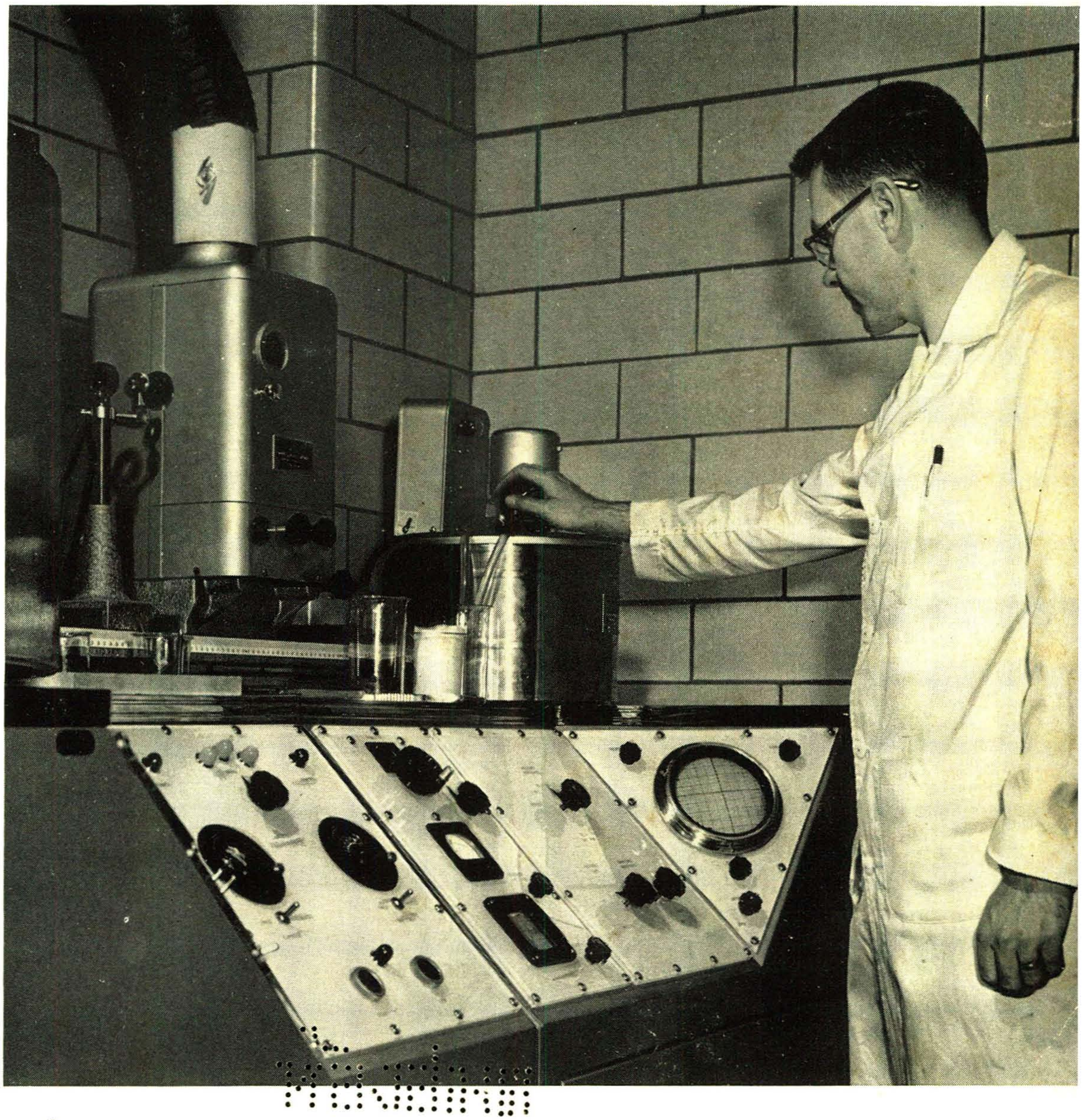
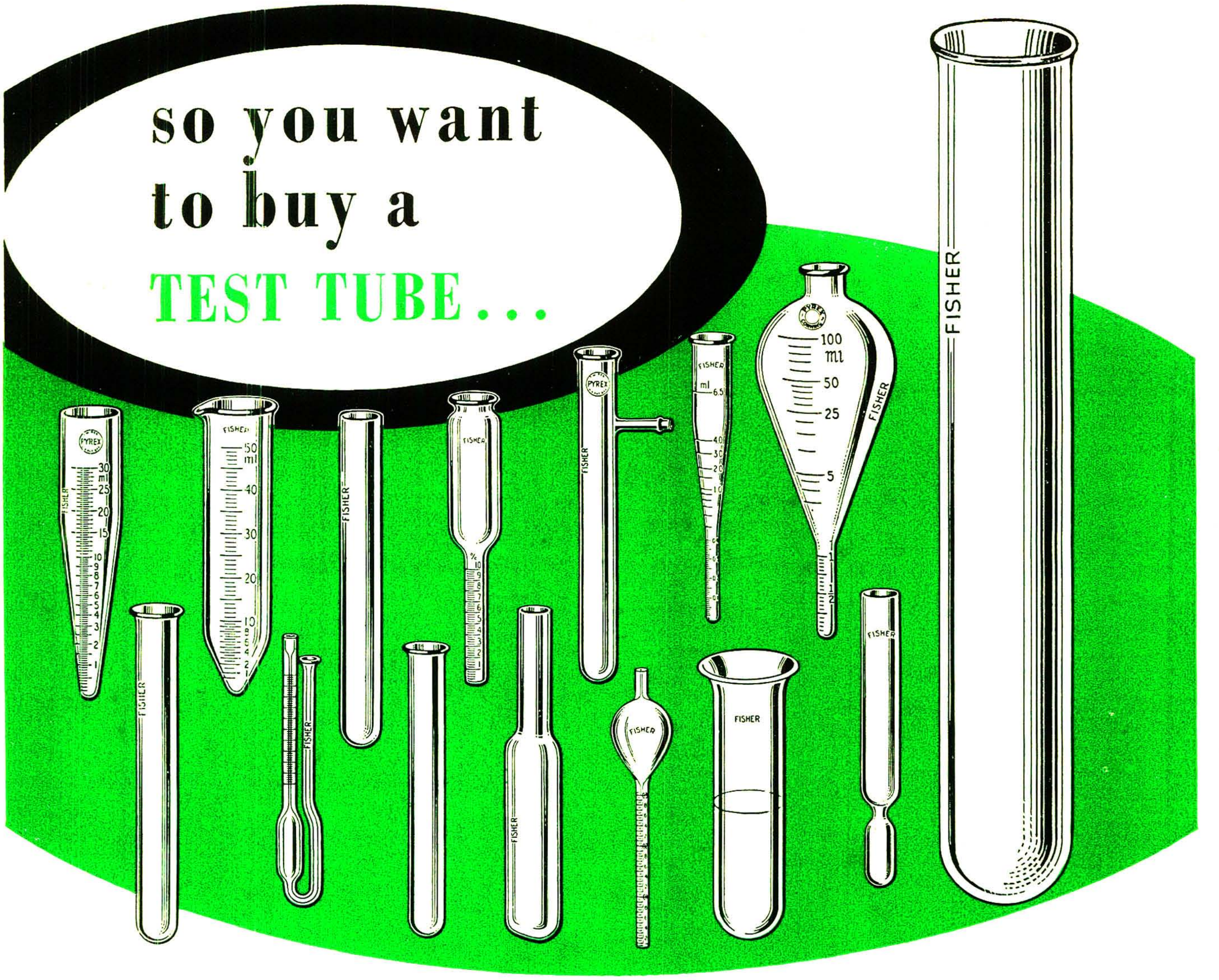
AUGUST 1954

ANALYTICAL CHEMISTRY



Kennecott's ultramodern new research center at Salt Lake City adds to growing research facilities in mountain states area. See pages 29A and 31A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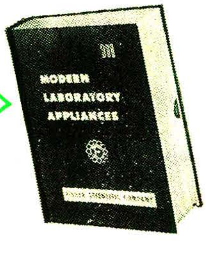
MODERN LABORATORY APPLIANCES

ANALYTICAL CHEMISTRY

Volume 26, No. 8 Issued August 16, 1954

This Month's Cover. The mountain states area and Kennecott copper can be justifiably proud this month as the company's new research center is dedicated. Located on the University of Utah's campus at Salt Lake City, these facilities will be an important addition to the research facilities of the area. The company apparently has spared no effort or expense to provide excellent housing and equipment for the technical staff. The principal objectives of this research center appropriately will be the effective coordination and expansion of the research activities of Kennecott's four western mining divisions. At the same time it is reasonable to assume that the university and the community will benefit greatly by having the research center and its staff in their midst. For further details of the laboratory see pages 29 A and 31 A

(Continued on page 4 A)

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CRYSTALLOGRAPHIC DATA

MEETING REPORT

AIDS FOR THE ANALYST

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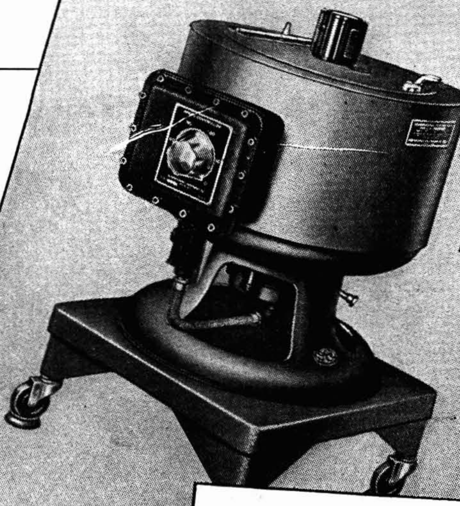

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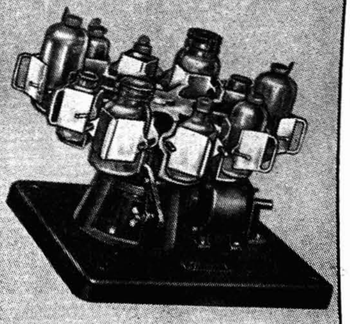

3

For the Industrial Laboratory

Designed particularly to meet the needs of the industrial scientist, these three machines are valuable assets in both research work and production control. Their effectiveness has been proven in countless applications — investigate their possibilities for your projects.

1. MODEL BE CENTRIFUGE equipped with a 3450 r.p.m. adjustable speed explosion-proof motor, for Class I Group D locations. Characteristic capacities: 11″ diameter high-speed perforated basket style head; four 250 ml. bottles; eight 100 ml. tubes. Also available with 1750 r.p.m. explosion-proof motor for petroleum testing.

2. LABORATORY CHEMICAL CENTRIFUGE. For purely scientific or preliminary to large scale commercial operations. Can be operated continuously and has adjustable speeds up to 3600 r.p.m. with 5″ dia. x 2½″ deep basket, furnished in manganese bronze, stainless steel, rubber-covered steel and Coors porcelain.

3. BOTTLE SHAKING MACHINE. Produces a motion similar to shaking by hand but much more rapid and effective. Various interchangeable heads are available with capacities up to ten one-liter bottles, quart-size fruit jars or other containers of similar shape. Of rugged design for continuous operation, the Shaker can be furnished with explosion-proof motor if required.

Send for Catalog C giving full details

INTERNATIONAL EQUIPMENT COMPANY

1284 SOLDIERS FIELD ROAD, BOSTON 35, MASS.

For further information, circle number 7 A on Readers' Service Card, page 37 A

Rapid... Accurate... Reproducible...

MOISTURE DETERMINATIONS

The NEW cenco *Infrared* MOISTURE BALANCE

for use with such materials as—

FLOUR
POPCORN
SORGHUM MILO
SOIL
HAY
RICE
FOUNDRY SANDS
DRY MILK PRODUCTS
OATS
PAPER
CLAY
SUGAR BEET PULP
SOYBEAN MEAL
CERAMICS
FOOD PRODUCTS

—●—

Measures either solid or liquid samples.

Here is an entirely new CENCO development which offers greater speed and efficiency in obtaining moisture determinations.

This unit measures moisture content by weighing and drying *simultaneously*. It utilizes an improved principle of operation in drying the sample by infrared radiation and weighing by a sensitive null-point torsion balance. As a result, extremely rapid, accurate and reproducible moisture determinations are easily made.

The CENCO Moisture Balance has been used successfully for determining moisture content in a wide variety of materials. New developments now make it possible to measure liquids as well as solid samples. Disposable pans are also available at low cost for use with greasy, oily, tacky, and adhesive materials eliminating the need for cleaning.

Operation of the Moisture Balance is quite simple. The scale of the torsion balance is calibrated directly in per cent moisture. Moisture content of samples is read directly on the scale as a percentage. The scale is graduated from 0 to 100% in .2% divisions. All necessary adjustments are conveniently located. Gradual loss of moisture is shown during the procedure and final reading indicates the percentage of moisture content of the sample.

Full details about this improved unit are contained in our bulletin No. 1210B. Write for your copy today.

No 26675 Cenco Moisture Balance, $226.50

No. 26678 disposable pans for solids or liquids,
Pkg. of 25, $2.20 4 pkgs. of 25, $8.00

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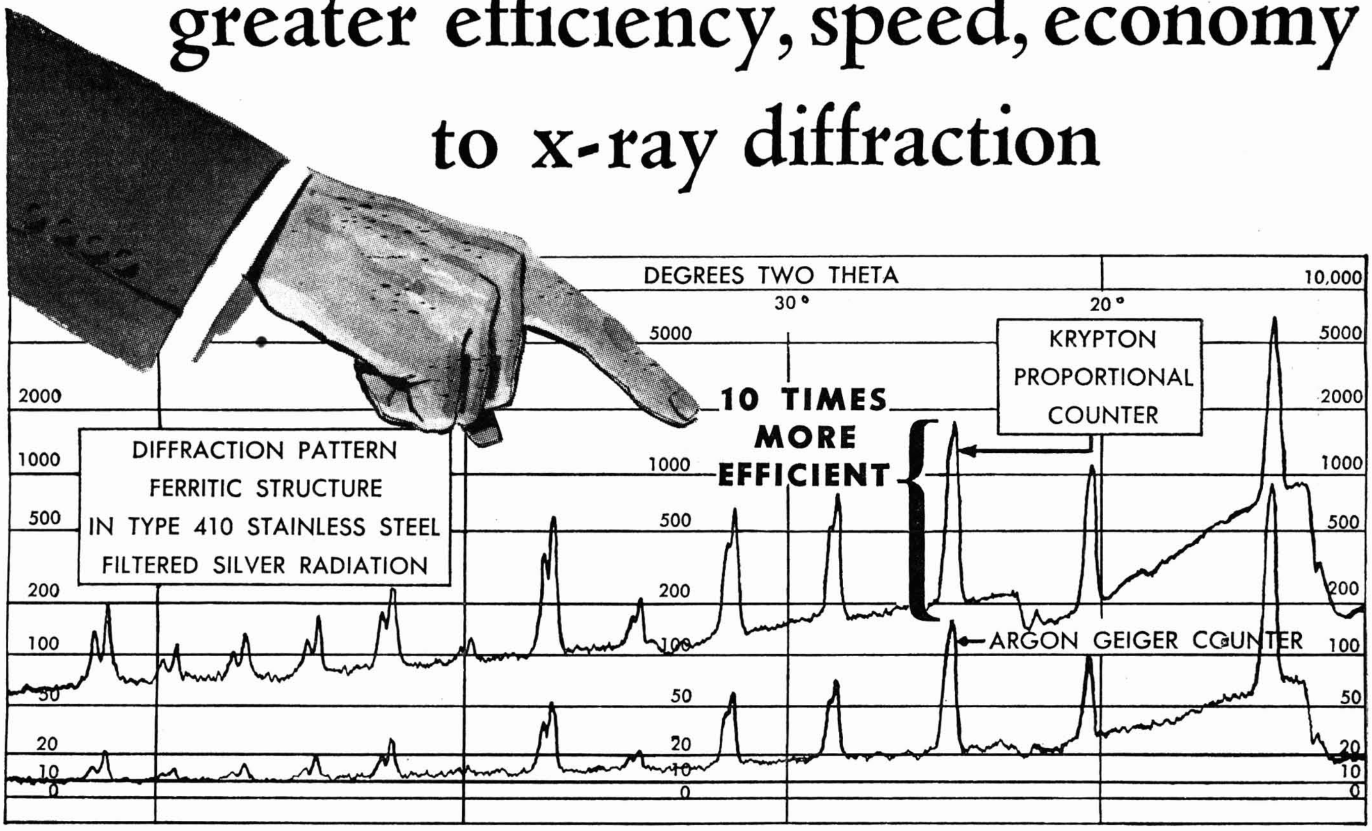
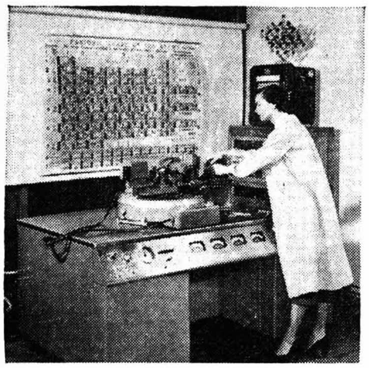
For further information, circle number 8 A on Readers' Service Card, page 37 A

Now! Proportional counter brings greater efficiency, speed, economy to x-ray diffraction



The improved efficiency of the new G-E krypton-filled proportional counter tube and amplifier is quickly apparent, even when recorded on semi-log paper.



Available with a wide range of accessories, the General Electric XRD-3 is a highly versatile tool for x-ray diffraction.

Two new accessories extend accuracy of General Electric XRD-3 diffraction units

HERE'S important news for present and prospective users of x-ray diffraction. This fast, accurate method for the non-destructive analysis of a wide range of materials has been advanced in effectiveness by two new accessories for the General Electric XRD-3. They are:

(1) NEW PROPORTIONAL COUNTER AMPLIFIER that converts present G-E Geiger tube to proportional counter operation. Connection to your present XRD-3 is extremely simple.

(2) NEW KRYPTON-FILLED PROPORTIONAL COUNTER TUBE has much higher absorption efficiency than the argon-filled tube. What's more, it has no noticeable thermal sensitivity. And tube failure due to very high intensities and unnecessarily high voltages is practically eliminated.

Both accessories, acting together, perform linearly over five times the range of argon-filled multi-chamber Geiger tubes, and about 20 times the range of linearity of typical single-chamber Geiger tubes. The new counter assembly has less than one micro-second resolution time.

The great reduction of error in the higher frequencies is the biggest, *but only one,* of the benefits of this new General Electric development. Your G-E x-ray representative will be glad to point out others. Call him today, or write X-Ray Department, General Electric Company, Milwaukee 1, Wisconsin, for Pub. UU84.

Progress Is Our Most Important Product

GENERAL ELECTRIC

Enroll in the Fall G-E Diffraction School
September 27 through October 1, 1954.

For further information, circle number 9 A on Readers' Service Card, page 37 A

Thank modern electronics for this:

A full-fledged line-operated pH Meter of remarkable accuracy at the UNPRECEDENTED price of

$115.00

. . . made possible by recent advances in electronic tubes and circuits.

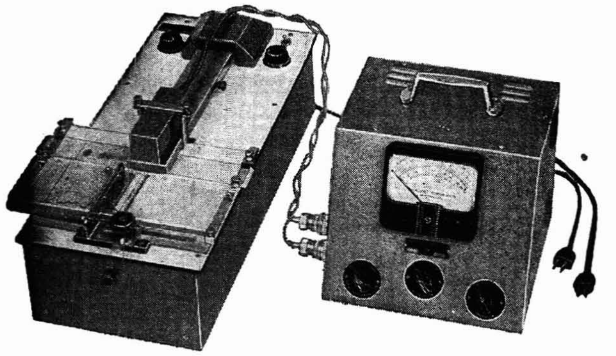
Write for Bulletin #225 to

PHOTOVOLT CORPORATION
95 MADISON AVENUE • NEW YORK 16, N. Y.

PHOTOVOLT pH METER
MOD. 115

- **SIMPLE** in operation and maintenance.
- **FAST** and dependable in daily service.
- **FULLY** stabilized for wide range of line voltage fluctuations.

PHOTOVOLT Densitometer
for
Partition Chromatography
and Paper Electrophoresis



A photoelectric precision instrument for the rapid and convenient evaluation of strips and sheets of filter paper in partition chromatography and paper electrophoresis.
Write for Bulletin #800 to

PHOTOVOLT CORP.
95 Madison Ave. New York 16, N. Y.

Also

Colorimeters	pH meters	Electronic Photometers
Fluorimeters	Reflection Meters	Multiplier Photometers
Nephelometers	Glossmeters	Interference Filters

LUMETRON
Photoelectric COLORIMETER and FLUORESCENCE METER
Mod. 402-EF

A high precision instrument of unusual flexibility for all tests involving . . .
TRANSMISSION
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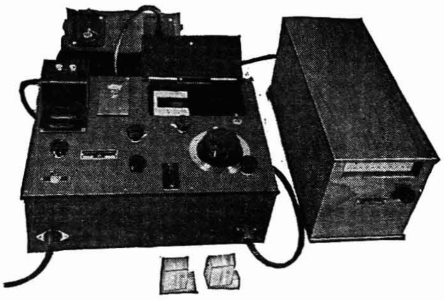
NEPHELOMETRY



Write for Literature *Prompt Delivery*

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95 Madison Ave. New York 16, N. Y.

Also

Colorimeters	pH Meters
Reflection Meters	Electronic Photometers
Densitometers	Multiplier Photometers

For further information, circle numbers 10 A-1, 10 A-2, 10 A-3 on Readers' Service Card, page 37 A

~~ABOUT~~ ~~NEARLY~~ ~~CLOSE TO~~ ~~APPROXIMATELY~~ ~~ALMOST~~

BE SURE!

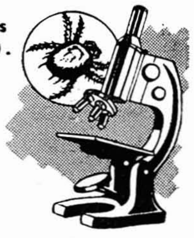
with a

NEW IMPROVED ROLLER-SMITH PRECISION BALANCE

Featuring increased response and speed and employing Alnico magnets for damping, the new and improved Roller-Smith Precision Balance is capable of weight determinations ranging from 3 milligrams to 150 grams, in sensitivities from 2 micrograms to 20 milligrams. Available in a wide selection of models and ranges. Its attractively designed die cast case, in gray hammer-tone finish, is now fitted with snap latch doors for easy access.

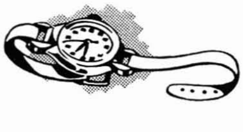
When the quality of your product . . . the success of your research . . . depends upon precise weight measurements in a matter of seconds, you can rely on Roller-Smith Precision Balances . . . universally accepted as the standard for speed, accuracy and simplicity of operation. Catalog No. 4540 illustrates and describes all models . . . shows wide selection of pans and accessories. Write for your copy today.

These are but a few of the thousands of operations performed daily by Roller-Smith Balances.

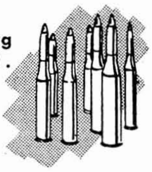


Detects difference in weight of anesthetized insects before and after eating. (Biological Laboratories).

Insures quality of drugs and antibiotics in the research laboratory. (Pharmaceutical Manufacturers).



Counts thousands of tiny screws by weight. (Watch Manufacturer).



Measures accurate powder charge and lead slug for match rifle ammo. (Firearm Manufacturers).

Protects quality of women's hosiery . . . determining synthetic fiber size by weight. (Hosiery Mills).

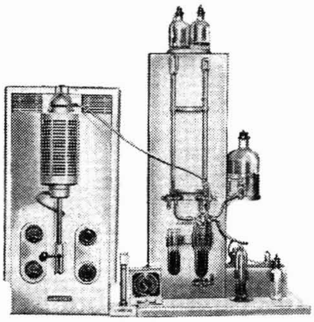
Instrument Division

ROLLER-SMITH CORPORATION
1825 WEST MARKET STREET
BETHLEHEM, PENNSYLVANIA

Since 1908—producers of high quality electrical instruments, aircraft meters, rotary switches, relays and precision balances.

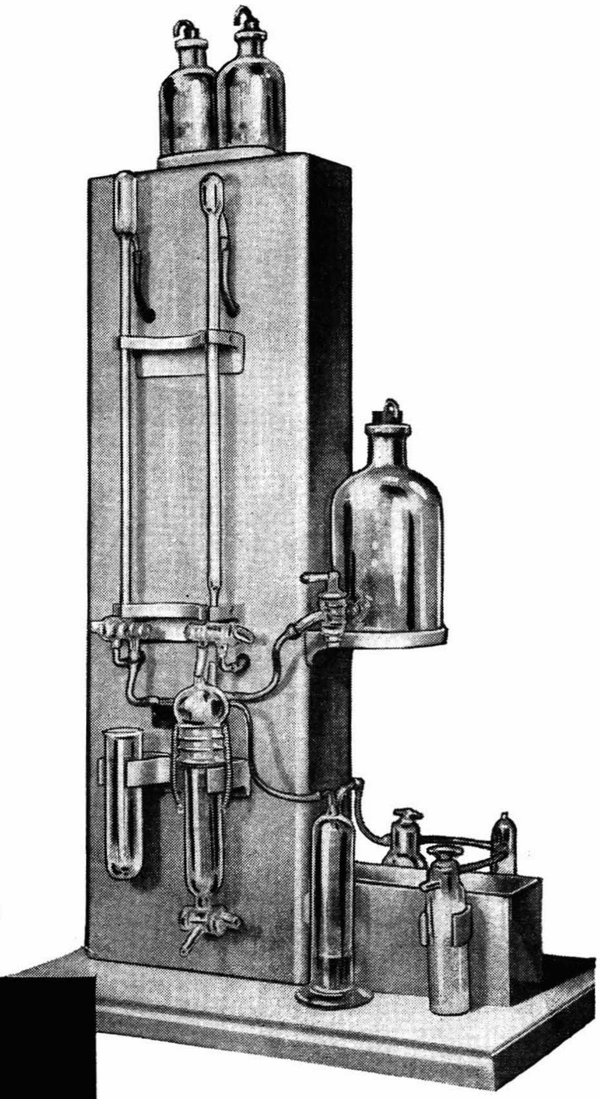
For further information, circle number 11 A on Readers' Service Card, page 37 A

Analyze both Sulfur and Carbon content in ONE operation



LINDBERG

Combined Sulfur-Carbon Determinator



Model DS-C—Takes minutes instead of hours. Reduces equipment cost.

Actually, this unit does the same work, in less time, than the two separate units you may now be using. It does combustion sulfur analysis (A.S.T.M. E30–47) and also has a gravimetric absorption system for carbon analysis.

Sulfur contents up to .30% can be analyzed with a one gram sample. Sulfur analysis can be made alone, in 3 minutes or less, by disconnecting the absorption system.

It's easy to clean this unit, because the sealed titration vessel has fill and drain tubing connections. This also reduces the chance of breakage, since the vessel does not have to be removed for cleaning.

Errors are eliminated because you do not have to remember the initial color or shade before titration. It has a mirror surface that permits color end point comparison.

The Lindberg Combined Sulfur-Carbon Determinator cuts equipment costs way down—and at the same time saves plenty of work hours. This makes it just about perfect for the small lab, or for the lab that must analyze both carbon and sulfur on every sample.

If you want to know more about this unit, just call your nearest Lindberg laboratory equipment dealer. He will be happy to give you full details.

LINDBERG LABORATORY EQUIPMENT DIVISION

Lindberg Engineering Company, 2440 West Hubbard Street, Chicago 12, Illinois

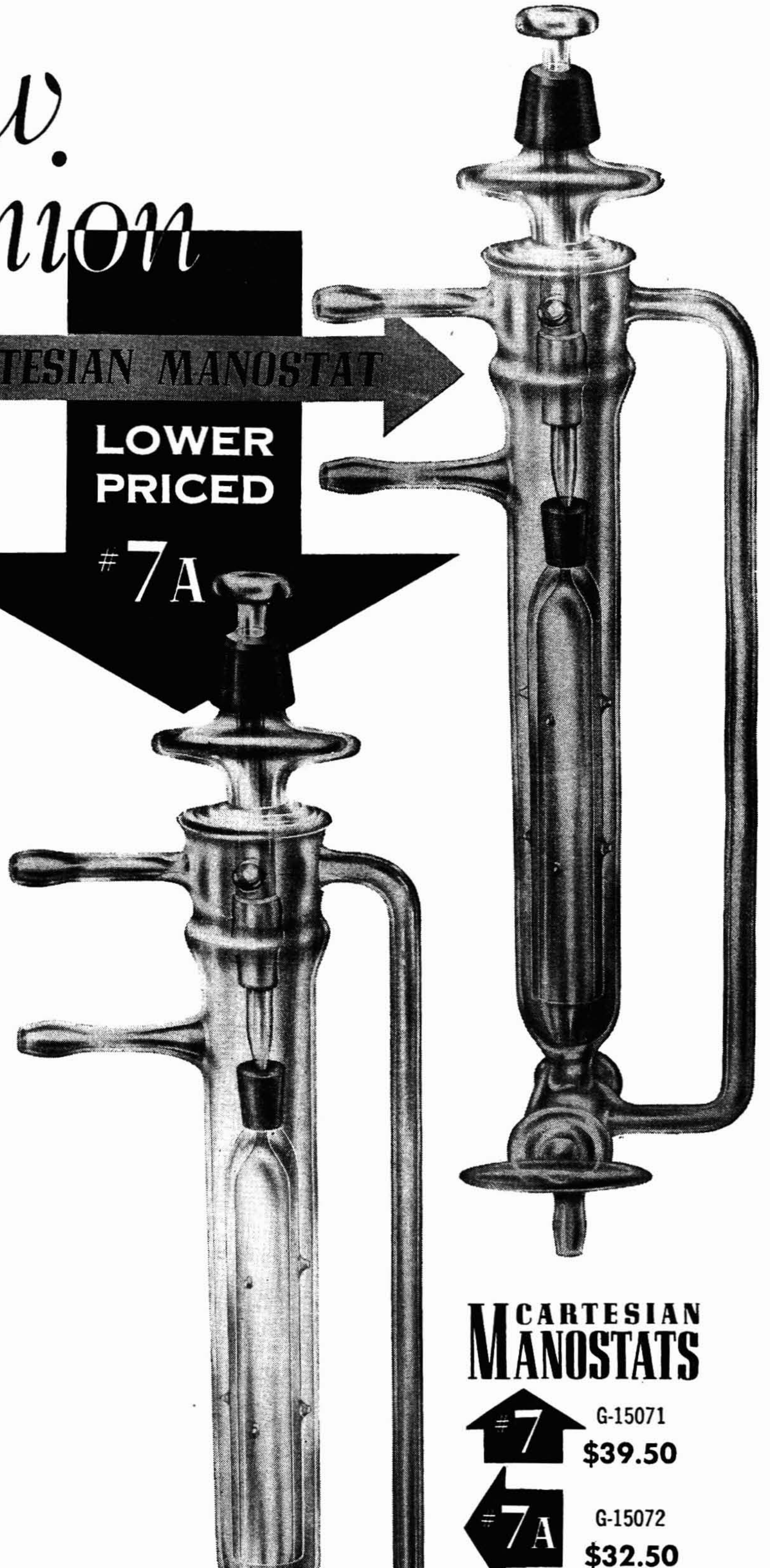
For further information, circle number 12 A on Readers' Service Card, page 37 A

New Companion

TO OUR #7 CARTESIAN MANOSTAT

LOWER PRICED

#7A



...they remember your vacuum setting even after shutting down system!

With the elimination of the 3-way stopcock at the base... which is required only in special cases such as flow control... we are now able to offer a new lower priced glass Cartesian Manostat as a companion to our model #7.

This new model, #7A, is otherwise identical in construction and performance to #7. Both Cartesian Manostats perform with human-like sensitivity, so uncanny are they in their operation.

Formerly, new settings had to be made every time the system was shut down. But now Cartesian Manostats #7 and #7A eliminate that time-consuming operation. Now, once a vacuum has been set in the instrument, the system may be shut down without disturbing the setting. This new feature provides simple and fool-proof operation.

These glass models are especialy suitable for laboratory applications because of their corrosion resistance.

how it works*

The operation is based on sealing off a given amount of gas inside the diver at the control pressure. The sensitive diver responds to the slightest increase in pressure in the system which causes the diver to drop and open the upper orifice which is connected to a source of pressure lower than the control pressure. This allows the excess gas to leave the system and restore it to the control point. A small bleed into the system from a source of higher pressure insures that the pressure in the system will never go below the control pressure.

When operated under vacuum, the quantity of gas maintaining the control pressure is sealed inside the diver even when the system is restored to atmospheric pressure, since the excess pressure forces the inside seat of the diver down upon the orifice of the internal central tube and prevents breaking of the mercury seal.

*For Theory of Operation See Following Article: Gilmont, R., *Ind. Eng. Chem. Anal. Ed.* **18**, 633, (1946); **23**,157 (1951).

price list:

G15071 Cartesian Manostat #7, all glass model ready for use with rubber connections. Mercury not included. ea. **$39.50**

G15072 Cartesian Manostat #7A, all glass model ready for use with rubber connections. Mercury not included. ea. **$32.50**

CARTESIAN MANOSTATS

#7	G-15071	**$39.50**
#7A	G-15072	**$32.50**

Automatic

VACUUM & PRESSURE CONTROL

for Laboratory

The EMIL GREINER Co.

20-26 N. MOORE STREET (EGCo®) NEW YORK 13. N.Y.

For further information, circle number 14 A on Readers' Service Card, page 37 A

THE ANALYST'S COLUMN

L. T. HALLETT, Science Editor

WE can still vividly remember from our graduate days 25 years ago with what disdain and misgivings our professor of analytical chemistry looked upon the introduction of dimethylglyoxime for the determination of nickel. The contamination of inorganic determinations with organic chemicals was considered poor technique and to be avoided. Since that time, and in spite of protestations of the classicists, analytical chemistry has been practically taken over by organic reagents, particularly with respect to colorimetric determinations.

The study of coordination compounds and the introduction shortly after World War II by G. Schwarzenbach of the volumetric determination of calcium and magnesium based upon the titration with the disodium salt of ethylenediamine tetraacetic acid (EDTA) has opened up a whole new approach to the determination of metals using the stable undissociated complexes formed by such reagents, now familiarly known as chelates. Chelating agents are primarily being used as sequestering agents in industrial applications, and thus are manufactured in quantity under various trade names. The analytical chemist has found a useful chemical tool and, fortunately, a plentiful supply. As is generally true with new approaches, the published literature to date does not begin to represent what the present applications are or what new determinations are likely to emerge from work already in progress. We do know that it is considerable, judging from manuscripts now being received in this field from workers in this country. There is considerable research being done in Britain and on the Continent, particularly in Czechoslovakia, where Rudolf Pribil in Prague, together with his coworkers, has published and is continuing to publish important contributions. He has communicated with us and summarizes some of the applications of EDTA as follows:

> Ethylenediaminetetraacetic acid as a volumetric reagent differs from a large number of other precipitating, complex-forming, or redox reagents by its wide range of specificity. At the time of writing, volumetric methods using this reagent

facts on Infrared *for the laboratory*

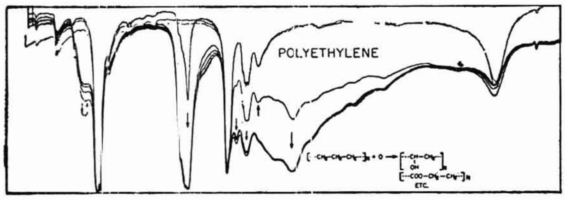
Want to watch a reaction?

Reaction rates, effects of catalysts, temperature, etc., the detection of intermediates, efficiency of stabilizers, aging properties of materials—these are all subjects of importance in the study of reaction mechanisms. Special infrared analytical techniques reveal valuable information about all of them.

The composite spectrum below depicts the oxidation reaction of polyethylene. The formation of hydroxyl and carbonyl groups is indicated by the gradual appearance of their characteristic absorption bands as the oxidation proceeds. The hydroxyl absorption band later decreases in intensity with the appearance of the carbonyl or peroxide stage.

The spectrum was prepared by means of the unique cycling feature of the Perkin-Elmer Model 21 Infrared Spectrophotometer and a Perkin-Elmer horizontal heated sampling stage. A sample of polyethylene was placed on the stage and heated to 150° C for 4 hours. Its spectrum was successively traced with no attention from the operator.

"Recording a reaction" is just one example of how a versatile infrared spectrophotometer plus the availability of the proper accessories can be invaluable in the solution of common laboratory problems. *Only* at Perkin-Elmer will you find all the instruments and accessories required to meet *all* research needs.

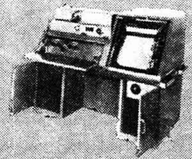


The Perkin-Elmer Corporation, 860 Main Avenue, Norwalk, Conn.
Southern Regional Office: New Orleans, Louisiana

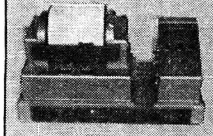
For Optical Design and Electro-Optical Instruments

PERKIN ELMER

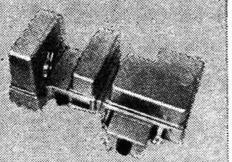
The ONLY complete range of infrared instruments and accessories to meet all research needs!



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

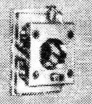


Model 21 Double Beam Infrared Spectrophotometer—The fastest and most efficient instrument commercially available for the recording of large numbers of spectra. Records directly in percent transmission. *Write for Bulletin 104.*



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

ACCESSORIES:

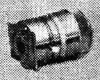


Demountable Cell—may be assembled to any thickness—for liquids, capillary films, mulls of solids—and films and powders.

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

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

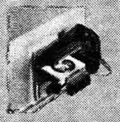
- **Microcell**—obtains good spectra with 25-100 micrograms—available in thicknesses from 0.025 to 3 mm.



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

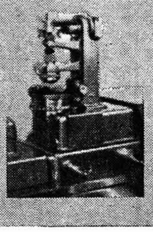
Reflectance Attachment—for specular reflectance studies of solid materials.

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



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

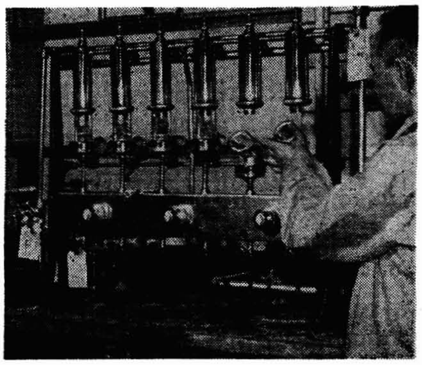
Polarizer—for studies of crystal and molecular orientations. **Rotable Cell**—To assist in sample orientation for polymerization studies.



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

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

For further information, circle numbers 16 A-1, 16 A-2, 16 A-3, 16 A-4 on Readers' Service Card, page 37 A



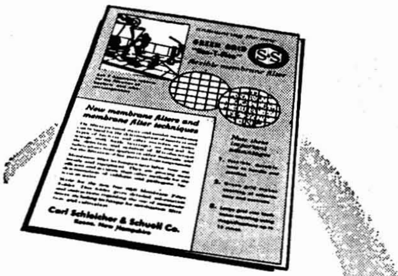
have been worked out for some 15 to 20 cations, for many of which only indirect methods of estimation had previously been known, and for some no suitable methods of any kind. This versatility of the reagent poses a number of highly interesting, but frequently rather complex problems concerning the estimation of several components in a single solution. These problems may be tackled essentially in the following four ways:

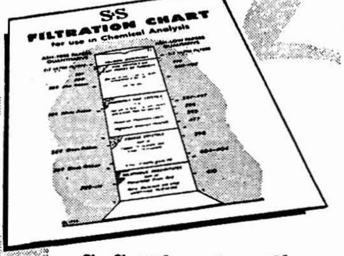
By determination of different cations at different pH of the solution, the complexes formed by ethylenediaminetetraacetic acid with various cations differ in the pH range of their existence. The majority of complexes formed by divalent cations dissociate at pH values below 4, whereas the complexes of tri- and quadrivalent metals are stable at pH 1 to 3. Complex formation may readily be followed polarographically. Determination based on the different stability of various complexes at defined pH value, however, requires indicators specific for the cation to be determined. . . .

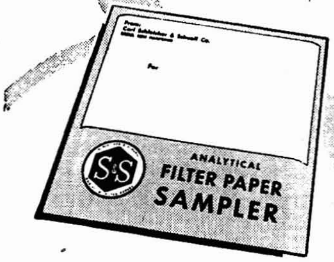
2. By a suitable choice of methods of isolation (extraction or precipitation procedures) either of the metal to be estimated or of interfering elements, selective isolation by precipitation or extraction may frequently be achieved by the use of suitable organic reagents. The simultaneous determination of cadmium and zinc may serve as an example of this type of procedure. The sum of both elements is first determined by titration with EDTA to Eriochrome Black T, the cadmium is then precipitated by the addition of diethyldithiocarbamate, and the EDTA liberated is titrated with magnesium sulfate without previous removal of the white cadmium precipitate. . . .

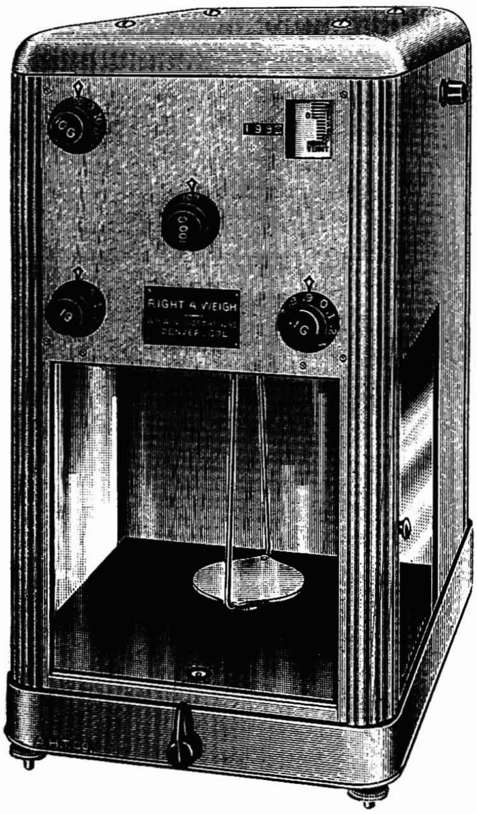
3. By the selective screening or "demasking" of certain cations, the use of potent complex-forming reagents for the selective screening of certain cations against EDTA and chelatometric indicators holds out more promise than the isolation methods discussed above. The greatest attention has hitherto been given to potassium cyanide, which is capable of forming complexes of the required stability with a large number of cations. The use of cyanide thus makes possible the determination of magnesium in the presence of zinc, copper, cadmium, nickel, and cobalt, or the determination of lead in the presence of zinc, etc. Much of the work in this field is due to H. Flaschka, who has worked out a number of microanalytical procedures on this basis. . . .

4. By the use of more selective reagents of the "complexone type," for the successive titration of several ions in a single solution, which is as yet largely a problem of the future. Here, too, it will be necessary to extend the number of available specific indicators, and it is to be presumed that the adjustment of acidity will be of considerable importance. One example making use of a new chelating reagent of the EDTA type may be cited, though the procedure is as yet of theoretical interest rather than of practical importance. Iron may be titrated with EDTA at pH 2 to 3 with salicylic acid as indicator. The possibility of further titration—e.g., of zinc of magnesium—after alkalization of the solution is, however, vitiated by the fact that under alkaline conditions iron is displaced from its complex with EDTA and precipitated. . . .









1867-F.

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Column—Of aluminum, mounted directly on cast aluminum base.

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Release and Arrest—Ball bearing arrest mechanism for beam and pan operated by single control which also turns on scale projection lamp. Control is turned to right for partial release during weight adjustments and to left for complete release at equilibrium.

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Weights—Of Stainless steel, Type 310, with high chromium-nickel content, which is non-magnetic and corrosion resistant. Including all weights required for total of 199.9 grams in increments of 100 mg, adjusted to well within the tolerances established by the U.S. National Bureau of Standards for Class S.

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ANALYTICAL CHEMISTRY

WALTER J. MURPHY, Editor

Helping Those Inclined toward Science

THE May issue of *Chemistry*, published by Watson and Helen Davis of Science Service of Washington, D. C., is devoted to reporting on many scientific instruments that high school students have built in recent years. Many of our readers will recall that *Chemistry* is the successor to the *Chemistry Leaflet* which Pauline Beery Mack, then of Penn State, distributed to many high schools, as a labor of love of profession, in an effort to stimulate interest in chemistry careers on the part of high school students.

In the introductory remarks to this special issue, the Davises point out that every one of the great instruments of science was once handmade from improvised materials. While the use of "every one" may or may not be factual, it certainly is true that the overwhelming majority have been developed in this manner. It is likewise true that many of the very first models have been reported on in the pages of ANALYTICAL CHEMISTRY.

The analysts of this country can very well take pride in the role that many have played in pioneering scientific instruments. It was natural for them to do so. They were the ones who most frequently saw at first hand the need for a special instrument. Those with special bent in the direction of physics, electronics, and plain gadgeteering have been the authors frequently of the prototypes of slick-looking and expensive-looking instruments that now so clearly identify modern analytical and research laboratories.

The future welfare of analytical chemistry, of instrumentation, of automation depends upon how many young men and women endowed with natural talents for science become interested in the broad field of instrumentation.

The National Science Talent Search, conducted by Science Service and financed by Westinghouse, has performed an excellent service to this country and to science in supplying the medium for youngsters interested in science careers. According to the Davises, building instruments is one of the favorite projects of these young people.

Reading the descriptions of the instruments built by winners and honorable mentions in some recent Science Talent Searches makes it very apparent that for the most part these young experimenters did more than follow published directions "from A to Z." In most cases it is evident that the students had read widely and combined the most appealing methods from numerous sources. Interestingly enough, the Davises report that the young men and women were particularly cost-conscious in constructing their various pieces of equipment. How better can one learn the scientific principles upon which such instruments are built?

Glancing through the May issue of *Chemistry* we find the following were constructed by Science Talent Search winners and honorable mentions: a spectroscope, a Tegla coil, an oscilloscope, a cloud chamber, a Geiger counter, a Van de Graaff generator, an electrical digital computer, and a machine for generating ultrasonic waves, to mention just a few. One other article of special interest was on a phase of chromatography which the young author defines "for the lack of a better name" as "centrifugal chromatography."

We all see the need for encouraging the type of young men and women who are attracted to the natural sciences at the secondary school level. It is at this age that the inspiration is given further impetus or usually is lost forever. The National Talent Search, the science clubs, and other activities designed to engender a love for and a curiosity about the natural sciences need, at times, highly trained people to assist in many ways. Is this not a form of science "action" that many analysts could engage in with much benefit to themselves and to those whom they would be helping to shape a career in science?

Broadening the Horizons

ONE of the very practical aspects of analytical chemistry is quality control. Some industries have gone further than others in turning to laboratory and statistical quality controls, one of the most notable being the pharmaceutical field. Others have looked at their manufacturing operations more as an art than a science, and in this category to a considerable extent is the candy industry.

Last year the Scientific Apparatus Makers Association working with Sears, Roebuck & Co. started a project that undoubtedly will result in the much wider use of analytical chemistry methods in the candy field. In June of this year, Robert W. Watson of Sears, speaking at the 70th annual convention of the National Confectioners' Association in New York, suggested that the objective of quality control in the candy field should be "the setting of standards not from a production but from a consumer point of view." At the same time, he cited substantial savings in various phases of production and merchandising where scientific controls have been introduced. Reporting on his company's experience in establishing a candy research section in its development and testing laboratories, Mr. Watson continued:

> Candy has been regarded as having intangible and variable qualities which could not be given definite expression. It is a common tendency, where we have an edible product, to regard it as a combination of chemical substances—which it most certainly is. Being such a combination, it obeys the laws of nature and never gives an unpredictable result, if studied sufficiently. Therefore, it is capable of prediction, control, and evaluation.
>
> Most of the resistance we initially encountered has been overcome, I am happy to say; because through a series of methods which are chemical, physical, and organoleptic (test analysis) in nature, we have given an evaluation to most of candies' qualities, both tangible and intangible.

The SAMA, of course, is interested primarily in the project, and rightfully so, in order to promote the sale of analytical instruments, laboratory reagents, etc. Through its efforts, however, it is bringing to many segments in a large consumer industry a knowledge of the practical values inherent in the adoption of modern analytical practices and at the same time is creating more opportunities for analytical chemists.

Determination of Olefin Group Types

Chromatographic and Infrared Absorption Techniques

ELEANOR L. SAIER, ABBOT POZEFSKY[1], and NORMAN D. COGGESHALL
Gulf Research & Development Co., Pittsburgh, Pa.

In the spectroscopic determination of functional group types there are fundamental limitations due to variations in position and intensity of functional group absorption. A detailed study has been made of the limitations and applications of the analysis for functional group-type olefins. A high degree of accuracy is not possible, owing to variations in absorption behavior among olefins of the same class, although very useful results may be obtained. A method of working in dilute carbon disulfide solutions with thick cells has been developed to eliminate the dependence on specific absorption cells. Chromatographic procedures were employed to obtain olefin-rich mixtures for direct examination. The procedure has been employed as an integral portion of a complete analysis for certain problems wherein specific paraffins, group-type olefins, and specific aromatics are determined.

THE realization that the absorptivity of a given functional group often is reasonably constant in a series of compounds has given impetus to the development of infrared spectroscopic methods for quantitative group-type analysis. Johnston and coworkers (*8*) applied this technique to the determination of several olefinic classes of compounds in gasolines. Anderson and Seyfried (*3*) extended the method to include five olefinic classes in addition to a group-type analysis for oxygenated compounds. In the past few years the literature on the application of this approach to the quantitative determination of C-H groups in hydrocarbon mixtures has been increasing (*5–7, 10*). The usefulness of group-type analyses using infrared absorption techniques is evidenced by the increased development and application of these methods in various laboratories. This paper concerns itself with such an analysis for the olefinic functional groups $RCH{=}CH_2$, $RR'C{=}CH_2$, $RCH{=}CHR'$ (*cis* and *trans*), and $RR'C{=}CHR''$, using chromatographic separations as a means of concentrating the olefins and minimizing interferences by nonolefinic components. This method does not yield direct information on the concentrations of tetrasubstituted and cyclic olefins. In the development of this method, the following points have been investigated and the results are discussed below:

The utilization of dilute carbon disulfide solutions of the olefins and a comparatively thick cell (approximately 1.5 mm.). This technique has a long-term convenience not encountered with methods using thinner cells.

Use of four analytical wave lengths for the $RR'C{=}CHR''$ group which shows variable absorption in the 11.9 to 12.7-micron region.

Evaluation of the accuracies of the present method.

Procedure for the chromatographic separation of paraffins, olefins, and aromatics, and the quantitative evaluation of the volume fractions of these three classes of materials from the chromatogram.

Effect of the chromatographic separation on the relative distribution of the five olefinic classes.

Desirability of separating the olefins and aromatics from the paraffins in order to improve the accuracy of any analysis of the paraffinic fraction.

Accuracy of the olefin analysis in the presence of moderate amounts of paraffins present as contaminants.

Application of the olefin matrix as determined for one cell to other thick cells.

The present method has been applied to gasolines and to paraffin-olefin-aromatic mixtures of dehydrogenation experiments, and the results are also discussed. The data presented permit a more critical evaluation of the limitations and accuracies of the present group-type olefin analysis than now appears in the literature.

EXPERIMENTAL

Spectra. A Perkin-Elmer model 12A spectrometer equipped with rock salt optics was used to obtain the quantitative spectral data. The Perkin-Elmer Model 21 spectrophotometer was also used qualitatively to examine samples and fractions from chromatographic separations. The olefins used for calibration in all instances were obtained from American Petroleum Institute Project 6, Carnegie Institute of Technology. Eimer and Amend Purity carbon disulfide was used as the solvent. The pure olefins generally were diluted at least 1 to 100 by volume in order to obtain a cell plus solvent corrected absorbance of 0.4 to 0.5 at their major analytical wave lengths. The absorbance of the same cell filled with the solvent only was taken as the correction at all analytical wave lengths. The limited availability of olefins from API Project 6 resulted in either four or five compounds of each class being used for calibration.

Chromatographic. The chromatographic column employed in concentrating the olefins is illustrated in Figure 1.

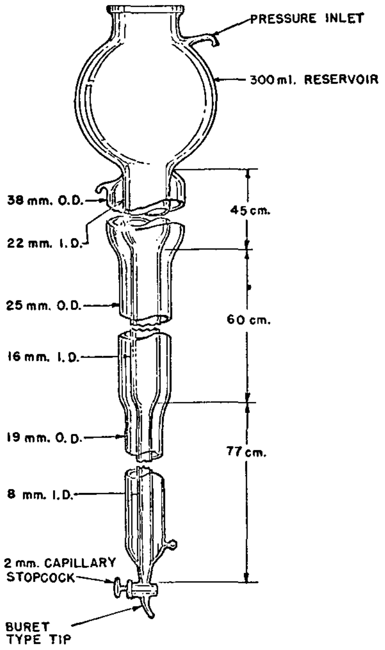

Figure 1. Chromatographic Column Used in Concentrating Saturates, Olefins, and Aromatics

Davison silica gel (Code 923) was used as the adsorbent. It is important to stress the use of this particular silica gel, as it is believed to be the most favorable one in repressing olefin isomerization and polymerization (*9*). In making a separation on a sample for which only the olefinic content was of interest, 10 ml. of spectral grade iso-octane (2,2,4-trimethyl pentane) was employed to prewet the column. The sample was added as soon as the iso-octane was into the adsorbent zone. (The ratio of

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[1] Present address, General Electric Co., Waterford, N. Y.

grams of adsorbent to milliliters of olefins plus aromatics was approximately 10 to 1.) After all the sample had entered this zone, approximately a half inch of fresh adsorbent was added to the column and followed with ethyl alcohol eluent. A sufficient pressure of nitrogen was maintained so that approximately 1 ml. per minute of sample issued from the bottom of the column. The effluent was collected in 0.9-ml. portions using the collector illustrated in Figure 2. The complete separation of a 100-ml. sample takes approximately 4 to 5 hours. The refractive indices are obtained for all cuts and plotted *vs.* cut number. In cases where the paraffinic fraction is to be analyzed, it is advisable not to use a separate prewetting agent. [An excellent discussion of chromatographic procedures and applications has appeared in this journal (*2*)].

CALIBRATION AND PROCEDURE

Spectral. Originally a 0.15-mm. cell was used with *n*-heptane as the solvent. However, as part of a more general investigation using comparatively thick cells, all the calibration data were redetermined in a 1.5-mm. cell with carbon disulfide as the solvent. (In changing from the 0.15-mm. cell with *n*-heptane as solvent to the 1.5-mm. cell using carbon disulfide as solvent, several synthetic solutions were tested by both methods. An analysis by either technique was usually within the accuracy of the general method. There was, however, a definite improvement in the results for the *cis*-RCH=CHR′ type resulting from the elimination of the considerable absorbance of heptane at the *cis*-RCH=CHR′ point.) In all olefin calculations the concentrations were expressed on a moles per liter basis. The detecting system of the spectrometer requires the use of comparatively wide slit widths, and there was reason to suspect deviations from Beer's law owing to instrumental effects. Consequently, each pure olefin was checked for these deviations within the practical absorbance range using the 1.5-mm. cell. In every case a plot of absorbance *vs.* concentration in moles per liter gave a straight line within experimental error up to an absorbance of approximately 0.45 to 0.5. Beer's law deviations due to solution effects are expected to be at a minimum. Since the olefin concentrations used in calibration at the dominant points were at most 1% by volume, the absorbance of the cell filled with solvent was taken as the correction at all analytical points. This procedure is a very close approximation to the true cell plus solvent correction.

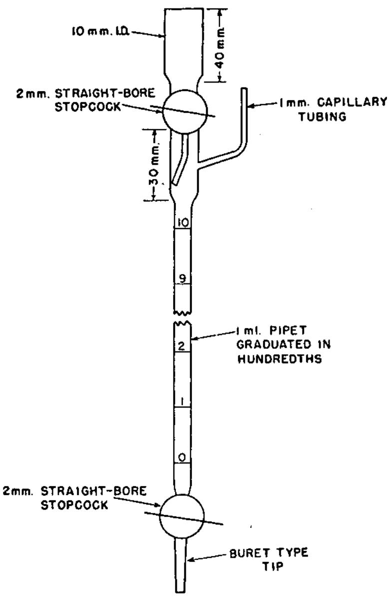

Figure 2. Receiver for Obtaining Measured Volumes of Liquid Issuing from Chromatographic Column

RCH=CH$_2$, RR′C=CH$_2$ AND RCH=CHR′ (*trans*) CLASSES. For the RCH=CH$_2$, RR′C=CH$_2$, and RCH=CHR′ (*trans*) classes, the group analytical wave lengths are approximately 11, 11.2, and 10.4 microns, respectively. The constancy of band positions and near-constancy of absorptivities are good. Thirteen olefins were used to calibrate for these three classes, and the average deviation of the absorptivities from the average of the class was 7.6% for RCH=CH$_2$, 4.4% for RR′C=CH$_2$, and 4.8% for RCH=CHR′ (*trans*). The maximum deviation of absorptivity of any member from the appropriate average of its class was approximately 11%. It is for these three classes then that one would expect to observe the better accuracy on synthetics, and this is the case. The use of carbon disulfide as the solvent gave some trouble with the RR′C=CH$_2$ class. At 11.2 microns one is on the side of a carbon disulfide absorption band, and it was necessary to obtain scanning data for the solution through this wave length and to correct each point for the cell plus solvent in order to find the absorption maximum. For the three classes above the analytical points for all, samples were obtained by scanning to find the absorption maxima.

RR′C=CHR″ CLASS. The RR′C=CHR″ class shows a variable region of maximum absorption (*3*). Five compounds (2-methyl-2-butene, 3-methyl-*cis*-2-pentene, 3-methyl-*trans*-2-pentene, 2-methyl-2-pentene, and 2,4,4-tri-methyl-2-pentene) were used for calibration, and the individual absorption maxima were found to occur at one of four wave lengths which were approximately 12.0, 12.1, 12.3, and 12.5 microns. The absorptivities of each olefin of this class were obtained at these four wave lengths. Two of the procedures employed in utilizing these calibration data in analyses were: (1) The class absorptivity was obtained by averaging the maximum absorptivity of each member regardless of wave length. The spectra of synthetic samples were obtained and the absorption maximum was located in the 11.9 to 12.7-micron region. Absorbance data were taken at this point and used in conjunction with the class absorptivity (*2*). The absorptivities of each compound at the four wave lengths mentioned above were averaged (four absorptivities were used per compound). This average was taken as the effective absorptivity of the compound in this region. The average of the effective absorptivities of the five pure compounds was taken as the class absorptivity. In practice, data are obtained at these four wave lengths for samples and the resultant absorbances are averaged and used in the calculations. Other schemes of utilizing the calibration data for calculations of the RR′C=CHR″ concentration were also tried. The results on synthetic samples indicated that in general the second method above gave the better results more consistently, and hence this procedure has been incorporated into the method.

RCH=CHR′ (*cis*) CLASS. Four compounds were used in calibrating for RCH=CHR′ (*cis*). The absorption maximum characteristic of this class was found to fall at approximately 14.4 microns for three of the compounds, and the maximum for the fourth one appeared at 13.9 microns. The latter band is close to the methylene wagging frequency characteristic of chain hydrocarbons. Consequently this point was not considered as a good one for which to take data. This would be especially true in the case of samples containing long chain olefins. Hence, the absorbance data were obtained at the absorption maxima of the other three compounds. The absorption maxima of these three compounds are rather broad and 14.44 microns was chosen as the analytical point for all samples. Carbon disulfide is to be preferred as the solvent as its absorbance at this point is very much smaller than that of *n*-heptane. The absorptivities of the members of the RR′C=CHR″ and RCH=CHR′ (*cis*) classes do not remain as constant as was found for the first three classes discussed above. One expects and finds that the accuracies for these two classes are the poorest.

TESTS ON SYNTHETICS AND ACCURACY. A five-component matrix was set up using the average absorptivity of each class at its own analytical wave length or wave lengths, and the average absorptivities of the other classes at the same points. This matrix as obtained with a 1.5-mm. cell is seen in Table I.

In solving the above matrix, the concentrations of the different olefin classes are found in moles per liter. The total olefin, in moles per liter, is then used to find the percentage distribution of each class. Synthetic blends of olefins were analyzed in order to obtain information on the expected accuracy of this analysis. Some typical results are shown in Table II.

Table I. Matrix Used in Group-Type Olefin Calculations

(Molar absorptivities in arbitrary units)

Wave Length, μ	*trans*-RCH=CHR′	RCH=CH₂	RR′C=CH₂	RR′C=CHR″	*cis*-RCH=CHR′
10.36	16.7	0.789	0.456	0.738	0.719
10.95	0.703	14.9	1.31	0.764	0.556
11.24	0.626	1.63	17.3	0.376	0.312
Av. of 4, 12.0–12.5	0.228	0.253	0.353	2.11	0.328
14.44	0.064	0.266	0.108	0.094	3.80

Table II. Analyses of Synthetic Blends[a] of Pure Olefins

(Concentrations in mole per cent)

Sample[b]	$RCH{=}CH_2$ Known	$RCH{=}CH_2$ Calcd.	$RR'C{=}CH_2$ Known	$RR'C{=}CH_2$ Calcd.	$RR'C{=}CHR''$ Known	$RR'C{=}CHR''$ Calcd.	*trans*-$RCH{=}CHR'$ Known	*trans*-$RCH{=}CHR'$ Calcd.	*cis*-$RCH{=}CHR'$ Known	*cis*-$RCH{=}CHR'$ Calcd.
1	18.6	19	34.3	34	10.8	8	14.5	12	21.8	27
2	17.2	18	28.9	31	20.3	16	11.2	12	22.4	24
3	27.2	31	19.1	22	16.9	23	12.3	14	24.5	10
4	23.2	26	16.3	18	29.0	34	10.6	13	20.9	9
5	17.1	20	28.8	30	20.4	19	11.2	14	22.5	17

[a] Each blend was prepared to contain several members of each class.

[b] Samples 1 and 2 were analyzed using the 1.5-mm. cell and CS_2 as solvent. Samples 3, 4, and 5 were analyzed in a 0.15-mm. cell with *n*-heptane as the solvent.

Considering the complexity of this type of analysis, the results of Table II show a reasonable accuracy for all classes except the *cis*-RCH=CHR′. The poor accuracy for this latter class must be considered an inherent limitation of the present method. In Table III are given the average errors based on the results of Table II and three other synthetics in terms of mole per cent of total sample.

Table III. Average Errors of Total Sample for Various Classes of Olefins, Based on Results of Synthetic Blends

(Mole %)

	RCH=CH₂	RR′C=CH₂	RR′C=CHR″	*trans*-RCH=CHR′	*cis*-RCH=CHR′
Average error	2.5	1.7	3.6	1.3	5.0

The agreement between blended and calculated compositions is fairly good for the $RCH{=}CH_2$, $RR'C{=}CH_2$, and *trans*-RCH=CHR′ classes, and that the RR′C=CHR″ and *cis*-RCH=CHR′ classes contribute the major discrepancies. This analysis was originally set up using a 0.15-mm. cell and *n*-heptane as the solvent. In terms of accuracy, the 0.15-mm. and 1.5-mm. cell procedures were equivalent. However, for reasons discussed in the next section the authors prefer the thicker cell technique.

USE AND INTERCHANGE OF COMPARATIVELY THICK ABSORPTION CELLS. In quantitive infrared analysis the tendency has been to use liquid cells of approximately the same path length as required for obtaining good qualitative spectra of paraffins—i.e., path lengths in the range of 0.1 to 0.2 mm. When using these thin cells, some or all of the following difficulties are frequently encountered:

When a given thin cell is used and dilutions are not employed, the cell absorbance contributes to the "apparent" absorptivities. These will therefore change if there is cell fogging or deterioration and frequent recalibrations may be necessary.

When dilutions are necessary in order to obtain good absorbance data at some of the analytical wave lengths, the problem arises of properly correcting for the solvent and cell and recalculating all the data to a common dilution basis.

Deviations from Beer's law are more likely to occur in concentrated solutions.

The use of comparatively thick cells offers a means of minimizing most of the above difficulties. The thicker the cell, the closer one can approach the situation that exists in ultraviolet spectrometry where it is possible to obtain relatively absolute data. At present the obtaining of calibration data in the infrared for nonroutine liquid analysis accounts for an appreciable part of the time spent in making such an analysis. If calibration data can be obtained with the cell and solvent properly corrected out, these data should have a long-term utility.

A cell approximately 1.5 mm. thick (cell A) was used to obtain all the calibration data which were incorporated into the matrix of Table I. Then a second cell (cell B) was assembled, and its thickness relative to the first cell was found by placing the same solution in both cells and obtaining absorbances at five or six wave lengths. The ratio of the absorbances of each cell at a given wave length, corrected for the absorbance of the appropriate cell filled with solvent, gave the ratio of the path lengths. A 2-mm. cell (cell C) was purchased from the Perkin-Elmer Corp. and compared in the same way to the original cell *A*. In no case was the absolute path length determined. The ratio of cell lengths were found to be as follows:

	Cell B	Cell C
Ratio of path length (relative to cell A)	0.84	1.28

It was of interest to see how readily the matrix which had been determined for one cell could be used on other cells. Absorbance data were obtained for several olefin mixtures in each of the three cells, and these data were corrected only for the appropriate cell plus solvent absorbance. Then the original matrix that appears in Table I was used with the corrected absorbance data for each cell to calculate the olefinic content. Of course, the total calculated moles of olefin differed with each cell because of varying path lengths, but the group-type distributions based on total observed olefins are as shown in Table IV.

Table IV indicates the feasibility of switching cells which are approximately of the same path length, and the continued use of the original matrix. The results from cells A and B, which differ in thickness by approximately 16%, agree fairly well. The agreement between cells A and C, which differ in thickness by approximately 28%, is somewhat poorer. This indicates the advisability of using cells of approximately the same thickness. The absolute olefin content as determined in one cell is related to that as determined in the other cell by the ratio of the path lengths (provided that the dilutions for both cells are placed on a common basis). For samples which are mixtures of olefins and nonolefins, the authors prefer to determine the relative olefin distribution spectrally and to report a separate total olefin content as determined by the capillary tube method for Criddle and LeTourneau (*4*) or by the chromatographic procedure described here.

Chromatographic. This analysis was applied to two types of samples—namely, products of dehydrogenation experiments and to gasolines. The samples contained saturates, olefins, and aromatics. For reasons outlined above, a chromatographic separation was employed. Sufficient sample was charged to the column so that approximately 10 or more 0.9-ml. cuts in the olefin region could be obtained. These cuts were selected by obtaining their spectra and observing when the characteristic olefin bands were present or from a plot of refractive index *vs.* cut number. The

Table IV. Analysis of Olefin Mixtures Using a Given Matrix on Data Obtained in Three Relatively Thick Absorption Cells of Differing Path Lengths

	Synthetic 1				Synthetic 2				Olefin Concentrate			Gasoline		
Type	Cell[a] A	Cell[a] B	Cell[a] C	Known	Cell A	Cell B	Cell C	Known	Cell A	Cell B	Cell C	Cell A	Cell B	Cell C
$RCH{=}CH_2$	19	19	24	17.6	18	19	20	17.2	46	46	48	21	20	20
$RR'C{=}CH_2$	34	32	28	32.5	31	30	25	28.9	23	25	23	11	11	8
$RR'C{=}CHR''$	8	9	8	11.3	16	16	18	20.3	24	22	24	34	35	35
$RCH{=}CHR'$ (*trans*)	12	13	16	13.7	12	12	14	11.2	5	4	5	11	10	11
$RCH{=}CHR'$ (*cis*)	27	27	25	24.9	23	23	24	22.4	2	3	0	23	24	26

[a] Data for matrix of Table I obtained using cell A. See text for ratios of cell path lengths.

Table V. Comparison between Olefin Portions of Synthetic Blends before and after Chromatography

(Mole %)

	$RCH{=}CH_2$		$RR'C{=}CH_2$		$RR'C{=}CHR''$		*trans*-$RCH{=}CHR'$		*cis*-$RCH{=}CHR'$	
Sample	Before	After	Before	After	Before	After	Before	After	Before	After
1[a]	44	46	19	23	29	24	5	5	3	2
2[b]	4	4	54	50	33	38	7	5	3	3
3[b]	20	22	30	32	14	13	14	15	22	18
4[b]	49	55	22	23	21	18	7	4	1	0

[a] 1.5-mm. cell with CS_2 solvent.
[b] 0.15-mm. cell with *n*-heptane solvent.

selected cuts were reblended in equal volumes and then analyzed for olefins.

EFFECT OF COLUMN ON OLEFIN DISTRIBUTION. It was important to see if the chromatographic separation affected the olefinic distribution by such things as selective separation, isomerization, or polymerization. Several synthetic samples were prepared and analyzed before and after chromatographic separation. The olefin mixture was analyzed spectrally, then blended with Philips spectral grade iso-octane and Merck reagent grade xylenes and chromatographically separated. In Table V the results of these analyses are presented.

The results in Table V give no definite evidence to indicate a general trend toward any separation within the olefins themselves on the column if the olefin cuts are reblended. The over-all average difference between the before and after results generally is of the same magnitude as the over-all average error in the olefin analysis. Thus, any change in olefin distribution due to the chromatographic separation is not much different from the inherent inaccuracies of the olefin analysis itself. The results tend to confirm the conclusions of Johnston and coworkers (*8*) that "there is little, if any, change in the olefin skeletal structure or double bond position."

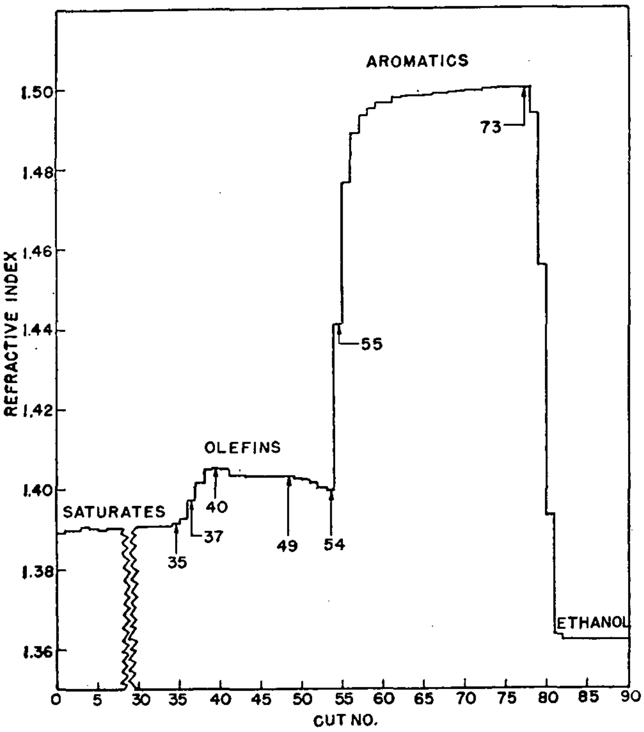

Figure 3. Chromatogram of Synthetic Sample Containing Complex Mixture of Saturates, Olefins, and Aromatics

USE OF CHROMATOGRAM FOR RECOMBINATION AND CALCULATION OF TOTAL SATURATES, OLEFINS, AND AROMATICS. Figure 3 is a plot of refractive index *vs.* cut number of a typical chromatographic separation. The sample used for this separation was a synthetic blend, and it differed from other synthetic blends that were chromatographed in that a complex mixture of paraffins and aromatics was used with the olefins instead of only iso-octane and xylenes. In previous separations the chromatogram was used to calculate total paraffin, olefin, and aromatic content on a volume per cent basis. The chromatogram of Figure 3 illustrates the calculation procedures for all chromatographic separations. The refractive indices of the truly paraffinic cuts will remain almost constant if the paraffins have approximately the same molecular weight. When the first olefin starts to issue from the column, the refractive index of this cut will show a definite increase unless the saturate portion contains a very high concentration of cycloparaffins. This is the beginning of the transition zone where the separation between paraffins and olefins is incomplete and in Figure 3 occurs at cut 35. At cut 55 the second sharp break in refractive index occurs and this indicates that aromatics are beginning to issue from the column, and an olefin-aromatic mixing zone is encountered. Spectra of the cuts in each transition zone confirm the point where olefins and aromatics first begin to come through the column. This spectral test should be applied if the saturates are very rich in cycloparaffins as the latter may have higher refractive indices than the olefins. In Figure 3 cuts 1 to 34 are considered pure paraffins. From cut 35 onward the cuts contain olefins and decreasing amounts of paraffins and the relative concentrations are computed assuming additivity of refractive indices. The refractive index of cut 34 is taken as typical of the paraffins and the refractive index of cut 40 is taken as typical of the olefins. In the chromatogram the refractive indices of cuts 54 and 73 are taken as typical of the olefins and aromatics, respectively, for the calculations of distribution in the second transition zone. On occasion it has been found that the refractive index of the olefin cuts will rise to a maximum and then fall off slightly until the aromatics start to come through. For chromatograms of this type the maximum refractive index of the olefin fraction is taken as typical of the olefins up to that cut, and the following cuts are assumed to be all olefin until the cut where aromatics start to become apparent. The refractive index of the cut just before the point is used in the calculation of olefin-aromatic distribution. The chromatogram in Figure 3 is an example of this behavior, and cuts 41 through 54 were assumed to be pure olefins in the calculation. This dropping off of refractive index in the olefin region is due in large part to a partial separation of the olefins on the column. In Figure 4 the spectra of cuts 37, 49, and 54 (see Figure 3 for the chromatogram) are shown in the 9.8- to 11.5-micron region. It is seen that there is an appreciable separation of olefins, and this is the reason why the olefin cuts are reblended instead of using a central heart cut as representative of the distribution. In Table VI results of the chromatographic analysis for total paraffin-olefin-aromatic are given for several synthetic samples.

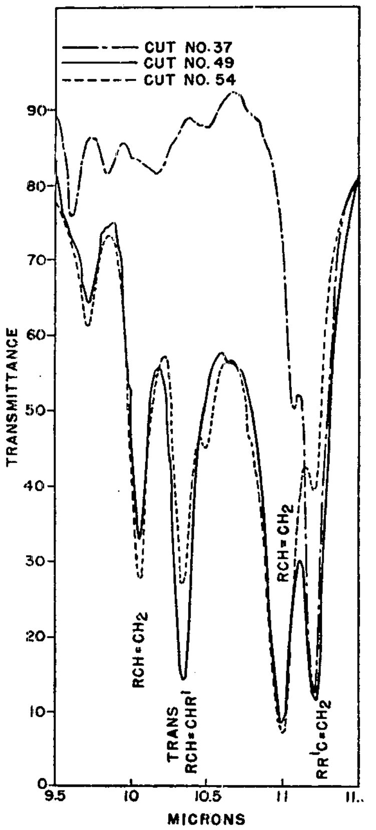

Figure 4. Region of 9.5 to 11.5 Microns of Selected Olefin Cuts

See Figure 3 for chromatogram. Illustrating partial separation of olefins on chromatograph column

If it is necessary to obtain an olefin fraction for spectral analysis, the use of this chromatographic method gives data which permit the above type of calculation. However, if only a total paraffin-olefin-aromatic determination is desired, the capillary tube method (*4*) is to be preferred, as it is much more rapid. In reblending olefinic cuts for spectral analysis, it has been found best to blend from the point where olefins begin to come through to the point just before aromatics are present. This procedure does result in some error as olefins are lost in the transition zone between olefins and aromatics, although this is not too serious, as seen in Table V. The first cuts used in reblending for the spectral analysis of group-type olefins contain some paraffins. In Figure 3 cuts 35 through 54 would be considered the usable olefin fraction, and by assuming additivity of the refractive indices the paraffin content in these cuts is calculated to be 13%. The group-type olefin bands generally have a much larger absorptivity than do paraffins at the same wave lengths. The presence of paraffins will introduce some error, but this has been found to be relatively small (see applications for further evaluation).

Several of the synthetic samples in Table V were also analyzed for total olefins and aromatics (which were xylenes) using ASTM Method D 875 (*1*). The results were in excellent agreement with those obtained from the chromatographic analyses. However, the same two methods, when applied to gasolines, gave the results tabulated in Table VII.

The agreement between olefin and aromatic contents is not good. It appears that in the chemical method more than just the olefins are being brominated, and this accounts for the higher olefin content as determined chemically. The authors' findings are similar to those reported and discussed by Criddle and Le Tourneau (*4*), and it is concluded that the chromatographic method gives a better analysis than the chemical method used above for samples as rich in olefins as these.

Table VI. Comparison between Blended Concentrations of Saturates, Olefins, and Aromatics and Concentrations Obtained by Chromatographic Fractionation

(Results in volume %)

	Saturates (Iso-octane), %		Olefins, %		Aromatics (Xylenes), %	
Sample	Blended	Calcd.	Blended	Calcd.	Blended	Calcd.
1	60.0	61.4	20.0	19.3	20.0	19.3
2	55.5	55.3	20.0	19.3	24.5	25.4
3	70.0	69.5	5.0	5.9	25.0	24.6
4	69.6	70.0	8.7	7.8	21.7	22.2

Table VII. Comparison of Chemical and Chromatographic Determination of Volume Per Cent Olefins and Aromatics in Gasolines

	Olefin		Aromatics	
Gasoline	ASTM D 875	Chromat.	ASTM D 875	Chromat.
Polyform distillate	39.8	26.9	8.9	17.3
Thermal cracked	54.1	36.9	0.0	11.8
Cat. blending stock	59.2	44.7	3.8	18.5

APPLICATIONS

In the application of these methods to dehydrogenation products, the saturates used as the reactants were analyzed by conventional infrared methods. The reaction products contained paraffins, olefins, and aromatics. An attempt was made to analyze distillation cuts of the total mixture using the group-type olefin method in conjunction with a specific paraffin analysis. Analysis of synthetic samples blended to simulate the actual samples showed that this procedure gave results for the paraffins which were in error by as much as 10% on total sample, although the olefin analysis was of the accuracy discussed above. These same synthetics were also analyzed as a pure olefin mixture, neglecting all paraffins. In the two cases the olefin analyses agreed very well. Apparently the approximation of the olefin

Table VIII. Olefin Analysis of a Synthetic and a Dehydrogenation Experiment Sample Containing Paraffins and Olefins

(Olefin content expressed as mole % of total olefin content).

	Synthetic			Sample	
	Known	Paraffin-olefin matrix calcd.	Olefin matrix calcd.	Paraffin-olefin matrix calcd.	Olefin matrix calcd.
$RCH{=}CH_2$	20.4	19	20	14	13
$RR'C{=}CH_2$	13.8	13	15	5	5
$RR'C{=}CHR''$	13.9	12	16	11	10
$RCH{=}CHR'$ (*trans*)	27.3	22	26	41	41
$RCH{-}CHR'$ (*cis*)	24.6	34	23	29	31

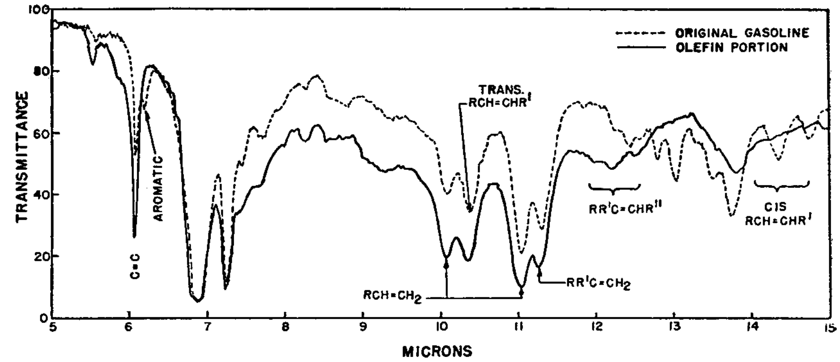

Figure 5. Infrared Spectra of Total Thermally Cracked Gasoline and Olefin Portion of Same Gasoline as Isolated Chromatographically

Table IX. Olefin Data for Three Representative Gasolines

(Different olefin types are given in mole % of the olefin portion. Total olefin portion given as volume % of total gasoline)

Gasoline	Total Olefins, %	RCH= CH$_2$, %	RR'C= CH$_2$, %	RR'C= CHR'', %	*trans*- RCH= CHR', %	*cis*- RCH= CHR', %
Polyform distillate	27	21	6	35	22	16
Thermal cracked	37	32	10	30	14	14
Cat. blending stock	45	9	13	42	20	16

absorbances at the paraffin points was rather poor and resulted in poor paraffin results. It was evident that the neglect of moderate paraffin contamination did not seriously affect the olefin analysis. Table VIII shows the olefin results of a synthetic sample in which paraffins are present to the extent of 38% by volume, and of an olefin concentrate from a dehydrogenation experiment in which the paraffin content was of the order of 20% by volume. A group-type olefin-specific paraffin matrix was used in one instance, and the calculation was repeated using the group-type olefin matrix alone.

Table VIII shows that moderate paraffin contamination in the olefin cuts of a chromatographic separation will not seriously affect the ordinary accuracy of the olefin analysis. However, in order to obtain better information on the paraffins, chromatographic separation was used. It was then possible to improve the paraffin accuracy so that the average error was approximately ±1% of total sample. The results for specific paraffins before and after reaction permitted the evaluation of any isomerization accompanying the dehydrogenation.

In the application to gasolines, only the olefinic distributions were determined spectrally. The chromatogram permitted the determination of total saturates, olefins, and aromatics. The results for three gasolines are presented in Table IX.

In Figure 5 the spectra of a total thermal cracked gasoline and of the olefin portion of the chromatographically separated gasoline are shown. The marked changes of absorption in the RR'C=CHR'' and RCH=CHR' (*cis*) regions are to be noted.

In any concentration procedure, of which chromatography is an example, errors made in the spectral analysis of the concentrated produce are reduced by the concentration factor when related back to total sample. Thus in Table IX the absolute error in the determination of any class of the polyform distillate is reduced by the factor of 0.27 when related back to total sample. This assumes that there is no error in the determination of the concentration factor.

ACKNOWLEDGMENT

The aid of the Analytical Section in providing the ASTM analyses of particular samples is gratefully acknowledged.

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Accurate Analysis with an Infared Double-Beam Spectrophotometer

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The purpose of this work was to examine the effect of instrumental factors on the analytical accuracy attainable with an infrared double-beam spectrophotometer. For xylene-ethylbenzene mixtures analytical results well within 1% accuracy can be obtained if instrument corrections are applied and averages of at least four recordings are taken. The technique of "difference spectra" can yield mean values with a deviation of not more than ±0.1%. Corrections for finite slit widths must be made. Empirical corrections are preferable to assumptions concerning distribution of spectral impurity and of response coupled with geometrical approximations to the shape of the absorption band. Over an appreciable range of concentrations the tangent to the absorbance-concentration curve in the optimum transmittance region is a closer approximation to the observed relationship than the chord drawn through a point on the curve. The technique of difference spectra is speedy and accurate, compared with the cell in-cell out method, where the spectra of two samples are very similar.

A RIGOROUS application of simultaneous equations presupposes an exact knowledge of every one of the coefficients. In spectrophotometry this condition is not fulfilled. The degree of analytical accuracy which can be achieved with a fully automatic infrared double beam spectrophotometer depends upon instrumental factors and the availability of nonoverlapping absorption bands. The instrumental factors include random errors and systematic corrections. It is shown for the example of mixtures of the xylene isomers with ethylbenzene that analytical results can be obtained with an accuracy of within ± 0.4% and even within ± 0.2% of the total if the random errors are reduced by averaging over four or more recordings and if the systematic corrections are applied to the readings taken from the records. The equations are then solved using the corrected experimental data. By the method of difference spectra at fixed wave lengths mean values can be obtained with a deviation of not more than ± 0.1% from the composition of test samples.

EXPERIMENTAL FACTORS

Random Errors. With a Perkin-Elmer Model 21 double beam instrument records in the rock salt region commonly repeat with an accuracy of the order of the width of the trace when no adjustments are made between consecutive runs. Figure 1 shows for a number of recording speeds three neighboring pyridine bands in the 5-micron region. These bands were scanned six times at each speed. It is clear that the autosuppressor has a slight effect upon the recorded position of the peak of each band. The two single scans are with and without autosuppression and a slight shift toward longer wave lengths is apparent when the autosuppressor is not applied. Throughout this investigation the autosuppressor is used and the reproducibility of the wave-length positions of the bands is extremely good. There are, however, small random fluctuations of intensity similar to those shown by White and Liston (*21*). With a recording speed of 1 minute per micron and slits of 0.05-mm. width the largest of these variations were 1.7% when two values of the amplifier gain were selected; at each amplification the bands were scanned four times. That these were irregular fluctuations was confirmed by scanning these bands 10 times and numbering each trace on the chart consecutively. Thus, for one band the tenth scan gave the smallest absorption intensity, for the next band the ninth and the tenth, and for the third band the ninth scan. Similarly, for one band the second and fourth records gave the highest absorption, for the next band the first, second, and third, and for the third band the first record. It is considered that frictional forces between the pen and the recording paper as well as frictional forces in the servomechanism have significant influence on such errors; this is borne out by close examination of the motion of the pen. Lack of stability in the output stage of the amplifier also contributes to these errors, since better agreement between consecutive recordings is obtained when the pen is set to the zero transmittance line before each scan. This agrees with recent findings of Bowman and Tarpley (*5*) and of Hausdorff, Sternglanz, and Williams (*9*). The balance control of the amplifier is used to move the effective zero transmittance point of the optical attenuator and the amount by which the amplifier is biased is referred to as the off-balance signal.

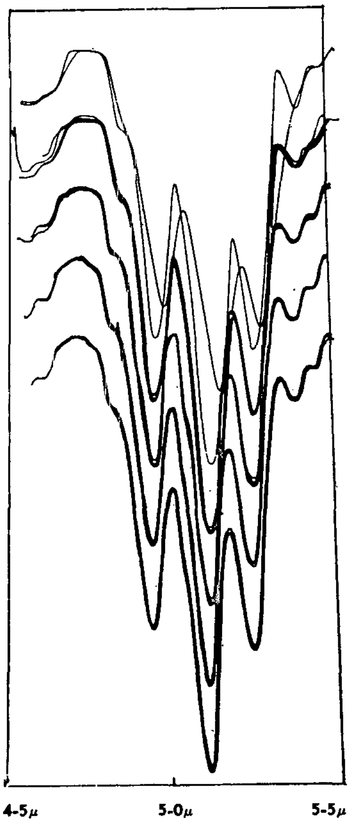

Figure 1. Six Consecutive Scans with Autosuppression of Three Neighboring Pyridine Bands in the 5-Micron Region

Recording speeds. 0.5, 1, 3, and 8 minutes per micron
Slit width. 0.05 mm.
Amplifier gain setting No. 5 used with Perkin-Elmer Model 21

Systematic Corrections. Optical Attenuator. The Perkin-Elmer double-beam instrument uses a comblike shutter which is moved in or out of one optical path with the object of reducing its intensity until it is equal to that of the beam containing the absorbing sample (*8, 16, 23*). From the position of this comb along its direction of motion normal to the reference beam, the percentage transmittance of the sample is recorded. It is sometimes said that the aperture of the optical attenuator must vary in direct proportion to its displacement relative to the position of the reference beam. Since the comblike shutter of the Perkin-Elmer Model 21 instrument shows deviations from linearity, appropriate corrections must be made to the absorbance scale. (Details concerning the nonlinearity of the "optical wedge" will be published elsewhere.) These empirical corrections are plotted in Figure 2. The correction curve in this figure was obtained by varying the slit width by known amounts when the shutter of the sample beam was closed and a test signal was injected to balance the energy in the reference beam. Very wide slits were used to avoid apparent wedge errors caused by the entrance and exit slits not closing simultaneously.

Finite Slit Width. Comparatively wide slits are used in infrared spectrophotometers. Finite slit width leads to spectral impurity and deviations from Lambert-Beer's law. Proposals have been made (*7, 18, 19*) for approximate corrections of the absorbance measured with finite slit widths. Since, however, empirical corrections can be employed, these are much to be preferred to assumptions concerning distribution of spectral impurity and response which are usually combined with geometrical approximations to the shape of the absorption band.

For each component of a mixture an analytical wave length is selected at which this component shows appreciably stronger absorption than any of the other components. To assess the deviations from Lambert-Beer's law, measurements of absorbance must be made with various concentrations of each component of a mixture at the analytical wave lengths. For a given error in transmittance the fractional error in measured concentration is least at 37% transmittance. Since the minimum of the fractional concentration-per cent transmittance curve is very broad and flat, a tangent to the absorbance-concentration curve may be drawn at any transmittance between 25 and 50% in order to correct the measured absorption coefficient for deviations from Lambert-Beer's law. To make the measurements which are necessary for the plotting of absorbance-concentration curves, a sealed cell of carefully calibrated path length must be used. [The thickness of the cells was determined by interference fringes (*15*).]

EXPERIMENTAL RESULTS

Xylene-Ethylbenzene Mixtures. Convenient analytical wave lengths for xylene-ethylbenzene mixtures (*14, 15, 22*) are 12.59 microns for *p*-xylene, 13.02 microns for *m*-xylene, 13.48 microns for *o*-xylene, and 14.36 microns for ethylbenzene. The analyses considered in this paper were made with "slit program 3"—i.e., a slit width of 0.156 mm. at 10 microns and 0.412 mm. at 14 microns. Attention must be paid to the relative proportions of the components of any particular mixture, as there is a comparatively weak *m*-xylene band at 14.45 microns and a weak and broad ethylbenzene band at 13.4 microns. However, the resolution of the instrument is good enough to show an absorption peak at 14.36 microns when the proportion of ethylbenzene is

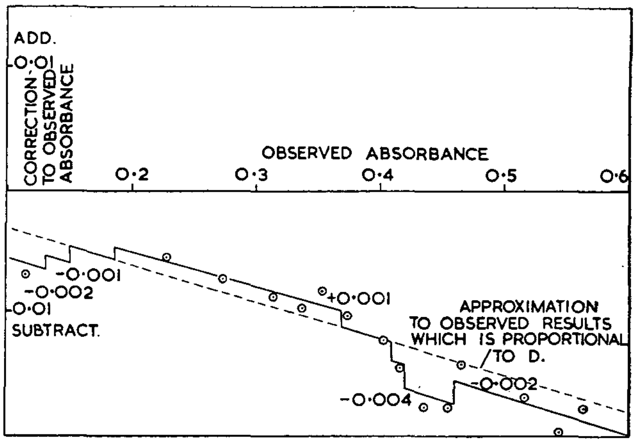

Figure 2. Corrections for Nonlinearity of Optical Wedge of Perkin-Elmer Model 21 Spectrophotometer

Trend of experimental points is approximated by the heavy lines which are used for correcting recorded data

Table I. Data Relating to the Construction of Absorbance-Concentration Diagrams

Component	Range of Concn. in Iso-octane, G./Ml.
p-Xylene	0.00102-0.02455
m-Xylene	0.00158-0.01897
o-Xylene	0.00045-0.01432
Ethylbenzene	0.00106-0.03476

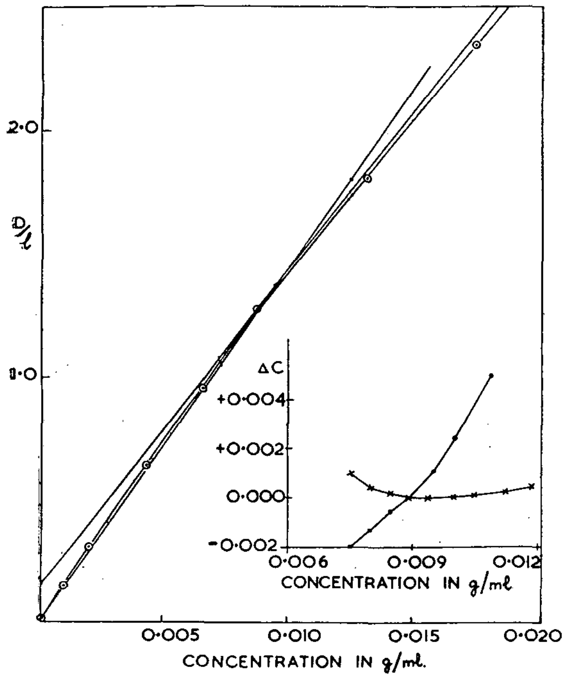

Figure 3. Absorbance-Concentration Diagram for Ethylbenzene with Tangent and Chord Drawn at a Point in Optimum Transmittance Region

Inset shows deviations from experimental data in the neighborhood of the selected concentration when tangent, x, is drawn and when chord, °, is drawn

about one fifth of that of *m*-xylene. It appears that in spite of the close neighborhood of the weak ethylbenzene band to the analytical wave length of *o*-xylene (13.48 microns), this isomer is the one which is determined with the relatively highest degree of accuracy, because the *o*-xylene band at 13.48 microns is by comparison very strong. The ethylbenzene band at 14.36 microns is comparatively weak and it may therefore happen that the analytical wave length for ethylbenzene falls on the side of the *m*-xylene band at 14.45 microns. This tends to increase the uncertainty of the ethylbenzene determination.

Deviations from Lambert-Beer's Law. Absorbance-concentration diagrams of the type shown in Figure 3 were constructed from measurements at the analytical wave lengths for each of the xylene isomers and ethylbenzene covering the range of concentrations given in Table I.

Over an appreciable range of concentrations the tangent to the absorbance-concentration curve in the optimum transmittance region is a closer approximation to the observed relationship than the chord drawn through a point on the curve. This is illustrated by the inset of Figure 3 where the crosses show the insignificant variation of the difference of concentration values between the tangent and the absorbance-concentration curve, whereas the dots show the rapid change of the corresponding differences for the chord. Therefore, the tangent method was adopted. The slope of the tangent is, for the particular component of a mixture, its absorbance per unit of the concentration scale at the analytical wave length of the material under consideration. To correct the absorbance of the mixture at the analytical wave lengths the intercepts of the corresponding tangents with the absorbance axis were subtracted. Each corrected absorbance must be multiplied by the dilution factor of the solution.

This factor is determined by the desirability of working in the optimum transmittance region. The concentration values calculated from equations containing the absorption coefficients were further corrected for the difference on the concentration scale between the empirical absorbance-concentration curve and its tangent (Figure 4). The final results for seven synthesized mixtures are given in Tables II and III, which are comprised of data relating to one four-component, four three-component, and two two-component mixtures. It is apparent from these tables that the totals fall between 99 and 101%, apart from one case of 102.9%, for a mixture which contains predominantly ethylbenzene (mixture F). In a case like this the base-line method gives higher accuracy than the setting up of simultaneous equations. The agreement between the measured and the actual concentrations of ethylbenzene is best in the case of the four-component mixture A where there was good resolution at all the analytical wave lengths (Figure 5). Mixture E offers a useful illustration of the pitfalls when components have overlapping absorption bands. Because the analytical wave length of ethylbenzene lies on the side of the *m*-xylene band at 14.45 microns one derives from a set of four equations a small amount of ethylbenzene (0.3%), although mixture E had been synthesized from the three xylene isomers without the addition of any ethylbenzene (Table III). To average over the random errors four scannings were taken of the spectra of the mixtures A to G.

The importance of maintaining a constant off-balance signal for accurate measurements was mentioned previously. Two industrial samples of xylene-ethylbenzene mixtures were examined without and with adjustment of this signal (Tables IV and V). Mean errors of 0.49 and 0.93% (depending on the number of

Table II. Absorption Coefficients and Intercepts on Absorbance Axis of Xylene Isomers and Ethylbenzene

	Absorption Coefficients in a 0.272-Mm. Cell							
	p-Xylene		*m*-Xylene		*o*-Xylene		Ethylbenzene	
Wave-Length, μ	Absorption coefficient	Intercept	Absorption coefficient	Intercept	Absorption coefficient	Intercept	Absorption coefficient	Intercept
12.59	72.4	0.016	1.070	...	0.477	...	2.88	...
13.02	0.866	...	67.0	0.033	0.883	...	5.04	...
13.48	0.175	...	0.465	...	112.3	0.014	11.87	...
14.36	0.033	...	5.63	...	0.246	...	35.7	0.033

Table III. Analysis of Synthesized Mixtures of Xylenes and Ethylbenzene by Infrared Spectrophotometry

	p-Xylene, %			*m*-Xylene, %			*o*-Xylene, %			Ethylbenzene, %			
Mixture	Actual	Meas.	Diff.	Actual	Meas.	Diff.	Actual	Meas.	Diff.	Actual	Meas.	Diff.	Total, %
A	34.3	33.6	−0.7	4.07	4.07	0.00	50.3	50.3	0.0	11.4	11.4	0.0	99.4
B	1.39	1.27	−0.12	4.65	4.78	+0.13	94.2	93.7	−0.5	0.00	0.00	0.00	99.7
C	1.15	1.17	+0.02	20.1	20.4	+0.3	78.8	78.4	−0.4	0.00	−0.75	−0.75	99.2
D	39.9	39.8	−0.1	2.79	2.90	+0.11	56.9	57.4	+0.5	0.00	+0.20	+0.20	100.3
E	39.9	40.1	+0.2	2.79	2.70	−0.09	56.9	58.0	+1.1	0.00	+0.30	+0.30	101.1
F	0.00	1.49	+1.49	27.1	27.4	+0.3	0.00	0.88	+0.88	72.9	73.1	+0.2	102.9
G	0.00	0.83	+0.83	51.6	50.4	−1.2	0.00	1.17	+1.17	48.3	48.4	+0.1	100.8

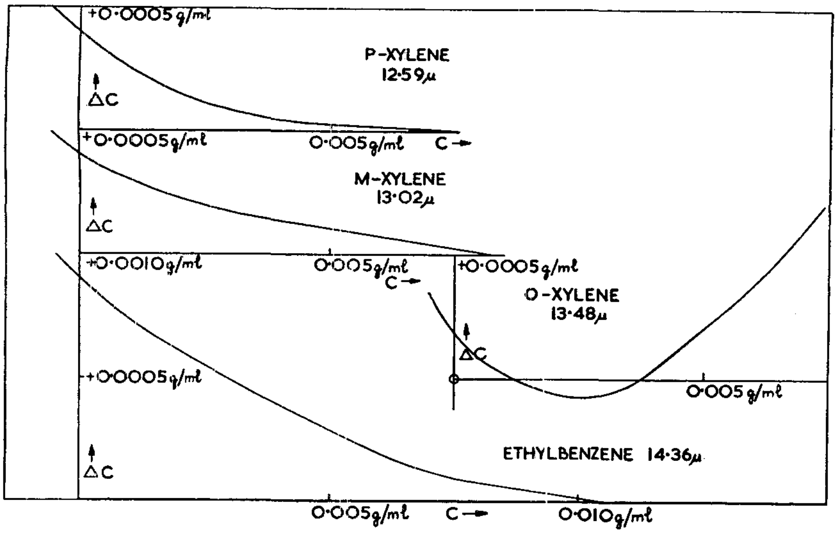

Figure 4. Empirical Corrections, Δc, of Concentrations Derived from Simultaneous Equations for Xylene Isomers and Ethylbenzene

individual recordings) were obtained without adjustment of the off-balance control (Table VI); a mean error of 0.2% was obtained when such adjustment was made before each scanning (Table VII). The content of paraffins in these two samples was estimated from their refractive indices on the assumption that 1% of paraffinic material reduces the refractive index (n_D^{20}) by approximately 0.001. The paraffinic material was also separated from a xylene cut and its absorption spectrum was recorded so that allowance could be made for its contribution to the absorbance at the analytical wave lengths.

Table IV. Repeatability of Analysis of Two Industrial Xylene-Ethylbenzene Mixtures by Infrared Spectrophotometry

(Without adjustment of the off-balance control of the instrument)

Sample	Analysis	*p*-Xylene, %	*m*-Xylene, %	*o*-Xylene, %	Ethylbenzene, %	Total, %, Including 9.0% Paraffins
1	1a	24.0	51.1	2.96	14.6	101.7
	1b	24.7	50.2	3.01	13.3	100.2
	1c	25.2	47.8	3.05	13.6	98.6
	1d	25.9	49.0	3.12	13.0	100.0
	1e	25.4	51.2	2.95	12.7	101.3
	1f	26.0	49.4	3.32	12.6	100.3
	1g	26.2	49.7	3.10	13.1	101.1
	1h	26.0	49.0	3.13	13.9	101.0
	1i	26.2	48.5	3.14	14.2	101.0
Mean		25.7	49.5	3.09	13.3	100.6
2	2a	25.6	50.7	4.14	12.6	102.0
	2b	27.4	56.1	3.66	13.1	109.3
	2c	24.1	48.4	3.63	11.6	96.7
	2d	25.4	52.9	3.66	12.4	103.4
	2e	24.9	56.5	3.84	11.7	105.7
	2f	26.1	53.8	3.80	12.4	105.1
Mean		25.6	53.1	3.79	12.3	103.7

Table V. Repeatability of Analysis of Two Industrial Xylene-Ethylbenzene Mixtures by Infrared Spectrophotometry

(With adjustment of the off-balance control of the instrument)

Sample	Analysis	*p*-Xylene, %	*m*-Xylene, %	*o*-Xylene, %	Ethylbenzene, %	Total, %, Including 9.0% Paraffins
1	1j	25.0	49.0	2.90	14.0	99.9
	1k	25.2	48.4	2.92	13.8	99.3
	1l	25.0	47.9	2.87	13.4	98.2
Mean		25.1	48.4	2.90	13.7	99.1
2	2g	25.3	51.4	3.52	12.1	101.3
	2h	25.9	51.2	3.41	11.9	101.4
	2i	25.4	50.8	3.49	12.6	101.3
Mean		25.5	51.1	3.47	12.2	101.3

It is important for analytical purposes to ascertain whether the infrared spectrum indicates additional constituents. Reference has already been made to the presence of paraffinic hydrocarbons in a mixture of C_8 aromatic compounds. Measurements of two further industrial samples of xylene-ethylbenzene mixtures reveal the presence of additional aromatic hydrocarbons. Sample 3 shows a weak band at 13.74 microns which might be caused by $^1/_2$% of toluene. If the contribution of this amount of toluene to the absorption is allowed for at 14.36 microns, it reduces the ethylbenzene concentration from 15.1 to 14.9%. The analysis of sample 3 would therefore yield 24.9% *p*-xylene, 44.4% *m*-xylene, 6.6% *o*-xylene, 14.9% ethylbenzene, approximately 0.5% toluene, and 9.0% paraffins, making a total of 99.3%. The spectrum of sample 4 shows a weak band at 14.83 microns and, since the origin of this band is uncertain, the provisional analysis of this sample is subject to slight revision. The present analysis is 7.8% *p*-xylene, 27.4% *m*-xylene, 49.9% *o*-xylene, 2.8% ethylbenzene, and 12% paraffins, making a total of 99.9%.

DIFFERENCE SPECTRA

By difference spectra is meant spectra obtained with a specimen of known composition in the reference beam. This technique is adopted to reveal differences in the spectra of the samples in the two beams, hence the name difference spectra. In the American literature (*2–4, 6, 10–13, 20, 24*) this technique is sometimes referred to as differential spectra.

A double-beam instrument permits the direct recording of difference spectra and this may be useful in determining with a

Table VI. Deviations from Mean of Data Given in Table IV

Sample	Analysis	*p*-Xylene	*m*-Xylene	*o*-Xylene	Ethylbenzene
1	1a	−1.7	+1.6	−0.13	+1.3
	1b	−1.0	+0.7	−0.08	0.0
	1c	−0.5	−1.7	−0.04	+0.3
	1d	+0.2	−0.5	+0.03	−0.3
	1e	−0.3	+1.7	−0.14	−0.6
	1f	+0.3	−0.1	+0.23	−0.7
	1g	+0.5	+0.2	+0.01	−0.2
	1h	+0.3	−0.5	+0.04	+0.6
	1i	+0.5	−1.0	+0.05	+0.9
Mean deviation		0.6	0.8	0.08	0.5
2	2a	0.0	−2.4	+0.35	+0.3
	2b	+1.8	+3.0	−0.13	+0.8
	2c	−1.5	−4.7	−0.16	−0.7
	2d	−0.2	−0.2	−0.13	+0.1
	2e	−0.7	+3.4	+0.05	−0.6
	2f	+0.5	+0.7	+0.01	+0.1
Mean deviation		0.8	2.4	0.14	0.4

Mean error for sample 1 over all nine determinations, 0.49%
Mean error for sample 2 over all six determinations, 0.93%

Table VII. Deviations from Mean of Data Given in Table V

Sample	Analysis	*p*-Xylene	*m*-Xylene	*o*-Xylene	Ethylbenzene
1	1j	−0.1	+0.6	0.00	+0.3
	1k	+0.1	0.0	+0.02	+0.1
	1l	−0.1	−0.5	−0.03	−0.3
Mean deviation		0.1	0.37	0.017	0.23
2	2g	−0.2	+0.3	+0.05	−0.1
	2h	+0.4	+0.1	−0.06	−0.3
	2i	−0.1	−0.3	+0.02	+0.4
Mean deviation		0.23	0.23	0.04	0.27

Mean error for sample 1 over all three determinations, 0.18%
Mean error for sample 2 over all three determinations, 0.19%

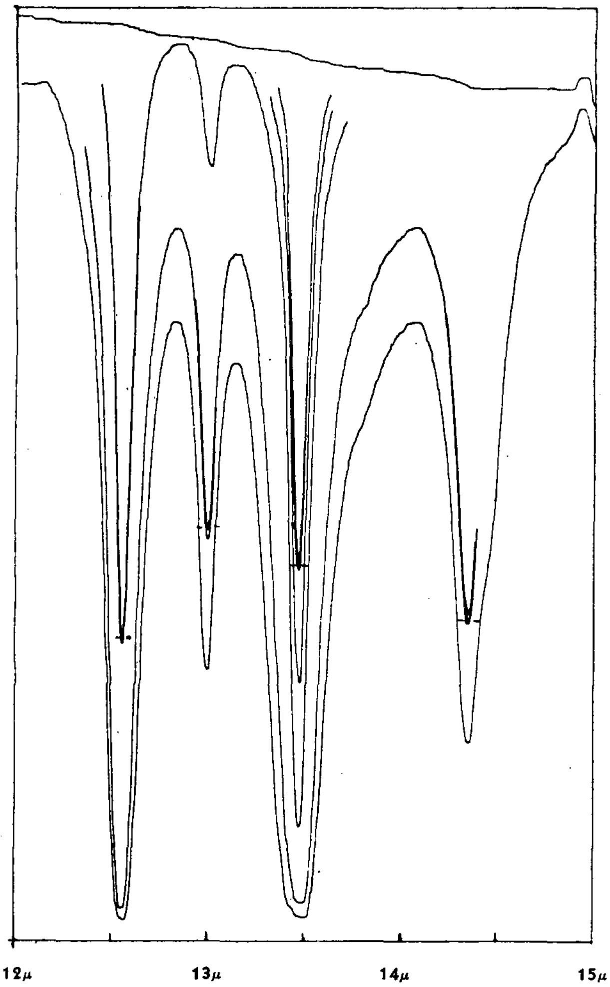

Figure 5. Spectrum of Mixture A in 12- to 15-Micron Region

Concentrations adjusted so that percentage transmittance was in region of 30 to 50 at each analytical wave length

Curve	Concentration, G./Ml.
Bottom	0.1168
Second	0.0778
Third	0.0195
Fourth	0.0097
Top	0.0065

Short horizontal lines indicate percentage transmittance values used for calculation

high degree of accuracy small percentages of one component in a mixture, a sample of which is placed in the reference beam. The technique can also save much time in the accurate analysis of two-component mixtures. To give an example, a commercial sample of *p*-xylene revealed by its spectrum (Figure 6) a small amount of *m*-xylene. If the concentration of a solution of this *p*-xylene material in iso-octane were adjusted to bring the absorption at 13.02 microns, the analytical wave length of *m*-xylene, within the optimum transmittance region (*x* in Figure 6), the contribution of *p*-xylene absorption at this wave length would introduce a large error in the *m*-xylene determination. On the other hand, when this particular *p*-xylene material was measured against a sample of pure *p*-xylene in the reference beam, the *m*-xylene band at 13.02 microns (Figure 7) was prominent, although the *m*-xylene content was only 0.64%; in addition a weak band appeared at 13.22 microns, indicating that there was some further impurity present.

A good illustration of the time saving that can be achieved with difference spectra is given by the analysis within 0.2% of blends of 60% iso-octane and 40% *n*-heptane. The procedure laid down by the ASTM (*1*) is to use four blends, each of which is prepared with an accuracy of at least 0.02 volume % for each component. One blend, reference standard A, contains 59.00% iso-octane and 41.00% *n*-heptane; reference standard C is made up to 61.00% iso-octane and 39.00% *n*-heptane. A test blend B contains 60.00% iso-octane and 40.00% *n*-heptane. With the aid of these three blends one is required to determine the iso-octane content of unknown blend D to within ±0.2%. According to the ASTM handbook one measures in close succession the absorbances of the four liquids in the order: (1) one of the reference standards, (2) the test blend B, (3) the unknown blend D, and (4) the other reference standard. The investigator is requested to "determine the absorbance of each of these liquids from four P_0 readings, resulting from incident radiant power, using the blank plate followed by four P readings, resulting from transmitted radiant power, with the liquid in the cell." The further instructions are to "reject the analysis unless the individual P_0 and P readings for each liquid agree with the corresponding average P_0 and P values within plus or minus 0.2% of the average . . . and to make at least two additional analyses in the same manner checking the wave-length setting between analyses." For the test blend the average values must agree with the known percentage to ±0.1%. This rather searching requirement can be fulfilled with any type of infrared spectrometer provided that intensity measurements are made with the sample cell removed from the beam (P_0 measurements) before and after each absorp-

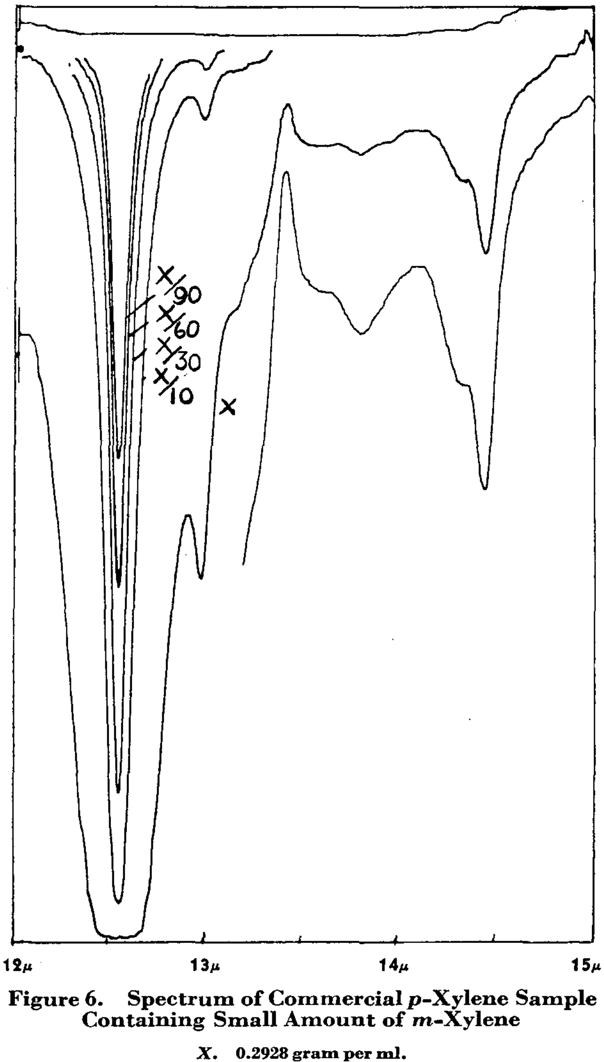

Figure 6. Spectrum of Commercial *p*-Xylene Sample Containing Small Amount of *m*-Xylene

X. 0.2928 gram per ml.
Cell length, 0.272 mm.

tion measurement (P measurement), but it is considered on the grounds of the present work that one series consisting of, say, six measurements of each sample would be sufficient to give the required accuracy, if two P_0 measurements were made separately for each P measurement, one before and one after.

Certainly a great deal of time can be saved with a double beam instrument by taking difference spectra. In this case a cell filled with the reference standard A for the iso-octane determination is used in the reference beam or a cell filled with the reference standard C is used for determining the *n*-heptane values. Fixed wave lengths of 8.54 and 13.82 microns, respectively, are chosen for iso-octane and *n*-heptane and again transmittance has to be adjusted to about 37%. A typical set of results is shown in Figure 8 with average values of 60.00% iso-octane and 40.05% *n*-heptane. For the *n*-heptane determination a cell filled with reference standard C was placed in the reference beam; for the iso-octane determination the cell was filled with reference standard A. There was a slight difference in the length of the cells in the sample and in the reference beam; the sample cell was 0.117 mm. long and the reference cell was 0.120 mm. long. The relative transmittance of each blend was measured from the base line of the transmission scale.

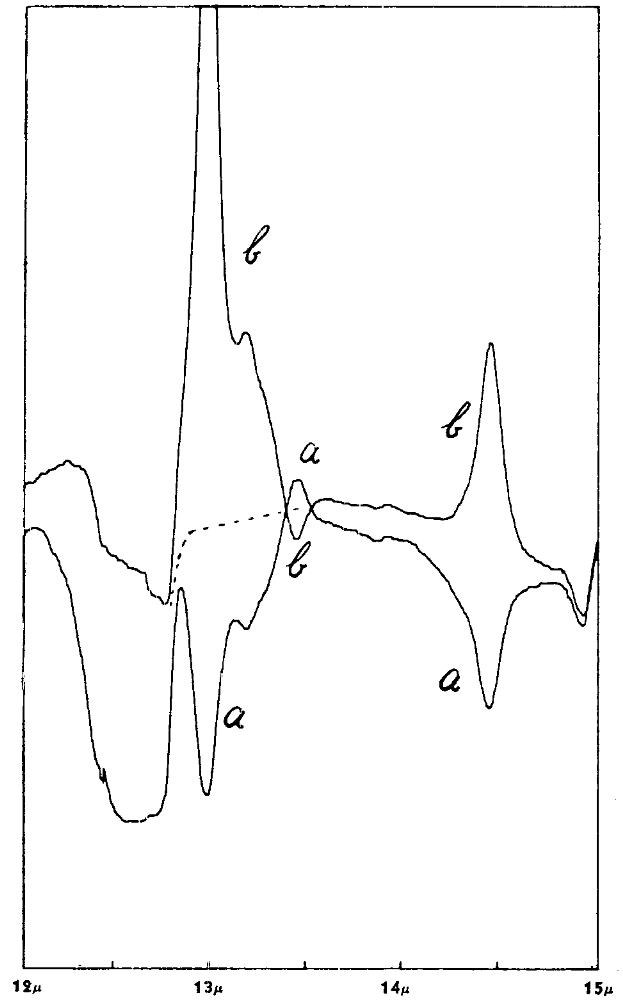

Figure 7. Difference Spectrum of Commercial *p*-Xylene Sample

a. Obtained with sample of pure *p*-xylene in reference beam
b. Obtained with pure *p*-xylene in sample beam and commercial *p*-xylene in reference beam
Broken line is an extrapolation for case of pure *p*-xylene in both beams
Commercial sample contains 0.64% *m*-xylene
Weak band at 13.22 microns indicates presence of unknown contaminant

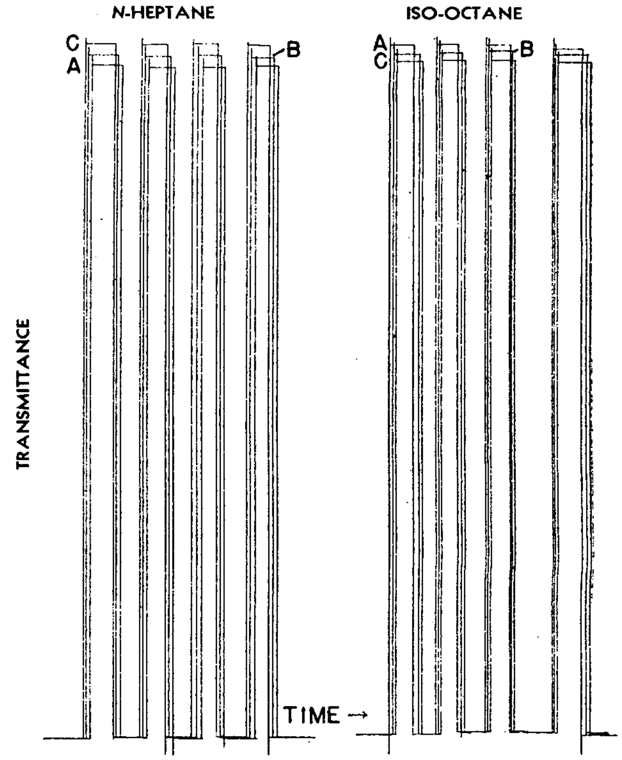

Figure 8. Determination of Iso-octane and *n*-Heptane at Fixed Wave Lengths in Test Blend

Relative transmittance of each blend measured from base line of transmittance scale

Iso-octane, 8.54 microns
A. 59%
C. 61%
n-Heptane, 13.82 microns
C. 39%
A. 41%

Table VIII contains eight individual iso-octane and eight individual *n*-heptane values for test blend B, yielding mean values of 59.94% iso-octane and 40.05% *n*-heptane. Both figures are well within ±0.1% of the known composition. Two of the eight individual iso-octane values were 59.74%. Following the ASTM stipulation to reject individual values which are outside a deviation of ±0.2% from the known composition, they would have to be omitted from the data considered for the arithmetical mean. The average of the six admitted values amounts then to 60.00%.

Table VIII. Determination of Iso-octane and *n*-Heptane in Test Blend B by Method of Difference Spectra

	Volume %	
Component	Individual	Mean
Iso-octane	60.05	60.00
	60.02	
	60.02	
	59.90	
	59.74[a]	
	59.85	
	59.74[a]	
	60.19	
n-Heptane	40.12	40.05
	40.17	
	40.05	
	40.10	
	39.83	
	39.97	
	40.11	
	40.08	

[a] Rejected as being outside the 0.2% deviation limit. If the two values of 59.74 are not rejected the mean volume percentage amounts to 59.94 instead of 60.00 and is still within the specified limit for the mean value.

Measurement of the same test blend at 8.54 and 13.82 microns, respectively, using the instrument virtually as a single beam instrument without another cell in the reference beam gave mean values of 60.00% iso-octane and 39.96% n-heptane, showing very close agreement within ±0.1%.

DISCUSSION

The experimental procedure to obtain an accurate analysis by infrared spectrophotometry is to employ the same slit width—i.e., the same slit program—for scanning around the analytical wave lengths of the spectra of a mixture and of its components. The absorbance values, D, of the mixture are read at the analytical wave lengths and corrections, ΔD, for attenuator deviation from linearity are applied. This yields $D' = D + \Delta D$. A further correction for deviations from Lambert-Beer's law is then applied with the aid of measurements at the analytical wave length for the respective component.

In this way the absorption values $A_i = D' - \Delta A_i$ are obtained for the components of a mixture. The concentration of each constituent is evaluated by inserting in the equation for the concentration of each component the A_i' values of all components of a mixture. $A_i' = \gamma_i(A_i)$, where γ_i is the dilution of the mixture to make the transmittance at each of the analytical wave lengths between 25 and 50%. To these results finally a concentration correction is applied for deviations from Lambert-Beer's law. When these three corrections are made the mean errors of the results for the example of mixtures of the xylene and ethylbenzene can be kept within 1%. It is of interest that a similar high degree of accuracy cannot be obtained by ultraviolet spectrophotometry (*17*) because here in spite of the smaller slit width there is more overlapping of bands with the result that the differences of some of the cross products from the simultaneous equations assume comparatively small values.

In the infrared case o-xylene is the isomer which can be determined with the relatively highest degree of accuracy, whereas in the ultraviolet case it is p-xylene.

The importance of corrections for deviation from Lambert-Beer's law was discussed by Williams, Hastings, and Anderson (*22*). It was pointed out there that the same instrument and the same resolution must be used for recording the spectra of mixtures and for plotting the absorbance-concentration curves of the components of the mixtures.

For the analysis of industrial samples it is considered that normalization of the results detracts from accuracy because of unknown components. Industrial xylene-ethylbenzene distillation cuts illustrate this contention; in such cases the contents of saturated hydrocarbons can be estimated from the refractive index of the mixture, whereas normalization alone of the experimental results for the aromatic hydrocarbons would introduce a corresponding error.

For measurements at fixed wave lengths with the single beam technique the small random errors are easily averaged when four or five consecutive recordings are made of pairs of P_0 and P measurements so that horizontal lines can be drawn through corresponding P_0 and P levels. It is then a matter of measuring with reasonable accuracy the distance between these levels and the base line of the recording chart.

The measurements of P from the recordings have to be accurate to less than 0.2 mm. if the most is to be made of the accuracy of the spectrometer. From the definition of absorbance

$$D = \log_{10}\frac{P_0}{P} = \frac{\log_e \frac{P_0}{P}}{2.303}$$

Therefore

$$\left(\frac{\delta D}{\delta P}\right)_{P_0} = \frac{PP_0}{2.303P_0}\cdot\frac{\mathrm{d}}{\mathrm{d}P}\left(\frac{1}{P}\right) = -\frac{1}{2.303P}$$

Hence for an error in D of $\Delta D = \pm 0.2\%$—i.e., about 0.001

$$\Delta P = 0.023 \text{ cm. for } P = 10 \text{ cm.}$$

$$\text{and } \Delta P = 0.016 \text{ cm. for } P = 7 \text{ cm.}$$

Similarly, $$\left(\frac{\delta D}{\delta P_0}\right)_P = +\frac{1}{2.303P_0}$$

Hence, for $\Delta D = \pm 0.2\%$ and $P_0 = 25$ cm.

$$\Delta P_0 = \text{is of the order of 0.6 mm.}$$

CONCLUSION

The infrared spectra of a mixture and of its components must be measured with the same instrument and the same resolution. Empirical corrections can be made for finite slit widths. The components of synthesized mixtures of xylenes and ethylbenzene can be determined within ±0.4% of the total. When industrial xylene-ethylbenzene distillation cuts are examined and their content of saturated hydrocarbons is taken into account, results are obtained with mean deviations of 0.2%.

The technique of difference spectra is illustrated by the measurement of 0.64% of m-xylene in a commercial sample of p-xylene. Measurements of about 60-40 iso-octane-n-heptane blends at fixed wave lengths show that an accuracy of 0.1% can be reached. In this latter case the single beam technique can also be employed successfully if a check is kept on the P_0 values and an appreciably larger number of measurements is made than with the double-beam technique.

ACKNOWLEDGMENT

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Graphical Absorbance-Ratio Method for Rapid Two-Component Spectrophotometric Analysis

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A simple, rapid, graphical method for the ultraviolet spectrophotometric analysis of two-component systems uses the ratio of observed absorbances at two selected wave lengths, one of which is an "isoabsorptive" point if possible. This permits a straight-line plot of the ratio of the observed absorbances *vs.* relative composition, as derived from Beer's law. The method may be applied even though no isoabsorptive point exists, by use of a plot of calculated ratio *vs.* composition. It can be extended to a three-component system if desired. Speed and ease in setting up an analysis are obtained, as knowledge of only three absorptivities is needed for a two-component analysis if an isoabsorptive point is used; these values may be readily obtained from the user's files, the literature, or another laboratory.

TWO-component spectrophotometric analyses generally require the solution of simultaneous equations, for seldom do the two components have absorption bands that do not overlap appreciably. Many schemes have been proposed to simplify the calculations and to lessen the amount of time and effort required both to set up the method and to use it in the analysis. In an effort to simplify further and to speed up these operations of setting up the method and of using it later, the "absorbance-ratio" method here described was devised and put into use.

This method has no relation to the similarly named "transmittance-ratio" method which makes use of highly absorbing "blanks" in the comparison beam of the instrument (*4*). The name absorbance-ratio refers to the ratio of the observed absorbancies (*5*) at two selected wave lengths using conventional blanks. It most nearly resembles the "graphical-offset" method of Shurcliff and Stearns (*7*), though resemblances to other methods may be noted in the equations and graphs, for all are based upon and derived from Beer's law.

By proper selection of the analytical wave lengths, a simple straight-line graph can be drawn to show the relationship between the absorbance ratio and the fraction or relative concentrations of the two components; a simple one-component calculation based on Beer's law gives the total amount present. In many applications, only the ratio of the two components is desired, and this latter step may be eliminated.

DERIVATION

Beer's law may be written in a generalized form for *i* components:

$$A_{\text{obsd.}} = b\sum_i a_i c_i \qquad (1)$$

or

$$A_{\text{obsd.}} = b\sum_i (a_1c_1 + a_2c_2 + a_3c_3 + a_4c_4 \ldots) \qquad (2)$$

where *A* is the absorbance (*5*) (optical density), *b* is the cell length, millimeters, *a* is the absorptivity (*5*) of component *i*, and *c* is the concentration of component *i*, in grams per 100 ml.

For two-component systems, at a wave length λ',

$$A'_{\text{obsd.}} = b(a'_1c_1 + a'_2c_2) \qquad (3)$$

and at another wave length, λ'',

$$A''_{\text{obsd.}} = b(a''_1c_1 + a''_2c_2) \qquad (4)$$

Instead of being solved for c_1 or c_2, these equations may be divided:

$$A'_{\text{obsd.}}/A''_{\text{obsd.}} = \frac{b(a'_1c_1 + a'_2c_2)}{b(a''_1c_1 + a''_2c_2)} \qquad (5)$$

As the same cell length is used for both concentrations, *b* may be eliminated from the equation. It may be shown that relative concentrations (x, y) may be used in place of absolute concentrations, since

$$x = \frac{c_1}{c_1 + c_2}, \qquad y = \frac{c_2}{c_1 + c_2} \qquad (6)$$

The equation then becomes

$$\frac{A'_{\text{obsd.}}}{A''_{\text{obsd.}}} = \frac{a'_1x + a'_2y}{a''_1x + a''_2y} \qquad (7)$$

USE OF ISOABSORPTIVE POINT

If two spectra, plotted as *log a* or *a vs.* wave length, have a point of intersection, the numerical values of the absorptivities are equal at this wave length; this has been termed an "isoabsorptive" point. (An isosbestic point is a special case of an isoabsorptive point, where the two components are interconvertible.) Figure 1 shows the spectra of *o*- and *p*-nitrophenol (at pH 5.2), which have two isoabsorptive points. If the wave length of the isoabsorptive point at 286 mμ be chosen as the analytical wave length to be used in the denominator of Equation 7, the denominator becomes a constant equal to the absorptivity value of the isoabsorptive point, since $x + y = 1$. Equation 7 then becomes:

$$\frac{A'_{\text{obsd.}}}{A''_{\text{obsd.}}} = \frac{a'_1x + a'_2y}{a''} \qquad (8)$$

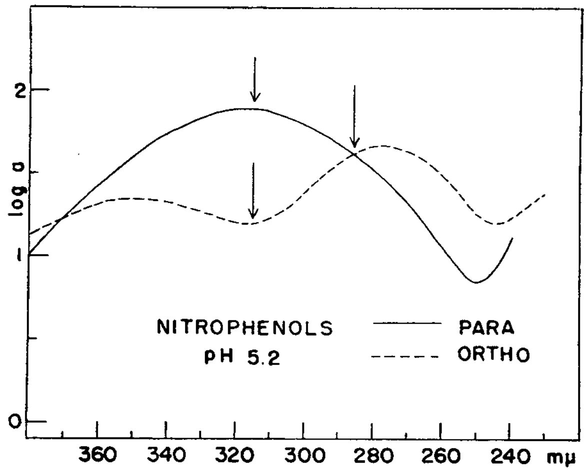

Figure 1. Spectra of *p*- and *o*-Nitrophenols

Showing isoabsorptive points

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With the denominator constant, a plot of the ratio of the observed absorbances, A'/A'', *vs.* x or y is a straight line. The ends of the line are given by a_o'/a'' and a_p'/a'', where subscripts o and p, for ortho- and para-, have replaced subscripts 1 and 2.

