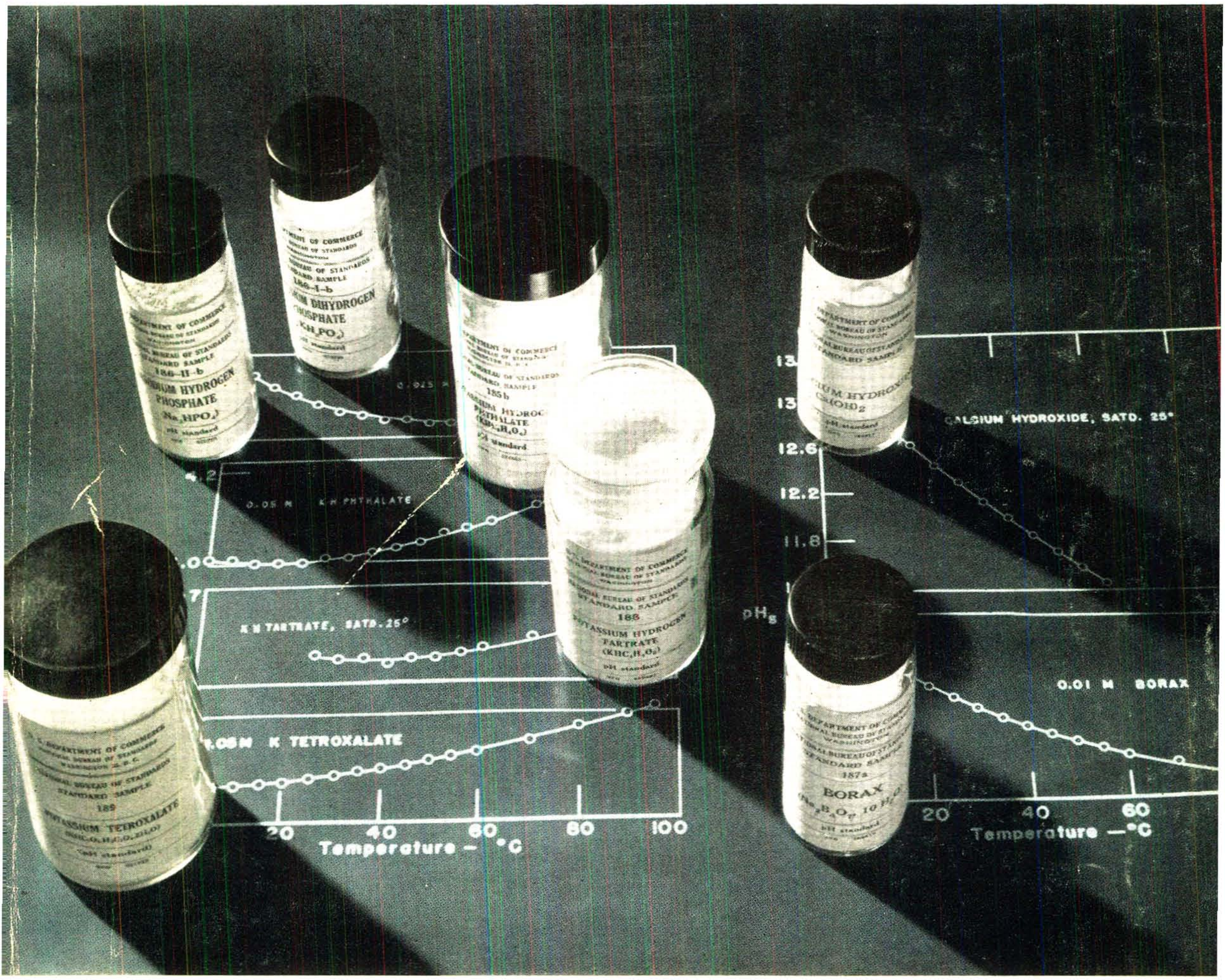
MAY 1957

ANALYTICAL CHEMISTRY



pH—WIDELY USED BUT LIMITED TOOL . . . . PAGE 15 A

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Sulfur Compounds (as S)	0 001 %
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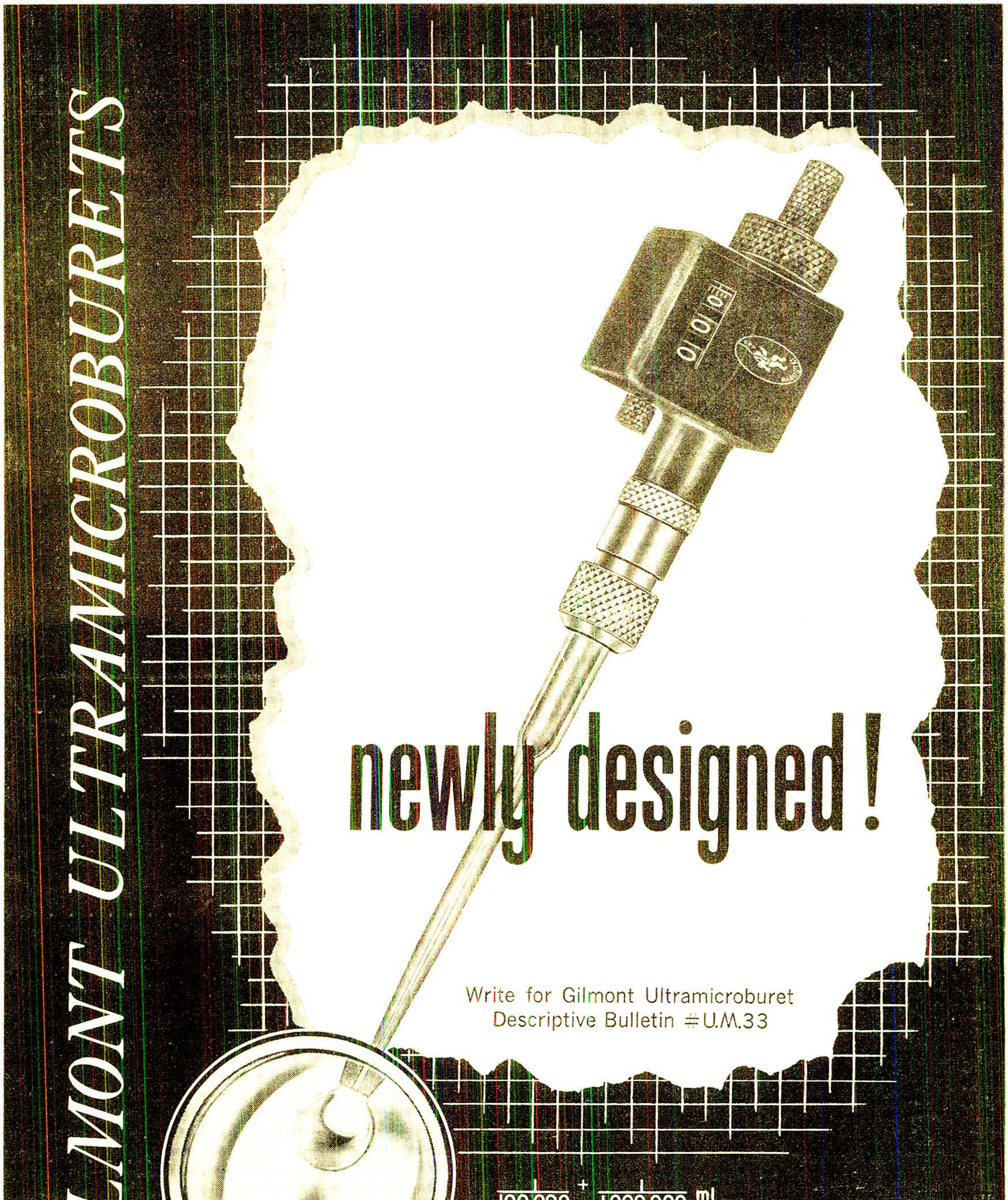
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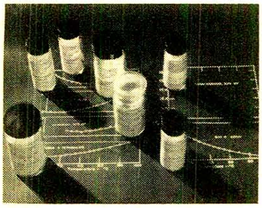

THIS MONTH'S COVER

The six standards issued by the National Bureau of Standards for pH measurement calibration are shown on the cover. The advantages and limitations of this useful tool are described in this month's Report for Analysts starting on page 15A.

Volume 29, No. 5

Issued April 23, 1957

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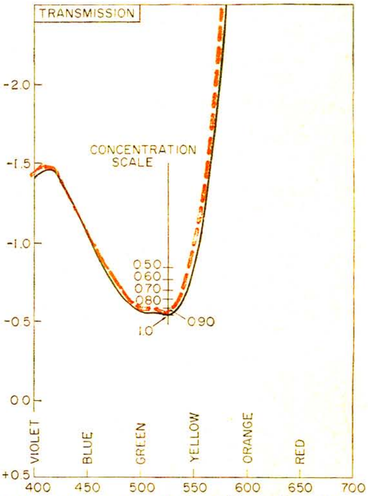
OPERATOR RUNNING CURVE of a color sample on the General Electric's easy-to-use Recording Spectrophotometer.



SCALE SHOWS sample is 10% weaker than known standard of Azo Phloxine GA Extra Conc. (C. I. 31).

Color-match Samples Without Question

PROBLEM 2

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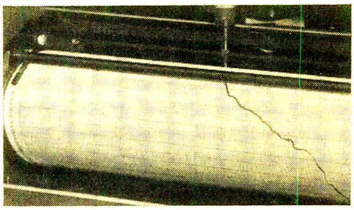
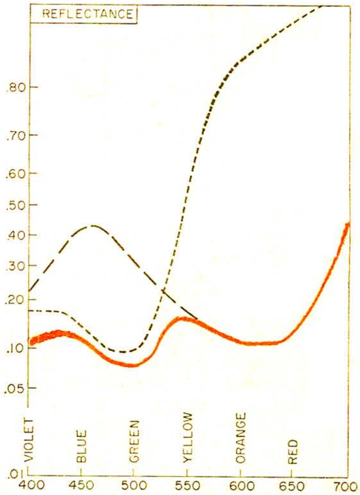
For information about the General Electric Recording Spectrophotometer, call your G-E Apparatus Sales Office or write to Section 585-40, General Electric Company, Schenectady 5, N. Y. For latest information on color measurements, ask to be added to mailing list 79.



CLOSE-UP of the General Electric Spectrophotometer drawing a curve of color.



CURVE OF UNKNOWN SAMPLE indicated in red. Curve shape indicates that blue and orange dyes should be used.

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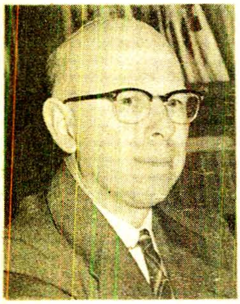
REPORT FOR ANALYSTS

pH and the Modern Analyst

pH, a very useful guide for the analyst, is, unfortunately, an inexact physical quantity with certain serious limitations. A recognition of the faults of pH, as well as its virtues, allows the analyst to use pH measurements most effectively in aqueous and nonaqueous media. This month's Report for Analysts presents a survey of this subject. It is based on a paper presented by the author at the recent Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.



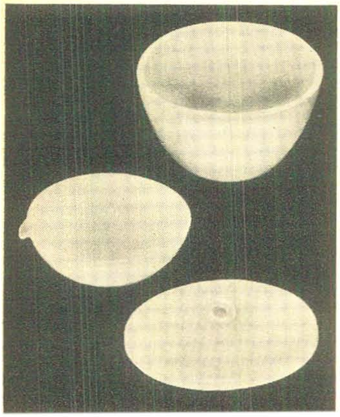
Roger G. Bates, National Bureau of Standards research chemist, is a native of Massachusetts. He attended the University of Massachusetts (B.S., 1934), Duke University, (M.A., 1936; Ph.D., 1937), and Yale University (Sterling Fellow). He joined the staff of the Chemistry Division at the National Bureau of Standards in 1939 and has been there since that time, with the exception of a year at Zurich on a U. S. Public Health Service fellowship. He has been chairman of the Commission on Electrochemical Data of the Analytical Section, International Union of Pure and Applied Chemistry, since 1953. His publications include a book, "Electrometric pH Determinations." He received the 1955 Hillebrand Prize of the Washington Section, ACS, and the Department of Commerce gold medal for exceptional service. Both honors relate to outstanding work in the field of pH and electrolytic solutions.

THE AGE of instrumentation has come to the analytical laboratory. The modern analyst now has at his disposal an elaborate array of costly tools through which molecules, atoms, and atomic fragments betray the compositions of gas, liquid, and solid systems with speed and simplicity. With this assortment of spectrometers and electroanalytical assemblies filling his laboratory, he has difficulty finding space for burets and crucibles. This, however, is of little concern to one who "titrates" with electrons and "weighs" with wave lengths.

One may well inquire where pH measurements fit into the new order. The pH meter, the heart of which is a galvanic cell with its glass and calomel electrodes, was one of the earliest and remains one of the most modest of our analytical instruments. Is the magic wand of the engineer about to transform this laboratory drudge into a Cinderella, a marvel of electronics immune to the limitations of present-day pH equipment?

Unfortunately, a radical improvement in the methodology of pH measurements seems remote. True, the welcome appearance of new electrodes with reduced errors is announced from time to time,

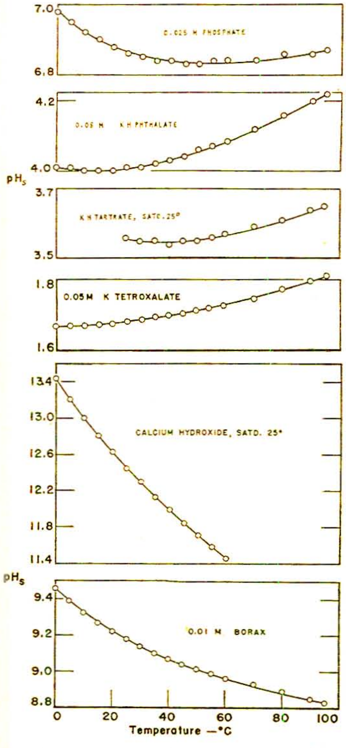
The complete series of NBS pH standards



and new measuring devices of increased stability are being developed continually. Fundamental difficulties remain, nonetheless, for the pH meter persists in its incorrigible habit of expressing results on a scale that has no exact theoretical meaning. Because no really convenient practical way of measuring acidity on the scales that we find theoretically most satisfactory is known at present, the pH meter seems unlikely soon to become a casualty of technological progress. The regrettable situation may be summed up in the following uncertainty principle: "We can't understand what we measure; we can't measure what we understand." Despairing of reform, the modern analyst must seek to recognize the limitations of pH numbers and to use these numbers most effectively.

pH Units and Scales

The analyst would like to have a means of determining quickly and accurately the hydrogen ion concentration of solutions of unknown composition. The logarithm of the reciprocal of this quantity, termed pcH, in equimolar acetate buffer solutions is shown in Figure I. The curve of paH (the logarithm of the reciprocal of the hydrogen ion *activity*) lies considerably higher than that of pcH at ordinary concentrations, whereas psH, the classical pH value of Sørensen, is uniformly 0.03 to 0.04 unit lower than paH.



pH variation with temperature of NBS pH standards

Galvanic cells are oxidation-reduction systems, and the use of two electrodes is inescapable. Two arrangements of these electrodes are possible. The electrodes may both be placed in the same solution, whereupon the measured electromotive force (e.m.f.) is strongly dependent upon two ions. Alternatively, one of the electrodes (the reference) may be isolated in a suitable medium of its own which makes contact (the liquid junction) with the test solution through a "bridge," usually a saturated potassium chloride solution. There are then three loci of potential difference—namely, the two electrodes and the liquid-liquid boundary. In this arrangement, the measured e.m.f. is dependent primarily upon the amount of a single ionic species—e.g., hydrogen—present in the "test" solution, but the unknown changing potential at the liquid junction introduces a considerable uncertainty into the measurement.

The pH cell is an arrangement of the second type. The only alternative would be to add a second ion in known concentration to the test solution, a very inconvenient measure at best and incapable of serving as a completely satisfactory pH method. For practical uses, then, one strives to make the liquid-junction potential constant, and to use the cell to determine *differences* of pH alone. If the residual liquid-junction potential were indeed nullified by this means, the e.m.f. would yield a relative *activity* of hydrogen ions, as the formal equations show. By definition, this activity, a_H, is $f_H c_H$, where c_H is the hydrogen ion concentration and f_H is the activity coefficient of hydrogen ions. Granting for the moment that constancy of the junction potential has been attained, we are led to the operational definition of pH:

$$\text{pH} = \text{pH}_S + \frac{E - E_S}{2.3026RT/F}$$

where E is e.m.f. and the subscript S refers to the standard solution with which the pH cell is adjusted before the measurement, and $2.3026RT/F$ has the value 0.05916 volt at 25° C.

The operational definition has had an enormous influence in justifying the widest possible application of pH measurements. In effect, it authorizes the conversion of every value of E to a corresponding value of pH. Thanks to the high-impedance pH equipment avail-

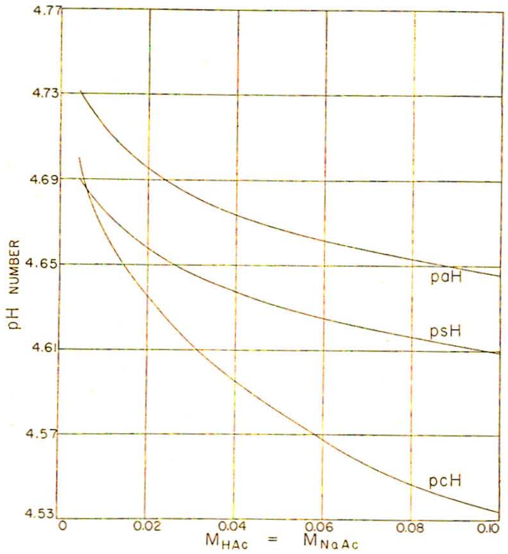


Figure 1. Comparison of pH numbers for acetate buffer solutions

able commercially, determinations of the e.m.f. of the glass-calomel assembly and of pH in soft solids, slurries, nonaqueous media, and the like, are commonplace. The numbers obtained are useful for their reproducibility but obviously bear hardly the remotest relation to hydrogen ion concentration. The propriety of calling them "pH values" is certainly questionable, although there seems little doubt that this practice will continue.

Interpretation of pH Measurements

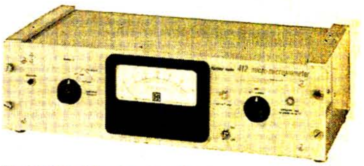
The analytical chemist needs the answers to two important questions. The first is—can the measured pH ever be given a fundamental interpretation, and, if so, under what conditions?—and the second—exactly how should the interpretation, when allowable, be made?

The measurement of pH is a measurement of a difference of e.m.f. If the latter is to reflect the true change of acidity, only one of the three possible sources of potential difference—namely, the glass electrode-solution interface—can change when the standard solution is replaced by the "unknown." The constancy of the liquid-junction potential is the key to the first question. Fortunately, the bridge of saturated potassium chloride solution is rather effective in bringing about this desired constancy. Nevertheless, the difference of potential across the liquid-liquid interface is caused by unbalanced diffusion of ions, and it can hardly be expected that all unknowns will match the standards closely with respect to ionic concentrations and mobilities. In particular, the highly mobile hydrogen and hydroxyl ions, if present in the standard and unknown solutions at different concentrations, have exaggerated effects. The same is true of any ion present in high concentration or any molecular species in amount sufficient to alter the essentially aqueous character of the medium.

The answer to the first question is, then, a qualified yes: experimental pH values can be justifiably given an interpretation if (1) both standard and unknown are dilute aqueous solutions $(< 0.2M)$ of simple ions, and (2) the pH is greater than 2 and less than 11, or matches closely that of the standard.

The answer to the second question facing the modern analyst—namely, how to interpret experimental pH values when an interpretation is allowable—is not readily found. It requires first of all an examination of the meaning of the pH_S values assigned to the standard solutions, for it is evident from the operational definition that pH derives its character largely from pH_S.

One must deal here with the great fundamental problem of pH measurements: Although the pH measurement may yield what is called a difference of hydrogen ion activity, a_H, neither the latter nor the single ionic activity coefficient, f_H, has exact thermodynamic significance. Hence, a_H can neither be determined uniquely nor applied exactly to the chemical equilibria one deals with in calculating end points, ionic concentrations, dissociation constants,



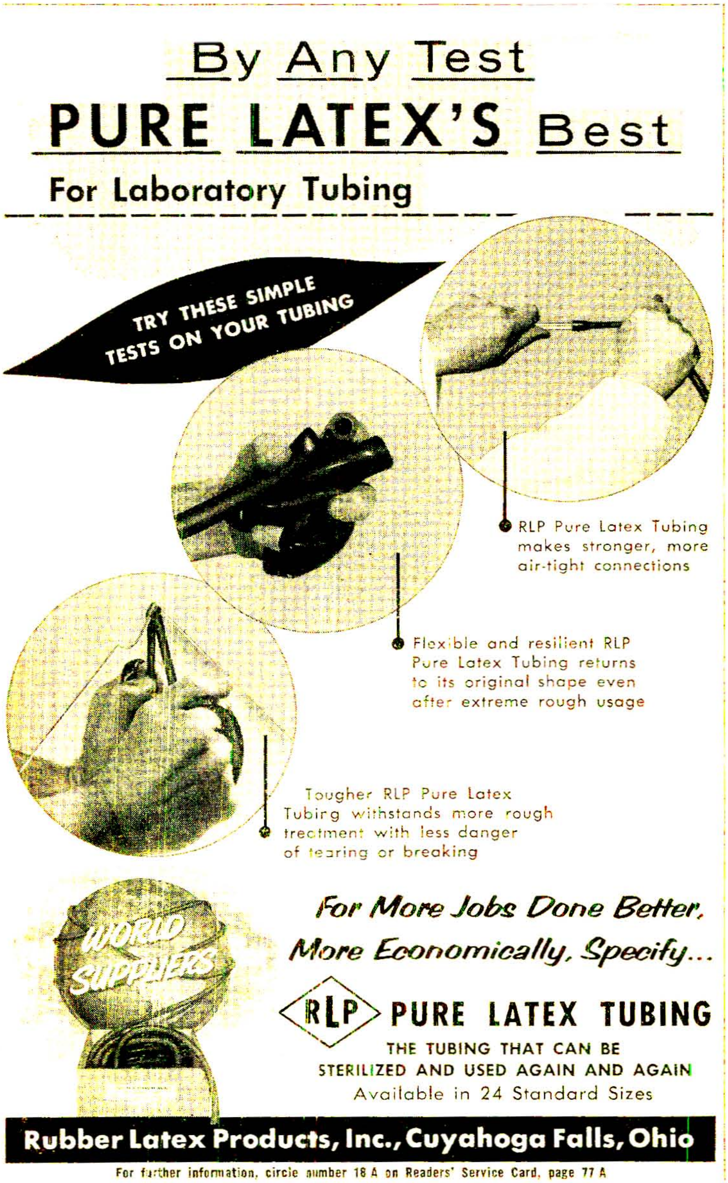
and the like. It is possible, however, to define arbitrarily the single ionic activity coefficient and to establish in this way a *conventional* scale of a_H that serves quite well. Perhaps the most logical procedure is to ascribe to the activity coefficient of a univalent ion the well-understood properties of the mean activity coefficient of a uni-univalent electrolyte in a similarly constituted medium. This approach was chosen as a basis for the establishment of the National Bureau of Standards pH standards. These NBS reference materials, now six in number, enable pH measurements to be standardized from 0° to 95° C. and over the pH range 1.6 to 12.4 at 25° C.

In the procedure for the assignment of standard values (*1*), an alkali chloride is added in known concentration to the buffer solution, and the e.m.f. between hydrogen and silver–silver chloride electrodes in a cell without liquid junction is obtained. Standard potentials and fundamental constants being known, the e.m.f. is an unambiguous measure of $-\log(f_H f_{Cl} c_H)$, a quantity that has been termed p**w**H for convenience. The effect of the chloride on p**w**H is eliminated by a suitable extrapolation, and f_{Cl} is made to disappear by introduction of the conventional definition of the single ionic activity coefficient. The result is a pH standard value, or pH_S. Inasmuch as $f_H f_{Cl}$ is equivalent to $f_{\pm}^2$, where $f_{\pm}$ is the mean activity coefficient of hydrochloric acid in the buffer solution, pH_S has in reality the dimensions of $-\log f_{\pm} c_H$, but it is often convenient to regard $f_{\pm} c_H$ as the conventional hydrogen ion activity.

The specific properties of the ions of strong electrolytes of a single charge type are different and, hence, so also are the mean activity coefficients of these electrolytes, even at rather low values of the ionic strength (μ). For example, the value of a, the "ion-size parameter" in the Debye-Hückel equation at 25° C., $-\log f_{\pm} = 0.508\sqrt{\mu}/(1 + 0.328a\sqrt{\mu})$, may vary from 3 to 6 for different strong uni-univalent electrolytes below $0.2M$. Hence, a single convention cannot yield exactly comparable pH_S or pH values for differently constituted standards and unknowns, even under the most favorable circumstances. As μ decreases, the differences in $f_{\pm}$ evidently also decrease. Accordingly, the NBS procedure selects standards of ionic strength 0.1 or less, where the assigned uncertainty of ±0.01 unit in pH_S will allow a considerable variation in the parameter a.

A similar restriction to the application of measured pH values to chemical equilibria is inescapable. Here again it is impracticable, or even impossible, to recognize specific differences of a secondary character, among the constituents of the solution. Differences of electric charge are, however, of primary influence on the activity coefficients, and allowance must be made for them. If $f_{\pm}$ is the conventional definition of the activity coefficient of a single univalent ion, the activity coefficients, f_i, of other ionic and molecular species of valence z_i may be expressed by $\log f_i = z^2_i \log f_{\pm}$. This expression is consistent with the ionic strength principle and with the valence relations of the Debye-Hückel limiting law.

The manner in which measured pH values are employed in chemical equilibria, when the favorable circumstances of the measurement justify this step, is now clear. The equilibrium is first formulated in its exact (thermodynamic) form, and the following substitutions are made: (1) $-\log f_H c_H$ is replaced by the experimental pH value; (2) the activity coefficients of the other species are expressed in terms of $f_{\pm}$; and (3)



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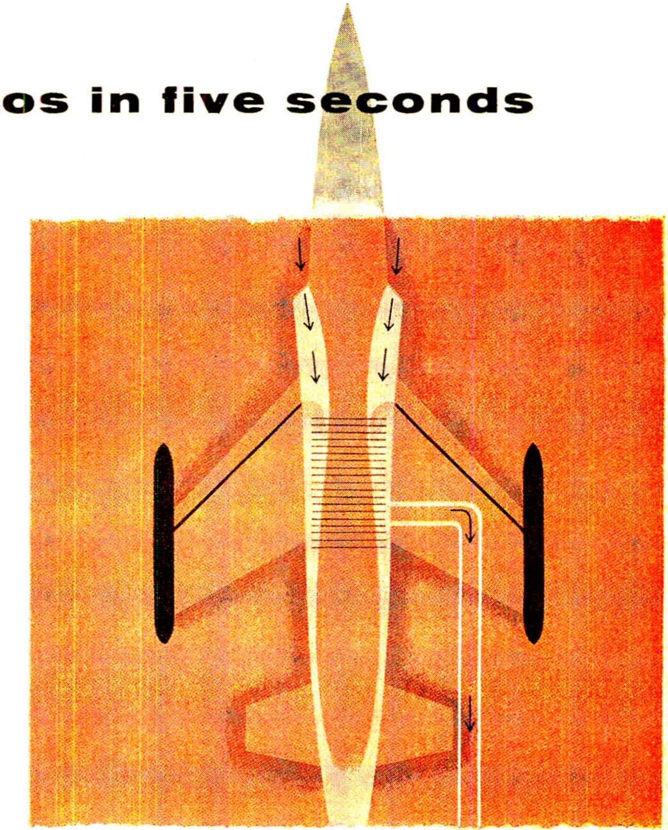

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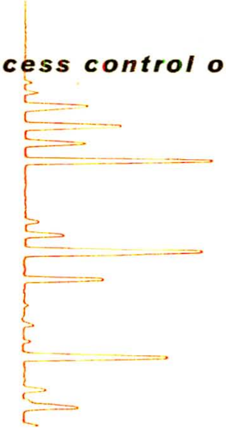

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$f_{\pm}$ is computed by the Debye-Hückel equation with an average value of 4 or 5 for a.

The accuracy of calculations of this sort is evidently limited when ions of charge greater than ±1 are involved. However, for certain equilibria, notably the dissociation of monobasic weak acids, this treatment may be very successful, thanks to a partial cancellation of activity-coefficient corrections. In spite of these limitations, pH measurements remain a most useful tool for the determination of equilibrium constants and other electrochemical data with moderate accuracy.

Nonaqueous Media

Perhaps the most difficult pH problem facing the modern analyst concerns the proper use of measurements in media that are not entirely aqueous. In its strictest sense, pH has no meaning in such solutions. What is the pH, for example, of a solution of a strong base in 90% ethanol? The ion-product constant for water is no longer 10^{-14}; neutrality, if it has any real significance here, is no longer at pH 7. Yet in its most general formulation—namely, the operational definition—a pH value exists for any medium in which the pH cell develops a reproducible e.m.f.

The hydrogen electrode and often the glass electrode display a definite potential in many solutions that contain little or no water. It may be presumed, therefore, that some quantity, which may be termed the "proton activity," has a definite value in these media. Bronsted regarded this proton activity or "proton availability" to be a manifestation of acidity in a fairly general sense, free from medium restrictions. Unfortunately, this concept is of more academic than practical interest, for all comparisons of acidity in two different media with the pH cell involve a large and indeterminate phase-boundary potential.

It seems clear, then, that the pH meter is incapable of furnishing a useful quantitative measure of changes in acidity relative to the aqueous reference solutions with which the instrument is customarily standardized. One is led to inquire whether the numbers constitute a qualitatively reliable index of the changes in acidity that occur as the composition of the solvent is altered, or whether they are useful solely because of their reproducibility. At least for ethanol-water mixtures up to 100% ethanol, the qualitative validity of pH measurements seems to have been demonstrated. The pH meter, for example, reveals the expected decrease in acidity of an acetate buffer solution and the increase in the acidity of an amine buffer solution as the solvent is en-

riched with alcohol. Likewise, the pH meter demonstrates the high acidity of alcoholic hydrochloric acid as compared with the aqueous solution.

It has been claimed that a comparison of acidities in pure ethanol and pure water is subject to a liquid-junction error of as much as 2 pH units. Nevertheless, it is believed that a determination of relative acidity in a nonaqueous medium may be successful, as long as the composition of the solvent does not change. If relative measurements of this type are indeed possible, the availability of a series of reference standards for a variety of nonaqueous and mixed solvents, whose pH values were consistent with the aqueous scale, would link all of these measurements to a common basis. Unfortunately, no independent practical means of establishing these reference values has been proposed.

In contriving such a pH scale, we would be motivated, perhaps falsely, by a desire for formal consistency with the procedures that are successful in aqueous systems. One must remember, however, that the pH meter with its aqueous standards can furnish reproducible numbers in many partially aqueous and nonaqueous media. A plurality of standards can be justified only if it provides results of increased usefulness.

Behavior of acids and bases in water and some other leveling solvents is subject to certain generalizations that do not apply to all other solvents. Acid-base interactions are influenced not only by the so-called strengths of these substances but by such factors as dielectric constant, association, and steric effects. Hence, it is unlikely that a measurement of a conventional proton activity relative to water would be of great practical value. Two acids of different structures and charge types would probably not participate to the same extent in a reaction with a given base, even though the pH values of their solutions were identical. Nor would a single acid react the same at identical pH values in different solvents, for the extent of a chemical reaction is determined by factors that do not necessarily influence the electrometric measurement. Where indicator reactions are concerned, one is accustomed to attribute these differences in reactivity to salt effects and medium effects.

In view of these limitations, it seems unwise to attempt to relate acid-base phenomena in nonaqueous and partially aqueous media to a scale which at best has no exact theoretical meaning, or to apply the term pH to these media in other than its operational sense. When the qualitative indication afforded by the operational pH will not suffice, the analyst may resort to the Hammett acidity function or to the electrometric function, pwH. Both functions relate the acidity to the aqueous standard state; both are free from the experimental uncertainties of the liquid junction; and both permit an escape from the fundamental ambiguity with which the pH value is beset.

Summary

The pH measurement is a useful tool for the analyst, providing him with reproducible numbers in both aqueous and nonaqueous media. Its interpretation, however, in terms of hydrogen ion activity or concentration, can be attempted only for certain aqueous systems of relatively ideal composition. It should not be applied to partially aqueous or nonaqueous media at the present time.

Literature Cited

(1) Bates, Roger G., "Electrometric pH Determinations," Chap. 4, Wiley, New York, N. Y., 1954.

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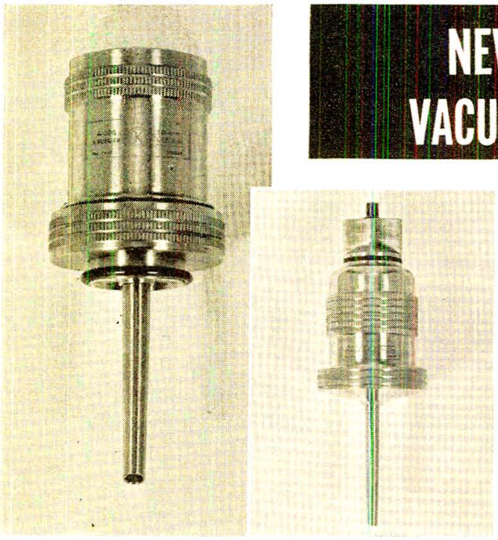

The simple design of these new precision-type filters makes it easy to disassemble and assemble them without tools. The filtering medium is a combination paper and asbestos pad of various grades to meet different filtration problems. Pad slips into pad housing quickly and a twirl of the threaded nut tightens it into position, the whole operation taking about a third as much time as in other similar filters. Although the vacuum filters have five components, they are so assembled that there are only two units to take apart for sterilization.

The Filters are made of Type 304 stainless steel to prevent deterioration. There are three laboratory models for small scale sterile filtration or pilot plant work.

FLOW RATE DATA

Pad No.	Flow Rate in Gal. Sq. Ft. Per Hour	Pore Size Range, Microns
HK-5	160	5
HK-6	110	2–4
HK-8	60	1–2
HAK-3	20	1/10
HAK-2	10½	1/50
HAK-1	7	1/100

FILTERS

Catalog No.	Mode	Type	Liquid Capacity	Each (Without Pads)
F-2110X	A-200 (35 mm.)	Vacuum	40 cc.	$24.50
F-2111X	A-300 (50 mm.)	Vacuum	110 cc.	28.50
F-2112X	A-400 (65 mm.)	Pressure/Vacuum	120 cc.	36.50

FILTER PADS

	For Model A-200		For Model A-300		For Model A-400	
Catalog No.	F-2110-4X		F-2111-4X		F-2112-4X	
Pad No.	HAK-1,2,3	HK-5,6,8	HAK-1,2,3	HK-5,6,8	HAK-1,2,3	HK-5,6,8
Per 100 Pads	$ 5.00	$ 4.00	$ 6.00	$ 5.00	$ 7.00	$ 6.00
Per 500 Pads	24.00	23.00	28.50	27.50	32.00	31.00

NOTE: Please be sure to specify catalog number; also pad number.

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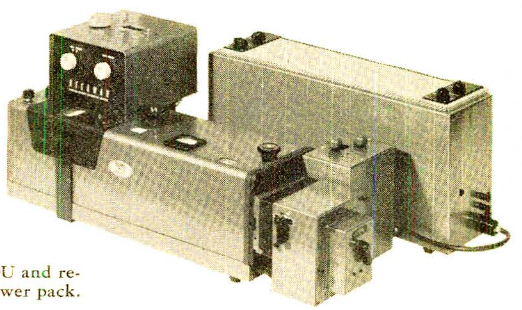
FOR MODEL DU SPECTROPHOTOMETER

If you operate a Model DU Spectrophotometer, you will find this new AC Power Supply an indispensable accessory. Not only does it eliminate the task of keeping the storage battery in good condition, but it eliminates the need for dry cells used in both the DU and photomultiplier circuits. It also provides a regulated voltage to operate the hydrogen lamp for work in the ultra-violet region, dispensing with the need for the power supply unit of the Ultraviolet Accessory Set.

The entire electronic circuitry is housed in a case approximately the same length as the DU monochromator. Operating controls are on top within easy reach.



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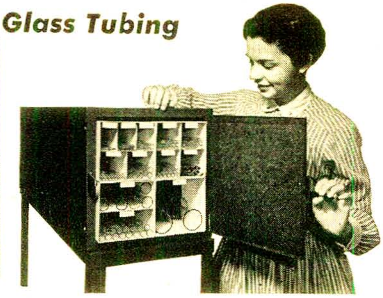
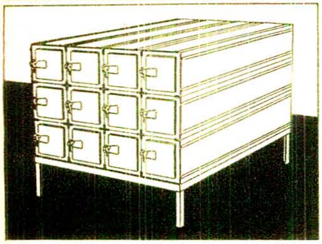
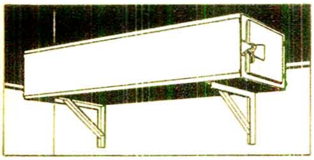
LABORATORY APPARATUS - INSTRUMENTS - CHEMICALS - GLASSWARE

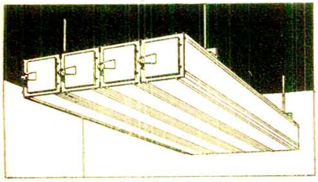
No. S-4349X AC Power Supply, 6½″ wide x 11″ high x 22″ long; weight 35 lbs. Input power 50/60 cycle, 115 volts, 350 watts. Price..... $595.00

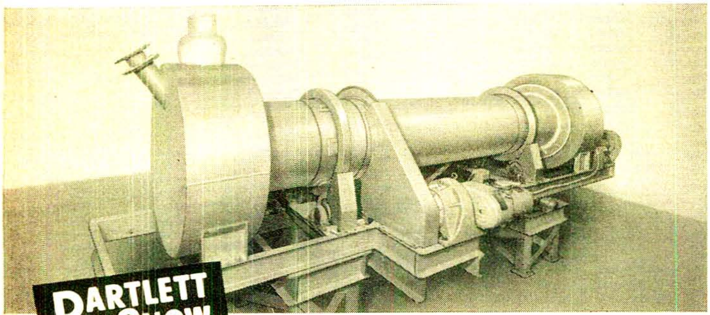
For further information, circle numbers 23 A-1, 23 A-2 on Readers' Service Card, page 77 A











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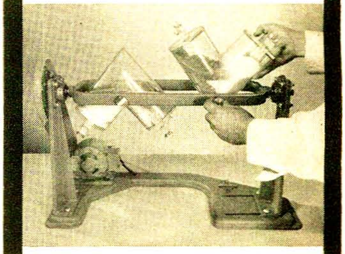

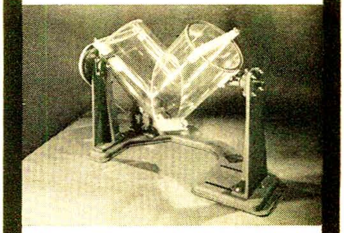

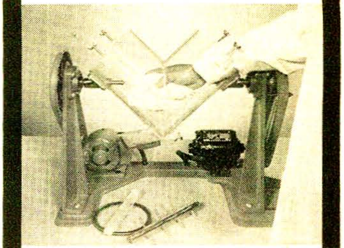

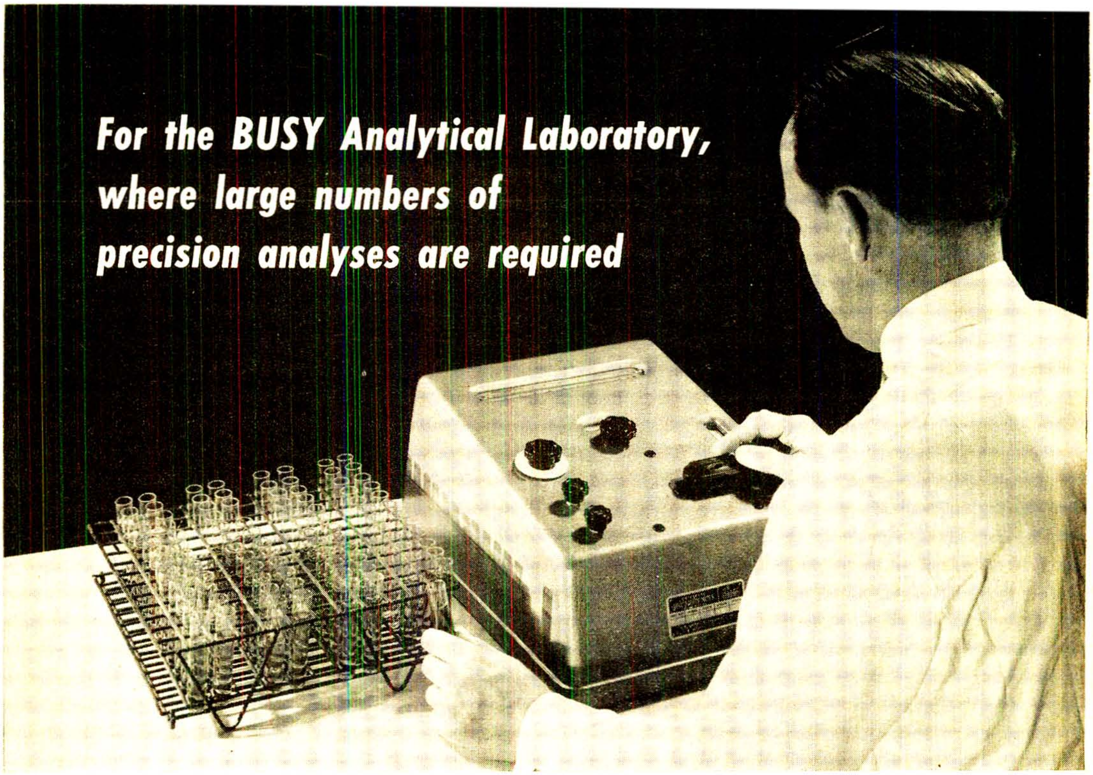
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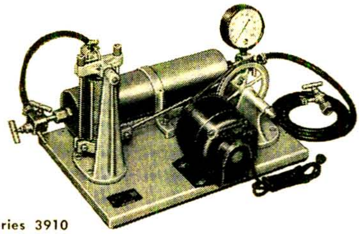

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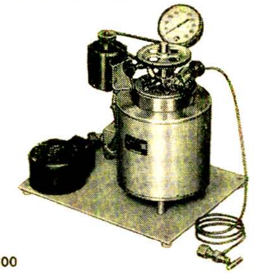
LOW PRESSURE, SHAKER TYPE — For catalytic hydrogenation and other reactions at pressures to 5 atm. using a 500 ml. glass reaction bottle held in a sturdy clamping device. Connections to a 4-liter gas tank permit quantitative control of hydrogen consumed. Heater available for temperatures to 100° C.



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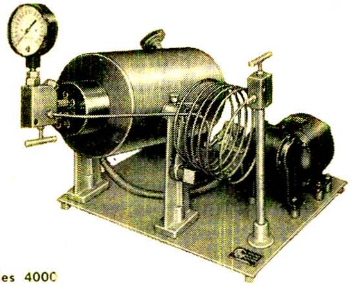
MEDIUM PRESSURE, STIRRER TYPE — For hydrogenation, alkylation, hydrolysis, polymerization, sulfonation and many other reactions requiring an autoclave with stirrer for pressures to 1000 psig. and temperatures to 350° C. Available with either 1 or 2 liter stainless steel bombs, both interchangeable in the same electric heater.



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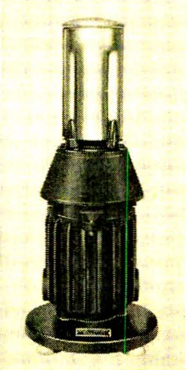

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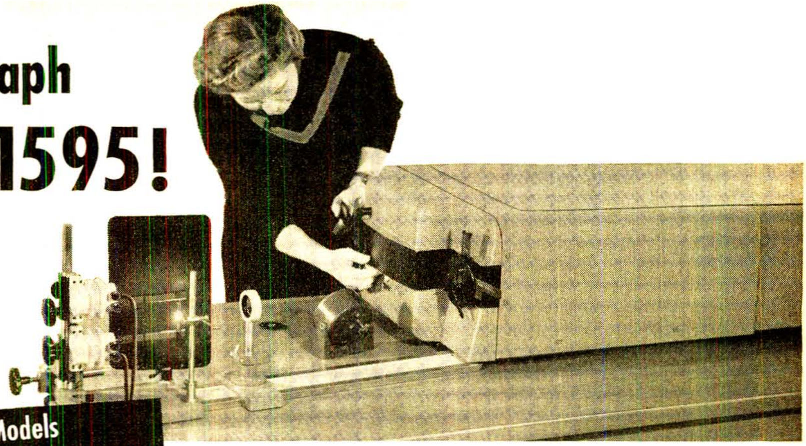

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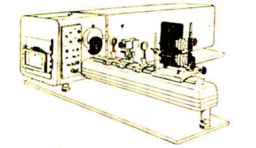

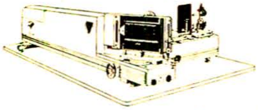

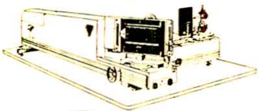

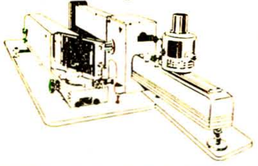

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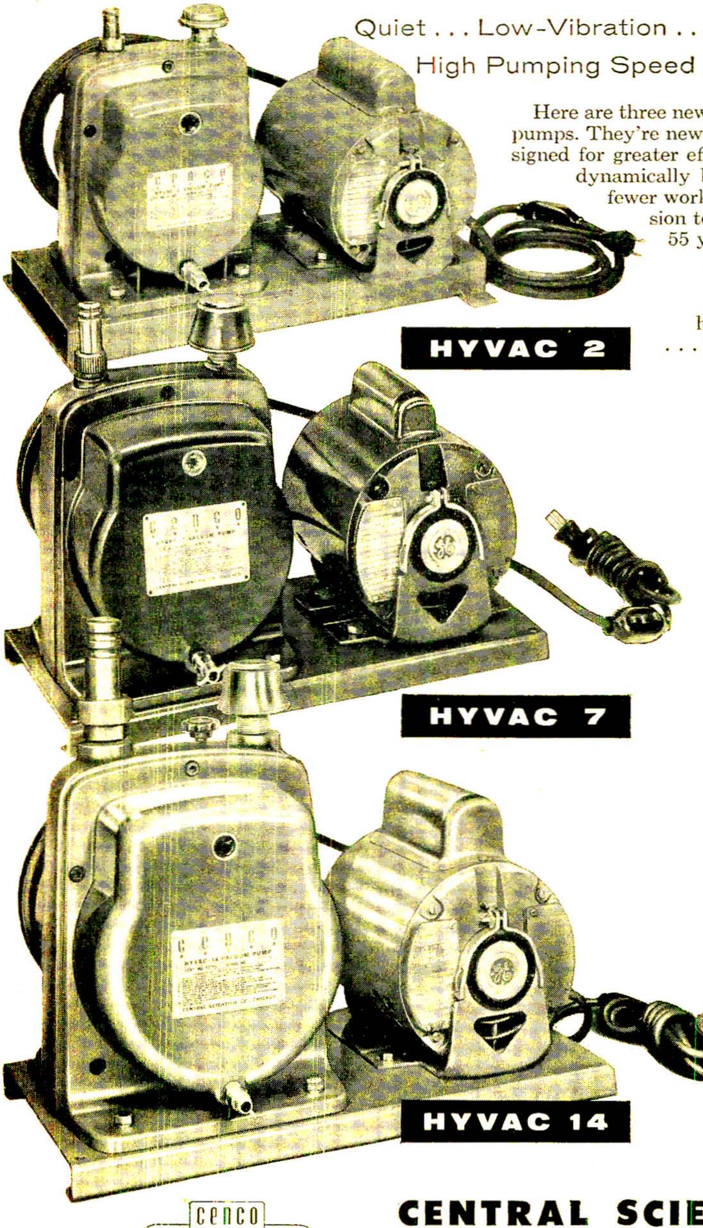

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HYVAC 2—No. 91305-1 60 cy. 115 v. with motor and base $175.00

This precision engineered pump produces a free air displacement of 20 liters per minute. Reaches a guaranteed pressure of 0.1 micron.

HYVAC 7—No. 91505-1 60 cy. 115/230 v. with motor and base $275.00. No. 91506-1 (with Gas Ballast Control) $285.00

The new Cenco-Hyvac 7 produces a free air displacement of 70 liters per minute and reaches a guaranteed pressure of 0.1 micron. Ratio of pumping speed at 1 micron to that at atmospheric pressure is 45%. Now available with or without gas ballast control.

HYVAC 14—(with Gas Ballast Control) No. 91705-1 60 cy. 115/230 v. with motor and base $350.00

This is the largest pump in the Cenco-Hyvac line and is provided with the gas ballast control feature. It achieves a free air displacement of 140 liters per minute and attains a guaranteed pressure of 0.1 micron.

All of these pumps are also available with motors for other voltage requirements or with explosion proof motors.

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For further information, circle number 28 A on Readers' Service Card, page 77 A

Analysts Aid Battle on Insects

Petroleum seekers get help also from analysts . . . New trace techniques developed . . . Yoe and Müller honored

MIAMI—With crop losses to insects now at the $4 billion a year level, there is urgent need for a large variety of efficient pesticidal chemicals. Safe and effective use of such chemicals requires adequate analytical techniques and methods. Recent legislation requires precise determination of pesticidal residues on crops. The role of the analyst, therefore, becomes increasingly significant in the area of crop production.

The subject of methods for analysis of pesticide residues was covered in a two-day symposium sponsored by the Division of Analytical Chemistry held here in April. Other symposia dealt with analytical contributions to research in petroleum geochemistry and Beckman Award winner Ralph H. Müller and Fisher Award winner John H. Yoe.

Pesticide Residues Challenge Analysts

The major research task involved in assessing possibilities of large-scale use of any pesticide is analytical, a report by F. A. Gunther, University of California, stated. His paper was read by W. E. Baier, Sunkist Growers. To isolate, measure, and identify these chemicals on or in plants or in the soil requires use of every tool known to biology, chemistry, and physics.

Legal requirements relating to residues were outlined by T. H. Harris, U. S. Department of Agriculture, and J. A. Noone, National Agricultural Chemicals Association.

Under the Federal Insecticide, Fungicide, and Rodenticide Act if it can be shown that these chemicals leave no residues on or in the crops, registration is granted. Where residues are left, tolerance limits or exemptions are established. In both cases the analyst is called upon to supply factual data.

Requirements of the Miller Pesticide Residue Amendment, Noone said, make methods of analysis and compilation of residue data the critical and limiting factors in maintaining and expanding uses of pesticides for food crops. Costs of conducting research in these areas are great and much will have to be done by federal and state research personnel. Noone suggested the desirability of incorporating residue studies in pesticide field testing programs.

C. H. Van Middelem, University of Florida, and Louis Lykken, Shell Chemical Co., emphasized the need for careful sampling. This calls for close cooperation between the chemist and entomologist in establishing standardized procedures for formulations, dosages, replications, sampling procedures, solvents, extraction times, and storage temperatures.

Analysts Aid Petroleum Geochemistry Research

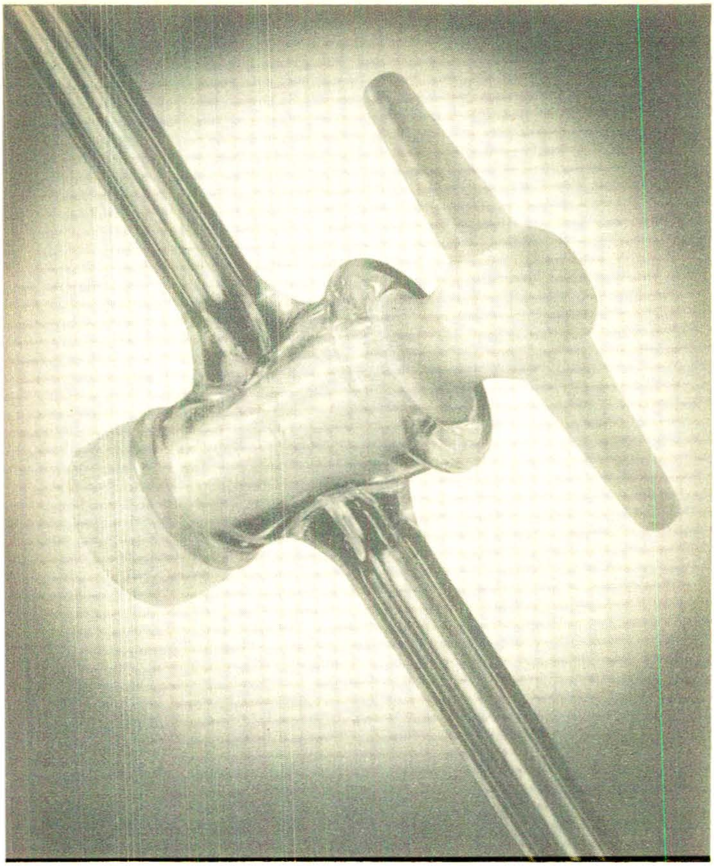
Analytical research on residues of chlorophyll and hemoglobin, known as porphyrins, is shedding light on the origins of petroleum and assisting the petroleum industry cope with this material which has adverse effects in petroleum processing. Porphyrins poison some catalysts, are corrosive in special fuels, and affect the flow of fluids in petroleum reservoirs.

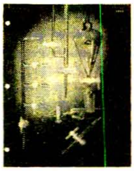
Chlorophyll derivatives in certain marine sediments can be determined spectrophotometrically following extraction with acetone, W. L. Orr and J. R. Grady, University of Southern California, learned. Extensive research on porphyrins by H. N. Dunning and J. W. Moore, Bureau of Mines, Bartlesville, Okla., gives support to the theory that bituminous materials have a biological origin (marine and terrestrial plants and animals). Results also support the theory of low-temperature history with asphaltic type formation preceding oil formation.

Similarly, thermal degradation studies of vanadium and nickel porphyrin complexes, carried out by G. W. Hodgson and B. L. Baker, Research Council of

Mrs. Richard Gordon looks at the Fisher Award in Analytical Chemistry etching given to her father, John H. Yoe, University of Virginia authority in colorimetric analysis. John W. Aldinger (left), Fisher Scientific Co., presented the award

Ralph H. Müller, Los Alamos Scientific Laboratory (right), instrumentation authority, receives $1000 Beckman Award in Chemical Instrumentation from Mark K. Howlett, Beckman Instruments, Inc.





Alberta (Canada), gives support to the low-temperature theory.

Studies on the organic materials in shales and limestones associated with oil fields show that they contain up to 5% organic matter. Research by T. P. Forsman and J. M. Hunt, Carter Oil Co., Tulsa, shows that most of the material is carbonaceous (kerogen) which is insoluble in organic solvents. Recently developed isolation techniques permit extraction of these small amounts of kerogen by hydrofluoric-phosphoric acid mixtures, certain alkalies, hydrochloric acid, and physical separations. X-ray diffraction is used to identify impurities at various stages of isolation.

Colorimetry Advances Reported

Rapid progress in a relatively old analytical technique, colorimetry, has been made possible through the development of analytical instrumentation, John H. Yoe stated in his Fisher Award address. Instrumentation includes pH meters, photoelectric colorimeters, spectrophotometers, ion exchange resins, water immiscible organic liquids, and radioactive isotopes.

An area marked by recent progress is that of colorimetric determination of inorganic constituents by organic compound reagents. To date more than 6000 organic compounds have been tested against 75 to 80 metallic ions for color reactions. These have been done by spot tests or micro glass cells in acid, alkaline, and neutral solutions. The research has resulted in discovery of a number of new and highly sensitive color reagents and development of procedures.

Reagents have been developed for palladium, platinum, iron, titanium, molybdenum, zinc, copper, uranium, magnesium, boron, osmium, fluorine, silver, gold, aluminum, cobalt, nickel, and zirconium.

The papers in this symposium were presented by several of Yoe's former students.

A spectrophotometric method for the determination of submicrogram amounts of nickel in human blood or other biological fluids, for example, was described by M. L. Cluett, E. I. du Pont de Nemours & Co., Inc. The method, which is based on complex formation between nickel and diethyldithiocarbamate, allows determination of 0.2 microgram of nickel with a precision of about 30%.

Tailor-made membrane electrodes, which respond to specific ions, are one possible end result of studies on permselective membranes, J. S. Parsons, American Cyanamid Co., reported. These membranes have been made and used as indicator electrodes for the potentiometric titration of sulfate with

Slowing down the leucocytes

Magnification of blood sample from leukemia victim, showing extreme white cell-to-red cell imbalance. White cell level 250 times greater than normal.

Beckman®/DK Automatic Recording Spectrophotometer speeds research in leukemia

Seeking to stop leukemia, medical scientists have learned how to slow it down. Inhibitors have been found that temporarily stop the abnormal production of *leucocytes,* white blood cells. But, because the body develops resistance to these present inhibitors, white cell metabolism must be better understood and more selective inhibitors discovered to permanently stop abnormal production of leucocytes.

Leucocyte-inhibitor reaction is studied by introducing a radioactive assimilate into the environment of leucocyte samples, both in the presence and in the absence of an inhibitor. To determine what metabolic use the leucocytes make of the radioactive substance and what effect the inhibitor has on this process is a big analytical job.

Beckman DK-2 gets the job done twenty times faster

A typical experiment of this type involves the collection of 1,000 fractions, measuring each fraction on a spectrophotometer for ultraviolet absorption, and plotting results – an almost insurmountable task without a high-speed automatic instrument. The medical researchers faced with making these thousands of analyses have found that the Beckman DK-2 Automatic Recording Spectrophotometer is 20 times faster than manual measurement and recording.

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barium acetate. The cation and anion selective membranes are made by molding commercially available ion exchange resins with a plastic binder.

New Instrumentation Advances

Study of obscure or less highly investigated phenomena may be the source of significant new advances in analytical instrumentation, R. H. Müller stated in his Beckman Award address. The classical techniques, he believes, may have been refined and developed to the point of diminishing returns. These include titrations and electrochemical and optical methods.

Some techniques which might be explored he feels, include thermal, magnetic, and nuclear effects. Activation analysis and use of radioactive tracers are the only nuclear methods in widespread use at present.

Further developments in the field of instrumentation will also depend in part on a generalized approach to instrumental research and a sound scheme for training people in the field.

Through instrumentation research, more will be learned concerning what goes on in a process. Results can then be recorded continuously and automatically with savings in time, manpower, and money, Müller said.

Several new or modified instruments were described in the symposium honoring Müller. An automatic instrument, composed of a derivative polarograph and a sampling and proportioning system, for example, has been developed to analyze high concentrations of uranium in process streams. C. J. Rodden, U. S. Atomic Energy Commission, stated that this derivative polarograph, based on the RC circuit, scans the applied voltage in a reverse direction to decrease peak oscillations. It can analyze process streams containing from 100 to 200 grams per liter of uranium with an accuracy of 6%.

Other derivative polarography developments, reported by D. S. Fisher and M. T. Kelley, Oak Ridge National Laboratory, include two models which utilize the combination of current amplifier and RC network. The current amplifier permits use of high values of current measuring resistors and low values of RC differentiating networks.

An instrument for continuous electrochromatography was described by H. H. Strain, Argonne National Laboratory. This system permits continuous resolution of mixtures of ionized or electrically charged solutes by electrical migration transverse to the flow of the background electrolytic solution. Separations are carried out in a thick porous industrial filter paper with a background solution added by

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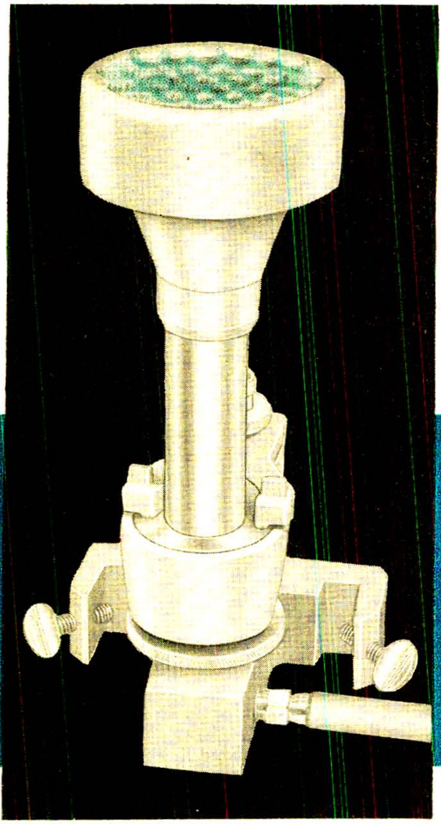

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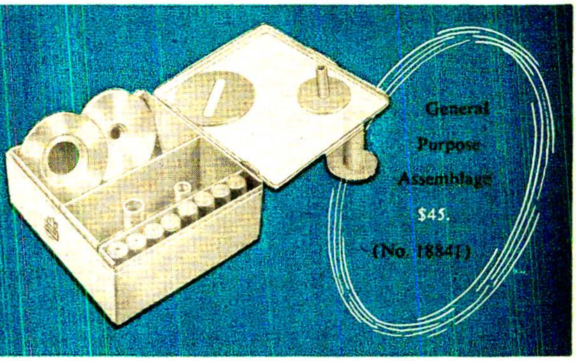

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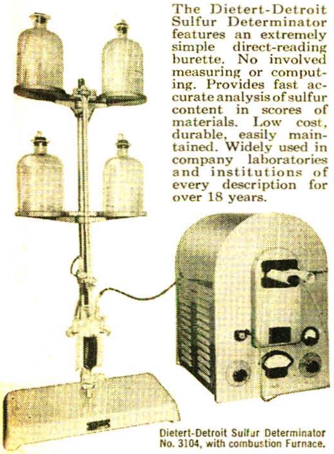

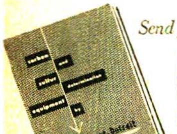

A major responsibility of scientists is to convince secondary school students that science is a challenging career, Paul M. Gross (center), vice presidnent, Duke University, stated at the Analytical Division dinner. Divisional officers R. P. Chapman (right), American Cyanamid, chairman, and Warren Brandt, Purdue University, secretary-treasurer, discuss this topic with Gross

capillary siphon flow. The filter paper, which is narrower at the top than at the bottom, is supported at a slight incline on solidified polystyrene foam. A cover of polyethylene sheeting prevents evaporation of the solution. The apparatus has been applied to such ions as silver and copper, cobalt and iron, silver and cadmium, and bismuth and aluminum.

More information concerning temperatures at which various intermediates and final reaction products are formed can be obtained from a simple differentiator, Clement Campbell, Picatinny Arsenal, reported. It consists of a precision, single-turn transmitting potentiometer mounted on the slide-wire shaft of a recorder used to obtain the thermogram.

A recording differential refractometer, originally designed for process control, such as monitoring effluents from adsorption and partition chromatography columns and ion exclusion columns, is sensitive enough (10^{-6}) for use as a laboratory instrument. This development is the work of P. B. Moseley and R. H. Osborn, Hercules Powder Co., and P. W. Collyer, Barnes Engineering Co.

A completely automatic, recording cryoscopic apparatus, described by E. L. Simons, General Electric Research Laboratory, has a unique way of controlling supercooling. A stream of precooled nitrogen gas impinges on the bottom of the cell containing the liquid to be frozen. Crystallization of the supercooled liquid is induced quickly. As the temperature rises toward the freezing point of the liquid, the nitrogen stream is automatically cut off.

D. M. Rosie, Esso Research and Engineering Co., found that, contrary to prior assumptions, the thermal conductivity differences between similar hydrocarbons even when measured against helium, may be significantly large. When correction is made for these thermal conductivity differences, precise quantitative results are obtained in using gas chromatographs with thermal conductivity cells.

A gas chromatography apparatus, suitable for analyses of impurities at the parts per million level was described by C. E. Bennett, E. I. du Pont de Nemours & Co., Inc. This instrument uses a direct-current amplifier in conjunction with a thermistor detector. Typical applications are traces of isopropyl alcohol in benzene, benzene in toluene, methanol in water, and cyclohexanol in toluene.

An automatically operated, modified gas chromatograph instrument for laboratory use was described by Nathaniel Brenner, Perkin-Elmer Corp. A one-inch diameter column, one meter long, fits directly into a standard gas chromatography apparatus. Use of automatic controls to operate sample injection and sample collection devices provides a system for continuous, automatic preparation of pure samples.

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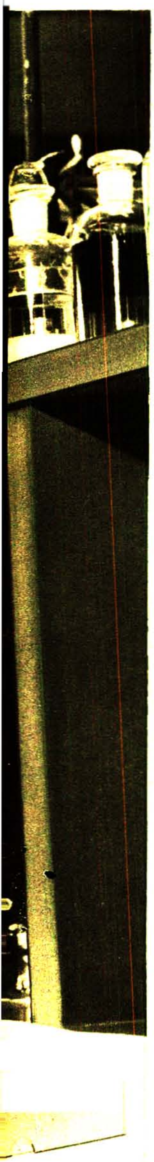

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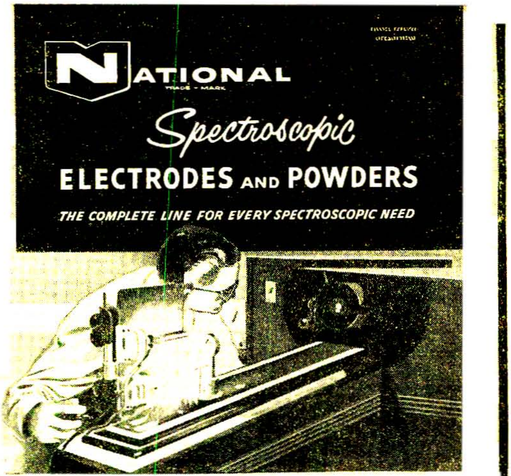

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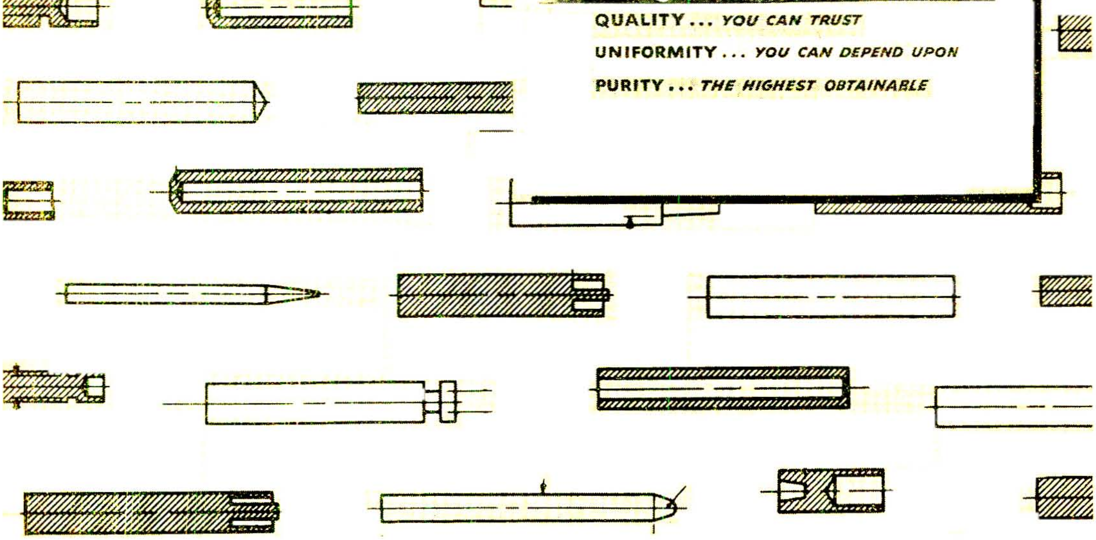

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Special Problems in Atomic Laboratories

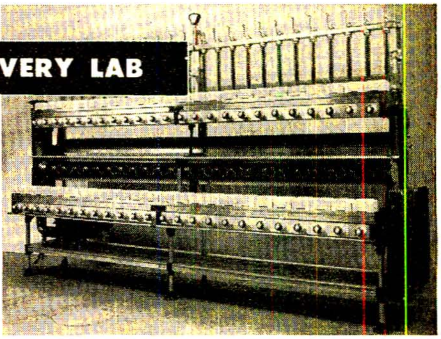
Thousands of scientists converged on Philadelphia's Convention Hall in mid-March for the 1957 Nuclear Congress. The week-long meeting included three technical conferences, as well as an international atomic exposition. Session topics ranged all the way from reactor operation and spent-fuel processing to plant instrumentation and the metallurgy of nuclear alloys. A number of papers were of special interest to analytical chemists.

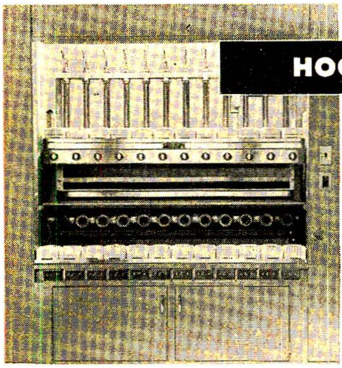
As pointed out in a report by Bernd Kahn of Oak Ridge National Laboratory and Abraham S. Goldin of Robert A. Taft Sanitary Engineering Center, a variety of techniques are available for the identification of radionuclides. Identification may be based on chemical separation (including separation of a related activity) or on radiation characteristics, such as type (alpha, beta, or gamma), half life, or energy. A combination of chemical and physical methods is generally more efficient than either approach alone. In many cases, however, determination of radiation characteristics may not be practical because the isotopes involved are present in extremely small quantities.

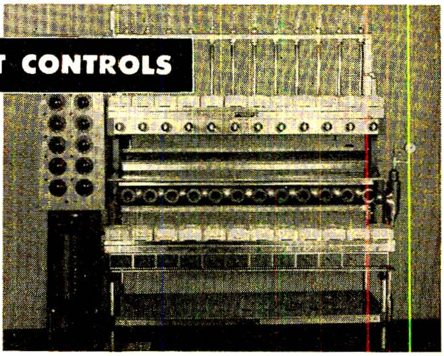
At these low levels, the activity must usually be concentrated from very large samples. At still lower activity levels or where large samples are not available, extremely specialized counting equipment must be used, in which the background is lowered to mere traces by heavy shielding and special circuitry.

For many materials, preliminary sample preparation is a major problem. The analysis of solid samples usually requires that they be totally dissolved. A soil is treated by carbonate fusion and then dissolved in acid; a biological material is either wet- or dry-ashed and then dissolved. These methods are tedious and not entirely satisfactory, even when they do not cause loss of radioactivity or add excessive amounts of inactive contaminants.

Although radiochemical separations based on conventional analytical methods have been published for every element, they must be modified to permit measurement at low levels of activity and allow application to different media, Kahn and Goldin emphasize. Especially with soils and biological materials, separation of the desired radionuclide from a large mass of inert matter can be extremely difficult. These inert materials usually are not considered in







standard methods—for example, for the analysis of pure neutron-irradiated uranyl nitrate solutions, cyclotron bombardment targets, and the like.

In radiochemical separations, a known amount of carrier material is usually added so the radioisotope, usually present in unweighably small amounts, can be manipulated. The recovery need not be quantitative, since the results can be corrected for chemical yield on the basis of the recovery of the carrier. As a result, rapid, less quantitative techniques can be used.

Analytical procedures have been worked out for radium-226, strontium-90, iodine-131, cobalt-60, and other materials. Methods are currently being developed for other isotopes, particularly among the fission products. Farthest advanced are methods for zirconium, niobium, cerium, and yttrium.

Remote-Control Analysis. Some of the more delicate operations carried out in nuclear analytical laboratories cannot be performed with the "mechanical hands" usually available. In other remote-control operations, these mechanical devices can be used, but require an inordinate amount of manual effort. According to M. T. Kelley and D. J. Fisher of Oak Ridge National Laboratory, specialized gadgets are often required as an aid to chemical analysis in hot labs.

One such piece of equipment is a servo-pipettor, a positive-displacement piston device which is reported to be more accurate and flexible than previously designed remote pipettors. The new units have a total capacity of either 1 ml. (mostly for measuring primary samples for chemical analysis) or 0.1 ml. (mostly for use with the falling-drop densimeter).

This densimeter, another useful device, measures the density of highly radioactive samples by timing the rate of fall of drops through a liquid of suitable density. The rate of fall is determined by a pair of photocells—one which starts a timer and the other which stops it when the drop passes a predetermined point. Density can be measured in this way with a precision of fall times of ±0.3%.

Some commercial spectrophotometers can be operated with master-slave manipulators, while others cannot without many changes, Kelley and Fisher indicate. For this reason, Oak Ridge scientists have developed a special remotely operated instrument using an incandescent light source, interference filters, and a detector unit.

The part of the instrument that must be inside the cell is suitably compact. Adjustments of meter sensitivity are made outside the cell without the use of manipulators. Although not as accurate as a good standard spectrophotometer, it has a precision of ± 5%, which is adequate for most of the laboratory's control work.

The laboratory also uses numerous small devices to facilitate operations with mechanical manipulators. These include special baskets so that beakers and flasks can be handled with no danger of spilling; Lucite blocks with suitably sized holes to support small beakers and flasks and permit them to be easily positioned; and split aluminum blocks attached to stopcocks to make them easier to turn by manipulators.

Metallography Lab. A hot laboratory installation for remote metallography can be built satisfactorily by modifying commercially available equipment, reported D. D. LaRocque and F. P. Crimi of GE's Knolls Atomic Power Laboratory. GE's recently installed setup required a minimum of equipment modification to permit operation with master-slave manipulators.

The internal working space of the cell occupies an area of 4 × 14 feet, divided into three modules. Use is made of six Argonne master-slave manipulators. The equipment includes five polishers, five polishing attachments, a mounting press, liquid filter system, research metallograph, table and shield for the metallograph, Castle manipulator, and a microhardness tester. The approximate cost of the original equipment (not including the cell and manipulating assemblies) was about $24,700, while the cost of the necessary modifications was about $7700.

With this installation, a metallographer can process a batch of five specimens in about 8 hours. By use of a "clean as we go" technique, the level of activity left in the cell after the processing of 35 specimens of highly radioactive fuel is 200 mrad per hour at 2 feet from the table top.

Analytical Symposium at NYU

A one-day analytical symposium has been scheduled for May 11 at New York University. This is to be the first of a series of annual symposia for the New York area.

The program appears below:

Introduction. E. A. WYNNE, Fisher Scientific Co.

Three-Dimensional Representation of

Spectrophotometric Data. H. JAFFE, Rockefeller Institute.

Recent Applications of Infrared to Chemical Analysis. C. LUTINSKY, Perkin-Elmer Corp.

Optical Crystallography in Pharmaceutical Analysis. J. MEANS, Chas. Pfizer & Co., Inc.

New Developments in Volumetric Analysis. B. NAIMAN, College of the City of New York.

Current Trends in Instrumental Analysis. S. Z. LEWIN, New York University.

Recent Trends in the Application of Ion Exchange in Analysis. H. P. GREGOR, Polytechnic Institute of Brooklyn.

Recent Trends in Thermo Analytical Methods. S. GORDON, Picatinny Arsenal.

Analytical Application of Solvent Extraction. G. H. MORRISON, Sylvania Electric Products, Inc.

Current Trends in Coulometric Analysis. L. MEITES, Polytechnic Institute of Brooklyn (tentative).

Quantitative Aspects of Paper Chromatography. W. H. MCMULLEN, Chas. Pfizer & Co., Inc.

Further details are available from the chairman of the analytical group, Edwin A. Wynne, Fisher Scientific Co., 1 Reagent Lane, Fair Lawn, N. J.

API Schedules Analytical Papers

Several papers of analytical interest will be presented on May 13 as part of the program of the American Petroleum Institute's Division of Refining. The meeting will be held at the Sheraton Hotel, Philadelphia. Other sessions will be devoted to discussion of corrosion, electrical equipment, fuels, training, instrumentation, data logging, isomerization, reforming, air pollution, and kerosine handling.

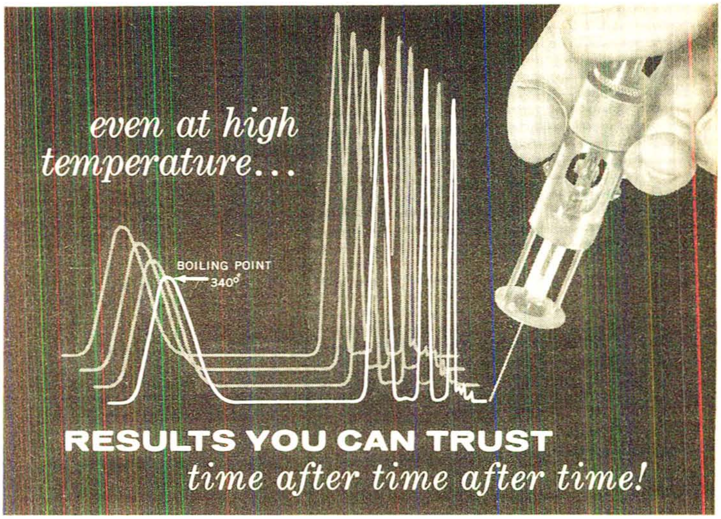
The papers dealing with analytical research are:

Spectrophotometric Determination of Nitric Oxide or Nitrogen Dioxide in Nitric Acid Plant Tail Gas. FRANCIS J. O'HARA AND ORVILLE N. HINSVARK, Girdler Co., Louisville, Ky.

Determination of Traces of Water in Hydrocarbons in the Gasoline Boiling Range. Sample Handling and Interferences. J. WEST LOVELAND AND THOMAS B. WEBSTER, Sun Oil Co., Marcus Hook Pa., AND CHARLES P. HABLITZEL AND GEORGE W. REED, Sun Oil Co., Toledo, Ohio.

Analysis of Biological Assessment of Petroleum-Based Insecticides. A. D. HARFORD, E. THORNTON, AND N. G. MCTAGGART, British Petroleum Co., Ltd., Middlesex, England, and JOHN W. HYDE, British Petroleum Co., Ltd., New York, N.Y.

Polarographic Estimation of Thiophenes and Aromatic Sulfides in Petroleum and Its Fractions. HARRY V. DRUSHEL AND JAMES F. MILLER, Mellon Institute of Industrial Research, Pittsburgh, Pa.



ANALYST'S CALENDAR

Apr. 29-May 1	**Eighth Annual Spectroscopy Symposium and Exhibit,** American Association of Spectrographers, Hotel LaSalle, Chicago, Ill. *Contact:* Theodore H. Zink, H. Cohn & Sons, 4528 West Division St., Chicago 51, Ill.
	48th Annual Meeting, American Oil Chemists' Society, Roosevelt Hotel, New Orleans, La. *Contact:* Lucy R. Hawkins, Executive Secretary, American Oil Chemists' Society, 35 E. Wacker Drive, Chicago 1, Ill.
May 7	**Society for Applied Spectroscopy,** dinner meeting, Hotel New Yorker, New York, N. Y. C. Sheer, Vitro Laboratories, "High Intensity D.C. Arc."
May 11	**Analytical Symposium,** New York University, New York, N. Y. See page 40 A.
May 13	**Division of Refining, American Petroleum Institute,** Sheraton Hotel, Philadelphia, Pa. Twelve Analytical Research Papers. See page 41A.
May 13 to 15	**12th Purdue Industrial Waste Conference,** Purdue University, Lafayette, Ind. Fifty Papers on Industrial Wastes and Their Treatment. *Contact:* Don E. Bloodgood, Purdue University, Lafayette, Ind.
May 13-16	**Symposium on Recent Developments in Research Methods in Instrumentation and 7th Annual Research Equipment Exhibit,** National Institutes of Health, Bethesda, Md. *Contact:* Public Relations Office, National Institutes of Health, Bethesda 14, Md.
May 20—24	**5th Meeting on Mass Spectrometry, ASTM Committee E-14,** Commodore Hotel, New York, N. Y. **Symposia of Theoretical and Analytical Interest.** *Contact:* R. A. Friedel or A. C. Sharkey, U. S. Bureau of Mines, 4800 Forbes St., Pittsburgh 13, Pa. See page 44A.
June 10 to 14	**Symposium on Molecular Structure and Spectroscopy,** The Ohio State University, Columbus, Ohio. *Contact:* Harald H. Nielson, Ohio State University, Columbus, Ohio. See page 44A.
June 13 to 15	**10th Summer Symposium, ACS Analytical Chemistry Division and** ANALYTICAL CHEMISTRY, Purdue University, Lafayette, Ind. Ref. April Part I, page 21A
June 24 to 28	**Congress on Modern Analytical Chemistry in Industry,** St. Andrew's University, Scotland.

Coming Events

July 10 to 17—**4th General Assembly and International Congress, International Union of Crystallography,** McGill University, Montreal, Canada.
July 16 to 25—**XIXth Conference and XVI Congress, International Union of Pure and Applied Chemistry,** Paris, France.
Aug. 7 to 9—**Sixth Annual Conference on Industrial Applications of X-Ray Analysis,** Denver Research Institute, University of Denver.
Aug. 20 to 22—**Conference on Liquid Scintillation Counting,** Northwestern University, Evanston, Ill.
Aug. 26 to 30—**Eighth Annual Infrared Spectroscopy Institute,** Fisk University, Nashville, Tenn.
Aug. 28 to 30—**International Symposium on Gas Chromatography, Instrument Society of America,** Michigan State University, East Lansing, Mich.
Sept. 8 to 13—**132nd National Meeting, ACS,** New York, N. Y.
Sept. 11 to 13—**Fourth Ottawa Symposium on Applied Spectroscopy,** Canadian Association for Applied Spectroscopy, Victoria Museum, Ottawa.
Oct. 14 to 16—**Association of Official Agricultural Chemists, Annual Meeting,** Shoreham Hotel, Washington, D. C.
Nov. 2 to 10—**International Congress and Exhibition of Measuring Instruments and Automation,** Nordwestdeutsche Ausstellungs-Gesellschaft m. b. H., Dusseldorf, Germany.

NEWS (Continued)

Rapid Chromatographic Analysis of Soap-Thickened Lubricating Greases. GEORGE W. POWERS, JR., AND FRANK J. PIEHL, Standard Oil Co. (Indiana), Whiting, Ind.

Sequential Probability Ratio Test as a Novel Statistical Procedure in Analytical Chemistry. ANTHONY F. BARTHOLOMAY AND BERT L. VALLEE, Harvard Medical School and Peter Bent Brigham Hospital, Boston, Mass.

Nonaqueous Titration of Zinc. A Rapid Method for Zinc in Lubricating Oils. T. L. MARPLE, G. MATSUYAMA, AND L. W. BURDETT, Union Oil Co. of California, Brea, Calif.

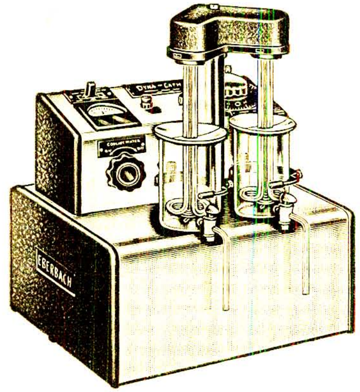
Determination of Five- to Seven-Carbon Saturates by Gas Chromatography. F. T. EGGERTSEN AND SIGURD GROENNINGS, Shell Development Co., Emeryville, Calif.

Wet-Ash Spectrochemical Method for Determination of Trace Metals in Petroleum Fractions. JOHN HANSEN AND C. R. HODGKINS, Esso Research and Engineering Co., Linden, N.J.

Determination of Trace Quantities of Hydrocarbons in the Atmosphere. E. R. QUIRAM AND W. F. BILLER, Esso Research and Engineering Co., Linden, N.J.

Influence of Olefin Structure on Bromine Number by Various Analytical Methods. E. H. UNGER, Socony Mobil Oil Co., Inc., Paulsboro, N.J.

Determination of Oil in Refinery Effluent Waters (Report of API Subcommittee on Refinery Effluent Water Analytical Methods). J. B. RATHER, JR., Socony Mobil Oil Co., Brooklyn, N.Y.



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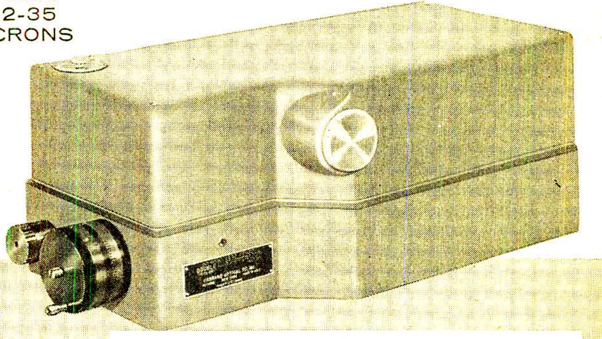

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ASTM Meeting on Mass Spectrometry

The fifth annual meeting of ASTM Committee E-14 on Mass Spectrometry will take place at the Commodore Hotel in New York City, May 20 to 24. The meeting will have an international aspect, with 61 papers scheduled to be presented by authors from seven countries. According to the program, subjects covered will include high molecular weight analysis, solids analysis, ionization potentials, isotopic abundance determinations, as well as new mass spectrometer techniques and developments.

A symposium on negative ions will be held on May 22 as part of the meeting; papers will discuss negative ion formation in molecular gases, hydrogen and oxygen, and some halogenated gases, among other topics.

Half-day discussion sessions for Subcommittee 5 on New Instruments and Techniques and for Subcommittee 7 on Solids have also been scheduled.

Special daytime activities, beginning with a coffee assembly on Monday morning, have been planned for the ladies.

Those interested may obtain further details of the program from R. A. Friedel, U. S. Bureau of Mines, 4800 Forbes St., Pittsburgh 13, Pa.

Molecular Structure—Spectroscopy Symposium

The Annual Symposium on Molecular Structure and Spectroscopy will be held at Ohio State University, June 10 to 14.

Subjects covered are: infrared instrumentation and applications; infrared spectra of molecules; molecular dynamics; intensities; and electronic band spectra.

The dinner, to be held on Wednesday evening, June 12, will feature Dudley Williams, Ohio State University.

There is no registration fee. Rooms for male registrants are available at Baker Hall, during the period June 10 to 14 only. Accommodations are available for a limited number of women guests on campus.

Further details are available from Harald H. Nielsen, The Ohio State University, Columbus 10, Ohio.

The program to date appears below:

Monday Morning, June 10

Infrared Instrumentation and Applications

Commercial Infrared Instrumentation. VAN ZANDT WILLIAMS, Perkin-Elmer Corp., Norwalk, Conn.

Instrumentation for High Resolution. E. K. PLYLER, Nationa[illegible]eau of Standards, Washington 25, [illegible]

Military Instrumentation. LLOYD G. MUNDIE, Willow Run Laboratories, Ypsilanti, Mich.

Tuesday Morning, June 11

Infrared Spectra of Molecules

Infrared Spectroscopy in the Field of Bacteriology. H. M. RANDALL, University of Michigan, Ann Arbor, Mich., AND DONALD W. SMITH, University of Wisconsin, Madison, Wis.

Spectroscopy of Molecules in the Infrared. K. NARAHARI RAO, Ohio State University, Columbus, Ohio, AND EDWARD D. PALIK, University of Michigan, Ann Arbor, Mich.

Structure of Some Inorganic Hydrides. M. KENT WILSON, Tufts University, Medford 55, Mass.

Wednesday Morning, June 12

Molecular Dynamics

Interaction of Rotational and Vibrational Motion in Polyatomic Molecules. C. F. CURTISS, University of Wisconsin, Madison, Wis.

Review of Work in Internal Rotation. D. G. BURKHARD, University of Colorado, Boulder, Colo.

Theory of the Overtone and Combination Bands of the Methane Molecule. KARL T. HECHT, University of Michigan, Ann Arbor, Mich.

Thursday Morning, June 13

Intensities

Some Problems in the Measurement and Interpretation of Infrared Intensities. JOHN OVEREND, University of Minnesota, Minneapolis, Minn.

Infrared Intensities. Perturbations and Interactions. DAVID F. EGGERS, JR., University of Washington, Seattle, Wash.

Friday Morning, June 14

Electronic Band Spectra

Recent Theoretical Studies of Bond Properties. C. A. COULSON, Oxford University, Oxford, England.

Electron Spin Resonance Studies of Unstable Free Radicals. DAVID J. E. INGRAM, University of Southampton, England.

Interaction of Two Excited Hydrogen Atoms in Either 2-*S* or 2-*P* States. BRUNO LINDER AND JOSEPH HIRSCHFELDER, University of Wisconsin, Madison, Wis.

X-Ray Diffraction Course

The 27th x-ray diffraction school for research and industrial workers will be held at Morrison Hotel, Chicago, June 3 to 7. Sponsor is Philips Electronics, Inc.

The course will involve both class and laboratory work, with prominent speakers discussing x-ray diffraction, diffractometry, and spectrography. Also included are discussions on new high and low camera techniques, electron microscopy, and electron diffraction.

While there is no registration fee, registration is limited. Details are available from Instruments Division, Philips Electronics, Inc., 750 South Fulton Ave., Mt. Vernon, N.Y.

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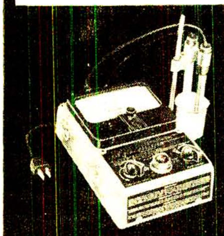

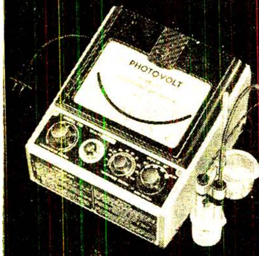

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- Accuracy 0.01 in pH 6-8 range, 0.05 in pH 2-12 range.

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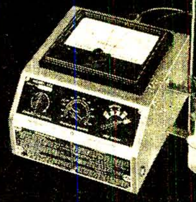

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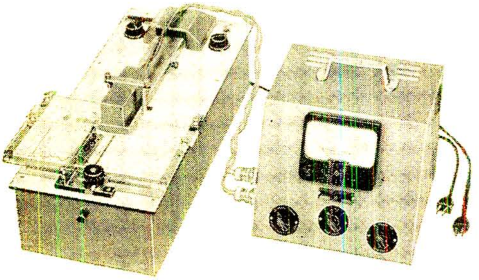

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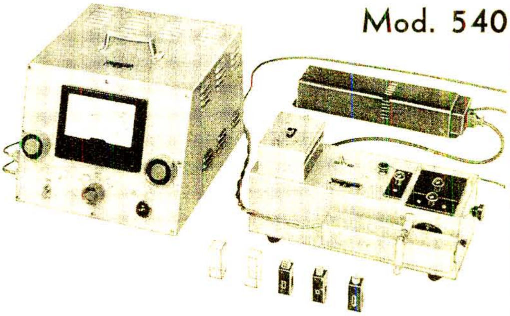

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Paper electrophoresis takes 2 important steps

Spinco announces developments which make the Model R Paper Electrophoresis System more useful than ever for such analyses as serum proteins, lipoproteins, glycoproteins, amino acids, carbohydrates, hemoglobins, proteins in spinal fluid, tears, and in other body fluids, enzymes, extracts, and a number of other inorganic and organic mixtures.

1

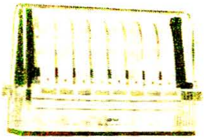
NEW PROCEDURE

Improved low-noise paper plus several changes in recommended procedure increase accuracy and reproducibility. Subtler changes in the distribution of electrophoretic components can now be recognized with certainty. In addition, for serum proteins, analysis time has been reduced by over five hours through a new dyeing technique.

2

NEW ANALYTROL

The Spinco Analytrol recording scanner and integrator, which quantitates the paper strips, now uses narrow bandpass filters and a high-sensitivity servo amplifier. This substantially improves reproducibility and makes the Analytrol a general-purpose paper scanner, recording colorimeter and recording densitometer.



PRESENT USERS can bring existing Model R Systems up-to-date by converting earlier-model Analytrols and taking advantage of the new procedure.

FOR A FLOW CHART of the new serum protein method and for more information on the new Spinco Model R Paper Electrophoresis System write to Spinco Division, Beckman Instruments, Inc., Stanford Industrial Park, Palo Alto, California. Ask for Data File R7.

Beckman® / Spinco Division

For further information, circle number 46 A on Readers' Service Card, page 77 A

the ANALYST'S column

L. T. Hallett, Editor

Work of the National Bureau of Standards in preparing standard samples and calibrating instruments for use by government and non-government organizations and individuals, is of direct concern to every analytical chemist. In the past, NBS efforts in this area have been somewhat hampered by lack of funds, since fees received had to be turned in to the U.S. Treasury and could not be used to support or improve calibration and testing services.

Recently, several changes have taken place which should aid NBS in rendering these valuable services. Many of the changes have been made possible by new legislation. Strong support for these changes came from advisory committees to the Bureau, such as those of the American Chemical Society, American Society for Testing Materials, and American Standards Association.

One of the principal changes was the creation of a revolving fund for calibration and testing services. Fees received for such work can now be used to support it. A development of long-range significance is the plan to relocate NBS about 20 miles from Washington. The new site will be equipped with new buildings and other facilities to meet the Bureau's needs for more space and modern facilities.

In the "standards" area, NBS feels that it can render the greatest service by developing standards and methods of calibration and test. Conversely, NBS would like to decrease certain types of routine or repetitive testing that other laboratories are equipped to undertake.

In connection with its programs, it is important to note that NBS carries out many projects in col-

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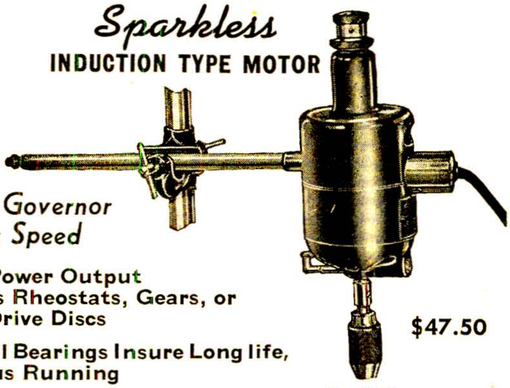

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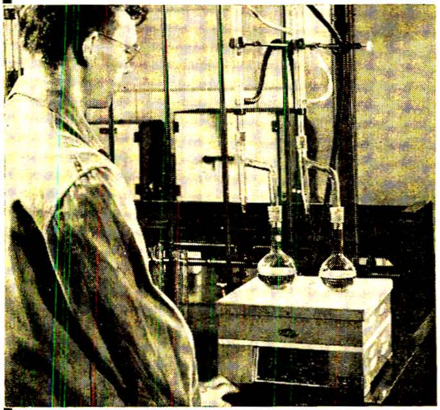

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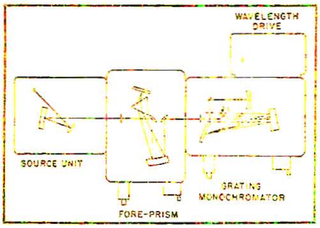
P-E Analytical News

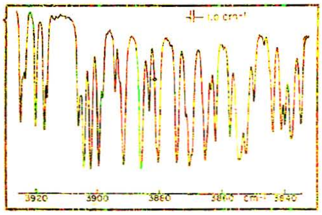
- *Two new high resolution instruments*
- *Spectrophotometry for patent protection*
- *Fuel gas analysis — fast and accurate*

FORE PRISM-GRATING SPECTROMETERS

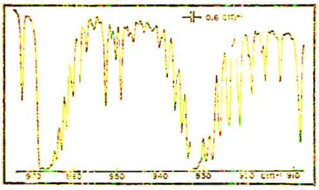
Two new instruments for spectroscopists whose work demands very high resolution and virtual freedom from scattered light are the Perkin-Elmer Models 12G single beam, single pass and 112G single beam, double pass recording infrared fore prism-grating spectrometers.



The optical layout for the Model 12G spectrometer is shown above. Two representative spectra obtained with the double pass instrument are shown below.



This 2.6μ water vapor spectrum was obtained with a 75 1/mm grating used in the fifth order. The grating monochromator slits were 80μ wide and running time was 50 minutes. The resolved bands at 3841 cm^{-1} are separated by 1.0 cm^{-1}.



This 10.7μ ammonia spectrum was obtained with a 75 1/mm grating used in the first order. A cell 10 cm long filled to 5 cm pressure held the sample. The grating monochromator slits were 215μ wide and running time was one hour. 0.6 cm^{-1} resolution was obtained.

This improved resolution makes application to research problems obvious. Errors due to finite slit width and scattered light are reduced. Wavelength range from 2.2 to 17μ can be covered with a single fore prism and a single grating. Wavelength range can be extended from the ultraviolet to the far infrared by substituting suitable prisms, gratings, sources and detectors.

INFRARED SPEEDS PATENT APPLICATION

A paper by patent examiners Donald Levy and Lucile Burd Wendt in the Journal of the Patent Office Society (Vol. XXXVII, No. 12) points out the value of infrared spectra in speeding patent prosecution.

Although the paper deals specifically with patent applications on antibiotics, the information and suggestions are of general interest in patent problems on all types of chemical compounds. Levy and Wendt point out that in many of today's complex molecules complete structural analysis that has heretofore been necessary in patent applications can often be replaced by good infrared spectra. The patent office has accepted the fact that the infrared spectrum of most organic compounds is nearly as characteristic as the structural diagram. The patent office recognizes that complete structural analysis of a new compound may take months or even years to accomplish. It has therefore shown a willingness to issue patents based on infrared spectral characteristics pending the complete disclosure of the structure of the material in question.

The authors indicate the type of spectral information that is required and point out some of the pitfalls which must be avoided in presenting infrared spectra. They also indicate that other material such as Raman, X-ray, and ultraviolet spectra should be used where possible to supplement the infrared data.

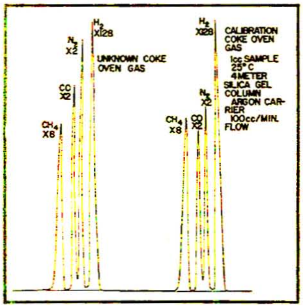
PRECISION CAN BE INEXPENSIVE

Until recently the chemist with fuel gases to analyze was faced with a dilemma. He either had to spend a lot of cash for a sensitive piece of equipment which would give accurate separation and analysis of all components, or he had to be satisfied with an inexpensive, insensitive apparatus which would give results on only a few components. There was no in-between.

Now the problem has been licked — by a low-cost, precise yet simple instrument which operates on the principles of gas chromatography. The P-E Model 154-B Vapor Fractometer completely separates and analyzes fuel gas components — from hydrogen through the pentanes — in less than one hour. Even isomers and close boilers, difficult or impossible to separate by other means, yield to this new tool.

Calculations are a breeze. The ability to reproduce gas sample sizes precisely make it unnecessary to compute band areas in quantitative determinations. Simple comparison of peak height measurements with those of calibration mixtures yields quantitative analyses of extreme accuracy.

At the American Gas Association's Chemical Engineering and Manufactured Gas Production Conference in Philadelphia last fall, P-E's Vincent J. Coates presented a paper on fuel gas analysis by Vapor Fractometry. Reprints are available from P-E.



(Illustration from V. J. Coates' paper shows fractogram of major components in coke oven gas.)

P-E engineers feel that within the next five years this inexperience and powerful new method will completely dominate the field in analyzing for fuel gases. Any questions? Just give us a call!

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We'll be glad to send you more information on any of these items. Or to put you on the mailing list for INSTRUMENT NEWS, a quarterly published by P-E to further research, material analysis and production through electro-optical instrumentation.

For further information, circle numbers 48 A-1, 48 A-2, 48 A-3 on Readers' Service Card, page 77 A

laboration with private and public test groups or associations. An example of this is the Cement Reference Laboratory, now in its 28th year. This is a joint project of the NBS, Bureau of Public Roads, ASTM, and the U. S. Army Corps of Engineers. Its objective is to promote uniformity and improvement of cement test methods.

Such joint projects can be initiated at the request of any interested public or private group.

The bureau's backlog of calibration and testing is still substantial. Time required to complete projects varies considerably, depending on the item.

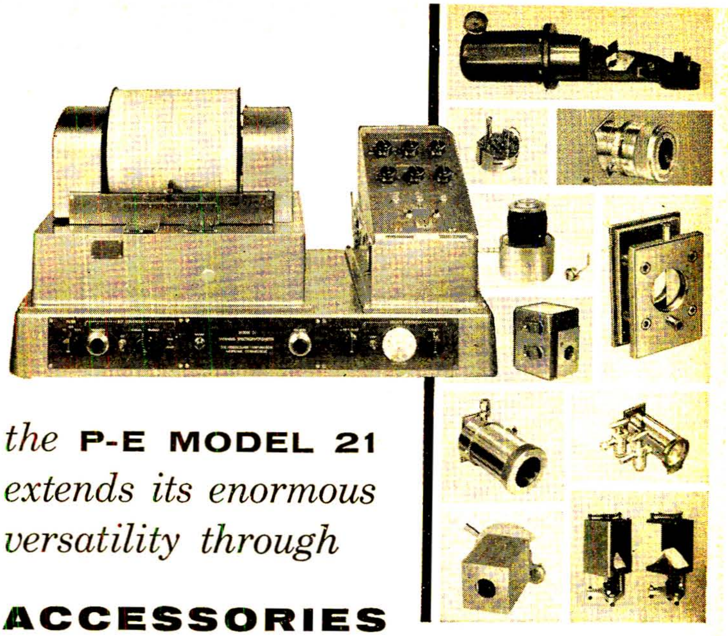
At a recent meeting with NBS officials, the ASTM and ASA advisory groups recommended that, since testing and calibration work are now on a self-supporting basis, NBS should provide sufficient facilities and personnel to render prompt service even though such a procedure might require increased fees. Sixty to 90 days, the committee feels, should suffice for all except special tests.

Another recommendation is that NBS should develop versatility in its personnel, so that they can adjust to shifts in the work load.

The committee also feels that industry and NBS should "loan" personnel to each other for tours of duty, so that each can become familiar with the other's needs. Such a step would also provide an effective means for interchange of information.

The advisory group feels that research should be conducted to improve tests and calibration methods, but that such programs should be kept in balance with practical objectives.

Experience has indicated that there is no substitution for certification by NBS, which has established its integrity and prestige over many years. It is to be hoped, therefore, that the new setup will permit NBS to render services more promptly and effectively than it has been able to do in the past.



New Illustrated 16-Page Booklet

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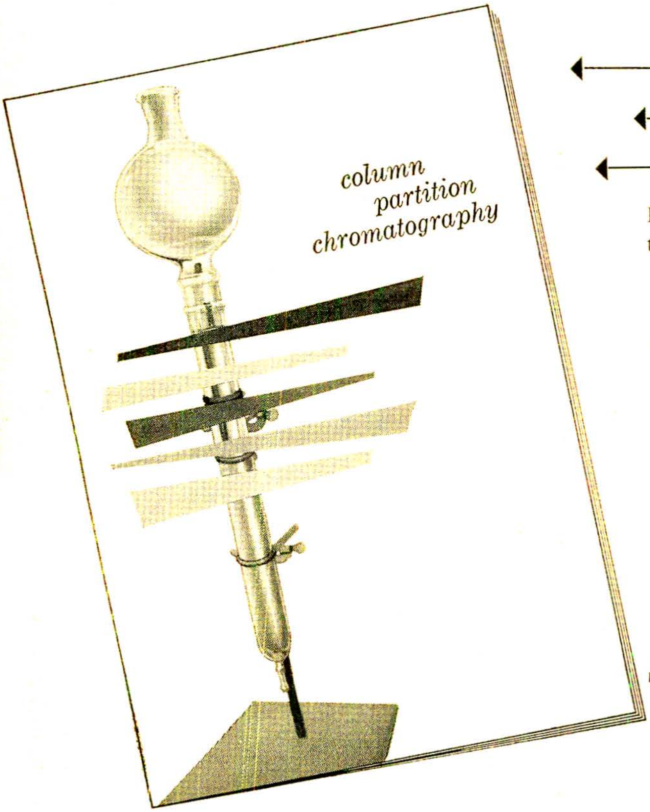
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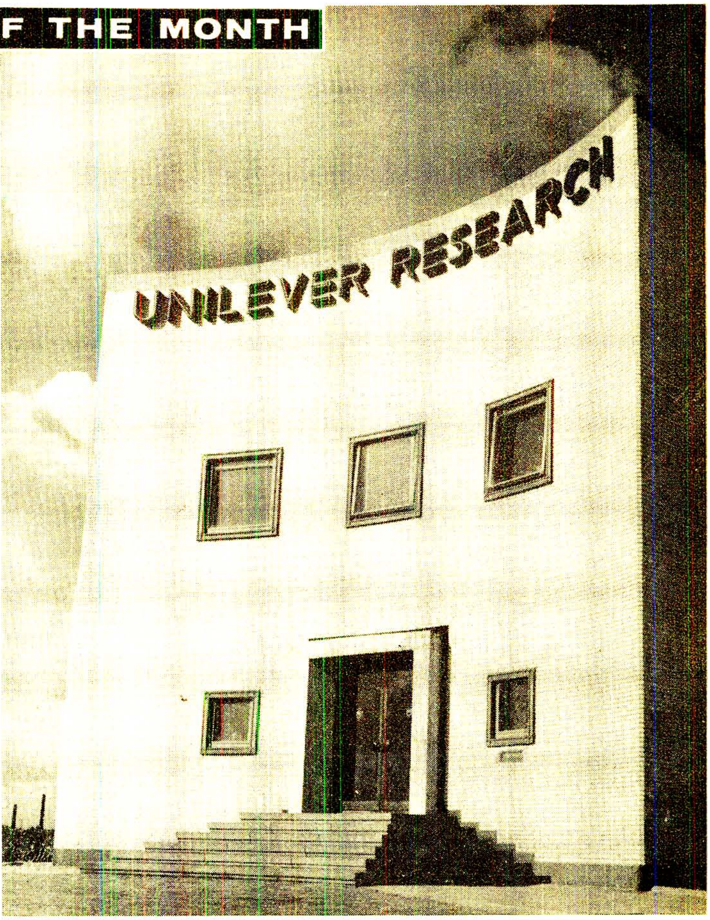


The three-story research building, adjacent to a Unilever plant, is fully equipped to do basic and applied research on edible fats and oils

New techniques and instrumentation are an integral part of Unilever's basic research program at Vlaardingen, Holland, site of its new facility.

Work here, which is centered on edible fats and oils, will supplement and complement that being carried out at the company's other research facilities. At Port Sunlight, England, for example, work is done on soaps and detergents; at Colworth House near Cambridge, England, research is done on low-fat foodstuffs; at Pears Factory in London, toilet preparations; at Edgewater, near New York, products for the American market.

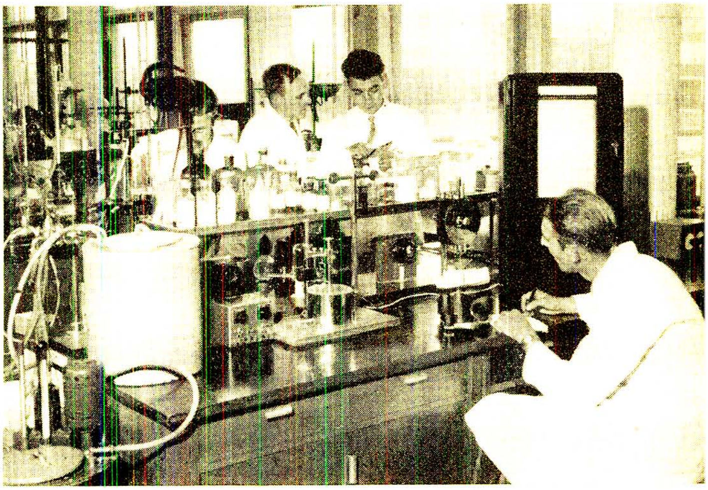
The Vlaardingen research center replaced the limited facilities at Zwijndrecht, Holland. The new laboratory adjoins a Unilever plant. Construction was started in April 1953. When it was occupied two years later, a new wing was added to provide facilities for synthetic detergent and microbiological research. The expanded laboratory was officially opened last November.

Unilever has developed empirical techniques for refining oils, converting oils to fats, and preparing margarine from skim milk and fat. Only through *fundamental* research does Unilever feel that it can make further substantial progress.

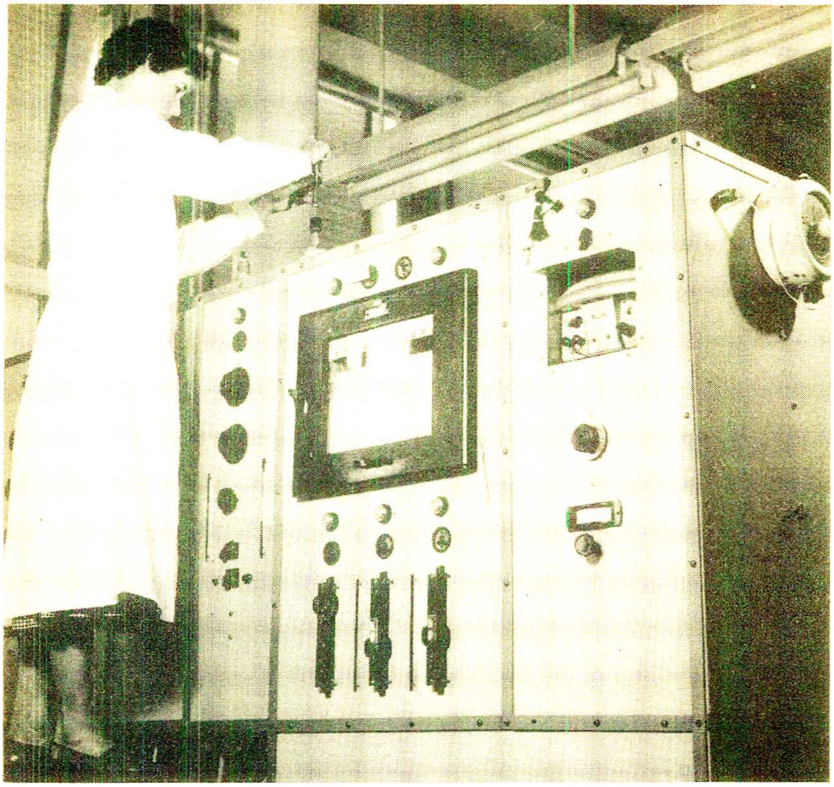
Typical areas to be explored are synthetic organic materials; physical chemistry of structures of oil-water interfaces; plastic, elastic, and rheological properties of margarine and fats; catalysis and catalysts involved in conversion of oil to fats by hydrogenation; and physiological and biological effects of fats on men and animals.

Among the techniques and instruments being used are infrared and ultraviolet spectrophotometers, chromatographs, and radiochemicals.

The new three-story and basement research center, with its still newer wing, occupies 7400 sq. meters. In addition to laboratories, the building includes offices, library, conference room, heating and air conditioning facilities, auditorium, canteen, supply room, glassblowing facilities, and workshops. Pilot plant facilities are also included.