The use of the isoabsorptive point is the very heart of the absorbance-ratio method, for it permits the setting up of a two-component analysis from knowledge of three absorptivity values only—i. e., the value at the isoabsorptive point and the two values of the two pure components at the other analytical wave length.

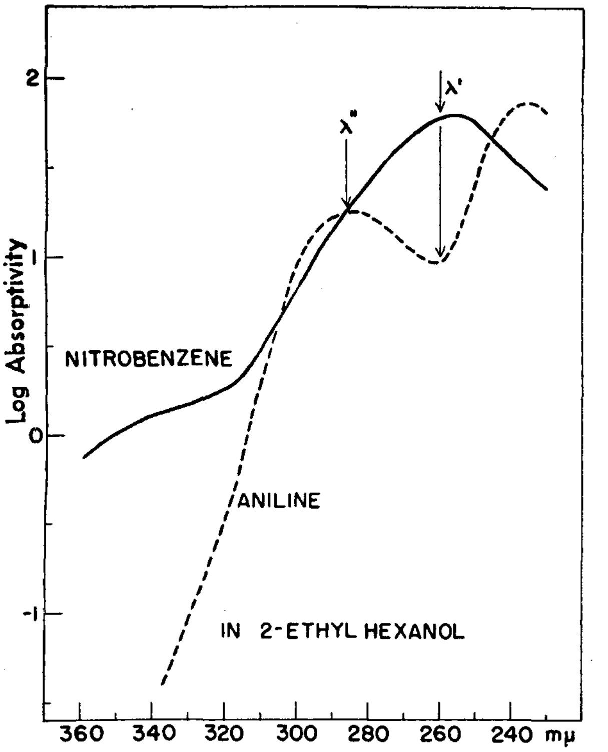

Figure 2. Spectra of Nitrobenzene and Aniline

Showing isoabsorptive points

A second example is shown in Figure 2, with the spectra of aniline and nitrobenzene, a combination which had been of interest in an industrial hygiene investigation (*1*). Three isoabsorptive points are seen; the center one is selected because of the high angle of intersection and the greater freedom from stray interferences which might occur with the shortest wave-length point. A similar plot may be set up, using the absorptivity values of aniline and nitrobenzene at the selected analytical wave lengths.

If no isoabsorptive point occurs between the spectral curves of the two components to be determined, the plot of absorbance ratio *vs.* x is not a straight line, but a curve connecting the extreme (100%) points which are determined by the ratio of the absorptivities of the pure components. This curve may be plotted by use of Equation 7, using the known absorptivity values and substituting values of 0.05, 0.10, 0.15, 0.20, etc., for x and the corresponding values of 0.95, 0.90, 0.85, 0.80, etc., for y. If the plot is to be used for many analyses, the extra effort of plotting this nonlinear curve will be compensated for by the ease of use.

In general, the criteria for selecting the analytical wave length which is not at the isoabsorptive point are much the same as for any analytical scheme. Wave lengths as long as possible are preferred to minimize the effect of possible interferences. A large spread between the curves is desirable, but not so large that the use of absorbance readings in the less accurate very high or very low ranges of the instrument would be used. (In actual use, readings that are too high or too low for the instrument's accurate range should not be taken, and a change in cell length or concentration should be made.)

The use of an absorbance-ratio graph determines relative concentrations, as fractions, and another step is necessary to determine absolute concentrations. Frequently this second step is not needed, for only the ratio of the two absorbing materials is desired. Examples are the examination of a plant product stream or the effluent from a chromatographic column. In such cases, no weighing of the sample or quantitative dilutions are needed; the concentration and/or cell length need only be adjusted so that the absorbance readings are in the desired accurate range of the spectrophotometer. The use of cells of adjustable length, such as micrometer Baly cells (*2*), is particularly advantageous in such cases.

UNAVAILABILITY OF STANDARDS

The spectroscopist is frequently called upon to determine (or estimate) two-component absorbing systems for which pure standard samples of either or both components are not readily available. If spectra are available in his files, the absorptivity values may be obtained from these, and the absorbance-ratio plot made. If both the spectra and the pure samples are not available, the only recourse is to published data or to those communicated from another laboratory. With the advent of punch-card systems, as described by Kuentzel (*6*), and of large-scale abstracting programs (such as those of ASTM Committee E-13), very much larger quantities of reliable spectrophotometric data are becoming generally available to spectroscopists. Such data may be used with the absorbance-ratio method when necessary to provide an estimate if not a determination of the quantities of the two or three absorbing components.

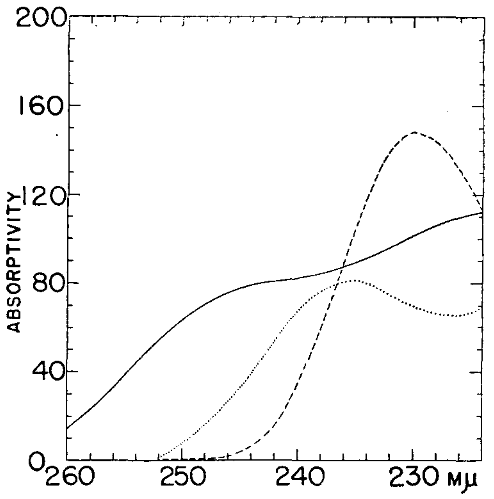

Figure 3. Spectra in 0.1*N* Hydrochloric Acid

—— Trimethylolmelamine
... Melamine
– – – Ammeline

EXTENSION TO THREE COMPONENTS

It is possible to extend the two-component absorbance-ratio method to three components, at the expense of some rapidity and convenience, but still with some advantage over the conventional solving of three simultaneous equations. The almost complete lack of true three-component isoabsorptive points requires the use of plots of absorbance ratio *vs.* relative composition, which are curves calculated from equations like Equation 7, rather than straight lines. Using three selected wave lengths, or usually more conveniently two sets of two selected wave lengths, two sets of three curves each may be drawn. The spectra of melamine, ammeline, and trimethylolmelamine, shown in Figure 3, prepared for use in a hydrolysis study (*3*), may serve as examples. The absorbance-ratio curves are shown in Figure 4, and were plotted from values calculated from equations like that of Equation 7. Since certain of the analytical wave lengths nearly correspond to two-component isoabsorptive points, certain of these curves are very nearly straight lines. Each curve corresponds to a two-component analysis (the third component being zero) for the three possible two-component combinations. Each ratio of two observed absorbances then corresponds to two possible extreme situations. The extremes of composition are read from the plots (like Figure 4) and become two points on a triangular composition plot, such as that of Figure 5. Because Beer's law is obeyed, the absorbances are additive, and the true analysis corresponds to one of the extreme points or to a point on a straight line connecting them. The desired composition lies at the intersection of these two lines, as shown in Figure 5.

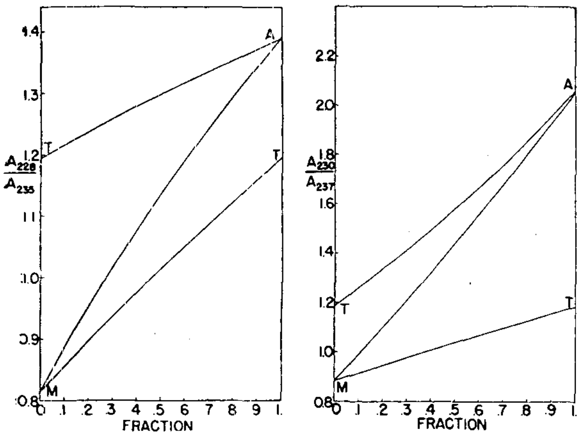

Figure 4. Three-Component Absorbance-Ratio Plots

A. Ammeline
M. Melamine
T. Trimethylolmelamine

As in the two-component methods, this gives the relative concentrations of the three components. To obtain the total concentration, a "composite" absorptivity value must be obtained at some wave length by multiplying each pure component's absorptivity by its fraction present and adding these; this "composite" absorptivity is then used in a conventional one-component Beer's law calculation to obtain the total concentration. The absolute concentration of each component is obtained by multiplying the total concentration by the fraction present. Clearly the three-component application is clumsier and slower than the two-component application; this is also true of the solving of three simultaneous equations as compared to the solving of two such equations. The graphical absorbance-ratio method is best applied to the determination of the relative concentrations of the three components.

ILLUSTRATIVE DATA

The absorbance-ratio method has been successfully applied to a large number of two- and three-component systems, both in research and analytical laboratories and in plant-control laboratories. Two sets of data on known mixtures have been selected to illustrate the application of this method to the systems used as examples in this paper. "Known" samples were prepared by mixing measured volumes of solutions of known concentrations of the pure components. Compositional data by preparation and by the absorbance-ratio method are given for aniline-nitrobenzene in Table I and for melamine-ammeline-trimethylolmelamine (*3*) in Table II, to illustrate the two- and the three-component applications.

Table I. Aniline and Nitrobenzene Mixtures

By Preparation, %		By Absorbance Ratio, %	
Aniline	Nitrobenzene	Aniline	Nitrobenzene
100.0	0.0	100.0	0.0
80.0	20.0	81.2	18.8
60.0	40.0	60.8	39.2
40.0	60.0	41.4	58.6
20.0	80.0	19.0	81.0
0.0	100.0	0.0	100.0

Table II. Melamine-Ammeline-Trimethylolmelamine Mixtures (*3*)

By Preparation, %			By Absorbance Ratio, %		
Melamine	Ammeline	Trimethylolmelamine	Melamine	Ammeline	Trimethylolmelamine
53.3%	46.7	0.0	53.5	46.5	0.0
53.2	0.0	46.8	54.0	0.0	46.0
0.0	49.8	50.2	0.0	50.4	50.6
63.1	18.4	18.5	64.8	19.1	16.1
36.2	31.7	32.1	34.8	31.1	34.1
22.2	19.4	58.4	24.8	20.0	55.2
22.1	58.3	19.6	22.4	58.2	19.4

ADVANTAGES

The graphical absorbance-ratio method for two components has the advantages of speed and ease in the setting up and use of the analytical method. Only knowledge of the three absorptivity values at the analytical wave lengths is necessary. This allows a laboratory with a large library of spectra to transmit a minimum of information—by telephone, for example—to a smaller laboratory or plant control unit to enable it to set up and use a plot of absorbance ratio *vs.* relative concentration. The advent of large amounts of reasonably reliable spectrophotometric data,

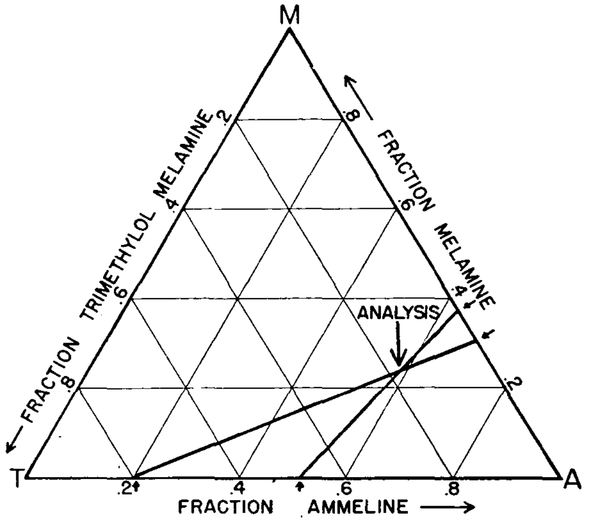

Figure 5. Three-Component Analysis Using Absorbance-Ratio Data

which will be widely distributed, will further the usefulness of this rapid graphical method for setting up two-component analyses even when pure standard samples are not readily available to the user. However, caution must be exercised in the use of data in such a manner, and a realistic view of the effects on the accuracy of the analysis must be taken.

ACKNOWLEDGMENT

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Detection and Estimation of Melamine in Wet-Strength Paper by Ultraviolet Spectrophotometry

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The use of melamine resins to impart wet strength to paper makes desirable a rapid method for the detection and estimation of the melamine content of paper samples. A spectrophotometric method has been developed which makes use of the strong absorption of the melamine ion at 235 mμ. The resin is effectively extracted from the paper and hydrolyzed to melamine by refluxing cut-up paper samples in 0.1*N* hydrochloric acid.

A RAPID METHOD for the detection and estimation of the melamine content of paper samples is desirable in using melamine resins to impart wet strength to paper. The strong absorption of melamine (2,4,6-triamino-*s*-triazine) in the ultraviolet (*1, 6*) near 235 mμ makes possible the detection and estimation of melamine by a spectrophotometric method of high sensitivity. The relatively large change in the spectrum of melamine between neutral and acetic conditions has been utilized for the determination of the ionization constant (*3*), and serves as an additional means of identifying melamine in solution. Refluxing cut-up paper samples in 0.1*N* hydrochloric acid effectively extracts and hydrolyzes the resin to the melaminum ion, which is then measured spectrophotometrically.

APPARATUS AND MATERIALS

A Cary automatic recording spectrophotometer, Model 11, No. 67, and fused quartz cells of various light path lengths were used for examination of the extracts in the range from 260 to 220 mμ. Appropriate adjustment of cell length and/or concentration was made in order to obtain absorbance readings at the analytical wave lengths in the accurate range of the spectrophotometer. An all-glass flask and reflux condenser assembly was used for both the extraction of paper samples and for the hydrolysis experiments.

The melamine (*1, 6*) and ammeline (*4*) samples were of high purity and identical with those used in previous investigations. The resin sample was a commercial trimethylolmelamine, a partially condensed resin, called Parez Resin 607 (*2*).

SPECTROPHOTOMETRIC METHODS

The ultraviolet spectra of melamine, ammeline, and trimethylolmelamine in acid solution have been presented in connection with the absorbance-ratio method (*5*). The strong band of the melaminum ion near 235 mμ has an absorptivity of 81.0 and may be utilized in a simple one-component analysis in the absence of interfering materials. A detectability of 4 γ may be obtained with an observed absorbance of 0.100 (in a 100-mm. cell 31 ml. in volume), if no other absorbing materials are present.

Because other ultraviolet absorbing materials are extracted from paper samples by the refluxing with 0.1*N* hydrochloric acid, some type of background correction is desirable. Examination of the extracts of various paper samples did not yield any reproducible value that could be used as a simple subtractive background correction. However, because the absorption of melamine falls off so rapidly toward longer wave lengths, becoming only $^1/_{200}$ as high at 260 mμ as at 235 mμ, all the observed absorption at 260 mμ can be taken as due to absorbing materials other than melamine. If it is assumed that such absorption does not decrease from 260 to 235 mμ, the absorbance at 260 mμ may be subtracted from that at 235 mμ, to give a first approximation of a background correction. Because ammeline, the acid hydrolysis product of melamine, may be present, the analytical wave length used should be 237 mμ (rather than 235 mμ), which is the isoabsorptive (*5*) wave length for melamine and ammeline. The absorptivity at 237 mμ is 79.0.

HYDROLYSIS OF MELAMINE AND OF PAREZ RESIN 607

During the refluxing with 0.1*N* hydrochloric acid to remove the resin from the paper sample, hydrolysis of the resin to melamine occurs, and to a much lesser extent, hydrolysis of melamine to ammeline. In order to study these hydrolysis reactions, a two-component analysis of melamine and ammeline was set up, using the graphical absorbance-ratio method (*5*). Because an isoabsorptive point occurs between melamine and ammeline at 237 mμ, this wave length was selected as one of the analytical wave lengths (the other being 226 mμ), so that a plot of the ratio of the absorbances at the analytical wave lengths *vs.* fraction of melamine or ammeline would be a straight line. The hydrolysis of the resin of melamine also involves the presence of measurable quantities of ammeline in its later stages, so a three-component analysis, using the graphical absorbance-ratio method, was set up. The details of the three-component application of this method have been described (*5*).

A sample of melamine was refluxed in a large excess of 0.1*N* hydrochloric acid and aliquots withdrawn and analyzed spectrophotometrically at suitable time intervals, using the two-component absorbance-ratio method described. The results are shown in Figure 1. A similar study was made on the resin, and the three-component modification of the absorbance-ratio method was used to obtain the resin content as a function of time, as shown in Figure 1.

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The hydrolysis of the resin, at pH = 1, is much more rapid than that of melamine, with a hydrolysis rate constant at 100° C. of 3.4×10^{-3} sec.$^{-1}$ compared to 2.0×10^{-5} sec.$^{-1}$. Thus, the acid extraction of paper samples effectively hydrolyzes the resin to melamine with a small but measurable amount of the melamine hydrolyzing further to ammeline. By using the isoabsorptive wave length of 237 mμ for the calculation of melamine, no error is introduced because of the ammeline present; the total amount of melamine plus ammeline is determined, and because the molecular weights have but one unit difference, this amount may be reported as melamine.

PROCEDURE

A sample of 1 to 2 grams of paper is cut into small pieces (about 1 cm. on a side) and weighed on an analytical balance. The weighed sample is placed in a flask of 200- to 300-ml. capacity having a ground-glass joint connection with a water-jacketed reflux condenser (the use of cork or rubber stoppers must be avoided because of contamination of the extract). A volume of 100 ml. of spectroscopically pure 0.1*N* hydrochloric acid, pH = 1, is added to the flask and refluxed for 1 hour. This is filtered through good quality filter paper or sintered glass and examined in the spectrophotometer. Appropriate adjustment of cell length and/or concentration is made so that the readings at the analytical wave lengths are in the accurate range of the instrument. The comparison or blank cell is filled with 0.1*N* hydrochloric acid. The range from 260 mμ to the lower wave-length limit of the instrument is scanned to ensure the observation of the maximum near 235 mμ.

The concentration of melamine in the paper sample is calculated from the following equation, derived from Beer's law:

$$\% \text{ melamine} = \frac{(A_{237} - A_{260})\,(f)\,(V)}{(a_{237})\,(b)\,(W)}$$

where A = the observed absorbance (*8*) at the subscript wave length
f = the dilution factor (usually 1)
V = the volume of HCl in ml. (usually 100)
a = the absorptivity (*8*) (at 237 mμ, 79.0)
b = the cell light path length in mm.
W = the sample weight in grams

RECOVERY TESTS

Because no other method for the determination of melamine in wet strength paper was available for checking this spectrophotometric method, comparison to Kjeldahl-nitrogen analyses were used to furnish the known values for recovery tests. Samples of papers containing melamine resin for wet strength were analyzed by the conventional Kjeldahl-nitrogen method and by the spectrophotometric method. The values for per cent nitrogen were calculated as if all the nitrogen content were due to melamine, although some nitrogen may be found in papers not containing melamine resin. The recovery figures for the spectrophotometric method are based on these values. These data are shown in Table I. The maximum difference from the nitrogen-analysis values was observed to be a relative 11%, and the average difference was 5.5%.

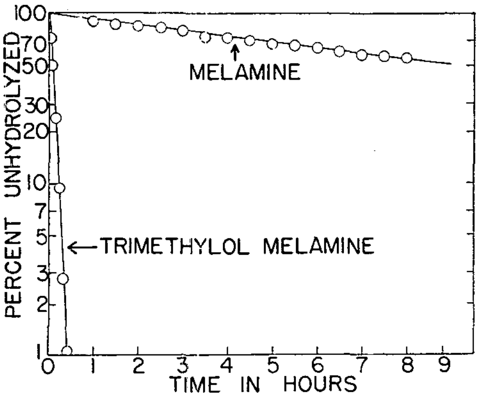

Figure 1. Hydrolysis of Trimethylolmelamine and Melamine Refluxed in 0.1*N* Hydrochloric Acid

Table I. Comparison of Kjeldahl-Nitrogen and Spectrophotometric Results

Type of Paper Sample	Kjeldahl Nitrogen, %	Calculated Resin, %	Calculated Melamine, %	Ultraviolet Melamine, %	Recovery, %
Facial tissue	0.25 0.25	0.65	0.38	0.38 0.39	100 103
Specialty wrap	0.28 0.28	0.73	0.42	0.40 0.43	95 102
Bleached southern kraft, bag	0.40 0.41	1.05	0.61	0.68 0.64	111 105
Unbleached southern kraft, bag	0.52 0.53	1.36	0.79	0.72 0.73	91 92
Army map	0.70 0.70	1.82	1.05	1.12 1.11	107 106
Specialty wrap	1.05	2.73	1.57	1.65	105

ADVANTAGES OF THE SPECTROPHOTOMETRIC METHOD

The principal advantage of the spectrophotometric method is the speed with which analyses may be performed. The amount of time spent in scanning the desired spectral range with a recording spectrophotometer or in taking several point readings on a nonrecording instrument, and calculating the per cent melamine is of the order of 10 minutes per sample. The samples may be refluxing while other operations are being carried on.

The presence of a maximum near 235 mμ in hydrochloric acid, which disappears in alkaline solution, serves as a confirmatory test for melamine. This is easily done by making the solution alkaline and re-examining the spectrum. The band at 235 mμ in acid becomes a slight shoulder in neutral or alkaline solution (*1*, *6*, *9*). If a band is not observed near 235 mμ in hydrochloric acid, the presence of melamine should not be reported.

The Kjeldahl-nitrogen method does not distinguish between melamine and urea resins, and is interfered with by the presence of nitrogen from casein, glue, amine-softeners, or other nitrogen-containing materials sometimes present in paper. These materials do not have ultraviolet spectra of appreciable intensity, or, like rosin, are not extractable by the acid solution, and hence do not interfere. The background correction using the absorption at 260 mμ fairly well compensates for other absorbing materials present.

The dye-staining test for melamine (*7*, *10*) gives only a qualitative indication of melamine present.

ACKNOWLEDGMENT

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Automatic Mass Spectrometric Analysis

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A rapid method of obtaining mass spectrometer analyses is of utmost importance in following pilot plant operation. Application of an automatic peak selector and an analog-to-digital converter makes possible direct tabulation of mass spectrometer ion currents for preselected analytical peaks. These data, furnished automatically by an electric typewriter or on punched cards or tape, may then be fed to a high speed computer for calculation and tabulation of the results. One such arrangement, using a Consolidated Spectro-Sadic, an IBM summary punch and card programmed calculator, is employed at the Esso Laboratories. With this system it is possible to report 30 gas analyses (20-component) per 8-hour shift. Only $1^1/_2$ men (11 man-hours) are required per shift to operate the mass spectrometer and computing equipment.

DURING 1953, a marked decrease in the time requirement for mass spectrometric analysis has been accomplished. In the past, the major portion of the time required to obtain a mass spectrometric analysis of a complex mixture has been that used to measure the analytical peaks on the recorder trace and to calculate the results. Actual sample-running time for a mass range of 2 to 100 requires only a few minutes as compared to 1 to 1.5 hours for the peak measurement and calculation steps.

A typical example is the analysis of a hydrocarbon sample for C_6 and lighter components. The instrument running time is 5 to 7 minutes, at the end of which a spectrum in the form of a photographic trace or a recorder chart is obtained.

The first calculation step is the determination of the C_{5+} components by unique peak solution (using mechanical calculators) and correction of the remainder of the analytical peaks. Equations using the corrected peaks are then solved. In many cases a Consolidated analog computer is used. The remaining components (hydrogen, methane, air, etc.) are then obtained by mechanical calculation after the necessary corrections have been made.

The total time of spectrum scanning, tabulation, and calculation by this procedure is from 1 to 1.5 hours per sample as contrasted to 5 to 7 minutes of instrument time.

A more rapid method of obtaining mass spectrometer analyses is of utmost importance as the work load increases. In order to obtain the results from the analysis of 30 gas samples (20-component) per 8-hour shift, two analog computers and six men would be required if the old method of measuring peaks from a record and calculation by employing analog computers were employed.

Thus, it becomes an economic necessity to devise a means of rapid conversion of the analog information (ion collector currents) to digital information in the form of punched cards, magnetic tape, or punched tape. Also an automatic method of calculation, using high speed computers, is required.

REDUCTION OF MASS SPECTROMETER ION CURRENTS TO DIGITAL INFORMATION

To date, two systems have appeared in the literature for reduction of mass spectrometer ion currents to digital form and calculation of the final results.

One of these employs the Spectro-Sadic (*5*), manufactured by the Consolidated Engineering Corp. At the present time three of these are in service. They are located at the Analytical Service Laboratory of Consolidated Engineering Corp., Pasadena, Calif.; Research and Development Department, Socony-Vacuum Laboratories, Paulsboro, N. J.; and the Esso Laboratories, Standard Oil Development Co., Linden, N. J. The second system (*6*), was developed by the Atlantic Refining Co., Philadelphia, Pa., in cooperation with G. B. Greene, Physics Research Corp., Pasadena, Calif. (now associated with Marchant Research, Inc., Oakland, Calif.) Both of these systems are easily adapted to present mass spectrometers.

The conversion of ion currents to digital form consists of two parts. The first part is the automatic selection of the analytical peaks. The second is the actual conversion of the ion collector currents for the preselected analytical peaks to digital information.

Both of the systems mentioned use presetting of the acceleration voltages for peak selection. The mass range covered is 12 to 122 or 40 to 150. Any 40 peaks within either one of these ranges can be programmed. It is not necessary to set up all 40 peaks but only the peaks desired for the type of analytical work being carried out.

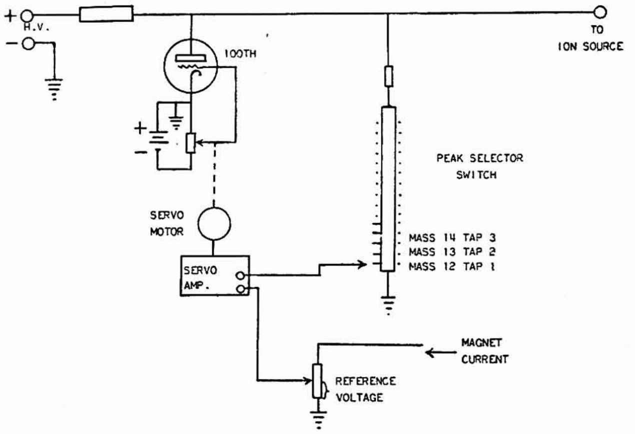

Figure 1. Peak Selection Circuit of the Spectro-Sadic

In Figure 1 is given a simplified circuit to achieve selection of the desired acceleration voltage in a Consolidated mass spectrometer. The condenser whose discharge varies the grid voltage of the 100TH tube has been replaced by a servo-operated potentiometer. In addition, a bank of resistors has been connected across the acceleration voltage supply. By means of a selector switch any one of 40 tie-in points can be selected. The values of the resistors are such that the voltage output at a tie-in point will focus a given mass. For instance, at tap point one the voltage output of the circuit will be 3673 volts, which for a magnetic current of 0.587 ampere on the instrument used in this laboratory, will focus mass 12 on the collector. Similarly, at tap point two will be 3391 volts for focusing mass 13.

One very important requirement in the use of a fixed acceleration voltage to focus a given mass-charge ratio, is that the magnetic field have a high degree of stability. This is not too important if a scanning technique of varying the ion acceleration voltage—for instance, discharging a condenser—is used. In order to compensate for the drift in magnetic field strength, the acceleration voltage used is referred to a reference voltage which

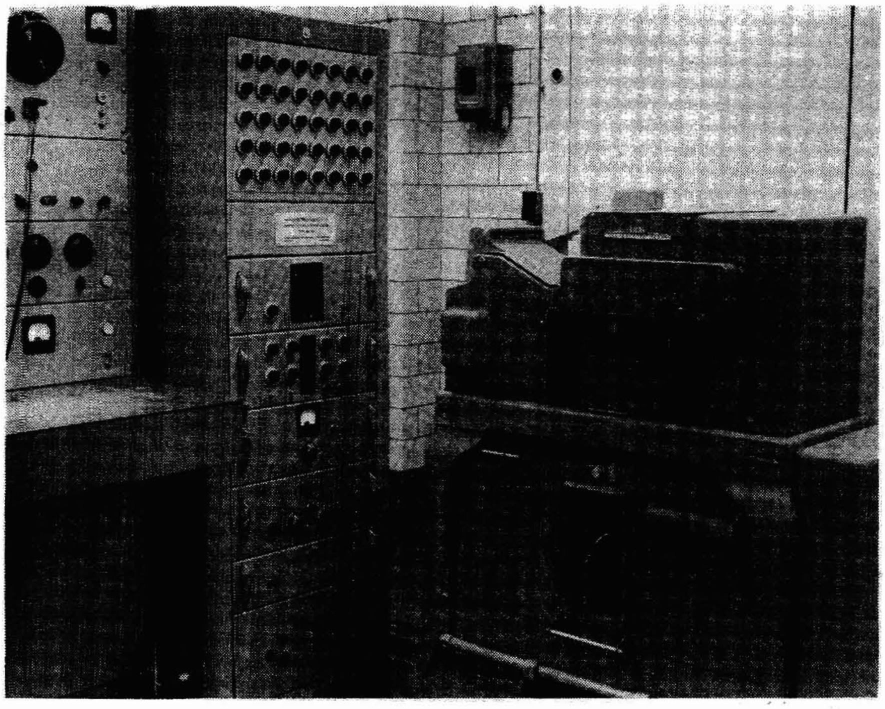

Figure 2. Spectro-Sadic

is derived from the magnetic current. As each new acceleration voltage is selected, a comparison is made to the reference voltage and a servo mechanism makes the necessary correction. This is also shown in Figure 1. The acceleration voltage goes to a servo-amplifier, where it is compared to the reference voltage from the magnetic current. If an unbalance exists, the servo drives a potentiometer which changes the grid voltage of the 100TH tube. This correction is not strictly correct, since it is a linear correction, while the effect of a drift in magnetic field is a square function. However, as only drifts of small magnitude are involved, this method works satisfactorily.

The Spectro-Sadic System. In actual operation this instrument goes through several program steps for each mass peak.

1. The ion beam is defocused (electrically), at which time the analog-to-digital converter is automatically zeroed.
2. The preprogrammed acceleration voltage is selected.
3. The ion beam is refocused.
4. The signal is applied to the analog-to-digital converter which reaches a balance.
5. The data are read out to IBM punch and/or electrical typewriter.
6. Step to next peak program.

As only the necessary analytical peaks (at a speed of 8 seconds per peak) are recorded, a definite decrease in the time required to run a sample is achieved. If desired, a photographic record of the selected analytical peaks can be obtained at the same time. In addition, by throwing a single switch, it is possible to return to photographic recording of all the peaks.

The Spectro-Sadic (*1*) is essentially a Thompson-Varley self-balancing potentiometer. However, instead of operating on the usual slide-wire basis, it incorporates a unique 10-position, bidirectional stepping switch in each of the three stages to provide a 0- to 999-digital output. The balancing process is accomplished by the stepping switches, which, being both reversible, and capable of simultaneous stepping in all three decades of the three-digit number, reach balance at high speed. Linearity of the output voltage is achieved by the use of fixed precision resistors to establish the discrete voltage levels. The switch contacts providing the digital output parallel the potentiometer contacts to establish a positive relation of the output to the original analog input. When the system is in balance, the digital voltage value is tabulated by any of a variety of devices. These may be card or tape punches, automatic typewriters, or any other read-out unit which may be actuated by contact closures. A chart record of the spectrum (the analytical peaks only) can be obtained concurrently if desired. A photograph of the instrument is given in Figure 2.

USE OF INVERSE MATRIX WITH PUNCH CARD CALCULATORS. Older calculation methods, employing analog computers, etc., did not use an inverse matrix for numerous reasons. When punch card calculators are employed, however, it is advantageous to use an inverse matrix.

Several methods for matrix inversion with punch card calcula-

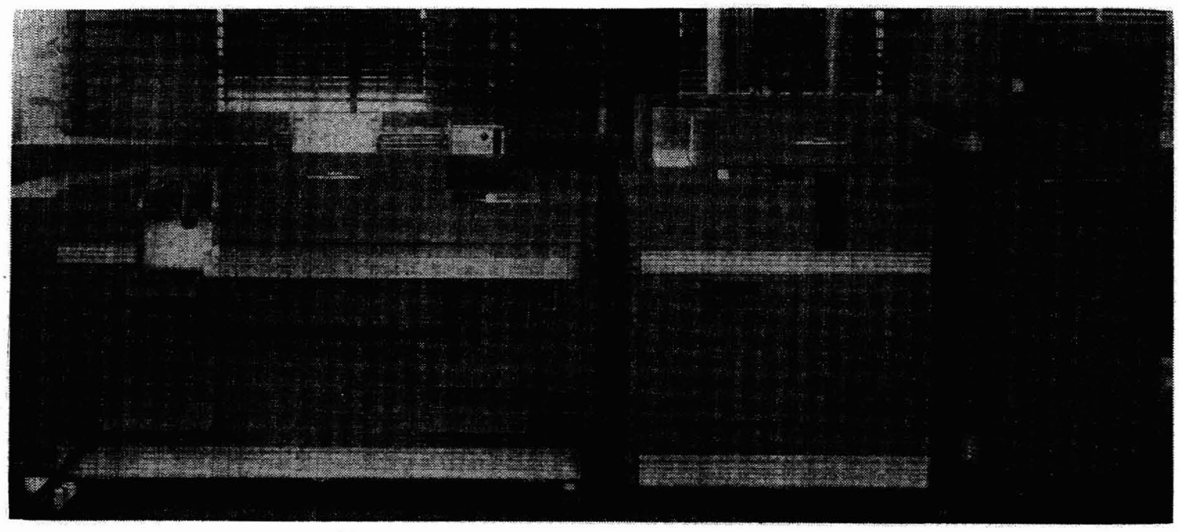

Figure 3. IBM Card Programmed Calculator

tors have appeared in the literature (*2*, *3*). The classical iterative method of approximations (Gauss-Seidel) is employed at the Esso Laboratories in conjunction with a card programmed calculator (CPC). This method requires less than 6 hours for the inversion of the 20 equations containing the required mass spectrometer calibration data. (Matrix inversion is required only once for each instrument calibration.) Although faster methods are available, the approximation method is preferred because of its simplicity. A photograph of a CPC setup is given in Figure 3.

COMPUTING PROCEDURE. Once the inverse matrix is available, the computation of mass spectrometer data proceeds in the following fashion.

A sample is charged to the mass spectrometer. Ion collector currents for the preselected analytical peaks are converted to digital information by the Spectro-Sadic and automatically key-punched by an IBM reproducing or summary punch. These cards (one for each analytical point) are fed, along with the program deck, to the card programmed calculator. The program deck contains the inverse matrix, molecular weight, compressibility, and other factors to permit the determination of all the desired information.

The method used for calculation with the card programmed calculator is the same as that for the IBM 602A as described in a previous publication from this laboratory (*4*). The time for this calculation on the card programmed calculator is 1 minute 20 seconds per sample. The results from a mathematical test problem are shown in Table I. This is a mathematical synthetic blend containing 19 components. It can be seen that the analysis is reported in mole per cent (fixed gas free) and weight per cent. Specific gravities and the compressibility factor for the sample are also given.

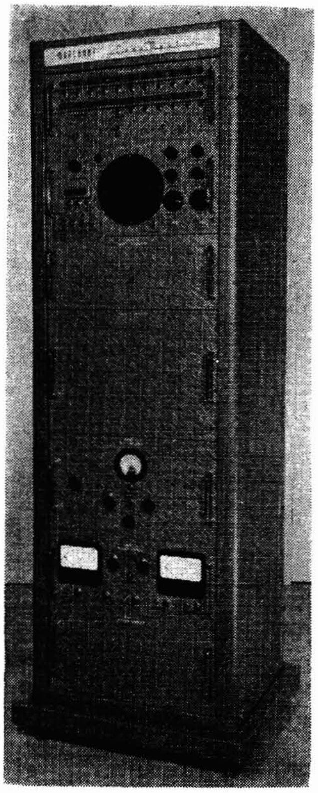

Figure 4. Encoder (Atlantic Refining Co.)

The Atlantic System. In the Atlantic setup the same method of peak selection is used as in the Spectro-Sadic. In fact, the development of this method was a joint effort of the Consolidated Engineering Corp. and the Atlantic Refining Co. From this point on, however, the Atlantic system is quite different, in that an entirely different method of recording the peak heights is used and the computer is an integral part of the mass spectrometer setup.

The Atlantic system consists of an encoder (the Marchant Codemaster), a digital computer (Miniac), and a typewriter. The encoder converts galvanometer deflections to derived binary numbers. At this point the data can be stored on a magnetic drum in the computer, can be converted to the decimal system and recorded by the typewriter, or can be punched on tape in a binary form.

The encoder is based on a newly developed cathode ray technique, involving a monoscope tube with an internal screen containing a 1024-line binary pattern. It can resolve 1024 units of voltage to the nearest half unit and is free from ambiguity.

Table I. Mass Spectrometer Analysis

Component	Mole % Inert Free	Wt. %	Mole %
Hydrogen	11.76	0.45	10.00
Methane	5.88	1.80	5.00
Ethane	5.88	3.37	5.00
Ethylene	5.88	3.15	5.00
Propane	5.88	4.95	5.00
Propylene	5.87	4.71	4.99
n-Butane	5.89	6.53	5.01
Isobutane	5.89	6.53	5.01
Butenes	5.88	6.29	5.00
n-Pentane	5.87	8.08	4.99
Isopentane	5.89	8.10	5.01
Pentenes	5.88	7.87	5.00
n-Hexane	5.87	9.65	4.99
Hexenes	5.88	9.44	5.00
Benzene	5.88	8.76	5.00
Toluene	5.88	10.33	5.00
Total	99.96	100.01	
Nitrogen	5.00		5.00
Carbon dioxide	5.00		5.00
Air	5.00		5.00
Total	15.00		100.00
Compressibility			0.9736
Gravity inert free			1.8115

The encoder is equipped with a logarithmic amplifier which provides single scale operation, an important adjunct to automatic operation, with constant precision regardless of the magnitude of the analog voltage. In this manner, one of the 1024 horizontal lines of the monoscope tube is chosen through vertical deflection to correspond to the instantaneous magnitude of the analog voltage. Actual reading is accomplished by sweeping the beam horizontally across the pattern along the line so chosen. The encoder ordinarily operates only upon interrogation by the Miniac computer. The encoder is shown in Figure 4.

Because the Miniac computer is a general-type digital computer, it can be used for many types of calculations other than mass spectrometry. Therefore, provision has been made for either calculating the results as the samples are run or for storing the peak values on punched tape for calculations at a later time. If it is desired to calculate the results as samples are run, the calibration data and instructions to the computer are fed into the computer on punched tape prior to running the sample. Under this system the final results are available some 3 to 4 minutes after scanning a sample.

An inverse matrix solution method is used for routine work. A 20 × 20 matrix may be solved in less than 2 minutes. In some

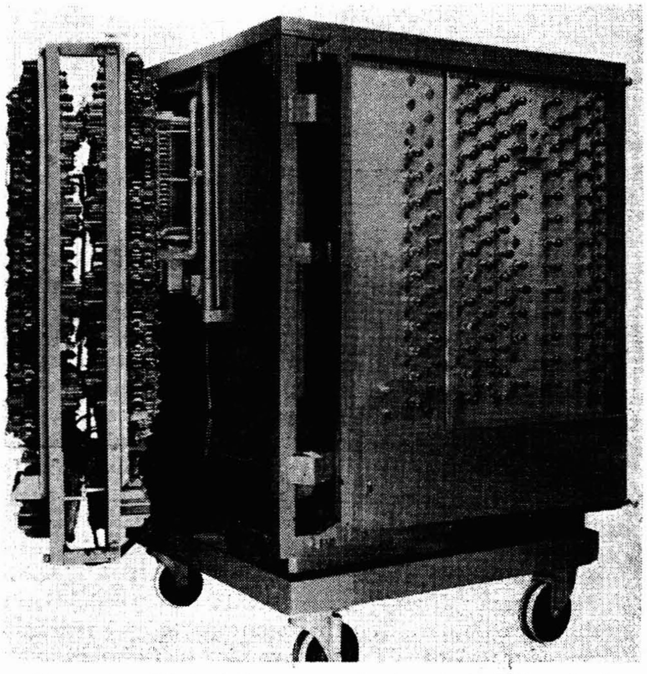

Figure 5. Digital Computer (Atlantic Refining Co.)

cases it is desirable to calculate particular solutions for each problem and this direct solution can be accomplished by reiteration in about 6 minutes. Two photographic views of the Miniac computer are presented in Figures 5 and 6.

Time Requirement Comparison. Three methods of obtaining mass spectrometric results have been employed over the past few years at this laboratory: photographic record plus analog computer, photographic record plus IBM 602A punched card calculation, and Spectro-Sadic digital conversion plus IBM (CPC) calculation. A comparison of the time requirements for each of these methods is shown in Table II.

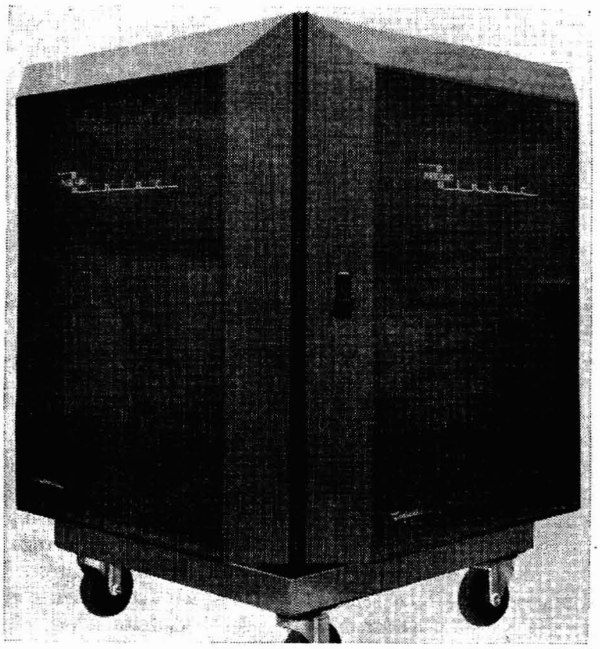

Figure 6. Digital Computer

It can be seen that the replacement of analog computers with the 602A reduced the time requirement from 1.65 to 0.92 man-hours per sample. Replacement of the photographic record with a digital converter and computation by the card programmed calculator reduced this still further, to 0.37 man-hour. These figures include time for instrument pump-out, sample charging, checking, etc.

Table II. Time Requirements for Various Methods of Measuring and Calculation of Mass Spectrometer Data

(Basis, 30 20-component gas samples)

Time Requirement, Man-Hours	Photographic Record Analog Computer	Photographic Record 602A (IBM)	Sadic CPC (IBM)
Instrument[a]	10	10	8
Chart measurement	10	10	0
Calculation	30	7.5	3
Total	50	27.5	11
Man-hr./sample	1.65	0.92	0.37

[a] This includes sample charging and pump-out.

It is now possible with $1^1/_2$ men, one mass spectrometer, digital conversion, and card programmed calculator computation to report 30 gas samples (20 components) per 8-hour shift.

ACKNOWLEDGMENT

The authors wish to thank the Atlantic Refining Co., Philadelphia, Pa., for the photographs and description of the encoder and digital computer used in their system.

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Spectrophotometric and Polarographic Determinations Of Soluble Silicate

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In searching for a rapid method for the determination of low percentages of silica in magnesium oxide and magnesium carbonate, the spectrophotometric method, based on the measurement of yellow molybdosilicic acid, has been reinvestigated including conditions for color development and for minimizing interferences. Measurement of the absorbance in the ultraviolet against an appropriate blank has increased the sensitivity so that it is nearly the same as that obtained by the more cumbersome procedure involving reduction to the blue complex. A hitherto unreported polarographic procedure of considerable promise has also been developed for the determination of silicates.

A MORE rapid method than the conventional gravimetric was desired for the determination of low percentages of silica in magnesium oxide and magnesium carbonate. A spectrophotometric method was the obvious approach because the literature contains many colorimetric and spectrophotometric procedures for the determination of silica involving measurement of the yellow molybdosilicic acid or of the blue reduced form. Heretofore, procedures had been proposed for the determination of silica in magnesium metal and its alloys (*15*) so the extension to magnesium oxide and carbonate appeared to be feasible. Despite the fact that "yellow" methods were reported to be less sensitive

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than "blue" methods, they promised greater speed as a result of their simplicity. Therefore, the possibility of using the yellow molybdosilicic acid was thoroughly investigated.

The published photometric procedures disagreed on the best wave length for measuring the absorbance of the yellow molybdosilicic acid. Recommended wave lengths in millimicrons were: 370 (*11*), 390 (*9*), 390 to 400 (*10*), 400 (*2*), 405 (*4*), 410 (*7*), 420 (*17*), and 425 (*5*). At the time of the initiation of this work only the paper of Armand and Berthaux (*2*) showed the spectrum. These authors found that when measured against distilled water the absorbance of the molybdosilicic acid increased continuously as the wave length was decreased from 500 to 305 mμ. A recent paper by Carlson and Banks (*6*) showed the same spectrum.

Most recently, Strickland (*20*), in his work on the preparation and properties of molybdosilicic acid, found that there were two forms of the acid. By using extremely dilute solutions, Strickland was able to measure the spectra of the α and β forms of the heteropoly acid against water down to 220 mμ. The β form which is usually formed in the recommended analytical procedures shows, in the region 275 to 305 mμ, a relatively constant absorbance which, at the same time, is much greater than that in the 370 to 420 mμ region previously used in spectrophotometric work.

Tungsten, vanadium, iron, and reducing agents have been reported to interfere in the silicon determination (*1*) as have phosphorus, arsenic, and germanium. Various methods have been proposed for the removal of the interference of the last three elements which are known to react with molybdate in acid solution to produce heteropoly acids similar to those of silicon. Complexing agents such as citrate (*1, 7, 18*), oxalate (*1, 19*), and tartrate (*1*) have been recommended to bleach the interfering color while leaving the silica color more or less unaffected. It has been reported possible to remove the phosphate interference by adding enough excess phosphate to form the colorless $H_3PO_4 \cdot 9MoO_3$ (*12*). A solvent extraction technique has also been recommended (*11*) for removing the phosphorus and arsenic interferences and more recently for their determination (*21*). Because of the controversial nature of the reports in the literature, methods for minimizing the interferences from phosphorus and arsenic have been re-examined.

The present paper reports a procedure for the determination of silica based on absorbance measurements in the ultraviolet region of the spectrum against a blank continuing all the color developing reagents. It was desirable, therefore, to reinvestigate the effects of pH and molybdate concentration for this region of the spectrum. Finally, the sources of difficulties, encountered when the method was applied to the analysis of magnesium oxide, have been examined.

While attempting to establish an independent method to corroborate the analytical results of the spectrophotometric method, the possibility of polarographic determination of silica by reduction of the molybdosilicic acid at the dropping mercury electrode was also examined. Boltz, DeVries, and Mellon (*3*) had reported that molybdophosphoric and molybdosilicic acids were reducible at the dropping mercury electrode in acetic acid–sodium acetate buffers. The molybdosilicic acid complex present in an acetic acid–sodium acetate buffer of pH 3.5 produced a single, double, and triple wave with increasing concentration and gave half-wave potentials in the neighborhood of −0.2. −0.5, and −0.55 volt *vs.* saturated calomel electrode. These studies were not directly applicable to analytical determinations because the polarograms were made on solutions prepared by dissolving the solid heteropoly acid directly in the supporting electrolyte, whereas in an analytical procedure the heteropoly acid would be formed in solution using excess molybdate which is reducible in an acetate buffer (*8*). The study by Strickland (*20*), comparing the polarographic behavior of the α and β forms of molybdosilicic acid in 0.1*N* potassium sulfate at a pH of approximately 3.5, was encouraging. The β-form, which is supposed to to be the one usually found under analytical conditions, gave rise to an ill-defined polarogram consisting of two waves with half-wave potentials of +0.3 and −0.1 *vs.* normal hydrogen electrode. The present investigation of the polarographic behavior of molybdosilicic acid formed under analytical conditions suitable for spectrophotometric work revealed a moderately well-defined reduction wave for the heteropoly acid which appeared at a potential corresponding closely to that for the first wave reported by Strickland. The height of this wave was directly proportional to the concentration of dissolved silica, and proved to be quite useful in confirming the spectrophotometric results.

APPARATUS AND REAGENTS

Apparatus. Absorbance measurements were made with a Beckman Model DU quartz spectrophotometer using matched 1.00-cm. silica cells. Most measurements were made in the 320 to 400 mμ region of the spectrum where the tungsten lamp (with blue filter) was used as light source in preference to the hydrogen discharge tube.

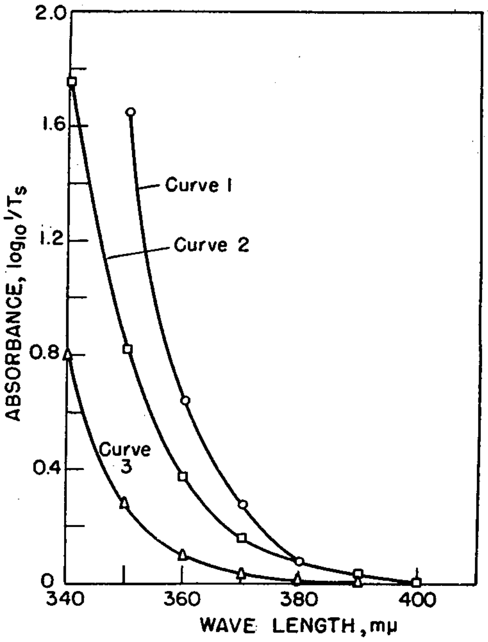

Figure 1. Absorption Spectrum of Molybdate in 0.1*N* Acid

All solutions contained 0.50 gram of molybdenum oxide in 100 ml. of 0.1*N* acid

1. HCl, $HClO_4$, HNO_3 and H_2SO_4
2. H_3PO_4
3. CH_3COOH

Polarograms were taken with a Sargent Model XXI polarograph. The capillary constant, $m^{2/3}t^{1/6}$, was 1.74 at 0 volt *vs.* S.C.E. All solutions were thermostated at 25° ± 0.1° C. while being purged with nitrogen and during the actual recording of the polarogram.

Measurements of pH were made with a Beckman Model G pH meter. When measuring the pH of solutions containing an appreciable amount of perchlorate, a calomel half-cell saturated with sodium chloride was used to avoid formation of solid potassium perchlorate at the tip of the reference electrode. The instrument was standardized at pH 3.57 with a solution of saturated potassium acid tartrate as recommended by Lingane (*13*).

Polyethylene bottles and beakers were used throughout this study. Solutions, after being mixed in volumetric flasks, were transferred to polyethylene bottles for storage.

Reagents. All chemicals used were of analytical reagent or C.P. purity. Concentrated solutions of salts were filtered after preparation in order to remove any insoluble particles.

Stock solutions of 10 mg. per ml. of soluble silica, arsenic(V), and phosphorus(V) were prepared by dissolving 4.7 grams of sodium metasilicate ($Na_2SiO_3.9H_2O$), 4.2 grams of sodium acid arsenate ($Na_2HASO_4.7H_2O$), and 12 grams of trisodium phosphate ($Na_3PO_4.12H_2O$), respectively, in distilled water and diluting the resultant solutions to 100 ml. These stock solutions were standardized gravimetrically, and standard solutions of 100 γ per ml. of desired constituents were prepared from them by dilution.

A working solution of 40 mg. per ml. of molybdenum(VI) oxide was prepared by dissolving 50 grams of ammonium molybdate tetrahydrate in distilled water and diluting the resultant solution to 1 liter.

EXPERIMENTAL

Spectrum of Molybdosilicic Acid. The adsorbance of a sample containing 4 p.p.m. of silica and 5 mg. per ml. of molybdenum oxide in 0.1*N* hydrochloric acid, made up according to the directions of Armand and Berthaux (*2*) and measured against a blank containing the same amount of molybdate and acid, was found to increase toward the ultraviolet region of the spectrum down to 340 mμ. Below 340 mμ, the blank could no longer be balanced. The blank might be strongly absorbant because of the formation of a molybdenum chloride complex with a strong ultraviolet absorption band, so similar solutions of molybdosilicic acid were prepared using various 0.1*N* acids and the spectra determined against distilled water. The results of this study, shown in Figure 1, indicate that the same spectrum was obtained in each of the strong acids except in phosphoric. In acetic acid the molybdate was also less absorbant. Solutions of normal molybdates tend to form polymolybdates whose complexities increase with increasing concentration of hydrogen ion so the absorbance of the blank is probably due to a polymolybdate.

Optimum Conditions of Acidity. In almost every paper published on the yellow method a study has been made to determine the optimum conditions of acidity and concentration of molybdate. It is generally agreed that the optimum pH lies between 1 and 2, and that the molybdate-to-silica ratio must be greater than 12 for measurements in the visible, but establishment of the conditions for the ultraviolet was necessary. Samples were made up to contain 5 p.p.m. of silica with 5 mg. per ml. of molybdenum(VI) oxide in various concentrations of acid. In each case a blank containing the same amount of molybdate and acid was used. The lower wave length limit was taken as the point where the blank could no longer be balanced. Although hydrochloric acid was first used in this study, a change was made to perchloric acid because it has the least tendency to form heavy metal complexes having absorption bands in the near ultraviolet. The results were the same with each acid and are shown in Figure 2 plotted as log A_s *vs.* λ (*14*). The wave length of maximum absorption shifted toward longer wave lengths as the acid concentration decreased from 1.4 to 1.18*N* and with further decreases in acid strength receded into the ultraviolet. At the same time, the peak absorbance increased and then decreased. This behavior is consistent with the results of previous workers who recommended a final pH of 1 to 2 for colorimetric work because at higher and lower pH's the absorbance peak is shifted toward the ultraviolet thereby resulting in less intense absorption in the visible.

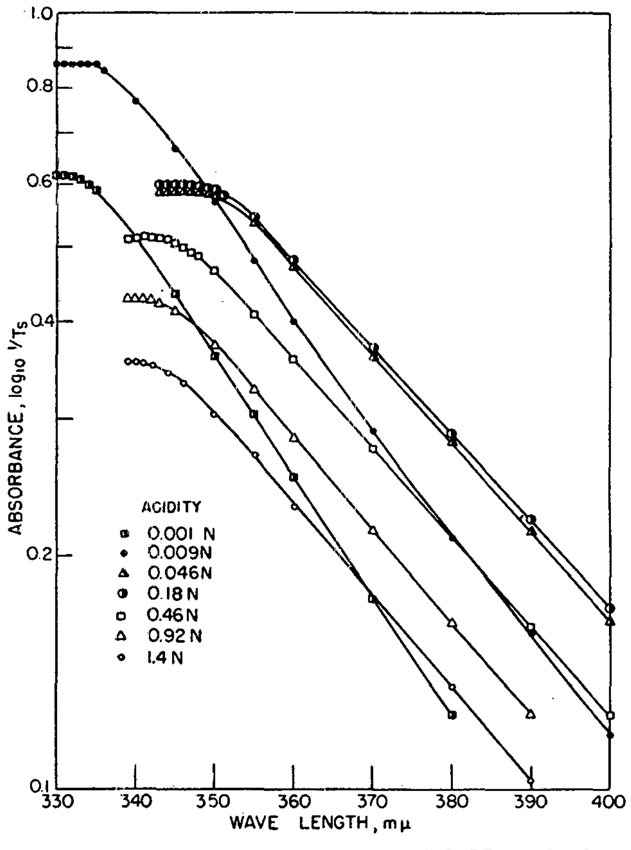

Figure 2. Variation of Spectrum of Molybdosilicic Acid with Acidity

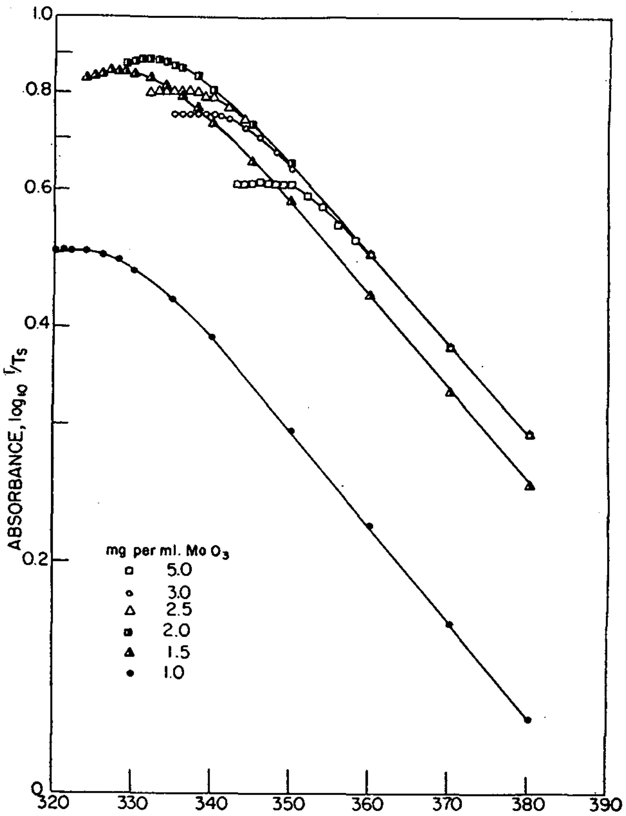

Figure 3. Variation of Spectrum of Molybdosilicic Acid with Molybdate Concentration

All solutions contained 500 micrograms of silica and 2 ml. of 60% perchloric per 100 ml.

Further studies showed that in acidities of 0.01 to 0.001*N* the sensitivity was good but varied widely with pH. In the 0.5 to 1.5*N* acid range the acidity could be adjusted easily, but the color development was erratic. In the range of 0.09 to 0.28*N* of perchloric acid the color development was independent of acid concentration. Therefore, a final concentration of 0.18*N* (1.2%) of perchloric acid was chosen because it represented a convenient dilution of the 60% acid supplied commercially and was near the middle of the optimum acid range.

Optimum Molybdate Concentration. The spectra of samples made up to contain silica in 1.2% of perchloric acid with varying amounts of molybdate were measured against appropriate blanks 0.5 hour after mixing. According to these results, shown in Figure 3, 2 mg. per ml. of molybdenum(VI) oxide gave the greatest sensitivity. When the effects of acid concentration were checked at this new concentration of molybdenum, 1.2% of perchloric again fell inside the optimum range.

Study of Interferences. In these samples the probability of encountering phosphate was high; arsenate, slight; and germanate, vanishingly small. For that reason only interferences from phosphate and arsenate were studied. Solutions were made up to contain 3 p.p.m. of phosphorus and 25 p.p.m. of arsenic with the optimum concentrations of perchloric acid and molybdate. The spectra of these heteropoly acids, determined against a blank containing the same amount of molybdate and acid, were very similar to the spectrum of the molybdosilicic acid, except that the absorbance index of the molybdosilicic acid at any given wave length was about ten times that of the molybdophosphoric acid and about one hundred times that of the molybdoarsenic acid.

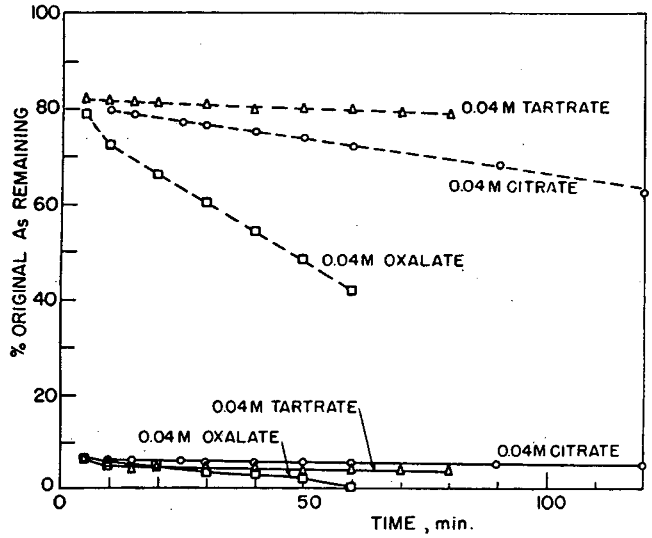

Figure 4. Comparison of the Bleaching Effect on Molybdosilicic Acid (- - - -) and on Molybdophosphoric Acid (—)

In order to compare the abilities of citrate, oxalate, and tartrate to remove phosphorus and arsenic interference, three samples were made up to contain 5 p.p.m. of silica, 3 p.p.m. of phosphorus, and 25 p.p.m. of arsenic, respectively, and a $0.04M$ concentration of one of the three complexing agents. (The molarity of 0.04 was in or close to the optimum range recommended in previous studies.) The change in absorbance of each solution with time was measured at 332 mμ against an appropriate blank. The molybdoarsenic acid was completely bleached at once by each of the reagents used while molybdophosphate lost over 90% of its absorbance at once and gradually lost more with time (Figure 4). In each of the three reagents the molybdosilicic acid absorbance was about 20% less at the start; it continued to fade rapidly in oxalate and citrate, but very slowly in tartrate. Therefore, tartrate appeared to be the best of the three.

The possibility of using excess phosphate to remove the phosphate and arsenic interferences was also investigated. In the presence of $0.1M$ or more phosphate, the interference from 25 p.p.m. of arsenic was eliminated entirely. In 0.1 to $0.2M$ phosphate, interference from 3 p.p.m. of phosphorus remained constant at about 4% of its value in the absence of excess phosphate while the absorbance of the molybdosilicic acid bleached to about 65% of its former intensity. Thus $0.1M$ phosphate produced nearly the same effect as tartrate, but tartrate was considered to be the better reagent because many cations can form precipitates with phosphate under a variety of conditions.

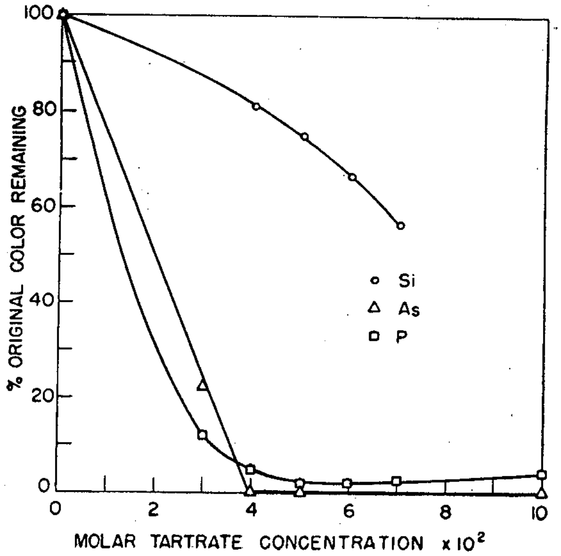

Figure 5. Bleaching Effect of Various Concentrations of Tartrate on the Heteromolybdic Acids of Silicon, Phosphorus, and Arsenic

To determine the optimum concentration of tartrate for removal of phosphorus and arsenic interferences, solutions of 5 p.p.m. of silica, 3 p.p.m. of phosphorus, and 25 p.p.m. of arsenic were made up according to the standard procedure. However, before the solutions were adjusted to their final volumes, varying aliquots of $0.5M$ sodium tartrate were added. After 0.5 hour the absorbance of each solution was measured at 332 mμ against a blank containing the same amount of tartrate as the sample. Figure 5 shows that a final concentration of $0.05M$ tartrate eliminated interference from arsenic, and minimized that from phosphorus while causing only about 25% reduction in the absorbance of the molybdosilicic acid. Therefore, a corresponding amount of tartaric acid, 4 ml. of a 20% solution, should be added for each 100 ml. of final volume.

Other Experimental Variables. Preliminary experiments had shown that best results were obtained when molybdate was added to the silicate, followed by development of the color by addition of perchloric acid and finally removal of interferences with tartaric acid. However, unless great care was exercised in avoiding slight variations in the details of mixing and diluting, the reproducibility was very poor. A procedure less sensitive to experimental manipulations was certainly desirable. Of the possible variables, the following appeared to be the most likely. Differences in the volume at the time of development of the color with acid would result in different concentrations of hydronium ion. Furthermore, because full development of the color required about 0.5 hour, the time at which the tartrate was added could be important. Together, these factors might make the method of mixing important. Hence, the following factorial experiment was carried out.

The volume of the silica sample was adjusted with distilled water, added from a buret, to 12, 37, 62, or 77 ml. immediately after adding the acid.

Tartrate was added 5, 15, 30, or 60 minutes after the acid.

In one set of experiments, each flask was swirled to mix the solutions during the addition of a reagent, whereas in another, the flasks were swirled only after the addition had been completed. In each case, the volume was adjusted to 100 ml., and mixed thoroughly immediately after adding the tartrate. The absorbance was measured after 15 to 20 minutes (against a blank

Table I. Absorbance Data for the Factorial Experiment

(Using 5 ml. of a 100 p.p.m. solution of silica and a final volume of 100 ml.)

Time of Mixing	Volume before Adding Tartaric Acid, Ml.	Addition of Tartaric Acid, Minutes 5	15	30	60
		Absorbance, mμ			
Immediate	12	0.597	0.587	0.590	0.531
	37	0.575	0.645	0.695	0.748
	62	0.653	0.819	0.885	0.915
	77	0.733	0.897	0.916	0.915
After addition	12	0.611	0.628	0.550	0.658
	37	0.665	0.741	0.785	0.795
	62	0.780	0.815	0.879	0.903
	77	0.875	0.885	0.920	0.915

prepared in the same manner as the sample) using a 0.90-mm. slit. Duplicates were not run because the desired information was available from the first set of experiments without further statistical analysis.

Table I shows that each of the factors exerted important effects on the final absorbance. However, when the sample volume was adjusted to 77 ml., the mixing technique was no longer important providing the solution had been allowed to stand at least 15 minutes before the tartaric acid was added. Further studies showed that the dilution of 77 ml. was not critical—i.e., a variation in volume ±7 ml. did not noticeably affect the final absorbance.

Calibration Curve and Optimum Range. A calibration curve was prepared by the following standard procedure. An aliquot of the standard 100 p.p.m. of silica solution was transferred to a 100-ml. volumetric flask. Five milliliters of a solution containing 40 mg. per ml. of molybdenum(VI) oxide were added and the solution was mixed. Two milliliters of 60% perchloric acid were added by pipet, the solution was again mixed, and the total volume adjusted to about 75 ml. with distilled water. After 30 minutes, 4 ml. of 20% tartaric acid were added by pipet and the solution was diluted to volume.

The absorbance of a solution prepared in this manner showed a 2% decrease in color during the first 45 minutes after mixing, but 1.6% occurred in the first 15 minutes. Therefore, the absorbances of the solutions were measured after 15 minutes.

Beers law was obeyed for the range 0.5 to 10 p.p.m. of silica. The average absorbance index (per p.p.m.) was 0.183 and the coefficient of variation 2.1%. When the data were plotted as absorbance (1 − transmittance) against the logarithm of the concentration of silica, as recommended by Ringbom (*16*), the concentration range of 1 to 5 p.p.m. was found to be optimum.

POLAROGRAPHIC STUDIES

In attempting to corroborate the absolute accuracy of the results of the spectrophotometric analyses, the possibility of determining silica by reduction of the molybdosilicic acid complex at the dropping mercury electrode was investigated. Exploratory polarograms were run on solutions prepared according to the spectrophotometric procedure. A steeply sloped wave with a half-wave potential of +0.15 volt *vs.* S.C.E. was found for molybdosilicic acid, whereas at more negative potentials, the wave was essentially the same as that for molybdate alone. Reduction of the blank did not begin until +0.05 volt.

Various attempts were made to improve the wave shape. By eliminating the addition of tartrate in the preparation of solutions the anodic dissolution of mercury was shifted to more positive potentials so that the molybdosilicic acid wave was more easily observed. In perchlorate solutions, the wave was fairly satisfactory, but the best-shaped wave was obtained by using 1*M* ammonium nitrate as supporting electrolyte with 0.001% of gelatin present as maximum suppressor. Furthermore, in nitrate solutions the spectrophotometric interferences, phosphorus and arsenic, were eliminated as precipitates of ammonium molybdophosphate and molybdoarsenate. A saturated potassium nitrate–agar bridge was used between the solution and the saturated calomel electrode.

A calibration curve was prepared according to this procedure. Into a 100-ml. volumetric flask the desired aliquot of 100 p.p.m. silica was pipetted. Then 25 ml. of 4*M* ammonium nitrate and 5 ml. of 40 mg. per ml. of molybdenum oxide were added and mixed thoroughly. After adding 2 ml. of 9.2*M* nitric acid, mixing and adding 1 ml. of 0.1% gelatin solution, the solution was made up to the mark. A portion of the solution was transferred to a polarographic cell where it was thermostated for 30 minutes and deaerated with nitrogen for the last 10 minutes before recording the polarogram.

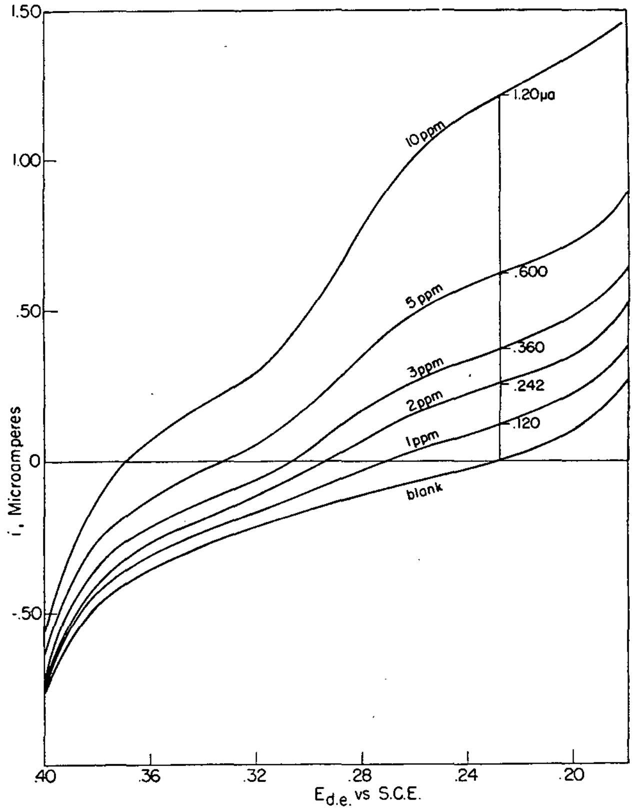

Figure 6. Polarographic Curves for Different Concentrations of Molybdosilicic Acid in a Supporting Electrolyte of 1*M* Ammonium Nitrate and 0.2*M* Nitric Acid

The curves used for the calibration are shown in Figure 6. Rather than using a graphical technique for evaluating the diffusion currents, the currents were measured at +0.23 volt *vs.* S.C.E. where the blank was zero. In the range of 1 to 10 p.p.m., which was investigated, the currents were proportional to the concentration of silica.

ANALYSES OF SAMPLES

Choice of Acid. In the preliminary tests samples were prepared by dissolving a large batch of magnesium oxide or magnesium carbonate in concentrated perchloric acid and subsequently taking aliquots of this concentrated solution. Because a large amount of heat was evolved when perchloric acid was used, a short study was made to determine if some other acid could be substituted.

The earlier decision to avoid hydrochloric acid was supported when a yellow solution was obtained which gave a pink color with thiocyanate. Presumably the yellow color was due to a ferric chloride complex. Nitric acid was avoided as the solvent for spectrophotometric determination because of the necessity of driving off the oxides of nitrogen which, if present, would exhibit a very high absorbance. Sulfuric acid was eliminated because large amounts of sulfate caused a bleaching of the color of the molybdosilicic acid as shown in Table II. Consequently, perchloric acid was deemed most suitable for spectrometric measurements:

Table II. Bleaching Effect of Sulfate on the Absorbance of Molybdosilicic Acid

SiO_2, P.P.M.	Sulfate Concn., M	A_s
3	...	0.390
3	0.32	0.098
3	0.64	0.041
3	0.96	0.022

Table III. Effect of Sample Weight on the Per Cent of Silica in Magnesium Oxide

Aliquot, Ml.	Sample Weight, G.	A_s	SiO_2, P.P.M.	SiO_2, %
Spectrophotometric (37.0 g./liter MgO in perchloric acid stock)				
75	2.78	0.773	4.22	0.0152
50	1.85	0.467	2.55	0.0138
25	0.925	0.188	1.03	0.0103
Polarographic (100 g./liter MgO in nitric acid stock)				
50	5.00	0.890	7.41	0.0149
25	2.50	0.437	3.64	0.0146
10	1.00	0.147	1.22	0.0122

Effect of Sample Weight on Analyses. In order to test the polarographic and spectrophotometric procedures, stock solutions of magnesium oxide in nitric acid and in perchloric acids, respectively, were prepared by dissolving the desired amount of the magnesium compound in the theoretical quantity of acid. Aliquots of these solutions were analyzed by the two methods. Table III shows that the final percentage of silica found was dependent upon the sample weight. However, the answers obtained by both methods on samples which contained 3 to 7 p.p.m. of silica generally agreed very well.

The consistently low answers obtained by spectrophotometric analysis of samples containing only a small amount of silicate seem to be due to a bleaching effect of magnesium ion on the high background absorbance of the excess molybdate. This conclusion was drawn from the following spectrophotometric study.

Various amounts of magnesium perchlorate were added to solutions of 0.5 and 5.0 p.p.m. silica before they were developed by the standard spectrophotometric procedure. These samples were measured both against a normal blank and against a blank containing the same amount of magnesium perchlorate as the sample.

Table IV shows that blanks prepared in the presence of magnesium perchlorate were less absorbant than blanks containing no added magnesium perchlorate. (The blank containing $1.0M$ magnesium perchlorate is an exception, but this positive absorbance may have resulted from silicate introduced by the magnesium perchlorate or from formation of a magnesium tartrate complex.) The lower absorbance of blanks containing magnesium may be due to formation of molybdate complex or to a change in the concentration or nature of the polymolybdate ion as a result of the change in ionic strength. A similar trend is shown by the absorbances for 0.5 p.p.m. silica which was almost nil in the presence of 0.2 to $0.6M$ magnesium perchlorate. Measurements made against blanks containing the same amount of magnesium perchlorate are discordant but the values for the absorbances of the samples are nearer to the expected value. The relative effect of added magnesium perchlorate was less on the 5 p.p.m. silica sample for the same adsorbance was obtained up to $0.6M$ magnesium perchlorate.

Table IV. Effect of Magnesium Perchlorate on Molybdosilicic Acid Color

Concn. of $MgClO_4$, M	Silica Added, P.P.M.	A_s vs. Normal Blank	A_s vs. Blank Containing Same Amt. of $MgClO_4$
0	0.5	0.095	...
	5.0	0.920	...
0.2	0.0	<0.00	...
	0.5	0.007	0.097
	5.0	0.820	0.916
0.4	0.0	<0.00	...
	0.5	0.009	0.100
	5.0	0.815	0.916
0.6	0.0	<0.00	...
	0.5	0.015	0.073
	5.0	0.820	0.880
0.8	0.0	<0.00	...
	0.5	0.050	0.101
	5.0	0.840	0.900
1.0	0.0	0.015	...
	0.5	0.068	0.052
	5.0	0.877	0.862

Accuracy sufficient for control work would appear to result if enough sample was employed to ensure close to 5 p.p.m. of silica in the final solution. For more accurate work it would be necessary to add a constant amount of a low-silica (or preferably, silica-free) magnesium perchlorate solution to the silica standards used in the preparation of a calibration curve.

SOLUBILIZATION OF SILICA

Although interest was primarily in the determination of soluble silica, several studies were made to determine methods of dissolving small amounts of silica, initially present as colloidal silica, prior to spectrophotometric determination.

Fluoride. Hydrofluoric acid could not be used in the presence of magnesium ion because magnesium (or calcium?) fluoride was formed in the solution and interfered with the absorbance measurements. Carlson and Banks (*6*) used a zirconium fluoride reagent for dissolving silica in the presence of calcium and then determined the silica by the molybdenum blue method. Before testing their method on insoluble silica, tests were made which showed that addition of this reagent to solutions of soluble silicates did not affect the value of the absorbance. Therefore, a suspension of approximately 100 p.p.m. of colloidal silica in 100 ml. of distilled water was prepared by weighing out 0.0100 gram of Mallinckrodt Silicic Acid, "Special Bulky," which had been dried at 120° C. When aliquots of the freshly shaken suspension were treated with the zirconium fluoride according to the method of Carlson and Banks, no silicate was found in these solutions when they were analyzed by the spectrophotometric method. However, when a reducing agent was added to these solutions the molybdenum blue color was formed. Therefore, it appeared that the mass action constant for the total reaction of solubilization and heteropoly acid formation was so small that the reaction only occurred when the heteropoly acid was removed by reduction.

Ammonium Hydroxide. A study was made to determine the feasibility of using ammonia to solubilize colloidal silica for ammonia can easily be prepared in a silicate-free form by saturating distilled water, in a polyethylene bottle, with ammonia gas.

Preliminary tests showed that colloidal silica was dissolved by treatment with ammonium hydroxide. In order to determine if this solubilization were reproducible and quantitative, samples of a synthetic colloidal silica solution prepared from silicic acid were treated with 10 ml. of silicate-free ammonium hydroxide in a polyethylene beaker in a hot water bath for 20 minutes. The samples were neutralized to phenolphthalein with a few drops of acid and cooled, and the soluble silicate was determined by the standard spectrophotometric technique. On five samples of approximately 4 p.p.m. of silica the range of absorbance values was 0.790 to 0.814; the average, 0.802; and the standard deviation, ±0.0094 or ±1.2%. When samples containing 2 to 10 p.p.m. of colloidal silica were given the same treatment, Beer's law was obeyed, but the average absorbance index was slightly higher than the value obtained with soluble silica probably because the powdered silicic acid contained less water than assumed by using metasilicic acid, H_2SiO_3, as the basis for calculation. On the basis of these studies the ammonia treatment, rather than the fluoride treatment, is recommended for solubilization of colloidal silica when the nature of the sample permits it to be made alkaline.

DISCUSSION

The method frequently used in control procedures for the determination of silicate in magnesium oxide and carbonate depends on the precipitation and weighing of silicic acid from a 10-gram sample. For a 10-gram sample containing the maximum allowable limit of 0.02% of silica, the final weight of precipitate is only 2 mg. Because the usual weighing error is ±0.1 mg., the gravimetric procedure is subject to at least a 5% error. It is well known that in any gravimetric determination of silica the final traces of silica are difficult to remove by the usual process of fuming with acid so that the gravimetric procedure probably leads to low results.

The reproducibility of analyses obtained on small samples of magnesium oxide or carbonate (0.5 to 1.0 gram) was significantly worse than that obtained on larger samples (5 to 10 grams); the latter, in turn, was worse than that obtained with aliquots from a given solution of oxide or carbonate corresponding either to 0.5- or 5-gram samples. This behavior was interpreted as an indication of heterogeneity of the materials despite the special efforts to ensure homogeneity. Therefore, a more representative result will be obtained by weighing out and dissolving a large sample followed by analysis of an appropriate aliquot rather than using a small sample in its entirety.

The sensitivity of the "yellow" method is comparable to that of the "blue" method when measurements are made at 332 mμ rather than to the region of 370 to 425 mμ that has previously been recommended. Furthermore, the yellow method is simpler to use because it does not involve a reduction to molybdenum blue.

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Thiocyanate Spectrophotometric Determination of Molybdenum and Tungsten

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The critical examination of the thiocyanate spectrophotometric procedures for molybdenum and tungsten is a part of a larger and more general program on the application of this medium to trace metal ion analysis. This investigation gives evidence for the 2-electron reduction of molybdenum by stannous chloride. The occurrence of several species in each valence state is shown and the valence state involved in the color development is proved. Other difficulties in the color development are discussed. The procedures described, if carefully followed, are more selective, sensitive, and reliable than other thiocyanate methods applied to the analysis of these metals.

THIOCYANATE has been employed fairly extensively in the spectrophotometric analysis of a number of metal ions. The application of thiocyanate to the determination of cobalt (*15*) and of iron (*13*, *14*) are two of the oldest colorimetric methods. The thiocyanate method has also been applied in the analysis of molybdenum, rhenium, tungsten, and more recently, uranium and niobium. The authors have studied the color development with thiocyanate in homogeneous acetone-aqueous system for 30 elements. The results of a study of molybdenum and tungsten in subgroup VI are reported here.

The choice of the acetone-aqueous system was based largely on the experience gained in previous work on uranium (*3*). In general, acetone gave the highest sensitivity in a homogeneous system, showed the greatest tendency to prevent interference from other anions, and showed a favorable general solubility for a wide variety of salts and acids. Stabilization of many valent states was more easily accomplished in acetone.

The authors believe that they have minimized the effect of previous history of the molybdenum and tungsten solutions on the color development. Some of the difficulties in color development caused by reaction kinetics, quantitative achievement of the proper valent state, and the presence of multiple species in a given valent state have been eliminated.

REAGENTS

Ammonium thiocyanate, c.p. reagent grade material, was recrystallized from a saturated methanol solution. The methanol solution of ammonium thiocyante was saturated at 50° C. in a water bath and the warm solution was filtered by drawing through a coarse-porosity glass filter disk into a filter flask. Polythene tubing was used to connect the disk and flask. (Rubber tubing introduces organic materials which form colored products.) The saturated methanol solution was cooled in an ice bath, and the crystals were filtered on a coarse-porosity glass filter disk. The crystals were dried thoroughly by means of dry air or nitrogen flowing rapidly through the crystalline mass for 24 hours.

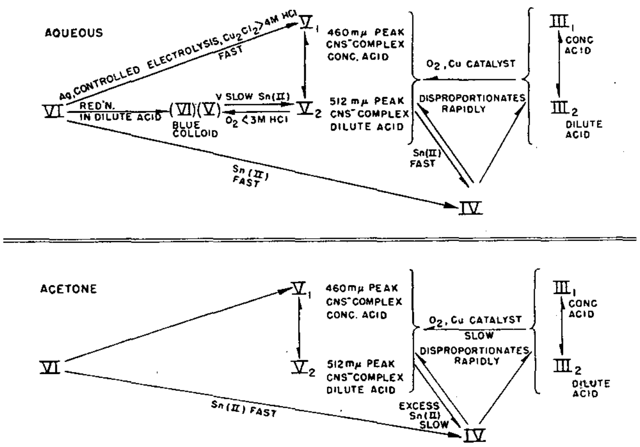

Figure 1. Molybdenum Reaction Scheme

The crystals were broken and then were stored in a drying cylinder, through which passed a moderate flow of dried gas. A tube of anhydrous calcium sulfate was used to dry the air or nitrogen gas stream. At 25° C. and a relative humidity of 10% or less, the crystals may be air-dried by spreading on a clean, inert surface. At 25° C. and a relative humidity greater than 50%, however, the crystals appeared wet after 24 hours in the open air. The wet crystals invariably yielded poorer color stability, varying somewhat with the metal analyzed and the storage time and storage temperature. The importance of working with recrystallized and dry-stored ammonium thiocyanate crystals cannot be overemphasized if precise and uniform results are to be obtained.

Standard solutions of tungsten(VI) were prepared by weighing pure tungstic oxide or anhydrous sodium tungstate into 50 ml. of 0.25*M* sodium hydroxide. The sodium tungstate was then added slowly and with stirring to approximately 900 ml. of concentrated hydrochloric acid and diluted to volume with concentrated hydrochloric acid. Concentrations of tungsten(VI) up to 0.006*M* were obtained and were stable over long periods.

Standard molybdenum(VI) was prepared by weighing and dissolving reagent grade molybdic oxide in a minimum of 8*M* hydrochloric acid.

APPARATUS

A Beckman Model DU quartz spectrophotometer and a Cary model 11 recording spectrophotometer were both used. One-centimeter quartz cells were used throughout.

MOLYBDENUM

The thiocyanate spectrophotometric method has long been considered one of the most reliable methods (*9*) for the analysis of trace amounts of molybdenum. The development of the molybdenum–thiocyanate complex and the extraction of the color into ether was applied 90 years ago (*2*) and more recently by King (*11*). Kapron and Hehman (*10*) developed the molybdenum–thiocyanate complex directly into butyl Cellosolve and butyl Carbitol aqueous mixtures. These investigators were using the molybdenum(V)–thiocyanate complex; the present authors also found this to be the most useful species.

A graphic summary of some of the molybdenum reactions in aqueous and acetone media is given in Figure 1. A detailed study of the kinetics of each of the various reactions was not undertaken, and Figure 1 is limited mainly to information which the authors feel is essential to the intelligent application of the color-developing procedures. It was found that only molybdenum(V) developed the characteristic colors which have been applied previously in the analysis of this element. Thus the major problem has been the quantitative reduction of molybdenum(VI) to molybdenum(V). A glance at Figure 1 will also give a quick survey of most of the difficulties involved. Previous methods have achieved only 50 to 75% of the maximum possible color intensity; the major difficulty has been traced to the reduction reaction or stabilization of molybdenum(V) in solution. Even observing the warning of Dick and Bingley (*4*) that iron- or copper-free molybdenum(VI) solutions developed only 65% of the color when reduced with tin(II), very slow and erratic color development will occur if the correct sequence of addition of reagents is not observed. Slow color development shown in Figure 2 occurred when molybdenum(VI) solution was first reduced with excess stannous chloride in acetone-aqueous medium, followed by the addition of cuprous chloride. The absorbance in this case reached a maximum after standing about 60 minutes. A similar slow color development occurs in aqueous medium, or a lower color intensity is obtained when ether extracted. Rapid and quantitative development of the color was always achieved by first reducing molybdenum(VI) to molybdenum(V) with copper(I) in 4*M* hydrochloric acid solution. In previous work, no attempt was made to obtain the maximum molar absorbance index for standard molybdenum solutions in any given medium.

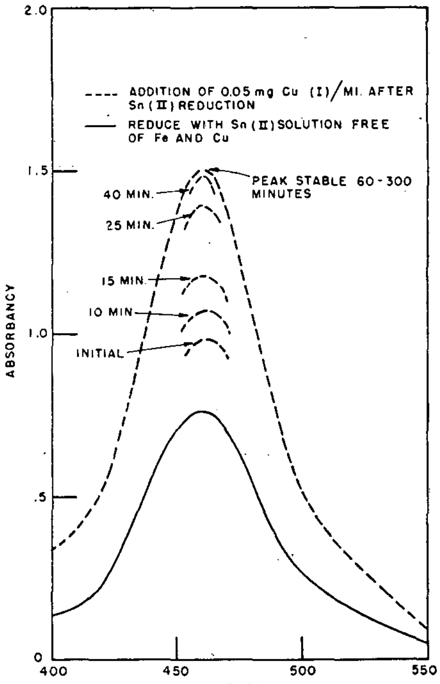

Figure 2. Effect of Copper on Reduction of Molybdenum with Stannous Chloride

Molybdenum initially in hexavalent state, 8.10 × $10^{-5}M$, 60 volume % acetone and 0.6*M* NH_4CNS

Birnbaum and Walden (*1*) have shown that stable standard molybdenum(V) solutions may be prepared by reduction of molybdenum(VI) in approximately 4*M* hydrochloric acid at 60° C. in a silver reductor. The reduction was complete and the stoichiometry of the reaction was checked by titration of the molybdenum(V) with standard ferric chloride. The thiocyanate complex developed an absorbance with the molybdenum(V) standard in aqueous, acetone, and ether media identical with that obtained by the copper(I) reduction procedure on molybdenum(VI) standards in the three media, in both the complete form of the spectra and the intensity.

The color of the molybdenum(V)-thiocyanate complex shown in Figure 3 was obtained directly upon the addition of 100- to 250-microliter aliquots of molybdenum(V) stock solutions to aqueous, acetone, or ether thiocyanate solutions. The addition of a moderate excess of tin(II) or tin(II) and copper(I) did not affect the color in acetone or ether. A large excess of tin(II), however, slowly reacted with molybdenum(V) to reduce the absorbance. Additions of excess tin(II) to the aqueous solution reacted more readily with the molybdenum(V) to reduce the absorbance and this excess tin has been the source of previous analytical difficulties in this medium.

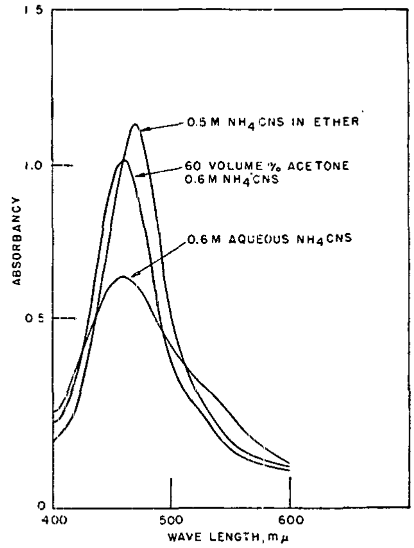

Figure 3. Comparison of Molybdenum(V)-Thiocyanate Complex Developed in Various Media

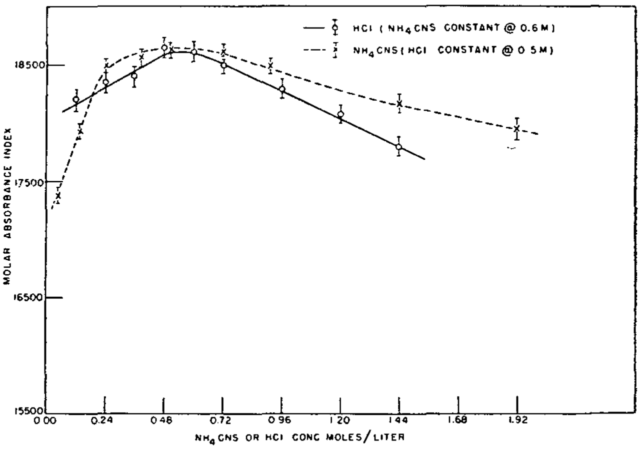

Figure 4. Effect of Acid and Thiocyanate on Molar Absorbance Index of Molybdenum

A search for evidence of mixed valent complexes and possible reactions of molybdenum(V) with acetone, ether, or thiocyanate indicated none of these complications. The observed rate of color development in all the media was complete and stable within 20 seconds, the time required for complete mixing. Also a 50% decrease in the molar absorbance index always was obtained for the total molybdenum concentration when the color was developed in previously mixed equimolar mixtures of molybdenum (VI) and molybdenum(V) and molybdenum(V) and molybdenum(III). Molybdenum(III) was prepared by reduction of a concentrated hydrochloric acid solution of molybdenum(VI) with granulated lead in an inert atmosphere. The solution of molybdenum(III) in $\geq 10M$ hydrochloric acid was bright red. The absorbance index also decreased when molybdenum(V) stock solution was partially oxidized (bromine) or reduced [tin(II)] in the presence of thiocyanate. The authors have concluded, therefore, that the 460 and 470 mμ absorbance peaks shown in Figure 3 are due to only a molybdenum(V)-thiocyanate complex, and represent the maximum obtainable molar absorbance index in the media described.

Figure 4 shows the effect of thiocyanate and hydrochloric acid concentration in the acetone medium on the molar absorbance index. For the acetone-aqueous medium (60 volume % acetone and $0.6M$ ammonium thiocyanate) the molar absorbance index and the standard deviation at the 460 mμ maximum were 18,700 ±150. Figure 5 shows the obedience of the total molybdenum concentration to Beer's law. The ether extraction procedure gave a molar absorbance index and standard deviation at the 470 mμ maximum of 19,500 ± 200.

It is now possible to employ the molar absorbance index obtained with the standard molybdenum(V) solution to explain the remarkable effects observed with copper and iron in developing the molybdenum(V)-thiocyanate complex. It was shown in Figure 2 that the iron- and copper-free solutions of molybdenum developed only 50% of the maximum color when reduced with moderate excess of tin(II). The 50% color development was demonstrated more easily at the higher molybdenum concentrations in the acetone thiocyanate medium. In ordinary work where traces (<1 part per million) of iron or copper were present, the color intensity ranged between 50 and 75% of the known maximum. In each of these low intensity color developments the scanned 460 mμ absorbance peak showed no changes in form anywhere in the visible region (800 to 300 mμ).

The following explanation is consistent with all the observed facts and also allows the hypothesis of a reaction scheme.

Reaction 1 shows the rapid direct 2-electron reduction of molybdenum(VI) to molybdenum(IV):

$$\text{Mo(VI)} + \text{Sn(II)} \xrightarrow{\text{rapid}} \text{Mo(IV)} + \text{Sn(IV)} \qquad (1)$$

It is assumed that this is rapidly followed by Reaction 2:

$$2\text{Mo(IV)} \rightarrow \text{Mo(V)} + \text{Mo(III)} \qquad (2)$$

It must be assumed that molybdenum(VI) is depleted quickly and/or no appreciable reaction with molybdenum(III) occurs.

It was shown independently, firstly, that mixtures of molybdenum(V) and molybdenum(III) do not react to form a mixed valent complex, and, secondly, that moderate excess of tin(II) will not reduce molybdenum(V) in the acetone thiocyanate medium. The half color intensity solutions were stable in the absence of copper or iron. If the above explanation is right, the correct reduction procedure may be prescribed immediately.

A relatively weak and preferably soluble one-electron reducing agent capable of only the step, molybdenum(VI) to molybdenum(V), is required. Thus, the reduction of molybdenum(VI) with copper(I) as recommended in the standard procedure did give the maximum molar absorbance index. In this procedure, tin(II) was added to reduce the copper(II) or iron(III) only after the molybdenum(V) was formed and complexed in the thiocyanate-acetone medium. Another possible method of developing the maximum color based on Reactions 1 and 2 is to reduce molybdenum(VI) quantitatively to molybdenum(III).

In chloride medium (>$3M$ hydrochloric acid), Reactions 1 and 2 are followed by:

$$\text{Mo(V)} + \text{Sn(II)} \rightarrow \text{Mo(III) or Mo(IV)} \qquad (3)$$

which in either case quantitatively reduces the molybdenum(VI) to molybdenum(III). Addition of the thiocyanate-acetone reagent developed no appreciable color with molybdenum(III). However, if the excess of tin(II) was relatively small, the addition of a trace of copper slowly developed the known maximum color, as shown in Figure 2. The removal of oxygen by saturating the solutions with carbon dioxide stopped the color development. Molybdenum(III) and no tin(II) present (prepared with lead reductor or by electrolysis) produced the correct maximum color when oxidized in either aqueous or acetone thiocyanate with a small excess of copper(II). As in the standard procedure, the copper(II) interference was finally removed with tin(II) after molybdenum(V)-thiocyanate complex was formed in the acetone medium. Although the silver reductor and controlled electrolysis may be employed to produce molybdenum(V) quantitatively, these methods of reduction are not readily adaptable to spectrophotometric work.

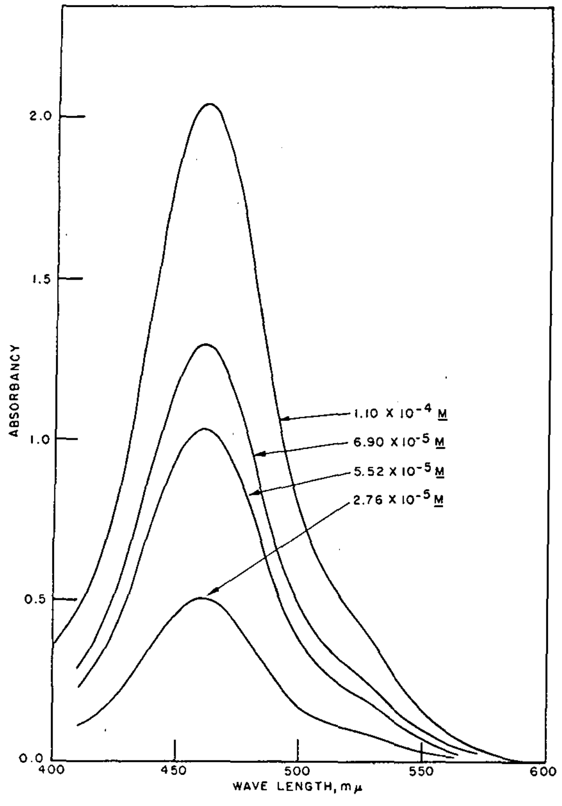

Figure 5. Molybdenum-Thiocyanate Complex

60 volume % acetone and $0.6M$ NH_4CNS molybdic acid reduced by Cu_2Cl_2

When starting with molybdenum(VI) solutions, there appeared to be very little difficulty with complex hydrolytic or polymeric unreactive species. In a 6-month period, storage of stock solutions of molybdenum(VI) in neutral, alkaline, or strong acid (>$0.5M$ hydrochloric or sulfuric acid) media did not reveal any difficulties with the color developing procedure. Solutions stored in dilute acid appeared to be easily reversible to a more reactive state by neutralizing or by warming slightly in concentrated hydrochloric acid. In general, molybdenum solutions caused less difficulty than tungsten. In dilute acid, (<$0.25M$) either in aqueous or acetone media, molybdenum(V) initially formed a red thiocyanate complex which slowly transferred to the more stable species. Figure 6 shows a spectrophotometric record of such a reaction in $0.12M$ hydrochloric acid. The red molybdenum(V)-thiocyanate complex has a maximum absorbance at 512 mμ and the orange molybdenum(V)-thiocyanate complex absorbance maximum is at 460 mμ. The isosbestic point of the two species is at 492 mμ. The standard molybdenum(V) stock solution used in the work of Figure 6 was prepared by reduction in a silver reductor according to the procedure of Birnbaum and Walden (*1*). The 0.7-minute and 4.3-minute curves of Figure 6 show the development of both species, and the 7.7-minute curve shows the end of the development of the 512 mμ species. The continued transference to the more stable 460 mμ peak is shown in the remaining curves.

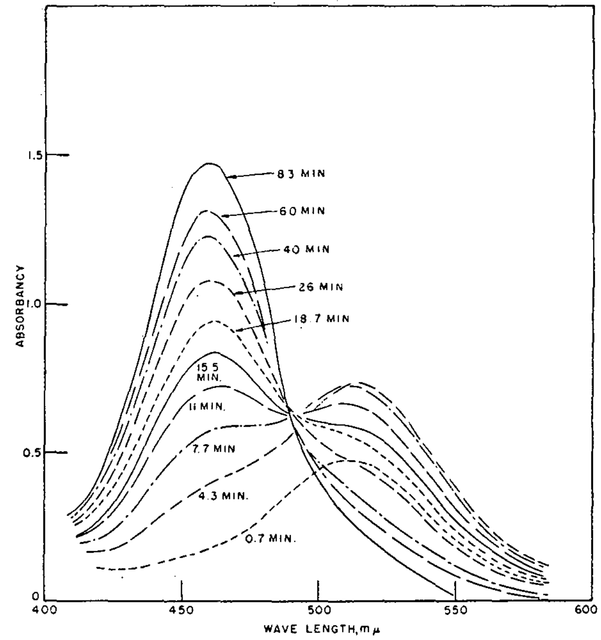

Figure 6. Molybdenum(V)-Thiocyanate Complexes

$8.19 \times 10^{-5}M$ Mo(V) in $0.12M$ HCl; 60 volume % acetone and $0.6M$ NH_4CNS

Color development in aqueous thiocyanate solutions was found to be highly unsatisfactory. The quantitative reduction of molybdenum(VI) to molybdenum(V) was very difficult to control. In dilute acids (1 to $4M$), the reduction of molybdenum(VI) to molybdenum(V) tended to produce the mixed valent molybdenum(VI) molybdenum(V) colloidal blue complexes. The quantitative reduction of this complexed molybdenum(VI) to molybdenum(V) is very slow and difficult. Also, the molybdenum(V) in the molybdenum blue complex does not readily form the characteristic molybdenum(V)-thiocyanate complexes. It is important, therefore, not to attempt to reduce molybdenum(VI) to molybdenum(V) in less than approximately $8.0M$ acid. After complete reduction to molybdenum(V) is accomplished, the solution may be diluted with water, and no molybdenum blue complex forms immediately. Dilute acid (<$8.0M$ hydrochloric acid) solutions of molybdenum(V) become increasingly more sensitive to air oxidation. Molybdenum blue is the stable product formed. Molybdenum(V) in 10 to $12M$ hydrochloric acid is green, stable, and capable of storage for several weeks in air before a noticeable amount of oxidation occurs. In dilute hydrochloric acid, molybdenum(V) is brown and quite sensitive to air oxidation. However, it was noted that freshly prepared molybdenum(V) brown chloro complex did not delay the quantitative formation of the 460 mμ molybdenum(V)-thiocyanate complex in the acetone medium if the final acid concentration was >0.6*M*. Aged in an inert atmosphere, brown molybdenum(V) showed an increasing tendency to form initially the red thiocyanate complex, which transferred as shown in Figure 6, if adequate acid was present, to the 460 mμ species.

STANDARD PROCEDURES FOR MOLYBDENUM

Homogeneous Acetone Thiocyanate Method. The solution of the sample may be effected in sulfuric acid or hydrochloric acid. If the sulfuric acid is reduced to approximately 1.0 ml. or less by fuming, there is no interference in the color development in a 25-ml. volume. To avoid the small errors indicated in Figure 4, the acid concentration of the samples should be consistent with those of the standards. The acid concentration, however, should not be less than that required to make the final solution of 25 ml. about 0.3*M*, and should not exceed 1.0*M*, which would cause phase separation in the final acetone solution. Cuprous reduction of molybdenum(VI) becomes slow in less than 4*M* hydrochloric acid medium. Add 5 drops of 0.1*M* cuprous chloride solution in concentrated hydrochloric acid. This solution is prepared as needed by adding dropwise 10% by weight stannous chloride in concentrated hydrochloric acid to cupric chloride, leaving a slight excess of cupric chloride. The latter can be detected by its green color in concentrated hydrochloric acid medium. Dilute the solution containing the molybdenum and cuprous chloride with a few milliliters of water, and add 15 ml. of 1.0*M* ammonium thiocyanate in acetone. Mix the solution and dilute with water, allowing for the addition of 5 drops of a 10% by weight solution of stannous chloride before finally diluting to 25 ml. with water and shaking. The correct color develops rapidly, and the absorbance at 460 mμ may be read immediately upon mixing the solution. Variation of the slit width of the Beckman Model DU from 0.25 to 0.050 mm. did not cause a change in intensity at 460 mμ.

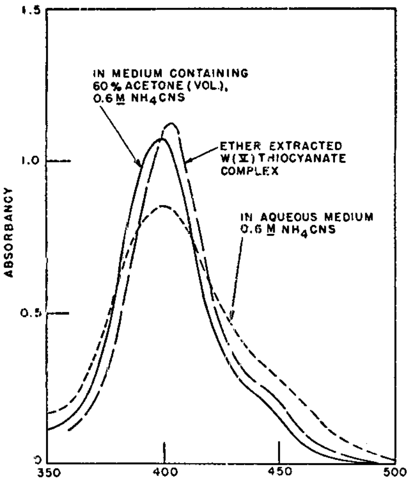

Figure 7. Comparison of Tungsten(V) Thiocyanate Absorbance Developed in Various Media

W(V) concentration 6.15 × $10^{-5}M$

Ether Thiocyanate Extraction Method. One milliliter of 0.1*M* cuprous chloride in concentrated hydrochloric acid was added to the molybdenum(VI) in approximately 8.0*M* hydrochloric acid. The volume in normal operation was limited to 3.0 ml. Molybdenum can be readily oxidized to molybdenum(VI) by bromine and the excess removed by boiling. The molybdenum (V)-thiocyanate complex was then formed by adding 3.0 ml. of 3.00*M* ammonium thiocyanate aqueous solution. Two 10-ml. portions of diethyl ether were used to extract the molybdenum, and the extracts were combined and diluted with ether to a 25-ml. volume. The absorbance maximum was at 470 mμ and the molar absorbance index was 19,500. The stability appeared to be inferior to that of the acetone solution. The absorbance should be measured within a few minutes after extracting, as it decreased slowly.

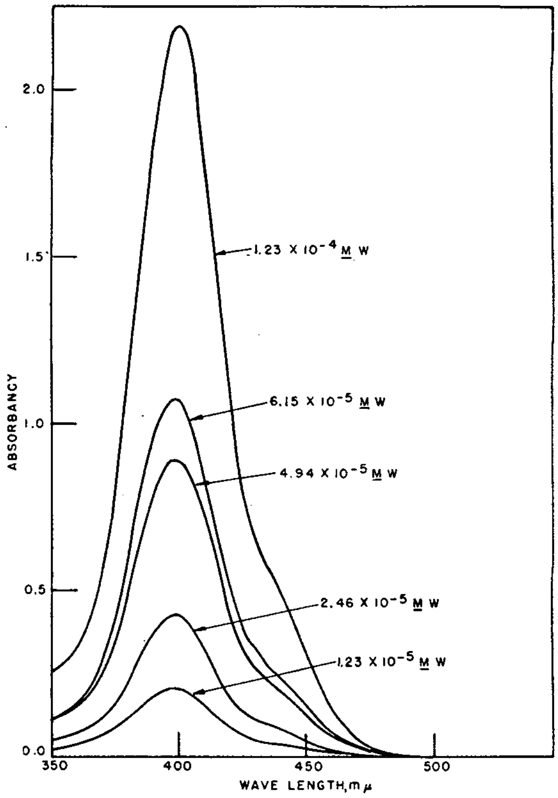

Figure 8. Tungsten-Thiocyanate Complex

60 volume % acetone and 0.6*M* NH_4CNS tungsten reduced with stannous chloride

Aqueous Molybdenum Thiocyanate Method. This method is not recommended because of the difficulty in obtaining quantitatively the quinquivalent state in solution and the marked decrease in sensitivity.

TUNGSTEN

The literature on the development of tungsten-thiocyanate methods has been compiled in previous works (*6-8*). Gentry and Sherrington (*8*) made the reduction of tungsten(VI) to tungsten(V) prior to the addition of the thiocyanate and reported improved color stability. Freund, Wright, and Brookshier (*6*) have studied the effect of the chloride ion and hydrogen ion concentration on the reduction of tungsten with stannous chloride. A minimum of 8*M* chloride ion and 10*M* total acid concentration used in this work is in essential agreement with the studies cited above.

One feature of the tungsten-thiocyanate complex system was the relatively small effect obtained by employing acetone or ether to develop the color. This is shown in Figure 7. The peaks are sharper and higher in acetone and ether media; however, the effect is small compared with the more strongly hydrated niobium, titanium, vanadium, cobalt, and molybdenum species. The tungsten thiocyanate complex color was also relatively unaffected by other complexing agents in the aqueous medium. Tartrate, citrate, oxalate, and sulfate were without effect (*8*) in the aqueous medium at relatively high concentrations. This and the fact that the tungsten reaches a maximum absorbance in aqueous solution at the low thiocyanate concentration of 0.50*M* indicate that the complex formed must be relatively stable. Increased thiocyanate concentration tended to decrease the absorbance obtained, as was also found in the case of molybdenum.

The development of the tungsten color in aqueous medium is free of interference from niobium and titanium, which require acetone to develop any color. Older studies (*7*, *8*) have confused the facts on niobium interference in the tungsten method. First, niobium does not develop a color with thiocyanate in aqueous medium, but readily does so in nonaqueous media (*5*, *12*). Secondly, niobium(V) and not niobium(III) develops the yellow color with a maximum absorbance at 383 mμ. Also niobium(V) is not reduced to niobium(III) with tin metal, tin amalgams, or hot stannous chloride in strong hydrochloric or sulfuric acids.

Figure 8 shows the tungsten thiocyanate spectra obtained in acetone medium on concentrations varying by a factor of 10. Beer's law was also obeyed by the total tungsten concentration in aqueous medium in the concentration region tested (maximum $1.23 \times 10^{-4}M$ per liter of tungsten). More than 20 experiments gave a molar absorbance index and standard deviation of 17,600 ± 130 at 398 mμ.

Some of the pertinent reactions of tungsten in aqueous medium are summarized in Figure 9. The reactions in acetone are more sluggish or do not proceed at appreciable rates. Oxidation of tungsten(III), however, to 75% tungsten(V) proceeds rapidly in both media. The importance of reducing tungsten(VI) in a strong acid medium ($>10M$) to tungsten(V) cannot be overemphasized. The formation of tungsten blue causes the color development to be slow and generally erratically low. Tungsten blue forms at much higher acidities than molybdenum blue and is thus more troublesome. The intense blue color formation on reduction should serve as a warning to the analyst that trouble will follow in color development. The blue species is a mixed valent tungsten(VI)–tungsten(V) compound, and is formed during reduction in solutions below approximately $9.0M$ in acidity. Dilution of either tungsten(VI) or tungsten(V) solutions alone with water produces no blue product, but dilution of the strong acid mixed valent solutions produces an immediate blue color. A second difficulty which has not been recognized as a separate problem is the existence of two forms of tungsten(V) as observed in the presence of thiocyanate, apparently analogous to the molybdenum(V) species (Figures 6 and 10). However, the tungsten(V) species cannot be quantitatively separated as in the case of the two molybdenum(V) forms (see Figure 10). The transition of the tungsten(V) species also occurs at much higher acidity than the corresponding molybdenum(V) forms.

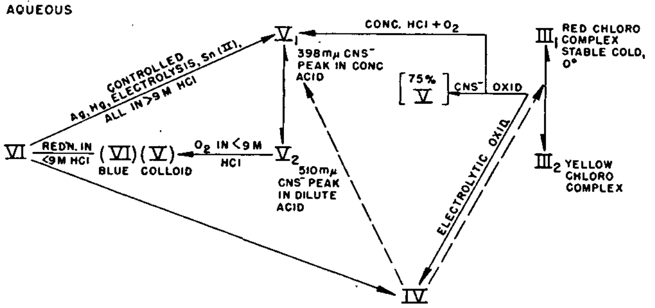

Figure 9. Tungsten Reaction Scheme

The analytically important features are the following. If the tungsten(VI) is reduced in dilute acid ($<9.0M$ hydrochloric acid), a mixed valent tungsten blue forms which is unreactive with thiocyanate. Second, if the analyst reduces tungsten(VI) quantitatively in strong acid to colorless or light blue tungsten(V) and then dilutes the acid solution with water ($<6.0M$ hydrochloric acid), a yellow chloro complex of tungsten(V) forms immediately. No tungsten blue forms unless tungsten(VI) is present. Addition of thiocyanate to the yellow tungsten(V) chloro complex in $6.0M$ hydrochloric acid develops an initial absorbance peak at 510 mμ, followed by its slow transfer to the 398 mμ complex, as shown in Figure 10. The time of color development increases with the amount of dilution, aging time after dilution, and the thiocyanate concentration. A third fact which has not been considered is the existence of several stable molar absorbance indexes for the tungsten(V) 398 mμ absorbance peak. Thus, if thiocyanate is added to tungsten(III) in the red or yellow species, exactly 75% is oxidized by thiocyanate to tungsten(V), and the molar absorbance index is stabilized (see Figure 11). If tungsten(VI) solution is reduced electrolytically, by shaking with mercury metal, by a silver reductor at 80° C., or by tin(II), all in concentrated hydrochloric acid medium, the color developed is the maximum intensity. In each case, the fractional and maximum spectra are identical except for the intensity. The maximum intensity as obtained by the four methods above is a molar absorbance index of 17,600 at the 398 mμ peak. Quantitative reduction to tungsten(III) red species was accomplished in each case at 0° C. in concentrated hydrochloric acid by electrolysis at a mercury cathode, by tin metal, and by lead metal in nitrogen atmosphere. The yellow species of tungsten(III) is formed from the red species at room temperature. The addition of the thiocyanate acetone medium to either the yellow or red tungsten(III) species developed a stable tungsten(V) thiocyanate absorbance spectra which was 75% of the known maximum. As shown in Figure 11, the color was formed on both yellow and red tungsten(III) in approximately 15 minutes. The presence of excess tin(II) in the acetone–thiocyanate medium did not affect the rate or per cent of the color formed.

STANDARD PROCEDURES FOR TUNGSTEN

Homogeneous Acetone–Thiocyanate Method. The tungsten (VI) solution must be adjusted before reduction to $>8M$ chloride ion concentration and $>10M$ total acid. It has been found convenient to fume tungsten(VI) samples to a 0.5-ml. volume of

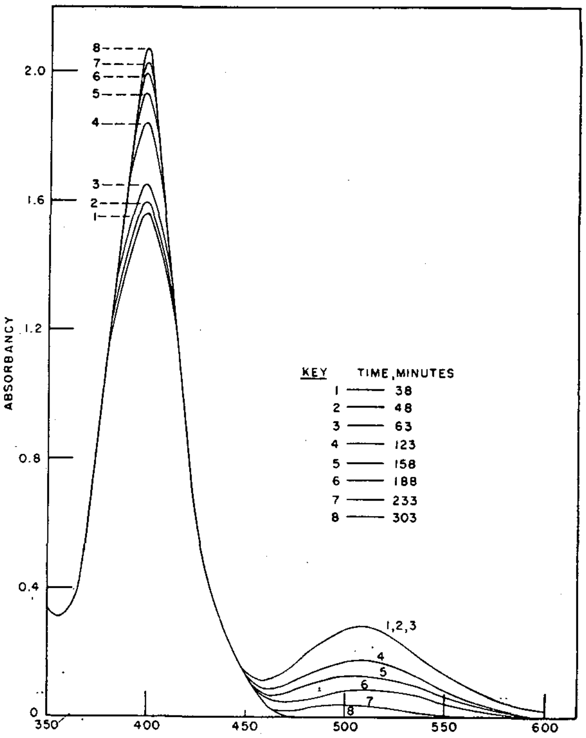

Figure 10. Tungsten(V)-Thiocyanate Complexes

$1.23 \times 10^{-4}M$ W(V) in $0.12M$ HCl; 60 volume % acetone and $0.6M$ NH_4CNS

concentrated sulfuric acid. No precipitation of tungstic acid occurs at the low concentrations of tungsten(VI) required for color development. The additional chloride and acid were then added as 2 ml. of 10% stannous chloride dissolved in concentrated hydrochloric acid. In 1-cm. cells, 10.5 γ of tungsten per milliliter developed unit absorbance. Another reduction method was the addition of 0.1 ml. of mercury metal and 2 ml. of concentrated hydrochloric acid. The total volume during reduction was limited to 3 ml. or less. The reduction was made at room temperature for 30 minutes for both tin(II) and mercury. Reduction time with mercury is a function of the mercury particle size during shaking. A Burrell wrist action shaker was used in the tests made in this laboratory. The color was then developed by adding 15 ml. of 1.0*M* ammonium thiocyanate dissolved in acetone. The solution was diluted to 25 ml. with water. In cases where mercury was used, the volume was corrected. Fifteen minutes were allowed for the maximum color to develop. The absorbance maximum is at 398 mμ.

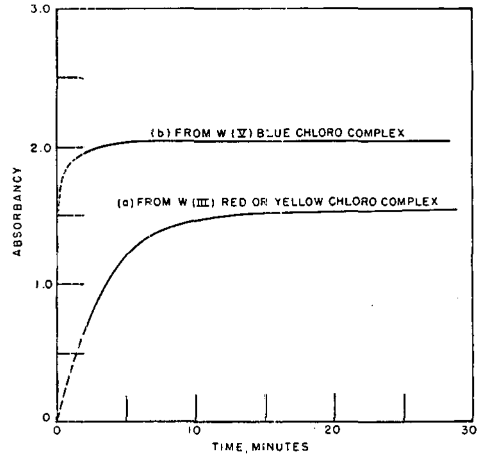

Figure 11. Effect of Initial Valence State on Formation of Tungsten (V)-Thiocyanate Complex

1.10×10^{-4} *M* tungsten
***a.* W(III) red chloro complex**
***b.* W(V) blue chloro complex**
60 volume % acetone and 0.6*M* NH_4CNS absorbancy measured at 398 mμ

Ether Thiocyanate Extraction Method. The same procedure is used in reducing tungsten to the pentavalent state. Five milliliters of 3.0*M* aqueous ammonium thiocyanate were added to the sample and extracted with two 10-ml. volumes of diethyl ether. The extracts were combined and diluted to 25 ml. with ether. The molar absorbance index is 18,300 at the 405 mμ peak. The absorbance should be measured immediately.

Aqueous Thiocyanate Method. This procedure may have certain advantages in the presence of elements which require a nonaqueous medium to develop any appreciable color. Such elements are titanium(IV), niobium(V), cobalt(II), and vanadium (III). The reduction again was the same as in (1). Five milliliters of 3.0*M* ammonium thiocyanate aqueous solution were added, and the solution was diluted with water to 25 ml. The color development was rapid, and the absorbance may be obtained immediately upon mixing. The molar absorbance index is 13,800 at the 398 mμ peak.

DISCUSSION

The spectra of tungsten(VI) and molybdenum(VI) in the thiocyanate acetone medium are quite different and in certain applications may be analytically useful. Figure 12 shows the molybdenum(VI)-thiocyanate complex in acetone medium. No absorbance was observed for tungsten(VI) above 330 mμ. The acetone–thiocyanate medium below 330 mμ masks any absorbance in the ultraviolet region. Molybdenum and tungsten can be oxidized to the +6 valence state by bromine. Excess bromine may be boiled off, although it does not form any colored products in the acetone–thiocyanate medium.

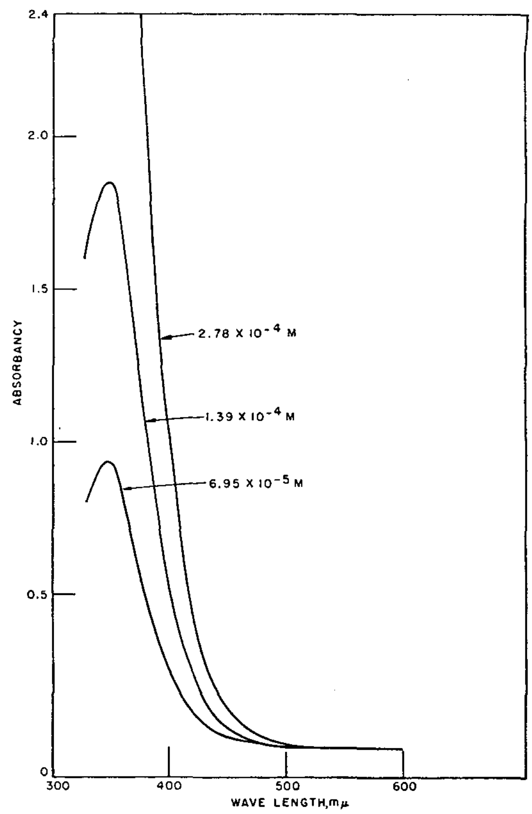

Figure 12. Molybdenum(VI)-Thiocyanate Complex

60 volume % acetone and 0.6*M* NH_4CNS

A feature of the cuprous chloride reduction of molybdenum was the elimination of tungsten interference. Cuprous chloride did not reduce tungsten(VI) to tungsten(V). Table I shows the limits of tungsten concentration which may be tolerated. Since molybdenum(III) forms virtually no color in the thiocyanate–acetone medium, reduction with tin(II) or mercury in strong hydrochloric acid eliminates molybdenum interference in the tungsten analysis.

Iron is a major source of difficulty in obtaining a stable color with molybdenum(V) thiocyanate. Even when scanning the

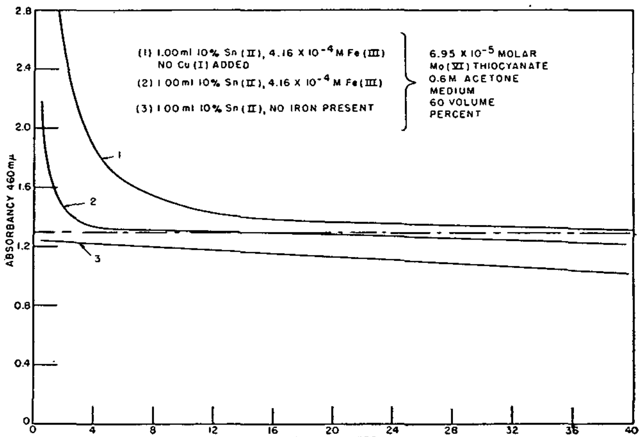

Figure 13. Effect of Time on Absorbance

— — — 6.95×10^{-5}*M* Mo(VI) standard thiocyanate acetone Procedure A, no iron present

Table I. Effect of Foreign Cations on the Molybdenum(V) and Tungsten(V) Spectrophotometric Analysis in Acetone–Thiocyanate Medium

Concn. of Cation Analyzed, $M/L \times 10^{-5}$	Concn. of Foreign Cation, M/L	Error, %	Remarks
Mo(V) 4.00	W(VI) 8.00×10^{-4}	0.0	As W(VI)/Mo(VI) ratio increased above 20, the correct Mo(V) thiocyanate absorbance developed immediately, but dropped appreciably (4%) in 20 minutes Drop was accompanied by growth of the W(V) thiocyanate peak. Results obtained with no error by reading absorbance 5 minutes after mixing
W(V) 8.00	Mo(III) 2.00×10^{-4}	0.0	Reduction with both Hg and Sn(II) by standard procedure
W(V) 8.00	Mo(V) 6.00×10^{-3}	+4.0	Sn(II) reduction was employed
Mo(V) 4.00	V(IV) 8.00×10^{-5}	+4.0	Error calculated from absorbance obtained immediately after mixing. Absorbance continued to grow slowly, owing to formation of V(III) thiocyanate complex
Mo(V) 4.00	Fe(III) 4.00×10^{-5}	0.0	Standard acetone thiocyanate procedure employs enough Sn(II) in acetone medium to reduce iron
Mo(V) 6.95	U(VI) 5.5×10^{-4}	+3.0	
Mo(V) 6.95	U(VI) 2.8×10^{-4}	+0.8	

460 mμ molybdenum(V) thiocyanate peak, iron interference appears as a small broadening of the peak. Thus a 30% increase in the 460 mμ peak due to iron(III) thiocyanate increased the resolution of the molybdenum(V) thiocyanate 460 mμ peak only 2%, from 13 to 15%. If a large excess of tin(II) is added to reduce the iron, the molybdenum(V)–thiocyanate complex is relatively unstable. Figure 13 shows the complex nature of reactions involved. In the absence of iron, the standard procedure A for molybdenum is applied as shown in curve 3 of Figure 13, except for the quantity of tin(II) added, which was increased to 1.0 ml. of 10% by weight tin(II) solution. The absorbance measured was immediately below the known correct value of 1.29. The curves of Figure 13 were obtained with the Cary recording spectrometer, which allows the accurate measurement of the high absorbance values. If will be noted that in curve 3, copper was employed to reduce the molybdenum(VI) to molybdenum(V) and the tin(II) was added after the thiocyanate acetone. In curve 2, the same color development procedure was applied with 1.0 ml. of 10% tin(II), but in the presence of $4.16 \times 10^{-4}M$ iron(III), which was added to the original molybdenum(VI) standard.

Curve 1 is the same reaction with the copper(I) deleted from procedure A and with the same concentration of iron(III). The presence of iron prevented the rapid overreduction of molybdenum(VI) to molybdenum(III) as shown in curve 3, and the absence of copper apparently slowed the reaction between tin(II) and iron(III) in the acetone medium. The procedure employed in curve 2 is thus recommended in cases where excess iron is present. However, the reaction rates of the solutions may be sensitive to other impurities, and the analyst must exercise care in applying the procedure. For precise results, the separation of large quantities of iron from molybdenum should be made. In this laboratory, the separation of 10,000 to 1 ratios of iron(III) to molybdenum(VI) were made with a Dowex 50, 100-mesh, 7.2% cross-linked resin, 0.5 inch (diameter) by 2.5 inch cylindrical column. The iron(III) and molybdenum(VI) mixture was first passed through a pH 2 equilibrated column as a dilute ~0.5M hydrochloric acid solution and the molybdenum(VI) was eluted with 75 ml. of 0.04M ammonium thiocyanate. The eluted solution of molybdenum(VI) was reduced to 0.50 ml. of concentrated sulfuric acid, and the color was developed by procedure A.

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Polarographic Determination of Maleate Unsaturation in Polyesters

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Unsaturated polyester resins have a polymerization mechanism which utilizes maleate and/or fumarate double bonds as the sites through which the linear polyester chains are cross-linked by vinyl-type monomers. The advent of these resins has presented the problem of detecting and determining their maleate and/or fumarate unsaturation. Application of the polarograph to simple solutions of the polymer is practical if the acid number of the material, a measure of its molecular weight, is taken into consideration. A method has been developed for the polarographic determination of the maleate and/or fumarate unsaturation in polyester formulations, expressed as per cent maleic anhydride.

SWANN (*3*) and Shreve and Heether (*2*) have developed adaptations of the Kappelmeier procedure (*1*) for the determination of phthalate content of alkyd resins. Each of these methods involves preliminary time-consuming saponification of the resin. The advent of unsaturated resins, with emphasis on maleate double bonds as the sites through which the linear polyester chains are linked, has presented the problem of detecting and determining this unsaturation. In the above-mentioned procedures, the determination of maleic acid is, at most, incidental to the determination of phthalic acid.

A new polarographic method for determining the maleate unsaturation of a polyester resin, as maleic anhydride, involving no preliminary reactions on the resin, is described in this paper.

Table I. *K* Determined on Several Known Resins

Sample	% Maleic Anhydride in Sample	K
1	16.6	9.37
2	36.2	9.52
3	25.9	9.50
4	17.3	9.24
5	24.6	9.31
6	18.6	9.14
7	24.1	9.13

$\overline{K} = 9.32$; $\sigma_K = 0.16$
$K_i = 9.32 \pm 0.31$ ($P = 0.95$)

SOLVENT SYSTEM

Polyester resins are soluble in common organic solvents such as acetone, methyl ethyl ketone, and ethyl acetate. Acetone is not a desirable solvent because of its high vapor pressure. The other two are subject to peroxide formation. Peroxides interfere with the determination, because they are reduced polarographically in the same potential range as the maleate unsaturation in polyesters. Although it might be possible to purify these solvents by distillation or other means, it was found that Mallinckrodt's analytical reagent grade ethyl acetate was satisfactory as received. The solvent system used in this study consisted of:

50% A.R. ethyl acetate (freshly opened)
25% 2B ethyl alcohol
25% 1.0*N* hydrochloric acid (aqueous)

Table II. Demonstration of Acid Number Correction

Resin No.	Acid No.	K (Observed)	K (Corrected)
1	45.4	8.16	7.81
2	34.2	7.50	7.91
3	26.4	7.03	8.06
4	23.7	6.78	7.95

$\overline{K}_0 = 7.37$ $\overline{K}_c = 7.93$
$\sigma_0^2 = 0.37$ $\sigma_c^2 = 0.01$
$F = 0.37/0.01 = 37$

The critical value of *F* at 99% confidence under these conditions is 29.5. Therefore, corrected values of *K* are significantly better than uncorrected values.

DIFFUSION CURRENT

Proportional to Concentration of One Resin. Polarograms of solutions containing various concentrations of one particular resin were prepared in order to determine whether or not the diffusion current of the observed wave is proportional to the amount of esterified maleic acid present in solutions of polyesters. Figure 1 shows that i_d is proportional to the amount of esterified maleic acid present in the solution.

Proportional to Maleic Acid Content of Different Resins. Polarograms were obtained in solutions of the same concentration of various resins of known formulation to test whether the diffusion current can be used to determine maleate unsaturation in a polyester resin. A constant, *K*, was calculated by the equation:

$$K = i_d/0.01PW$$

where

i_d = diffusion current
W = sample weight
P = per cent maleic anhydride in resin, calculated from the proportion of maleic anhydride used in the synthesis of the resin, considering the loss of water during the reaction but assuming no other significant losses

The results of this series of experiments are summarized in Table I. The constant, *K*, varies not more than ±3.3% within 95% confidence limits.

Dependence on Molecular Weight. Normally, polyesters react to an acid number of about 40. A deviation from this acid number will cause a change in the molecular weight of the compound with an attendant variation in the observed diffusion current. If the approximate correction factor, derived below, is applied to the diffusion current, the molecular weight error is largely eliminated. The data from a series of similar resins with different acid numbers are tabulated in Table II. These resins differ from those used in the preparation of Table I, in that they are formulated with a different unsaturated acid. Because the correction factor, derived below, is approximate, it is suggested that *K* be determined separately for resins formulated from different acids and/or glycols, and corrected to an acid number of 40 as described below.