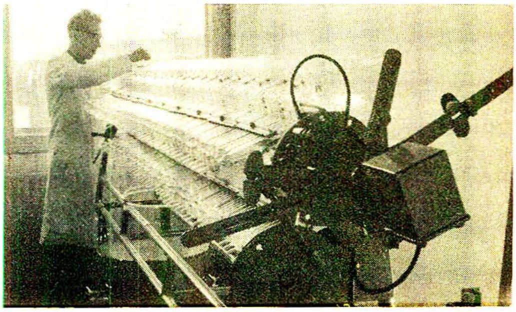
The general laboratories are well equipped and well lighted



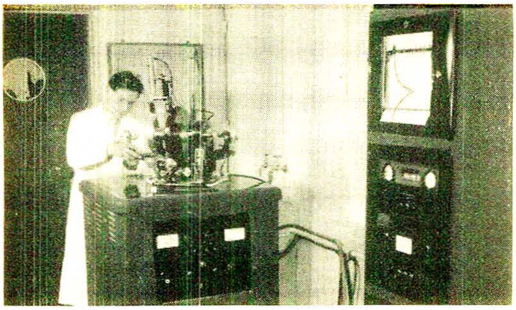
Gas chromatography is one technique widely used in basic studies

◄

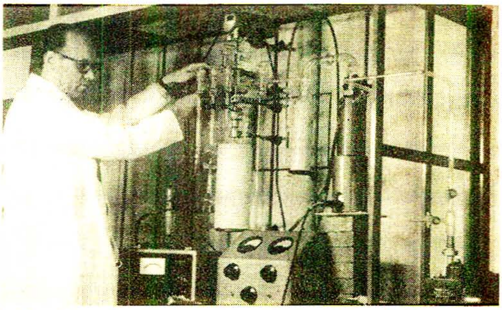
The newest in instrumentation, such as the infrared spectrophotometer, is used to learn more about fats and oils



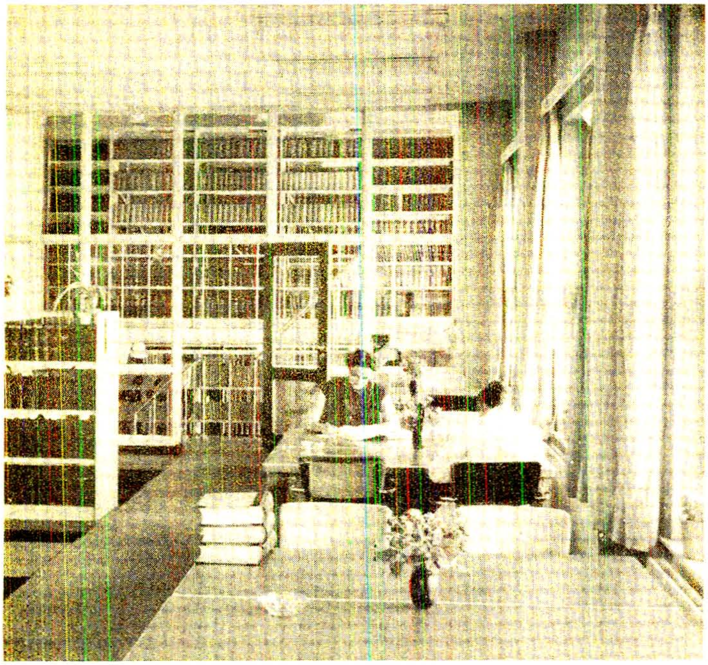
A countercurrent liquid-liquid extractor unit plays an important role in Unilever's research program



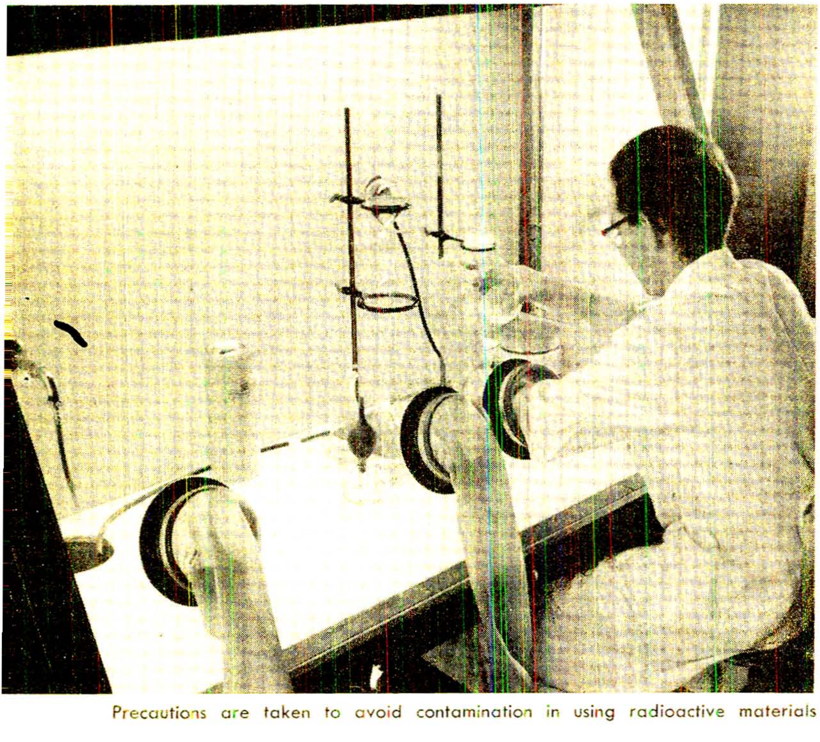
X-ray diffraction is one of the modern analytical techniques used in the basic research program



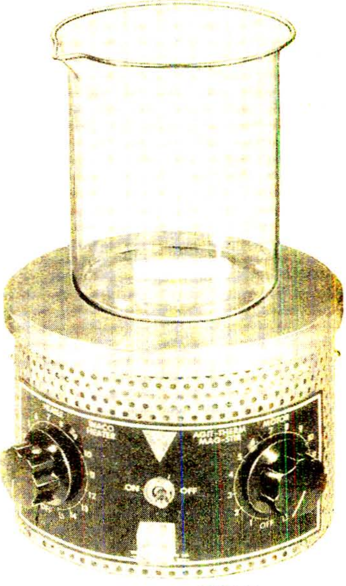
Radioactive chemicals are synthesized to yield research tools needed in Unilever's program

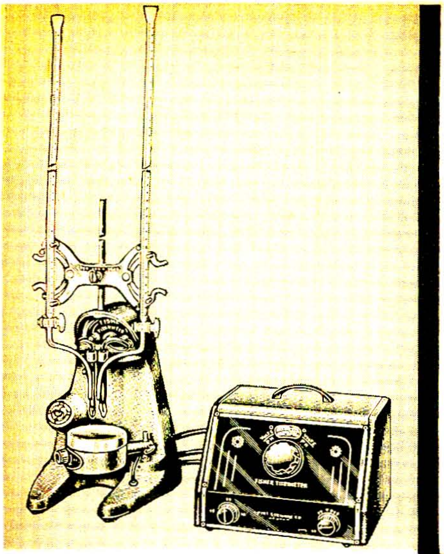


Adequate library facilities are provided to assist in the research program



Precautions are taken to avoid contamination in using radioactive materials





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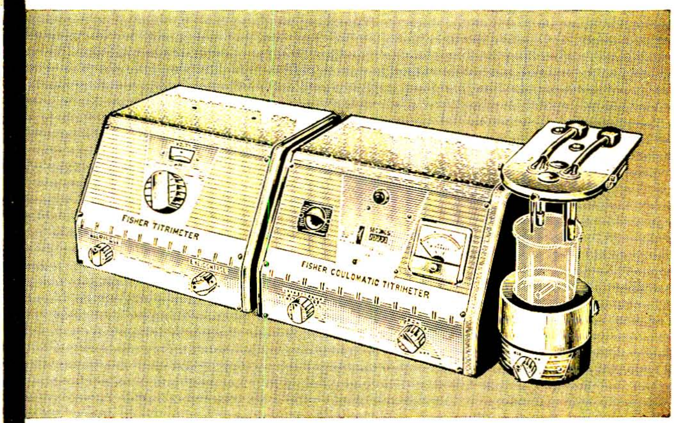

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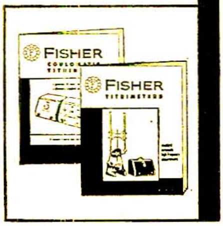

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by Ralph H. Müller

Recording differential refractometers used for process control and research

In the August 1954 column we had the opportunity to describe the Sinclair-Phoenix forward-scattering smoke photometer. Once more, through the courtesy of Edward J. Fuhrmeister, president of the Phoenix Precision Instrument Co., 3803-05 North Fifth St., Philadelphia 40, Pa., we are privileged to describe another series of important optical instruments—the differential refractometers.

The precise measurement of refractive index, as well as its wave length dependence (dispersion), has been a commonplace for more than a century. This quantity has been a precise means of identification and has played an important role in the elucidation of molecular structure. Many elegant instruments have been designed for this purpose, indeed, a first class refractometer is an example of the best in optical instruments.

It is characteristic of modern instrumentation that whereas little improvement can be made in an almost perfect classical instrument, a new approach can open up vast and unexplored possibilities. The automatic recording of refractive index, or changes thereof, is one of these. Refractivity has been one of the last of the classical optical techniques to be recorded. The earlier methods toward this end measured refraction by the obvious means of following the angular deviation in a hollow prism containing the liquid. Many forms of this principle are eminently practical and are widely used in process control. More than ten years ago Claesson in Sweden developed and refined the differential scheme, in which a standard and unknown liquid are compared in an essentially rectangular compartment divided by a diagonal window. A lateral displacement of the light beam occurs as a result of any difference in the respective refractive indices. This principle is employed in the Phoenix refractometers. We can write about this with mixed enthusiasm and respect. Having designed and built an instrument of this kind some years ago, we have healthy respect for the development of a rugged and reliable instrument.

Operation of Refractometers

Figure 1 is a schematic of the Phoenix refractometer. Light from source *M* is rendered monochromatic through a series of narrow-band pass filters labeled *MF*, which are mounted in an indexing turret allowing rapid selection and isolation of the desired wave length. The monochromatic light after passing through slit *S* is collimated by a lens system, *L*, and enters the differential cell which is divided into two compartments: one for solution, and the other for solvent. At the cell partition, the light beam suffers deviation corresponding to the difference between the refractive index of the solvent (usually not flowing) and the solution which is flowing continuously through the other compartment.

After collimating the beam through

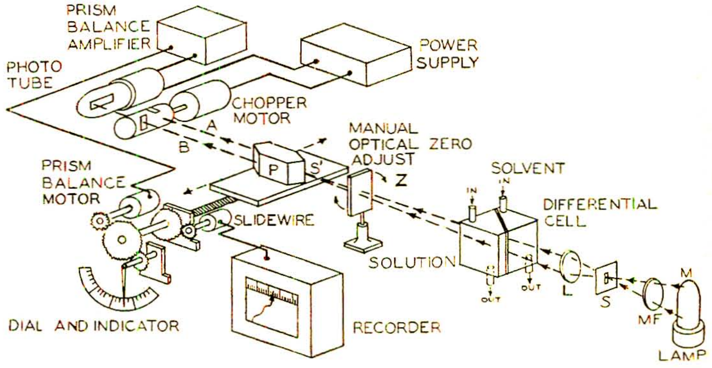


Figure 1. Schematic of Phoenix refractometer

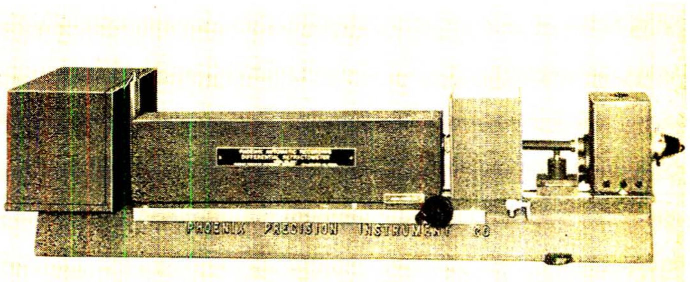


Figure 2. Automatic recording differential refractometer

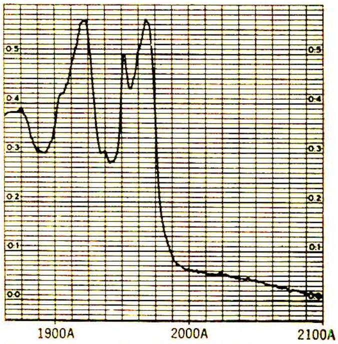
Cary / instrument abstracts

Applied Physics Corporation Pasadena California

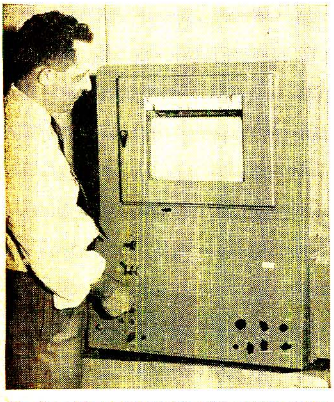
Extension of Spectrophotometer Range to 1860A Opens New Region for Analysis

The extended ultraviolet wavelength range of the Cary Model 14 Recording Spectrophotometer has opened a new region which will permit analysis of a number of compounds not previously adaptable to ultraviolet spectrophotometry with standard instruments.

Accurate direct reading absorbance* to 1860A is now provided with the Model 14 through the use of optical elements of increased ultraviolet efficiency in the double monochromator. The spectrum of methyl ethyl ketone vapor, shown, indicates just one class of compounds whose spectra in this region provide analytical possibilities. In addition to ketones, it is likely that alcohols, mono-olefines, aromatics and other compounds will also have useful spectra in this region.



This spectrum of methyl ethyl ketone vapor illustrates the performance of the Model 14 in the lower wavelength regions.



The Cary Model 14 Spectrophotometer provides performance to 1860A, with possibilities for even shorter wavelengths. Heretofore such performance was possible only on custom made instruments.

The prism-grating double monochromator of the Model 14 is noted for its high resolving power with low scattered light (less than a part per million) in the ultraviolet, visible and near infrared regions. By using the new, more efficient optical elements in this double monochromator, the extended range is achieved.

This development is the result of constant effort to improve the performance, reliability and usefulness of Cary instruments by taking full advantage of advancements in materials, components and technology.

For additional information on the new Model 14 and other Cary instruments, write for Bulletin ACS-25.

*By use of readily interchangeable slidewires, the Model 14 will also record directly in transmittance, log absorbance or other special functions.

IMPROVED VIBRATING REED ELECTROMETER

Faster, simpler measurement of radioactive isotopes, mass spectrometer ion current, small pH changes, etc.... these and other laboratory problems involving measurement of very small charges, currents, and voltages are now made still simpler with the new Cary Model 31 Vibrating Reed Electrometer than by other methods. The new design provides ten operating ranges from 1 millivolt full scale to 30 volts full scale.

The wider choice of ranges means that users can cover a wide range of input currents or voltages with the standard Model 31 and one or two input resistors, thus in many cases eliminating the need for special instrument modifications and accessories.

The Cary Model 31 replaces the former Model 30 and provides all of the features of the Model 30 plus the added advantages of the new ranges. A descriptive bulletin (No. ACE-25) and information on application to specific problems are available.

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the cell, the lens system focuses the slit image, S', on the apex of the hexagonal prism, P, which is mounted on a table that has precision-ground ways and allows lateral displacement of the beam-splitting prism with respect to the slit image, S'. When the slit image, S', is centered precisely on the apex of the prism, the system is in balance, as the image is split into two parallel beams of equal intensity, A and B, which emerge from the opposite sides of the prism.

Each beam is alternately interrupted by a synchronous chopper, and enters a diffuser system where the average light intensity of each beam is monitored by a photomultiplier tube. Any change in the refractive index of the flowing solution will cause a displacement of slit image S' and a corresponding change in the intensities of emergent beams A and B, resulting in an unbalance signal.

This signal is detected by the photomultiplier, amplified and transmitted to the servo system, which determines the direction of unbalance and drives the prism table laterally to restore the system to balance. The lateral position of the prism table is a linear measure of the refractive index difference between the solvent and solution. The shaft which actuates the prism table drive is geared to a potentiometer slidewire for recorder operation. A pointer is geared to the same shaft and indicates refractive index on the front panel dial. The recorder may be remotely located if desired.

All operating controls, mechanical and electrical, are readily accessible and easy to use. Coarse and fine photomultiplier gain controls are provided to permit measurements on dark as well as clear liquids and gases. Two test buttons are provided for injecting up and down scale test signals, to check gain settings of the photomultiplier tube and proper operation of the complete optical servo system. A refractive index zero control, Z, is provided, which allows the operator to set the instrument to read zero when the solvent is in each half of the differential cell.

A typical example is in the Phoenix Model R-1000-T shown in Figure 2. A separate cabinet contains a standard recorder and all power supplies. The recorder is of the high-level bridge type which eliminates batteries, standard cell, and standardizing mechanisms.

An important feature of these refractometers is the calibrated range extension with constant zero control. It is apparent that with sensitivities of 3 units in the sixth decimal point a very limited range of refraction difference would result for a given solvent ref-

New Torsion Laboratory Balances

Model HT-1 was developed to fill the demand for a balance which combines large capacity with unusually high sensitivity. The beam is graduated to 1 gram and no weights are needed for weighings of 1 kilo or less.

Model LA-3 has several new features. The Torsion bands are made of a new, extremely corrosion resistant, stronger alloy (Elgiloy), which results in longer, trouble-free life for the balance. A single beam with vernier permits accurate weighings from 0.01 gram to 10 grams without the use of loose weights. The stainless steel calibrated beam assembly is positioned directly over the Torsion mechanism to minimize the effects of vibration. Sensitivity is easily adjusted with the high poise weight, and weighing operations are faster with the new oil dashpot.

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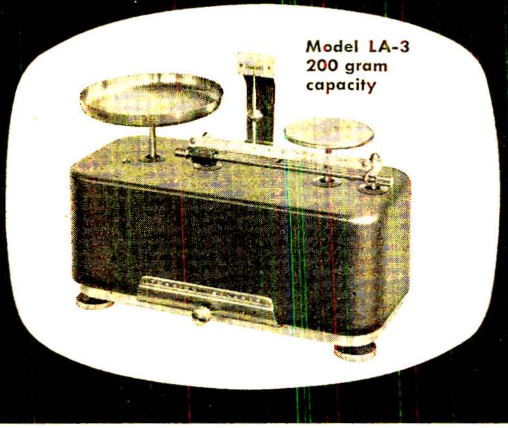
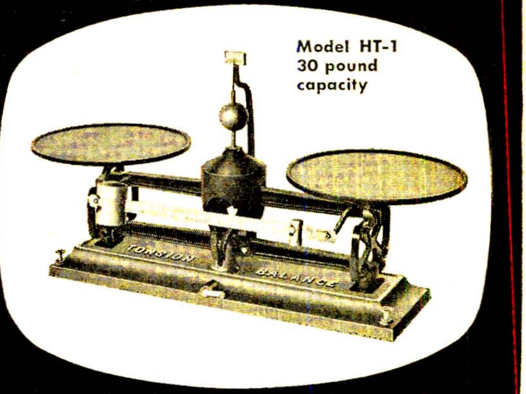


Model LA-3
200 gram
capacity



Model HT-1
30 pound
capacity

LA-3 SPECIFICATIONS

Capacity: 200 gm.
Sensibility Reciprocal*: 0.02 gm.
Beam: 10 gm. by 0.01 gm. with vernier
Pan: 5″ diameter stainless steel
Dashpot: New oil dashpot for faster weighing
Finish: Smooth, chemically resistant gray
Dimensions: 5½″ x 11½″ x 9″ high
Net Weight: 8 lbs.
Shipping Weight: 11 lbs.

HT-1 SPECIFICATIONS

Capacity: 14 kg. (30 lbs.)
Sensibility Reciprocal*: 0.75 gm. (.046 oz.)
Beam: Single graduated beam with 2 slide weights, beam reading 1 gm. to 1 kg.
Plates: 10″ diameter iron plates (ring-bottom scoops with counterpoise available)
Finish: Smooth, chemically resistant gray
Dimensions: 27½″ x 10″ x 15″ high
Net Weight: 39 lbs. • **Shipping Weight:** 60 lbs.

*Sensibility Reciprocal (S.R.) is the amount of weight required to change the rest position of the indicator one full scale division.

The Torsion Balance Company

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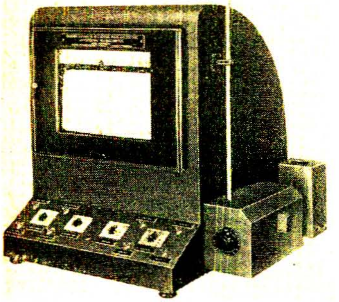

Figure 3. Automatic recording mass collecting differential refractometer

erence. For this reason, all Phoenix refractometers are equipped with a calibrated optical range extension mechanism that allows multiple full scale deflections to be restored on scale without changing sensitivity or losing the original starting zero. This arrangement makes it possible to measure with a sensitivity of 3 in the sixth decimal place over a span of 7000 units in the sixth decimal place, without changing cells or reference solutions.

Mass Collecting Differential Refractometer

Of vital importance to the analyst is the Model CR-1000-T automatic recording mass collecting differential refractometer shown in Figure 3. This instrument has a supplementary feature in which the mass collector permits the recording of refractive index as a function of the mass of the liquid sample passed. The automatic weighing element drives the Y axis of an x-y recorder, the x axis drive being proportional to the differential refractive index. A choice of eleven interchangeable sensing elements can be purchased ranging from 0-1.5 to 0-80 ounces, all for a chart travel of 30 inches. For any one weight range, a three-position calibrated mass range switch can change the chart span for a desired fraction of total weight. Special sensing elements covering ranges up to 3000 pounds are available for process and industrial control application. The great utility of this instrument for following the output of fractionation columns and the effluents of liquid phase chromatographic columns and ion exchange columns is evident.

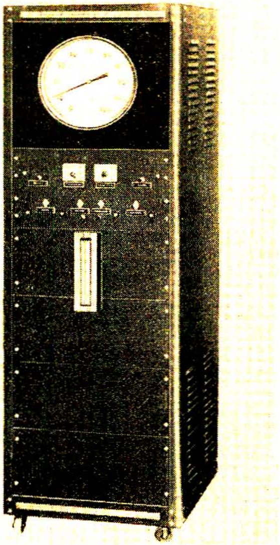

Figure 4. Process refractometer

Of the many special purpose models, space permits the illustration of only one other example. In Figure 4 is shown the P-1000-C, one form (indicating) of a process refractometer. This is specifically designed for process plant analysis and control. Complete fail-safe features are provided with appropriate alarms, to take care of light source, photomultiplier, or high voltage supply failures. Of the many applications to process monitoring and control, a few may be mentioned—controlling fractionating tower separation of cyclohexane and n-hexane, controlling concentration of acids, sugar, and salt solutions, the blending of gasoline additives, alcohol-water analysis, hydrogenation of food oils and fats, and the identification of compounds as they are released, such as coal tar.

For the readers who may be inclined to believe that this columnist's interests are confined to rare and esoteric devices, it may be of interest to note that these various differential refractometers are being used in some 152 domestic university, governmental laboratories; and industries, and some 50 or more by foreign organizations.

Although these instruments are doing workhorse jobs in industry, it is apparent that they represent a powerful research tool. The extraordinary sensitivity, combined with ruggedness and reliability, is up to the most exacting needs of pure research.

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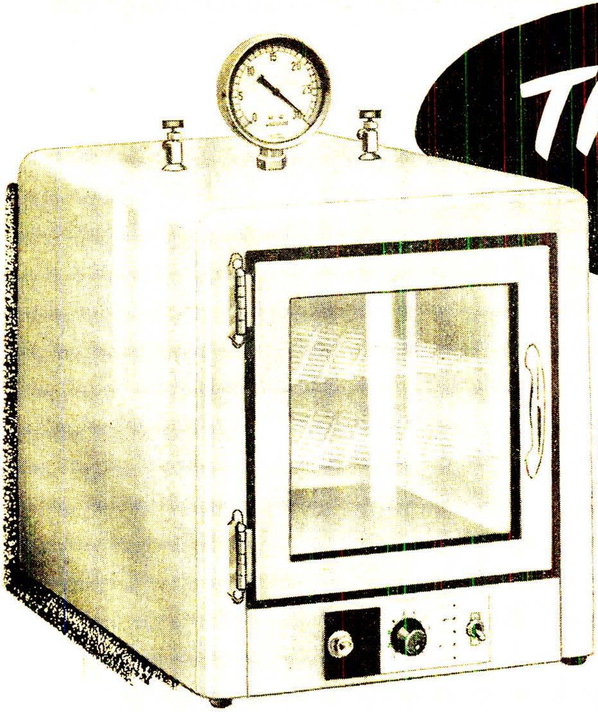

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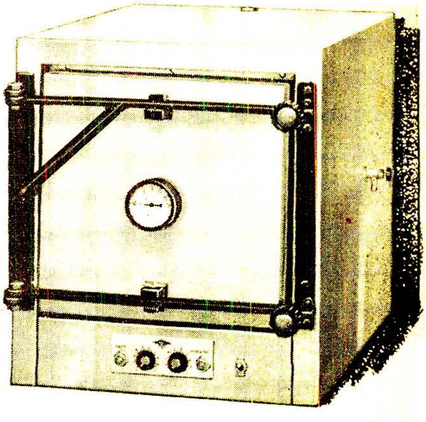

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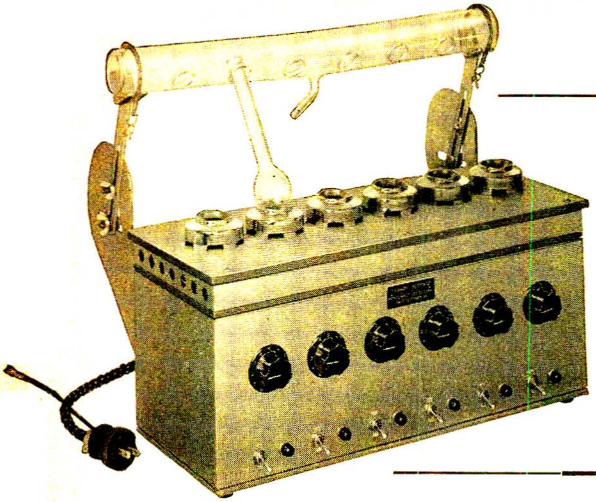

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Thomas-LABCONCO HIGH TEMPERATURE KJELDAHL DIGESTING APPARATUS

KJELDAHL DIGESTING APPARATUS, Micro, Electric, Thomas-Labconco. With six 200-watt heaters, each with separate rheostat control, pilot lamp and "on-off" switch, for completely independent operation at temperatures up to 450° C. Controls are mounted in a Stainless steel housing, and finish is corrosion resistant throughout. With fume duct of Pyrex brand glass. Support is adjustable to accommodate Kjeldahl flasks 10 ml, 30 ml or 100 ml capacity, making the apparatus suitable for micro or semimicro analysis. Heat production is adequate for larger Kjeldahl flasks* or for pressure digestions using sealed tube procedures. Fume duct is in accordance with *"Recommended Specifications for Microchemical Apparatus,"* Division of Analytical Chemistry, American Chemical Society; see *Analytical Chemistry, Vol. 23, No. 3 (March, 1951), p. 524.*

The disc-shaped heaters, consisting of heating elements embedded in refractory cement, are spaced 3 inches from center to center on the transite top of the Stainless steel housing and are separated from the controls by a ventilated air chamber $1\frac{1}{8}$ inch high, beneath which is a second transite strip. Each heater has a removable, circular top of Stainless steel with opening 26 mm diameter and concavity for supporting the bottom of a 30 ml Kjeldahl flask. Readily insertable wire gauze discs are available for use in openings of heater tops to support 10 ml Kjeldahl flasks and tubes less than 26 mm in diameter.

Individual switches, pilot lamps and temperature control knobs, with dials graduated in 10 arbitrary divisions, are mounted on front panel and are insulated by a transite panel from the six 50-ohm rheostats mounted in ventilated rear compartments. Housing is $19\frac{1}{8}$ inches long x $7\frac{5}{8}$ inches deep x $10\frac{3}{16}$ inches high to tops of heaters.

Fume duct, 516 mm long x 51 mm outside diameter, has six openings 22 mm diameter for flask necks and slopes toward center for drainage through the central outlet tube, $\frac{7}{16}$-inch outside diameter. The fume duct is held in position by the Stainless steel, spiral springs of two slotted aluminum clamps supported by wing-shaped brackets at the back corners of the housing. The flexible attachment of the clamps to L-shaped slots in the brackets by two bolts with wing-nuts and washers permits easy adjustment to support flasks or test tubes up to 12 inches long at any preferred angle over a wide range.

7498-E. Kjeldahl Digesting Apparatus, Micro, Thomas-Labconco, Electric, as above described, with six independently controlled 200-watt heaters. Complete with six heater tops to support 30 ml Kjeldahl flasks, fume duct made of Pyrex brand glass, two clamps to support duct, two additional bolts for locking clamps in desired position, and 4 ft., 3-wire connecting cord with 2-prong attachment plug cap and grounding tail. For use on 115 volts, a.c. or d.c. Maximum power consumption 1200 watts **242.25**

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*For use with Kjeldahl flasks 100 ml or larger, the Apparatus can be furnished at same price with heater tops to fit in place of the tops regularly furnished.

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Low-Cost Instrumentation

INSTRUMENTS used for analysis have always been expensive, often costing many thousands of dollars. Laboratories fortunate enough to have adequate funds have been able to justify such purchases because of the added information obtainable in no other way or the speed with which the determination can be carried out.

Small laboratories and many small liberal arts colleges do not have such funds available. In some instances colleges and universities have managed to obtain such equipment as gifts or at bargain prices through private or government-sponsored projects started in World War II. The market for instruments selling for $10,000 to $100,000 is limited. Fortunately for the instrument maker, developments in simplified circuitry using miniature tubes, printed circuits, and transistors have permitted drastic reductions in the cost and size of instruments.

This year we are seeing the fruition of many years and months of development to extend the market of instruments to those who cannot afford to spend more than $5000. Recent instrumental developments in the field of gas chromatography, infrared, and mass spectrography will be particularly useful to organic analysis. While these instruments do not have the resolution of their larger counterparts, they are adequate for 75% of the samples run.

These instruments, particularly infrared, were developed not only with the small laboratory and college and university in mind, but on the basis that these instruments will become a part of every organic research man's equipment, much as we would formerly think of a pH meter as part of his equipment.

The burdens of routine work in instrumental laboratories are certainly a problem. All too frequently the length of time required to get an analysis is frustrating. Often the results are received too late to be of value. There is much work where an elaborate curve is of little value in identification or where a reaction is followed step by step by following the increase or decrease of a particular constituent through decrease or increase of a certain peak.

Development of simplified, low-cost instruments will permit the main analytical laboratory to devote more time to special problems and research. However, we do not feel that such development should divorce and isolate the organic chemist from the main spectroscopy or other analytical group. He still needs their advice and counsel in interpretation of curves and preparation of samples. He still needs guidance to know when his problem requires the experience of the spectroscopist and the versatility of more expensive equipment.

Now that relatively low-cost instruments of various types are within reach of many, we see a future for the application of instrumental methods of analysis to many specific determinations in which the instrument can be further simplified because the system to which it is applied contains few or controllable components. Such applications will be made by collaborative efforts of the instrument maker and the large laboratories equipped and staffed to envision such future applications.

Certainly future growth in instrumental analysis seems destined to be phenomenal within the next few years.

Chemical Analysis of Surfaces by Nuclear Methods

SYLVAN RUBIN, THOMAS O. PASSELL, and L. EVAN BAILEY
Stanford Research Institute, Menlo Park, Calif.

▶ Nuclear scattering and nuclear reactions induced by high energy protons and deuterons have been applied to the analysis of solid surfaces. The theory of the scattering method, and determinations of oxygen, aluminum, silicon, sulfur, calcium, iron, copper, silver, barium, and lead by the scattering method are described. Carbon, nitrogen, oxygen, fluorine, and sodium were also determined by nuclear reactions other than scattering. The methods are applicable to the detection of all elements to a depth of several microns, with sensitivities in the range of 10^{-8} to 10^{-6} gram per square centimeter.

In the analysis of the surfaces of solids and investigations of the effects of surface treatments, extremely high sensitivity is required because of the small quantities per unit area involved. Futhermore, detection methods must be selective for only the surface layers.

The short range of heavy ionizing particles in solid matter makes them particularly adaptable as tools for the analysis of the compositions of surface layers to depths from a few atomic layers to several microns. A variety of nuclear interactions can be used for this purpose.

Nuclear properties can be used to distinguish between specific elements or isotopes; the interaction energies are too large to be influenced significantly by chemical or crystalline binding energies, so that no information is obtained on compounds or crystal structure by these methods.

The large particle energies permit individual particles to be detected, so that very high sensitivities are achievable. Surface concentrations as small as 10^{-8} gram per square centimeter are readily detectable in many cases. Furthermore, film thicknesses and continuous variation of concentration with depth can be measured with a depth resolution of about 10^{-2} micron.

Nuclear reactions can be produced by bombardment with energetic protons, deuterons, or alpha particles, causing the emission of other energetic particles or of gamma radiation, or the production of radioactive isotopes. The elements in the surface can be identified by the energies of the various particle groups and gamma rays emitted, and/or by the half lives of the isotopes produced. In general, these reaction methods are best applied to the light elements, from which adequate reaction yields are obtainable for incident particle energies less than 2 m.e.v.

Another nuclear interaction is elastic scattering of the incident particle. The scattering nucleus can be identified in this case by the fractional loss in momentum of the scattered particle, which is a function of the scattering mass. This method can be used for all elements, but it requires very high momentum resolution, and therefore is generally less rapid than the nuclear reaction methods.

This paper discusses the principles, instrumentation, and results obtained in the application of these methods to the analysis of a variety of types of samples.

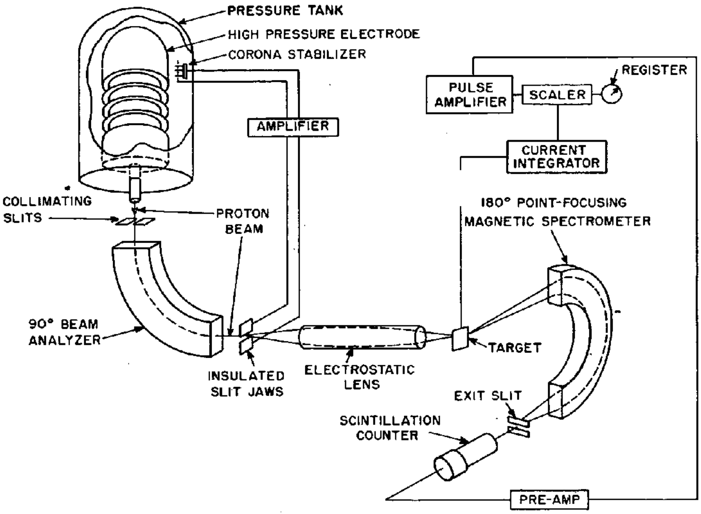

Figure 1. Schematic drawing of apparatus as used in scattering analyses

EQUIPMENT

Proton or deuteron beams are obtained from a 2,000,000-volt Van de Graaff accelerator (Model AH, High Voltage Engineering Corp., Cambridge, Mass.), equipped with a 90° analyzer magnet, which produces a collimated beam with an energy spread of about 0.1%. Beam currents up to about 1 μa. are obtainable. The beam is focused on the target by a two-section electrostatic quadrupole lens, which can provide a spot on the target about 0.2 mm. high by 2 mm. wide. The target chamber is fixed rigidly to the spectrometer magnet (7) which is used for the elastic scattering measurements. Samples are mounted on standard bayonet mounts which are inserted into the target chamber through a vacuum lock and coupled to an insulated target positioning assembly. Positioning adjustments include horizontal and vertical displacement and rotation about a vertical axis. The entire spectrometer magnet assembly can also be rotated about a vertical axis through the target to select a suitable scattering angle. Figure 1 is a schematic drawing of the apparatus as used in scattering analyses.

The same target chamber is also used for nuclear reaction analyses. It has a number of ports, 1 inch in diameter, with O-ring seals through which scintillation counters and other equipment can be inserted. A vacuum of about 0.1 micron of mercury is maintained in the target chamber and connecting system.

The incident beam is monitored by a precision charge integrator connected to the insulated target. The circuit is essentially that developed by Bouricius and Shoemaker (*3*), with minor modifications. Provision is made for connecting a leak resistor to make the integrated charge decay at the same rate as a short-lived radioactive product, so that this type of measurement can be accurately normalized. The target assembly is surrounded by a guard ring at −90 volts to prevent secondary electron emission from giving erroneous charge measurements. The incident beam charge is integrated by charging one of several low-leakage condensers, ranging in capacity from 0.001 to 10 microfarads, from −10 volts to ground potential, at which point a relay is operated to terminate the run and rest the integrator.

The beam energy is determined by measuring the analyzer magnetic field by means of a flip-coil fluxmeter (*5*) which is calibrated with the accurately known proton resonance energies of the aluminum-27 (p,γ) reaction (*4*). The same fluxmeter system, using another flip coil in the spectrometer magnet, is also used to measure the ratio of the fields of these two magnets. This is the basis for the determination of the relative momentum of the scattered and incident particles. The fluxmeter is sensitive to about 1 part in 10^4.

The magnet currents are each regulated to about 1 part in 10^4 or better; however, the over-all resolution of the scattering momentum ratio is about 2500, most of which is due to the spread in beam energy from the accelerator. A choice of exit slit widths in the spectrometer gives calculated spectrometer resolution factors of 3300, 1106, and 560. The solid angle of the spectrometer is 0.0025 steradian.

Particles and radiation are detected with scintillation counters. A thin, thallium-activated sodium iodide crystal is mounted behind the spectrometer exit slit on a Lucite light pipe 2 inches in diameter, where it detects all particles selected by the spectrometer. For nuclear reaction detection, a large-solid-angle detector is used, consisting of a thin sodium iodide scintillation crystal $^1/_4$ inch square, about 3 inches from the target, on the end of a Lucite rod inserted through one of the side ports of the target chamber. A layer of 0.001-inch aluminum foil on a cap slipped over the end of the tube enclosing the Lucite rod stops scattered deuterons and keeps out light. Gamma radiation is measured with a $1^1/_2 \times 1$ inch sealed sodium iodide crystal. Du Mont 6292 photomultiplier tubes are used with all these crystals. A conventional linear amplifier and single channel analyzer are used with the scintillation crystals to distinguish particle groups or gamma rays of different energies.

ELASTIC SCATTERING METHOD

Theory. The velocity, V_s, of a particle of mass M_1 and initial velocity V_0, elastically scattered at an angle θ by a particle of mass M_0 initially at rest, is

$$V_s = \frac{V_0}{M_0 + M_1}\,[M_1 \cos\theta + (M_0^2 - M_1^2 \sin^2\theta)^{1/2}] \qquad (1)$$

or

$$\frac{V_0 - V_s}{V_0} = \frac{\Delta V}{V_0} \cong \frac{M_1}{M_0 + M_1}(1 - \cos\theta) \qquad (2)$$

The elements in the sample are identified by the change in velocity of the scattered particles. If the element is present only in a very thin (with respect to the energy loss of a 1- or 2-m.e.v. proton or deuteron) film on the surface of the sample, it will produce a narrow peak in the momentum distribution of the scattered particles.

However, the incident particles also lose energy by ionization in the sample, in proportion to their depth of penetration before scattering from a nucleus. Therefore an element in a thick layer, or homogeneously distributed in the sample will produce a step in the momentum distribution, the front edge of the step being located at the theoretical momentum for particles scattered by that element. This feature makes it possible to determine the variation of the concentration of an element with depth, with depth resolution of the order of 0.01 micron.

The yield of scattered particles from a thick target depends on the concentration, the scattering cross section of the element, the stopping power of the sample for the particles, and geometrical factors of detector resolution and solid angle.

In a target material containing various elements a_i, in the relative atomic proportions n_i, the following formula gives the number of particles, Y_i, scattered from a given element, a_i, and counted in the momentum interval determined by the resolution factor, R_s (*9, 10*):

$$Y_j = 1.2 \times 10^{13}\left(\frac{d\sigma}{d\Omega}\right)_j \frac{q\Omega E_1 n_j}{R_s}\left[\Sigma_i n_i\left(\epsilon_{i1} + \frac{\epsilon_{i2}}{k_j}\,\frac{\cos\theta_1}{\cos\theta_2}\right)\right]^{-1} \qquad (3)$$

where $\frac{d\sigma}{d\Omega}$ is the differential scattering cross section (in center-of-mass coordinates)

R_s is the spectrometer resolution factor (*7*)

E_1 is the incident particle energy (in the same energy unit as ϵ)

q is the incident charge (in microcoulombs for singly ionized particles)

Ω is the spectrometer solid angle (in center-of-mass coordinates)

ϵ is the atomic stopping cross section of each atomic species, with subscript 1 referring to the particle before scattering, subscript 2 after scattering

k is the ratio of the particle energy after scattering to the energy before scattering

θ_1 and θ_2 are the angles between the normal to the target and the direction of the incident and scattered beams, respectively

For elements of $Z > 30$, the Rutherford formula for the elastic scattering cross section is accurate to within a few per cent:

$$\frac{d\sigma}{d\Omega} = \left(\frac{zZe^2}{2Mv^2}\right)^2 \sin^{-4}\frac{\theta}{2} = 1.3 \times 10^{-27}$$
$$(zZ)^2E^{-2}\sin^{-4}\frac{\theta}{2} \text{ sq. cm./steradian} \qquad (4)$$

For light elements the scattering cross sections deviate considerably from the Rutherford formula, and show resonance effects at certain bombarding energies. At proton energies up to 2 m.e.v., strong resonance effects occur in the light elements up to and including aluminum and sulfur. No significant resonances are present in iron and heavier elements. No detailed data are available on the intermediate elements between sulfur and iron.

The stopping cross section, ϵ, for protons of various energies is given in Figure 2, as smoothed average functions of atomic number Z of the stopping element, based on the data of Fuchs and Whaling (*6*). More precise data are given by Bader and associates (*2*), with references to other stopping cross section measurements.

The stopping cross sections for particles other than protons, and for various energies of the incident particle, can be calculated from the proton cross section by the approximate expression

$$\epsilon \cong \frac{CM^{1/2}z^2}{E^{1/2}}$$

which is useful for $E \gg 0.3$ m.e.v. for protons and deuterons. The relative stopping cross section for alpha particles will be diminished below 1.5 m.e.v. because of capture and loss of electrons by the alphas.

The concentrations of a given element can be determined from the measured scattering yield, either by application of the above equations, or, in many cases, more conveniently by comparison with measurements on reference samples of known concentrations. The latter method is especially useful for light elements because of the large deviations of the actual scattering cross sections from Equation 4. However, experimentally determined proton scattering cross sections for most of the light elements in this energy range have been published.

For the analysis of heavy elements, deuteron or alpha particle scattering may be preferable, as the resolving power of this method for nuclear masses is proportional to the mass of the scattered particle. Although the scattering yield with deuterons or alphas is less than that of protons by factors of 2 and 4, respectively, the relatively large scattering yield from heavy elements makes this loss unimportant except when the maximum sensitivity is required.

Scattering Analyses. Most of the scattering analyses described here were made with protons. Deuterons have also been available from the accelerator during the past year, but have been used chiefly for the observation of *d,p* and *d,n* reactions.

Samples up to 1 inch square can be accommodated on the target holders. Reference targets are often mounted with the samples.

Scattering measurements with the magnetic spectrometer are usually made at a scattering angle of 150° to the incident beam, to give the maximum change of velocity with mass. The target face is vertical with the normal bisecting the line between the incident beam and the spectrometer. The beam is focused to a fine horizontal line on the target with the electrostatic lens to make a suitable source for the spectrometer. The exit slit of the spectrometer is set for a suitable compromise between resolution and yield. The beam energy is kept fixed, usually between 1.2 and 1.5 m.e.v., where the accelerator gives optimum beam current and focusing.

Data are taken by varying the magnetic field of the spectrometer in uniform steps manually by means of a Helipot control and counting the relative number of scattered particles, at each step, for a constant incident charge to the target. These data, when plotted against the fluxmeter ratio scale, are referred to as momentum profiles of the targets. The fluxmeter scale is calibrated by means of known elements in the samples or by reference targets such as copper or aluminum, which also provide standardization of yield measurements.

The minimum detectable concentrations depend on the atomic number of the element. A heavy element in a thin film on the surface can be detected with the greatest sensitivity, being limited essentially only by background from the counting crystal. The poorest sensitivity is obtained in determining light elements in a sample consisting primarily of heavy elements. In this case, the large background of scattering from the heavy elements is added to a small yield from the light elements, requiring very good statistical accuracy in the yield measurements to detect the latter.

Sample Preparation. A sample to be analyzed by elastic proton scattering must have several characteristics. In the approximate order of importance, these are:

Resistance to degradation by the heating of the proton beam; metals, glass, and inorganic salts with melting points above 300° to 400° C. are satisfactory in this respect.

The sample must have a relatively smooth surface. A badly rusted surface for example, is too rough for a good scattering analysis. Salts which can be compressed into smooth surfaced wafers have been successfully used.

The sample must have surface area dimensions available for analysis of at least 0.5 by 1 mm. This limitation is imposed by the size of the proton beam at the sample (target). The only area which is analyzed is that which is directly bombarded by the beam. Beam sizes up to 1 by 4 mm. have been used, but the larger beam sizes limit the momentum resolution obtainable.

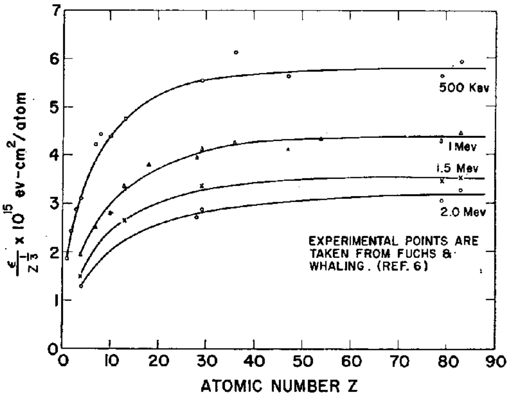

Figure 2. Stopping cross sections, ε, for protons of various energies vs. atomic number, Z, of element

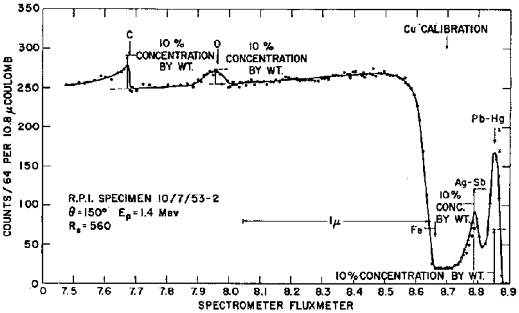

Figure 3. Momentum profile of scattered protons from a steel sample exposed to detonation of an explosive

10% concentration levels are calculated from the scattering cross section of each element relative to iron. The depth scale of 1 micron, shown for iron, is applicable to each of the other elements, measured from their "front edges"

The nuclear reaction methods are less demanding of the target properties. Because more diffuse beams can be used, target heating and degradation is less of a problem. Relatively rough surfaces, corresponding to a badly rusted piece of steel, have been successfully analyzed. Larger areas can be analyzed, as a large area beam (about 0.5 sq. cm.) has little if any deleterious effect on sensitivity or accuracy.

General "good housekeeping" precautions are necessary to minimize surface contamination. In some instances special cleaning techniques have been used, but each case is so different that no general discussion of sample cleaning is appropriate here.

Results of Scattering Analyses. The following scattering analyses have been selected as illustrative of the types of problems encountered.

Steel Surface. Figure 3 shows a momentum profile of scattered protons from a steel sample exposed to the detonation of an explosive. Before analysis the sample surface was cleaned by condensing vapor phase pyridine on it for a short time, followed by vapor phase cleaning with tetrachloroethylene. This cleaning procedure should have removed most surface contaminants from handling or the accumulation of dust.

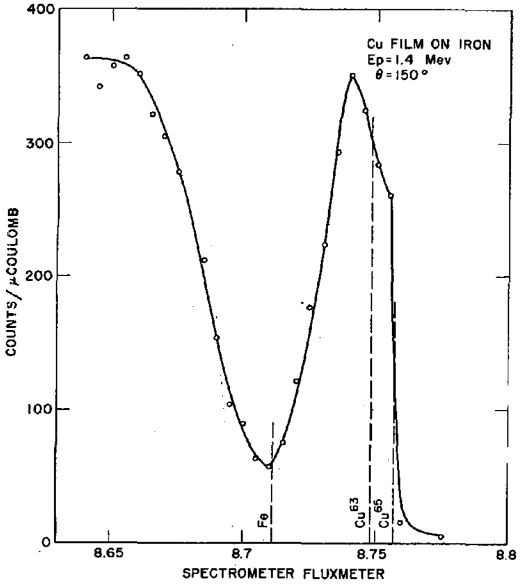

Figure 4. Momentum profile obtained from analysis of a thin copper film on a polished iron backing

Made with the maximum spectrometer resolution of 3300. Copper isotopes are not quite resolved

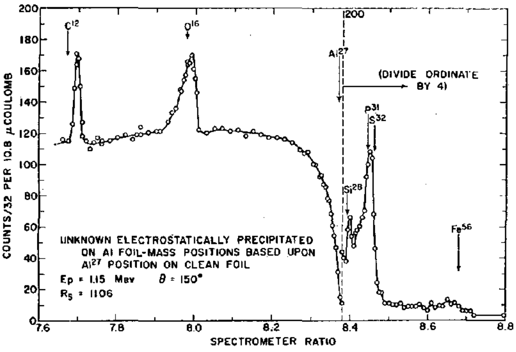

Figure 5. Momentum profile of scattered protons from an aerosol deposited on aluminum foil

The most notable feature of the profile is the plateau due to scattering from iron. A so-called "front edge" of this plateau is evident at the vertical arrow designated Fe, representing the maximum energy a proton (of initial energy corresponding to fluxmeter reading of about 9.25) can have after elastically scattering from an iron nucleus (mostly iron-54 and iron-56). With sufficient momentum resolving power, the front edges due to iron-54 and iron-56 and perhaps iron-57 could have been separated from one another.

Narrow maxima due to elements with nuclear masses greater than those of the iron nuclides are evident to the right of the iron cutoff. The fact that narrow peaks appeared rather than step functions tells us that the materials are present in thin layers on the surface. The surface concentrations involved are of the order of micrograms per square centimeter. The positions of these two maxima correspond to elements with masses in the silver to antimony and the mercury to lead regions respectively. The lead and/or mercury probably arose from the decomposition of the lead azide or fulminate of mercury detonators. No offhand explanation can be given for the presence of the silver-region elements. However, this sample had been provided by another laboratory, and information is not available on all substances involved in its preparation.

Small peaks due to the presence of surface carbon and oxygen are also evident. The high background plateau from iron decreases the sensitivity for detection of these elements as it would for any other elements lighter than iron.

The depth resolution possible in this method of analysis is evident from a 1-micron scale shown on the iron plateau. In other words, the proton counts on the plateau directly above the left arrow of the micron scale were scattered from a 1-micron depth in the iron. If the iron at that depth were diluted with some other element, the plateau level would have dropped proportionately. Because of the increase in stopping power with increase in atomic number, the depth resolution also increases with increasing atomic number. Therefore, scattering data for the higher atomic number elements are more sensitive to the effects of surface irregularities and contamination than are similar data for the lighter elements.

Electroplated Film. Figure 4 shows the proton scattering profile obtained from analysis of a thin copper film electroplated on a polished iron target. This example demonstrates the effect of a surface layer in displacing the position of the front edge of iron, and the usefulness of the scattering method in the determination of film structure. The first effect is evident from the figure, where the front edge of iron is displaced to a lower value than its usual position with no surface layer. The following conclusions on the structure of the copper film can be drawn: The surface of the film is very smooth, as evidenced by the very sharp rise of the copper front edge, and the thickness of the film is not uniform, as evidenced by the decreased slope of the iron front edge compared with the sharp rise exhibited by a polished iron surface. A perfectly uniform copper layer would have displaced the iron front edge but not influenced its slope.

The height of the copper maximum is 80% of the height expected for a perfect layer with no holes. Therefore about 20% of the copper film surface consists of holes which extend all the way through the film.

Aerosols. In the study of the elements contained in aerosols (such as smog), it is often convenient to deposit the material by jet impaction or electrostatic precipitation onto some clean surface. A proton scattering analysis of such a deposit electrostatically precipitated on aluminum foil is shown in Figure 5. Figure 6 shows the signal obtained from the foil alone.

This particular aerosol exhibits maxima which have been assigned to carbon-12, oxygen-16, silicon-28, and sulfur-32. Some signal was obtained (above the foil background) on out to the region of iron, but these elements were not resolved, because of their proximity to each other (in mass) and/or their low abundance. The oxygen peak corresponds to a thin deposit of 5 γ per sq. cm. Silicon and sulfur are present in thin films of 0.13 and 0.3 γ per sq. cm., respectively. The carbon peak shown arises from the well-known carbon build-up and was not originally present on the sample. Carbon build-up has been greatly reduced by placing a liquid nitrogen-filled cold finger near the target. The hydrocarbon vapors, which are ordinarily absorbed and cracked on the target where the beam hits it, are reduced in pressure by condensation on the cold finger.

The thick target momentum distribution to the right of the aluminum cutoff from the clean aluminum foil is due to silicon and iron impurities known to be present in this grade of foil. This background could be eliminated by using purer aluminum foil.

Glass Surface. The results of analysis of three soft-glass surfaces subjected to different washing procedures are shown in Figures 7, 8, and 9. The dichromate wash (Figure 8) decreased the surface concentration of calcium to about half its value in the untreated glass (Figure 7), whereas the heavy element (probably cesium or barium) was unaffected. On the other hand, a sulfuric and nitric acid wash leached the heavy element (Figure 9), leaving calcium relatively unaffected.

These results illustrate the use of the proton scattering method in the study of surface reactions such as leaching, adsorption, and corrosion. The cases used here as an illustration are favorable for this purpose, in that the glass surface is very smooth, glass does not deteriorate appreciably when bombarded for the time necessary in the analysis, and the elements of interest were the heaviest ones present in the material.

USE OF NUCLEAR REACTIONS FOR ANALYSIS

These methods consist of the application of well-known nuclear disintegration phenomena to surface analysis. The papers by Lauritsen and associates (*1*) and by Endt and Kluyver (*4*), on the energy levels of light nuclei, provide extensive data on the nuclear interactions of all the light nuclides.

The use of nuclear reactions is advantageous for detection of light elements, in comparison with the scattering method, because in general its sensitivity (using charged incident particles with energies under 2 m.e.v.) decreases drastically with increase in atomic number. On the other hand, the sensitivity of the scattering method increases with increase in atomic number, primarily because of increase in the Rutherford

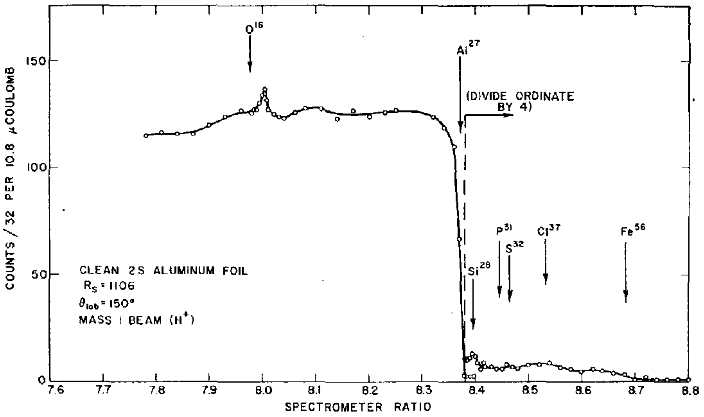

Figure 6. Momentum distribution of scattered protons from clean aluminum foil

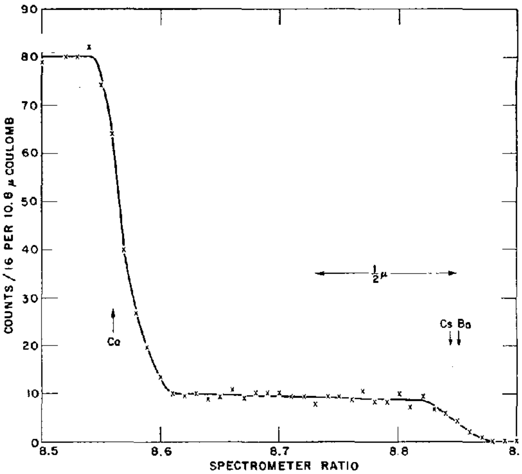

Figure 7. Scattering analysis of an untreated soft-glass surface

Depth scale of 0.5 micron is computed from the stopping power of glass for 1.4-m.e.v. protons

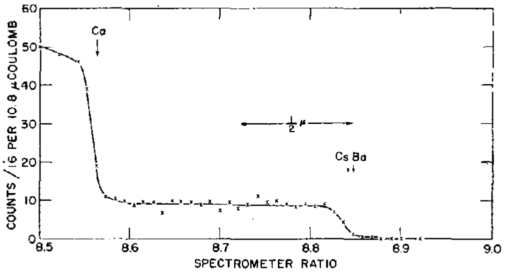

Figure 8. Scattering analysis of a soft-glass surface treated with dichromate cleaning solution

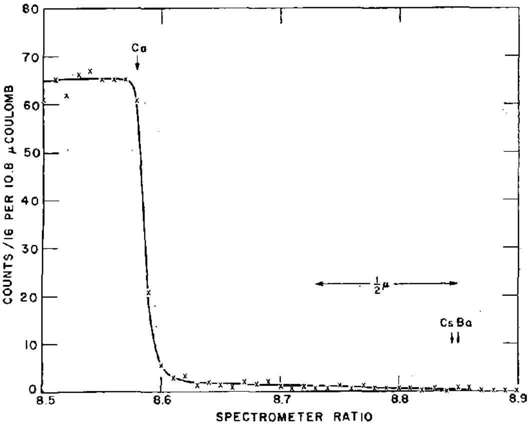

Figure 9. Scattering analysis of a soft-glass surface treated with a mixture of nitric and sulfuric acids

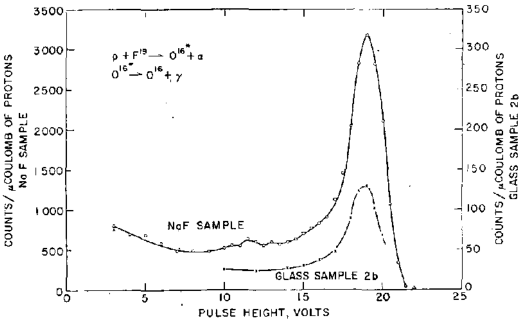

Figure 10. Pulse height spectrum of 6- and 7-m.e.v. gamma rays from the F^{19}(p, $\alpha\gamma$)O^{16} reaction

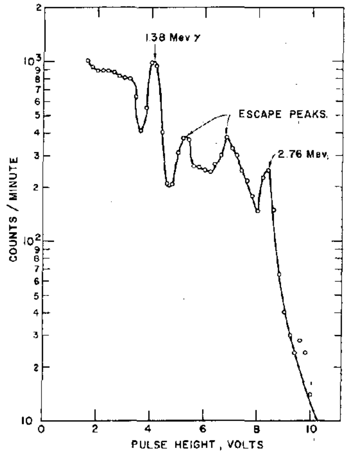

Figure 11. Pulse height spectrum of gamma rays from the decay of sodium-24

scattering cross section with increasing Z.

Another feature of the reaction methods is the simplicity of the detection equipment required. Large solid angle scintillation detectors are commonly used, as the high resolution of energy or momentum necessary for a scattering analysis is not required.

The fact that each element is usually treated as a separate problem extends the time necessary for an extensive or comprehensive analysis of a sample. However, in many analyses, only one or a few elements are of interest, so this is not a serious limitation. In most cases the signal from the element of interest can be isolated completely from the signals of the other elements, hence background problems are seldom a limiting factor.

Fluorine in Opal Glass. Sections of opal glass ($^3/_4 \times {}^3/_4 \times {}^1/_8$ inch) were bombarded by a proton beam of 1.4-m.e.v. energy. The 6- and 7-m.e.v. gamma rays resulting from the fluorine-19 (p, $\alpha\gamma$) oxygen-16 reaction were observed in a scintillation crystal 1.5 inches in diameter by 1 inch thick. Since these gamma rays are emitted with mean lifetimes of less than 10^{-11} second, the number of gammas resulting from a given number of bombarding protons was measured. Figure 10 shows the pulse height spectrum observed using a single-channel pulse height analyzer.

The amount of fluorine present was determined by observing the gamma yield (above a given arbitrary pulse height discrimination level) of the sample relative to the yield from a fluorine sample of known composition. The standard chosen in this case was sodium fluoride, because it has about the same stopping power as the glass samples. Therefore the effective thickness of the surface layer was essentially the same in both the standard and the unknown samples.

In this instance, the chief concern was with relative concentrations on different samples, so no further effort was expended on the standardization of the method for measuring absolute concentrations.

Samples of the other elements in opal glass were bombarded with the same energy proton beam to determine the background radiation in the critical 4- to 7- m.e.v. region. Background was essentially nil. Fluorine concentrations in these experiments were of the order of 3% by weight and were measured to a precision of within ±0.1%. No other proton-induced reaction (at proton energies under 2 m.e.v.) has a higher yield for gammas than fluorine-19(p, $\alpha\gamma$)oxygen-16.

The methods of gamma detection used here are not necessarily optimum for fluorine detection in glass or any other surfaces. For example, the use of a much larger scintillation crystal and a more favorable solid angle would have increased the sensitivity of this analysis for fluorine by a factor of 10^2 to 10^3. There is no particular significance in the use of a proton energy of 1.4 m.e.v., except that most of the resonances (of those accessible to a 2,000,000-volt Van de Graaff) in the fluorine-19(p, $\alpha\gamma$)-oxygen-16 cross section are at energies less than 1.4 m.e.v.

Sodium in Glass. The glass surfaces were analyzed for surface sodium. Sodium concentrations were of the order of 6% by weight. The chief objective was to look for differences in the surface concentration of sodium among the glass samples.

Sodium was measured quantitatively, using the sodium-23(d, p)sodium-24 reaction. Sodium-24 is radioactive with a half life of 15 hours, going by beta decay to magnesium-24, which emits two cascade gamma-rays for every disintegration. The yield of these gammas was measured to determine the sodium concentrations of the various samples. This scheme was very satisfactory for the detection of sodium, as no other long lived gamma activities were produced in appreciable quantities in the 1.4-m.e.v. deuteron bombardment of the glass samples. That the activity detected was due to sodium-24 was verified by: observation of the 15.0-hour half life, and observation of the gamma-ray energy spectrum (see Figure 11). Each sample was bombarded by a known quantity of 1.4-m.e.v. deuterons. The bombarded samples were removed from the target chamber and counted in a gamma-ray scintillation counter. Care was taken to assure that the counting geometry was the same for each sample. The sodium concentrations were determined by comparing the activities of the samples with the activity of a sample of known sodium concentration.

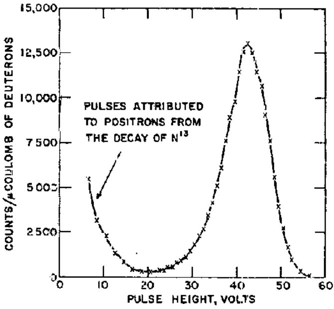

Figure 12. Pulse height spectrum of protons from 1.4-m.e.v. deuteron bombardment of a thick carbon target

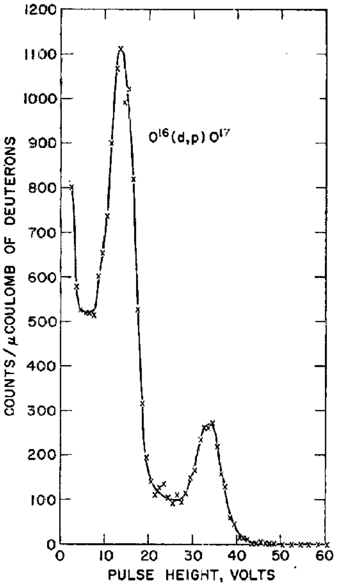

Figure 13. Pulse height spectrum of protons from the 1.4-m.e.v. deuteron bombardment of a thick zinc oxide target

Quantitative Measurement of Carbon and Oxygen Deposited in Detonation of an Explosive Charge. A piece of steel exposed to an explosive charge exhibits two markedly different surfaces, one smooth (near the center of the explosion) and the other a somewhat mottled, darkened surface at the periphery of the smoother region. It was of interest to determine differences in chemical composition between the two surfaces, especially in the content of carbon, nitrogen, and oxygen from the detonation products.

The reactions carbon-12(*d*, *p*)carbon-13, oxygen-16(*d*, *p*)oxygen-17, and nitrogen-14(*d*, *p*)nitrogen-15 were used to detect the presence or absence of carbon, oxygen, and nitrogen. Each reaction has a characteristic proton energy spectrum through which the element of interest is identified. The energy spectra from carbon and oxygen are shown in Figures 12 and 13. The presence or absence of these elements in the steel samples is determined by comparing the proton spectra from the steel samples with the proton spectra from the samples of known chemical composition. Figure 14 is the proton spectrum from the 1.4-m.e.v. deuteron bombardment of a steel sample located at the periphery of the explosion. In this figure the proton groups from the reactions oxygen-16(*d*, *p*)oxygen-17 and carbon-12(*d*, *p*)carbon-13 can be seen. The concentrations of oxygen and carbon are determined by comparing the proton yields in a given group with the yield from the samples of known composition. In computing these concentrations, corrections were made for the differences in stopping power of the different samples.

The large steel sample was cut into smaller pieces of size approximately $^1/_2 \times {}^1/_2$ inch, which were inserted separately into the target chamber and bombarded by the 1.4-m.e.v. deuteron beam. Secondary protons were detected by a scintillation counter and their energy spectrum was determined with a pulse height analyzer. The sodium iodide crystal in this case was only 0.050 inch thick. Scattered deuterons were stopped in an aluminum absorber before they entered the scintillator.

Tests which would have detected nitrogen concentrations of 0.1% by weight indicated that no nitrogen was present. These tests consisted of looking both for high energy protons from the reaction nitrogen-14(*d*, *p*)nitrogen-15 and for the 118-second positron activity from the reaction nitrogen-14(*d*, *n*)oxygen-15.

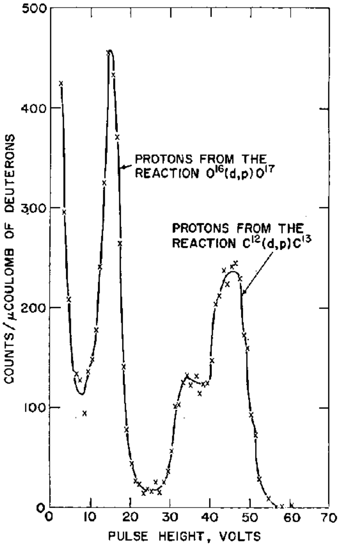

Figure 14. Pulse height spectrum of protons from the 1.4-m.e.v. deuteron bombardment of a steel sample exposed to an explosive charge

The failure to detect high energy protons from *d*, *p* reactions also indicates that neither beryllium nor boron was present.

Various systematic errors are present in this analysis, especially in the determination of absolute concentrations. In computing concentrations, carbon and oxygen were assumed to be distributed uniformly through the 5-micron surface depth. As these elements are no doubt more abundant at the surface, the quoted concentrations for the 5-micron layer would tend to be high. Some of the counts attributed to protons from the reaction oxygen-16-(*d*, *p*)oxygen-17 come from the beta (positron) decay of nitrogen-13, which is produced by the reaction carbon-12-(*d*, *n*)nitrogen-13. This would cause the largest relative error where the oxygen concentration is lowest. The use of a thinner scintillation crystal would have facilitated discrimination against pulses caused by the nitrogen-13 positrons.

Other Reactions Useful in Analyses. During the above-mentioned analyses, other reactions were observed which should prove useful in certain instances, even though they were not exploited in this work.

BORON-11(*d*, *n*) CARBON-11. The 20-minute half life of carbon-11 (a positron emitter) allows it to be readily detected by standard beta counting techniques.

It can be more easily detected in quantitative fashion by observing the 511-k.e.v. annihilation quanta produced when the positron and a free electron mutually annihilate. To simplify the determination of the counting geometry, it is necessary to ensure that all positrons are stopped in the immediate vicinity of the source.

NITROGEN-14(*d*, *n*)OXYGEN-15. The nuclide oxygen-15 has an inconveniently short life of 2.1 minutes. In order to get a reproducible counting rate of oxygen-15 from a given nitrogen sample, the deuteron beam must not vary appreciably in intensity. As this is sometimes difficult to achieve with a Van de Graaff, another reliable means of obtaining reproducibility has been used. The charge on the capacitor in the beam current integrator is caused to decay at the same rate (through a leak resistor) as the nuclide under investigation. Thus a given amount of charge in the capacitor always is directly proportional to a given number of radioactive nuclei in the target. If the same amount of charge is reached in each bombardment, the same number of radioactive nuclei will be produced (from a given sample). Wide variations of beam intensity of almost any description can be tolerated with this type of system. Snowdon describes the use of the "leaky integrator" in measuring 11-second fluorine-20 from the reaction fluorine-19(*d*, *p*)fluorine-20 (*8*).

MAGNESIUM-26(*d*,*p*)MAGNESIUM-27; ALUMINUM-27(*d*, *p*)ALUMINUM-28; SILICON-30(*d*, *p*)SILICON-31; AND OXYGEN-16(*d*, *n*)FLUORINE-17. These reactions appear to be useful under favorable circumstances, although their feasibility has not been directly determined.

As many variations in incident beam energies, particle and radiation detectors, and geometrical arrangement are possible, a complete coverage of all experimental situations is not attempted. However, this discussion may bring this powerful tool for the chemical analysis of surfaces to the attention of those not aware of its potentialities.

ACKNOWLEDGMENT

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Study of Accuracy in Chemical Analysis Using Linear Calibration Curves

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► In situations characterized by linear calibration curves such as the relation between "found" and "added" in studies of accuracy in chemical analysis, the usual method for deriving confidence intervals for the slope and the intercept of the fitted straight line may lead to erroneous conclusions. The difficulty results from the interdependence of multiple conclusions drawn from the same data, especially when there is a strong correlation between the parameters involved. The method of joint confidence regions eliminates these difficulties and has the further advantage of allowing for the evaluation of the uncertainty of the calibration line as a whole, as well as of any values or functions of values derived from it.

THE STUDY of an analytical procedure generally starts with determining satisfactory operating conditions. Once this has been done, the precision and accuracy of the method can be effectively studied by analyzing a series of prepared samples covering the range of concentrations over which the method is applicable. This procedure, which involves the statistical theory of fitting straight lines based on the method of least squares, has been described by Youden (*18*, *19*) and applied by Linnig, Mandel, and Peterson (*9*) and by Lark (*8*). Essentially, the slope of the fitted straight line can be compared to a value based on stoichiometric or other theoretical considerations; the intercept, to "blank" determinations; and the "standard error of estimate," to a measure of precision obtained from replicate determinations. Thus, the method generally involves tests of significance of the slope and the intercept of a fitted straight line. Such tests can readily be carried out in accordance with classical theory (*1*, *2*, *12*, *19*).

Lark (*8*) has pointed out that the tests of significance on slope and intercept can lead to erroneous conclusions, because these tests, when carried out independently of each other, ignore the strong correlation that exists between the estimated slope and intercept of a straight line obtained by least squares calculations. In Table I, the values labeled "found" differ from those denoted "added" merely by random fluctuations. Thus, the "true" relation between found and added is a straight line passing through the origin with a slope equal to unity. This line is denoted *T* in Figure 1. The line *E*, on the other hand, which is the least squares fit of the equation $y = b + mx$ to these data, has, as the result of the random errors, an intercept different from zero and a slope different from unity. It is easily seen that if by the interplay of chance effects, the fitted line has a slope less than unity, it will tend to have a positive intercept and vice versa. Thus, if the error in the slope is negative, the error in the intercept will tend to be positive, and vice versa. The theory of least squares shows this to be generally true for any set of linear data, for which the average of the x values (values "added") is positive; in these cases, the errors of slope and intercept are always negatively correlated, regardless of the precision of the data.

Table I. Illustrative Data

"Added"	"Found"
15	25.4
30	26.8
45	43.6
60	62.8
75	82.5
90	84.0

In this paper a rational basis is provided for judging the reliability of slope, intercept, and any value derived from the calibration line. The concepts are presented in terms of the data obtained by the authors in the study of an analytical method for which interesting chemical interpretations were suggested for some of the statistical conclusions (*9*). However, reference will also be made to the data of Table I to illustrate situations where the high reproducibility of the analytical method just referred to would produce effects too small to be distinguished graphically. For greater continuity of presentation, all mathematical and computational matters are relegated to a later section.

ACCURACY IN CHEMICAL ANALYSIS

Linnig, Mandel, and Peterson (*9*) obtained the data given in Table II for the determination of fatty acid in rubber.

Table II. Determination of Fatty Acid in Rubber

	Fatty Acid, Mg.	
Titration	Added	Found
1	20.0	28.0
2	20.0	24.5
3	50.0	58.5
4	50.0	57.8
5	150.0	157.8
6	153.7	163.2
7	250.0	257.8
8	250.0	259.3
9	500.0	512.4
10	500.0	509.2
Solvent blank	0.0	7.40

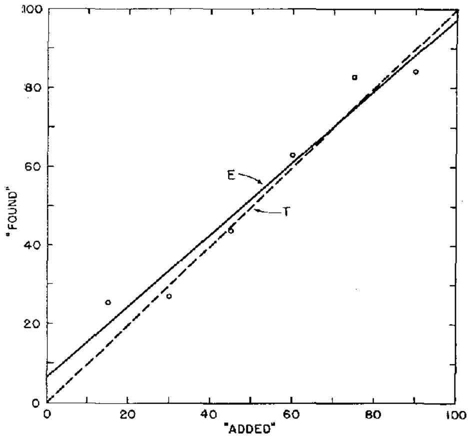

Figure 1. Effect of experimental errors on fitted straight line

Data of Table I
T. Theoretical line
E. Fitted line

From a chemical viewpoint the following questions are pertinent:

1. Does this analytical procedure require a blank correction?
2. Is the value for the blank that was determined experimentally (b = 7.40 mg.) an acceptable correction for the removal of the constant type of error suggested by the data?
3. Does the removal of the constant-type error (by means of a blank correction) lead to an otherwise accurate method? More specifically, is there, in addition to a constant-type error, also an error of a relative type—i.e., one that increases as the amount of material to be titrated increases?

These questions relate to the values of the intercept and the slope of a plot of "found" *vs.* "added," similar to the one shown in Figure 1 (*9*).

Now, if answers to these questions are obtained by means of a statistical analysis, these answers should be compatible with the data, not only individually but collectively. For example, it has been suggested (*9*) that the existence of a relative type of error (slope different from unity) in titration data of the type given in Table II is related to the choice of an indicator that does not change at the equivalence point. Therefore, in order to determine the adequacy of a particular indicator, one would test statistically the significance of the departure of the slope from unity. On the other hand, one may wish to judge the adequacy of a blank titration as a correction for a constant error by testing the significance of its difference from the observed intercept. Chemically, these may be entirely unrelated questions; but from the viewpoint of experimental evidence, they are related in that they are obtained from the same set of data. This is especially so because, as has been indicated, there exists a strong statistical correlation between the errors in the slope and the intercept. Consequently, the answers to both questions must be jointly compatible with the data, and this requires the use of joint confidence regions.

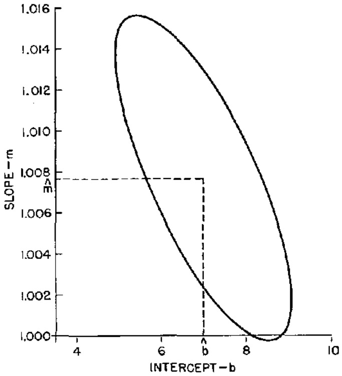

Figure 2. Joint confidence ellipse for slope and intercept

Data of Table II
$\hat{m}$. Least squares estimate of slope
$\hat{b}$. Least squares estimate of intercept

JOINT RELIABILITY OF SLOPE AND INTERCEPT

A joint confidence region for slope and intercept is shown in Figure 2. On the abscissa point $\hat{b}$ represents the value for the intercept obtained by the method of least squares. Similarly, $\hat{m}$ on the ordinate is the least squares estimate of the slope. Point ($\hat{b}$, $\hat{m}$) establishes, therefore, the line of "best fit." However, even this line of best fit is probably in error, the magnitude of its discrepancy from the true line depending on the experimental errors in the measurements to which the line was fitted. Consequently, points other than ($\hat{b}$, $\hat{m}$) are admissible, and theory shows (*12*, p. 296) that these points lie in an ellipse having the point of best fit as center. The boundary of the ellipse is determined by the magnitude of the experimental errors and by the degree of confidence, the "confidence coefficient," with which one wishes to state that the true point lies in the interior of the ellipse. The tilt of the ellipse with respect to the axes is a consequence of the negative correlation between the errors in slope and intercept. As a result of the tilt, the ellipse favors points with a higher slope and lower intercept than the best fit (upper left area) and points with a lower slope and higher intercept (lower right area); while points corresponding to lower slopes and lower intercepts (lower left) or to higher slopes and higher intercepts (upper right) tend to fall outside the admissible region.

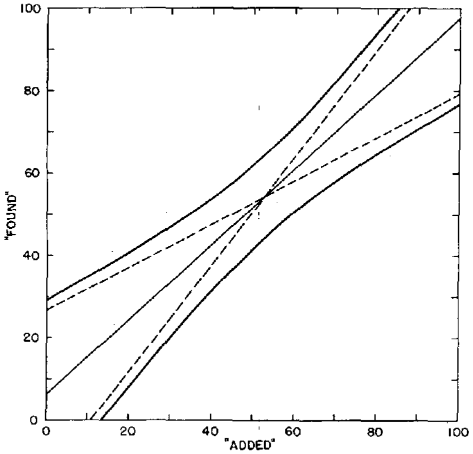

Figure 3. Confidence band for calibration line

Data of Table I. Straight line is least squares fit. The two branches of hyperbola define the confidence band. Broken lines are the asymptotes

APPLICATION TO CHEMICAL EXAMPLE

Figure 2 represents the 95% joint confidence ellipse corresponding to the data in Table II. The three questions that arose in connection with these data can readily be answered by means of this figure.

1. The question as to whether a blank is required is answered by determining whether the ellipse contains points for which $b = 0$. As all such points are on a vertical line at $b = 0$, they are well outside the ellipse, and it is at once apparent that $b = 0$ is unacceptable. Consequently, a blank is required to correct for a constant-type error.

2. Is the experimental blank an adequate correction for the constant-type error? To answer this question, draw a vertical line at $b = 7.40$ (the value of the experimental blank). This line intersects the ellipse and is, in fact, close to its center. Consequently, there is no reason to doubt the validity of this blank as a means of correcting for the constant-type error.

3. Is there a relative-type error? Answering this question is equivalent to deciding whether the value, $m = 1$, is acceptable. Consider the horizontal line, $m = 1$. The points on this line falling inside the ellipse are extremely close to the boundary of the ellipse. Therefore, the hypothesis, $m = 1$, is of doubtful validity, and there exists a strong likelihood that, in addition to an error of the constant type, there is a relative type of error. It has been suggested in relation to these data (*9*) that the reason for finding results higher than the stoichiometric values may be the opacity of the solution, causing the change of color of the indicator to be observed somewhat beyond the equivalence point.

The selection of any particular value for the intercept, even though acceptable, restricts the range of acceptable slope values. Thus, as seen in Figure 2, if it is decided to use a blank correction of 7.40 mg., the range of slope values that are compatible with this blank extends approximately from 1.0013 to 1.0117—i.e., it is no longer equal to the total range enclosing the entire ellipse (approximately 1.000 to 1.016).

As the least-squares solution, $m = 1.00765$, is well within this restricted range, the procedure which consists of first correcting the data by means of the experimental blank and then dividing by 1.00765 is entirely acceptable. At the same time it is apparent that merely subtracting the experimental blank is not satisfactory, because this amounts to accepting the joint hypothesis, $b = 7.40$ and $m = 1$, which corresponds to a point outside the ellipse.

If the acceptability of the blank had been judged on the basis of a confidence interval obtained by the usual method—i.e., not based on the joint confidence region—then this judgment would, in a sense, have exhausted the confidence coefficient. If now a judgment concerning the true value of the slope were also attempted, then the joint judgment, concerning both intercept and slope, would no longer be associated with the initially chosen confidence coefficient. In view of the strong correlation between slope and intercept, any proposed value for the intercept restricts the choice of acceptable values for the slope and vice versa. This fact is ignored in the usual method of examining slope and intercept separately.

RELIABILITY OF CALIBRATION LINE

The study of an analytical procedure by the method of linear regression leads to values for the slope and the intercept of the calibration line, and by the method described in the preceding section specific questions regarding these parameters can be satisfactorily answered. This approach is particularly useful when the values of the slope and the intercept can be correlated with chemical aspects of the problem such as the need for, or adequacy of, a blank correction or the appropriateness of a particular indicator.

From the viewpoint of routine testing, one may be interested in the calibration line as such without a critical study of specific values for the slope and the intercept. This question of practical interest can be stated as follows: How reliable is the calibration line over its entire range of applicability? The answer is obtained by the method illustrated in Figure 3, which is based on a 95% joint confidence region for the slope and intercept of the data shown in Figure 1. These data, being less precise than those of Table II, are more suitable for graphical illustration of the concepts here discussed. The two branches of the hyperbola define the limits within which the calibration line is known at any one of its points. The line is most accurately known in the middle region of the range in which it was studied, the uncertainty of its position increasing with increasing departure from the middle. Computational details are relegated to the section on formulas and computations.

However, it is important to note at this point that the hyperbola, in addition to providing an uncertainty band for the calibration line, also yields the answer to two further classes of problems. Just as the estimated straight line can be used for the estimation of the "true" y corresponding to a given x as well as for the estimation of the x corresponding to a given y, so the hyperbola can also be used to give the confidence intervals corresponding to these two situations. The first problem is solved by drawing a vertical line through the given x; the segment of this line situated between the two branches of the hyperbola is the desired confidence interval for the "true" y corresponding to the chosen value of x. The procedure for solving the second problem is entirely analogous, the confidence interval being the segment bounded by the two branches of the hyperbola on the horizontal line drawn through the given y value. Incidentally, it is worth noting that the uncertainty intervals for x, given y, are asymmetrical with respect to the value of x situated on the calibration line. Of course, there is no impelling reason for an uncertainty interval to be symmetrical, because the uncertainty may well be greater in one direction than in the opposite one. This is the case here, the calibration line being most precisely known in the center and becoming gradually less well known at increasing distances from the center. Therefore, the uncertainty intervals for x, given y, are shorter on the side toward the center than on the other side. As may be expected, in the case in which the slope of the line is not significantly different from zero, the confidence interval for x, given y, becomes infinitely long and, of course, meaningless.

The procedure just described can be repeated for any number of given x and/or y values, using the same calibration line with its associated hyperbola, without ever causing the joint reliability of all the confidence intervals thus obtained to drop below the chosen confidence coefficient.

RELIABILITY OF QUANTITIES DERIVED FROM CALIBRATION LINE

The two classes of problems discussed in the preceding section constitute special cases of a wider class of interval estimation problems that can be solved by means of the joint confidence ellipse of slope and intercept. As will be shown in the final section, a confidence interval can be derived for any arbitrary function, linear or nonlinear, of slope and intercept. Only the linear case appears to have been considered in its most general form in the literature (*3*). An example of the nonlinear case is found in the study of the viscosity of polymer solutions.

The following equation is sometimes used to relate viscosity and concentration for dilute solutions (*11*)

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c$$

where c is concentration, η_{sp} is specific viscosity, and $[\eta]$ is intrinsic viscosity. The constant, k', which characterizes the solute-solvent system, can be estimated as the ratio of the slope, $k'[\eta]^2$, of the straight line to the square of its intercept, $[\eta]$. The uncertainty of k' is, therefore, influenced by that of both the estimated slope and the estimated intercept.

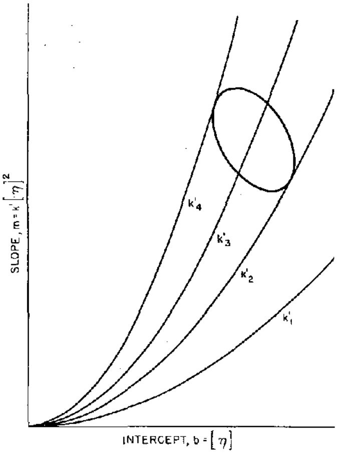

Figure 4. Confidence interval for nonlinear function of slope and intercept in viscosity study

Parabolas represent the equation $m = k'b^2$ for various values of k'. The confidence interval for k' consists of all values of k' contained between k'_2 and k'_4

The following method is proposed for solving this problem. The relation

$$k' = \frac{k'[\eta]^2}{[\eta]^2} = \frac{m}{b^2}$$

can be written $m = k'b^2$ and represents, for any given value of k', a parabola in the b, m plane (Figure 4). Different values of k' result in different parabolas some of which intersect the ellipse, while others do not. For a value of k' to be acceptable, it must correspond to a parabola which contains acceptable combinations of b and m—i.e., points inside the ellipse. Thus, the totality of acceptable values of k' is that set of k' values for which the corresponding parabolas intersect the ellipse—i.e., the values contained between k'_2 and k'_4 corresponding to the tangent parabolas. Thus, k'_1 is unacceptable, while k'_3 is acceptable.

While the problem of determining the limiting values k'_2 and k'_4 can be solved mathematically, it may be simpler in many cases, including the one under discussion, to use graphical methods involving trial and error on some values of k'.

The function of interest in the present example is the ratio of the slope to the square of the intercept. Other functions may also be of interest. If this is the case, confidence intervals can be derived for all such functions by the same general method. It can then be stated that the confidence intervals thus obtained from a single set of straight line data are all jointly valid with a probability at least equal to the selected confidence coefficient.

FORMULAS AND COMPUTATIONS

Equation of Joint Confidence Ellipse. This equation for slope and intercept can be written at once, provided the usual least squares calculations for slope and intercept are carried out in a systematic way.

Suppose that N pairs of corresponding values for x and y are given and that it is required to fit a straight line

$$y = b + mx$$

to these data. The usual assumptions are made —viz., that the x values are known without error and that the errors in the y measurements are independent of each other and have a common variance. The usual least squares formulas are then applicable and require the computation of the following quantities:

Given N pairs of x,y values, compute:

(a) From the x values:

$$S = \Sigma x \text{ and } Q = \Sigma x^2$$

(b) From the y values:

$$Y = \Sigma y \text{ and } L = \Sigma y^2$$

(c) From corresponding x and y values:

$$P = \Sigma xy$$

It is useful to represent the quantity, $NQ - S^2$, which depends on the x values only, by a separate symbol

$$\Delta = NQ - S^2 \qquad (1)$$

Then, the estimates of slope and intercept, $\hat{m}$ and $\hat{b}$, are given by

$$\hat{m} = \frac{NP - SY}{\Delta} \qquad (2)$$

$$\hat{b} = \frac{QY - SP}{\Delta} \qquad (3)$$

The standard error of estimate, which is a measure of the experimental error of the y measurements, is the square root of the quantity

$$s^2 = \frac{1}{N-2}\left[L - \frac{Y^2}{N} - \frac{\Delta}{N}\hat{m}^2\right] \qquad (4)$$

The equation of the ellipse is

$$N(b - \hat{b})^2 + 2S(b - \hat{b})(m - \hat{m}) + Q(m - \hat{m})^2 = 2Fs^2 \qquad (5)$$

In this equation, F represents the critical value of the "variance-ratio," with 2 and $N - 2$ degrees of freedom, corresponding to the desired "confidence coefficient." For example, if the desired confidence is 95% and N is 10, the value of F is obtained from the "variance ratio" table at a level of significance equal to $100 - 95 = 5\%$, for 2 and 8 degrees of freedom. This value is 4.46.

In practice, it is not necessary actually to draw the ellipse, because it can be closely approximated by three sets of parallel tangents, as shown in the following section.

In terms of the data of Table II, the formulas just given lead to the following quantities:

$N = 10$
$S = 1943$
$Q = 676{,}924$
$\Delta = 2{,}991{,}267$
$m = 1.00765$
$b = 6.99$
$s^2 = 2.121$
$F = 4.46$

The equation of the ellipse is, therefore

$$10(b - 6.99)^2 + 3886(b - 6.99)(m - 1.00765) + 676{,}924\,(m - 1.00765)^2 = 18.919$$

Practical Construction of Joint Confidence Region. Referring to the symbols defined in the preceding section, the following additional quantities are required.

$$K^2 = 2Fs^2 \qquad (6)$$

$$W = \frac{\sqrt{NQ}}{S} \qquad (7)$$

$$L_m = K\sqrt{\frac{N}{\Delta}} \qquad (8)$$

$$L_b = K\sqrt{\frac{Q}{\Delta}} \qquad (9)$$

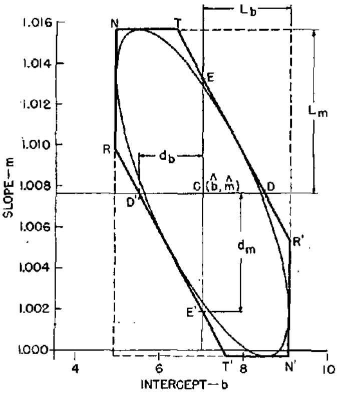

Figure 5. Graphical construction of joint confidence region

Data of Table II

$$d_m = K\sqrt{\frac{2W}{Q(1+W)}} \qquad (10)$$

$$d_b = d_m \frac{L_b}{L_m} \qquad (11)$$

Construct a system of coordinate axes (Figure 5) in which the abscissa represents the intercept and the ordinate the slope. The scales need not be equal for the two axes. They should be such that a rectangle of sides $2L_m$ (in the vertical direction) and $2L_b$ (in the horizontal direction) covers most of the area available for the graph. The center of the rectangle is the point, $C = (\hat{b}, \hat{m})$. After drawing the rectangle, locate the points E and E' above and below C, at distances $\pm\, d_m$ from C; and the points D and D' to the right and left of C, at distances $\pm d_b$ from C. Draw the sloping lines ED and $E'D'$ and extend them to their points of intersection with the rectangle. The sloping lines, as well as the four sides of the rectangle, are all tangent to the ellipse. The hexagon, $RNTR'N'T'$, enclosed between these lines inside the rectangle is an excellent approximation for the ellipse, as evidenced by Figure 5.

Formulas 6 through 11, when applied to the data of Table II, give

$K^2 = 18.919$
$W = 1.3391$
$L_m = 7.953 \times 10^{-3}$
$L_b = 2.0693$
$d_m = 5.655 \times 10^{-3}$
$d_b = 1.47$

These values were used in constructing Figure 5.

Confidence Band for Calibration Line. The hyperbola shown in Figure 3 is obtained by adding to and subtracting from the fitted value, y, corresponding to any given x, a quantity depending on the distance of this x from the average, $\bar{x}$. This quantity is

$$K\sqrt{\frac{1}{N}\left[1 + \frac{(x - \bar{x})^2}{\Delta/N^2}\right]}$$

Thus, the equation of the upper branch of the hyperbola is

$$y = \hat{b} + \hat{m}x + K\sqrt{\frac{1}{N}\left[1 + \frac{(x - \bar{x})^2}{\Delta/N^2}\right]} \qquad (12a)$$

and the equation of the lower branch is

$$y = \hat{b} + \hat{m}x - K\sqrt{\frac{1}{N}\left[1 + \frac{(x - \bar{x})^2}{\Delta/N^2}\right]} \qquad (12b)$$

The derivation of these formulas is outlined in the final section.

It is helpful to draw the asymptotes to the hyperbola. The equations for the two asymptotes are

$$y = \hat{b} + \hat{m}x + K\sqrt{\frac{N}{\Delta}}(x - \bar{x})$$

and

$$y = \hat{b} + \hat{m}x - K\sqrt{\frac{N}{\Delta}}(x - \bar{x}) \qquad (13)$$

The quantity, $K\sqrt{\frac{N}{\Delta}} = L_m$, has already been calculated for the construction of the ellipse.

If a confidence interval is desired for y corresponding to any given value of x, say x_0, it may be determined by drawing a vertical line through $x = x_0$. The desired interval is the portion of that line which falls between the two branches of the hyperbola. Conversely, if a confidence interval is desired for x corresponding to any given value of y, say y_0, it is determined by drawing a horizontal line through $y = y_0$. The desired interval is the portion of that line which falls between the two branches of the hyperbola. It has already been pointed out that this procedure can be repeated for any number of x and y values, with the assurance that the probability that all intervals will be jointly valid is never less than the chosen confidence coefficient. In many cases, the scale of the graph will make it necessary to obtain these intervals by computation rather than graphically.

To judge the reliability of the calibration line over its entire range of applicability, it is useful to note that, for the case of equally spaced values of x, the length of the uncertainty interval for y at both extremes of the calibration line (extreme values for which measurements were made) is approximately twice its length at an x value near the center.

Application to the data of Table II gives the following equation for the confidence hyperbola

$$y = 6.99 + 1.00765x \pm 4.35\sqrt{\frac{1}{10}\left[1 + \frac{(x - 194.3)^2}{29{,}913}\right]} \quad (14)$$

To show how this equation yields information about the precision of the calibration line

$$y = 6.99 + 1.00765x$$

let us calculate the uncertainty of a value x "read" from the line for a value of $y = 250$ mg. Substituting this value in the equation and squaring, we obtain

$$(250 - 6.99 - 1.00765x)^2 = 1.8919\left[1 + \frac{(x - 194.3)^2}{29{,}913}\right]$$

This quadratic equation in x has the roots $x_1 = 239.83$ and $x_2 = 242.48$.

This interval of uncertainty reflects only errors in the calibration curve and does not include errors in the measurement of y.

SOME THEORETICAL CONSIDERATIONS

While the basic theory of joint confidence regions has been known for a number of years, its practical usefulness seems to have been largely overlooked. Textbooks on applied statistics either ignore the issue entirely or treat it very sketchily. The present discussion is an attempt to fill this gap and to present a concise outline of the theoretical ideas and principles necessary to an understanding of the techniques already discussed in this paper. It is hoped that this exposition will also throw some light on the manner in which the various principles are related to each other.

1. It is interesting to contrast problems involving two unknown parameters, such as intercept and slope, with problems involving a single parameter. In the latter case, there is essentially only one possible confidence statement; for example, if the parameter is the slope, m, of a straight line, $y = mx$, passing through the origin, then the confidence interval for y corresponding to $x = x_0$ is the range of values extending from x_0m_1 to x_0m_2, where m_1 and m_2 are the confidence limits for m. If another value x_0' had been considered, the corresponding confidence interval would be proportional to the first, with a proportionality factor, x_0'/x_0. Thus, all such intervals are uniquely determined by values m_1 and m_2 or by each other. The joint confidence for any number of intervals thus obtained is therefore equal to the confidence for each single one, since any one interval determines all others.

On the other hand, in the case of two or more parameters, such as the slope and intercept of the line, $y = b + mx$, a confidence statement for y corresponding to x_0 does not mathematically imply a confidence statement corresponding to another value x_0'. For example, if it is stated that for $x = 2$, $b + mx$ lies between 5 and 15—i.e.,

$$5 < b + 2m < 15$$

no statement can be inferred from these inequalities for $x = 3$—i.e., for $b + 3m$. Thus, if statements of uncertainty are made both for $x = 2$ and $x = 3$, their joint reliability will be less than that corresponding to each statement taken separately. If more values of x are considered, the joint reliability will further decrease. The joint confidence ellipse ensures that no matter how many individual confidence intervals are derived from it, the joint confidence of all these intervals is never less than the selected confidence coefficient, say 0.95.

2. The usefulness of the joint confidence ellipse for slope and intercept in the study of linear relationships was recognized by Working and Hotelling (*17*) as early as 1929. Some aspects of their paper appear to have been largely ignored in subsequent writings. These authors show that the totality of all straight lines whose slopes and intercepts correspond to points inside the ellipse—i.e., the admissible lines—are contained between the branches of a hyperbola, and they point out that this hyperbola is wider than the one corresponding to the sampling errors in y for any particular x. They consider the wider hyperbola as setting limits for the "sampling errors of the trend line as a whole" (*17*). However, the ellipse discussed by Working and Hotelling involves the population standard deviation of the experimental errors, σ, and therefore, does not allow for sampling errors in the estimation of the standard error of estimate, s. Neither do these authors consider the problem of determining the uncertainty of an x value "read" from the calibration line for a given y.

3. The latter problem is examined in detail by Eisenhart (*4*). This author summarizes the theory of confidence intervals, based on Student's t, for the parameters of a straight line and the uses of hyperbolic uncertainty bands for the interval estimation of x, given y, as well as for y, given x. It will be shown that some of these problems can also be treated by the method of joint confidence regions underlying Working and Hotelling's "wider" hyperbola, leading to more satisfactory solutions for some types of applications than those based on Student's t.

4. A further aspect of linear regression is that of evaluating the uncertainty of some given function of the slope and the intercept, such as in the viscosity problem described in an earlier section. For functions that are linear with respect to b and m, a general solution based on the joint confidence ellipse is given by Durand (*3*). For functions that are of the form, $L_1(b,m)/L_2(b,m)$, where both L_1 and L_2 are linear, a solution is available using a theorem by Fieller (*5, 7*), the basic principle of which is concisely presented by Finney (*6*). However, this solution is not based on the joint confidence ellipse and suffers, therefore, from the restriction that only one conclusion can be drawn from a given set of data, using a preselected confidence coefficient.

5. The method presented in this paper and illustrated by the viscosity problem constitutes an entirely general procedure. It contains as special cases the treatment of linear functions by the method of Durand (*3*), as well as those nonlinear functions that can be covered by Fieller's theorem. Among the latter, there is the interval estimation of x, given y which, under the generalized procedure leads also to the "wider" hyperbola of Working and Hotelling (*17*).

The principle of the general method is as follows: Given a set of data for a straight line and any arbitrary function of slope m and intercept b, say $z = f(b,m)$, first determine the joint confidence ellipse as described. Next, consider any value of z, say z_0. For this value, function $z_0 = f(b,m)$ represents a curve in the b,m plane. By varying z_0, a family of such curves is obtained. A confidence interval for z is then obtained by collecting all numerical values of z for which the corresponding curves intersect the ellipse.

This procedure can be repeated for any arbitrary number of functions of b and m, using the same ellipse. Provided that the functions contain no random errors other than those affecting estimates b and m, the confidence intervals obtained will all be jointly valid with a probability not less than the selected confidence coefficient.

6. By the procedure that has just been outlined, a single mathematical operation yields the solution to both the problem of determining a confidence band for the regression line, as dealt with by Working and Hotelling, and the problem of determining confidence intervals for y, given x, and for x, given y.

Identify z with the expression, $(y - b)/m$—i.e., x—for a fixed value of y

$$z \equiv x = \frac{y - b}{m}$$

This equation represents a straight line in the b,m plane. The values of z for which this line intersects the ellipse will be contained between two values, say x_1 and x_2, for which this line is tangent to the ellipse given by Equation 5. By means of elementary analytical geometry it can be shown that x_1 and x_2 are the solutions of the following equation in x

$$(y - \hat{b} - \hat{m}x)^2 = K^2(Nx^2 - 2Sx + Q) \tag{15}$$

The interval extending from x_1 to x_2 is, of course, a confidence interval for x for the fixed value of y considered. On the other hand, Equation 15 also represents a hyperbola entirely analogous to the "wider" hyperbola obtained by Working and Hotelling, but allowing for sampling errors in the estimate, s, of σ.

If z had been identified with the expression, $b + mx$, the same identical hyperbola would have been obtained. Thus, Equation 15 also yields confidence intervals for y, given x. By replacing the quantity, $Nx^2 - 2Sx + Q$, by its equivalent, $N(x - \bar{x})^2 + \frac{\Delta}{N}$, it is easily verified that Equations 12a and 12b are merely a different way of writing Equation 15. Figure 3 is based on these equations.

7. Fieller's theorem (*5–7*) could have been used to derive confidence intervals for x, given y, as the expression $x = (y-b)/m$ is of the form, $L_1(b,m)/L_2(b,m)$, with L_1 and L_2 linear. This technique would have led to an equation entirely similar to Equation 15, with the sole difference that quantity t^2s^2 appears in the place of K^2. As $K^2 = 2Fs^2$, the relation between the solutions obtained by Fieller's theorem and the use of the ellipse is that of the use of t *vs.* $\sqrt{2F}$. This same relation applies also to the comparison between the method described by Eisenhart, based on Student's t, and that derived from the joint confidence ellipse for confidence intervals of y, given x. In fact, it can be shown that in all cases in which confidence intervals can be derived on the basis of Student's t, they bear a constant relationship to corresponding intervals based on the joint confidence ellipse for the slope and the intercept—namely, that the length of the latter intervals is longer by the ratio, $\sqrt{2F}/t$. For a confidence coefficient of 0.95, this ratio equals 1.295 for $N = 10$ and it decreases slowly to the limiting value, 1.247, as N increases indefinitely.

Against the disadvantage of the method based on the joint confidence ellipse to yield somewhat longer confidence intervals, one must weigh two important advantages. In the first place, as mentioned before, it is possible by this method to obtain confidence intervals for any function, linear or nonlinear, of b and m. Secondly, the confidence intervals derived from the ellipse are all jointly valid, regardless of their number, with a joint confidence coefficient that is never less than the one on which the ellipse is based.

8. While the general method described above permits one to derive from a single set of data an unlimited number of jointly valid confidence intervals for y, given x, and for x, given y, it fails to solve a twofold problem discussed by others (*1, 2, 4, 12, 15*) in connection with linear regression: that of predicting in what range a "future" y, to be measured at a given x, will lie; and conversely, the problem of evaluating the uncertainty of x corresponding to a "future" y measurement. In both cases, an error is involved that is not accounted for in the joint confidence ellipse of slope and intercept—namely, the error of a future y measurement. The former problem is strictly speaking, not concerned with confidence intervals, because it deals with the uncertainty of a random variable, not a population parameter. The relation of intervals of this type to classical confidence intervals and application to a chemical example are described by Weiss (*16*).

The second problem, on the other hand, is a genuine case of interval estimation, and of particular interest to the chemist. It can be solved by an extension of the method here described through introduction of a three-dimensional ellipsoid in place of the plane ellipse (*10*). The solution thus obtained does not allow for the treatment of more than a single "future" measurement, but it does permit the construction of an unlimited number of jointly valid confidence intervals involving the slope, the intercept, and the "true" y corresponding to the "future" measured y. The method can be easily extended to include any finite number of "future" measurements.

9. Durand (*3*) notes that the use of joint confidence regions for the determination of confidence intervals for linear combinations of regression coefficients is closely related to a technique recently developed by Scheffé (*14*) and extended by Roy and Bose (*13*) for examining simultaneously all combinations of a number of observed means. The general result derived by these authors consists essentially in replacing t with $N - k$ degrees of freedom by $\sqrt{kF_{k,N-k}}$, where N is the total number of measurements and k is the number of parameters. The case discussed in this paper involves two parameters: the slope and the intercept. Making $k = 2$ in the general formula, we find $\sqrt{2F_{2,N-2}}$ as the quantity to be substituted for Student's t in the construction of confidence intervals. Since we have already found this relationship in comparing the technique based on the joint confidence ellipse with that based on Fieller's theorem in a nonlinear case, it appears that the relationship is more general than is implied in Durand's statement.

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Spectrophotometric Determination of Copper in Titanium

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▶ The chloroform-alcohol extraction of a copper(I) neocuproine complex has been used for the spectrophotometric determination of copper in titanium. Comparison photometric measurement permits determination on a 0.5-gram sample of 0.005 to 0.40% copper. Accuracy is within 4% with a coefficient of variation of 0.5 to 3%, depending upon the level of absorbance. Chromium(III) is the sole metallic interference, and methods for the removal of this interference are presented.

COMMERCIAL TITANIUM may contain copper in amounts ranging from tenths of thousandths to several per cent, depending upon the type of material and its history. A method for determining copper in titanium is needed for application to the several orders of magnitude over which the concentration might range. None of the methods previously reported as applicable to titanium samples (*6*) meets such a requirement with speed or accuracy. Electrodeposition has been suggested (*2*), but a large sample is required, and preliminary separations must be made if common alloying agents used in titanium are present. Mikula and Codell (*14*) have reported a polarographic procedure for the simultaneous determination of copper, nickel, and cobalt; however, the useful concentration range is 0.2 to 5% for each of the components. A spectrophotometric method would probably be better suited to the broad range of copper concentrations which titanium materials present.

Of the many color-forming reagents which have been proposed for the determination of copper, 2,2′-biquinoline (*5*) and its structural analog, 2,9-dimethyl-1,10-phenanthroline (neocuproine), appear to be the most specific, most sensitive, and simplest to use. The excellent results obtained by Gahler (*8*) in the analysis of steels and by Crawley (*7*) on tungsten materials have prompted the selection of neocuproine for the present investigation.

The extraction of a copper(I) neocuproine complex into water-immiscible alcohols has been shown to be specific and independent of pH over a wide range (*16*). Gahler (*8*) noted that, in addition to aiding phase separation, the use of a mixed chloroform–ethyl alcohol solvent increases sensitivity, and the mixed solvent has been applied here. An extension of the concentration range over which the neocuproine method might be applied has been sought by means of comparison spectrophotometry, the name applied to the practice of making measurements against a reference solution containing a known concentration of the absorbing species. Further study has been made of possible metallic interferences.

The titanium samples which have been used for this investigation are materials which have been prepared and distributed by Watertown Arsenal for a program of cooperative analysis under the direction of the Panel on Methods of Analysis, Metallurgical Advisory Committee on Titanium, sponsored by the Ordnance Corps. While these are by no means standard samples—none are as yet in existence for titanium—they are in circulation among the cooperating laboratories as reference samples. Their present use will provide information on materials of some definite interest and utility.

APPARATUS AND REAGENTS

Absorbance measurements were made in matched 13-mm. cells with a Coleman Model 10S spectrophotometer, using a fixed band width of 35 mμ. A Leeds & Northrup line-operated pH indicator was coupled to the spectrophotometer as a vacuum-tube voltmeter to act as the photometric device.

The pH measurements were performed with a Beckman Model G pH meter or with Hydrion short-range pH paper. The paper readings were adequate for normal use.

2,9 - Dimethyl - 1,10 - phenanthroline (neocuproine) was obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio, and used as a 0.2% solution in ethyl alcohol.

A solution containing 2.5 grams of reagent grade anhydrous copper(II) sulfate in 400 ml. of water, to which had been added 20 ml. of sulfuric acid, 7 ml. of nitric acid, and 0.1 gram of urea, was electrolyzed at platinum electrodes. The weighed copper deposit was stripped from the cathode by 200 ml. of hot water containing 10 ml. of nitric acid. The dissolved copper was diluted to 1 liter, and aliquots were diluted to prepare stock copper solutions of known concentration.

National Bureau of Standards Sample No. 154 titanium dioxide, certified to contain less than 0.001% copper, was used in the preparation of a stock solution containing 2.96 grams of titanium and 60 grams of ammonium sulfate per liter.

A combined reducing reagent was prepared from hydroxylamine hydrochloride and sodium citrate pentahydrate by dissolving 50 and 300 grams, respectively, in water and diluting to 1 liter.

Because of evidence of copper contamination in the local supply of distilled water, all reagents were prepared with water which had been redistilled from an all-glass apparatus. This same redistilled water was used throughout the investigation.

ANALYSIS OF TITANIUM SAMPLES

Dissolve a sample of suitable size, normally 0.5 gram, in a 600-ml. beaker with a mixture of 80 ml. of water, 20 ml. of sulfuric acid, and 5 ml. of fluoboric acid, keeping the solution heated just below the boiling point for about 0.5 hour. After the sample has dissolved, add nitric acid dropwise until the dark green fluotitanate(III) color is discharged. Add a few drops in excess, and warm gently until all material is in solution. Add 10 ml. of perchloric acid, and evaporate rapidly to dense fumes of perchloric acid. Add hydrochloric acid dropwise until orange fumes of chromyl chloride cease to be evolved. Evaporate rapidly to fumes of sulfur trioxide. (In mixtures containing both perchloric and sulfuric acid, it is a simple matter to distinguish between the appearance of perchloric acid fumes, which evolve first, and those of sulfur trioxide.) Cool the solution to room temperature; add 50 ml. of water and warm gently until salts dissolve. Filter the solution through a Whatman No. 42 paper into a 100-ml. volumetric flask and wash the paper with distilled water. When the solution has cooled to room temperature, dilute to the mark with water.

Withdraw a 25-ml. aliquot and transfer it to a 150-ml. beaker. Add 10 ml. of

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Table I. Analysis of Watertown Arsenal Titanium Samples

Sample	Type	Sample Size, Grams	Aliquot Taken	Cu Found, %
WA-2A	3% Al–5% Cr	2.000	1/4	0.0030, 0.0029, 0.0029
WA-4	7% Cr–3% Mo–0.2% Fe	0.500	1/4	0.183, 0.181, 0.185
WA-5	10.5% Cr–4.5% Fe	2.000	1/4	0.0094, 0.0092, 0.0092
WA-7	2% Cr–2.7% Fe–2.1% Mo–0.1% W	0.500	1/4	0.017, 0.017, 0.016
WA-13	Iodide Ti	4.000	1/4	0.0049, 0.0049, 0.0049
WA-44	2.3% Sn–0.15% Fe	0.500	1/4	0.134, 0.133, 0.136
WA-66	Iodide Ti	4.000	1/4	0.0011, 0.0011, 0.0011
AA-375[a]	Cu-Ti alloy	0.887	1/1000	8.68, 8.68, 8.76

[a] Not a WA sample, but included to permit examination of high copper alloy. Copper in sample, 8.72%.

Table II. Direct Electrolytic Determination of Copper in Titanium Samples

Sample[a]	Type	% Cu Found	% Cu Anticipated
WA-66	Iodide Ti + 0.0136 gram Cu added	0.137, 0.135, 0.136	0.137[b]
WA-4	Cr-Mo alloy	0.163, 0.165, 0.158 0.161, 0.164, 0.185	0.183[c]

[a] 10-gram samples used.
[b] Direct addition of standard copper solution to solution of sample containing 0.0011% copper from Table 1.
[c] Photometric value from Table I.

the hydroxylamine-citrate solution. Adjust the pH between 4 and 6 by dropwise addition of ammonia. Transfer the solution to a 125-ml. separatory funnel. Add 10 ml. of 0.2% neocuproine solution in ethyl alcohol. Extract with 10 ml. of chloroform, shaking for about 30 seconds. Draw off the chloroform layer into a 25-ml. volumetric flask containing 2 or 3 ml. of absolute alcohol. Repeat the extraction of the aqueous phase, first with a 3-ml. and then a 2-ml. portion of chloroform, and collect the chloroform layers in the volumetric flask. Dilute to volume with absolute alcohol and mix well.

Prepare a suitable reference solution by carrying either a reagent blank or a standard amount of copper through the above procedure. Measure the absorbance of the unknown solution at 452 mμ as compared to the reagent blank or copper reference. Determine the copper concentration of the extracts from an algebraic or graphic calibration prepared by carrying known amounts of copper through the procedure.

As Beer's law is obeyed in the region where a comparison copper reference may be employed, the absorbance measured against a copper reference represents the copper content of the unknown in excess of that present in the reference solution.

The results obtained on the Watertown Arsenal titanium samples are shown in Table I.

CONFIRMATORY EXPERIMENTS

In the absence of reliable information with which to compare the photometric results, additional data were sought. Direct electrolysis was attempted on a chrome-molybdenum titanium alloy (WA-4) immediately after dissolution. An iodide titanium sample was treated similarly, except that an increment of copper was added to the dissolved sample. The data, which are summarized in Table II, indicate that direct electrolysis is not feasible when alloying elements are present. Preliminary separations prior to electrodeposition of copper would probably introduce larger errors than does the photometric method.

The only practical means of confirming the photometric result appeared to lie in the method of standard addition. Known amounts of copper were added to aliquots of samples previously analyzed, and the total copper was determined photometrically. The recoveries shown in Table III agreed with anticipated totals within 3%.

EXPERIMENTAL STUDY

The suitability of the wide-band spectrophotometer was tested on chloroform–ethyl alcohol extracts of the copper(I) neocuproine complex. Whereas narrow-band width measurement

Table III. Test of Validity of Analysis of Watertown Arsenal Titanium Samples

Sample[a]	Copper, Mg. Added	Copper, Mg. Present	% Transmittance	Absorbance, A	Cu[b] Found, Mg.	Error, %[c]
WA-13	0	0.0123	...	...	...	...
(0.0049%)	0.0117	0.0240	68.7	0.163	0.0245	+2.1
2.5 × 1/10	0.0234	0.0357	57.5	0.240	0.0361	+1.1
	0.0585	0.0708	34.6	0.461	0.0693	−2.1
WA-5	0	0.0364	57.1	0.243	0.0366	+0.6
(0.0093%)			57.4	0.240	0.0361	−0.6
4.0 × 1/10	0.0091	0.0455	49.8	0.303	0.0456	+0.2
			49.8	0.303	0.0456	+0.2
	0.0272	0.0636	39.3	0.406	0.0611	−3.9
			39.0	0.409	0.0616	−2.5
	0.0453	0.0817	29.8	0.526	0.0792	−3.1
			29.8	0.526	0.0792	−3.1
WA-7	0	0.0676	35.4	0.451	0.0679	+0.4
(0.017%)			35.7	0.447	0.0673	−0.4
4.0 × 1/10	0.0091	0.0767	32.1	0.494	0.0744	−2.4
			31.8	0.498	0.0751	−1.3
	0.0272	0.0948	24.2	0.616	0.0928	−2.1
			24.2	0.616	0.0928	−2.1
	0.0453	0.1129	18.4	0.735	0.1106	−2.0
			18.7	0.728	0.1097	−2.8

[a] Includes sample number, copper content from Table I, sample weight in grams, and aliquot size.
[b] Divide absorbance by experimental slope of the Beer's law curve (6.64).
[c] Equals copper found less copper present divided by copper present.

showed the absorbance maximum to be at 457 mμ (*8*), the use of the wide-band spectrophotometer provided maximum absorbance at a nominal wave length of 452 mμ. This setting was used in subsequent measurements.

Beer's law is obeyed whether the copper is extracted from a simple aqueous solution or from the titanium stock solution. The slope of the curve (the absorbance produced by 1 mg. of copper in 25 ml. of the extract) is 6.64. This value was used in subsequent calculations of concentration.

The extraction of copper is unaffected by pH within the range from 3 to 9. For the present study, a pH of 4 to 5 was chosen to avoid hydrolysis of the titanium-citrate solution, although strict pH control was found to be unnecessary.

Comparison Photometric Measurements. Direct photometric measurements are limited to concentrations of absorbing species such that the absorbance produced lies within the range of accurate photometric measurement (*3, 15*). By use of the comparison photometric method, wherein absorbance measurements are made against a moderately absorbing reference, the instrument is used to measure only the absorbance difference between the sample and the reference solution. In addition to an extension of the concentration range over which a photometric method may be applied, increased accuracy and precision result from the effective lengthening of the photometric scale (*3, 4, 10, 11, 13*). Additionally, operations otherwise required to regulate the amount of absorbing species may be eliminated. This simplifies procedures and eliminates extra steps which might introduce manipulative errors.

For application of comparison methods to the determination of copper, solutions containing 0.0635, 0.1270, 0.1905, and 0.2540 mg. of copper were extracted with neocuproine, and the absorbance of each extract was determined against the next lower in concentration, with a reagent blank used for the lowest concentration. The extract containing 0.190 mg. of copper was the highest in concentration for which the transmittance of the spectrophotometer could be set at 100%. The results (Table IV) show that Beer's law is still obeyed at these higher concentrations of copper.

Table IV. Conformance to Beer's Law; Measurement Against Absorbing Reference Solution

Total Cu, Mg.	Reference Cu,[a] Mg.	ΔC[b]	Absorbance, A	Slope, $A/\Delta C$
0.0635	0	0.0635	0.418	6.58
0.1270	0.0635	0.0635	0.427	6.72
0.1905	0.1270	0.0635	0.421	6.63
0.2540	0.1905	0.0635	0.426	6.71
			Av.	6.66
			σ =	±0.07 or 1.05%

[a] Reference solution of reagent blank containing indicated added copper.
[b] Difference in copper content of sample and reference solution, mg. copper per 25 ml.

A series of solutions was prepared, each containing 0.2 to 0.4 mg. of copper, and the absorbance of these solutions was determined with reference to the copper extract containing 0.190 mg. of copper. A duplicate series was prepared, and the copper content of one-fifth aliquots was determined directly against a reagent blank. The results obtained by comparison photometry are contrasted in Table V with those found by dilution.

Interference Study. According to Smith and McCurdy, copper is the only metal ion extracted under the conditions of the neocuproine procedure. Gahler has shown that sulfide, cyanide, and large amounts of phosphate prevent complete recovery of copper by making it unavailable to the color reagent. The absence of interference by some 50 diverse metal ions at the 50-γ level was shown by Luke and Campbell (*12*). The present authors felt that interferences might be noted at the higher ratios of alloying element to copper likely to be encountered in titanium materials.