DERIVATION OF ACID NUMBER CORRECTION

If it is assumed that the relative deviation of the acid number of a polyester resin from the reference acid number is equal to and opposite in sign from the relative deviation of the molecular weight from the molecular weight corresponding to the reference acid number; that the molecular weight of a large molecule is approximately proportional to the volume of the molecule; that the diffusion coefficient is approximately inversely proportional to the cross-sectional area of the molecule; and that the average molecular shape is spherical; we have:

$$\frac{dM}{M} = \frac{-dA}{A} \tag{1}$$

$$M = 4/3c\pi r^3; \; r = \left(\frac{M}{4/3c\pi}\right)^{1/3} \tag{2}$$

$$D = e/\pi r^2; \; r = \left(\frac{\pi D}{e}\right)^{-1/2} \tag{3}$$

where

M = molecular weight
A = acid number
D = diffusion coefficient
c = a constant
e = a constant
r = radius of molecule

Then:

$$\left(\frac{M}{4/3\pi c}\right)^{1/3} = \left(\frac{\pi D}{e}\right)^{-1/2} \text{ or } D^{1/2} = fM^{-1/3} \tag{4}$$

where f = a combined constant
Substituting Equation 4 in the Ilkovič equation,

$$i_d = knCD^{1/2}m^{2/3}t^{1/6} \tag{5}$$

where

k = a constant
n = electron change per molecule
$m^{2/3}t^{1/6}$ = electrode constant
C = concentration of reducible species, moles per liter

we obtain:

$$i_d = gnCM^{-1/3} \tag{6}$$

where

$g = kfm^{2/3}t^{1/6}$

For a given weight concentration of a resin of particular formulation, it is obvious that the product, nC, will remain constant, so that Equation 6 simplifies to:

$$i_d \doteq hM^{-1/3} \tag{7}$$

where

$h = gnC$

h will remain constant for any one weight concentration of a resin containing a specific amount of maleic anhydride, regardless of the molecular weight of that resin.

Differentiating Equation 7 we obtain:

$$di_d = -hM^{-4/3}dM/3 \qquad (8)$$

Dividing Equation 8 by Equation 7:

$$di_d/i_d = -dM/3M \qquad (9)$$

or one third the relative deviation of the molecular weight from that corresponding to the reference acid number is equal to and opposite in sign from the relative deviation of the observed diffusion current from the diffusion current corresponding to the reference acid number. Combining Equations 9 and 1, we obtain:

$$di_d/i_d = dA/3A \qquad (10)$$

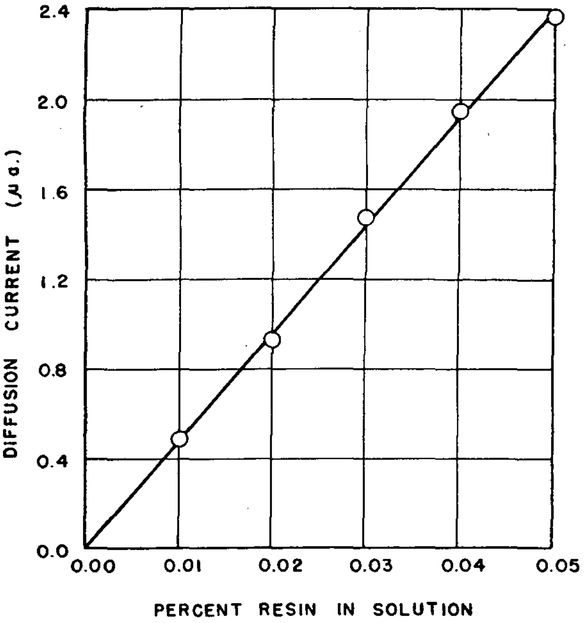

Figure 1. Linear Relationship between i_d and Concentration of a Known Resin

The relative deviation of the diffusion current measurement from the diffusion current corresponding to the reference acid number is seen to be one third the relative deviation of the acid number from the reference acid number. In order to translate this statement into a useful correction factor, let:

i_0 = observed diffusion current
i_c = corrected diffusion current
A_0 = observed acid number
A_c = reference acid number (usually $A_c = 40$)

Assuming that the deviations are relative to the averages of the reference and observed values, from Equation 10 we can say that

$$(A_c - A_0)/3(A_c + A_0) = (i_c - i_0)/(i_c + i_0) \qquad (11)$$

dividing and cross-multiplying:

$$A_c i_c + A_c i_0 - A_0 i_0 - A_0 i_c = 3A_c i_c + 3A_0 i_c - 3A_c i_0 - 3A_0 i_0 \qquad (12)$$

combining terms and solving for i_c, we obtain:

$$i_c = i_0(2A_c + A_0)/(A_c + 2A_0) \qquad (13)$$

INTERFERENCES

In the course of the development of this procedure, it was observed that none of the following compounds, often present in unsaturated polyester resins, cause interferences:

Adipic acid
Phthalic acid
Sebacic acid
Ethylene glycol
Propylene glycol
Diethylene glycol
Styrene

Pentaerythritol and glycerol interfere with the determination by greatly increasing the molecular weight of the compounds. This would indicate that the method may not be applicable to alkyd resins in general, but is satisfactory for most linear unsaturated polyester resins.

EXPERIMENTAL DETAILS

A Leeds and Northrup Electro-chemograph, Type E, was used throughout this study.

Temperature was controlled to 25° ± 0.1° C.

Oxygen was removed by passing nitrogen through the solutions, with a fritted-glass bubbler, for 15 minutes prior to polarographing.

Reagents. Ethyl acetate, Mallinckrodt A. R. No. 4992, freshly opened 1-pound bottles; 1N hydrochloric acid; and denatured ethyl alcohol, formulation 2B.

Procedure. Weigh out a 1.0-gram sample of resin into a 100-ml. beaker. Dissolve the sample in freshly opened ethyl acetate and transfer it to a 100-ml. volumetric flask. Dilute to the mark with ethyl acetate.

Place a 5-ml. aliquot of the sample solution in another 100-ml. volumetric flask. Add 25 ml. of 2-B ethyl alcohol and 25 ml. of 1.0N hydrochloric acid to the aliquot and dilute to the mark with ethyl acetate. Place a part of the solution in a polarographic cell, remove oxygen, and polarograph.

Measure the wave which occurs between −0.55 and −0.97 volt (S.C.E.), correcting for residual current determined on a balnk.

Calculations. To calibrate the electrode, use a similar known resin, follow the procedure above, and calculate a value for the constant, K.

$$K = i_d/0.01PW$$

where i_d = diffusion current, P = per cent maleic anhydride in resin, and W = sample weight.

Substitute the value for the diffusion current in the equation:

$$P = i_d/0.01KW$$

This will give a good estimate of the maleate unsaturation in the sample.

In order to improve the accuracy of the determination, correct the diffusion current of both the known and the unknown resins by use of Equation 13. Determine the acid number on the resin itself, not the resin plus styrene or other monomeric material which may be present.

ACKNOWLEDGMENT

The author is greatly indebted to R. W. Stafford for his help in the preparation of this paper, to W. G. Deichert for providing the background information on the subject of polyester resins, and to H. M. Day for his cooperation in providing resin samples of known composition.

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Polarographic Determination of Molybdenum(VI)

Tartaric Acid as Supporting Electrolyte

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This investigation was undertaken to develop a rapid method for the polarographic determination of molybdenum(VI) in the presence of tungsten(VI). A supporting electrolyte of tartaric acid has been found very suitable for such a determination. In the presence of tartaric acid, molybdenum(VI) is reduced in two steps, the total height of the two waves being proportional to the molybdenum concentration. Tungsten(VI) is not reduced under these conditions. A systematic study of the system has shown that the reducible molybdate species must be adsorbed before reduction can occur. Because of this adsorption, the presence of indifferent salts decreases slightly the total wave height; the use of the method of standard additions is therefore most convenient for the determination. Methods for overcoming interference due to iron(III) and chromium(III) are described. Nickel(II), cobalt(II), and other substances reduced at potentials more negative than −0.75 volt *vs.* the saturated calomel electrode do not interfere. The method is rapid, accurate, convenient, and subject to few interferences.

SEVERAL methods for the polarographic determination of molybdenum(VI) have been described (*1, 4, 5, 12, 14*). The majority of these methods require preliminary separation of many of the common elements associated with molybdenum before the polarographic method can be applied. A common interfering element is tungsten(VI). Recently Meites (*10*) and Pribil and Blazek (*11*) have described methods for the determination of molybdenum in the presence of tungsten, the former using a citrate buffer and the latter an ethylenediaminetetraacetic acid solution as supporting electrolytes.

The present paper describes the use of tartaric acid as a supporting electrolyte for the polarographic reduction of molybdate. It is shown that molybdate produces two waves in 0.1*M* tartaric acid, the sum of the heights of the two waves being proportional to the molybdenum(VI) concentration. As tungsten does not give a polarographic wave in this supporting electrolyte, the reduction of molybdate was investigated systematically, and a method for the determination of molybdenum in the presence of tungsten has been developed. Methods for overcoming interferences due to large amounts of iron(III) and chromium(III) are given. Nickel, manganese, cobalt, and other substances that are reduced at more negative potentials than −0.75 volt *vs.* S.C.E. in this supporting electrolyte will not interfere in the determination.

EXPERIMENTAL

All current-voltage curves in this research were obtained on a Leeds and Northrup E Electrochemograph. In those cases where data were required to test a wave for reversibility, a manual polarograph similar to that described by Lingane and Kolthoff (*9*) was used. All diffusion currents were corrected for residual currents. A single compartment polarizing cell similar to that described by Hume and Harris (*3*) was used as the electrolysis cell. The reference electrode was a saturated calomel electrode (S.C.E.) which was connected to the electrolysis cell through a potassium chloride–agar bridge. The experiments were carried out in a water thermostat at 30.0° ± 0.1° C. The value of $m^{2/3}\,t^{1/6}$ for the capillary used was 1.41 mg.$^{2/3}$ sec.$^{-1/2}$. All chemicals in the experiments were of analytical reagent grade and were used without further purification. A Beckman Model G pH meter was used for pH measurement.

The diffusion currents obtained with the Leeds and Northrup Electrochemograph were compared against those obtained with the manual instrument to check the usefulness of the automatic instrument in obtaining quantitative data.

Several concentrations of lead nitrate in a supporting electrolyte of 0.5*N* potassium nitrate with methyl red as a maximum suppressor were prepared and the total current—i.e., the diffusion current plus the residual current—was measured on both instruments at −0.6 volt *vs.* S.C.E. after oxygen was removed. With the recording instrument, peak current values—i.e., the maximum of the current oscillations—were taken. Using the zero damping position on the Electrochemograph, the ratios of the current obtained with the manual instrument to the peak current obtained with the recording instrument were constant at 0.799 ± 0.003 for current ranges of 30, 20, 15, 10, and 7, and lead ion concentrations varying from 2×10^{-3} to $5 \times 10^{-4}M$. Assuming the current values obtained with the manual polarograph represent true average currents, the peak current values obtained with the Electrochemograph represent closely the maximum current which flows at the end of the drop life. Although the theoretical ratio of average current to maximum current is 0.857, Taylor, Smith, and Cooter (*13*) found the ratio to be 0.81. It appears that the response of this recording polarograph is fast and faithfully reproduces the variation of current during the latter part of the drop life. It is obvious that this instrument can be used to obtain precise quantitative data, and the procedure of measuring current peaks is recommended when using the instrument with no damping of the current oscillations.

POLAROGRAPHIC BEHAVIOR OF MOLYBDENUM(VI) IN TARTARIC ACID

Molybdenum(VI) is reduced at the dropping mercury electrode in 0.1*M* tartaric acid (pH 2.0) producing two waves with half-wave potentials of −0.22 and −0.52 volt *vs.* S.C.E. (Figure 1, *a*). Both waves are irreversible. The height of the first wave is approximately one half that of the second wave, indicating that molybdenum(VI) is probably reduced first to the +5 state then to the +3 state. The final rising portion of the curve at −1.1 volts represents the discharge of hydrogen. No constant diffusion current region is reached for the first reduction wave, and that reached for the second wave is constant only over a rather small potential range. As the potential becomes more

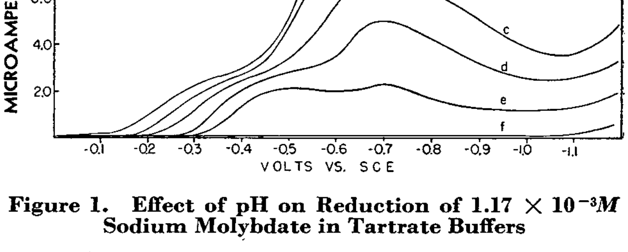

Figure 1. Effect of pH on Reduction of 1.17 × $10^{-3}M$ Sodium Molybdate in Tartrate Buffers

a. 0.1*M* tartaric acid, pH 2; *b.* 0.1*M* tartaric acid + sodium hydroxide, pH 2.3; *c.* 0.06*M* tartaric acid and 0.04*M* sodium tartrate, pH 2.80; *d.* 0.05*M* tartaric acid and 0.05*M* sodium tartrate, pH 3.35; *e.* 0.04*M* tartaric acid and 0.06*M* sodium tartrate, pH 3.79; *f.* 0.1*M* sodium tartrate, pH 7.77

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Table I. Diffusion Current Constant of Molybdenum(VI) in 0.1*M* Tartaric Acid

Concentration of Molybdate, Millimolar	i_d (μa.) at −0.65 Volt *vs.* S.C.E.	$i_d/Cm^{2/3}t^{1/6}$
0.0	0.13	..
0.186	1.33	5.07
0.372	2.64	5.04
0.930	6.69	5.10
1.86	13.30	5.05
3.72	26.67[a]	5.08
		Av. 5.07 ± 0.02

[a] Measured at −0.75 volt.

negative, a decrease is observed in the diffusion current of the second wave (Figure 1, *a*). This is not a regular maximum as is shown by the effect of 0.01% solutions of gelatin and agar. Both of these maximum suppressors lower the total wave height by about one third and accentuate the decrease in current. The decrease has been attributed to a desorption of the reducible species from the dropping mercury at the more negative potentials.

The total limiting current, after correction for the residual current, is proportional to the molybdate concentration (Table I). The total diffusion current values were measured at a potential of −0.65 volt *vs.* S.C.E. except for 3.72 *mM* molybdate, where it was measured at −0.75 volt. At the higher molybdenum concentrations, the potential at which the limiting current plateau is reached is shifted slightly in the negative direction.

The diffusion coefficient for the reducible molybdate species calculated from these data assuming an electron transfer of 3, gives a value of 7.8 × 10^{-6} sq. cm. per second. This value is about 34% lower than the diffusion coefficient of the chromate ion (1.1 × 10^{-5} sq. cm. per second) and indicates that the molybdate species in the solution is larger than the simple molybdate ion. Undoubtedly the molybdate exists in the solution as a tartrato complex of a polymerized molybdate species. The degree of polymerization of the molybdate species does not appear to change with increasing concentration, as is usual for molybdate, since a constant value is obtained for the diffusion current constant.

The total diffusion current was found to be directly proportional to the square root of the pressure on the dropping mercury electrode. Moreover, the temperature coefficient of the diffusion current was found to be low (1.0% per degree in the range 25° to 35° C.). Both of these factors indicate a diffusion-controlled process.

The decrease in the diffusion current with increasing negative potential may be best explained by assuming that an adsorption of the reducible species is necessary before reduction can occur. With increasing negative potential a slight desorption occurs and the current becomes less because not all of the ions reaching the electrode are adsorbed and reduced. To substantiate this hypothesis, the effect of camphor on the reduction wave was studied. Camphor is strongly adsorbed on the dropping electrode and its effect on the reduction of substances which are adsorbed before being reduced is well known (*6, 8*).

Figure 2 shows the effect of camphor on the wave for 3.72 × $10^{-4}M$ molybdate in 0.1*M* tartaric acid. With 0.001% camphor, the concentration of camphor is so small that its adsorption is negligible and virtually the same curve is obtained for the molybdate reduction as that without any camphor present. As the concentration of camphor is increased, however, the area available for adsorption of the molybdate species is decreased, causing the total reduction wave to decrease considerably and the decrease in current beyond about −0.6 volt to become much more sharp and pronounced and to be shifted to less negative potentials. Such a shift was also found by Laitinen and Onstott (*8*) in the systematic investigation of a somewhat similar adsorption phenomenon.

Beyond the minima in Figure 2, *b* and *c*, the camphor itself begins to be desorbed at these concentrations, and the adsorption and subsequent reduction of molybdate again occur so that the current gradually increases up to the value it would have in the absence of camphor. When the solution is saturated with camphor (Figure 2, *d*) the wave is inhibited. Apparently under these conditions camphor is not completely desorbed until a more negative potential is reached than that at which the liberation of hydrogen starts (>1.1 volts). Saturated octyl alcohol also completely represses the wave.

The potential range in which the desorption process (desorption wave) occurs appears to be independent of the temperature in the range from 25° to 35° C., and practically independent of the concentration of molybdate. However, at higher concentrations of molybdenum(VI), the half-wave potential for the reduction of molybdate is shifted to slightly more negative potentials, and the desorption wave is also shifted slightly in this direction.

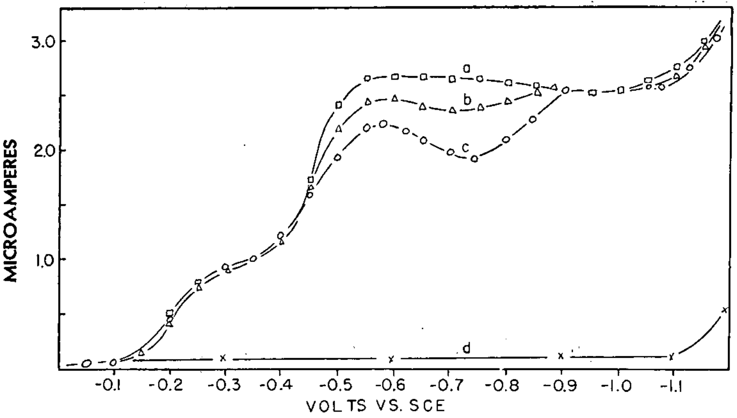

Figure 2. Effect of Camphor on Molybdate Reduction Wave

3.72 × $10^{-4}M$ sodium molybdate in 0.1*M* tartaric acid; *a.* 0.001% camphor; *b.* 0.002% camphor; *c.* 0.005% camphor; *d.* saturated with camphor

The half-wave potentials of the molybdate waves are shifted toward more negative values as the pH of the solution is increased (Figure 1). In addition, the height of the second wave is lowered considerably and the wave becomes more ill defined. The desorption of the reducible species apparently becomes greater as the pH is increased. Above a pH of 4 the second wave is hardly discernible. No reduction of molybdate occurs in neutral or alkaline tartrate solutions.

The pH of the solution should be between 1.5 and 2.3 for the determination of molybdate. Below the lower limit the discharge of hydrogen begins to interfere. Above a pH of 2.3, and in the presence of tungsten, no constant diffusion plateau is reached because of the early discharge of hydrogen and the negative shift in the molybdate wave, as described below. Even without tungsten present the wave begins to become ill defined much above this pH value.

DETERMINATION OF MOLYBDENUM IN PRESENCE OF TUNGSTEN

Tungsten is not reduced at the dropping mercury electrode in 0.1*M* tartaric acid. Large amounts of tungsten, however, lower the diffusion current of the molybdate wave slightly. Furthermore, the presence of tungsten causes the wave, due to the discharge of hydrogen, to start at more positive potentials and the limiting current, due to the molybdate reduction, to be reached at more negative potentials. However, diffusion current values could be obtained for the molybdate reduction with concentrations of tungsten up to about 0.05*M* (Figure 3). Provided the concentration of molybdate in the unknown could be adjusted by proper dilution to be in the neighborhood of $2 \times 10^{-4}M$, molybdate could be determined in the presence of about 250 times as much tungsten.

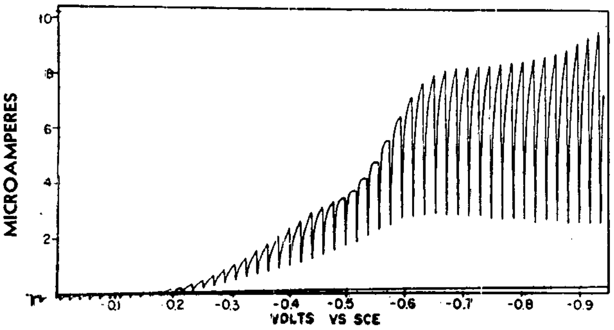

Figure 3. Reduction Wave for $1.32 \times 10^{-3}M$ Sodium Molybdate in 0.1*M* Tartaric Acid and 0.05*M* Sodium Tungstate

In the presence of a constant amount of tungstate the diffusion current of molybdate is proportional to its concentration. It should be possible, therefore, to use the method of standard additions (*7*) for the determination of molybdenum in the presence of tungsten. Table II shows some results obtained by this method. The diffusion current was corrected for residual current by extrapolation.

Table II. Determination of Molybdenum(VI) in Presence of Tungsten(VI) Using Method of Standard Additions

Molybdate Added, Millimolar	Concentration Tungstate, Molar	Molybdate Found, Millimolar	Error, %
0.372	0.00	0.379	+1.9
0.186	0.01	0.181	−2.7
0.372	0.01	0.379	+1.9
1.18	0.01	1.18	0.0
0.235	0.05	0.232	−1.3
0.372	0.05	0.369	−0.8

The presence of the alkali chlorides, sulfates, or perchlorates causes a decrease in the total diffusion current. For example, in the absence of anything but 0.1*M* tartaric acid the total diffusion current at −0.65 volt for $1.17 \times 10^{-3}M$ sodium molybdate was 8.39 μa. In the presence of 0.2*M* sodium chloride and 0.1*M* tartaric acid it was 8.13 μa.; with 0.1*M* sodium sulfate and 0.1*M* tartaric acid it was 7.71 μa., and with 0.2*M* sodium perchlorate and 0.1*M* tartaric acid it was 8.13 μa. Since the reduction current is governed by the adsorption of the reducible species on the electrode, large amounts of such electrolytes might be expected to decrease the area available for the adsorption or cause a decrease in the rate of adsorption. Hence, the effect of such salts on the diffusion current is not too surprising.

It was found that i_d/C for the molybdate reduction was still constant in the presence of a constant amount of these nonreducible salts. Thus, the effect of the presence of such salts can be circumvented by use of the method of standard additions, and the determination of molybdate can be made in concentrations of these salts up to 0.5*M*. Nitrate interferes causing a rather large increase in current and distortion of the wave, probably caused by the catalytic reduction of nitrate under these conditions (*4*). It therefore must be removed.

Table III. Effect of Ferric Chloride on *Molybdate* Wave[a]

Concentration of Ferric Iron, Moles	Diffusion Current (μa.) for Iron Wave at 0.0 Volt *vs.* S.C.E.	$i_d/C \times 10^3$	Diffusion Current for Molybdate Wave at −0.65 Volt
0.0	...	..	8.39
0.002	4.32	2.16	8.38
0.005	11.00	2.20	8.39
0.006	13.02	2.17	8.39
0.010	21.89	2.19	8.38

[a] $1.17 \times 10^{-3}M$ sodium molybdate in 0.1*M* tartaric acid.

Table IV. Determination of Molybdenum in Presence of Iron[a]

Molybdate Added	Molybdate Found	Error, %
3.72×10^{-4}	3.81×10^{-4}	+2.4
9.30×10^{-4}	9.11×10^{-4}	−2.0
1.86×10^{-3}	1.89×10^{-3}	+1.6

[a] Supporting electrolyte 0.1*M* tartaric acid and 0.05*M* ferric chloride; ferric iron reduced with sulfur dioxide.

EFFECT OF OTHER IONS

A possible application of the proposed method would be for the determination of molybdenum in steel. In view of such an application the effect of iron, chromium, manganese, nickel, copper, and vanadium was investigated.

Iron(III) is reduced in 0.1*M* tartaric acid to iron(II) producing a well-defined wave with a half-wave potential of 0.12 volt *vs.* S.C.E. The diffusion current is proportional to the concentration of iron(III) so that both molybdate and iron can be determined simultaneously in solutions containing up to about 20 times as much iron as molybdate (Table III). With larger amounts of iron the reduction of molybdate begins to be masked, and the precision for the molybdate determination is considerably decreased. It was found that sulfur dioxide, when bubbled through tartaric acid solutions containing iron(III) and molybdate, quickly reduced the iron without affecting the molybdate. Since iron(II) does not interfere with the molybdate wave, the determination of molybdenum may be made after reducing iron(III) in this manner and removing the excess sulfur dioxide by boiling. Table IV gives some results obtained in this manner.

For freshly prepared solutions containing chromium(III) chloride in 0.1*M* tartaric acid, a single polarographic wave is produced which starts at about −0.6 volt *vs.* S.C.E. and therefore would interfere with the molybdate wave. On standing, however, the green chromium(III) solution is transformed slowly into a violet form which is reduced at a more negative potential. The green chromium complex is probably the dichlorotetraquochromium(III) ion $[Cr(H_2O)_4Cl_2^+]$ and the violet complex the hexaquochromium(III) ion $[Cr(H_2O)_6^{+++}]$ (*2*). The rate of transition from one form to the other is slow, so that chromium will interfere with the determination of molybdate unless the solution is allowed to stand for a long period before electrolysis.

The transformation of chromium(III) to an innocuous form may be hastened by passing sulfur dioxide through the tartaric acid solution containing the molybdenum and chromium. A color transition from the green form to a blue-gray color occurs after a few minutes and a new chromium species, probably a sulfite complex, is formed which does not interfere with the molybdate wave. The half-wave potential of the wave for the sulfite complex of chromium(III) is even more negative than that for the hexaquochromium(III) complex. Further study of this system would be interesting.

Neither cobalt nor manganese produces waves in 0.1*M* tartaric acid before the discharge of hydrogen. Nickel produces a single wave, but the wave does not begin until a more negative potential is reached than that at which the molybdate wave is read. Thus nickel, cobalt, and manganese will not interfere in the molybdate determination.

Copper, which produces a single wave in 0.1*M* tartaric acid (half-wave potential of +0.15 volt *vs.* S.C.E.), causes a slight decrease in the molybdate limiting current but does not interfere in the proposed determination when present in concentrations up to $2mM$ or a maximum copper to molybdenum concentration ratio of about 10 to 1. Both species can be determined up to this limit, since the diffusion current of copper is proportional to its concentration. At higher copper concentrations a maximum appears in the copper wave which masks the molybdate reduction. An effective maximum suppressor could not be found which eliminated this maximum and did not seriously lower and distort the molybdate wave. Thus, the concentration of copper in the unknown cannot be larger than about 10 times that of molybdate.

Vanadium(V) produces three waves in $0.1M$ tartaric acid with half-wave potentials of about +0.4, 0.0, and −0.6 volt *vs.* S.C.E., caused by reduction to the +4, +3, and +2 oxidation states respectively. Since the half-wave potential for the third reduction wave is very close to the potential where the molybdate wave is read (−0.65 volt) the presence of vanadium will interfere in the determination of molybdenum unless its concentration is about $^1/_{50}$ that of the molybdate.

PROCEDURE

The appropriate amount of unknown solution to give a final molybdate concentration between 1.5×10^{-4} and $4 \times 10^{-3}M$ is placed in a beaker. The volume of this solution should not exceed 30 ml. Five milliliters of $1M$ tartaric acid is then added. The pH of the solution should be between 1.5 and 2.3. If chromium or a large amount of iron is present, the solution is heated to 80° to 90° C. while sulfur dioxide is carefully bubbled through the solution. After 10 minutes the passage of sulfur dioxide is stopped, and the solution is gently boiled for a few minutes to remove excess sulfur dioxide. The solution is then cooled to room temperature, transferred quantitatively to a 50-ml. volumetric flask, and diluted to volume. After thorough mixing, a suitable aliquot is placed in the polarograph cell, oxygen is removed by passage of air-free nitrogen, and temperature is allowed to reach equilibrium. The polarogram is then recorded.

A known volume of standard molybdate solution is then added, and air free nitrogen is bubbled through the solution again for 2 to 3 minutes. The second polarogram is then recorded. It is best to add a volume of molybdate which will approximately double the wave height. The current is read at the plateau occurring between −0.6 and −0.75 volt. (The exact potential range in which this plateau is obtained changes somewhat with change in concentration of molybdate, tungstate, and various indifferent salts.) The concentration of the molybdate is calculated by the equation:

$$C_{\text{molybdate}} = \frac{ivC_{\text{stnd}}}{\Delta i(V + v) + iv}$$

where i = original diffusion current of unknown
V = volume of original unknown solutions
v = volume of standard molybdate added
$C_{\text{stnd.}}$ = concentration of standard molybdate
Δi = increase in current caused by standard addition

ACKNOWLEDGMENT

The assistance of Robert H. Moss in preparing some of the illustrations is gratefully acknowledged.

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Polarographic Determination of Dissolved Oxygen In Dilute Sulfite Waste Liquor

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Dissolved oxygen measurements by the Winkler method or its modifications are unreliable in water containing sulfite waste even at low waste concentrations. The feasibility of a polarographic method was recently demonstrated, but the limitations of the method were not established. In an examination of the effects of waste concentration, pH, and operating potential the sulfite waste reduced the diffusion current and shifted the oxygen waves to more negative potentials with increasing waste concentration. These effects were a minimum at low pH values. The sulfite waste had an immediate oxygen demand only in alkaline solution by current-time measurements at a given potential. Dissolved oxygen can be measured by the polarographic method within the limits of experimental error in water containing up to about 3.0% sulfite waste.

SULFITE waste is known to interfere with the determination of dissolved oxygen by the Winkler method and its modifications, even at the very low concentrations that exist in surface waters. Dissolved oxygen measurements are required in connection with programs for stream pollution control, for which the waste concentration may be well below 0.4%. Dissolved oxygen measurements may also be desired, however, in isolated instances where the waste concentration is greater, as in accidental spills, in impounding ponds, and in studies of B.O.D. and waste treatment.

Busch and Sawyer (*1*) and Rand and Heukelekian (*4*) have recently demonstrated the feasibility of a polarographic method for dissolved oxygen in water containing sulfite waste. The present study was undertaken to define the limitations of the polarographic method and the conditions under which reasonably accurate measurements can be made.

Table I. Iodine-Consuming Capacity of Sulfite Waste Liquor

(In terms of p.p.m. SO_2)

Iodine-Consuming Capacity, P.P.M. SO_2	Procedure
251, 254, 239	Direct reaction with standard iodine in acid solution. Excess iodine back-titrated immediately with standard thiosulfate
	Waste diluted with an equal volume of 5.0% NaOH, allowed to stand for a definite period of time, then acidified, standard iodine added, and excess back-titrated immediately with standard thiosulfate
4300, 3980, 4000	1 min. in alkaline solution
4320, 4020, 4020	10 min. in alkaline solution
4190, 4210, 4210	60 min. in alkaline solution
1740, 1780, 1480	50.0% sulfite waste distilled into excess NaOH. Distillate was acidified, standard iodine added, and excess back-titrated with standard thiosulfate
2050, 1940, 1950	20.0% sulfite waste distilled into excess NaOH. Distillate was acidified, standard iodine added, and excess back-titrated with standard thiosulfate

APPARATUS AND EXPERIMENTAL PROCEDURE

Current-voltage and current-time curves were recorded automatically with a Leeds and Northrup Electrochemograph. A saturated calomel electrode with a saturated potassium chloride bridge and agar plug served as a reference electrode in all experiments. The electrolytic cell was a 65-ml. specimen bottle into which the mercury electrode capillary, salt bridge, and a thermometer protruded for 1 inch through openings in a plastic cover plate. The temperature of the samples was maintained at 25.0° ± 0.2° C. for experiments at pH 4.1 and 6.9. For experiments at pH 9.2, the temperature was measured but not controlled. The value of *m* in the Ilkovič equation (*2*) was not determined, but the head of mercury was adjusted to the same value for all experiments. The drop time was 3.00 seconds in 0.1M potassium chloride at 25.0° C. on open circuit. All pH measurements were made with a Beckman glass electrode pH meter, Model H 2.

Methyl red was used as a maximum suppressor in all experiments at pH 9.2. It was later found that the methyl red contributed a small wave at about −0.5 volt *vs.* the saturated calomel electrode. Thymol blue was used in subsequent experiments at pH 6.9 and 4.1. At pH 9.2 in 0.05M borax buffer, 3 p.p.m. of methyl red satisfactorily suppressed the oxygen maximum. At pH 6.9 in 0.05M phosphate buffer and at pH 4.1 in 0.05M acetate buffer, 3 and 17 p.p.m. of thymol blue were required, respectively.

A calcium-base, digester strength, spent sulfite liquor, containing about 13% solids, from the cooking of spruce wood by the Mitscherlich-type process was used to prepare all test solutions. The waste was obtained from the Sulfite Pulp Manufacturers' Research League, Inc., Appleton, Wis.

The sulfite waste liquor was not boiled, aerated, or modified in any manner. The iodine-consuming capacity of this waste was determined by various procedures to characterize some of its chemical properties. The results are presented in Table I, together with a brief description of the various procedures used for analysis. The iodine-consuming capacity of the waste is expressed in parts per million of sulfur dioxide. The great increase observed in the iodine-consuming capacity on treating the waste with alkali over that observed in the direct reaction procedure is indicative of the complexity of the waste liquor. It further suggests that the polarographic behavior of the waste in alkaline solution may be somewhat different from its behavior in acid solution.

The pH of diluted sulfite waste varied from 2.6 for a 100% solution to 3.2, 3.7, and 4.4 for 10.0, 1.0, and 0.1% waste solutions, respectively.

All test solutions were prepared by diluting the sulfite waste with a buffer or distilled water of known dissolved oxygen content. The initial dissolved oxygen for each experiment was calculated from the known dissolved oxygen of the buffer and the dilution, assuming the waste to have a zero dissolved oxygen. The solutions were then siphoned into a 65-ml. electrolysis cell containing the required quantity of maximum suppressor. All solution transfers and preparations were made with delivery tips beneath the surface of the liquid and with a minimum of agitation to prevent oxygen uptake. The completely filled cell was then placed in a water bath and positioned beneath the electrode tips. Test solution displaced by the thermometer and electrode tips formed a thin liquid seal between the cell and plastic cover plate. Current-voltage or current-time curves were then recorded with the Leeds and Northrup polarograph.

Test solutions for residual current measurements were prepared by two procedures. In some experiments, purified nitrogen gas was passed through the diluted sulfite waste prior to its transfer to the electrolysis cell in order to deoxygenate it. In other experiments, nitrogen gas was passed through the buffer to remove all dissolved oxygen before the required quantity of sulfite waste liquor was added.

Residual current measurements made in diluted sulfite waste at pH 4.1 and 6.9 showed no difference in the curves for measurements made in solutions prepared by the two procedures. This was taken to indicate a small or negligible dissolved oxygen in the sulfite waste liquor.

INSTRUMENT CALIBRATION FOR DISSOLVED OXYGEN

Calibration experiments were conducted in the buffer solutions at −0.3 volt *vs.* the saturated calomel electrode (S.C.E.) by the procedure described above, except that sulfite waste was not added to the buffer. The diffusion current, i_d, was determined by measuring the limiting current in the buffer and correcting it for the residual current at the same potential. Dissolved oxygen was also measured by the Winkler method on corresponding samples of the buffer. The calibration constant, *K*, for dissolved oxygen was then calculated from the ratio of the dissolved oxygen measured by the Winkler method to the diffusion current:

$$K = \frac{\text{D.O.}}{i_d}$$

All experiments at pH 4.1 and 6.9 were made with one capillary; a second capillary was used at pH 9.2. Calibration for dissolved oxygen was made at −0.3 volt *vs.* S.C.E. in 0.05M acetate, phosphate, and borate buffers at pH 4.1, 6.9, and 9.2, respectively. The average value of *K* was found to be 2.28 for solutions buffered at pH 4.1 and 6.9 with a standard deviation of 0.021 based on a total of 10 measurements. For solutions buffered at pH 9.2, *K* was found to be 2.18, with a standard deviation of 0.022 based on six measurements.

The temperature coefficient of *K* was not determined for solu-

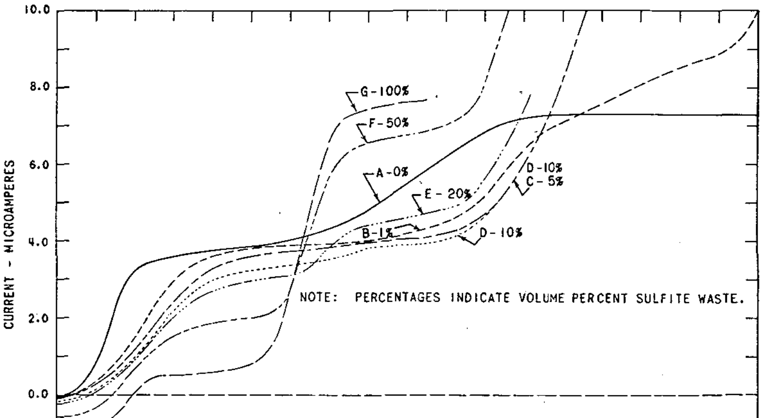

Figure 1. Polarograms Measured in Unbuffered Sulfite Waste Solutions

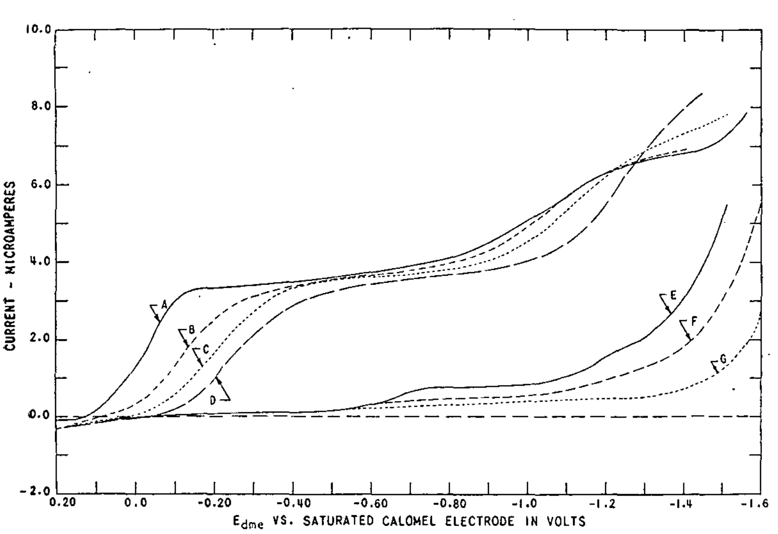

Figure 2. Current-Voltage Curves for Sulfite Waste Solutions Buffered at pH 4.1 with 0.05M Acetate Buffer

T = 25.0° C.

Curve	Sulfite Waste, Vol. %	Initial D.O., P.P.M.
A	0.00	7.61
B	0.03	7.56
C	0.30	7.54
D	5.68	7.13
E	2.91	0.00
F	0.99	0.00
G	0.00	0.00

tions buffered at pH 4.1 and 6.9, as the measurements were all made at 25.0° C. At pH 9.2, a number of calibration determinations in the temperature interval 23.5° to 31.0° C. showed the temperature coefficient of K to be -0.013 per ° C. at 25.0° C.

The 95% confidence limits for a single K determination was found to be 2.28 ± 0.048 for pH 4.1 and 6.9, and 2.18 ± 0.056 at pH 9.2. These limits establish the magnitude of the experimental error for a single K determination at -0.3 volt to be ±2.1% at pH 4.1 and 6.9 and ±2.6% at pH 9.2.

The calibration experiments for dissolved oxygen were made at -0.3 volt, a potential selected arbitrarily on the first oxygen plateau that extends from about -0.2 to -0.6 volt (see curve A in Figures 1 and 2). Because all the experimental errors are independent of choice of potential, one may expect the $CL_{K_{95}}$ at any other potential on the oxygen plateau to have a range comparable to that determined at -0.3 volt, and hence similar limits for the experimental error.

CURRENT-VOLTAGE CURVES

Measured in Unbuffered Sulfite Waste Solutions. Current-voltage curves measured in unbuffered water containing 1.0 to 100.0% by volume of sulfite waste liquor are given in Figure 1, curves B to G, in which the current is plotted against the potential of the dropping mercury electrode, E_{dme}. A normal dissolved oxygen polarogram (curve A) in 0.1M potassium chloride is included for comparison.

The effect of the sulfite waste on the characteristics of the normal oxygen polarogram is very definite. As illustrated in Figure 1, the first oxygen wave becomes flatter and shifts to more negative potentials as the sulfite waste concentration increases. This effect is most pronounced at waste concentrations of less than 1%, as illustrated by curves A and B.

At higher waste concentrations, curves C to G, the second oxygen wave is completely eliminated. In addition, another wave appears in the -0.5- to -0.8-volt range, superimposed on the first oxygen plateau, that has all the characteristics of a sulfur dioxide wave. The height of this wave increases, but not proportionately, with an increase in waste concentration.

Because of the sulfur dioxide wave, the only potential suitable for possible dissolved oxygen measurements in unbuffered sulfite waste solutions is in the -0.4- to -0.55-volt range for solutions containing up to 50% waste, and in the -0.4- to -0.6-volt range for solutions containing up to 20% waste.

Measured in Buffered Sulfite Waste Solutions. Current-voltage curves measured in solutions buffered at pH 4.1 and containing 0.03 to 5.68 volume % sulfite waste and about 7.5 p.p.m. of dissolved oxygen are presented in Figure 2, curves B to D. Curves E to G are residual current measurements made in solutions containing up to 2.91% sulfite waste. A normal oxygen polarogram, measured in the buffer solution, is presented as curve A for comparison.

Except for the sulfur dioxide wave in the -0.5- to -0.8-volt range, the current-voltage curves measured in sulfite waste solution buffered at pH 4.1 are essentially the same as those observed in unbuffered waste solutions. The trends observed are the same, for the first oxygen wave becomes flatter and shifts to more negative potentials. In addition, as the waste concentration increases, the second oxygen wave becomes less distinct.

A well defined wave observed at about -0.7 volt in the residual current (curve E, Figure 2) for a solution containing 2.91% waste appears to be due to the reduction of sulfur dioxide. The same wave does not occur in curve D for a solution containing 5.68% waste and 6.13 p.p.m. of dissolved oxygen initially. This observation suggests that sulfur dioxide was completely oxidized by oxygen before curve D was measured. This possibility of an oxygen demand by the waste requires further study.

The residual current curves, E to G, do not differ in the potential range 0.0 to -0.6 volt for solutions containing up to 2.91%

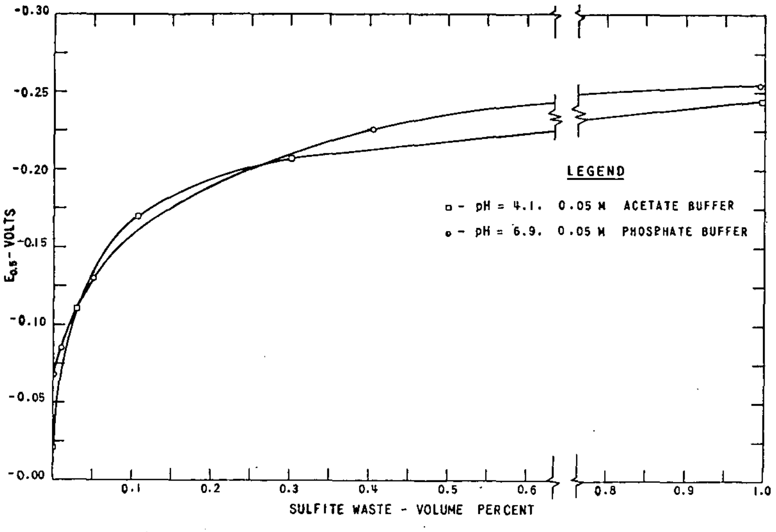

Figure 3. Half-Wave Potential of Oxygen Wave in Buffered Sulfite Waste Solutions

T = 25.0° C.

waste. At potentials more negative than −0.6 volt, the residual current increases with an increase in waste concentration.

Except for the residual current curves, the current-voltage curves measured in sulfite waste solutions buffered at pH 6.9 and 9.2 are similar to those measured at pH 4.1 (Figure 2). There is a change with pH, however, in the residual current measurements. At pH 4.1, the sulfite waste contributes to the residual current only as potentials more negative than −0.6 volt, as illustrated in Figure 2. At pH 6.9, however, the waste contributes to the residual current only at potentials more negative than about −1.3 volts, whereas at pH 9.2 the sulfite waste has no significant effect on the residual current. It appears that as the pH increases, the sulfite waste starts to contribute to the residual current at more negative potentials, and that the contribution to the residual current increases with waste content.

Waves due to the reduction of sulfur dioxide at the dropping mercury electrode do not appear in any of the current-voltage curves measured in solutions buffered at pH 6.9 and 9.2.

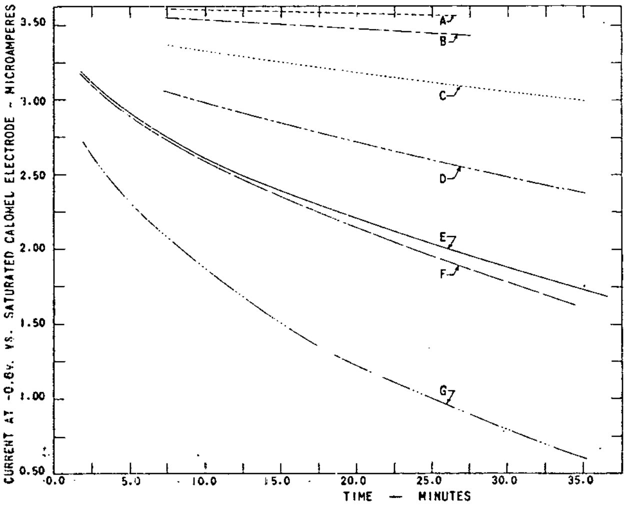

Figure 4. Current-Time Curves at −0.6 Volt *vs.* S.C.E.

Measured in sulfite waste solutions
Buffered at pH 9.2 with 0.05*M* borax buffer

Curve	Sulfite Waste, Vol. %	Initial D.O., P.P.M.	Temperature, ° C.
A	0.20	7.42	27.0
B	0.60	7.40	27.0
C	1.49	7.29	27.5
D	2.95	7.14	28.0
E	4.80	6.95	28.5
F	4.80	6.86	29.5
G	9.15	6.60	29.0

In order to characterize and emphasize the progressive change in the current-voltage curves with an increase in sulfite waste concentration, the half-wave potential, $E_{0.5}$, of the first oxygen wave was measured as a function of sulfite waste concentration for solutions buffered at pH 4.1 and 6.9. The results are presented in Figure 3, in which $E_{0.5}$ is plotted as a function of waste concentration. As illustrated in Figure 3, the most significant increase in $E_{0.5}$ occurs at low waste concentrations, below about 0.3% waste. At higher waste concentrations, $E_{0.5}$ increases slowly as the waste concentration increases.

OXYGEN DEMAND OF SULFITE WASTE SOLUTIONS

Current-time curves were measured in the buffered waste solutions at each pH to establish the magnitude of the immediate oxygen demand of the waste. All measurements were made at −0.6 volt, a potential that appeared to be the middle of the oxygen plateau in solutions containing sulfite waste. Any decrease in the current with time was taken to indicate a decrease in dissolved oxygen.

Current-time measurements in solutions buffered at pH 4.1 and 6.9 and containing up to 5.69% sulfite waste and about 7.5 p.p.m. of dissolved oxygen showed no change in the current at −0.6 volt for about 30 minutes after the solution was prepared. These results indicate that the sulfite waste has a negligible oxygen demand at pH 4.1 and 6.9 during the time interval at which the current-voltage curves were being measured. These findings also eliminate the possibility of sulfur dioxide oxidation by oxygen at pH 4.1 before the current-voltage curves were measured, a possibility suggested by the sulfur dioxide wave, in the residual current curve in Figure 2, that did not appear in the polarogram.

Current-time curves measured at −0.6 volt in solutions buffered at pH 9.2, and containing initially 7.42 to 6.60 p.p.m. of dissolved oxygen and 0.20 to 9.15% sulfite waste are presented in Figure 4, in which the current is plotted as a function of time in minutes.

Unlike the results observed in solutions buffered at pH 4.1 and 6.9, the current at −0.6 volt decreased with time in solutions buffered at pH 9.2, as illustrated in Figure 4, indicating a decrease in dissolved oxygen due to reaction with the waste. The rate at which the current decreases becomes greater as the waste content increases, as can be seen by comparing curves *A* and *G*, in the extreme case, representing 0.20 and 9.15% sulfite waste solutions.

EFFECT OF SULFITE WASTE CONCENTRATION ON CALIBRATION CONSTANT

It is instructive, in the present case, to compare the calibration constant determined in the buffer with that determined in buffered sulfite waste solutions at various potentials. The results for measurements made at −0.3, −0.5, −0.6, and −1.6 volts in sulfite waste solutions buffered at pH 4.1, 6.9, and 9.2 are presented in Table II together with the initial composition of each solution.

Special treatment was required to obtain a calibration constant, *K*, at pH 9.2 because of the oxygen demand of the waste. The initial dissolved oxygen for each experiment was determined in

Table II. Effect of Sulfite Waste Concentration on Calibration Constant, *K*

(At −0.3, −0.5, −0.6, and −1.6 volts *vs.* S.C.E. in solutions buffered at pH 4.1, 6.9, and 9.2 at 25.0° C.)

Sulfite Waste, Vol. %	Initial D.O., P.P.M.	*K*			
		−0.3 v.	−0.5 v.	−0.6 v.	−1.6 v.
		pH = 4.1			
0.00	7.56	2.28	2.25	2.25	..
0.03	7.56	2.52	2.28	2.29	..
0.10	7.55	2.70	2.29	2.28	..
0.30	7.54	2.91	2.29	2.27	..
0.99	7.50	3.12	2.32	2.30	..
2.94	7.34	3.49	2.36	2.30	..
5.68	7.13	3.53	2.37	2.32	..
		pH = 6.9			
0.00	7.74	2.28	2.20	2.12	..
0.00	7.77	2.28	2.18	2.10	1.22
0.01	7.74	2.37	2.30	2.23	1.24
0.05	7.74	2.44	2.28	2.24	1.22
0.40	7.71	2.93	2.36	2.39	1.26
0.90	7.70	3.42	2.46	2.43	1.25
2.56	7.54	3.71	2.54	2.48	..
5.69	7.30	3.88	2.51	2.45	..
		pH = 9.2			
0.00	7.33	2.18	..	2.13	..
0.00	7.25	2.18	..	2.13	..
0.05	7.38	..	..	[2.22][a]	..
0.20	7.42	..	..	[2.30]	..
0.60	7.40	..	..	[2.30]	..
1.00	6.98	..	..	[2.24]	..
1.49	7.29	..	..	[2.34]	..
2.94	6.91	..	..	[2.32]	..
4.80	6.95	..	..	[2.47]	..
4.80	6.86	..	..	[2.44]	..
9.15	6.60	..	..	[2.63]	..

[a] Brackets indicate values determined from diffusion currents extrapolated to zero time and corrected to 25.0° C.

the usual manner. The diffusion current at −0.6 volt, similar to that presented in Figure 4, was carefully extrapolated to zero time. These extrapolations were made on semilog paper, for the current-time curves plotted in this manner were found to be nearly linear and the extrapolation was made over a very short time interval. The calibration constant was then calculated from the initial dissolved oxygen and the extrapolated value of the diffusion current. The calibration constant was then corrected to 25.0° C. on the assumption that the temperature coefficient was the same as that in the pure buffer.

In general, the calibration constant increased with an increase in sulfite waste concentration, as illustrated in Table II. The increase above that of the buffer is much greater, in most cases, than the limits of experimental error as determined by the 95% confidence limits for a single calibration measurement.

In comparing the trend in K with increasing sulfite waste concentration, it is observed that the variation in K is least at pH 4.1 at −0.5 and −0.6 volt and at pH 6.9 at −1.6 volts.

For solutions buffered at pH 4.1, the calibration constant increased at −0.5 volt from 2.25 for the buffer to 2.37 for a 5.68% waste solution. This represents a 5.3% increase in K over that of the buffer, as compared with 2.1% for the limit of experimental error. This gradual increase in K as the waste concentration increases is more definite than can be explained on the basis of a 1 in 40 chance for the measurements to be beyond the CL_{K95} for a single K determination. In fact, it is found to be well beyond the experimental error based on 99.9% confidence limits for a single K determination. However, the variation in the calibration constant is within the limits of experimental error for sulfite waste concentrations up to about 0.30%. At −0.6 volt, K increases from 2.25 for the buffer to 2.32 for a 5.68% waste solution. This represents a 3.1% increase in K over that of the buffer, as compared to 2.1% for the experimental error based on 95% confidence limits. The increase in K above that of the buffer, furthermore, is somewhat greater than the experimental error, 2.9% based on 99% confidence limits for a single K determination, so it represents a definite trend. The increase in K at −0.6 volt is within the limits of experimental error at the 95% level of significance for waste concentrations up to 2.94%.

At pH 6.9, the variation in K at −1.6 volts appears to be within the limit of experimental error for sulfite waste solutions up to 0.90%. It was not possible to measure K at higher waste concentrations.

The observed increase in K at each pH and potential reflects a decreasing current response per unit of dissolved oxygen with increasing sulfite waste concentration. Because of this, dissolved oxygen measurements made in diluted sulfite waste will tend to be low if the variation of K with waste concentration, choice of operating potential, and pH is not taken into account. The usual polarographic methods employed for dissolved oxygen measurements do not provide for this.

DISCUSSION

It was observed that the sulfite waste alone acted as a suppressor for the oxygen maximum. In this respect, the effect of sulfite waste on the characteristics of irreversible polarographic waves should be somewhat similar to that of other maximum suppressors. In the case of gelatin (*3, 6*), waves generally become flatter and shift to more negative potentials, and the diffusion current is reduced as the concentration of gelatin increases. It has been reported (*3*) that various other maximum suppressors cause effects similar to those observed in the presence of gelatin. These effects have been attributed either to a binding of the reducible substance by the maximum suppressor or to adsorption of the suppressor at the electrode surface with the possibility of a subsequent effect on the kinetics of the electrode process. The latter viewpoint is strongly supported by Strassner and Delahay (*6*). The behavior of gelatin and other maximum suppressors is remarkably similar to that reported here for sulfite waste. On this basis, it is believed that one or more components in the sulfite waste are adsorbed on the surface of the dropping mercury electrode, and that the observed variation in K and in the half-wave potential of the oxygen wave with an increase in waste concentration can be attributed to the surface active components of the waste that are adsorbed on the electrode.

Other industrial or domestic wastes containing organic components may affect the characteristics of the dissolved oxygen polarogram in a manner similar to that observed for dilute sulfite waste liquor. Rand and Heukelekian (*4*), in fact, observed that a number of industrial wastes distorted the oxygen polarogram. They did not, however, describe or characterize the distortion effects nor attempt to determine the cause of distortion.

Dissolved oxygen measurements of buffered solutions by the procedure used here are limited to a small range of sulfite waste concentration under carefully controlled conditions. Low pH values at an operating potential of about −0.6 volt *vs.* S.C.E. appear to be the optimum operating conditions, for the variation in K with increasing waste concentration appears to be least under these conditions. More specifically, for the pH values, operating potentials, and waste concentration ranges considered, the optimum operating conditions for measuring dissolved oxygen within the limits of experimental error in diluted sulfite waste are:

pH	Potential, Volts *vs.* S.C.E.	Max. Sulfite Waste Concn., Vol. %	Exptl. Error, %
4.1	−0.5	0.30	2.1
4.1	−0.6	2.94	2.1
6.9	−1.6	0.90	Ca. 3.0

At other pH values and potentials, the increase in K above that of the buffer was greater than the expected experimental error for the lowest waste concentration considered, ca. 0.01%. If errors greater than the expected experimental error can be tolerated, the waste concentration range in which dissolved oxygen can be measured may be extended somewhat.

The studies made by Rand and Heukelekian (*4*) on the polarographic determination of dissolved oxygen in unbuffered sulfite waste solutions are not comparable with the present studies, for they used a mercury pool reference electrode and boiled the waste under nitrogen to ensure working with a waste free from dissolved oxygen. Such a procedure may alter the polarographic behavior of the sulfite waste.

Busch and Sawyer (*1*), in a study on the replication of dissolved oxygen measurements by the polarographic method in sulfite waste solutions, reported dissolved oxygen values 1.6% low for a 0.021% waste solution in B.O.D. dilution water with an operating potential of −1.6 volts. If residual current measurements are made, their method may be extended to waste solutions up to 0.90% with a similar accuracy on the basis of the results presented here at −1.6 volts at pH 6.9.

Although the present method for dissolved oxygen in dilute sulfite waste is a substantial improvement over modifications of the Winkler method, the limitations imposed by the variation of K with pH, waste concentration, and choice of operating potential are rather severe. A modified polarographic technique designed to compensate for the variation of K such as the method of standard addition (*2*), is indicated. Such a method should also be appropriate for use in the presence of many other industrial wastes.

TENTATIVE PROCEDURE

On the basis of the results presented here, the following procedure is presented as a guide for the routine determination of dissolved oxygen in water samples containing sulfite waste liquor.

Reagents. Acetate buffer, 5.0*M*. Dissolve 122.0 grams of sodium acetate trihydrate in 240 ml. of glacial acetic acid, and dilute to 1 liter. The pH of the buffer diluted 1 to 100 with water is 4.1.

Nitrogen gas (and alkaline pyrogallol gas scrubbing train).
Thymol blue, 0.5%.

Electrodes and Other Equipment. A dropping mercury electrode assembly similar to that described by Seaman and Allen (*5*) is desirable. Any manual or recording polarograph may be used.

Operating Potential, -0.6 volt *vs.* S.C.E.

Procedure. Add 0.5 ml. of concentrated acetate buffer and 4 drops of thymol blue to an electrolysis cell. Pipet 50.0 ml. of the water sample into the cell and gently stir the mixture with the tip of the pipet. Place the electrolysis cell in the constant temperature bath to adjust the temperature of the sample. Adjust the dropping mercury electrode according to the procedure described by Seaman and Allen (*5*). Measure current passing through the sample at -0.6 volt *vs.* S.C.E. before and after deaeration with nitrogen gas.

Calibration. To calibrate the instrument for dissolved oxygen, measure the current by the above procedure on distilled water. Add 3.0 ml. of the concentrated buffer to a standard B.O.D. bottle and fill the bottle with distilled water. Measure dissolved oxygen by the Winkler method. Calculate the calibration constant, K, from the ratio of the Winkler dissolved oxygen to the difference in the current before and after deaeration with nitrogen.

Calculations. Calculate the dissolved oxygen in a water sample by multiplying the difference in the current, i_d, measured before and after deaeration by the calibration constant, K: D.O. = Ki_d.

Precision and Accuracy. Determine the precision and accuracy of the method for every apparatus and electrode.

Limitations. This procedure is limited to water samples containing less than about 5% sulfite waste in terms of the sulfite waste liquor used in this study. If previous knowledge or experience does not indicate a low sulfite waste concentration, it may be possible to establish the effective concentration of the waste by determining the iodine-consuming capacity of the water sample before and after alkaline treatment. Additional work is needed to establish the validity of such a method.

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Polarographic Determination of Tungsten in Rocks

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This work was undertaken to develop a simpler and faster method than the classical gravimetric procedure for the determination of tungsten in rocks and ores. A new polarographic wave of tungsten is obtained in a supporting electrolyte of dilute hydrochloric acid containing tartrate ion. This permits the determination of tungsten both rapidly and accurately. No precipitation of the tungsten is necessary, and only the iron need be separated from the tungsten. The accuracy is within the limits of a polarographic procedure; comparison of polarographic and gravimetric results is given. The method reduces appreciably the amount of time ordinarily consumed in determination of tungsten.

WHEN tungsten is determined on rocks and ore concentrates, the classical gravimetric methods are usually employed. Tungsten is precipitated as tungstic acid after an acid attack to put the sample in solution, and the tungstic acid is ignited to the oxide. The impure oxide is then dissolved and corrected for contamination by silica, iron, and molybdenum. Analyses for trace amounts of tungsten in rocks have been made colorimetrically by measuring the color produced by the stannous chloride–thiocyanate reaction (*5*).

Lingane and Small (*3*) investigated the polarography of tungsten in hydrochloric acid media. In $4M$ hydrochloric acid +6 tungsten (VI) undergoes stepwise reduction to the (V) and the (III) state. The first diffusion current starts from zero applied electromotive force, and the half-wave potential of the second wave is 0.66 volt *vs.* saturated calomel electrode. Kolthoff and Parry (*2*) reported a kinetic polarographic wave of tungsten in the presence of hydrogen peroxide, but it is not a linear function of the tungsten concentration. Stackelberg *et al.* (*4*) determined tungsten in steel polarographically by precipitating the tungsten as the acid, igniting the acid to the oxide, dissolving the oxide in potassium hydroxide, and running the polarogram in about $9M$ hydrochloric acid with the half-wave potential at -0.60 volt *vs.* S.C.E.

In the proposed method the sample is fused with sodium carbonate, leached with water, and filtered; tartrate is added, and the solution is acidified with hydrochloric acid. The polarogram is run in dilute hydrochloric acid and the per cent of tungsten is calculated from the diffusion current constant obtained on standard tungsten solutions.

EXPERIMENTAL DATA

Apparatus. Polarograms were recorded with a Rutherford Polaro-analyzer. All measurements were made at 25° C. A modified H-cell with an external saturated calomel electrode was used.

Reagents. Reagent grade chemicals were used. The tungstic oxide that was added to the samples was prepared from sodium tungstate.

Sodium tartrate, $1M$.

Cinnamic acid, 5% in alcohol. This solution should not be more than 5 days old.

Standard tungsten solution, about $1.0 \times 10^{-2}M$. This solution was made from sodium tungstate and standardized gravimetrically (*1*).

CHARACTERISTICS OF POLAROGRAPHIC WAVE

Initially a solution of $8M$ hydrochloric acid was used as the supporting electrolyte for tungsten (*3*). However, a difference was observed in the number of microamperes produced by a millimole of tungsten between the tungsten in some of the samples and the tungsten in the standard solutions. From the ratio of these differences it was clear that in the $8M$ hydrochloric acid, the tungsten in some of the samples formed polytungstates but that the tungsten in the standard solutions did not. It is, of course, necessary for the tungsten to be of the same molecular species—that is, the same number of atoms of tungsten in the ion or molecule containing the tungsten—in both the sample and the standard solution in order to calculate the per cent tungsten from the diffusion current. Therefore, tungsten was added to the samples both as a standard sodium tungstate solution and as tungstic oxide prior to the fusion so that the tungsten for the standard would be conditioned in the same manner as the tungsten in the sample. This did not solve the difficulty. The added tungsten formed polytungstates (again the microamperes due to a millimole of tungsten varied), but they were not the same polytungstates as those formed by the tungsten in the sample. The polytungstate formed seemed to depend on the constituents of the sample, the chemical treatment of the sample, and the manner in which the tungsten was added to the sample.

However, in a supporting electrolyte of 4.6*M* hydrochloric acid and 0.1*M* tartrate, the formation of polytungstates is prevented. Tungsten, in this solution, produces the same number of microamperes per millimole of tungsten, regardless of the constituents of the sample and regardless of whether the tungsten was that present in the sample or that added as standard to an aliquot of the sample.

The polarographic current-voltage curve obtained using a solution of 0.8m*M* tungsten in 4.6*M* hydrochloric acid and 0.1*M* sodium tartrate is shown in Figure 1. Tungsten is reduced stepwise, the half-wave potential of the first wave being −0.35 volt and that of the second wave −0.68 volt *vs.* the S.C.E.

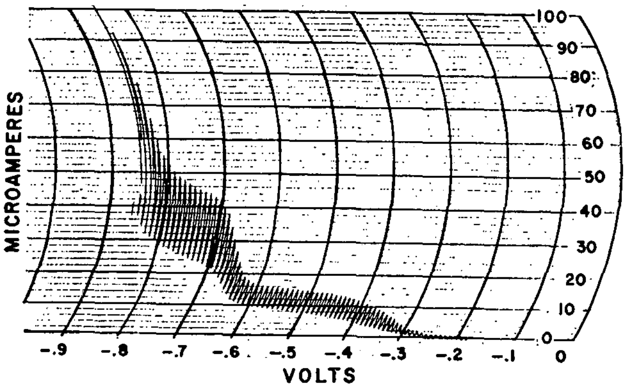

Figure 1. Polarogram of 0.8*mM* Tungsten in 4.6*M* Hydrochloric Acid and 0.1*M* Tartrate

The diffusion current is directly proportional to the tungsten concentration in the range from 0.05 to 1.0 m*M* tungsten (Table I). Solutions more concentrated than 1.0 m*M* exceed the solubility of tungsten and precipitated before polarograms could be made. The accuracy is within the polarographic limit of 2%. The height of the second wave is double that of the first wave. The diffusion-current constant for the second wave is 4.40, the value for $m^{2/3}\,t^{1/6}$ being 1.59. As the acidity decreases the diffusion current per millimole of tungsten decreases, and the half-wave potentials become more negative. The diffusion current shown in Table II is the total diffusion current for both waves. In the weak acid (1.4*M*) the discharge of hydrogen precedes the second wave. The half-wave potential of the first wave is affected by a slight change in the acid concentration. However, no significant change in that of the second wave was noted in the range from 3.7 to 5.1*M*.

PROCEDURE

Solution of Sample. Mix a 0.5-gram sample intimately with 5 grams of sodium carbonate and fuse in a crucible of at least 25-ml. capacity. When the crucible is cool, add 20 ml. of water, cover the crucible, and leach overnight on the steam bath. Filter into a 50-ml. volumetric flask, washing with water as thoroughly as possible, make to volume, and shake thoroughly. Discard the residue.

Preparation of Polarographic Solution. Pipet a 10-ml. aliquot into a 50-ml. volumetric flask, and add 5 ml. of sodium tartrate solution and 0.1 ml. of thymol blue. Add concentrated hydrochloric acid dropwise until the first trace of pink appears in the solution. Add 20 ml. of concentrated hydrochloric acid with a serological pipet and cool to room temperature. Add 0.25 ml. of cinnamic acid solution, swirling the contents of the flask immediately after the addition. Make to volume and shake thoroughly.

Table I. Proportionality between Concentration of Tungsten and Diffusion Current

4.6*M* HCl, 0.1*M* tartrate, $m^{2/3}t^{1/6}$ = 1.20 mg.$^{2/3}$ sec.$^{-1/2}$ at −0.78 volt *vs.* S.C.E.

Tungsten Concn., *mM*	Diffusion Current per Millimolar Concn., μa.
0.05	7.00
0.1	7.00
0.2	7.05
0.4	7.02
0.8	6.94
1.0	6.95
	Av. = 6.99 ± 0.05

Table II. Effect of Hydrochloric Acid Concentration on Half-Wave Potential and Diffusion Current of Tungsten

HCl, Molarity	$E^{1/2}$, Volt (1st Wave)	$E^{1/2}$, Volt (2nd Wave)	Total Diffusion Current, μa. at −0.78 Volt
1.4	−0.57	...	2.70
2.8	−0.47	−0.71	5.90
3.2	−0.43	−0.69	6.60
3.7	−0.41	−0.68	7.60
4.1	−0.39	−0.68	8.30
4.6	−0.35	−0.68	8.70
5.1	−0.33	−0.68	8.70
5.6	Zero applied e.m.f.		

Tungsten concentration 0.8 *mM*.

Determination of Tungsten. Transfer a suitable volume of the solution to a polarographic cell and remove oxygen by passing nitrogen through the solution for about 5 minutes. Measure the diffusion current at −0.78 volt *vs.* S.C.E. Calculate the per cent tungsten in the sample from the diffusion-current constant or a standard curve for tungsten made from standard solutions of tungsten in 4.6*M* hydrochloric acid and 0.1*M* tartrate.

RESULTS AND DISCUSSION

The samples were selected at random from samples submitted for tungsten analysis and were analyzed in duplicate. The results obtained by the polarographic procedure are in close agreement with the results from the gravimetric procedure. The average deviation of the two polarographic results was 0.57 mg., which is within the limits of reproducibility of a polarographic method.

The stability of the tungsten-tartrate solution depends on the acid concentration. The weaker the acid, the longer the tungsten remains in solution. Solutions made up in the morning were all usable at the end of the working day. In the range from 3.7 to 5.2*M*, tungsten had precipitated by the second morning; in the range from 2.8 to 3.2*M*, tungsten had precipitated by the third morning; but in the 1.4*M* solution no tungsten had precipitated. The effect of the tartrate is destroyed in 5.6*M* acid.

The curve produced by the tungsten-tartrate solution is not affected by the sodium carbonate in the solution. In a solution to which potassium bisulfate and ammonium hydroxide have been added, the second wave has no satisfactory plateau and coincides with the discharge of hydrogen. However, in a solution to which potassium bisulfate and an excess of sodium carbonate have been added, the current-voltage curve of the tungsten-tartrate ion complex is not affected. Nitrate ion affects the curve and should not be present.

A current-voltage curve similar to the curve obtained with the tartrate solution is also produced by complexing the tungsten with Versene. However, the Versene-tungsten ion complex could not be used in the determination of tungsten because the complex begins to deteriorate almost immediately and produces a peculiar wave.

Vanadium, of course, is also in the alkaline filtrate from the carbonate fusion. The half-wave potentials of vanadium at 0.0 and −0.80 volt *vs.* S.C.E. in 0.1*M* hydrochloric acid indicate that vanadium should not interfere in the measurement of the current voltage curve for tungsten. Actually, however, in the more concentrated acid solution, vanadium gives an ill-defined wave, ex-

Table III. Comparison of Polarographic with Gravimetric Results

Description of Sample	Tungsten, %			
	Polarographic			Gravimetric
	1	2	Av.	
1. From edge of tailings pond	1.23	1.27	1.25	1.25
2. Grab sample of mill heads, Idaho	0.32	0.43	0.37	0.40
3. From a tungsten mine, Alaska	3.25	3.06	3.15	3.11
4. From a tungsten mine, Alaska	5.97	5.80	5.88	5.30
5. Dredge concentrate of placer gravel, Alaska	3.20	3.37	3.28	3.40
6. Dredge concentrate of placer gravel, Alaska	0.32	0.32	0.32	0.30
7. Dredge concentrate of placer gravel, Alaska	1.00	0.96	0.98	0.96

tending from zero applied electromotive force to −0.80 volt, which makes the measurement of tungsten impossible. Addition of cinnamic acid to the solution eliminates the current due to vanadium. Cinnamic acid has no effect on the wave of the tungsten and does not contribute any current to the system. Cinnamic acid is only slightly soluble in acid solution and precipitates copiously immediately when added to the acid, but this causes no difficulty. Several soluble complexing agents (cupferron, quinoline, and diphenylamine) for vanadium were tried, but the complexing agents themselves produced interfering waves.

Most of the iron is removed by the filtration. However in many samples, some of the iron remains in the ferrous state after the carbonate fusion. Potassium nitrate added to the flux to oxidize all the iron to ferric later interfered with the tungsten current-voltage curve. Ferrous iron in the solution may obscure the indicator end point slightly, but it does not interfere with the determination of tungsten.

Of the other elements that may be present in the filtrate from the carbonate fusion, attention need be given only to molybdenum. All the others either are not reduced in hydrochloric acid or their half-wave potentials are more negative than that of tungsten. Molybdenum, however, would necessitate a separation if its molar concentration greatly exceeded that of tungsten.

The acid concentration must be carefully controlled so that the final acidity of samples and standard solutions is the same. The half-wave potential and particularly the height of the tungsten wave are sensitive to changes in the molarity.

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Radioactivity Assay of Water and Industrial Wastes with Internal Proportional Counter

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A method for determining low levels of nonvolatile radioactive contamination in water is proposed. The suspended and dissolved radioactivities are separated by filtration and evaporation. This permits counting both the alpha and beta radiation at levels less than the maximum permissible concentration of unknown isotopes in drinking water. When a 250-ml. sample of water containing about 50 μμc. per liter is prepared and counted for 30 minutes, the activity may be assayed with an accuracy (at the 95% confidence limit) of 10% for alpha and 20% for beta radiation. Levels as low as 10 μμc. per liter (beta) and 2 μμc. per liter (alpha) are detectable. Such sensitivity and accuracy are made possible by counting the dry solids spread over a large area and by using instruments with efficient counting characteristics.

A METHOD for separately assaying the gross alpha and beta radioactivity of waters and industrial wastes is presented. Filtered or evaporated samples are counted with an internal proportional counter which is particularly applicable for assaying low levels in the order of 1 to 10 μμc. of alpha activity and 10 to 100 μμc. of beta activity per liter of water.

This counter has the properties desirable for high efficiency counting. Graf *et al.* reported (*7*) that it gives a counting rate as much as 7 to 11 times greater than that from an end-window counter. Window and air absorption losses are eliminated because the sample is within the counting volume, and the geometry of counting is 50%. Because some internal counters will accept large (5 cm. in diameter) dishes, the losses from self-absorption for equal sample volumes are minimized. This is important for samples which have an appreciable (>200 p.p.m.) dry solids content.

The counter will count alpha activity in the presence of up to at least 500,000 counts per minute of beta activity without interference. Beta activity may be counted at the higher beta operating voltage, provided the alpha activity is negligible or alpha interference is eliminated with an absorber. A detailed evaluation of the counting efficiency of the counter has been made (*11*).

INSTRUMENTATION

A commercially available internal proportional gas-flow counting set was used. This counting set consisted of a Nuclear Measurements Corp., Indianapolis, Ind., PCC-10 converter plus a Nuclear Instrument and Chemical Corp., Chicago, Ill. scaler, Model 161. A cross section of the counting chamber is shown in Figure 1. It consists of a center wire assembly in a hemisphere-and-piston chamber. The chamber will accept dishes, 5 cm. in diameter by 1 cm. in depth, and may be readily taken apart for maintenance.

One of the criteria of reproducibility and accuracy in counting is that a curve of count versus voltage (*5*) has a broad and flat plateau. The slope, length, and position of the plateau depend on the area of the source, and on the size and position of the center wire loop. To count samples of extended area, it is

Table I. Backscattered Radiation

Isotope	Maximum Energy, M.e.v.	Backscatter Factor[a]	
		MF + Al + Cu[b]	Al + Cu[c]
Sulfur-35	0.167	1.09	1.15
MFP[d]		1.25	1.29
Thallium-204	0.762	1.28	1.31
Phosphorus-32	1.704	1.37	1.39

[a] Ratio of activity with backscatter to activity without backscatter.

[b] Membrane filter (4.6 mg./sq. cm.) + aluminum (0.0035 inch) + copper ($\geq$ 0.040 inch).

[c] Aluminum (0.0035 inch) + copper (0.040 inch).

[d] Mixed fisson products, 2.5 years old.

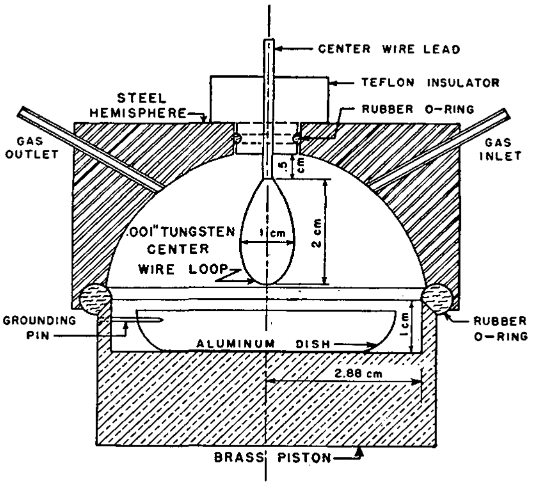

Figure 1. Internal Counter Chamber

necessary to establish a plateau using an extended source. The position and size of the center wire loop selected for the optimum plateau characteristics are shown in Figure 1. For a radioactive source 5 cm. in diameter, the plateau is greater than 150 volts in length with a slope of less than 3% per 100 volts.

The use of metal counting dishes causes backscattering (*5*) which improves the counting efficiency. With aluminum dishes (milk bottle caps) on the piston head, the backscatterer consists of 0.0035 inch of aluminum and more than 0.040 inch of brass. When suspended solids are counted, the backscattering is changed by the addition of the filter. The amount of backscattered radiation from this combination with and without a membrane filter was determined for a range of beta energies. The results, presented in Table I, show that backscatter and the efficiency of counting are energy dependent.

Self-absorption (*4*), the absorption of radiations by the sample solids, reduces the efficiency of counting and is independent of the counter. The extent of self-absorption by sample salts in aluminum dishes counted in the internal counter is shown in Figure 2. The salts used were magnesium ammonium phosphate hexahydrate for phosphorus-32, cerous carbonate pentahydrate plus strontium carbonate for mixed fission products, MFP, and lead iodide for iodine-131. Reduction in efficiency of counting becomes apparent at thicknesses of sample solids of 1 mg. per sq. cm. or more. At a thickness of 10 mg. per sq. cm. the count is reduced by 27, 36 and 45% for phosphorus-32, mixed fission products and iodine-131, respectively.

The counting dish may reduce the efficiency of counting by affecting the electric field. Dielectric or ungrounded metallic sample dishes tend to reduce the counting rate. For an ungrounded metallic dish the counting rate has been observed to decrease with time by as much as 35% in about 15 minutes. It is important, therefore, that the sample dish be properly grounded. When lightweight aluminum dishes are used, a positive grounding of the dish may be obtained by impaling the side of the dish on a grounded pin within the counting chamber as shown in Figure 1. Heavier dishes or planchets are grounded by their own weight. Dielectrics may be made conducting by spraying them with a very thin conducting film.

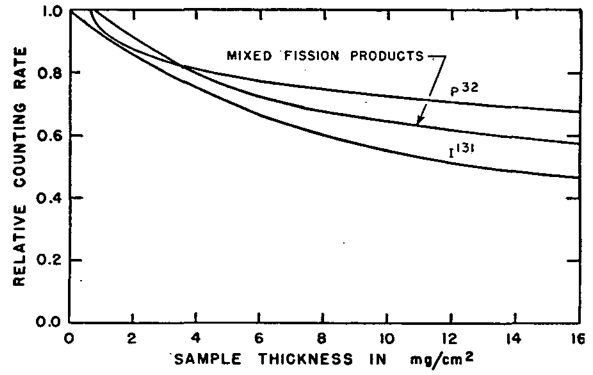

Figure 2. Self-Absorption in an Internal Counter

Efficiency. The alpha counting efficiency of the counter for samples having negligible self-absorption is 51 ± 1% because the geometry is 50% and the backscattered radiation is between 0 and 2% (*14*).

The beta counting efficiency of the counter for samples having negligible self-absorption will vary from more than 50% to over 75% because the backscattered radiation varies from a few per cent to over 25% of the total radiation, depending on the energy of the radiation, the atomic number, and thickness of the sample backing. The phosphorus-32 counting efficiency was determined from backscatter experiments and checked by counting standard solutions of phosphorus-32 from the National Bureau of Standards. For an unknown beta emitter, whose backscatter factor cannot be determined, the counting efficiency may be estimated by assuming an intermediate backscatter value.

PROCEDURE

Preparation of Samples. The suspended matter in a sample (200 to 1000 ml.) was usually removed by filtration through a porous cellulose acetate membrane (*3*) or, at some sacrifice of efficiency (*1*), through a smooth hard-surfaced filter paper. The suspended matter on a membrane was oven-dried at 103° C., cooled, and counted. The suspended solids were determined by the Gooch method (*2*) to obtain the sample thickness for self-absorption correction.

A sample of filtrate (200 to 1000 ml.), containing preferably less than 100 mg. of solids, was evaporated directly in a tared metal dish to avoid loss of radioactive material (*16*), for which an automatic evaporator (*12*) was proved to be convenient for direct evaporation of water samples. By this means a sample could be evaporated unattended at a rate of 20 ml. per hour. The temperature of evaporation did not exceed 90° C. until all but a few milliliters of water remained. The sample was then dried at 103° C., cooled, weighed, and counted. When the sample was sufficiently radioactive, a volume containing at least 1000 counts per minute was pipetted directly into the counting dish for drying and counting.

Counting. PLATEAU AND BACKGROUND. The alpha and beta operating voltages (*5*) were chosen at the middle of the alpha and beta plateaus, respectively, using a uranium oxide source, 5 cm. in diameter, for the alpha plateau and a similar source covered with aluminum foil (10 mg. per sq. cm.) for the beta plateau. A check on proper instrument functioning was made by counting these sources at their respective operating voltages three times a day. Each of the alpha and beta backgrounds was determined three times a day by counting clean sample dishes at the proper voltages.

SAMPLE ACTIVITY. The sample was counted at both the alpha and the beta operating voltages for two 16-minute periods each, separated by a short flushing time. If the two counting rates in a test did not agree within counting statistics (*8*), a third count was taken immediately.

When the alpha activity was less than 5 counts per minute, the observed beta count was corrected by subtracting the alpha

Table II. Reproducibility of Duplicate Radioactivity Assays

Sample	Assay		Radioactivity, Counts per Minute		Difference, Counts per Minute	
			Test 1	Test 2	Observed	Error[a]
Rain	Beta	Soluble	45.4	42.6	2.8	4.0
		Insoluble	242.9	240.7	2.2	8.7
Snow	Alpha	Soluble	0.41	0.45	0.04	0.33
		Insoluble	1.23	1.17	0.06	0.45
	Beta	Soluble	20.3	22.2	1.9	3.3
		Insoluble	8.2	5.0	3.2	3.2
River	Alpha	Soluble	5.1	6.5	1.4	1.7
		Insoluble	4.4	6.1	1.7	1.7
	Beta	Soluble	20.5	18.0	2.5	3.4
Waste	Alpha	Soluble	4.1	4.5	0.4	1.0
		Insoluble	14.5	15.5	1.0	2.3
	Beta	Soluble	31.0	31.5	0.5	4.2
		Insoluble	221.9	227.9	6.0	7.3
Sewage	Beta	Soluble	2004	1977	27	35
		Total	2553	2579	26	40

[a] Counting error at the 95% confidence level.

count. When the alpha activity was 5 counts per minute or more the sample was covered with an aluminum foil (7 mg. per sq. cm. thick) and the observed beta count was corrected for aluminum foil absorption by extrapolating an absorption curve (*5*) to zero thickness.

CALCULATIONS. The counting rate, because the counter efficiency and sample volume are known, can be converted to micromicrocuries per liter.

The counting rate error, E_{95} (at the 95% confidence level) was obtained (*6*), and converted to micromicrocuries per liter.

REPRODUCIBILITY AND ACCURACY

The reproducibility achieved with the assay method on a variety of typical samples is shown in Table II. A comparison of the last two columns of Table II indicates that the difference in duplicate assays is consistent with the counting error E_{95}.

Table III. Accuracy of Radioactive Assays

Source	Activity	Radioactivity, μμc./l.			Counting[b] Error, %
		Added	Observed	Corrected[a]	
Uranium	Alpha	1.34	2.12[c]	2.12	73
			0.56[c]	0.56	270
			0.56[c]	0.56	270
		27	17.9[c]	17.9	17
			23.4[c]	23.4	15
		54	39	49	10
Thallium Tl^{204}	Beta	9	14[c]	14	69
			5[c]	5	185
		45	50[c]	50	19
			42[c]	42	23
			48	55	20
			36	41	27
		225	208	239	6
			182	209	6
			204	234	6

[a] Self-absorption correction for Tl^{204} taken from MFP curve in Figure 2. Alpha (uranium) self-absorption was calculated.

[b] Statistical error of counting at 95% confidence level.

[c] Distilled water sample, all other samples in Cincinnati tap water.

The accuracy of the assay was tested by adding known quantities of uranium salts and of thallium-204 to 250 ml. of distilled or Cincinnati tap water. The activity of the uranium is known (*9, 10*). The activity of the thallium is based on the assay of weightless samples. The results, presented in Table III, indicate that rather poor accuracy is obtained at the low levels of 1 to 2 μμc. per liter of alpha activity and about 10 μμc. per liter of beta activity. At higher levels, equal to about 50 μμc. per liter or half of the maximum permissible level of unknown isotope in water, the error is 10% for the alpha and 20% for the beta assays.

DISCUSSION

The value of this assay method is limited by the errors introduced by the random nature of the radioactive disintegration process, the factors used in converting the observed counting rate to absolute activity, and the variations in sample preparation.

In theory, any radioactivity, however slight, could be detected if counted long enough. In practice, a counting period of 32 minutes was selected as a convenient time for low-level counting.

The conversion factors of geometry, self-absorption, and backscatter may introduce errors in the determination of radioactivity. For counters having good plateau characteristics, the geometry factor is reliable.

The self-absorption factor may introduce large errors, so it is desirable to minimize the error by counting thin samples. For radioactivity of known isotopes or unknown sources at levels of 1000 μμc. per liter or more, the self-absorption factor may be determined from curves such as those in Figure 2. At lower levels, self-absorption may be estimated on the basis of an assumed energy.

The backscatter factor for beta emitters varies with energy as shown in Table I. When possible, the backscatter factor should be determined (*15*), or a backscatter factor may be assumed on the basis of an estimated energy.

SUMMARY AND CONCLUSIONS

A method for separately assaying the alpha and beta radioactivity in water and industrial wastes is presented. The suspended solids in a sample are removed by filtration or centrifuging for an assay of insoluble radioactivity. The supernatant or filtrate of a relatively large sample is evaporated in a large counting dish to deposit the dissolved solids in a thin layer so as to minimize self-absorption losses.

The radioactivity is counted in an internal proportional counter, the counting efficiency of which varies from 50 to 52% for alpha activity and from 50 to 75% for beta activity, depending on the amount of backscattered radiation. At low levels of radioactivity, the statistical error of counting has a predominant effect on the accuracy of the assay. At a radioactivity level of 50 μμc. per liter (one half of the maximum permissible level (*13*) of unknown isotopes in drinking water), this error is ± 10% for alpha activity and ± 20% for beta activity at the 95% confidence level. Lower levels of activity are detected but with less accuracy.

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Quantitative Radiochemical Method for Determination of Major Sources of Natural Radioactivity in Ores and Minerals

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When an ore sample contains radioactivity other than that attributable to the uranium series in equilibrium, a quantitative analysis of the other emitters must be made in order to determine the source of this activity. Thorium-232, radon-222, and lead-210 have been determined by isolation and subsequent activity analysis of some of their short-lived daughter products. The sulfides of bismuth and polonium are precipitated out of solutions of thorium or uranium ores, and the α-particle activity of polonium-214, polonium-212, and polonium-210 is determined by scintillation-counting techniques. Polonium-214 activity is used to determine radon-222, polonium-212 activity for thorium-232, and polonium-210 for lead-210. The development of these methods of radiochemical analysis will facilitate the rapid determination of some of the major sources of natural radioactivity.

THE radioactivity of an ore sample can be attributed to many isotopes occuring in nature: the uranium, thorium, and actinouranium series, potassium-40, lutecium-176, rhenium-187, rubidium-87, samarium-152, and tin-124. In this paper the only elements considered as measurable contributors are those of the uranium series, the thorium series, and, where the total activity is low, potassium-40.

The amount of natural radioactivity is determined in most laboratories by measuring the relative intensity of the beta-gamma radiations with a Geiger-Müller counter (*4*) compared with a standard uranium source measured under similar conditions and usually reported as equivalent uranium (per cent eU). The value of equivalent uranium is defined as the ratio of the net counting rate of a sample to the net counting rate per per cent of a uranium standard in equilibrium with all of its disintegration products, both measured under similar geometry. Thus it will equal the actual uranium content only when the sample is in equilibrium and other emitters are not present.

The activity of a sample thus determined is very useful, but does not identify the source of this activity. The determination of equivalent uranium and uranium in a given sample may differ considerably owing to lack of equilibrium in the radioactive series, to the presence of radioactive isotopes other than uranium and its equilibrium amounts of disintegration products, and to statistical deviation of the analytical processes. When this difference is greater than that expected from the precision of either method or the combination of both, the reason for such disagreement should be determined and explained.

Even though a series is not in complete equilibrium, many of the immediate short-lived daughter products will be in equilibrium with their long-lived parent isotopes. Thus the two series can be separated into the major isotopes and groups of established equilibrium shown in Figure 1. The basic requirement for a group is that each daughter product be in equilibrium with the parent of the group. In many cases radon will emanate from the ore, especially after it has been ground, resulting in a partial and continual loss of the radon group isotopes. Hence, in the following list, the radon group is not included with radium-226 under a heading "the radium group."

1. The uranium-238 group, consisting of uranium-238, thorium-234, protoactinium-234, and uranium-234, where uranium-238 is the long-lived parent ($T = 4.5 \times 10^9$ years).
2. The thorium-230 isotope ($T = 8.0 \times 10^4$ years).
3. The radium-226 isotope ($T = 1620$ years).
4. The radon-222 group, consisting of radon-222, polonium-218, lead-214, bismuth-214, and polonium-214, with radon-222 the long-lived parent ($T = 3.825$ days).
5. The lead-210 group containing lead-210, bismuth-210, and polonium-210, with lead-210 the long-lived parent ($T = 22$ years).
6. The thorium-232 isotope ($T = 1.39 \times 10^{10}$ years).
7. The radium-228 group, containing radium-228, thorium-228, radium-224, radium-220, polonium-216, lead-212, bismuth-212, polonium-212, and thallium-208, with radium-228 the long-lived parent ($T = 6.7$ years). (See Figure 1.)

Radiochemical methods for the direct determination of thorium-230 and thorium-232 are not included in this paper. It will be assumed that thorium-232 is in equilibrium with the radium-228 group, unless there is reason to believe otherwise, and that the analysis of the latter will be valid for thorium-232.

With these qualifying assumptions and the fact that inter-group equilibrium is established, the quantities of the parent members may be calculated if one of its products can be determined.

Thus when the equivalent uranium and the actual chemical uranium content do not agree, quantitative radiochemical analysis of certain isotopes can be used to determine which groups, relative to certain standards, produce the radioactivity inherent in a sample, and thus determine the source of disequilibrium.

The content of the uranium-238 group is determined by the standard chemical methods (*2*, *5*). The α-particle activity of polonium-214 is used to determine the content of the radon-222 group; the alpha activity of polonium-212 is used to determine the radium-228 group and thorium-232; and polonium-210 activity is used to determine the lead-210 group.

APPARATUS

The measurement of equivalent uranium (*4*) is made with a Geiger-Müller tube in a lead shield of 1.5-inch wall thickness connected to a conventional scaling unit. A mica window tube 2.5 to 3.3 mg. per square centimeter with a $1^{1}/_{8}$-inch effective window diameter is used, supported by a stand notched for support of the tray containing the sample to be measured. The samples and standard are contained in a half-ounce metal pillbox (diameter $1^{15}/_{16}$ inch and thickness $^{5}/_{8}$ inch).

The determination of the amounts of polonium isotopes present is made by α-particle count with a scintillation detector, using silver-activated zinc sulfide phosphor placed on the sensitive area of a 5819 photomultiplier tube and covered with thin aluminum foil. An appropriate aluminum absorber is used between the precipitate and the detector when counting polonium-214 and polonium-212. The thickness of this absorber is such that in combination with the built-in aluminum light shield on the detector, just enough absorption is created to prevent any 5.3 m.e.v. alpha particles of polonium-210 from reaching the phosphor.

The determination of the radium content is performed on the radon train apparatus described in the method of Curtiss and Davis (*1*, *3*).

REAGENTS AND STANDARDS

Bismuth Carrier. Bismuth trioxide (1.34 grams) is dissolved in 5 ml. of hydrochloric acid and diluted to 200 ml. with distilled water; 1 ml. of solution contains 6 mg. of bismuth.

Lead Solution. Lead nitrate (0.96 gram) is dissolved in 200 ml. of distilled water; 1 ml. of solution contains 3 mg. of lead.

Uranium and Thorium Ore Standards. All the ore standards were obtained from the National Bureau of Standards. Five

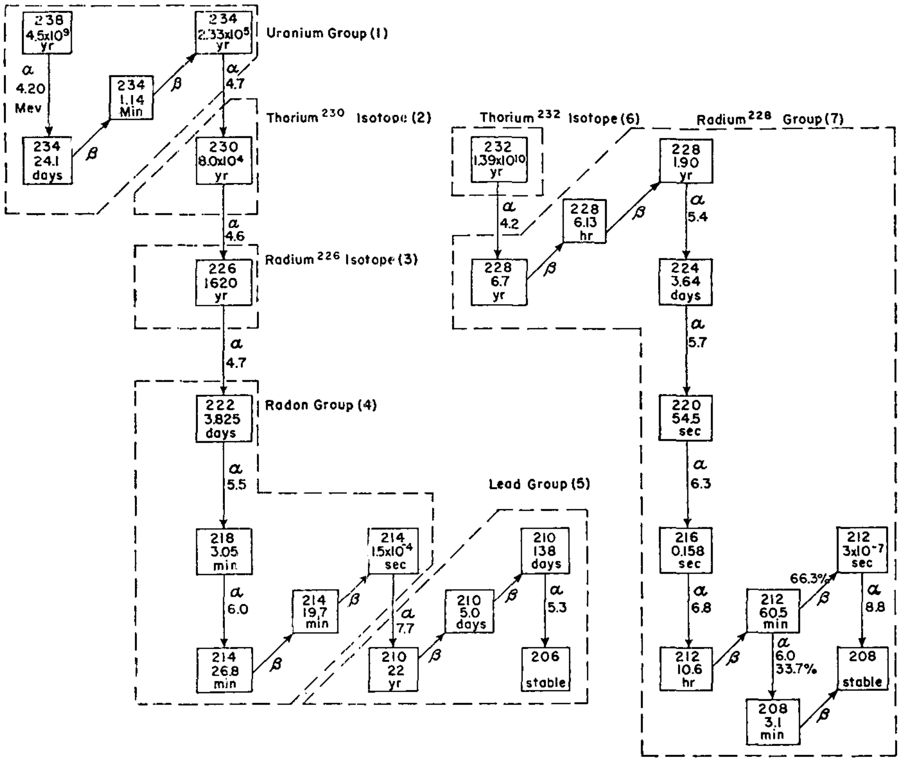

Figure 1. Classification of Natural Radioactivity in Separate Groups

different standards were used to determine the experimental alpha-activity constants in the two radioactive disintegration series:

1. One per cent uranium in dunite rock base.
2. NBS No. 2230-1, 3.08% uranium.
3. NBS No. 2230-2, 6.92% uranium.
4. One per cent thorium in dunite rock base.
5. NBS No. 2601, monazite sand, 8.48% thorium.

Radium Solution Standard. National Bureau of Standards solutions containing 10^{-9} and 10^{-11} gram of radium were used for comparative constants in the determination of radium.

PROCEDURE

A 0.1- to 0.5-gram sample, depending on total activity and ease of solution, is fused to almost red heat with 4 grams of sodium peroxide in a nickel crucible. It is important that approximately the same amount of flux and the same conditions of fusion be used for all samples in order to ensure a more consistently uniform sulfide precipitation.

The time of fusion is recorded. The melt is taken up in water, neutralized with hydrochloric acid, then made up to an acidity of 1.0N with hydrochloric acid in a total volume of 100 ml. With this treatment the sample should be completely in solution. Then 1 ml. each of the bismuth carrier and lead solution are added (6 mg. of bismuth and 3 mg. of lead) and the solution, cooled to 45° to 50° C., is gassed with hydrogen sulfide for 10 minutes. The bismuth is used as a carrier of the polonium and bismuth isotopes. The lead is intended to dilute the coprecipitation of the radioactive lead isotopes.

The bismuth-polonium sulfide precipitate is filtered on a 7.0-cm. No. 42 paper in a No. 0 Büchner funnel using a suction flask. The precipitate is washed to the center of the paper with water and the sides of the paper are completely washed down with alcohol. The damp precipitate and paper are glued to an aluminum ring $1^{7}/_{8}$ inches in diameter and dried with moderate heat.

The time is recorded as the mean between the beginning of filtration and the time when the *entire solution* has passed through the filter paper. It is desirable that no more than 6 to 8 minutes be required for this operation.

This precipitate contains the isotopes polonium-218, bismuth-214, polonium-214, bismuth-210, and polonium-210 when radium is present and polonium-216, bismuth-212, and polonium-212 when thorium is present. The amount of these isotopes present is determined by alpha-particle count with the scintillation detector.

Radon Group (Thorium Series Absent). When a radon-222 determination is desired, the foregoing preparation must be rapid. Between the time of fusion and the time of precipitation of the radon-222 group the controlling isotope is lead-214—that is, the radioactivity in the solution decays with a half-life of 26.8 minutes—the half-life of lead-214, as radon itself was expelled during the fusion. It is desirable that no more than 30 minutes be used in this operation, and no more than 6 to 10 minutes'

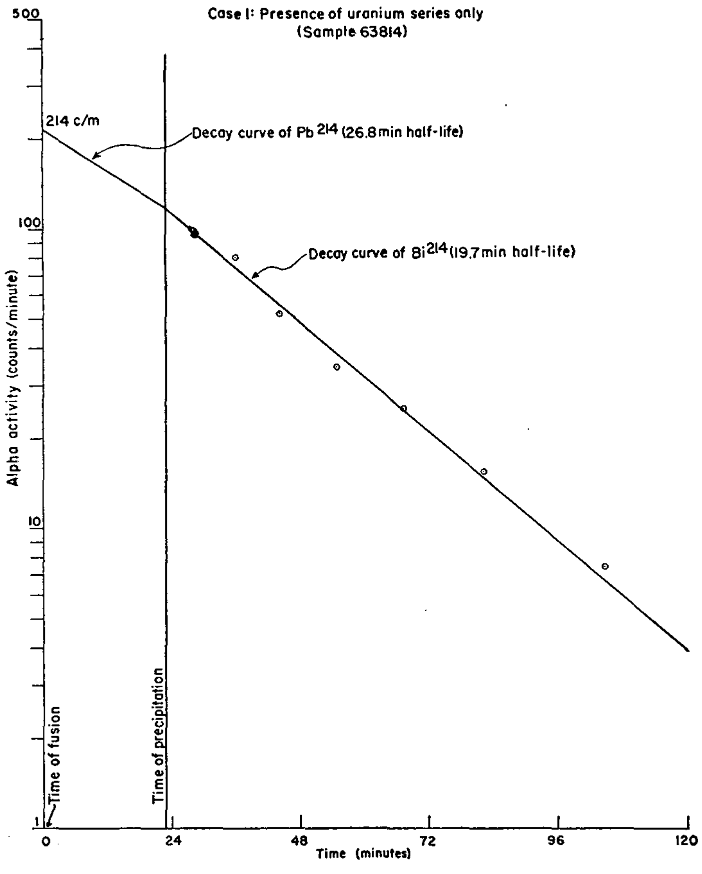

Figure 2. Decay Curve of Lead-214 Product Alpha Activity and Decay Curve of Bismuth-214 through 5.1 Mg. per Square Centimeter Aluminum Absorber

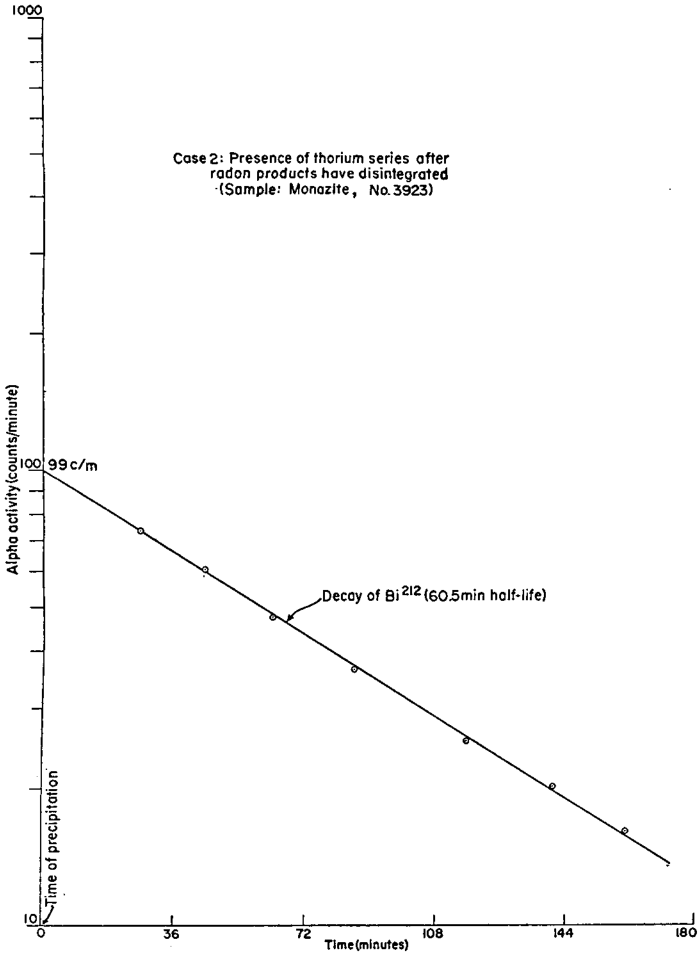

Figure 3. Decay Curve of Bismuth-212 Product Alpha Activity through 5.1 Mg. per Square Centimeter Aluminum Absorber

additional time should elapse before the count is initiated. After precipitation, the controlling isotope is bismuth-214 with a half-life of 19.7 minutes.

The count itself is made on the 7.68 m.e.v. alpha particles emitted by polonium-214 ($T = 1.5 \times 10^{-4}$ second). At least three determinations of counting rate immediately following each other should be taken. A plot on semilogarithmic graph paper is made of these counting rates against time to determine the radon content at the time of fusion (see Figure 2).

If no isotopes of the thorium series are present in the sample, the plot will be a straight line with the slope of decay curve of bismuth-214 (T = 19.7 minutes). This line is extrapolated back to the time of precipitation. Another line is drawn with the slope of the decay curve of lead-214 (T = 26.8 minutes) from the point of intersection of the bismuth-214 decay curve and the ordinate representing the time of precipitation to the ordinate representing the time of fusion. The final extrapolated point represents the activity of lead-214 at the time of fusion. However, if one assumes that at this time there was equilibrium between radon-222, polonium-218, and lead-214, the activity is the same for these three nuclides. This value of lead-214 is then compared with the count (obtained in the same manner) of a source of radon-222 in equilibrium with a standard uranium ore. (A standard uranium ore usually has a positive emanating power. Hence, for absolute determinations of radon, corrections must be made for this source of error. However, where the emanating power is known to be low, this can be neglected for most practical purposes.)

Thorium-232 (as Radium-228 Group). When only thorium analyses are required, no speed requirements are necessary in the time between fusion and precipitation. In fact more accurate results can be obtained if the radon group products are allowed to decay before precipitation (about 4 to 5 hours is sufficient). After precipitation, however, rapid filtration and initiation of count are desirable.

After allowing for the decay of bismuth-214, if present, bismuth-212 with a half-life of 60.5 minutes is the controlling isotope that starts to decay when the sulfide precipitate is filtered. The count is made on the 8.78 m.e.v. alpha particles from polonium-212; a small part is also due to 6 m.e.v. bismuth-212 alpha particles. The same methods of counting and absorber are used as in the determination of radon. If insignificant amounts of radon are present or if its products have been allowed to decay, the plot of consecutive counting rate determinations will result in a straight line (Figure 3). This line is extrapolated to the ordinate representing the time of precipitation and represents the activity of bismuth-212. The assumption is then made that all the isotopes in the thorium series are in equilibrium. The resulting value is compared with that of a 1% thorium standard obtained in the same manner.

Combined Radon and Thorium Analyses. In the presence of significant quantities of both radon-222 and thorium-232 products, the resulting curve of counting rate against time describes initially a decay somewhere between bismuth-214 and bismuth-212. As bismuth-214 decays to a small fraction of its initial value, the pure bismuth-212 decay curve is defined (see Figure 4). This bismuth-212 curve is extrapolated back to the ordinate representing the time of precipitation. The decay curve of bismuth-214 is obtained after subtracting the difference between the curve representing the bismuth-212 decay and the curve representing the combined decay of bismuth-214 and bismuth-212. With these corrected and extrapolated points the quantities of radon and thorium can be determined as previously shown.

Lead-210 Group. The products of radon-222 and thorium-232 are allowed to decay for 1 day and an alpha count is again made on the sulfide precipitate. In determining this count, no absorber is used and decay curves need not be drawn. Polonium-210 with a half life of 138 days is the emitter of the alpha particles counted and a wait of several days can be made with no correction required for its decay. This counting rate is then compared with a source of polonium-210 prepared in the same manner from a standard uranium ore.

Radium-226. The method of Curtiss and Davis (*1, 3*) is used to determine the radium-226 content of an ore. The sample to be analyzed must be completely in solution. The radon contained in the solution is boiled under vacuum and passed into an ionization chamber. The count resulting from the ionization of the gas in the chamber is compared with the count obtained from the radon-222 in a standard radium solution of 10^{-9} gram.

A different method of solution than that described in (*1, 3*) reference is usually used. A 0.1- to 1.0-gram sample is fused with sodium peroxide and acidified to a 3 to 4% hydrochloric acid solution.

RESULTS

The radiochemically determined thorium and chemically determined uranium content is reported as per cent of thorium or uranium. The chemically determined uranium content is also converted from per cent to curies $\times 10^{-9}$ per gram of sample and reported as such for comparison with the other amounts to be described. The radiation from 1 gram of 1% pure uranium-238 is equivalent to 3.42 × 10^{-9} curie. The content of radium-226, radon-222, and lead-210 is reported separately as curies × 10^{-9} per gram of sample for radium-226, radon-222, and lead-210, respectively.

Table I shows the experimental alpha-activity constants of the thorium-232 and uranium-238 series standards used in the subsequent radiochemical determinations of ore samples for these isotopes.

Comparison of thorium analyses determined by the foregoing radiochemical methods with those determined by classical chemical methods is given in Table II. Ores containing various thorium minerals were analyzed.

Table I. Alpha-Activity Constants Used in Determinations of Isotopes[a]

(Average and standard deviation of 16 determinations on the two thorium standards and 14 determinations on the three uranium standards)

	Counts/Minute	
Th, %	10^{-9} Curie Rn^{222}/g. sample	10^{-9} Curie Pb^{210}/g. sample
61.2	90.0	87.7
59.5	89.5	85.1
60.0	87.2	86.0
59.6	90.3	82.2
58.5	91.0	86.3
61.1	85.3	83.4
58.8	89.7	86.8
61.0	91.0	83.6
59.5	88.2	87.6
60.0	88.9	86.8
61.0	94.7	88.5
60.5	89.2	78.7
64.5	88.0	80.0
58.5	88.9	80.8
61.6	..	..
60.5	..	..
Av. 60.4 ± 1.5	89.4 ± 2.1	84.5 ± 3.1

[a] 0.250-gram amounts of sample.

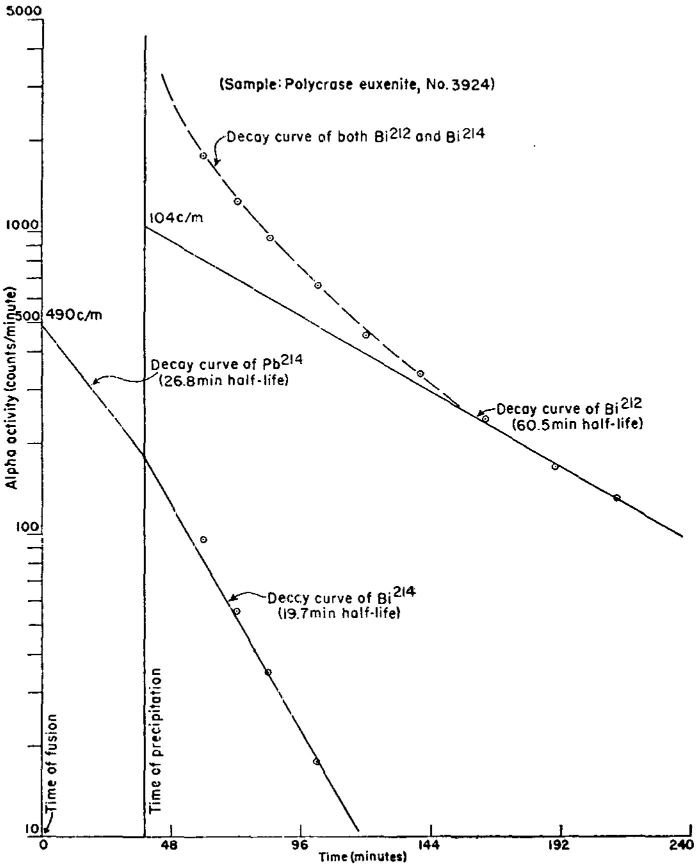

Figure 4. Relationship of Combined Decay Curve of Bismuth-212–Bismuth-214 Product Alpha Activity to Differentiated Decay Curves of Lead-214, Bismuth-214, and Bismuth-212 Product Activities

Table II. Comparison of Chemical and *Radiochemical* Thorium Determinations of Various Thorium Ores

		Th, %	
No.	Sample	Chemical analysis[a]	Radiochemical analysis
3926	Aeschynite	5.74	5.76
		5.54	5.50
3924	Polycrase and euxenite	4.43	
		4.60	4.55
		..	4.56
			4.32[b]
3923	Monazite	4.21	4.13
		4.23	3.92
A 13	Black sand	3.12	3.12
		3.29	3.26
		..	3.11
A 26	Black sand	1.67	1.75
		1.79	1.82
3181	Ward's thorianite	2.74	3.03
		2.86	2.94
3063	Thorianite	1.75	1.74
		1.65	1.75
		..	1.72

[a] Chemical analyses by Harry Levine, U. S. Geological Survey.

[b] Rn^{222} and Pb^{210} for this sample: $\frac{13.7 \times 10^{-9} \text{ curie } Rn^{222}}{\text{g. of sample}}$ and $\frac{13.4 \times 10^{-9} \text{ curie } Pb^{210}}{\text{g. of sample}}$, respectively.

Analyses of various ore samples for chemically determined uranium and radiochemically determined thorium, radium-226, radon-222, and lead-210 are given in Table III. The table is divided into groups where the majority of the radioactivity is due to thorium, excess radium, and deficient radium. Where the samples contain only the uranium series in equilibrium, the activities of each member of the series should be the same. These particular analyses clearly show disequilibrium, the seriousness of which can be seen from the activities of the parent uranium and the three daughter products shown.

The data shown in Table III are calculated from the following equations:

$$Th^{232}, \% = \frac{(Po^{212} \text{ alpha activity, } c/m) \dfrac{(0.250 \text{ g.})}{(\text{mass of sample})} \dfrac{(1430)}{(K)}}{60.4 \; c/m/\% \text{ Th}}$$

$$Rn^{222} \; (10^{-9} \text{ curies/g. of sample}) = \frac{(Po^{214} \text{ alpha activity } c/m) \dfrac{(0.250 \text{ g.})}{(m \text{ of sample})} \dfrac{(1430)}{(K)}}{89.4 \; c/m/ \; 10^{-9} \text{ curies } Rn^{222}\text{/g. of sample}}$$

$$Pb^{210} \; (10^{-9} \text{ curies/g. of sample}) = \frac{(Po^{210} \text{ alpha activity, } c/m) \dfrac{(0.250 \text{ g.})}{(m \text{ of sample})} \dfrac{(1430)}{(K)}}{84.5 \; c/m \; 10^{-9} \text{ curies } Pb^{210}\text{/g. of sample}}$$

where the denominators are the counting rates for 0.250 gram of the particular standard in question. The value 1430 ± 14 counts per minute is a standard calibration constant of a polonium source in equilibrium with lead-210 and K is the sensitivity standard value of the same source obtained at the time of the determination to correct the detector to standard conditions.

A useful check for the amounts of radon, lead, and thorium determined by alpha measurements is based on the fact that the normal distribution of the isotope groups for a sample in equilibrium, measured in this laboratory with its conditions of geometry, is such that approximately 40% of the beta-gamma count is due to uranium-238 and its products down to radium-226, about 40% is due to the products between radon-222 and lead-210, and about 20% is due to lead-210 and its daughter products. When thorium-232 in equilibrium with its decay products is present in a uraniferous sample, the measured beta-gamma activity is equal to the sum of the activities produced by the beta-gamma contributing groups—namely, the uranium-238, radon-222, and lead-210 groups, plus the thorium-232 group activity. This last activity is equivalent to the activity of an equilibrium uranium sample, the uranium content of which is 20% of the thorium present in the sample.

Thus the sum of the equivalent activities of each beta-gamma contributing group converted from curies × 10^{-9} per gram to per cent gives a calculated value of per cent equivalent uranium (% eU_c). $eU_c = \dfrac{(0.4)\ (U^{238}) + (0.4)\ (Rn^{222}) + (0.2)\ (Pb^{210})}{3.42 \times 10^{-9}\ \text{curie/g.}}$

and, in the case of the presence of thorium, $eU_c = \dfrac{(0.4)\ (U^{238}) + (0.4)\ (Rn^{222}) + (0.2)\ (Pb^{210})}{3.42 \times 10^{-9}\ \text{curie/g.}} + (0.2)\ (\%\ Th^{232})$.

Table III. Chemical Analyses of Uranium and Radiochemical Analyses of Thorium-Radium-226, Radon-222, and Lead-210 in Various Ore Samples[a]

Sample No.	U, %	Th, %	U, Curies × 10^{-9}/g. Sample	Ra^{226}, Curies × 10^{-9}/g. Sample	Rn^{222}, Curies × 10^{-9}/g. Sample	Pb^{210}, Curies × 10^{-9}/g. Sample
			Samples Containing Thorium			
52336	0.005	1.2	0.02	0.034	...	...
52337	0.002	0.41	0.007	0.02	...	...
63526	0.010	0.44	0.034	0.092	0.2	0.1
63527	0.005	0.06	0.02	....	...	...
63528	0.008	0.15	0.03	0.02	0.07	0.01
67150	0.001	7.1	0.003	....	...	0.03
			Samples with Deficient Radium-226			
63814	19.9		68.0	8.82	4.70	7.05
64124	0.45		1.5	1.2	.0.75	0.41
64125	0.48		1.6	1.6	1.1	0.62
			Samples with Excess Radium-226			
64123	0.10		0.34	5.88	4.8	4.4
64126	0.008		0.03	1.7	1.6	1.0
64128	0.13		0.44	19.8	17	17
64129	0.14		0.48	5.91	4.8	4.8
64130	0.17		0.58	2.9	2.5	2.7
64131	0.009		0.03	0.72	0.51	0.68
64132	0.005		0.02	2.2	1.9	1.2
64133	0.064		0.22	1.9	1.5	1.2
64630	0.036		0.12	0.61	0.54	0.34
64631	0.034		0.12	0.85	0.61	0.44

[a] Uranium analyses by the staff of the Geochemistry and Petrology Branch, Denver Laboratory.

When uranium-238, radon-222, and lead-210 are in curies × 10^{-9} per gram of sample and thorium-232 in per cent, per cent equivalent uranium$_c$ should be approximately equal to the value of equivalent uranium (% eU) determined by beta-gamma measurements.

Table IV illustrates the comparison of per cent equivalent uranium determined by beta-gamma counting methods and per cent equivalent uranium$_c$ calculated as shown. The results show an agreement within the limits of error of such methods.

LIMITATIONS

The analysis for radon-222 is restricted to those samples that go into solution with sodium peroxide immediately. If an ore sample contains large amounts of heavy metals that coprecipitate with bismuth sulfide, too large a precipitate is obtained and the effect is excessive self-absorption of the alpha particles, causing low results. However, the thorium-232 could be determined on these ores by a reprecipitation of the bismuth sulfide after an overnight wait for the bismuth-212 to regenerate.

Table IV. Comparison of Total Beta-Gamma Activity (% *eU*) with the Summation of the Activity of Each Beta-Gamma Contributing Group (% *eU*$_c$)

Sample No.	(0.4 U)	(0.4 Rn)	(0.2 Pb)	(0.2) × % Th	eU_c,[b] %	eU, %, by Beta-Gamma Activity
52336	0.008	0.014	0.007	0.24	0.25	0.23
52337	0.003	0.008	0.004	0.082	0.085	0.084
63526	0.014	0.08	0.02	0.088	0.12	0.13
63527	0.008	...	...	0.012	0.01	0.021
63528	0.01	0.03	0.02	0.030	0.05	0.041
63814	27.2	1.88	1.41	...	8.9	8.7
64123	0.14	1.9	0.88	...	0.85	0.84
64124	0.60	0.30	0.082		0.29	0.30
64125	0.64	0.44	0.12		0.35	0.36
64126	0.01	0.64	0.20	...	0.25	0.23
64128	0.18	5.6	3.4	...	2.8	2.9
64129	0.19	1.9	0.96	...	0.89	0.90
64130	0.23	1.0	0.54	...	0.52	0.50
64131	0.01	0.20	0.14	...	0.10	0.10
64132	0.008	0.76	0.24	...	0.29	0.26
64630	0.048	0.22	0.068	...	0.098	0.088
64631	0.048	0.24	0.088	...	0.11	0.12
67150	0.001	0.01	0.01	1.4	1.4	1.4

[a] Uranium, radon, and lead are in curies × 10^{-9}/gram of sample; thorium is in per cent.

[b] $eU = \dfrac{(\text{cols. } 2 + 3 + 4)}{3.42} + \text{column 5.}$

The lower analytical limit for most samples with respect to total activity is about 0.020% equivalent uranium. Samples that are believed to contain only thorium can be analyzed at a slightly lower equivalent uranium. In analyzing for a combination of radon-222 and thorium-232, the lower analytical limit, for the same degree of accuracy, is considerably higher than the 0.020% equivalent uranium mentioned previously. For samples containing approximately 1% uranium-238 or thorium-232, the error in reproducibility of results is about 5% for radon-222 and thorium-232 and about 8% for lead-210.

DISCUSSION

The fact that a uranium-bearing ore is or is not in equilibrium with its decay products is of prime importance to the geochemist. In order to make a radioactivity assay of the ore in terms of uranium, equilibrium is a prerequisite. For a large number of problems it is necessary to have a quantitative measure of the amount of disequilibrium, especially for radium, radon, and lead. For instance, in any radioactive-age method it is necessary to know the state of equilibrium of a given sample. For these and a host of other problems the foregoing methods can prove to be a useful tool in determining the degree of equilibrium within a sample.

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Continuous Recording of Concentration of Organic Matter in Waste Water

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A method has been developed for continuously determining dissolved organic matter in a stream of waste water, recording concentration directly in parts per million by weight of organic carbon. Concentration changes as low as 1 p.p.m. of carbon can be detected. Initial response to a change in sample composition occurs in 10 minutes; 67% response is attained in an additional 4 minutes. The process involves filtration of the sample, precipitation of carbonates, oxidation of organic carbon, stripping and purification of the resulting carbon dioxide, and measurement of the carbon dioxide. All operations are performed on a continuous basis. The method has been successfully demonstrated in the analysis of a typical plant waste stream, a record of which is presented. Development of a fully automatic analyzer appears to be entirely practical.

THE mounting problem of river pollution by industrial wastes has led to a need for a rapid and continuous means of accurately determining the composition and concentration of plant waste effluents. This is particularly true of organic wastes, as B.O.D. (biochemical oxygen demand) (*1*) measurements are, at present, a primary criterion of water pollution. Many states have, in fact, set up regulations on average and peak B.O.D. values for industrial wastes.

Any practical monitor of waste stream composition must be based on a rapid and reliable analytical technique, capable of incorporation into a continuously recording instrument. B.O.D. measurement, unfortunately, is of notoriously poor reproducibility in analysis of chemical plant waste. Requiring an elapsed time of 5 days, it is of little value for purposes of control. Measurement of chemical oxygen demand or oxygen consumed (C.O.D.), while more rapid than the B.O.D. technique, also shows poor reproducibility and is poorly adapted to continuous operation (*1*). It was decided, therefore, to measure total organic carbon concentration, a precise technique for which has been developed by Oemler and Mitchell (*5*). While no direct relationship exists between organic carbon and B.O.D., the maximum possible B.O.D. value can easily be computed on the assumption that the organic matter measured would be completely oxidized in a B.O.D. measurement. Unlike B.O.D., organic carbon measurement provides actual concentration data, of value in locating the source of pollution and in determining the necessary corrective measures. The measurement may be restricted to the determination of dissolved organic matter only, since control of this quantity is the major problem in most chemical plant waste streams.

An experimental model of a continuously recording organics analyzer has been built and demonstrated in actual plant tests. A reliable plant instrument can be developed on the basis of the information now available.

DESCRIPTION OF METHOD

The method of analysis was selected after a careful examination of a variety of chemical and physical techniques. Oxidation of the organic matter to carbon dioxide was the only method found offering adequate sensitivity, while still responding to all organic compounds. Chromic acid oxidation was chosen on the basis of available literature (*2–6*, *8*) and because of many practical difficulties encountered in trials of vapor-phase oxidation techniques.

A flow sheet of the organics analyzer is given in Figure 1.

Waste water is sampled and pumped to the instrument at a rate sufficient to minimize the transportation lag. A portion of this stream is metered with a second pump, through a filter, to a mixer, where it joins a stream of alkaline barium hydroxide solution. Dissolved carbon dioxide and carbonates, which would interfere with the subsequent organic carbon determination, are precipitated here. A majority of the stream is discarded, carrying with it any barium carbonate precipitate formed.

A possibility of sample loss exists at this point, by adsorption on the precipitate or filter. While no such effect has been observed in any of the samples so far analyzed, a check would be justified in the case of easily absorbed sample materials.

A small portion of the decarbonated sample is metered, through a second filter, to another mixer, where it joins a stream of chromic acid in sulfuric acid solution. The mixture is heated to 250° C., at which temperature it is held for 2.5 minutes. The hot reaction mixture is stripped of carbon dioxide in a small falling-film column with a metered stream of oxygen.

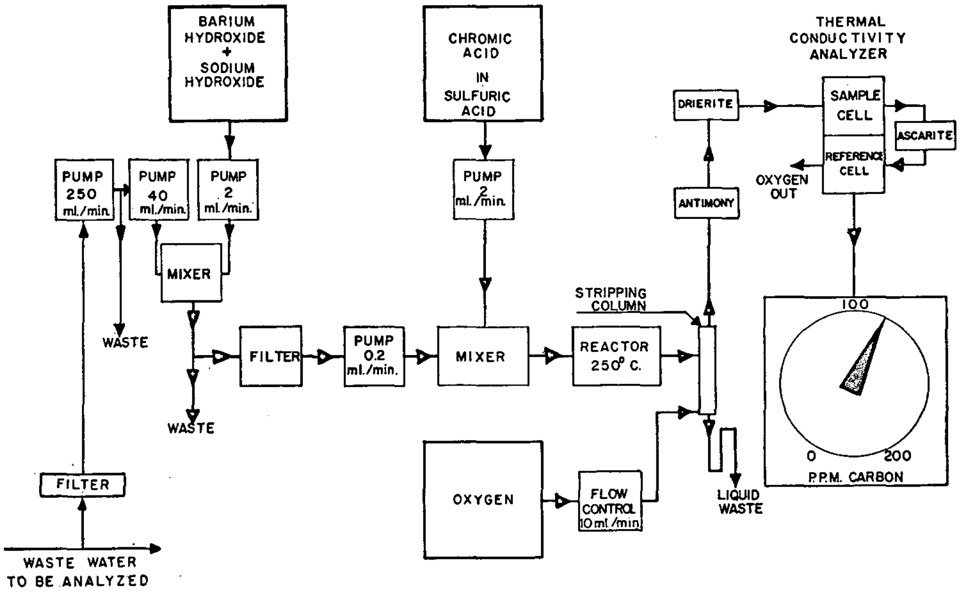


Figure 1. Flow Diagram of Organics Analyzer

Chlorine, formed by the oxidation of any chlorides in the sample, is removed from the gas stream by an antimony scrubber. Water vapor is removed with Drierite. The purified gas is passed through one side of a differential thermal conductivity analyzer, stripped of carbon dioxide with Ascarite, and then passed through the reference side of the analyzer. The organic carbon content of the original sample is plotted on a recorder as a function of this differential thermal conductivity measurement.

The process was designed for an instrument having a full-scale span as low as 50 p.p.m. or as high as 1000 p.p.m. of organic carbon, and is applicable to ordinary samples of low inorganics concentration. It is, of course, capable of modification for more specialized applications.

The various fluid-flow rates selected for the process represent a necessary compromise between ease of metering and small transfer lags, on the one hand, and reagent supply requirements and practical equipment size on the other. The low rates chosen, while presenting some difficult metering problems, have been found to be entirely practical and to offer some definite advantages in equipment design, as indicated below.

DETAILS OF UNIT OPERATIONS

Sampling. To reduce the response time of the analyzer, it is desirable to maintain a high linear flow rate between the sampling point and the instrument. Because only a small sample is ultimately used for the analysis, in practice, an excess of sample is pumped to the analyzer. This is, in fact, desirable for flushing away spent reagents from the analyzer. The use of a pump capable of handling suspended material, such as the Vanton Flex-i-Liner pump, was found desirable, so that the sample can be forced under pressure through the primary filter at the analyzer. A primary flow rate of 250 ml. per minute is used in the present equipment.

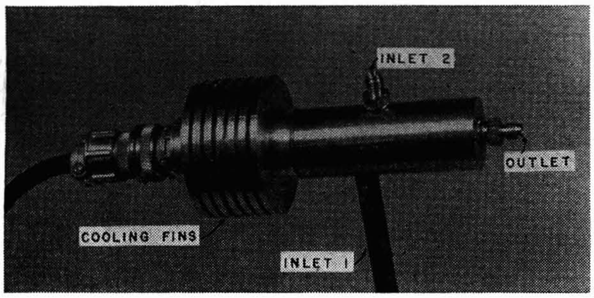


Figure 2. Vibrating Mixer Assembly

The choice of filter is determined by the character of the particular sample. As the sample is filtered a second time after the carbonate precipitation operation, only a coarse filtration is required here, sufficient to prevent fouling of the sample metering pump. An easily cleaned unit, such as that produced by the Cuno Engineering Corp., is expected to be applicable to the majority of cases. The filter can be continuously self-cleaning, using a motor drive.

Primary Sample Metering. A sample flow in excess of that required for actual analysis is desirable for use in flushing away precipitate formed in the process of carbonate removal. The sample must be metered at this point, however, to permit correction of the error introduced by its subsequent dilution with barium hydroxide solution. High metering precision is not required. With a sample flow of 40 ml. per minute, at this point, and a barium hydroxide flow of 2 ml. per minute, a sample metering error of 25% will produce an instrument error of only 2%. This degree of accuracy is easily attained with any of a variety of commercial metering pumps, a convenient unit being the Research Appliance Co.'s Micro-Bellows pump. The flow pulsations proposed by this pump are readily damped by discharging into a short, vertical length of $^1/_4$-inch pipe, followed by about 1 foot of $^1/_8$-inch bore tubing.

Carbonate Precipitation. Because carbon dioxide or carbonates are frequently present in the sample water, they must be removed if low concentrations of organic carbon are to be measured without error. Low concentrations of carbonates have been found to be readily removed quantitatively by continuous precipitation with alkaline barium hydroxide, provided that adequate mixing and holdup time are allowed. A reagent volume of 2 ml. per minute of 0.1*M* sodium hydroxide and 0.1*M* barium hydroxide in 40 ml. per minute of sample provides sufficient excess reagent for all samples so far encountered. A Micro-Bellows pump can be used to meter this reagent.

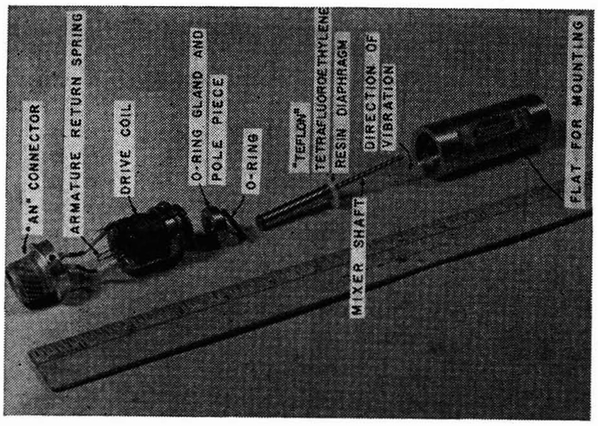


Figure 3. Vibrating Mixer Components

The mixer used for the precipitation operation is shown in Figures 2 and 3. It comprises a $^3/_{16}$-inch bore stainless tube fitted with inlet and outlet ports, in which is vibrated laterally a stainless rod $^1/_8$ inch in diameter, driven through a Teflon tetrafluoroethylene resin diaphragm by a 60-cycle coil around a mild steel armature. Violent mixing of the liquids is obtained in this unit, and the vibration effectively eliminates any tendency of the barium carbonate to deposit in the lines.

At the flow rates employed, a $^1/_8$-inch pipe nipple, 8 inches long, provides sufficient holdup time after mixing for the precipitate to reach an easily filterable particle size.

Filtration. In the preliminary work on the process, it was found possible to filter off the barium carbonate continuously, by sucking a small portion of the sample through a sintered stainless steel disk or filter paper cartridge so oriented that its surface was continuously flushed by the excess stream of sample. With actual waste samples, however, the filter was quickly plugged

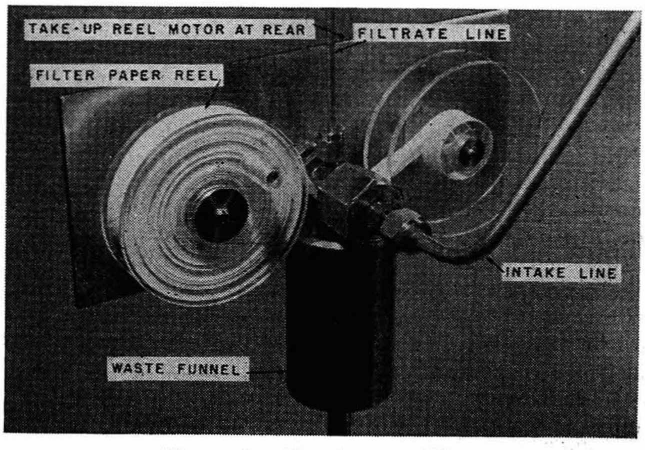


Figure 4. Continuous Filter

with slimy material, presumably algae, almost invariably present in the sample. Increased filter area was not practical because of the time lag introduced by any appreciable increase in holdup volume.

A practical solution to the filtration problem is shown in Figure 4. A filter-paper tape (Whatman No. 54) is pulled over a port in a smooth stainless steel cylinder at a rate of about $^1/_2$ inch per hour, being wound on a reel by a small clock motor. The sample to be filtered floods the underside of the paper, dropping off freely to prevent any possibility of plugs forming. The filtrate is sucked through the paper into the port in the stainless cylinder. Because of the low flow rate of the filtered sample—0.2 ml. per minute—no danger of air being pulled through the paper exists. The small reel of paper shown is sufficient for a month's operation.

Secondary Sample Metering. Practical limits on reagent consumption and size of the oxidation reactor require that the sample taken for oxidation be of the order of 0.2 ml. per minute. For adequate control of reaction conditions, this flow must be as nearly continuous as possible. To avoid excessive lags, the volume of the pump and line carrying this flow should be very low, preferably not more than a few tenths of a milliliter. The metering must be accurate, as it directly determines the accuracy of the analysis. Positive displacement is required, as back-pressure variations are to be expected in the system.

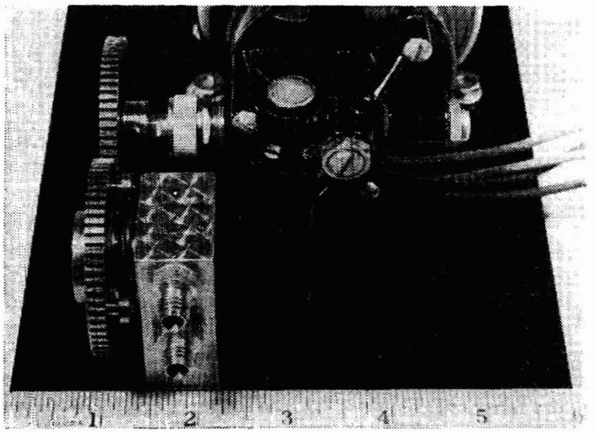


Figure 5. O-Ring Pump and Motor

No commercial pump has been found entirely satisfactory for this application. A timer motor-driven pump of the tubing-milker variety, produced by Wallace and Tiernan Co., gives adequate metering performance, but has severely limited service life. Its delivery is greatly influenced by back pressure. Its production has been discontinued by the manufacturer. A pump under development at this laboratory, shown in Figures 5 and 6 shows promise of greater serviceability. In this pump, fluid contained in a narrow semicircular groove in a stainless cylinder is retained by an O-ring stretched over the top of the groove. Three ball-bearing rollers, riding the outer surface of the O-ring, squeeze the O-ring into the groove. Rotation of the roller carrier produces the pumping action, forcing the trapped fluid along the groove and out a terminal port. This pump has a displacement of 0.003 ml. per revolution and provides metering accuracy of 99.5% against back pressures up to 10 pounds per square inch. It is capable of pumping against a maximum of 20 pounds per square inch. While the service life of the O-ring is expected to be limited, the design is such as to permit its rapid replacement.

When the O-ring pump is used in conjunction with polyethylene tubing lines of $^1/_{16}$-inch bore, the transfer lag at 0.2 ml. per minute is easily limited to 2 minutes.

Sample-Reagent Mixing. At the low flow rates employed, turbulent flow cannot be attained in practical tubing sizes. Experiments with a variety of orifice and jet mixer devices always showed smooth, laminar flow of the parallel streams of 0.2 ml. per minute of water and 2 ml. per minute of sulfuric acid, in spite of the strong chemical affinity of the two fluids. Passage through a plug of glass wool was found to produce mixing, but was not used because of the danger of plugging with barium sulfate. Excess barium hydroxide, from the carbonate removal process, forms barium sulfate at this point. While, in the final acid concentration, this salt is soluble, precipitation inevitably occurs during the process of dilution involved in mixing.

Although a motor-driven rotary mixer was successfully used for this mixing operation, packing leakage difficulties led to the substitution of the diaphragm-sealed vibrating mixer described above. Carpenter 20 stainless steel is used in its construction, because of the highly corrosive sulfuric acid concentrations attained during mixing.

Oxidation Reaction. Several papers have been published on the quantitative oxidation of aqueous organic matter by chromic acid (*2–6, 8*). Oemler (*5*) has developed an analytical procedure specifically designed for analysis of waste water. Using chromic acid concentrations ranging from 2.5 to 5%, these workers have found refluxing periods of the order of 30 minutes necessary for complete oxidation. Special modifications of procedure have been necessary to handle especially refractory compounds, such as acetic acid, and volatile materials escaping from the reaction mixture.

It was reasoned that, by using a large excess of reagent and by operating at temperatures much higher than those normally employed, the oxidation reaction could be performed more rapidly and with better conversion of refractory materials. If a continuous flow through a tubing reactor is used, rather than batch reaction in a reflux flask, little difficulty should be encountered in retaining volatile materials within the reaction zone. Tests have borne out this hypothesis.

The oxidizing reagent used was a solution of 0.1*M* chromic oxide in 95% sulfuric acid This solution can be mixed with water in all proportions at room temperature, without precipitation of chromic oxide. Higher chromic oxide concentrations cannot be used because of the danger of its precipitation in the flowing stream upon dilution with the sample water. If one volume of sample is mixed with 10 volumes of this solution, approximately 29 times the stoichiometric amount of reagent is available for oxidation of 200 p.p.m. of organic carbon as methylene. Such a mixture boils at about 280° C.

Oxidation experiments were performed by mixing 0.2 ml./minute of solutions of known organics concentration (approximately 100 p.p.m.) with 2 ml. per minute chromic acid solution and feeding to a short glass preheater, in which the mixture was raised to reaction temperature in about 30 seconds. The effluent from the preheater was passed through a section of 4-mm. glass

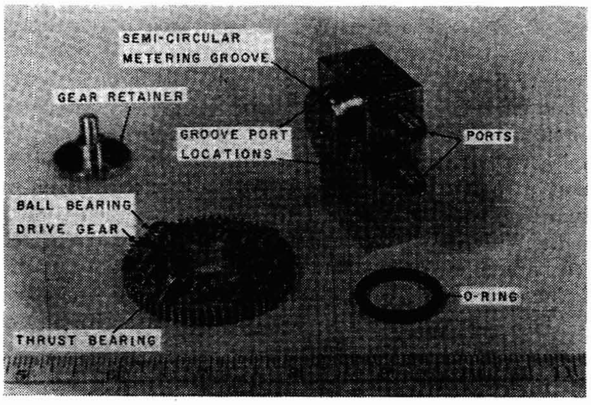


Figure 6. Components of O-Ring Pump

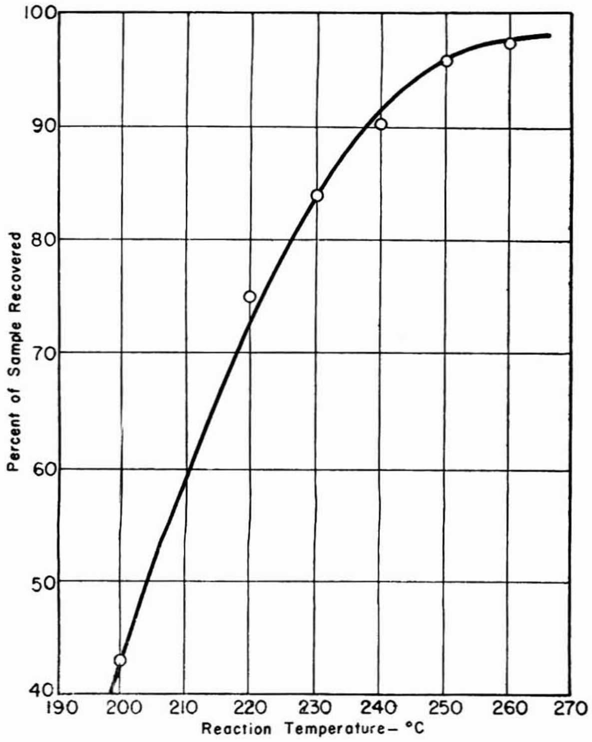


Figure 7. Effect of Temperature on Acetic Acid Oxidation

tubing in an air bath held at reaction temperature. The length of this tubing was variable, to permit adjustment of reaction time. The effluent from the reactor was stripped with a metered stream of oxygen, dried, and analyzed by thermal conductivity.

Rather than attempting to maintain prescribed absolute values of flow rates in the various streams involved in an instrument of the type under consideration, it is generally more practical empirically to calibrate the over-all process against samples of known composition. For the purpose of the present tests, however, calculations were based upon actual flow measurements, each made with an estimated accuracy of 98%.

Because the literature indicates that acetic acid is one of the compounds most resistant to chromic acid oxidation, it was chosen for the sample in most of the following tests.

The effect of reaction temperature on the completeness of acetic acid oxidation, using a 5-minute reaction period, is shown in Figure 7. Because boiling produces troublesome pressure and flow variations in the reactor, operation at maximum temperature was not desirable. Thermostating the reactor at 250° C. allows sufficient tolerance for minor variations in flow and concentration.

At 250° C., negligible gain is realized by increasing reaction time beyond 2.5 minutes, as shown in Figure 8. Most samples, in fact, were completely oxidized in 30 seconds. Recovery of volatile materials, however, was severely reduced with less than 2.5-minute-contact. Diethyl ether was 90% recovered with 2.5-minute reaction.

A reaction period of 2.5 minutes at 250° C. was used for all further measurements. Analyses were subsequently made with the finished apparatus, in which the over-all instrument had been calibrated against a standard solution of acetic acid. At least 98% accuracy was obtained with known solutions of adipic acid, benzoic acid, dextrose, ethanolamine, and nitroethane.

Nitrogen compounds, incidentally, produce no interference, as the nitrogen is retained in the liquid phase, presumably via a Kjeldahl reaction.

No reason has been found to doubt that the oxidation conditions will be equally effective for all water-soluble organic compounds. In any specific application, however, a test on the particular compounds involved is obviously desirable.

Stripping of Carbon Dioxide. At temperatures above 200° C., carbon dioxide was found to be quantitatively stripped from sulfuric acid solution with the simplest possible apparatus. The hot solution was merely allowed to flow down the walls of a 60-mm. vertical length of 8-mm. glass tubing, through which the stripping gas is rising. While no attempt was made to determine the limits of this process, no variations of flow in the range of interest here resulted in less than 100% recovery of carbon dioxide. The length of the stripping column appeared to be equally noncritical.

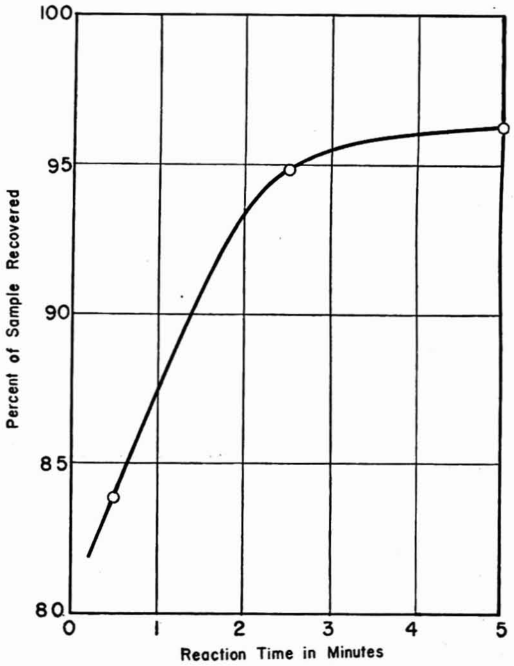


Figure 8. Effect of Reaction Time on Acetic Acid Oxidation

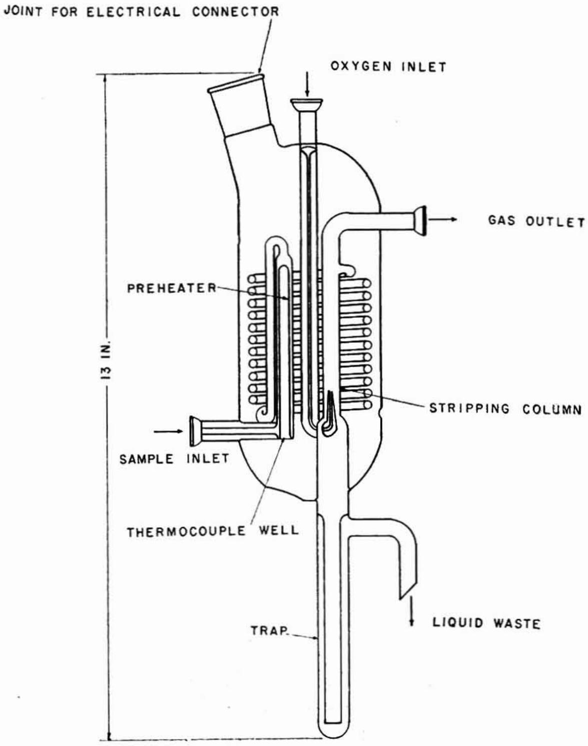


Figure 9. Oxidation Reactor

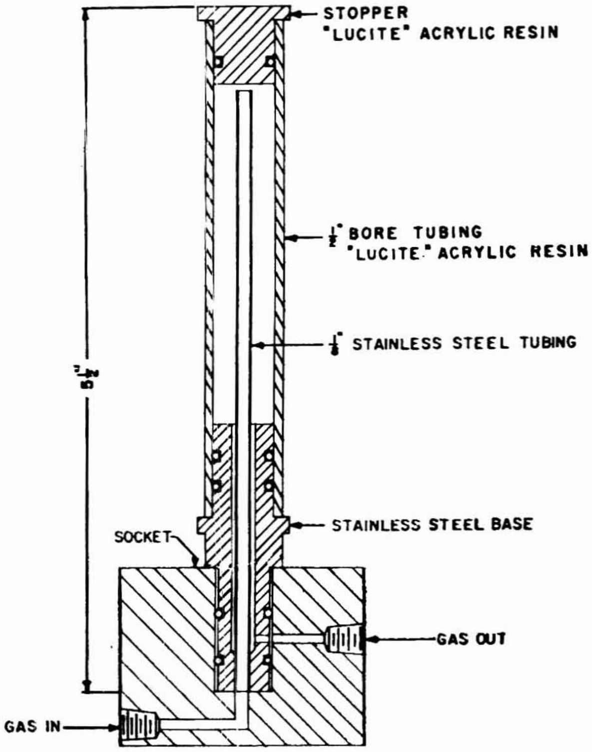
Reactor Design. The reactor used in the analyzer is shown in Figure 9. The extremely corrosive nature of the hot reaction mixture limits the choice of possible construction materials to glass and platinum. Cost considerations narrow the choice to glass.

The preheater, tubing reactor, and stripper are enclosed in a single glass jacket to facilitate temperature control and to produce a compact and reasonably durable unit. The reaction mixture enters the unit through the ball joint at the lower left and is brought to temperature in the Nichrome-wrapped preheater (50 watts). A thermocouple well in the preheater permits automatic temperature control of this operation. A helix of 4-mm. tubing, having a volume of 8 ml., retains the mixture for the reaction period. (Approximately 2 ml. per minute of oxygen is evolved by thermal decomposition of the reagent, doubling the volume requirements for the 2 ml. per minute of solution alone.) The contents of the reactor discharge into the vertical stripping column, to the right, in which the carbon dioxide is stripped by the stream of oxygen entering through the jet at the bottom of the column. The spent reaction mixture discharges to the waste through the trap at the bottom of the unit.

In order to maintain the reaction temperature after the mixture leaves the preheater, the jacket is filled with Santocel insulation. To minimize the temperature gradient across the insulation and thus improve temperature regulation, a Nichrome heater (100 watts) is wound around the jacket, supplied with a Variac.

This means of temperature control was found to be superior to any but the more elaborate proportioning controls, as any temperature cycling, as produced by on-off controllers, tended to be reflected, via pressure cycles, in the recorder. With the system employed, line voltage variations between 90 and 120 volts produced negligible effect on reactor performance with no adjustment of the Variac.

Oxygen Metering. Control of the 10 ml. per minute oxygen stripping gas is easily obtained with commercial flow-regulating equipment. With the cylinder regulator set at 10 pounds per square inch, the gas is passed through a Moore differential flow controller, operated in conjunction with a Foxboro



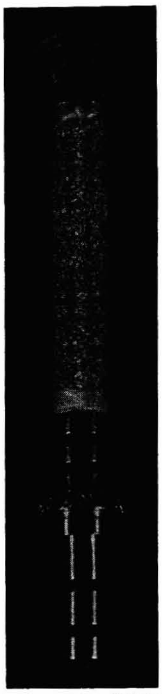


Figure 10. Absorption Tube

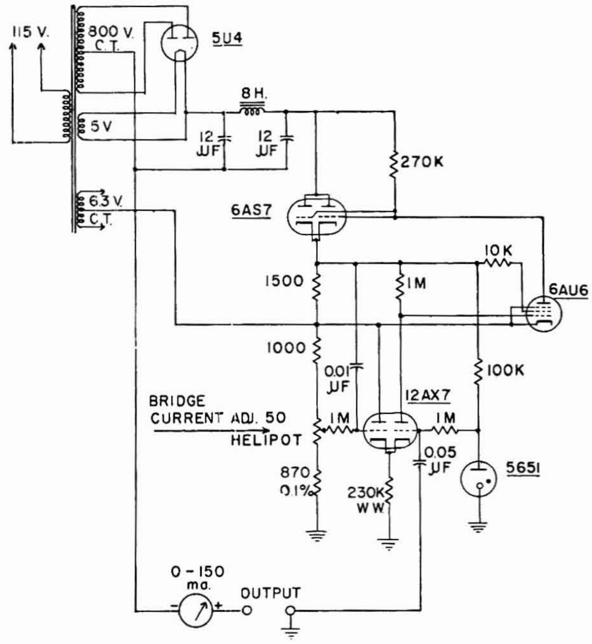


Figure 11. Current Regulator for Thermal Conductivity Bridge

Resistance in ohms except where noted
K. Kilo-ohms
M. Megohms

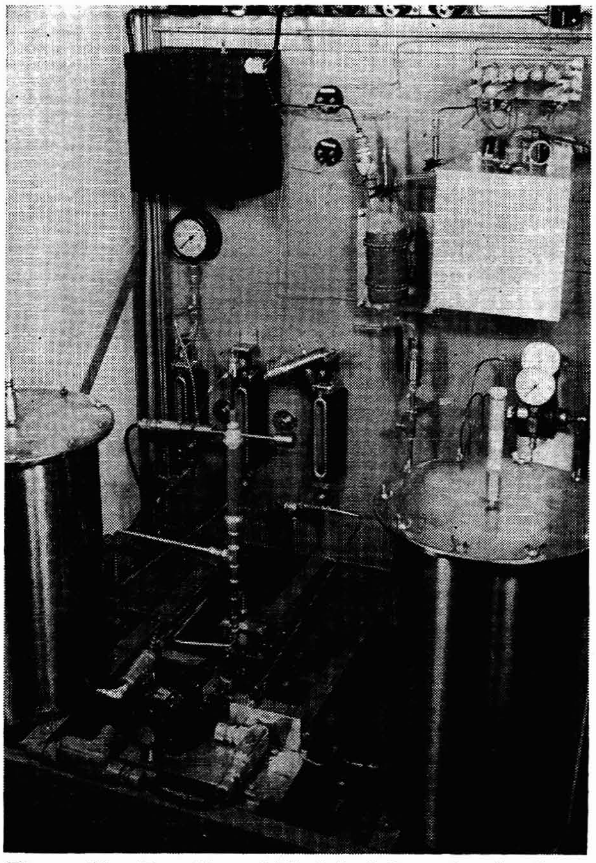


Figure 12. Breadboard Model of Organics Analyzer

Bordon restrictor valve (the reset valve from a Foxboro pneumatic controller). This system has been found to be remarkably stable, maintaining a constant flow for weeks without attention.

Because of the oxygen evolution from the reaction mixture, complete control of the flow is not attained by this system. In practice, however, variations from this source have not been found important.

Chromic Acid Metering. Because of the high ratio of reagent to sample employed, a smooth flow of reagent is essential to uniform section conditions, although the absolute value of the metered flow is not at all critical. Fortunately, the concentrated sulfuric acid solution employed is easily metered, being somewhat viscous and a reasonably good lubricant. In concentrated form, it is not particularly corrosive. A gear pump of Type 316 stainless steel can be used for its metering. A somewhat simpler and longer-lived pump has been developed at this laboratory for the application, a description of which will be published separately.

Gas Purification. ACID SPRAY. A very small amount—about 2 ml. per day—of acid spray is entrained in the gas leaving the stripping column. While small in amount, this spray tends to accumulate and cause troublesome corrosion of the subsequent metal tubing. A vertical 6-inch length of glass tubing has been found sufficient to settle most of this spray, which is drained off through a small glass trap. That not trapped is absorbed in a small (1-ml.) tube of 20-mesh metallic zinc.

CHLORINE. Chlorides, frequently present in the sample water, are oxidized to chlorine in the oxidation reaction. This gas, which would interfere with the subsequent thermal conductivity measurement, is quantitatively absorbed by black powdered antimony (7). This material was selected over the usual liquid scrubbers or heated metal gauzes for the sake of reduced maintenance requirements. The material is prepared for convenient use by heating to sintering temperature, grinding, and screening to about 16 to 20 mesh. (Caution. Antimony is posionous. These operations should be performed in a well-ventilated hood.) The effectiveness of this reagent was demonstrated in the finished instrument by adding 1000 p.p.m. of sodium chloride to a runner sample; the recorder reading was not affected.

WATER VAPOR. A tube of Drierite is used to remove the small amount of water vapor carried in the gas stream.

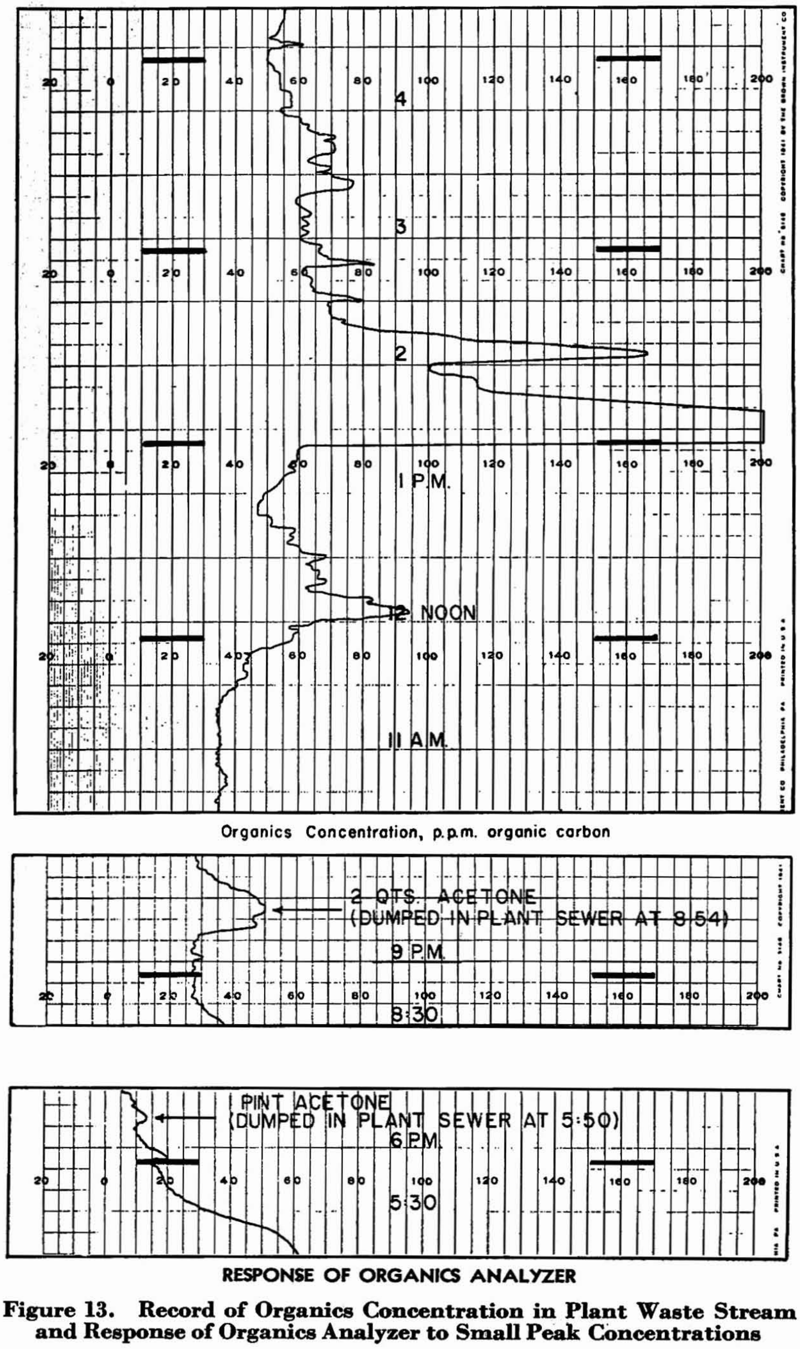
ABSORPTION TUBES. The vessel shown in Figure 10 has been found extremely convenient for containing the gas-purifying reagents, being durable, transparent, and easily replaced.

Thermal Conductivity Measurement. Analysis of gases by thermal conductivity is frequently considered to be practical only in the higher concentration ranges—i.e., above 5% full scale. In the present process, 200 p.p.m. of organic carbon in the sample water produces 1% by volume carbon dioxide in the oxygen stripping gas. Using a Gow-Mac Type M/T-T-8 thermal conductivity cell, no difficulty was encountered in obtaining 1.5-mv. output for this concentration, sufficient for full-scale deflection on a modern electronic recorder. After warm-up, no zero drift is evident at this sensitivity. A number of refinements over ordinary practice were necessary, however, to obtain this performance.

THERMOSTATING. The thermal conductivity cell was enclosed in a small water-tight brass box and submerged in a water bath. Bath temperature was controlled, using convection circulation, at about 40° C., the on-off controller producing water temperature cycles of about ±3° C. Because of the very low gas flow rate, no special effort was necessary to bring the gas to cell temperature.

DIFFERENTIAL MEASUREMENT. At this sensitivity, the thermal conductivity unit is highly sensitive to small pressure fluctuations, of the order of 1 mm. of water. By using the differential measurement technique, such fluctuations, invariably present, are almost entirely cancelled out. The differential measurement, of course, also tends to cancel the effect of other extraneous gases present which are not absorbed with the carbon dioxide by the Ascarite absorbent between the sample and reference cells.

BRIDGE CURRENT CONTROL. Slight imperfections in the thermal conductivity bridge render its output sensitive to supply current variations. In the present unit, a 1% current variation



RESPONSE OF ORGANICS ANALYZER

Figure 13. Record of Organics Concentration in Plant Waste Stream and Response of Organics Analyzer to Small Peak Concentrations

produces an output variation of 0.075 mv., equivalent to 5% of the recorder span. While no entirely satisfactory commercial regulator was found, the circuit shown in Figure 11, having an output of 100 ma., has been found to provide stability such that 20% line voltage fluctuations produce no visible recorder deflection. This is a current, rather than voltage regulator, having an output impedance at low frequencies in excess of 10 megohms. Consequently, the bridge current is made effectively independent of contact and lead resistances.

SHOCK MOUNTING. The cell is appreciably sensitive to shock and vibration at this level of sensitivity. Shock mounting is desirable if vibration is likely to be present.

Zero and Span Adjustments. In a practical automatic instrument, means must be provided for adjustment of the recorder zero and span. Although no significant zero drift has been observed in the thermal conductivity unit, a slowly variable blank error is inevitably present from impurities in the chromic acid reagent. A simple potentiometer in the thermal conductivity bridge circuit is used to zero the recorder, while operating the analyzer with no sample flow.

Because slow drifts of the various metered flows are to be expected in practice, it is desirable to provide means of feeding a standard sample to the analyzer, against which the recorder can be calibrated. Adjustment to the correct reading is most conveniently made by adjustment of the recorder potentiometer span, a feature now available in commercial equipment.

These operations can be readily made automatic with a suitable timer and solenoid valve arrangement.

PLANT TESTS OF ANALYZER

A "breadboard" model of the complete analyzer, shown in Figure 12, was tested in the analysis of an actual plant waste stream. The value of the instrument was quickly made evident by the revelation of peak organics concentrations, of which the plant personnel had been entirely unaware. A typical record is shown in Figure 13. It is evident that the magnitude and duration of these peaks could be determined only by continuous measurement. Also shown is a demonstration of the sensitivity of the analyzer, in which 1-point and 2-quart samples of acetone were deliberately dumped in the 1000-gallon-per-min. waste stream, 10 minutes upstream from the sampling point. (While peaks other than those deliberately produced are evident in the record, the deliberate peaks can be isolated by measuring on the record the known 20-minute transportation lag from the time of pollution to initial deflection of the recorder.) The use of this instrument has made it possible for the plant personnel to track down and eliminate the sources of contamination.

DESIGN OF AUTOMATIC PROTOTYPE ANALYZER

A continuous chemical analyzer of this type necessarily presents some maintenance problems not encountered in the usual plant instrument. Periodic replenishment of reagents is unavoidable. Failure of components may result in leaks or line stoppages. Metered flows may deviate from the proper values. In an effort to minimize these problems and to simplify maintenance, the instrument layout shown in Figure 14 was developed.

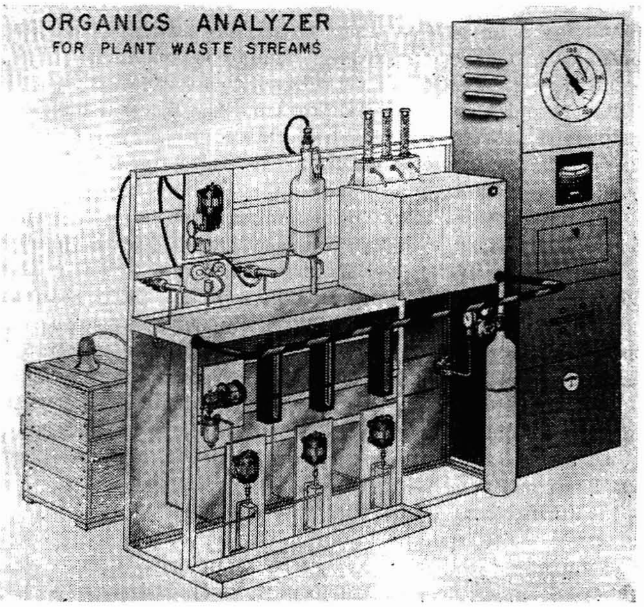


Figure 14. Organics Analyzer for Plant Waste Streams

The equipment is physically divided into two units, the chemical and electrical racks, in order both to minimize corrosion hazards to the electrical equipment and to increase flexibility of layout. The liquid reagents, barium hydroxide, chromic acid, and standard sample, are contained in separate 6-gallon polyethylene carboys, which can be shipped to the supplier for refilling. The large sampling pump (not shown) is also separate for layout flexibility.

For ease of servicing, the mixers, continuous filter, and oxidation reactor are at waist height, suspended over a splash pan through which excess sample water flows to flush away wastes. The continuous filter, O-ring pump, and sample-acid mixer are closely grouped, to minimize the transfer lag in the 0.2 ml. per minute sample line. The thermostated thermal conductivity cell and gas absorption tubes are at the right. On the front of the rack are the motor-driven Cuno filter, metering pumps, rotameters, oxygen cylinder, and oxygen flow controller. The pumps, suspended over a floor-level drip pan, are mounted at a low point to facilitate priming.

The electrical rack contains the recorder, reactor temperature controller, switch panel, zeroing and standardizing gear, and the regulated supply for the thermal conductivity bridge.

It is expected that maintenance will comprise daily replacement of the recorder chart and the Drierite absorption tube and weekly replacement of other reagents. The paper supply to the continuous filter will require monthly replacement. Apart from actual component failure, no additional servicing other than that required for conventional instruments is anticipated.

It is expected that practical experience in the field will result in the eventual development of components which will render automatic chemical analyzers of this type so reliable as to permit their valuable application to a large variety of plant process stream analyses and control problems now beyond the scope of the simpler direct physical methods of measurement.

ACKNOWLEDGMENT

Much of the work on the selection of the analytical scheme was performed by L. M. Magner, of this laboratory, who also evaluated the vapor phase oxidation approach. H. C. Carlson, of the Engineering Service Division, rendered much valuable assistance in the development of the liquid-phase oxidation process. F. A. Keidel, of this laboratory, performed the basic evaluation of the precipitation process for removal of carbonates from the sample stream. The assistance of these and many other individuals in the Du Pont Co. is gratefully acknowledged.

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Studies with *N*-Halo Reagents

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N-chloro-, N-bromo-, and N-iodosuccinimides were used in the differentiation of alcohols, amines, and some position isomers, and the detection of amino alcohols. In general, the tests were carried out in carbon tetrachloride solution, on a water bath at 80° C. Primary alcohol tests using N-bromosuccinimide yield a permanent orange color, whereas the color disappears in secondary alcohol tests to give an orange-mottled precipitate. No observable color change occurs with most tertiary alcohols. Thirty saturated alcohols were tested, as well as 25 other alcohols and hydroxy compounds. With N-iodosuccinimide primary amines yield a permanent brown color, whereas the color fades with secondary amines. Tertiary amines give a brown color and are confirmed by an orange precipitate using N-bromosuccinimide. Some position isomers have been differentiated with N-halosuccinimides; no color changes occurred with any of the meta-disubstituted isomers. The N-halosuccinimides have been shown to be valuable classification reagents.

The halosuccinimides have been the subject of much research. Most of these investigations have been concerned with the use of these compounds as halogenating agents. During a course of investigations in this laboratory it was noted that *N*-bromosuccinimide could also be used to differentiate primary, secondary, and tertiary saturated alcohols. The test is applicable over a wide range of alcohols. It is rapid and very simple to perform, a possible advantage over previous proposed tests (*10, 13, 19*). While this work was in progress it occurred to the authors that the halosuccinimides might be useful in differentiating other groups of compounds. The present report deals with the use of *N*-bromosuccinimide, *N*-chlorosuccinimide, and *N*-iodosuccinimide in the differentiation of primary, secondary, and tertiary alcohols and amines and some position isomers, and the detection of amino alcohols.

DIFFERENTIATION OF PRIMARY, SECONDARY, AND TERTIARY ALCOHOLS

Procedure and Results. Three drops of an alcohol (or an equivalent amount of solid) were dissolved in 1 ml. of a solution of 2 drops of bromine in 100 ml. of carbon tetrachloride in a 6-inch test tube, and treated with *N*-bromosuccinimide (15 to 30 mg.). Another milliliter of the solvent solution was used to wash down the walls of the tube. The tube was placed in a 600-ml. beaker containing water heated to 77° to 80°.

At this temperature the solution will gently boil and any color changes from the initial pale yellow will occur in the mixture within 13 minutes. For most compounds tested, changes occurred within 5 minutes. Primary alcohols give a permanent orange color. If the alcohol is secondary, an orange color will appear but will fade (rapidly) to colorless on continued boiling. An orange-mottled precipitate is apparent upon cooling. Tertiary alcohols usually show no color changes, although the behavior of *tert*-amyl alcohol has been erratic. Decolorization of the bromine–carbon tetrachloride solution prior to heating shows that the alcohol is not of the saturated type. Table I groups the 30 saturated alcohols which were tested and gives the identifying characteristics for each class. Table II lists the results when the test was applied to 25 other hydroxy compounds.

Discussion. The results listed in Table I are self-explanatory. A continuous boiling period of 6 or 13 minutes was required for the disappearance of the color in the case of 2-methylcyclohexanol and 4-methylcyclohexanol, respectively.

The results listed in Table II are worthy of comment. Allyl, propargyl, and benzyl alcohols appear to fade in the manner of secondary alcohols. These exceptions are not surprising, as these α,β-unsaturated compounds are often exceptions to many general rules regarding reactions. Furthermore, Lucas (*13*) reported that allyl alcohol gave a secondary test, and the same result was noted with the present test. The α-hydroxy esters conform to the rules of the *N*-bromosuccinimide test, as do five tertiary alcohols listed in this table (dimethylbenzylcarbinol excepted). From this it appears that this test in many cases can be applied to more complex alcohols and other hydroxy compounds.

The reaction of *N*-bromosuccinimide with alcohols and other hydroxy compounds has been the subject of a number of reports. Although this discussion is limited to reactions of *N*-bromosuccinimide, the reactions of alcohols with similar reagents have been reported—i.e., *N*-bromoacetamide (*12, 18, 20*), *N*-chlorosuccinimide (*5, 8*), and *N*-bromophthalimide (*1*). Fieser and Rajagopalan (*4*) first demonstrated the use of *N*-bromosuccinimide for oxidizing a secondary alcohol group to a keto group, using the reagent in aqueous solution. Their first work was the selective oxidation of the 7-hydroxyl group in cholic acid to the 7-keto derivative. In 1952, Barakat and Mousa (*1*) reported treating methyl, ethyl, isopropyl, and benzyl alcohols (5, 6, 7, and 4 ml., respectively) with *N*-bromosuccinimide (2 grams each). From the filtered reaction mixtures they obtained the 2,4-dinitrophenylhydrazones of formaldehyde, acetaldehyde, acetone, and benzaldehyde. They indicated the alcohols were converted to

Table I. Differentiation of Saturated Alcohols by *N*-Bromosuccinimide

PRIMARY	
Methanol[a]	An orange color appears usually within 3 minutes during boiling and remains on cooling. Unreacted bromoimide is present at the bottom; succinimide floats at the top.
Ethanol	
1-Propanol	
1-Butanol	
2-Methyl-1-propanol	
1-Pentanol	
3-Methyl-1-butanol	
1-Hexanol	
1-Heptanol	
1-Octanol	
2-Ethyl-1-hexano	
1-Decanol	
1-Dodecanol	
1-Hexadecanol	
1-Octadecanol	
SECONDARY	
2-Propanol	An orange color is produced during boiling and usually disappears (rapidly) within 5 minutes. An orange-mottled precipitate will appear on cooling; succinimide floats at the top.
2-Butanol	
3-Methyl-2-butanol	
2-Pentanol	
3-Pentanol	
Cyclopentanol	
2-Hexanol	
Cyclohexanol	
3-Heptanol	
2-4-Dimethyl-3-pentanol	
2-Methylcyclohexanol	
4-Methylcyclohexanol	
2-Octanol	
TERTIARY	
2-Methyl-2-propanol	No observable change
2-Methyl-2-butanol	Results erratic

[a] Color develops slowly.

hypobromites, which dehydrobrominated to yield the carbonyl compounds. These authors stated that primary and secondary alcohols and primary amines can be detected using N-bromosuccinimide, although they gave no experimental details for a detection or differentiation procedure. Presumably the combination of an orange-red color obtained when these (seven total) compounds reacted and the 2,4-dinitrophenylhydrazones obtained constituted the method for detection.

The alcohol differentiation tests described in the present paper can possibly be explained on the basis that the primary and secondary alcohols give hypobromites which split out hydrogen bromide to yield aldehydes and ketones. With hydrogen bromide present, unchanged N-bromosuccinimide has been reported in other instances to yield succinimide and bromine (*23*), which is probably responsible for the color. The aldehyde formed could react with additional unchanged alcohol to form a hemiacetal which has been postulated to react with N-bromosuccinimide (*6*) to give a hypobromite. Here primary compounds would produce twice as much halogen as secondary ones, which could account for the fading of color in the secondary test. The presence of bromine is critical in this test, as the solvent system must contain a small amount of bromine to prevent color fading with some primary alcohols. The lack of color formation with tertiary alcohols can be explained by the fact that there is no hydrogen atom on the α-carbon and consequently hydrogen halide is not removed, bromine is not produced, and the alcohol is not oxidized. The inertness of N-chlorosuccinimide toward *tert*-butyl alcohol was observed by Seliwanow (*21*), and he suggested that a tertiary alcohol may be detected in this manner.

Table II. Differentiation of Other Alcohols and Hydroxy Compounds by N-Bromosuccinimide

PRIMARY	
Allyl alcohol	Pale orange color which disappears during heating
Propargyl alcohol	Faint orange color which disappears during heating
Benzyl alcohol	Pale orange color which disappears during heating
Cinnamyl alcohol	Complete solution, no color change
Furfuryl alcohol	Prim. test initially with black ppt., complete black solution on continued heating
Tetrahydrofurfurol	Permanent yellow-orange color, prim. test
2-Phenylethanol	Yellow changes to permanent orange, prim. test
3-Phenylpropanol	Yellow changes to orange, gradual fading in 10-min. heating
2,3-Dibromo-1-propanol	Permanent orange color, prim. test; on standing overnight orange ppt. settles
Ethylene glycol monomethyl ether	Permanent orange color, prim. test
Ethylene glycol monoethyl ether	Permanent orange color, prim. test
Ethylene glycol mono-n-butyl ether	Permanent orange color, prim. test
Ethylene glycol monophenyl ether	Faint prim. test
SECONDARY	
DL-Phenylmethylcarbinol	Orange color fades rapidly, sec. test
Ethyl DL-lactate	Orange color fades rapidly, sec. test
Ethyl DL-α-hydroxybutyrate	Orange color fades rapidly, sec. test
Ethyl DL-mandelate	Orange color fades rapidly, sec. test
Ethyl DL-α-hydroxyhydrocinnamate	Orange color fades rapidly, sec. test
Benzhydrol	Orange color fades on standing, orange ppt.
TERTIARY	
Diacetone alcohol	No observable change, tert. test
Trichloro-*tert*-butyl alcohol	No observable change, tert. test
Triphenylcarbinol	No observable change, tert. test
2,5-Dimethyl-3-hexyne-2,5-diol	No observable change, tert. test
α-Terpineol	Succinimide forms, no color change
Dimethylbenzylcarbino	Slight yellow color

Table III. Differentiation of Saturated Amines by N-Iodosuccinimide[a]

PRIMARY	
n-Propylamine	The color which develops during heating in the water bath is usually brown, although it ranges among deep yellow, orange-brown, and red-brown. No color fading occurs.
Isopropylamine	
n-Butylamine	
Isobutylamine	
sec-Butylamine	
n-Amylamine	
Isoamylamine	
Cyclohexylamine	
n-Heptylamine	
n-Octylamine	
2,4,4-Trimethyl-2-amylamine	
n-Decylamine	
n-Dodecylamine	
n-Octadecylamine	
SECONDARY	
Diethylamine	The color which develops during heating in the water bath is usually brown, although it ranges among deep yellow, orange-brown, and red-brown. The color then fades while heating to pale yellow or tan or colorless.
Di-n-propylamine	
Diisopropylamine	
Di-n-butylamine	
Diisobutylamine	
Di-*sec*-butylamine	
Di-n-amylamine	
Diisoamylamine	
Dicyclohexylamine	
Di-n-octylamine	
TERTIARY	
Triethylamine	The color becomes very dark brown or brown-violet upon heating in the water bath. This test must be confirmed by the immediate appearance of an orange precipitate when N-bromosuccinimide is added to a sample of the tertiary amine in carbon tetrachloride.
Tri-n-butylamine	
Tri-n-amylamine	
Triisoamylamine	
Tri-n-hexylamine	
Tri-n-heptylamine	

[a] All tests were run heating in a water bath at 80–90° C. for 10 minutes. The color changes occur within this period of time.

[b] Furnished through the courtesy of Rohm & Haas Co., Philadelphia.

DIFFERENTIATION OF SATURATED AMINES AND SOME POSITION ISOMERS AND DETECTION OF AMINO ALCOHOLS

Procedure and Results. Six drops of the liquid amine (or an equivalent amount of the solid) were introduced into a test tube containing 1 ml. of carbon tetrachloride. A small amount (ca. 30 mg.) of N-iodosuccinimide and a few particles of benzoyl peroxide were added and the walls of the tube were washed with an additional milliliter of carbon tetrachloride. The reactants were placed in a water bath at 80° C. At this temperature the solvent gently boiled and the reaction(s) was observed for 10 minutes.

The test was interpreted as follows: If the amine was primary, the color that developed during heating was usually brown, although it ranged from deep yellow and orange-brown to red-brown. No color fading occurred. In the case of a secondary amine, the color that developed during heating was usually brown (deep yellow, orange-brown, or red-brown) and this color faded to pale yellow, tan, or colorless during the period of heating. The tertiary amines tested exhibited a permanent dark brown or brown-violet color upon heating in the water bath. Their detection must be confirmed by the immediate appearance of an orange precipitate when N-bromosuccinimide is added to a fresh sample of the tertiary amine in carbon tetrachloride. The results of the test when applied to 30 saturated amines are listed in Table III.

When the method was applied to the differentiation of some position isomers, equivalent conditions and amounts of the sample and reactants were used where indicated (see Table IV). The dihydroxybenzene tests were carried out at room temperature in the presence of benzoyl peroxide. This series was the only group of position isomers which required benzoyl peroxide.

The test can also be used to detect amino alcohols. The reagent used was N-bromosuccinimide without benzoyl peroxide. A positive test for these compounds was the presence of a brown ring floating on the top of the solution after heating. Upon cooling, succinimide appeared at the top of the solution. The compounds tested in this group were ethanolamine, diethanolamine, triethanolamine, and diethylaminoethanol. All gave the characteristic brown ring test.

Discussion. In applying the amine differentiation test to unknowns, it is difficult to detect the difference between primary and tertiary amines with *N*-iodosuccinimide. Therefore *N*-bromosuccinimide must be used to confirm a tertiary amine.

The present test can be used equally as well as the benzoyl peroxide tests (*15*, *16*), the chloranil test (*22*), the quinhydrone test (*11*), or the well-known Hinsberg test (*9*) for differentiating saturated amines. The function of benzoyl peroxide in the present test is catalytic. This was evident when the tests with *N*-iodosuccinimide were carried out without benzoyl peroxide. The same color changes occurred, but were not as pronounced as when benzoyl peroxide was used. The benzoyl peroxide test reported by de Paolini and Ribet (*16*) required the addition of Fehling's solution in an alkaline medium for differentiating aliphatic amines.

Table IV. Differentiation of Position Isomers by *N*-Halosuccinimides

Compound	Conditions and Reagents Used[a]	Result
1-Naphthol	NIS $+ \Delta$	Purple
2-Naphthol	NIS $+ \Delta$	Yellow to light pink
1-Naphthylamine	NBS $+ \Delta$	Purple
2-Naphthylamine	NBS $+ \Delta$	No color change
Catechol	NIS $+ Bz_2O_2$	Purple
Resorcinol	NIS $+ Bz_2O_2$	Light tan
Hydroquinone	NIS $+ Bz_2O_2$	Pink
o-Aminophenol	NCS $+ \Delta$	Dark brown
m-Aminophenol	NCS $+ \Delta$	No color change
p-Aminophenol	NCS $+ \Delta$	Dark red
o-Bromoaniline	NCS $+ \Delta$	Dark blue-brown
m-Bromoaniline	NCS $+ \Delta$	No color change
p-Bromoaniline	NCS $+ \Delta$	Orange-brown
o-Nitroaniline	NCS $+ \Delta$	Green-yellow
m-Nitroaniline	NCS $+ \Delta$	No color change
p-Nitroaniline	NCS $+ \Delta$	No color change; yellow precipitate
o-Toluidine	NCS $+ \Delta$	Brownish black
m-Toluidine	NCS $+ \Delta$	No color change
p-Toluidine	NCS $+ \Delta$	Red-brown
o-Anisidine	NCS $+ \Delta$	Brownish black
p-Anisidine	NCS $+ \Delta$	Red-brown
o-Phenetidine	NCS $+ \Delta$	Dark brown
p-Phenetidine	NCS $+ \Delta$	Brownish purple
o-Phenylenediamine	NCS $+ \Delta$	Dark green-brown
m-Phenylenediamine	NCS $+ \Delta$	No color change
p-Phenylenediamine	NCS $+ \Delta$	Purple

[a] NIS. *N*-Iodosuccinimide. NBS. *N*-Bromosuccinimide. Bz_2O_2. Benzoyl peroxide. NCS. *N*-Chlorosuccinimide.

The authors do not propose this test in preference to the Hinsberg test in any qualitative organic flow chart. Preferably they propose its use in conjunction with the Hinsberg test. There are several advantages to this arrangement: Occasionally difficulties are encountered in the Hinsberg test when too much benzenesulfonyl chloride is added. The *N*-iodosuccinimide test is amenable to the differentiation of several amines at the same time; this includes the simultaneous observation of the color changes of known and unknown amines. The rapidity of the *N*-bromosuccinimide confirmatory test can be used to advantage in confirming the tertiary amine result in the Hinsberg test.

The chemistry of these amine reactions with *N*-iodosuccinimide is not well known at present when compared with the Hinsberg reactions. Nevertheless, some suggestions can be made as to reaction mechanisms. Mechanisms can be postulated which would cause the production of twice as much iodine in the primary test as in the secondary test. This involves the substitution of the positively charged iodine for one of the active hydrogens in the primary amine. This could be followed by the splitting out of the hydrogen iodide and the formation of an imine. Upon metathesis of the hydrogen iodide with additional *N*-iodosuccinimide, succinimide and iodine are released. The iodine, which would impart a color to the solution, could add across the point of unsaturation of the imine. At this point two possible reactions could occur, both yielding hydrogen iodide again as one end product. The first possibility would be a repetition of the series of reactions just described up to the point of iodine formation. The second possibility would involve a condensation of the *N*-iodoamine with unchanged amine to form a hydrazo compound and hydrogen iodide. In all, 4 moles of the *N*-iodosuccinimide would be used per mole of the amine, and iodine would be one of the end products. In the case of secondary amines, which have only one active hydrogen, the suggested series could take place only once. The addition of iodine to the double bond may be responsible for the color fading. The fading may not be detected with primary amines, since twice as much iodine is formed.

The reactions regarding tertiary amines could involve the addition of iodine to the nitrogen of the amine, resulting in a quaternary salt. This could be followed by a dehydrohalogenation involving one of the hydrogens on a carbon alpha to the functional group. Similar reactions have been suggested by Meisenheimer (*14*) and Price, Pohland, and Velzen (*17*). However, in aqueous solution, they reported the cleavage of a carbon-nitrogen double bond and the formation of a secondary amine and an aldehyde. While it is difficult to conceive of this latter reaction occurring in a nonpolar solvent (such as was used in the present study), Crane, *et al.* (*3*) and Cosgrove and Waters (*2*) reported the presence of secondary amines and aldehydes when tertiary amines were caused to react with *N*-2′,4′,6′-tetrachlorobenzanilide and with chlorine in carbon tetrachloride. Furthermore, they stated the reaction produced much hydrogen chloride. De Paolini and Ribet (*16*) demonstrated a similar type of reaction using benzoyl peroxide and tertiary amines in 95% ethanol. In any event, the production of hydrogen iodide (in the present study) could form iodine in the presence of the *N*-iodosuccinimide. If the tertiary amine is converted to a secondary amine, more halogen would be liberated for tertiary amines than in the case of the secondary amine test.

Some deductions can be made concerning the color reactions observed in the isomer differentiation studies. As no color changes were produced with the meta isomers irrespective of the *N*-halosuccinimide used, the color formation with other isomers was not due to the halogen. Consequently it could arise from the formation of a chromophoric group. The chromophore formation is supported by the fact that all of the compounds listed in Table IV contain auxochromes, hydroxy, or amino groups. Furthermore, the *o*-, *m*-, and *p*-xylenes were tested and no visible color was produced. Since ortho and para isomers are much more easily oxidized than meta isomers, the color could be due to oxidation products or to more complicated products formed between these and the original compound.

In all, these postulated mechanisms are reasonable, in that they account for the color changes observed. The reactions suggested for *N*-iodosuccinimide are closely analogous to those which have been found and reported for reactions of its *N*-chloro- and *N*-bromo- counterparts with hydroxy and amino compounds (*1*, *2*, *5–8*).

Irrespective of reaction mechanisms, it is clear that the *N*-halosuccinimides are valuable analytical reagents, in addition to their well-known uses in synthesis. They represent one homologous series of compounds which can be used in differentiating alcohols, saturated amines, and some position isomers and detecting amino alcohols.

Students under the direction of P. L. Pickard, University of Oklahoma, and J. B. Entrikin, Centenary College of Louisiana, have used some of these differentiation tests; the results were very satisfactory.

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Titration of Bismuth with Ethylenediaminetetraacetic Acid

Spectrophotometric End Points

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Prior to the development of ethylenediaminetetraacetic acid, the volumetric methods for determining bismuth were indirect and unsatisfactory. Since this reagent offers a simple and direct titration but suffers from a lack of good indicators, an attempt has been made to extend its usefulness by application of the photometric titration technique. The progress of the titration may be assessed by following spectrophotometrically the disappearance of the yellow bismuth-thiourea complex, or the appearance of the blue complex formed by cupric ion with the titrant. Quantities of bismuth from 0.5 to 100 mg. can be titrated accurately when present in a volume of 100 ml. Large quantities of lead do not interfere with the titration, and bismuth can be determined rapidly in a mixture with tin, lead, arsenic, and antimony by a simple procedure.

BISMUTH is usually determined gravimetrically or colorimetrically. The volumetric methods previously available are indirect, based on precipitation of bismuth with oxalate, chromate, molybdate, etc., followed by titration of the anions. Such methods are not considered completely reliable (*4, 10*). Thus a direct volumetric method, in which bismuth itself is titrated, is of interest. Pribil and Matyska have recently shown that bismuth may be titrated amperometrically with ethylenediaminetetraacetic acid (*6*). A visual titration based on the disappearance of the yellow bismuth-thiourea complex upon the addition of ethylenediaminetetraacetic acid has also been described (*3*), but the recommended quantities of bismuth are large (100 to 200 mg.).

Photometric titrations with ethylenediaminetetraacetic acid have recently been reported by Sweetser and Bricker (*7, 8*), Malmstadt and Gohrbandt (*5*), and Underwood (*9*). In the present paper, the photometric technique may be applied with advantage to the titration of bismuth with this reagent. As little as 1 mg. of bismuth can be titrated easily. Furthermore, the bismuth complex with ethylenediaminetetraacetic acid is very stable. Thus, moderate quantities of numerous other ions do not interfere, and in certain cases, separations prior to the actual titration need not be performed with great rigor. Two photometric methods for obtaining the end point are described: the disappearance of the bismuth-thiourea complex may be followed, or cupric ion may serve as indicator. In the latter case, the formation of the cupric complex of ethylenediaminetetraacetic acid (less stable than the bismuth complex) indicates the end point in the bismuth titration. The use of both indicators is described because they supplement each other in extending the useful range of the method.

APPARATUS AND REAGENTS

The titration cell was similar to that described by Goddu and Hume (*2*), with a light path of about 2.2 cm. Such a cell can be mounted in the test tube attachment supplied for use with the Beckman Model DU spectrophotometer. The cell is thus entirely enclosed within the sample compartment, minimizing difficulties due to stray light. Holes drilled in the cover of the compartment to admit stirrer and buret were fitted with felt gaskets. The stirrer and the 5-ml. Exax buret were painted black for a short distance on either side of the level where they entered the compartment.

pH measurements were made with a Beckman Model G pH meter equipped with a glass electrode.

Standard bismuth solutions (generally $0.01M$) were prepared by dissolving Baker's analyzed bismuth metal (99.8%) in the minimal quantity of 1 to 1 nitric acid with gentle heating, followed by dilution with distilled water containing sufficient nitric acid to make the final solution about $0.5M$ in acid (to prevent hydrolysis of the bismuth).

All the titrations were carried out at a pH of about 2, although the pH is not extremely critical. A chloroacetate buffer is appropriate because of the pK value of chloroacetic acid. However, chloroacetate solutions slowly liberate, on long standing, sufficient chloride ion to form a precipitate with bismuth (BiOCl). Thus, buffer solutions were not kept on hand, but rather, appropriate quantities of solid chloroacetic acid were added as desired, followed by pH adjustment with ammonia or sodium hydroxide in the final solutions to be titrated. Eastman Kodak Co., Rochester, N. Y., practical grade, monochloroacetic acid, distilled to remove dark-colored impurities, was employed.

The disodium salt of ethylenediaminetetraacetic acid (Bersworth Chemical Co., Framingham, Mass., disodium versenate, analytical reagent) was dissolved in distilled water to prepare solutions of the titrant (0.1 or $0.01M$) which were standardized by photometric titration against the standard bismuth solutions.

All other materials were reagent grade or the equivalent.

TITRATIONS WITH CUPRIC ION AS INDICATOR

The titration of a bismuth-copper mixture with ethylenediaminetetraacetic acid is very similar to the titration of an iron-copper mixture previously reported from this laboratory (*9*). Figure 1 shows the type of titration curve obtained at a wave length where the cupric complex of the titrant absorbs strongly. The end points may be obtained for both bismuth and copper in a single titration. In this study, however, the emphasis has been placed on bismuth titrations alone, with the copper merely serving as indicator.

Procedure for Pure Bismuth Solutions. To a bismuth solution containing from 5 to 100 mg. of bismuth, add 2 grams of solid chloroacetic acid and 1 ml. of a 1*M* cupric nitrate solution. Adjust the volume of the solution to about 100 ml., and adjust its pH to about 2, using 1 to 1 ammonia or 5*M* sodium hydroxide. (The pH requirement is not extremely critical, satisfactory titrations having been performed at pH values of 1.5 to 2.4; below pH 1.5, the end point becomes less sharp, and above pH 2.5 there is a danger of precipitating bismuth.) Transfer the solution to the titration cell, and position it in the spectrophotometer. Set the instrument to zero absorbance at 745 mμ, using the slit width and sensitivity controls in the usual manner. Titrate with a 0.1*M* ethylenediamine tetraacetate solution previously standardized against a known bismuth solution. Read the absorbance after addition of appropriate increments of titrant, obtaining as many points as desired to define the two straight lines whose intersection gives the end point.

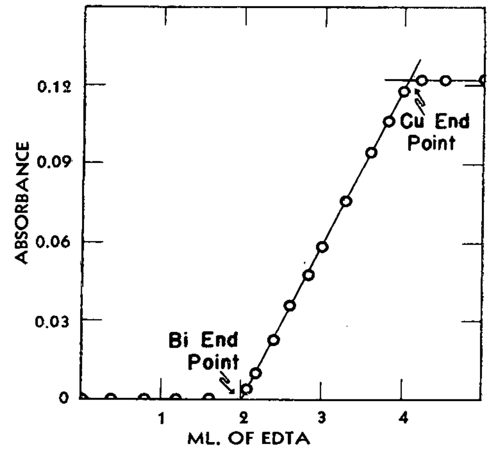

Figure 1. Titration of Bismuth-Copper Mixture with 0.1M Ethylenediaminetetraacetic Acid

41.8 mg. Bi, 13.1 mg. Cu; 745 mμ

Results. The results shown in Table I were obtained with pure bismuth solutions. The errors are within the range reasonably expected in good volumetric usage. In obtaining these results, the absorbance readings were corrected for dilution before the titration curves were plotted, although this affected the end points only very slightly.

Table I. Titration of Pure Bismuth Solutions

Copper Indicator			Thiourea Indicator		
Bi taken, mg.	Bi found, mg.	Error, parts/1000	Bi taken, mg.	Bi found, mg.	Error, parts/1000
4.18	4.16	5	0.418	0.412	14
4.18	4.15	7	1.05	1.06	10
10.5	10.5	0	2.09	2.09	0
10.5	10.6	9	4.18	4.16	5
20.9	20.9	0	6.27	6.26	2
20.9	20.9	0	8.36	8.38	2
41.8	41.9	2	10.50	10.40	9
62.7	62.6	2			
83.6	83.6	0			
105.0	105.0	0			

TITRATIONS WITH THIOUREA AS INDICATOR

Where the quantity of bismuth is sufficient to permit convenient titration with a 0.1*M* ethylenediamine tetraacetate solution, cupric ion is a better indicator than thiourea, because it is subject to fewer interferences. However, for titration of smaller quantities of bismuth with a 0.01*M* reagent solution, thiourea indicator is recommended for this reason—using copper ion as indicator, the slope of the titration curve beyond the bismuth end point decreases by a factor of 10 when the concentration of the titrant is changed from 0.1 to 0.01*M*. Because the molar absorbance index of the copper complex is rather small, this tenfold decrease in slope results in absorbance readings which are attended by considerable photometric error. The bismuth-thiourea complex absorbs so strongly that the above considerations are unimportant for the bismuth concentrations involved in this study.

One difficulty which is encountered with the thiourea indicator should be pointed out, although it is easily circumvented. The intensity of the yellow color formed when this reagent reacts with bismuth is dependent upon the pH of the solution, decreasing as the pH is raised. At room temperature, the extent of the decrease is also a function of time—i.e., if the pH is raised, the color very slowly decreases to its equilibrium value. Thus, if an acid bismuth solution containing thiourea is adjusted to pH 2 preparatory to a titration, there follows a troublesome drifting in absorbance readings throughout the titration, and a poor titration curve is obtained. However, if the bismuth solution is heated to about 70° C. for 10 to 15 minutes, after its pH has been adjusted to 2, there is no drifting whatsoever after the addition of thiourea. When the pH of an acidic bismuth solution is raised, there occurs an hydrolysis reaction which is slow at room temperature, and that the bismuth hydrolysis product has less tendency to react with thiourea than does the simple bismuth ion.

The wave length at which the titration is performed may be varied depending on the intensity of the bismuth-thiourea color. The absorbance maximum of the thiourea complex actually occurs in the ultraviolet (about 340 to 350 mμ, shifting somewhat as the ratio of bismuth to thiourea changes), but the yellow color is sufficiently intense to permit measurements at 400 mμ except near the extreme lower limit of the method.

Because there is no reference solution with which to compare the solution being titrated, once the titration has been started, it is necessary to guard against the possibility of the absorbance readings' falling below zero during the titration. This is the reason for setting the instrument before the addition of thiourea.

Procedure for Pure Bismuth Solutions. To the bismuth solution, containing from 0.5 to 10 mg. of bismuth, add 0.5 gram of solid chloroacetic acid and dilute the solution to about 100 ml. Adjust the pH to a value of about 2, using 1 to 1 ammonia or 5*M* sodium hydroxide. (Satisfactory titrations are obtained at pH values between 1.5 and 2.4.) Heat the solution to about 70° C., holding it at this temperature for 10 to 15 minutes. Cool the solution to room temperature, and transfer it to the titration cell. Position the cell in the spectrophotometer, and adjust the slit width and sensitivity controls to obtain an absorbance reading of zero. Then add 5 ml. of a 1*M* solution of thiourea in water. The absorbance will increase immediately to its maximal value, after which the titration may be commenced.

Results. A titration curve obtained in this manner is shown in Figure 2. The results of a number of titrations of pure bismuth solutions are also compiled in Table I. Although the results are not so accurate as those shown in Table I for the copper indicator, they are satisfactory in view of the small quantities of bismuth.

INTERFERENCES

The study of interfering ions was centered about the elements tin, lead, arsenic, and antimony, with which bismuth is commonly associated in samples encountered in practical analysis. A few other ions were also studied. A simple procedure prior to the actual titration permits the determination of small quantities of bismuth in lead-tin alloys containing arsenic and antimony.

Pribil and Matyska (*6*) pointed out that tin interfered in their amperometric titrations of bismuth with ethylenediaminetetraacetic acid. Such interference was also noted in the present study. Removal of tin as hydrous stannic oxide from a nitric acid solution of the sample is not satisfactory because of the tendency for bismuth to coprecipitate. Volatilization of the tin by fuming its hydrobromic acid–bromine solution with perchloric acid has been found very satisfactory. The standard procedure presented in the ASTM manual (*1*) can be used with only the minor modification of omitting phosphoric acid from the recommended solutions. (This is necessary because of the tendency of bismuth to precipitate in the presence of phosphate when the pH is raised to 2 prior to the titration.) Because arsenic and antimony are also removed during the volatilization of tin, the interference of these elements required no further study.

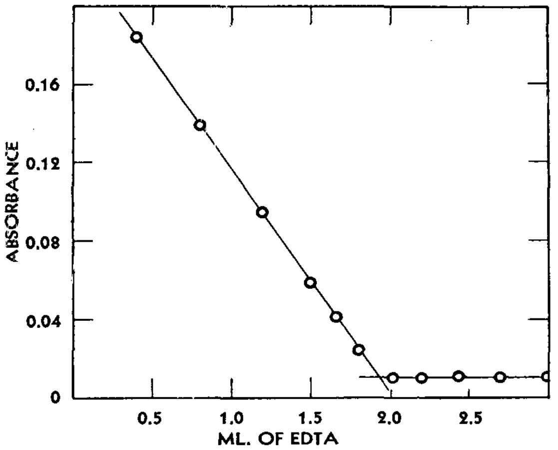

Figure 2. Titration of Bismuth with 0.01*M* Ethylenediaminetetraacetic Acid

4.18 mg. Bi; 400 mμ

The stability of the lead complex of ethylenediaminetetraacetic acid is approximately the same as that of the cupric complex. Thus lead can exert no interference so far as the actual titration process is concerned, but large amounts of lead can interfere with respect to the indicator systems. When thiourea is used as the indicator under the conditions given in the above procedure, the maximal permitted quantity of lead is about 1 gram. Larger quantities of lead form a precipitate with the thiourea. With 1 gram or less of lead, there is no noticeable interference. When copper is used as the indicator, still larger quantities of lead can be tolerated. Because lead and copper react with the titrant simultaneously, and because the lead complex is colorless, the effect of lead is to lower the slope of the rising portion of the titration curve past the bismuth end point. The extent to which this is troublesome depends upon the quantity of copper indicator present. Under these conditions, 3 grams of lead affects the slope only slightly and the end point not at all. The presence of 5 grams of lead affects the slope more markedly, and the end point is less sharp. Thus this method possesses the advantage of being relatively insensitive to large quantities of lead, especially when the indicator is cupric ion.

Obviously copper will not interfere when cupric ion is serving as indicator. With thiourea indicator, however, as little as 5 mg. of copper interferes by forming a precipitate with the indicator. Merely separating the precipitate does not suffice, because some bismuth is coprecipitated. Ferric ion interferes when either indicator is used, because its complex with the titrant is stable enough to form during the titration of bismuth. In addition, ferric ion appears to interact with thiourea.

To test the method under fairly realistic conditions, bismuth was determined in mixtures with tin, lead, arsenic, and antimony. The mixtures were prepared by weighing out the pure metals and hence the analysis of actual alloys was simulated. The following procedure was used to obtain the results presented in Table II.

Table II. Determination of Bismuth in Mixtures Containing Tin, Lead, Arsenic, and Antimony

Metals Taken, Mg.	Bi Found, Mg.	Error, Parts/1000
Sn 302 Pb 700 Bi 53.5	53.1	8
Sn 310 Pb 717 As 93 Bi 34.8	34.4	11
Sn 295 Pb 847 As 67 Sb 72 Bi 49.3	49.4	2
Sn 250 Pb 900 As 85 Sb 102 Bi 50.7	50.7	0
Sn 325 Pb 736 As 54 Sb 37 Bi 24.7	24.4	12
Sn 400 Pb 614 Bi 30.2	30.3	3
Sn 367 Pb 624 As 102 Sb 78 Bi 11.7	11.6	8

Procedure. For samples containing 0.5 to 10% bismuth, 1-gram portions may be taken for analysis. The size of the sample may be adjusted within wide limits depending on its bismuth content. Place the accurately weighed sample in a 250-ml. wide-mouthed Erlenmeyer flask. Add 10 ml. of a mixture prepared by adding 20 ml. of liquid bromine to 180 ml. of 48% hydrobromic acid. Cover the flask, and warm gently until the sample dissolves, avoiding excessive loss of bromine. Additional bromine may be added dropwise if required for complete solution and oxidation of tin. After the sample has completely dissolved, add about 10 ml. of perchloric acid (70 to 72%), and heat over a flame in the hood to expel tin, arsenic, and antimony bromides. When copious fumes of perchloric acid appear, heat intermittently so that condensation on the upper flask wall will wash the solid bromides back into the solution. Bumping is especially troublesome at this stage; therefore, the mixture must be kept in constant motion. After the lead and other bromides have been converted to perchlorates, the solution becomes clear and colorless. Finally, heat the solution until copious white fumes of perchloric acid appear. Turbidity in the solution seems to indicate that the tin has not been removed completely. If this is found, add more bromine–hydrobromic acid mixture, and repeat the above process.

Cool the solution, and dilute it to a convenient volume—e.g., 50 to 75 ml. Beyond this point, the procedure is the same as that given for pure bismuth solutions, with the choice of indicator depending upon the quantity of bismuth present and the interferences which may be expected.

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Estimation of Rubber in Asphalt

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As a corollary to the growing tendency to add elastomers to bitumen and asphalt, a method by which these polymers can be estimated quantitatively in mixtures is needed. The method of van Heurn and Begheyn has been adapted to a problem of current interest. By prolonged extraction with xylene or higher boiling solvents, raw or vulcanized natural or synthetic rubbers are separated from the stone chippings in asphalt. The rubber in this soluble fraction then reacts with a large quantity of sulfur and the rubber content is determined from a sulfur analysis of the purified ebonite. The influence of reaction time and temperature, the type of rubber and bitumen, and the viscosity of the mixture on the experimental error has been specified. Determination can be made of 2 to 10% of a previously, unidentified natural or synthetic rubber in asphalt and bitumen mixtures. The result is generally 10 to 20% higher than the true value. If the mixture has been heated above 265° C. prior to analysis, most of the rubber is irretrievably lost, but this pretreatment is revealed by a simultaneous hardening of the bitumen.

THE incorporation of natural rubber in asphalted roads (*1*) is being studied in this laboratory. The practical importance of the problem has had the effect of removing the estimation of rubber in asphalt from the academic sphere to the practical world of routine tests.

Following a recent convention, the word "bitumen" is used for the organic constituents of a mixture, while "asphalt" here means bitumen with (stone) chippings.

It is not easy to estimate natural rubber in the presence of several other organic compounds like bitumen and coal tar, as well as inorganic materials like chippings and fillers from the rubber. The common tetrabromide method of determining the rubber content cannot be used because bitumen likewise shows an insoluble bitumen bromide (*2*). Nor is it warranted, in the presence of other organic compounds, to resort to the oxidation of the rubber to acetic acid as a means to the desired end. Again, the addition of hydrochloric acid to the rubber in the bitumen-rubber mixture followed by the chlorine determination is prohibited in this case, because unsaturated compounds are also likely to be present in bitumen.

A tentative experiment was performed with the object of separating the rubber and bitumen chromatographically. Although separation was effected with the help of a carbon column, this technique was handicapped by the fact that the rubber could be recovered only after very prolonged elution, and then only in part. Moreover, this method is highly sensitive to the molecular weight of the rubber.

If the incorporated rubber is in a vulcanized form, the bitumen-rubber mixture can be extracted with carbon disulfide, leaving the insoluble rubber behind, but this method is reliable only if it is known for certain that there are no other compounds which are insoluble in carbon disulfide. Of this, of course, there can be no guarantee in advance with a random sample.

In order to circumvent all these drawbacks, the laborious method devised by van Heurn and Begheyn (*2*) for the analysis of rubber-bitumen mixtures was employed. This method effects the conversion of the rubber to insoluble ebonite by the use of sulfur in excess, the ebonite then being isolated from sulfur and bitumen by extraction with xylene. The sulfur content of the ebonite thus purified is then determined, because small amounts of contaminations always remain enclosed. The rubber content is then derived from the quantity of ebonite and the sulfur content.

The present authors were faced with the wider aspect of analyzing mixtures of bitumen or asphalt not only with unvulcanized natural rubber (*2*) but also with partly or fully vulcanized natural and synthetic rubbers. The original method has been adapted to this purpose by a number of apparently minor changes. Only oxidized rubber and bitumen-rubber mixtures heated to a very high temperature cannot be analyzed in this way.

EXPERIMENTAL

Equipment. The equipment used consisted of an oven heated electrically to 155° C. with a sand bath; a Soxhlet apparatus made of borosilicate glass; borosilicate glass tubes about 7.5 cm. long and about 2.0 cm. in diameter; glass rods; and Alundum extraction thimbles (thermal alumina 501, Thermal Syndicate, England).

Reagents. Distilled xylene, precipitated sulfur, and solid paraffin wax, free from sulfur, were used.

Materials. The following grades of bitumen and rubber were the subject of examination:

Bitumen. Most of the experiments were done with bitumen N 180–200, sulfur content 5.8%, purchased from Shell ex Pernis, 1951, and Mexphalte N 50–60, sulfur content 5.6%, purchased from Shell ex Pernis, 1950. In one experiment (see Table III) a blown bitumen was used, R 85–40, purchased from Shell ex Pernis, 1950.

Crepe of low protein content with 96% rubber hydrocarbon.

Natural rubber latex, the dry substance of which contained 97% rubber hydrocarbon (determined by oxidation with chromic acid) and 0.4% ash.

Pulvatex, unvulcanized natural rubber powder with 78% rubber and 17% inorganic carrier.

Mealorub, partly vulcanized rubber powder with 91% rubber, approximately 1.5% combined sulfur, and 3% ash.

GR-S latex, the dry matter of which contained 95 ± 3% of rubber consisting of 75 parts by weight of butadiene and 25 parts by weight of styrene.

Ground tires with 56% of rubber, 69% of which consisted of natural rubber and 31% of GR-S.

Reclaimed rubber; Liverpool Reclaim with 40% rubber.

Rubbone C, oxidized rubber with 19% oxygen.

Rubbone N, highly broken down rubber with approximately 0.4% oxygen.

Procedure. PRELIMINARY TREATMENT OF SAMPLE. In order to expel any inorganic contaminations—fillers from the rubber and/or chippings—the sample is extracted in an Alundum thimble in a Soxhlet apparatus for about 48 hours. van Heurn and Begheyn (*2*) in their study on mixtures of bitumen with natural rubber applied an extraction time of only 8 hours. The longer period proposed here is, however, essential in the analysis of unidentified mixtures, which may contain insoluble rubbers, as not all vulcanized rubbers dissolve completely after 8 hours. The xylene is then evaporated from the extract and, while the solution is still sufficiently fluid, it is poured into a weighed porcelain dish. The xylene is further evaporated off on a water bath and finally on a sand bath at roughly 140° C. The percentage of xylene-soluble material is calculated from the increased weight of the porcelain dish. If the sample contains vulcanized natural rubber, this is broken down and dissolved by the boiling xylene. Should there be any GR-S present in the asphalt, it is necessary to extract at a higher temperature with, for example, *o*-dichlorobenzene instead of xylene to dissolve the GR-S.

In the types of bitumen used here no organic matter was found in the insoluble fraction. On the other hand, pitch and tar have been reported to contain fractions insoluble in boiling xylene; these must be separated from the rubber fraction before analysis (*2*). This can be conveniently done by filtering the hot xylene solution over asbestos fiber and diatomaceous earth in a Gooch crucible. This point deserves special attention if unidentified mixtures are analyzed. All further treatments refer to this "xylene-soluble fraction." A sufficient quantity of the dried extract is weighed off to obtain 50 to 100 mg. of rubber, which usually means about 2 grams of sample. If the rubber content is not known even approximately, there is assumed to be 2% relative to the bitumen and, if necessary, an exact determination is performed later. The sample is weighed into a borosilicate glass tube.

Solid paraffin wax is next added to the sample in order to lower the viscosity. About 12% of the quantity of weighed-in sample is used. This manipulation is an amendment of the original procedure (*2*) and is essential for the analysis of known mixtures containing Reclaim or Mealorub but no fillers (see Table II). In this case the foregoing xylene extraction can be omitted. The material is then heated for roughly 20 minutes to 120° C. and is mixed thoroughly with a stirring rod, which remains with the sample in the tube.

Vulcanization to Ebonite. A quantity of sulfur equal to twice the weight of the specimen is now added and the tube is placed in an oven in a sand bath, the latter having previously been heated to a slightly higher temperature (160° to 170° C.) because of the inevitable cooling which ensues upon introducing the tubes. As soon as the bitumen has melted, the sulfur is stirred into it and the whole is then maintained at 155° C. for 4.5 hours, the mixture being stirred every hour to ensure thorough intermingling of the sulfur with the bitumen.

Extraction of Ebonite Fraction and Sulfur Determination. After the material has cooled, the tube and glass rod (which is cut off) are placed upside down in a weighed Alundum thimble and extracted, slowly at first but afterwards at an accelerated rate, with xylene. The Alundum thimble is stoppered with a wad of cotton wool. When the xylene has become colorless, the ebonite still clinging to the tube and rod is removed and transferred to the Alundum thimble, after which extraction is continued until the xylene is again colorless. This method is much more efficient than the usual extraction of free sulfur from ebonite with acetone. As traces of sulfur in hot xylene are revealed by a faint yellow hue and as the time of extraction is kept variable, all free sulfur is actually removed from the sample.

The extraction thimble is dried at 150° C. and then weighed, the difference in weight representing the percentage of insoluble material, which consists of ebonite contaminated by a small amount of bitumen. The sulfur content of this specimen is determined by the Carius test, the Carius tubes being heated to approximately 320° C. for about 20 hours.

Calculation. The rubber content of the soluble fraction extracted with xylene is derived from a, the quantity of insoluble material produced by reaction of the polymer with sulfur and expressed as a percentage of the initial material extracted with xylene, and b, the sulfur content of this ebonite fraction.

Because the ebonite fraction still contains a certain amount of bitumen, the true ebonite content has to be calculated from the sulfur content, b. If b is taken to be 32%, the amount of ebonite present is $\frac{b}{32} \times a\%$, instead of $a\%$. This percentage of ebonite corresponds to $\frac{ab}{32} \times \frac{68}{100}\%$ of rubber, where 68 is the molecular weight of the rubber and 100 that of an ebonite containing 32% of sulfur.

If there is a sulfur-containing inorganic filler in the asphalt which cannot be isolated by extraction, this filler will be enclosed in the ebonite, with the result that the sulfur content found will be too high. In that event, the procedure is to determine the ash content of the ebonite and the sulfur content of the ash. It is then necessary to correct b for this sulfur content.

The bitumen studied in this laboratory did not produce any insoluble sulfur-containing material after heating to 155° to 160° C. Only at 170° C. did a reaction of this type take place to a minor degree (see Table II). This again cannot be generalized and should be controlled for bitumen of other origin. The ebonite formed in samples of unknown composition can, if required, be analyzed qualitatively for natural or synthetic rubber.

RESULTS

Reaction of Unvulcanized Natural Rubber with Sulfur. In order to ascertain how ebonite is formed as the result of the reaction between natural rubber and sulfur under these experimental conditions, crepe of low protein content and sulfur were heated with solid paraffin wax (as a substitute for the bitumen) and treated in the manner described. The subjects of these investigations were mixtures of 95–5 and 50–50 parts of paraffin wax and of rubber. The results are recorded in Table I.

Table I. Reaction of Raw Rubber with Sulfur

Reaction Time, Hr., at 155° C.	Insoluble, %	S in Insoluble, %	Rubber, %	
			Found	Av.
	Mixture of 5% Rubber and 95% Paraffin Wax			
2.5	7.6	28.7	4.6	4.7
	7.8	29.1	4.8	
	7.5	29.5	4.7	
	7.3	29.6	4.6	
4.5	8.1	32.4	5.6	5.3
	7.8	32.1	5.3	
	7.7	31.1	5.1	
	8.0	29.8	5.1	
6.5	8.0	33.8	5.8	5.6
	7.9	33.0	5.6	
	8.0	32.0	5.5	
	7.9	32.6	5.5	
12.5	8.0	34.7	5.9	5.7
	7.4	34.7	5.5	
	7.8	35.2	5.8	
	7.5	34.0	5.4	
	Mixture of 50% Rubber and 50% Paraffin Wax			
4.5	78	33.3	55	52
	74	32.1	51	
	76	31.7	51	
	76	32.8	53	
6.5	79	33.6	57	56
	79	32.9	55	
	79	33.2	56	
	79	33.1	56	

After 4 to 5 hours of heating at 155° C., calculation from the sulfur content shows 106% of the quantity of rubber present in the xylene-soluble fraction. van Heurn and Begheyn found 100% of the rubber present after heating for 4 to 5 hours at 160° C. Hence approximately one sulfur atom is combined with one C_5H_8 group. After longer reaction periods, the quantity of combined sulfur increases slightly (*3*, *6*). After heating for 12.5 hours at 155° C., the apparent percentage of rubber derived from the sulfur content is, on an average, 114% of the amount of rubber actually present. Therefore, although the reaction proceeds approximately in accordance with the general formula

$$(C_5H_8)_n + nS \longrightarrow (C_5H_8\,S)_n$$

it does not do so stoichiometrically; it is known that not only addition of sulfur takes place but also substitution and evolution of hydrogen sulfide (*6*). As a matter of fact, in this work the value for rubber was generally found 10 to 20% too high (see Table II).

The excess of sulfur above one atom per C_5H_8 group after a fixed reaction time depends then on small changes in temperature and other experimental conditions. It therefore seems advisable especially when using the method repetitively—e.g., for control purposes where greater precision is required—in the analysis of mixtures of the same type of rubber and asphalt to calibrate the procedure against samples of known composition. The values obtained in the calibration test could then be used to correct other values obtained with the same materials.

The results reported here differ in a number of details from the work of van Heurn and Begheyn (*2*). This can be explained as follows:

> Sulfur determination by the Carius method gives more correct values than oxidation in an open system with nitric acid, the method used by van Heurn and Begheyn. According to the authors' experience the latter method gives results which are systematically too low with hard rubber. It is probably for this reason that they found values which were generally too low for the rubber content.
>
> The reaction of sulfur with rubber is like that of chlorine or oxygen with rubber—a mixture of substitution, addition, and cyclization (*3–5*) reactions which do not lead to a product $(C_5H_8S)_n$ but actually products of gradually changing compositions. Four and one-half hours at 155° C. was chosen as a fixed point, because the sulfur content increases only slowly with much longer times, while it is very susceptible to small changes in temperature at shorter reaction times. This result is in agreement with van Heurn and Begheyns' findings (Table 7 of their paper). For chemical reasons (*4, 5*) the present authors prefer a longer reaction time at 155° C. to 2 hours at 160° C. (Table 3 of their paper). Moreover, the danger of errors attributable to insoluble sulfurized bitumen increases with higher temperatures.

Table III. Estimation of Synthetic Rubber and Mixtures of Synthetic and Natural Rubber in Bitumen

Sample						Rubber Content, %			
Bitumen		Rubber		Insoluble, %	S in Insoluble, %				
%	Grade	%	Type			Found	Av.	Calcd. on RHC	Error
95.3	50/60	4.7	GR-S latex	7.4–7.2	31.6–32.0	5.1–5.2	5.2	4.6	+11
92	50/60	8	Ground tires	11.5	22.3	5.5	5.5	4.5	+22
92	85/40	8	Ground tires	11.1–11.9	16.8–16.2	4.0–4.1	4.1	4.5	− 9
85	50/60	15	Reclaim	16.4–16.6	18.0–18.2	6.4–6.3	6.4	6.0	+ 6

In these ratios of 95–5 and 50–50, the proportion of paraffin wax to rubber is immaterial. A few experiments were made without the addition of paraffin wax and it was found that after a 4.5-hour heating, the combined sulfur corresponds to 115% of the rubber originally present in the xylene-soluble fraction, even higher than when wax was added.

Estimation of Natural Rubber in Mixtures of Bitumen and Rubber. The mixtures of bitumen and rubber were made by first heating the bitumen until it was of thin liquid consistency, then adding the rubber, and mixing the two well together by stirring. The majority of samples were subsequently heated for 1 to 3 hours to 170° to 230° C., a procedure which did not affect the results of the determination. When rubber is added to asphalt before it is poured onto the road, it is likewise heated to approximately 170° C.

The three forms of natural rubber suitable for incorporation in asphalt are unvulcanized latex; Pulvatex (unvulcanized rubber as a powder with an inorganic carrier); and Mealorub (partially vulcanized powdered rubber).

The results of these estimations will be found in Table II. The figures refer to the lowest and highest values of four to six analyses per mixture. The theoretical value is calculated from the rubber content of the starting material, assuming that each double bond reacts with only one atom of sulfur. Only in the case of the sample containing Mealorub and bitumen 50/60 was the quantity of rubber estimated far too low, but even here satisfactory results are obtained if the viscosity of these specimens is reduced by adding 12% of paraffin wax at the beginning of the analysis.

Table II. Estimation of Rubber in Bitumen-Rubber Mixtures

Sample						Rubber Content, %			
Bitumen		Rubber		Insoluble, %	S in Insoluble, %				
%	Grade	%	Type			Found	Av.	Calcd. on C_5H_8	Error
100	50/60	0	..	0.5	5.5	0.06	..	0	..
100	50/60	0	..	1.0–1.5[a]	14	0.4	..	0	..
97.7	50/60	2.3	Latex	4.0–3.9	30.1–30.8	2.6–2.5	2.6	2.2	+18
95	50/60	5	Latex	8.6–8.4	31.4–30.7	5.8–5.5	5.7	4.9	+16
90	50/60	10.1	Latex	16.4–16.9	30.6–31.4	10.6–11.3	11.0	9.8	+12
95	180/200	5	Pulvatex	7.3–7.5	30.2–29.8	4.7–4.8	4.8	3.9	+23
95	50/60	5	Pulvatex	7.2–7.5	28.8–30.2	4.4–4.8	4.6	3.9	+18
95	180/200	5	Mealorub	8.3–8.2	30.1–30.5	5.3–5.3	5.3	4.6	+15
95	50/60	5	Mealorub[b]	5.3–5.4	16.9–16.9	1.9–1.9	1.9	4.6	−59
95	50/60	5	Mealorub[c]	7.3–7.8	31.3–31.2	4.8–5.1	5.0	4.6	+ 9

[a] Heated for 5 hours at 170° C.; other samples heated only 4.5 hours at 155° C.
[b] Viscosity of these samples was too high.
[c] Paraffin wax (12%, relative to whole sample) was added to these samples.

The sample with bitumen 180/200, which is of lower viscosity, did produce the correct values with Mealorub. The inference is that, if the sample contains Mealorub, the viscosity of the specimen must be either low or else reduced by the addition of paraffin wax. To make sure that the viscosity was low enough, therefore, paraffin wax was always added to samples of unknown composition.

Estimation of Natural Rubber in Road Carpet Mixture. The rubber content of a road carpet mixture which contained 86% chippings and 14% bitumen was estimated. The calculated rubber content of this sample was 0.35%, relative to the total amount of the constituents. The specimen was dissolved in carbon disulfide and the solution poured off from the stones. The stones were washed several times with carbon disulfide to make sure that all the bitumen and rubber had been collected. The carbon disulfide solutions were collected and evaporated until dry. An alternative to this decantation of carbon disulfide would have been extraction with xylene.

The rubber content of the evaporated sample was estimated as ebonite in the ordinary way; 22.3 to 23.5% of insolubles, expressed as a percentage of the initial decanted material, was found. The sulfur content of this insoluble portion was 5.2 to 5.4%, which corresponds to 2.5 to 2.7% of rubber, relative to the bitumen. Relative to the total sample this comes to 0.35 to 0.38%, which is in excellent agreement with the quantity calculated as being present.

Synthetic Rubber, Reclaimed Rubber, and Ground Tires. A minor môdification of the computation is required if GR-S (75 parts by weight of butadiene and 25 parts by weight of styrene) is used, but the variation is within the margin of error. Table III lists the results obtained with mixtures of bitumen and GR-S latex, bitumen and reclaimed rubber, and bitumen and ground tires. While these mixtures were being made, they were heated to 170° to 200° C. for 3 to 6 hours. The results are reasonably good.

Oxidized Rubber and Degradated Rubber. To discover whether this technique can also be used for oxidized rubber and depolymerized rubber, one sample of each was examined—viz., Rubbone C with 19% oxygen, and Rubbone N, which contains the normal amount of oxygen occurring in rubber. Ninety-six per cent of Rubbone N but only 53% of Rubbone C was traced, which means then that rubber of low viscosity is for the most part identified but only a portion of oxidized rubber is traceable. The method is, therefore, unsuitable for rubber derivatives containing oxygen.

Overheating of Bitumen-Rubber Mixtures. Before the bitumen-rubber compound is mixed with the mineral aggregate in road construction, it is heated. In order to determine to what temperature these compounds can be heated with

Table IV. Effect of Overheating on Reactivity of Bitumen-Rubber Mixture

(Mixture. 95% bitumen 50/60 and 5% Pulvatex)

Preheating of Sample				Rubber Content, %			
Temp., ° C.	Time, Hr.	Insoluble, %	S in Insoluble, %	Found	Average	Calcd. on C_5H_8	Error, %
230	1	7.4–7.4	28.9–28.6	4.5–4.5	4.5	3.9	+15
260	2.5	6.6–6.5	21.4–21.9	3.0–3.0	3.0	3.9	−23
295	2	1.7–1.7	0.7–1.3	0.02–0.05	0.04	3.9	−99

impunity so far as this test is concerned, a few specimens were heated to a high temperature. One sample of bitumen-Pulvatex was heated to 230°, 260°, and 295° C.; at 295° C. the bitumen hardened to such an extent that it would have been unusable for road making. The results of these experiments (see Table IV) show that after 2 hours of heating at 295° C., nearly all traces of the rubber vanished. Natural rubber is known to undergo cyclization and degradation at this temperature. Obviously then, these degradation products do not form insoluble rubber derivatives with sulfur.

Since synthetic rubber changes thermally in a different way, it may be that this, on the contrary, would be identifiable after being heated. This implies that the negative result of a rubber estimation in bitumen is conclusive only if the mixture has not been overheated in the course of the procedure.

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Determination of Germanium in Coal, Coal Ash, and Flue Dust

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This investigation was undertaken to develop a rapid and accurate method for the determination of small amounts of germanium such as exist in coal and waste products. A chemical method is described in which the germanium is converted to Ca_2GeO_4, separated as germanium tetrachloride by distillation, and determined as cinchonine germanomolybdate. A spectrochemical method for coal and coal ash is also described, in which bismuth is added as an internal standard and a direct current arc is used as the means of excitation. For small amounts of germanium, the spectrochemical method is more sensitive and also less time-consuming than the chemical method after synthetic standards have been prepared and working curves established.

In CONNECTION with a survey of coal deposits and byproducts of coal combustion, a search was made for a method of determining germanium in these materials. It was found that a comprehensive study of the chemical reactions of both organic and inorganic compounds of germanium had been made by Johnson (*3*, *4*) and Krause and Johnson (*5*) in this country; Davies and Morgan (*1*) in Great Britain investigated a number of analytical procedures. Headlee and Hunter (*2*) and Rusanov and Bodunkov (*6*) described procedures for spectrographic determination of germanium.

The present paper evaluates some of these methods and describes a new procedure for treating material so as to prevent volatilization of germanium compounds and to render them soluble in hydrochloric acid.

CHEMICAL METHODS

The preliminary treatment for coal consisted of oxidizing the coal with concentrated sulfuric and nitric acids and also of igniting similar samples with calcium carbonate at 1000° C. Samples of coal ash and of flue dust were fused with sodium carbonate and duplicates of these samples were ignited with calcium carbonate at 1000° to 1050° C. In all cases, the ignited samples were treated with hydrochloric acid and the germanium was separated from interfering elements by distillation. The germanium was then determined in the distillate.

In considering methods for determining the amount of germanium in the distillate, one of the methods recommended by Davies and Morgan (*1*) was investigated. It consisted of precipitating the germanium as cinchonine germanomolybdate and weighing it as such. In the present investigation, it was found necessary to change this procedure somewhat because the distillate amounted to more than 40 ml. The nitric acid concentration was kept low to reduce the possibility of precipitating molybdic acid, and the solution was kept ice cold because a lower blank was obtained than when working at room temperature.

ANALYTICAL PROCEDURE

Mix 5 grams of the 100-mesh coal sample with fine reagent grade calcium carbonate and transfer the mixture to a porcelain dish or to a wide-form crucible. If the amount of germanium in the sample is more than 3 mg., use a sample smaller than 5 grams. Above 3 mg. of germanium, the precipitate becomes bulky and difficult to filter; this increases the time required to make the determination. Place the dish containing the mixture in a muffle furnace. Hold the furnace at 480° C. until all the volatile matter has been removed from the coal, then heat to 1000° C. and hold at this temperature for 1 hour. Coal ash samples can be placed directly in the muffle at 1000° C. Flue dust should be heated at 1050° C. for 1 hour.

Remove the sample from the muffle, cool, and transfer the ignited residue to a distilling flask. Add 100 ml. of water and 2 ml. of potassium chromate solution. Place a 250-ml. tall-form beaker containing 100 ml. of ice-cold water under the condenser so that the tip of the condenser extends to within 1/4 inch of the bottom of the beaker. Keep the water in the beaker ice cold by surrounding it with ice. Next, add 200 ml. of concentrated hydrochloric acid to the distilling flask, bubble carbon dioxide through the acid, and start the distillation by applying heat. Continue the distillation until 50 ml. has distilled over.

Transfer the distillate to a 600-ml. beaker and adjust the volume of the solution to 250 ml. with distilled water. Cool in ice water and neutralize with ammonium hydroxide (methyl red indicator). To prevent local overheating and consequent loss of germanium, stir the solution continuously while the ammonium hydroxide is being added. Conduct the neutralization by adding ammonium hydroxide until a distinct yellow is obtained, and then add 2*N* nitric acid until the first pink color appears. Dilute the solution to 400 ml. with distilled water and cool to 10° to 15° C. in ice water.

Add 20 ml. of 25% ammonium nitrate solution, 16 ml. of 2% ammonium molybdate solution and 30 ml. of 2*N* nitric acid, and stir until thoroughly mixed. Add 9 ml. of cinchonine solution and stir. Let stand for 3 hours in ice water, filter through a weighed, fine-texture, Selas crucible, and wash 5 times with ammonium nitrate solution. Dry the crucible and precipitate in an oven at 160° C. for 2 hours, cool in a desiccator, and weigh. The increase in weight represents cinchonine germanomolybdate.

Two blanks should be run with each lot of samples and the germanium found in the sample should be corrected by the amount of the average blank.

Calculation:

$$\frac{(\text{Wt. of ppt.} - \text{wt. of blank}) \times 2.955}{\text{Wt. of sample}} = \%\ \text{Ge}$$

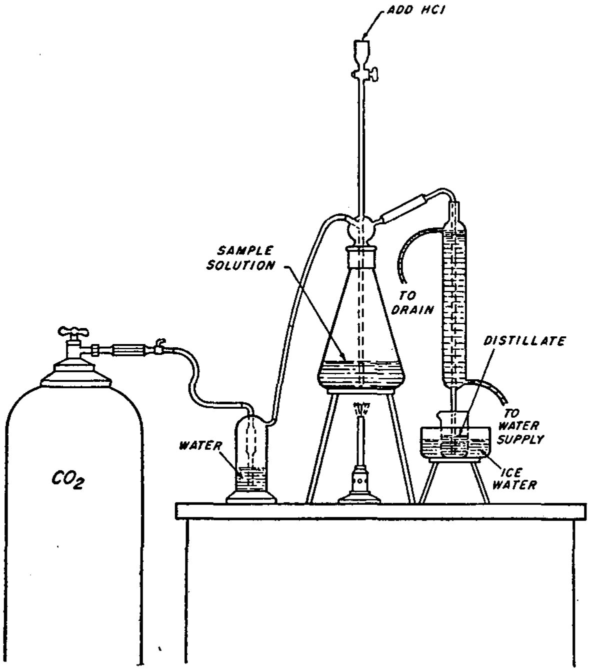

Figure 1. Apparatus for Distilling Germanium Tetrachloride

Special Reagents Required. AMMONIUM NITRATE, 25%. Dissolve 250 grams of ammonium nitrate in water and dilute to 1000 ml.

AMMONIUM MOLYBDATE, 2%. Dissolve 20 grams of $(NH_4)_6Mo_7O_{24}.H_2O$ in 1000 ml. of distilled water.

NITRIC ACID, 2*N*. Dilute 127 ml. of nitric acid to 1000 ml. with distilled water.

CINCHONINE, 2.5%. Dissolve 25 grams of cinchonine in 1000 ml. of 2.5*N* nitric acid.

NITRIC ACID, 2.5*N*. Dilute 159 ml. of nitric acid to 1000 ml. with distilled water.

AMMONIUM NITRATE SOLUTION. Dissolve 25 grams of ammonium nitrate in 1000 ml. of water that contains 50 ml. of 2*N* nitric acid.

POTASSIUM CHROMATE SOLUTION. Dissolve 50 grams of potassium chromate in 100 ml. of distilled water.

EXPERIMENTAL WORK

The accuracy and precision of the cinchonine germanomolybdate method was determined with solutions containing known amounts of germanium. Solutions were prepared from two separate lots of germanium(IV) oxide by dissolving a weighed amount of each lot in sodium hydroxide and diluting to 1000 ml. with distilled water. Each milliliter of solution 1 contained 0.069 mg. of germanium and each milliliter of solution 2 contained 0.091 mg. of germanium. The analysis of aliquots of these samples checked whether they were distilled through the apparatus in Figure 1 or not.

A series of synthetic samples containing known amounts of germanium was analyzed by the procedure described. The calculations were based on the assumption that the cinchonine germanomolybdate molecule contained four cinchonine radicals. According to this assumption, the germanium content of the compound is 2.385% (factor 0.02385). The results obtained with this factor, Table I, were low by approximately 20%.

Table I. Use of Factors 0.02385 and 0.02955 for Calculating Germanium Content

Ge Added, Mg.	Ge Found, Mg. (Factor 0.02385)	Deviation, Mg.	Ge Found, Mg. (Factor 0.02955)	Deviation Mg.
0.69	0.52	−0.17	0.65	−0.04
0.91	0.78	−0.13	0.95	+0.04
0.91	0.72	−0.19	0.89	−0.02
0.91	0.70	−0.21	0.87	−0.04
0.91	0.75	−0.16	0.92	+0.01
0.91	0.74	−0.17	0.87	−0.04
1.04	0.83	−0.21	1.03	−0.01
1.37	1.14	−0.23	1.41	+0.04

Table II. Theoretical Composition and Actual Analysis of Compound

	Theoretical Composition, %			Molecular Wt.
	C	Mo	Ge	
$(C_{19}H_{22}ON_2)_4H_4(GeMo_{12}O_{40})$	29.97	37.66	2.385	3046
$(C_{19}H_{22}ON_2)_2H_4(GeMo_{12}O_{40})$	18.58	46.87	2.955	2457
	Actual Analysis of Ppt., %			
	20.85	44.02	...	

Since this factor gave low results, the germanium content was recalculated, assuming two cinchonine radicals in the molecule. This compound has a germanium content of 2.955% (factor 0.02955). The results obtained with this factor (Table I) were correct within the limits of experimental error.

Table II shows the theoretical percentages of carbon, molybdenum, and germanium for the formulas $(C_{19}H_{22}ON_2)_4H_4(GeMo_{12}O_{40})$ and $(C_{19}H_{22}ON_2)_2H_4(GeMo_{12}O_{40})$. Since the factor derived from the latter formula gave correct results, it was decided to make a chemical analysis of the cinchonine germanomolybdate precipitated under the conditions outlined in the analytical procedure. The carbon and molybdenum contents were found to be 20.85 and 44.02%, respectively (Table II). A higher carbon content and a lower molybdenum content were obtained than indicated by the formula. Until further work is done, such as determining the molecular weight of the compound, the factor 0.02955 must be considered empirical.

SPECTROCHEMICAL METHODS

At the time this investigation was undertaken, only two quantitative spectrochemical methods for germanium in coal or coal ash were found in the literature One was a total energy method developed by Headlee and Hunter (*2*) and the other was an internal standard method for coal ash devised by Rusanov and Bodunkov (*6*). The methods described here are similar to that of Rusanov and Bodunkov (*6*) with respect to the internal standard element but the techniques of the methods are different.

EXPERIMENTAL WORK

Because the composition of coal varies considerably, it was necessary to add as an internal standard an element that does not occur in coal and that has physical characteristics similar to those of germanium. Bismuth was found to be suitable for this purpose.

The standards used for the calibration of the methods were prepared synthetically. The coal standards were made by mixing a weighed amount of C.P. germanium(IV) oxide with a weighed amount of germanium-free coal. A portion of this first standard was then mixed with a portion of the coal to produce a second standard. This dilution procedure was repeated to obtain five standards covering the range 0.0005 to 0.0065% germanium.

The coal ash standards were prepared in a similar manner, the matrix being a sample of germanium-free coal ash. Nine standards were made covering the range of 0.0013 to 0.67% germanium.

The procedure developed for the analysis of coal differed slightly from that for the analysis of coal ash. To every 7 parts of a coal sample, 1 part of bismuth(III) oxide was added. To every 3 parts of a coal ash sample, 4 parts of pure graphite powder and 1 part of bismuth(III) oxide were added. Each combination was thoroughly mixed and then packed into a sample electrode, which was a high purity graphite rod, 2 inches long and $^1/_4$ inch in diameter, having a center post and a 1 mm.-deep crater.

The samples were excited by a rectified direct current arc discharge; the counter electrodes being high purity graphite rods $^1/_4$ inch in diameter, having 120° conical tips. The excitation conditions are shown in Table III. (The use of counter electrodes of $^1/_8$-inch diameter gave less reproducible results, despite the smoother burning arc produced.)

A grating spectrograph having a first-order plate factor of about 3.4A per mm. was used for these analyses. Each sample was analyzed in triplicate.

RESULTS

The results of the analysis of four coal samples and eleven coal ash samples are shown in Tables IV and V.

The reproducibility of the methods was investigated by using one coal sample and four coal ash samples. The results are shown in Table VI. The reproducibility of the results for germanium in coal ash is comparable to that generally obtained with direct current arc excitation at similar concentration levels. The reproducibility of the results for germanium in coal is poor. The reason for this had not been determined but it is believed that the large amount of combustible matter in the coal may cause erratic excitation of the sample.

Table III. Excitation Conditions for Spectrochemical Determination of Germanium

Discharge Conditions	Coal Ash Analysis	Coal Analysis
Capacitance, microfarads	60	60
Inductance, microhenries	400	400
Resistance, ohms	15	15
Output potential, volts	340	340
Current, amperes	12	12
Time, seconds	90	90
Sample electrode	Lower and positive	Lower and negative[a]
Analytical gap, mm.	3	3

Spectrograph Conditions	
Coal analysis (0.0005 to 0.008% Ge)	16-Micron entrance slot 25% Incident light transmitted to entrance slit First-order spectrum 2170–3900 A.
Coal ash analysis (0.001 to 0.05% Ge)	10-Micron entrance slit 25% Incident light transmitted to entrance slit First-order spectrum 2170 to 3900 A.
Coal ash analysis (0.03 to 0.4% Ge)	14-Micron entrance slit 100% Incident light transmitted to entrance slit Second-order spectrum 2525 to 3350 A.

[a] Reversed polarity is used here to increase line-to-background ratios.

Table IV. Determination of Germanium in Coal

(Comparison of Kjeldahl, calcium carbonate, and spectrochemical methods)

	Ge, %		
Sample No.[a]	Kjeldahl method	Calcium carbonate method	Spectrochemical method
6	0.001	0.004	0.0037
7	0.001	0.005	0.0031
8	<0.001	0.004	0.0040
10	<0.001	0.005	0.0030
11	0.003	0.006	....
12	0.002	0.007	....
13	<0.001	0.006	....
14	<0.001	0.003	....

[a] Germanium content of ash from coal samples 6, 7, 8, 10, and 11 was determined and is shown in Table V.

Table V. Determination of Germanium in Coal Ash and Flue Dust

		Ge, %		
Sample No.	Ash in Coal, %	Sodium carbonate method	Calcium-carbonate method	Spectrochemical method
1	3.29	0.001	...	0.0020
2	17.55	0.001	0.001	0.0016
3	1.34	0.21	0.24	0.25
4	3.55	0.025	0.033	0.037
5	1.77	0.030	0.039	0.034
6	8.32	0.027	0.049	0.048
7	17.44	0.015	0.029	0.023
8	6.87	0.046	0.053	0.057
9	16.88	0.011	0.016	0.014
10	5.92	0.014	0.020	0.018
11	4.98	0.041	0.100	0.063
15	Flue dust	0.025	0.017	....

Table VI. Spectrochemical Determination of Germanium

(Results of reproducibility tests)

Material	Mean Value of Concn., Ge, %	No. Detns.	Max. Spread, Ge, %	Av. Deviation, Ge, %
Coal	0.0028	22	0.0020	±0.0006
Coal ash	0.0034	23	0.0010	±0.0002
Coal ash	0.026	23	0.009	±0.001
Coal ash	0.052	24	0.012	±0.002
Coal ash	0.25	24	0.04	±0.01

DISCUSSION

The investigation was continued by analyzing a number of coal, coal ash, and flue dust samples for germanium. Table IV compares the results obtained by the sulfuric and nitric acid oxidation method (Kjeldahl method), the calcium carbonate method, and the spectrochemical method for various coal samples. In all cases, the results obtained with the calcium carbonate method are higher than those obtained with the Kjeldahl method and are in better agreement with the results obtained with the spectrochemical method for the four samples run by that method. An examination of these data shows that not all the germanium is recovered with the Kjeldahl procedure. Since the results obtained with the calcium carbonate method are as high as or slightly higher than those obtained with the spectrochemical method, it is believed that all the germanium in coal is recovered with the calcium carbonate method. For coals containing from 0.001 to 0.010% germanium, the accuracy of the calcium carbonate method, in conjunction with the cinchonine germanomolybdate precipitation, is judged to be ±0.001% germanium.

Table V compares the results obtained with the sodium carbonate method, the calcium carbonate method, and the spectrochemical method for various samples of coal ash and flue dust. The results obtained with the calcium carbonate method are appreciably higher in nearly every case than those obtained with the sodium carbonate fusion method and they are in better agreement with the results obtained with the spectrochemical method. Sample 11 is an exception, but the distillation of the dissolved calcium carbonate residue was conducted without the addition of potassium chromate and the high germanium content may be due to the presence of arsenic.

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Anthrone in the Estimation of Hexose Sugars

With Special Reference to Pentose Interference

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A method has been developed whereby errors in the estimation of hexose sugars resulting from the premature and/or irregular mixing of the reagent and test solution are eliminated. A spinning disk is used to produce a centrifugal force which keeps reactants in separate layers until the moment of mixing. With controlled anthronation the study of interference from pentoses was greatly facilitated. Increase in pentose-hexose ratio and/or concentration of sulfuric acid in the reagent produces a shift from 625 to 680 mμ in maximum absorption. With less concentrated acid it remains unchanged at 625 mμ and the total interference of pentoses is greatly reduced.

THE wide use of the anthrone reagent introduced by Dreywood (*4*), in the estimation of sugars, oligosaccharides, and derivatives of polyhexose units (*1*, *2*, *5*, *6*, *8–12*) confirms the usefulness of this reagent. Numerous modifications in procedure, adopted to obtain reproducible results, are evidence of the difficulty in controlling the anthronation reaction. It appears that the concentration of acid in the reagent, and the manner in which the reagent and test solution are brought together determine the nature and intensity of the color developed, and so affect the reproducibility of results. The method described here affords some degree of precision.

During investigations of the anthrone reaction there was evidence that the presence of pentose sugars could cause serious interference with the determination of hexoses (*7*). When pentose alone is anthronated under conditions similar to those used for hexose a transient blue-green color develops and rapidly deteriorates to yellow. Under special conditions, this blue-green color can be made to persist long enough for it to form the basis of a method of pentose estimation (*3*). The more stable yellow complex is equivalent at 625 mμ to a 6% equimolar hexose. However, an anthronated pentose-hexose mixture may give a complex which differs vastly from that obtained on separately mixing anthronated hexose and pentose. The data indicate that pentose interference in hexose determinations depends largely on the composition of the anthrone reagent. The methods described greatly reduced interference but with some materials, care is necessary for the interpretation of results.

METHOD

The anthrone reagent normally is prepared as a solution in 92 to 95 volume % sulfuric acid. When this reagent is mixed with the aqueous solution of test sample, considerable heat is evolved. Slight variations in the mixing technique have been found to give marked differences in the intensity of color development. Morse (*10*) and Barnett and Miller (*1*) added the reagent so that a separate layer was formed below the test solution, and then rapidly mixed the two layers. Viles and Silverman (*12*) added the reagent rapidly with continuous mixing. Koehler (*8*) used this method, but cooled the test tubes during mixing. Black (*2*) and Fairbairn (*6*) avoided heating through hydration by using a lower concentration of acid, and then heated the mixture on a water bath to obtain full development of color.

Difficulties have been experienced in this laboratory in reproducing results when these techniques were used. The use of weaker acid helps to minimize the effect of irregular mixing, but is accompanied by loss of sensitivity and slower color development (Table I). Below a certain concentration of acid (approximately 56 volume %) separation of anthrone and decomposition of the complex occurs.

The use of more concentrated acid appears to be essential if the method is applied to certain complex polyhexoses, and it is desirable for general routine purposes where there is no interference from pentoses. The problem was to devise a means of getting the reagent into proximity with the test solution so that instantaneous mixing could be attained. This can be done with the aid of a small conical flask centrally mounted on a spinning disk (Figure 1). The reagent is added down the side of the rotating flask, and centrifugal force collects it around the wide bottom of the flask. This allows ample time for delivery of the viscous reagent without the risk of premature reaction. When addition is complete, the flask is removed from the disk, shaken quickly, and then allowed to stand in a water bath for optimum color development. Using this method, the standard error of a single reading on an absorptiometer, graded from 0 to 1, is 0.004, and is equivalent to a deviation of about 1γ of hexose.

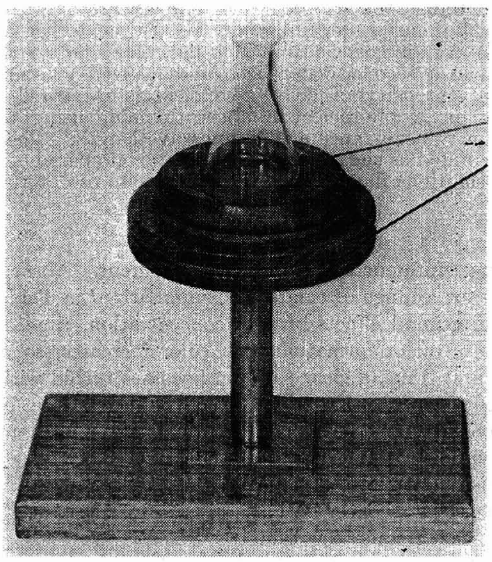

Figure 1. Spinning Disk Used in Anthronation Procedure

Apparatus. A disk (11-cm. diameter), with four spring clips for holding a 30-ml. conical flask in a recess at the center, is mounted on a vertical shaft (10 cm. high). The disk also acts as a pulley for a belt driven by a stirrer motor. The spinning movement of the disk is started and stopped by moving the stand away from or toward the motor, thus tightening or loosening the tension in the belt.

The spectral measurements were made on a Beckman Model DU spectrophotometer, with 1-cm. Corex-glass cells and anthronated blanks. Maximum intensities of color developed were measured on Hilger absorptiometer H 760.

Chemicals. One hundred milligrams of anthrone (British Drug Houses laboratory reagent) is dissolved in 100 ml. of sulfuric acid diluted to the required concentration using analytical grade (specific gravity 1.838 at 20° C.), shaken to ensure homogeneity,

Table I. Absorptiometer Readings for Glucose Anthronated under Varying Conditions

(Means of duplicate estimations)

Acid Vol.[a]	Temp., ° C.	Time, Min.	Glucose, γ 30	60	90	120	180
96.4	80	5	0.882	0.750	0.634	0.536	0.342
94.5	80	6	0.867	0.752	0.640	0.542	0.342
81.0	90	7	0.907	0.815	0.714	0.642	0.493
75.2	90	20	0.923	0.835	0.742	0.668	0.510
69.4	90	15	0.913	0.826	0.757	0.670	0.560

[a] Ratio of reagent to test solution is 3 to 1 except for 69.4 acid vol. % which was 5 to 1.

Table II. Wave Lengths for Maximum Absorption for Complexes Produced by Anthronation

Molecular ratio, arabinose to glucose	0.75:1	1:1	1.5:1	1.7:1	2:1	2.4:1	3:1	3.5:1	4:1
Maximum absorption, mμ	635	645	650	665	670	675	680	675	670

and allowed to stand for at least 12 hours. Anthrone reagent keeps well when stored away from light and at temperatures of 0° to 3° C. Before using, the reagent is warmed to 20° C.

The following sugars were used: glucose (B.D.H. analytical grade), L-arabinose, D-xylose, D-ribose and fructose (both B.D.H. and Light's, laboratory grades), and D-levulose (C.P., Pfanstiehl Chemical Co., Waukegan, Ill.).

Anthronation Technique. The reaction is carried out in 30-ml. Erlenmeyer flasks, selected for uniformity, with 3 ± 0.003 ml. of test solution in each flask. Each flask in turn is placed on the disk and allowed to revolve at about 400 r.p.m. From a pipet with rapid delivery 9 ± 0.05 ml. of reagent is added on the side in such a way that it "slides" along the walls and forms a separate layer in the flask. As the flask is removed from the disk the two layers are immediately mixed with a sharp shake. Then the flask is placed on a wire platform, at a depth of 1.5 cm., in a water bath at a selected temperature of 80° or 90° C. for 5 to 30 minutes, depending on the acid concentration of the reagent. At the correct time each flask is cooled to room temperature in a second water bath and allowed to stand for 30 minutes. Intensity of color developed is measured in 1-cm. cuvettes on a photoelectric absorptiometer using filters for maximum transmittance at 625 mμ wave length. The readings are interpreted as sugar values from graphs prepared of standard glucose solutions included in the same group of determinations.

DISCUSSION

Factors Influencing Color Development. Absorptiometer readings for a range of conditions, summarized in Table I, illustrate the general effects of acid concentration, time, and temperature on color formation. As color increases, so deterioration occurs; thus, a clear solution becomes turbid with decomposition products. Experience soon indicates the degree of color, which can be developed safely without interference from this source. In general, the lower the concentration of acid, the greater the time and/or temperature required to develop the optimum color. When optimum color is developed, the color intensity for a given quantity of hexose tends to be less with more dilute acids.

Pentose Interference. Measurements with combinations of arabinose, xylose, and ribose with glucose or fructose in concentrated acid indicate the same extent of interference in all cases (7). The spectral curves shown in Figure 2 are typical for mixtures of pentoses and hexoses under a range of conditions. The interference appears to be due to an interaction between the two types of sugar molecules and/or their products; it reaches a maximum value when the pentose-hexose molecular ratio is 2.7 (±0.3) to 1. Moreover, the form of the absorption curve is changed.

Effect of Pentose-Hexose Ratio. Solutions containing 60 γ of glucose, and varying amounts of arabinose were anthronated with concentrated (96.4 volume %) reagent. The absorption curves were determined and are given in Table II. The maximum absorption wave length was found to shift from 625 mμ for pure hexose to 680 mμ for the 3 to 1 ratio of arabinose to glucose. Absorption measurements at 625 mμ therefore do not measure the full interference by arabinose.

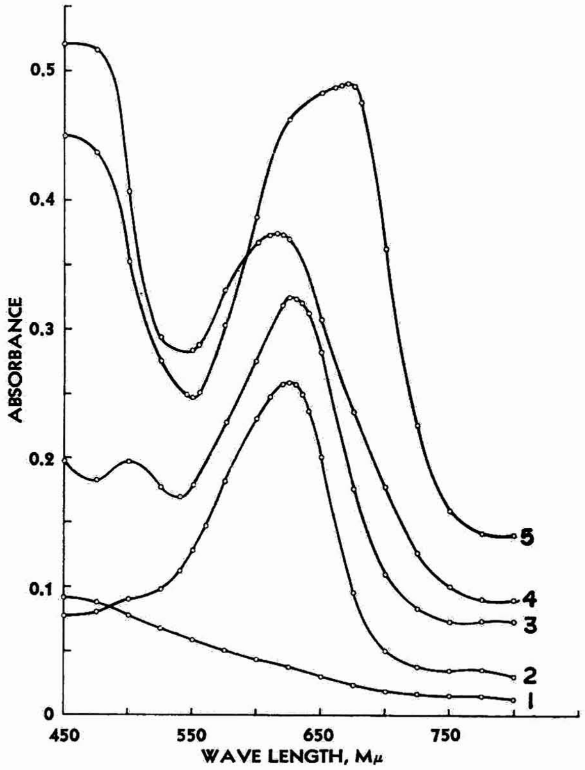

Figure 2. Absorption Spectra for Sugar-Anthrone Complexes at 22° C.

For all curves final concentration of anthronated sugars was 150 γ of arabinose and/or 75 γ of glucose in 12 ml. of solution.

Table III. Pentose Interference

Acid, Vol.[a] %	Temp., ° C.	Time, Min.	Pentose-Glucose Ratio, γ 25:30 Diff.[b]	Dev.[c]	25:60 Diff.	Dev.	50:60 As Hexose, γ Diff.	Dev.	100:60 Diff.	Dev.	100:120 Diff.	Dev.
						Arabinose						
96.4	80	5	7.5	<2	11.3	<2	16.9	<4	35.0	<15	48.8	<15
94.5	80	6	6.0	<2	9.0	<2	16.2	<4	26.2	< 9	33.8	< 9
81.0	90	7	2.0	<1	2.5	<1	4.0	<2	10.8	< 5	12.0	< 5
75.2	90	11	3.7	0	2.5	0	8.8	0	12.5	< 2	12.5	< 2
69.4	90	15	2.0	<1	1.5	<1	6.3	<2.5	10.0	< 4	16.3	< 4
69.4	80	30	2.0	<2	4.6	<2	9.2	<5	13.3	< 5	18.2	< 5
						Xylose						
75.2	90	30	1.9	<1	2.5	<1	4.4	<2	10.0	< 4	16.3	< 4
						Ribose						
81.0	90	10	0	0	2.5	0	4.0	0	9.0	< 2	14.5	< 2

[a] With 69.4% acid, ratios of test solutions to reagent were 2:10 to maintain a final concentration of acid sufficient to prevent breakdown; for others, ratios were 3:9.

[b] Actual difference between amount of apparent hexose in pentose-hexose mixture estimated by anthronation procedure using glucose as reference standard, and amount of glucose known to be present.

[c] Deviation expected when pentose is included in mixture, determined from pure pentose solution, and expressed as if absorption was due to glucose.

Effect of Reagent Concentration on Error. Absorption curves for complexes obtained with dilute and concentrated reagents are shown in Figure 2. For curves 1, 2, and 3 dilute (81 volume %) sulfuric acid was used in the reagent. Curves 1, 2, and 3, respectively, are typical for pentose alone (150 γ anthronated arabinose), hexose alone (75 γ anthronated glucose), and the mixture of arabinose and glucose (the same concentrations as for curves 1 and 2) mixed before anthronation. They indicate some mild interaction, for the total absorption of the mixture is greater than can be accounted for with the absorption contribution from the individual components (curves 1 and 2). The wave length of maximum absorption, however, remains unchanged at 625 mμ.

For curves 4 and 5 concentrated (96.4 volume %) sulfuric acid was used in the reagent. Curve 4, typical for a mixture of pentoses and hexoses, was obtained from independently anthronated solutions of arabinose (300 γ) and glucose (150 γ), mixed to same concentration as curve 5, just before the measurement. Curve 5 was obtained when arabinose (150 γ) and glucose (75 γ) were mixed before anthronation. The effect of the concentrated acid on interaction between pentose and hexose is drastic. Deviation of curve 5 from curve 4 indicates a change in maximum absorption by some 50 mμ and also a great increase in absorbance of the solution.

In each case and for all curves, final concentration of anthronated sugars was 150 γ of arabinose and/or 75 γ of glucose in 12 ml. of solution.

The measurements of actual interference by pentoses are shown in Table III. These results indicate that the error was increased rapidly as the strength of the acid in the reagent was increased; also, the percentage error was less with weak sugar solutions than with strong ones for any given concentration of acid. Weaker solutions also have the advantage that the 625 mμ transmittance filter works more effectively than with stronger solutions. Thus an error of approximately 50% with a high sugar and a high acid concentration can be reduced to less than 10% using sugars in the same ratio, but at only one quarter of the concentration, and acid of 81 volume % instead of 96.4 volume %.

These data show that it is desirable to use a considerably less concentrated acid than that used in hexose determination when hexoses are being estimated in a hexose-pentose mixture, and also, that there is an advantage in using weaker sugar solutions. As the concentration of acid is decreased, increased time is required for good color development and this too may increase the pentose interference. In practice, 81 volume % acid with a slight increase in both time and temperature gives satisfactory results. For plant material, semiquantitative chromatographic determination of pentose offers a simple means of assessing error; this approach has been used extensively and was found expedient.

ACKNOWLEDGMENT

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Determination of Diphenylmercury Alone or in Presence of Phenylmercuric Compounds

Application to Ethyl Analogs

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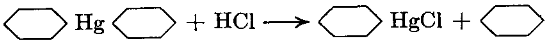
In an investigation of phenylmercuric fungicides, it became desirable to determine why some formulations appeared to give better results than others. One possible explanation was that diphenylmercury, a relatively inactive material against the fungus under investigation, might be formed. The described procedures make possible the analysis of diphenylmercury alone or in the presence of phenylmercuric compounds. A procedure is also given for the estimation of diethylmercury alone or in the presence of ethylmercuric compounds.

THE diphenylthiocarbazone reaction has been used for the determination of phenylmercuric compounds by Gran (*2*) and both the ethyl and phenyl compounds by the authors (*3*). Webb *et al.* (*5*) reported that, in macro amounts, diphenylmercury reacts slowly with diphenylthiocarbazone (dithizone) in benzene to form phenylmercuric dithizonate at room temperature. However, the authors found that in micro amounts diphenylmercury does not react with dithizone in chloroform at room temperature in the presence of 0.3*N* acetic acid.

When it became desirable to separate diphenylmercury and phenylmercuric compounds, the diphenylmercury interfered in the published procedure. The 3*N* hydrochloric acid used caused a partial decomposition of the diphenylmercury with the formation of phenylmercuric chloride according to the equation:

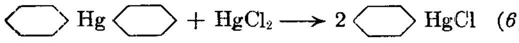


(*6*) (1)

When a chloroform solution of diphenylmercury is shaken with 9*N* hydrochloric acid, this reaction becomes quantitative. This permits diphenylmercury to be determined as a phenylmercury compound. In chloroform solution, phenylmercuric salts may be separated from diphenylmercury by extraction into the aqueous phase with acidified thiosulfate solution in a manner similar to that used by Cholak and Hubbard for mercury (*1*). This permits direct determination of diphenylmercury by the dithizone reaction.

A $0.05N$ hydrochloric acid solution, $1N$ in sodium chloride, does not decompose a chloroform solution of diphenylmercury. By use of this reagent the analysis of phenylmercuric salts with dithizone in the presence of diphenylmercury is possible.

An alternative procedure for the determination of diphenylmercury is based on the reaction with mercuric chloride:



(*6*) (2)

The determination of mercury using this reaction will be the subject of a separate paper.

The analysis of ethylmercuric salts and diethylmercury is conducted in a way similar to that outlined in the separation of diphenylmercury and phenylmercuric compounds, except that it is necessary to use $12N$ hydrochloric acid for the reaction in Equation 1. Under the conditions described, the reaction in Equation 2 does not occur with diethylmercury.

REAGENTS

Reagent 1. Fifty milliliters of $1N$ hydrochloric acid containing 2.5 ml. of 20% hydroxylamine hydrochloride is added to 200 ml. of $5N$ sodium chloride and 750 ml. of redistilled water. The stock solutions of hydroxylamine hydrochloride and sodium chloride are dithizone extracted. The pH of the reagent is about 1.15.

Reagent 2. Glacial acetic acid is diluted at the rate of 40 ml. per liter of water.

Reagent 3. Sodium thiosulfate; a 12% solution prepared in water daily.

Reagent 4. Hydrochloric acid, $9N$.

Reagent 5. Hydrochloric acid, $3N$.

Reagent 6. Ethanolic mercuric chloride, 600 γ per ml.

Reagent 7. Acetic acid, approximately 35 ml. per 2 liters of solution.

Reagent 8. Eastman Kodak white label diphenylthiocarbazone dissolved in chloroform at the rate of 1 mg. per ml. This stock solution is diluted in chloroform as needed. When 1 to 30 γ of organic mercury compound is to be determined, the diluted dithizone should contain approximately 3.3 mg. per 100 ml. In case of larger amounts (90 to 120 γ), a solution of 10 mg. per 100 ml. is necessary.

The standard materials used were Eastman white label diphenyl and diethylmercury and phenylmercuric chloride. The diethylmercury contained an appreciable amount of contaminant that reacted with dithizone but could be extracted with acidified thiosulfate. Similarly, the phenylmercuric chloride contained a small amount of mercury that was removed by extraction with $3N$ hydrochloric acid. The ethylmercuric chloride came from E. I. du Pont de Nemours & Co. and Bios Laboratories. Both were recrystallized from methanol and melted at 191° to 192° C. (*4*). The phenylmercuric acetate was Berk's C.P. product.

PROCEDURE

Diphenylmercury in Absence of Phenylmercuric Compounds. A chloroform solution of the sample not exceeding 10 ml. in volume is transferred to a small separatory funnel. The amount of organic mercury compound is such that a mixed color is formed with the dithizone in the end reaction. Sufficient chloroform is added to make a total of 10 ml. in the separator. Ten milliliters of $9N$ hydrochloric acid is added and the funnel immediately shaken for 30 seconds. The chloroform phase is transferred to a second separator containing 50 ml. of reagent 7. Exactly 1 ml. of the diluted standard dithizone solution is added and the separator shaken again for 30 seconds. The chloroform phase is now transferred to a suitable volumetric flask (10 to 15 ml.), and diluted to volume and the percentage transmittance is determined at approximately 620 mμ. Diethylmercury may be determined by the same procedure, except that $12N$ hydrochloric acid is used in place of $9N$ for the hydrolysis step.