Of the metallic elements commonly found in titanium alloys, the following were examined: iron(III), aluminum, chromium(III), manganese(II), molybdenum(VI), and vanadium(IV). To each of a series of solutions containing 0.06 mg. of copper was added 15 mg. of one of the metals to be studied (each as the chloride or sulfate except for the use of ammonium molybdate). When the extraction procedure was performed without acid fuming, complete recovery of copper was found except in the case where chromium(III) was present.

To determine the effective level of chromium interference, successively larger quantities of chromic chloride were added to solutions each containing 0.06 mg. of copper. The recovery data presented in Table VI indicate that only 2 mg. of chromium may be tolerated in the final aliquot. In the presence of

Table V. Comparison Method vs. Dilution Method

Cu, Mg. Present	Comparison[a] Absorbance, A	Comparison[a] Mg. Cu found	Dilution[b] Absorbance, A	Dilution[b] Mg. Cu found
0.227	0.245	0.227	0.290	0.218
	0.243	0.227	0.292	0.220
	0.248	0.228	0.292	0.220
0.272	0.530	0.270	0.351	0.264
	0.536	0.271	0.349	0.263
	0.535	0.271	0.354	0.266
0.317	0.830	0.315	0.415	0.312
	0.821	0.314	0.419	0.316
	0.836	0.316	0.412	0.311
0.363	1.056	0.349	0.480	0.361
	1.046	0.348	0.484	0.365
	1.046	0.348	0.482	0.362

[a] Comparison reference solution made by carrying solution containing 0.190 mg. of copper through extraction procedure.
[b] Original solution diluted fivefold to permit transmittance to lie in 10 to 90% range.

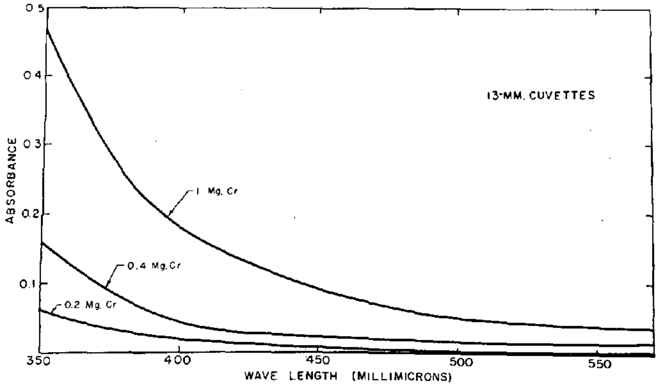

Figure 1. Absorption spectra of chromium(III) neocuproine complex in 40% alcohol

larger amounts of chromium, and as a routine precaution, the solution must be fumed with perchloric acid and chromyl chloride must be evolved on dropwise addition of hydrochloric acid.

Because chloroform-neocuproine extracts of chromium(III) solutions show no absorbance and give no qualitative test for chromium, spectral studies were performed on 40% alcohol solutions of chromium(III) chloride and neocuproine. The absorbance of such solutions was determined against a reference containing an equal concentration of neocuproine in 40% alcohol. Chromium (III) chloride at the concentrations employed shows zero absorbance over the entire wave length region available to the Coleman spectrophotometer. The absorption curves presented in Figure 1 show that chromium-neocuproine interaction occurs in the aqueous layer only, making less of the color-forming reagent available to copper.

DISCUSSION

While many methods have been used to dissolve titanium, the sulfuric-fluoboric procedure described here has been found to be the most rapid and the least likely to lead to hydrolytic separation of titanium.

The procedure developed by Gahler for the determination of copper in steel applies equally well to titanium materials, and, as many investigators undoubtedly suspect, it appears to be a universal method subject only to the anion interferences noted by Gahler and that due to chromium, as reported here.

The interference from chromium is somewhat anomalous in that it does not occur in the presence of large amounts of iron. NBS samples 101c and 153, containing 18 and 4% chromium, respectively, have been analyzed in this laboratory with and without the volatilization of chromium. The results were 0.122 and 0.097% copper, independent of the presence of chromium, as compared to certificate values of 0.124 and 0.097%, respectively. Neither the minimum amount of iron required to suppress chromium interference nor the mechanism by which this occurs have been determined.

Table VI. Extent of Interference by Unremoved or Uncomplexed Chromium

Cr Added[a]		Cu Recovered,
Mg.	%	%[b]
0	0	100
1	0.8	100
2	1.6	99
4	3.2	95
5	4.0	90
10	8.0	80
15	12.0	77
20	16.0	66
25	20.0	59
15[c]	15.0	97

[a] Calculated as per cent chromium present in 25-ml. aliquot of 500-mg. titanium sample made up to 100 ml.

[b] Based on 0.0585 mg. of copper added.

[c] Chromium removed by volatilization as chromyl chloride.

Chromium interference also may be avoided by addition of sulfurous acid prior to reduction of copper with hydroxylamine (*9*). As the mechanism for the interference of chromium involves chromium(III), reduction of chromium (VI) appears to be incidental to the action of sulfite in this instance. Sulfite complexes of chromium(III) have been described (*1*), and it is believed that the formation of such complexes prevents interaction of chromium(III) with neocuproine. While sulfurous acid could be used to prevent interference from chromium in the analysis of titanium, the authors prefer to remove the interfering species.

All results obtained in this investigation have been used to determine the precision of the method at several levels of absorbance. The standard deviation, expressed percentagewise as the coefficient of variation (*v*), varies according to the error function predicted for photometric measurement against a nonabsorbing reference solution (*11*). For absorbance in the range of 0.4, *v* is approximately 0.5%; *v* rises to as much as 3% at absorbances of 0.1, and 2.5% at absorbances of 0.8. When absorbance is measured by the comparison photometric technique, *v* lies between 0.5 and 1.2%. An improvement in precision at high and at low absorbances could be obtained by using an instrument with greater sensitivity and stability in the photometric scale.

The accuracy of the method, as determined by recoveries of standard additions, is within 3%. Results on synthetic solutions were accurate to 1%, except in the example where the absorbance was greater than 1 and the resultant error was approximately 4%. The application of precision photometry permits the determination of copper from 0.005 to at least 0.4% by a rapid, simple, and accurate procedure. Variation of sample size extends the applicability to the range from 0.0001 to more than 1% copper.

ACKNOWLEDGMENT

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Spectrophotometric Determination of Iron with 2-Fluorobenzoic Acid

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▶ The color of the water-soluble amethyst complex formed by the reaction of ferric ions with 2-fluorobenzoic acid can be used as the basis of a spectrophotometric method for the determination of iron. The effect of pH, concentration of reagents, and the presence of diverse ions are discussed. Results similar to those obtained by the salicylic acid method for the determination of iron can be expected, with the advantage that only the ferric ion reacts.

THE REACTION between ferric ions and an organic compound containing a phenolic group generally results in the production of a colored complex. Mehlig has made use of the complex formed between salicylic acid and ferric ions for the quantitative determination of iron (*2*, *3*). According to Welcher, the reaction between sodium salicylate and iron in an acetic acid solution is not restricted to the ferric ion; an identical color is also obtained with ferrous ion (*4*). In a study of the hydrogen bonding within 2-fluorobenzoic acid, Whittaker noted that this reagent produced an amethyst color with ferric ions similar to that produced by salicyclic acid (*5*). As this color is not affected by the presence of ferrous ions, an investigation was undertaken to determine the possible application of this reagent to the quantitative determination of iron.

APPARATUS AND REAGENTS

A Beckman Model DU spectrophotometer operating on a band width of 0.05 mμ and utilizing 1-cm. cells was employed for all spectrophotometric measurements. A Coleman Model 3D pH meter was used for all determinations of pH.

The 2-fluorobenzoic acid, prepared according to Blatt (*1*), was purified by steam distillation and recrystallization from water to give a product with a melting point of 126° C. A saturated solution was prepared by dissolving 7 grams of the reagent in 1 liter of warm water and cooling to room temperature.

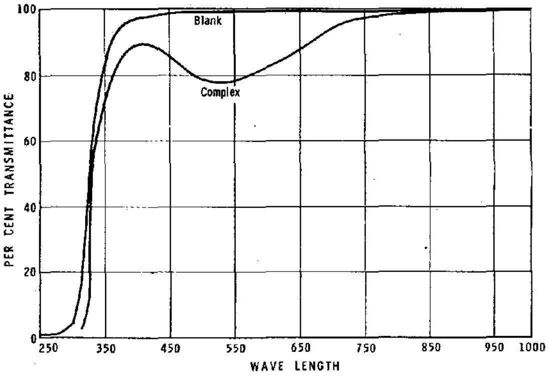

Figure 1. Absorption spectra of 2-fluorobenzoic acid and its iron complex

The standard iron solutions were prepared by dissolving 100 mg. of electrolytic iron in hydrochloric acid. The iron was then oxidized to the trivalent state by the addition of bromine water, the excess of which was removed by boiling. The solution was then diluted with water until the weight of the entire solution was 1 kg.

The ammonium formate solution was prepared by dissolving 75 grams of the salt in 1 liter of water.

METHOD FOR IRON

In Absence of Interfering Substances. Add 20 ml. of the reagent solution to the unknown solution which contains between 0.1 and 1 mg. of iron. Destroy the resultant color by the dropwise addition of concentrated hydrochloric acid, then add 5 ml. of the ammonium formate solution and dilute to 50 ml. with water.

Measure the absorbance of the system at 525 mμ using distilled water as a blank. Convert the absorbance reading to iron concentration by means of a previously prepared calibration curve.

EXPERIMENTAL

The absorption spectra (Figure 1) indicate that the wave length of maximum absorption by the complex and of minimum absorption by the reagent is 525 mμ. This wave length was used, therefore, for all absorbance measurements.

Effect of pH on Degree of Complexation. Experiments showed that the pH of the solution had a considerable effect upon the degree of complexation. To determine the pH which would give maximum absorption by the complex, several solutions containing identical quantities of iron were prepared, and 20 ml. of 2-fluorobenzoic acid solution were added to each. The resulting color was just destroyed by the dropwise addition of concentrated hydrochloric acid, then restored by the addition of varying amounts of ammonium formate solu-

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tion. Each solution was then diluted to 50 ml. and the pH and absorbance were measured. Figure 2 indicates that the pH range of 3.0 to 3.5 is most suitable for quantitative determinations of iron. Within this pH range and in the presence of an excess of reagent, the color of the complex was stable for 24 hours.

Beer's Law. In order to determine the applicability of Beer's law to this complex, solutions of known iron concentration were prepared from the standard iron solution in a series of 50-ml. volumetric flasks. The solutions were treated as for the pH study, except that the color was restored by the addition of 5 ml. of the ammonium formate. At 525 mμ maximum absorbance was obtained when 20 ml. of the complexing reagent was used. The complex follows Beer's law for concentrations from 0 to 20 p.p.m. of iron.

An average value of 27.7 was obtained for the absorptivity. On the basis of the assumed formula, $C_{21}H_{12}O_6F_3Fe$ (molecular weight, 473), a value of 13,100 was obtained for the molecular extinction coefficient.

A	c	$a = \frac{A}{bc}$
0.0200	0.00062	32.25
0.1500	0.00562	26.87
0.3010	0.01154	26.08
0.4179	0.01606	26.02
0.5200	0.2000	26.00
0.0400	0.00129	28.77
		Av. 27.66

27.7 × 473 = 13,100

Effect of Diverse Ions. To determine which of the more common ions interfere, the method described above was used, except that the ion under investigation was added prior to the reagent. Although the absorbance of colored ions in the solution can be compensated for by using a blank solution containing this ion, their presence makes the adjustment of the pH difficult. Table I lists such ions, as well as noncolored interfering ions.

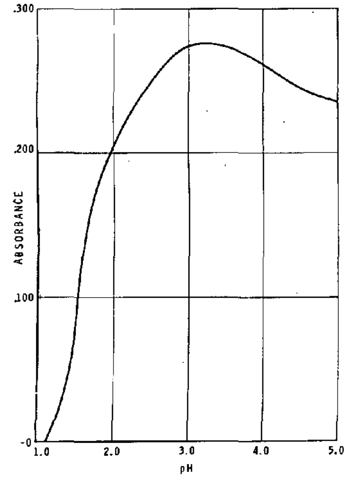

Figure 2. Effect of pH on absorbance of iron complex

Table I. Noncolored Interfering Ions

Ion	Type of Interference
Ag^+	Ppt.
Al^{+++}	Forms colorless complex
AsO_4^{---}	Forms colorless complex
Bi^{+++}	Ppt.
F^-	Forms colorless complex
Hg_2^{++}	Ppt.
Nb^{+5}	Ppt.
Pb^{++}	Ppt.
PO_4^{---}	Forms colorless complex
SiO_4^{-4}	Ppt.
Sn^{+4}	Ppt.
Ta^{+5}	Ppt.
Th^{+4}	Ppt.
Ti^{+4}	Forms yellow complex
UO_2^{++}	Forms orange complex
VO_3^-	Forms yellow complex

STRUCTURE OF COMPLEX

A possible structure of the complex was determined by assuming that it was the 2-fluorobenzoate anion, which complexed with the iron and not the free acid. The degree of complexation would then be a function of the pH of the solution and the equilibrium constant for the reaction would be expressed as follows:

$$x\text{HBz} + \text{Fe}^{+++} \rightarrow x\text{H}^+ + \text{complex}$$

$$K = \frac{[\text{H}^+]^x . \text{ complex}}{[\text{Fe}^{+++}] . [\text{HBz}]^x} \qquad (1)$$

where x is the combining ratio and HBz represents the 2-fluorobenzoic acid. Upon rearranging the terms and taking the logarithms of each side, the equation reduces to the following:

$$\log \text{complex} = -x\text{pH} + \log(K)(\text{Fe}^{+++})(\text{HBz})^x \qquad (2)$$

If the conditions of the experiment are such that the changes in the molar concentration of the iron and the 2-fluorobenzoic acid are small in comparison with their concentrations, then the second member of the right side of the equation becomes a constant and the equation reduces to that of a straight line. The slope of this line is then the combining ratio of the iron and the 2-fluorobenzoic acid. Furthermore, as the absorbance values are proportional to the molar concentration of the complex, absorbance can be substituted for the molar concentration. When these simplifications and substitutions are made, the equation then becomes:

$$\log A_s = -x\text{pH} + C \qquad (3)$$

In a highly acid solution, where the changes in the molar concentration of the iron and the 2-fluorobenzoic acid are negligible, the curve obtained is a straight line with a slope of 2.9. This value is close enough to 3 to consider that 3 moles of the 2-fluorobenzoate ion are combined with 1 mole of the iron.

RESULTS

Several NBS samples were analyzed by this method. Samples of brass, glass, and fluorspar were taken to provide a variety.

The glass was prepared for the analysis by treatment with perchloric and hydrofluoric acids (*6*). The residue from the evaporation was moistened with hydrochloric acid, taken up in distilled water, transferred to a volumetric flask, and diluted to volume. Aliquots of this solution were then pipetted into 50-ml. volumetric flasks and the color was developed. The fluorspar samples were treated in the same manner except that it was not necessary to add hydrochloric acid.

The brass samples were treated with nitric acid, and the tin was removed as metastannic acid. The filtrate was

Table II. Results of Analysis of NBS Samples

	% Iron	
Sample	Present	Found
Sheet brass 37D	0.076	0.075
		0.076
		0.074
Cast bronze 52B	0.032	0.033
		0.032
		0.033
Ounce metal 134B	0.26	0.24
		0.25
		0.25
	% Iron(III) Oxide	
	Present	Found
Fluorspar 79D	0.15	0.15
		0.16
		0.16
Glass 93	0.076	0.077
		0.077
		0.076

Table III. Precision of Method by Ten Determinations on Same Sample

	% Fe_2O_3 Found	Dev. from Av.
	2.56	+0.01
	2.51	−0.04
	2.53	−0.02
	2.54	−0.01
	2.57	+0.02
	2.57	+0.02
	2.55	0.00
	2.54	−0.01
	2.55	0.00
	2.53	−0.02
	Av. 2.55	——
Fe_2O_3 by titration, %	2.57	——

then treated with ammonium hydroxide and the resultant precipitate, containing the iron, was washed free of copper. The precipitate was dissolved from the paper and the solution evaporated almost to dryness to remove the excess acid. The cooled solution was then filtered into a volumetric flask and the color developed in the manner indicated earlier.

The results of these analyses are listed in Table II.

PRECISION

The precision of the method was tested by analyzing 10 samples of a cement by the method outlined above for the determination of iron in glass. The results of these analyses are presented in Table III. A statistical analysis of the data indicates that this method is capable of results with a maximum deviation from the mean of 0.04% and an average deviation of 0.02%. Expressed in terms of the amount present, the average deviation is 0.8%.

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Spectrophotometric Determination of Uranium with Thiocyanate in Butyl Cellosolve–Methyl Isobutyl Ketone–Water Medium

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▶ A spectrophotometric method for the determination of uranium in ores and leach liquors consists of separation of uranium from interfering ions by extraction into methyl isobutyl ketone, using aluminum nitrate as a salting agent, followed by development of the color in a portion of the extract with a solution of ammonium thiocyanate in a butyl Cellosolve–water solvent. The yellow uranyl thiocyanate complex forms immediately, and the color is stable for at least 48 hours. The optimum range of uranium concentration at 375 mμ is from 0.4 to 2.0 mg. of uranium oxide (U_3O_8) in the sample aliquot. The coefficient of variation of absorbance measurements on standard solutions at 375 mμ was 0.34%. Titanium is the only serious interference, but procedures are given which make it possible to analyze samples containing as much as 5 mg. of titanium in the sample aliquot.

Various modifications of the spectrophotometric determination of uranium with thiocyanate have been proposed. Currah and Beamish (*4*) first used thiocyanate as a colorimetric reagent for the determination of uranium. The yellow uranyl thiocyanate color was developed in an aqueous solution, and stannous chloride was recommended to prevent the interference of iron(III). Nelson and Hume (*12*), who examined the procedure with respect to errors inherent in the analytical method and possible interferences, developed a more reproducible and sensitive method. Henicksman (*11*) made a thorough investigation of interferences and first recognized the serious interference of vanadium.

Although the method may be applied to the analysis of certain materials, such as monazite concentrates (*20*), without preliminary separation of the uranium, most of the recent papers have been concerned with the removal of anionic and cationic interferences. Crouthamel and Johnson (*2*) found that the stannous chloride reductant, in the presence of uranium and ammonium thiocyanate in aqueous solution, generated an interference peak around 375 μ, which became more serious as the thiocyanate solution aged. By developing the color in an acetone-water solvent, Crouthamel and Johnson were able to inhibit this attack of thiocyanate by stannous chloride. The use of an acetone-water solvent eliminated the majority of the anionic interferences in the aqueous thiocyanate method, increased the sensitivity, enhanced the stability of color, and made the correct color development independent of pH in the acid region. However, several elements, such as vanadium and titanium, cannot be tolerated.

The extraction of the colored uranyl thiocyanate complex into amyl alcohol or ethyl ether in order to eliminate some of the interferences was recommended by Gerhold and Hecht (*7*), and dibutoxy tetraethylene glycol has recently been used in a similar manner (*18*). The ethyl acetate extraction of uranium from a nitrate solution, first recommended by Grimaldi and Levine (*9*), has been utilized in several procedures which involve recovery of the uranium from the ethyl acetate phase and determination with thiocyanate in water (*8, 10*) or in an acetone medium (*6*).

A method (*5, 13*) for the analysis of uraniferous ores and leach liquors consists of extraction of the uranium from an aluminum nitrate solution into ethyl acetate, followed by color development in a portion of the ethyl acetate extract with a solution of ammonium thiocyanate and stannous chloride in an acetone-water solvent.

This method offers several advantages over the other reported modifications of the determination of uranium with thiocyanate. Interferences are eliminated by the preliminary separation of uranium more efficiently than by extraction of uranyl thiocyanate after the color development. Less time is required than for other procedures involving a preliminary extraction separation, because the color is developed directly on the extract. Higher sensitivity is obtained in the acetone–ethyl acetate–water solvent. A slightly modified version of this method has been used at the Oak Ridge National Laboratory (*19*), and from the University of Utah it was reported (*15*) that "highly accurate results may be quickly obtained by this procedure."

However, this procedure has several limitations. The chromogenic reagent is stable for only 3 hours and is usually prepared no more than 1 hour before use. The yellow color of the uranyl thiocyanate complex is stable for only 10 minutes and becomes more intense on standing. While the increase amounts only to 3% after 1 hour, this behavior limits the number of samples which can be prepared at one time. The procedure is not applicable when the sample aliquot contains more than 2 mg. of vanadium, because the tolerable limit of vanadium is exceeded, and most alkaline leach liquors require an initial neutralization with nitric acid for quantitative extraction of uranium into ethyl acetate. The acetone–ethyl acetate–water solution of ammonium thiocyanate tends to creep in the cells and volatilizes to leave a residue of ammonium thiocyanate around the edge of the absorption cells.

This paper describes the experimental work leading to a revised method, in which all the previous difficulties are eliminated. The substitution of butyl Cellosolve for acetone in the chromogenic reagent reduces the volatility of the colored solution and eliminates the creeping of the solution in the absorption cells. Instead of stannous chloride, ascorbic acid is used as the reducing agent. As a result of using a milder reducing agent, the chromogenic reagent and the colored solutions do not deteriorate for at least 48 hours. The tolerable limit of vanadium is greatly increased, as the seriously interfering vanadium(III) species is not formed in the colored solution. The use of methyl isobutyl ketone as the extractant for uranium results in a more selective separation from other cations and makes it possible to analyze alkaline leach liquors directly without prior neutralization.

After this work was essentially completed, Paley (*14*) reported a similar procedure in which the uranium is extracted into methyl ethyl ketone and the color is developed by mixing the organic phase with a solution of ammonium thiocyanate and ascorbic acid in acetone. However, in his procedure, two extractions are required and it is advised that the color intensity be measured within 30 minutes. Vanadium, titanium, bismuth, and molybdenum are extracted and interfere, so that special separations are required.

APPARATUS AND REAGENTS

All quantitative measurements were made with the Beckman Model DU spectrophotometer using 1-cm. Corex and silica cells.

The extraction separations were performed in 40-ml. vials, 4.25 inches long and 1 inch in diameter. Although the vials were washed and re-used, the screw caps, which are lined with aluminum foil, are so inexpensive that they may be discarded after use. The extractions were performed on a variable-speed, box-carrier shaking machine, whose platform was fitted with a wooden insert to hold the vials in a horizontal position.

Machlett Autopipets, 15- and 20-ml. capacity, were used to deliver the chromogenic reagent and the extractant.

Standard uranium solutions were prepared from MS-ST grade uranium oxide (U_3O_8) dissolved in perchloric acid.

The salting agent was prepared in a 4-liter beaker by slowly heating a mixture of 500 ml. of deionized water and 1880 grams of reagent grade aluminum nitrate nonahydrate, obtained from the J. T. Baker Chemical Co. The solution was cooled slightly, 200 ml. of 1 to 1 ammonium hydroxide were slowly added, and the mixture was stirred until the precipitate dissolved. After cooling to room temperature, the solution was diluted to 2 liters with deionized water. The salting agent for samples containing titanium was prepared in a similar manner; however, before diluting to volume, 60 grams of reagent grade tartaric acid were dissolved in the mixture, 60 ml. more of 1 to 1 ammonium hydroxide were added, and the mixture was stirred until the precipitate dissolved.

The chromogenic reagent was prepared by dissolving 46 grams of reagent grade ammonium thiocyanate, obtained from Baker and Adamson, and 2 grams of reagent grade *l*-ascorbic acid in a solution of 11 parts of butyl Cellosolve and 4 parts of water to a final volume of 150 ml.

Purified grade butyl Cellosolve (ethylene glycol monobutyl ether) and methyl isobutyl ketone were used as solvent and extractant, respectively.

RECOMMENDED PROCEDURE

Aqueous samples are diluted to a concentration of 0.2 to 2.0 grams of uranium oxide (U_3O_8) per liter if absorbance measurements are to be made at 375 mμ, or analyzed as received if the absorbance measurements are to be made at longer wave lengths. Organic samples, such as those from solvent extraction studies, are best treated by stripping the uranium into aqueous carbonate solution before proceeding with any dilution. Ore and concentrate samples are decomposed by any suitable method and diluted to a convenient volume after neutralizing any large amounts of caustic or acid.

An aliquot of the sample (no more than 3 ml.) is transferred into a 40-ml. vial. If the sample is strongly acid or alkaline, or is in a concentrated buffer solution, especially carbonate-bicarbonate, the pH is adjusted to 0 to 3 by the dropwise addition of nitric acid or concentrated sodium hydroxide. Approximately 15 ml. of the appropriate aluminum nitrate reagent are added, followed by exactly 20 ml. of methyl isobutyl ketone. The vial is capped and shaken for 2 minutes. The organic and aqueous phases are completely separated by centrifugation. Ten milliliters of the organic phase are transferred by pipet into another vial, and 15 ml. of the chromogenic reagent are added. The vial is capped and the solution is mixed well. A reagent blank is prepared in the same manner as the samples. The absorbance is measured against the reagent blank at 375 mμ (slit width, 0.10 mm.) or, if the absorbance is greater than 1.0, at 420 mμ (slit width, 0.060 mm.).

EXPERIMENTAL

Color Developing Reagent. During the investigation of a spectrophotometric procedure for the determination of molybdenum with thiocyanate (*21*), it was observed that a butyl Cellosolve–water solvent had several properties which made it superior to the acetone-water solvent used in the similar determination of uranium with thiocyanate. The butyl Cellosolve–water solvent exhibited no tendency to creep in the absorption cells, the solvent did not volatilize appreciably, and the stability of the molybdenum(V) thiocyanate color was enhanced. It seemed that butyl Cellosolve might be profitably substituted for acetone in the preparation of the chromogenic reagent for the determination of uranium.

A mixture of at least 11 parts of butyl Cellosolve to 4 parts of water forms a homogeneous solution with 10 ml. of the ethyl acetate used to extract uranium from the sample aliquot. The greater the water concentration in the Cellosolve-water mixture, the more ammonium thiocyanate can be dissolved. A mixture of 11 parts of butyl Cellosolve to 4 parts of water was chosen as the solvent for the ammonium thiocyanate reagent for all future work.

Ten-milliliter aliquots of an ethyl acetate solution containing 0.025 gram of uranium oxide (U_3O_8) per liter as uranyl nitrate were added to 15 ml. of the solvent containing 0.67% (w./v.) of stannous chloride and various concentrations of ammonium thiocyanate. The intensity of the resulting color was measured against a blank of similar composition at 375 mμ. The following results were obtained:

M NH_4SCN	1	2	3	4
Absorbance	0.134	0.157	0.173	0.186

A 4M solution of ammonium thiocyanate in the butyl Cellosolve–water solvent is a saturated solution, and is the obvious choice, because it yields the most intense color. The limit of solubility of either sodium or potassium thiocyanate is about the same as the ammonium salt.

The colored solutions did not volatilize or creep in the absorption cells. The color intensity was 3% greater with the reagent consisting of 4M ammonium thiocyanate in the butyl Cellosolve–water solvent as compared to the use of 6M ammonium thiocyanate in an acetone-water solvent.

Reducing Agent. In most variations of the thiocyanate procedure for uranium, stannous chloride is used to eliminate any iron(III) interference by reducing the iron to the ferrous state. However, stannous chloride reduces vanadium to the trivalent state, which, in the presence of thiocyanate, has a strong absorption band in the near-ultraviolet region of the spectrum. A milder reducing agent such as ascorbic acid, which would reduce any traces of iron but reduce vanadium only to the quadrivalent state, should increase the tolerable limit of vanadium.

In order to compare ascorbic acid and stannous chloride, mixtures of 1.00 mg. of uranium oxide (U_3O_8) and various concentrations of vanadium (IV or V) were prepared. The proper amount of aluminum nitrate was added to each solution, and the mixtures were extracted with ethyl acetate in the usual manner. The color was developed in a 10-ml. portion of the ethyl acetate extract with 15 ml. of the chromogenic reagent containing 0.67% (w./v.) of either stannous chloride or ascorbic acid, so that the concentration of reductant in the colored solution was 0.4% (Table I).

Table I. Effect of Reductant on Vanadium Interference

Vanadium Added, Mg.		Resultant % Error		
V(V)	V(IV)	$SnCl_2$	Ascorbic acid	
		0.4	0.4	0.8
2.0	...	5.9	2.2	1.4
4.0	...	5.9	3.0	1.4
...	2.0	1.4	0.3	0.0
...	5.0	4.3	0.5	0.5

While the reducing normality of each reagent was approximately the same, a lower interference was observed with the ascorbic acid reductant. A similar test indicated that increasing the ascorbic acid concentration to 0.8% (w./v.) in the colored solution resulted in a further diminution of the vanadium interference as is also shown in Table I.

The chromogenic reagent adopted for further studies consisted of 46 grams of ammonium thiocyanate and 2 grams of *l*-ascorbic acid dissolved in a solution of 11 parts of butyl Cellosolve and 4 parts of water to a final volume of 150 ml. This reagent is stable for at least 2 days—i.e., uranium standards analyzed with the same reagent gave identical absorbance readings for at least 2 days. Therefore the use of ascorbic acid instead of stannous chloride not only increases the tolerable limit of vanadium, but, even more important, eliminates the deterioration of the chromogenic reagent.

Extraction Medium. The solvent extraction system used for the separation of uranium during the investigations leading to the development of the butyl Cellosolve–ascorbic acid–thiocyanate reagent consisted of an aqueous phase of nearly saturated aluminum nitrate solution and ethyl acetate as the organic phase. The optimum acidity recommended (*9*) for extraction of uranium by ethyl acetate from aluminum nitrate solutions is 7 volume % nitric acid. While sulfuric acid leach solutions may be extracted by using 1- or 2-ml. aliquots and 10 to 15 ml. of saturated aluminum nitrate solution, carbonate liquors have to be acidified in order to obtain complete extraction of uranium. An extraction reagent which could be used without careful control of the acidity was desired. It has been reported (*3*) that the distribution coefficient of uranyl nitrate into methyl isobutyl ketone is not appreciably affected by the acid content of the aluminum nitrate reagent and the separation of uranium from fission products is greatly improved by using "acid deficient" aluminum nitrate—i.e., by neutralizing some of the acid formed by the hydrolysis of the salt.

The effect of aluminum nitrate concentration and of added ammonium hydroxide in the salting agent on the extraction of uranium by methyl isobutyl ketone and the separation of uranium from vanadium was evaluated.

One-milliliter aliquots of solutions containing 1.00 mg. of uranium oxide per ml. and between 0 and 25 mg. of vanadium(IV) per ml. were extracted with 20 ml. of methyl isobutyl ketone using as the salting agent 15 ml. of aluminum nitrate solutions varying between 1.6 and 2.7M in aluminum nitrate and containing up to 10 volume % of concentrated ammonium hydroxide. A 10-ml. portion of the methyl isobutyl ketone extract and 15 ml. of the butyl Cellosolve–ascorbic acid–thiocyanate reagent were mixed and the resultant color intensity was measured against a suitable blank at 375 mμ.

The optimum concentration of aluminum nitrate for the extraction of uranium was found to be 2.3 to 2.7M containing up to 10 volume % of concentrated ammonium hydroxide. At values of less than 2.3M aluminum nitrate, the efficiency of the uranium extraction decreases. The optimum concentration of aluminum nitrate for the separation of uranium from vanadium was found to be 2.3 to 2.5M aluminum nitrate containing up to 10 volume % of concentrated ammonium hydroxide. At values greater than 2.5M aluminum nitrate, the interference of vanadium (IV) became more serious. A salting agent containing 2.5M aluminum nitrate and 5 volume % of ammonium hydroxide is recommended. This reagent is acidic (pH 0.7) and will buffer dilute acid or basic samples between pH 0.5 and 1.0.

Choice of Wave Length. As in the other versions of this method, no absorption peak for the uranyl thiocyanate complex was observed in the visible region of the spectrum. Crouthamel and Johnson have reported (*2*) that absorbance measurements should not be made at wave lengths shorter than 375 mμ in the acetone-water solvent because uranium and several other ions fluoresce in this region of the spectrum. It was found in this laboratory that measurements below 360 mμ are erratic, and very wide slit widths are required to zero the instrument for the reagent blank. However, reproducible calibration data which obey Beer's law were obtained at 360, 375, 400, and 420 mμ, and presumably could be obtained at any other wave length in this region. The data reported in this paper were all taken at 375 mμ, but in practice, solutions which are highly colored are measured at 420 mμ.

Color Stability. Absorbance measurements at various time intervals showed that the yellow color of the uranyl thiocyanate complex formed immediately in the methyl isobutyl ketone–butyl Cellosolve–water medium, and was stable for at least 48 hours after about 15 minutes required to reach a constant absorbance. A study on the effect of temperature showed a change in absorbance of only 1% between 15° and 25° C.

Efficiency of Extraction. One-milliliter aliquots of standard uranium solutions ranging in concentration from 0.10 to 10.0 mg. of uranium oxide per ml. were diluted with 15 ml. of aluminum nitrate reagent. After extraction of the uranium with 20 ml. of methyl isobutyl ketone, the aqueous layer was analyzed fluorometrically (*1*) to determine the amount of uranium unextracted.

An average extraction of 99.2% was

Table II. Efficiency of Extraction of Uranium from Aluminum Nitrate into Methyl Isobutyl Ketone According to the Recommended Procedure

U_3O_8 Taken for Extraction, Mg.	U_3O_8 Found after Extraction, Mg.	Extraction, %
0.100	0.00058	99.4
0.200	0.0019	99.1
0.500	0.0055	98.9
1.00	0.0078	99.2
1.50	0.012	99.2
2.00	0.016	99.2
2.50	0.023	99.1
5.00	0.040	99.2
10.0	0.066	99.2
	Av.	99.2
	Coefficient of variation	0.14%

obtained (Table II). Not only is the extraction nearly quantitative, but it is reproducible over the concentration range studied.

Calibration Data. Calibration data were obtained by treating 1-ml. aliquots of standard uranium solutions, ranging in concentration from 0.100 to 5.00 grams of uranium oxide per liter, according to the recommended procedure. For the eight solutions prepared, the range of absorbance index obtained was 0.370 to 0.374, the average was 0.371, and the coefficient of variation was 0.34%. The absorbance index is in such units that 1 ml. of a 1.00 gram of uranium oxide per liter of solution treated according to the recommended procedure yields a solution with an absorbance of 0.371 at 375 mμ.

In order to determine the optimum range of uranium concentration for a minimum spectrophotometric error, a Ringbom (*16*) plot was made from the data obtained. The optimum range found was from 0.2 to 1.0 mg. of uranium oxide in the 25 ml. of colored solution.

Interferences. The possible interference of various anions with the extraction of uranium into methyl isobutyl ketone was evaluated. Synthetic solutions containing 1.00 mg. of uranium oxide in either 1M chloride, carbonate, bicarbonate, phosphate, and sulfate or 4M tartrate were treated according to the recommended procedure. There was no interference with the extraction of uranium due to the presence of these anions.

The extent of separation of uranium from the various cations reported to interfere in the thiocyanate method was determined. Synthetic mixtures containing 1.00 mg. of uranium oxide and 100 mg. of the possible interference in a volume of 3 ml. were treated according to the recommended procedure. The absorbance for the solutions containing cobalt(II), chromium(VI), copper(II), iron(III), molybdenum(VI), manganese(II), nickel(II), lead(II), and thorium(IV) was the same as expected for uranium alone within the limits of reproducibility, and the presence of mercury resulted in about a 1% increase in absorbance. Forty milligrams of zirconium(IV) caused a negative error equivalent to 0.01 mg. of uranium oxide. The presence of 20 mg. of vanadium(IV) in the sample aliquot caused a positive error equivalent to 0.02 mg. of uranium oxide. Titanium precipitated in the extraction vial and occluded uranium, causing negative results. The presence of at least 5 mg. of titanium in the sample aliquot can be tolerated with a maximum negative error of 0.02 mg. of uranium oxide either by the addition of 1 ml. of 3M tartaric acid at pH 1 to the aliquot before adding the aluminum nitrate reagent or by use of the aluminum nitrate–tartaric acid mixture described under the reagents.

Table III. Comparative Analyses

Sample	U_3O_8, % Spectrophotometric	Standard value
Standard ore (NBL 3)	3.40	3.32 ± 0.08[a]
Concentrate 1	72.3	72.3[b]
Concentrate 2	81.5	81.3[b]
	U_3O_8, Grams/Liter	
ESP 2031	1.14	1.15[c]
JTL 242A	1.84	1.83
JTL 250	2.22	2.21
GXT 1573	0.992	0.989
HFF 968	0.300	0.307
WES 732	1.13	1.15
KPQ 2523	2.90	2.91

[a] Certified average value and range limits at 95% confidence level.
[b] Based on volumetric analysis.
[c] Results obtained by former spectrophotometric method (*5*, *13*).

RESULTS

In order to test the method, a standard uranium ore, two uranium concentrates, and a number of process samples in both acid and carbonate medium were analyzed according to the recommended procedure (Table III). The spectrophotometric analysis of the only suitable standard ore sample was within the range limits of the certified value at the 95% confidence level. Excellent agreement with the volumetric method (*17*) was obtained on the determination of uranium in concentrates. The average per cent deviation of the results obtained by the proposed spectrophotometric procedure on the process samples was 0.9% from the analyses obtained by the spectrophotometric method formerly used.

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Quantitative Analysis of Anatase-Rutile Mixtures with an X-Ray Diffractometer

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► An analytical procedure based on x-ray diffraction intensities is presented for the determination of the relative amounts of anatase and rutile in their mixtures.

Titanium dioxide may be incorporated into a plastics molding compound to adjust the dielectric constant to a desired value. Either anatase or rutile may be used; these allotropic forms differ in dielectric behavior. Neither is available commercially in a pure state; a preparation consisting largely of one form is apt to contain, in addition to other impurities, an admixture of the other. In order to permit proper formulation of filled resins, therefore, it is desirable to establish a method for determining the relative amounts of anatase and rutile in mixtures. The application of photometry to this problem has been discussed (*2,6*). This paper develops a method using the more precise technique of diffractometry.

APPARATUS AND MATERIALS

The instrument used was a Norelco Geiger-counter x-ray diffractometer equipped with voltage and current stabilizers, counters, and a strip-chart recorder; it was operated at a voltage of 35 kv. with a filament current of 25 ma. Scanning speed was 0.25° per minute; the width of the receiving slit was 0.003°. For rapidity and convenience, most of the intensity data were obtained from the strip chart and showed a satisfactory agreement with the results obtained by direct counting. The accuracy and reproducibility of this type of instrument have been discussed by Klug and coworkers (*3, 5*). The strongest reflections for anatase and rutile are conveniently located for Cu$K\alpha$ radiation at the Bragg angles 12.68° and 13.73°, respectively.

The materials studied are two commercial products, one of which is largely anatase (A) and the other largely rutile (R). When total titanium dioxide was determined by the method of Rahm (*7*), the percentages found in three determinations were A. 98.00, 97.68, 98.08; average: 97.92. R. 98.70, 98.73, 98.62; average: 98.68. The values for the weight fractions of anatase in anatase-rutile mixtures determined by the method described are insensitive to several per cent variations in the total titanium dioxide content.

Particle diameters smaller than 5 microns are desirable to ensure adequate reproducibility of diffraction intensity measurements (*4*). Electron micrographs taken at a magnification of 36,000 diameters indicate that particle diameters are 0.04 to 0.6 micron for anatase and 0.08 to 0.5 micron for rutile. The particle sizes are, therefore, sufficiently small for reproducibility of intensity measurements.

RESULTS AND METHOD OF CALCULATION

For a given sample, the ratio (I_A/I_R) of the intensity of the strongest anatase reflection to the intensity of the strongest rutile reflection is independent of fluctuations in diffractometer characteristics. This ratio therefore provides a useful index of sample composition. The first three columns of Table I show the weights of A and R in the samples; the average values of I_A/I_R were found from a total of 53 determinations.

The intensity data show that the A material contains a small amount of rutile and the R material a small amount of anatase. If A were pure anatase, the value of I_A/I_R for sample 11 would be infinite; and if R were pure rutile, the value of this ratio for sample 1 would be zero. It is not difficult, however, to estimate the impurities in A and R to a sufficient degree of accuracy to establish an analytical method for anatase and rutile.

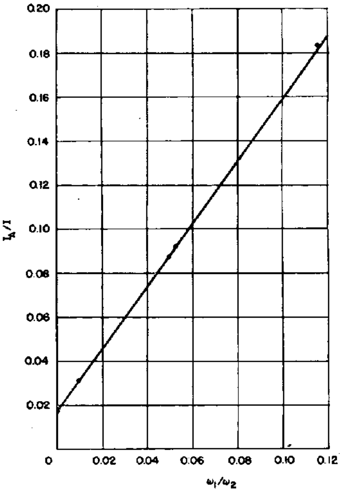

Figure 1. Intensity ratio as a function of weight ratio for small w_1

Table I. Compositions and X-Ray Intensity Data for Anatase-Rutile Mixtures

Sample No.	w_1, Weight of A, G.	w_2, Weight of R, G.	I_A/I_R Intensity Ratio	x_A, Weight Fraction of Anatase	$f = \frac{1}{1 + 1.265 \frac{I_R}{I_A}}$ Intensity Function
1	0	1.997	0.0165	0.0112	0.0115
13	0.0099	0.9898	0.0312	0.0205	0.0240
16	0.0399	0.8002	0.0869	0.0564	0.0573
14	0.0501	0.9500	0.0920	0.0588	0.0677
2	0.202	1.749	0.183	0.110	0.126
3	0.451	1.335	0.431	0.252	0.253
4	0.626	1.121	0.680	0.350	0.349
5	0.822	1.022	0.941	0.438	0.426
6	0.996	0.918	1.21	0.510	0.489
7	1.290	0.622	2.31	0.658	0.645
8	1.502	0.518	3.28	0.724	0.722
9	1.726	0.355	5.31	0.807	0.809
10	2.856	0.268	9.54	0.889	0.883
15	0.9501	0.0496	13.51	0.919	0.915
11	2.050	0	55.9	0.972	0.978

The first three columns of Table I give the weight of A (97.9% TiO_2, largely anatase), the weight of R (98.7% TiO_2, largely rutile), and the ratio of the intensity of the strongest anatase reflection to that of the strongest rutile reflection for the various sample mixtures. The last two columns give the weight fraction of anatase and a function of the intensity ratio that approximates the weight fraction of anatase.

For a given sample, the relation between the weight ratio and the intensity ratio for anatase and rutile is given by the expression

$$\frac{w_A}{w_R} = K\frac{I_A}{I_R} \qquad (1)$$

where w_A and w_R are the weights of anatase and rutile, respectively, in the sample. It is known that, for mixtures of allotropes, intensity of scattering for each component is substantially proportional to its weight fraction (*1*). It may be expected, therefore, that K will be approximately constant over narrow ranges of concentration.

The weight of pure anatase in the sample is given by the equation

$$w_A = a_1w_1 + a_2w_2 \qquad (2)$$

where w_1 is the weight of A, w_2 is the weight of R, a_1 is the weight fraction of anatase in A, and a_2 is the weight fraction of anatase in R. A similar expression gives the weight of pure rutile in the sample:

$$w_R = r_1w_1 + r_2w_1 \qquad (3)$$

where r_1 and r_2 are the weight fractions of rutile in A and R, respectively. Substitution of Equations 2 and 3 in 1 gives

$$\frac{a_1w_1 + a_2w_2}{r_1w_1 + r_2w_2} = K\frac{I_A}{I_R} \qquad (4)$$

r_1 is small compared with unity; therefore, for small w_1, r_1w_1 may be neglected in comparison with r_2w_2. The following approximate equation can thus be derived:

$$\frac{I_A}{I_R} = \frac{1}{K_1}\frac{a_2}{r_2} + \frac{1}{K_1}\frac{a_1}{r_2}\frac{w_1}{w_2} \text{ (for small } w_1\text{)} \qquad (5)$$

Here K_1 denotes the value of K in the region where w_1 is small compared with w_2. Figure 1 is a graph of I_A/I_R *vs.* w_1/w_2. The fact that the points lie near a straight line is an indication that K_1 is approximately constant in this concentration range. The equation for the line is

$$\frac{I_A}{I_R} = 0.0165 + 1.425\,\frac{w_1}{w_2} \qquad (6)$$

Similarly a_2 is small compared with unity and, for small w_2, the term a_2w_2 may be neglected in comparison with a_1w_1; the equation obtained is

$$\frac{I_R}{I_A} = K_2\frac{r_1}{a_1} + K_2\frac{r_2}{a_1}\frac{w_2}{w_1} \text{ (for small } w_2\text{)} \qquad (7)$$

where K_2 is the value of K in the region where w_2 is small compared with w_1. Figure 2 is a graph of I_R/I_A *vs.* w_2/w_1 in this region. The straight line drawn may be represented by the equation

$$\frac{I_R}{I_A} = 0.0230 + 0.820\,\frac{w_2}{w_1} \qquad (8)$$

There are now six unknown quantities—a_1, r_1, a_2, r_2, K_1, and K_2—which may be related by the following six equations. The first four are obtained by comparing coefficients in Equations 5 through 8; the last two give the total amounts of titanium dioxide in A and R as determined by chemical analysis.

$$\begin{aligned} \frac{1}{K_1}\frac{a_2}{r_2} &= 0.0165 \\ \frac{1}{K_1}\frac{a_1}{r_2} &= 1.425 \\ K_2\frac{r_1}{a_1} &= 0.0230 \\ K_2\frac{r_2}{a_1} &= 0.820 \\ a_1 + r_1 &= 0.979 \\ a_2 + r_2 &= 0.987 \end{aligned} \qquad (9)$$

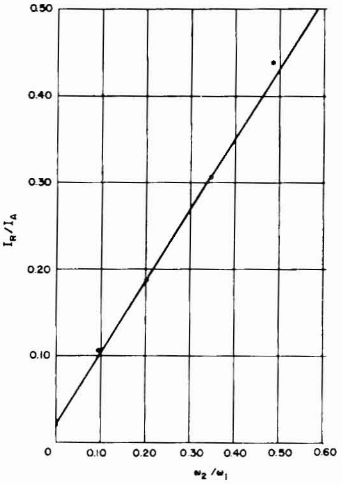

Figure 2. Intensity ratio as a function of weight ratio for small w_2

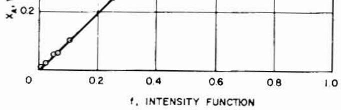

Figure 3. Weight fraction x_A as function of

$$f = \frac{1}{1 + 1.26\,\frac{I_R}{I_A}}$$

Solution of these simultaneous equations yields

$$\begin{aligned} a_1 &= 0.952 \\ r_1 &= 0.027 \\ a_2 &= 0.011 \\ r_2 &= 0.976 \\ K_1 &= 0.68 \\ K_2 &= 0.80 \end{aligned} \qquad (10)$$

It is seen that the A material contains 95.2% anatase and 2.7% rutile and that the R material contains 97.6% rutile and 1.1% anatase. It is now possible to calculate the weight fraction of anatase in the titanium dioxide for each sample; these values, given in the fourth column of Table I, may be considered reliable to within about 0.01 unit.

For the analysis of anatase-rutile mixtures, it is convenient to devise a function of the intensities that is approximately equal to the weight fraction x_A of anatase present. This weight fraction is given by

$$x_A = \frac{w_A}{w_A + w_R} \qquad (11)$$

The combining of Equations 11 and 1 yields

$$x_A = \frac{1}{1 + \frac{1}{K}\frac{I_R}{I_A}} \qquad (12)$$

If the variation of K with concentration is now neglected and if K is taken as 0.79, or $1/K$ as 1.26, an approximation to x_A is obtained that may be designated as f:

$$f = \frac{1}{1 + 1.26\,\frac{I_R}{I_A}} \qquad (13)$$

This quantity f is tabulated in the last column of Table I and a graph of x_A *vs.* f is shown in Figure 3. It can be seen that f is, in fact, approximately equal to x_A. A better fit for $x_A \leq 0.2$ could be obtained by taking $K = 0.68$ in this region of concentration.

The weight fraction of anatase in an anatase-rutile mixture may be determined by calculating f from the observed x-ray intensities and by referring to Figure 3.

The most important contribution to the experimental error in f arises from the lack of reproducibility of scattering intensities recorded by the diffractometer. Optimum precision can be obtained by the use of slow scanning speed, and by averaging several values of I_A/I_R, where the ratio contains two intensity values from the same run. It was found from 18 determinations that the standard error in f due to lack of instrument reproducibility is about 2%; the inclusion of other experimental errors suggests a standard error for f of 3 to 4%. Two experimental determinations of known mixtures led, however, to errors of only 0.9 and 0.2%.

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Steroid X-Ray Diffraction Powder Data

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▶ X-ray diffraction powder data and powder pattern photographs are presented for 32 steroids.

To continue the studies on the identification of steroids by x-ray powder diffraction, 32 additional compounds were investigated. Their interspacing data and powder pattern photographs are here reported. The earlier papers (1–3) in this series gave powder data for 106 steroids.

The x-ray patterns were obtained in 5 hours, using nickel-filtered copper x-radiation produced at a potential of 35 kv. and a current of 20 ma. (1,2). The methods of recrystallization used were the same as those discussed and used in the last paper of this series (3). The majority of the steroids were recrystallized from ethyl alcohol, the exceptions being noted in Table I.

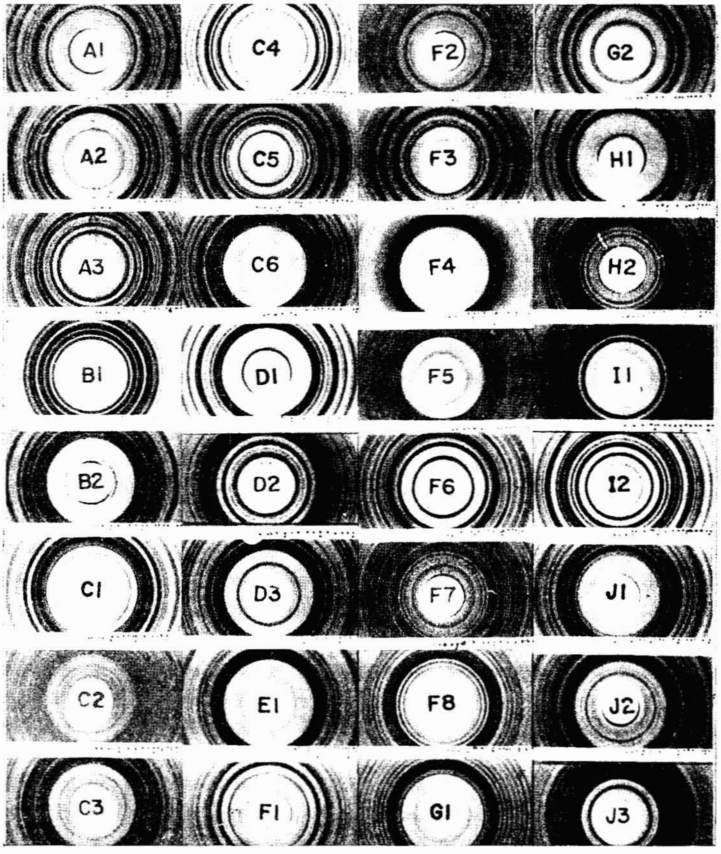

Figure 1. X-ray diffraction powder patterns of steroids

Key found in Table I

Table I. Index to Steroid X-Ray Diffraction Powder Data

Pattern No.	Name	Melting Point (Uncorr.), ° C.
	I. C_{18} STEROIDS	
A1	Equilenin	257–261
A2	Estrone methyl ether	167–169
A3	1-Methyl estrone	251–256
	II. C_{19-29} STEROIDS	
	B. Monohydric Alcohols	
B1	Androstane-17-ol	164.5–166.5
B2	Neosterol (75.5% ergosterol and 24.5% $\Delta^{7,22}$-ergostadien-3β-ol)[a]	164–168
	C. Dihydric Alcohols	
C1	$\Delta^{5,7}$-Androstadiene-3β, 17β-diol[b]	Dec. 225–228
C2	$\Delta^{5,7}$-Androstadiene-3β, 17β-diol-dibenzoate	218–220
C3	17-Ethynyl-Δ^{5}-androstene-3,17-diol	245–246
C4	Δ^{5}-Androstene-3β, 17-diol-diacetate	160–162
C5	Δ^{4}-Cholestene-3β, 6β-diol-diacetate	133.5–135
C6	Allopregnane-3β, 20-diol-diacetate	141–145
	D. Monoketones	
D1	Δ^{16}-Allopregnene-20-one	155.5–157.5
D2	Δ^{1}-Cholestene-3-one	103–106
D3	Androstane-17-one	115–120
	E. Diketones	
E1	Allopregnane-3, 20-dione	202–205
	F. Monohydroxymonoketones	
F1	Δ^{4}-Pregnene-20β-ol-3-one	166–168
F2	Δ^{4}-Androstene-17-ol-3-one-17-acetate-3-enol acetate (testosterone diacetate)	151–154
F3	Δ^{4}-Androstene-17-ol-3-one-17-propionate-3-enol propionate (testosterone dipropionate)[a]	123–126
F4	Androstane-17-ol-3-one-17-acetate (dihydrotestosterone acetate)	157–159
F5	Androstane-17β-ol-3-one-17-hexahydrobenzoate (dihydrotestosterone hexahydrobenzoate)	161–163
F6	Pregnane-3β-ol-20-one-3-acetate	112–115
F7	Allopregnane-3β-ol-20-one-3-acetate	144–146
F8	Etiocholane-17β-ol-3-one-17-acetate	146–148
	G. Dihydroxymonoketones	
G1	Pregnane-3α, 17α-diol-20-one	215–218.5
G2	Allopregnane-3, 21-diol-20-one-21-acetate	210–203.5
	H. Trihydroxymonoketones	
H1	Δ^{5}-Pregnene-3β, 17, 21-triol-20-one-3,21-diacetate (17-hydroxy-21-acetoxy pregnenolone acetate)	267–270
H2	Allopregnane-3β, 17α, 21-triol-20-one-21-acetate[c]	231–235
	III. BILE ACID ESTERS	
	I. Carboalkoxy Esters	
I1	Methyl 3-acetoxy-12-ketocholanate	145–148
I2	Methyl 3-keto-12β-acetoxycholanate	118–119
	IV. STEROIDAL SAPOGENINS AND DERIVATIVES	
J1	Δ^{4}-Hexogenone	Dec. 233–235
J2	Hecogenin	261–262
J3	Smilogenone	181–186

[a] Acetone.
[b] Ethyl alcohol and ethyl ether.
[c] Methanol.