Alternative Procedure for Diphenylmercury. As the amount of phenylmercuric chloride formed in the alternative procedure is twice that formed in the preceding one, the amount of sample should be estimated accordingly. Half a milliliter of reagent 6 is added to the separator containing the chloroform solution of the sample diluted to approximately 10 ml. with chloroform. The solutions are swirled to mix. Twenty milliliters of reagent 5 is added and the mixture shaken for 30 seconds to extract the excess mercury into the aqueous phase. The chloroform phase is then transferred to another separator which contains 50 ml. of reagent 7. Exactly 1 ml. of the diluted dithizone reagent is added, and the mixture is shaken for 30 seconds. The percentage transmittance is determined as above.

Phenylmercury in the Presence of Diphenylmercury, or Ethylmercury in the Presence of Diethylmercury. The chloroform solution of the ethyl- or phenylmercuric compound, which may contain the diphenyl- or diethylmercury as contaminant, is placed in a small separator. The quantity of organic mercury compound is adjusted so that a mixed dithizone color is formed. Sufficient chloroform is added to make a total of 10 ml. Twenty milliliters of reagent 1 is added and the mixture is shaken for 1 minute. The chloroform phase is then transferred to a second separator containing 50 ml. of reagent 7, and 1 ml. of diluted standard dithizone solution is added. The funnel is then shaken for 30 seconds. The resultant chloroform phase is diluted to a convenient volume and the percentage transmittance determined at 620 mμ. Only the phenyl- or ethylmercuric compound reacts in this portion of the procedure.

Diphenyl- or Diethylmercury in the Presence of Phenyl- or Ethylmercuric Salts. Because the ethyl- or phenylmercury salts react with dithizone, they must be removed from the mixture. The sample in chloroform solution is added to a sufficient volume of chloroform in a small separator to total 10 ml. One milliliter of reagent 3 is added, followed by 50 ml. of reagent 2. The separator is immediately shaken for 1 minute. This step removes the phenyl- or ethylmercury. The estimation of the diphenyl- or diethylmercury is done by the procedure given for these compounds alone.

The concentration of the dithizone is regulated so that a mixed color is formed. Standard curves are prepared from known amounts of the pure materials. The calibration curves follow Beer's law. The procedures seem to work equally well with small (1 to 30 γ) and larger amounts (90 to 120 γ). When the ratio of the compounds to one another is large, it is advantageous to use two concentrations of dithizone.

The amount of phenylmercuric acetate present in the determination of diphenylmercury did not exceed 2000 γ. In the reverse determination, the diphenylmercury did not exceed 4000 γ.

Table I. Approximate Solubilities of Several Organic Mercury Compounds at Room Temperature

	Solubility (γ/Ml.)		
	In water	In chloroform	In reagent 1
C_6H_5HgOAc	4,300	105,000	23
C_6H_5HgCl	24	5,450	19
$(C_6H_5)_2Hg$	6	453,000	0
C_2H_5HgCl	975	62,800	862
	(1.4)[a]	(38,000)[a]	
$(C_2H_5)_2Hg$	101	Complete	20

[a] Calculated from literature data.

DISCUSSION

The separation described depends on the quantitative extraction of the phenylmercuric compound from chloroform solution into the acidified thiosulfate. The original solutions of the compounds must be in chloroform. Alcoholic solutions cannot be used. The solubility of the diethyl- or diphenylmercury in chloroform is so much greater than in water that the extraction loss is negligible. Table I shows data on solubilities. Water solubilities of phenylmercuric acetate and chloride agree fairly well with accepted values. The solubility of ethylmercuric chloride in water and chloroform is much higher than previously reported (*4*). The solubilities were repeatedly determined by machine shaking of the compound in the solvent for over 20 hours during at least 2 days. The solutions were filtered through sintered glass. The organic mercury compounds were determined as described in this paper. Also in some cases the chloride from the water saturated solution of ethylmercuric chloride was determined gravimetrically by precipitation with silver.

If the same dithizone solution was used to prepare standard curves of diphenylmercury and phenylmercuric acetate, it was found that by calculating to equivalent phenylmercury (C_6H_5Hg), the standard curves would superimpose. The same was true with ethylmercuric chloride and diethylmercury. Typical data are shown in Table II.

Cholak and Hubbard (*1*) used a dilute sulfuric acid–sodium thiosulfate reagent to extract mercury from the chloroform to

Table II. Comparison of the Absorbance of Equivalent Alkylmercuric Dithizonate from Aryl or Alkylmercuric Chloride

Procedure	Material, γ	Equivalent to, γ	Absorbance
C_6H_5HgOAc, direct	C_6H_5HgOAc	C_6H_5Hg	
	6.1	5	0.606
	18.2	15	0.432
	30	25	0.258
$(C_6H_5)_2Hg$, doubling	$(C_6H_5)_2Hg$		
	3.2	5	0.611
	9.6	15	0.429
	16.0	25	0.248
$(C_6H_5)_2Hg$, hydrolysis	6.4	5	0.606
	19.2	15	0.430
	31.9	25	0.252
C_2H_5HgCl, direct	C_2H_5HgCl	C_2H_5Hg	
	5.8	5	0.634
	17.3	15	0.459
	28.8	25	0.280
$(C_2H_5)_2Hg$, hydrolysis	$(C_2H_5)_2Hg$		
	5.6	5	0.629
	16.9	15	0.456
	28.2	25	0.280

the aqueous phase. However, a dilute acetic solution was to be preferred in the extraction of phenyl- or ethylmercuric compounds from the chloroform to the aqueous phase because of less decomposition of the thiosulfate. In this step, the addition of the thiosulfate to the separatory funnel should be followed immediately by the acetic acid and the separator promptly shaken, as standing even for a minute had a deleterious effect on the separation. Only thiosulfate of the highest purity should be used. The presence of 10 γ of added sulfide (which may be an impurity) seriously interfered with the separation.

Good separation of diphenylmercury from phenylmercuric acetate was obtained when the ratio of diphenylmercury to phenylmercury was 1 to 150, or conversely, when the ratio was 1 to 300. Similar separations of diethylmercury from ethylmercuric chloride were obtained. The investigation was mainly concerned with the phenyl compounds because they are cheaper, and diethylmercury is a volatile, toxic material. The data in Table III give the results obtained when mixtures of diphenylmercury and phenylmercuric compounds were analyzed by the described procedure. The results were considered satisfactory for this type of work. Based on these and other results, the analysis will not be in error greater than 2 γ or 5%, whichever value is the greater.

Table III. Analysis of Mixtures

C_6H_5HgOAc, γ		$(C_6H_5)_2Hg$, γ	
Calculated	Found	Calculated	Found
192	197	6.4	6.7
640	640	6.4	6.9
960	962	6.4	6.8
6.4	6.6	192	190
6.4	6.7	640	636
6.4	7.1	1,280	1,287
6.4	7.1	1,920	1,937
6.4	7.1	960	944
40	42	40	42

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Separation of Platinum and Palladium and Their Subsequent Colorimetric Determination with *p*-Nitrosodimethylaniline

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The wide variation in the rate of reaction of platinum and palladium with *p*-nitrosodimethylaniline to give highly colored products has been utilized to develop a sensitive additive absorbance colorimetric procedure for these metals. Palladium and platinum can be determined individually with average relative errors of 1.0 and 1.5%, respectively, when in the concentration range of optimum photometric measurement. Samples containing palladium to platinum ratios of 10 to 1 to ratios of 60 to 1 platinum to palladium may be analyzed by this method with good accuracy. Larger proportions of palladium may be determined by utilizing a differential measurement technique. Relatively large amounts of palladium may be quantitatively separated by extraction of the palladium-*p*-nitrosodimethylaniline complexes in chloroform. A method is proposed for the simultaneous separation of platinum and palladium from other platinum metals interfering with their colorimetric determination; these metals are extracted as their diethyldithiocarbamate salts into chloroform, the solvent is evaporated, and the residues are ashed with concentrated nitric acid and peroxide. Final determination of the metals is easily made by means of the additive absorbance method.

The color reactions between *p*-nitrosodimethylaniline and palladium and platinum have been individually proposed as means of determining small amounts of these metals (*4, 5*). As is the case with the other existing colorimetric methods for platinum, this reaction is also interfered with by relatively small amounts of palladium and to varying extents by other platinum metals.

In this paper *p*-nitrosodimethylaniline is recommended as a colorimetric reagent for the determination of both platinum and palladium in trace concentrations. A method for selectively separating these metals from commonly associated elements interfering with their colorimetric determination is also proposed. During the course of the experimental work embodied in this re-

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port, it was found that *p*-nitrosodimethylaniline is useful for the separation of relatively large amounts as well as small quantities of palladium. The procedure for this separation is described.

APPARATUS AND REAGENTS

Standard Palladium Solution. A standard palladium solution was prepared from palladium powder (specified 99.9% pure) obtained from the American Platinum Works. Exactly 0.5 gram of this powder was dissolved and treated as described for the standard platinum solution (*4*). The final substance was take up in distilled water and 4 ml. of concentrated hydrochloric acid and made up to 50-ml. volume. This gave a stock solution containing about 10 mg. of palladium per ml. in 1*M* hydrochloric acid. The solution was standardized with dimethylglyoxime and was found to contain 9.94 mg. of palladium per milliliter.

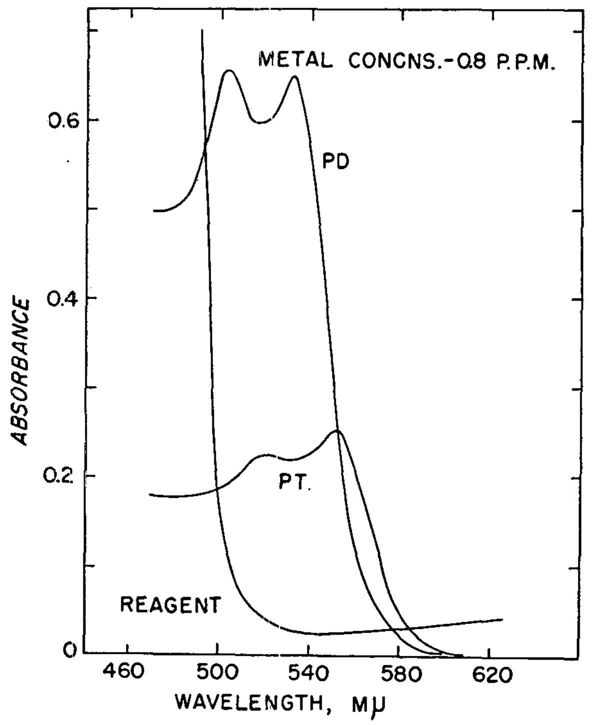

Figure 1. Complexes of *p*-Nitrosodimethylaniline

All equipment and chemicals were the same as those described in an earlier publication (*4*).

SIMULTANEOUS COLORIMETRIC DETERMINATION OF PLATINUM AND PALLADIUM

The absorption spectra of the red-colored solutions resulting from the reaction of platinum and palladium with *p*-nitrosodimethylaniline by the analytical procedure recommended for platinum (*4*) are similar in appearance (Figure 1). No reaction occurs between platinum (II) and *p*-nitrosodimethylaniline for several hours at room temperature, while palladium gives an immediate red color under the same conditions. In view of this, a colorimetric method for the simultaneous determination of both metals utilizing their differences in reactivity appeared feasible and was successfully devised. The technique consists of determining the amount of palladium in one sample aliquot by its color reaction with *p*-nitrosodimethylaniline at room temperature; a color-forming solution containing another aliquot of sample when heated gives a total color attributable to both platinum and palladium. Under prescribed reaction conditions the difference between the color intensity of the solution containing the colored complexes of both metals and that of the solution containing only the palladium complex indicates the absorbance attributable to the platinum complex.

Table I. Analysis by the Additive Absorbance Method

Pd, P.P.M.		Pt, P.P.M.		Ratio Pd-Pt
Added	Found	Added	Found	
0.80	0.80, 0.80	0.08	0.08, 0.07	10-1
0.80	0.80	0.20	0.21	4-1
0.60	0.60	0.20	0.20	3-1
0.60	0.59	0.40	0.42	1.5-1
0.40	0.40	0.40	0.40	1-1
0.40	0.40, 0.40	0.80	0.80, 0.84	1-2
0.40	0.40	2.40	2.44	1-6
0.20	0.20	1.60	1.59	1-8
0.04	0.04	2.40	2.38	1-60

DISCUSSION

A study of several variables in the palladium-*p*-nitrosodimethylaniline reaction was found necessary in order to ascertain the necessary conditions for obtaining quantitatively additive color intensities. It was found that the color intensity of the palladium complex decreases markedly when heated in the presence of sodium acetate-acetic acid buffers; however, similar tests with sodium acetate-hydroloric acid buffers showed that the color remains unchanged on heating only within the narrow pH range 2.2 ± 0.2. Although at pH 3 a buffer of the latter type gives maximum color intensity when used for the determination of platinum, only a slight loss in sensitivity occurs when a buffer of pH 2.2 ± 0.2 is employed (*4*).

The colored palladium complex developed by the procedure described below obeys Beer's law at 525 mμ in the concentration range studied. At this wave length the color intensity is measured in a "trough" between the two absorption maxima (Figure 1). The sensitivity of the color reaction for palladium as described in this paper is 0.0015 p.p.m. by the Sandell notation (*12*); however, the practical sensitivity is 0.0067 p.p.m. when measured in a 1-cm. cell. The range of most accurate spectrophotometric measurement is about 0.25 to 1.0 p.p.m. palladium; in this range the color can be reproduced with an average relative precision of 1%.

The palladium color developed with large excess of reagent shows two absorption maxima, one at 505 and one at 535 mμ. Overholser and Yoe (*5*) have shown that the absorption curve of the palladium-*p*-nitrosodimethylaniline complex prepared with only a slight excess of reagent exhibits only one maximum at about 495 mμ. Presumably, the color formed in the presence of a large excess of reagent is the combination of two or more complexes similar to those previously observed for platinum (*4*).

APPLICATION

A number of synthetic samples composed of palladium and platinum in relative amounts varying from palladium to platinum ratios of 10 to 1 to ratios of 60 to 1 platinum to palladium were analyzed in order to test the additive absorbance method. The results are summarized in Table I.

DIFFERENTIAL ANALYSIS MODIFICATION

By utilizing differential measurements, samples may be analyzed containing palladium to platinum in ratios considerably higher than those possible with the simple additive absorbance method. In this procedure the color caused by both the platinum- and palladium-*p*-nitrosodimethylaniline complexes is spectrophotometrically compared with the color of a reference palladium complex solution of known concentration. The concentration of palladium used in the reference solution is usually made some convenient value slightly less than that found by analyzing a sample aliquot. A correction for the small amount of palladium in the sample not accounted for in the reference solution must be applied when the calculations are made. The results recorded in Table II were obtained in the analysis of some known synthetic mixtures using this differential measurement technique.

It was observed that sample solutions not measured immediately after filling the absorption cells gradually decreased in differential absorption. Refilling the cells with fresh original colored solutions resulted in correct intensity measurements. Good results were obtained when intensity measurements were made promptly after filling the absorption cells.

In connection with the differential analysis method, a study was conducted to determine the upper limit of platinum that may be present in a palladium sample without interfering with the colorimetric determination of the latter. It was found that relatively large quantities of platinum usually caused palladium analyses to be low. This is contrary to that which might be predicted, because $PtCl_6^{--}$ at relatively high concentrations is yellow-colored and hence should cause a positive interference—i.e., high results. Up to 60 p.p.m. of platinum may be tolerated in a 0.40–p.p.m. palladium solution without introducing an error which exceeds 3%. As shown in Table III, palladium may be determined in platinum samples in ratios of as much as 1000 to 1 platinum to palladium with a relatively low absolute error.

Table II. Analysis Using Differential Measurements

Pd, P.P.M., Added in Sample and Used in Reference	Pt, P.P.M.		Ratio Pd-Pt
	Added	Found	
2.00	1.20	1.18	1.67–1
2.40	0.24	0.23	10–1
2.40	0.20	0.24	12–1
2.40	0.16	0.14	15–1
2.40	0.08	0.07	30–1

Table III. Effect of Large Amounts of Platinum

Pd, P.P.M.		Pt, P.P.M., Added	Ratio Pt-Pd
Added	Found		
0.40	0.39	60	150–1
0.040	0.045	40	1000–1

Table IV. Extraction of Palladium with *p*-Nitrosodimethylaniline

Pd Added, γ	Pd Found, γ
200	198
500	494
1000	1010

Colored palladium–*p*-nitrosodimethylaniline solutions containing relatively large amounts of unreacted platinum slowly increase in intensity on standing at room temperature. This color increase may be explained by the slow reduction of the platinum(IV) to platinum(II) by the excess reagent, with subsequent formation of the colored platinum(II) complex. This effect, in the order of 2% increase for 30 minutes at room temperature, indicates that solutions of this composition should be measured as soon as possible after the recommended period for color formation.

RECOMMENDED PROCEDURES

Additive Absorbance Method. PALLADIUM. The sample containing between 12 and 40 γ of palladium is adjusted to pH 2 to 3 and made up to a total volume of 10 ml. One milliliter of a concentrated sodium acetate-hydrochloric acid buffer solution of pH 2.2 ± 0.2, prepared as described (*4*), is added. The resulting mixture is treated with 1.00 ml. of a 5 mg. per ml. alcoholic *p*-nitrosodimethylaniline reagent solution and 5 ml. of wash liquid, distilled water, or absolute ethyl alcohol (depending on the heating technique used for the subsequent determination of platinum). This solution is allowed to stand for 5 minutes at room temperature, then diluted to 50.0 ml. with 95% ethyl alcohol. The intensity of the orange-red color is measured at 525 mμ against a reagent blank and the palladium concentration determined from a standard calibration curve or absorbance index.

PLATINUM. A sample containing palladium and platinum in an amount which will give a total color intensity falling in the range of most accurate spectrophotometric measurement (about 20 to 60% transmittance or 0.2 to 0.7 absorbance unit) is adjusted to pH 2 to 3, and made up to a total volume of 10 ml. It is then treated with 1.0 ml. of concentrated sodium acetate–hydrochloric acid buffer (pH 2.2 ± 0.2) and 1.00 ml. of 5 mg. per ml. reagent solution. Five milliliters of distilled water are added and the solution is heated for 20 minutes at 100° C., or 4 ml. of ethyl alcohol may be added and the solution heated for 60 minutes at 85° C. [see (*4*)]. The solution is immediately cooled to room temperature, diluted to volume with 95% ethyl alcohol, and measured at 525 mμ against a reagent blank which has been heated in the exact manner. The color intensity of the platinum may be calculated by the following relationship:

$$A_s^{\mathrm{Pt}} = A_s^{\mathrm{Pd+Pt}} - A_s^{\mathrm{P}}$$

where

$A_s^{\mathrm{Pd+Pt}}$ = absorbance attributable to platinum and palladium

A_s^{Pd} = absorbance attributable to palladium

(This is determined in another sample aliquot as described. A concentration factor must be used if the two aliquots are not the same volume.)

A_s^{Pt} = absorbance attributable to platinum

DIFFERENTIAL ANALYSIS MODIFICATION

The procedure described for the additive absorbance method is followed, except that a heated reference solution containing a known amount of palladium is used in the measurement of the color intensity of the platinum complex. The reference palladium solution should contain an equal or slightly lower concentration of this metal than that determined to be present in the unknown sample but should not have an absorbance which exceeds about 1.5. Correction must be made for any difference in the concentration of palladium in the reference solution compared to the amount actually found in the sample. Similar calculations are employed as those described previously.

SEPARATION OF PALLADIUM FROM PLATINUM WITH *p*-NITROSODIMETHYLANILINE

The selective separation of palladium from platinum in the trace concentration range has been performed by various techniques (*1, 2, 10, 11, 13, 15, 16*). While some of the more convenient of these methods may be used only when very small amounts of palladium are to be isolated, the extractive properties of the palladium complexes of the red *p*-nitrosodimethylaniline may be utilized to separate relatively large amounts of this metal.

The orange to intense red color which results when a large excess of *p*-nitrosodimethylaniline reacts with palladium may be quantitatively extracted into chloroform. Ethyl acetate, diethyl ether, benzene, diphenyl ether, carbon tetrachloride, ethylene dichloride, and carbon disulfide were found to be unsatisfactory for this purpose. Purified or C.P. chloroform must be employed for the extraction; low palladium recoveries were obtained when U.S.P. grade chloroform was used in some experiments. (The losses were thought to be due to a film usually found in the separatory funnel after extraction.) Table IV lists the results of experiments designed to test the efficiency of the extraction of relatively large quantities of palladium.

The data were obtained by evaporating to dryness the chloroform extract containing the palladium complex, ashing the residue with concentrated nitric acid and peroxide, and colorimetrically determining the amount of palladium in the inorganic residue. *p*-Nitrosodimethylaniline may also be used to separate quantitatively palladium in amounts less than 200 γ; however, as the additive absorbance method described may be applied directly to samples containing low ratios of palladium to platinum, separation of this metal in amounts of less than 200 γ is unnecessary. It was found difficult to extract palladium quantitatively in amounts exceeding 1 mg. When quantities in this range were attempted, a significant portion of the colored complex collected at the water-chloroform interphase as a red film, making the separation uncertain. Utilizing this extractive technique, small amounts of platinum may be determined in the presence of much larger quantities of palladium. Palladium is reacted with *p*-nitrosodimethylaniline at room temperature and extracted with chloroform. The aqueous phase is then analyzed for platinum using the procedure previously described (*4*). (The additive absorbance method may be used here to compensate for reasonably large quantities of this metal.) The results of analysis of some known synthetic samples containing high palladium to platinum ratios, using a preliminary extractive separation of palladium, are listed in Table V.

Table V. Separation of Large Quantities of Palladium with *p*-Nitrosodimethylaniline

Pd, γ		Pt, γ		Ratio
Added	Found	Added	Found	Pd-Pt
500	494	20	18	25-1
500	502	10	10	50-1
500	510	4	5	100-1
1000	969	10	7	125-1

The palladium was determined in these mixtures by evaporating the chloroform extract to dryness, ashing the residue with nitric acid and peroxide, and subsequently analyzing for the metal with *p*-nitrosodimethylaniline (*4*). Mixtures which include more than 500 γ of palladium are analyzed with some difficulty, and poor results are obtained if 1 mg. or more of this metal is present. Platinum was determined by evaporating the aqueous phase to dryness, ashing any organic residue with the nitric acid and peroxide procedure to be described, and measuring the amount of platinum colorimetrically using *p*-nitrosodimethylaniline (*4*).

p-Nitrosodimethylaniline cannot be used to separate platinum quantitatively by an extractive method because it is known that this metal does not react completely (*4*).

PROCEDURES

Separation of Palladium. About 10 ml. of sample solution of pH 2 to 5, preferably containing not more than 500 γ of palladium, are placed in a small separatory funnel and treated with 0.5 ml. of a 5 mg. per ml. alcoholic *p*-nitrosodimethylaniline reagent solution. Five milliliters of 95% ethyl alchol are added and the solution is allowed to stand for 5 minutes with frequent agitation. The resulting orange to red color is extracted with 10 ml. of chloroform. The aqueous phase is again treated with 0.5 ml. of reagent and 5 ml. of ethyl alcohol, allowed to stand 5 minutes, and extracted with another 10-ml. portion of chloroform. (If more than about 500 γ of palladium are to be extracted, two additional extractions may be necessary to ensure quantitative removal.)

Ashing. The chloroform extract embodying the palladium complexes or the aqueous phase containing platinum and some unreacted reagent are evaporated to dryness in a small beaker on a steam bath. If the residue contains relatively large amounts of unreacted reagent, the beaker is heated carefully on the edge of a hot plate until dense green fumes are no longer evolved. The charred residue is then treated with 5 ml. of fuming nitric acid and heated almost to dryness. Another 5-ml. portion of fuming nitric acid is added and the solution is evaporated to about 2 ml. If the resulting solution is pale yellow or amber, 30% hydrogen peroxide is carefully added, dropwise, to the hot (not boiling) mixture until it becomes colorless. This solution is then evaporated almost to dryness and treated with three successive 5-ml. portions of concentrated hydrochloric acid, and each mixture is again evaporated almost to dryness. (The hydrochloric acid treatment eliminates oxides of nitrogen and converts the metal to the corresponding chlorides.) To ensure complete removal of any oxidizing substances which would interfere with the subsequent colorimetric determination of platinum, it is usually necessary to treat the salt residue with 5 drops of 1% sodium bisulfite solution and carefully evaporate just to dryness. The metal salt is then dissolved in distilled water with gentle heating, cooled, and diluted almost to the desired volume. The solution is adjusted to pH 2 to 3 (by removing droplets of liquid and testing with pH paper) and made up to a final volume with distilled water.

COLORIMETRIC DETERMINATION OF PLATINUM AND PALLADIUM AFTER SIMULTANEOUS SEPARATION FROM OTHER PLATINUM METALS

The colorimetric method for platinum (*4*), applied in studies reported previously in this paper, suffers varying interference from other metals of the platinum group. In order to utilize this method better for samples containing other platinum group metals, a procedure for quantitatively separating platinum from these elements was devised. Since the additive absorbance technique provides a convenient way for simultaneously determining platinum and palladium, a method was developed for simultaneously separating these two metals from commonly associated elements which interfere with their colorimetric determination.

DISCUSSION

Pollard (*6–9*) has shown that palladium and platinum may be individually separated from other platinum metals by extraction of their diethyldithiocarbamate salts into benzene. This method was evaluated as a possible technique for simultaneously separating these metals. Pollard found that stannous chloride was satisfactory for the reduction of platinum(IV) to the reactive divalent state. This reducing agent was first employed in the separation herein described; however, low platinum results were often obtained when *p*-nitrosodimethylaniline was used in making the final colorimetric measurement. In these cases white basic stannous salt precipitates were usually noted after solutions of the ashed extraction residues were adjusted to pH 2 to 3 prior to colorimetric measurement.

Organic reducing agents such as hydrazine and hydroxylamine hydrochloride were found to have no apparent effect on platinum(IV) at room temperature. However, addition of an alkali iodide solution to a highly acid solution of chloroplatinate ions was observed to give an immediate formation of a rose-brown color, with apparent liberation of iodine. [Hydrochloroplatinic acid has been reported by Walche (*14*) to be reduced to hydrochloroplatinous acid by alkali iodides; it is probable, however, that iodoplatinous acid is formed in highly acid medium, as it is known that iodide reacts slowly with chloroplatinate in slightly acid medium to give a rose-colored solution of the iodoplatinate (*12*).] Tests showed that sodium diethyldithiocarbamate reacts quickly with this colored solution to form a cream-colored turbidity, indicating formation of the platinum complex. This turbidity was found to be readily extracted into chloroform, imparting to it a brownish yellow color.

The use of iodide as the reducing agent for platinum somewhat complicates the simultaneous extraction of palladium with sodium diethyldithiocarbamate, because highly insoluble palladium iodide precipitates from solution when a slight excess of iodide is present. However, if a large iodide excess is added, the palladium iodide precipitate dissolves, probably because of the formation of the soluble PdI_4^{--} complex. (This situation presumably also exists with platinum. A relatively small excess of iodide is apparently sufficient to keep platinum iodide from precipitating because of the greater tendency to form the soluble PtI_4^{--}.) This large excess of iodide is required if more than about 10 p.p.m. (50 γ in 5 ml.) of palladium are to be extracted. When relatively large amounts of rhodium and iridium (10 to 20 times the palladium concentration) are present, it is usually convenient to add solid iodide to maintain a sufficient excess. It was found that not more than about 60 γ (in 5 ml.) of palladium can be extracted quantitatively when 1 mg. of rhodium and/or iridium is present; however, 100 γ or more of palladium are completely extracted from solutions containing relatively small amounts of these metals.

A preliminary separation of palladium is necessary when it is desired to determine very small quantities of platinum in samples containing relatively large amounts of palladium and significant quantities of iridium and rhodium. Preliminary experiments indicated favorable results in making this separation by precipitating the palladium as palladium iodide but a complete investigation of this method was not undertaken.

Platinum is completely extracted with sodium diethyldithiocarbamate in amounts up to about 200 γ (in 5 ml.). Extractions were not attempted on larger quantities but it is believed that this does not represent the upper limit of the method.

Table VI. Simultaneous Separation of Platinum and Palladium with Sodium Diethyldithiocarbamate

Pt, γ			Pd, γ			Other Metals Present in Total Sample, γ
Total Added, γ	Sought in aliquot	Found in aliquot	Total Added, γ	Sought in aliquot	Found in aliquot	
60.0	30.0	30.8 28.5	...	..	..	....
60.0	24.0	22.5	...	..	..	....
60.0	30.0	29.0	...	..	..	500 Rh
60.0	30.0	28.0	...	..	..	1000 Ir
60.0	30.0	29.8	...	..	..	500 Rh + 500 Ir
60.0	30.0	31.0	60.0	24.0	23.8	....
20.0	10.0	10.5	100.0	40.0	40.4	....
60.0	30.0	33.0	50.0	20.0	18.8	500 Rh + 500 Ir
200.0	80.0	84.0	20.0	10.0	9.0	1000 Rh + 10000 Ir

A dozen or more base metals are known to react with sodium diethyldithiocarbamate *(3)*; however, these reactions were observed in weakly acid, neutral, or weakly basic solutions in contrast to the highly acid solutions from which platinum and palladium are extracted by the method of separation proposed. The effect of these base metals on the completeness of extraction of platinum and palladium was not studied. The other platinum group metals do not react with sodium diethyldithiocarbamate; hence, interference from these substances is completely eliminated. Osmium and ruthenium do not interfere with the colorimetric determination if the sample has been heated with oxidizing acids, since these metals volatilize as their tetroxides. Gold must be removed before attempting the simultaneous separation.

APPLICATION

Summarized in Table VI are the results of analyses of some known synthetic mixtures. Samples containing both palladium and platinum were analyzed by selectively extracting the metals using the sodium diethyldithiocarbamate procedure to be given and determining the amount of these elements in the ashed extraction residue by the additive absorbance method.

Procedure. A sample of about 5 ml. containing not more than approximately 200 and 100 γ of platinum and palladium, respectively, and no organic or oxidizing substances, is placed in a small separatory funnel. (If the aliquot contains relatively large amounts of iridium and rhodium, only about 60 γ of palladium can be extracted quantitatively. If the percentage of platinum in the sample is low so that a large amount is required, a preliminary separation of palladium may be necessary if it is present in large quantities.) This solution is treated with 5 ml. of concentrated hydrochloric acid and 4 ml. of 2% potassium iodide solution. Samples containing 50 γ or more of palladium or large amounts of rhodium and iridium may require more potassium iodide solution or a little solid salt in order to prevent the precipitation of palladium iodide. The rose-brown colored mixture should be allowed to stand for about 5 minutes with frequent agitation. It is then treated with 2 ml. of 1% sodium diethyldithiocarbamate solution and again allowed to stand for 5 minutes with frequent shaking. The white or cream-colored turbid mixture is extracted with two 5-ml. portions of chloroform. The reduction and extraction procedure is repeated using 2 ml. of 2% potassium iodide solution, 2 ml. of 1% sodium diethyldithiocarbamate solution, and two 5-ml. portions of chloroform. The chloroform extracts are combined and evaporated to dryness, and the resulting residue is ashed by the nitric acid–peroxide method described previously in this paper. The platinum and palladium in the sample may then be determined colorimetrically using the additive absorbance method discussed.

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Spectrophotometric Study of *p*-Nitrosodimethylaniline as a Sensitive Colorimetric Reagent for Platinum

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The orange-red color produced by heating excess *p*-nitrosodimethylaniline with platinum is the basis of a colorimetric procedure which is several times more sensitive for this metal than any in the literature; the practical limit of sensitivity of the reaction is about 0.015 p.p.m. when measured in a 1-cm. cell. The colored solutions were found to be stable for at least 24 hours and follow Beer's law at the concentration level studied. The optimum concentration range for photometric measurement is 0.7 to 2.4 p.p.m. of platinum; over this range the colored solutions may be reproduced with average and maximum relative errors of 1.4 and 3.0%, respectively. A study of possible interference by many cations and some common anions shows a tolerance about equivalent to that of existing colorimetric methods for platinum. The reaction variables have been investigated in order to establish optimum conditions for the color reaction. The color is believed to be due to at least two different platinum complexes, one of which was isolated as a solid and identified. The colored solutions exhibit absorption maxima at 550 and 525 mμ when compared with a reagent blank; intensity measurements are made at the latter wave length.

THE two colorimetric methods most widely used for platinum, the tin(II) chloride and potassium iodide procedures, utilize the color resulting from the formation of inorganic complexes (*1*, *9*). In this paper *p*-nitrosodimethylaniline is recommended as a colorimetric reagent of high sensitivity for platinum. This compound has already been used by Yoe and Overholser (*11*) for the colorimetric determination of palladium and during the course of this study it was proposed by Currah *et al.* (*2*) as a colorimetric reagent for ruthenium. It will be shown in a subsequent paper that *p*-nitrosodimethylaniline may be successfully utilized for the determination of minute amounts of both platinum and palladium without the need of separating them.

APPARATUS

Absorbance measurements were made with Beckman Models DU and B spectrophotometers with matched 1.00-cm. Corex cells. The Model DU was operated at constant sensitivity, using slit widths of the order of 0.02 to 0.1 mm., corresponding to effective band widths of about 1 to 4 mμ. The Model B was operated at varying sensitivities using slit widths of 0.1 to 0.2 mm., representing effective band widths of about 1 to 6 mμ.

All pH measurements were made with a Beckman Model G pH meter, with glass electrode.

A constant temperature bath of useful range 20° to 65° C. was employed in most of the experiments to cool heated solutions to room temperature in a uniform manner. A temperature of 25° ± 0.05° C. could be maintained easily with this bath.

Spectrographic examinations of standard platinum metals and salts were made with an Applied Research Laboratories 2-meter grating spectrograph using a direct current arc.

SOLUTIONS

Standard Platinum Solution. Platinum wire obtained from the American Platinum Works and specified 99.9% pure was examined spectrographically for impurities. Faint lines attributable to copper and silver were found, indicating only traces of these metals. No other impurities were noted. A standard chloroplatinate solution was prepared by dissolving exactly 1 gram of the "pure" platinum in 50 ml. of aqua regia with gentle heating. The solution was evaporated almost to dryness and treated with three successive 10-ml. portions of 1 to 1 hydrochloric acid, each time evaporating almost to dryness in order to free the solution of oxides of nitrogen. The final material was transferred to a 100-ml. volumetric flask, 4 ml. of concentrated hydrochloric acid were added, and the solution was diluted to volume. This gave a stock solution that was about 0.5*M* in hydrochloric acid and 10 mg. of platinum per milliliter; it was standardized gravimetrically by precipitating the platinum from 25-ml. aliquots and subsequent ignition to the metal (*5*). Triplicate analyses in good agreement gave an average value of 9.99 mg. of platinum per milliliter. Less concentrated platinum solutions were prepared by appropriate dilutions. Standard solutions of less than 100 p.p.m. were made up fresh daily because it was found that such dilute platinum solutions slowly decreased in effective concentration. This effect has also been observed by Leutwein (*8*) and Ayres and Meyer (*1*).

Reagent Solutions. Distillation Products Industries No. 188 *p*-nitrosodimethylaniline (*N*,*N*-dimethyl-*p*-nitrosoaniline) was further purified by recrystallization from 25% ethyl alcohol. In certain studies a particular concentration of this material was chosen; however, most of the experiments called for a reagent concentration of 5 mg. per milliliter in fresh absolute ethyl alcohol. Reagent solutions made with alcohol that had been standing in contact with air for some time were found to be unsatisfactory because color-forming solutions prepared with it discolored badly when heated. Solutions made with fresh absolute ethyl alcohol and kept well stoppered were satisfactory for at least a month.

Buffer Solutions. Buffer solutions containing sodium acetate and hydrochloric acid or sodium acetate and acetic acid were made up in concentrated form, so that 1 ml. when made up to 50 ml. gave the desired stabilized hydrogen ion concentration. The buffer in the recommended procedure was prepared by mixing 50 ml. of 4*M* sodium acetate and 53 ml. of 4*M* hydrochloric acid, resulting in a solution of pH 2.2 ± 0.2.

Solutions of Diverse Ions. Stock solutions used for the study of interferences contained either 1 or 10 mg. of metal or ion per milliliter. All sources were ACS reagent grade or C.P., except gold and the platinum metals and their salts. Gold foil, rhodium chloride, palladium metal, and potassium osmate, obtained from the American Platinum Works, were used to prepare chloride salt solutions of gold, rhodium, palladium, and osmium, respectively. Ammonium chloroiridite and ammonium chlororuthenite (Johnson, Matthey and Co., Ltd., Specpure brand) were dissolved in aqua regia and treated as in the preparation of the platinum stock solution.

Chemicals. U.S.P. absolute alcohol was used throughout the study unless otherwise specified. All other chemicals used were ACS reagent grade or C.P.

THE COLOR REACTION

The reaction of platinum chloride with a yellow-green aqueous alcoholic solution of *p*-nitrosodimethylaniline to give an intense red color takes place very slowly at room temperature. The application of heat and the use of a large excess of reagent in small color-forming volumes results in a more rapid formation of the color. In order to obtain uniform color development, it was found necessary to control several variables in the reaction.

Heating Time. Alternate methods for developing the color were devised, each giving satisfactory results. The first procedure, used in the greater portion of the study, employed a heating time of 60 minutes. Addition of ethyl alcohol to the color-forming solution to make it 37% in that component stabilizes the temperature at 85° C. while heating on a steam bath. The

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second method differs in that the color was developed in a solution to which no additional ethyl alcohol had been added. This heating technique requires 20 minutes in boiling water (100° C.). Using either of these heating procedures it was noted that only 1 to 2% increase in color intensity occurred in 24 hours after the orange-red color-forming solutions were cooled to room temperature and made up to volume with ethyl alcohol. Figure 1 shows the effect of heating time on the color intensity. Heating times longer than 90 minutes at 85° C. and 45 minutes at 100° C. result in a noticeable discoloration of the excess reagent present, probably because of the gradual oxidation of this compound. Any slight discoloration of the reagent which occurs during heating is accounted for by measuring the colored solution against a reagent blank which undergoes identical heating treatment. It was found that the reaction of the platinum is about 93% complete using the heating time recommended. This was determined by extracting the colored components with chloroform and analyzing for the unreacted platinum left in the aqueous phase by a colorimetric modification of the platinum(IV)-tin(II) chloride procedure (*1*).

Reagent Concentration. A large molar excess of reagent over platinum was found necessary to produce colored solutions which followed Beer's law when measured against a reagent blank. Use of a smaller excess than that recommended will produce the color but its formation will be much slower and the intensity significantly lower.

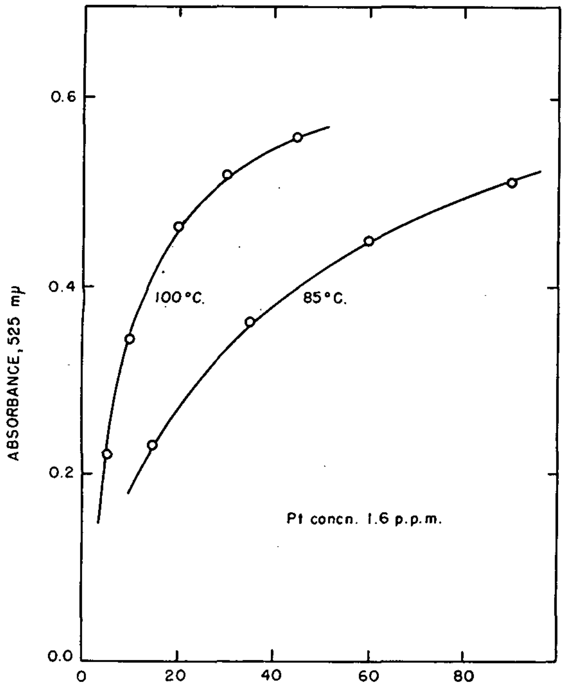


Figure 1. Effect of Heating Time on Formation of Platinum-*p*-Nitrosodimethylaniline Complexes

Solvent Effects. It was found essential in both color-forming procedures to dilute the final solutions to volume with 95% ethyl alcohol in order to prevent precipitation of the excess reagent when the heated solutions were cooled to room temperature. Addition of 5 ml. of ethyl alcohol to the color-developing mixture in the 85° C. method assists in stabilizing the temperature of the solutions at about 85° C. when steam bath heating is used. In studying the effect of varying alcohol content of the color-forming solution in the 85° C. procedure, it was found that increasing the alcohol from 30 to 80% results in a decrease in color intensity of about one fourth. Addition of ethyl alcohol is not feasible with the 100° C. method because it is quickly boiled off at this temperature.

Volume of Solution Heated. In order to approach maximum color development more quickly, the volume of liquid heated was kept as small as practicable. The procedure to be given specifies that the total color-forming solution volume is 17 ml., which includes 1 ml. of concentrated buffer, 10-ml. sample aliquot, 1 ml. of alcoholic reagent solution, and 5 ml. of wash liquid, either distilled water or ethyl alcohol.

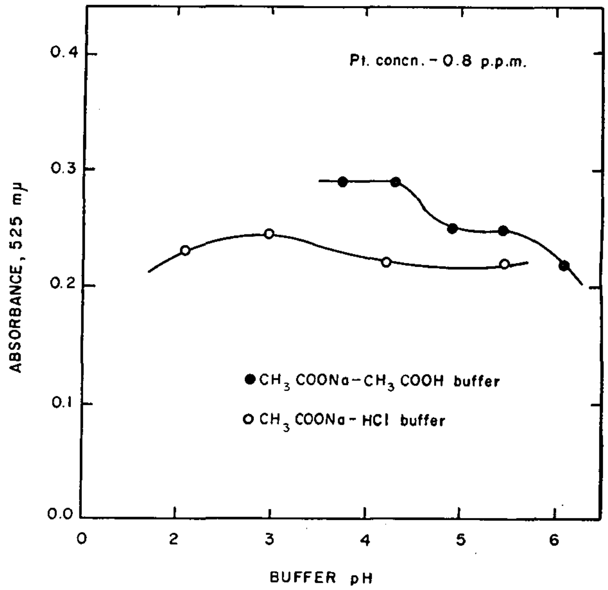


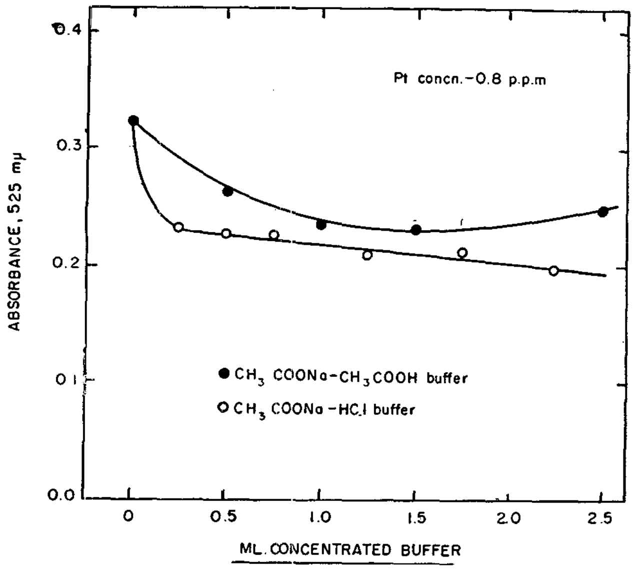
Figure 2. Effect of pH on Intensity of Platinum-*p*-Nitrosodimethylaniline Color

Effect of pH and Buffer. Color-forming solutions of low pH do not approach maximum color intensity even with continued heating, while solutions of high pH quickly give discolored brown solutions when heated. Clear red solutions of maximum color intensity are obtained with a sodium acetate–acetic acid buffer of pH 3.8 or a sodium acetate–hydrochloric acid buffer of pH 3.0. The variation in color intensity with the pH of the aqueous buffer is shown in Figure 2. A sodium acetate–hydrochloric acid buffer of pH 2.2 is prescribed in the procedure because the additive absorbance method for platinum and palladium to be described in a subsequent paper must be carried out with these conditions. The system follows Beer's law over a wide concentration range; when prepared with sodium acetate–hydrochloric acid buffer the pH range is 2 to 5.

The concentration of buffer used in the color-forming solution was found to have a pronounced effect on the intensity of the color produced, undoubtedly a result of the variation of the ionic strength of the solution. Increase in the concentration of both sodium acetate–acetic acid and sodium acetate–hydrochloric acid buffers caused lower color intensities. Only a little more loss in sensitivity occurred, however, when more than 0.5 ml. of either buffer (approximately 2*M* in both components) was added. One milliliter of buffer was chosen as a satisfactory compromise between loss in color intensity and buffering capacity. Figure 3 shows the effect of buffer concentration on the color intensity.

Sensitivity and Precision. In both color-forming techniques the color intensity was found to be proportional to the platinum concentration up to at least 3.2 p.p.m. platinum. The sensitivity of the reaction when expressed by the notation of Sandell (*9*) is

0.0029 γ per square centimeter; 2.9 γ per square centimeter corresponds to unit absorbance at 525 mμ in the Beckman spectrophotometer. The practical limit of sensitivity of the reaction is about 0.015 p.p.m. when measured in a 1-cm. cell. The range of most accurate spectrophotometric measurements is 0.7 to 2.4 p.p.m. platinum, which indicates that the proposed color reaction is more sensitive than the stannous chloride–platinum(IV) chloride and potassium iodide procedures.



[Figure 3. Effect of Amount of Buffer on the Intensity of the Platinum-*p*-Nitrosodimethylaniline Color

When controlled according to optimum conditions, solutions containing the same platinum concentrations developed colors which gave absorbance readings showing average and maximum relative errors of 1.4 and 3.0%, respectively, for both the 85° and 100° C. modifications. See Table I.

Table I. Precision of Complex Color Formation

(Platinum concentration 1.0 p.p.m.; heating time, 60 minutes at 85° C.)

	Absorbance, 525 Mμ		Deviation from Av. Absorbance
	0.276		0.005
	0.273		0.002
	0.269		0.002
	0.269		0.002
	0.267		0.004
	0.271		0.000
	0.273		0.002
	0.264		0.007
	0.263		0.008
	0.278		0.007
	0.274		0.003
	0.274		0.003
Av.	0.271	Av. deviation	0.0038
		Max. deviation	0.008

Av. relative deviation, 1.4%
Max. relative deviation, 3.0%

In order to obtain optimum precision of color development, the three variables—temperature, heating time, and cooling time—must be controlled in a reproducible manner. With a 60-minute heating period at 85° C., a deviation of ±5 minutes may be allowed without causing color intensity changes which exceed the maximum relative error of the method. In the case of the 100° C. modification, ±2 minutes deviation in a 20-minute heating period will give similar results. The technique used satisfactorily in this study to cool hot reaction mixtures in a reproducible manner consisted in removing the solutions from the heating bath and immediately placing them into a constant temperature bath regulated at room temperature. When only a few solutions were to be cooled simultaneously, a large vessel of water, agitated, and at room temperature, was found adequate.

Effect of Diverse Ions. Various ions were selected for study of their influence on the color reaction. The metallic ions tested were osmium(VI), iridium(IV), ruthenium(III), rhodium(III), palladium(II), gold(III), tellurium(VI), chromium(III), nickel(II), iron(III), copper(II), and cobalt(II). Anions included were nitrate, bromide, iodide, and sulfate. The diverse ions were added, individually, to solutions containing 1.2 p.p.m. of platinium (in the final solution), in varying amounts and the color was developed by the 100° C. method. Tolerance concentrations for the various foreign ions were taken as those amounts which caused absorbance errors not exceeding 3%, the maximum relative error of the method. Measurements were made on solutions containing interfering substances in the concentration range

Table II. Effect of Diverse Ions

(All solutions contained 1.2 p.p.m. of platinum)

Interfering Substance	Concn., P.P.M., for 3% Relative Error	Per Cent Relative to Platinum
Pd(II)[a]	0.02	1.7
Rh(III)	0.05	4.2
Ir(IV)	0.08	6.7
Os(VI)[b]	0.07	5.8
Ru(III)[b]	0.05	4.2
Au(III)	1.5	125
Fe(III)	0.6	50
Cu(II)	1.2	100
Te(VI)	>100	>8300
Cr(III)[c]	3.6	300
Ni(II)[c]	30	2500
Co(II)	120	
Nitrate	$>10^3$	
Bromide	$>10^3$	
Sulfate	120(300)[d]	
Iodide[c]	180	

[a] May be determined simultaneously with platinum using an additive absorbance method to be described in a subsequent publication.

[b] Eliminated as interference by volatilization as tetroxides in the presence of oxidizing acids.

[c] All substances produced an increase in absorbance at 525 mμ, except in the cases of chromium, nickel, and iodide which gave low readings.

[d] Final ethyl alcohol concentration of 35% instead of the usual 70%.

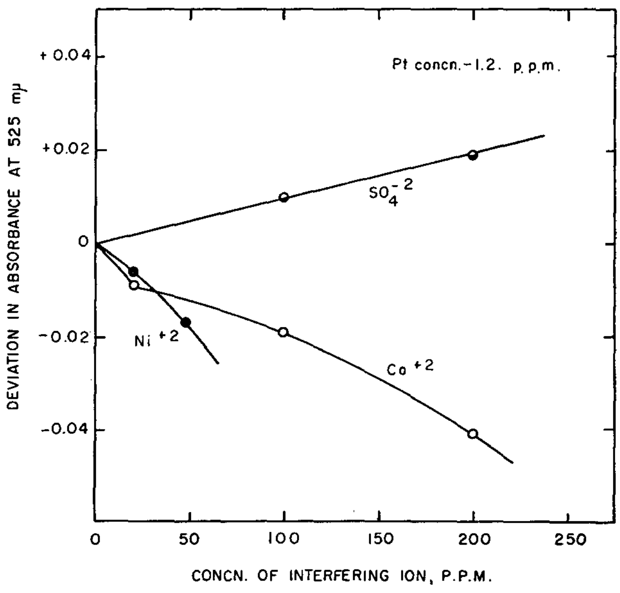


Figure 4. Effect of Diverse Ions on Intensity of Platinum-*p*-Nitrosodimethylaniline Color

necessary to give approximately 3% error and the limiting concentrations determined by graphic extrapolation as illustrated in Figure 4. The results are summarized in Table II.

In the following paragraphs are recorded the observed reactions of the platinum metals when a test solution of 10 ml. containing 60 γ of metal was caused to react in a solution consisting of 1 ml. of concentrated buffer pH 2.2, 1 ml. of 5 mg. per milliliter alcoholic reagent solution, and 5 ml. of fresh absolute ethyl alcohol. These color-developing solutions were heated for 60 minutes at 85° C., cooled to room temperature, and made up to 50 ml. with 95% ethyl alcohol, giving a final concentration of 1.2 p.p.m. of metal.

Palladium. On addition of palladium an intense blood-red color developed almost immediately. The color intensity of the solution was so high that it was unsuitable for direct spectrophotometric measurement; however, in a solution containing 0.6 p.p.m. of palladium no significant change took place in the color during the heating period. [The palladium solution was standardized by the dimethylglyoxime method (*3*, p. 41).]

Rhodium. No color change occurred immediately at room temperature, but upon standing for a few minutes, a faint orange color slowly developed. Heating the solution 4 to 5 minutes caused the formation of a deep red color which increased in intensity for about 30 minutes, after which little or no increase was noted. The final solution was clear, cherry-red in color. It is believed that this reaction might be used as a sensitive colorimetric method for rhodium.

Iridium. Reaction of the reagent with the iridium salt was not apparent at room temperature. After 20 minutes of heating the solution began to darken slightly and subsequently developed a brownish green color. The solution was distinctly brown after the heating period.

Osmium. The reaction appeared very similar to that for iridium. The color of the final solution was yellow-green with a brown tinge.

Ruthenium. No color change was evident in the solution after standing for several minutes at room temperature. A deep emerald-green color, in contrast to the yellowish green of the color-forming solution before heating, developed after about 2 minutes of heating. No significant change in the color or intensity was noted for some time during the heating process, but toward the end a brownish tinge appeared.

Interference by sulfate ion was manifested in two ways. Below 500 p.p.m. sulfate ion, a color enhancement was apparent. Larger concentrations resulted in turbid solutions because of the low solubility of sulfate in the final 70% alcoholic solution. By diluting the color-forming solutions with 48% ethyl alcohol (final ethyl alcohol concentration about 35%), it was found that the sulfate tolerance could be increased to 300 p.p.m., with no turbidity evident at a sulfate concentration of 1000 p.p.m.

RECOMMENDED PROCEDURE

The 85° C. Method. A sample containing between 35 and 120 γ of platinum as the chloride salt is adjusted to pH 2 to 3 and made to a total volume of 10 ml. (Highly acidic samples are adjusted to pH 2 to 3 with 1*M* sodium hydroxide, neutral or weakly acidic solutions with 0.1*M* hydrochloric acid.) It is treated with 1 ml. of concentrated sodium acetate–hydrochloric acid buffer and 1 ml. of 5 mg. per milliliter reagent solution and the walls of the flask containing the resulting mixture are washed down with 5 ml. of fresh absolute alcohol. (Although maximum sensitivity is obtained using a sodium acetate–hydrochloric acid buffer of pH 3, the additive absorbance method for platinum and palladium to be described in a subsequent paper requires the use of a buffer of pH 2.2 ± 0.2.) The solution is then heated on a steam bath for 60 minutes at 85° ± 2° C. This heating is conveniently carried out in a 50-ml. borosilicate glass volumetric flask. The resulting solution is immediately cooled in some reproducible manner and made up to a 50-ml. volume with 95% ethyl alcohol. A blank solution is prepared using distilled water instead of the aliquot containing platinum. This blank is used to correct for the excess reagent in the sample solution. (One blank solution may be used over a period of several hours for a number of determinations.) The absorbance of the sample solution is measured at 525 mμ against the blank and the platinum concentration determined from a calibration curve or standard absorbance index which has been obtained using known amounts of platinum.

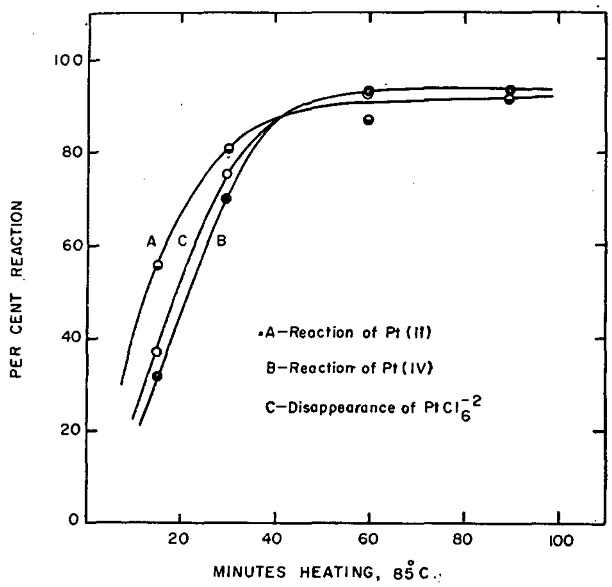


Figure 5. Reaction Rates of Platinum with *p*-Nitrosodimethylaniline

The 100° C. Modification. The same technique of solution preparation is followed as described for the 85° C. method, except that the flask is rinsed down with 5 ml. of distilled water instead of ethyl alcohol. (A slight turbidity may develop at this point but this will disappear as soon as the solution is heated. When the final solution is made up to volume with ethyl alcohol, any reoccurring turbidity will be eliminated.) The solution is heated in boiling water for 20 minutes and then carried through the same procedure as given for the 85° C. method.

THE COLORED SPECIES

Absorption spectra of the red-colored solutions developed by the recommended procedure are identical and reach the same intensity when either quadrivalent or divalent platinum is used as the starting material. It is believed that the red color is the result of the reaction of divalent platinum with *p*-nitrosodimethylaniline following the reduction of platinum(IV) by the excess reagent. Since no change in the intensity of the 262-mμ absorption maximum attributable specifically to the chloroplatinate ion (*7*) was observed when a solution containing $PtCl_6$ was carried through the color-forming procedure without *p*-nitrosodimethylaniline as is the case when the reagent is present, it is presumed that the excess reagent acts as the reducing medium during the color-forming reaction. Additional evidence of reduction was found when divalent platinum was shown to react at a faster initial rate than quadrivalent platinum (Figure 5). [These data were obtained by extracting the red color with chloroform and determining the unreacted platinum by an independent method of analysis (*1*)]. After 35 to 40 minutes of heating (85° C. procedure) the extent of the reaction of platinum(II), curve *A*, Figure 5, and platinum(IV), curve *B*, is approximately equal. It is believed that at this point the reduction reaches equilibrium and the color reaction alone governs the reaction rate. The decrease of the chloroplatinate ion concentration (curve *C*, Figure 5) was found to proceed at a rate which closely approximated the rate of formation of red color from platinum(IV). [The concentration of chloroplatinate ion remaining unreacted was determined by extracting the red complex and the excess reagent with chloroform and analyzing the aqueous phase by an ultraviolet spectrophotometric procedure (*7*)]. It appears, therefore, that reduction is the rate-determining step, since chloroplatinate ion disappears at a rate which is slower than the formation of red color from divalent platinum.

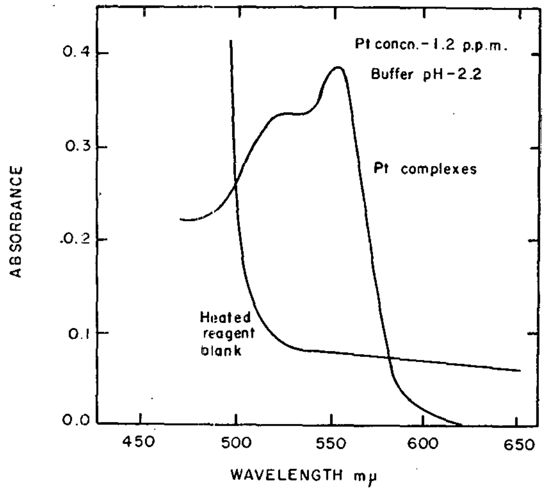


Figure 6. Absorption Curve of Platinum–*p*-Nitrosodimethylaniline Complexes

When platinum(II) or (IV) is heated with approximately equimolar quantities of *p*-nitrosodimethylaniline, a red color forms which shows a single absorption maximum at about 510 mμ. If this reaction is carried out in a large excess of reagent, such as that used in the recommended analytical procedure, the resulting red color then shows two absorption maxima, one at 550 and one at 525 mμ, and at times a third at 475 mμ. It was found that the absorption peaks at 525 and 550 mμ maintain a constant intensity ratio when the color is developed by the recommended procedure; however, the relative intensity of these maxima is changed by altering such variables as type and concentration of buffer, ethyl alcohol concentration, and heating time (during the early stages). Figure 6 shows the absorbance curve of the color formed by the reaction of platinum(IV) with *p*-nitrosodimethylaniline using the procedure recommended. A similar curve may also be obtained using a sodium acetate–hydrochloric acid buffer of pH 4; however, use of a sodium acetate–acetic acid buffer, pH 4, results in a color whose absorbance curve is almost the mirror image of that found when the sodium acetate–hydrochloric acid buffer is used. In these instances the absorption maxima are found to remain at the same wave lengths but their relative intensities vary. On the basis of these observations it may be concluded that chloride ion plays an important part in the formation of the color represented in Figure 6. The absorption maxima at 525 and 550 mμ would thus appear to indicate at least two colored platinum complexes. The origin of the 475-mμ maximum is less clear but it is believed to be associated with an oxidized form of the reagent molecule, either in the uncombined state or perhaps combined with platinum.

An attempt was made to establish the empirical formulas of the colored substances in solutions using the "continuous variations" technique devised by Job (*6*) and extended by Vosburgh and coworkers (*4, 10*); however, the data found in this study were erratic and difficult to interpret conclusively. Presumably the conflicting experimental data obtained are due to the fact that equilibrium conditions were not the same for all of the solutions containing varying mole ratios of reagent to metal used in the study.

A sample of one pure platinum complex, a dark reddish purple material, was obtained by chromatographic separation. The dark red color resulting from the reaction of 10 mg. of platinum in a scaled-up version of the recommended procedure was first extracted with chloroform. A crude dark red solid was then secured by evaporating this extract to dryness and leaching out some of the unreacted reagent (also extracted) with diethyl ether. This crude preparation (50 to 60 mg.) was next dissolved in 25 ml. of acetone containing 1 ml. of chloroform and the resulting red solution was slowly poured onto a column of 80- to 200-mesh alumina 1 cm. in diameter and 25 cm. long. A dark reddish purple band was observed to be formed at the top of the alumina column. During the slow addition of acetone, a band of unreacted yellow reagent and a band of unidentified reddish brown material passed out in the eluent. The dark reddish purple band was observed to move slowly down the column upon continued acetone development until no other band was evident. This reddish purple material was then eluted with absolute ethyl alcohol and the residue resulting from the evaporation of this solvent was again chromatogrammed in the same manner as previously described. The final blood-red eluent was carefully evaporated to dryness, leaving a film of dark green crystals which represented a yield 27% of theoretical. Analysis of this complex gave results which indicated its structure as $Pt[(CH_3)_2N—C_6H_4NO]_4Cl_2$. Calculated for $C_{32}H_{40}O_4N_8Cl_2Pt$: carbon, 44.33%; hydrogen, 4.65%; platinum, 22.52%. Found: carbon, 44.77%; hydrogen, 4.40%; platinum, 23.16%. An absorption spectrum of this material exhibited a single maximum at 518 mμ, very probably corresponding to the 525-mμ "maximum" found in the complex colored solutions (Figure 6), since the isolated complex represented a substantial part of the colored constituent.

Absorption spectra of reddish purple acetone eluent fractions taken off just prior to the elution of the dark reddish purple band showed the presence of material having strong absorption at 550 mμ, with little absorption at 525 mμ. It was not found possible to isolate in pure form the complex which showed its maximum at 550 mμ in sufficient quantity to attempt an analysis.

ACKNOWLEDGMENT

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Colorimetric Determination of Zinc and Copper with 2-Carboxy-2′-hydroxy-5′-sulfoformazylbenzene

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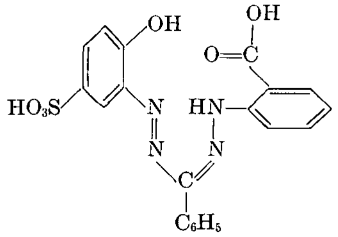
The purpose of this investigation was to develop a new colorimetric method for zinc and copper utilizing the compound 2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene (Zincon). Both elements form a blue complex with this reagent. The zinc complex is stable over the pH range 8.5 to 9.5 while the copper complex is stable in the pH range 5.0 to 9.5. This difference in effect of pH permits the determination of zinc and copper in the presence of each other. Both complexes follow Beer's law over the concentration range 0.1 to 2.4 p.p.m. of the element. The sensitivity is 0.003 γ per sq. cm. for both zinc and copper. An ion exchange procedure is described for the separation of zinc from interfering ions.

DURING an investigation of a number of organic compounds, selected as possible analytical reagents because of their structure, the compound 2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene (I) was observed to give a dark blue precipitate (blue solution at high dilution) with zinc and color reactions with copper, cobalt, and nickel. These observations prompted an investigation of this compound as a possible colorimetric reagent for zinc and copper. A brief discussion of the color formation with zinc has already been presented (*13*).



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Various colored metal complexes with formazyl compounds have been described (*1*, *4*, *9–11*). The only mention of compounds of this type as colorimetric reagents is in a note by Wizinger (*9*).

At present, the most widely used colorimetric method for zinc is the one employing dithizone which has a sensitivity of 0.0016 γ per sq. cm. (*7*). The new method has a sensitivity of 0.003 γ per sq. cm. and replaces the complexing and extraction of the dithizone method with an ion exchange separation.

Zincon is proposed as a short name for the compound 2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene. According to *Chemical Abstracts'* nomenclature the name is *o*-{2-[α-(2-hydroxy-5-sulfophenylazo)-benzylidene]hydrazino}benzoic acid.

APPARATUS AND REAGENTS

A Beckman spectrophotometer, Model DU, operated at maximum sensitivity, was used for all absorbance measurements. The ultraviolet-sensitive phototube was employed at and below 625 mμ. Matched 1.00-cm. Corex cells were used. A Beckman pH meter, Model G, was employed for all pH measurements. Both the straight- and goose-neck type of ion exchange columns were used. The tube containing the resin was a 7-cm. length of borosilicate glass tubing, 5 mm. inside diameter, in both cases. The desired rate of flow was obtained by applying air pressure to the top of the resin column.

Standard solutions of zinc and copper were prepared so as to contain 0.100 mg. of the respective ion per ml. All buffer solutions were prepared according to the directions of Clark (*2*).

Reagent solutions were prepared by dissolving 0.130 gram of finely powdered Zincon in 2 ml. of $1M$ sodium hydroxide and diluting to 100 ml. This gives a concentration of $0.002M$, based on a purity of 68% for the reagent. These solutions were deep red in color and were stable for about one week. Zincon may be obtained from the LaMotte Chemical Products Co., Towson, Baltimore 4, Md.

A sample of Dowex 1 anion exchange resin (50 to 100 mesh), supplied by the Dow Chemical Co., Midland, Mich., was used in all the ion exchange studies. The columns described above were filled by adding the resin in a slurry with water to give a height of 5 cm.

DETERMINATION OF ZINC

Color Formation. Upon addition of zinc to an alkaline solution of the reagent a blue color is formed immediately. Absorption curves of both the reagent and the zinc complex are shown in Figure 1. Maximum absorbance for the zinc complex occurs at 620 mμ. The absorbance was found to be the same at 620 and 625 mμ. Because the reagent absorbs slightly in this region, a blank was used in all cases.

The color of the zinc complex has a maximum intensity in the pH range 8.5 to 9.5 as shown in Figure 2. The curve for the complex was obtained by using 1.00 p.p.m. of zinc, an excess of reagent, and varying amounts of dilute hydrochloric acid and ammonium hydroxide. The reagent curve was obtained in the same manner, using the same amount of reagent, but no zinc. A Clark and Lubs buffer, pH 9.0, was found to be satisfactory for maintaining the hydrogen-ion concentration in this region.

The complex was found to follow Beer's law over the range 0.1 to 2.4 p.p.m. of zinc using Procedure A. The optimum concentration range for absorbance measurements is 0.5 to 2.0 p.p.m.

The reagent-to-metal ratio of the complex in solution was found to be 1 to 1 by the slope ratio method (*3*), mole ratio method (*12*), and the continuous variations method (*8*).

For the slope ratio method two plots of absorbance versus

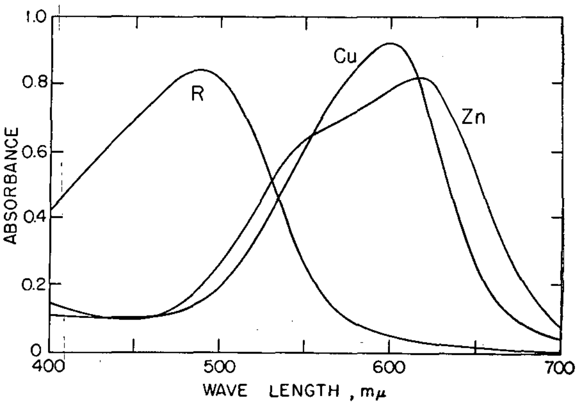

Figure 1. Absorbance Curves for $4.0 \times 10^{-5}M$ Solutions of Reagent (R), Zinc Complex (Zn), and Copper Complex (Cu), at pH 9

Absorbance curves measured every 10 mμ, beginning at 400 mμ versus a water blank

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concentration were obtained—one with solutions containing an excess of zinc (6×10^{-5} *M*) and varying concentrations of reagent and the other with solutions containing an excess of reagent (4×10^{-5} *M*) and varying concentrations of zinc (Figure 3). The ratio of the slopes of these two lines is 0.97 indicating a 1 to 1 ratio.

In the mole ratio method the reagent concentration was maintained constant at 4.0×10^{-5} *M* and the ratio of moles of zinc to moles of reagent varied from 0.08 to 1.5. The results, as shown in Figure 4, indicate a 1 to 1 ratio.

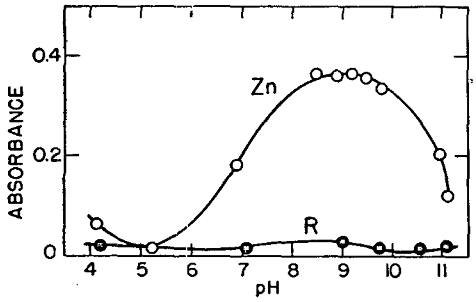

Figure 2. Effect of pH on Reagent (R) and Zinc Complex (Zn); 1.00 P.P.M. Zinc, Excess Reagent, 625 mμ

The continuous variations method was applied by mixing *X* ml. of a 5.0×10^{-4} *M* reagent solution and ($10.0 - X$) ml. of a zinc solution of the same concentration and diluting to 50 ml. with the Clark and Lubs buffer, pH 9.0. The maximum value of *Y* (observed absorbance minus calculated absorbance) occurs at $X = 5.0$ (Figure 5), again indicating a 1 to 1 ratio.

From the data obtained in the slope ratio method the dissociation constant for the complex was found to be about 10^{-6}.

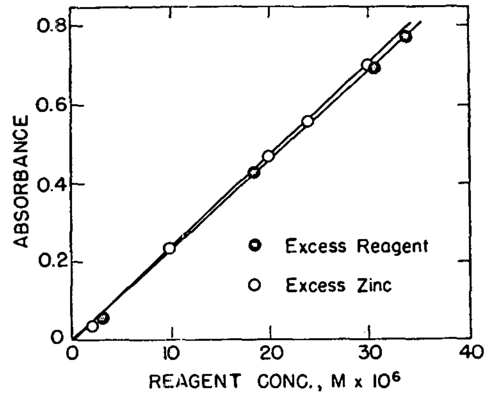

Figure 3. Slope Ratio Method Applied to Zinc Complex; pH 9.0, 625 mμ

The effect of the reagent concentration on the color formed with 1.00 and 2.00 p.p.m. of zinc was studied over the range 6×10^{-6} to 18×10^{-6} *M*. Above a concentration of 12×10^{-6}*M* a decrease in the sensitivity and precision was noted and this concentration is used in the standard procedure.

The volume of the pH 9.0 buffer used was found to have no effect on the absorbance of a 2.00 p.p.m. zinc solution (determined by Procedure A) over the range 5 to 25 ml.

The order of addition of the buffer and the reagent was found to have no effect on the intensitv of the complex color.

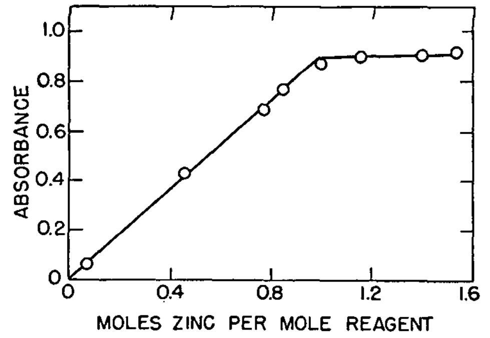

Figure 4. Mole Ratio Method Applied to Zinc Complex; pH 9.0, 625 mμ

Procedure A. Transfer to a 50-ml. volumetric flask a 10-ml. aliquot of the sample, in an approximately neutral solution, containing 25 to 100 γ of zinc. Add 10 ml. of a Clark and Lubs buffer pH 9.0, and 3.0 ml. of the Zincon reagent solution. Dilute to the mark, mix thoroughly, and measure the absorbance in a spectrophotometer at 620 mμ against a reagent blank. The amount of zinc can then be estimated from a calibration curve obtained with known amounts of zinc treated as above.

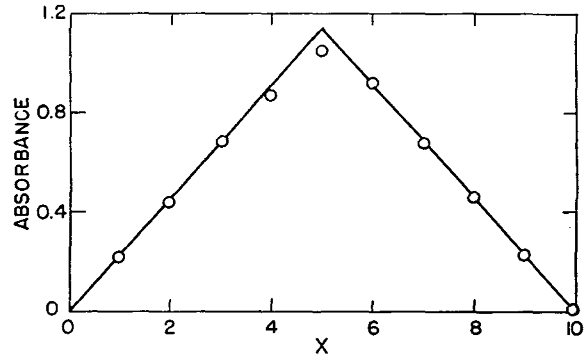

Figure 5. Continuous Variations Method Applied to Zinc Complex; pH 9.0, 620 mμ

The average of 11 determinations of 1.00 p.p.m. of zinc by this procedure was 0.99 p.p.m. with a standard deviation of 0.01.

The practical sensitivity of this procedure was found to be 1 part of zinc in 70,000,000 parts of solution. Six solutions of this concentration gave an average value of 0.005 absorbance unit. This corresponds to a sensitivity of 0.003 γ per sq. cm. as defined by Sandell (*7*).

A solution containing 1.00 p.p.m. of zinc and treated by Procedure A showed only a 2% decrease in absorbance over a period of 24 hours.

The following ions were found to cause an interference in the above procedure when present in a ratio of metal-to-zinc of 1 to 1 or less: aluminum(III), beryllium(II), bismuth(III) cadmium(II), cobalt(II), chromium(III), copper(II), iron(III) manganese(II), molybdenum(VI), nickel(II), and titanium(IV) A detailed study of diverse ions was not carried out because these results indicate that zinc must be separated from a large number of common metal ions before it can be determined by this method.

Separation of Zinc. The possibility of separating zinc using the anion exchange resin Dowex 1 has been suggested by Kraus (*5*, *6*). This information indicated that zinc could be separated from most other ions (except gallium and indium) by adsorption and washing with 1*M* hydrochloric acid and elution with 0.01*M*

Table I. Analysis of Zinc Solutions by Procedure B

Composition, γ		Zinc Added, γ	Zinc Recovered, γ	Difference, γ
		50.0	51.0	+ 1.0
		50.0	50.4	+ 0.4
		50.0	49.3	− 0.7
		100	100	0
Cu(II)	50	50.0	50.5	+ 0.5
	500	50.0	52.3	+ 2.3
	5000	50.0	73	+23
Fe(III)	500	50.0	51.8	+ 1.8
	5000	50.0	47.4	− 2.6
Co(II)	1000	50.0	50.4	+ 0.4
Ni(II)	1000	50.0	50.4	+ 0.4

hydrochloric acid. A series of experiments showed that small amounts of zinc (about 50 γ) were quantitatively adsorbed from $1M$ hydrochloric acid and quantitatively eluted by $0.01M$ hydrochloric acid. These experiments also showed that washing with $1M$ hydrochloric acid removed copper(II) and iron(III) up to 500 γ, and cobalt(II) and nickel(II) up to 1000 γ (See Table I).

Procedure B. Wash the resin column with 30 ml. of $0.01M$ hydrochloric acid (2 ml. per minute) and carry out a zinc determination by Procedure A on the eluate. The absorbance of this solution is the column blank. Wash the column with 5 ml. of $1M$ hydrochloric acid (1 ml. per minute) followed by the sample (25 to 100 γ of zinc) in 1 to $3M$ hydrochloric acid (1 ml. per minute). Follow this with 50 ml. of $1M$ hydrochloric acid (2 ml. per minute), and elute the zinc with 30 ml. of $0.01M$ hydrochloric acid (1 ml. per minute) into a 50-ml. volumetric flask. Determine the zinc by Procedure A, correcting for the column blank.

Initially it may be desirable to run another 30-ml. portion of $0.01M$ hydrochloric acid through the column and to determine the zinc by Procedure A in order to check for completeness of removal of the zinc. However, in all results reported in this paper, this second portion of $0.01M$ hydrochloric acid was found to have the same absorbance value (within the experimental error) as the column blank.

Table II. Analysis of NBS Samples by Procedure B

Material	NBS		Found	
	ZnO, %	Zn, %	ZnO, %	Zn, %
Opal glass 91	0.08	...	0.075 0.076 0.078 0.078 0.080	...
			Av. 0.077	
			σ 0.002	
Mg-base alloy 171	..	1.05	...	1.00 1.01 1.02 1.06
				Av. 1.02
				σ 0.03
Al alloy 85a	..	0.019	...	0.020 0.021

The results of the analysis of National Bureau of Standards Samples by Procedure B are summarized in Table II.

DETERMINATION OF ZINC AND COPPER

Color Formation with Copper. As with zinc, an immediate blue color is formed when copper is mixed with an alkaline solution of the Zincon reagent. An absorption curve of the copper complex is shown in Figure 1. Maximum absorption occurs at 600 mμ and this wave length was used for analytical measurements.

The absorbance of the copper complex remains constant over the pH range 5.0 to 9.5. This stability towards pH changes permits the determination of zinc and copper in the presence of each other. The absorbance of a solution containing zinc, copper, and reagent buffered at pH 5.2 will be due entirely to the copper complex because the zinc complex does not absorb at this pH (Figure 2). At pH 9.0 the absorbance of such a solution will be due to both the copper and the zinc complexes. Thus, the absorbance at pH 5.2 gives the copper directly and the difference between the absorbances at pH 5.2 and 9.0 gives the zinc. To facilitate the subtraction of absorbance values, all measurements were made at 600 mμ. The zinc complex follows Beer's law over the range 0.1 to 2.4 p.p.m. of zinc at this wave length, with only a small loss (about 10%) in sensitivity.

The copper complex was found to follow Beer's law over the range 0.1 to 2.4 p.p.m. of copper at both pH 5.2 and 9.0. The optimum concentration range in both cases is 0.5 to 2.0 p.p.m. The reagent-to-metal ratio in solution was found to be 1 to 1 at both pH 5.2 and 9.0 by both the mole ratio method (*12*) and the continuous variations method (*8*). The sensitivity of this reagent for copper is the same as for zinc—i.e., 0.003 γ per sq. cm. A solution containing 1.00 p.p.m. of copper and excess reagent showed less than a 1% decrease in absorbance over a period of 24 hours.

Procedure C. Transfer to a 50-ml. volumetric flask a 10-ml. aliquot of the sample, in an approximately neutral solution, containing 25 to 100 γ of zinc plus copper. Add 10 ml. of a Clark and Lubs buffer, pH 5.2, and 3.0 ml. of the Zincon reagent solution. Dilute to the mark, mix thoroughly, and measure the absorbance in a spectrophotometer at 600 mμ against a reagent blank. The amount of copper can then be estimated directly from a calibration curve. Treat a second 10-ml. aliquot as described above, except use a Clark and Lubs buffer, pH 9.0. The absorbance due to zinc is the difference between these two absorbance values and the amount of zinc can then be estimated from a calibration curve.

The interferences with this procedure are essentially the same as for the determination of zinc (without the ion exchange separation).

The results of the analysis of several synthetic solutions by Procedure C are given in Table III.

Table III. Analysis of Synthetic Solutions by Procedure C

Added, γ		Found, γ	
Zinc	Copper	Zinc	Copper
100	5.0	100	4.7
50.0	50.0	49.1	50.7
50.0	50.0	47.4	52.1
20.0	20.0	20.8	20.0
5.0	100	4.8	101
5.0	100	4.7	100

ACKNOWLEDGMENT

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An Automatic Differential Potentiometric Titrator

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A simple and inexpensive automatic differential potentiometric titrator is described which does not require any instrument adjustments prior to a titration. It is not necessary to know and set the end-point potential, because the electronic circuit computes the second derivative voltage of the ordinary potentiometric curve, and this voltage is ideally suited to trigger a relay system which turns the buret off at the inflection point (end point) of the titration. The instrument gives excellent precision and accuracy for the two oxidation-reduction systems used in testing the titrator. The titrator is applicable for automatic potentiometric titrations where the end-point potential is not known or changes with different titration conditions.

THE use of automatic titrators is becoming increasingly popular, chiefly because precise titrations can be performed more rapidly with good automatic instruments than by manual titrations. Many automatic potentiometric titrators are described in the literature and a comprehensive bibliography is given by Lingane (*6*).

There are essentially two basic types of automatic titrators and both are commercially available. One type, originally presented by Lingane (*5*), automatically anticipates and seeks the equivalence-point potential and turns the buret off when it is reached. There are commercial instruments available (*1, 6*) which use this basic principle. Another type of automatic titrator records the potentiometric titration curve of potential against milliliters of titrant. The end point is read from the plot after the titration is completed. A recording instrument of this type is described by Robinson (*8*) and a commercia' model is available (*7*).

Another type of automatic potentiometric titrator is now presented which is considerably different from those previously described. It is known that the inflection point of a potentiometric curve is often equal to or sufficiently close to the equivalence point to cause negligible error in a titration (*4*). This new titrator automatically determines the inflection point and turns the buret off when it is reached. This is accomplished by electronically producing a voltage which is proportional to the second derivative of the ordinary electrode potential titration curve, and the second derivative voltage is ideally suited for triggering a relay system which turns the buret off at the inflection point.

It is necessary to deliver the titrant at a constant or uniform rate. A constant flow rate buret (*6*), a uniform flow rate buret (*3*), or coulometric generation of titrant at constant current is suitable.

Several advantages characterize the differential automatic titrator: The equipment is very simple, compact, and inexpensive; the end-point potential does not have to be known; various reference electrodes can be used and their potentials do not have to be known; and no instrument adjustments are required—it is only necessary to push the start button.

The present model of the instrument also has certain disadvantages. It is not suited for titrations where the solution or electrodes reach equilibria very slowly, because the system does not anticipate and slowly hunt for the equivalence point. The glass electrode cannot be used because of its high resistance. This can be remedied by redesigning the input amplifier stage.

INSTRUMENTATION OF DIFFERENTIAL TITRATOR

The differential automatic titrator consists of two basic circuits. One is an amplifier-differentiator circuit which produces an output voltage proportional to the second derivative of the ordinary potentiometric titration voltage fed into the input. The other circuit is a relay system which uses the second derivative voltage to turn the buret off at the inflection point (end point) of the potentiometric curve.

Amplifier-Differentiator Circuit. The schematic diagram of the amplifier-differentiator circuit is given in Figure 1. The voltage between the electrode pair is fed directly to the control grid of a triode amplifier, which is one half of a 6SL7 twin-triode tube. The amplified voltage is differentiated by a simple resistance-capacitance differentiator, R_1C_1, consisting of a 0.5-microfarad polystyrene condenser and a 1-megohm resistor. The output voltage of the first resistance-capacitance differentiator is closely proportional to the first derivative of the electrode potential curve. The characteristics of a similar amplifier and resistance-capacitance differentiator are discussed by Blaedel and Malmstadt (*2*).

The output voltage of the first resistance-capacitance differentiator is fed directly to the grid of the second triode amplifier stage, which is the other half of the twin-triode tube. The amplified first derivative voltage is differentiated by a second resistance-capacitance differentiator, R_2C_2, also consisting of a 0.5-microfarad polystyrene condenser and a 1-megohm resistor. The output voltage from the second differentiator is closely proportional to the second derivative of the electrode potential curve.

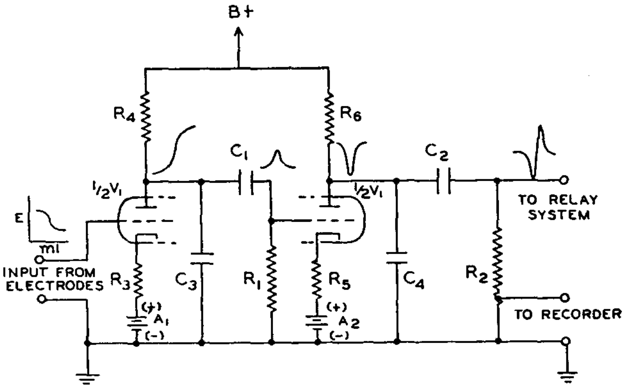

Figure 1. Amplifier-Differentiator Circuit

R_1. 1-megohm, 0.5-watt resistor
R_2. 1-megohm resistor and a 2000-ohm resistor in series
R_3, R_5. 2000-ohm, 0.5-watt resistors
R_4, R_6. 1-megohm, wire-wound, 0.5-watt resistors
C_1, C_2. 0.5-microfarad, 300 WVDC, polystyrene condensers
C_3, C_4. 0.02-microfarad, 450-volt paper condensers
A_1, A_2. 1.5-volt flashlight batteries
B_+. 270-volt B batteries or electronic-regulated supply
V_1. 6SL7 twin-triode tube

The typical voltage curves which exist at various points of the circuit when titrant is added at a constant rate in the end-point region of a potentiometric titration are illustrated in Figure 1.

Resistance, R_2, consists of a 1-megohm resistor and a 2000-ohm resistor in series. This provides for a small fraction of the second differential output voltage to be observed on a recording potentiometer or millivoltmeter.

The amplifier-differentiator circuit is designed so that for relatively sharp end points the amplitude of the output voltage is 15 volts or more. The large output voltage is desirable for the type of relay system illustrated in Figure 2.

Relay System. The relay system shown in Figure 2 is the most simple and reliable of several systems that were tested.

The output voltage from the second differentiator is fed directly to the grid of a miniature 2D21 thyratron tube. The 110-volt alternating current line voltage is applied across the thyratron tube in series with the coil of a SPDT 110-volt alternating current relay. When no voltage is applied to the grid, the thyratron conducts on the positive cycles of the 60-cycle line voltage. If a rather large condenser, C_1, is put in parallel with the coil of the alternating current relay, it remains closed in the position shown when the grid voltage is zero.

If the grid voltage of the thyratron goes about 1.5 volts negative, illustrated as point *a* on the second derivative input voltage, Figure 2, the thyratron deionizes, stops conducting current, and relay 1 opens. When relay 1 opens, condenser C_2 is charged by battery B_1 through resistance R_1. The thyratron remains cut off until the grid becomes slightly more positive than minus 1.5 volts, illustrated by point *b* on the input voltage. At point *b* the thyratron again conducts and closes relay 1. This puts the charged condenser, C_2, across the single-pole single-throw 6-volt direct current relay 2 and momentarily opens the contacts of relay 2.

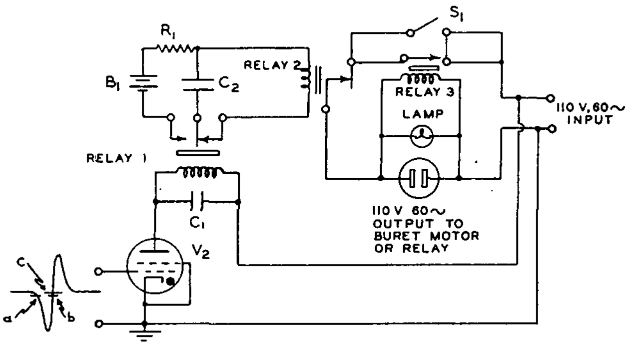

Figure 2. Relay System

R_1.	2000-ohm resistor
C_1.	8-microfarad, 150-volt electrolytic condenser
C_2.	500-microfarad, 20 WVDC electrolytic condenser
S_1.	Push button (spring return) SPST switch
Relay 1.	110-volt alternate current, SPDT relay
Relay 2.	6-volt direct current, SPST, normally closed relay
Relay 3.	110-volt alternate current, SPST, normally open relay
B_1.	10-volt bias cell
Lamp.	110-volt alternate current indicator lamp
V_2.	2D21 thyratron tube

The 110-volt line output to the buret motor or relay is normally dead because switch, S_1, and the contacts of relay 3 are open. In order to start delivery of titrant the 110-volt output to the buret motor or relay must be activated. This is done by depressing the push button (spring return) switch, S_1, which puts the 110-volt alternating current across the coil of 110-volt alternating current relay 3, and the contact points of relay 3 immediately close. Consequently the 110-volt alternating current line voltage remains across the 110-volt outlet even though S_1 opens when released. Titrant is therefore continuously delivered from the time the start switch, S_1, is depressed to the time that condenser, C_2, discharges through the coil of relay 2, and this corresponds to the inflection point of the titration. When the contacts of relay 2 open, the contacts of relay 3 open. Therefore, even though C_2 discharges rapidly through the coil of relay 2 and the contacts are only briefly open, the 110-volt buret outlet remains dead because the contact points of relay 3 open. The buret outlet remains dead until S_1 is depressed for the next titration.

There are several features about the relay system to consider. The condenser, C_2, is charged by battery B_1 through resistance R_1. R_1 is not always essential in the circuit, but it acts as a safety device to prevent false end points when the noise level on the second derivative voltage is large. The noise level on the second derivative voltage is usually negligible if the electrodes are properly positioned and there are suitable flow rates of titrant (Figure 3). However, if the stirring is inefficient or flow rate too fast, it is possible to have high local concentrations of titrant around the indicator electrode which can result in random voltage pulses in the region of the end point. If R_1 were not in the charging circuit for C_2, it would be possible to charge C_2 with a momentary sharp voltage pulse and cause relay 2 to open. However, if R_1 is of such a size that 1 or 2 seconds are required for C_2 to be charged to sufficient voltage to operate relay 2, it is unlikely that any random and sharp voltage pulses at the input of the thyratron can result in the operation of relay 2. The value for R_1 depends on the usual time required to go from *a* to *b* on the second derivative voltage curve, Figure 2. This time depends on several factors, including the titrant flow rate and the sharpness of the voltage change at the end point. For most titrations the time from *a* to *b* is greater than 3 seconds.

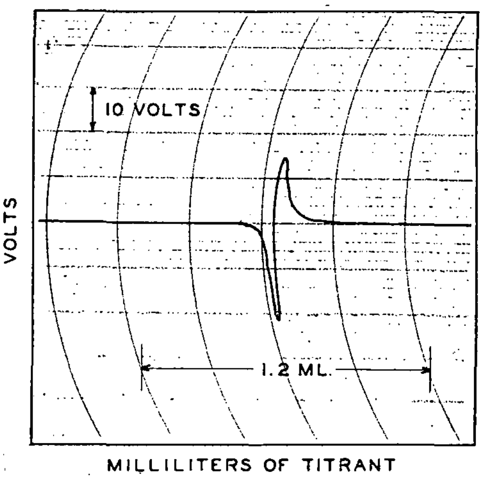

Figure 3. Recorded Second Derivative Titration Curve

The relay circuit as shown in Figure 2 requires the input second derivative voltage initially to swing negative. Therefore the electrodes must be connected so the grid voltage at the input of the amplifier-differentiator circuit swings negative with respect to the cathode. This does not present any serious problem because the direction of voltage change of the indicator electrode is usually known.

In some cases it might be convenient to leave the electrodes connected in one direction regardless of the direction of change of voltage at the end point. This is possible by a somewhat more complicated relay system.

The actual inflection point is shown as point *c* on the voltage input curve, Figure 2. This is slightly different than point *b* where the buret turns off, although the difference is negligible. If a case should arise where the difference between *b* and *c* is significant, a slightly modified relay system can be devised to turn the buret off at exactly point *c*.

Power Supplies. The amplifier-differentiator circuit requires a 6-volt filament supply and approximately a 250-volt B supply. The 6-volt filament voltage for the 6SL7 is best supplied by a storage battery. Six-volt alternating current introduces too much "noise" into the circuit. The B supply can be readily obtained from either B batteries or a small regulated electronic supply. Current drain on the B supply is less than 1 ma. The relay system requires only the 110-volt alternate current line voltage.

Delivery of Titrant. Motor-driven syringe burets (*6*) are very satisfactory for use with the differential titrator. The motor is plugged directly into the 110-volt alternate current outlet of the relay system.

The uniform flow rate buret (*3*) is also readily adapted for use with the automatic titrator. The solution from the tip of the buret is run through a small-diameter gum rubber tubing which can be rapidly opened and closed by a pinch-clamp device operated by a 110-volt alternate current relay. The flow rate is readily changed by using different sintered-glass tubes through which the titrant passes. The system is simple, inexpensive, and the milliliters of titrant delivered are read directly from an ordinary-type buret.

Coulometric generation of titrant at constant current (*6*) is an excellent and accurate method of delivery.

EXPERIMENTAL RESULTS

The operation of the automatic differential potentiometric titrator is illustrated by the results obtained from titrations using two common redox systems—ferrous solutions against both dichromate and ceric solutions. After the delivery of titrant is automatically stopped, the titrated solution is allowed to equilibrate and the equilibrium potential is measured.

The precision of the instrument is best illustrated by the reproducibility of the potential measurements for a given system. The accuracy of the instrument is shown by the comparison of the theoretical equilibrium potential at the equivalence point to the measured potentials.

Table I. Precision of Automatic Titrator for Ferrous-Dichromate Titrations

(10-ml. aliquots of 0.1*N* ferrous solution automatically titrated with 0.1*N* dichromate solution)

Determination	End-Pt. Potential, Volt (Pt-Cal. Electrode Pair)
1	0.630
2	0.630
3	0.650
4	0.648
5	0.656
Av.	0.643
Std. deviation	0.012

Preparation of Solutions. Solutions of dichromate, cerate, and ferrous iron were prepared by weighing out 4.9 grams of potassium dichromate, 56 grams of ammonium hexanitrato cerate, and 39 grams of ferrous ammonium sulfate; the dichromate and ferrous iron were dissolved and diluted with water to 1000 ml., while the cerate was dissolved in 56 ml. of concentrated sulfuric acid and then diluted to the mark in a 1-liter volumetric flask.

Recording of Titration Curves. A typical recorded second derivative curve for the titration of ferrous iron with dichromate is shown in Figure 3.

This curve is obtained by connecting the platinum-calomel electrode pair to the input of the titrator and by connecting a millivoltmeter recorder across the recorder leads at the output of the amplifier-differentiator circuit (Figure 1). The relay system is disconnected to allow continuous delivery of titrant past the end point. The low noise level on the recorded curve indicates the stability of the titrator. Titrant is delivered from a syringe microburet at the rate of 1.2 ml. per minute. A flow rate of 1.2 ml. per minute was also used for the titrations described in the following sections.

Ferrous-Dichromate System. In order to test the precision and accuracy of the automatic titrator without introducing buret errors the equilibrium end-point potentials are measured. The precision of the end-point potentials is converted to precision in terms of milliliters of standard titrant by using an expanded plot of potential against milliliters of titrant in the end-point region.

The expanded plot is obtained by adding the titrant in the end-point region from a Kirk ultramicroburet. The initial solution contains 10 ml. of 0.1*N* ferrous iron solution, 10 ml. of 6*N* sulfuric acid solution, and 5 ml. of 85% phosphoric acid, and is diluted in the titration vessel to about 50 ml. A calomel and a platinum wire electrode are placed in the titration vessel and connected to a Leeds & Northrup potentiometer, Model 7552. The standard dichromate solution is added from a 50-ml. buret to the ferrous solution to within 0.1 ml. of the equivalence point. The titration is then completed by adding the standard dichromate from the ultramicroburet. Care is taken to allow the solution to reach equilibrium before the potential is read. The expanded potentiometric curve in the region of the end point is shown in Figure 4, *A*.

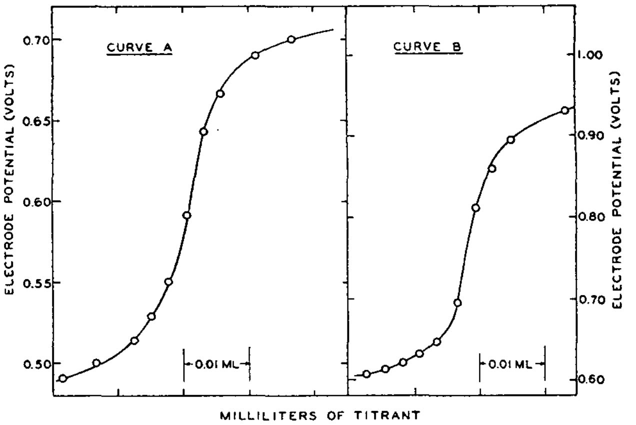

Figure 4. Expanded Potentiometric Titration Curves of End-Point Region

A. **Ferrous against dichromate**
B. **Ferrous against ceric**

Five 10-ml. aliquots of 0.1*N* ferrous iron are titrated with standard 0.1*N* dichromate, using the automatic titrator to determine the end point. After the buret automatically shuts off, the solution is given time to equilibrate and the potential of the solution is measured. The precision of the results are shown in Table I. The standard deviation of the electrode potential at the end point is 0.0120 volt, which is equivalent to 0.00086 ml. of 0.1*N* dichromate solution. The average end-point potential is 0.039 volt higher than the potential at the end point determined by the classical method and represents a difference of 0.002 ml.

Table II. Precision of Automatic Titrator for Ferrous-Ceric Titrations

(10-ml. aliquots of 0.1*N* ferrous solution are automatically titrated with 0.1*N* ceric solution; two different reference electrodes are used)

	Potential, Volt	
Determination	Pt-calomel electrodes	Pt-Pt (10% Rh) electrodes
1	0.818	0.860
2	0.817	0.865
3	0.821	0.865
4	0.820	0.867
5	0.824	0.868
6	0.826	...
7	0.825	...
8	0.823	...
Av.	0.822	0.866
Std. deviation	0.0033	0.0034

Ferrous-Ceric System. An expanded plot of the end-point region of the ferrous-ceric system is made. Ten milliliters of 0.1*N* ferrous solution in the presence of 5 ml. of concentrated sulfuric acid and diluted to about 50 ml. with distilled water are titrated with standard 0.1*N* ceric solution in the manner described for the ferrous against dichromate system.

Eight 10-ml. aliquots of ferrous iron are titrated with standard ceric solution using the automatic titrator and the calomel-platinum electrode pair. Upon completion of each titration the solution is allowed to equilibrate and the potential of the solution is measured. The precision of the results are shown in Table II. The standard deviation of the electrode potential at the end point is 0.0033 volt, which is equivalent to 0.00018 ml. of 0.1N ceric solution. The average end-point potential is 0.068 volt higher than the theoretical end-point potential and represents an error of 0.0015 ml.

Bimetallic Electrodes. It is easy to substitute various reference electrodes for the calomel electrode because the potential of the reference electrode does not have to be known for use with the automatic titrator. Five 10-ml. aliquots of 0.1N ferrous solution are titrated with standard ceric solution. The reproducibility of the end-point potential with a platinum indicator electrode and a platinum–10% rhodium reference electrode connected to the input of the automatic titrator is given in Table II. The end-point potential of the platinum electrode is measured with reference to a saturated calomel electrode.

The standard deviation of the electrode potential at the end point is 0.0034 volt, which is equivalent to 0.00019 ml. of 0.1N ceric solution. The average end-point potential is 0.112 volt higher than the potential at the end point determined by the classical method and represents a difference of 0.004 ml.

Flow Rate Studies. In order to test the effect of the delivery rate of titrant on the precision and accuracy of the results, standard ceric solution was added to ferrous solutions at five different flow rates varying from 0.4 to 2.8 ml. per minute. The reproducibility of the end-point potential at all of the rates is about the same. There is, however, a rise in end-point potential with increase of flow rate. At the fastest flow rate studied, 2.8 ml. per minute, the end point is overshot by less than 0.02 ml. of 0.1N ceric solution.

These results indicate that for certain potentiometric titrations delivery rates of about 3 ml. per minute are possible without introducing significant error.

Procedure for Performance of Titrations. The stirrer, a small, motor-driven glass propeller, is placed in a 150-ml. beaker, slightly offset from center and approximately one half inch from the bottom. The right-angled delivery tip of the buret is placed immediately above the propeller and about 0.1 inch from the shaft of the stirrer, so that the delivery flow is directed at the shaft. The reference and indicator electrodes are placed on the opposite side of the titration vessel about 0.25 inch from the bottom and close but not touching the sides of the titration vessel. The complete assembly is mounted so that the bottom of the titration vessel is above the table surface, thus allowing the vessel to be replaced without disturbing the electrode, buret, and stirrer assembly.

The solution to be titrated is diluted with distilled water to approximately 50 ml., which allows sufficient volume to completely cover the electrodes, thus eliminating appreciable electrical noise during the titration. The stirrer is rotated as rapidly as possible without introducing too much air into the solution. It is advisable to ground the stirrer and buret motor to prevent pickup of electrical noise at the electrodes. The start button of the automatic titrator is pushed; completion of the titration is automatically determined.

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Automatic Recorder for Continuous Determination of Oxygen in Gases Using the Dropping Mercury Electrode

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A constant control is needed to show the presence of oxygen in the head gas of reactors used for synthetic rubber production. By means of a continuous automatic analyzing system, the oxygen content of the exit gas from a nitrogen purification unit as well as in the hydrocarbon feed used in preparing synthetic rubber was placed on a more reliable basis. This eliminates the error found in periodic sampling procedures and fulfills the need for more accurate and additional analyses of gases used in commercial systems where the presence of oxygen is detrimental.

OXYGEN plays an important role in the polymerization reactions of olefins and diolefins. Small traces of this gas have been found to act as both polymerization inhibitors and activators, depending on the polymerization reactions involved. It is the general practice at the Government Laboratories to reduce this variable to a minimum by purging polymerization equipment with butadiene or oxygen-free nitrogen prior to initiation.

Because it is believed that a polarographic method is superior to the classical manometric and Winkler methods for determining small quantities of oxygen, a potentiometric method (*5*) for the determination of oxygen in gases was developed at the Government Laboratories and used extensively in the analysis of gases for purging polymerization units and laboratory assemblies (*1*). An automatic recording instrument was desirable in recording instantaneous changes in the oxygen content of the head gas in a 500-gallon reactor during purging and charging procedures. It was also desirable to record transient phenomena in the stream from a nitrogen purification unit (*6*). Such recordings were not obtainable with the use of the manual apparatus. The design and operation of an electronic unit which automatically records the low concentration of oxygen in gases are described.

THEORY

Molecular oxygen is irreversibly reduced at the dropping mercury electrode at applied potentials near zero (*2*, *3*). The diffusion current is reached at approximately −0.3 volt *vs.* the saturated calomel electrode. In neutral or alkaline solutions, the reaction proceeds according to the following equation:

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \qquad (1)$$

At potentials more negative than −0.5 volt, the second reduction step occurs:

$$H_2O_2 + 2e^- \rightarrow 2OH^- \qquad (2)$$

The polarographic behavior of dissolved oxygen has been the basis of several methods for the determination of oxygen in gases and water solutions (*7*, *9*). Generally, the diffusion current at a constant applied potential is used as a measure of the amount of oxygen. A dilute aqueous solution, saturated with air and containing approximately $0.1N$ electrolyte, is $2.5 \times 10^{-4}M$ with respect to oxygen, corresponding to 8 p.p.m., and gives rise to a diffusion current on the order of 4 μa. with an electrode of usual characteristics (*4*). The limit of sensitivity of the polarographic technique is usually around 10^{-3} μa.; but because at a concentration of oxygen below 1%, by volume, the residual current is in the same order of magnitude, the ordinary polarographic method becomes inaccurate for concentrations of oxygen less than 1%. However, a null-current measurement of the potential of the dropping mercury electrode shows considerable response to small changes in oxygen concentration.

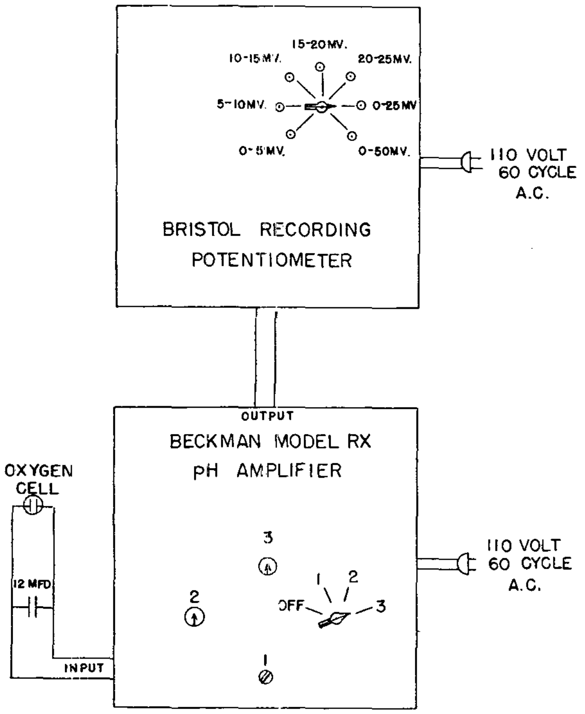

Figure 1. Automatic Recording Oxygen Analyzer

The theoretical aspects of the method have been reported by Laitinen, *et al.* (*5*). The method is based on measurement of the equilibrium potential between mercury drops forming in an electrolyte medium containing molecular oxygen and a reference electrode of constant electromotive force. Consideration of the characteristics of the dropping mercury electrode and transfer of charge during the electrolytic reduction of oxygen has led to the following expression:

$$(E - E_{\text{max.}}) = \frac{6nFCD^{1/2}t^{1/2}}{\sqrt{21\pi}\,k} = 7.128 \times 10^4\,\frac{nCD^{1/2}t^{1/2}}{k} \qquad (3)$$

where E is the potential of the dropping mercury electrode at equilibrium, $E_{\text{max.}}$ is the potential corresponding to the electrocapillary maximum (zero oxygen), nF is the number of coulombs of electricity involved per mole, C is the concentration of oxygen in millimoles per liter, D is the diffusion coefficient in square centimeters per second, t is the time in seconds, and k is the capacity in microfarads per square centimeter of the double layer on the positive side of the electrocapillary maximum.

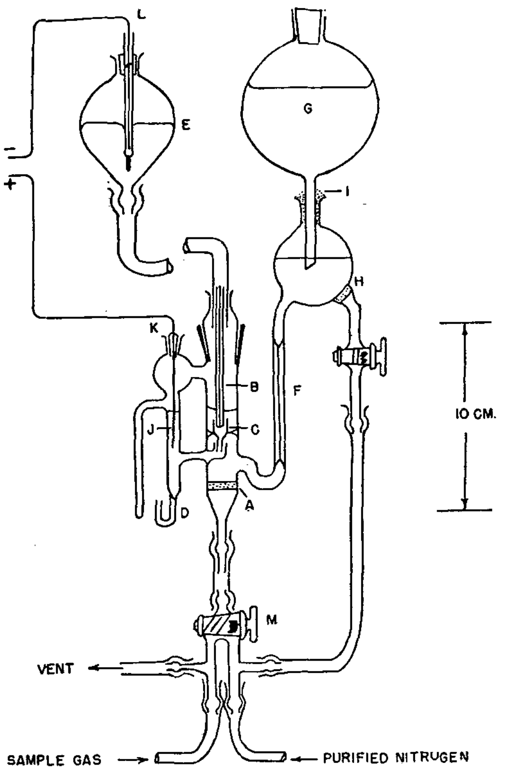

Figure 2. Oxygen Cell

If values of $n = 2$, $D = 2.6 \times 10^{-5}$, and $k = 42.2$ ($0.1N$ potassium chloride), are assigned the final expression becomes

$$(E - E_{\text{max.}}) = 1.72 \times 10^4\,Ct^{1/2} \qquad (4)$$

where the potential shift, $\Delta E = E - E_{\text{max.}}$, is measured in millivolts, the concentration, C, in millimoles per liter, and the drop time, t, in seconds.

Equation 4 relates the potential of the system with the oxygen dissolved in the electrolyte. To determine the actual oxygen content of any nonreducible gas, it is necessary only to bring the electrolyte into equilibrium with the gas before measuring the potential.

The expression then takes the form:

$$\text{Percentage of oxygen in gas} = \frac{\Delta E}{\frac{10\alpha}{22.4} \times 1.72 \times 10^4 t^{1/2}} \qquad (5)$$

where α is the adsorption coefficient of oxygen in the electrolyte expressed in cubic centimeters per liter, and the total gas pressure is 1 atmosphere.

At 25° C., $\alpha = 28.3$; using a drop time of $t = 4$ seconds, the equation reduces to:

$$\text{Percentage of oxygen} = 2.30 \times 10^{-3}\Delta E \qquad (6)$$

(The value of 28.3 applies only to oxygen dissolved in water. In $0.1N$ potassium chloride, a lower value would be expected.)

An oxygen content of 0.1% corresponds to a potential shift of about 40 mv., reproducible within 2 mv. From 0 to 1% of oxygen the method is accurate to within 0.01% (absolute). In actual practice there is a slight deviation from linearity at concentrations near 1% of oxygen. Therefore, a calibration curve of ΔE versus percentage of oxygen may be employed for routine analyses.

The question may arise as to the possible interference due to the anodic current-voltage curve of mercaptans. It is the belief of the authors that the vapor pressure of Sulfole B-8 is too low for traces of mercaptan to be detected in the reactor head gas.

APPARATUS

The oxygen analyzer (Figure 1) consists of a Bristol recording potentiometer, operating on the output of a Beckman Model RX pH amplifier in which the glass–calomel electrode system is replaced by the oxygen cell. The polarographic oxygen cell has to fulfill the following requirements (*1, 5*):

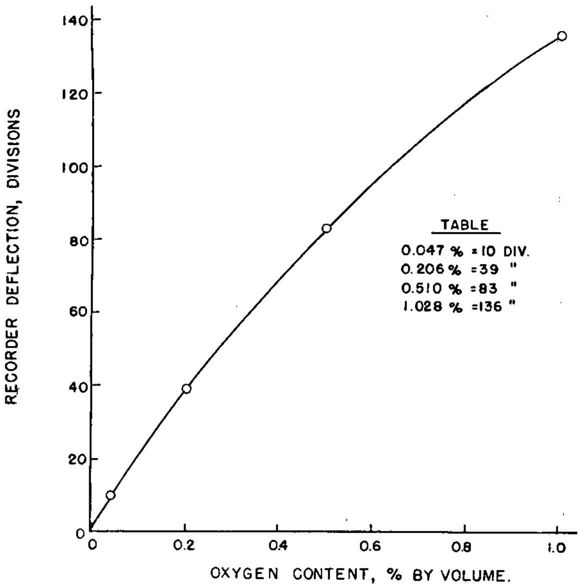

Figure 3. Calibration of Oxygen Analyzer

Arrangements have to be made to bring the electrolyte rapidly in equilibrium, with respect to its oxygen content, with the sample gas.

The dropping electrode has to be shielded from any turbulence caused by flow of gas through the solution.

The reference electrode has to have constant reversible potential and possess relatively low resistance. It has to be placed so that the reducible products, if any, of the electrode cannot affect the dropping electrode.

The mercury from the dropping electrode has to be removed in a manner to minimize contact with the electrolyte. Any mercurous chloride formed through interaction of the mercury with the electrolyte might affect the dropping electrode potential.

To permit continuous operation, it is advisable to construct the cell in such a manner as to permit cautious partial replacement of the electrolyte. This prevents accumulation of contaminants over a long period of time.

The electrolytic cell (Figure 2), designed to provide rapid equilibration of the supporting electrolyte with the gas being tested, consists of a fritted-glass disk, *A*, within a cylindrical tube, through which the gas bubbles into the electrolyte. The dropping mercury electrode, *B*, is suspended directly above the disk and is shielded from turbulent flow by a small funnel, *C*, which also directs the mercury drops into an exit tube and trap, *D*. Fresh mercury from reservoir *E* is supplied to the electrode capillary through polyethylene tubing. The mercury height (approximately 60 cm.) is adjusted to give a constant drop time of 4 seconds. The electrolyte ($0.1N$ potassium chloride) is automatically maintained at a constant head of 12 cm., and is continuously admitted to the cell at approximately 1 ml. per minute through the capillary at *F*. A 1-liter bulb, *G*, acts as a reservoir for the electrolyte, which is maintained air-free by nitrogen bubbling through the fritted-glass disk, *H*. A cotton plug, *I*, prevents air from diffusing into the system. A silver–silver chloride reference electrode, *J*, completes the cell. Electrical connections are made at *K* and *L*, the dropping electrode serving as cathode. The electrolyte is alternately equilibrated with purified nitrogen and the sample gas by means of a three-way stopcock, *M*.

The potential obtained with pure nitrogen bubbling through the cell corresponds to the electrocapillary maximum potential, $E_{\max.}$, and is approximately −0.500 volt *vs.* the silver–silver chloride electrode. As oxygen is introduced into the cell, the potential shifts to less negative values; the magnitude of the shift, $E - E_{\max.}$, is proportional to the amount of oxygen present.

A shift in the potential of the electrocapillary maximum may be expected in the presence of foreign electrolytes introduced by the gas stream, the water used to make up the supporting electrolyte, or the mercury for the dropping electrode. However, attainment of the theoretical value is not a requisite in the method, since the determination constitutes a differential measurement of potentials, and the system is calibrated accordingly.

The potential of the cell is recorded on a Bristol recording potentiometer. A 12-microfarad oil-filled condenser is connected in parallel with the cell terminals on the Beckman RX pH amplifier to reduce fluctuation of voltage associated with the growth of mercury drops.

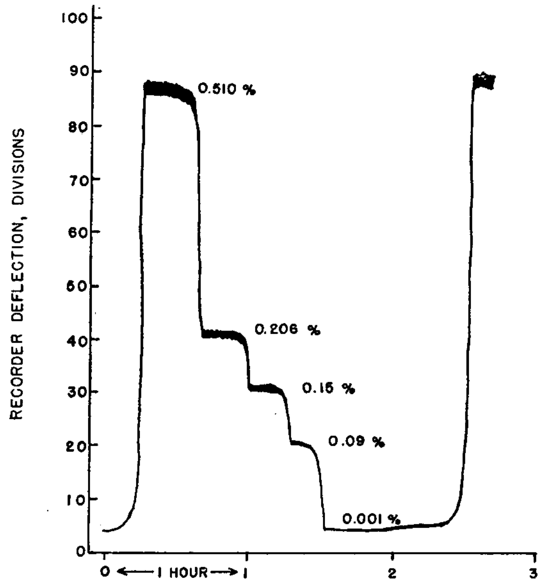

Figure 4. Oxygen Content of Nitrogen

The amplifier is operated with the right-hand switch in the No. 3 position (see Figure 1). Controls 1, 2, and 3 are used as coarse and fine adjustments of the zero position. The recorder has provisions for various ranges; generally the 0- to 25-mv. range is used and covers the range 0 to 0.5% oxygen. For greater sensitivity the 0 to 25-mv. range may be spanned in increments of 5 mv., corresponding to approximately 0.1% oxygen for full scale deflection at maximum sensitivity. To record concentrations above 0.5% the 0- to 50-mv. range position is used. Because of the limiting sensitivity of the oxygen cell, it is not practical to record concentrations above 1% oxygen by volume.

PROCEDURE

With prepurified nitrogen bubbling through the cell and the recorder set on the 0- to 50-mv. range, adjust controls 1, 2, and 3 on the amplifier until the recorder pen is on scale near the left side of the chart. Turn the selector switch on the recorder to the appropriate range for standardization and allow it to record for 5 minutes to establish the reference line. Standardize the instrument by bubbling a known mixture of nitrogen and oxygen through the cell. If the recorder deflection does not coincide with the calibration curve, recalibrate the cell, using additional known mixtures of nitrogen and oxygen.

RESULTS AND DISCUSSION

Figure 3 shows a calibration curve for the oxygen analyzer using four standard mixtures of nitrogen and oxygen—0.047, 0.206, 0.510, and 1.028% oxygen by volume. Airco prepurified nitrogen, containing 0.001% oxygen, was used as the zero reference.

Figure 4 shows a sequence of gases of increasing oxygen contents. The instrument responds immediately to a change in oxygen concentration and attains equilibrium within approximately 10 minutes.

Figure 5 shows the reproducibility of the zero setting by alternately admitting the reference gas and the nitrogen-oxygen mixtures. The 0- to 50-mv. range was used in recording the 1.028% level.

Figure 6 shows the changes in the oxygen level of the head gas in a 500-gallon reactor during purging and charging procedures.

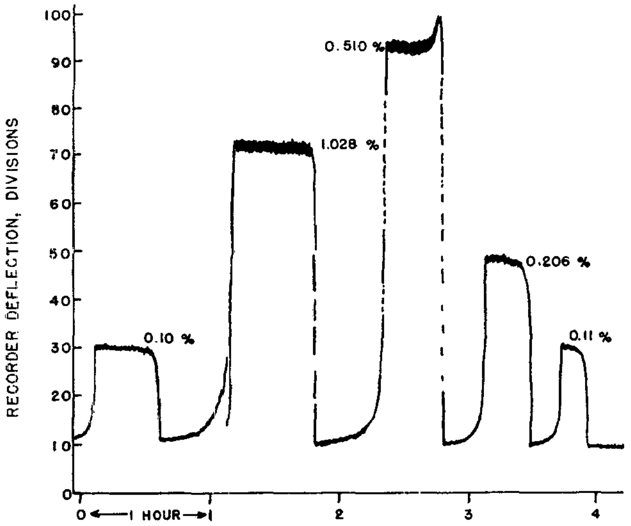

Figure 5. Oxygen Content of Nitrogen

The instrument was zeroed (A in Figure 6) at the second chart division with prepurified nitrogen bubbling through the cell and the selector switch on the 0- to 50-mv. range. The reactor was evacuated and then pressured with 15 pounds of butadiene. At this point, B, the concentration of oxygen was approximately 1.0% by volume. The reactor was again evacuated and another 15 pounds of butadiene added. The drop in oxygen content is shown along BC in Figure 6. The selector switch was turned to the 0- to 25-mv. range at C, doubling the sensitivity. The curve along D represents the lag in sampling and equilibration in the oxygen cell. The concentration of oxygen at this point was 0.03%. At E the soap solution was charged. The oxygen content rose sharply to an apparent concentration of 0.25%, F, but immediately dropped to a level slightly higher than 0.03%, G. Apparently, a portion of air from the soap charging line had reached the gas sampling line before it was mixed with the head gas. Sulfole B-8 was then charged and an appreciable quantity of air was admitted, raising the oxygen content to 0.1%, H. Styrene was then charged and more air was admitted raising the oxygen level to 0.16%, I. The reactor was purged twice with purified nitrogen by pressuring to 30 pounds per square inch and venting to 2 to 3 pounds per square inch. Point J (0.04% oxygen) represents the dilution of the oxygen in the reactor by the first nitrogen purge. The second nitrogen purge, K, reduced the oxygen content to 0.02%. The zero point of the instrument was checked at L using prepurified nitrogen. The butadiene was then charged, M, and resulted in further dilution of the oxygen to approximately 0.01% at N. The oxygen content remained at this level during the completion of the charge.

Figure 7 shows the continuous analysis of the nitrogen stream (*8*) from a plant purification unit designed to remove oxygen from regular grade nitrogen containing approximately 0.1 to 0.2% oxygen. The oxygen is removed by countercurrent scrubbing of the gas with a solution of sodium hyposulfite in a 16-foot packed column. The analysis was made under conditions of high consumption near the depletion of activity of the solution in the column. The highest rate of nitrogen consumption in the pilot plant occurs when pressure tests are being made on the 500-gallon reactors. The instrument was zeroed at A in Figure 7 and then switched to the column gas at B. At low consumptions of the nitrogen, the oxygen content is maintained at 0.01 to 0.02%, BC. Points D and E (0.09 amd 0.21% oxygen, respectively) represent surges in the oxygen level during pressure tests on the 500-gallon reactors. The zero check at F showed no drift in the reference point of the instrument.

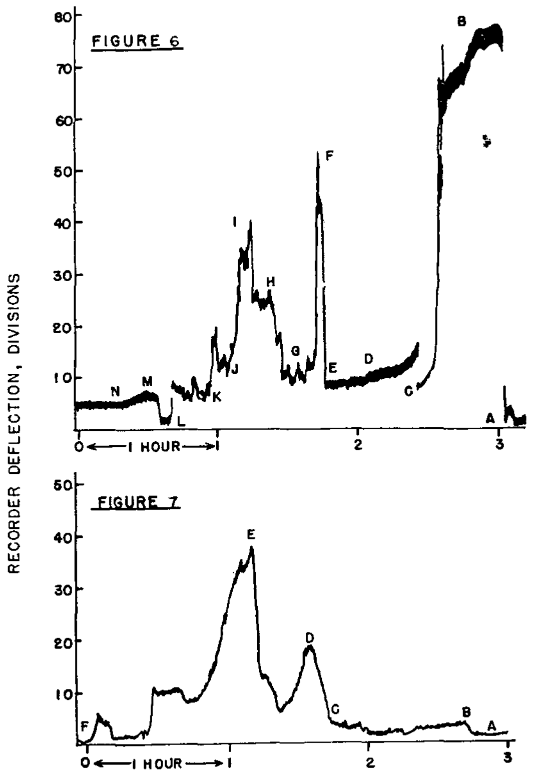

Figure 6. Oxygen Content of Head Gas in 500-Gallon Reactor

Figure 7. Oxygen Content of Nitrogen from Purification Unit

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Testing Cationic Surface Active Germicides for Use In Industrial Water Systems

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THE increased use of and interest in surface active germicides point out the need for a reliable test method for determining the killing levels of such agents. Frequently the tube methods of testing the killing power of this type of compound give poorly reproducible results. Lack of reproducibility may be attributed to sampling at the end of the contact period and lack of suitable inhibitors to inactivate the germicide at the end of the contact period.

The appearance of "skips," whereby growth occurs at fairly high concentrations with no growth at intermediate levels, seems to be due to the methods of transferring the test solution to a culture medium at the end of the contact period. Various workers have attributed erratic results to adherence of organisms to solid surfaces, to improper sampling, and to "carry-over" of the germicide. Many methods, modifications, and criticisms of established techniques for evaluating the germicidal action of quaternary ammonium compounds are to be found in the literature.

For some time laboratory workers have observed that the agar plate inhibition test is not suitable for the evaluation of surface active materials: agar has "neutralizing" action of its own. This has been confirmed by work in this laboratory. At low concentrations surface active germicides, in contact for 1 hour with *Aerobacter aerogenes*, can be completely neutralized by the addition of standard tryptone glucose extract agar. To neutralize the surface active germicides at higher levels, it is necessary to add an inhibitor. The use of inhibitors (or neutralizing agents) in the culture medium is a well established procedure in testing quaternary-type germicides. Weber and Black (*4*) have investigated several inhibitors. The purpose of the inhibitor is to prevent the carry-over of bacteriostatic quantities of the germicide into the subculture medium and to neutralize any unreacted quaternary on the bacterial cell, thereby definitely stopping any further germicidal action after the specified period of contact.

The proposed method attempts to overcome these difficulties by culturing the entire reaction mixture of chemical and organisms in the test container at the end of the contact period and inactivating the germicide by means of an efficient inhibitor contained in the culture medium.

The method has been used primarily for the direct comparison of surface active germicides intended for use in industrial water systems where the volume of water to be treated may run into thousands and even millions of gallons. Thus to be economically practical, the dosage levels must be extremely low. Complete sterilization of such systems would be exceedingly difficult and from a practical viewpoint this is unnecessary. Hence, an arbitrary figure of 99.99% kill has been adopted to represent a satisfactory killing action. There is no urgent necessity for rapid killing action in these systems; hence a contact period of 1 hour has been adopted. This constitutes a convenient working interval, eliminates the error caused by small variations in timing sometimes found when 5- or 10-minute test periods are used, and brings out the maximum effectiveness of the chemical under the conditions of testing

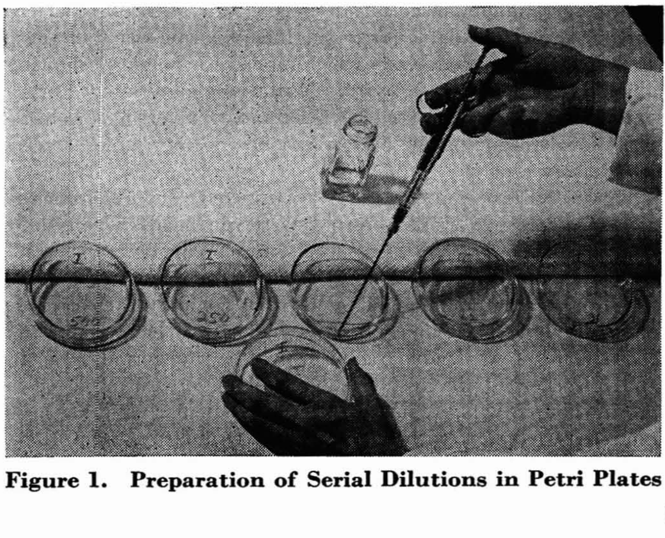

Figure 1. Preparation of Serial Dilutions in Petri Plates

It is hoped that adaptation of the method to suitable conditions of time, culture, and other factors will make it useful and convenient in a variety of applications.

PROCEDURE

In principle, the test comprises the preparation of serial dilutions of the chemical in a series of Petri plates, addition of the test organisms, and, after the desired period of contact at room temperature, flooding the plate with agar containing an excess of neutralizing agent. The plates are incubated for a suitable period and the colonies of surviving bacteria are counted. The percentage kill is determined by calculating against the number of bacteria in the original inoculum as determined by the standard plate count method.

Serial Dilution of Chemicals. The required number of sterile Petri plates (100 × 15 mm.) are placed in a row and sloped at an angle of about 30° by placing a support under the plates on the side farthest from the operator. Using a constant volume, hand-operated syringe type automatic pipet (Aloe Scientific Co., St. Louis, Mo.) calibrated to deliver 1 ml., and working with aseptic technique, 1 ml. of sterile distilled water (or physiological saline) is placed in the bottom of each plate (Figure 1). With the same pipet, 1 ml. of 0.1% stock solution of the chemical to be tested is placed in the first plate. The liquid is mixed well by drawing it into the automatic pipet and ejecting it five times, being careful to hold the tip of the pipet in contact with the inner angle of the plate at the deepest part of the liquid. Care should be taken to avoid splashing. After mixing, 1 ml. of the solution from the first plate is transferred to the second plate, mixed five times as above, and 1 ml. transferred to the third plate. This process is repeated through the required number of plates. The last 1 ml. is discarded. This process gives serial dilutions throughout the plates in amount of 1 ml. and covering a range of 500, 250, 125 p.p.m., etc.

Between operations the syringe pipet may be cleaned and decontaminated satisfactorily by aspirating several times in 70% alcohol.

Inoculum. The inoculum is prepared by adjusting an 18- to 22-hour broth culture of *Aerobacter aerogenes* to approximately 1,000,000 organisms per ml. in distilled water (or saline) immediately before use in the test. The adjusted culture should be used within 5 minutes after its preparation.

Using the automatic pipet, 1 ml. of the inoculum is placed in the center of the solution in each plate, starting with the first plate, being careful not to touch the solution or the plate with the tip of the pipet, nor to permit any droplets to fall within the plate at any point other than in the solution. When the inoculum is added to the last plate, the tip of the pipet is placed in the deepest part of the solution at an angle such that there is no danger of touching the rim of the plate with the contaminated sides of the cannula and the culture is mixed with the chemical dilution by aspirating five times.

The plunger of the pipet is held in the compressed position while the pipet is transferred to the preceding plate where the contents are mixed in a similar manner. Proceeding in this manner, the contents of all plates are mixed in order. Chemical concentrations in the plates in the amount of 2 ml. per plate cover the range of 250, 125, 62.5 p.p.m., etc. A control plate, containing 1 ml. of water and 1 ml. of culture is included in each series. The plates are now placed flat on the laboratory table and allowed to stand for 1 hour from the time the inoculum was placed in the first plate.

Neutralization of Chemical. At the end of this period of contact between the bacteria and the germicide, the activity of the chemical is destroyed by adding at least 10 ml. of a special neutralizing agar of the following composition: 24 grams of Difco tryptone glucose extract agar; 5 grams of Daxad 11 (polymerized sodium salts of short-chain alkyl naphthalenesulfonic acid, Dewey and Almy Chemical Co., Cambridge, Mass.); and 1000 ml. of distilled water. The mixture of the germicide and bacteria in the plate is evenly distributed throughout the melted agar by rotating the contents of the plate so that any bacteria that may have survived the contact with the chemical will be distributed uniformly throughout the agar. When the agar has solidified, the plates are inverted and incubated for 48 hours at 37° C., after which time the plates are counted.

A count of 100 colonies per plate has been arbitrarily selected as the dividing line between effective and ineffective killing action. This number of survivors represents a 99.99% kill, as there were approximately 1,000,000 organisms in the test plates.

Determination of Efficiency of Neutralizing Agar. After an extensive survey of inhibitors for several types of cationic surface active germicides, it was found that 0.5% Daxad 11 in standard tryptone glucose extract agar was entirely satisfactory for neutralization of the germicide at a concentration of 500 p.p.m. The medium is clear, homogeneous, and noninhibitory to *Aerobacter aerogenes*. The other inhibitors tested were less desirable for one or more of the following reasons: less effective neutralization, discoloration of the medium, and voluminous precipitates which interfered with colony counts. This is not the first use of sulfonic acid derivatives as neutralizing agents for surface active germicides. Lawrence (*2*), in studying a series of these compounds, recommended the use of Suramin Sodium, trisodium salt of 3,3′-ureidobis [8-(3-benzamido-*p*-toluido)-1,3,5-naphthalenetrisulfonic acid], for this purpose.

PROCEDURE. One milliliter of the proper concentration of germicide—i.e., 10 times the final concentration desired in the agar—is mixed thoroughly with 8 ml. of melted neutralizing agar in a Petri plate. After sufficient mixing, 1 ml. of standard inoculum of *Aerobacter aerogenes* (approximately 1,000,000 organisms) is added, and mixed again, and the agar allowed to solidify. Plates are incubated for 48 hours at 37° C. and their appearance is compared with that of a control plate (water or saline) prepared in a similar manner. In other tests the inoculum was varied to contain approximately 1,000,000, 100,000, 10,000, and 1000 organisms, respectively. In the plates inoculated with 1000 organisms, direct comparisons were made with the controls by actual counts of the colonies.

Table I. Efficiency of Neutralizing Agar[a] on 500 P.P.M. of Surface Active Germicides

	Colonies of *A. aerogenes* Developing on Neutralizing Agar			
		Dilution of Inoculum		
Germicide	1:1000	1:100	1:10	Undiluted
QAC 1	1220	Gross appearance of plates identical with corresponding dilutions in control plates		
QAC 2	1252			
QAC 3	1146			
QAC 4	1116			
QAC 5	1240			
QAC 6	1136			
Amine salt 1	1104			
Amine salt 2	926			
Control (no germicide)	1276			

Standard plate count of inoculum 1,240,000/ml.

[a] Neutralizing agar. 0.5% Daxad 11 in standard tryptone glucose extract agar.

Table II. Variations in Killing Levels of Quaternary Determined by Two Methods

Tube Dilution Method		Plate Method	
No. of tests	100% killing range, p.p.m.	No. of tests	99.99% killing range, p.p.m.
1	> 2		
1	2–4		
2	4–8	1	4–8
1	8–16	6	8–16
2	16–31	2	16–31
1	31–62		
2	>1000		

RESULTS AND DISCUSSION

The efficiency of the neutralizing agar (Daxad-tryptone glucose extract agar) against several quaternaries and two other surface active germicides is shown in Table I. The agar does not interfere with the growth of the test organism and appears to neutralize completely the action of 500 p.p.m. of the quaternary ammonium germicides, but is possibly less effective at that concentration of the amine salts.

Table II shows an extreme example of the variation in results encountered when the killing level was determined by a tube method (modified FDA phenol coefficient type) using a 1-hour contact period. A comparison of these results with those obtained using the proposed plate method killing test shows a distinct improvement in the degree of reproducibility.

Table III. Replicate Killing Ranges (99.99%) of Cationic Surface Active Germicides

QAC 1		QAC 2		QAC 3		QAC 4	
No. of tests	P.p.m.	No. of tests	P.p.m.	No. of tests	P.p.m.	No. of tests	P.p.m.
1	1–2	4	1–2	1	4–8	3	1–2
3	2–4	1	2–4	5	8–16	1	2–4
2	4–8	1	4–8	1	16–31	1	4–8
		2	8–16				

QAC 5		QAC 6		Amine Salt 1		Amine Salt 2	
No. of tests	P.p.m.	No. of tests	P.p.m.	No. of tests	P.p.m.	No. of tests	P.p.m.
3	16–31	3	4–8	6	31–62	1	2–4
3	31–62	1	8–16			5	4–8

Agar plate method killing test conditions. Serial dilution of chemical; organism, *A. aerogenes;* contact time, 1 hour; killing range upper level denotes >99.99% kill, lower level <99.99% kill.

Table III shows the degree of reproducibility encountered with several surface active germicides when tested by the proposed agar plate method for "effective" killing levels against *Aerobacter aerogenes* with a 1-hour contact period. The dividing line between "effective" kill and "ineffective" kill has been arbitrarily placed at 100 colonies per plate for ease in determining the end point. A kill of 99.99% is satisfactory for most industrial uses, as complete sterility is rarely required.

It seems clear from the results given in Table III that the results are within expected ranges of reproducibility for a serial dilution type test. At no time, in the course of several hundred tests, have the workers encountered the annoying "skips" or erratic results of the tube method.

From a theoretical viewpoint the proposed method overcomes the principal weaknesses inherent in the tube method of testing quaternary ammonium germicides. The tube method is widely recognized as dependable for testing many germicides, but there is no doubt of its weaknesses when applied to chemicals showing a high degree of surface activity. With these materials the problem of sampling the treated bacteria and transferring to sterile broth for determining the presence or absence of viable bacteria has been a vexing one.

The useful procedure has been to transfer a loopful from the "seeding tube" to sterile broth. With chemicals which show little surface activity, a fairly large sample can be transferred. However, with the reduced surface tension encountered in testing quaternary ammonium compounds the volume transferred is markedly less, particularly in the higher concentrations, and consequently fewer viable organisms will be transferred. Jacobs and coworkers (*1*) have shown that a single organism placed in broth will usually fail to initiate growth, particularly if it has been injured by contact with a germicide. Ordinarily, from 10 to 100 organisms may be required to initiate growth. Therefore any variation in the amount of sample carried over from the seeding tube may effect the results obtained.

Some workers have sought to minimize this error by transferring 0.1 ml. by use of a pipet. However, even this refinement in technique fails to give a representative sample in the case of the surface active materials. It has been shown by Quisno and coworkers (*3*) that for some reason a few bacteria survive at the juncture of the liquid surface and the wall of the medication tube, while none survive in the main body of the medication mixture. Therefore, it is probable that sampling from the main body of the liquid in the seeding tube, whether by loop or by pipet, is unreliable. The present method would appear to eliminate the sampling problem, since the entire reaction mixture is taken as the sample and no transfer of the mixture to another tube or plate is involved.

The question of the minimum number of organisms required to initiate growth in broth culture is not a factor in the proposed plate test, since all surviving bacteria are introduced into the culture medium and those bacteria capable of cell division will develop as individual colonies in the agar.

The proposed method has been adopted as a routine screening procedure for surface active materials in this laboratory. In addition to the serial dilution technique using the syringe pipet, the test has been adapted for use with closer chemical ranges and more exact work using dilutions made with 1- and 5-ml. graduated pipets. There is a small inherent error associated with the automatic syringe pipet, depending on the length and diameter of the cannula.

With suitable variations it has also been possible to study the effect of ions, pH, organic matter, and foreign material on surface active agents. In addition, it has been used with other types of troublesome bacteria and fungi isolated from specific industrial water systems.

A limited number of tests on mercurial germicides, using thioglycolate agar as a neutralizing medium, suggests that the technique may also be useful for the evaluation of these materials.

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Miniature Mixer Settler for Continuous Countercurrent Solvent Extraction

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THE widespread use of continuous countercurrent solvent extraction owes much to the laboratory scale development of suitable flowsheets. In addition, solvent extraction is often the preferred method for the separation of reaction products from organic syntheses, or of fine pharmaceuticals. In general, such problems have been solved in the laboratory by the use of batch countercurrent extraction techniques (*3*). Equipment for batch countercurrent extraction varies over a wide range of complexity, but in principle performs batchwise stirring, settling, and countercurrent phase transfer by some characteristic pattern. The outstanding advantages of such units are the ability to approach 100% stage efficiency and, by the taking of equilibrium stage samples, to obtain a reliable equilibrium curve for the systems under investigation. Batch countercurrent extraction may however, be both laborious and time-consuming and may require careful technique. Devices used may be fragile or not suitable for the handling of highly toxic or valuable substances. Dynamic flow patterns and residence times may not be applicable to large scale continuous equipment.

The existing need for a compact, continuous countercurrent, multistage extraction unit to operate in the range of holdup and feed requirements of laboratory batch countercurrent equipment has not been adequately met in the past by small scale continuous-extraction devices. This paper describes the miniature mixer settler, a unit which is believed to fulfill this need. The unit has been developed over a period of 3 years in connection with other work.

DESCRIPTION OF EXTRACTION UNIT

The miniature mixer settler is similar in operating principle to the pump-mix mixer settler described by Coplan, Davidson, and Zebroski (*2*). The contactor consists of a number of stages, each containing a mixing section and a settling section. Every mixing section has an impeller driven by a shaft that enters the mixing section at the top of the stage. The impeller is similar to a small centrifugal pump, liquid being drawn up through an axial tube and discharged through radial holes. Because the capacity of the pump is designed to be greater than the heavy phase flow, the mixed phase–heavy phase interface in the mixing section will fall below the impeller tip and mixed phases from the top of the mixing section will be recirculated through the impeller. The net result is a "make and break" effect between the interface and the impeller tip. In this way the level of the impeller tip in each stage uniquely determines the interface in the settling section of the previous stage. The only leveling device required is a weir to drain heavy phase from the last stage.

In pump-mix mixer settler operation, therefore, the heavy phase is pumped from stage to stage through the bank with the light phase flowing in the opposite direction by gravity. The light phase pressure drop from stage to stage is negligible and permits horizontal operation of the bank. A conventional mixer-settler countercurrent flow pattern is followed; light phase from the settling section of stage $n + 1$ and heavy phase from the settling section of stage $n - 1$ flow into the mixing section of stage n. The mixed phases then flow through a port to the settling section of stage n.

Good operation is characterized by steady interfaces in all settling sections and by make and break interface-impeller action in the mixing sections. Feed streams are introduced continuously at the ends of a bank or into any stage or stages in a bank, making possible extraction with reflux or center feed. Similarly, products and raffinates may be collected at both ends or removed continuously from any stage. The unit may be shut down and started up without disturbing equilibrium, and light and heavy phase stage samples may be taken from settling sections either during operation or upon shutdown. The entire bank may be conveniently immersed in a bath for operation at controlled temperatures. Operator attention during a run is ordinarily limited to the taking of end stream or stage samples.

The over-all size of a 16-stage unit with impellers is 3 × 14 × 8 inches. The total holdup per stage is about 8 ml. Flow rates to the unit are in the range of 0.05 to 4 ml. per minute. Depending on the system, impellers are operated at 1500 to 3000 r.p.m. Bank efficiency is in excess of 85%.

It was desired that the material of construction of the miniature mixer settler be resistant to most solvents and aqueous solutions and be transparent. In the past, Fluorethene has been used for this purpose, but present units have been built from a plastic, Homalite (Homalite Corp., Wilmington, Del.), which satisfactorily meets these specifications.

An isometric view of a complete unit is shown in Figure 1. Figure 2 shows a magnified view of an impeller in a mixing section.

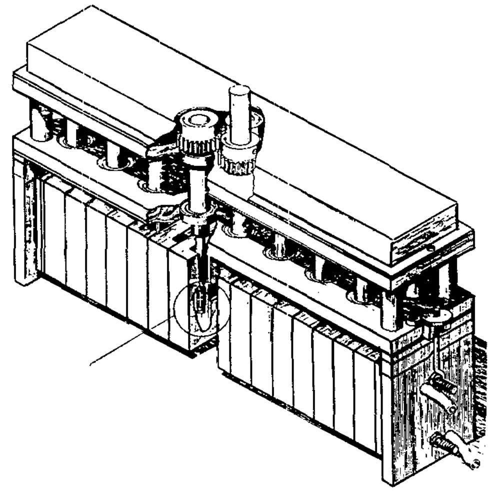

Figure 1. Isometric View of 16-Stage Miniature Mixer Settler

Each stage in the unit, consisting of a $^3/_8 \times {}^3/_8 \times 2^1/_2$ inch mixing section and a $^3/_8 \times {}^1/_4 \times 2^1/_2$ inch settling section with associated ports, is milled from a $^3/_4 \times 2 \times 3$ inch sheet of Homalite. Two types of stages are made, one the mirror image of the other. These are placed together alternately, the front, milled face of one stage touching the back face of its mirror image (Figure 3). The ends are secured by metal end plates appropriately drilled. Two longitudinal rods, threaded at each end, go through all the stages and the end plates. Nuts on the ends provide the pressure necessary to hold the unit together and prevent leakage. Stage surfaces must be flat and free of tool marks.

In this way, units may be built up of as many stages as desired. Units of greater than 20 stages have not been made, but there is little doubt that longer units could be operated. If a great many stages are desirable, multiunit assemblies may be preferable.

The end plates also serve as supports for the impeller head. The impellers must be centrally located with respect to the mixing chambers and should be without appreciable wobble or whip. Each impeller shaft is supported by two bearings and is driven by a gear train at the top of the impeller head. The gear train is designed so that each impeller rotates in the same direction with respect to the port connecting mixing and settling sections. A General Electric Thymotrol drive has been found convenient for control of impeller speed.

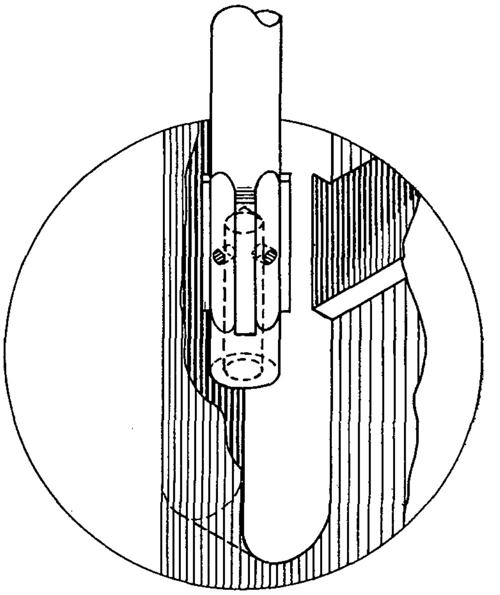

Figure 2. Magnified View of Impeller in Mixing Section

Showing axial and radial holes

The accurate flow control demanded in many runs in the range of 0.05 to 4 ml. per minute was made possible by a feed system composed of 50-ml. syringes driven by a rack and pinion arrangement. The pinion was turned at desired speeds by a suitably geared down synchronous motor. A wide variety of flows and flow ratios could be obtained by varying pinion speed or size and by manifolding several syringes on one feed stream. Syringes were refilled manually at regular intervals. Flow ratios with the syringe drive were routinely good to 0.5%.

EXPERIMENTAL

In order to measure the efficiency of a solvent extraction unit, it is desirable to employ a liquid-liquid system which conforms as nearly as possible to the following ideal conditions:

1. The solute obeys the Nernst distribution law.
2. The liquid phases are immiscible.
3. Volume changes due to the mass transfer of solute are negligible.

The third condition implies the use of dilute solutions, which in turn requires that a sensitive analytical method be available for the solute. It is convenient if the system exhibits a distribution coefficient close to 1, a reasonable density difference between the phases, and a relatively low viscosity for each of the liquids used. Such a system is, of course, somewhat arbitrary and the efficiency so measured reflects the performance of the unit for that system only.

Table I. Analytical Extinction Coefficients for Aniline and Phenol

Solute	Solvent	λ, A.	Molar Extinction Coefficient
Aniline	Iso-octane	2875	1830
	Water	2800	1370
Phenol	Iso-octane	2710	2060
	Water	2700	1520

Table II. Distribution of Aniline between Iso-octane and 0.8*M* Sodium Perchlorate

y, Mole/Liter	x, Mole/Liter	D
0.102	0.132	0.773
0.0685	0.088	0.778
0.0342	0.044	0.777
0.0205	0.0264	0.776
0.00684	0.0088	0.777
0.00337	0.0044	0.776
	D Av.	0.775

A system exhibiting these properties was found to be that of water-aniline–iso-octane (2,2,4-trimethylpentane). Aniline as the solute distributed between the aqueous and organic phases in a manner closely approaching ideality, with a distribution coefficient sufficiently close to 1 to allow a flow ratio (organic/aqueous) near unity. Iso-octane and water are not appreciably miscible and, furthermore, ultraviolet spectrophotometry provided a sensitive and accurate analytical method for the solute. The density difference between the two phases was 0.38 gram per ml.

In order to investigate the efficiency of the unit at a flow ratio considerably different from 1, phenol was substituted for aniline in an otherwise identical system. Here the distribution coefficient was near 0.1, and a flow ratio of about 7 was employed. It was found that the addition of an inert organic-insoluble salt enhanced the settling properties of the system. Sodium perchlorate was chosen because its solutions have a high transparency in the ultraviolet region.

Materials. Aniline (boiling point 183° to 186° C.) and phenol were used as received from the Baker Chemical Co. The sodium perchlorate was recrystallized and prepared in a 4.0*M* stock solution with deionized water of pH 6 to 7, which was used for all aqueous solutions. Care was taken that neither acidic nor basic contamination entered the system, as either would affect both the distribution coefficients and the analytical procedure. The iso-octane was of spectrophotometric grade purity, from the Eastman Kodak Co.

Analytical. The analyses were performed with a Cary recording spectrophotometer, Model 11MS, and a Beckman quartz spectrophotometer, Model DU. Known solutions of each solute were prepared and the spectra studied. The analytically important peaks and the corresponding extinction coefficients are listed in Table I.

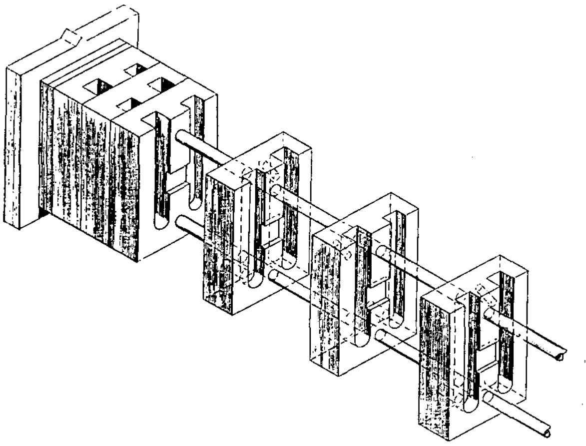

Figure 3. Isometric View of Stage Construction and Assembly

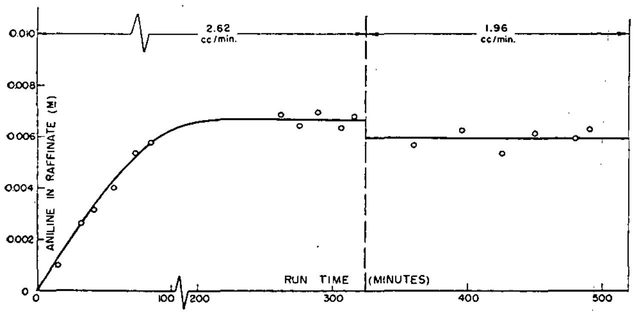

Figure 4. Relationship between Raffinate Aniline Concentration and Total Flow Rate to Bank as a Function of Run Time

Aniline run 1

Table III. Distribution of Phenol between Iso-octane and 0.8*M* Sodium Perchlorate

y, Mole/Liter	x, Mole/Liter	D
0.0171	0.132	0.129
0.0113	0.088	0.128
0.00568	0.044	0.129
0.00347	0.0264	0.131
0.00120	0.0088	0.136
	$D_{\text{Av.}}$	0.130

Table IV. Distribution of Aniline between Iso-octane and 0.4*M* Sodium Perchlorate by Exhaustive Extraction

No. of Extractions	y, Mole/Liter	x, Mole/Liter	D
1	0.0612	0.0808	0.757
2	0.0343	0.0449	0.764
3	0.0189	0.0253	0.747
4	0.0104	0.0141	0.738
5	0.00565	0.00763	0.740
6	0.00226	0.00308	0.734
7	0.000555	0.000757	0.733

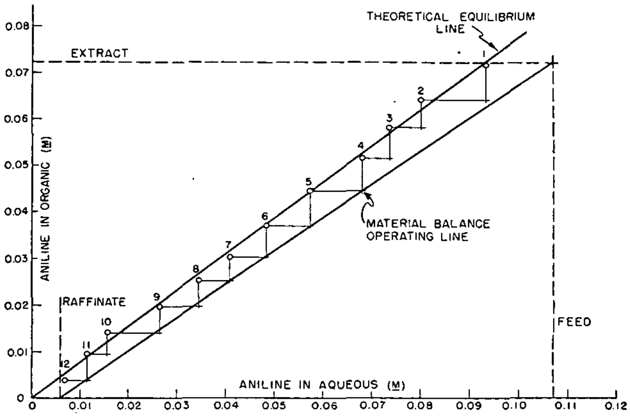

Figure 5. McCabe-Thiel-Type Plot from Individual Stage Samples

Aniline run 1. Organic-aqueous flow ratio 1.40. Total flow rate to bank 1.96 ml. per minute

Both solutes obeyed Beer's law within the range of analytical importance (10^{-4} to $10^{-3}M$). Furthermore, the presence of up to 1.0*M* sodium perchlorate had a negligible effect on the spectrum of each solute, whereas somewhat less than this amount was found sufficient to promote rapid settling of the phases.

Distribution Data. The theoretical equilibrium line for each solute was determined by batch distributions performed at room temperature by exhaustive equilibration of a volume of iso-octane to an aqueous phase of known solute concentration and 0.8*M* sodium perchlorate. The results for aniline and phenol are shown in Tables II and III, where y and x refer to the molar concentration of the solute in the organic and aqueous phases, respectively, and D is the distribution coefficient, y/x. For aniline an exhaustive batch extraction was also performed in order to determine whether "inextractable species" were present. The presence of only 0.4*M* sodium perchlorate in the exhaustive extraction resulted in a somewhat lower, but still nearly constant, distribution coefficient. These extraction data are listed in Table IV.

The time required to reach equilibrium in a single contacting was found to be less than 15 seconds. As this was considerably less than the holdup time per stage in the contacting unit for the flow rates used, rate effects were considered unimportant for this work. Because of the volatility of iso-octane, provision had to be made for inhibiting the evaporation of the solvent from the bank. A blotter, perforated for the impellers and placed across the top of the bank, was found satisfactory for this purpose.

In addition, the organic end stream was collected in a container whose air vent was partially plugged with glass wool. As a result of these precautions, evaporation of the iso-octane was held to a tolerable minimum.

The extraction method used was to introduce a solute-bearing aqueous stream at one end of a 12-stage bank, and to extract this solute into the organic solvent entering at the opposite end. As for this system the equilibrium and operating lines were linear, and the feed and extract concentrations and flow ratios were known, the raffinate solute concentration (the "loss") became a direct measure of the efficiency of the unit. For a further study of bank operation, stage samples were withdrawn when equilibrium had been reached, as denoted by constant end stream concentrations. Continuous volume measurements of the raffinate and extract streams provided a check on both the flow ratio and the total flow to the bank. The impellers were operated between 2500 and 2800 r.p.m. for all runs.

Performance Data. In the first aniline run, the bank was operated at a total flow rate of 2.62 ml. per minute, with a flow ratio (organic/aqueous) of 1.40, until a constant aniline concentration in the raffinate (as shown in Figure 4) indicated that dynamic equilibrium had been reached. This average loss value was then used to determine bank efficiency for this flow rate. A similar operation was carried out at a lower flow rate (see Figure 4). When equilibrium had been established for the final throughput rate (1.96 ml. per minute total to the bank), the feed and solvent streams were turned off, the impellers were stopped, and the impeller head was removed. Organic and aqueous stage samples were withdrawn from the settling sections and analyzed for aniline. Figure 5 presents the stage data in a conventional McCabe-Thiel–type plot, with average values of raffinate and extract concentrations also shown, as well as the theoretical equilibrium line from batch distribution measurements, and the operating line as calculated from material balance at the end of the run.

Figures 6 and 7 present similar data for the phenol run. A flow ratio of 6.85 was used, with the total flow set at 1.96 ml. per minute in order to compare bank operation between the two systems under similar throughput conditions.

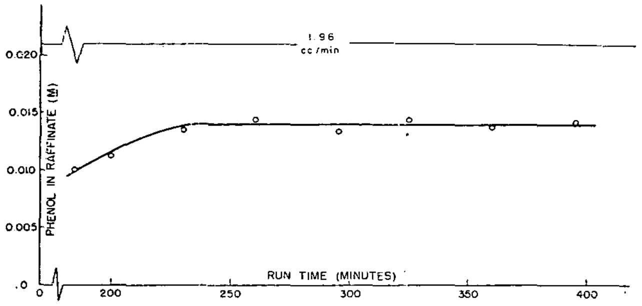

Figure 6. Relationship between Raffinate Phenol Concentration and Total Flow Rate to Bank as a Function of Run Time

Phenol run

Table V. Run Results for 12-Stage Miniature Mixer Settler

Solute	Total Flow Rate to Bank, Ml./Min.	Flow Ratio, Organic/Aqueous	Solute Concentration, M			Theoretical Stages	% Efficiency
			Feed	Extract	Raffinate		
Aniline	0.97	1.55	0.1025	0.0646	0.00235	11.4	95
Aniline	1.96	1.40	0.107	0.0723	0.00594	10.5	88
Phenol	1.96	6.85	0.0937	0.0117	0.0140	10.5	88
Aniline	2.20	1.55	0.1025	0.0642	0 00296	10.3	86
Aniline	2.62	1.40	0.107	0.0718	0.00667	9.6	80
Aniline	3.40	1.63	0.1025	0.0609	0.00329	8.5	71

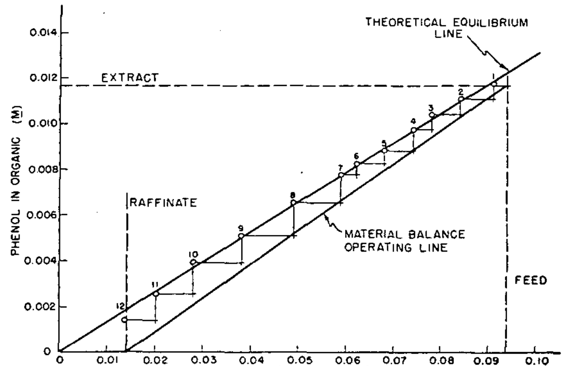

Figure 7. McCabe-Thiel–Type Plot from Individual Stage Samples

Phenol run. Organic-aqueous flow ratio 6.85. Total flow rate to bank 1.96 ml. per minute

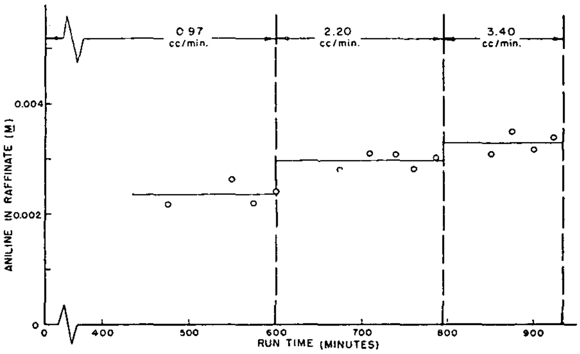

Figure 8. Relationship between Raffinate Aniline Concentration and Total Flow Rate to Bank as a Function of Run Time

Aniline run 2

A second aniline run was carried out to test the bank efficiency over a relatively wide range of total flow rates, up to the flow rate at which flooding occurred. Figure 8 shows the variation in raffinate loss as the throughput rate was increased, with an average raffinate concentration indicated for each total flow rate.

CALCULATIONS AND RESULTS

In the evaluation of performance of a continuous countercurrent multistage extractor, the number of equilibrium stages obtained in any system must be determined. For a mixer settler the bank efficiency is then the ratio of the number of equilibrium stages obtained to the number of actual stages in the bank. Barson and Beyer (*1*) have given an expression for solvent extraction calculations in special cases where pure solvent is used. The extraction expression they derive for the number of theoretical stages, N, is:

$$N = \log\left(\frac{1 - (x_1 - x_2)(a - m)}{mx_2}\right)\Big/\log(m/a)$$

where a = slope of operating line = $\dfrac{y_1}{x_1 - x_2}$

m = slope of equilibrium line (equivalent to $D_{\text{av.}}$)

x_1 = solute concentration in feed

x_2 = solute concentration in raffinate

y_1 = solute concentration in extract

All concentrations are expressed in moles per liter.

Based on this equation, each set of equilibrium values of raffinate and extract concentrations was used to calculate the per cent efficiency of the 12-stage bank corresponding to that particular set of conditions. These results are summarized in Table V, and presented in graphical form in Figure 9. The efficiency is seen to be a function of total flow rate to the bank and is independent of flow ratio or solute within these limits.

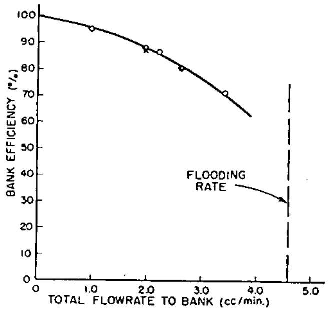

Figure 9. Relationship between Bank Efficiency and Total Flow Rate to Bank for All Runs

× **Phenol run**
⊙ **Aniline run**

The McCabe-Thiel-type diagrams (Figures 5 and 7) indicate that equilibrium was generally established in each stage of the bank for both runs shown, as the stage data fall on the theoretical equilibrium line in each case. Losses in bank efficiency were apparently due to poor settling and resultant back-mixing, as indicated by the position of some of the stage operating points above the operating line. In the second aniline run, where the total flow rate was increased to flooding, the bank became hydraulically inoperable at a flow rate of 4.6 ml. per minute, as evidenced by a lack of flow of the organic phase, and resultant overflow of the stages involved. This stoppage of flow was due to blocking of the light phase ports by small aqueous droplets, resulting from inadequate settling.

Such visual evidence of back-mixing would tend to confirm the belief, based on the stage data and operating points, that the loss in theoretical stages was due not to inefficient mixing, but to poor settling at the higher throughput rates. Relatively simple stage modifications, such as increasing the size of the settling section or the size of the light phase port, should permit high efficiency operation at much higher flow rates if this is desirable.

The miniature mixer settler has shown high efficiency and operability with systems other than those reported on in detail here. At moderate flow rates and with systems having reasonable settling properties, consistent performance of the unit at 85 to 95% efficiency may be expected.

For those interested, complete production blueprints of the unit are available from this laboratory.

ACKNOWLEDGMENT

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Anodic Polarographic Wave of Vanadium(IV) Aged in Alkaline Solution

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THE oxidation of vanadium(IV) at the dropping mercury electrode has been studied by Lingane and Meites (*1*). They found a single reversible wave with half-wave potential of −0.432 volt versus the saturated calomel electrode, and a diffusion current constant, $I (= i_d/\text{cm.}^{2/3}t^{1/6})$ of −1.466 in solutions which were 1*M* in sodium hydroxide and 0.08*M* in sodium sulfite. As the free alkali was decreased, the half-wave potential became more positive, while the diffusion current constant remained about the same. In solutions 0.25*M* or less in sodium hydroxide, they found that the single reversible wave changed to two irreversible waves, which was ascribed to the presence of two vanadite ions, $V_4O_9^{--}$ and $V_2O_5^{--}$. In the authors' polarographic study of the system they obtained results in full agreement with those of Lingane and Meites. It was noted, however, that the irreversible double wave obtained in solutions 0.25*M* or less in sodium hydroxide changed to a single wave when the solutions were aged before measuring the current-voltage curve. Consequently, some experiments on the effect of aging on the anodic wave of vanadium(IV) in alkaline medium were performed.

EXPERIMENTAL

Standard vanadyl sulfate solution was prepared by dissolving Fisher reagent grade $VOSO_4 \cdot 2H_2O$ in 0.1*M* perchloric acid. The solution was standardized by potentiometric titration with ceric sulfate in 3*M* perchloric acid.

Current-voltage curves of aged vanadium(IV) solutions were measured in solutions of varying pH. Fifty milliliters of a buffer solution of alkalinity ranging from pH 9 (ammonia buffer) to 0.5*M* sodium hydroxide was placed in a screw-cap bottle sealed with a neoprene gasket and all oxygen removed by bubbling with pure nitrogen for 1 hour (with ammonia buffers the nitrogen was prewashed with the same buffer in several wash bottles). The solutions were made up to an ionic strength of 0.5, by the addition of sodium perchlorate where necessary. Then 5 ml. of air-free 0.015*M* vanadyl sulfate solution (0.1*M* in perchloric acid) was inserted through the gasket into the solution with a hypodermic syringe. The mixture was well shaken and allowed to stand for several days to allow the establishment of equilibrium. The current-voltage curve of the aged solution was measured by flushing out a closed polarograph cell with nitrogen for 15 minutes and then forcing the solution from the sealed bottle into the cell by means of nitrogen pressure through two 6-inch needles connected by Tygon tubing. A flow of nitrogen was maintained through the polarographic cell while the solution was being transferred. The current-voltage curve at the dropping mercury electrode was then measured manually, after which the pH of the solution was measured.

RESULTS

The current-voltage curves showed a single anodic wave throughout the pH range. The half-wave potential and diffusion current constants are given in Table I, as well as values of the quantity $E_{3/4} - E_{1/4}$. This quantity is equal to 0.056/*n* at 25° C. if the polarographic wave is described by the equation: $E_{d.e.} = E_{1/2} - (0.059/n) \log i/(i_d - i)$, and is thus a criterion of

Table I. Polarographic Characteristics at 25° C. of Anodic Vanadite Wave after Aging in Alkaline Medium

Electrolyte	pH	$E_{1/2}$ (*vs.* S.C.E.)	I	$E_{3/4} - E_{1/4}$
0.05M NH_3-NH_4^+	9.1	−0.25	−1.12	. . .
0.05M NH_3	10.1	−0.34	−1.06	0.06
0.05M Na_2CO_3	10.5	−0.34	−1.1	. . .
0.25M NH_3	10.7	−0.39	−1.02	0.055
0.5M NH_3	10.9	−0.42	−1.02	0.05
0.05M NaOH	12.1	−0.42	−0.83	0.06
0.1M NaOH	12.4	−0.42	−0.75	. . .
0.14M NaOH	12.6	−0.37	−1.01	(0.09)
0.27M NaOH	12.8	−0.38	−1.11	0.065
0.5M NaOH	13.7 (calcd.)	−0.42	−1.11	. . .

the reversibility of the wave (*2*). The values of $E_{3/4} - E_{1/4}$ given in the table indicate that these anodic waves may be considered reversible as far as the criterion is concerned.

DISCUSSION

The half-wave potentials in the aged solutions vary only slightly between −0.42 and −0.34 volt when the pH is decreased from 13.7 to 10 and are of the same order of magnitude as those reported by Lingane and Meites. For the diffusion current constants, values of −1.466 to −1.41 were reported in unaged solutions compared to values of −1.1 and less observed in aged solutions. The decrease in the diffusion current constant throughout the pH range in aged solutions, as well as the disappearance of the double waves, suggested that a slow association process takes place in alkaline solutions of vanadium(IV).

ACKNOWLEDGMENT

The work was carried out in a test of the possible replacement of iron(II) by vanadium(IV) in low temperature polymerization recipes under the sponsorship of the Reconstruction Finance Corp., Office of Synthetic Rubber, in connection with the synthetic rubber program of the United States Government.

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New Solvent System for Separation of Amino Acids By Paper Chromatography

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DURING purification studies on a plant growth factor from coconut (*5*), fractionation progress was followed by paper chromatographic resolution and detection of the ninhydrin-positive components of the various concentrates. The more common solvent systems available for the separation of ninhydrinpositive materials were found to be unsatisfactory for this work.

Consden *et al.* (*3*) and Block *et al.* (*1*) describe the use of various phenolic, organic base (both buffered and unbuffered), and butyl alcohol solvent systems. The phenolic systems were found to be undesirable for routine work because of their corrosive nature and because they are generally equilibrium systems, the composition of which is affected markedly by temperature fluctuations. The common *n*-butyl alcohol–acetic acid system (*1*) was found to be unsatisfactory because of the slow movement of the solvent front after several hours of development. Since the decrease in solvent front movement was accompanied by the development of the odor of ethyl acetate in the chromatographic chamber, *tert*-butyl alcohol was substituted for *n*-butyl alcohol in an attempt to reduce esterification. While this substitution did decrease esterification, and enhance the solvent front movement, the resolution of the ninhydrin-positive components was greatly impaired. The high cost of organic bases such as lutidine and collidine renders these solvents impractical for daily, routine investigations.

The new system, which has been used successfully in this laboratory for the resolution of ninhydrin-positive compounds, consists of methyl ethyl ketone, propionic acid, and water in the volume ratios 75:25:30. The solvents are completely miscible and hence the composition of the system is not altered by temperature fluctuations. The solvent front moves about 40 cm. in 20 hours on ascending chromatograms, and can be air-dried in 30 minutes to allow spraying with a butyl alcohol solution of ninhydrin. The movement of 24 amino acids has been studied and the R_f differences among the individual amino acids have been found to be as great as those reported with any of the existing unidirectional systems. Replicate R_f determinations were found to agree within ±2%.

In application to natural product work in this laboratory, this solvent system has allowed resolution of eight ninhydrin-positive spots in a unidirectional chromatogram of an acid hydrolyzate of a purified coconut meat fraction (*2*). In another experiment, this same hydrolyzate were resolved further into 12 spots by development of the chromatogram with the same solvent system in a second direction. This new solvent system can be used for routine, unidirectional paper chromatograms of amino acids, or in combination with one of the published systems for two-directional chromatograms where the separation of complex mixtures of amino acids or peptides is desirable.

EXPERIMENTAL

Preparation of Samples. Solutions of 24 amino acids (Table I) were prepared by dissolving approximately 20 mg. of each amino acid in 1 ml. of 1.0N hydrochloric acid and diluting to 10 ml. with water. These solutions were kept frozen when not in use. Asparagine and glutamine gave two ninhydrin-positive spots 2 weeks after preparation of the solutions. This observation seemed to indicate partial conversion to the corresponding dibasic acids.

Operating Procedure. Whatman No. 1 sheets (46 × 52 cm.) were used as supplied by the manufacturer throughout this work. Two to 4 γ of each amino acid were applied to the paper on the base line at points 1.5 cm. apart. Ascending chromatograms were run with a solvent system which consisted of 75 ml. of methyl ethyl ketone, 25 ml. of propionic acid, and 30 ml. of water. The papers were run for 20 hours in a Chromatocab (Model A, Research Equipment Corp., Oakland, Calif.) at 22° to 24° C. The solvent front generally moved about 40 cm. during this period of time.

After 20 hours, the papers were removed and air-dried for 30 minutes. The papers were sprayed with a butyl alcohol solution of ninhydrin (0.125%) which contained one crystal (5 mg.) of

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phenol per 100 ml., and were air-dried for 20 minutes. A 10-minute heating period in an 85° C. oven was usually sufficient to bring out all of the spots. Finally, the spots were sprayed with an ethyl alcohol solution of copper nitrate (*4*) to convert them to a permanent, salmon-pink color. A list of R_f values is given in Table I.

Table I. R_f Values of Amino Acids on Whatman No. 1 Paper at 22° to 24° C.[a]

Amino Acid	Average R_f[b]
DL-Leucine	0.81
DL-Isoleucine	0.78
DL-Phenylalanine	0.75
DL-Tryptophan	0.69
γ-Amino butyric acid	0.68
DL-Methionine	0.65
DL-Valine	0.62
L-Tyrosine	0.57
β-Alanine	0.55
L-Proline	0.51
DL-Alanine	0.47
L-Glutamic acid	0.44
DL-Threonine	0.43
Glycine	0.39
L-Hydroxyproline	0.39
DL-Aspartic acid	0.36
DL-Glutamine	0.34
DL-Serine	0.34
L-Arginine	0.30
L-Asparagine	0.30
L-Histidine	0.28
L-Lysine	0.25
L-Cysteine	0.15 (Streaking)
L-Cystine	0.14

[a] Ascending chromatograms run in the solvent system, 75 ml. of methyl ethyl ketone, 25 ml. of propionic acid, 30 ml. of water.

[b] These values represent the averages of triplicate determinations. Individual values differed from the averages by about ±0.02 R_f unit.

Continued investigations with this solvent system have indicated that the mobility of the individual amino acids is dependent upon the relative volumes of the chromatographic chamber and solvent mixture used, as well as upon temperature. Evidently, when a relatively small volume of solvent is used in a large chromatographic chamber, unequal evaporation of the components of the solvent system occurs and the composition of the remaining liquid (particularly that on the paper) is changed sufficiently to alter the observed R_f values. With the amino acid leucine, for example, observed R_f values were 0.81 under the experimental conditions reported above, whereas at 27° to 30° in glass jars with volumes of 37.6, 14.0, and 2.0 liters and 130 ml. of solvent in each jar, the observed values were 0.78, 0.64, and 0.56, respectively. These chromatograms were run for 14 to 16 hours, and the solvent front moved about 40 cm. during this time.

The effect of temperature changes were also rather marked. For example, with 130 ml. of solvent in the largest of the three jars mentioned above, the 0.78 value for leucine at 27° to 30° was reduced to 0.71 at 25° to 27° and to 0.64 at 18.5° to 21.5°. Conditions which would be expected to favor removal of the most volatile component, methyl ethyl ketone, from the solvent mixture—i.e., larger jar volumes and higher temperatures—are thus seen to result in higher R_f values. This result is consistent with the higher water content of the unevaporated liquid portion of the solvent remaining after removal of a part of the methyl ethyl ketone.

The absolute R_f values were found to be consistent and reproducible under a given set of experimental conditions. Furthermore, altered conditions affected the various amino acids studied approximately equally, so that the relative order of R_f values was usually not changed. Further studies on the effect of the above variables on the absolute R_f values of amino acids with several solvent systems are being carried out.

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Calculation of the Integral Attenuation Index Between 400 and 700 Millimicrons

And of Corresponding Wave Length for Filtered Raw Sugar Solutions

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ACCORDING to Judd (*3*), the term "color" as used in the sugar industry is likely to have different meanings and, to avoid confusion, only the accepted psychophysical definition of color should be employed. In this sense color may be expressed in terms of luminance (photometric brightness), excitation purity, and dominant wave length. In previous work by the writers and associates (*7, 8*) on Filter-Cel–filtered solutions of refined and later of raw sugars, the wave lengths chosen in the computation of the trichromatic coefficients were those given by Hardy (*2*) in his method of color determination on the basis of ten selected wave lengths for each primary. All of these are in the range of 422.2 to 646.2—that is, in the visible range between 400 and 700 mμ. It was found that a high correlation exists between the attenuation indices ($-\log T/bc$) (*1*) of the solution, at wave length 560 mμ, and the following evaluation of the color: $k_1 - (k_2 \times \text{luminance}) - (k_3 \times \text{purity}) - (k_4 \times \text{dominant wave length})$, where T is transmittancy, b thickness of solution in centimeters, c concentration of refractometer solids in grams per milliliter, and k_1, k_2, k_3, and k_4 are constants independent of wave length. [The expression, $-\log T/bc$, is now termed absorbancy index only if the solution is completely free from light-scattering particles, but attenuation index if it does contain such particles. The sugar solutions prepared by the writers had been filtered with Celite analytical filter aid and were practically, though not completely, free from scattering particles. No filtering agent or technique has so far been found that will leave no trace of Tyndall effect in the solution (*6*).]

The result confirmed the findings of Peters and Phelps (*5*), and goes far toward justifying the use of the attenuation index at 560 mμ as a measure of the degree to which the filtered sugar solution of unit concentration appears colored—that is, different from distilled water, taken as colorless.

Some industrial sugar chemists use wave lengths other than 560 mμ for this estimate, and some are particularly interested in the quantity of coloring matter present in sugar products rather than color as seen by the eye. Color comparators ("colorimeters") have been constructed with this purpose in view, and use visual methods whereby the thickness and concentration of a solution of the unknown sugar required to produce the color of a known standard are determined. With chemically pure material this may be done at any wave length preferred, but with sugar products the concentration ratio varies from wave length to wave length. This difficulty was overcome by Peters and Phelps by integrating with respect to wave length the product of spectral transmittancy, spectral energy of noon sunlight, and spectral luminosity of the human observer, and taking this integral as a measure of the concentration of coloring matter. They also showed that the specific absorptive index, now called attenuation index, at the wave length of the centroid (560 mμ) is a nearly equivalent measure of the concentration of coloring matter.

Several sugar laboratories have in the past estimated the concentration of coloring matter of sugar products by integrating the attenuancy, based on the attenuation indices, instead of integrating the luminosity-energy-transmittancy products. The idea back of this practice is that, although attenuancy at any wave length desired is a strict measure of concentration of chemically pure material, for sugar products each wave length yields a somewhat different measure. It was therefore decided to test the applicability of this method by including all wave lengths that can contribute to color within the visible spectrum, and take an average.

It is the purpose of this investigation to find what single wave length yields attenuation indices that correlate best with this average. The integral of the luminosity-energy-transmittancy products used by Peters and Phelps should correlate perfectly only with the light-dark aspect of the colors of sugar solutions, and it is undoubtedly true that the wave length 560 mμ is close to the optimum for correlation with this aspect of color. It is possible that the wave length found in the present study may yield a better correlation with the color of the solution judged directly by the eye, both toward yellow and toward dark, and so afford a better measure of the concentration of coloring matter.

METHOD

From previous investigations the writers have spectral transmittancy data for 97 raw sugars from a number of different producing regions all over the world. Of the original 102 samples listed in Table I of the second paper mentioned (*7*), the curves for Nos. 1, 25, 26, 27, and 28 have been lost, but similar samples of the same characteristics were among the remaining ones, so that the use of the missing curves would not have affected the conclusions in a significant way. The data have been converted to attenuation indices—that is, reduced to the basis of 1-cm. thickness and a concentration of 1 gram of refractometer solids in 1 ml. of solution. For each solution the curve of attenuation indices is plotted against wave length, read at every 10 mμ, and averaged over the wave length range 400 to 700 mμ. Then the wave length at which the solution has an attenuation index equal to this average was read by interpolation. Of the total number of samples, 9 fell between 495 and 500 mμ, 37 between 501 and 505 mμ, 46 between 506 and 510 mμ, and 5 between 511 and 513 mμ. The mean wave length for all 97 was at 505.3 mμ.

Although it might be presumed that the attenuation index for this wave length would yield optimum correlation with this average for the whole visible spectrum, it was decided to submit this assumption to a statistical test. The analysis was carried out at the request of the writers under the direction of Lorge (*4*).

The attenuation indices previously computed were recorded for each of 30 wave-length intervals of 10 mμ. The sum of these attenuation indices multiplied by 10 gives the area, *A*, of the field under the attenuation index curve between 400 and 700 mμ. This area, *A*, divided by 300, gives the average attenuation index. It was found that the area *A* could be approximated by $Ka + b$, where a is the attenuation index at some fixed wave length and K and b are constants depending on choice of this wave length.

RESULTS

The constants K and b were derived from 46 samples selected at random for wave lengths between 475 and 555, 10 mμ apart, and for combined wave lengths—namely, 505 and 515 mμ—and for 515 and 535 mμ. The values of K and b, and the respective correlation coefficients between A and $Ka + b$ are shown in Table I, together with similar results based on the use of two wave lengths combined.

Table I. Equations for Different Wave Lengths

Number of Equation	Wave Length, Mμ	Equations	Correlation Coefficient
1	475	$A = 195.712\, a_{475} + 29.992$	0.9956
2	485	$A = 219.998\, a_{485} + 28.540$	0.9964
3	495	$A = 246.878\, a_{495} + 26.554$	0.9972
4	505	$A = 277.754\, a_{505} + 21.951$	0.9970
5	515	$A = 310.105\, a_{515} + 19.711$	0.9968
6	525	$A = 346.328\, a_{525} + 15.809$	0.9964
7	535	$A = 381.935\, a_{535} + 14.916$	0.9939
8	545	$A = 422.908\, a_{545} + 12.006$	0.9917
9	555	$A = 467.482\, a_{555} + 8.441$	0.9884
10	$\begin{Bmatrix}505\\515\end{Bmatrix}$	$A = 8.646\, a_{505} + 19.013$ $+301.275\, a_{515}$	0.9968
11	$\begin{Bmatrix}515\\535\end{Bmatrix}$	$A = 425.951\, a_{515} + 21.221$ -142.255	0.9965

The correlation coefficients show an initial rise with the wave length, reach a maximum around 495 mμ, and then fall again with increasing wave length. Those for two wave lengths combined are of about the same magnitude as those for either of the two wave lengths and show no further improvement, and consequently the idea of combining two different wave lengths was abandoned.

Since the highest correlation was found for wave lengths around 495 mμ, but the previous calculations had given a mean wave length of 505.3 mμ, the deviations resulting by using Equations 3 and 4 were calculated for all 97 samples.

The ranges of the percentage deviations in calculating the total area from the attenuation indices at 495 mμ and at 505 mμ by equations 3 and 4 are given in Table II.

The coefficient of variation—i.e., the standard deviation in per cent of the total area, on the basis of all individual results—is 2.703 for the values obtained at 495 mμ, and 2.568 for those found at 505 mμ, a lower value at the latter wave length, in spite of the fact that at 495 mμ the correlation coefficient was 0.9972, against 0.9970 at 505 mμ.

The mean wave length for the 97 samples calculated previously

Table II. Number of Samples within Various Ranges of Percentage Deviations According to Equations 3 and 4

Deviation, % Within	Equation 3, 495 mμ	Equation 4, 505 mμ
1	25	31
2	54	54
3	71	72
4	81	84
5	89	91
6	93	93
7	95	93
8	96	94
9	96	95
10	96	96
13	96	97
15	97	97

is 505.3 mμ, checking with that giving the smaller coefficient of variation, 2.568 at wave length 505 mμ.

The two prediction equations, at 495 mμ and 505 mμ, may not be significantly different from each other. Errors in rounding out could have produced the observed differences between Equations 3 and 4. In terms of relative error, Equation 4 is better than Equation 3.

It may be concluded that wave length 505 mμ is the one at which the mean attenuation index gives the minimum error when it is used to calculate from Equation 4 the total area below the attenuation index curve within the visible region of the spectrum.

Various attempts to reduce the observed deviations to less than 13% in one case did not lead to improvements. Those workers who are inclined to place reliance on the average attenuation index over the visible spectrum (400 to 700 mμ) may find it advantageous to use wave length 505 mμ as the one giving an approximate average measure of the concentration of coloring matter in raw sugars.

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Hydrolysis of Polysaccharides by a Cation Exchange Resin and Identification of Monosaccharide Components by Paper Chromatography

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CATION exchange resins have been used for hydrolysis of di- and polysaccharides (*1*, *7*, *9*) and proteins (*8*). More recently, carbohydrate-protein complexes have been hydrolyzed in a similar manner prior to identifying monosaccharide components by paper chromatography (*3*). The present paper describes the detailed analytical aspects of this technique, including control experiments designed to test the effect of the hydrolysis medium on monosaccharides representative of various chemical classes (pentoses, methylpentoses, aldohexoses, ketohexoses, hexuronic acids, hexosamines, and acetylated hexosamines), as well as di-, tri-, and polysaccharides. The treated and untreated solutions were analyzed qualitatively by chromatography. A comparison of the results provided information concerning the degree of decomposition of the monosaccharides and the hydrolysis of di-, tri-, and polysaccharides under various conditions. In this way, suitable conditions were established for the identification of monosaccharides by chromatography after the hydrolysis of carbohydrates or carbohydrate-protein complexes.

EXPERIMENTAL

Resin. Permutit Q, a polystyrene sulfonic acid type cation exchange resin, was acid-regenerated by shaking with 4.4*N* hydrochloric acid (900 ml. per liter of resin) in a separatory funnel. It was repeatedly washed with large volumes of distilled water until free of chloride ions. The final pH of the washings was 6. The resin was then air-dried.

Effect of Hydrolysis Medium on Mono-, Di-, Tri-, and Polysaccharides. Two milliliters of 1% solutions of each of the saccharides listed in Tables I and II were heated at 100° C. in sealed tubes for 48 and 96 hours with 1-gram portions of resin. As controls, 2 ml. of 1% solutions of the monosaccharides (Table I) were heated (in the absence of resin) for 96 hours at 100° C. to determine the degree of decomposition due to heating alone, and also incubated with 1 gram of resin at 22° C. for 48 hours (likewise in sealed tubes) to determine the degree of adsorption of the monosaccharides by the resin. Three-microliter aliquots of the treated solutions were taken directly from the tubes for analysis by paper chromatography. (However, in the case of sucrose and raffinose, 6 and 9 μl., respectively, were used, as sucrose contains two, and raffinose three different monosaccharide units).

Table I. Relative Intensities[a] of Sugar Spots after Treatment with and without Resin

Substances	Time, Hours			
	48	96	96	48
	Treatment of Solution			
	Resin at 22° C.	Without resin at 100° C.	Resin at 100° C.	
Pentoses				
Arabinose	++++	++	+	++
Xylose	++++	+	+	++
Ribose	++++	+++	−	+
Methylpentoses				
Fucose	++++	+++	++	++
Rhamnose	++++	+++	+	+++
Aldohexoses				
Galactose	++++	+++	+++	++++
Glucose	++++	+++	+++	++++
Mannose	++++	+++	+++	++++
Ketohexoses				
Fructose	++++	+	−	−
Sorbose	+++	++	−	−
Hexuronic acids				
Galacturonic acid	++++	−	−	+
Glucuronic acid	++++	−	−	+

[a] Control untreated solutions, containing amounts of sugar which would have been present if treatment had no effect, were also placed on chromatograms as markers. Control spots were given a rating of ++++ regardless of intensity. Spots obtained after treatment were compared visually and given relative ratings.

Effect of Hydrolysis Medium on Amino Sugars and Acetyl Derivatives. Two milliliters of 1% solutions of glucosamine and *N*-acetyl glucosamine were subjected to the three treatments described above for monosaccharides. The resin which was recovered from the last treatment was thoroughly washed with water, and then eluted three times with 2-ml. portions of 0.5*N* hydrochloric acid. The eluates were evaporated to dryness, and the residues were dissolved in 0.5 ml. of water.

Table II. Relative Intensities[a] of Sugar Spots Produced by Resin Hydrolysis of Di-, Tri-, and Polysaccharides

Substances	Time of Hydrolysis, Hours					
	48	96	48	96	48	96
	Products of Hydrolysis					
	Galactose		Glucose		Fructose	
Cellobiose			++++	++		
Maltose			++++	++		
Sucrose			++++	++	−	−
Raffinose	+++	++	+++	++	−	−
Glycogen			+++	++		
Starch			+++	++		

[a] Control untreated solutions, containing amounts of monosaccharide which would have been present if hydrolysis and recovery were quantitative, were placed on chromatograms as markers. Control spots were given a rating of ++++ regardless of intensity. Spots obtained after resin treatment were compared visually and given relative ratings.

In addition, to determine whether amino sugars could be recovered from mucopolysaccharides, 50 mg. each of chondroitin sulfuric acid and heparin were hydrolyzed with 12 times their weight of resin and 5 ml. of water at 100° C. in sealed tubes. The resin was eluted with 0.5N hydrochloric acid, the eluates were evaporated to dryness, and the residues were dissolved in 0.1 ml. of water. Six-microliter aliquots of each of the solutions were used for chromatographic analysis.

Paper Chromatography. The solutions were analyzed by unidimensional ascending paper chromatography. Rectangular sheets (27 × 38 cm.) of Schleicher and Schuell No. 589 white ribbon paper were used. The sheets were cut so that the long sides were in the machine direction. Aliquots of the solutions were placed at individual points of origin along a line 4 cm. above one of the narrower edges of the paper.

The long sides of the paper were approximated, stapled securely, and the resultant cylinder was developed in a butyl alcohol-pyridine-water solvent (*2*). The solvent was allowed to rise to the top of the paper three times in the same direction (*5*), each development requiring about 22 hours. Reducing sugars and uronic acids were identified by spraying the dried paper uniformly with aniline hydrogen oxalate (*4*); amino sugars by spraying with acetyl acetone dimethylaminobenzaldehyde (*6*).

In order to estimate the effect of the various treatments on the saccharides of known structure, the intensities of the spots resulting from 3-μl. aliquots of the treated solutions were compared visually with those from 3 μl. of 1% untreated solutions of the corresponding sugars (or known monosaccharide components in the case of di-, tri-, and polysaccharides) placed on the same piece of paper and developed at the same time.

Because the various control untreated sugars gave spots of different colors and intensities, they were all given an arbitrary rating ++++, regardless of the intensity, and the resin-treated material compared with these as standards. The treated materials (Tables I and II) were rated ++++, +++, ++, +, or −, depending on whether the spots showed no, a very slight, a moderate, or a drastic reduction of intensities, or were completely invisible, respectively. (The spots rated as + were still easily visible.)

RESULTS AND DISCUSSION

Monosaccharides (Table I, Figure 1). Pentoses, methylpentoses, and aldohexoses were easily identified on paper chromatograms after their solutions were heated at 100° C. with the resin for 48 or even 96 hours, although the intensities of the spots indicated varying degrees of decomposition (last two columns of Table I). None of these substances was significantly adsorbed by the resin at 22° C. (column 2). The slight decomposition of the aldohexoses can thus be attributed to heating in the presence of water at 100° C. (column 3), but the resin appeared to catalyze the decomposition of pentoses and methylpentoses.

Ketohexoses were not detectable after heating with the resin for 48 hours. Thus the decomposition observed by heating with water alone is catalyzed further by the resin. However, mineral acid hydrolysis also completely destroys ketohexoses.

Hexuronic acids are destroyed by heating at 100° C. with or without resin for 96 hours, but enough was preserved for identification when the hydrolysis was limited to 48 hours. Under all these conditions decomposition was accompanied by development of dark brown solutions. When the solutions were chromatographed, no interference was caused by the brown material, since the uronic acids traveled as usual and were the only substances observed above the origin.

Glucosamine and N-acetyl glucosamine were destroyed by heating without resin at 100° C. However, glucosamine was protected from destruction by the presence of resin even after heating for 96 hours. This effect may be explained by the adsorption of glucosamine on the resin. N-Acetyl glucosamine was

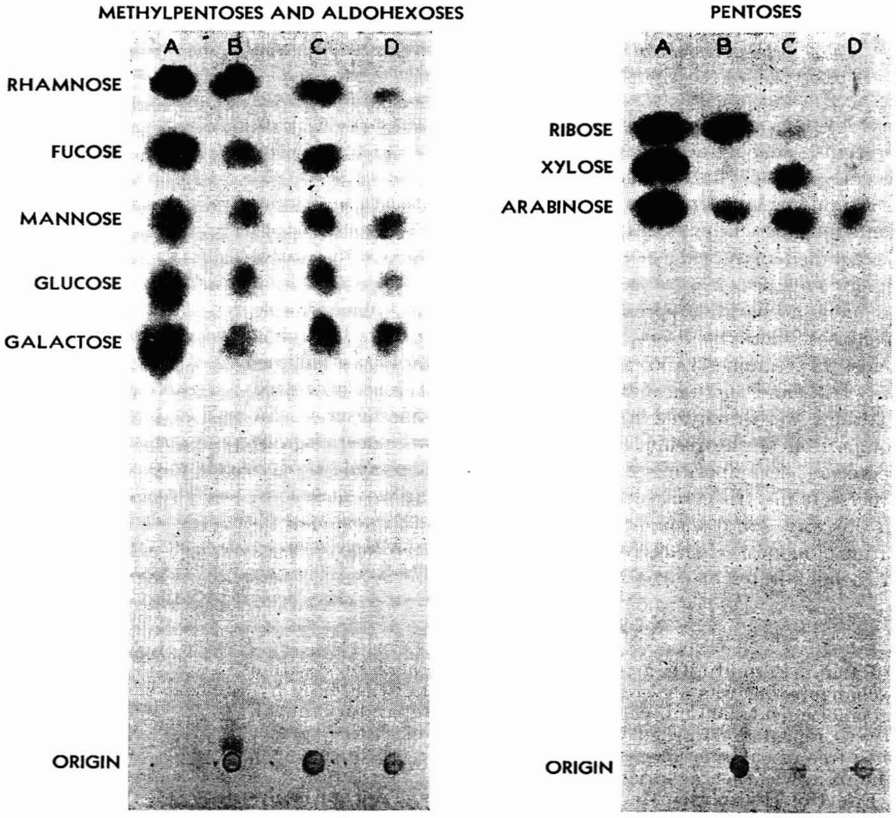

Figure 1. Paper Chromatogram Showing Positions and Intensities of Spots for Methylpentoses (Greenish Brown), Aldohexoses (Reddish Brown), and Pentoses (Pink)

Columns demonstrate effects of various treatments on these monosaccharides
A. Untreated
B. Incubated without resin at 100° C. for 96 hours
C and *D.* Incubated with resin at 100° C. for 48 and 96 hours, respectively
Original solutions were 1%, and 3-μl. aliquots were used for chromatography
Chromatograms were sprayed with aniline hydrogen oxalate
All monosaccharides were run on same piece of paper from common line of origin; photograph was cut in two for convenience in labeling

deacetylated under the influence of the resin and the free glucosamine was likewise absorbed and protected. It was found possible to elute the hexosamine from the resin with 0.5*N* hydrochloric acid and then to identify it on chromatograms as the hydrochloride.

These results indicated that, with the exception of ketoses, the monosaccharides were detectable after heating with the resin for 48 hours.

Di-, Tri-, and Polysaccharides. The di-, tri-, and polysaccharides were hydrolyzed with the resin for periods of time ranging from 12 to 96 hours. In general, maximum intensities of sugar spots were obtained after 48-hour hydrolysis. Sucrose, cellobiose, maltose, starch, and glycogen gave rise to glucose only, and raffinose gave rise to glucose and galactose (Table II). In agreement with the fact that ketohexoses were easily destroyed, no fructose was detected in the hydrolyzate from sucrose or raffinose.

Since uronic acids were only just detectable after their solutions were treated with the resin for 48 hours (Table I), polysaccharides known to contain these substances as structural units (pectin, chondroitin sulfuric acid, and heparin) were hydrolyzed for periods of time ranging from 12 to 96 hours and the hydrolyzates were chromatographed. The uronic acids in these three substances were easily detectable up to 72 hours, with maximum intensities at 48 hours. The data suggest that the hydrolysis of the polysaccharides is initially a slow process, so that the free uronic acid liberated during the latter part of the hydrolysis is not completely destroyed.

Hexosamines eluted from the resin after the hydrolysis of heparin and chondroitin sulfuric acid were identified as glucosamine and galactosamine, respectively. (As *N*-acetyl galactosamine is a component of chondroitin sulfuric acid, this provided further evidence that the resin deacetylates *N*-acetylhexosamines).

The resin hydrolyzates of carbohydrate-protein complexes were almost colorless (in contrast to the dark brown solutions obtained after hydrolysis with 1*N* hydrochloric acid at 100° C. for 8 hours), except when glucuronic acid was a component. Monosaccharide components were clearly identified without further treatment of the solutions (*3*).

The paper chromatographic technique provided clear separations of galactose, glucose, mannose, fucose, and rhamnose in a single mixture (Figure 1). Ribose when added to such a mixture could also be identified despite its proximity to fucose, owing to the differences in color produced by aniline hydrogen oxalate. The clarity of the separations is a result of the combination of several factors—the solvent used, the technique of triple development, and the fact that the solvent was allowed to move in the machine direction of the paper.

None of the monosaccharides yielded decomposition products which could be identified on the chromatograms; and di-, tri-, and polysaccharides yielded only those monosaccharides which were expected on the basis of their known structural units. The overall analytical technique, involving hydrolysis in the presence of a cation exchange and paper chromatography of the hydrolyzates is therefore dependable and free from artifacts.

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Determination of Moisture in Sodium Bicarbonate

Karl Fischer Method

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THE presence of small amounts of moisture in sodium bicarbonate inhibits the flowability of the product and promotes lump formation during storage (*5*). The occurrence of these undesirable effects has created a need for an accurate and sensitive method for measuring the moisture content of commercial sodium bicarbonate.

The U. S. Pharmacopoeia (*8*) directs the drying of 3-gram portions of sodium bicarbonate contained in a low-form weighing bottle over concentrated sulfuric acid in a desiccator for 4 hours prior to assay. No recommendation is made to utilize the weight loss from this operation as an index of the moisture content of the sample. In fact, tests of this type have indicated the inadequacy of the desiccation period under such conditions. Actually, dessication periods of 24 hours rarely showed weight loss values (moisture) greater than 0.02%, with values of 0.01% predominating in virtually all cases. Occasionally samples showed a slight gain in weight resulting from the initial desiccation treatment and, in such cases, an additional 24-hour dessication treatment was conducted to obtain a measurable weight loss of the sample. Analyses obtained by a procedure of this type are unsatisfactory and are often open to considerable question and doubt.

A review of general methods for determining moisture in solids (*1*) suggested potential application of the Karl Fischer method (*3*) described by Wernimont (*9*) involving the use of the dead-stop end point (*4*). Application of this method to sodium bicarbonate involves an extraction technique with anhydrous methanol (*6, 7*) and takes into account the interference of bicarbonate (*2*) which is also extracted slightly from the sample along with the moisture.

It was the purpose of the work to adapt the Karl Fischer technique of moisture determination to sodium bicarbonate and to give a typical analysis of the commercial product.

EXPERIMENTAL

The general procedure for determining moisture in sodium bicarbonate by the Karl Fischer method involved extraction of the moisture in the sample with dry methanol, filtration to separate the extract, titration of an aliquot of the extract with Karl Fischer reagent to measure the moisture and a small amount of

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sodium bicarbonate which is dissolved, and acidimetric titration of an aliquot of the extract to measure the dissolved bicarbonate for use as correction in the Karl Fischer titration.

Experiments were conducted to define optimum conditions for extracting moisture from the sample quantitatively. Consideration was given to the duration of the extraction period and the duration of the digestion or settling period which followed extraction. These experiments indicated optimum recovery of moisture from the sample by extracting the mixture vigorously and continuously for 1 minute and digesting for 5 minutes prior to filtration.

The accuracy of the method was measured by analyzing three series of synthetic samples containing known amounts of moisture. These samples were prepared by weighing 100-gram portions of freshly prepared, free flowing sodium bicarbonate into a series of wide-mouthed sample bottles equipped with tight-fitting screw caps, and adding the requisite weight of distilled water to each specimen with a dropping pipet having a finely drawn tip. Immediately after the addition, the bottles were closed tightly and mixed thoroughly by vigorous shaking. The level of moisture added to the three series was within the calculated range of 0.01 to 0.10%; as the moisture was increased from 0.01 to 0.10% the observed flowability of the samples decreased and the samples became lumpy. Periods of 24, 48, and 72 hours of conditioning in the respective moist environments were allowed to transpire before the moisture tests by the Karl Fischer method were conducted. These conditioning periods provided time for reaching equilibrium between the free moisture and the sodium bicarbonate components.

The precision of the method was measured by conducting duplicate analyses of a series of typical production lots of sodium bicarbonate which had been stored for varying periods under normal conditions.

MOISTURE EXTRACTION AND TITRATION APPARATUS

The extraction flask is a conventional 500-ml. separatory funnel equipped with a ground-glass stopper and a medium-porosity sintered-glass filter disk sealed permanently to the inner walls of the funnel near the vertex. Provision is made for attaching a drying tube charged with Drierite to the top opening of the funnel to protect the system from atmospheric contamination of moisture during the transfer of the extract to the reservoir. The reservoir is a dispensing funnel of 125-ml. capacity graduated at 50- and 100-ml. volumes and is connected to the extraction flask by a tight-fitting rubber stopper. The stopper is fitted with a drying tube charged with Drierite to which an aspirator pump is attached. A two-way stopcock at the bottom of the reservoir facilitates removal of extract from the reservoir directly into the Karl Fischer titration cell or into a beaker for acidimetric titration. The apparatus for the Karl Fischer titration is of conventional design involving the dead-stop principle.

REAGENTS

The reagents required for the test include Karl Fischer reagent, reagent grade anhydrous methanol, Fleisher's methyl purple indicator solution, and standardized 0.1*N* hydrochloric acid.

PROCEDURE

Rinse the extraction flask and reservoir with four 15-ml. portions of absolute methanol, using suction and the drying tube devices after each rinse.

Place 100 grams of the sodium bicarbonate sample in the extraction flask and add 130 ml. of absolute methanol. Stopper the flask immediately and shake vigorously for 1 minute after the sample has been completely wetted with the methanol. Rapidly replace the stopper with the drying tube device and allow the solids to settle for 5 minutes.

Attach the reservoir to the extraction flask, apply gentle suction to the system with a water aspirator and withdraw 100 ml. of the extract. Disconnect the water aspirator, close the cock at the bottom of the extraction flask, and measure a 50-ml. aliquot of the extract into the Karl Fischer titration cell. Stir the extract and titrate directly to a dead-stop end point with standardized Karl Fischer reagent. Record this titration which measures the moisture plus dissolved sodium bicarbonate.

Withdraw the remaining 50-ml. aliquot of the extract into a 250-ml. beaker. Add 125 ml. of distilled water and titrate to a steel gray end point with standardized 0.1*N* hydrochloric acid solution, employing Fleisher's methyl purple indicator.

Conduct a blank determination involving all of the operations detailed above with a portion of the absolute methanol used for the extraction.

ANALYSIS OF SYNTHETIC MIXTURES AND TYPICAL PRODUCTION LOTS OF SODIUM BICARBONATE

Analysis of the synthetic mixtures of sodium bicarbonate and determination of moisture by the Karl Fischer method are shown in Table I. The calculated recovery of moisture from the samples conditioned 24, 48, and 72 hours is shown in this table and ranges between 72 and 103%. The absolute accuracy of the method is unknown because of the lack of a standard basic material or a suitable alternative method for determining moisture in the control material. This limitation was resolved by selecting a freshly prepared, free-flowing product and adding weighed amounts of water, then subjecting the entire mixture to the test procedure. Residual moisture in the control samples, subjected to the same conditioning periods as the synthetic mixtures, was determined by the Karl Fischer method described.

Random specimens of refined sodium bicarbonate stored under plant conditions were analyzed in duplicate by the Karl Fischer method. The moisture content of these commercial specimens ranged between 0.01 and 0.16% with a calculated precision within ±0.005%.

Table I. Recovery of Moisture from Sodium Bicarbonate

H_2O Control, %	H_2O Added, %	Total H_2O Present, %	Total H_2O Found, %	Recovery, %
		24-Hour Conditioning Time		
0.025	0.018	0.043	0.039	91
	0.039	0.064	0.058	91
	0.055	0.080	0.079	99
	0.061	0.086	0.084	98
		48-Hour Conditioning Time		
0.025	0.019	0.044	0.043	98
	0.036	0.061	0.058	95
	0.051	0.076	0.074	97
	0.071	0.096	0.099	103
		72-Hour Conditioning Time		
0.005	0.010	0.015	0.015	100
	0.018	0.023	0.019	83
	0.038	0.043	0.031	72
	0.056	0.061	0.046	75
	0.086	0.091	0.075	82
	0.099	0.104	0.083	80

ACKNOWLEDGMENT

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Spectrographic Determination of Sodium and Potassium in Coal Ashes

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THE authors' company is investigating the underlying causes of fireside deposit formation in high-duty boiler units, and emphasis has been placed on these causes as they are related to coal and coal ash chemistry. The most promising approach toward reducing the time required for the many necessary analyses appeared to be through the development of quantitative spectrographic methods for determining sodium and potassium, the constituents which apparently are a cause of the deposit difficulties. Flame photometric methods for determining the alkali metals have been popular, but have the disadvantage of requiring a prior dissolution of the sample. Helz (*7*) and Helz and Scribner (*8*) have described methods for determining the alkali group elements in portland cement using both silver and cobalt as internal standards. Other workers, in analyzing cracking catalysts (*4*) and coals (*9*), have relied upon external standards for quantitative calibrations.

This paper describes a spectrographic method of determining sodium and potassium in coal ashes over a range of 0.3 to 5.0%.

EXPERIMENTAL

Apparatus. The equipment used in this investigation was a Jarrell-Ash, Wadsworth mounting, 3.4-meter grating spectrograph, a National Spectrographic Laboratories Spec-Power source unit, an Applied Research Laboratory developing machine, and a Jarrell-Ash densitometer.

Choice of Analytical Lines and Internal Standards. It was considered practical to use methods that could be applied directly to a powdered sample with a minimum of sample preparation, and because of its convenience and simplicity, a direct current arc was chosen as the excitation source for this work.

As it has been shown (*3*) that excellent results can be obtained if the volatilization and excitation characteristics of the internal standard are similar to those of the element to be determined, it was of importance to choose the proper internal standard for sodium and potassium.

Table I. Precision Studies

	Intensity Ratios		
	K 4044.1 / Rb 4215.6	Na 3303.0 / Rb 4215.6	Na 3303.0 / Li 3232.6
	1.90	2.10	0.96
	1.64	1.60	1.05
	1.75	1.51	1.04
	1.82	1.50	1.03
	1.77	1.45	1.00
	1.69	2.34	0.99
	1.72	1.50	0.96
	1.71	1.61	0.95
	1.70	1.77	..
Average	1.73	1.61	1.00
Average deviation, %	3.2	12.8	3.2
Standard deviation, %	4.5	20.4	3.9

The alkali lines lying in the near ultraviolet (sodium 3303.0, 3302.3; potassium 4044.1, 4047.2) were of the proper intensity to be used at concentration levels of 0.3 to 5.0%. The sodium lines are relatively free from interferences (zinc 3302.9 is the only serious interference); but cyanogen bands and the iron 4045.8 line interfere with the potassium lines in this region. In order to reduce these interferences with the potassium lines, the sample was diluted with a lithium carbonate buffer and excited in a low amperage direct current arc. This buffer not only reduced the interferences with the potassium lines but also reduced the cyanogen intensity to such an extent that the rubidium 4215.6 line (referred to below) was relatively free from interferences.

Initially the rubidium 4215.6 line was investigated as an internal standard for both sodium and potassium. Moving plate studies were made for the three elements and are shown in Figure 1. Since the potassium-rubidium intensity ratios were fairly constant with time, it was concluded that this line combination was satisfactory in so far as excitation and volatilization characteristics were concerned. The sodium-rubidium ratio varied irregularly, but the variations were not considered excessive in view of previously reported studies on the rare earths (*3*).

Precision studies, tabulated in Table I, however, showed that while potassium-rubidium ratios were of satisfactory precision, the sodium-rubidium ratios showed large deviations. As precisions of 12.8% were not acceptable for the sodium determination, attention was given to the use of lithium as an internal standard for this element. Barium carbonate was chosen as a buffer material in order to minimize self-absorption and extraneous effects, and to maintain an even-burning arc.

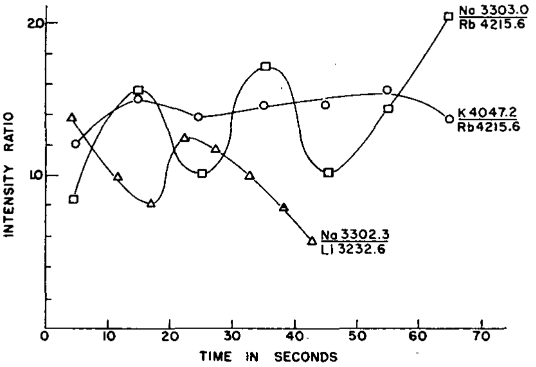

Figure 1. Time Versus Intensity Ratio

Although moving plate studies showed the sodium-lithium ratios to fluctuate almost as much as the sodium-rubidium ratios, nevertheless, the integrated sodium-lithium ratios showed a great improvement in precision, as is indicated in Table I. This may be explained in part by a comparison of the excitation potentials of these lines. The excitation potential of lithium 3232.6 is much more favorable than rubidium 4215.6 for use with the sodium lines, but on the other hand the excitation potential of rubidium 4215.6 is more favorable for use with the potassium lines (*5*).

Effect of One Alkali on Determination of the Other. In determining sodium in portland cement, Helz (*7*) found that the potassium concentration had a marked effect on the sodium-cobalt ratio. Workers in flame photometry have also observed the effect of potassium on sodium-lithium ratios (*1*). The reverse effect of sodium on the potassium determination has not been so clearly defined, and in flame photometry apparently it is not agreed whether the potassium line is enhanced or repressed by the addition of sodium in the flame. Hence, it was thought advisable to investigate this experimental variable.

A synthetic standard sample was prepared (see Quantitative Calibrations) containing 2.50% sodium oxide added as the sulfate and no potassium. The sample was mixed with the barium carbonate buffer containing 1.50% lithium carbonate. Known variable amounts of potassium sulfate were added to this mixture; the samples were arced in triplicate and photographed,

Table II. Operating Conditions for Sodium and Potassium Determination in Coal Ashes

	Potassium	Sodium
Sample charge	20.0% ash 2.56 Rb_2CO_3 77.4 Li_2CO_3	14.3% ash 1.30 Li_2CO_3 79.2 Ba_2CO_3 5.2 K_2SO_4
Wave length photographed, A.	3400–4600	2700–3900
Weight of charge, mg.	10	
Anode	3/16-inch diameter graphite, regular grade, 1.5 inches long drilled to depth of 4 mm.	
Cathode	1/8-inch diameter carbon rod, 1.5 inches long and pointed	
Gap, mm.	7	
Source	220-volt direct current, 4 amp.	
Time	1 minute	
Order	2nd	
Slit, mm.	0.030	
Sector	Steps 3, 4, 5	
Emulsion	SA No. 1 film	
Development	2.5 minutes at 21° C. in Eastman D-19	

and the intensities were measured, all according to the conditions indicated in Table II. A parallel procedure was followed for a synthetic mixture containing 2.50% potassium oxide and variable amounts of sodium sulfate.

The results of these experiments are illustrated in Figure 2. The potassium additions had the effect of increasing the sodium-lithium intensity ratios to a significant extent. In order to determine how this effect is brought about, the absolute intensities of the sodium and lithium lines are shown in Figure 2 as a function of the potassium addition. Apparently the effect of the potassium is to increase the intensity of the sodium line and to decrease slightly the intensity of the lithium line.

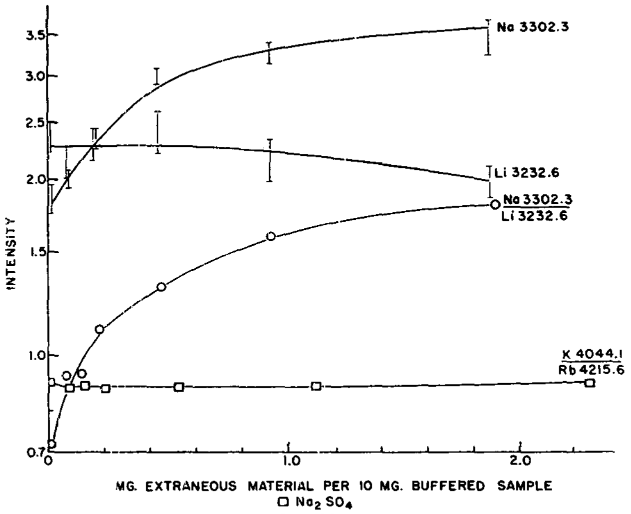

Figure 2. Effect of Additions of One Alkali on Intensity of the Other

The effect of additional potassium on the sodium-lithium intensity ratio becomes less at higher concentrations of potassium, and this agrees with observations previously made in studies on extraneous element effects (*2*). The method used by Duffendack (*2*) for eliminating this effect was applied in this case by including a fixed amount of potassium as potassium sulfate in the barium carbonate buffer mixture.

Except for a small initial reduction in the potassium-rubidium ratio, the subsequent additions of sodium as sodium sulfate to the potassium standard showed very little effect. As a result, no special precautions were taken in so far as this determination was concerned.

Quantitative Calibrations. Synthetic standard samples were prepared by dry grinding the proper amounts of alkali sulfate into an alkali-free synthetic coal ash prepared from spectrographically pure metal oxides. The composition of the alkali-free base material was as follows: 42% silicon dioxide, 30% ferric oxide, 20% aluminum oxide, 5.0% calcium oxide, 2.0% magnesium oxide, and 1.0% titanium oxide. Known samples containing 5.0, 2.50, 1.25, 0.62, and 0.31% of each alkali calculated as the oxide were prepared. These samples were then mixed with the proper buffer, excited, and photographed under the conditions listed in Table II.

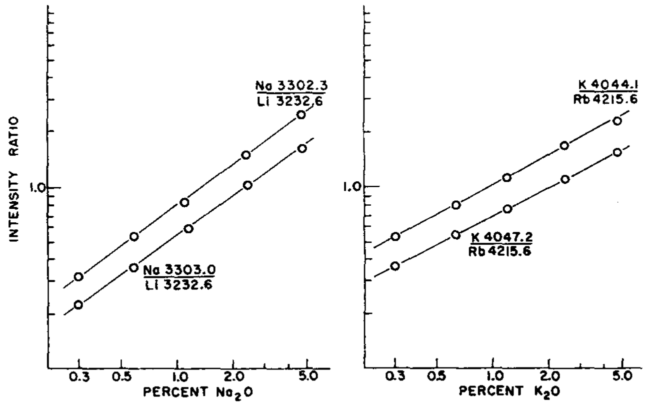

Figure 3. Calibration Curves for Alkali Determination

The per cent transmittance data were converted to intensity ratios according to standard procedures (*1*). No background was observed with these line pairs. In order to reduce emulsion calibration errors, intensity ratios for two line pairs $\left[\frac{\text{Na 3303.0}}{\text{Li 3232.6}}, \frac{\text{Na 3302.3}}{\text{Li 3232.6}}, \frac{\text{K 4044.1}}{\text{Rb 4215.6}}, \frac{\text{K 4047.2}}{\text{Rb 4215.6}}\right]$ of each element were calculated and two working curves for each element were obtained. When samples are analyzed, only that ratio nearest unity is used. Figure 3 shows the working curves which were obtained when log intensity ratio was plotted against log concentration.

Procedure for Analyzing Samples. The sample, ground to pass 200 mesh, is mixed in the proper proportions with buffer and internal standard. This is most easily accomplished by preparing a large amount of the buffer mixture (*a*) containing 3.20% of rubidium carbonate (Rb_2CO_3) and 96.8% of lithium carbonate (Li_2CO_3), and (*b*) containing 1.50% of lithium carbonate 92.5% of barium carbonate, 6.0% of potassium sulfate (K_2SO_4). For the potassium determination a sample to buffer ratio of 1 to 4 is used; for sodium a ratio of 1 to 6 is used. Duplicate 10-mg. samples are weighed into electrodes, the samples are excited, and the film processed under conditions listed in Table II.

Time Requirements. One man can complete the sample preparation (not including grinding the sample to 200 mesh), excitation, and densitometry for one sample in duplicate for both sodium and potassium in approximately 1.5 hours. This represents a considerable saving in man-hours over the classical wet method of analysis.

SCOPE OF METHOD

This method applies not only to coal ashes, but to other products from the combustion of coal, such as tapped slag, fly ash, and tube deposits. There have been occasions when the alkali content was found to be greater than the 5% concentration limit of the working curves. In these cases, satisfactory results have been obtained by increasing the ratio of buffer mixture to sample and multiplying the result by the proper factor.

EFFECT OF LITHIUM IN COAL ASH

During the preliminary investigation of the method, many coal ashes and fireside deposits were examined qualitatively for lithium. In no case was the lithium 3232.6 line detected and it was estimated from a synthetic standard that the limit of detection was 0.05% lithium as Li_2O.

Table III. Comparison of Spectrographic and Chemical Results

Sample	Na_2O, %		K_2O, %	
	Spectrographic	Chemical	Spectrographic	Chemical
1	3.15	3.3	..	..
2	1.71	1.4	1.45	1.7
3	0.83	0.9	2.22	2.4
4	0.79	0.8	..	..
5	0.70	1.1	4.7	4.9
6	0.40	0.6	1.13	1.2
7	..	..	1.81	2.4

However, variable amounts of lithium oxide at the concentration level recently reported by Headlee (*6*) would cause small, variable errors in the sodium determination. In the event that the coal contains significant amounts of lithium, the method is modified by (*a*) adding 0.20% lithium oxide to the standard and (*b*) doubling the amount of lithium carbonate used in the sodium buffer.

PRECISION AND ACCURACY

The standard deviation for the method, as determined from data selected at random over a period of 3 months, was 4.1% for the potassium and 4.3% for the sodium determination.

The accuracy of the method is somewhat difficult to determine because there is a lack of standard samples of these materials and because of the difficulty of chemical analysis for sodium and potassium. The results of analyses of laboratory coal ash samples when analyzed spectrographically and chemically are compared in Table III. There is a tendency for the spectrographic results to be consistently lower than the chemical values. However, in view of the difficulty in obtaining agreement on the chemical sodium and potassium determinations on silicate rocks which was reported recently (*10*), the comparison appears adequate.

SUMMARY AND CONCLUSIONS

A spectrographic method for determining sodium and potassium that is applicable to the analysis of coal ashes, tapped slag, fly ash, and tube deposits has been developed. It was advisable to determine each element on a separate sample, so that the influence that potassium exerted on the sodium determination could be minimized. The cyanogen and iron interferences with potassium and rubidium lines were eliminated by using lithium carbonate as a buffer.

Rubidium was found to be an excellent internal standard for potassium, and the potassium-rubidium ratio was apparently independent of the sodium content. The time requirement of 1.5 hours for the determination, in duplicate, of both elements represents a substantial saving in time over the classical chemical methods for these elements. The accuracy of the method, as measured from a comparison of spectrographic and chemical results, is satisfactory.

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Rapid Photometric Determination of Chromium In Alloy Steels and Bronzes

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THE need for a more rapid, accurate, routine photometric determination of chromium in ferrous alloys of all compositions has long been recognized. There is a particular need for a determination applicable to stainless steels (8 to 30% chromium), alloy cast irons (0.5 to 15% chromium), and chromium-bearing bronze alloys (0.5 to 10% chromium).

Fowler and Culbertson (*1*) have developed a photometric method based on the absorption of the orange-red sexivalent chromate ion. However, the presence of a number of color-producing ions and the necessary provisions required therefore limited application for the purposes of this work.

It has been suggested by Vredenburg and Sackter (*3*) that the aqua-colored chromic ion complex in a solution of nitric, sulfuric, and phosphoric acids will lend itself to photometric measurement. The presence of molybdenum and copper in the alloys investigated constituted a source of interference. The time required for decomposition further restricted the use of this method on alloys studied in the experiments.

Trace concentrations of chromium can be determined by photometric analysis through the use of *s*-diphenyl-carbazide (*2*). The alloys investigated had chromium contents of such magnitude as to render this reagent unsuitable.

METHOD

A number of experiments were made by dissolving and subsequently oxidizing the selected alloys through the use of perchloric acid. The resultant sexivalent chromium was reduced with metallic zinc to an aqua-colored complex, and the solution was boiled to stabilize this complex in the trivalent state. The absorbance of this solution was measured in acid media on a Brociner-Mass photometer at a wave length of 585 mμ. Cupric ion was reduced by the zinc to elemental copper. Hydrogen peroxide was added to prevent interference in the presence of molybdenum. Phosphoric acid was then used to decolorize ferric ion and to dissolve any intermediary products that may have been formed by the action of hydrogen peroxide.

Nickel increased the absorbance of the solution. However, the increase (at 585 mμ) was constant over a wide range of nickel content. This nickel effect was compensated by using a calibration curve standardized from nickel-bearing materials. It was found that one curve suffices for nickel concentrations from approximately 5 to 400 mg. per 200 ml., which range includes all the alloys investigated.

PROCEDURE

Apparatus. Brociner-Mass photometer; cell size, 17 mm. Lumetron No. 400 photometer; cell size, 17 mm.

Procedure for Chromium in Alloy Steels. Weigh sample so that 10 to 150 mg. of chromium will be present, and place in a 600-ml. beaker. Decompose with 10 ml. of concentrated nitric acid and 10 ml. of concentrated hydrochloric acid. Heat on a hot plate until action commences; then warm gently until decomposition is complete. Add small amounts of acid as required. Add 10 ml. of perchloric acid (70%), and cover the beaker with inverted watch glass to allow refluxing acid to run down sides of the beaker. Fume until the chromium is completely oxidized, indicated by the formation of red sexivalent chromium salts. Cool, from 1 to 2 minutes, and cautiously add 70 ml. of distilled water without removing the watch glass. Swirl salts into solution.

If the solution is free of tungsten (at this stage present as the dense precipitate of tungsten trioxide) and contains less than about 0.75% silicon (present as silicon dioxide at this point), it may be filtered through Whatman No. 41-H paper into a second 600-ml. beaker. If either tungsten or more than about 0.75% silicon is present, it is advisable to filter with suction through Whatman No. 41-H paper.

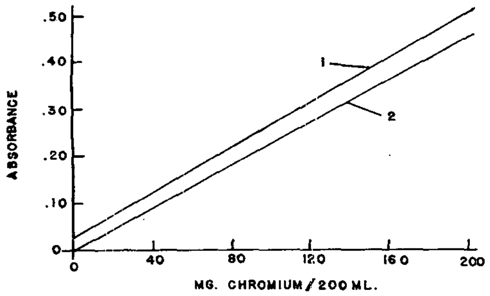

Figure 1. Absorbance *vs.* Milligrams of Chromium per 200 Ml.

1. Calibrated for nickel-bearing material
2. Calibrated for nickel-free material

Wash the paper with distilled water until it is clean, adding washings to the filtrate. Add to the filtrate approximately 10 ml. of concentrated sulfuric acid and 15 to 30 grams of metallic zinc. The zinc used must be any form of electrolytic grade having a large surface area. Keep the beaker covered with a watch glass during the reduction in order to maintain a reducing atmosphere over the solution. Allow the reaction to continue from 12 to 17 minutes, adding small quantities of zinc only to replenish the metal consumed by the reaction. Filter through Whatman No. 41-H paper into a second beaker. Wash with distilled water twice, adding washings to filtrate. Add 4 ml. of hydrogen peroxide (30%), and raise to a boil. Boil for 3 minutes. Remove from hot plate, add 4 ml. of concentrated phosphoric acid and mix. Filter through Whatman No. 41-H paper into a 200-ml. volumetric flask. Wash the paper twice again with distilled water, allowing washings to go into the flask. Cool to room temperature, fill to mark, and shake. Measure absorbance at 585 mμ. Record the measurement against water blank and calculate the chromium content by using the formula

$$\% \text{ Cr} = \frac{\text{grams of chromium/200 ml. (from curve)}}{\text{Weight of sample}} \times 100$$

Table I. Results on National Bureau of Standards Materials

Sample	Chrome Present, %	Chrome Found, %	Deviation, %
NBS 121A	18.69	18.70	0.01
		18.70	0.01
		18.32	0.37
		18.45	0.24
NBS 161	16.90	17.05	0.15
		17.06	0.16
		17.06	0.16
		17.05	0.15
NBS 36A	2.41	2.35	0.06
		2.35	0.06
		2.41	0.00
		2.38	0.03
NBS 153	4.14	4.14	0.00
		4.10	0.04
NBS 132	4.11	4.16	0.05
		4.14	0.03

Procedure for Bronzes. Weigh the sample so that 10 to 150 mg. of chromium will be present, and place in a 600-ml. beaker. For each 2 grams of sample, decompose by the addition of 20 ml. of nitric acid (1 to 1) and 10 ml. of perchloric acid (70%). Cover the beaker with an inverted watch glass and fume until the chromium is completely oxidized, indicated by the formation of red sexivalent chromium salts. Cool, from 1 to 2 minutes, and cautiously add 70 ml. of distilled water without removing the watch glass. Swirl salts into solution. Add approximately 10 ml. of concentrated sulfuric acid and 15 to 30 grams of metallic zinc. Keep the beaker covered with a watch glass during the reduction in order to maintain a reducing atmosphere over the solution.

Allow the reaction to continue from 12 to 17 minutes, adding small quantities of zinc only to replenish the metal consumed by the reaction. Raise to a strong boil, coagulating copper into a mass filterable condition. Filter through Whatman No. 41-H paper into a second beaker. Wash with distilled water twice, adding washings to filtrate. Raise solution to a boil. Boil for 3 minutes. Filter a second time, using Whatman No. 41 paper which has been treated with a small amount of macerated filter pulp, into a 200-ml. volumetric flask. Wash the paper twice with distilled water, allowing washings to go into the flask. Cool to room temperature, fill to mark, and shake. Measure absorbance at 585 mμ against a water blank. Calculate the chromium content using the formula

$$\% \text{ Cr} = \frac{\text{grams of chromium/200 ml. (from curve)}}{\text{Weight of sample}} \times 100$$

Table II. Results on Synthesized Standards

Sample[a], Specialloy No.	Chrome Present,[b] %	Chrome Found,[c] %	Deviation, %
1224-4x	4.21	4.22	0.01
		4.22	0.01
		4.21	0.00
1224-5x	5.03	5.03	0.00
		5.09	0.06
		5.04	0.01
1224-6x	6.17	6.15	0.02
		6.15	0.02
		6.13	0.04
1224-7x	7.10	7.07	0.03
		7.07	0.03
		7.05	0.05

[a] Made by research department of Specialloy, Inc.
[b] Determined by ferrous ammonium sulfate titrations.
[c] Determined by method described.

Preparation of Standard Reference Curves. The first curve constructed was for ferrous alloys bearing no more than 5 mg. of nickel per 200 ml. National Bureau of Standards 36a (2.41% chromium) was used as the base material for calibration. Samples of this standard, 0.3 gram, were weighed into each of several beakers and varying aliquots of ferrochrome standard solution were added so as to construct a curve that covered the chromium range from 0 to 200 mg. of chromium per 200 ml.

Ferrochrome standard solution was prepared by fusing a 0.5-gram sample of NBS No. 64a with 8 grams of sodium peroxide in an iron crucible. After the melt was cooled, it was dissolved in 150 ml. of water and acidified with sulfuric acid, treated with an excess of potassium permanganate, and boiled for 10 minutes. The potassium permanganate was then destroyed with a minimum of hydrochloric acid and the resulting clear solution was made up to volume in a 250-ml. volumetric flask.

A second curve, applicable to nickel-bearing ferrous alloys, was constructed in precisely the same manner, except that for each plotted point an increment of a solution containing nickel ions was added. The amount of nickel added was the arbitrary value of 200 mg. (equivalent to a nickel content of 40% based on a 0.5-gram sample). This solution was prepared by dissolving electrolytic nickel in nitric acid and fuming with sulfuric acid. The curve derived in this manner is for use in chromium determination of nickel-bearing ferrous alloys in the range of approximately 5 to 200 mg. per 200 ml.

Table III. Effect of Concentrations of Nickel in Steel

Sample	Nickel, %	Chrome Present, %	Chrome Found, %
NBS 121A	20.00 (added)	18.69	18.69
	40.00 (added)	18.69	18.69
NBS 161	64.3	16.90	17.06

A third curve, for bronzes, was constructed by using alloy standards prepared by the research department of Specialloy, Inc. This special processing was required, since NBS standard samples of chromium-bearing copper-base alloys were not available. The chromium content of these special standards was determined by classical methods, while the procedure followed in calibrating the curve was that described by this work.

DISCUSSION OF RESULTS

Table I summarizes the results obtained on various NBS standards of ferrous materials tested. Table II summarizes the results obtained for standard samples manufactured by Specialloy, Inc. The effect of varying concentrations of nickel in steel was studied and the results are shown in Table III.

In addition to the metals mentioned above carbon, manganese, phosphorous, sulfur, vanadium, titanium, tin, lead, zinc, aluminum, cadmium, niobium, tantalum, and selenium do not affect the absorbance of the solution. Cobalt does not interfere if present in concentrations under 0.5%. Tungsten is removed as the trioxide by filtration following the perchloric acid fuming.

The trivalent chromium complex was stable for at least 6 hours, as indicated by observing a constant absorbance over this period.

CONCLUSION

The method exhibits the degree of reproducibility and speed which was sought, together with the degree of accuracy required. Furthermore, in practice a large number of samples could be handled conveniently at one time. This simplicity of operation results in relatively low analysis costs.

The results of this study indicate that the application of this procedure exhibits a high order of efficiency, in that one procedure covers a wide range of chromium-bearing materials.

ACKNOWLEDGMENT

The authors gratefully acknowledge the advice and assistance of Bernard Hauser and Mitchell Silverstein.

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Formation of Bromate in the Oxidation of Iodide by Bromine

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IN THE oxidation of iodide to iodate for iodometric titration, aqueous bromine is used in a number of procedures. There is some disagreement regarding the pH range suitable for the oxidation of iodide and for the removal of excess bromine by boiling.

In some methods (*1, 2*) bromine is added to weakly acidic solutions of iodide and the solutions are boiled. In other procedures (*4, 5*) bromine is added to alkaline solutions which are then acidified before boiling. Under these conditions a slow return of the end point is observed after liberation of iodine from potassium iodide and titration with sodium thiosulfate. Waters and Beal (*5*) have attributed the return of the end point to the use of too much bromine. Heim (*2*) has reported that if the solution is made weakly acidic before the addition of bromine (pH of 1.2 to 3.2), no return of the end point occurs. Heim suggested that compounds of bromine in higher oxidation states are formed in alkaline solution and that traces of these are slowly reduced by iodide, causing return of the end point. It is well known that bromate is not readily reduced by bromide unless the acidity is high (*3*). Results reported here confirm Heim's suggestions.

EXPERIMENTAL

Solutions of potassium carbonate (6.5 grams in 50 ml.) were treated with 3 ml. of saturated bromine water then acidified to known pH with concentrated phosphoric acid. The solutions were boiled for 20 minutes, then cooled. These solutions, corresponding roughly to those obtained in the United States Pharmacopoeia XIV method (*4*), were transferred to an H-type polarograph cell. Oxygen was removed by bubbling with nitrogen and polarograms were obtained with the dropping mercury electrode. Similar experiments were made adding bromine only after acidification. Polarograms were compared with those obtained without the addition of bromine, and without the addition of bromine but with addition of known amounts of potassium bromate after acidification. In some cases 3 ml. of 5% aqueous phenol was added after boiling.

In a series of experiments similar to those above, the solutions were acidified strongly with 25 ml. of 6*M* sulfuric acid after boiling. Nitrogen gas was bubbled through the solutions to remove bromine and the expelled gases were passed through a drying tower filled with anhydrous magnesium perchlorate. The dried gases were mixed with ethylene gas and passed into a trap in a dry ice–acetone bath. Excess ethylene and nitrogen were pumped off and the material remaining in the trap was introduced into

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Table I. Bromate Remaining after Boiling

pH	Concentration, Millimole/Liter		
2.0	0.10,	0.05,	0.06
2.0[a]	0.06,	0.14,	0.02
3.0	0.14,	0.15,	0.16
3.0[a]	0.13,	0.06,	0.07
4.0	0.15,	0.12,	0.13
4.0[a]	0.10,	0.09,	0.08

[a] Phenol was added to these solutions.

Table II. Ratios of Peak Heights

Mass Numbers	Pure Ethylene Bromide	Gas from Trap
79/81	1.0	1.0
93/95	1.28	1.26
107/109	1.06	1.06

a Consolidated Engineering Corp. Model 21-103 mass spectrometer.

A Beckman Model H pH meter was used for determination of pH. Polarograms were measured with a Sargent Model III polarograph.

DISCUSSION

At each pH used, the concentration of bromate remaining after boiling was estimated by comparison of the diffusion current with diffusion currents obtained with similar solutions containing added bromate. Results for cases in which bromine was added before acidification are given in Table I. In all cases where bromine was added after acidification no detectable difference was found between blank runs and those with bromine added. The half-wave potentials of the solutions to which bromine had been added were the same as for similar bromate solutions within 0.01 volt. These results indicate that bromate is formed in alkaline solution and is not completely removed by boiling. Evidence that the oxidizing agent is a bromine compound rather than iodate formed from iodide in the reagents is shown in Table II.

The material in the trap had the same mass spectrum as ethylene bromide and no indication of any iodine compound was found. Because of difficulties with absorption in the mass spectrometer inlet system, mass spectra were not used for quantitative measurements of bromine.

From the above it appears that oxidation of iodide to iodate by bromine must be carried out after acidification to avoid the formation of bromate which is difficult to remove and which would interfere with the titration of the resulting iodate.

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Separation of Fluoranthene and Chrysene by Molecular Distillation

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THE separation and purification of polynuclear hydrocarbons by crystallization are tedious and often unsuccessful because of the tendency of such compounds to form solid solutions. Separation by conventional fractional distillation at reduced pressure frequently leads to difficulties owing to the high melting points of many of these hydrocarbons, which solidify and clog condensers, stopcocks, and receivers. The successful isolation of coronene from coal-hydrogenation oil by a codistillation technique (*9*) in the molecular still prompted an investigation into the general applicability of the tool for separating mixtures of polynuclear hydrocarbons.

The method that may be used for separating closely related polynuclear hydrocarbons is a modification of the technique of molecular distillation devised by Hickman and called "analytical distillation" (*6, 10*). In this procedure, the substance under investigation is dissolved in a solvent (carrier oil) and subjected to repeated distillations in a cyclic molecular still. Successive distillations are performed at progressively higher temperatures. The rate of elimination of solute is proportional to the product of its concentration and its distillability. The latter is a function of its vapor pressure and increases with temperature, but the concentration of solute decreases as the distillation proceeds. A plot of the concentration of solute in the distillate as a function of temperature has been proved experimentally (*2*) and theoretically (*6*) to resemble a probability distribution curve. This curve is called the "elimination curve" of the substance. Under strictly standardized conditions, the temperature at which the distillate contains the maximum concentration of solute (elimination temperature) is reproducible to within 1° or 2°. Thus, the technique may be used as an analytical tool for the identification of the solute (*3, 5, 7*).

The object of the present investigation was to determine the elimination curves of the two closely related polynuclear hydrocarbons fluoranthene and chrysene and to attempt their separation by molecular distillation. The difference between the elimination temperatures of two similar materials may conceivably be increased by:

Dilution of the mixture that is to be separated with a compounded carrier medium having the same distillability as the mixture. This technique, called "amplified distillation," has been successfully employed by Weitkamp (*11*) for the separation of methyl esters of fatty acids.

Use of an azeotrope-forming carrier which has a selective affinity for one of the components or which forms azeotropes with both components, the difference in distillability of the azeotropes being greater than the difference in distillability of the two pure components. Azeotrope formation at very low pressures has yet to be definitely demonstrated.

Gradual reduction in cycle time as the distillation progresses. This device might shift the elimination temperature of the more volatile component to a lower value; once the distilland is freed of this component, the elimination temperature of the other component may be shifted to a higher value. This method has been studied by Embree (*2*).

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Table I. Molecular Distillation of Fluoranthene (Experiment 1)

		Grams
Charge.	Polyethylene glycol 200	186.7
	Polyethylene glycol 300	186.7
	Polyethylene glycol 400	163.6
	Tetraethylene glycol	201.6
	Fluoranthene	11.3
		749.9

Fraction	Rotor Temp., ° C.	Pressure, µ Hg	Fraction Weight, Grams	Fluoranthene Concn., %	Fluoranthene Weight, Grams
1	80	37	15.3	2.48	0.38
2	90	29	30.2	2.96	0.89
3	100	34	56.5	3.38	1.91
4	110	38	111.6	3.31	3.69
5	120	34	99.3	2.73	2.71
6	130	89	42.2	1.95	0.82
7	140	35	45.9	1.32	0.61
8	150	34	31.2	0.99	0.31
9	160	32	31.0	0.11	0.03
10	170	34	35.0	0.07	0.03
11	180	34	50.8	0.05	0.03
Residue			187.5		
Loss			12.6		
Total			749.9		11.41

The most suitable carrier oils for the hydrocarbons appeared to be polyglycols, which are commercially available in a wide variety of molecular-weight ranges and are soluble in water, thereby facilitating the recovery of hydrocarbon material. Furthermore, hydrooarbons frequently form azeotropes with glycols and are appreciably soluble in glycols, even at room temperature.

EXPERIMENTAL

Materials. A technical grade of fluoranthene manufactured by the Reilly Tar and Chemical Corp. was used. Ultraviolet spectrophotometric analysis showed that it contained 94.21% of fluoranthene and 1.01% of chrysene; the balance of the material was not characterized because it did not interfere in any way. The technical grade chrysene manufactured by the Reilly Tar and Chemical Corp. contained 96.49% of chrysene and 3.51% of fluoranthene. Polyethylene glycols 200, 300, and 400, and tetraethylene glycol, manufactured by the Carbide and Carbon Chemical Co., were used; the numbers following the name of the glycol refer to the average molecular weights.

Apparatus and Procedure. Distillations were conducted in a centrifugal, cyclic, batch, molecular still, Type CMS-5, manufactured by Distillation Products, Inc. The polynuclear compounds were dissolved in glycol and sucked into the glass reservoir of the still. After degassing at a rotor temperature of 50° to 70° C. the pressure was decreased and the temperature of the rotor was fixed for the collection of the first fraction. (Pressures were determined by a MacLeod gage; the Pirani gage furnished with the molecular still performed unsatisfactorily.) When degassing was complete, internal recycling was stopped by closing the ball valve and opening the stopcock to the distillate receiver. This operation started a cycle which ended when all the liquid had passed over the rotor and the residue had been collected in the aluminum cup. The residue was allowed to drain back into the glass reservoir, and a second cycle was started. The second cycle was complete when all the liquid had again passed over the rotor. At this moment, internal recycling was resumed; the first distillate fraction, collected during the two full cycles, was removed. A new distillate receiver was connected and evacuated by means of a side line. When the rotor reached the next predetermined temperature, internal recycling was stopped and collection of the second fraction was started. Distillation rate and cycle time were determined by means of a stopwatch.

All but the last fractions were collected in this way. The last fractions, usually not more than three in each run and containing virtually no detectable amounts of polynuclear compounds, were collected by allowing uninterrupted recycling for a time approximately equal to that taken for collecting the previous fraction. The technique was changed because the time intervals gradually decreased as the amount of material in the still was reduced so that, while collection of the first fraction required about 30 minutes, the last fractions were collected in less than 5 minutes, and the first and second cycles could not be segregated.

Analytical Method. All fractions were analyzed with a Beckman ultraviolet spectrophotometer Model DU. Samples of about 1 gram of polyglycol containing a small quantity of polynuclear hydrocarbon were diluted with 95% ethyl alcohol (benzene-free), and each reading was corrected for absorbance by the glycols. This correction is significant for concentrated solutions.

The ultraviolet spectra of pure fluoranthene and pure chrysene were determined and found to be identical with those previously reported (*4*). Determination of the amount of hydrocarbon in a solution containing only one hydrocarbon requires one absorbance measurement; values at 360.0 mµ for fluoranthene and 267.3 mµ for chrysene were used. For determining the composition of a mixture of the two hydrocarbons, the concentration of each was

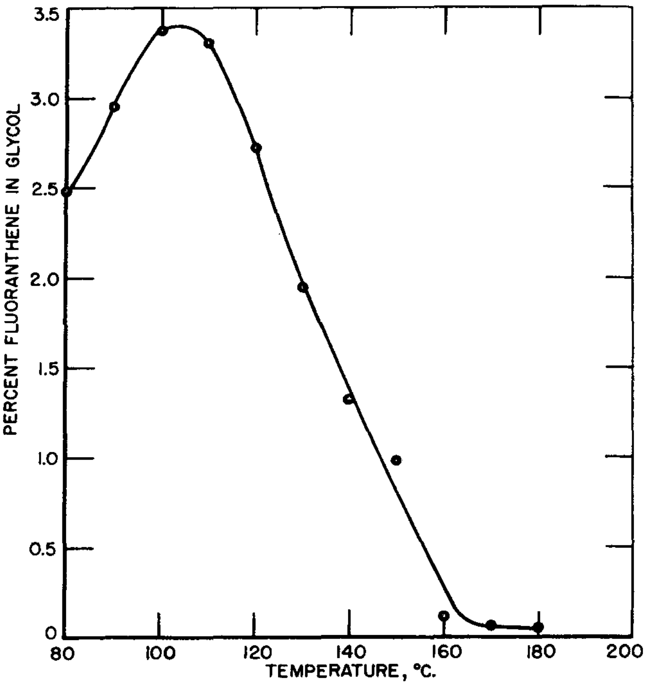

Figure 1. Elimination Curve of Fluoranthene

Table II. Molecular Distillation of Chrysene (Experiment 2)

		Grams
Charge.	Polyethylene glycol 200	225.0
	Polyethylene glycol 300	202.0
	Polyethylene glycol 400	200.0
	Chrysene	0.300
		627.3

Fraction	Rotor Temp., °C.	Pressure, µ Hg	Fraction Weight, Grams	Chrysene Concn., %	Chrysene Weight, Mg.
1	80	85	3.0	0.0087	0.26
2	90	78	6.2	0.0080	0.50
3	100	85	12.7	0.0099	2.17
4	110	74	24.2	0.0179	4.33
5	120	108	45.2	0.0306	13.77
6	130	99	42.4	0.0590	25.02
7	140	95	29.1	0.0979	28.49
8	150	102	31.1	0.1151	35.79
9	160	102	36.1	0.1484	53.57
10	170	101	40.4	0.1454	58.74
11	180	103	33.9	0.0925	31.36
12	190	108	35.3	0.0708	24.99
13	200	105	44.7	0.0365	16.32
14	210	105	42.0	0.0072	3.02
17	220	...	45.1	0.0040	1.80
16	230	...	47.8	0.0044	2.10
17	240	115	28.4	0.0018	0.51
18	250	140	23.1	0.0021	0.49
Residue			52.2		
Loss			4.4		
Total			627.3		303

Table III. Molecular Distillation of Mixture of Fluoranthene and Chrysene (Experiment 4)

		Grams
Charge.	Tetraethylene glycol	386.9
	Polyethylene glycol (160°–185° at 1–10μ)	386.9
	Fluoranthene	1.1029
	Chrysene	0.2917
		775.1946

Fraction	Rotor Temp., ° C.	Pressure, μ Hg	Fraction Weight, Grams	Fluoranthene Concn., × 10² %	Fluoranthene Weight, mg.	Chrysene Concn., × 10³ %	Chrysene Weight, mg.	Fluoranthene (Glycol-Free Basis), %
1	100	17.0	64.1	34.44	220.76	17.52	11.23	95.15
2	100	15.0	75.8	30.08	228.01	23.94	18.15	92.62
3	100	16.0	57.6	28.23	162.61	26.31	15.16	91.47
4	110	1.2	87.4	26.48	231.44	47.80	41.78	84.71
5	120	0.4	51.1	22.93	117.17	86.56	44.23	72.60
6	130	0.6	35.4	19.51	69.07	159.02	56.29	55.10
7	140	2.6	19.0	11.36	21.58	183.70	34.90	38.21
8	150	0.8	18.4	5.97	10.99	137.27	25.26	30.32
9	160	1.7	29.9	2.90	8.62	62.23	18.61	31.78[a]
10	170	..	39.2	1.18	4.63	20.60	8.80	36.43[a]
11	180	10.0	62.5	0.64	4.00	5.73	3.58	
12	190	4.0	71.5	0.40	2.86	1.87	1.34	
13	200	2.5	88.6	0.39	3.46	0.94	0.83	
14	210	3.5	32.9	0.84	2.76	0.49	1.61	
Residue			25.3					
Loss			16.6					
Total			775.3		1088.01		281.05	

[a] Values after fraction 10 are inaccurate because of interfering absorbance of polyglycol.

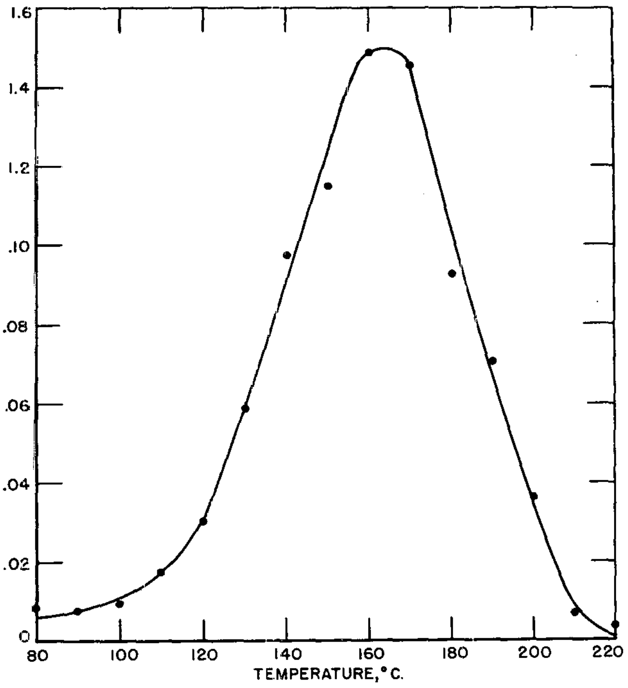

Figure 2. Elimination Curve of Chrysene

calculated from the observed absorbances at 267.3 and 340.0 mμ by means of the simultaneous equations:

$$A_{267.3} = 568.848\,c + 45.300$$

$$A_{340.0} = 1.724\,c + 38.300\,f$$

where c and f are the concentrations of chrysene and fluoranthene in grams per liter, and $A_{267.3}$ and $A_{340.0}$ are the observed absorbances of the mixture at the wave lengths noted. The measurements at both wave lengths must be made (or adjusted) to the same dilution. The coefficients of c and f are the four specific extinction coefficients (*4*) (absorbance in a 1-cm. cell per concentration in grams per liter) for the two pure hydrocarbons at the two chosen wave lengths. All measurements were made in a 1-cm. cell and concentrations were chosen to give absorbance values in the range 0.2 to 0.9. No normalizing factors were employed.

Experiments. The elimination curve at 30- to 35-micron pressure secured with 12 grams of fluoranthene in 750 grams of a mixture of glycols is plotted in Figure 1 from the data in Table I.

A solution of 0.3 gram of chrysene in 627 grams of mixed glycols was distilled at approximately 100-micron pressure with the results shown in Table II and Figure 2. Although the pressure in this experiment was higher than that in Experiment 1, the difference in elimination temperatures was great enough to assume that separation of the two hydrocarbons is possible at the lower pressures. Accordingly, the following experiments were performed.

A mixture of 1.2 grams of fluoranthene and 0.3 gram of chrysene was diluted with 800 grams of a solvent mixture containing equal parts of tetraethylene glycol and polyethylene glycol 200, 300, and 400, and distilled at a pressure of 50 to 80 microns. The elimination temperature for fluoranthene was 110° C. and that of chrysene was 150° C. Seventy-six per cent of the fluoranthene was recovered with an average purity of 92%; 48% of the fluoranthene had an average purity of 95%.

A mixture of 1.1 grams of fluoranthene and 0.29 gram of chrysene was distilled from 793.8 grams of a solvent containing equal parts of tetraethylene glycol and a polyethylene glycol fraction boiling at 160° to 185° C. (1 to 10 microns). The first three fractions were collected at a constant rotor temperature of

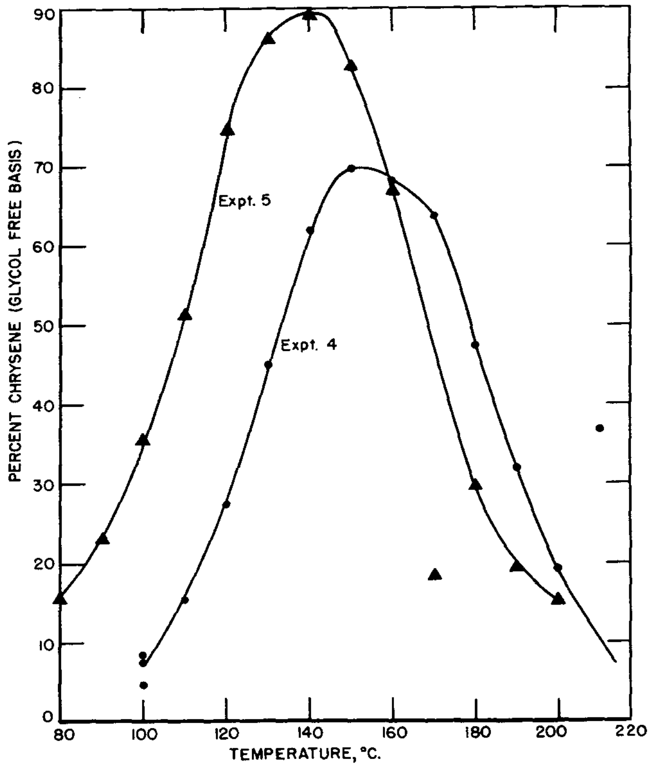

Figure 3. Molecular Distillation of Fluoranthene-Chrysene Mixture

100° C. according to the following technique. The condensed distillate was recycled to the reservoir, while the residue was collected in the cup until approximately half the material remained in the reservoir. At this point the recycling of distillate was discontinued and the fraction was collected until the reservoir was exhausted. The contents of the residue cup were then returned to the reservoir and the process was repeated at the same rotor temperature for the next fraction. This procedure served to concentrate the fluoranthene before the product was collected. Unfortunately, chrysene was also concentrated at this rotor temperature. The remaining fractions were collected in the usual way. The results are given in Table III and Figure 3.

Table IV. Molecular Distillation of Mixture of Fluoranthene and Chrysene (Experiment 5)

		Grams
Charge.	Fractions 7-14 of Experiment 4	344.7 (containing 58.95 mg. of fluoranthene
	Polyethylene glycol 200	345.2 and 94.21 mg. of chrysene)
		689.9

Fraction	Rotor Temp., ° C.	Pressure, μ Hg	Fraction Weight, Grams	Fluoranthene		Chrysene		Chrysene (Glycol-Free Basis), %
				Concn., × 10³ %	Weight, mg.	Concn., × 10³ %	Weight, mg.	
1	80	2.3	47.3	12.34	5.84	2.29	1.08	15.61
2	90	8.2	61.0	18.57	11.33	5.58	3.40	23.08
3	100	12.0	52.4	22.27	11.67	12.30	6.45	35.60
4	110	5.8	46.3	23.68	10.96	24.64	11.41	51.01
5	120	5.3	42.6	15.33	6.53	45.59	19.42	74.84
6	130	13.3	39.3	8.40	3.30	52.15	20.50	86.13
7	140	3.7	34.6	4.76	1.65	38.93	13.47	89.09
8	150	2.2	36.9	3.66	1.35	17.52	6.47	82.74
9	160	9.5	44.8	2.79	1.25	5.68	2.54	67.02[a]
10	170	7.9	91.3	4.73	4.73	1.18	1.08	
11	180	7.8	58.2	1.74	1.01	0.74	0.43	
12	190	11.0	52.1	1.77	0.92	0.43	0.22	
13	200/220	20.0	36.3	3.23	1.17	0.58	0.21	
Residue			20.8					
Loss			26.0					
Total			689.9		61.71		86.68	

[a] Values after fraction 9 are inaccurate because of interfering absorbance of polyglycol.

Fractions 7 through 14 from experiment 4 (from 140° C.) were diluted with an equal volume of polyethylene glycol 200 and distilled in the usual fashion. The results are shown in Table IV and Figure 3. Of the chrysene (21% pure, solvent-free basis) originally charged to the still in experiment 4, 5.5% was recovered with an average purity of 90% and 25% with an average purity of 82%. Chrysene was recovered from the fraction collected at its elimination temperature by precipitation with water, extraction with benzene, evaporation of the benzene, solution with alcohol, and precipitation with water. The crude product was filtered, washed with ethyl alcohol, dried, and sublimed. Its melting point was 253° to 255° C. [literature 254.1° to 254.4° (*1*)].

DISCUSSION

The results demonstrate that it is possible to separate fluoranthene and chrysene by dissolving the mixture in a suitable polyglycol mixture and subjecting the solution to molecular distillation in a cyclic still. The very low pressure possibly has the effect of increasing the relative volatility of the mixture of hydrocarbons. No attempt was made to determine whether true azeotrope formation occurred or whether there was only codistillation of solute and solvent. The major component of the mixture (fluoranthene) was recovered in good yield and was fairly pure. Repeated distillation was necessary to secure relatively pure chrysene. The rate of product removal in experiment 4 was excessively rapid for the first fractions; about 200 drops were collected per minute, which is four times as much as recommended for good results. Hickman and Trevoy (*8*) have recently pointed out that very small rates (1 to 10 drops per minute) are sometimes conducive to high relative volatilities ("superalphas"). By changing the molecular weight distribution of the glycols one should be able to avoid the excessive rates of distillation experienced here.

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Analytical Applications of the Cyanohydrin Reaction

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RECENT work (*1*) on the kinetics of cyanohydrin formation has shown that in buffered acetate media both propionaldehyde and acetaldehyde react quantitatively with hydrogen cyanide. These rate studies suggested that certain analytical applications could be devised—namely, the quantitative analysis for halide ions in the presence of cyanide and the quantitative determination of acetaldehyde and propionaldehyde.

EXPERIMENTAL

At the pH of sodium cyanide solutions, the reaction is almost instantaneous. However, at this pH the equilibrium would be shifted and the reaction might not be quantitative. In order to obtain information about the completeness of reaction, the following procedure was used.

Twenty-five milliliters of 0.12*N* aldehyde solution (an excess) were added to 10 ml. of a 0.2*N* solution of sodium cyanide. The solution was acidified with 6 ml. of 6*N* nitric acid. On the addition of 0.1*N* silver nitrate, a precipitate was formed in the case of the acetaldehyde and propionaldehyde solutions but not in the case of formaldehyde solutions, indicating that the reaction was complete only in the latter case.

The procedure was modified for propionaldehyde and acetaldehyde solutions as follows: six drops of bromocresol purple indicator (pH range 5.2 to 6.8) were added to a solution containing an aldehyde and sodium cyanide. The solution was slowly titrated with 0.1*N* nitric acid over a 10 to 15-minute interval to a definite yellow. Six milliliters of 6*N* nitric acid were added, followed by the addition of 25 ml. of 0.1000*N* silver nitrate. No precipitate was observed. On titration of the resulting solution with 0.1000*N* potassium thiocyanate, the titration value corresponded exactly to that obtained when 25 ml. of the silver nitrate were titrated directly with potassium thiocyanate. The same results were obtained in the use of both propionaldehyde and acetaldehyde, indicating that the reactions with sodium cyanide were complete at the pH of the indicator.

Propionaldehyde was used to test the procedure for the determination of chloride in the presence of cyanide as follows: Ten milliliters of a 0.1000*N* standard sodium chloride solution were added to 10 ml. of approximately 0.2*N* sodium cyanide solution and 1.5 ml. of technical grade propionaldehyde (calculated to be an excess). Indicator, 0.1*N* nitric acid, 6*N* nitric acid, and 25 ml. of 0.1*N* silver nitrate (an excess) were added according to the procedure already described. The silver chloride was filtered and washed. The filtrate was titrated in the usual way with standard potassium thiocyanate. The original sodium chloride solution was also analyzed by the Volhard method. Each determination was run in triplicate. The results for the 0.1000*N* standard sodium chloride solution were 0.0999*N* and 0.1000*N* in the absence and presence of cyanide, respectively. Thus, the procedure is suitable for the quantitative determination of chloride in the presence of cyanide. It may be suitable for other halides as well.

The quantitative removal of acetaldehyde and propionaldehyde using hydrogen cyanide solutions has been described (*1*). The use of sodium cyanide solutions would be preferable because of the smaller hydrogen cyanide losses and the rapidity of the reaction in basic solution. No specific experiments were performed to validate a procedure using sodium cyanide solutions, but from the above experimental work, a suitable procedure is readily suggested. One would prepare a standard solution of sodium cyanide, add a sample of aldehyde solution to an excess of the standard sodium cyanide solution, adjust the pH using bromocresol purple and then determine the unreacted cyanide by the procedure in (*1*).

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Simplified Procedure for Extraction and Determination of Vitamin A in Liver

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CURRENTLY used methods for determining vitamin A in liver tissue were critically evaluated during the course of developing a modified (*1*) liver-storage type vitamin A bioassay procedure (*4*, *7*, *11*). None of the published methods proved to combine the accuracy and precision desired with the speed and ease of performance needed for routine analyses. Consequently, a simplified procedure was developed which involved drying the liver by grinding with anhydrous sodium sulfate, adding ethyl ether, and determining the vitamin A content of an aliquot by means of the standard Carr-Price (antimony trichloride) reaction.

This new method eliminates the need for saponification (*2*), a step which leads to low results unless carefully conducted. Ethyl ether was used, since it has been shown (*2*) to extract vitamin A more completely from biological samples than other solvents. The use of anhydrous sodium sulfate to dry liver tissue has been reported (*6*, *14*), but these methods differ either in the type of solvent or in the details of extraction of the liver lipides.

ANALYTICAL PROCEDURE

A 3- to 5-gram portion of liver tissue, or an entire rat liver, is ground in a mortar with three to five times its weight of anhydrous sodium sulfate until completely dry. If the grinding is started while the livers are in the frozen state, less sodium sulfate is required and the drying is more rapid. Too much sodium sulfate is undesirable, because it results in a fine, slow-settling suspension in the ether layer during the subsequent extraction. The dry powdered liver is transferred quantitatively to a 250-ml. Perma-red glass-stoppered Erlenmeyer flask. Exactly 100 ml. of peroxide-free anhydrous ethyl ether are added and the flask is shaken for 2 minutes. It is then either set aside until the solids have separated from the ether layer (ca. 1 hour) or the suspended solids are removed by centrifugation. An aliquot of the ether layer is transferred quantitatively to an Evelyn colorimeter tube and the solvent is removed by evaporation under nitrogen. The residue is dissolved in 1 ml. of chloroform, the tube is positioned in the colorimeter, and 2 drops of acetic anhydride are added. Ten milliliters of a saturated solution of antimony trichloride in chloroform (ca. 20 to 25%) are then added and the intensity of the resulting blue color is determined using a 620 mμ filter. The amount of vitamin A present is determined by reference to a standard curve prepared using the United States Pharmacopoeia vitamin A reference standard.

Livers containing less than 0.2 γ of vitamin A per milligram of liver lipide (5 to 10 γ per gram of liver tissue) cannot be satisfactorily analyzed by this procedure. Ether-soluble materials in the liver extract result in turbidity on addition of the antimony-trichloride reagent. About 20 mg. of total ether-extractable material in the colorimeter tube are sufficient to induce this disturbing turbidity. This is not solely a triglyceride effect, since 60 mg. of either cottonseed oil or lard do not give turbidity under similar conditions.

The method, however, is very satisfactory for use in conjunction with the modified rat liver-storage bioassay procedure (*1*), since livers from the bioassay contain between 100 and 1500 γ of vitamin A per liver.

RECOVERY EXPERIMENTS

Assays of livers from vitamin A-deficient rats by the antimony trichloride-blue color procedure indicated no perceptible blue color potency. Results of recovery experiments using livers from vitamin A-deficient animals are given in Table I. Aliquots of an ethyl ether solution of vitamin A acetate were evaporated onto the whole liver before grinding it with anhydrous sodium sulfate. The fortified livers were analyzed by the simplified procedure. Excellent recovery was realized at all three levels added (30, 150, and 300 γ). The over-all average recovery of 98.6 ± 0.56% standard error showed that there was no significant loss of vitamin A during the analysis. Also, there was no indication of extraction of materials from the liver which interfere with the vitamin A determination.

CONFIRMATION OF IDENTITY

The possibility of the presence of nonvitamin A substances yielding a blue color with antimony trichloride was considered.