Table II. X-Ray Diffraction Powder Data for Steroids

I. C_{18} STEROIDS

A1. Equilenin

d, A.	I/I_1
12.4	0.11
7.00	0.06
6.44	0.20
5.65	0.03
5.17	1.00
4.82	0.06
4.44	0.06
4.18	0.06
3.72	0.53
3.32	0.20
3.21	0.06
3.08	0.03
2.96	0.03
2.78	0.04
2.59	0.01
2.48	0.03
2.41	0.04
2.35	0.06
2.27	0.01
2.22	0.01
2.17	0.01
2.12	0.04
2.05	0.03
1.96	0.03
1.91	0.01
1.85	0.01
1.80	0.01
1.73	0.01

A2. Estrone Methyl Ether

d, A.	I/I_1
9.16	0.06
7.31	0.04
6.52	0.03
5.79	1.00
5.07	0.40
4.60	0.11
4.40	0.20
4.06	0.11
3.82	0.01
3.64	0.03
3.44	0.73
3.33	0.20
3.13	0.04
2.97	0.15
2.87	0.06
2.71	0.11
2.60	0.11
2.50	0.11
2.41	0.06
2.31	0.08
2.27	0.08
2.22	0.11
2.18	0.08
2.15	0.11
2.11	0.04
2.04	0.08
1.95	0.06
1.92	0.08
1.87	0.06
1.82	0.04

A3. 1-Methyl Estrone

d, A.	I/I_1
8.68	0.03
8.12	0.38
6.71	0.56
6.35	0.05
6.01	0.05
5.54	0.75
5.35	0.08
4.90	1.00
4.50	0.08
4.30	0.08
4.05	0.38
3.87	0.56
3.68	0.15
3.38	0.28
3.25	0.28
3.14	0.03
3.08	0.20
2.98	0.20
2.89	0.11
2.76	0.01
2.63	0.15
2.53	0.11
2.46	0.05
2.40	0.20
2.35	0.15
2.30	0.15
2.23	0.05
2.15	0.20
2.09	0.08
2.03	0.08
1.96	0.15
1.93	0.11
1.86	0.15
1.79	0.20

II. C_{19-29} STEROIDS

B. Monohydric Alcohols

B1. Androstane-17-ol

d, A.	I/I_1
12.8	0.05
9.87	0.05
7.53	0.41
6.54	0.73
5.83	1.00
5.54	0.55
5.02	0.73
4.76	0.55
4.29	0.27
4.01	0.20
3.79	0.08
3.65	0.15
3.44	0.05
3.32	0.05
3.19	0.20
3.08	0.05
3.00	0.05
2.73	0.20
2.63	0.11
2.53	0.08
2.45	0.08
2.36	0.02
2.21	0.20
2.14	0.08
2.09	0.11
1.98	0.08
1.90	0.08
1.81	0.02
1.77	0.02

B2. Neosterol

d, A.	I/I_1
13.3	0.08
11.4	0.11
9.51	0.01
6.82	0.01
6.15	0.73
5.80	0.53
5.31	1.00
5.04	0.63
4.62	0.20
4.34	0.87
4.14	0.11
3.93	0.30
3.80	0.06
3.64	0.06
3.42	0.35
3.28	0.30
3.00	0.08
2.94	0.08
2.87	0.11
2.78	0.08
2.73	0.08
2.67	0.15
2.43	0.04
2.36	0.06
2.29	0.15
2.21	0.04
2.18	0.15
2.12	0.01
2.08	0.08
2.02	0.03
1.97	0.03
1.93	0.11
1.85	0.04
1.77	0.04
1.72	0.06

C. Dihydric Alcohols

C1. $\Delta^{5,7}$-Androstadiene-3β, 17β-diol

d, A.	I/I_1
14.3	0.05
12.5	0.05
8.35	0.08
7.44	0.11
6.17	0.11
5.82	0.08
5.47	1.00
5.21	1.00
4.90	0.08
4.75	1.00
4.25	0.55
3.91	0.11
3.75	0.11
3.62	0.05
3.35	0.27
3.09	0.20
3.01	0.20
2.92	0.11
2.73	0.08
2.49	0.11
2.34	0.03
2.25	0.05
2.17	0.05
2.03	0.08
1.80	0.08

C2. $\Delta^{5,7}$-Androstadiene-3β,17β-diol dibenzoate

d, A.	I/I_1
12.3	0.08
8.27	0.15
6.61	0.06
6.03	0.73
5.51	1.00
4.98	0.40
4.58	0.25
4.17	1.00
3.96	0.30
3.76	0.17
3.60	0.17
3.41	0.06
3.25	0.46
3.14	0.11
3.01	0.25
2.92	0.04
2.83	0.11
2.75	0.15
2.68	0.11
2.59	0.20
2.49	0.08
2.40	0.34
2.31	0.04
2.26	0.04
2.20	0.04
2.14	0.06
2.11	0.11
2.07	0.06
2.04	0.06

C3. 17-Ethynyl-Δ^5-androstene-3,17-diol

d, A.	I/I_1
12.1	0.06
10.6	0.04
8.51	0.15
6.44	0.40
5.74	1.00
5.21	0.20
4.76	0.25
4.52	0.13
4.30	0.53
4.12	0.30
3.86	0.18
3.75	0.11
3.56	0.03
3.36	0.06
3.24	0.20
3.10	0.15
2.94	0.11
2.86	0.04
2.79	0.20
2.67	0.15
2.60	0.08
2.49	0.10
2.41	0.08
2.35	0.10
2.26	0.08
2.20	0.08
2.15	0.15
2.12	0.13
2.08	0.13
2.02	0.08
1.95	0.04
1.89	0.01
1.86	0.11

C4. Δ^5-Androstene-3β,17-diol diacetate

d, A.	I/I_1
14.7	0.27
7.40	0.27
6.89	0.03
5.93	1.00
5.55	0.15
5.08	0.37
4.76	1.00
4.59	0.37
4.20	0.20
4.02	0.27
3.76	0.10
3.64	0.15
3.51	0.20
3.42	0.15
3.32	0.20
3.20	0.10
2.92	0.15
2.84	0.10
2.74	0.10
2.64	0.15
2.54	0.10
2.40	0.15
2.32	0.15
2.30	0.15
2.13	0.03
2.02	0.10
1.98	0.07
1.91	0.10
1.86	0.03

C5. Δ^4-Cholestene-3β,6β-diol diacetate

d, A.	I/I_1
15.6	0.06
12.5	0.08
10.8	0.11
8.98	0.01
7.73	0.08
7.03	0.11
6.26	0.40
5.75	0.04
5.29	0.04
5.21	1.00
4.76	0.11
4.39	0.04
4.32	0.20
3.85	0.08
3.68	0.15
3.54	0.04
3.38	0.04
3.24	0.03
3.15	0.01
2.83	0.01
2.70	0.02
2.55	0.02
2.37	0.01
2.32	0.03
2.23	0.02
2.17	0.03

C6. Allopregnane-3β,20-diol diacetate

d, A.	I/I_1
16.5	0.03
10.7	0.04
8.89	0.15
7.22	0.20
6.17	1.00
5.80	0.30
5.57	0.40
5.37	0.20
4.98	0.40
4.56	0.20
4.35	0.15
4.20	0.11
3.86	0.30
3.61	0.08
3.36	0.04
3.04	0.11
2.90	0.08
2.81	0.11
2.67	0.01
2.61	0.04
2.52	0.06
2.44	0.08
2.30	0.04
2.18	0.06
2.10	0.06
2.07	0.01
1.97	0.03
1.86	0.01
1.75	0.04

D. Monoketones

D1. Δ^{16}-Allopregnene-20-one

d, A.	I/I_1
11.8	0.27
10.4	0.04
8.31	0.01
6.21	0.27
5.57	1.00
5.08	0.11
4.65	0.08
4.24	0.40
4.06	0.15
3.78	0.05
3.65	0.15
3.38	0.04
3.28	0.20
3.18	0.11
3.08	0.08
2.89	0.11
2.72	0.04
2.65	0.05
2.55	0.02
2.39	0.05
2.29	0.08
2.19	0.11
2.12	0.05
2.08	0.05
2.03	0.04
1.86	0.01
1.80	0.02
1.64	0.01

D2. Δ^1-Cholestene-3-one

d, A.	I/I_1
12.8	0.08
9.56	0.30
8.72	0.11
7.87	0.11
6.74	0.35
6.03	0.01
5.49	1.00
4.98	0.73
4.70	0.30
4.30	0.30
3.97	0.08
3.64	0.20
3.38	0.01
3.22	0.15
3.10	0.11
2.93	0.04
2.77	0.03
2.66	0.03
2.53	0.15
2.46	0.06
2.39	0.01
2.31	0.04
2.25	0.04

D3. Androstane-17-one

d, A.	I/I_1
9.31	0.15
6.24	0.30
5.85	0.40
5.54	1.00
5.23	0.20
4.82	1.00
4.67	0.08
4.11	0.08
3.84	0.04
3.51	0.15
3.35	0.20
3.19	0.30
3.00	0.15
2.94	0.06
2.85	0.08

(*Continued on page 765*)

Table II. X-Ray Diffraction Powder Data for Steroids *(Continued)*

D3. Androstane-17-one (*Contd.*)

d, A.	I/I_1
2.77	0.08
2.59	0.08
2.50	0.04
2.36	0.11
2.32	0.11
2.24	0.06
2.15	0.06
2.08	0.08
2.05	0.08
1.98	0.04
1.94	0.04
1.88	0.06
1.79	0.04
1.77	0.04

E. Diketones

E1. Allopregnane-3,20-dione

d, A.	I/I_1
10.9	0.04
6.09	0.40
5.91	0.30
5.59	1.00
5.11	0.30
4.54	0.03
4.34	0.08
4.12	0.08
3.72	0.04
3.58	0.04
3.42	0.03
3.29	0.04
3.21	0.20
3.11	0.15
3.01	0.06
2.87	0.08
2.76	0.06
2.67	0.06
2.58	0.08
2.48	0.01
2.37	0.06
2.28	0.03
2.17	0.04
2.10	0.04
2.03	0.01
1.96	0.06
1.80	0.01
1.68	0.01

F. Monohydroxy-monoketones

F1. Δ^4-Pregnene-20β-ol-3-one

d, A.	I/I_1
13.2	0.27
10.0	0.09
8.15	0.09
7.37	0.36
5.89	1.00
4.93	0.67
4.70	0.27
4.53	0.04
4.08	0.20
3.80	0.20
3.62	0.09
3.42	0.04
3.32	0.09
3.09	0.02
3.00	0.20
2.68	0.02
2.48	0.04
2.44	0.13
2.31	0.04
2.22	0.13
2.07	0.09

F2. Δ^4-Androstene-17-ol-3-one-17-acetate-3-enol acetate

d, A.	I/I_1
14.2	0.27
8.47	0.05
7.47	0.55
5.83	1.00
5.32	0.27
4.88	0.15
4.72	0.73
4.52	0.27
4.33	0.05
3.93	0.41
3.71	0.20
3.51	0.27
3.35	0.11
3.25	0.20
2.90	0.20
2.78	0.20
2.60	0.15
2.45	0.04
2.35	0.15
2.24	0.15
2.16	0.08
2.09	0.05
2.01	0.11
1.96	0.11
1.82	0.04
1.64	0.02

F3. Δ^4-Androstene-17-ol-3-one-17-propionate-3-enol propionate

d, A.	I/I_1
14.3	0.05
7.97	0.27
7.14	0.11
6.11	0.27
5.76	1.00
5.55	0.08
4.76	0.73
4.53	0.27
4.32	0.02
4.04	0.20
3.95	0.55
3.76	0.08
3.63	0.15
3.51	0.15
3.37	0.11
3.20	0.04
3.09	0.02
2.91	0.11
2.77	0.15
2.65	0.11
2.56	0.04
2.49	0.08
2.37	0.08
2.26	0.20
2.18	0.02
2.05	0.05
1.99	0.05
1.90	0.04
1.84	0.04
1.75	0.01
1.71	0.02
1.70	0.02

F4. Androstane-17-ol-3-one-17-acetate

d, A.	I/I_1
15.0	0.20
9.98	0.04
7.70	0.04
6.13	0.27
5.49	0.27
5.14	0.20
4.27	1.00
3.75	0.08
3.48	0.01
3.08	0.08
2.74	0.15
2.51	0.08
2.37	0.04
2.21	0.03
2.05	0.03

F5. Androstane-17β-ol-3-one 17-hexahydrobenzoate

d, A.	I/I_1
12.1	0.15
10.8	0.15
6.49	1.00
5.99	0.40
5.49	0.87
5.02	1.00
4.65	0.20
4.09	0.23
3.87	0.17
3.73	0.15
3.60	0.15
3.49	0.20
3.28	0.11
3.09	0.35
3.01	0.30
2.90	0.06
2.78	0.23
2.62	0.20
2.41	0.15
2.34	0.11
2.30	0.11
2.22	0.11
2.17	0.15
2.12	0.04
2.08	0.15
2.02	0.08
1.98	0.08
1.91	0.15

F6. Pregnane-3β-ol-20-one-3-acetate

d, A.	I/I_1
9.51	0.15
7.22	0.05
6.57	1.00
5.78	0.08
5.51	0.21
5.15	0.73
4.84	0.08
4.54	0.08
4.31	0.41
4.03	0.11
3.92	0.11
3.68	0.15
3.59	0.15
3.43	0.20
3.29	0.15
3.23	0.11
2.99	0.15
2.88	0.11
2.78	0.05
2.66	0.11
2.57	0.15
2.41	0.11
2.36	0.11
2.28	0.11
2.19	0.08
2.16	0.11
2.11	0.15
2.02	0.20
1.95	0.08
1.87	0.02
1.81	0.04
1.78	0.05

F7. Allopregnane-3β-ol-20-one-3-acetate

d, A.	I/I_1
13.3	0.20
10.3	0.11
7.94	0.06
7.34	0.11
6.74	0.11
6.07	1.00
5.55	0.73
4.94	0.30
4.68	0.73
4.39	0.30
4.16	0.30
3.95	0.20
3.82	0.20
3.69	0.08
3.54	0.08
3.30	0.20
3.16	0.08
2.97	0.06
2.80	0.06
2.63	0.08
2.56	0.08
2.46	0.15
2.36	0.04
2.33	0.03
2.26	0.08
2.18	0.08
2.00	0.06
1.91	0.06
1.88	0.01
1.83	0.01
1.76	0.01

F8. Etiocholane-17β-ol-3-one-17-acetate

d, A.	I/I_1
15.1	0.09
8.08	0.09
7.37	0.27
6.59	0.37
6.01	1.00
5.80	0.49
5.54	0.49
5.18	0.27
4.88	0.49
4.40	0.36
4.12	0.49
3.90	0.27
3.75	0.13
3.63	0.36
3.37	0.09
3.12	0.09
2.97	0.04
2.91	0.13
2.63	0.27
2.50	0.04
2.43	0.04
2.34	0.13
2.33	0.04
2.18	0.09
2.11	0.09
2.00	0.20
1.94	0.04
1.88	0.04

G. Dihydroxy-monoketones

G1. Pregnane-3α,17α-diol-20-one

d, A.	I/I_1
10.5	0.06
6.84	0.15
6.40	0.04
5.80	1.00
5.61	0.03
5.28	0.20
5.14	0.15
4.76	0.15
4.46	0.08
4.18	0.08
3.86	0.11
3.65	0.15
3.43	0.15
3.20	0.06
2.94	0.06
2.82	0.06
2.72	0.08
2.62	0.08
2.54	0.11
2.36	0.04
2.17	0.04
2.14	0.06
2.02	0.03
1.92	0.03
1.89	0.03

G2. Allopregnane-3,21-diol-20-one-21-acetate

d, A.	I/I_1
9.66	0.27
8.94	0.24
6.61	0.05
6.37	0.08
5.84	1.00
5.17	0.08
4.85	0.73
4.27	0.15
4.11	0.15
3.96	0.15
3.83	0.04
3.65	0.11
3.52	0.04
3.29	0.20
2.99	0.20
2.82	0.04
2.69	0.15
2.59	0.08
2.54	0.11
2.47	0.04
2.34	0.04
2.29	0.02
2.22	0.11
2.17	0.02
2.10	0.05
2.05	0.05
1.98	0.15
1.88	0.08
1.81	0.02
1.75	0.02
1.67	0.05

H. Trihydroxy-monoketones

H1. Δ^5-Pregnene-3β,17,21-triol-20-one-3,21-diacetate

d, A.	I/I_1
12.1	0.25
5.87	1.00
4.98	0.73
4.55	0.15
4.53	0.55
4.04	0.08
3.74	0.05
3.58	0.27
3.51	0.04
3.29	0.08
3.16	0.08
3.05	0.05
2.99	0.41
2.85	0.15
2.73	0.15
2.67	0.15
2.57	0.04
2.50	0.04
2.43	0.13
2.40	0.13
2.36	0.13
2.28	0.15
2.15	0.04
2.08	0.20
2.03	0.13
1.98	0.05
1.93	0.13
1.84	0.08

H2. Allopregnane-3β,17α,21-triol-20-one-21-acetate

d, A.	I/I_1
11.9	0.15
8.35	0.11
7.23	0.20
6.47	0.11
5.99	1.00
5.65	0.40
5.51	0.15
5.10	0.40
4.94	0.08
4.56	0.40
4.39	0.15
3.97	0.15
3.78	0.20
3.58	0.15
3.30	0.06
3.13	0.08
3.00	0.30
2.84	0.15
2.76	0.15
2.67	0.06
2.55	0.08
2.47	0.20
2.34	0.08
2.27	0.06
2.23	0.04
2.16	0.04
2.07	0.15
2.00	0.15
1.93	0.08
1.87	0.08
1.83	0.06

III. BILE ACID ESTERS

I. Carboalkoxy esters

I1. Methyl 3-acetoxy-12-ketocholanate

d, A.	I/I_1
14.5	0.06
7.31	0.53
6.20	1.00
5.65	1.00
5.25	0.30
5.10	0.37
4.72	0.33
4.50	0.13
4.27	0.23
4.09	0.15
3.88	0.15

(Continued on page 766)

Table II. X-Ray Diffraction Powder Data for Steroids (*Continued*)

d, A.	I/I_1
I1. Methyl 3-acetoxy-12-ketocholanate (*Contd.*)	
3.72	0.30
3.52	0.17
3.34	0.20
3.12	0.11
3.01	0.06
2.85	0.11
2.72	0.03
2.64	0.15
2.57	0.01
2.47	0.08
2.34	0.03
2.28	0.04
2.21	0.04
2.05	0.11
2.02	0.11
I2. Methyl 3-keto-12β-acetoxycholanate	
12.4	0.15
10.9	0.07
9.66	0.01
8.76	0.75
6.92	0.37
6.64	1.00
6.01	0.20
5.49	0.20
5.29	0.50
5.15	0.50
4.60	0.27
I2. Methyl 3-keto-12β-acetoxycholanate (*Contd.*)	
4.08	0.20
3.94	0.37
3.73	0.15
3.62	0.15
3.50	0.27
3.33	0.07
3.16	0.20
3.03	0.03
2.88	0.15
2.74	0.07
2.65	0.07
2.54	0.10
2.40	0.07
2.31	0.07
2.17	0.10
2.10	0.07
2.01	0.15
1.98	0.15
IV. STEROIDAL SAPOGENINS AND DERIVATIVES	
J1. Δ^4-Hecogenone	
13.6	0.15
6.89	0.20
6.22	0.20
5.84	1.00
5.39	0.20
5.17	0.37
4.93	0.37
4.67	0.37
J1. Δ^4-Hecogenone (*Contd.*)	
4.16	0.27
3.90	0.20
3.69	0.10
3.62	0.37
3.46	0.10
3.36	0.20
3.10	0.03
2.95	0.15
2.82	0.10
2.66	0.15
2.57	0.10
2.45	0.05
2.34	0.10
2.22	0.10
2.17	0.10
2.08	0.10
1.99	0.05
1.96	0.10
J2. Hecogenin	
15.0	0.20
11.1	0.03
8.23	0.11
7.20	0.03
5.99	0.11
5.54	1.00
5.01	0.11
4.73	0.11
4.42	0.20
4.24	0.08
4.00	0.08
3.77	0.11
3.62	0.08
J2. Hecogenin (*Contd.*)	
3.42	0.06
3.10	0.20
2.99	0.06
2.81	0.04
2.72	0.11
2.52	0.08
2.47	0.06
2.40	0.04
2.34	0.08
2.30	0.08
2.23	0.08
2.16	0.04
2.09	0.08
2.03	0.04
1.92	0.01
1.86	0.03
J3. Smilogenone	
15.8	0.11
9.26	0.30
7.22	0.30
6.84	0.20
5.87	1.00
5.59	0.20
5.31	1.00
5.08	0.30
4.64	0.40
4.29	0.20
3.96	0.20
3.56	0.30
3.30	0.11
3.11	0.15
2.88	0.15
J3. Smilogenone (*Cont.*)	
2.75	0.15
2.60	0.15
2.58	0.08
2.36	0.06
2.31	0.08
2.17	0.06
2.08	0.08
2.00	0.15
1.93	0.04
1.88	0.06
1.82	0.01
1.76	0.04

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Monochromatic Diffraction-Absorption Technique for Direct Quantitative X-Ray Analysis

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▶ In a diffraction-absorption method of quantitative x-ray analysis, a polychromatic beam was employed for the absorption measurement. Use of a polychromatic beam limits the precision and may introduce large errors. An alternative method, employing an essentially monochromatic beam, which eliminates these difficulties, is reported. A number of known samples were analyzed by the diffraction-absorption methods and by the internal standard. It is concluded that the diffraction-absorption methods are reproducible and capable of giving results comparable to those obtained with the internal standard; for some problems, they may provide the only suitable method of analysis.

A METHOD of direct quantitative x-ray analysis for α-quartz, using a Norelco diffractometer (*7*), was developed as an alternative to the commonly used internal standard technique (*2*, *3*). A general theoretical equation was derived, expressing concentration as a function of diffracted intensity and x-ray absorption:

$$x_1 = \left(\frac{I_1}{(I_1)_0}\right)\left(\frac{\mu_s^*}{\mu_1^*}\right) \qquad (1)$$

where

I_1 = integrated intensity diffracted by a sample with mass absorption coefficient μ_s^* containing weight fraction x_1 of component 1

$(I_1)_0$ = integrated intensity diffracted by a sample with mass absorption coefficient μ_1^* comprised wholly of component 1

A similar equation was found to hold experimentally.

The measured diffracted beams were, of course, essentially monochromatic, but absorption measurements were made employing the polychromatic beam emitted by a copper target x-ray tube. For simplicity, this method is here called the polychromatic diffraction-absorption technique. A monochromatic technique using the beam diffracted by a crystal monochromator for absorption measurements is also a possibility. In this case, however, the measurable x-ray absorption range is smaller and it was believed to be too small for practical α-quartz analysis. Experience with the polychromatic technique has since indicated that the range of absorption met in practice is not excessively large.

The use of a monochromatic technique should eliminate two errors associated with the polychromatic technique. Strictly accurate results depend on the exact proportionality of absorption coefficients for the wave lengths involved in diffraction and absorption measurements. The only way to assure exact proportionality is to make both measurements at the same wave length—i.e., a monochromatic technique. In the polychromatic technique there is an approximate proportionality for all elements except those occurring between corresponding absorption discontinuities for the two wave lengths. Approximate proportionality causes slight errors in the final result, but in most cases these do not exceed 3% of the amount of α-quartz present. If, however, the sample contains even small amounts of elements not in the region of proportionality, relatively large errors will occur in the final result. Even strongly diffracting compounds of nickel, zinc, and other elements subject to absorption discontinuity effects are difficult to detect by x-ray diffraction methods alone when the concentration of the element is small.

A monochromatic technique has the advantage of eliminating any possibility of this error. On the other hand, if there is any possibility that a sample will be affected by absorption range limitations, the absorption measurements will indicate that to be the case.

The present paper describes the development of such a technique. The polychromatic technique was repeated simultaneously for comparison purposes. The same samples and diffraction readings were used for both techniques.

EXPERIMENTAL TECHNIQUE

Binary mixtures were prepared as described (*5*) with quartz percentages by weight of 5, 10, 20, 40, 60, 80, and 100. Four such sets were prepared in duplicate or triplicate with the following quartz associates: tridymite, gypsum, calcium hydroxide, and calcium fluoride, giving absorption ratios, relative to pure quartz, from 1.0 to about 3.0.

The experimental mixtures were packed into rectangular cavities (2 × 1 × 0.158 cm.) in uniform aluminum slides. The apparent density of the powder was determined by weighing the slide before and after filling.

Diffraction Measurement. For this measurement the copper target x-ray tube current was reduced to 7 ma. at 35 kv. All diffracted intensities were compared with the intensity diffracted by a selected aluminum plate. The aluminum diffraction line chosen for this purpose corresponded to an atomic spacing of 2.34 A. The automatic pen recorder was used for all diffraction measurements, diffraction lines being scanned at 0.25° per minute.

Monochromatic Absorption Measurements. A calcite crystal was found to be a suitable monochromator. Kilovoltage and milliamperage were 40 and 20, respectively. The usual nickel filter was removed.

The absorption ratio—i.e., ratio of mass absorption coefficients—is calculated from the equation ρ = Rho

$$\frac{\mu_s^*}{\mu_1^*} = \frac{\rho_1 \log_e (T_s/T_0)}{\rho_s \log_e (T_1/T_0)} \qquad (2)$$

where

ρ_1 = apparent density of a pure sample of component 1

ρ_s = apparent density of a sample containing weight fraction x_1 of component 1

T_0 = intensity of incident x-ray beam

T_1 = intensity transmitted by pure sample of component 1

T_s = intensity transmitted by sample containing weight fraction x_1 of component 1

Because of the relatively high absorption of CuK_α radiation by the samples, incident intensity was necessarily large and, therefore, had to be measured indirectly. Consider a number of foils of uniform thickness t and linear absorption coefficient μ. The intensities, T_n and T_{n+1}, transmitted by n and $n+1$ foils, respectively, are

$$T_n = T_0 \, e^{-n\mu t} \qquad (3)$$

$$T_{n+1} = T_0 \, e^{-(n+1)\mu t} \qquad (4)$$

and

$$\frac{(T_n)^{n+1}}{(T_{n+1})^n} = T_0 \qquad (5)$$

If a suitable value for n can be found, so that T_n and T_{n+1} both fall in the linear portion of the Geiger response curve, T_0 can be calculated.

For monochromatic radiation thin brass foils (0.0049 cm.) with $n=3$ were used for T_0 determination, and intensities were measured by manual counting. Although it was not possible to select foils with identical x-ray transmission properties, this factor does not introduce serious errors into the final results. T_s/T_0 is of the order of 10^{-3} and less and under these conditions the relative error in log (T_s/T_0) is small compared to that in T_0.

Polychromatic Absorption Measurement. T_0 was again determined indirectly using aluminum plates (0.056 cm.) with $n=1$. X-ray tube kilovoltage and milliamperage were 15 and 10, respectively, and the angular setting of the Geiger tube was 0.5°, 2θ. This gave a calculated effective wave length of 0.87 A. with a short wave length limit of 0.83 A. Intensities were again measured by manual counting.

EXPERIMENTAL RESULTS

The diffraction-absorption relation is best visualized when μ_s^*/μ_1^* is plotted against $I_1/(I_1)_0$ on log-log paper. The theoretical relation (Equation 1) gives a straight line with a slope of -1, for which $I_1/(I_1)_0 = x_1$ when $\mu_s^*/\mu_1^* = 1.0$.

Table I gives the calculated slopes for each percentage for the monochromatic and polychromatic techniques. In determining the average slopes the 5% results were ignored, because for this low quartz concentration diffracted intensities are weak and intensity measurements unreliable when made with the automatic pen recorder (*4*).

Table I. Experimental Slopes

Quartz, %	Monochromatic Technique	Revised Polychromatic Technique
5	−1.53	−2.05
10	−0.94	−1.45
20	−0.94	−1.45
40	−1.03	−1.51
60	−1.07	−1.49
80	−0.98	−1.89
Av. slope (ignoring 5%)	−0.99	−1.55
Standard deviation	0.05	0.16

For both techniques when $\mu_s^*/\mu_1^* = 1.0$, $I_1/(I_1)_0 = (x_1)_{\text{exp.}} > x_1$ where $(x_1)_{\text{exp.}}$ is a constant for any given percentage. The experimental diffraction-absorption relations are given by Equations 6 and 7. The monochromatic slope has been assumed to be -1.

Monochromatic

$$(x_1)_{\text{exp.}} = \left(\frac{I_1}{(I_1)_0}\right)\left(\frac{\mu_s^*}{\mu_1^*}\right) \qquad (6)$$

Revised polychromatic

$$(x_1)_{\text{exp.}} = \left(\frac{I_1}{(I_1)_0}\right)\left(\frac{\mu_s^*}{\mu_1^*}\right)^{0.652} \qquad (7)$$

The values of $(x_1)_{\text{exp.}}$ are slightly different for each technique (Table II). Smooth curves may be constructed showing the relation between $(x_1)_{\text{exp.}}$ and x_1 and used to determine quartz percentage from the calculated value of $(x_1)_{\text{exp.}}$.

Figure 1 compares the theoretical diffraction-absorption relation (Equation 1) with the experimental results (Equations 6 and 7). For simplicity only the 20% curves are shown.

Table II. Values of $(x_1)_{\text{exp.}}$

Quartz, %	Monochromatic Technique	Revised Polychromatic Technique
5	0.059	0.057
10	0.125	0.124
20	0.248	0.241
40	0.459	0.451
60	0.668	0.656
80	0.847	0.828

Causes of Experimental Deviation. SUBHARMONICS IN BEAM DIFFRACTED BY MONOCHROMATOR. When the calcite crystal is properly oriented to diffract the first order of Cu$K\alpha$, it will also diffract the second order of Cu$K\alpha/2$, the third of Cu$K\alpha/3$, and so on, provided these subharmonics are present in the polychromatic beam impinging on the crystal (*6*). Under the experimental conditions the second, third, and fourth subharmonics were present. Considering only the effect of the subharmonics on sample measurements, measured absorption coefficients will be less than true monochromatic coefficients, because of differential absorption of the subharmonics. This effect will become more pronounced as sample absorbing power increases. The effect on T_0 determination should be smaller, because an absorption edge occurs for the brass foils between Cu$K\alpha$ and Cu$K\alpha/2$. The over-all effect on monochromatic absorption measurements should, then, be mainly due to sample measurements and the curves should be rotated counterclockwise to give less negative slopes.

To test whether subharmonics have any appreciable effect, a number of 50% samples were prepared, and, in addition to the usual diffraction and absorption measurements, an extra set of monochromatic absorption measurements was made with kilovoltage reduced sufficiently to eliminate subharmonics from the beam incident on the crystal.

A comparison of normal monochromatic, test monochromatic, and normal polychromatic results is given in the first line of Table III. The figures given are the intercepts of the curves with $\mu_s^*/\mu_1^* = 1.0$ and their slopes. Subharmonics did affect the monochromatic results, and the slopes were less negative under their influence, as predicted. Consequently, the agreement in slope between theoretical and experimental monochromatic results was fortuitous.

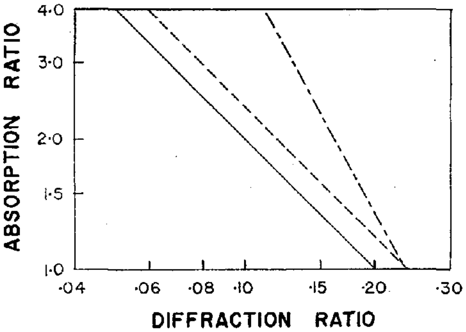

Figure 1. Comparison of experimental and theoretically predicted diffraction-absorption curves

——— Theoretical
— — — Monochromatic
— - — - Polychromatic

GEIGER COUNTER NONLINEARITY. When x-ray intensities are measured with a Geiger counter, they are proportional to true intensities only for very low counting rates. If subscripts T and M are used to refer to true and measured intensity values, respectively, and τ is the resolving time of the Geiger counter, the relation between true and measured values for diffraction measurements may be written:

$$(I_1)_T = \frac{(I_1)_M}{1 - (I_1)_M\,\tau} \tag{8}$$

and Equation 1 becomes

$$x_1 \times \frac{(1 - (I_1)_M\,\tau)}{(1 - (I_1)_{0M}\,\tau)} = \left(\frac{I_1}{(I_1)_0}\right)_M \times \left(\frac{\mu_s^*}{\mu_1^*}\right)_T \tag{9}$$

The factor multiplying x_1 is greater than unity and therefore one effect of nonlinearity is to shift the curves parallel to the intensity axis. As it is not constant, a slight rotation is also predicted, in this case toward more negative values of the slopes.

Nonlinearity may also have an effect on absorption measurements and a mathematical expression for the relation between the true absorption ratio and the measured ratio may be derived on the same basis as the diffraction correction and inserted in Equation 9. This expression is, however, difficult to evaluate quantitatively for two reasons, one being that it is a function of not only transmitted sample intensities but also the measurements made on the absorbing foils in the indirect determination of T_0. Also, transmitted intensities of otherwise identical samples vary considerably because of variations in apparent density arising in slide preparation.

To determine the effect of nonlinearity, experimental intensity readings were all corrected using Equation 8 and the published value of 270 microseconds (*8*) for the resolving time of the Geiger counter. Results of applying this correction are shown in Table III, in the second line for diffraction readings only, and in the third for both diffraction and absorption. The effect of correcting diffraction is as predicted above and absorption corrections produce little change except in the case of the polychromatic technique.

MISCELLANEOUS EFFECTS IN POLYCHROMATIC ABSORPTION MEASUREMENTS. Because the polychromatic beam consists of a continuous band of wave lengths, polychromatic absorption measurements are subject to the same type of error arising in monochromatic measurements when subharmonics are present. Variation in Geiger counter sensitivity with wave length also affects results, as does the approximate proportionality of absorption coefficients discussed earlier. The over-all effect of the first two is complicated by the indirect measurement of T_0, but if any combination of the three causes an appreciable difference between theory

Table III. Causes of Experimental Deviation

Successive Corrections Applied to Experimental Readings	Monochromatic (Normal)		Monochromatic (Subharmonics Eliminated)		Polychromatic (Normal)	
	Intercept[a]	Slope[b]	Intercept	Slope	Intercept	Slope
None	0.578	−1.048	0.574	−1.363	0.569	−1.615
Diffraction corrected for nonlinearity	0.547	−0.991	0.543	−1.286	0.537	−1.527
Absorption corrected for nonlinearity	0.547	−0.995	0.542	−1.284	0.538	−1.640
Polychromatic absorption corrected on basis on Table IV	...	...	...	...	0.520	−1.497

[a] Intercept of curve with $\mu_s^*/\mu^* = 1.0$.
[b] Slope of curve.

and experiment, observed absorption ratios are significantly different from ratios calculated for monochromatic Cu$K\alpha$ radiation. A comparison of the ratios is given in Table IV, and the polychromatic absorption ratios are corrected on this basis to obtain the results given in the fourth line of Table III. Closer agreement is obtained with the monochromatic results in which subharmonics were eliminated and diffraction and absorption ratios were corrected for nonlinearity. In terms of the angles made with the intensity axis, separation between the two curves is only about 4°

Table IV. Comparison between Observed Polychromatic Absorption Ratios and Those Calculated for Cu$K\alpha$ Radiation

Sample	Polychromatic Ratios	Cu$K\alpha$ Ratios
Quartz-tridymite	1.043	1.000
Quartz-gypsum	1.638	1.417
Quartz-calcium hydroxide	2.074	1.909

Microabsorption. If all errors peculiar to the absorption measurements were systematically corrected in this way, it should be possible to arrive at monochromatic and polychromatic relations which are the same within the limits of experimental error. Although there is still some difference between the two, it has been reduced considerably, as angular separation was about 12° for normal, uncorrected results. It seems plausible to ascribe most of the residual difference between theory and experiment to the diffraction measurement. Possible causes are preferred orientation, line broadening, and microabsorption. The presence of preferred orientation may be established by a careful comparison of relative intensities of several quartz diffracted lines and that of line broadening by an examination of line profiles. Neither of these phenomena was observed experimentally. In the original paper (*5*) microabsorption (*9*) was believed to be a major cause for the difference between theory and experiment and this conclusion should still be valid.

Analysis of Known Mixtures. Two sets of synthetic samples were prepared to test the accuracy of the method. The first set was prepared using materials susceptible to analysis by either diffraction-absorption method and by the internal standard. The second set all contained, in the matrix, compounds of elements expected to cause absorption edge difficulties.

Table V summarizes results obtained with the first set and establishes the practicability of the diffraction-absorption methods. The diluents used in the known mixtures occur commonly in routine quartz analysis in this laboratory. Feldspars and clays also occur commonly, and because of their low absorption coefficients should present no problems in quartz analysis.

Occasionally samples have been received containing appreciable amounts of mullite and fluorite (calcium fluoride). Mullite also has a small absorption coefficient, but that of fluorite is large and samples containing large amounts of this material cannot be analyzed by the monochromatic technique as described. In the experimental determination of the monochromatic diffraction-absorption relation, results obtained with samples containing 40% or more by weight of fluorite had to be discarded because of this factor. This result is a direct consequence of the presence of subharmonics in the x-ray beam and a test made with a pure fluorite sample with kilovoltage reduced to eliminate subharmonics has indicated that analysis of samples containing considerably larger amounts of fluorite should be possible under strict monochromatic conditions. A disadvantage is the reduced intensity, which necessitates fairly long counting times.

Also in Table V are summarized the results obtained in analysis of the second set of synthetic samples. The elements leading to absorption edge difficulties were all added in 5% amounts. As predicted above, large errors result when such samples are analyzed by the polychromatic technique.

Table V. Analysis of Known Mixtures

	Set 1		Set 2	
	Total quartz, %	Total absolute error	Total quartz, %	Total absolute error
Actual	692.5	0.0	323.5	0.0
	(100.0)	(0.0)	(100.0)	(0.0)
Internal standard	751	65.5	...	...
	(108.4)	(9.5)	...	...
Monochromatic	678	40.5	322.5	31
	(97.9)	(5.8)	(99.7)	(9.6)
Polychromatic	729.5	42	408.5	87
	(105.3)	(6.1)	(126.3)	(26.9)

DISCUSSION

Methods of Improving Monochromatic Diffraction-Absorption Analysis. The monochromatic technique as described is limited to samples with a relatively small range of absorption coefficients. Four methods are possible to extend the range: reduction of sample thickness, use of a proportional counter as an x-ray detector, use of shorter wave length radiation, and elimination of subharmonics from the beam incident on the monochromator.

Reduction of sample thickness may make sample preparation more difficult because of lack of rigidity of the thinner sample. A laboratory press may be used instead of manual methods for packing the sample. However, this will increase sample densities and some, at least, of the advantage gained by reducing thickness will be lost.

Proportional counters for detection of x-rays are being manufactured commercially and are coming into increasing use. Taylor and Parrish (*8*) compare the proportional counter with the Geiger counter and discuss its advantages. In particular, the xenon proportional counter has about the same counting efficiency at all wave lengths as the Geiger counter and has a linear response to very high counting rates. If available monochromator intensity is assumed to be the same as in the actual experiment, sample thickness must again be reduced. Otherwise transmitted sample intensities will be the same low values which were obtained experimentally and the linear response at higher counting rates will not be utilized. Under these conditions an increase in the measurable absorption range is obtained and errors due to nonlinearity should be eliminated.

Use of shorter wave length radiation allows the samples to be more easily penetrated by the x-ray beam, and again a greater range of sample absorption may be measured. Disadvantages are the smaller dispersion of the x-ray diffraction spectrum and the shift of the spectrum to smaller Bragg angles.

Table VI shows the calculated effects of the three factors on the measurable absorption range. μ_l is the linear absorption coefficient of quartz and μ_s the largest measurable linear absorption coefficient under the experimental conditions outlined.

CONCLUSIONS

The monochromatic diffraction-absorption technique described gave

Table VI. Calculated Effects of Changing Experimental Conditions on Range of Absorption Measurable by Monochromatic Technique

	Changes from Original Conditions			
	None	Sample thickness	Detector and sample thickness	Radiation
Radiation	CuK_α	CuK_α	CuK_α	MoK_α
Detector	Geiger	Geiger	Proportional	Geiger
t	0.15	0.10	0.10	0.15
μ_1	38.5	38.5	38.5	4.08
μ_s	56.2	65.0	84.3	21.8
$\frac{\mu_s - \mu_1}{\mu_1}$	0.46	0.69	1.19	4.34
% increase in absorption range	0	50	160	840

results comparable in accuracy to those obtained by either the polychromatic or the internal standard technique. When compared with the polychromatic technique it is not susceptible to the errors introduced by the presence in the sample of elements on the high atomic number side of the first absorption edge of the characteristic radiation used. These errors may be fairly large before there is any reason to suspect them. The monochromatic technique is not affected by the random errors associated with approximate proportionality of absorption coefficients at different wave lengths. The main limitation of the monochromatic method is the restricted range of absorption it can measure, but samples possibly subject to this limitation will be detected by the absorption measurement. About 5% of samples received in this laboratory for quartz analysis fall in this category.

When the diffraction-absorption methods and the internal standard method are compared, preparation and analytical times are about the same. If the amount of sample available is much less than 500 mg., it should be mixed with starch to produce the necessary bulk to fill the slide cavity completely for diffraction-absorption analysis. Internal standard analysis may be made with as little as 100 mg. of sample by filling the remainder of the cavity with starch.

In general, the choice of method for other quantitative problems will be determined by the expected range of sample absorption, the presence or absence of elements affected by absorption edges, and whether it is desirable to dilute or adulterate the sample. For determining only one component of mixtures, any one of the three techniques may be suitable. In some cases it may be difficult to find a suitable internal standard and this problem will become more serious if more than one component is to be determined. Black (*1*) has described a method for determining a number of components in multicomponent mixtures. This method is fast and accurate but is probably limited in its application, as it was used for a specialized analytical problem, in which a number of factors combined to produce the speed and accuracy. In the general case of multicomponent analysis, diffraction-absorption may be the only suitable method of obtaining an accurate quantitative determination.

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Mass Spectra of Trimethylsilyl Derivatives

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▶The mass spectra of 26 aliphatic trimethylsilyl ethers and eight related silicon compounds have been obtained. Fragmentation peaks have been correlated with molecular structures. Structures have been proposed for rearrangement ions appearing in the spectra. By the use of trimethylsilyl derivatives, compounds of several classes including alcohols, phenols amines, and thiols can be determined in the presence of compounds that normally interfere.

Although mass spectrometric methods have been used to analyze mixtures of alcohols (*1, 6, 7, 9, 16, 17*), determination of individual C_5 to C_{10} primary alcohols in the presence of hydrocarbons requires preliminary separation before chemical or spectroscopic methods can be applied. A method, utilizing the trimethylsilyl ether derivatives of alcohols, has been developed for rapid, direct analysis of individual alcohols in hydrocarbon solutions (*12*). The trimethylsilyl ether derivatives of alcohols, $(CH_3)_3SiOR$, are readily prepared (*11*) and produce distinct mass spectra free of interference by hydrocarbons.

The mass spectra of 26 aliphatic trimethylsilyl ethers and eight related silicon compounds were obtained. Trimethylsilyl ethers have higher volatility than hydrocarbons and oxygenated compounds containing fewer carbon atoms. For example, the mass spectrum of a C_{10} alcohol from a conventional room-temperature mass spectrom-

Table I. Mass Spectra of Trimethylsilyl Derivatives

[R^{a}—OSi(CH$_3$)$_3$]

Compound^{a}	Primary Straight-Chain									
	Methyl^{b}	Ethyl	Propyl	1-Butyl	1-Pentyl	1-Hexyl	1-Heptyl	1-Octyl	1-Nonyl	1-Decyl
Carbons	4	5	6	7	8	9	10	11	12	13
Molecular weight	104	118	132	146	160	174	188	202	216	230
Mass/charge										
29	87.6^{c}	138	198	179	267	275	278	174	113	54.9
31r^{d}	40.7	30.2	29.0	23.6	33.5	20.5	17.0	8.9	6.1	2.8
43	180	210	207	151	177	189	194	137	92.0	65.0
45r^{e}	149	334	296	262	269	241	201	112	58.5	34.9
47r	11.4	82.1	73.0	79.0	75.4	87.8	75.6	42.8	26.4	15.1
59r	867	333	130	109	128	125	117	65.7	38.3	22.5
61r	39.5	83.4	83.7	86.0	107	110	107	68.4	40.8	24.4
65.5	...	...	...	...	...	...	...	...	...	...
66	1.1	1.1	1.8	...	...	0.9	1.6	1.4	0.1	0.7
69	0.7	1.1	1.6	2.0	84.4	12.7	36.4	133	70.0	26.8
73	41.2	313	567	484	551	528	490	290	173	105
75r	19.6	750	1040^{f}	1000^{f}	1080^{f}	1050	984	569	352	212
83	...	...	1.0	...	1.6	78.8	5.4	14.8	46.7	35.4
87	...	12.1	5.1	20.4	12.3	45.6	40.2	20.4	11.4	6.6
89	1230^{f,g}	2.7	5.3	114	192	179	170	97.5	54.7	33.5
101	...	11.0	12.5	9.7	60.3	54.9	67.8	46.0	29.2	20.8
103	...	1140^{f,g}	199	217	282	281	277	164	103	60.4
104	P 3.9^{h}	109	19.5	21.1	27.0	27.5	25.3	15.9	10.1	5.6
115	...	...	5.3	12.2	8.9	45.6	47.9	21.3	15.4	9.1
117	...	5.5	957^{g}	2.5	2.8	9.6	4.0	2.4	1.7	1.0
118	...	P 9.8	103	...	0.4	1.2	0.7	0.3	0.2	...
130	...	...	...	...	1.0	...	...	1.9	0.6	...
131	...	...	4.4	947.^{g}	1.9	2.2	15.1	2.7	1.7	1.7
132	...	...	P 6.1	112	...	...	1.4	0.2	...	...
145	...	...	...	5.0	1060^{g}	4.4	1.3	1.2	1.3	2.9
146	...	...	...	P 8.1	140	...	...	...	...	...
147	...	...	...	...	35.7	7.4	1.3	8.0	...	1.0
159	...	...	...	...	4.4	1130^{f,g}	4.4	0.5	0.6	3.1
160	...	...	...	...	P 13.0	160	...	...	...	...
161	...	...	...	...	1.7	50.1	1.6	...	...	...
162	...	...	...	...	0.4	4.4	...	...	...	...
173	...	...	...	...	...	...	1090^{f,g}	3.2	...	...
174	...	...	...	...	...	P 10.4	165	...	...	...
187	...	...	...	...	...	...	2.8	686^{f,g}	1.0	...
188	...	...	...	...	...	...	P 6.6	112	...	...
201	...	...	...	...	...	...	...	...	438^{f,g}	...
202	...	...	...	...	...	...	...	P 2.3	92.9	...
215	...	...	...	...	...	...	...	...	...	265^{f,g}
216	...	...	...	...	...	...	...	...	P 2.5	49.3
230	...	...	...	...	...	...	...	...	...	P 1.0
Sensitivity of base, div./micromole	315	270	261	248	286	291	290	280	322	309

Compound^{a}	Primary Branched							
	2-Me-1-propyl	2-Me-1-butyl	3-Me-1-butyl	2,2,Dime-1-propyl	2-Me-1-pentyl	3-Me-1-pentyl	2-Et-1-butyl	2-Et-1-hexyl
Carbons	7	8	8	8	9	9	9	11
Molecular weight	146	160	160	160	174	174	174	202
Mass/charge								
29	130	231	150	197	176	229	254	304
31r^{d}	24.5	17.8	17.3	17.9	17.1	22.3	18.2	14.1
43	225	141	191	150	208	145	211	184
45r^{e}	245	208	219	194	186	193	207	177
47r	65.2	66.5	70.8	59.6	64.3	69.3	74.7	68.3
59r	92.1	84.3	115.	83.7	80.7	111	86.7	92.4
61r	80.2	80.9	78.6	65.8	82.4	78.6	84.3	98.1
65.5	...	...	...	...	...	...	...	...
66	1.1	0.8	0.9	0.7	1.0	1.0	1.2	1.7
69	1.6	10.9	128	3.3	20.0	4.1	18.0	74.0
73	810	687	517	941^{f}	675	455	747	761
75r	1000^{f}	943^{f}	674	669	897^{f}	536	1000^{f}	1010^{f}
83	1.4	1.6	1.4	1.6	22.6	619^{f}	13.8	34.8
87	4.1	4.4	21.0	4.1	5.2	19.1	6.6	8.7
89	10.4	47.2	523	52.0	54.2	326	53.5	73.8
101	6.2	15.8	31.3	28.1	13.0	24.1	13.4	18.1
103	444	495	630	572	525	274	557	686
104	42.2	47.6	30.6	59.6	51.8	26.5	56.3	69.7
115	7.1	4.2	9.3	1.1	13.3	23.8	9.7	13.6
117	1.1	1.6	2.5	...	8.1	5.5	15.6	14.9
118	...	0.3	0.4	...	0.9	1.0	1.5	1.2
130	...	6.4	1.1	...	1.4	1.0	1.7	3.3
131	763^{g}	...	...	...	2.4	1.0	1.5	4.3
132	92.4	...	1.8	1.0	0.3	...	...	0.3

(*Continued on page 772*)

Table I. Mass Spectra of Trimethylsilyl Derivatives (*Continued*)

Compound^{a}	Primary Branched							
	2-Me-1-propyl	2-Me-1-butyl	3-Me-1-butyl	2,2,Dime-1-propyl	2-Me-1-pentyl	3-Me-1-pentyl	2-Et-1-butyl	2-Et-1-hexyl
145	6.4	731^{g}	797^{f,g}	496^{g}	2.6	3.5	3.5	13.4
146	P 6.3	95.9	104	65.1	...	1.8	...	2.5
147	...	32.5	34.4	22.7	2.0	3.0	1.6	4.2
159	...	3.6	2.5	2.2	550^{g}	423^{g}	584^{g}	1.8
160	...	P 9.5	P 3.1	P 7.7	78.6	59.7	82.8	...
161	...	1.4	0.4	1.2	24.7	18.9	26.2	0.4
162	...	0.4	...	0.3	2.1	1.7	2.2	...
173	...	...	...	...	2.0	1.2	2.0	3.6
174	...	...	...	...	P 9.5	P 5.9	P 3.0	...
187	...	...	...	...	...	...	...	623^{g}
188	...	...	...	...	...	...	...	102
201	...	...	...	...	...	...	...	...
202	...	...	...	...	...	...	...	P 10.4
215	...	...	...	...	...	...	...	...
216	...	...	...	...	...	...	...	...
230	...	...	...	...	...	...	...	...
Sensitivity of base, div./micromole	243	194	208	255	292	210	308	305

Compound^{b}	Secondary						Tertiary	
	2-Propyl	2-Butyl	2-Pentyl	3-Me-2-butyl	2-Hexyl	3-Heptyl	2-Me-2-propyl	2-Me-2-butyl
Carbons	6	7	8	8	9	10	7	8
Molecular weight	132	146	160	160	174	188	146	160
Mass/charge								
29	89.6	150	116	103	260	349	101	200
31r^{d}	22.6	21.9	18.1	17.7	19.5	20.6	18.2	19.2
43	215	178	190	225	175	141	158	200
45r^{e}	313	284	257	239	328	253	254	277
47r	80.0	74.6	80.5	63.7	94.5	86.7	76.3	85.2
59r	82.3	92.3	88.1	86.6	87.1	117	58.5	15.0
61r	88.6	84.8	88.1	68.7	110	107	91.8	104
65.5	...	...	...	...	...	...	...	2.0
66	0.9	1.0	1.0	0.8	0.9	1.7	...	1.5
69	1.5	1.4	3.6	3.0	25.6	45.9	1.5	3.3
73	699	1030^{f}	1010	1160	1000	1310^{f}	790	1140^{f}
75r	1200^{f}	821	818	565	834	747	1190^{f}	947
83	0.7	0.6	0.8	0.8	3.4	3.0	1.0	0.9
87	5.3	23.6	19.4	24.0	27.4	9.2	2.0	3.3
89	1.6	2.4	3.1	2.9	5.0	5.6	2.7	2.5
101	14.5	19.9	29.3	29.2	26.2	37.5	15.1	32.2
103	0.7	2.7	17.5	3.9	28.0	83.4	0.8	1.6
104	...	0.6	2.2	0.7	3.2	8.1	...	...
115	5.1	6.2	4.7	1.5	28.1	56.2	16.6	19.7
117	943^{g,i}	831^{i}	1070^{f,i}	1170^{f,i}	1300^{f,i}	6.9	0.9	1.6
118	102	104	127	137	142	0.7	...	0.2
130	...	1.6	...	1.7	1.7	12.6	3.5	5.8
131	15.1	315^{g}	6.1	0.7	1.3	891^{i}	773^{g}	754
132	P 1.9	42.4	1.4	...	...	105	86.8	90.0
145	...	...	279^{g}	182^{g}	1.2	50.2	...	292^{g}
146	...	P 11.9	40.2	30.4	...	6.5	P ...	39.3
147	...	...	15.3	11.2	...	6.8	...	1.7
159	...	...	...	...	237^{g}	570	...	...
160	...	...	P 10.8	P 11.3	33.7	80.4	...	P 0.8
161	...	...	...	...	10.6	25.5	...	...
162	...	...	...	...	0.7	2.3	...	...
173	...	...	...	...	...	112^{g}	...	...
174	...	...	...	...	P 9.4	17.2	...	...
187	...	...	...	...	...	...	...	...
188	...	...	...	...	...	P 8.8	...	...
201	...	...	...	...	...	...	...	...
202	...	...	...	...	...	...	...	...
215	...	...	...	...	...	...	...	...
216	...	...	...	...	...	...	...	...
230	...	...	...	...	...	...	...	...
Sensitivity of base, div./micromole	278	256	282	230	345	325	234	299

[a] Source O, synthesized at Bureau of Mines.
[b] Alcohol from which trimethylsilyl ether is derived.
[c] Peak height in divisions per liquid volume (0.00068 cc.) when mass 27, n-heptane = 492 div.
[d] Rearrangement peaks except for methyl.
[e] Rearrangement peaks.
[f] Base peak, most intense peak in spectrum.
[g] Parent mass minus 15.
[h] Parent peaks indicated by P.
[i] Ion resulting from fragmentation at functional carbon—for secondary alcohol derivatives.

Table II. Mass Spectra of Trimethylsilyl Derivatives and Related Compounds

[R[a]—OSi(CH$_3$)$_3$]

Compound	*n*-Butyl[a] Mercaptan	*o*-[a] Cresol	*m*-[a] Cresol	*p*-[a] Cresol	Phenol[a]	Propylene[a] Glycol	Hexa-methyl-disilazane	Hexa-methyl-disiloxane
Source[b]	O	O	O	O	O	O	O	D
Carbons	7	10	10	10	9	9	6	6
Molecular weight	162	180	180	180	166	220	161	162
Mass/charge								
29	279[c]	56.6	52.5	54.3	76.8	71.2	53.3	75.9
31r[d]	22.4	20.9	13.1	12.8	16.4	22.5	26.4	24.9
43	177	128	114	119	166	132	101	109
45*r*	188	179	159	166	192	239	131	190
47*r*	43.4	27.5	29.3	25.1	37.1	54.0	4.7	16.4
59*r*	90.6	68.3	54.4	48.7	42.8	138	109	189
61*r*	47.8	18.9	20.1	17.1	38.3	35.3	4.4	12.2
65.5	...	...	...	...	...	...	245	6.6
66	4.0	8.6	9.9	8.1	16.9	196	38.5	286
66.5	...	...	...	...	...	28.5	18.1	42.5
73	696	198	122	154	135	944[e]	200	331
75*r*	212	101	120	108	131	136	10.8	40.2
75.5	...	...	...	...	111	...	...	...
77	62.4	76.8	65.8	69.3	183	8.7	0.2	1.9
87	2.8	2.4	2.9	2.7	1.2	11.4	9.5	41.2
89	6.7	34.0	28.2	25.0	11.5	12.4	1.6	7.4
91	938[e]	545	192	155	128	0.8	1.3	10.8
101	3.7	2.9	2.1	1.9	3.5	23.1	142	17.1
103	5.1	14.7	14.2	12.9	3.2	108	22.6	21.0
104	4.3	5.7	5.7	7.0	1.0	11.8	4.0	3.2
105	60.0	49.3	72.5	66.8	10.0	11.9	4.7	18.3
115	1.0	1.6	1.4	1.2	...	21.0	30.7	17.0
117	3.6	1.2	1.4	1.3	1.2	695	52.3	28.8
118	...	...	...	...	...	77.1	7.0	6.7
119	28.8	3.5	4.9	4.4	2.6	34.0	3.6	8.8
121	2.5	13.6	7.6	6.8	675	0.9	...	0.3
130	...	...	...	...	...	2.5	386	...
131	5.1	4.2	2.9	2.4	3.2	42.7	58.5	103
132	...	...	...	...	...	7.4	37.8	16.1
133	8.9	16.7	4.1	5.5	6.9	71.6	6.3	39.7
135	...	185	18.0	48.6	60.0	5.8	...	2.5
145	1.6	3.8	4.4	3.8	...	...	11.6	...
146	...	...	...	...	...	...	1820[e,f]	14.9
147	717[f]	15.9	6.9	6.2	3.1	834	299	2390[e,f]
151	1.4	...	...	...	1820[e,f]	2.1	...	4.7
159	...	...	...	...	...	1.1	...	...
160	...	...	...	...	...	...	1.0	...
161	...	11.5	8.5	7.3	...	...	P 45.1	...
162	P 218[g]	...	...	...	...	...	7.9	P 0.8
165	...	864[e,f]	1520[e,f]	1410[e,f]	...	...	...	...
166	...	...	...	...	P 499	...	...	...
180	...	P 532	P 523	P 545	...	...	...	...
191	...	...	...	...	...	101	...	...
205	...	...	...	...	...	32.6[f]	...	...
220	...	...	...	...	...	P 0.8	...	...
Sensitivity of base, div./micromole	230	185	327	320	414	309	494	668

[a] Compound from which trimethylsilyl ether is derived.

[b] O, synthesized by Bureau of Mines; D, Dow Corning Corp., DC-200.

[c] Peak height in divisions per liquid volume (0.00068 cc.) when mass 27, *n*-heptane = 492 div.

[d] Rearrangement peaks.

[e] Base peak, most intense in spectrum.

[f] Parent mass minus 15.

[g] Parent peak indicated by P.

eter is not usable, but the spectrum of a trimethylsilyl ether prepared from a C$_{10}$ alcohol can be obtained without difficulty.

Trimethylsilyl ethers show several intense rearrangement peaks in addition to the expected fragmentation peaks. Numerous other instances of intense rearrangement peaks in mass spectra, mainly of oxygen-containing compounds, have been reported (*8*, *10*, *14*, *15*). Earlier work by Dibeler on a similar silicon compound, hexamethyldisiloxane, (CH$_3$)$_6$Si$_2$O, also showed many rearrangement peaks (*3*).

EXPERIMENTAL

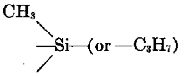
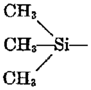
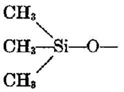
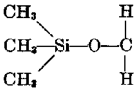
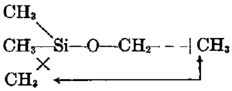
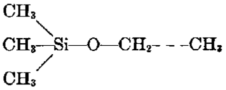
The spectra were obtained on a Consolidated Electrodynamics Corp., Model 21-103, mass spectrometer. All samples were introduced from a constant-volume pipet (0.00068 cc.) through a mercury orifice system (*2*). Preparation of the alcohol derivatives has been described by Langer (*11*). Physical constants for compounds previously reported agree with literature values (*13*). Heart cuts were used in all instances for mass spectrometer calibrations.