Table I. Recovery of Vitamin A Added to Livers from Vitamin A–Depleted Rats

Animal No.	Vitamin A Added, blue color units	Vitamin A Recovered, blue color units	Recovery, %	Average Recovery, %
		Controls, No Vitamin A Added		
96	0	NBC[a]	...	
394	0	NBC	...	
363	0	NBC	...	
6	0	NBC	...	
549	0	NBC	...	
5	0	NBC	...	
		Low Level Added, 0.10 Ml. of ca. 300 γ/Ml.		
406	105	108	103	
570	105	105	100	
546	105	103	98	
361	107	105	98	99.1
547	107	104	97	
240	107	105	98	
542	107	107	100	
		Intermediate Level Added, 0.50 Ml. of ca. 300 γ/Ml.		
399	526	514	98	
551	526	507	96	
390	526	525	100	97.5
376	526	532	101	
387	537	510	95	
384	537	510	95	
		High Level Added, 1.00 Ml. of ca. 300 γ/Ml.		
564	1053	1035	98	
545	1053	1087	103	
544	1053	1079	102	99.2
388	1053	1035	98	
396	1075	1028	96	
395	1075	1050	98	

Over-all average recovery = 98.6 ± 0.56% S.E. (σ = 2.4%)

[a] No blue color.

Ether extracts from a number of animals on a routine liver storage bioassay (each of which had received 300 or 600 γ of vitamin A as alcohol, acetate, or palmitate) were pooled and the solvent was removed under nitrogen. This composite sample of rat liver lipide was saponified and both the unsaponifiable fraction and the original lipide extract were analyzed as indicated in Table II.

Table II. Test of Identity of Vitamin A in Rat Liver Lipides

(Composite ethyl ether extract from animals receiving 300 or 600 γ of vitamin A as alcohol, acetate, or palmitate)

Analysis	Liver Lipides, Units per Gram	Unsaponifiable Fraction of Liver Lipides, Units per Gram
$SbCl_3$-blue color	2970	2860
E_{328} (uncorr.) × 1900	4035	3330
E_{328} (corr.) × 1900 (USP XIV)	...	2480
Morton-Stubbs correction factor[a]	...	74.4%
Dehydration[b]	...	3015
Vitamin A as ester[c]	90%	...

[a] Correction factor = $\frac{A \text{ corr.}}{A}$ × 100 (*12*).

[b] Determined as described by Shantz, Cawley, and Embree (*13*).

[c] Determined as described by Kascher and Baxter (*9*).

The vitamin A content of the liver lipides was 2970 units per gram by conventional blue-color procedures compared with a blue-color potency of 2860 units per gram in the unsaponifiable fraction. Spectrophotometric analyses indicated an E_{328} uncorrected potency of 3330 units per gram. The E_{328} corrected potency (U.S.P. XIV procedure) resulted in a value of 2480 units per gram with a Morton-Stubbs correction factor (*12*) of 74.4%. The ratio of blue-color potency to U.S.P. XIV potency of 1.15 is identical with the mean ratio of 1.15 considered (*3*) characteristic of good quality vitamin A–bearing liver oils. As a further proof of identity the unsaponifiable fraction was dehydrated with acid and the anhydro vitamin A formed was analyzed spectrophotometrically as described by Shantz, Cawley, and Embree (*13*). Since this procedure is specific for vitamin A, the correspondence of the potency, 3015 units per gram, by dehydration with that obtained by the other procedures is further indication that under these conditions the blue-color potency is a reliable measure of the vitamin A present. The vitamin A in the liver lipide fraction was 90% in the ester form. This corresponds well with the value of 86 to 86.5% previously reported from these laboratories (*8*).

In this sample of rat-liver fat any blue-color yielding substances were formed from vitamin A, since nearly pure vitamin A or its esters had been fed. The approximate agreement of the various procedures for estimating vitamin A shows that the blue-color method is satisfactory for the determination of vitamin A in rat livers under the conditions of the modified liver-storage bioassay.

COMPARISON WITH OTHER METHODS

Comparison of methods for the determination of vitamin A in liver tissue was complicated by the difficulty of obtaining samples of uniform composition. Aliquots of chopped or homogenized liver tissue were analyzed by the various procedures according to a Latin square design and the results were subjected to analysis of variance. By this procedure the variation between samples was isolated and a statistical comparison of methods was made.

Five procedures for the determination of the vitamin A content of liver tissue were compared. Similar sized samples (3 to 5 grams) were used in all cases and the vitamin A content of the extract was determined colorimetrically. The procedures are summarized briefly as follows:

Method A. Simplified procedure as described in this paper.

Method B [Glover, Goodwin, and Morton (*6*)]. Sand and anhydrous sodium sulfate were added to the liver and the mixture was ground until dry and homogeneous. The dried powder was extracted once with 150-ml. and then twice with 75-ml. portions of anhydrous ethyl ether. Extraction was facilitated by stirring for 2 minutes on a warm water bath. The extracts were separated from the residue by decantation and filtration and the residue was washed. The combined extracts and washings were evaporated to dryness under nitrogen and vitamin A was determined.

Method C (Soxhlet). The mixture obtained by grinding the liver with anhydrous sodium sulfate was placed in a thimble in a Soxhlet apparatus and was continuously extracted with anhydrous ethyl ether for 3 hours. The extract was evaporated to dryness under nitrogen and vitamin A was determined.

Method D [(Benham (*2*)]. In a flask, 4 ml. of 5% alcoholic potassium hydroxide were added for each gram of liver. The flask was heated on a steam bath with occasional shaking until saponification was complete. An equal volume of water was added and the mixture was extracted with one 100-ml. and two 50-ml. portions of anhydrous ethyl ether. The combined ether extracts were washed with one 100-ml. and two 10-ml. portions of water. The washed extracts were diluted to a known volume, and dried with anhydrous sodium sulfate, and the vitamin A content of an aliquot was determined.

Method E [Week and Sevigne (*14*)]. The mixture obtained by grinding with anhydrous sodium sulfate was extracted four times with 50-ml. portions of petroleum ether (boiling point, 40° to 60° C.). The extracts were filtered, the residue was washed, the combined extracts and washings were evaporated to dryness under nitrogen, and vitamin A was determined.

Uniformity of distribution of vitamin A in samples and reduction of sampling errors to the minimum were prime objects in these comparison experiments. Pork and beef livers were used because of the quantity of sample needed.

In a preliminary experiment, samples of minced fresh pig's liver were analyzed in duplicate by each of the five methods on each of 5 days. The analysis of variance showed that the difference between samples within days (error variance) was large and the difference between average units per sample determined on different days (days variance) was likewise large. Even with the great variation between samples, the variance due to difference in methods was significant due primarily to low values obtained by Method E. This inferior method was, therefore, omitted from further comparisons.

In view of the large sampling variation in the first experiment, a refined sampling technique was devised for the second comparison test. Fresh calf liver was thoroughly homogenized in a Waring blender and the homogenate was passed through cheesecloth under slight pressure to remove large particles and fibrous tissue. The filtered homogenate was thoroughly mixed and poured into damp Visking cellulose sausage casings (23/32 inch in diameter). The casing was tied off in sections containing ample amounts for a 1-day analysis. The sections were wrapped carefully in foil, frozen as quickly as possible, and stored at −20° C.

Table III. Comparison of Methods Using Homogenized Calf Liver

Latin Square Used to Randomize Sampling Errors

(For details of methods see text)

Day	Order of Samples Selected			
	1st	2nd	3rd	4th
1	D	B	A	C
2	B	A	C	D
3	A	C	D	B
4	C	D	B	A

Methods. A. Simplified procedure.
Methods. B. Glover *et al.*
Methods. C. Soxhlet.
Methods. D. Benham.

Table IV. Comparison of Methods Using Homogenized Calf Liver

Method	Units of Vitamin A/Gram				Average Units Per Gram
	1st day	2nd day	3rd day	4th day	
A. Simplified procedure	718	702	671	679	671.6
	661	666	631	683	
	646	687	668	692	
	651	670	651	669	
B. Glover *et al.*	675	670	662	673	651.3
	658	632	660	675	
	641	647	633	693	
	611	628	632	631	
C. Soxhlet	690	693	645	712	661.6
	652	635	641	688	
	649	677	654	677	
	633	648	623	669	
D. Benham	603	625	602	629	607.3
	596	603	585	636	
	586	613	570	661	
	564	604	586	653	
Average units/gram	639.6	650.0	632.1	670.0	647.9

σ = 19.6 or 3.0% S.E. = 2.44 or 0.38%

Analysis of Variance

Source of Variation	Sum Squares	df	Mean Square	F
Treatment				
Method	38,597	3	12,866	33.59^b
Day	13,032	3	4344	11.34^a
Interaction	3765	9	418	1.09
Error	18,394	48	383	...
Totals	73,788	63		

[a] Significant.
[b] Highly significant.

At the time of analysis a section of the cylindrical casing containing the homogenized liver was cut into 3- to 5-gram samples, the casing was removed, and the still-frozen homogenate was weighed. The assignment of the samples to the four methods compared was randomized by following the Latin square schedule given in Table III. The initial row of the Latin square was altered on each of 4 days. This procedure was followed to minimize not only the error variance (within methods variation on a given day) but also the variance between days. The order of sampling was quadruplicated each day so that four samples by each of four methods on 4 days or a total of 64 determinations were run. The results of these determinations and their treatment by analysis of variance are given in Table IV.

The data showed excellent agreement within methods and within days as evidenced by an error mean square which was about one fourth that obtained in the preliminary experiment. In addition, the day-to-day variance was greatly reduced, from an F value of 128 to 11.3. These results showed that the method of sampling, using homogenized liver, was much superior to that previously used. By reduction of the variance due to sampling, the variance due to method proved to be highly significant as evidenced by an F value of 33.6. It remained to determine which of the four methods was the best.

Table V. Comparison of Methods Using Homogenized Calf Liver

[Analysis of variance of adjacent samples (paired observations)]

Source of Variation	df	Sum Squares	Mean Square	F
Comparison of Method A (simplified procedure) and Method B (Glover *et al.*). Mean of Method A = 671.6 (15 observations). Mean of Method B = 652.6 (15 observations).				
Error	14	3,089.7	220.7	...
Sample	14	20,663	1,475.9	6.69
Method	1	2,707.5	2,707.5	12.27^a
Total	29			
Comparison of Method A (simplified procedure) and Method C (Soxhlet). Mean of Method A = 671.7 (15 observations). Mean of Method C = 658.2 (15 observations.)				
Error	14	982.9	70.2	...
Sample	14	13,035	931.0	13.3^a
Method	1	1,360	1,360.0	19.4^a
Total	29			
Comparison of Method B (Glover *et al.*) and Method D (Benham). Mean of Method B = 650.0 (15 observations). Mean of Method D = 607.5 (15 observations).				
Error	14	4,762.8	340.2	...
Sample	14	14,044	1,003	2.95
Method	1	13,611	13,611	40.0^b
Total	29			

[a] Significant.
[b] Highly significant.

In the design of the Latin square used to assign consecutive samples to each method, methods A and B, A and C, and B and D, but not A and D, were always assigned to adjacent samples—i.e., 15 times out of 16 samples. The comparison of adjacent samples by analysis of variance for paired observations and statistical analyses for these pairs of methods are given in Table V. This method was used in preference to Student's t-test, since an estimate of the sample variance is obtained in addition to the method variance. It is evident that Method D, involving saponification, is distinctly inferior to the other three methods. Method A (simplified procedure) gives significantly higher recoveries of vitamin A than either Method B or Method C.

Thus, drying with anhydrous sodium sulfate followed by addition of ethyl ether and analysis of an aliquot yields somewhat higher results than either extraction three times with hot ethyl ether or Soxhlet extraction.

PRECISION OF METHOD

An estimate of the precision of the simplified procedure can be made from the recovery experiments included in Table I. The standard deviation of a single determination was ±2.4% with a standard error of 0.56% (19 values). Similarly, the data of Table IV indicated that the four methods have a comparable precision. Based on the total error mean square which includes both variation between samples and the true method variation, a standard deviation of 3.0% with a standard error of 0.38% (64 values) was obtained. The liver storage bioassay for vitamin A (*1*) specifies 10 analyses per dose level and would yield a standard deviation (owing to method) of about 2.5% and a standard error of about 0.6%.

DISCUSSION

One of the inferior procedures involves hot saponification of the liver followed by a single extraction with petroleum ether (Skellysolve F) (*5*). A recovery from the liver of only 25 to 35% of orally administered vitamin A was obtained by this method in contrast to the 60 to 70% recovery observed with the simplified procedure. This is confirmation of Benham's conclusions (*2*) that an excess of alkali and the use of petroleum ether both result in lower and variable results.

The new, simplified procedure used in conjunction with the modified liver-storage bioassay (*1*) yields data from which a dose-response curve is obtained which is linear and passes through the point of zero dose–zero response (origin). The use of less accurate analytical techniques usually leads to considerable destruction of vitamin A which is proportionately greater at the lower concentrations of vitamin A in the liver. Such data results in a dose-response relationship with a positive y-intercept at zero response—i.e., a dose of 1 to 20 γ of vitamin A must be fed before storage is observed. Unsuspected complications of this type led Koch and Kaplan (*10*) to the erroneous conclusion that the threshold dose of storage (y-intercept of dose-response curve) was proportional to the potency of the material fed.

The new, simplified procedure thus results in significantly higher recovery of the vitamin A from liver, compared with currently used procedures. This results from an improved extraction technique with fewer manipulations and involving less destruction by avoiding both heat and prolonged manipulation of the extract. It combines both speed and precision which recommends it for use as a routine analysis. It also serves as an essential part of a liver-storage type bioassay which was developed for the accurate and economical determination of vitamin A in oils and pharmaceuticals (*1*).

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Spectrophotometric Determination of Arsenic, Phosphorus, and Silicon in the Presence of Each Other

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DURING the investigation leading to the spectrophotometric determination of traces of silica in magnesium oxide and magnesium carbonate (*1*) as the yellow molybdosilicic acid, various methods for removal of the interference from phosphorus and arsenic were investigated. Selective extraction of the heteropoly acids of arsenic and phosphorus was one of the methods considered. The literature on extraction of heteropoly acids has recently been summarized by Wadelin and Mellon (*3*), and the technique was used for the determination of phosphorus. Hure and Ortis (*2*) had used ethyl acetate to extract molybdophosphoric acid from a mixture of the heteropoly acids of silicon and phosphorus. This technique was briefly investigated and shown to be feasible but more time-consuming than simply using tartaric acid to bleach selectively molybdoarsenic and molybdophosphoric acids. However, while investigating the solvent extraction technique, a method was developed for the separation and determination of arsenic, phosphorus, and silicon, as the yellow heteropoly acids formed with molybdate. This note reports the preliminary investigations leading to this method and the brief tests conducted on the procedure.

As the authors do not intend to continue this investigation further, the results have been reported so that interested persons may use the proposed or a modified procedure for the analysis of traces of arsenic, phosphorus, and silica in one sample.

APPARATUS AND REAGENTS

Absorbance measurements were made with a Beckman Model DU quartz spectrophotometer using matched 1.00-cm. silica cells.

Stock solutions of 10 mg. per ml. of soluble silica, arsenic(V), and phosphorus(V) were prepared by dissolving 4.7 grams of sodium metasilicate ($Na_2SiO_3.9H_2O$), 4.2 grams of disodium arsenate ($Na_2HAsO_4.7H_2O$), and 12 grams of trisodium phosphate ($Na_3PO_4.12H_2O$), respectively, in distilled water and diluting the resultant solutions to 100 ml. These solutions were standardized gravimetrically, and standard solutions of 100 γ per ml. of desired constituents were prepared by dilution.

EXPERIMENTAL

Preliminary Studies. The standard procedure previously developed for development and measurement of the color of the heteropoly acids was employed (*1*). An aliquot of the desired standard solution was pipetted into a 100-ml. volumetric flask. Five milliliters of a solution containing 40 mg. per ml. of molybdenum(VI) oxide were added and the solution mixed. Two milliliters of 60% perchloric acid were added, and the solution was made up to 100 ml., and thoroughly mixed. Finally the absorbance was measured at 332 mμ against a blank containing all the reagents used in developing the color.

Solutions prepared by the method described above had a pH of 0.7. Hure and Ortis (*2*) reported that ethyl acetate would extract molybdoarsenic and molybdophosphoric acids at pH 1. In order to check the possible quantitative aspects of an extraction technique, solutions of 5 p.p.m. of silica as silicate, 10 p.p.m. of phosphate, and 50 p.p.m. of arsenate were made up according to the standard procedure, and 20-ml. aliquots of each of the three heteropoly acids were taken. In one study, they were extracted once with 20 ml. of ethyl acetate; in a second, extracted twice.

The absorbance of the aqueous phase was measured at 332 mμ against an extracted and an unextracted blank. The results of this study are shown in Table I.

The ethyl acetate extracts the molybdophosphoric and molybdoarsenic acids to some degree. However, if a single or double extraction was used to remove arsenic and phosphorus before measuring the remaining molybdosilicic acid, appreciable errors

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Table I. Extraction Studies with Ethyl Acetate

Conditions	Blank	Absorbance of Aqueous Phase at 332 mμ 5 p.p.m. SiO_2	10 p.p.m. PO_4	50 p.p.m. AsO_4	Blank
No extraction	Normal	0.964	1.49	1.15	...
One extraction	Normal	0.994	0.165	0.193	...
Two extractions	Normal	1.19	0.265	<0	0.450
Two extractions	Normal blank after two extractions	0.715	<0	<0	...

Table II. Analyses of Mixtures of Phosphorus and Silicon

Taken, P.P.M. SiO_2	P	Found, P.P.M. SiO_2	P
2.0	0.5	2.0	0.48
2.0	1.0	1.9	1.0
2.0	2.0	1.6	2.2

could be expected no matter which blank was used. Because a blank solution showed a high absorbance when subjected to two extractions, it may be that ethyl acetate dissolved in the aqueous phase was absorbing at 332 mμ. Therefore, the possibility of using a less soluble acetate prepared from a longer chain alcohol was investigated. Isoamyl acetate was chosen for it is water insoluble and readily available. Qualitative tests showed that molybdophosphoric acid was extracted quantitatively into this medium but molybdoarsenic acid was not extracted. From some empirical qualitative experiments it was found that both molybdoarsenic and molybdophosphoric acids were extracted if some ethyl alcohol was added to the aqueous phase. From these qualitative experiments, the total concentration of silica, phosphorus, and arsenic in the aqueous phase could probably be determined, and then selectively phosphorus and arsenic be extracted and determined in the organic phase. A few experiments were carried out to test this possibility.

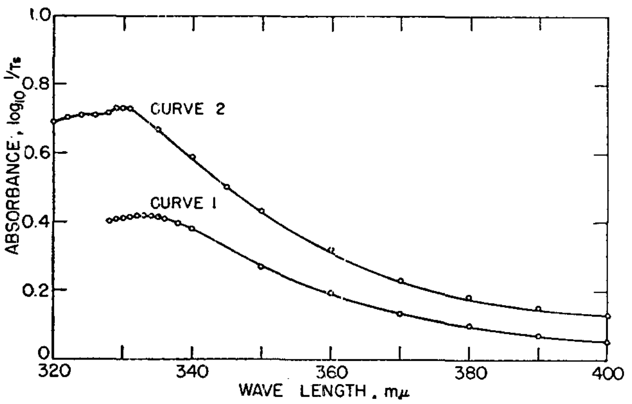

Figure 1. Absorption Spectra of 3.2 P.P.M. of Phosphate as Molybdophosphoric Acid

1. In aqueous phase against blank containing all color-developing agents
2. In amyl acetate extract against amyl acetate blank

Determination of Phosphorus in the Presence of Silica. A preliminary study showed that the color of the molybdophosphoric acid in the isoamyl acetate extract was stable for 10 to 30 minutes after extraction. The spectrum of the molybdophosphoric acid in the isoamyl acetate extract was determined against an isoamyl acetate blank and is compared in Figure 1 with the spectrum of the molybdophosphoric acid in the aqueous phase determined against an acid molybdate blank. Beer's law was found to hold in the organic phase at 330 mμ when 20 ml. of 0.5, 1, and 2 p.p.m. phosphorus solutions were developed according to the standard procedure and extracted during 2 minutes of shaking with 20 ml. of isoamyl acetate.

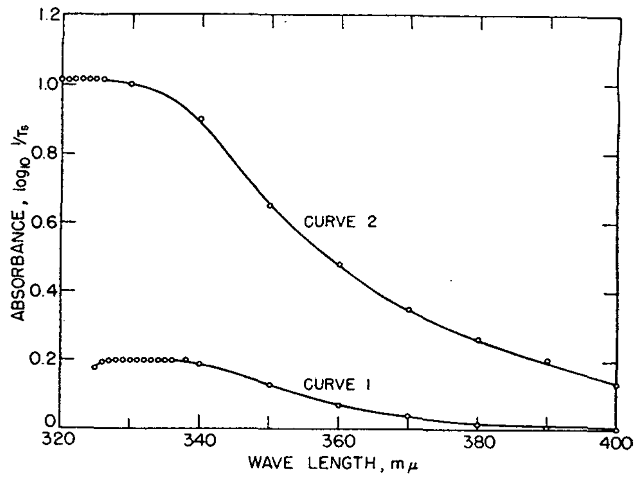

Figure 2. Absorption Spectra of 10.0 P.P.M. of Arsenate as Molybdoarsenic Acid

1. In aqueous phase against blank containing all color-developing agents
2. In amyl acetate extract against amyl acetate blank

Mixtures of silicate and phosphate were made up from the stock solutions and their colors developed according to the standard procedure. Total absorbance in the aqueous phase was determined at 332 mμ. The phosphorus was then determined by extracting with isoamyl acetate for 2 minutes and measuring the absorbance in the organic phase at 330 mμ. Silica was determined by correcting total absorbance in the aqueous phase for phosphorus using the previously determined absorbance index of molybdophosphoric acid in the aqueous phase. The analyses of three mixtures are shown in Table II. The trends with change in concentration need checking for they may or may not be real.

Determination of Arsenic in the Presence of Silica. Because molybdoarsenic acid is extracted by isoamyl acetate only when the aqueous phase is made alcoholic, the optimum alcohol concentration for quantitative extraction was determined. This was accomplished by extracting for 2 minutes with 20 ml. of isoamyl acetate, 20-ml. aliquots of a 25 p.p.m. molybdoarsenic acid in the presence of various amounts of alcohol. The absorbance of the aqueous phase was measured against a normal blank before and after extraction. From these data the apparent percentage of extracted arsenic was determined. When the aqueous phase was made 16 to 17.5% in alcohol, complete extraction was obtained. At lower concentrations of alcohol, the extraction was incomplete; at high concentrations, negative absorbance values were obtained on the aqueous phase. These negative values are probably due to the fact that molybdate is extracted into the organic phase. Because molybdate is strongly absorbant in the ultraviolet, the extracted solution may easily be less absorbant than the unextracted blank.

The color of the molybdoarsenic acid extracted into isoamyl acetate from a 17% alcohol solution was found to fade slowly for 0.5 hour and then remain constant for at least 2 hours. The spectrum of the heteropoly acid, determined in isoamyl acetate against pure isoamyl acetate, is compared in Figure 2 with the spectrum in the aqueous phase.

To complete the preliminary work, the optimum alcohol concentration for extraction of the molybdoarsenic acid was again determined by measuring the absorbance at 323 mμ of the extracts from solutions at various strengths of alcohol. The results checked the previous study, and a graphical presentation of both studies is shown in Figure 3.

Table III. Analyses of Mixtures of Arsenic and Silicon

P.P.M. SiO_2	P.P.M. As	P.P.M. SiO_2	P.P.M. As
1.0	3.0	1.1	2.6
1.0	5.0	1.0	5.1
1.0	8.0	0.8	8.4
3.0	3.0	3.5	2.7
3.0	6.0	3.2	6.1
3.0	9.0	3.1	9.2

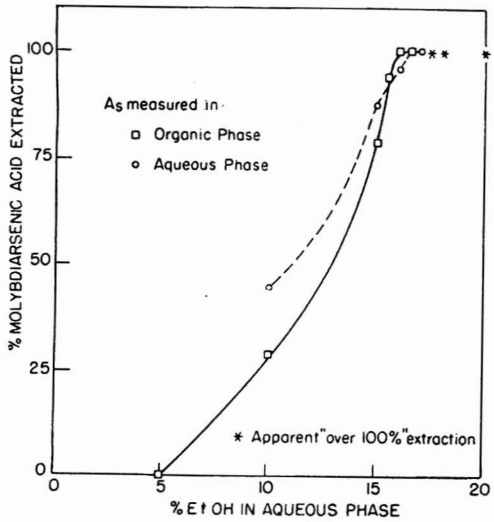

Figure 3. Effect of Ethyl Alcohol Concentration on Extraction of Molybdoarsenic Acid by Amyl Acetate

Beer's law was checked in the aqueous phase by making up 3, 5, 8, 10, and 15 p.p.m. of arsenic according to the standard procedure. The absorbances of these solutions, when plotted against concentration, gave a straight line which did not go through zero, but crossed the zero absorbence at a concentration of 1.5 p.p.m. of arsenic. When 20-ml. aliquots of these solutions containing 17% alcohol were extracted for 2 minutes with 20 ml. of isoamyl acetate and the absorbances of the extracts measured at 323 mμ against an isoamyl acetate blank, Beer's law was obeyed and an absorbance index for molybdoarsenic acid in isoamyl acetate was determined.

Mixtures of silicate and arsenate were made up from the stock solutions and the color developed according to the standard procedure. A procedure similar to that described for analysis of silicate and phosphate mixtures was used to analyze the silicate and arsenate mixtures. Results are summarized in Table III.

SUMMARY AND CONCLUSION

A means of separating the heteropoly molybdo- acids of arsenic, silicon, and phosphorus by means of solvent extraction has been devised. The technique has been successfully tested for the spectrophotometric analysis of artificial mixtures of silicon and phosphorus and silicon and arsenic.

While a mixture of all three elements was not analyzed, it seems entirely possible to determine arsenic, silicon, and phosphorus in one sample. The sum of all three heteropoly acids, which have identical spectra in the near ultraviolet region, could be determined on one sample. Then aliquots of this sample could be treated to remove phosphorus, and then arsenic, selectively, into isoamyl acetate in which medium these two elements can be individually determined. Finally the silica could be determined by correcting the absorbance in the aqueous phase for the contribution of arsenic and phosphorus.

ACKNOWLEDGMENT

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Analysis of Phosphate Mixtures by Filter Paper Chromatography

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PREVIOUS papers *(10, 11)* from these laboratories described a technique for separating and determining phosphate anions by means of filter paper chromatography. Because a number of laboratories are now using this technique, and the methods of these laboratories have been greatly improved in accuracy and convenience, an up-to-date description appeared in order.

Various methods exist for the analysis of phosphate mixtures but they do not have as wide a range of usefulness as the method under consideration. Bell's *(3, 4)* procedure is not as accurate; the mixture cannot be more than 25% pyroposphate and trimetaphosphate can be determined only by difference. The method of Raistrick, Harris, and Lowe *(9)* will not tolerate more than 4% orthophosphate while the various x-ray methods, such as the one developed by Raistrick *(8)*, are limited to crystalline mixtures. As compared with these methods, the chromatographic procedure permits the direct determination of more species of phosphate anions, with as good or better accuracy.

MATERIALS

Orthophosphate, K_2HPO_4, reagent grade.

Pyrophosphate, $Na_4P_2O_7$, supplied by Albright and Wilson, Birmingham, England.

Tetrametaphosphate, $(NaPO_3)_4.4H_2O$, supplied by Albright and Wilson.

Filter paper chromatographic tests showed that these materials were not contaminated by other phosphates *(10)* and that the amounts of phosphorus present were in accordance with the formulas.

Trimetaphosphate, $(NaPO_3)_3.H_2O$, supplied by Albright and Wilson.

Although no other phosphates *(10)* were present in this material, the water content was lower than indicated by the formula, corresponding in fact to 0.94%.

Triphosphate, $Na_5P_3O_{10}.6H_2O$, supplied by Albright and Wilson.

In the triphosphate sample (according to the chromatographic analysis), 2.3 and 1.5% of the phosphorus were present as pyrophosphate and orthophosphate, respectively.

Although it was undesirable to determine the impurities in the triphosphate sample by the analytical procedure that was being evaluated, no other course appeared practical. Attempts were made to prepare pure anhydrous sodium triphosphate, but some pyro- and orthophosphate were always present. However, it can be shown that this chromatographic analysis of the "pure" triphosphate sample is consistent with the analyses obtained in this laboratory of phosphate mixtures containing this material.

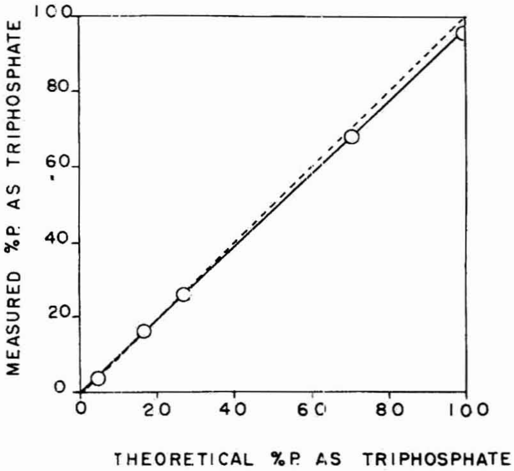

Figure 1. Comparison of Theoretical and Measured Percentages of Phosphorus Found as Triphosphate

Assuming that the material on hand was pure $Na_5P_3O_{10}.6H_2O$, mixtures of tri-, pyro-, and orthophosphate were prepared in which the percentage of phosphorus present as triphosphate was varied from 4.2 to 70.3%. In Figure 1, the percentage of triphosphate phosphorus found by the analysis is plotted against that calculated on the above assumption. If the assumption of purity were correct, the points should fall along the diagonal shown in broken line. However, they are everywhere below this line and fall on another line consistent with the author's analysis of the material itself. Therefore, it was concluded that the percentage of the total phosphorus present in the form of tri-, pyro-, and orthophosphate was 96.2, 2.3 and 1.5%, respectively. Alternative hypotheses considered appeared unlikely on chemical and other grounds.

PROCEDURE

Apparatus. The apparatus consists of a well insulated box containing glass jars (inside dimensions 12 × 7 × 18 inches) with typical stand and trough assemblies as shown in Figure 2. Each jar is fitted with a plate glass lid sealed on with petrolatum.

The trough is filled with the solvent mixture (hereafter referred to as the solvent). To help keep the jar saturated with the vapor of the solvent, two sheets of filter paper are placed on opposing sides of the tank and dipped into a quantity of the solvent in the bottom of the jar. In this way the solvent is wicked up the sides of the tank. This step, which was suggested by Mortimer (*7*) has proved very effective.

Preparation of Chromatogram. The phosphate solutions are spotted on the chromatograms along the starting line (Figure 3) with a micropipet. This starting line is approximately 14 inches from the bottom of the chromatogram but is below the spacing rod as indicated in Figure 3. Considerable care is required in applying the phosphate solution to the chromatogram. Between 60 and 90 γ of phosphorus must be applied to the paper for quantitative results, but the chromatograms must not be overloaded. Overloading causes the phosphates to streak down the chromatogram. Thus the solution of the phosphate mixture is applied to a chromatogram 4.5 inches wide in spots of $^1/_8$-inch diameter separated by $^1/_2$ inch. For convenience the concentration of the solution should be approximately 0.25 atomic weight of phosphorus per liter.

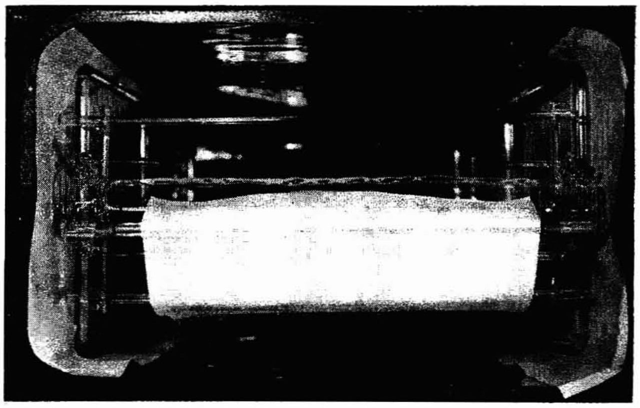

Figure 2. Chromatographic Tank with Stand and Trough Assembly

Once the solution has been applied and the spots have dried, the chromatogram is placed in the jar in the position indicated by Figure 3, and the solvent flow commences.

CONDITIONS FOR SEPARATING VARIOUS MIXTURES

The length of time which the chromatogram is run, the solvent, and the type of filter paper used depend upon the components of the phosphate mixture. This information is summarized in Table I, but an explanation may be of value.

Running Time. The length of time which a chromatogram is run is determined by experience and is the time required to separate the components of the mixture. However, with acid solvents (pH 1.5 to 2.0), the condensed phosphates may hydrolyze if the run is longer than 48 hours.

Solvent. Many solvent mixtures have been studied (*6, 11*), but in general it is found that a single phase alcohol-water-acid (or base) system is superior. The selection of a suitable solvent, however, is largely an empirical proposition.

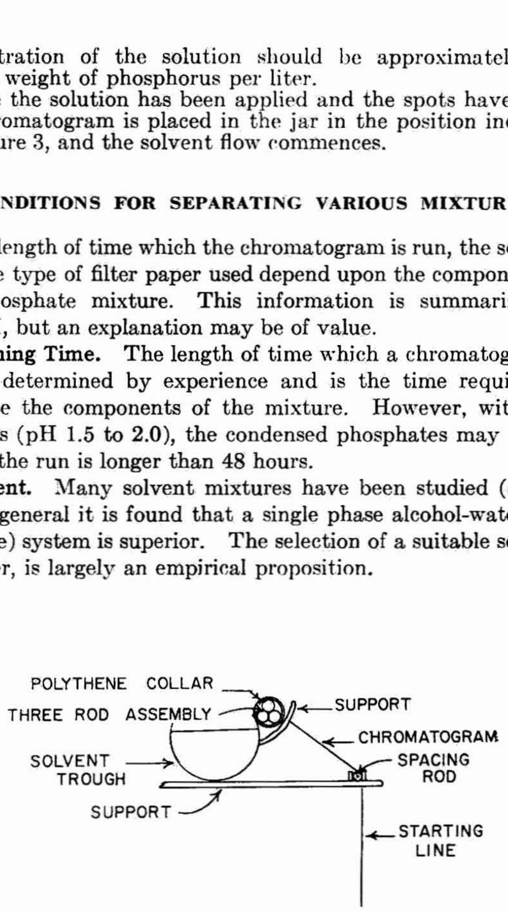

Figure 3. Position of Chromatogram

In acid media, the solvent tertiary butyl alcohol (80 ml.)–water (20 ml.)–formic acid (5 ml.), gives excellent resolution but is too slow to permit the separation of phosphates having more than four phosphorus atoms per molecule. Thus, for phosphates of higher molecular weight, a less viscous but also less efficient alcohol must be used. Using the solvent isopropyl alcohol (80 ml.)–water (20 ml.)–formic acid (5 ml.), phosphates with six or less phosphorus atoms per molecule are believed to be separated and determined. With this solvent, however, the resolution is incomplete, and a faint streak of phosphates exists between the components. This situation is undesirable, but as yet no remedy has been found. Owing to this streaking the standard deviation is increased from 0.8 to 2%.

Table I. Chromatographic Separations on Filter Paper

Procedure No.	Possible Phosphate Components[a]	Filter Paper	Solvent	Running Time, Hours	Remarks
1[b]	Ortho-, pyro-, tri-, H.P.[c]	Schleicher and Schuell 589 orange ribbon	*tert*-Butyl alcohol (80 ml.)–water (20 ml.)–formic acid (5 ml.)	30	Very clear bands
2[b]	Ortho-, pyro-, tri-, trimeta-, tetra-, tetrameta-, H.P.[c]	Schleicher and Schuell 589 black ribbon	*tert*-Butyl alcohol (80 ml.)–water (20 ml.)–formic acid (5 ml.)	30–40	Very clear bands but danger of overloading thin filter paper chromatogram
3[d]	Ortho-, pyro-, tri-, trimeta-, tetra-, tetrameta-, penta-, hexa-, H.P.[c]	Schleicher and Schuell 589 orange ribbon	Isopropyl alcohol (80 ml.)–water (20 ml.)–formic acid (5 ml.)	48	Bands joined by streak of phosphates
4[d e f]	Pyro-, tri-, tetra-, penta-, hexa-, septa-, octa-, nona-, H.P.[c]	Schleicher and Schuell 589 black ribbon	(*a*) *tert*-Butyl alcohol (80 ml.)–water (20 ml.)–formic acid (5 ml.) (*b*) *n*-Propyl alcohol (60 ml.)–water (20 ml.)–concentrated ammonium hydroxide (20 ml.)	16 48	Bands joined by streak of phosphates

[a] Listed in order in which they occur on chromatogram—first found closest to bottom of chromatogram. All components named need not be present. Any or all specified components can be determined under these conditions, but if a phosphate is not named, it cannot be determined.

[b] If procedure is carefully followed, resulting chromatograms will show clean-cut bands of phosphates with no background.

[c] H.P. refers to any higher polyphosphate groups which, under these conditions, would remain on or close to starting line of chromatogram. With Procedure 2 H.P. refers to all phosphates having more than four phosphorus atoms per molecule while in Procedure 4 H.P. refers to all phosphates having more than nine phosphorus atoms per molecule. H.P., therefore, deals with the polyphosphates which, if present, cannot be separated under specified conditions, and must be treated as a group.

[d] Procedures not yet fully developed because of lack of pure samples of tetra-, penta-, hexa-, septa-, octa-, and alcohol nonaphosphates.

[e] In specified basic solvent, pyro- and triphosphate are not separated from each other; thus such a mixture is successively chromatographed in two solvents to overcome this difficulty. Initial run in acid solvent separates pyro- from triphosphate. Chromatogram is then removed from tank, dried, and re-run in *n*-propyl alcohol–water-ammonia solvent. Since pyro- and triphosphate have same R_f values in this basic solvent, they remain separated.

[f] If any or all of ortho-, trimeta-, and tetrametaphosphates are present in this phosphate mixture, they will have run off bottom of the chromatogram by end of run. This difficulty can be overcome by using chromatogram which is longer than 14 inches or by decreasing running time. If latter step is taken some of polyphosphates listed will not be separated. An alternative method would be to use Procedure 2 in conjunction with Procedure 4.

In basic media the solvent *n*-propyl alcohol (60 ml.)–water (20 ml.)–concentrated ammonium hydroxide (20 ml.), provides the best resolution, and is believed to permit the separation of phosphates having nine or less phosphorus atoms per molecule. Again, however, the streaking between bands is present and the standard deviation for such an analysis is only 2%.

Filter Paper. Finding or preparing suitable filter paper for quantitative chromatography was one of the greatest difficulties encountered. To summarize the problem, briefly, an examination of earlier techniques showed that they could be materially improved if (1) the phosphorus blank on the paper could be reduced or made more uniform and (2) if the impurities in the paper tending to complex with condensed phosphate anions could be decreased. Both factors required a purer paper. Efforts were made to achieve this by (*a*) an investigation of washing techniques and (*b*) testing lots of paper submitted by various filter paper companies in an effort to meet the requirements, which are much more exacting than those ordinarily met in filter paper chromatography. Under (*a*) some 50 methods were investigated. Even the most painstaking gave results which were largely unpredictable although occasionally good. Under (*b*) the papers first meeting the requirements were Schleicher and Schuell, No. 589 Black and No. 589 Orange Ribbon. Two lots of each type have been satisfactory.

The black and orange ribbon papers, although similar in purity, differ chromatographically. The black paper permits comparatively rapid resolution of the phosphate components, but care must be taken to avoid overloading—i.e., streaking. With orange paper, the resolution is much slower, but the danger from overloading is considerably decreased. Thus orange paper is used wherever feasible, as it is much easier to handle.

General. Thus the type of paper, running time, and solvent are selected by considering the components of the phosphate mixture. Qualitative chromatograms are run on unknown mixtures to identify components before an analysis is attempted. In Table I the conditions under which various combinations of phosphates can be separated are summarized. For example, using Procedure 1, ortho, pyro, tri, or any combination of these three can be separated and determined. Any other phosphates present in the mixture will remain as a group on or near the starting line and can be determined only as a group.

TREATMENT OF DEVELOPED CHROMATOGRAMS

General. Once the chromatogram has been run as indicated above, the procedure consists of identifying the phosphate bands on the chromatogram, cutting out the bands, eluting the phosphates from the paper, and colorimetrically determining the amount of phosphorus in each band by a modification of the Boltz and Mellon (*5*) procedure.

Identification of Bands on Chromatogram. The phosphate bands are identified on the chromatogram by spraying with an acid molybdate solution and heating the chromatogram to form the phosphomolybdate complex. By exposing the dried chromatogram to ultraviolet light for approximately 1 minute the complex is reduced to form a blue color (*2*). This method is much simpler and more sensitive than the use of hydrogen sulfide gas as the reductant (*11*).

Colorimetric Determination of Phosphorus. The determination of the amount of phosphorus in the bands is simple. The bands are cut out, and the phosphate is eluted by soaking the paper in 25.00 ml. of 0.1*N* ammonium hydroxide. After 1 hour or more, a 20.00-ml. aliquot of this solution is pipetted into a 50.00-ml. volumetric flask. If, however, more than 50 γ of phosphorus are expected, a 10.00-ml. aliquot is removed. To this aliquot then, 5 ml. of 10*N* sulfuric acid are added, and the solution is heated in a bath at 100° C. for 30 minutes. This heating period is required to hydrolyze the cyclic and polyphosphates quantitatively to orthophosphate.

To the cooled hydrolyzed solution, 1 ml. of 12.5% ammonium molybdate is added, the flask is shaken, and then 1 ml. of 0.6% hydrazine hydrochloride is added. The volume is then adjusted to 50.00 ml., and the flask is placed in a bath at 100° C. for exactly 10 minutes. The flask is then cooled rapidly by placing it in a bath of cold water. The absorbance of the solution is then measured on a Beckman spectrophotometer at 830 mμ, using distilled water as the reference solution.

This colorimetric analysis is also carried out on blanks. The filter paper blanks are approximately equal in area to the bands of phosphates. In addition, a solvent blank is run on 20.00 ml. of 0.1*N* ammonium hydroxide. The filter paper and solvent blanks have similar absorbances (reference solution is distilled water) and this value is subtracted from the values obtained for the phosphate bands. The blanks then are the effective reference solution, but it is felt that the use of distilled water is a check on errors in the blanks which would be revealed by a more than slight variation from day to day.

From the absorbances, the amount of phosphorus present is calculated using the calibration curve. This straight line relationship was determined by using standard solutions of KH_2PO_4, $Na_4P_2O_7$, and $(NaPO_3)_3$.

Table II. Analytical Results for Mixtures of Pyro-, Tri-, and Orthophosphates

		Solution 1			Solution 2			Solution 3			Solution 4		
		% P as ortho-	% P as pyro-	% P as tri-	% P as ortho-	% P as pyro-	% P as tri-	% P as ortho-	% P as pyro-	% P as tri-	% P as ortho-	% P as pyro-	% P as tri-
Calcd. composition		7.1	25.3	67.7	20.2	75.7	4.1	31.7	42.4	25.8	78.6	5.5	15.9
Av. measured composition		7.1	24.9	68.0	20.0	75.6	4.3	31.9	41.7	26.3	78.6	5.3	16.1
Individual analytical compositions	1	7.7	24.6	67.8	19.1	76.8	4.1	31.0	41.8	27.2	78.5	4.8	16.7
	2	7.7	24.6	67.7	20.9	74.5	4.7	31.5	41.4	27.1	78.0	6.1	15.8
	3	6.5	24.8	68.6	20.0	75.5	4.5	31.9	42.2	25.8	77.6	6.4	16.0
	4	6.9	25.8	67.3	20.8	75.8	3.4	32.0	42.7	25.4	78.3	4.8	17.0
	5	6.8	24.8	68.4	19.4	74.7	5.8	33.0	40.6	26.3	78.4	5.2	16.3
	6	7.1	24.7	68.2	20.0	76.5	3.5	32.1	41.7	26.1	80.6	4.5	14.8

Table III. Analytical Results for a Mixture of Poly- and Cyclic Phosphates

		% P as Ortho-	% P as Pyro-	% P as Tri-	% P as Trimeta-	% P as Tetrameta-
Calcd. composition		19.9	20.1	15.0	25.2	19.8
Av. measured composition		19.8 [a] $\sigma = 0.73$	20.2 $\sigma = 0.62$	15.4 $\sigma = 0.60$	24.9 $\sigma = 0.42$	19.8 $\sigma = 0.78$
Individual analytical compositions	1	21.0	19.9	15.3	24.6	19.1
	2	19.4	20.8	16.1	25.0	18.8
	3	19.5	20.8	15.0	24.8	20.0
	4	20.1	20.8	14.3	25.6	19.3
	5	20.4	19.2	15.6	24.2	20.6
	6	18.3	19.9	15.9	25.0	20.9

[a] σ = Standard deviation (*1*) based on six determinations.

EXPERIMENTAL AND DISCUSSION

Four standard solutions containing ortho-, pyro-, and triphosphate were prepared and analyzed six times over a number of days. The results of these determinations and their averages are shown in Table II. Similarly a solution containing ortho-, pyro-, tri-, trimeta-, and tetrametaphosphate was analyzed six times over a number of days. The individual determinations in chronological order, their averages, and standard deviations (*1*) are shown in Table III.

The statistical analyses of all results for ortho-, pyro-, and triphosphate indicated that there was no variation in precision and no significant departure from the calculated distribution of phosphorus. The average standard deviation is 0.83 based on 75 degrees of freedom. In addition, no difference is noticed between analyses carried out on different days. However, the analyses of about 20 chromatograms are normally required for an operator to attain this degree of precision.

The analyses of the solution which also contained trimeta- and tetrametaphosphate (Table III) are in accordance with the calculated distribution of phosphorus.

Solutions of phosphate glasses have been analyzed by this chromatographic procedure, and results have been obtained on bands occupying positions which might logically be ascribed to tetra-, penta-, hexa-, septa-, octa-, and nonaphosphates as well as to the phosphates of lower molecular weight. This does not mean that all phosphate glass solutions can be analyzed. The composition of such solutions varies with the molar sodium to phosphorus ratio, and complete analysis is only possible when this ratio is greater than 1.5 roughly. As the sodium to phosphorus ratio decreases to 1.0 the percentage of phosphates with nine or less phosphate atoms per molecule decreases until none is present. The precision of these glass analyses is ±2%, but the accuracy is unknown. Pure samples of phosphates, with four or more phosphorus atoms per molecule, have not as yet been obtained, and hence it is impossible to prepare standard solutions to test the accuracy.

A number of household detergent mixtures have been analyzed by this method, and as yet no excessive difficulties have been encountered. The per cent distribution of phosphorus is determined chromatographically in the normal way, but it is necessary to determine the total phosphorus by analyzing a dilute solution of the detergent, since the foaming in concentrated solutions makes accurate volume measurements impossible. A detergent may be encountered in which some of the interfering chemicals mentioned in the following section are present. If so, this method of analysis would be unsuitable without modification.

The main weakness of this analytical method is the effect of polyvalent cations on the filter paper chromatograms. In moderate quantities—e.g., up to 1.5% magnesium—interference is not evident, but as the concentration of these cations increases the chromatograms become streaked owing to the formation of complexes. It is possible that a cation exchange column could be used to remove these ions. Citric acid and glycerol also tend to complex with condensed phosphates, and the resultant product fails to form the reduced blue phosphomolybdate complex.

The colorimetric determination of phosphorus has an appreciable tolerance for many ions as indicated by Boltz and Mellon (*5*).

The interfering tendencies of silicates are important when considering the analysis of detergent mixtures. Fortunately silicates do not affect the chromatographic separation of phosphates and the colorimetric determination of phosphorus tolerates at least 1000 parts per million of silicate. One silicate, $Na_2O.SiO_2.9H_2O$, has a R_f value similar to orthophosphate, but the latter is still quantitatively recovered. The presence of soap in the detergent interferes with the analyses but this difficulty is easily surmounted by an alcohol extraction.

Although polyvalent cations interfere, this chromatographic analytical procedure has much to recommend it. An operator can make 30 to 40 determinations per day. Components (up to four phosphorus atoms per molecule) are directly determined with equal accuracy, while longer chain polyphosphates do not interfere since they can be grouped together. The distribution of phosphorus among the components (up to four phosphorus atoms per molecule) does not affect the accuracy, and the standard deviation of the procedure (0.83 based on 75 degrees of freedom) compares favorably with the accuracy of other procedures for phosphate mixtures.

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Determination of Indium in Aluminum Bronze Alloys by Flame Photometry

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IN THE course of an investigation of the physical properties of indium-aluminum-copper alloys, it was necessary to determine the amount of indium in the alloy. The range of concentration was 0.5 to 2.5%. A review of the literature indicates that, whereas indium may be weighed as In_2O_3 after ignition of the hydroxide at 1100° to 1200° C., the separation of interfering elements may be tedious and difficult. Saltman and Nachtrieb (*4*) and Hauser (*2*) mentioned that indium could be analyzed spectrographically, and as another laboratory had reported difficulty in the analysis of the above-mentioned alloys by classical wet methods, it appeared that analysis by flame photometric procedure might result in a saving of time and yet yield adequate results. The flame spectrum of indium has two strong lines, 451.1 and 410.2 mμ, and it was believed that one of these lines might prove sensitive enough for flame photometric analysis.

This paper describes the application of a flame-photometric procedure to the analysis of a series of alloys for indium. In the course of this work the various possible interferences by elements which might be present in the alloy were studied.

APPARATUS AND MATERIALS

The instrument used in this study was a modified Beckman flame photometer equipped with a Model 4300 photomultiplier attachment and a Model 4020 hydrogen burner. The amplifier has been modified to include a fine adjustment on the dark current and a "bucking" circuit for opposing the potential caused by the flame background (*1, 3*). Using this bucking circuit, it was possible to eliminate the unwanted background potential from the total potential, thereby leaving the full scale for measurement of the analytical radiation.

Stock solutions of indium were prepared by dissolving 1.000 gram of indium metal in a small amount of nitric acid, boiling to expel the oxides of nitrogen, and diluting to 1 liter. This gave a solution of 1000 p.p.m. of indium. The metal used was indium shot obtained from the Indium Co. of America. The indium was checked by the spectrograph and found to contain only traces of aluminum and nickel. A stock solution of copper containing 10 mg. per ml. was prepared by dissolving 10.0 grams of analytical grade copper foil in nitric acid, boiling, and diluting to 1 liter. A 1000-p.p.m. aluminum solution was prepared by dissolving 13.9 grams of aluminum nitrate nonahydrate in water and diluting to 1 liter.

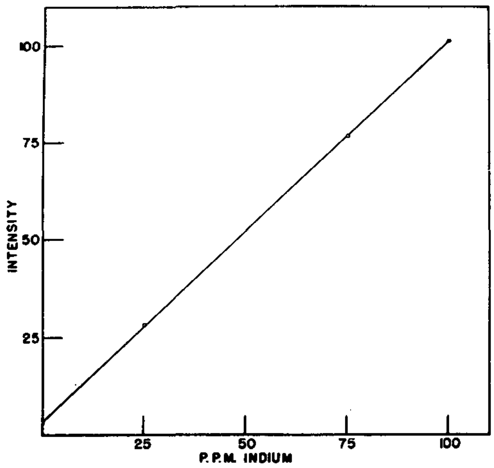

Figure 1. Relative Intensity (451.1 mμ) *vs.* Concentration of Indium

EXPERIMENTAL

An examination of the flame spectrum of indium showed the 451.1 mμ line to be approximately twice as intense as the one at 410.2 mμ. It was therefore decided to use the 451.1 mμ line.

Interferences. The study of various possible interferences was carried out by preparing a working curve from a standard series in the range 0 to 100 p.p.m. of indium and no other added elements. Two other series of solutions were prepared containing 10 and 50 p.p.m. of indium and various concentrations of the contaminants studied. The apparent concentration of the indium in these solutions was determined from the working curve and this concentration was compared to the amount added. The difference between these two values was a measure of the interference.

COPPER. Copper imparts a green color to the flame which affects the flame background intensity at 451.1 mμ. This effect was found to be constant above 800 p.p.m. (equivalent to 80% of copper in the alloy). Because all the samples to be analyzed were greater than 85% copper, the effect of this interference could be nullified by adding copper to the standard series; therefore 900 p.p.m. of copper were added to all standard solutions.

ALUMINUM. While aluminum has no flame spectrum in this region its presence does degrade the indium 451.1 mμ intensity. This effect became constant at 30 p.p.m. and remained so up to 500 p.p.m. It was not investigated at higher concentrations. The alloys studied contained approximately 11% of aluminum; therefore 50 p.p.m. of aluminum were added to the standards.

ZINC. The presence of zinc in the solution showed no effect in the range 0 to 100 p.p.m. of zinc.

NITRIC ACID. The possibility that varying amounts of nitric acid used in dissolving the sample might affect the emission was studied. The emission of a 1*N* nitric acid solution containing 900 p.p.m. of copper, 50 p.p.m. of aluminum, and 50 p.p.m. of indium was not appreciably different from that of a similar solution containing no excess nitric acid.

HYDROCHLORIC AND SULFURIC ACID. Up to 1*N* hydrochloric acid does not effect the radiation, but 1*N* sulfuric acid does degrade the flame. However neither acid is necessary for the solution of the sample.

RECOMMENDED PROCEDURE FOR DETERMINATION OF INDIUM IN ALUMINUM BRONZE ALLOYS IN RANGE 0.1 TO 10.0%

Instrumental Procedure. The instrument is allowed to warm up for 1 hour and the oxy-hydrogen flame is allowed to burn for 10 minutes. The slit is set at 0.04 mm. and the wave length dial is adjusted to the maximum emission for the 451.1 mμ line. The gas pressure for maximum emission must be determined for each individual burner. The sensitivity and the bucking circuit are adjusted so that the span of the slide wire represents 100 p.p.m. of indium. The 0.0 p.p.m. of indium solution should read higher than 0.0 on the instrument scale. It is then possible to determine whether drift has taken place.

Preparation of Standards. The standard series is prepared by adding the required amount of indium stock solution (0.0 to 10.0 ml.) together with 9 ml. of the copper stock solution and 5 ml. of the aluminum stock solution and diluting to 100 ml. The emission of these solutions is determined on the flame photometer and the readings are plotted against concentration. The results obtained from these solutions are given in Table I and Figure 1. Although the above data indicate that the radiation is a linear

Table I. Data for Working Curve

Indium Concentration, P.P.M.	Intensity, Average of 5 Readings
0.0	3.2
25.0	28.1
75.0	76.6
100.0	101.1

Table II. Results on Prepared Samples

	Added, P.P.M.						Reported, P.P.M.	
No.	Cu	Al	Zn	Pb	Fe	In	In	Error
1	822	59	25	2	0	86.0	86.1	+0.1
2	935	46	27	3	0.2	8.0	8.1	+0.1
3	850	53	30	0	0	67.0	66.0	−1.0
4	930	60	0	0	0	11.0	10.8	−0.2
5	820	95	40	3	0.5	35.0	34.5	−0.5
6	930	68	0	0	0	2.0	2.3	+0.3
7	850	100	38	2	0.6	8.8	8.8	0.0
8	900	30	0	1	0	80.8	81.3	+0.5
9	845	73	52	0	0	29.5	29.0	−0.5
10	910	57	0	2	0	28.0	28.0	0.0
11	830	100	0	0	0	70.0	69.5	−0.5

function of concentration from 0 to 100 p.p.m., it was found that the range for this relationship was at least 0 to 1000 p.p.m. for an indium solution to which no other elements had been added.

Analysis of Samples. A 0.1000-gram sample of alloy is dissolved in a small amount of nitric acid, and the solution is boiled and diluted to 100 ml. The emission of this solution is determined on the flame photometer and the concentration of the indium in the alloy is determined by interpolation from the working curve. The calculation of per cent indium is easy if a 0.1000-gram sample has been dissolved and diluted to 100 ml., as 1 p.p.m. is then equivalent to 0.1% of indium in the alloy.

DISCUSSION

A series of samples containing various concentrations of indium and the other elements mentioned earlier in the paper was prepared. These solutions were then analyzed by this procedure. Table II gives the results obtained. In order to calculate the precision of the procedure, the standard deviation of the readings used to obtain the working curve was calculated. A value of 0.33 p.p.m. was obtained using the readings from four working curves (approximately 100 readings). The samples all fall within the 3σ limit indicating that the procedure is accurate to within ±0.1% indium. The sensitivity of the method may be increased by increasing the slit width; however, if this is done the effect of copper must be re-examined. The minimum detectable amount of indium for an oxy-hydrogen burner appears to be approximately 0.2 p.p.m.

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Absorption Spectrum of Aqueous Monochloramine Solutions

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MONOCHLORAMINE, NH_2Cl, an intermediate in the formation of hydrazine in the Raschig synthesis, is commonly determined iodometrically. Inasmuch as it is conceivable that aqueous chloramine solutions might, on standing, give decomposition products which would interfere with iodometric analysis, the present study was undertaken to determine the feasibility of analysis for monochloramine by spectrophotometric means.

According to Metcalf (*2*), aqueous solutions of monochloramine give a maximum absorption at 2450 A. and have a molecular extinction, E, of 416 at this wave length. Moreover, on the assumption that iodometric analysis gives a true measure of chloramine content, the molecular extinction (in solutions containing acetate or phosphate buffer) remains essentially constant over an extended period of time. However, Metcalf states that when the titers of monochloramine solutions fall to about one half their original values (no quantitative data are given), extinctions no longer correspond to the iodometric titers.

The authors have definitely established the adherence to Beer's law at the wave length of maximum absorption of buffered aqueous solutions of monochloramine in the concentration range of 5×10^{-4} to $3 \times 10^{-3}M$, the concentration of the chloramine being calculated by iodometric analysis. Conformity to Beer's law is observed even in solutions which had been permitted to stand for 136 hours. Moreover, possible products of the decomposition of aqueous monochloramine solutions—e.g., hydrazine, hydroxylamine, nitrate, and nitrite ions—do not absorb to any extent at the wave length of maximum absorption by monochloramine. The results, therefore, demonstrate that monochloramine may be determined spectrophotometrically.

EXPERIMENTAL

The Spectrophotometer. A Cary recording spectrophotometer, Model 11, was employed for the spectrophotometric studies. The following instrument settings were used: slit control switch at 10, chart range 0 to 2.4 and Hi-Lo knob at the Lo position. The chart drive gears were kept at "60 driving, 60 driven," which gave a chart speed of 10 seconds per division. The large scanning gear was employed and provided a scanning rate of 5 A. per second. One-centimeter cells of fused silica were used in all measurements.

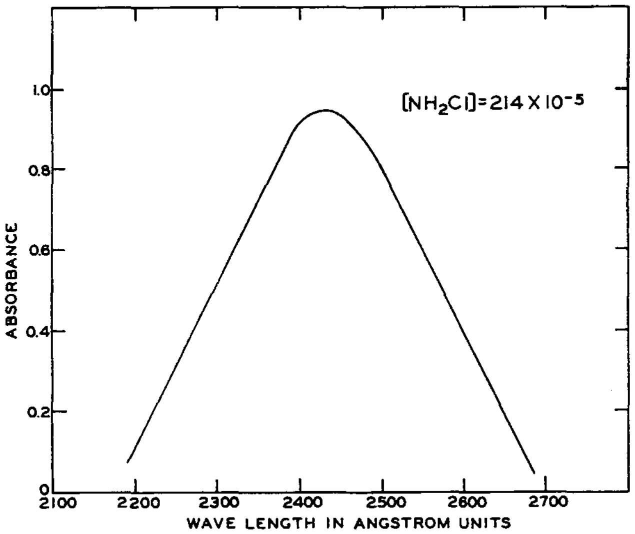

Figure 1. Absorption Spectrum of Chloramine in Aqueous Solution

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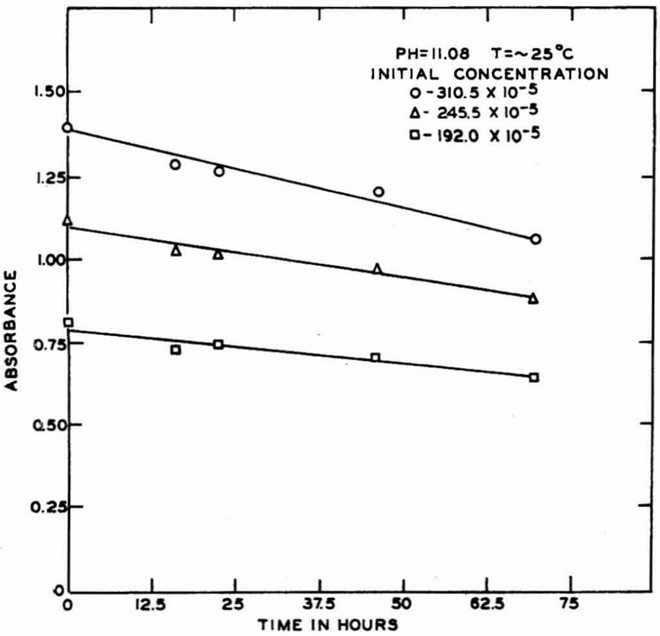

Figure 2. Decomposition of Aqueous Chloramine Solutions

Preparation of Monochloramine Solutions. All reagents and glassware were precooled in a refrigerator; the preparation of the monochloramine solutions was carried out at 0° C.

To a 500-ml. separatory funnel immersed in the ice bath, the reagents were added in the following order: 100 grams of ice, 100 ml. of 0.5*M* sodium hypochlorite solution, 100 ml. of reagent grade diethyl ether, and slightly more than 100 ml. of 0.5*M* aqueous ammonia. The resulting mixture was shaken gently and the aqueous layer was removed and discarded. To the ether layer remaining in the funnel there were added 100 ml. of cold distilled water; the monochloramine was extracted into the aqueous phase. The concentration of the monochloramine in the aqueous solution was then determined iodometrically using starch as an indicator.

SPECTROPHOTOMETRIC DATA

The absorption spectrum of monochloramine is characterized by one well defined peak with a maximum at 2430 A. (Figure 1). With 1-cm. cells this maximum appears in monochloramine solutions as dilute as $5 \times 10^{-4}M$.

A study was made of the effect of varying the pH of monochloramine solutions between values of 9 and 11 on the position of the absorption maximum and the value for the molecular extinction. To obtain solutions of appropriate pH values, buffer systems consisting of boric acid, potassium chloride, and sodium hydroxide were employed (*1*). Aliquots of an aqueous monochloramine solution were diluted with buffer to approximately the desired concentration and then the exact concentration was determined iodometrically. Buffers of pH 8.89, 9.81, and 11.08 were used. Each solution was examined spectrophotometrically with time, the appropriate buffer solution serving as a blank in each instance.

The initial monochloramine concentration in each buffer was $3.1 \times 10^{-3}M$ and the absorption maximum appeared at 2430 A. in each case, the molecular extinction values falling in the range 450 to 460. After about 5 hours the solutions were again examined spectrophotometrically and the monochloramine content was determined iodometrically. The solutions had decomposed to some extent, the greatest loss in monochloramine being observed in the solution of pH 8.89, where the monochloramine concentration had dropped from 3.1×10^{-3} to $2.8 \times 10^{-3}M$. However, the data indicated that over relatively short periods of time there is little difference in the stabilities of monochloramine solutions maintained at various pH values in the range 9 to 11. The position of the absorption maximum remained essentially constant, as did the value for the molecular extinction after corrections had been made for decomposition.

The stabilities of monochloramine solutions of various concentrations buffered at pH 11 were investigated. The initial monochloramine concentration ranged from 64.5×10^{-5} to $310.5 \times 10^{-5}M$. The experimental data for the three most concentrated solutions are shown in Figure 2, where the absorbances at 2430 A. are plotted against time. After 6 days, approximately 30% decomposition had occurred in each of the solutions. At the same time each of the solutions was being examined spectrophotometrically, the oxidizing power (assumed to be a measure of the monochloramine content) was determined iodometrically. A plot of absorbance at 2430 A. against concentration of monochloramine (as determined by iodometric titration) is shown in Figure 3. It is evident that each series of points falls fairly well on a straight line passing through the origin. This demonstrates the adherence of monochloramine solutions to Beer's law over the range of concentrations examined, and the validity of the iodometric procedure as a means for determining the concentration of monochloramine. The average molecular extinction for monochloramine in aqueous solution at the wave length of maximum absorption, 2430 A., was found to be 458.

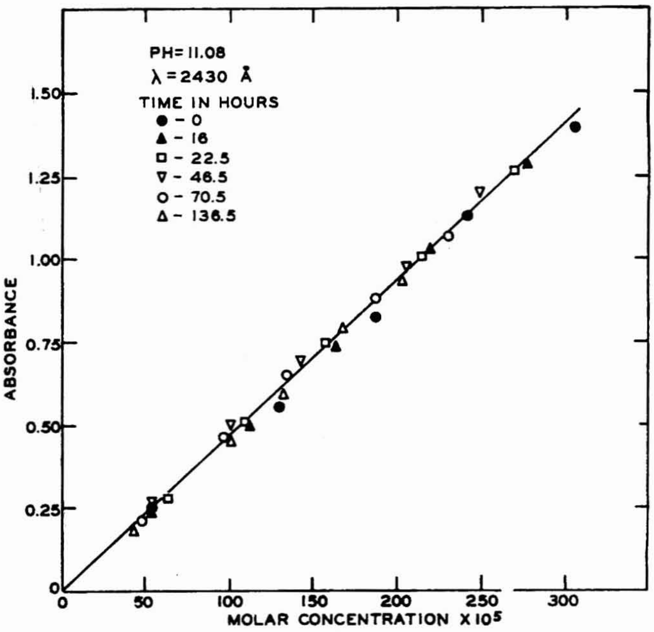

Figure 3. Conformity of Aqueous Chloramine Solutions to Beer's Law

Spectrophotometric examination of water solutions of hydrazine hydrate, hydroxylamine sulfate, sodium nitrate, and sodium nitrite showed that these substances, all possible products of the decomposition of aqueous chloramine solutions, do not absorb to any degree at 2430 A., the wave length at which absorption by monochloramine solutions is a maximum.

ACKNOWLEDGMENT

The authors are indebted to Gary Ehrlich for technical assistance.

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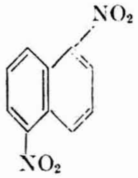
85. 1,5-Dinitronaphthalene

Contributed by WALTER C. McCRONE, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Ill., And JOHN H. ANDREEN, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.



Structural Formula for 1,5-Dinitronaphthalene (1,5-DNN)

CRYSTALS of 1,5-dinitronaphthalene from all ordinary solvents are monoclinic rods elongated parallel to *c*. Sublimed crystals are usually flattened 010 plates (Figure 1). There is no evidence of polymorphism for this compound.

CRYSTAL MORPHOLOGY

Crystal System. Monoclinic.

Form and Habit. Tablets lying on the clinopinacoid {010} showing the clinodome {011}, prism {110}, and occasionally the basal pinacoid {001}.

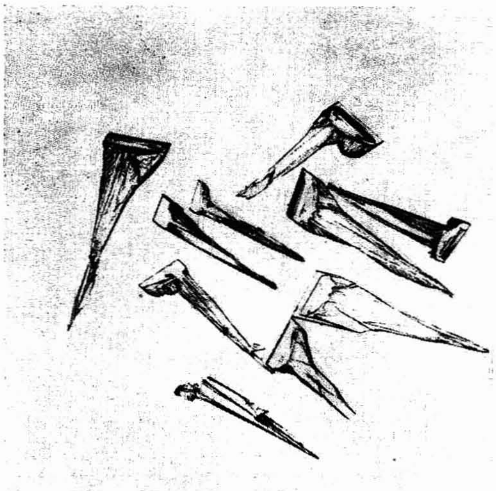


Figure 1. Sublimate of 1,5-Dinitronaphthalene from Kofler Block

Figure 2. Crystals of 1,5-Dinitronaphthalene from Melt

Axial Ratio. $a:b:c = 0.482:1:0.227$.

Interfacial Angles (Polar). $110 \wedge \bar{1}10 = 130° 8'$. $011 \wedge 01\bar{1} = 155° 14'$.

Beta Angle. 105.5°.

X-RAY DIFFRACTION DATA

Cell Dimensions. $a = 7.85$ A.; $b = 16.26$ A.; $c = 3.70$ A.

Formula Weights per Cell. 2 (2.004 calculated from x-ray data).

Formula Weight. 218.16 (218.6 calculated from x-ray data).

Density. 1.595 (flotation in CH_2I_2 and benzene); 1.592 (x-ray).

Principal Lines

d	I/I_1	*d*	I/I_1
8.12	9	2.36	1
7.60	1	2.28	5
6.87	9	2.22	3
5.53	9	2.18	1
4.40	1	2.14	6
4.24	1	2.06	2
4.06	8	2.02	2
3.79	2	1.994	3
3.69	7	1.959	1
3.60	9	1.920	2
3.47	9	1.877	2
3.25	10	1.841	3
3.10	1	1.794	3
2.98	7	1.767	2
2.88	2	1.718	1
2.75	3	1.684	1
2.69	3	1.628	2
2.64	3	1.554	2
2.57	2	1.519	2
2.47	1	1.486	1
2.40	5	1.438	1

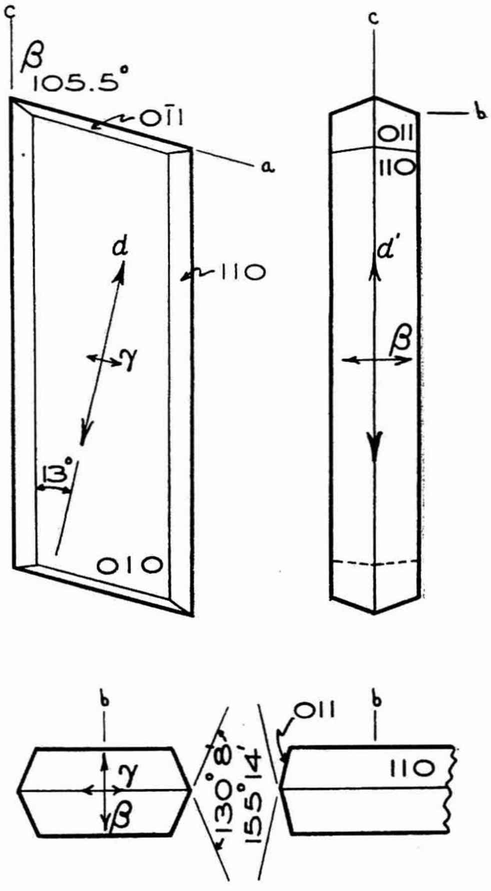


Figure 3. Orthographic Projection of a Typical Crystal of 1,5-Dinitronaphthalene

OPTICAL PROPERTIES

Refractive Indices. (5893 A.; 25° C.). $\alpha = 1.513 \pm 0.002$. $\beta = 1.755 \pm 0.005$. $\gamma = 1.817 \pm 0.005$.

Optic Axial Angles (5893 A.; 25° C.). $2H = (-)56°$. $2V = (-)48°$ (calculated from β and $2H$); $2E = 90°$

Dispersion. $r > v$, strong.

Optic Axial Plane. 010.

Extinction. $\alpha \Lambda c = 13°$ in obtuse β.

Molecular Refraction (R) (5893 A.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.690$. R(calcd.) = 54.1; R(obsd.) = 55.1.

FUSION DATA. 1,5-dinitronaphthalene sublimes easily in the Kofler block to give characteristic plates lying on the clinopinacoid (Figure 1). On further heating, melting occurs at 216–217° C. The melt does not supercool more than a few degrees and crystallization is very rapid. Using oil immersion, many crystals grown from the melt show optic axis and even BXa figures with $2H = (-)56°$, $r > v$ strong (Figure 2).

ACKNOWLEDGMENT

Much of the work described above was performed under a 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 progress of this work.

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.

MEETING REPORT

Society for Applied Spectroscopy

THE Society for Applied Spectroscopy held its ninth annual meeting in New York, May 27 and 28. In addition to an exhibit of spectroscopic instruments, a group of papers on the theme of "Frontiers in Spectroscopy" was presented.

Isotope Analysis by Emission Spectroscopy. J. R. MCNALLY, JR., Oak Ridge National Laboratory, Oak Ridge, Tenn.

This paper covers applications of high resolution spectroscopy to the determination of isotropic concentrations in materials. Material was presented on the source and instrumental problems associated with this field of analysis, and illustrations were given of the precision obtainable and the future potentialities in this field.

An RF Linear Decelerator Spectrometer. WALT DONNER, Mass Spectrometry Research, Beckman Instruments, Inc., Fullerton, Calif.

An RF linear decelerator mass spectrometer was described, featuring resolution to 100 and a dynamic range of 2000 to 1.

Ions are formed by electron impact in a somewhat conventional ion chamber, utilizing an electron beam at right angles to the ion beam, temperature regulation, and pressure differential for high signal to background ratio. All of the ions are then accelerated through 2500 volts, collimated, and then passed through a series of 24 RF gaps, spaced such that the preferred (or resonant) particles are decelerated by an amount equal to the peak RF voltage at each gap, all other particles emitting from the RF analyzer with correspondingly higher energies. The resultant "energy dispersed" beam is then separated in an electrostatic deflection system, the preferred (lowest energy) beam being collected in a Faraday bucket, and observed on a vibrating reed electrometer. A linear mass scan is achieved by varying the frequency applied to the gaps.

Typical mass spectra and stability figures were given.

Reflection of Infrared Radiation from Free Liquid Surfaces. E. D. MCALISTER, Eastman Kodak Co., Rochester, N. Y.

Simple modifications of a commercially available double-beam spectrophotometer employing a sodium chloride prism provide full scale readings for 5 or 10% reflection with signal to noise ratios of about 100 to 1. This expedient enables detailed study of the anomalies in reflectivity corresponding to regions of high absorption coefficient even though the reflectivity is only 1 or 2%.

The possibility of measuring the absorption coefficient (when large enough to cause an appreciable anomaly in reflection) by measuring the reflectivity for two different angles of incidence was discussed. Some suggestions concerning the nature of surface layers of molecules and of surface contaminations given by these studies were discussed. Typical spectrograms were shown.

Sensitivity of Detection of Deuterium Oxide by Infrared Absorption Spectroscopy. W. A. PATTERSON.

This paper describes some preliminary experiments on the detection of heavy water in ordinary water, using the Baird Associates infrared spectrophotometer.

Using 0.5-mm. calcium fluoride cells, the differential method of infrared analysis, a reversed cell technique, and wide fixed slits, deuterium as an additive in water can be readily detected in percentages as low as 0.01% with a probable precision of ±0.001%. Under present conditions an ultimate sensitivity of 0.003% deuterium oxide seems probable. The determination of ultimate sensitivity has been restricted by bad scattered light conditions when spectrophotometric slits are widened. If this scattered light problem can be solved, an ultimate sensitivity of 0.001% deuterium oxide does not seem out of the way.

Importance of Collision Process in Spectrochemical Analysis. LESTER W. STROCK, Sylvania Electric Products, Inc., Bayside, L. I., N. Y.

The departure of calibration curve slopes from unity has been interpreted as due to excitation energy exchange on collisions between atoms in different states of excitation. The extent to which the phenomenon affects spectrochemical results was illustrated by typical but actual calibration curves based on synthetic silicate standards.

The critical role of a varying sample matrix was pointed out. An attempt was made to account for the effect of the collision process in the intensity equation.

New Multichannel Direct-Reading Spectrograph. FREDERICK BRECH, FRED A. MCNALLY, AND LOREN P. NEAL, Jarrell-Ash Research Laboratory.

A multichannel direct-reading spectrograph based on the Wadsworth mount was described. Spectra are displayed on two levels on each of which several fixed position exit slits and photomultipliers may be located. By this arrangement, two detector tubes may be sited on two lines with a small wave-length separation without the use of optical separator elements. With the circuits employed, the signal from each photomultiplier is converted to fixed amplitude pulses whose frequency is proportional to the signal strength. The working curve for each channel is displayed on a separate dial face the rotation of which from a fiduciary position may be employed when necessary to compensate for a shift of the working curve.

Details of the instrument and sample analyses performed with it were discussed.

Raman Spectrometer Assembled from Available Components. S. M. DAVIS, R. F. STAMM, G. L. ROYER, AND H. C. LAWRENCE, American Cyanamid Co., Bound Brook, N. J.

A photoelectric Raman recording spectrometer has been assembled from commercially available optical and electrical components.

The light source is a Toronto-type mercury arc supplied by Applied Research Laboratories. The arc controls and housing were built in our shop. The sample tubes, filter jacket, and condensing lens system have been described by one of the authors. The monochromator started with a Perkin-Elmer Model 12 spectrometer equipped with a 60° light flint glass prism and off-axis parabola. The standard Littrow mirror was replaced by a plane diffraction grating whose dispersion augments that of the prism. The slits were modified to correct for the curvature caused by the prism. An RCA 1-P-21 photomultiplier was mounted inside the monochromator directly behind the exit slits. The standard Perkin-Elmer 13-cycle chopper and Model 81 amplifier modified to have 1-, 2-, 5-, and 12-second time constants were used. The output from this is recorded on a standard L&N Speedomax recorder which had been modified with an automatic range changing device supplied by Warren Electronics.

Some performance data were given.

Progress of the X-Ray Spectrograph. F. A. BEHR, North American Philips Co., Inc.

The advent of the x-ray spectrograph into the analytical field is not new. The method was thoroughly studied and widely applied a generation ago. However, the instrument has been commercially available for only a few years.

Research and commercial control have found the method useful and its acceptance has been rapid. Several hundred units are in use at the present time and there is a rapidly growing wealth of information available touching on such factors as fields of applicability, techniques, and analyses of data. These points were summarized.

The future progress of the method can be predicted in the light of the past progress, the inherent features, and the known lines of instrumentation changes in design and contemplation. There are certain limitations imposed by the basic physics involved, and the practical limits that these impose are becoming evident.

Analysis of Nonferrous Alloys by the X-Ray Spectrograph. Garton L. Crumrine, North American Smelting Co.

A brief review of the analysis of aluminum-base, copper-base, and lead-tin base alloys was given. The methods now in use in production control and comparative results with wet chemical methods were presented.

Determination of Metallic Elements in Nonmetallic Matrices. A. A. Shurkus, Applied Research Laboratories.

The determination of metallic elements in nonmetallic matrices has been studied, using both emission spectroscopy and x-ray fluorescence. This paper compared the results obtained using these two supplementary methods.

New Spectrophotometer for Use with Volumes of 0.01 to 5 Ml. Frederick Brech and David Glick, Jarrell-Ash Co., Newtonville, Mass., and Department of Physiological Chemistry, University of Minnesota, Minneapolis, Minn.

A double-beam instrument was described for use in the ultraviolet and visible regions between approximately 200 and 700 mu. A grating monochromator with a reciprocal dispersion of 4.4 mu per mm. provides two beams, each focused on a separate exit aperture. One beam passes through a cuvette containing the sample and the other passes through a reference cell. A rotating alternator permits each beam in turn to fall on the same area of a single photomultiplier, the output of which is coupled to a logarithmic amplifier. This provides a signal of the form log A/B which is displayed on a meter graduated linearly with optical density, and also carrying transmission scales. A feature of the instrument is that it employs special cuvettes with a 1-cm. light path having volumes of 0.010-ml. microcuvettes of this type with light paths up to 5 cm. can be accommodated. Macrocuvettes with light paths from 1 to 5 cm. having volumes of several milliliters can also be used. Examples of the use of the instrument in biochemical and histochemical research were detailed.

Applications of the Microvolume Technique to Emission Spectrochemistry and Metallurgy. J. K. Hurwitz, Mines Branch, Ottawa, Ontario, Canada.

There has been a growing metallurgical interest in segregation of alloying constituents and trace elements in casting and in the study of solid-state diffusion phenomena. To obtain the necessary analytical data, a rapid quantitative spectrographic technique has been developed. In principle, the specimen is moved over a spark discharge while the photographic plate is lowered so that each point on the spectrum corresponds to the analysis of a point on the specimen. A theory has been developed which takes into consideration the effects of the measurable instrumental variables and predicts quantitatively the observed intensity changes in the spectrum when a region of rapidly changing composition is traversed. The practical significance of this theory was indicated. Illustrative examples of the analysis of segregates were given, and an outline of the method to be applied to specimens in which diffusion has occurred was described. The results of a prespark-effect investigation in the spectrochemistry of zinc-base alloys indicate a procedure by which this effect may be eliminated. Future developments in the microvolume technique were discussed.

Illumination of the Spectrograph. R. H. Bell, Lucius Pitkin. Inc.

The selection of a suitable lens system for the illumination of the spectrograph was discussed, particularly in relation to the proper "sampling" of the light source and the ways in which the practical resolving power of the spectrograph is affected. Results of tests on the use of ground diffusion screens, and gratings, both transmission and reflection, were presented. It is believed that the proper illumination of the spectrograph should be given much more consideration than it has been given previously.

Evacuable Die for the Pressed Potassium Bromide Technique Harry Hausdorf, The Perkin-Elmer Corp., Norwalk, Conn.

In February 1953 a general paper on this invaluable technique was presented at the Society for Applied Spectroscopy. Since, the author had the opportunity to compare various types of dies for pressing potassium bromide and sample into thin transparent disks. The experience gained during this evaluation period led to the choice of a design of a special evacuable die which provides optimum results. This die was shown and described.

Performance of the Perkin-Elmer Model 21 in the Spectral Region 210 to 2300 mu. V. J. Coates, T. Miller, and A. Savitzky, Perkin-Elmer Corp.

The Perkin-Elmer Model 21 double-beam recording infrared spectrophotometer employs a completely achromatic optical system. The controls provided on this instrument allow the operator to vary its operating conditions over a wide range, optimizing its performance for a given problem. It might be expected that by the addition of the proper sources, prism, and detectors satisfactory performance can be obtained in the ultraviolet, visible, and near infrared portions of the spectrum, without affecting its infrared performance, which now extends to 37.5 microns.

On an experimental basis, a standard instrument has been converted for operation in this region while maintaining its function as an infrared spectrophotometer. The design of the various attachments and the problems involved in providing simple interchange were discussed. The performance obtained with this system was shown.

Novel Solution Excitation Apparatus for Spectrochemical Analysis of Alloys. Stuart Milliman and Hyman Kirtchik, Materials Laboratory, Development Department, General Electric Co., Evendale, Ohio.

The spectrographic analysis of a wide variety of metal alloys in the form of fabricated pieces presents sampling problems not easily overcome by normal excitation techniques. Standard points to plane methods are not practicable when the size of finished part samples falls below a minimum thickness of mass, causing excess heating of alloys containing large amounts of elements of relatively low thermal conductivity. Normal segregation in metal products may require repeated determinations or multiple super-imposed exposures to obtain representative sampling. The adjustment of excitation parameters to obtain large sparking areas is prevented in many cases by the small surfaces of samples such as nuts, bolts, washers, and gaskets. A separate analytical method for every different size group of samples is an overwhelming task when a quality control program must be maintained for a product containing many parts.

The common methods used to overcome these sampling problems are techniques of solutions, filings, grindings, powder extracts, briquets and pressed solid samples. This laboratory has investigated those of metallic acid solutions. A novel solution excitation chamber has been devised which maintains a continuous flow of liquid sample to the lower electrode of a standard high voltage spark system. It supplies a relatively large volume of sample to the analytical gap, providing high sensitivity and adequate reproducibility. The device contains no moving parts, external electrical or air line connections, and is used with any standard dual clamp excitation stand as a normal carbon rod-to-rod sparking technique. There are no critical dimensions required and construction can be finished in a day at a cost of a few dollars. The method requires that the solution be an electrolyte and its primary disadvantage of incomplete solution for certain elements is common to many solution techniques, although an unfiltered flow of fine suspensions to the analytical gap is provided.

Results of experimental techniques were discussed for the analysis of low-alloy steels, stainless steels, and titanium alloys.

50,000 Sources of Excitation. J. T. Rozsa and O. W. Uguccini, National Spectrographic Laboratories, Inc.

The variety and complexity of spectrographic excitation sources have been steadily increasing during the past decade. Since the major consideration is the output at the analytical gap, a method of classification based upon their secondary amperage is suggested for all sources. The duration of current flow per half cycle, the amplitude of the wave form, the frequency, and the unidirectional aspect afford considerable clarification and enhance the opportunity for standardization of techniques.

Applications of the Recording Spectrometer to Emission Spectroscopy. Frank B. Gray, Jr., and Victor S. Underkoffler Leeds & Northrup Co.

A brief description of the recording spectrometer was given. Representative performance data in the ultraviolet and visible region were included.

The following applications were covered:

Hydrogen-Deuterium Ratio Determinations. The parameters involved in the isotope ratio measurements were discussed as well as the application of this method to problems in the medical, biological, and chemical fields.

OH atlas for the ultraviolet. Compilation of an atlas for the complex molecular band spectra of OH in the ultraviolet has been prepared by use of this instrument.

Emission spectra showing the second positive systems of N_2. Rapid scanning at 250 A. per minute shows the band heads and an indication of the bands associated with them. Slow scanning at 5 A. per minute shows the detail within the bands themselves.

Line intensity comparison in the band spectra from flames. This reveals particularly valuable information in evaluating the temperatures of hot gases and the departure from equilibrium conditions in the combustion regions of flames.

AIDS FOR THE ANALYST

Prevention of Frothing in Fischer Assay Analysis. R. P. Hensel, Research and Development Division, Pittsburgh Consolidation Coal Co., Library, Pa.

THE Fischer assay is a standard method widely used to measure yields of coke, tar, light oil, and gas resulting from the low-temperature carbonization of coal. The method involves heating at the standard prescribed rate a 50-gram sample contained in an aluminum retort, to which a suitable collection system for the distillation products is attached. The apparatus and procedure are fully described by Fischer and Schrader [*Angew. Chem.*, **33**, 172 (1920)].

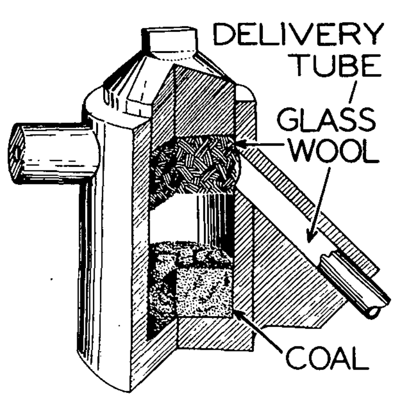


Figure 1

Serious difficulty is encountered when assays are attempted on highly swelling coals. The rapid evolution of gas combined with the extreme fluidity of the molten bed leads to excessive frothing, usually resulting in an overflow of the charge into the delivery orifice and thence to the tar trap. Selvig and Ode [IND. ENG. CHEM., ANAL. ED., 7, 88 (1935)] recommend reducing the weight of the sample to 30 grams; however, experience shows that certain coals perform unsatisfactorily with as little as 20 grams of sample, and reduction of sample size materially increases the significance of subsequent errors in handling and weighing.

Glass wool acts as an extremely effective froth breaker. A weighed loose-fitting plug of Pyrex brand No. 7220 glass wool (circa 8 grams) inserted into the retort and extending approximately 12 mm. below the delivery orifice (Figure 1) permits successful assays on a full charge of even the highest swelling materials.

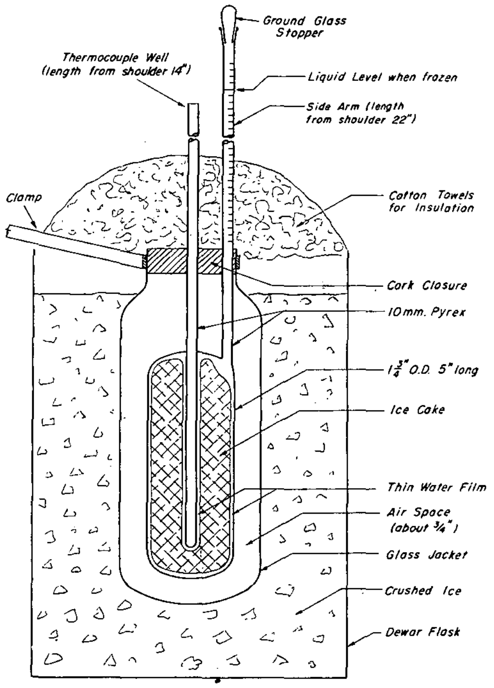
The normal procedure of weighing the coke residue directly is impractical, as some penetration of the bed into the glass wool occurs in the course of the run. Separation of this mixture is difficult; consequently, the coke residue is best determined by subtracting the initial weight of the glass wool from the combined weight of residue and wool at the termination of the run.

A Cryostat. Ernest P. Hall and William L. Nelson, Mellon Institute of Industrial Research, Pittsburgh 13, Pa.

THE cryostat depicted has been found invaluable for the maintenance of a thermocouple reference junction at 0° C. over an extended time. The cryostat was developed by J. R. Anderson, Physical Processes Department, Carbide and Carbon Chemicals Division, South Charleston, W. Va., from a design suggested by Wojciech Swietoslawski.

The cryostat consists of a glass bulb (the ice-water container) with two attached tubes, one for filling with water and indicating by the water level the condition of the annular ice-water cell and the other for the entry of thermocouples. The ice-water cell in the bulb provides a thin layer of water between the ice cake and the thermocouple well. The lower part of the cryostat (in a wide, stoppered tube) is placed within a Dewar flask, packed with ice, and wrapped with towels to extend the life of the cell.

Conductivity grade water used in the cryostat was prepared by demineralizing distilled water to less than 0.1 p.p.m. impurities (as sodium chloride). The cryostat can be prepared for use in about 1.5 hours using a modification of Swietoslawski's freezing technique [Swietowslawski, W., *J. Phys. Chem.*, **47**, 590–6 (1943)]. [The bulb is partially immersed with occasional shaking, in an air-agitated salt-ice bath until slushy ice crystals have just formed. The bulb is removed and all but about 5 cc. of these crystals are melted by warming in the hand. The bulb is again immersed in the freezing bath (the side arm being kept just out of the bath so that it does not become closed) and a solid ice cake of the desired thickness is frozen. After freezing, the bulb is again momentarily warmed in the hand, so that a very thin water film is formed between the ice cake and bulb wall. Placed in the glass jacket and paced with ice, the cryostat is now ready for use.] Maintenance (draining water and refilling the flask with ice twice daily) requires little more time than does an ordinary ice bath, the inadequacy of which as a constant reference point is well known.



Insulation and maintenance as stated greatly prolong the life of the ice-water cell. The authors have repeatedly obtained 20 days of service.

Over a period of several days in hot weather, the heat flow to the cell (as indicated by the change in the water level in the tube) was less than 69.1 cal. per day. This rate of heat influx is so low that equilibrium conditions can be maintained for many days.

CONTRIBUTION from the Coal Waste Fellowship sponsored by the Western Pennsylvania Coal Operators Association.

Simple Refractometer Cell. William G. Young and Joseph M. Rule[1], Department of Chemistry, University of California, Los Angeles, Calif.

IN DETERMINING the refractive index of many allylic halides and other corrosive liquids, it is advisable to protect the refractometer from the liquid, as the optical surface may be slowly damaged [Winstein, S., and Young, W. G., *J. Am. Chem. Soc.*, **58**,

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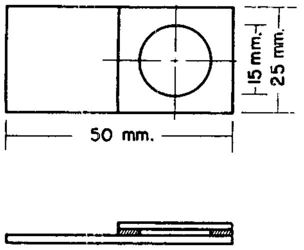
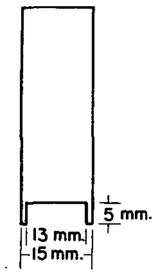
[1] Present address, Grasselli Chemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

105 (1936)]. A cell (Richards, L. M., M.A. dissertation, University of California at Los Angeles, p. 20, 1938) previously developed in this laboratory had the disadvantages of requiring several drops of liquid and of allowing rapid evaporation of low boiling materials. A new design has been developed which remedies the faults of the previous cell and has proved satisfactory for use with liquids having refractive indices in the ranges 1.30 to 1.48 and 1.54 to 1.70. Values in the intermediate range may not be determined with this cell, because the refractive index of the glass interferes. For determining refractive indices over the entire range of the refractometer, the cell must be constructed from special glass having a refractive index greater than 1.70, as was the case in the first cell.



Refractometer Cell



Lapping Tool "A"

The new cell was constructed from a corrosion-resistant microscope slide and two square cover glasses. The microscope slide was cut to length (40 mm.), and the edges were polished with the aid of 400-mesh Carborundum. A square cover glass of thickness No. 1 (0.005 inch) was cemented to a fourth piece of glass with Apiezon wax, and the unit was mounted upon the stage of a drill press. A hole (15 mm.) was lapped through the cover glass using the brass lapping tool, *A*, and 150-mesh Carborundum. The assembly was then removed from the drill press and washed with water. After drying, the unit was placed in an oven (100° C.) to soften the thermoplastic wax, and the drilled cover glass separated from its glass support. After being washed with benzene, the drilled cover glass was coated on one side with sodium silicate and then placed upon the previously cut and polished microscope slide. The two components were pressed together, and the excess silicate was removed with a cellulose cleansing tissue. The cell was placed between two large rubber stoppers and allowed to dry under pressure. After drying, any excess silicate was removed with the aid of a razor blade.

In using the cell, 2 drops of liquid were placed in the depression and a cover glass was placed over the cell. The covered cell unit was then attached to the refractometer with 1-bromonaphthalene in the same manner as a calibrating prism. The reading observed while using the cell was identical with the one obtained by placing the liquid directly upon the refractometer prisms.

This cell may be constructed with about 0.5 hour of actual labor, and the material cost is negligible.

Work made possible by research grant from General Laboratories, U. S. Rubber Co.

Improved Hydrogen Discharge Lamp. Vincent A. Campanile and Vernon Lantz[1], Shell Development Co., Emeryville, Calif.

The increase in the use of refractive dispersion for the analysis of hydrocarbon mixtures has created a need for a strong, convenient source of the hydrogen *F* and *C* spectral lines commonly employed for the measurement of this physical property. Commercially available hydrogen discharge lamps are fragile, give weak lines, and have a short useful life. A hydrogen lamp has been developed in this laboratory which represents a considerable degree of improvement in each of these respects. In addition, the new lamp incorporates a convenient means for charging with hydrogen, based on the fact that this gas can pass through palladium at red heat.

Available hydrogen lamps and other lamps described in the literature (*1-4*), produce a point source of light suitable for spectroscopic work. However, in measuring refractive dispersion of hydrocarbon liquids, the hydrogen light must be intense and cover the entire face of the refractometer prism; this is particularly required when samples are slightly colored.

To obtain strong lines from a hydrogen lamp, a high current density must exist in the discharge section of the lamp which, together with the high voltage necessary to start and maintain the current, means that considerable heat must be dissipated during operation. However, with conventional air-cooled units, the current cannot be increased to give the rather strong radiation required to measure refractive dispersion of hydrocarbon mixtures, because of limitations in heat dissipation. By providing the lamp with a water-cooled jacket it was possible to increase the current and thus the intensity of radiation appreciably. The operating current is supplied by a 115/9000-volt, 60-ma. luminous-tube transformer with the primary winding connected through a relay controlled by a pushbutton switch. In this manner, the lamp need be energized only when making measurements, thus reducing the electrical shock hazard to a minimum and adding appreciably to the life of the unit. The lamp (Rankin Glassblowing Co., 3990 Franklin Canyon Road, Martinez, Calif.) is convenient to use with either the Zeiss Pulfrich or Bausch and Lomb precision refractometers.

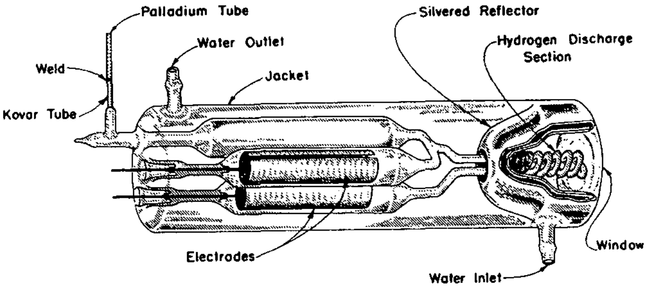


Figure 1. Improved Hydrogen Discharge Lamp

CONSTRUCTION OF LAMP

A sketch of the lamp is given in Figure 1, and Figure 2 shows the unit attached to the Bausch & Lomb instrument. The lamp consists of two electrode chambers, containing aluminum electrodes, and a reservoir connected with a 400- to 500-mm. length of 2-mm. inside diameter by 4-mm. outside diameter borosilicate glass tubing arranged in the form of a helix having an inside diameter of 10 mm. The helix is located within a Dewar-type reflector, which is evacuated and sealed after silvering. The electrode chamber and the helical radiator are sealed into a water jacket constructed of 57-mm. outside diameter borosilicate glass tubing. The end of the jacket sealed to the reflector is made flat and smooth to form a clear window to permit passage of light. The palladium tube for charging the lamp is made from a short length of 2-mm. outside diameter material of 0.016-inch wall thickness, flame-sealed on one end. The open end is butt-welded electrically to Kovar metal tubing of the same diameter, the Kovar tubing is sealed into Corning glass tubing No. 705-2, and this entire assembly is then fitted onto the evacuating tube. The completed lamp is evacuated to a pressure of less than 10^{-3} mm. of mercury and baked 24 to 48 hours before sealing.

OPERATION

To charge the lamp with hydrogen, circulation of cooling water is started and the palladium tube is heated to redness with a small hydrogen flame, being certain that no voltage is impressed on the electrodes. When the tube reaches red heat, the flame is extinguished, and a small stream of hydrogen is directed at the

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[1] Deceased.

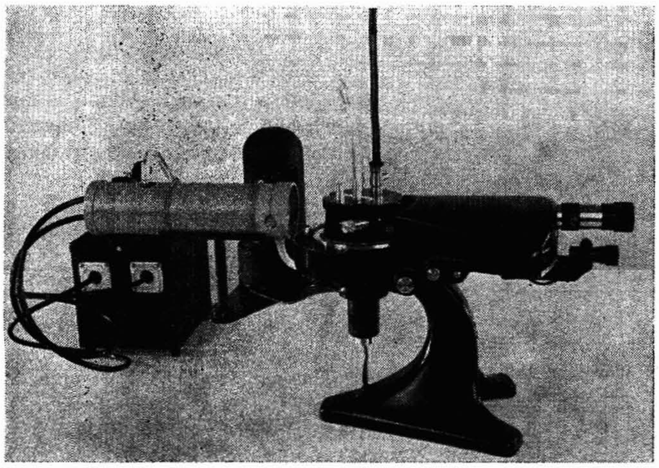

Figure 2. Hydrogen Lamp in Use with Bausch and Lomb Refractometer

hot palladium tube, allowing the gas to diffuse through the tube and into the evacuated lamp. The flow of hydrogen is continued until the lamp contains an excess of gas, as indicated by an absence of discharge when voltage is applied to the electrodes. The hydrogen pressure is then reduced by heating the palladium tube with a gas or alcohol flame, allowing hydrogen to escape from the lamp until a pink discharge is produced when voltage is applied. Care should be taken not to apply voltage to the electrodes while flaming the palladium tube.

The optimum hydrogen pressure is reached when the light and dark bands appearing in the discharge have receded to within approximately 6 to 7 cm. from the electrodes. To protect the palladium tube from possible damage and to avoid possibility of electrical shock while the lamp is in use, it should be covered with a short length of Tygon tubing. This same conditioning treatment at infrequent intervals makes possible the operation of the lamp at high intensity for years.

ACKNOWLEDGMENT

The authors wish to acknowledge their appreciation to J. H. Boyd and Edward Meyer for the construction of experimental models of the hydrogen lamp.

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All-Glass Adjustable-Head Liquid Reservoir for Flow Control. George J. Janz and Eric H. Stevens, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y.

An all-glass adjustable-head liquid reservoir has been designed whereby a liquid can be delivered at a constant metered rate to a system in which a substantial back-pressure may develop. A schematic presentation of this device and its use in practice are shown in Figure 1. The unique feature of the apparatus is an adaptation of the relatively well-known principle of a constant-head liquid reservoir to permit manual adjustment of the head as required to maintain constant flow in case of back-pressure changes in the system.

The air or inert gas used to drive the liquid through the flowmeter, *F*, is delivered through a needle valve, *B*. The liquid head in the pressure regulator, *P*, is adjusted to give the desired rate of flow through the meter; and the manometer, *M*, indicates the pressure drop across the meter.

A liquid reservoir, *R*, fits on the bottom chamber through a standard-taper ground-glass joint having an extension as shown. A center tube is held concentric by the supports, *S*, and extends slightly below the level of the outer tube. The capillary coil, *A*, is interchangeable, so that the meter can be adapted to a very wide range of flows. In operation the liquid reservoir is first filled, and the bottom chamber is inverted to seat the standard-taper joint. The flowmeter is next placed in position for use with stopcock *D* in position 1–3, so that it is at atmospheric pressure. The liquid will rise in the lower chamber to the bottom of the outer concentric tube. The stopcock is turned to position 2–3, admitting gas pressure to force the liquid through the capillary coil, *A*, into the system. When the liquid in the bottom chamber falls below the level of the outer concentric tube, gas flows up the outer concentric tube and liquid flows down the inner tube, until the level has returned to the bottom of the outer tube. This level will remain essentially unchanged until the liquid in the reservoir is depleted.

In this laboratory the apparatus was designed to handle flows of liquids at rates from 5 to 50 grams per hour over periods from 2 to 6 hours. The size of the capillary coil suitable for the desired flow rates was found by trial and error in each case. The reservoir *R*, a 200-ml. flask, was fitted to the bottom chamber, *F*, through a 24-40 standard-taper joint. The diameters of the tubing for the outer, middle, and inner concentric portions of the bottom chamber were 35, 18, and 8 mm., respectively.

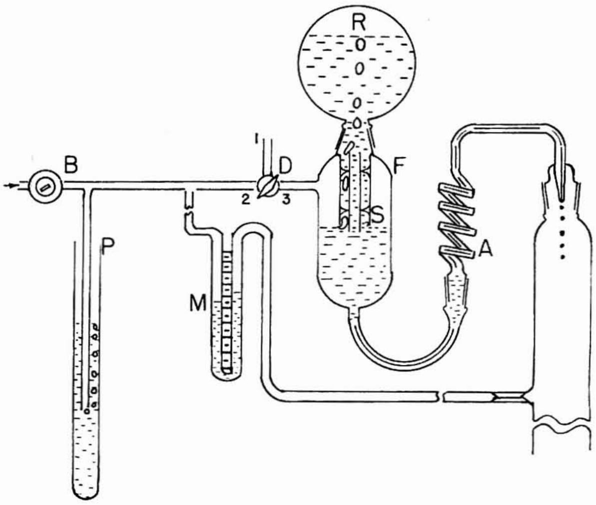


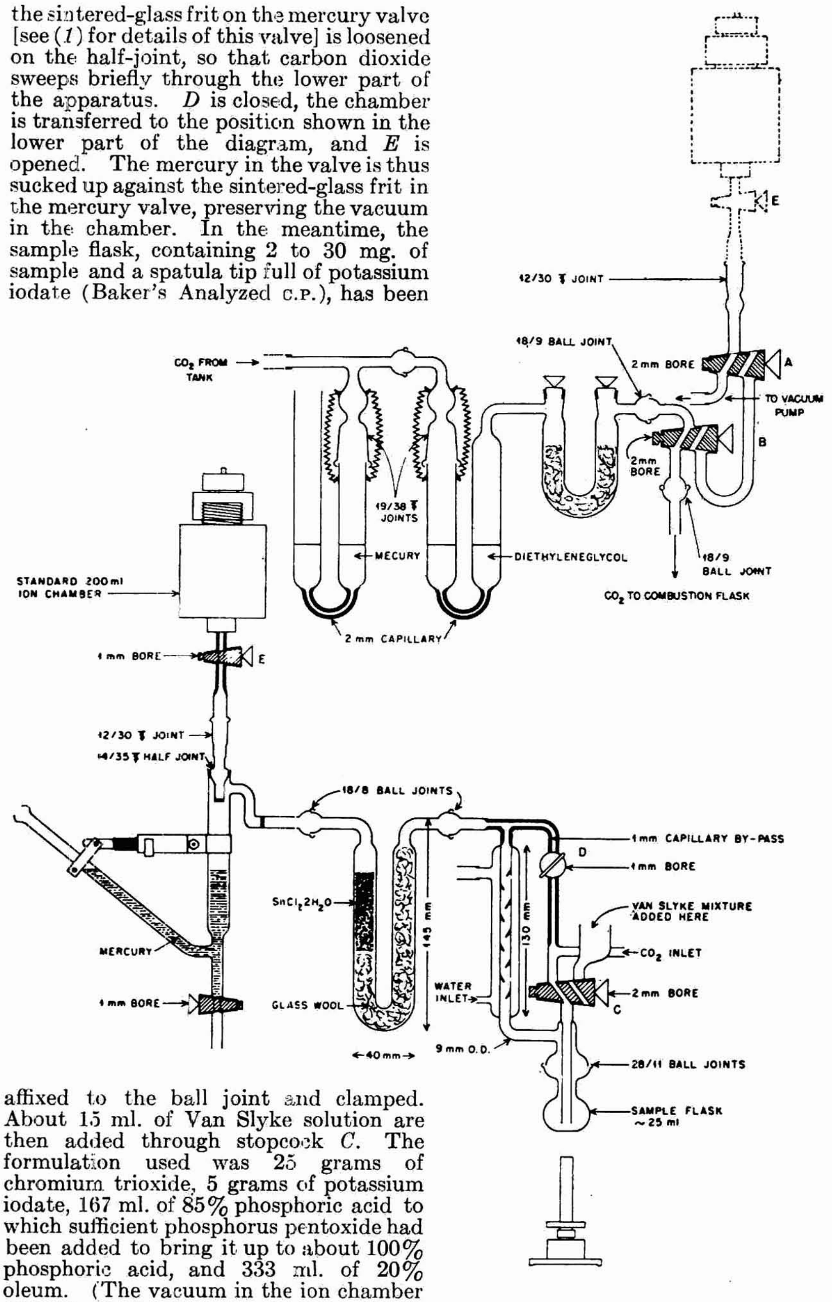
Figure 1. Liquid Reservoir

The flow rate will remain constant as long as the difference in pressure registered by the manometer is unchanged. Thus in the event of back-pressure in the system, it can be corrected by adjusting the regulator, *P*, so that the required pressure differential is maintained. This adjustment is not possible in the liquid flowmeters generally used. The present type thus is more reliable where flowmeter calibration charts are to be used for accurate data on the liquid input rate.

Apparatus for Wet Combustion of Organic Compounds Containing Carbon-14. John G. Burr, Jr., Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

The method reported is currently used at the Oak Ridge National Laboratory for the wet combustion of organic compounds containing carbon-14 to carbon dioxide preparatory to assay. This method was originally described by Neville (*1*), but the apparatus has been refined since that time.

The ion chamber is placed in the position shown by the broken line in the upper part of the diagram. By manipulation of stopcocks *A* and *B*, the chamber is alternately evacuated and filled with tank carbon dioxide, which enters through the train shown in the upper part of the diagram; this train consists, in order, of a pressure regulator, a bubble counter, and a U-tube filled with glass wool. This procedure removes from the chamber any previous sample of radioactive carbon dioxide. After final evacuation of the chamber, stopcock *E* is closed and stopcocks *A* and *B* are turned so as to fill the stem of the chamber with carbon dioxide. Stopcocks *B* and *D* are then turned and the sintered-glass frit on the mercury valve [see (*1*) for details of this valve] is loosened on the half-joint, so that carbon dioxide sweeps briefly through the lower part of the apparatus. *D* is closed, the chamber is transferred to the position shown in the lower part of the diagram, and *E* is opened. The mercury in the valve is thus sucked up against the sintered-glass frit in the mercury valve, preserving the vacuum in the chamber. In the meantime, the sample flask, containing 2 to 30 mg. of sample and a spatula tip full of potassium iodate (Baker's Analyzed C.P.), has been affixed to the ball joint and clamped. About 15 ml. of Van Slyke solution are then added through stopcock *C*. The formulation used was 25 grams of chromium trioxide, 5 grams of potassium iodate, 167 ml. of 85% phosphoric acid to which sufficient phosphorus pentoxide had been added to bring it up to about 100% phosphoric acid, and 333 ml. of 20% oleum. (The vacuum in the ion chamber draws in the liquid.)



With stopcocks *C* and *D* closed, the sample flask is heated with a free flame until the freely boiling mixture stops foaming and the bubbles become dark and coarse. The burner is removed and the mixture allowed to stop boiling. Stopcock *C* is then opened completely and a vigorous stream of carbon dioxide is admitted through *B* and *C* until the ion chamber is at atmospheric pressure as shown by the level of the mercury in the side arm of the valve. Stopcock *E* on the ion chamber is then closed, and ion chamber is removed from the valve. The sample flask is immediately removed (with gloved hands), and the contents are poured into running water. The flask is rinsed with water and dried with acetone and air; it is then ready for another sample.

Corrosion of the mercury in the valve and subsequent clogging of the frit are largely prevented by filling one arm of the U-tube in the lower part of the drawing with stannous chloride dihydrate (*3*). Samples very high in nitrogen (like dinitrophenylhydrazones) form an excessive amount of nitric acid upon combustion; this acid may be removed if a standard lead dioxide mortar (*2*) is inserted in the system just following the stannous chloride trap.

The advantages of this apparatus over Neville's earlier one lie in provision for an easily removable frit in the mercury valve; the use of stannous chloride dihydrate in the combustion line trap (this greatly extends the usable period of the mercury valve frit); increased flexibility provided by the use of ball joints; an improved form for traps, pressure regulators, and bubble counters which eliminates the possibility of sucking back of the trap liquids; and a more compact and rugged arrangement of parts.

The radioactivity in the ion chamber is measured as described by Raaen and Ropp (*3*).

ACKNOWLEDGMENT

The apparatus described has evolved from the work and suggestions of a large number of people. These include O. K. Neville, A. R. Jones, G. A. Ropp, A. J. Weinberger, D. N. Hess, V. F. Raaen, C. J. Collins, W. A. Bonner (Stanford University), W. G. Brown, (University of Chicago), and H. W. Davis (University of South Carolina).

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Two-Point Converter for Single-Point Recorder.

Ernst P. Hall and William L. Nelson, Mellon Institute of Industrial Research, Pittsburgh 13, Pa.

AN INEXPENSIVE device for externally converting a curve-drawing thermoelectric recorder from single-point to two-point recording has been developed and used to record two temperatures on the same recorder chart. Two-point operation is achieved by a system of automatically switching from one thermocouple pair to another on a timed cycle, identifying each thermocouple pair by the length of line on the recorder chart (dot-dash for a two-point recorder).

The converter is constructed as shown in Figure 1 by mounting the blades of a double pole–double throw knife switch on an insulating block, so that they short between the two sets of light spring brass contacts as they move from one pair of contacts to the other. The solenoid (Guardian 4ACI, 110 volts) and return spring are mounted so that the switch will be moved from position *A* to position *B* by energizing the solenoid, and returned to position *A* by the return spring when the solenoid is de-energized. The solenoid is controlled by a timer-operated microswitch. A war surplus 4 r.p.h. timer motor (similar to Synchron No. BH 889) is fitted with a brass disk or cam and the microswitch is attached so that a notch cut in the periphery of the cam will permit the microswitch to open as the timer motor rotates the notch past the microswitch plunger.

The over-all operation is shown by Figure 1. As the timer rotates cam section *A* (cutout) past the microswitch, the solenoid circuit is opened and the return spring pulls the switch blades to contacts *A*, connecting thermocouple *A* to the recorder. When cam section *B* is rotated past the microswitch, the solenoid is energized, pulling the switch blades away from contacts *A* (momentarily shorting contacts *A* with contacts *B*) to contacts *B*, connecting thermocouple pair *B* to the recorder. In this manner the temperatures indicated by thermocouples *A* and *B* are alternately recorded on the recorder chart.

A means of identifying the switch position on the recorder chart is usually necessary, and this may easily be accomplished by varying the lengths of cam segments *A* and *B*. As shown,

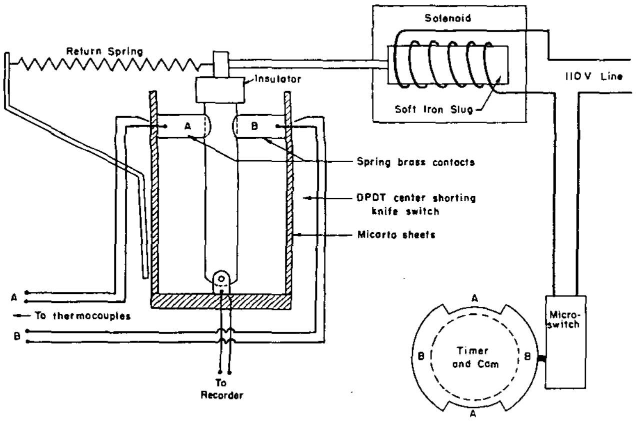


Figure 1

the recording cycle of 7.5 minutes (two cycles per timer cam revolution) is divided 2.5 minutes on thermocouple *A* and 5 minutes on thermocouple *B*, resulting in an identifiable dotted line for temperature *A* and a dashed line for temperature *B* on the recorder chart. In some cases where sudden changes or rapid cycling in temperatures are to be recorded, the over-all length of the recording cycle may be objectionable. Shortening the cycle (by using a motor of higher revolutions per hour or cutting a different cam) will minimize this objectional feature; however, for a strip chart speed of 1 inch per hour on the average recorder, it is recommended that the shortest time interval or dot be about 1 minute and that the dash be at least twice as long as the dot.

No difficulties have been encountered from contact resistance or contact potential at the converter switch. The center shorting feature of the converter switch is necessary to prevent the recorder from "wandering free" in the brief time interval between contacts.

The substitution of a ratchet-driven rotary switch (shorting type) with appropriate timer and cam changes should permit recording three or more temperatures with a recorder designed for single temperature recording.

CONTRIBUTION from the Coal Waste Fellowship sponsored by the Western Pennsylvania Coal Operators Association.

Improved Hydrogen Discharge Lamp for Use in Refractometry.

R. W. King and A. E. Hirschler, Research and Development Department, Sun Oil Co., Norwood, Pa.

REFRACTIVE dispersion is a physical property frequently used in the petroleum industry for hydrocarbon-type analysis. It is usually defined as the difference between the refractive index of the sample for the blue (*F*) line of the hydrogen spectrum and the refractive index for the red (*C*) line. For many years such refractive dispersions were measured using a conventional Abbe refractometer with Amici compensating prisms and white light, the compensator orientation at total achromatization being a measure of dispersion. However, the Zeiss Pulfrich and the recently introduced Bausch & Lomb precision refractometers, if provided with a suitable source of illumination for the *C* and *F* lines of the hydrogen spectrum, can be used for more accurate dispersion measurements than those obtained by the method of compensator readings.

The principles of the hydrogen discharge tube are so well known (*3, 4*) that the description of another model would be superfluous if it did not offer certain advantages over other types. The lamp described combines a simplification of the design of Campanile and Lantz (*2*) with a continuous-flow method of operation described by Arnold and Donn (*1*). It uses a relatively low current source, is water cooled, exceptionally rugged and easily constructed, and produces a hydrogen spectrum of high purity. It may be operated continuously for long periods without attention. Its advantage over commercially available types is most pronounced when refractometric measurements are made at irregular intervals, for no time need be wasted in preliminary manipulations before the arc is struck. These tubes have been used successfully for several years in this laboratory as a source of illumination for the routine measurement of dispersion.

CONSTRUCTION OF TUBE

A scale drawing of the tube is shown in Figure 1. It is constructed entirely of borosilicate glass and is about 8 inches long and 2.25 inches in diameter. It consists of two electrode chambers connected by a length of tubing 2 mm. in inside diameter, arranged in the form of a spiral, the entire assembly being inserted in a water jacket. The electrodes are fabricated of pure aluminum sheet as shown in *A*, Figure 1. The aluminum blank is first crimped to a piece of tungsten wire and then bent into cylindrical shape. The external contacts for the power supply are constructed as shown in *B* (Figure 1), and are sealed in place with de Khotinsky cement.

During assembly of the lamp, it is important that the lower end of the discharge section be placed as close as possible to the flat window at the end of the water jacket. The external surface of the jacket is silvered to the dashed line in order to increase the intensity of the illumination, and the entire tube, with the exception of the window and electrode terminals, is given a coat of flat black lacquer.

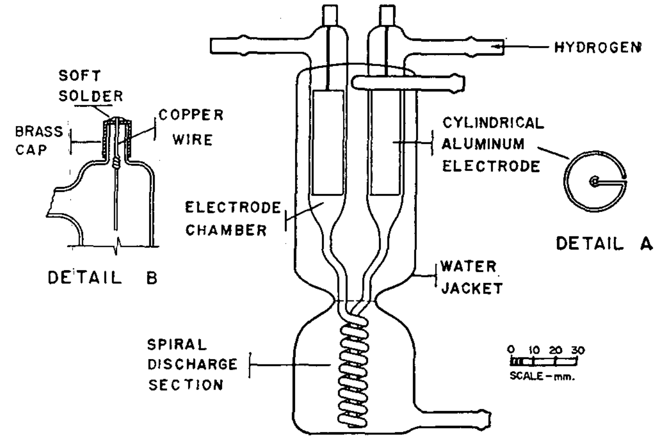


Figure 1. Hydrogen Discharge Lamp

In construction of the tube, care must be exercised to prevent foreign particles from adhering to the inside of it or to the electrodes, as such impurities affect the quality of light obtained from the finished lamp.

OPERATION AND USE

The useful life of any sealed discharge tube of reasonable volume is necessarily short because of absorption of the hydrogen by the electrodes. Consequently, such tubes must frequently be recharged.

To avoid this inconvenience, a slow stream of hydrogen is passed continuously through the tube at about 3 mm. of mercury pressure. The arrangement of the accessories for operating the lamp in such a manner is shown in Figure 2. The hydrogen is supplied by a pressure cylinder fitted with a conventional regulator and needle valve. The three-way stopcock permits the vacuum on the pump to be broken without affecting that in the tube. The hydrogen and vacuum lines are lengths of Tygon tubing. Tygon was found to be superior to rubber tubing for this purpose, and imparts more flexibility than would be obtainable with an all-glass system.

To eliminate any possiblity of electrical shock, it is advisable to ground the hydrogen cylinder and vacuum pump thoroughly. Details of the operation of such an arrangement have been described (*1*). In brief, screw clamps *A* and *B* are adjusted to give the desired pressure and rate of flow of hydrogen, and the lamp electrodes are energized by connecting them across the secondary of a 9000-volt, 60-ma. transformer. A lavender light is produced, which may be easily adjusted to maximum intensity by manipulation of the screw clamps. The vacuum pump runs continuously while the tube is in use. When operated in this manner, the lamp is capable of producing illumination of a little over 2 candlepower.

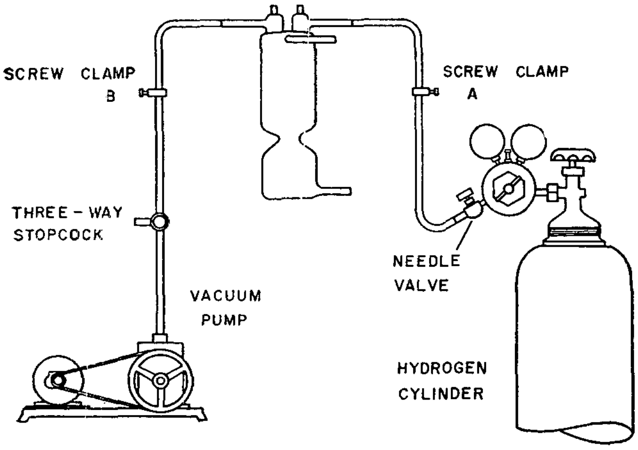


Figure 2. Arrangement of Accessories for Operating Lamp

The tube described has been used for several years for precise measurements of refractive index using a hollow prism spectrometer, the Bausch & Lomb precision refractometer, and the Zeiss Pulfrich instrument. In use with refractometers, the lamp should be placed in such a position that the spiral discharge section is perpendicular to the face of the illuminating prism or to the axis of the mirror used on the refractometers. When desired, Corning filter No. 2404 may be used to isolate the hydrogen red line at 657 mμ, and Wratten filter No. 45 will serve to isolate the blue line at 486 mμ.

LITERATURE CITED

(1) Arnold, G. B., and Donn, L., Anal. Chem., **19**, 666 (1947).
(2) Campanile, V. A., and Lantz, V., *Ibid.*, **26**, 1394 (1954).
(3) Hogness, T. R., Sidwell, A. E., and Zscheile, F. P., *J. Phys. Chem.*, 41, 379 (1937).
(4) Munch, R. H., *J. Am. Chem. Soc.*, 57, 1863 (1935).

Glass and O-Ring Vacuum Valves.

George W. Preckshot and Vernon E. Denny, Department of Chemical Engineering, University of Minnesota, Minneapolis, Minn.

Need for apparatus cleanliness prompted the design of a glass O-ring type of value suitable for use under pressures ranging from high vacuum to about 1 atmosphere. The value is particularly useful where liquids are also present and where metals and stopcock and valve greases interfere with experimental results. The O-ring is selected for the known conditions of operation and may be made of rubber, neoprene, silicone rubber, or Teflon. These valves are leakproof, lubricant-free, rapid-operating, of large bore, and particularly adapted for vacuum work.

Operation. Pictured in Figure 1 are two types of these valves, connected to a vessel and shown in cross section, disassembled.

a is the simplest type of discharge valve. *b* is a closure valve used between vessels or as a discharge valve where recovery of the liquid is necessary. Operation of the valves is identical.

Valve *a* consists of a cylinder, *A*, containing O-rings in its larger section and a piston, *B*, containing the open tubulation and triangular ports on the left half. The valve is assembled by inserting the open end of piston *B* into cylinder *A* through the O-rings until the spring hooks on the piston rest against the open end of *A*. This puts the triangular ports to the left of the leftmost O-ring and closes the valve. The valve may be opened partly or fully by withdrawing *B* a smaller or greater distance, such that the triangular ports are partly or totally to the right of the rightmost O-ring.

Assuming that the vessel is evacuated and the valve is suddenly opened, the flow of air will be from the outside through the angular space between the solid portion of *B* and the cylinder walls of *A*. The gas flow then is through the triangular ports of *B* into the tubular section and through the tubular section into the vessel.

The operation of valve *b* is made easier by a screw arrangement which permits fine adjustment of piston *B* into cylinder *A*. The left set of O-rings effects a seal between the vessel and the branch arm. The right set effects a seal between the branch arm and the atmosphere.

Construction. The simplest valve to construct is shown in Figure 1, *a*.

Cylinder *A* is made of a section of borosilicate glass tubing joined between two pieces of tubing of smaller diameter. The inside diameter of the larger tube minus the outside diameter of the inner tube may be chosen 1 mm. less than twice the diameter of the O part of the O-ring for the desirable seals. The tubing of larger diameter is made roughly 0.5 to 0.75 inch long to contain two to three O-rings. Two-part glass spacers may be used to reduce the number of O-rings or to maintain alignment. The O-rings can be slipped into place conveniently through the shorter section of the smaller tubing.

Piston *B* is made from tubing and rod having an outside diameter 0.5 to 1 mm. smaller than the inside diameter of cylinder *A*. It is fabricated by joining a short section of tubing to the rod. Four V-notches are cut into the open end of the tubing, then a desired length of the same tubing is sealed to the open ends of the V-notches. Care must be taken to make good coaxial seals. The sharp edges of the V-notches are carefully fire-polished. Circular ports may be carefully blown or drilled into the open tube of the piston, if the careful throttling action of the V-ports is not required. Hooks are provided for springs for operation at pressures above 1 atmosphere.

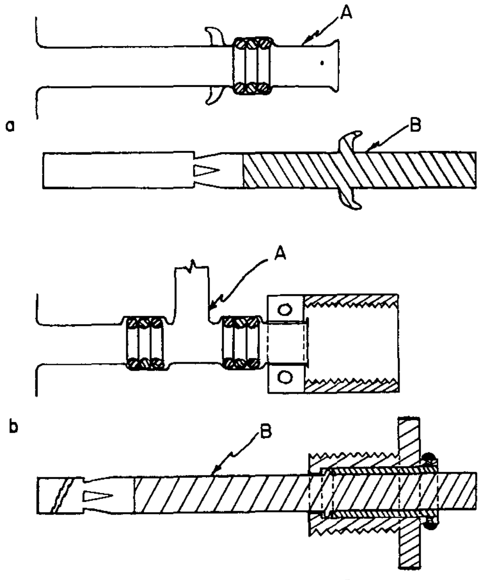


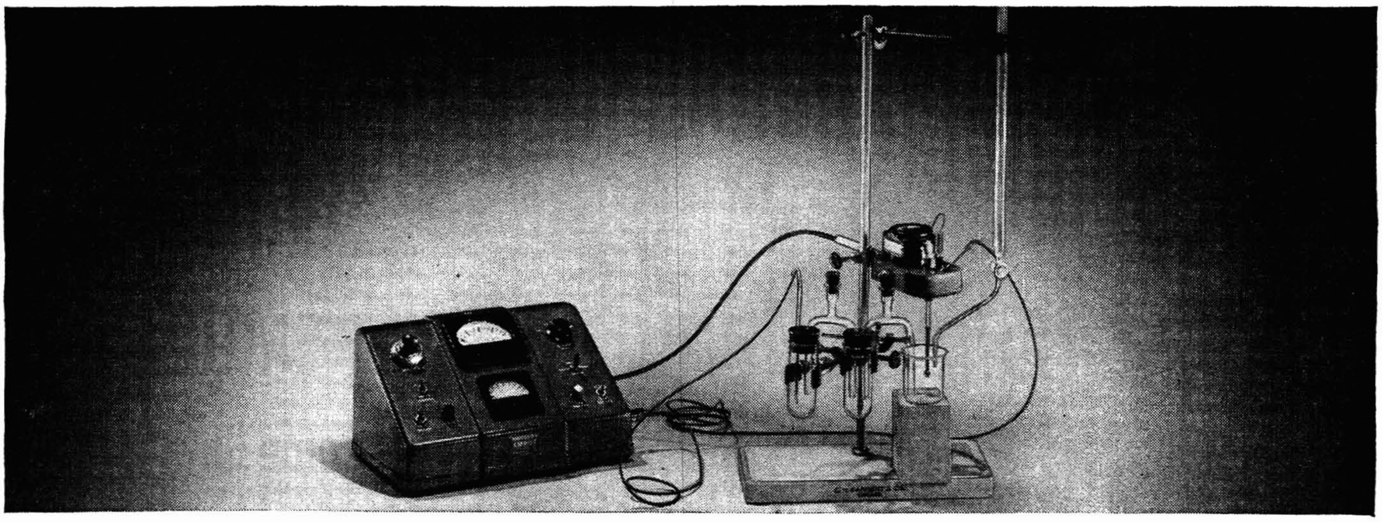
Figure 1. Vacuum Valves

The more complicated type of valve is shown in Figure 1, *b*.

The cylinder section, *A*, contains two such sections of O-rings, between which is attached the discharge tube. Beyond the rightmost of these O-ring sections is a coaxial brass tube fastened to *A* with a gasketed split flange. The tube contains 0.75 to 1 inch of thread to accommodate the male valve operating wheel attached to *B*.

The construction of *B* is similar to that described in the previous paragraph. The knurled operating wheel slips over the open end of *B* and engages against the left side of the slightly raised shoulder. Two screws through the hand wheel secure a follower which bears on the right side of the glass shoulder and permits the rotation of the piston within the valve handle but does not allow it to slip off. This arrangement permits more careful movement of the piston in its cylinder and thus facilitates better valve operation.

Amperometric Titrations



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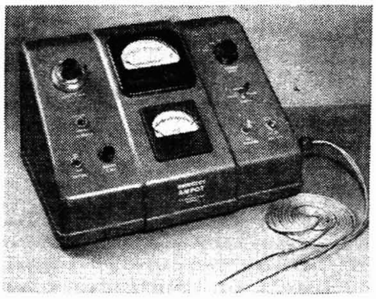

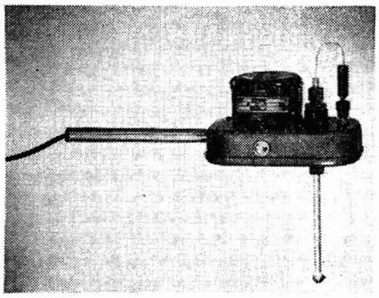

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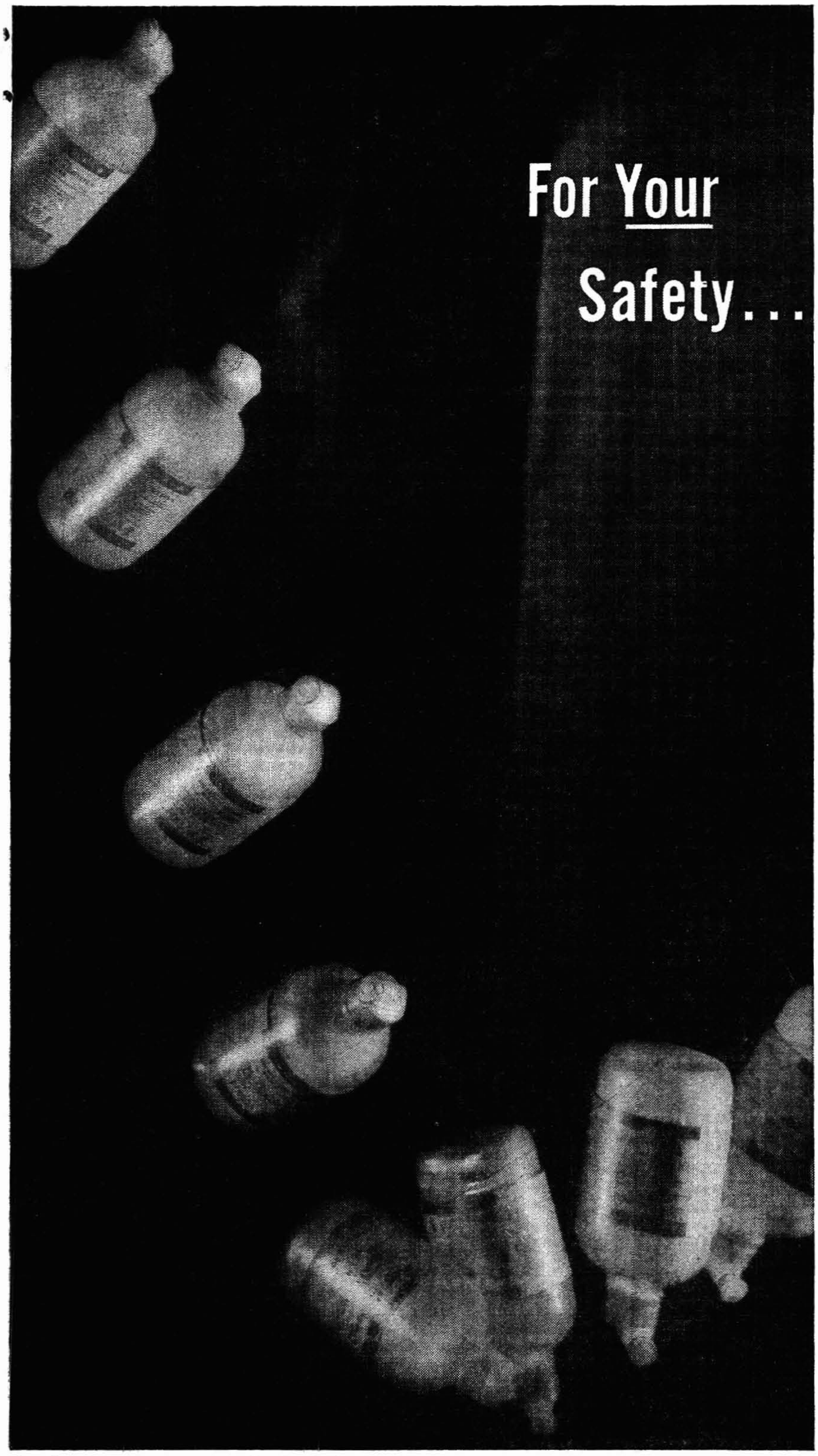


New York Program of Division of Analytical Chemistry

The program of the Division of Analytical Chemistry for the 126th ACS national meeting in New York, Sept. 12 to 17, includes joint symposia with the Divisions of Agricultural and Food, Industrial and Engineering, and Water, Sewage and Sanitation Chemistry. G. Frederick Smith is chairman of the Division, and R. P. Chapman is secretary.

Guest speaker at the divisional dinner on Wednesday evening will be Branch Rickey, president of the Pittsburgh Pirates baseball club in the National League. Mr. Rickey recently created a stir in baseball tradition with an article in *Life* magazine in which he attempts a statistical analysis of what makes a winner in the game of baseball.

MONDAY MORNING AND AFTERNOON

Hotel Barbizon-Plaza, Theatre

General

G. Frederick Smith, *Presiding*

9:00— 1. G. Frederick Smith. Introductory Remarks.
9:10— 2. Herman J. Weiser, Jr. Determination of Triphosphate in the Presence of Other Phosphates.
9:30— 3. L. E. Netherton, A. R. Wreath, and D. N. Bernhardt. Determination of Ortho-, Pyro-, and Triphosphate in the Presence of Each Other.
9:50— 4. Nathaniel L. Crump and Nathaniel C. Johnson. A Rapid Determination of Perchlorates.
10:10— 5. Earl W. Balis, John E. Fagel, Jr., and Edward L. Simons. The Combustion of Tungsten Carbide by High Frequency Induced Radiant Heating.
10:30— 6. R. S. McDonald, J. E. Fagel, Jr., and E. W. Balis. Vacuum Fusion Analysis of Ti, Zr, and Mo. The Determination of Oxygen by the Iron Bath Technique.
10:50— 7. A. D. Kirshenbaum and A. V. Grosse. Extension of the Isotopic Method for the Determination of Oxygen in Titanium to the 0.02 to 0.20 Weight % Oxygen Range.
11:10— 8. L. M. Foster and C. D. Gaitanis. The Determination of Phosphorus in Aluminum and Aluminum Oxide by Radioactivation Analysis.
11:30— 9. Robert Meyrowitz. Immersion Liquids of High Index of Refraction Containing Arsenic Tribromide as the Solvent.

W. G. Batt, *Presiding*

2:00—10. T. S. Ma and Robert Roper. A Simple Technique for Quantitative Paper Chromatography.
2:20—11. T. S. Ma and Robert E. Lang. The Micro-Kjeldahl Method for Nonaminoid Nitrogen.
2:40—12. William H. Hill and Marian S. Johnston. Analysis of Borohydrides.
3:00—13. William L. Porter and Nancy Hoban. An Ultramicro Technique for the Enzymatic Hydrolysis of Sugars Prior to Papergram Analysis.
3:20—14. Paul D. Garn and Stewart S. Flaschen. Differential Thermal Analysis as an Analytical Tool.
3:45—15. Saul Gordon and Clement Campbell. Thermogravimetric and Differential Thermal Analyses of Inorganic Compounds. Instrumentation and Study of Selected Compounds.
4:10—16. Clement Campbell and Saul Gordon. Thermogravimetric and Differential Thermal Analysis of the Nitrates of the Alkali Metals, Alkaline Earths, and Their Subgroups.
4:30—17. George H. Morrison, E. G. Dorfman, and James F. Cosgrove. Purification of Germanium Tetrachloride by Solvent Extraction.

TUESDAY MORNING

SECTION A

Hotel Statler, Georgian Room

Symposium on Analytical Methods and Instrumentation in Air Pollution

Joint with Divisions of Industrial and Engineering and Water, Sewage, and Sanitation Chemistry in Participation With ACS Committee on Air Pollution

Morris Katz, *Presiding*

9:00—18. Morris Katz. Introductory Remarks.
9:15—19. Chester T. O'Knoski and George J. Doyle. Light Scattering Studies in Aerosols with a New Counter-Photometer.
9:45—20. Gerald Oster, Yasunori Nishjima, and Howard Sabin. Production and Measurement of Uniform-Size Aerosols.
10:15—21. Frank T. Gucker, Jr., and George J. Doyle. The Amplitude of Vibration of Aerosol Droplets in a Sonic Field.
10:45—22. Earl R. Gerhard and H. F. Johnstone. Microanalytical Determination of Sulfuric Acid Aerosol.
11:15—23. J. L. Monkman. Use of Micro Gas Chamber Apparatus in Identification of Particulate Air Pollution.

TUESDAY AFTERNOON

Hotel Statler, Georgian Room

Symposium on Analytical Methods and Instrumentation in Air Pollution

Joint with Divisions of Industrial and Engineering and Water, Sewage, and Sanitation Chemistry in Participation With ACS Committee on Air Pollution

Morris Katz, *Presiding*

2:00—24. Saul W. Chaikin, Arthur C. Wilbur, and Thomas D. Parks. The Analysis of Particulate Fluoride.
2:30—25. George D. Clayton and Paul M. Giever. Transmissometer Measurements of Visibility in Air Pollution Studies in Detroit.
3:00—26. J. Cholak, L. J. Schafer, W. J. Younker, and D. Yeager. Air Pollution in a Number of American Cities.
3:30—27. W. C. L. Hemeon. Estimation of Health Hazard from Air Pollution.
4:00—28. Richard L. Pond and R. R. Paxton. A Comparison of Two Methods of Dustfall Measurement—Water Jars and Greased Plates.

WEDNESDAY MORNING

SECTION A

Hotel Barbizon-Plaza, Theatre

General

H. K. Alber, *Presiding*

9:00—29. Charles M. Maddin. Spectrochemical Analysis of Acid Solvents and Brine Solutions.
9:20—30. Leo Schubert and Charles E. White. Quercetin as a Quantitative Colorimetric Reagent for Tin (IV).

9:40—31. Kuang Lu Cheng. Spectrophotometric Determination of Palladium with 2-Nitroso-1-naphthol.
10:00—32. Richard N. Wilhite and A. L. Underwood. Ultraviolet Photometric Titrations of Bismuth and Lead with Ethylenediaminetetraacetic Acid.
10:20—33. Warren M. Wise and Warren W. Brandt. The Spectrophotometric Determination of Vanadium with Benzohydroxamic Acid in 1-Hexanol.
10:40—34. Henry Ph. Heubusch and Ralph R. Liberto. The Development of a Field Test for the Determination of Iron in White Fuming Nitric Acid.
11:00—35. R. F. Goddu, N. F. LeBlanc, and C. M. Wright. The Spectrophotometric Determination of Esters and Anhydrides by the Hydroxamic Acid Reaction.
11:25—36. James W. Fulton and Jane Hastings. The Photometric Determination of Copper by Neocuproine in Aluminum and Lead-Tin Solder.

WEDNESDAY AFTERNOON

SECTION A

Hotel Barbizon-Plaza, Theatre

General

Al Steyermark, *Presiding*

2:00—37. Takeru Higuchi and Carl R. Rehm. Conductometric Titration of Sulfuric and Hydrochloric Acids and Their Mixtures in Anhydrous Acetic Acid.
2:20—38. Donald A. Keyworth and Kenneth G. Stone. A Study of Oxidations Using Copper(III) Reagents.
2:40—39. Justin W. Collat and L. B. Rogers. Fluorimetric Determinations of Mixtures of Aluminum and Gallium as Oxinates.
3:00—40. Stanley K. Freeman. The Infrared Spectrophotometic Analysis of Allethrin.
3:20—41. James S. Fritz. Titration of Bismuth with Ethylenediaminetetraacetic Acid.
3:40—42. Murrell L. Salutsky and H. W. Kirby. Preparation of Carrier-free Yttrium Tracer.
4:00— **Business Meeting**
6:30— **Divisional Dinner**

THURSDAY MORNING

SECTION A

Hotel Barbizon-Plaza, Theatre

General

J. W. Stillman, *Presiding*

9:00—43. Maurice C. Lambert. Absorption of Polychromatic X-Rays as a Function of Atomic Number and Source Voltage.
9:20—44. Maurice C. Lambert. Chemical Analysis by X-Ray Photometry.
9:40—45. Charles W. Pifer, Ernest G. Wollish, and Morton Schmall. A Study of the Sensitivity of Certain Potentiometric Titrations.
10:00—46. Paul Delahay and Gleb Mamantov. Chronopotentiometry-Voltammetry at Constant Current. I. Theoretical Principles.
10:20—47. Charles N. Reilly, Grover W. Everett, and Richard H. Johns. Chronopotentiometry-Voltammetry at Constant Current. II. Experimental Evaluation.
10:40—48. Virginia Z. Deal and Garrard E. A. Wyld. Potentiometric Determination of Very Weak Acids. I. Titration with Hydroxides in Nonaqueous Media Using the Glass-Calomel Electrode System.
11:00—49. John T. Porter, II, and W. Donald Cooke. The Electrolytic Decomposition of Dilute Amalgams.
11:20—50. Sidney Siggia, Dale W. Eichlin, and Richard C. Rheinhart. Potentiometric Titrations Involving Chelating Agents, Metal Ions, and Metal Chelates.
11:40—51. Gerald C. Whitnack, Joan Reinhart, and E. St. Clair Gantz. Polarographic Behavior of Some Alkyl Phthalate Esters.

THURSDAY AFTERNOON

SECTION A

Hotel Barbizon-Plaza, Theatre

General

L. T. Hallett, *Presiding*

2:00—52. Louis Meites. Analytical Procedures Employing Controlled Potential Electrolysis. Purification of Supporting Electrolytes for Polarographic Trace Analysis.
2:20—53. Louis Meites. Analytical Procedures Employing Controlled Potential Electrolysis. Rapid Determination of Traces of Nickel and Zinc in Copper and Its Salts.
2:40—54. Ralph N. Adams. Current Scanning Polarography with the Dropping Mercury Electrode.
3:00—55. Ward B. Schaap and Arthur E. Messner. Polarography in Anhydrous Ethylenediamine.
3:20—56. Louis Meites. Analytical Procedures Employing Controlled Potential Electrolysis. Precise Controlled Potential Coulometric Analysis.
3:40—57. Louis Meites. Analytical Procedures Employing Controlled Potential Electrolysis. A New Method for the Polarographic Analysis of Solutions Containing Two Substances Which Give Superimposed Waves.
4:00—58. Donald D. DeFord, Robert S. Braman, and Robert F. Breese. Continuous Automatic Analysis in Flow Processes by Means of Coulometric Titrimetry. I. Separation and Titration of Hydrochloric Acid–Acetic Acid Mixtures.
4:20—59. Donald D. DeFord and Hans Horn. Coulometric Titrations with Electrolytically Generated Manganic Ion.
4:40—60. Walter H. Jura. Polarographic Determination of *S*-(1,2 Dicarbethoxyethyl) *O,O*-Dimethyldithiophosphate (Malathion).

FRIDAY MORNING

Hotel Barbizon-Plaza, Theatre

General

R. P. Chapman, *Presiding*

9:00—61. Harry Teicher. The Precipitation of Barium Carbonate.
9:20—62. Paul T. Gilbert, Jr. Applications of the Beckman Flame Spectrophotometer.
9:40—63. Barry W. Mulligan and Bourdon F. Scribner. Flame Photometric Determination of Alkalies in Refractory Materials. Preparation of Samples by the Sealed Tube Method.
10:00—64. Paul T. Gilbert, Jr. Determination of Cadmium by Flame Photometry.
10:20—65. Paul T. Gilbert, Jr. Determination of Indium by Flame Photometry.
10:40—66. Gerald A. Guter and George S. Hammond. The Separation of Lithium from Other Alkali Metal Ions.
11:00—67. Leonard S. Buchoff, Nathan M. Ingber, and James H. Brady. Colorimetric Determination of Low Concentrations of Dissolved Oxygen.
11:20—68. Leo D. Frederickson, Jr. Characterization of Hydrated Aluminas by Infrared Spectroscopy. Application to the Study of Bauxite Ores.

Other Symposia of Interest

TUESDAY MORNING

Hotel Statler, Sky Top

Symposium on Paper Chromatography of Biologically Active Fermentation Products

Joint with Fermentation Subdivision of Division of Agricultural and Food Chemistry

Marvin J. Johnson, *Presiding*

9:00— Marvin J. Johnson. Introductory Remarks.

9:15— Eldon D. Nielson. Paper Chromatography of Products of Steroid Fermentations.

9:35— Gilbert M. Shull. Paper Chromatography of Steroid Fermentation Products.

10:15— Richard P. Miller, N. E. Davis, and Harold L. Bird, Jr. Paper Chromatography as an Aid in the Identification of Antibiotics.

10:45— Thomas J. Oliver, Arthur C. Sinclair, Robert J. Theriault, and Ann V. Zeiger. The Use of Paper Chromatography for Identification of Antibiotics in a Screening Program.

11:15— Henry Koffler and J. F. Pagano. Paper Chromatography of Certain Basic Antibiotics and of Antibacterial Peptides.

WEDNESDAY MORNING AND AFTERNOON

Hotel Statler, Georgian Room

Symposium on Air Pollution

Joint with Divisions of Industrial and Engineering and Water, Sewage, and Sanitation Chemistry in Participation With ACS Committee on Air Pollution

R. D. Hoak, *Presiding*

9:00— R. D. Hoak. Introductory Remarks.

9:10— Norton Nelson, Marvin Kuschner, and Sidney Laskin. The Experimental Evaluation of Airborne Materials for Carcinogenicity.

9:40— Paul Kotin. Acute, Subacute, and Chronic Effects of Experimental Exposure to Airborne Pollutants.

10:10— G. R. Spencer, G. K. Garlock, E. C. Stone, R. L. Albrook, and D. F. Adams. A Field Survey for Detection of Bovine Fluorosis.

10:40— E. R. Gerhard and H. F. Johnstone. The Photochemical Oxidation of Sulfur Dioxide to Sulfur Trioxide and Its Effect on Fog Formation.

11:10— Gustave Freeman. Toxicity to Animals and Man of Organophosphorus Insecticides.

2:00— W. M. Noble, G. Cann, and G. P. Larson. The Pattern of Damage Produced on Vegetation by Smog. The Use of This Pattern in Detection of Smog-Forming Hydrocarbons in Car Exhaust Gases.

2:30— Andrew A. Nichol. Anomalies in Fluoride Concentrations Found in Field Material.

3:00— D. F. Adams, J. W. Hendrix, H. G. Applegate, H. A. Ferchau, and R. M. Gnagy. Some Effects of Hydrogen Fluoride on Plants.

3:30— P. W. Zimmerman. Comparative Susceptibility of Various Species of Plants to Hydrofluoric Acid in Contrast to Other Gases.

4:00— Philip W. West and A. R. Choppin. A Mobile Laboratory and Its Use in Atmosphere Surveys.

THURSDAY MORNING

Hotel Statler, Georgian Room

Symposium on Processes and Equipment In Air Pollution Control

Joint with Divisions of Industrial and Engineering and Water, Sewage, and Sanitation Chemistry in Participation with ACS Committee on Air Pollution

Paul L. Magill, *Presiding*

9:00— Paul L. Magill. Introduction.

9:20— R. G. Calkins. Filter-Scrubber Dust Collectors.

9:50— William B. Harris and M. G. Mason. Operating Economics of Air Cleaning Equipment Utilizing the Reverse Jet Principle.

10:20— Joseph A. Leary, Robert A. Clark, R. Philip Hammond, and Charles S. Leopold. Aerosol Collection by Wetted Fiberglas Media.

10:50— C. A. Snyder and R. T. Pring. Filtration of Hot Gases. Design Considerations.

11:20— Wayne T. Sproull. Laboratory Performance of a Special Two-Stage Precipitator for Collecting High Resistivity Dust or Fume.

THURSDAY AFTERNOON

Hotel Statler, Georgian Room

Symposium on Processes and Equipment In Air Pollution Control

Joint with Divisions of Analytical and Water, Sewage, and Sanitation Chemistry in Participation with ACS Committee on Air Pollution

Paul L. Magill, *Presiding*

2:00— H. J. White. Fundamental Performance Factors in the Electrical Precipitation Process.

2:30— Leslie Silverman, Edward W. Connors, Jr., and David M. Anderson. Mechanical Electrostatic Charging of Fabrics for Air Filters.

3:00— John I. Yellott and P. R. Broadley. Development of High Temperature, High Pressure Fly Ash Separation Equipment.

3:30— Amos Turk. Catalytic Reactivatio of Activated Carbon in Air Purification Systems.

4:00— L. V. Cralley and J. Paul Jenny. Air Pollution Control in the Aluminum Industry.

4:30— R. J. Ruff. Stack Sampling as Related to Full Scale Catalytic Fume Combustion Systems.

ANALYST'S CALENDAR

American Chemical Society. 126th National Meeting, New York, N. Y., September 12 to 17.

Optical Society of America. Annual meeting, Los Angeles, Calif., October 14 to 16.

First International Instrument Congress and Exposition. Instrument Society of America, Philadelphia, Pa., September 13 to 25.

Gordon Research Conferences. New London, New Hampton, and Meriden, N. H., June 14 to September 3.

Twelfth Annual Pittsburgh Diffraction Conference. Mellon Institute, Pittsburgh, Pa., November 3 to 5. Joint with American Crystallographic Association.

Instrument Society of America. Third Analytical Instrument Clinic. Commercial Museum and Convention Hall, Philadelphia, Pa., September 13 to 15.

Sixteenth Midwest Regional Meeting, American Chemical Society, Omaha, Neb., November 4 to 6, 1954.

Sixth Annual Conference on Electronics and Nucleonics in Medicine. American Institute of Electrical Engineers, Institute of Radio Engineers, and Instrument Society of America. Hotel New Yorker, New York, N. Y., November 19 and 20.

Symposium on Analytical Chemistry. Birmingham, England, August 25 to September 1.

Symposium on Modern Methods of Analytical Chemistry. Louisiana State University, Baton Rouge, La., January 31 to February 3, 1955.

Editor's Note: The Sixth Annual Oak Ridge Summer Symposium on Modern Analytical Chemistry originally scheduled for Aug. 23–27 was canceled early this year. We regret that it was erroneously included in the Calendar in recent issues.

Instrument Clinic

The third analytical instrument clinic of the Instrument Society of America will be held in Philadelphia, Pa., September 13 to 15 in connection with the First International Instrument Congress and Exposition [ANAL. CHEM., **26**, 32 A (April 1954)].

Two or more experts will conduct 3-hour lecture and demonstration sessions on the latest and most advanced analytical instruments.

Instruments included are: X-Ray Quantometers, Littrow-Echelle spectrograph, infrared spectrophotometers, process monitoring mass spectrometer, ion resonance mass spectrometer, nondispersion infrared analyzers, and nuclear magnetic resonance spectrometer.

Advance registration is required. Program and registration forms are available from Axel H. Peterson, Mellon Institute, 4400 Fifth Ave., Pittsburgh 13, Pa.

Government Lab Observes 68th Anniversary

Chemists of Internal Revenue's Alcohol and Tobacco Tax Division listen to their chief, Richard L. Ryan, describe a chromatographic technique adopted by the division to speed determination of beverage constituents. Meeting of all division's regional chemists in Washington marked the celebration of the 68th anniversary of the laboratory, the second oldest in Government

Calorimetry Conference

The Ninth Annual Calorimetry Conference is to be held at the General Electric Research Laboratory, Schenectady, N. Y., September 17 and 18. General chairman is E. J. Prosen, National Bureau of Standards, Washington, D. C. Inquiries should be addressed to Warren DeSorbo, Metallurgy Research Department, Research Laboratory, General Electric Co., P.O. Box 1088, Schenectady, N. Y. Room reservations should be made with the Hotel VanCurler Schenectady, N. Y.

Friday Morning

9:00 **Introductory Remarks.** J. H. HOLLOMON, Metallurgy Research Department, General Electric Research Laboratory, Schenectady, N. Y.

9:10 **Trends in Calorimetry.** GUY WADDINGTON, Bureau of Mines, Bartlesville, Okla. First Hugh M. Huffman Memorial Lecture.

9:40 **Calorimeter with Continuous Heating and Adiabatic Control.** L. J. TODD AND DONALD H. ANDREWS, Johns Hopkins University, Baltimore, Md.

10:05 **Adiabatic Calorimeter for the Temperature Range 2.5° to 20° K.** J. A. MORRISON, National Research Laboratories, Ottawa, Canada.

10:30 **Specific Heat of the Alkali Metals.** H. PRESTON-THOMAS, National Research Laboratories, Ottawa, Canada.

10:55 **Standard Reference Materials.** EDWARD WICHERS, National Bureau of Standards, Washington, D. C.

11:20 **Calorimetric Investigations of the Thermodynamic Properties of Gases Adsorbed on Solids between 10° and 150° K.** E. L. PACE, Morley Chemical Laboratory, Cleveland, Ohio.

11:45 **The N.P.L. No. 1 Bomb Calorimeter.** A. K. MEETHAM, National Physical Laboratory, Teddington, Middlesex, England.

12:10 **Rotating-Bomb Calorimeter with Direct Drive.** D. W. SCOTT, W. D. GOOD, AND W. N. HUBBARD, Bureau of Mines, Bartlesville, Okla.

12:30 **Determination of the Heats of Combustion of Organometallic Compounds.** P. WASZECIAK, R. E. MILLER, AND H. STANGE, Mathieson Chemical Corp., Niagara Falls, N. Y.

Friday Afternoon

2:00 **Two Calorimetric Methods for Energy Measurements in Solids.** A. W. OVERHAUSER, Cornell University, Ithaca, N. Y.

2:30 **Microcalorimetric Study of the Recrystallization of Copper.** PAUL GORDON, University of Chicago, Chicago, Ill.

2:55 **Twin Adiabatic Microcalorimeter for Measurement of Stored Energy in Copper.** F. B. RIGGS, Harvard University, Cambridge, Mass.

3:20 **New High Temperature Reaction Calorimeter.** O. J. KLEPPA, University of Chicago, Chicago, Ill.

4:00 **Experimental Tests of the Born-von Kármán Specific Heat Theory.** J. R. CLEMENT, Naval Research Laboratory, Washington, D. C.

4:30 **Extrapolation of High Temperature Heat Capacity Data.** MICHAEL HOCH AND HERRICK L. JOHNSTON, Ohio State University, Columbus, Ohio.

4:55 **Use of the Heat of Reaction in Polymerization Problems.** B. R. THOMPSON, Carbide and Carbon Chemicals Co., South Charleston, W. Va.

5:15 **Heat Capacity of Gold-Nickel Alloy and Its Deviation from the Rule of Additivity.** R. A. ORIANI AND W. DESORBO, General Electric Research Laboratory, Schenectady, N. Y.

Saturday Morning

9:00 **Thermal Effects Associated with the Antiferromagnetic Ordering of MnF_2, FeF_2, CoF_2, NiF_2.** J. W. STOUT AND EDWARD CATALANO, University of Chicago, Chicago, Ill.

9:30 **Thermal and Magnetic Properties of Anhydrous Manganous Chloride in the Liquid Helium Temperature Region.** L. D. ROBERTS AND R. MURRAY, Oak Ridge National Laboratory, Oak Ridge, Tenn.

9:55 **Thermal Effects Associated with Magnetic Transformations in Ferrites.** E. F. WESTRUM, JR., University of Michigan, Ann Arbor, Mich.

10:20 **Calorimetry Below 1° K.** J. G. DAUNT AND G. DEVRIES, Ohio State University, Columbus, Ohio.

11:00 **Heat Capacity of Lanthanum at Liquid Helium Temperatures.** A. BERMAN, M. W. ZEMANSKY, AND H. A. BOORSE, Columbia University, New York, N. Y.

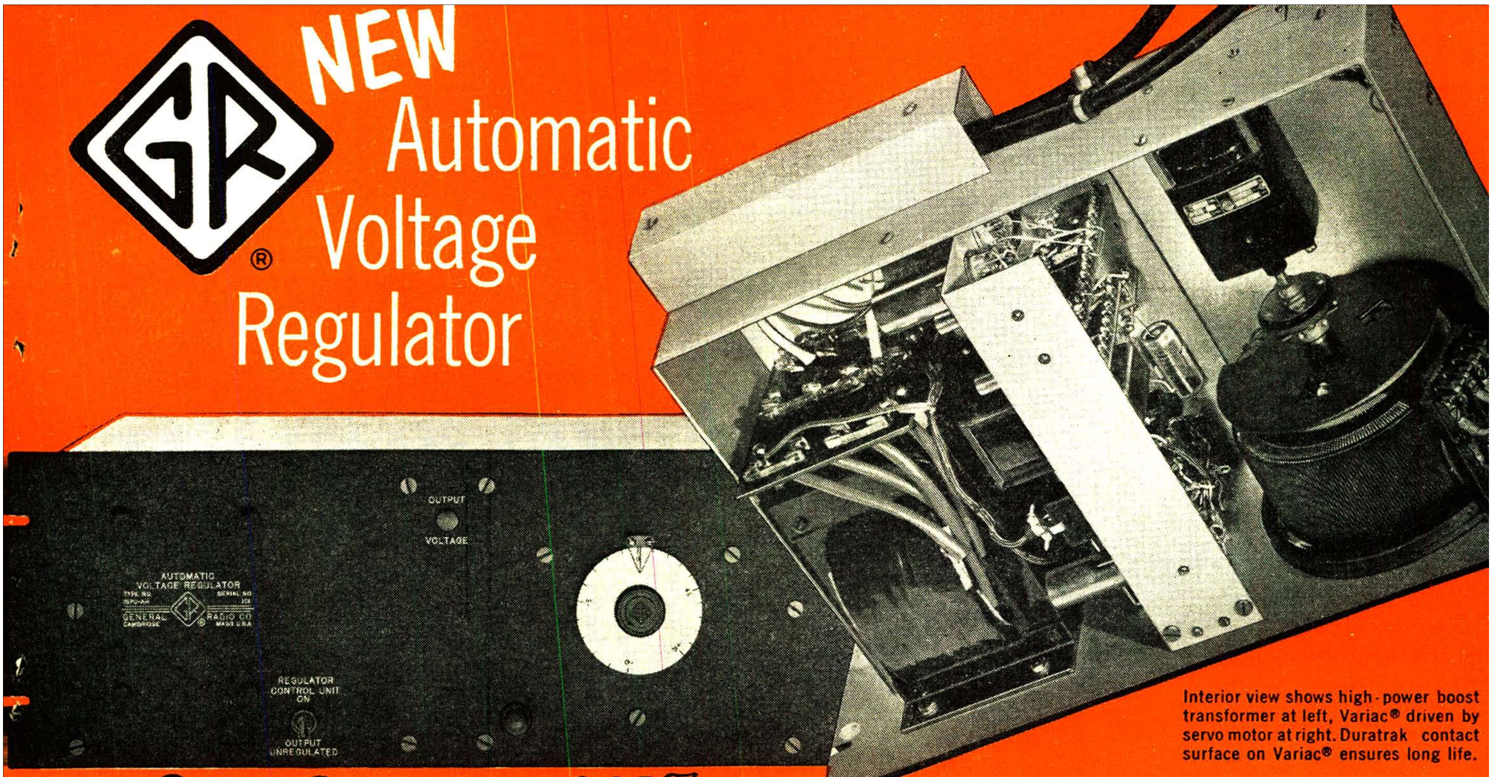
11:25 **Calorimeter for Radiation and Gas Conduction Heat Transfer Measurements between Surfaces at Room Temperature and at Liquid Nitrogen Temperatures.** F. J. ZIMMERMAN, Arthur D. Little, Inc., Cambridge, Mass.

11:50 **Tin Solution Calorimetry.** J. S. L. LEACH, Massachusetts Institute of Technology, Cambridge, Mass.

Saturday Afternoon

1:30 Business Meeting, Edward J. Prosen, Chairman.

NEW Automatic Voltage Regulator



Interior view shows high-power boost transformer at left, Variac® driven by servo motor at right. Duratrak contact surface on Variac® ensures long life.

Output Constant to ±0.25%
Extra Fast Response: 0.1 sec. per volt
Handles up to 6 KVA

For a Detailed Description of this New Instrument, write for the July Issue of the General Radio Experimenter

The Type 1570-A Automatic Voltage Regulator combines *Accuracy* for laboratory use with *High Power-Handling Capacity* for control of industrial processes.

The application of proportional-control servomechanisms to voltage regulator design has resulted in a unique, highly-efficient instrument which should prove of considerable value to those requiring constant a-c line voltage.

This Regulator consists essentially of a Variac® continuously-adjustable autotransformer, a servomechanism sensing circuit which samples the output voltage, and a servo-motor which varies the Variac to correct for input line-voltage changes. This instrument is rugged, requires minimum maintenance, — the G-R trademark guarantees it's been *engineered and built right*.

Features you get with the GR 115-volt, 60-cycle Automatic Voltage Regulator . . .

SPEED *This instrument does things in fractions of a second — response is 10 volts per second*

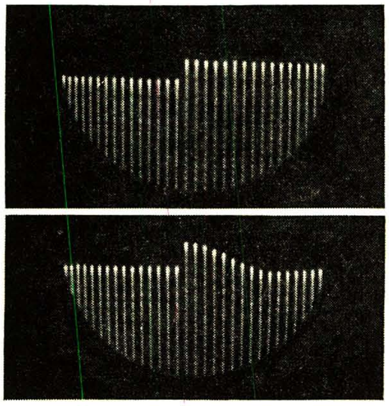
HIGH ACCURACY *Output held constant to within ±0.25% of voltage selected*

±10% SELECTION IN OUTPUT VOLTAGE *Output may be set for any desired value from 104 to 127 volts*

CORRECTS LINE VOLTAGE FLUCTUATIONS OVER WIDE RANGE *±10% of selected output voltage, ±20% or ±40% at reduced accuracy and power rating*

HIGH POWER *Handles 50-amps (6 KVA)*

EXCELLENT TRANSIENT RESPONSE *Adjustments permit setting response characteristic desired — adjustable for no overshoot (see oscillograms)*



Oscillograms illustrate high-speed response of typical G-R Automatic Voltage Regulator. Illustrated at top, is sudden 1% change in 60-cycle voltage input to Regulator. Bottom oscillogram shows instrument correcting for this change in 8 cycles (0.13 seconds)

ADDS NO HARMONIC DISTORTION *Unlike most saturable-core reactors*

SUPPLIES ANY LOAD *No restrictions on power factor*

EFFICIENCY *Better than 98%*

VOLTAGE CORRECTION INDICATED *Panel dial provides continuous indication*

USEFUL FOR CONTROL OF THREE-PHASE POWER *three of these instruments in conjunction will control both amplitude and phase of three-phase systems*

WEIGHT *55 lbs* DIMENSIONS *19" x 7" x 12⅞"*

Type 1570-A Automatic Voltage Regulator
. . . supplied in either 115-v or 230-v model

Type		Price
Type 1570-ALM (115v) **Type 1570-AHM** (230v)	Table-Top	**$470.**
Type 1570-ALR (115v) **Type 1570-AHR** (230v)	Relay-Rack	**$465.**

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POLARISCOPES
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PULSE GENERATORS

SIGNAL GENERATORS
SOUND & VIBRATION METERS
STROBOSCOPES
TV & BROADCAST MONITORS
U-H-F MEASURING EQUIPMENT
UNIT INSTRUMENTS
VARIACS
V-T VOLTMETERS

Experience Discussion on New Products and Techniques

2:00 **New Information Concerning Carbon-Composition Thermometers.** J. R. Clement, Naval Research Laboratory, Washington, D. C.

Present Status of Temperature Scale below 5.2° K and the Effects of Differences between Scales on Calorimetric Data. J. R. Clement, Naval Research Laboratory, Washington, D. C.

Shield and Bath Control. J. N. Ratti, Engineering and Research Corp., Riverdale.

Automatic Bath Temperature Control. M. D. Fiske, General Electric Research Laboratory.

Production of Isothermal Temperature Reservoirs between 0.2° and 1° K. with the Magnetic Refrigerator. C. V. Heer, C. B. Barnes, and J. G. Daunt, Ohio State University, Columbus, Ohio.

Wire Tape. G. T. Furukawa, National Bureau of Standards, Washington, D. C.

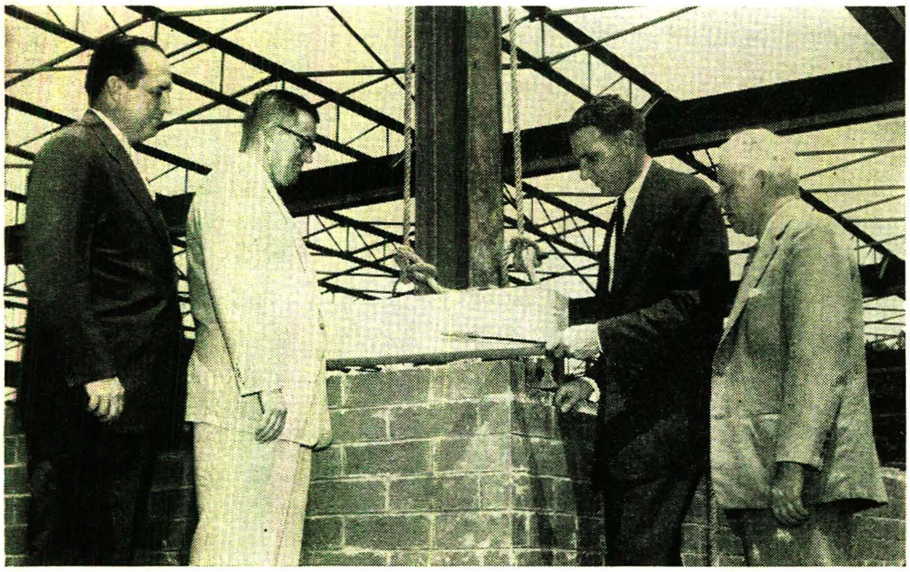
Thermoelectric Stability of Thermocouple Materials. J. M. Berry, General Electric Research Laboratory.

Thermoelectric Effects of Strain. J. M. Berry, General Electric Research Laboratory.

Calibration Procedures; Use of Gold Thermopile Leads at High Temperatures; Leakage Currents *vs.* Thermopile Accuracy. F. B. Riggs, Harvard University, Cambridge, Mass.

Simple Circuitry for Thermistors Used as Thermometers. C. R. Droms, General Engineering Laboratory, General Electric Co.

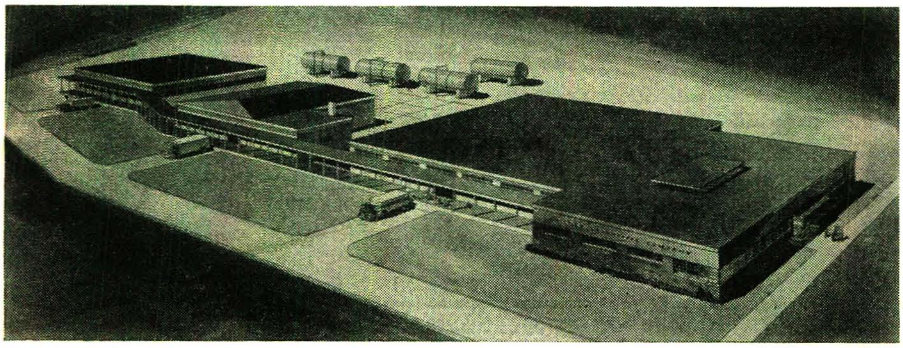
High Temperature Differential Solution Calorimeter. R. A. Oriani, General Electric Research Laboratory.



New Reagent Chemicals Facilities for Fisher

James A. Fisher, vice president of Fisher Scientific Co., uses a gold spatula to lay the cornerstone for Fisher's new chemical division plant at Fair Lawn, N. J. Others in the photo (left to right): A. L. Abbitt, vice president and plant manager; W. T. Williamson, Fair Lawn Borough manager; and C. A. Flanders, chief chemist of the new plant

Below. The three-building unit, scheduled for completion in late fall, will provide 70,000 square feet of manufacturing area for reagent chemicals, analytical and development laboratories, warehouse space, packaging rooms, library, and office. Fisher says it is the largest plant in the country designed exclusively for reagent chemicals and will increase fourfold the company's present facilities at Edgewater, N. J.



NEW BOOKS

Methods of Biochemical Analysis. Edited by *David Glick.* Vol. I. x + 521 pages. Interscience Publishers, Inc., 250 Fifth Ave., New York, N. Y., 1954. $9.50. Reviewed by H. B. Vickery, The Connecticut Agricultural Experiment Station, New Haven, Conn.

This is the first of a series of annual volumes in which the editor, with the assistance of a distinguished advisory board of both American and foreign biochemists, proposes to meet the need for detailed reviews of important analytical techniques currently used in biochemical research. Although the contributors (some 30 names are listed) have been given free rein with respect to their treatment of the various topics, each of the 17 chapters begins with an introduction in which the general significance in biochemistry of the substance or group of substances is set forth together with a statement of the principles upon which the analytical methods rest and often with an outline of the history of the subject. The various techniques that have been used for the qualitative and quantitative determinations are then given in logical order, in the cases of the most important methods with full procedural detail. A valuable feature of some of the chapters is a statement of preference on the part of the contributor for one or other of the methods, the reasons being given.

There is little doubt that this volume and its successors will find wide use. Those who are engaged in research in one of the fields covered will welcome the comprehensive discussion of the analytical problems involved; those contemplating entering one of these fields will be able better to judge which of the methods available in the literature can best be used to attain his particular ends in view of the equipment available to him. Students and junior assistants will find the book extremely helpful as an introduction to the literature of a given subject, for each chapter is provided with an excellent bibliography, several of which run to more than 100 references. The bibliography of the chapter on the chromatography of mixtures of sugars and that of the chapter on catalase are especially thorough and complete.

Few of the chapters are written at the level of a handbook of analytical methods, but the critical reader would perhaps welcome more information on the accuracy and precision of many of the methods. Nevertheless, it is probable that sufficient information upon which to form a judgment could be obtained by reference to the original literature.

The key references given should make this possible in all cases.

The book is well produced and free from blemishes. There are many figures and illustrations or diagrams of equipment, and a number of useful tables of data are included. The topics covered range from sulfhydryl groups and phenols through antibiotics, several vitamins, numerous steroids, choline, sugars, nucleic acid, and several enzymes to serum lipoproteins. Although classical techniques are not neglected, modern methods, especially chromatography, are emphasized. Subsequent volumes may be expected to extend the discussion to many more fields of interest.

Symposium on Fluorescent X-Ray Spectrographic Analysis. 72 pages. American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa., 1954. $1.75.

Seven papers presented at the 56th Annual Meeting of the American Society for Testing Materials, held in Atlantic City, N. J., June 1953, in the Symposium on Fluorescent X-Ray Spectrographic Analysis, are included in the volume. The symposium was sponsored by ASTM Committee E-2 on Emission Spectroscopy.

Identification and Qualitative Chemical Analysis of Minerals. *Orsino C. Smith.* 2nd ed. ix + 385 pages. D. Van Nostrand Co., Inc., 250 Fourth Ave., New York 3, N. Y., 1953. $7.50. Reviewed by Raleigh Gilchrist, National Bureau of Standards, Washington 25, D. C.

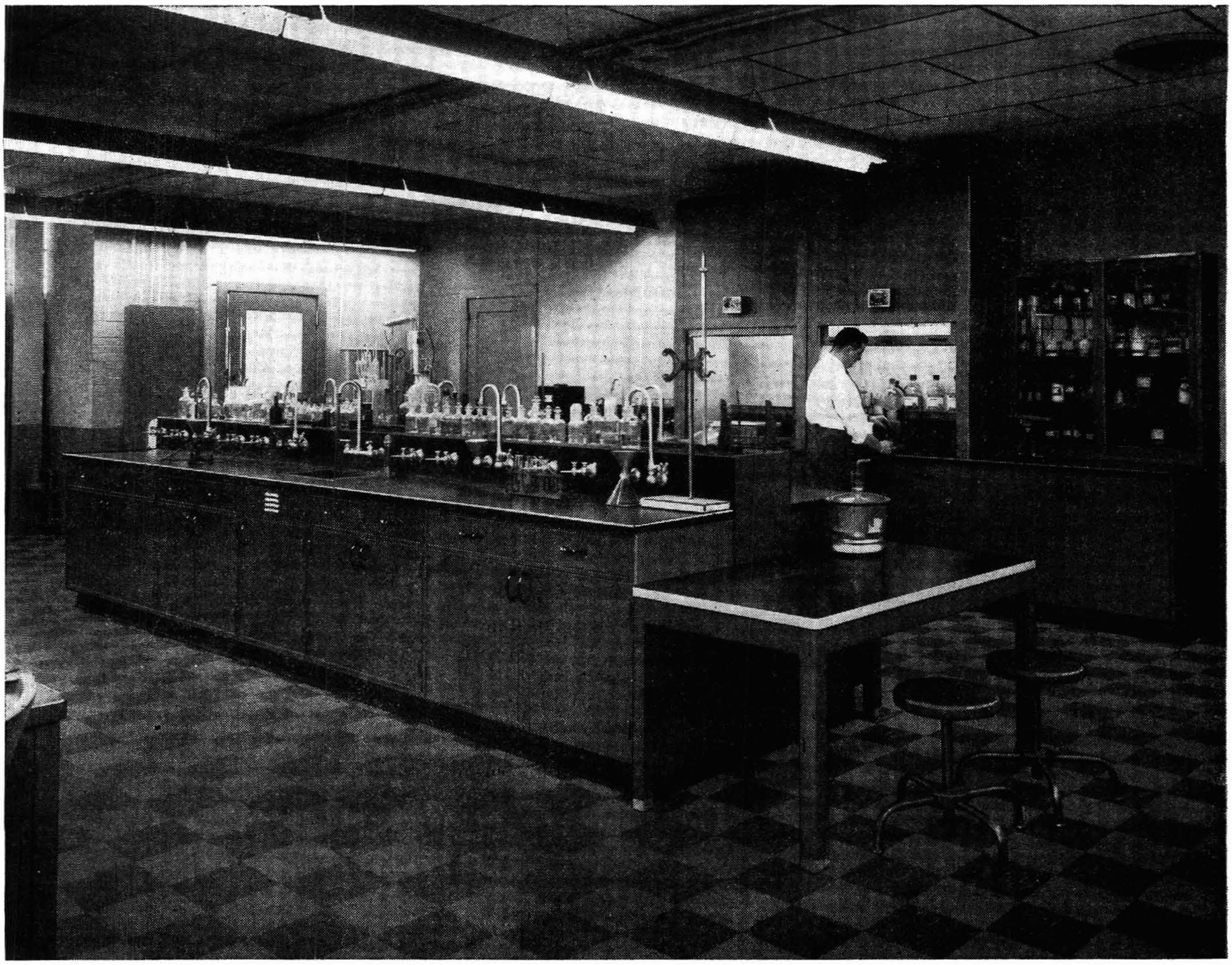
The subject matter of the book is presented in eight chapters, instead of in seven as previously, and covers the physical properties of minerals in general, history and uses of blowpiping, blowpipe reactions, ultraviolet light and fluorochemistry, mineral chemistry, tables of chemical reactions, qualitative chemical tests, and mineral identification tables. Thirty-eight figures and twenty-eight colored plates are included, as well as a general index and a mineral index.

This second edition is essentially the same as the first, except that a condensed account of the blowpipe and blowpiping has been added, and a number of tests not given in the earlier edition have been included, as well as Geiger-counter methods for locating radioactive minerals and standard methods of analysis of uranium and other radioactive elements. No changes in the mineral identification tables have been made at this time, although it is realized that modern methods of determining the composition and structure of minerals indicate that a number of substances still classified as distinct minerals are really variations of other minerals.

A feature of the book, as in the first edition, is the reproduction in color of 300 minerals, 120 blowpipe reactions, and a number of fluorescent minerals. The value of the book lies in the compact assembly of the physical properties and chemical tests necessary in identifying some 2000 minerals.

Sulfur, a Bibliography of Analytical Methods. *A. W. Scholl* and *R. L. Young.* 324 pages. A. W. Scholl, 669 South Terrace, Huntington 5, W. Va., 1954. $10 paper bound.

This book contains 3400 references to the analytical chemistry of sulfur, arranged alphabetically by first author, title, reference, and the abstract reference. An index of secondary authors and patents is also included.



Yesterday this was an Empty Room

To convert an empty room into a modern, completely equipped, operating chemical laboratory figuratively overnight is quite a feat . . . even for Fisher! But we did it.

At 3:30 one afternoon came urgent instructions from an eastern metals firm. At 4:45 our shipping department was getting out the order. The *next* morning the customer was uncrating the complete laboratory assembly, and by that afternoon every section of Fisher Unitized Furniture was in place.

We'd prefer not to be quite so rushed. But we *could* do it again *because* Fisher scientifically planned laboratories are made up to your exact specifications from modular, unitized steel laboratory furniture of most practical design.

More than 21 basic units are available from stock. Put together to meet your requirements, the result is an integrated laboratory, completely modern in appearance and efficiency.

Providing complete laboratories is only one facet of our interesting business. Implementing them with apparatus, instruments, supplies, reagent chemicals, glassware, even to suggested procedures and techniques, are others. Everything but providing the chemist, metallurgist or technician himself!

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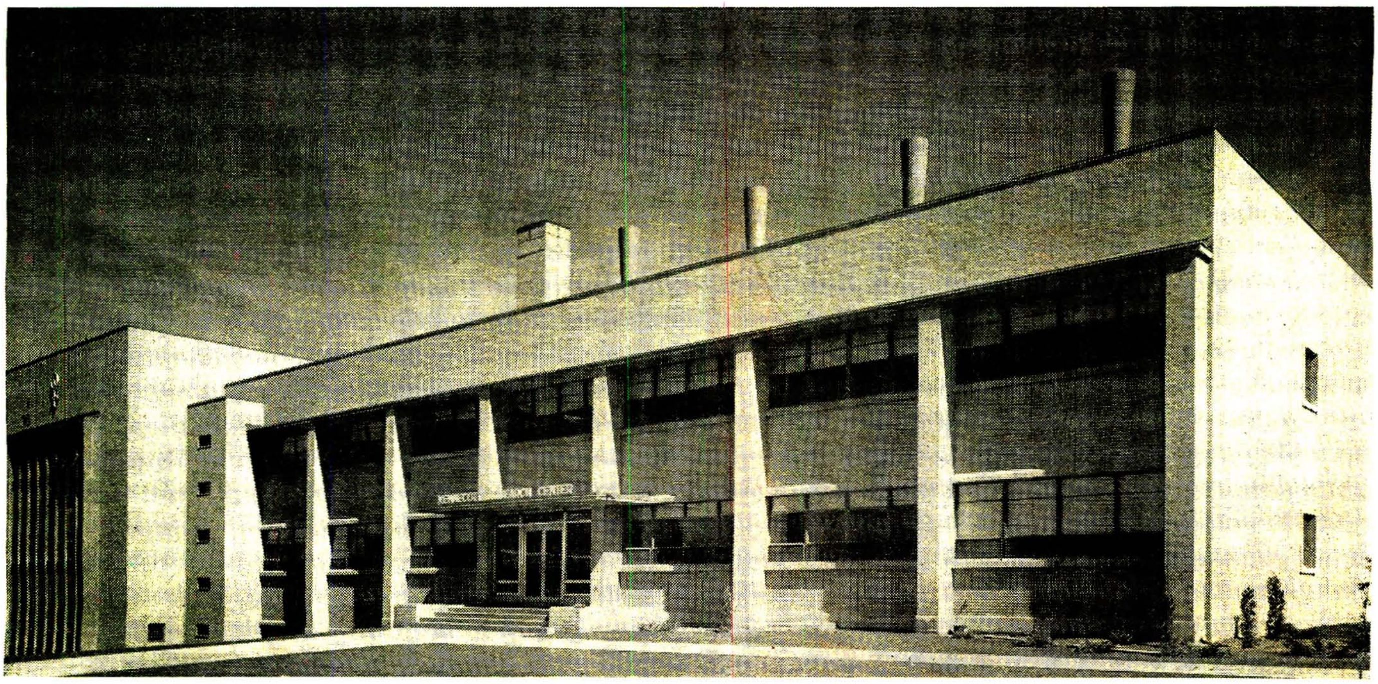
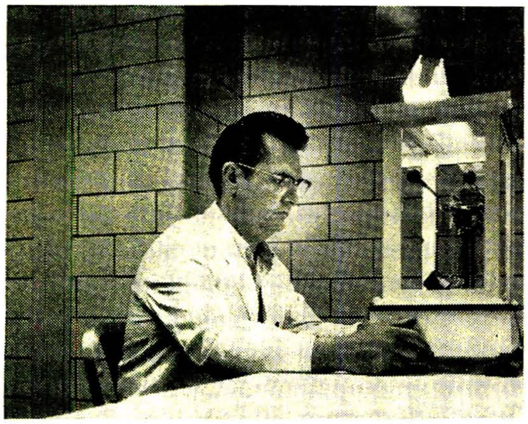
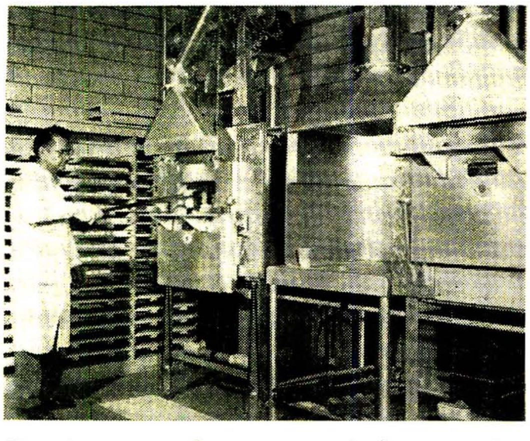
For further information, circle number 28 A on Readers' Service Card, page 37 A



Built primarily of concrete, brick, and steel, Kennecott's new Research Center provides 40,000 sq. feet of space. The pilot plant occupies 12% of this area with the remainder utilized for laboratories and offices. The laboratories have ceramic tile walls, asphalt tile or cement floors, and Transite ceilings. Each is equipped with individual ventilation and temperature control as well as utility outlets. Fluorescent lighting is used and the windows are of tinted glass to reduce glare



An interesting construction feature of the new building is a 4-inch expansion joint to separate the pilot plant from the laboratory, thereby eliminating vibrations that would affect sensitive instruments. For example, balances may be operated successfully only a few feet from the joint shown at the left of the picture



Electric assay furnaces used for assaying precious metals are capable of maintaining temperatures of 2070° F. The temperature in the furnaces is controlled electronically and no fume emanates into the working area, because of an adequate hood system

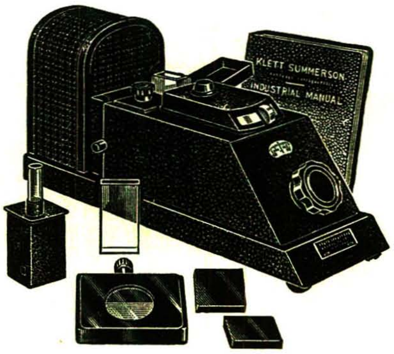
LABORATORY OF THE MONTH

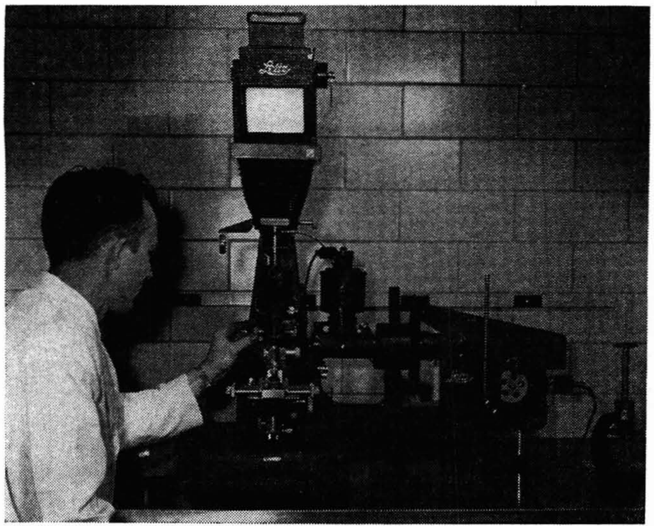
- ***New mountain states research unit to aim for improved methods and knowledge of mining, milling, and refining operations***

THIS month Kennecott Copper Corp. is dedicating its ultramodern $1,250,000 Research Center located on the campus of the University of Utah at Salt Lake City. This new unit will be an important addition to the growing research facilities of the Mountain States.

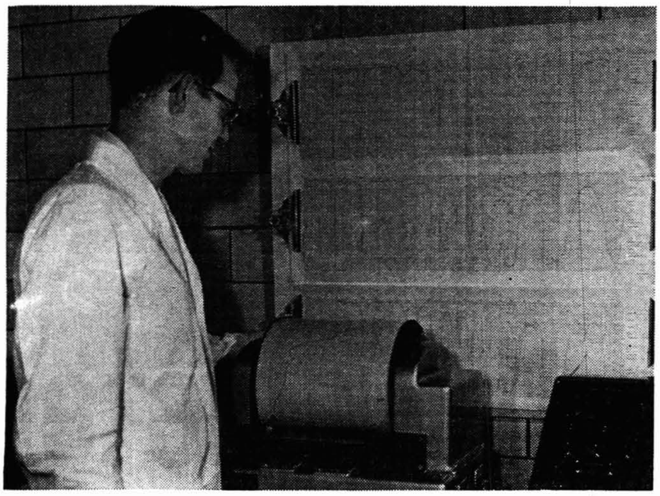
The primary purpose of the laboratory is to study the problems and improve methods used in Kennecott's mining, milling, and refining operations, and to develop the results into commercial application. According to company officials, an important objective is more effective coordination. Whereas in past years Kennecott has conducted research on specific problems at each of its properties, these studies now will be coordinated through the Research Center. A research area of special interest to the chemical field will be the laboratory's work in developing new flotation agents such as oils, xanthates, and starches to improve recovery and grade of concentrates.

(Continued on page 31 A)

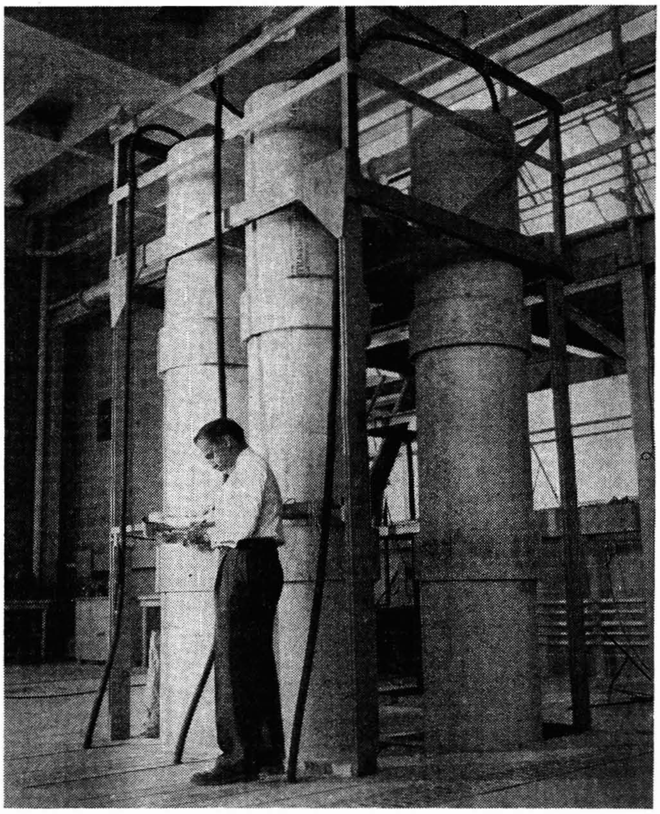




Microscope with camera is used for transmitted or reflected light studies. As in present set up for reflected light, the microscope measures mineral grain down to 0.001 mm.

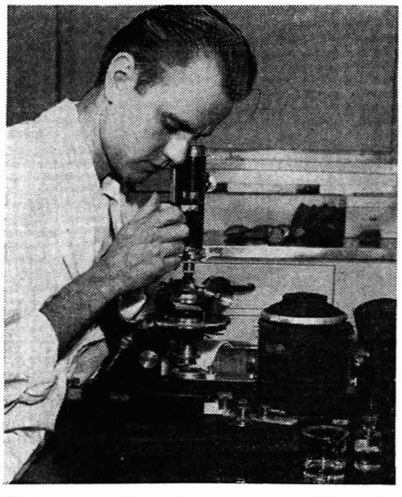


Infrared spectrophotometer is especially useful for identification and analysis of organic compounds. It is currently being used in a quality control study of flotation reagents

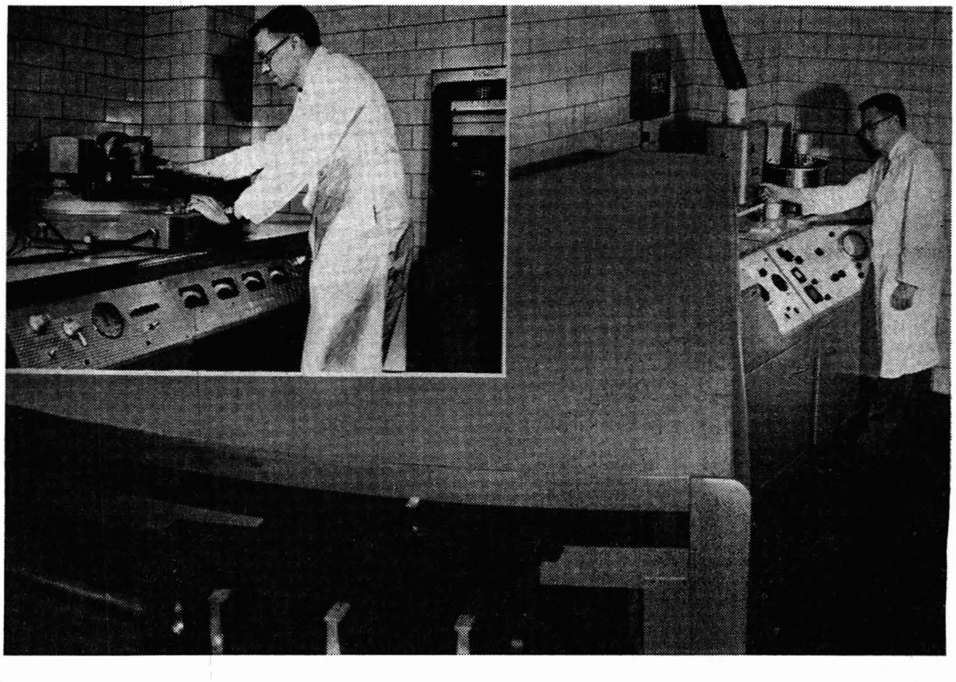


Each of two percolation columns shown above in Kennecott's new Research Center contains 1 ton of waste rock for the pilot plant study of a process developed in the hydrometallurgical laboratory

Mineral concentrations as small as 0.01 to 0.0001% can be determined with the comparative spectrograph (at right) operated in Kennecott's new Research Center. Inset top left shows center's x-ray diffraction unit with fluorescent attachment used to determine micro quantities of elements or metals present in ore samples ▼



Petrographic microscope with universal stage being used in the new research center for the identification of minerals in rock sections




NEW!

Forward-scattering photometer may prove indispensable for measuring and controlling outdoor and indoor air pollution

by Ralph H. Müller

The Phoenix Precision Instrument Co. of 3803–05 North Fifth St., Philadelphia 40, Pa., manufactures several important photometric instruments. We restrict our discussion to the Sinclair-Phoenix forward scattering smoke photometer. Later, we intend to describe the light-scattering photometer and automatic recording mass collecting differential refractometer.

Through the courtesy of Edward J. Fuhrmeister, the following information and illustrations have become available. The forward-scattering photometer is the latest, improved, commercial version of the apparatus described by David Sinclair [*Air Repair*, **3,** 51 (1953)] and built at the Johns-Manville Research Center, Manville, N. J. The photometer is a complete self-contained instrument for measurement of the mass concentration (dust load) of particulate matter in the atmosphere. An ingenious optical system measures the forward scattering of light from the particles of smoke, dust, fume, etc., drawn continuously through a darkfield illumination chamber. When the composition and particle size of the smoke remain relatively constant, the reading of the instrument is directly proportional to the mass concentration.

The range of concentration observable with this instrument is about 100,000 times, enough to include all outdoor and most indoor air pollution. This large range is obtained on a single scale by logarithmic amplification of the photocurrent from a photomultiplier tube illuminated by the forward-scattered light. For more detailed and precise measurement over a very restricted range, a linear amplifier is available. For either method, the Phoenix company furnishes a wide selection of indicators or recorders, including spotlight galvanometers of moderate and high sensitivity, a servo-scale expander, and electronic pen strip chart recorders of the one- or two-pen variety.

The optical principles involved in the Sinclair-Phoenix photometer are almost self-evident in the schematic diagram of Figure 1. In the optical projection system, the diaphragm stop, *D′*, defines a cone of darkness which fills the aperture of the scattered light-collecting lens *L″*. The latter, however, is free to collect all radiation scattered by particles in the forward direction (left to right in Figure 1). Other stops, *E, S, A, I′, W,* etc., minimize stray light arising from multiple reflection and other cases.

The assembly shown in Figure 2 is suitable for measuring the mass concen-

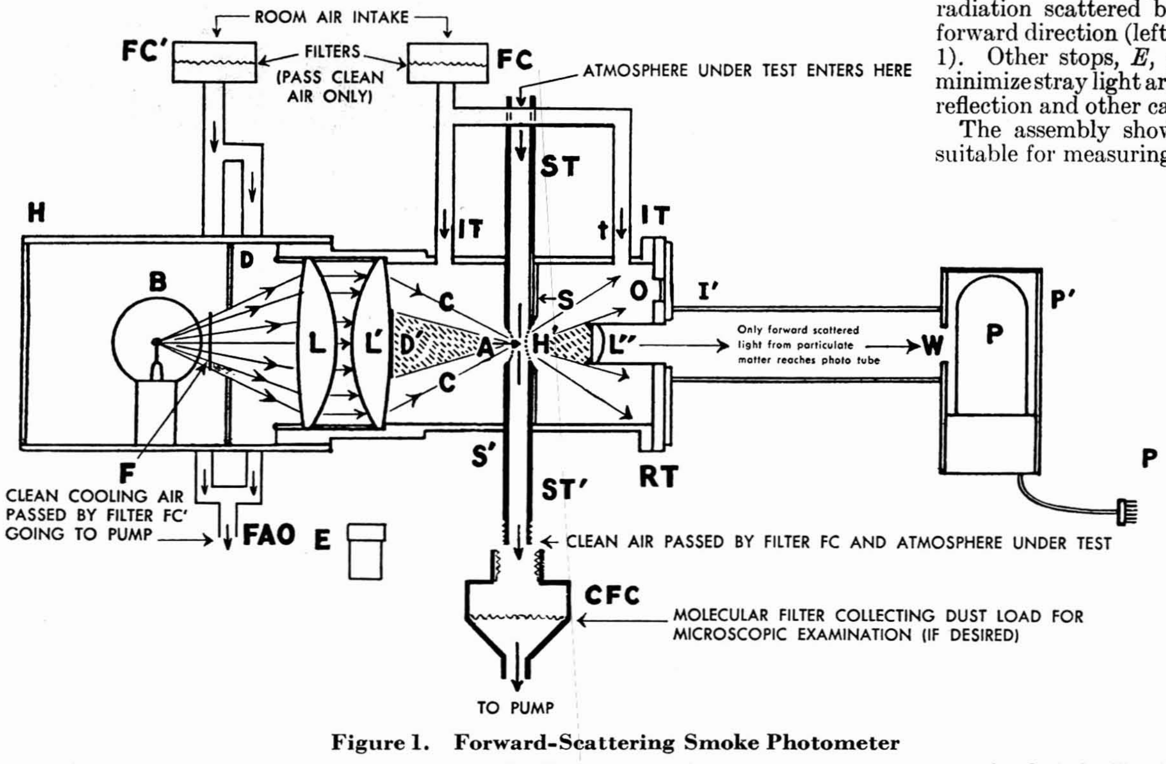


Figure 1. Forward-Scattering Smoke Photometer

A.	Stray light limiting diaphragm
B.	Lamp
C.	Converging cone of light
CFC.	Mass collector filter carrier
D.	Feathered edge diaphragm
D′.	Diaphragm stop, produces converging cone of darkness
E.	Removable eyepiece which replaces photomultiplier tube for visual observation of smoke particles, also used for alignment
F.	Heat-absorbing filter
FAO.	Lamp filtered air outlet
FC.	Optical system protector filter and carrier
FC′.	Light source system protector filter and carrier
H.	Sealed light source housing
H′.	Diverging cone of darkness
I′.	Light trap tube
IT.	Filtered air inlets
L,L′.	Condenser lenses
L″.	Scattered light collecting lens
O.	Optical calibration filters
P.	Photomultiplier tube
P′.	Shielded photomultiplier tube housing
P3.	Cable to logarithmic amplifier
RT.	Rotatable light trap tube flange
S.	Stray light diaphragm
S′.	Sealed optical housing
ST.	Smoke inlet tube
ST′.	Smoke and filtered air outlet tube
W.	Photomultiplier tube diaphragm

tration on a logarithmic basis. A strip chart recorder can be connected to this system. The record will be an enlargement of the meter readings (11 inches full scale).

For a more precise indication over a very limited concentration range, the arrangement of Figure 3 is to be preferred. At the extreme left is the Sinclair-Phoenix forward-scattering aerosol and smoke photometer. This is connected to the Phoenix electron multiplier photometer and detector which is used in place of the standard logarithmic detector and amplifier. At the right is a strip chart recorder, although for certain applications a galvanometer or servo-scale expander may be preferred.

The actual value of the mass concentration corresponding to the reading of any of these instruments depends upon the type of particulate matter in the atmosphere, its particle size, shape, refractive index, and color. Each factor must be determined by the user. There are many possibilities—among them, the weighing of material collected on a suitable collector.

Also, the instrument may be calibrated in the laboratory by using an aerosol of known size and physical properties. The standard calibration using dioctyl phthalate oil fog of 0.3-micron droplet diameter showed that a mass concentration of 10^{-3} γ per liter gave the minimum perceptible reading of about $^3/_{64}$ inch on the large type indicating meter, while 100 γ per liter gave full scale deflection. Calculations based on the theory of light scattering show that the lower limit of concentration corresponds to an atmospheric visibility of 930 miles and the upper limit to 50 feet. Any atmospheric pollution such as smoke, dust, or haze, would occur well within this visibility range.

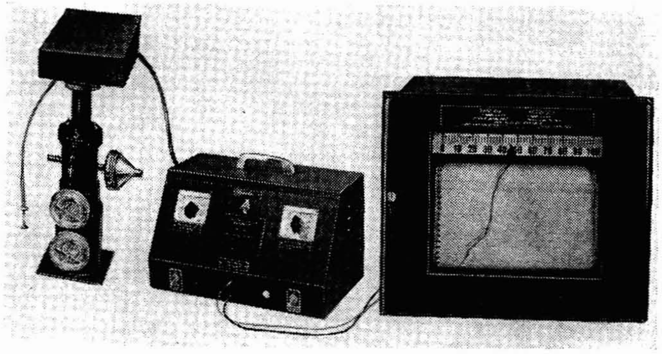


Figure 3. Arrangement for Precise Indication over Limited Concentration Range

The instruments can be expected to prove indispensable in the study, measurement, and control of air pollution in and around cities, industrial areas, offices, apartment buildings, plants, mines, and the holds of ships. Perhaps more important is their use in the research aspects of pollution problems, where filter design, air wash, and ventilation systems can be controlled.

In municipal air pollution studies, the continuous sampling and recording will be indispensable and should eliminate much uncertainty characteristic of grab sampling. Such studies represent a small but highly important part of the general problem. One need merely look at the results of mass spectrographic analysis of airborne contaminants to understand the complexity of this problem. There are still bitter discussion, acrimonious claim, and pointless name calling in this business—typical of the preinstrumentation phase of any large scale argument.

A large portion of California can justify the extravagant claims of its chambers of commerce. But, whatever aberration leads its citizens to attempt a fusion of heavy industry and idyllic natural resources, it does not work out and exodus is attaining alarming proportions. Recently, a distinguished chemist drove to southern California to consider a research post on this problem. His family accompanied him for a long overdue vacation. Their open-mouthed gasp at the beauties of Pasadena and environs was a mistake. They reacted with violent sneezing, coughing, and copious weeping. Residents comforted them with the statement that this day's smog was by no means the worst. A good man has been lost to this problem.

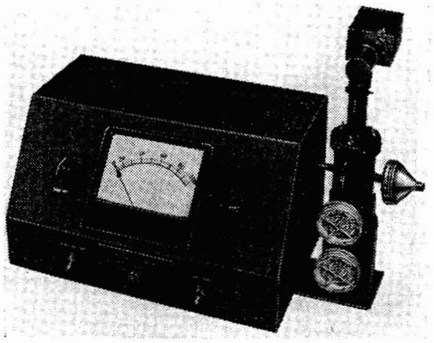
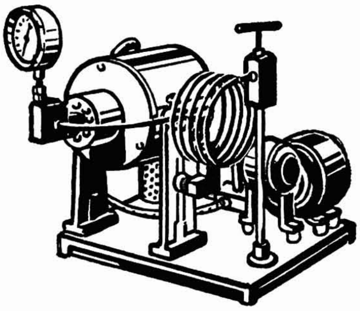
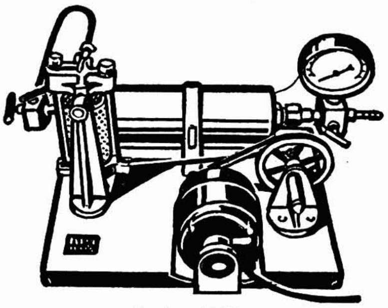


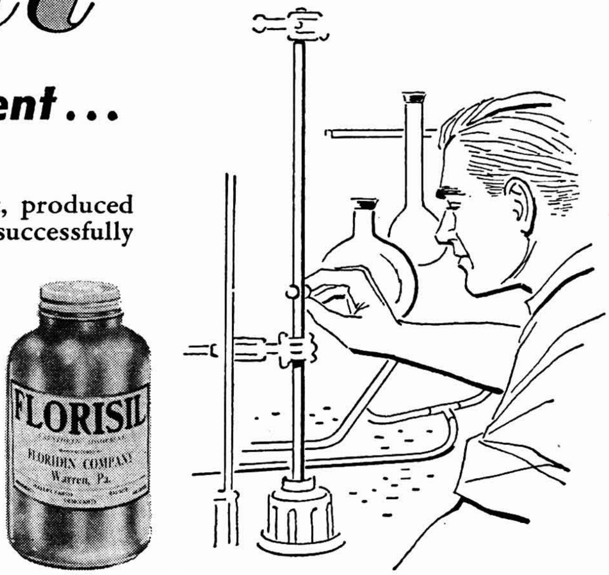
Figure 2. Photometer for Logarithmic Measuring

Man has had a century's experience with the studied design of the industrial slum. In the early days of the industrial revolution, coal smoke was the exclusive contaminant. Less than a quarter of the era can be said to be the chemical age, but it presents contamination possibilities, wherein only the fruits of an atomic era can supply a swift, unanswerable, and irrevocable termination.

Automatic instrumentation is the answer, in our opinion, precisely because it leaves out, very largely, the human element, which is the real bottleneck.



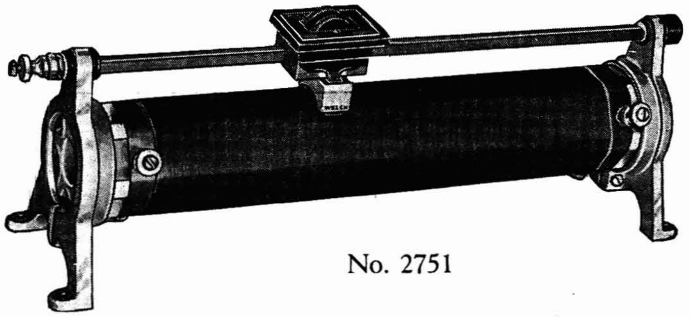



FLORISIL
FLORIDIN COMPANY
Warren, Pa.

Welch AIR-FLOW SLIDE-WIRE RHEOSTATS

90% REDUCTION in Reactance and Inductive Effects
200% GAIN in Heat Dissipation

Smoothly Operating Fine Adjustment
Durably Constructed



No. 2751

The sturdy construction and good heat dissipation of these rheostats make them ideally suited for general laboratory use. Thirteen sizes are offered.

Contact with the nickel-chromium-iron resistance wire is made by two graphite-copper brushes having a large contact area to give smooth current control and very little wear. The slider moves the full length of the rheostat, moves rapidly with ease, and has a freely turning fine adjustment at the center.

The wire is wound on a thick-walled Coors porcelain tube having a deeply grooved outer surface to provide air ducts for convection cooling. By using this non-magnetic core the disturbing magnetic effects on nearby unshielded meters is reduced, the inductive effect and consequent arcing is less, and the reactance in A.C. circuits is lowered. The core is 32 cm long and 5.6 cm in diameter. The end supports are of metal.

Available with the following nominal ratings:

Ohms	Amperes
2.5	13
5	9.2
10	6.5
20	4.5
40	3.2
85	2.2
170	1.6
340	1.12
680	.80
1300	.57
2600	.40
3800	.34
5500	.30

$15.35 EACH

Manufacturers of
Scientific Instruments and
Laboratory Apparatus

W. M. WELCH SCIENTIFIC COMPANY
DIVISION OF W. M. WELCH MANUFACTURING COMPANY
ESTABLISHED 1880
1515 SEDGWICK STREET, DEPT. A CHICAGO 10, ILLINOIS, U.S.A.

For further information, circle number 36 A on Readers' Service Card, page 37 A

ANALYTICAL
CHEMISTRY

August 1954

Readers' Information Service

These handy cards will bring information of value to chemists, engineers, and other technologists in laboratory, pilot plant, and production.

Circle Desired Items. Numbers on the adjoining tear-out cards are keyed to items in the NEW PRODUCTS section on the immediately following pages. For further information on any new product or service or for a copy of literature listed in NEW PRODUCTS, circle the corresponding number and mail card. For information about any of the products listed in the ADVERTISED PRODUCTS INDEX below, the reader should refer to the advertising pages and write directly to the company concerned.

See page 40 A for New Products for Analysts

ADVERTISED PRODUCTS INDEX

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Balances	11 A
Balances, Analytical	6 A 18 A
Balances, Triple-Beam	30 A-1
Balances for Moisture Determinations	8 A
Bottle Shaking Machines	7 A
Burets	3rd Cover
Centrifuges	7 A
Colorimeters	10 A-3 30 A-2 48 A-2 4th Cover
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pH Meters	10 A-1
Pipets	3rd Cover
Polyethylene Bottles	52 A-2
Polyethyleneware	52 A-3

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	17	18	19					
MANUFACTURERS' LITERATURE	20	21	22	23	24	25	26	27
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MANUFACTURERS' LITERATURE	20	21	22	23	24	25	26	27
	28	29	30	31	32	33	34	35
	36	37	38	39	40			

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ACS editors screen all manufacturers' product announcements and industrial literature, publishing only what is *really* new and containing valuable scientific or technical data.

You can trust the judgment of ACS editors not to clutter Readers' Information Service with items of doubtful value simply to prove "readership."

Every chemist, every chemical engineer should make certain he keeps up to date by:

(1) Subscribing and reading those ACS publications which serve his particular field.

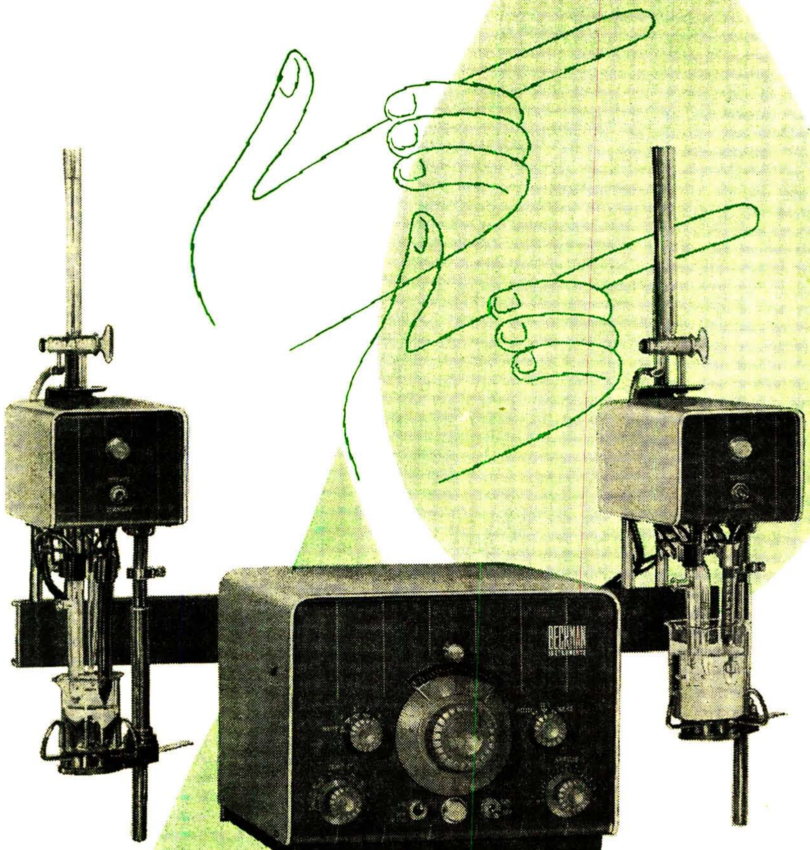
(2) Examining carefully the advertising pages in ACS publications, for they contain scientific and technical data second only in importance to the editorial pages.

(3) Building up a substantial reference file of manufacturers' literature to provide valuable information quickly.

Use this handy return card to save yourself time. It will bring information of use to chemists and engineers in laboratory, pilot plant, and production. The items listed in this special section have been selected by the editors of ANALYTICAL CHEMISTRY for their value and timeliness in helping you to keep abreast of the latest developments in the field.

See page 40 A for New Products for Analysts

Like having two extra hands!



BECKMAN

the new Beckman

Automatic Titrator

Your laboratory needs the Automatic Titrator if you run: Mass Titrations—Potentiometric Titrations—Titrations on Colored or Turbid Samples—Nonaqueous Titrations.

This automatic instrument runs titrations with the intelligence of a human operator, but without fatigue and without error. It adds titrant rapidly at first, then approaches the end of the titration cautiously—and stops exactly at the end-point. The important thing is that *every* titration is routine with the Beckman Automatic Titrator. It does them all accurately, automatically, and without attention.

Send in the coupon for more information

Here are typical applications where the Beckman Automatic Titrator does the job better:

- Ascorbic and Citric Acids in Fruits and Vegetables
- Oxygen Dissolved in Water (Winkler Method)
- Total SO_2 in Sulfite Liquor by Palmrose Method
- Sulfides and Mercaptides in Petroleum Products
- Total Acidity in Milk
- Bicarbonate in Blood
- Borate in Brine and Salts
- Copper in Ores and Alloys
- Iodine Number of Fats
- Hydroxyl Number in Resins
- Peroxide Value of Fats and Oils
- Free Fatty Acids in Fats and Oils
- Iodine Titration with Thiosulfate
- Analysis of Pickling and Plating Solutions
- Total Nitrogen by the Kjeldahl Method
- Permanganate Number of Wood Pulp
- Ceric Sulfate in Steel and Iron Ore Analysis
- Saponification Number of Fats and Oils
- Bromine Number for Unsaturation in Petroleum Products

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Beckman *division*
BECKMAN INSTRUMENTS, INC.
FULLERTON 1, CALIFORNIA

For further information, circle number 39 A on Readers' Service Card, page 37 A

NEW PRODUCTS FOR ANALYSTS

Equipment, Apparatus, Instruments, Reagents, Materials

Colorimeter-Spectrophotometer

A combination colorimeter and spectrophotometer, called the Spectronic 20 because of its 20 mμ band pass, has been announced by Bausch & Lomb Optical Co. The instrument employs a diffraction grating to produce high wavelength accuracy and spectral purity, according to the company. It can be used in both routine and research work.

The Spectronic 20 analyzes any liquid or solid which transmits light by subjecting the sample to light of specified wave lengths. Readings can be taken from a double scale in terms of either transmittance or optical density. By turning a control knob, the operator can adjust the diffraction grating for any wave length in the instrument's range of 375 to 950 mμ. For the range from 650 to 950 mμ an infrared tube and filter replace the standard tube.

Basic components of the instrument are a grating monochromator, a photoemissive detector to pick up light which passes through the sample and transmit it in the form of photoelectric current, and an electronic amplifying system. **1**

Laboratory Reagents

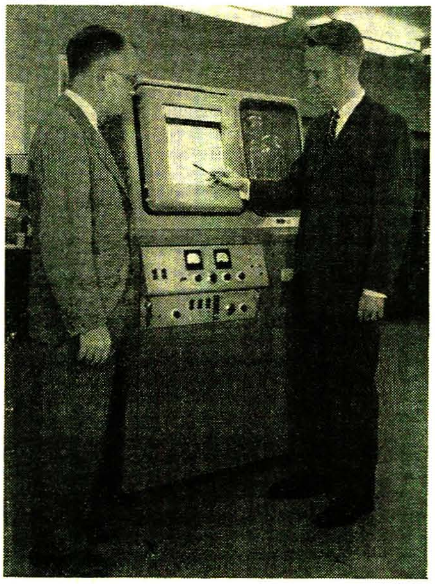
Six new laboratory reagents are now being offered by Merck & Co., Inc. Included are the following:

Osmium tetroxide (acid osmic)
Ammonium bicarbonate
Capryl alcohol
Cupric acetate
Sodium ammonium phosphate crystals
Sodium sulfide pentahydrate **2**

Mass Spectrometer

A portable, cycloidal-focusing mass spectrometer, Model 21-620, for making high speed analyses of gaseous and light liquid mixtures, has been developed by Consolidated Engineering Corp. It is designed for monitoring process streams, as well as conventional laboratory uses.

Cycloidal focusing of ions depends upon ion mass and the strength of crossed uniform electric and magnetic fields. It is independent of the velocity or direction of motion of the injected ions.



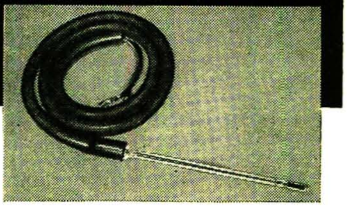
Quantitative separation may be obtained from mass 2 through mass 150. Scanning is possible to mass 180. Spectra are recorded to show as peaks the distribution and relative quantity of ions resulting from conventional electron bombardment. Interferences between these peaks from distortion due to ion energy spread has been eliminated, according to the company, by the independence of initial ion energies in the cycloidal instrument. **3**

Atom Models

Sets of scaled atom models manufactured by E. Leybold's Nachfolger in Germany are being distributed by Arthur S. LaPine & Co. Each set provides 28 structural unit types which can be used to study the structure of organic molecules.

Distinguishing colors are used for the various elements, which include hydrogen, carbon, oxygen, nitrogen, sulfur, phosphorus, silicon, fluorine, chlorine, bromine, and iodine. The first five elements listed are supplied in different types of structural units for various bonds and ring arrangements. Connections are made by snap-on fasteners. Small removable spring

For further information, see coupon on page 37 A



metal wedges make rigid connections for multiple bonds. A hook-and-eye arrangement on the hydrogen structural unit permits construction of hydrogen bridged molecules.

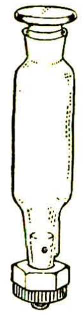
The models provide magnification of spheres of action of single atoms to 1.5×10^8. Dimensions of the models are claimed to be proportional to the mean of the latest experimentally measured values. **4**

Scaler

A general purpose scaler for operation with Geiger, scintillation, or proportional counters has been announced by Nuclear Instrument and Chemical Corp. The instrument, known as Model 192 Ultrascaler, permits either manual or automatic counting procedures, including either predetermined time or predetermined count operation and time-count operation where the count will be stopped at a preset time or preset number of counts, whichever occurs first.

For check purposes, the Ultrascaler has a 60-cycle calibrating circuit. It is also provided with electrically reset timer, register, and preset time clock. **5**

Separatory Funnel



A glass separatory funnel with a valve that is claimed to eliminate stopcock lubrication and freezing problems has been developed by Fischer & Porter Co. The Ultramax valve consists of a Teflon plug which turns on the natural glazed surface of an unground, precisely formed section of borosilicate glass tubing. The inert plug will not freeze, regardless of the fluid being handled.

The tip of the valve is an integral part of the Teflon plug, reducing the possibility of breakage. Parts are interchangeable. Funnel sizes from 30 ml. to 2 liters are available in globe, Squibb, or cylindrical shapes.

The cylindrical shape can be used for centrifuging to speed up separations. Because valve lubricants are unnecessary, product contamination is avoided. This makes the unit especially useful for vitamin assays, says the company. **6**

o-Phenanthroline

o-Phenanthroline for iron analysis is now available from Fisher Scientific Co. as a certified reagent made to ACS specifications. The reagent indicates redox end points clearly and distinctly,

For further information, see coupon on page 37 A

according to Fisher, and gives a Beer-Lambert curve for traces of iron.

Fisher also offers *o*-phenanthroline-ferrous sulfate complex in 0.025*M* solution, packaged by volume. **7**

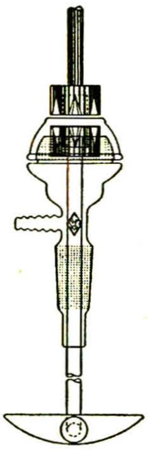
Vapor Equivalent Apparatus

An apparatus for measuring the volume of vapor which is equivalent to a unit volume of liquid after it is vaporized has been developed by Phillips Petroleum Co. The instrument was designed for the determination of the vapor equivalent and molecular weight of liquid residues from natural gas samples, but can be applied to any liquid which has a vapor pressure of more than 4 mm. of mercury at the temperature of the vaporization bulb.

The compact unit comprises a vaporization bulb with an integral multiplying manometer and a removable sample entry system consisting of an orifice and matching pycnometer. It is mounted in a glass constant temperature bath.

The procedure for using the instrument consists of filling the pycnometer with sample, admitting the sample to the evacuated vaporization bulb, and reading the pressure on the multiplying manometer. The molecular weight is then calculated from the previously determined specific gravity. The apparatus measures vapor equivalent as gaseous milliliters per liquid milliliter. **8**

Magnetic Stirrers



A magnetic stirrer designed so that the magnetic field is located above the vessel being stirred, leaving the underside free for application of heat or cold, has been developed by Scientific Glass Apparatus Co., Inc. Liquids with a consistency up to that of glycerol can be agitated.

The Lew magnetic stirrer employs an upper magnet located outside the vessel and attached to a motor shaft that can be inserted in a motor chuck. A lower magnet, covered with polytetrafluoroethylene, is mounted in a well at the top of a borosilicate glass adapter which fits into the neck of the flask. Stirring rod and blade are connected to this lower magnet. A removable borosilicate glass semiball cap fits over the well. As there is no direct contact between the rotor and motor, a hermetically sealed vessel can be obtained. Speed of rotation is governed by motor speed.

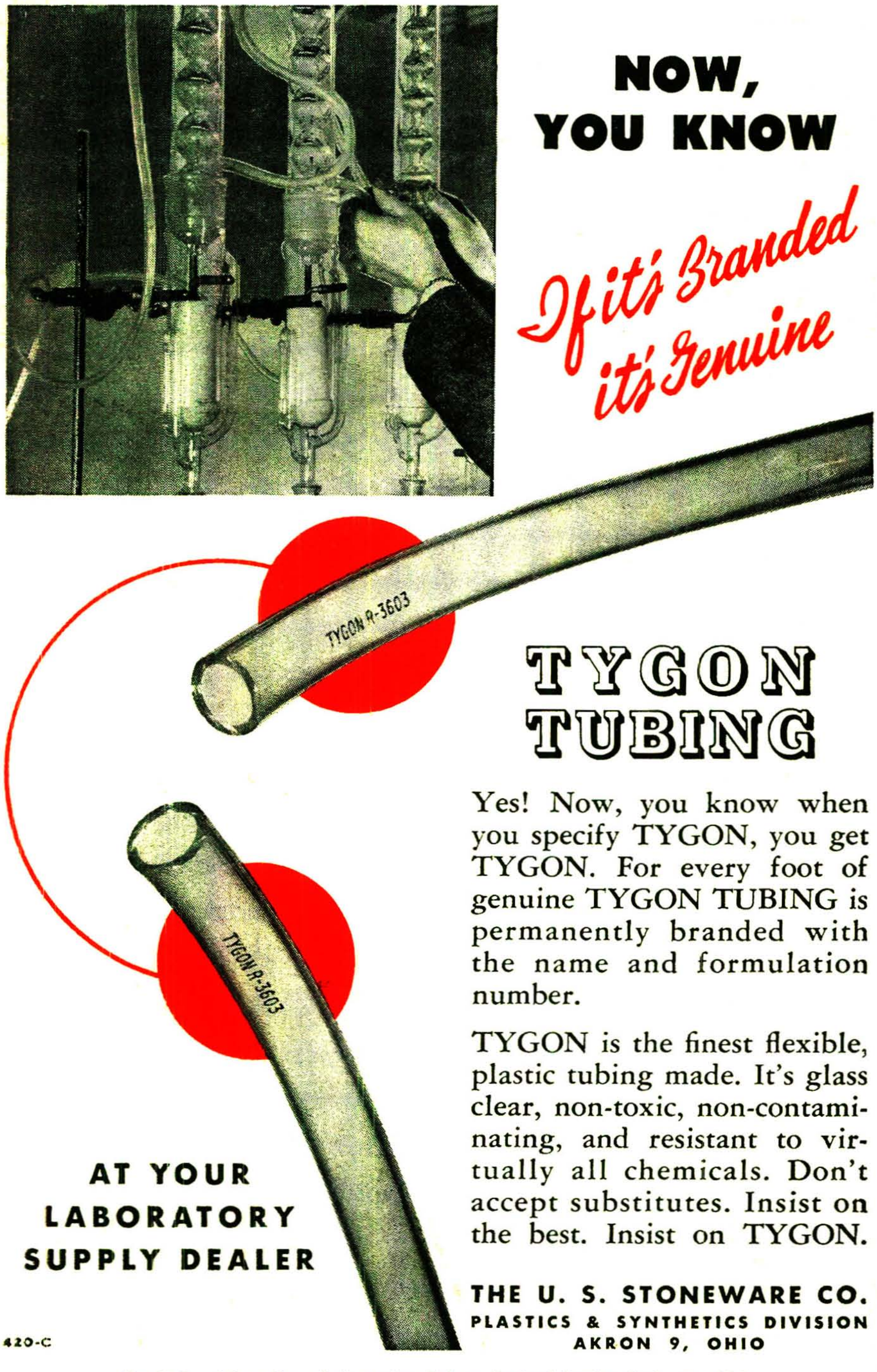
The stirrer is available with a side connection for vacuum or pressure use (illustrated) and in a model without the side connection for atmospheric work. Either type can be provided with six-pole or eight-pole dual magnets. The eight-pole type can be used in vessels of up to 50-liter capacity. **9**

Electrophoresis Apparatus

An apparatus for zone electrophoresis in supporting media is available from Kelab Aktiebolag of Sweden. Electrophoresis is carried out in the supporting medium contained in a vertical tube. When it is finished, the separated components are forced out of the medium by buffer flow obtained by applying air pressure to the tube and collected in fractions for analysis.

Two advantages are claimed for the

For further information, see coupon on page 37 A



apparatus over trough equipment for electrophoresis: sampling is said to be easier and more accurate because the medium need not be cut into segments and eluted, and one column can be used for many electrophoretic experiments without repacking. Capacity of the apparatus is 0.5 to 2 ml. **10**

Quartzware

Quartz shapes for microanalytical work are being produced by Microchemical Specialties Co. Items include beakers, boats, flasks, graded seals, ground joints, and capillary pipets. The shapes are transparent and are said to provide high transmission of ultraviolet and visible radiation. Melting point and chemical resistance are high. **11**

Microscope

A wide field microscope is being produced by Testa Mfg. Co. for general purpose work. Its use is not limited to inspection of specimen slides, for it can be used to examine whole mounts, crystals, textiles, foods, parts, and other objects.

The Model A microscope is adjustable to 15×, 45×, and 75×. In addition to normal position for desk or bench work, the arm or tube can be inclined or reversed to operate in any direction of a 360° circle. The tube may be removed and used as a pocket microscope. **12**

Viscometer

A torsional viscometer designed in Switzerland for rapid detection of viscosity changes is now available in the United States from Drage Products. Frictional forces are transmitted through a rotating measuring element to a rotatable mounted motor, the torque of which is opposed by a constant modulus hairspring.

A pointer attached to the motor casing directly indicates viscosity. The instrument has speeds of 20, 64, and 200 r.p.m. A recording attachment is available as an accessory. **13**

Electrophoresis Apparatus

For paper electrophoresis determinations, Labline, Inc., is marketing the Series 54 Electrograf. The instrument has a migrating chamber molded in one piece from transparent plastic which will hold 20 $1/2$-inch-wide or 12 1-inch-wide filter strips. The cham-

For further information, see coupon on page 37 A

ber measures 15 inches long, 11 inches wide, and 4 inches deep.

Voltage control is from 0 to 450 v.; current control is from 0 to 50 ma. The power supply can operate four migrating chambers simultaneously.

Plastic buffer troughs and electrode troughs are isolated from each other to protect the migrating materials from unfavorable pH changes due to accumulation of electrode products. Cotton wicks connect electrode troughs with buffer troughs. An automatic leveler between buffer troughs prevents syphoning through the filter paper strips. Platinum electrodes are sealed in the buffer troughs.

For safety, the migrating chamber is provided with a mechanical interlock to prevent operation unless the cover is in place. **14**

Stress Measurement

An instrument for measuring stresses caused by shrinkage or expansion in chemically deposited metals, electroplated metals, or paint, lacquer, and plastic films has been developed by Joseph B. Kushner Electroplating School. The apparatus can measure stresses ranging from 100,000 pounds per square inch in tension to 50,000 pounds per square inch in compression.

Stresometer is actuated by the deflection of a simple, flat metal disk which dishes in or bulges out as the material deposited on the outside of the disk shrinks or expands. The deflection at the center of the disk is magnified by a hydraulic arrangement so that it can be read on the linear stress scale of the instrument.

The unit can be used for electroplating control purposes and for research and development work. Stress readings may be taken continuously as a function of time or individually. **15**

Recording Spectrophotometer

Designed to give continuous transmittance records in the ultraviolet, visible, and near-infrared regions of the spectrum is the Model DK recording spectrophotometer now in production by Beckman Instruments, Inc. The instrument records per cent transmittance versus wave length over a range from 220 to 2700 mμ. A lead sulfide detector is used for the near-infrared spectrum; a hydrogen discharge lamp and photomultiplier detector are utilized in the ultraviolet region.

Operating on a double-beam optical principle, the unit employs a single quartz prism monochromator. Source light is chopped mechanically at 480 cycles per second, switched 15 times a second from reference cell to sample cell, and then sent to the single detector. This design is said to combine advantages of double-beam and single-beam systems. All tubes are common to the sample and reference signals, eliminating difficulties of matching phototubes, and circuitry is simplified. Such features of double-beam operation as elimination of effects of source and supply voltage fluctuations, freedom from tube characteristics and recorder standardizations, and drift-free amplification are realized.

Scanning speeds for the entire range of the instrument can be 5, 15, 50, 150, or 500 minutes. High speed is useful for samples without fine structure, low speeds where high resolution and photometric accuracy are required. **16**

Photofluorimeter

Coleman Instruments, Inc., has brought out a new photofluorimeter, Model 12C. The instrument is based on the design of Coleman's old Model 12. It is said to offer increased sensitivity and improved stability, which enable it to be used accurately at faint fluorescence levels and low concentrations. **17**

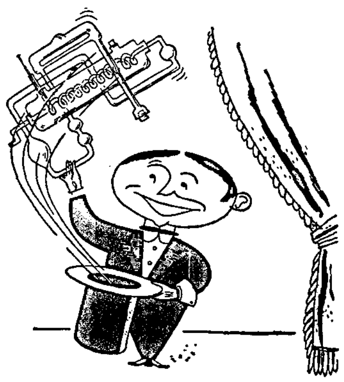
Electrophoresis Apparatus

Specialized Instruments Corp. is offering its Model R paper electrophoresis system, consisting of an automatic electronic curve-drawing integrator, two eight-strip electrophoresis cells, and a regulated power supply.

The power supply is capable of operating with either constant voltage or constant current output and is arranged to energize one or both electrophoresis cells.

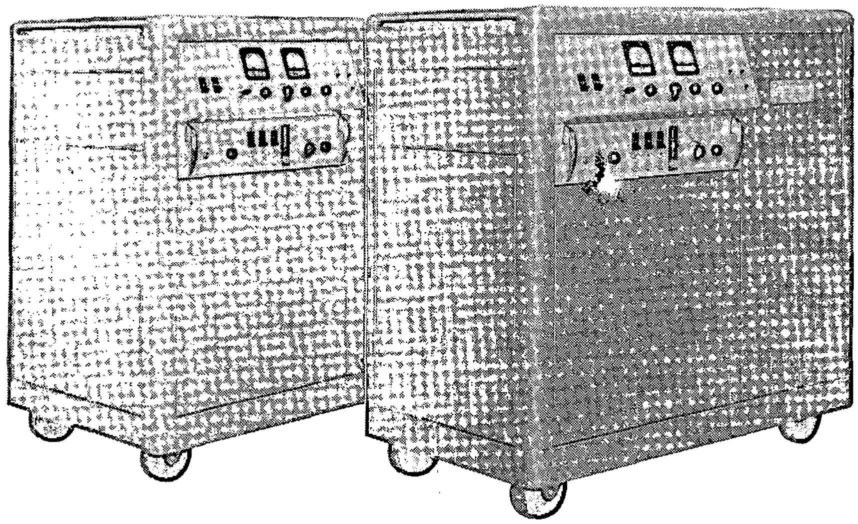
Cell units, of transparent plastic, have detachable racks which can be opened flat for installation of paper strips and for oven drying the strips at the conclusion of a run. Strips make electrical contact with each of the electrode chambers by means of a longitudinal wick which controls strip moisture and permits rapid placement and removal. An equilibrium channel built into the cell base automatically equalizes electrolyte level in the electrode chambers. A sample applicator for placing a metered quantity of specimen through a slot in the top of the cell cover and stainless steel dyeing trays are included.

For further information, see coupon on page 37 A



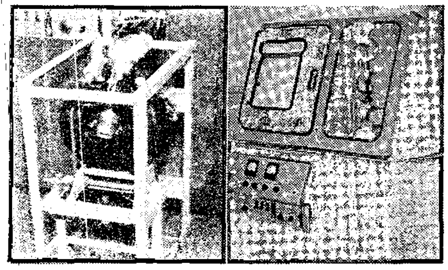
CEC increases the scope of *industrial mass spectrometry* through two great instruments for process monitoring and control

Consolidated's Model 21-610 mass-spectrometer and its companion, the new Model 21-620, far excel all other instruments of comparable price in performance capabilities and reliability in industrial environment. The extreme sensitivity of the 21-610—accurate to a few parts per million—qualify it for highly critical purity studies as well as process monitoring and control applications. Fitted with an accessory hand-held probe, either model serves as a leak detector for any gas within its mass-range. The 21-620's resolving power up to mass 150 further extends the applicability of an industrial mass-spectrometer to research laboratories and medical centers, as well as to plants of chemical, petro-chemical, petroleum and gas industries. Nearly identical in appearance, the 21-610 features the Diatron ion analyzer and the 21-620, a new cycloidal focusing analyzer.



21-620 Except for slightly less sensitivity, the 21-620 has all the capabilities of the 21-610 plus many others. Where the task is to analyze "heavy" gases or liquids, either in plant locations or in the laboratory, the 21-620 process monitor mass-spectrometer is the ideal control instrument.

21-610 The 21-610 is completely self-contained, needing only 110 volts and a small quantity of cooling water for operation. Moderately priced, easily movable, and economical to operate, the 21-610 is industry's ideal instrument for chemical research, process control and leak detection.



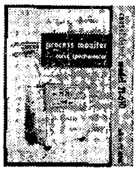
CEC Service Engineers quick change of ion analyzers (right) adds flexibility to Consolidated's two process monitoring mass-spectrometers. A cycloidal focusing analyzer assembly of the 21-620 type is being mounted in the vacuum rack in place of the Diatron analyzer of the 21-610.

The basic instrument can be augmented by many available accessories, thus broadening its application scope. At the far right, are a gas or light-liquid sample inlet system and chart recorder.

Consolidated Engineering
CORPORATION
300 North Sierra Madre Villa, Pasadena 15, California
Sales and Service through **CEC INSTRUMENTS, INC.,** *a subsidiary with offices in: Pasadena, Atlanta, Chicago, Dallas, Detroit, New York, Philadelphia, Washington, D. C.*

ANALYTICAL INSTRUMENTS FOR SCIENCE AND INDUSTRY

Investigate the application of industrial mass-spectrometry to your business. For full details about CEC's two companion process monitoring mass-spectrometers, send for Bulletin CEC 1824A-X2.



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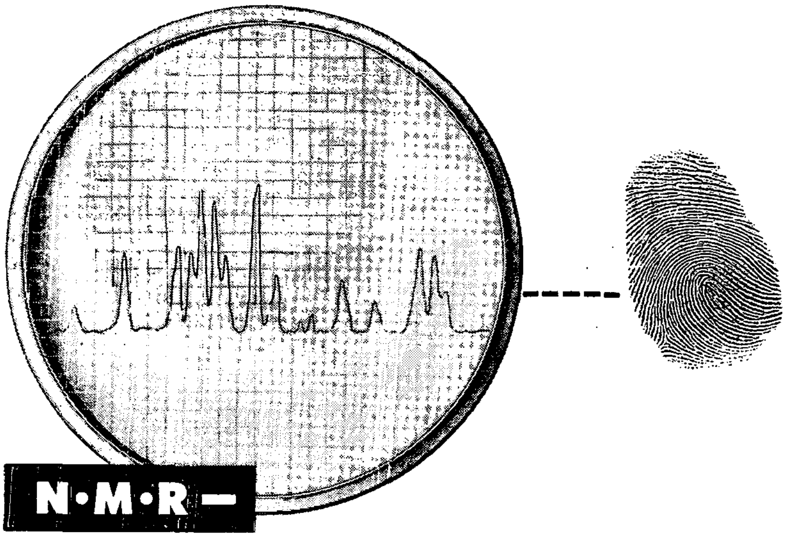


N·M·R—

as revealing as your fingerprint

Because it offers a completely fresh approach to the study of chemical systems, Varian's Model V-4300 High Resolution n·m·r (nuclear magnetic resonance) Spectrometer has become an instrument of major importance to analytical chemists everywhere. Now at work in research laboratories throughout America, this remarkable new device detects signals from H^1, F^{19}, P^{31}, B^{11}, C^{13}, H^2, N^{14}, and several other nuclei, revealing the character of the chemical environment.

High Resolution n·m·r techniques permit rapid, non-destructive analysis of small liquid samples, including melted solids, solids in solution and liquefied gases. Prominent applications include identification of functional groups, equilibrium and kinetic studies, assignment of structural formulas and analysis of multi-component mixtures.

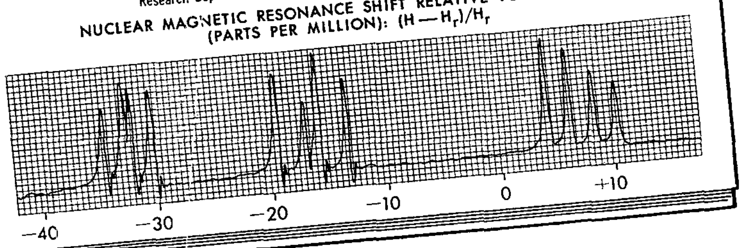
THIS IS N·M·R AT WORK
(Number 5 of a series)
F^{19} SPECTRUM OF TRIFLUOROCHLOROETHYLENE

DATA
Sample: $CF_2{=}CFCl$
Volume: .03 cc.
Frequency: 30 mc.
Field: 7500 gauss
Sweep Rate:
50 milligauss/sec.
Zero of Reference:
Magnetic field at F^{19} nuclei in perfluorocyclobutane

INTERPRETATION
This n·m·r spectrum is typical of the configuration $CF_2{=}CFX$ or $CF_2{=}CFR$, the exact spacing of the various lines depending upon the substituent. The three main groups of lines arise from the restricted rotation about the double bond, which makes all of the fluorine nuclei structurally non-equivalent. The fine structure within each group is a manifestation of the magnetic interactions between pairs of fluorine nuclei coupled by the electron spins. Analyses of such spin-spin multiplets frequently lead to useful structural conclusions and make possible identification of compounds.

The sample was supplied through cooperation of the Petroleum and Chemical Research Department, M. W. Kellogg Company, Jersey City, New Jersey.

NUCLEAR MAGNETIC RESONANCE SHIFT RELATIVE TO REFERENCE (PARTS PER MILLION): $(H-H_r)/H_r$



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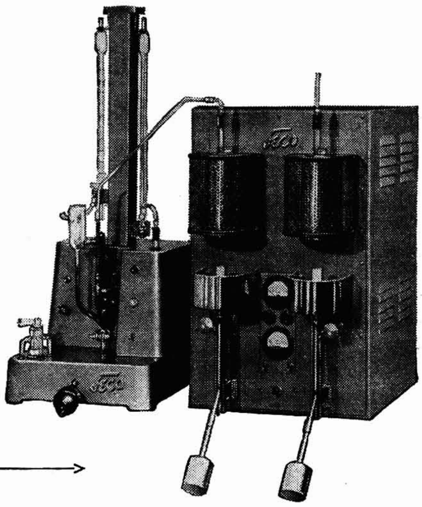

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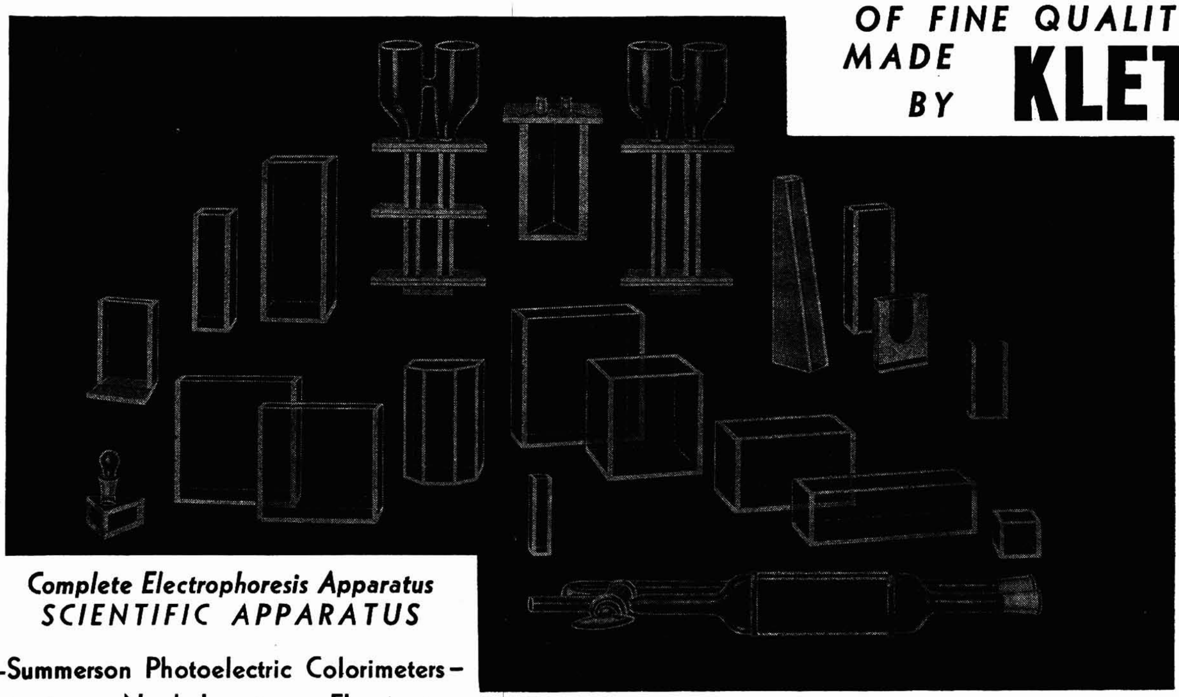

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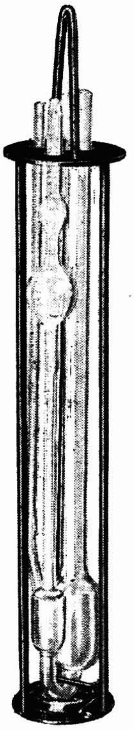

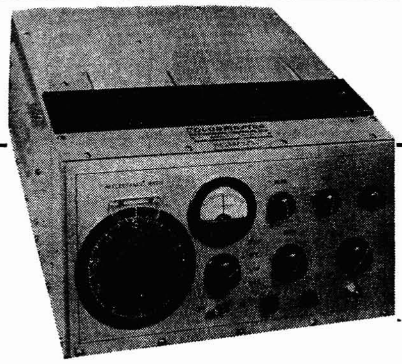

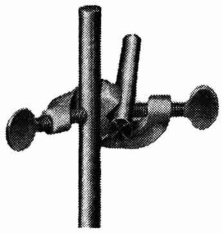
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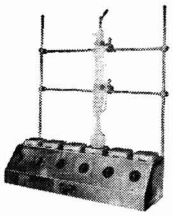
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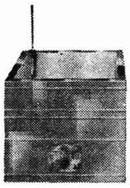
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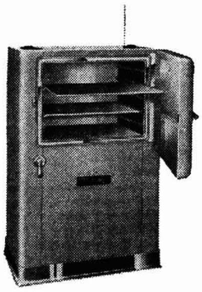
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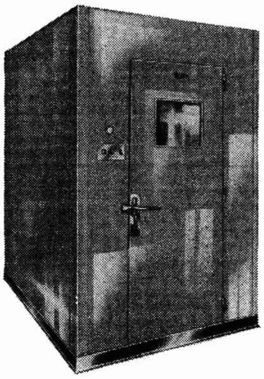
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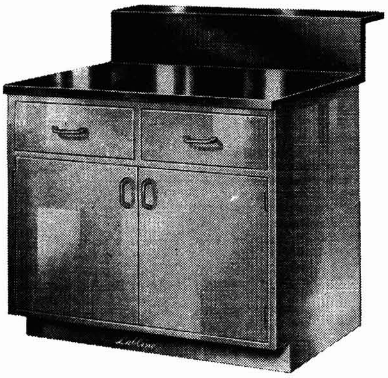
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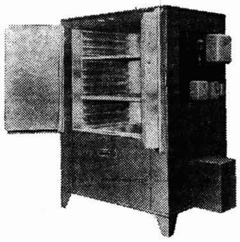
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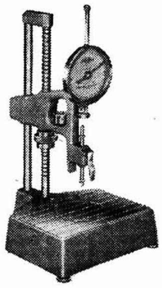
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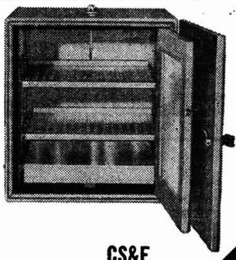
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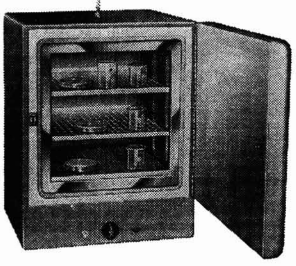
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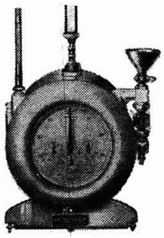
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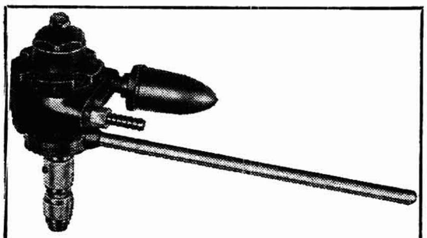

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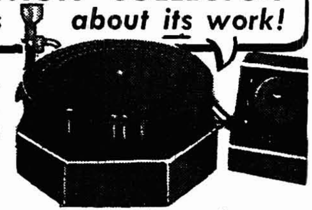

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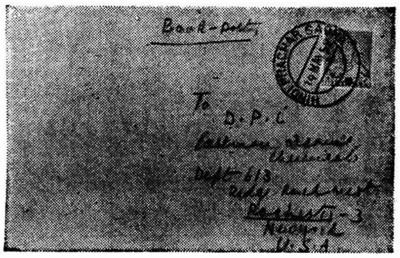


Book-Post

To D.P.C.

Dept 6/3

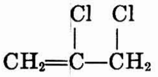
U.S.A.

This envelope came in postmarked Hindi Prachar Sabha a while back but bearing no sender's name or address, inside or out. All that was in it was a sheet of thin paper on which some devoted soul and poor typist had summarized an article about how *Thioacetamide* (CH_3CSNH_2), neat, manageable, water-soluble solid, can replace classical, gaseous, unpleasant hydrogen sulfide for the precipitation of insoluble sulfides.

We thank our self-effacing correspondent from the bottom of our heart. We also blush. Here we have been making *Thioacetamide* (Eastman 1719) for years and years and had never gotten around to mentioning how it can ease one of the oldest and most noxious occupational hazards of our valued friends, the inorganic analysts. (Whoever says that we wanted them to turn to emission spectroscopy so that another division would sell more photographic plates and film is being unkind and unrealistic.)

Thanks to the prod from India, we have now prepared a rather extensive abstract on *Thioacetamide* analytical procedures for various Group II and III metals. This we shall be pleased to send as a gift to all interested. Our friend in India, if he will but identify himself unequivocally, can also have 100 grams of the reagent for his trouble and postage outlay. To others we make a slight charge of $3.00 for 25 grams, or $1.50 for 10 grams.

Allene dispenser . . .



$$CH_2{=}\overset{\overset{\textstyle Cl}{|}}{C}{-}\overset{\overset{\textstyle Cl}{|}}{C}H_2$$

The nation's big producer of synthetic glycerine used to do a little business on the side in allene ($CH_2{=}C{=}CH_2$), but quit. Now allene, a gaseous, rather reactive hydrocarbon, may have some interesting commercial potential. Furthermore, a lot of organic chemists remember it from college days when the professor used it as one of the proofs that the carbon atom is tetrahedral. Consequently, we were not surprised when another smart chemical firm came to us for fifty pounds of allene, this being the sensible thing to do when one needs an organic hard to get from bulk producers.

We were sorry, we told them, but we preferred not to undertake the manufacture of a gas with poor shelf life. Persistent folks, they countered with the suggestion that we make them some *2,3-Dichloropropene*. This boils at 92-95 C and can be counted on to retain its identity over a more reasonable period of time. React it with zinc to pull out the two chlorines and you have your allene when you are ready for it.

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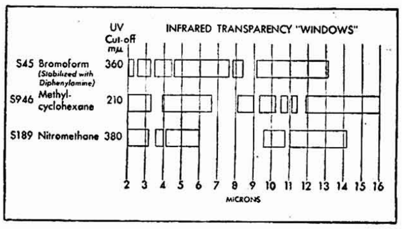

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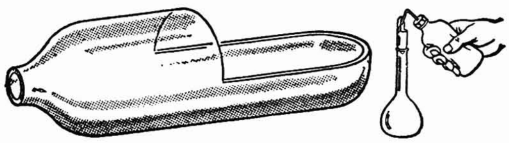

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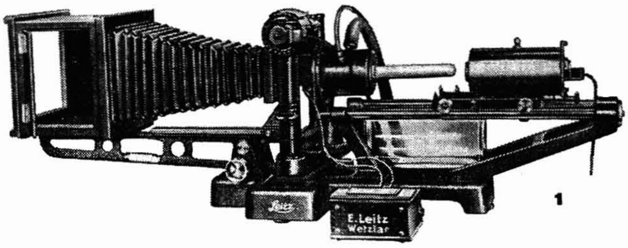

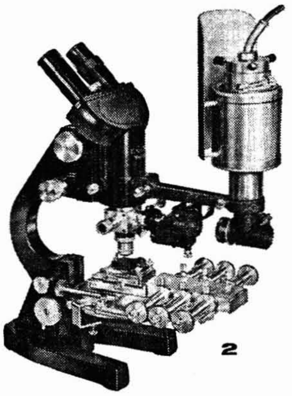

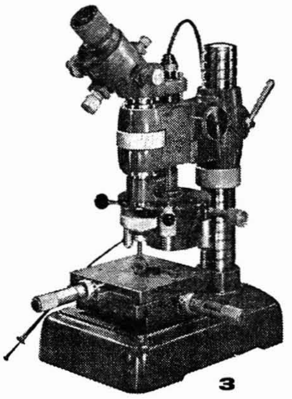

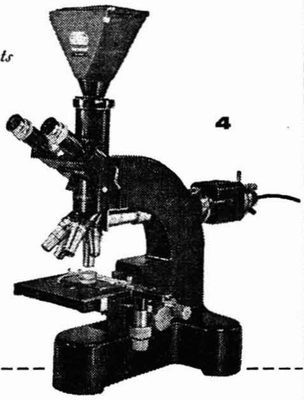

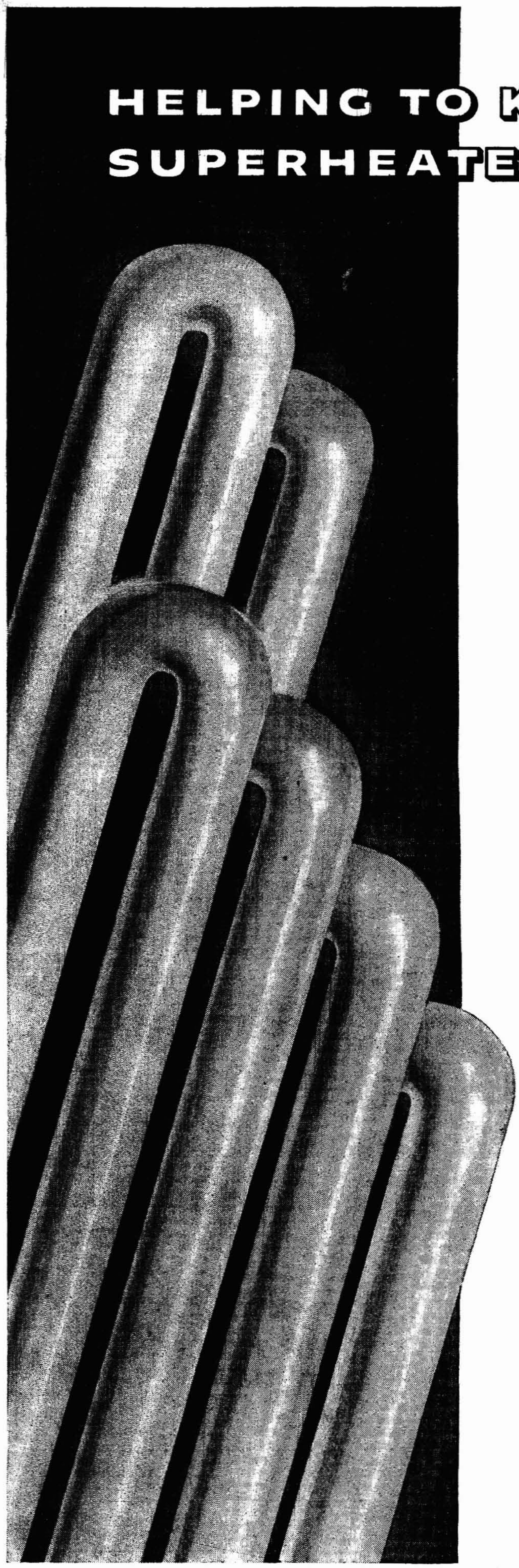

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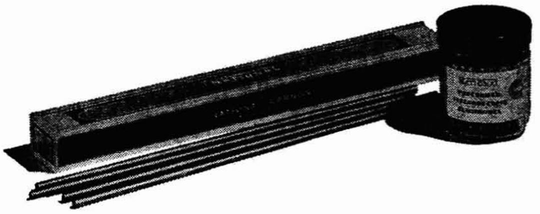
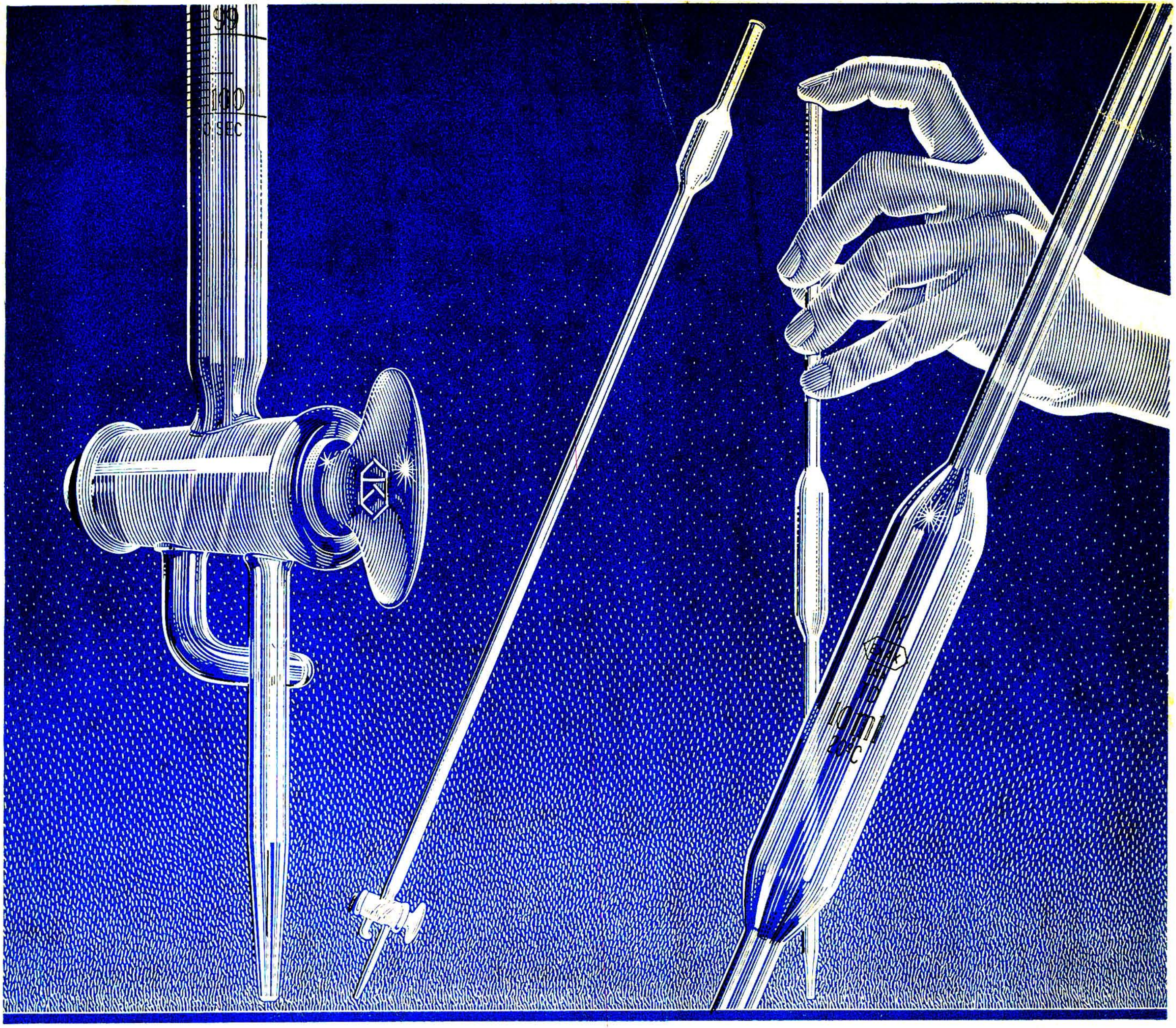


For further information, circle number 54 A on Readers' Service Card, page 37 A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