MASS SPECTRAL CORRELATIONS

Fragment Ions. PRIMARY STRAIGHT-CHAIN TRIMETHYLSILYL ETHERS. Important peaks in the spectra of the trimethylsilyl ethers are given in Tables I and II. A characteristic mode of fragmentation was found for all the normal (C$_4$ to C$_{10}$) aliphatic trimethylsilyl ethers: Parent

Table III. Fragmentation Peaks in Mass Spectra of Normal Aliphatic Trimethylsilyl Ethers

Example. 1-hexyl derivative

m/e	Structures	Relative Intensities
43		17
73		45
89		16
103		25
Parent minus 15	 or	100
Parent		0.9

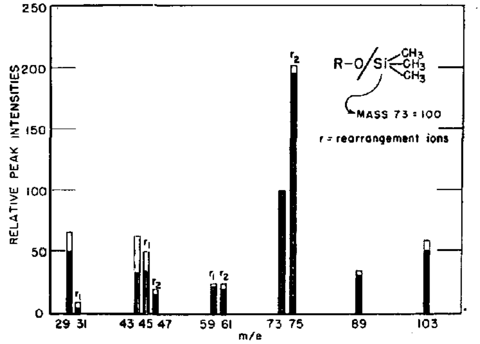


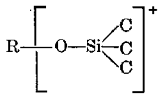
Figure 1. Pattern deviation, normal C_5 to C_{10} aliphatic trimethylsilyl ethers

mass peaks are weak, but a very intense peak resulting from the loss of one of the four methyl groups appears 15 mass units below the parent mass. Peaks at masses 73, 89, and 103 also are characteristic of this series, and these peaks have been correlated with the trimethylsilyl ether structure. The spectrum of the 1-hexyl ether is given as an example in Table III. Mass 43, which is an important peak in the mass spectra of many compounds, is a major peak for the trimethylsilyl ethers.

Patterns of the C_5 to C_{10} normal aliphatic trimethylsilyl ethers are similar for normal fragmentation masses 103, 89, 73, 43, and 29, and for rearrangement masses 75, 61, and 45 (Figure 1). The methyl, ethyl, branched, and secondary trimethylsilyl ethers do not show this pattern similarity. The intensity of mass 89, $(CH_3)_3SiO^+$, is different for the C_1, C_2, and C_3 normal aliphatic compounds. For the methyl derivative, mass 89 is the parent-minus-15 ion and is therefore very strong; for the ethyl and propyl trimethylsilyl ethers, mass 89 is much less intense than for any of the C_4 to C_{10} normal alcohol derivatives. Thus, the ion $(CH_3)_3SiO^+$ is unimportant unless the hydrocarbon chain consists of four or more carbon atoms.

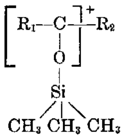
The most intense (base) peak is the parent-minus-15 ion for the derivatives of the normal alcohols C_1, C_2, and C_6 to C_{10} (Table I). Mass 75, a rearrangement ion, is the base peak for the C_3, C_4, and C_5 normal alcohol derivatives, although the parent-minus-15 peaks are almost equally intense.

PRIMARY BRANCHED TRIMETHYLSILYL ETHERS. Below mass 103 the same major peaks appear in the spectra of the primary branched- and straight-chain alcohol derivatives. However, the pattern variation is larger for the branched than for the normal derivatives. The two derivatives from γ-branched alcohols, 3-methyl-1-butanol and 3-methyl-1-pentanol, produce more mass 89 positive ions than other branched- or straight-chain derivatives (Table I).



A strong peak corresponding in mass to the alkyl radical minus two hydrogen atoms, is also in the spectra of the γ-branched derivatives.

SECONDARY TRIMETHYLSILYL ETHERS. The five ethers derived from straight-chain secondary alcohols show intense peaks resulting from a break at the functional carbon.



(R_2 is the larger hydrocarbon group)

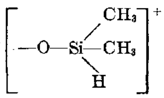
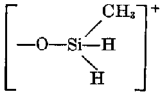
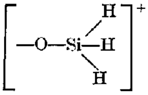
This fragmentation produces the base peak at mass 117 for 2-pentyl and 2-hexyl trimethylsilyl ethers and a strong peak at mass 131 for 3-type trimethylsilyl ethers. The branched-chain secondary alcohol derivative (3-methyl-2-butanol) behaves similarly by losing the larger alkyl group and producing the second most intense peak in the spectrum at mass 117. Mass 73 is more intense for the straight-chain secondary than for the corresponding primary alcohol derivative and is the base peak for 2-butyl and 3-heptyl trimethylsilyl ethers. Parent-minus-15 mass peaks are less intense for the derivatives of the secondary alcohols.

TERTIARY TRIMETHYLSILYL ETHERS. The mass spectra of the two tertiary alcohol trimethylsilyl ethers are similar. The parent-minus-15 ion for tertiary butyl and parent-minus-29 ion for tertiary amyl produce intense peaks at mass 131 in both spectra. All other peaks down to mass 75 are weak.

Rearrangement Ions. Several intense rearrangement peaks appear in the mass spectra of all the normal alcohol derivatives with the exception of methyl. Mass 75 is the most prominent rearrangement peak and always one of the three largest peaks in the spectrum. Rate of effusion determinations (*4*, *5*) made on mass 75 rule out the possibility of an impurity. With *n*-butyl trimethylsilyl ether, identical effusion rates were obtained for masses 131, 75, and 73, indicating that the mass 75 fragment is derived from the parent mass 146.

Two series of rearrangement peaks are found in the mass spectra of derivatives of normal aliphatic alcohols. The peaks in the two series are designated by r_1 and r_2 in Figure 1. The first series, r_1, is that found by Dibeler in hexamethyl disiloxane, $(CH_3)_6Si_2O$, and includes masses 59, 45, and 31 (*3*). These same mass ions were also found by Zemany and Price in the mass spectrum of tetramethylsilane, $(CH_3)_4Si$ (*18*). These authors concluded that the rearrangement fragments contain Si—H bonds. The second series, r_2, also has peaks differing by 14 mass units and includes masses 75, 61, and 47. This series is also explained by rearrangement structures similar to those proposed by Dibeler, with the addition of an oxygen atom (*3*).

Derivatives of the branched primary, secondary, and tertiary alcohols investigated show the same two series of rearrangement peaks as the normal compounds. Mass 75 is the base peak in the spectra of all the derivatives of β-branched primary alcohols given in Table I.

Rearrangement Series		Apparent Structure
r_1	r_2 (with —O—)	
59	75	 $[\text{—O—Si(CH}_3)_2\text{H}]^+$
45	61	 $[\text{—O—Si(CH}_2)\text{H}_2]^+$
31	47	 $[\text{—O—SiH}_3]^+$

Isotope determinations indicate that this is the correct assignment. Rearrangement peaks in the mass spectrum of hexamethyldisilazane, $(CH_3)_6Si_2NH$, parallel those in the spectrum of hexamethyldisiloxane.

Analyses of Alcohols by Trimethylsilyl Ethers. Because of their high volatility, normal aliphatic trimethylsilyl ether derivatives of C_4 to C_{10} alcohols can be analyzed by the mass spectrometer without difficulty. Relative intensities of the parent–minus-15 peak, useful in such analyses, are given in Figure 2. These peaks are not fragmentation peaks in the spectra of hydrocarbons and oxygenated compounds normally analyzed by the mass spectrometer. With derivatives of normal C_4 to C_9 alcohols, the total contribution to the characteristic parent–minus-15 peak of a compound by its homologs is less than 5% of the peak intensity. This slight interference can be corrected on the basis of the spectra of the pure compounds. Considerably less than 1% of any of the normal aliphatic trimethylsilyl ethers should be detectable in the presence of hydrocarbons. Mass 75 is of uniform intensity for the C_3 to C_7 normal alcohol derivatives and therefore serves as a convenient check on the total alcohol content.

Individual alcohol derivatives can be identified as to "type" by means of the mass spectral correlations described previously. These can be summarized as follows.

Only secondary and tertiary alcohol derivatives have strong peaks (other than the usual parent–minus-15 peak) above mass 103.

The intensity ratio of mass 75 to 73 is different for primary, primary branched, and secondary alcohol derivatives according to class. The ratios are given in Table IV.

Mass 89 is useful in determining the position of branching. Of the primary alcohols, only those having γ-branching show intense peaks at mass 89.

Secondary and tertiary alcohols can be identified as to type from the original alcohol spectrum (*6*).

The trimethylsilyl derivative of propylene glycol has the expected very weak parent peak and an intense parent–minus-15 peak. In contrast, both the parent and parent–minus-15 peaks are intense for the trimethylsilyl derivatives of phenol, butyl mercaptan, and the cresols. *m*- and *p*-cresol show similar fragmentation patterns, while *o*-cresol has a much less intense parent–minus-15 peak and a more intense mass 91 than *m*- and *p*-cresol. Trimethylsilyl derivatives should aid in the analyses of mix-

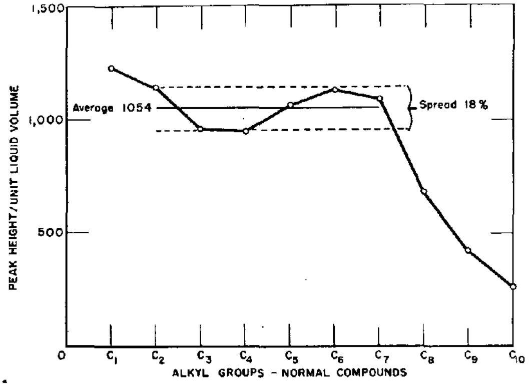


Figure 2. Trimethylsilyl ethers, parent–minus-15 peak intensities

Table IV. Type Identification of Alcohols by Trimethylsilyl Ether Derivatives

Alcohol Type (Trimethylsilyl Derivatives)	Peak Intensities: Ratio $\frac{\text{Mass } 75}{\text{Mass } 73}$ Average	Spread	Mass 73[a] (Vol. Sensitivity) Average	Spread
Primary-straight chain				
1-Butyl to 1-decyl	2.0	0.1	513	38
Primary-singly branched				
Butyl to octyl including methyl and ethyl branching	1.3	0.2	665	210
Secondary-(2-type)				
2-Butyl to 2-hexyl	0.82	0.04	1013	40

[a] *n*-Heptane mass 27 = 492 divisions/liquid volume.

tures containing these classes of compounds as well as in the analysis of alcohols.

ACKNOWLEDGMENT

The authors wish to express appreciation to Janet L. Shultz for the tabulation of the mass spectra.

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Infrared Spectra of Aliphatic Peroxyacids

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▶The infrared spectra of peroxypropionic acid and peroxybutyric acid were recorded in the vapor phase from 2 to 15 microns. In addition to the C-H and carbonyl bands, the most prominent absorptions were found at 3.05 microns, 6.9 microns, and 8.5 microns.

In the course of an investigation of the photo-oxidation of hydrocarbons at low concentration in air, samples of peroxypropionic and peroxybutyric acids were prepared and their infrared spectra recorded in the vapor phase.

Giguère and Olmos have published the spectra of peroxyformic and peroxyacetic acids (*2*). Their spectrum of peroxyacetic acid vapor is similar to the spectra reported here. Minkoff has published spectra which he attributes to peroxyacetic, peroxypropionic, and peroxybutyric acids (*3*). However, as he himself indicates, his samples were impure. His spectrum of peroxyacetic acid is similar to the spectrum obtained by Giguère and Olmos, but his spectra of peroxypropionic and peroxybutyric acids are not similar either to the peroxyacetic acid spectrum or to the spectra reported in this work. The chief impurity in Minkoff's samples appears to have been the ordinary aliphatic acids. These have been found to be persistent contaminents of the peroxyacids.

THE SPECTRA

The spectra of peroxypropionic and peroxybutyric acid are shown in the upper portion of Figures 1 and 2. These acids are unstable; for that reason the spectrum of a fresh sample shows bands of decomposition products. After the spectra had been run, the samples were allowed to decompose in the cell and the spectra were rerun. Bands of the unstable peroxyacids can be identified if a comparison is made of the spectra obtained before and after decomposition. For comparison the spectra of pure propionic and butyric acid vapors were also recorded and are shown in the lower portion of Figures 1 and 2.

The spectra were recorded on a Perkin-Elmer single-beam, single-pass spectrometer with the use of a Perkin-Elmer 1-meter gas absorption cell. For each of the peroxyacids the vapor pressure of the absorbing gas was about 3 or 4 mm. of mercury. The acid vapors were mixed in the absorption cell with 1 atmosphere of dry, carbon dioxide-free air which served to retard the decomposition of the peroxyacids.

The peroxyacids show absorption bands usually ascribed to the stretching vibrations of $C=O$ (5.7 microns), O—O (11.5 microns), and O_2—H (3.05 microns), as well as other frequencies which apparently originate in the oxygenated part of the molecule. These are given in Table I. The chief distinguishing bands of peroxyacids appear, from these spectra, to be at wave lengths of 3.05, 6.9, and 8.5 microns.

The 3.05-band in particular is a useful indication of the presence of peroxyacid in complex reaction mixtures. It is probably due to the OH vibration and may, therefore, indicate that these spectra are those of the monomer and not the dimer. Giguère and Olmos (*2*) discuss in some detail the assignment of bands in the spectra of peroxyformic and peroxyacetic acids.

PREPARATION AND CHEMICAL PROPERTIES

The peroxyacids were prepared by the method of Fischer, Düll, and Volz (*1*) which is essentially as follows. Aldehyde, in ice-cold carbon tetra-

Table I. Infrared Absorption Bands of Peroxyacids

Frequency, Cm.$^{-1}$	Wave Length, Microns	Intensity[a]
	Peroxypropionic Acid	
3280	3.05	M
2940	3.40	S
1760	5.68	S
1450	6.90	S
1180	8.48	S
1000	10.00	W
875	11.43	M
805	12.42	W
	Peroxybutyric Acid	
3280	3.05	M
2940	3.40	S
1760	5.68	S
1450	6.90	S
1175	8.52	S
862	11.6	W

[a] S = strong; M = medium; W = weak.

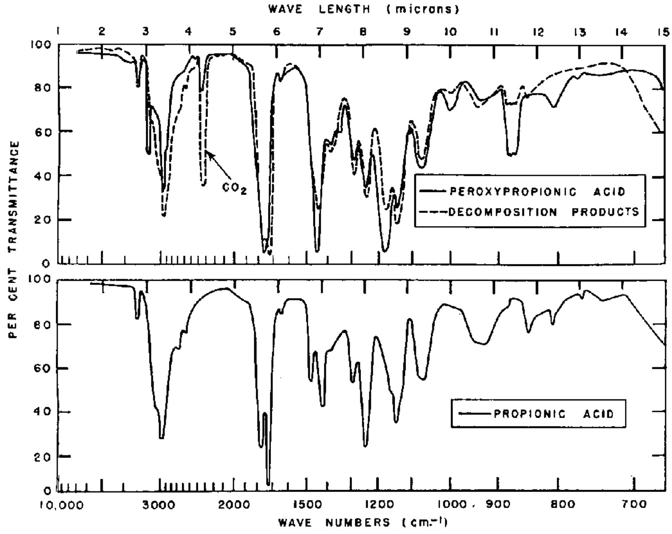

Figure 1. Peroxypropionic acid and decomposition products

Peroxypropionic acid spectrum recorded at several millimeters of mercury vapor pressure. Spectrum of decomposition products is same sample recorded 4.5 hours later. Propionic acid spectrum recorded at 1.3 mm. of mercury vapor pressure

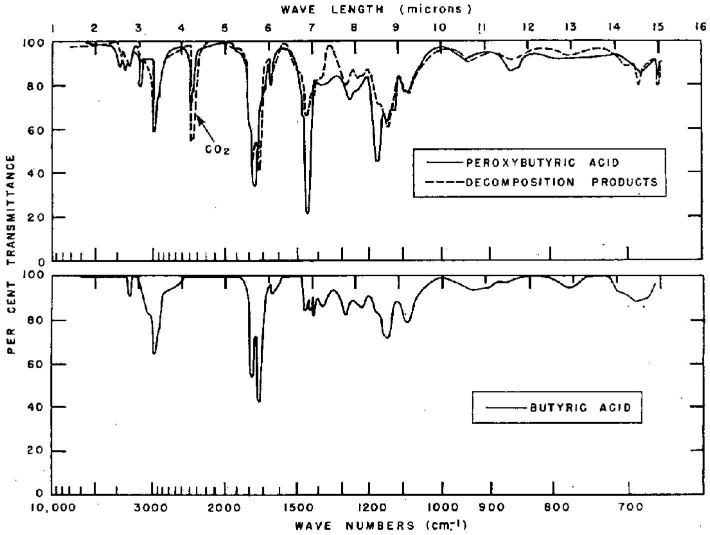

Figure 2. Peroxybutyric acid and decomposition products

Peroxybutyric acid spectrum recorded at several millimeters of mercury vapor pressure. Spectrum of decomposition products is same sample recorded 1.5 hours later. Butyric acid spectrum recorded at 1.0 mm. of mercury vapor pressure

chloride solution, was oxidized to its corresponding peroxyacid by bubbling a stream of ozonized oxygen through the solution. The peroxyacid was extracted from solution with aqueous base. It was converted back to peroxyacid by the addition of cold sulfuric acid and extracted from aqueous solution with ether. Finally, the ether extract was fractionally distilled under vacuum at room temperature.

Three fractions were obtained from the distillation. Their spectra showed the chief components to be ether, peroxyacid, and the simple acid. The second fraction was used for recording the spectra reported herein. This fraction had an oxidizing power as shown by the iodometric technique equivalent to approximately 50% by weight of peroxyacid, and an acid content as shown by titration with base equivalent to approximately 90% by weight—assuming the chief impurity to be the corresponding simple aliphatic acid.

DECOMPOSITION PRODUCTS

Both of the peroxyacids were observed to decompose while their spectra were being recorded. The spectra recorded after decomposition showed the presence of the corresponding simple acid and carbon dioxide.

The decomposition of the peroxypropionic acid was sufficiently slow to permit running of the whole spectrum on a single sample of vapor. However, the peroxybutyric acid vapor decomposed so quickly that it was necessary to run the spectrum in sections of 2 or 3 microns each, with the use of a fresh sample for each section. At room temperature the half-life of the peroxypropionic acid was several hours, and the half-life of the peroxybutyric acid was 10 or 15 minutes. No particular significance is attached to this rate of decomposition, as it may have been occurring on the walls of the cell.

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Photometric Determination of Arsenic and Phosphorus in Copper-Base Alloys

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▶ In the photometric determination of arsenic by the formation of a mixed heteropoly acid with molybdenum and vanadium, the factors influencing formation of the complex were examined and conditions designed to give results independent of temperature from 17° to 35° C. were established. The method was then extended to permit the simultaneous determination of both arsenic and phosphorus in deoxidized copper without prior separation. Phosphorus is determined first by developing the molybdovanadophosphoric acid complex in nitric acid of sufficient strength to prevent formation of the corresponding arsenic complex. Both complexes are then developed at a lower acid concentration and the arsenic concentration is determined from appropriate calibration curves. With this procedure arsenic and phosphorus have been determined in concentrations up to 0.60 and 0.10%, respectively.

When the technique of Gullstrom and Mellon (*4*) was attempted for the photometric determination of arsenic in copper, it seemed pertinent to determine the temperature sensitivity and the influence of copper on the behavior of the complex. This work was initiated following the authors' experience (*2*) with the corresponding heteropoly acid of phosphorus in the determination of phosphorus in steel, where the temperature insensitivity of the complex is markedly upset by the presence of iron.

Preliminary study of the reaction between vanadate, molybdate, and orthoarsenate, under the conditions specified by Gullstrom and Mellon, showed that the resultant arsenic complex was sensitive to temperature even after subtraction of the reagent blank. This effect was most pronounced at temperatures above 20° C., the net absorbance at 30° C. being approximately 25% lower than at 20° C. A critical examination of the factors and conditions affecting the color development of the mixed heteropoly arsenic acid was then undertaken with a view to establishing, if possible, conditions which would give the same magnitude of temperature variation in both the colored solution and the reagent blank, thus producing a constant net absorbance at least over a convenient temperature range.

Determination of both arsenic and phosphorus by a simple technique based on absorbance in the visible region, involving neither preliminary separations nor extractions with organic solvents, also seemed desirable. Arsenic has been determined in synthetic solutions as molybdoarsenic acid by measuring the absorbance in the ultraviolet region after extraction with butyl alcohol (*6*). Interference from phosphorus may be overcome by a preliminary selective extraction of the molybdophosphoric acid with a mixture of chloroform and butyl alcohol. De Sesa and Rogers (*3*) have suggested the possibility of determining phosphorus and arsenic in the same sample by successive extractions—first from water, then from alcohol—of the simple heteropoly acids with isoamyl acetate and measurement of the absorbance of each in the ultraviolet region.

With the conditions described here for the arsenic determination, phosphorus also forms a colored mixed heteropoly acid. Although the absorption spectra of these complexes of arsenic and phosphorus are similar (eliminating the possibility of a separate determination of the absorbance of each complex by a change in wave length), further experiments showed that the photometric method could be applied to the simultaneous determination of arsenic and phosphorus by proper control of the acidity.

APPARATUS AND REAGENTS

Measurements throughout this investigation were made with a Spekker Absorptiometer Type H 760 (Hilger and Watts Ltd.) under the following conditions: 1-, 2-, or 4-cm. glass cells; tungsten filament lamp; Kodak violet filter No. 543 (peak transmittance at 430 mμ); water setting on drum, 1.000. With this instrument net absorbances are represented by the differences between the drum readings of blank and colored solutions.

Nitric Acid. Concentrated, 2.00*N* and 4.0*N*.

Mixed Color Reagent. Dissolve 3.60 grams of sodium vanadate in 800 ml. of cold water, then add 48.0 grams of sodium molybdate dihydrate. Filter if necessary and dilute to 1 liter.

Neutralized Copper Nitrate Solution. Dissolve 15 grams of high-purity copper in a minimum quantity of concentrated nitric acid. Boil to expel nitrous oxide fumes and dilute to about 300 ml. Neutralize with ammonium hydroxide to the first appearance of a permanent precipitate. Add 2.0*N* nitric acid until the precipitate just dissolves and dilute to 500 ml. with water.

PROCEDURES

Phosphorus-Free Alloys. Dissolve 1.5 grams of the sample in 10 ml. of concentrated nitric acid, boil off nitrous oxide fumes, and evaporate to a small volume to expel most of the acid. (Solution in concentrated nitric acid oxidizes all the arsenic to the quinquevalent state, eliminating the need for a subsequent oxidation.) Dilute to about 30 ml. and neutralize carefully with dilute ammonium hydroxide until a faint permanent precipitate appears. Add 2.0*N* nitric acid dropwise with thorough shaking until the solution just clears. Dilute to 100 ml. in a volumetric flask. Transfer a 50-ml. portion to a second 100-ml. flask. One of these solutions is for color development, the other for the sample blank.

To one flask add 10.0 ml. of 2.0*N* nitric acid followed by 25.0 ml. of mixed color reagent. Let stand for 10 minutes and dilute to 100 ml. To the second flask add 10 ml. of 2.0*N* nitric acid and dilute to 100 ml. Prepare a reagent blank by mixing 10.0 ml. of 2.0*N* nitric acid and 25.0 ml. of mixed color reagent in a third 100-ml. volumetric flask. Let stand 10 minutes and dilute to 100 ml.

Measure the absorbances of the solutions at the same temperature. Determine the net absorbance by subtracting the absorbances of both blanks from that of the colored solution. Calculate the amount of arsenic by comparison with a calibration curve, which is prepared to cover the range from 0 to 0.75% arsenic by adding appropriate amounts of disodium hydrogen arsenate solution to samples of pure copper and developing the color as described above.

Additions of 2.0*N* nitric acid and mixed color reagent must be made

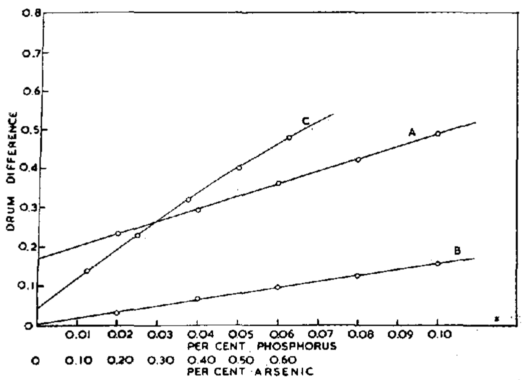

Figure 1. Calibration graphs

A. Phosphorus in 1.6*N* acid (4-cm. cell)
B. Phosphorus in 0.2*N* acid (2-cm. cell)
C. Arsenic in 0.2*N* acid (2-cm. cell)

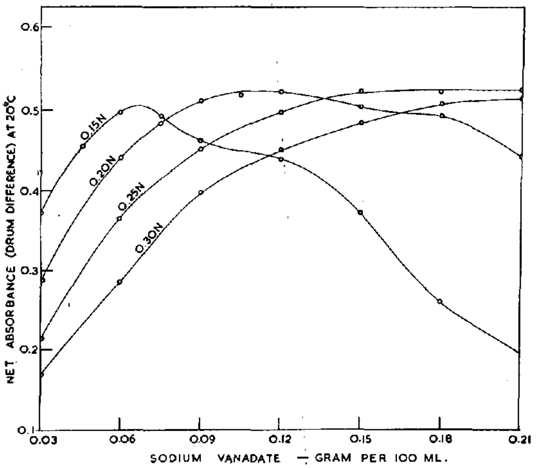

Figure 2. Effect of variation in acid and vanadate concentrations on arsenic color complex at 20° C.

accurately in this procedure. Also, the temperature difference between the reagent blank and colored solution should not be more than 0.5° C. when the absorbance measurements are made.

Alloys Containing Phosphorus and Arsenic. Dissolve according to the procedure given for phosphorus-free alloys. Again, the use of concentrated nitric acid assures conversion of all the phosphorus to the orthophosphate. After dilution to 100 ml., transfer 20-ml. aliquots (equivalent to 0.3 gram of sample) to each of three 100-ml. volumetric flasks. To the first flask add 40 ml. of 4.0*N* nitric acid and 25.0 ml. of mixed color reagent and dilute to 100 ml. Let stand for 15 minutes and measure the absorbance in a 4-cm. cell. This solution gives the absorbance for phosphorus at a nitric acid acidity of 1.6*N*.

To the second flask add 10.0 ml. of 2.0*N* nitric acid and 25.0 ml. of mixed color reagent. Dilute to 100 ml. Place this solution and a reagent blank (prepared in the same way but without a sample aliquot) in a water bath at a temperature between 17° and 30° C. and measure the absorbances in 2-cm. cells. The colored solution in this case gives the absorbance for arsenic plus phosphorus at 0.2*N* nitric acid acidity.

Prepare the sample blank by adding 10 ml. of 2.0*N* nitric acid to the third flask and diluting to 100 ml. Measure the absorbance of this solution in 2- and 4-cm. cells.

Calibration Curves. The simultaneous determination of arsenic and phosphorus requires three separate calibration curves. Vanadate and molybdate from different sources do not always give identical absorbances; therefore, it is desirable to check the calibration whenever the reagents are changed. The curves prepared as described below are shown in Figure 1.

A. Phosphorus Complex in 1.6*N* Acid. Add appropriate amounts of potassium dihydrogen phosphate to 10 ml. of the neutralized copper nitrate solution (equivalent to 0.30 gram of copper), followed by 40 ml. of 4.0*N* nitric acid and 25.0 ml. of mixed color reagent. Dilute to 100 ml. and let stand for 15 minutes. Prepare a sample blank containing the same amounts of copper and acid but no phosphate or color reagent. Measure the absorbances of blank and colored solutions (which need not be at the same temperature) in 4-cm. cells.

B. Phosphorus Complex in 0.2*N* Acid. To correct the total absorbance in 0.2*N* acid for the phosphorus contribution, a phosphorus calibration curve in 0.2*N* acid is also required.

Add appropriate amounts of potassium dihydrogen phosphate to 10 ml. of the neutralized copper nitrate solution, followed by 10.0 ml. of 2.0*N* nitric acid and 25.0 ml. of mixed color reagent. Prepare a combined blank containing the same amounts of copper, acid, and color reagent but no phosphate. Dilute both the colored solution and the blank to 100 ml. and bring to the same temperature in a water bath (within the range from 17° to 30° C.) Measure the absorbances in 2-cm. cells.

C. Arsenic Complex in 0.2*N* Acid. Add appropriate amounts of disodium hydrogen arsenate to 10 ml. of the copper nitrate solution, followed by 10.0 ml. of 2.0*N* nitric acid and 25.0 ml. of mixed color reagent. Prepare a sample blank containing copper and acid only, and a reagent blank containing acid and color reagent only. Dilute all solutions to 100 ml., bring to the same temperature in a water bath (17° to 30° C.), and measure the absorbances in 2-cm. cells. The absorbance due to the arsenic complex is obtained by subtracting the sum of the absorbances of sample and reagent blanks (net blank absorbance) from the absorbance of the colored solution.

Calculations. Percentages of phosphorus and arsenic in the alloy are obtained from the calibration curves and the following relationships:

Absorbance due to phosphorus = absorbance of solution at 1.6*N* − absorbance of sample blank (4-cm. cells, curve *A*, Figure 1).

Using this result, read the phosphorus correction from curve *B*, Figure 1.

Absorbance due to arsenic = absorbance of solution at 0.2*N* − (absorbance of reagent blank + absorbance of sample blank + phosphorus correction) (2-cm. cells, curve *C*, Figure 1).

PRELIMINARY EXPERIMENTS

Arsenic Determination. Initial experiments in nitric acid solution with 1 gram of sodium molybdate and 0.03 gram of sodium vanadate per 100 ml. of solution confirmed the statement of Gullstrom and Mellon that it is necessary to work in a weakly acid solution, because with increasing acidity the absorbance of the solution decreases rapidly.

At the start the molybdate concentration was kept constant at 1.0 gram per 100 ml. of solution because a large excess is necessary for the development of a heteropoly acid. The acid concentration was varied from 0.15- to 0.30*N* and the sodium vanadate concentration from 0.015 to 0.18 gram per 100 ml. of solution.

The results (Figure 2) can be summarized as follows:

> Acid concentration is highly critical for a given concentration of vanadate.
>
> The same maximum net absorbance can be attained irrespective of acid concentration, but the higher the acid concentration, the greater the amount of vanadate necessary for the development of this maximum.
>
> Further increases in the amount of vanadate beyond that required to produce the maximum bring about a marked reduction in the net absorbance of the solution in 0.15- and 0.20*N* solutions. This effect could not be investigated at higher acidities because the amounts of vanadate required caused the absorbance of the reagent blank to become prohibitively high.

Concurrently, the temperature effect was studied over the range from 10° to 35° C. for all combinations of acid and vanadate concentration plotted in Figure 2. Examination of the results showed that selection of an acid concentration of 0.2*N* together with a sodium vanadate concentration in the vicinity of 0.09 gram per 100 ml. gave minimum temperature dependence. Further work with sodium vanadate concentrations between 0.075 and 0.12 gram per 100 ml. in 0.2*N* nitric acid solution showed that results substantially independent of temperature could be obtained between 17° and 27° C. with from 0.08 to 0.11 gram of sodium vanadate. The amount of vanadate obviously is not highly critical within these limits, but the same amount must be added to both colored solution and reagent blank.

When the acid concentration was standardized at 0.2*N* and the sodium vanadate at 0.090 gram per 100 ml., a study of varying molybdate concentration showed that the net absorbance reaches a maximum at 1 gram of sodium molybdate and remains constant up to 1.6 grams. A concentration of 1.2 grams per 100 ml. of solution was selected for the procedure. A temperature survey showed that the effect of the increased molybdate was to minimize the effect of temperature further. Substantially constant results could now be obtained from 17° to 35° C.

A study of the influence of copper on the temperature sensitivity of the complex under these optimum conditions indicated that the copper nitrate background color remained constant from 15° to 40° C. The copper also had no effect on the temperature sensitivity of the complex when the optimum concentrations of reagents were used.

Phosphorus and Arsenic in Same Alloy. In developing a procedure for phosphorus, the optimum conditions of acidity and reagent concentration established for arsenic were used. Experimental work was concerned essentially with developing the phosphorus and arsenic complexes together in 0.2*N* nitric acid and with establishing conditions for determination of the phosphorus complex without interference from arsenic. It was desired to use aliquots from the same original solution to determine arsenic and phosphorus together and phosphorus alone, and to use the same concentration of mixed color-reagent as well.

Preliminary experiments showed that a yellow complex could be developed satisfactorily with orthophosphate in the presence of copper. Conditions for the arsenic procedure were used. Although the amount of vanadate was several times higher than usual for the determination of phosphorus (*1*), the absorbance was independent of temperature from 15° to over 30° C.

Although the interdependence of acid and vanadate concentrations was not examined at acid normalities above 0.3 for the arsenic determination, it seemed possible that, with the vanadate concentration selected, the development of the arsenic complex might be completely inhibited if the acid concentration was sufficiently high.

In studying the effect of acid concentration, both the arsenic and the phosphorus complexes were developed at room temperature in the presence of 0.75 gram of copper, with 0.09 gram of sodium vanadate and 1.2 grams of sodium molybdate per 100 ml. of final solution. The amounts of arsenic and phosphorus added (as orthoarsenate and orthophosphate) were 5 mg. and 1 mg., respectively, these amounts being chosen to correspond approximately with the maximum amounts of arsenic and phosphorus likely to be encountered in phosphorus deoxidized arsenical coppers. As the nitric acid concentration was varied from 0.2- to 2.0*N*, the molybdovanadophosphoric acid color was completely developed within 10 minutes at 20° C. at acid concentrations up to 1.6*N*. Under these same conditions the development of color due to the arsenic complex was increasingly inhibited, so that the color was negligible at 1.6*N* and completely extinct at 2.0*N* acid concentration (Figure 3). Furthermore, the absorbance due to either

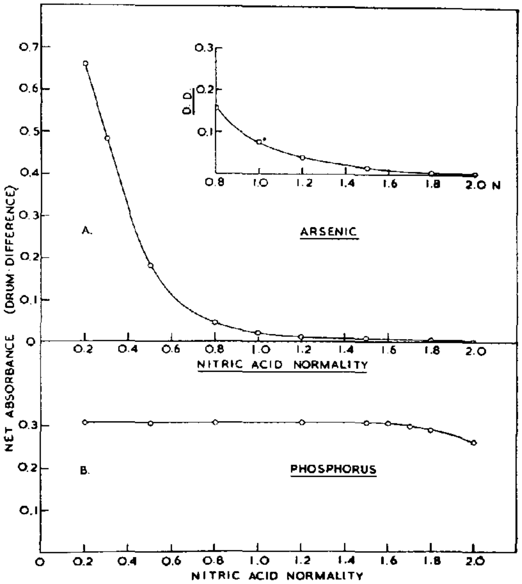

Figure 3. Effect of acid concentration on development of arsenic and phosphorus complexes for 10 minutes at 20° C.

A. 5 mg. of arsenic (1-cm. cell)
Insert. Same complex in 4-cm. cell
B. 1 mg. of phosphorus (1-cm. cell)

the reagent blank or the molybdovanadophosphoric acid complex was not affected by temperature variations at this acidity.

DISCUSSION

Arsenic Determination. The sensitivity of this method is such that it may also be applied to the determination of small amounts of arsenic in brasses and similar alloys in the range from 0 to 0.10%, using 4-cm. cells in the Spekker Absorptiometer. When small amounts of arsenic are sought, however, the compensation achieved by using a reagent blank may be insufficient to permit the determination to be made over a wide temperature range from the one calibration graph. Accurate results can still be obtained, though, if the absorbance of the sample is measured at the same temperature as that used for calibration.

In applying the method to the determination of arsenic in brasses, the effect of elements commonly present in brasses was re-examined. Zinc does not interfere, and small amounts of tin not precipitated in dilute nitric acid solution can be tolerated. The method is not applicable in its present form to alloys containing appreciable amounts of tin. The following elements can also be tolerated, at least up to the percentages given, without introducing an error greater than 0.005%:

	%		%
Lead	4	Manganese	0.2
Nickel	2	Cadmium	0.2
Aluminum	2	Bismuth	0.05
Iron	0.5	Antimony	0.05

Phosphorus and Arsenic Determination. Because of the widely divergent conditions used in other photometric procedures for phosphorus, it seems pertinent to discuss further the question of arsenic interference in the determination of phosphorus by a method based on the reaction between orthophosphate, vanadate, and molybdate. Although the present method requires an acid concentration as high as 1.6*N* to make the arsenic interference negligible, much lower acid concentrations can safely be used if the vanadate concentration is correspondingly reduced. Thus, in the three ASTM methods for the determination of phosphorus in various copper-base alloys, acid concentrations range from 0.45- to 1.15*N*, and ammonium vanadate concentrations from 0.01 to 0.025 gram per 100 ml. of final solution. No interference from arsenic results even at acid concentrations of 0.45*N* under these conditions, whereas Lutwak's modification (*5*) of the ASTM procedure, employing a lower acid concentration (0.35*N*) and 0.01 gram of ammonium vanadate per 100 ml., is subject to slight interference if arsenic is present.

Blanks. The success of the simultaneous determination is entirely dependent upon the use of the appropriate blanks at each stage of the procedure. When the mixture of vanadate and molybdate is added to a nitric acid solution of copper, arsenate, and phosphate, the total absorbance measured comprises contributions from four constituents. The copper nitrate, excess color developing reagent, and the two complex acids obviously are colored. But there is also a contribution of unknown cause from the combination of copper and the color developing agent, because the absorbance of a solution containing acid, reagents, and copper (combined blank) is greater than the sum of the absorbances of sample blank and reagent blank.

The combined blank is the only blank containing all constituents (other than the mixed heteropoly acids) contributing to the absorbance of the solution and is, therefore, the only blank permitting evaluation of the contribution of the phosphorus heteropoly acid at 0.2*N*. This blank, however, can obviously have no place in the subsequent analysis of actual samples.

Unlike the phosphorus calibration at 0.2*N*, which is merely a correction graph and also has no counterpart in the analysis of a sample, the arsenic calibration requires a net blank representing the sum of the absorbance of two blanks: the reagent blank through which compensation for temperature is achieved and the sample blank to account for background variation.

Table I. Determinations of Arsenic in Synthetic Samples

Arsenic, %			
Present	Found	Diff.	Temperature, ° C.
0.100	0.096	−0.004	25
0.250	0.250	0.000	20
0.350	0.347	−0.003	18
0.500	0.500	0.000	28
0.750	0.750	0.000	22

At 1.6*N* the absorbance of the reagent background is much lower than at 0.2*N* and is independent of temperature. A reagent blank at this normality is therefore unnecessary, and only a sample blank is used. The absorbance of the copper nitrate background is independent of both acid concentration and temperature, so that the actual analytical procedure can be simplified further by preparing only one sample blank, either at 0.2- or at 1.6*N*, and measuring the absorbance in both 2- and 4-cm. cells.

Consideration of these facts shows that the phosphorus calibration graph at 0.2*N* should pass through the origin, that the zero point on the arsenic calibration curve represents the difference between the combined and net blanks—i.e., the absorbance of the copper - vanadium - molybdenum complex—while the zero point on the phosphorus calibration curve at 1.6*N* represents, in addition, the absorbance of the excess reagents at this normality. Because the same procedure is adopted in both calibration and sample analysis, the fact that curves *A* and *C* of the calibration graph (Figure 1) do not pass through the origin introduces no error.

ACCURACY

The accuracy of the method for arsenic and its independence of temperature were checked by analyzing a series of synthetic standards prepared by adding high-purity, elemental arsenic to pure copper and dissolving in concentrated nitric acid. The results are given in Table I.

A sample of tough pitch copper (No. 23d, certificate value, 0.42% arsenic)

Table II. Simultaneous Determination of Arsenic and Phosphorus in Copper-Base Alloys

	Present, %		Found, %	
Sample No.	Arsenic	Phosphorus	Arsenic	Phosphorus
1	. . .	0.066	Nil	0.066
2	0.07	0.055	0.07	0.054
3	0.19	0.035	0.19	0.035
4	0.27	0.022	0.26	0.024
5	0.31	0.017	0.31	0.016
6	0.41	. . .	0.41	Nil
7[a]	0.10	0.100	0.10	0.098
8[a]	0.30	0.050	0.29	0.050
9[a]	0.60	0.020	0.60	0.020
10[a]	0.60	0.100	0.58	0.099

[a] Synthetic samples.

from the Bureau of Analyzed Samples Ltd., England, were also analyzed at different temperatures. The same result of 0.41% arsenic was obtained over the range from 17° to 35° C.

Phosphorus and arsenic were determined simultaneously on accurately analyzed standards as well as synthetic standards (prepared from pure copper, orthoarsenate, and orthophosphate). The results are given in Table II.

ACKNOWLEDGMENT

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Prewaves and Postwaves in the Polarography of Phenyl Ketones

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► The pre- and postwaves which have been reported to accompany the normal polarographic waves found for aromatic carbonyl compounds are due to the effect of ultraviolet radiant energy on the solvent used to prepare stock solutions of the carbonyl compound; the carbonyl compound apparently serves as a photochemical sensitizer or catalyst. Irradiation of a solution of propiophenone in 95% ethyl alcohol showed the gross reaction producing the prewave to be zero order in nature and the material produced to be polarographically identical with that formed in normally aged ketone stock solutions. The electroactive species producing the prewave was destroyed or transformed to a nonreducible species by sodium bisulfite. The postwave was due to acetaldehyde. The ketone wave itself was unaffected by irradiation or added bisulfite.

Previous investigators (*1*, *4*, *8*) of the polarographic behavior of aromatic carbonyl compounds have noted that on aging, stock solutions of aldehydes and ketones in ethyl alcohol developed a polarographic prewave—i.e., a wave which appeared at less negative potential than the normal wave due to carbonyl group reduction. The cause of this phenomenon was not determined. In a study of benzaldehyde, Tokuoka (*8*) attributed the prewave to peroxides formed during aging; however, this conclusion was not based on specific experimental investigation of the prewave. Postwaves have apparently also been observed.

In the course of an investigation of the polarography of aromatic ketones (*7*), additional polarographic waves were noticed when aged stock alcoholic solutions of ketones were used to prepare test solutions. As the appearance of these extraneous waves indicated that one or more reactions leading to formation of additional electroactive species had occurred, a study was made to determine the cause of these prewaves and postwaves.

From a series of qualitative tests involving the probable factors for the reaction—i.e., ketone, alcohol, air, and light—it was concluded that radiant energy was the primary cause of extraneous waves. Consequently, quantitative irradiation experiments utilizing ultraviolet radiant energy were performed on solutions of propiophenone in 95% ethyl alcohol.

EXPERIMENTAL

Chemicals. Eastman Kodak white label grade propiophenone was purified by distillation through a 1 × 28 cm. helix-packed column; the product had a boiling point of 114° C. (28 mm.) and n_D^{25} of 1.5245. Reagent grade 95% ethyl alcohol was used. Other chemicals used were also of reagent grade. The nitrogen used for deoxygenating polarographic test solutions was purified and equilibrated by bubbling it successively through sulfuric acid, alkaline pyrogallol solution, distilled water, and, finally, a portion of the test solution.

Apparatus. The irradiation apparatus consisted of a Westinghouse sun lamp affixed to an inverted U-stand; a manually operated shutter was clamped immediately below the lamp. The reaction vessel consisted of a tall, calibrated, 250-ml. beaker immersed in an ice bath; the center of the lamp outer wall was 30 cm. from the level of the beaker lip.

Polarographic data were obtained on a Leeds & Northrup Type E Electro-Chemograph and a water-jacketed H-cell (*6*) containing a saturated calomel reference electrode (S.C.E.); the cell was maintained at 25.0° ± 0.1° C. For the 0° runs, an unjacketed H-cell, maintained at 0.0° ± 0.1° C., was used. The data in Table I were obtained with a capillary having m = 1.172 mg. per second and t = 5.48 seconds at open circuit in distilled water (h = 60 cm., T = 25° C.); the capillary used to obtain the data in Table II had m = 0.952 and t = 5.97. All polarographic test solutions had an ionic strength of 0.45M and contained 9.5% ethyl alcohol; presence of the latter casts some doubt on the absolute validity of the pH measurements reported.

Irradiation Procedure. A stock solution of ketone (5.45 mM) in 95% alcohol was placed in the uncovered reaction vessel and irradiated for 10-minute intervals by opening the shutter; the distance from the light source to solution level was originally 34.75 cm. At the end of each time interval, the shutter was closed and, after stirring, a 5-ml. sample was removed and placed in a 50-ml. volumetric flask. The solution level dropped 0.25 ± 0.05 cm. after the removal of each sample. The exposure time, t, was corrected for the increase in distance, d, between the radiant energy source and the solution level by means of the relationship, $E = It$, where E is the amount of exposure, I is the radiant energy intensity, and I varies as d^{-2}. The temperature of the reaction mixture was always found to be 1.0° ± 0.1° C. Ten samples were thus collected, diluted 1 to 10—i.e., to 0.545 mM—with ammonia buffer ($NH_4Cl + NH_3$, pH = 8.9) and polarographed in the usual way.

EXPERIMENTAL RESULTS

Preliminary Studies. Solutions of propiophenone in 95% ethyl alcohol were stored in the dark and in daylight—i.e., near a window—and examined polarographically (pH 8.2 ammonia buffer) at the end of 1 week. The solution stored in the dark gave only the normal ketone wave, while that exposed to daylight also gave a prewave. Subsequently, 95% ethyl alcohol, exposed to daylight for the same period of time, was used to prepare a ketone stock solution; polarographic examination showed that no electroactive material, other than the ketone, was present.

The ketone stock solution which had been exposed to daylight was allowed to stand under similar conditions for 5 more weeks, after which time the solution (4.90 mM in ketone) was examined polarographically in both acetate and ammonia buffers (Table I). The half-wave potential, $E_{1/2}$, of the prewave was pH-independent over the pH range of 4 to 9. Its diffusion current (average, 0.86 μa.) was essentially constant over the same pH range. The ketone wave exhibited the same behavior as fresh propiophenone solutions (*7*). In addition to the prewave and normal wave, a postwave (occurring after the normal carbonyl group reduction wave) of constant $E_{1/2}$ was observed in alkaline solution; the postwave is masked by background electrolyte discharge in acidic solution.

Irradiation Studies. The electroactive species generated by controlled artificial irradiation of a 5.45 mM stock solution of propiophenone in 95% ethyl alcohol kept at 1.0° ± 0.1° C. produced, after dilution to 0.545 mM with ammonia buffer, a polarographic prewave, which was identical with the one derived from aged stock solutions. The magnitude of the prewave increased linearly with irradiation time (Table II) and consequently the gross photochemical reaction exhibits zero-order kinetics—i.e., $d(i_d)/dt = k$, where k is the reaction constant, i_d is a measure of the electroactive material being produced, and t is the reaction time. k = 0.092 μa. per minute, where the polarographic current times 10, the dilution factor, is taken as a measure of the concentration of the reducible material formed. If it is assumed that the electroactive species producing the prewave has a diffusion coefficient of 0.7×10^{-5} sq. cm. sec.$^{-1}$ and undergoes a two-electron reduction, k corresponds to 0.022 mmole liter^{-1}min.$^{-1}$ By relating k to ketone concentration, one obtains k' = 0.0040 mmole/mmole ketone/liter minute.

Table I. Effect of pH on $E_{1/2}$ and i_d of Polarographic Waves Appearing in Exposed Propiophenone Solutions[a]

Run No.	pH	Prewave $E_{1/2}$, -v.	Prewave i_d, μa.	Normal Wave $E_{1/2}$, -v.	Normal Wave i_d, ua.	Postwave $E_{1/2}$, -v.	Postwave i_d, μa.
1	3.9	0.99	0.69	1.27	0.90	Buffer discharge	
2	4.7	0.98	0.78	1.27	0.63	Buffer discharge	
3	5.7	0.97	0.93	1.36	0.66	Buffer discharge	
4	8.1	0.98	0.96	1.45	1.14	ca. 1.74	..
5	8.7	1.01	0.87	1.48	1.86	ca. 1.72	..
6	9.2	1.00	0.93	1.49	1.86	1.71	0.36

[a] Polarographic test solution had ketone concentration of 0.490 mM. Runs 1 to 3 made in acetate buffer; 4 to 6 in ammonia buffer.

Table II. Effect of Ultraviolet Radiant Energy on Subsequent Polarographic Behavior of a Solution of Propiophenone in Alcohol

		Polarographic Data,[a] Ammonia Buffer, pH 8.9				
		Prewave		Normal Wave		
Run No.	Exposure Time, Min.	$E_{1/2}$, -v.	i_d, μa.	$E_{1/2}$, -v.	i_d, μa.	I
1[b]	10.0	1.15	0.08	1.483	2.15	3.60
2[b]	19.9	1.04	0.10	1.483	2.22	3.72
3	29.6	1.03	0.27	1.487	2.20	3.69
4	39.2	1.01	0.36	1.485	2.18	3.68
5	48.6	1.03	0.45	1.485	2.20	3.69
6	57.9	1.01	0.52	1.484	2.15	3.60
7	67.1	1.02	0.62	1.482	2.14	3.58
8	76.2	1.02	0.70	1.483	2.10	3.37
9	85.1	1.01	0.79	1.480	2.13	3.40
10	93.8	1.01	0.90	1.484	2.11	3.37
11	93.8	1.01	0.98	1.485	2.25	..
12	93.8	1.04	0.80	1.508	1.40	..

[a] Polarographic data for runs 1 to 10 obtained at 25° C. and corrected head of 63.2 cm. Runs 11 and 12 made at 78.2-cm. (25° C.) and 63.2-cm. corrected head (0° C.), respectively.

[b] These runs gave such small prewaves that calculations were extremely difficult and are probably in considerable error.

As with naturally aged samples, there was indication of a slight postwave whose $E_{1/2}$ was approximately that of the postwave formed in the naturally aged stock solution. Variation of i_d both with height and with temperature indicated that the electroreduction producing the prewave is a diffusion-controlled process. The normal ketone wave was unaffected by the irradiation; in particular, its i_d did not change in magnitude. Comparison of runs 10, 11, and 12 (Table II) as to effect of height and temperature on i_d shows that both the prewave and the normal wave are diffusion-controlled. The temperature coefficient of the prewave was 0.5 per °C., while that of the normal wave was 1.6% per °C.; the current for both waves was proportional to $(h_2/h_1)^{1/2}$—i.e., 1.11.

Addition of a small amount of sodium bisulfite to the irradiated (100 minutes) solution destroyed or deactivated the electroactive species producing the prewave and postwave without affecting the normal wave of the ketone carbonyl group.

DISCUSSION

Effect of Irradiation and Aging. The irradiation experiments showed that formation of the electroactive material producing the extra waves, as an apparent result of aging, is, in fact, due to exposure to ultraviolet radiant energy. Furthermore, because the magnitude of the prewave can be made greater than that of the normal carbonyl group reduction by continued irradiation of the stock ketone solution, and the normal ketone wave is unaffected, the solvent must be the source of the prewave-producing material. The fact that the ketone must be present in order for the reaction to take place is evidence that the ketone acts as a sensitizer (*3*) or catalyst.

The prewave-producing material itself is probably not peroxidic in nature, as stated by Tokuoka (*8*), as peroxides are known to react when exposed to ultraviolet radiant energy—e.g., diethyl peroxide goes to biacetyl (*2*). Since bisulfite deactivates the electroactive species by either reducing it or combining with it, and the wave height becomes greater than that of the ketone wave without affecting the latter, the electroactive material must be an oxidation product of ethyl alcohol. At first, it was thought that biacetyl was produced (possibly through a peroxide intermediate); however, the polarographic behavior (*5*) of biacetyl, as well as that of possible peroxides and hydroperoxides, does not satisfactorily correspond with that of the prewave-producing material. Unfortunately, as no polarographic data which agree with those of the oxidation product could be found in the literature, it was impossible to identify the material from the information available. The $E_{1/2}$ of the postwave and its subsequent destruction with bisulfite indicate the wave to be undoubtedly due to some acetaldehyde which is also formed during the photochemical oxidation of ethyl alcohol.

The reaction leading to the prewave-producing material shows zero-order kinetics. This is in agreement with the polarographic results, in that the kinetic data also suggest that the ketone must be a catalyst or sensitizer and that the ethyl alcohol must be the progenitor of the prewave-producing material.

As the present authors were interested only in determining the cause of the prewave and the postwave, and in ascertaining whether it affected the normal ketone wave, no studies were made in solvents other than ethyl alcohol and no further attempts were made to identify the prewave electroactive species. This could presumably be identified by isolating it or its reduction product and characterizing either of them by usual methods. Another possible approach might be a polarographic study of all possible oxidation products and comparison of their behavior with that of the electroactive material. The latter method would probably be more tedious than the more direct approach.

ACKNOWLEDGMENT

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Carbon Replica Technique for Examination of Paint Surfaces in Electron Microscopy

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► The organic nature of paint surfaces necessitates the elimination of organic solvents for replication. The use of a water-soluble plastic as the primary replica with evaporated carbon as the final replica, followed by shadowing, has proved successful. Examples illustrating the attack of organic solvents on baked paint surfaces are presented and details of the methylcellulose-carbon replica technique are described.

REPLICATION TECHNIQUES have received wide acceptance for the study of surface structure of materials. The simple plastic film technique has been particularly successful. Recent work reported by Agar and Revell (*1*) has demonstrated that a true plastic replica of the surface (with the top surface of the replica flat) requires a film thickness approximately twice the thickness of the structure height. This criterion is not always achieved when using Formvar replicas, but it is possible to obtain satisfactory results even if the surface structure penetrates to the top surface of the replica. However, with very rough surfaces, thick replicas are required to prevent rupture in the electron beam. This introduces electron transmission difficulties when attempting to study such surfaces as paint coatings because of the roughness encountered, and suggests the use of multiple step replica techniques.

Multiple step replica techniques have the disadvantage of loss of detail due to repeated replication. Bradley's work (*3*) on the carbon replica technique, however, indicates that the primary Formvar replica is capable of a surface resolution of about 30 A. While there seems to be some question with respect to the final resolution following multiple replication, the resolution is adequate for the study of paint surfaces reported here.

REPLICATING SYSTEMS

In the study of surfaces of inorganic materials, the use of aromatic or aliphatic solvents for the plastic replicating medium is satisfactory. For surfaces of organic coatings however, solvents cause an uncertainty in the reproduction process because they can attack the organic phase. When this takes place, part of the surface may be pulled away during stripping of the replica or the film surface may be distorted or softened. Water-soluble plastics are a satisfactory substitute to eliminate this condition. On the other hand, these plastics cannot be used as final specimen supports because they rupture easily under the electron beam, but they are satisfactory as primary replicas for multiple replicating systems. A number of multiple replicating systems using water-

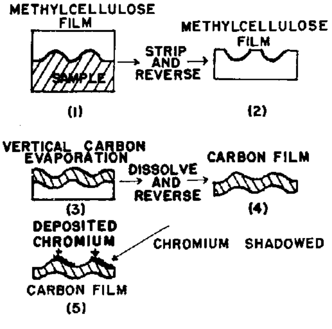

Figure 1. Methylcellulose-carbon replica technique

soluble plastics have been employed. Some of the more common ones include poly(vinyl alcohol)–silica, methylcellulose-Formvar, and methylcellulose-silica. As the stability of the final replica in the electron beam is of major significance, the development of the evaporated carbon film technique by Bradley (*2*) suggests an ideal material for the final replica when a water-soluble plastic is used as the primary replica.

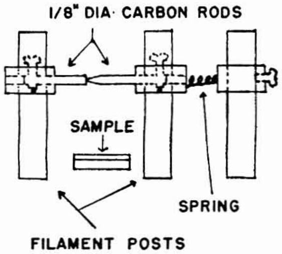

Figure 2. Carbon evaporation apparatus

The use of evaporated carbon has advantages over silica or plastic as the final replica in a two-step replica technique. Carbon evaporates with less difficulty than silica and forms a chemically inert substrate which is more stable than silica under the electron beam. It is also more stable than a plastic film of comparable thickness. Furthermore, carbon films are sturdy enough to permit handling without the need of additional backing or special specimen screen supports.

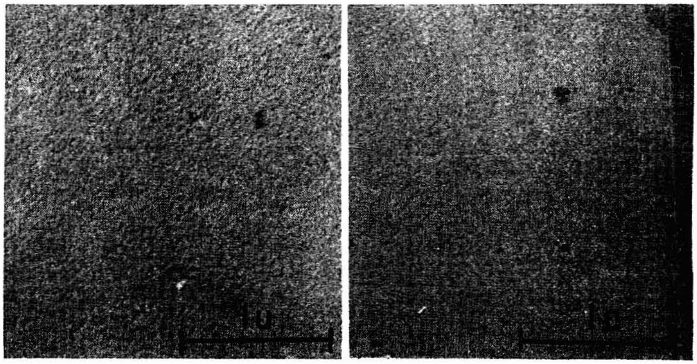

Figure 3. Replicas of polished glass surface

Chromium shadowing, × 25,000

A. Nitrocellulose replica *B.* Methylcellulose-carbon replica

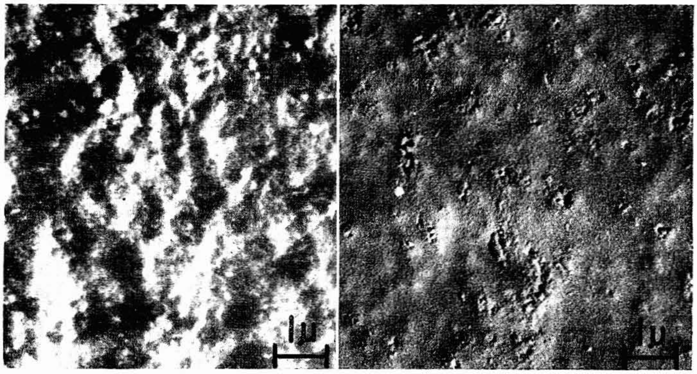

Figure 4. Replicas of same paint surface

Chromium shadowing, × 8000

A. Nitrocellulose replica *B.* Methylcellulose-carbon replica

METHYLCELLULOSE-CARBON REPLICA TECHNIQUE

Preparation of Primary Replica. A schematic representation of the steps used in the preparation of the carbon replica of a paint surface is given in Figure 1. True reproduction by the two-step replica technique is dependent on the characteristics of the primary replicating medium; therefore, careful control of the solution concentration is essential. Too low a concentration results in stripping difficulties which produce mechanical strains, while too high a concentration results in excessive shrinkage of the film at the surface of the sample, resulting in the development of wrinkles. For paint surfaces a 5% aqueous methylcellulose solution (Methocel, The Dow Chemical Co.) is employed. The solution is applied uniformly with the aid of a dropper maintaining the paint surface at an angle of approximately 20° to the horizontal. When dry, the film is stripped from the test surface with a small piece of Scotch tape. The stripped film is then attached with Scotch tape to a microscope slide and placed in the vacuum evaporator for coating with carbon.

Carbon Evaporation Procedure. The method of carbon evaporation consists of passing 60-cycle alternating current of approximately 50 to 60 amperes through $^{1}/_{8}$-inch diameter graphite rods (National Carbon, pure spectrographic grade) in a vertical position above the specimen with one rod tapered to a fine point. The carbon rods are held in close contact by a spring, as shown in Figure 2, so that they do not separate during the evaporation process. Intense local heating occurs at the regions of contact. In order to ensure that the vacuum is maintained at 0.1 micron of mercury or less, even while the hot regions are degassing, vacuum readings are checked closely, and a preliminary warming of the carbon rods at a lower temperature than that needed for evaporation is performed as an additional precaution.

A satisfactory carbon thickness is maintained by visually observing the color (light brown) of the condensed carbon developed on a piece of white porcelain through the window port of the vacuum evaporator bell jar. More elaborate methods of controlling the carbon thickness have been described (*3*).

When the evaporation is completed, the carbon–plastic coated slide is removed, cut into 0.3-cm. squares with a sharp razor, and placed on the surface of a Petri dish filled with distilled water until the methylcellulose is completely dissolved. Two to 3 hours is required for complete dissolution of the methylcellulose with frequent replacement of the distilled water. Specimen screens (200-mesh, woven stainless steel wire disks, $^{1}/_{8}$ inch in diameter) are placed on top of the floating carbon sections and removed with forceps. When dry, the carbon-coated screens again are placed in the vacuum evaporator for shadowing with chromium.

The selection of the shadowing angle for paint surfaces generally is not too critical. However, in the case of exceedingly smooth surfaces, such as high gloss paint films, an evaporation angle of approximately 5° to 7° with the horizontal is required to show surface irregularities of very small dimensions normal to the surface. When the shadowing process is completed, the metal-coated specimen is ready for examination in the electron microscope.

Electron Microscope Technique. An RCA-type EMU electron microscope equipped with self-biased electron gun and binocular viewer was employed. A platinum objective aperture with an opening of 40 microns in diameter was used to increase the contrast in the final image. All precautions necessary for the maintenance of a high resolution image were exercised. Kodak Medium Plates were used and developed in Kodak Versatol Developer. All electron micrographs of the paint surfaces were processed to the negative print stage to make heights and depressions more readily interpreted.

QUALITY OF REPRODUCTION

A comparison for quality of reproduction using the methyl-cellulose-carbon technique with the negative nitrocellulose technique was made employing a highly polished glass surface. The initial negatives were taken at an electronic magnification of ×3500 and enlarged optically to ×25,000. The electron micrographs (positive prints) in Figure 3 illustrate approximately the same areas of the glass plate obtained by the two techniques. These electron micrographs show that the reproduction obtained by the water-soluble plastic as the primary replica in conjunction with evaporated carbon gives the same degree of film structure as is obtained with nitrocellulose.

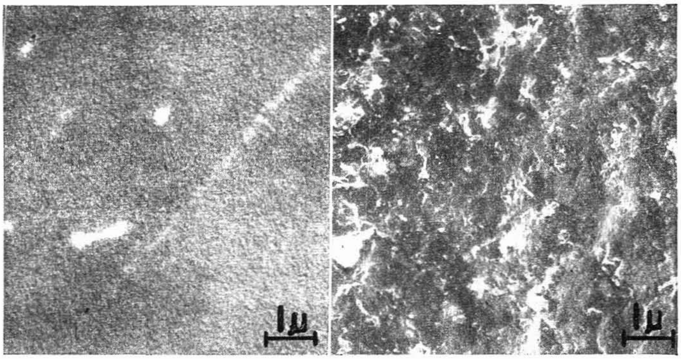

Figure 5. Methylcellulose-carbon replicas of paint surface

Chromium shadowing, × 8000

A. Original surface B. Surface after nitrocellulose replication

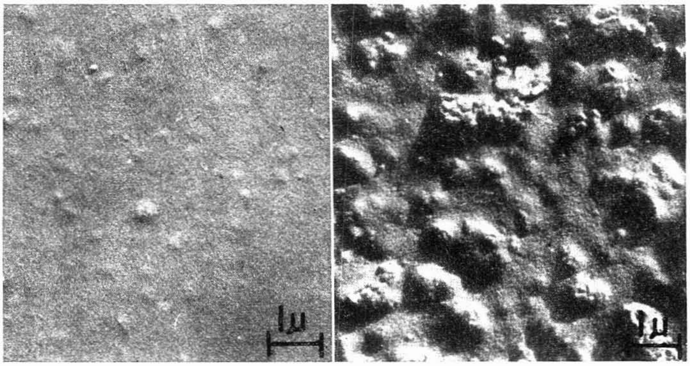

Figure 6. Methylcellulose-carbon replicas of glossy and mat paint surfaces

Chromium shadowing, × 8000

A. Glossy finish B. Mat finish

APPLICATIONS

Organic paint surfaces require a multiple replicating system as discussed above. For most work the electronic magnification is maintained at ×1400 and enlarged optically to a final magnification of ×8000. An example to illustrate the unsatisfactory reproduction of a baked paint surface with a nitrocellulose replica is shown in Figure 4,*A*. The same paint surface by the positive methylcellulose-carbon technique is shown in Figure 4,*B*. Figure 4,*A*, shows a roughened surface, while Figure 4,*B*, shows a moderately smooth surface.

In order to substantiate that the roughened surface was the result of attack by the replicating medium, a particularly smooth paint surface was examined. The methylcellulose-carbon replica technique was employed first; the electron micrograph is shown in Figure 5,*A*. The negative nitrocellulose technique was then applied to the same surface and the replica discarded. The methylcellulose-carbon technique was again applied to the same area of the paint surface exposed to the nitrocellulose replica; this electron micrograph is shown in Figure 5,*B*. A comparison of the micrographs shows that the nitrocellulose replicating medium attacks the organic phase of the paint surface.

Further examples of the versatility of the positive carbon replica technique are shown in Figure 6, where *A* represents a smooth surface commonly ascribed as a "glossy" surface, while *B* represents a rough surface commonly ascribed as a "flat" or "mat" surface.

It is essential in this technique that the replicating media do not interact with the surface to be observed and thereby introduce artifacts. A particular advantage of the technique is that the replicated surface is left undamaged and can be used for additional studies.

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Separation of Hydrogen, Oxygen, Nitrogen, Methane, and Carbon Monoxide by Gas Adsorption Chromatography

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▶ A molecular sieve column, Type 5A, for use in a gas chromatographic apparatus was developed for the separation of hydrogen, oxygen, nitrogen, methane, and carbon monoxide. The column was used to determine quantitatively the oxygen consumed in the cool flame oxidation of hydrocarbons. It was also used to determine qualitatively and quantitatively the production of hydrogen, methane, and carbon monoxide in this type of oxidation. The system is rapid and has good reproducibility.

THE OXYGEN CONSUMPTION and the light gas production during the oxidation of hydrocarbons in cool flames have usually eluded analysis because of the dilution by air accompanying these gases. Gas chromatography incorporating a molecular sieve adsorption column has successfully resolved this problem.

A stoichiometric mixture of hexane and air, heated to a temperature of 270° C., produced a cool flame. It was desired to ascertain the oxygen consumption and to determine the amounts of possible products of the oxidation, including hydrogen, methane, and carbon monoxide.

Gas chromatography has been successfully used by the authors for the qualitative and quantitative determination of these gases in the presence of a great quantity of air. Other products accompanying this type of oxidation are excluded. The method has the advantages of reliability, reproducibility, and simplicity. Greene and coworkers (*1*) have previously used gas chromatography for these gases. However, the separation of these gases by their procedure was not sufficient for the determination of cool flame products. This work describes the separation for hydrogen, nitrogen, oxygen, methane, and carbon monoxide by elution at constant temperature from a column packed with a molecular sieve. Hydrogen sensitivity is poor when using helium as a carrier gas; however, substitution of argon for helium would give satisfactory results.

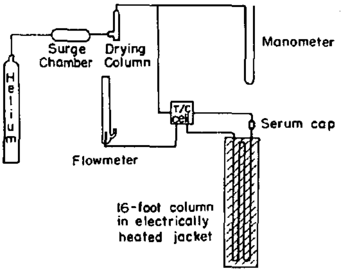

Figure 1. Schematic diagram of apparatus

EXPERIMENTAL WORK

The apparatus (Figure 1), consisted of a needle valve, surge chamber, drying column, manometer, chromatographic column in an electrically heated jacket, and a detector (Gow-Mac thermal conductivity cell) with a 0- to 25-mv. recording potentiometer. The chromatographic column consisted of four 4-foot lengths of borosilicate glass tubing, 5 mm. in inside diameter, joined together with capillary tubes. The tubes were packed according to the method of James and Martin (*2*) with molecular sieve, Type 5A (Linde, Tonawanda, N. Y.), ground to 30 to 60 mesh and reactivated at 350° C. under vacuum. The column was placed in an electrically heated jacket at 100° C. The samples were introduced by a hypodermic needle through a serum cap. Helium carrier gas flow rate was 25 ml. per minute.

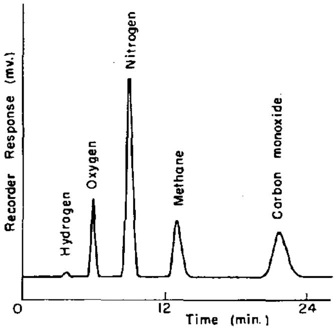

Figure 2. Separation of gas mixture on 16-foot molecular sieve, Type 5A, column

The results shown in Figure 2 were obtained using a 1-ml. sample containing 20% each of hydrogen, carbon monoxide, and methane and 40% of air by volume. The results shown in Figure 3 were obtained using a 5-ml. sample of the cool flame exhaust gas from the hexane and air mixture. The separa-

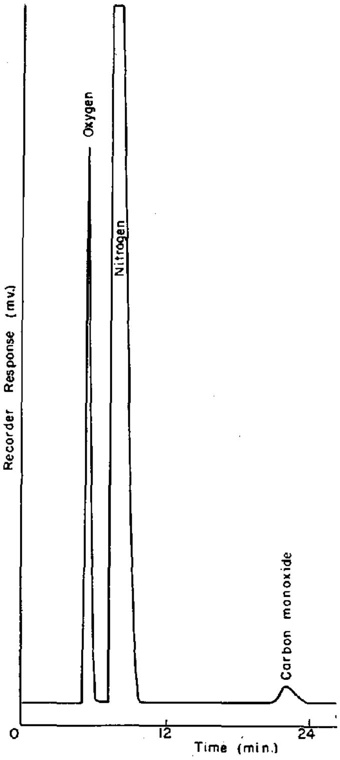

Figure 3. Separation of 5 ml. of cool flame gas mixture on 16-foot molecular sieve, Type 5A, column

tions and reproducibility of duplicate samples were excellent.

ACKNOWLEDGMENT

The writers express their appreciation to the Firestone Tire and Rubber Co. for the Research Fellowship granted them.

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Quantitative Aspects of Microchromatography

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▶ Chromatography as a quantitative method requires a consideration of some aspects which influence its reliability. These include stability of chromatograms under varying conditions of light, heat, and humidity, and uniformity of filter paper blank, because certain grades of paper may vary as much as 32% from the total transmittance of the blank paper. Absorbance values are somewhat erratic for chromatograms stored under atmospheric conditions, while minimum deviations resulted for those kept in a dark desiccator. Heating the chromatograms for 5 minutes at 60° C. caused a noticeable loss in amino acids as judged from the intensity of color produced by reaction with ninhydrin.

THE DEGREE of sensitivity attainable in one-dimensional chromatography makes this method desirable in quantitative micromeasurements of amino acids. If the problems ordinarily encountered could be minimized, this method would probably be preferable because of its simplicity and accuracy. This paper presents the results of a study carried on in two areas which proved of sufficient significance to merit special consideration—namely, limitations in the use of the so-called "base line" in the direct reading of absorbance values, and the stability of chromatograms under varying conditions of light, heat, and humidity.

A number of investigators have considered problems involved in the choice of suitable filter paper for chromatography (*1–3, 6, 10*). It is obvious that the grade of filter paper used is dependent on the method of analysis and the expected accuracy of the results. If a quantitative micromeasurement is based on absorbance values of the chromatograms, then any variation in the zero reading of the blank filter paper will seriously affect the accuracy of the results. Redfield (*8*) states that the filter paper blank can be well controlled, because the shape of the base line can be taken into account for each strip on the segments where no amino acid is present as compared to the adjacent areas occupied by the amino acids. He found it suitable to use a constant value of 10% transmittance for this base line.

The problems encountered in producing reproducible color intensities in amino acid chromatograms (*4, 8, 9, 12*) have likewise been investigated. Because of the sensitivity expected in absorbance measurements, variables in this area would probably be significant factors in the reliability of quantitative measurements. Wellington (*13*) reports that a variation in relative humidity between 40 and 70%, common in laboratories not equipped with air conditioning, is sufficient to explain the day-to-day variability in the ninhydrin reaction reported by earlier workers. While the effect of heating the chromatograms seems of less concern in quantitative measurements, some studies have been made in this regard (*5, 12*). The effects of each of these factors on amino acid chromatograms will be considered.

PROCEDURE

To determine the extent to which the use of a constant value for the base line could be relied upon, 15 selected grades of filter paper were used. In each case, the extent to which the absorbance varied for the filter paper blank was determined for both the crosswise and length-wise cuts of the paper. Absorbance measurements were made with a Model 525 Photovolt densitometer consisting of a transmittance unit in series with a microammeter. A 570-mμ filter was inserted in the transmittance unit, followed by three different sizes of apertures in succession—a 2-mm. diameter circle, and two slits, one 6 × 1 mm. and one 25 × 1 mm. The absorbance values were read at 1-mm. intervals over a 100-mm. length of filter paper. The lowest absorbance observed over the 100-mm. length of the paper was taken as the zero reading for each particular strip. Deviations from this zero reading are recorded in Table I.

In the preparation of chromatograms to be subjected to varying conditions of light, heat, and humidity, the horizontal method of chromatographic analysis was used (*11*). The strips were Whatman No. 4, $^1/_2$ inch wide and 23 inches long. The irrigating solvent was 1-butanol–glacial acetic acid–buffer (25 to 12 to 12); the buffer was potassium chloride–hydrochloric acid (pH 3.8). If the ninhydrin was applied as a spray, a 0.3% solution in aqueous butanol was satisfactory. If the ninhydrin was added to the irrigating solvent, the proportions were 25 to 12 to 6 to 6 of 1-butanol–glacial acetic acid–buffer–2.5% aqueous solution of ninhydrin.

In this part of the experiment three different types of amino acids were used—namely, histidine, serine, and ornithine. Each filter paper strip was spotted with 1 μl. of an 8mM solution of one of these amino acids. After the irrigating solvent had traveled the length of the strip, which required approximately 14 hours, the strips were dried at room temperature in a forced air hood. As the ninhydrin had been added to the irrigating solvent, the spots were revealed either by heating the strips for 5 minutes at 60° C. or maintaining them for 3 hours at 25° C. Strips containing spots revealed by both these treatments were mounted side by side on a frame and compared in their reactions to four additional treatments.

One set of chromatograms was kept in the dark under atmospheric conditions; another set was kept continuously in artificial light of about 70 cp. and 40° C. A third set was exposed to daylight in a room free of fumes but under atmospheric conditions. In this latter case the illuminance reached a maximum of about 300 cp. and, of course, was reduced to zero during the night. The humidity of the room in which these chromatograms were stored ranged from 48 to 71%. Another set of chromatograms was placed in a desiccator and kept in the dark. The absorbance values of the chromatograms were read with the densitometer, using the 570-mμ filter and the 6 × 1-mm. aperture. By marking the strips it was possible to read the absorbance of each spot in the identical position from day to day. This method eliminated any error which might result from a variation in density of the filter paper. Except for the time required to make the readings, which was about 5 minutes, the chromatograms were kept constantly under the conditions described above.

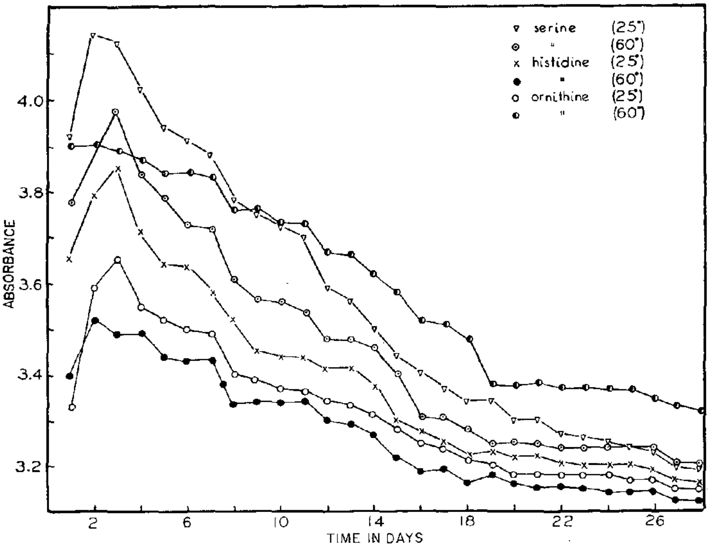

Figure 1. Effect of daylight on amino acid chromatograms produced by heating for 5 minutes at 60° C. or for 3 hours at 25° C.

RESULTS AND DISCUSSION

Uniformity of Filter Paper Blank. Table I indicates the extent to which the filter paper blank varied in absorbance from the zero point. It also gives a measure of the thickness of the paper. The more transparent grades permitted the use of the range of 2.00 to 3.00 units; those of greater density necessitated the use of a range of 3.00 units and above. The various grades of filter paper are listed in the order of increasing deviation with the use of the 2-mm. aperture. There is some variation in the zero readings of the lengthwise and crosswise cuts of the paper. Eight grades of lengthwise cuts have lower deviations from the zero reading while five grades of crosswise cuts were lower. Two grades do not vary for either the lengthwise or crosswise cuts. Obviously, the 25 × 1-mm. slit gives the lowest blank readings, but this aperture is too large for microdeterminations. In general, the "fast flow rate" papers vary most significantly. For example, if Whatman No. 4 is used with the 2-mm. round aperture, the absorbance variation is 0.17 unit for the crosswise cut. This is equivalent to a 68% transmittance or a variation of as much as 32% in the blank reading. Although previous investigators (*1*, *3*, *6*) have preferred either Whatman No. 1 (medium) or No. 4 (fast) as giving the best results so far as resolving capacity and other factors are concerned, it would

Table I. Variation in Zero Reading of Filter Paper Blank

Whatman Paper					
Grade	Cut[a]	Flow Rate	2-Mm. Aperture	6-Mm. Aperture	25-Mm. Aperture
7	L	Medium	3.00–3.05	2.00–2.04	2.00–2.03
40	L	Medium	3.00–3.05	2.00–2.04	2.00–2.03
44	L	Medium slow	3.00–3.05	2.00–2.04	2.00–2.03
31 DT	C	Fast	3.00–3.05	3.00–3.04	2.00–2.03
44	C	Medium slow	3.00–3.05	2.00–2.05	2.00–2.03
42	C	Slow	3.00–3.05	2.00–2.05	2.00–2.03
50	L	Slow	3.00–3.06	2.00–2.04	2.00–2.03
50	C	Slow	3.00–3.06	2.00–2.04	2.00–2.03
40	C	Medium	3.00–3.06	2.00–2.06	2.00–2.02
5	L	Slow	3.00–3.06	3.00–3.06	2.00–2.03
20	L	Slow	3.00–3.06	3.00–3.06	2.00–2.03
2	L	Medium slow	3.00–3.06	2.00–2.07	2.00–2.03
7	C	Medium	3.00–3.06	2.00–2.07	2.00–2.03
31 DT	L	Fast	3.00–3.07	3.00–3.06	2.00–2.03
3 MM	C	Medium	3.00–3.07	3.00–3.06	2.00–2.04
5	C	Slow	3.00–3.08	2.00–2.04	2.00–2.03
11	C	Medium slow	3.00–3.08	2.00–2.04	2.00–2.03
1	L	Medium	3.00–3.08	2.00–2.05	2.00–2.03
2	C	Medium slow	3.00–3.08	2.00–2.05	2.00–2.03
42	L	Slow	3.00–3.08	2.00–2.05	2.00–2.03
3 MM	L	Medium	3.00–3.09	3.00–3.05	2.00–2.04
1	C	Medium	3.00–3.09	2.00–2.05	2.00–2.05
11	L	Medium slow	3.00–3.09	2.00–2.06	2.00–2.03
20	C	Slow	3.00–3.09	3.00–3.06	2.00–2.05
41 H	C	Fast	3.00–3.10	2.00–2.07	2.00–2.05
4	L	Fast	3.00–3.10	2.00–2.08	2.00–2.05
54	L	Fast	3.00–3.10	2.00–2.11	2.00–2.07
54	C	Fast	3.00–3.12	2.00–2.07	2.00–2.05
41 H	L	Fast	3.00–3.13	2.00–2.10	2.00–2.05
4	C	Fast	3.00–3.17	2.00–2.10	2.00–2.09

[a] L designates lengthwise cut; C, crosswise cut.

Table II. Effect of Humidity on Absorbance Values of Amino Acid Chromatograms

Amino Acid	Produced at, ° C.	Dark Storage in	Initial Absorbance	Av. Absorbance, 28 Days[a]	Range of Absorbance, 28 Days[a]	Magnitude of Absorbance Range
Histidine	25	Desic.	3.45	3.67 ± 0.013	3.65 to 3.70	0.05
	60	Desic.	3.63	3.53 ± 0.015	3.49 to 3.54	0.05
	25	Atm.	3.53	3.85 ± 0.030	3.81 to 3.92	0.11
	60	Atm.	3.60	3.62 ± 0.042	3.52 to 3.74	0.22
Serine	25	Desic.	3.34	3.55 ± 0.009	3.52 to 3.57	0.05
	60	Desic.	3.62	3.59 ± 0.013	3.57 to 3.62	0.05
	25	Atm.	3.38	3.88 ± 0.048	3.81 to 3.98	0.17
	60	Atm.	3.75	3.90 ± 0.035	3.83 to 3.98	0.15
Ornithine	25	Desic.	3.54	3.62 ± 0.012	3.59 to 3.64	0.05
	60	Desic.	3.74	3.72 ± 0.016	3.68 to 3.77	0.09
	25	Atm.	3.62	4.01 ± 0.031	3.94 to 4.08	0.14
	60	Atm.	3.66	3.67 ± 0.039	3.59 to 3.75	0.16

[a] Values taken from 4th day on.

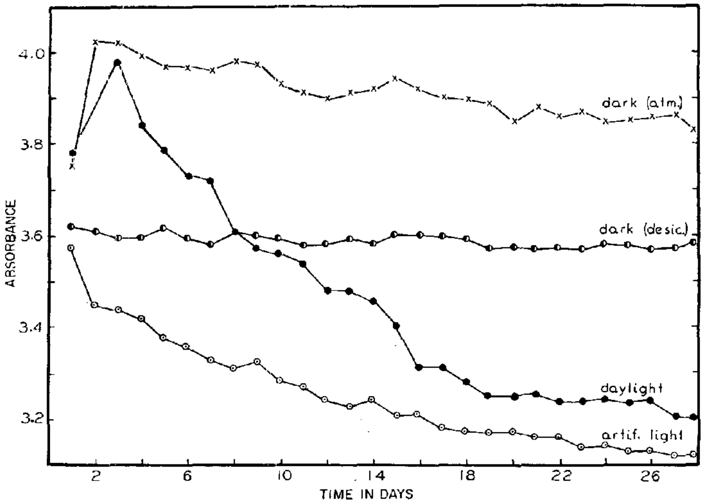

Figure 2. Replicate chromatograms of serine heated for 5 minutes at 60° C. and kept under four different storage conditions

seem that either of these grades would not be entirely suitable for use in quantitative measurements based on absorbance values.

Washing the filter paper in acid did not seem to lower the blank reading to any significant extent.

Application of Chromogenic Reagent. The method of combining the ninhydrin directly with the irrigating solvent, as proposed by Nicholson (*7*), gave results more readily reproducible than the usual spraying technique. When the ninhydrin added to the irrigating solvent produced a solution of the same concentration as that applied by spraying (in this case, a 0.3% solution), the resulting colors and R_f values were identical with those obtained by spraying the chromatograms. The areas of color were distinct and well defined.

Effects of Light, Heat, and Humidity. Figure 1 gives the results of the chromatograms exposed to daylight. The increased absorbance during the first two days indicates that the chromatograms were not fully revealed until that time. Dent (*4*) has shown that full color production takes place if the sprayed papers are dried for 24 hours at room temperature. For serine and histidine the absorbance is somewhat greater for those chromatograms kept at room temperature than for those heated at 60° C. This difference is probably due to a loss as a result of heating, and is in agreement with the work of Fowden and Penny (*5*). The unevenness in fading is partly accounted for by the change in intensity of the sunlight from day to day as well as by the variation in humidity.

Figure 2 is the comparison of replicate chromatograms of serine produced at 60° C. for 5 minutes and subjected to each of the four conditions described earlier. Variations in initial absorbance may be accounted for by the variation in time interval in reading each of the chromatograms immediately after removing them from the oven. It is evident that atmospheric conditions affect the intensity of the chromatograms. The curve for the chromatograms subjected to artificial light is less erratic than the curve for those stored under atmospheric conditions. This is probably due to the higher temperature of 40° C. produced by the artificial light.

Table II is a comparison of the chromatograms stored in the dark under atmospheric conditions and those kept in the dark in a desiccator. The initial absorbance reading is given in column 4; however, in computing the average for the 28-day period, the readings were taken after the fourth day when maximum production had been reached.

All chromatograms produced at 25° C. show an increase in absorbance. Those produced at 60° C. and stored in the desiccator show a decrease in absorbance. Furthermore, the deviation and range of those chromatograms stored in the desiccator are considerably less than for those stored in the dark under atmospheric conditions. The desiccant inhibits the production of the color of the spot, although it also stabilizes the intensity of the fully revealed chromatogram.

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Chromatography of Organic Acidic Compounds on Multibuffered Paper

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▶ Acidic organic compounds have been separated by a paper chromatographic technique similar to one applied to organic bases. Many acidic compounds form a salt at a particular pH level with alkaline buffers, applied in sequence of their ascending pH on a filter paper strip in marked zones. Upon equilibration, chloroform is used as the single mobile phase for descending chromatography. As the stronger acidic compounds are often immobilized at lower pH levels than the more weakly acidic ones, it was possible to separate benzoic acid, several barbiturates, and some phenolic compounds from each other. These compounds could be visualized on the paper under short wave ultraviolet light.

THE literature of paper chromatography, including paper chromatography of acidic compounds, has been covered by Block, Durrum, and Zweig (*1*), Lederer (*4*), Turba (*10*), and Hais and Macek (*3*). The most recent developments were reviewed by Strain and Sato (*9*).

While filter papers completely impregnated with buffers have been widely used for the separation of compounds of related structure, the technique of multibuffered paper chromatography has been developed for the separation of organic basic compounds. The procedure, employed for the separation of acidic compounds, was somewhat similar to the one described for organic bases (*7*).

METHOD

Apparatus. Usual equipment for descending paper chromatography. Short-wave Mineralight (maximum emission at 2553 A.).

Reagents. Chloroform, reagent grade. Clark and Lubs buffers, double strength (*2*). MacIlvaine buffers, double strength (*5*). Soerensen buffers, double strength (*8*).

PROCEDURE

The paper was prepared by application of buffers at varied pH levels in marked zones (*7*). For the separation of acidic compounds, Clark and Lubs buffers were applied at 0.2 pH intervals for the pH range of 7.8 to 9.4, while Soerensen buffers were used for the pH range 9.8 to 12.6, spaced at 0.3 pH intervals. A solution of the sample, equivalent to about 15 γ, was placed at the starting line and the strip was introduced into the chromatographic chamber containing water at the bottom and, in addition, an open beaker with chloroform. To hasten saturation with vapor, the chamber was partially lined with filter paper which dipped into the water. It was allowed to come to equilibrium overnight.

Chloroform, as the single mobile phase, was then placed in the solvent trough for descending chromatography. When the solvent front had moved down almost to the end of the paper, which usually required about 3 hours, the strip was removed and air-dried. It was inspected under short wave ultra-

Table I. pH of Immobilization of Barbiturates

Compound	pH Range of Buffered Paper	pH of Immobilization	R_f
Barbituric acid	8.3–12.6	8.3	0
	Unbuffered	. .	0
Isopropylbarbituric acid	8.3–12.6	8.3	0
	Unbuffered	. .	0
Barbital	7.8– 9.4	9.2	0.7
Phenobarbital	7.8– 9.4	9.2	0.75
Allylbarbituric acid	9.8–12.6	10.2	0.3
Diallylbarbituric acid	9.8–12.6	10.2	0.3
Probarbital	9.8–12.6	10.5	0.35
Aprobarbital	9.8–12.6	11.0	0.45
Butabarbital	9.8–12.6	11.7	0.6
Cyclopal	9.8–12.6	11.7	0.6
sec-Bromallylbarbituric acid	9.8–12.6	12.2	0.7
Amobarbital	9.8–12.6	12.5	0.75
Pentobarbital	9.8–12.6	12.5	0.8
Secobarbital	9.8–12.6	12.5	0.8
Hexobarbital	9.8–12.6	Past 12.6	0.95

violet light, where compounds such as barbiturates, benzoic acid, or esters of *p*-hydroxybenzoic acid appear as dark spots on light background. The spots were circled with pencil, to mark them for photographic reproduction. Hexylresorcinol was rendered visible by spraying with amino reagent [100 mg. of 4-methoxy-2-nitroaniline dissolved in 25 ml. of glacial acetic acid and diluted to 50 ml. with sulfuric acid, 10% w./v. A mixture of equal parts of this reagent was sprayed with 0.2% aqueous sodium nitrite solution. This was followed by a spray of 5% sodium carbonate solution (*6*)].

EXPERIMENTAL

Barbiturates (as the free acids), benzoic acid, and phenolic compounds were dissolved in either chloroform or ethyl alcohol and the equivalent of about 15 γ was chromatographed as described. In Table I the pH values are listed at which each one of the barbiturates was immobilized. When chloroform is used as the mobile phase, barbituric acid and isopropylbarbituric acid will not move on the paper. Some of the barbiturates, such as barbital and phenobarbital, could not be separated on multibuffered paper, as they move to the same pH.

In Table II, acidic compounds such as benzoic acid and several phenolic-type compounds and their R_f values are listed.

Table II. pH of Immobilization of Benzoic Acid and Phenolic Compounds

Compound	pH Range of Buffered Paper	pH of Immobilization	R_f
Benzoic acid	5.2– 6.9	6.3	0.6
Methylparaben	9.8–12.6	11.6	0.7
	Unbuffered	..	0.7
Propylparaben	9.8–12.6	12.6	0.9
	Unbuffered	..	0.9
Hexylresorcinol	9.8–12.6	12.2	0.75
	Unbuffered	..	0.75

MacIlvaine buffer, double strength, was applied at pH 0.2 intervals for the chromatography of benzoic acid, which was immobilized at pH 6.3. As is evident from Table II, phenolic-type compounds were not affected by the buffers on the paper. For example, methylparaben, when applied to a paper, buffered at 9.8 to 12.6, stopped at a pH of 11.6 with an R_f value of 0.7. When chromatographed on an unbuffered paper, it moved again to the same R_f. Propylparaben and hexylresorcinol behaved in a similar manner. It appears, therefore, that the movement of these phenolic-type compounds is dependent solely upon the solvent system.

Controlled Separation of Acidic-Type Compounds. Attempts were made to separate combinations of known mixtures of some acidic compounds from each other by buffering a small area of the paper at a selected pH value, so as to stop the movement of one of the components, allowing the other one to move down the strip.

In Figure 1, strip 1, such a controlled separation between benzoic acid and aprobarbital is shown. As benzoic acid is immobilized at any pH above 6.3, a 3-cm. wide upper zone on the paper was buffered at pH 9.8. As aprobarbital will stop at any pH above 10.2, a center portion of the paper was buffered at pH 12.5, to stop its move-

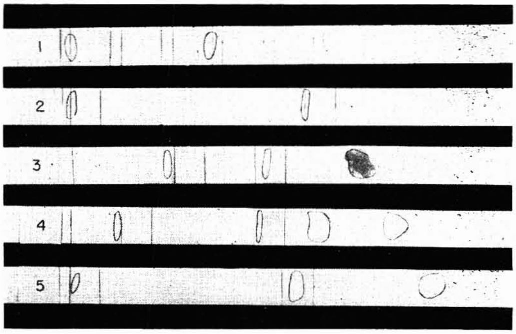

Figure 1. Separation of benzoic acid, barbiturates, and phenols

1. Benzoic acid–aprobarbital
2. Benzoic acid–aprobarbital
3. Benzoic acid–phenobarbital-hexylresorcinol
4. Benzoic acid–barbital-methylparaben-propylparaben
5. Benzoic acid–diallylbarbituric acid–pentobarbital

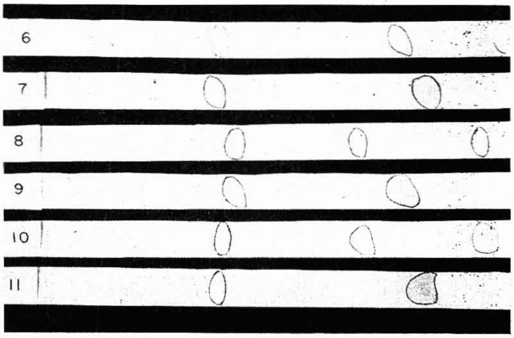

Figure 2. Separation of barbiturates from phenolic compounds

6. Diallylbarbituric acid–methylparaben-propylparaben
7. Diallylbarbituric acid–hexylresorcinol
8. Aprobarbital-methylparaben-propylparaben
9. Aprobarbital-hexylresorcinol
10. Probarbital-methylparaben-propylparaben
11. Probarbital-hexylresorcinol

ment. When a mixture of these compounds was placed on such a strip, benzoic acid stopped at the pH 9.8 area, with aprobarbital moving to the pH 12.5 zone.

An even wider separation of these compounds could be effected by using the same buffers as in strip 1, but placing the pH 12.5 zone farther down the paper (strip 2).

Phenobarbital, benzoic acid, and hexylresorcinol were easily separated by buffering an upper zone at pH 6.9, a central zone at pH 11.0, and leaving the remainder of the paper unbuffered. Three bands were observed, with benzoic acid at the first buffered zone, phenobarbital at the second, and hexylresorcinol moving down into the unbuffered area.

Strip 4 was prepared in the same manner as strip 3. Benzoic acid stopped at the top, barbital moved to the pH 11.0 zone, and methylparaben (R_f 0.7) and propylparaben (R_f 0.9) moved to the unbuffered portion of the paper.

In strip 5 an upper zone was buffered at pH 9.8 and a central one at pH 11.7. Benzoic acid moved to the first zone, diallylbarbituric acid to the second, and pentobarbital went down almost with the solvent front (R_f 0.9).

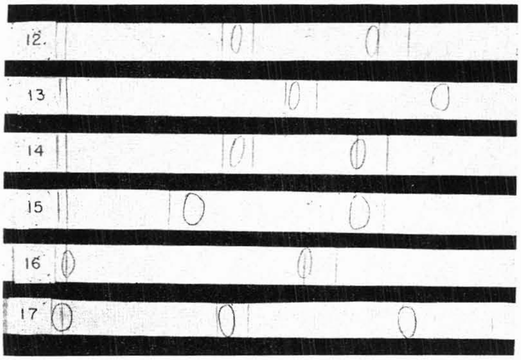

Figure 3. Controlled separation of barbiturates

12. Phenobarbital-aprobarbital
13. Diallylbarbituric acid–secobarbital
14. Diallylbarbituric acid–aprobarbital
15. Allylbarbituric acid–butabarbital
16. Barbituric acid–barbital
17. Barbituric acid–probarbital-cyclopal

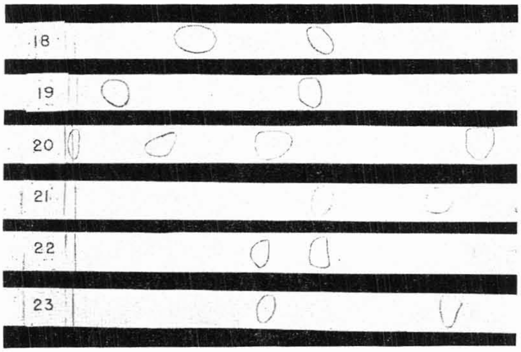

Figure 4. Separation on completely buffered paper

18. Probarbital-butabarbital
19. Butabarbital-cyclopal
20. Isopropylbarbituric acid–allylbarbituric acid–aprobarbital-methyprylon
21. Amobarbital-hexobarbital
22. Amobarbital-*sec*-bromallylbarbituric acid
23. *sec*-Bromallylbarbituric acid–hexobarbital

Because the movement of some of the barbiturates is affected by buffers, while the movement of phenolic compounds is impeded, a controlled separation between both types could be achieved.

All strips in Figure 2 were prepared by buffering a small upper zone with a pH 12.6 buffer, leaving the remainder unbuffered. As can be seen from strips 6 to 11, all barbiturates were immobilized at the buffered zone, with the phenolic compounds moving to their respective R_f values, as shown in Table II.

As phenobarbital is stopped at pH 9.2 and aprobarbital is immobilized at pH 10.2, a wide separation between these compounds could be accomplished, as shown in strip 12, Figure 3, which was prepared by buffering an upper zone at pH 10.0 to stop the phenobarbital and a lower one at pH 11.7 to halt aprobarbital.

Strips 13 through 17 exemplify five other examples of such controlled separations. In strip 13 the upper zone was buffered at pH 11.7; the remainder was unbuffered.

Strip 14 had an upper portion at pH 10.3 and a lower one at pH 12.6. In strip 15 the upper zone was buffered at pH 10.8 and the lower at pH 12.5.

Strip 16 had an upper portion at pH 8.3 and a middle portion at pH 10.0.

Strip 17 had a central zone at pH 10.8 and a lower one at pH 12.6.

As several of the barbiturates (Table I) could not be separated from each other on multibuffered paper, it was thought that buffering of the entire paper at a pH slightly below that at which these barbiturates are immobilized, might allow separations.

In strip 18, Figure 4, the entire paper was buffered at pH 10.8. The R_f value for probarbital was found to be 0.25, while that for butabarbital was 0.5.

Strip 19 was buffered at a pH 11.7. The R_f value of butabarbital was 0.1, and that of cyclopal was 0.5.

In strip 20, buffered at pH 10.2, the separation of three barbiturates of related structure from each other, as well as Noludar (Methyprylon, 3,3-diethyl - 5 - methyl - 2,4 - piperidinedione)—a sedative of entirely different configuration—can be seen. Isopropylbarbituric acid (R_f 0), allylbarbituric acid (R_f 0.2), aprobarbital (allylisopropyl barbituric acid) (R_f 0.45), and Noludar (R_f 0.9).

Strips 21, 22, and 23 were all buffered at pH 12.2. Amobarbital had an R_f of 0.6 in all three strips, the secondary bromallylbarbituric acid showed an R_f of 0.5, while the R_f of hexobarbital was 0.9.

The illustrations present examples of the type of separations that can be accomplished by the technique of multibuffered papers. Many other controlled separations can be carried out (Tables I and II).

ACKNOWLEDGMENT

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The System Naphthalene-Thianaphthene

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▶ A solid solutions treatment for calorimetric melting point data was verified for the system naphthalene-thianaphthene. The solid solutions phase diagram, including liquidus and solidus lines, was also determined. Theoretical analysis permitted an accurate prediction of the solid-liquid equilibrium. The heat of fusion was determined as a function of composition. The use of these data for the evaluation of purity of naphthalene is presented.

THE USE of freezing point as a specification for the evaluation of purity depends upon knowledge of the character of the impurities present and their behavior in solution with the major component. The formation of solid solutions is a serious deviation of a system from the results predictable by the ordinary form of the melting point equation:

$$\text{Log}_{10}N_1 = 2.00000 - \frac{A\Delta t}{2.30259}\left\{1 + B\Delta t\right\} \quad (1)$$

where N_1 = mole per cent purity

$\Delta t \equiv t_o - t_f$ = freezing point depression, ° C.

$A \equiv \frac{\Delta H_f}{RT_o^2}$ degrees^{-1}

$B \equiv \left(\frac{1}{T_o} - \frac{(\Delta C_p)_m^\circ}{2\Delta H_f}\right)$ degrees^{-1}

where ΔH_f = heat of fusion of the major component, calories per mole

T_o = freezing or melting point of 100.0 mole % major component, ° K.

$(\Delta C_p)_m$ = difference in molar heat capacity between liquid and solid at T_o

The system naphthalene-thianaphthene was described in the liquidus region (*2*), and the only reference to solid solution formation (*8*) gave no specific information in the solidus equilibrium region. The present investigation used both the calorimetric (*1*) and the freezing curve methods to determine the equilibrium regions bounded by the liquidus and solidus curves. Application of the analytical treatment (*6*) of calorimetric-melting point data for a dilute impurity forming solid solutions was verified for this system.

EXPERIMENTAL

Apparatus and Procedure. An adiabatic calorimeter was used (*5*). The method of Aston, Cinnes, and Fink (*1*) for plotting energy input *vs.* equilibrium melting temperatures was used to determine the liquidus and solidus temperature. Cooling curves were plotted at two concentrations so that the equilibrium points were approached from both sides.

The cooling curve method employed an air-jacketed test tube and stirrer, and an NBS-calibrated, short-range thermometer to define the liquidus line over short composition intervals.

Materials. Refined, liquid naphthalene (Barrett Division, Allied Chemical & Dye Corp.) was further purified by slow freezing in an insulated Dewar flask, discarding the central core. This procedure was repeated four times in successively smaller Dewar flasks.

The thianaphthene (Jefferson Chemical Co., Inc.) was purified by fractional distillation. Its freezing point was 31.40° C.

Molecular Sieve, 4A powder (Linde Air Products Co.) was used to dry samples; 2 grams were required for every 50 grams of sample.

SOLID SOLUTIONS TREATMENT TO NAPHTHALENE

A calorimetric purity determination was carried out (*5*) on a 36-gram sample of the purified naphthalene. Equilibrium temperature was plotted against the reciprocal fraction melted (Figure 1). The melting point obtained by extrapolating the best straight line through these points was 80.081° C., while the derived melting point of 100.00 mole % naphthalene was only 80.193° C. Other reported naphthalene freezing points are 80.290° C. (*7*) and 80.287° C. (*4*).

Figure 1 indicates the presence of solid solutions. The treatment of Mastrangelo and Dornte (*6*) was applied

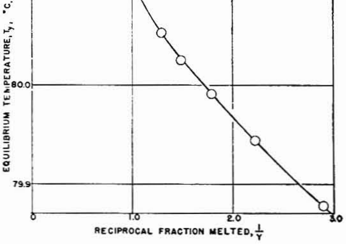

Figure 1. Equilibrium melting curve for naphthalene sample

Table I. Solid Solutions Treatment for Dilute Impurity in Naphthalene

y	$\frac{K}{1-K}+y$	$\left(\frac{K}{1-K}+y\right)^{-1}$	t_y, ° C.	t_y (Line), ° C.[c]
0.34206	0.55892	1.7893	79.8781	79.878
0.44860	0.66546	1.5027	79.9443	79.944
0.55510	0.77196	1.2954	79.9911	79.991
0.66410	0.88096	1.1351	80.0246	80.025
0.77241	0.98927	1.0108	80.0538	80.054
1.00000	1.21686	0.82179	80.098[a] 80.287[b]	

$$K = \frac{1}{2}\left\{\frac{t_{1\cdot 00} - t_{0\cdot 50}}{t_{0\cdot 50} - t_{0\cdot 33}} - 1\right\} = \frac{2}{3}\left\{\frac{t_{1\cdot 00} - t_{0\cdot 50}}{t_{0\cdot 50} - t_{0\cdot 25}} - \frac{1}{2}\right\}$$

$$t_{1\cdot 00} = 80.106,\ t_{0\cdot 50} = 79.969,\ t_{0\cdot 33} = 79.868 \text{ (Figure 1)}$$

$$K = \frac{1}{2}\left\{\frac{0.137}{0.101} - 1\right\} = 0.17821$$

$$\frac{K}{1-K} = 0.21686$$

[a] Extrapolated from solid solutions plot.
[b] Calculated by solid solutions treatment.
[c] Read from sensitive plot of t_y vs. $\left(\frac{K}{1-K}+y\right)^{-1}$.

to these same data with the results shown in Tables I and II. The terminology used has been described in (*6*). Table I illustrates the calculation of distribution constant K of the impurity between the solid and liquid phases from $t_{1\cdot 00}$, $t_{0\cdot 50}$, and $t_{0\cdot 33}$, or from $t_{1\cdot 00}$, $t_{0\cdot 50}$, and $t_{0\cdot 25}$, where t and subscripts refer to equilibrium temperatures at various fractions melted. A plot of equilibrium temperatures *vs.* the function $\left(\frac{K}{1-K}+y\right)^{-1}$ gives a straighter line, from which better values of $t_{1\cdot 00}$, $t_{0\cdot 50}$, and $t_{0\cdot 33}$ can be obtained and hence, a better value of K recalculated.

Table II illustrates the calculation of t_0, the melting point of 100 mole % naphthalene (nitrogen saturated, 1 atm.), and X''_2 the total mole fraction of impurity. By this method t_o was 80.287° C.; this melting point is in excellent agreement with the other literature values. The total mole fraction of impurity was 0.0042. The impurity was identified as thianaphthene by mass spectrometry and its concentration was 0.004 mole fraction by infrared spectroscopy, confirming the calorimetry result.

PHASE DIAGRAM

To confirm the predictions of the solid solutions treatment (*6*) and to evaluate the freezing point as a measure of the purity of naphthalene, the phase diagram for the system naphthalene-thianaphthene, on the naphthalene side, was determined (Figure 2). The average deviation of experimental points from the smooth curves was ±0.5 mole %. The smooth liquidus line incorporates the data of Franck (*2*).

Table II. Calculations by Solid Solutions Treatment of Naphthalene

(1) Calculation of t_o.

$$t_o = t_{1\cdot 00} + (t_{1\cdot 00} - t_{0\cdot 50})\frac{(1+K)}{(1-K)}$$

$$t_o = 80.098 + 0.130\left(\frac{1.18421}{0.81579}\right)^{a} = 80.098 + 0.189$$

$$t_o = 80.287° \text{ C.}$$

[Literature values. Glasgow, Streiff, and Rossini (*3*) = 80.290; Herrington, Densham, and Malden (*4*) = 80.287 ± 0.002° C.]

(2) Calculation of X''_2, total mole fraction of impurity.

$$X''_2 = \frac{\Delta H}{RT_o^2}(t_{1\cdot 00} - t_{0\cdot 50})\frac{1+K}{(1-K)^2}$$

$$X''_2 = 0.0181\,(0.130)\,\frac{1.18421}{0.66551}$$

X''_2 = 0.0042 mole fraction impurity (confirmed by infrared spectrometry)
Purity = 99.58 mole %.

[a] New values of $t_{1\cdot 00} - t_{0\cdot 50}$ and K calculated from solid solutions plot.

Table III. Liquidus Curve by Test Tube Freezing Point Method

Freezing Point, t, ° C.	Naphthalene, Mole %[a]
79.78	99.20
79.31	98.18
78.98	97.33
77.69	94.34
76.50	91.60
72.07	81.60
67.57	72.69
63.90	65.52
58.84	56.56
55.69	51.28
48.37	38.58
42.16	27.89
36.46	18.97
32.83	13.53
30.54	9.83
30.22	7.59
30.39	5.92
30.74	3.00

[a] By synthesis.

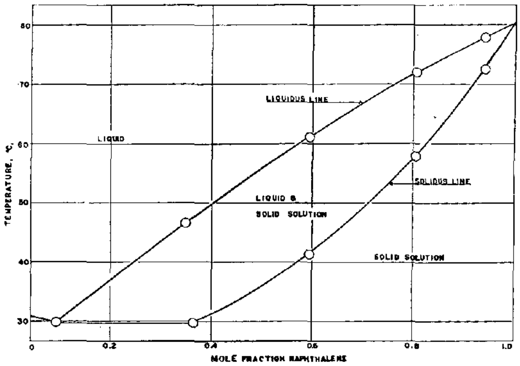

Figure 2. Naphthalene-thianaphthene phase diagram

Table IV. Solid-Liquid Phase Diagram

Composition, Mole % Naphthalene	Liquidus Line, ° C.	Solidus Line, ° C.	Method
100.00	80.287	80.287	Calorimetric
99.58	80.098	79.27	Calorimetric
94.44	77.89	72.30	Calorimetric
80.95	72.20	58.00	Calorimetric
59.74	61.26	41.10	Freezing curve
34.70	46.60	...	Calorimetric
34.70	46.63	...	Freezing curve
37.07	...	29.88	Calorimetric
9.2	29.88 (eutectic)	(29.88)	Freezing curve

Table V. Temperature Dependence of Thianaphthene Equilibrium Distribution Constant

t, ° C.	$N_n(\mathrm{l})$[a]	$N_n(\mathrm{s})$[b]	$N_{tn}(\mathrm{l})$[c]	$N_{tn}(\mathrm{s})$[d]	$K = \frac{N_{tn}(\mathrm{s})}{N_{tn}(\mathrm{l})}$	$\frac{1}{T, ° K.} \times 10^3$	$-\log K$	$-\log K$ (Calcd.)[e]	% Dev.
75	0.878	0.962	0.122	0.038	0.3115	2.87226	0.50651	0.5065	0.00
70	0.770	0.923	0.230	0.077	0.3348	2.91409	0.47524	0.474	0.26
65	0.670	0.878	0.330	0.122	0.3697	2.95718	0.43217	0.437	1.10
60	0.578	0.831	0.422	0.169	0.4005	3.00156	0.39742	0.402	1.14
55	0.488	0.782	0.512	0.218	0.4258	3.04729	0.37088	0.367	1.06
50	0.404	0.718	0.596	0.282	0.4732	3.09444	0.32490	0.327	0.64
45	0.324	0.651	0.676	0.349	0.5163	3.14307	0.28713	0.287	0.05
40	0.246	0.573	0.754	0.427	0.5663	3.19326	0.24699	0.247	0.0
35	0.169	0.481	0.831	0.519	0.6245	3.24506	0.20439	0.204	0.20
30	0.092	0.370	0.908	0.630	0.6938	3.29859	0.15866	0.159	0.21

[a] $N_n(\mathrm{l})$ = mole fraction of naphthalene in liquid phase (liquidus line).
[b] $N_n(\mathrm{s})$ = mole fraction of naphthalene in solid phase (solidus line).
[c] $N_{tn}(\mathrm{l})$ = mole fraction of thianaphthene in liquid phase.
[d] $N_{tn}(\mathrm{s})$ = mole fraction of thianaphthene in solid phase.
[e] Values read off sensitive plot of log K *vs.* $\frac{1}{T}$.

Table III lists the data obtained by the freezing curve method. The solutions were saturated with nitrogen and the time-temperature measurements were extrapolated to zero concentration of solid for the freezing point. Table IV lists the data obtained by the calorimetric method (nitrogen saturated) on various mixtures of naphthalene and thianaphthene. The freezing curves were obtained by maintaining the shields at 10° C. below the temperature of the calorimeter to provide a constant temperature gradient between the calorimeter and shield over the entire cooling range.

To check the internal consistency of the phase diagram data, values of the equilibrium distribution constant, K, (thianaphthene distributed between the solid and liquid phases) were calculated at 5-degree intervals from the concentrations read from a sensitive plot of the liquidus and solidus lines. Negative logarithms of these K values were plotted against the reciprocal of the absolute temperature. The slope of

Table VI. Calculated Phase Diagram

t, ° C.	Observed		Obsd.,	Calcd.,	Calculated		$N_n(\mathrm{s})$ (Obsd. – Calcd.), %
	$N_n(\mathrm{l})$	$N_n(\mathrm{s})$	K	K	$N_n(\mathrm{l})$	$N_n(\mathrm{s})$	
75	0.878	0.962	0.3115	0.3115	(0.878)	0.962	0
70	0.770	0.923	0.3348	0.3357	(0.770)	0.923	0
65	0.670	0.878	0.3697	0.3656	(0.670)	0.879	0.1
60	0.578	0.831	0.4005	0.3963	(0.578)	0.833	−0.2
55	0.488	0.782	0.4258	0.4296	(0.488)	0.780	0.2
50	0.404	0.718	0.4732	0.4710	(0.404)	0.719	−0.1
45	0.324	0.651	0.5163	0.5162	(0.324)	0.651	0
40	0.246	0.573	0.5663	0.5663	(0.246)	0.573	0
35	0.169	0.481	0.6245	0.6258	(0.169)	0.480	0.2
30	0.092	0.370	0.6938	0.6935	(0.0921)	0.370	0
						Av.	±0.08

where

$N_n(\mathrm{l})$ = mole fraction of naphthalene in liquid
$N_n(\mathrm{s})$ = mole fraction of naphthalene in solid

$$K = \frac{1 - N_n(\mathrm{s})}{1 - N_n(\mathrm{l})}$$

$$N_n(\mathrm{s})(\mathrm{calcd.}) = 1 - \{[1 - N_n(\mathrm{l})]\ \mathrm{obsd.} \times K\ (\mathrm{calcd.})\}$$

K (calcd.) was obtained from sensitive plot of – log K (obsd.) *vs.* $\frac{1}{T}$

Table VII. Heats of Fusion

Mole Fraction Naphthalene	ΔH (Obsd.), Cal./Gram	ΔH (Calcd.)[a] Cal./Gram	$\frac{\Delta H\ (\mathrm{Obsd.} - \mathrm{Calcd.})}{\Delta H\ (\mathrm{Calcd.})} \times 100$	$\frac{\Delta H\ (\mathrm{Obsd.})}{34.92}$	$\frac{\Delta H\ (\mathrm{Calcd.})^b}{34.92}$	Method
1.0000		35.081	..		1.0046	Extrapolation
0.9958	34.92	34.92	0.0	1.0000	1.0000	Integral
0.9444	33.02	33.06	0.12	0.9456	0.9466	Fractional
0.8095	28.70			0.8219		Fractional
0.8095	29.30			0.8391		Fractional
0.8095 (av.)	29.00	29.05	0.17	0.8305	0.8318	Average
0.5974	25.55	24.97	1.68	0.7316	0.7151	Freezing curve
0.3470	22.64					Fractional
0.3470	22.89					Freezing curve
0.3470 (av.)	22.77	22.77	0.0	0.6520	0.6520	Average

[a] ΔH (calcd.) cal./gram = $22.231 + 12.850 N^3$, where N = mole fraction of naphthalene.
[b] $\frac{\Delta H\ (\mathrm{calcd.})}{34.92} = 0.63663 - 0.36799 N^3$.

this line multiplied by $-2.3R$ gave the heat of fusion of thianaphthene (3700 calories per mole), assuming an ideal solution. A similar plot using the distribution constant for naphthalene yielded a heat of fusion of 4500 cal. per mole for naphthalene, compared with 4496 cal. per mole (*5*). Table V lists these concentrations and the derived K and $-\log K$ values. Table VI lists the phase diagram data recalculated from smoothed values of K and shows that the original curves are in excellent agreement with the smoothed data (±0.08 mole %).

HEATS OF FUSION

The heats of fusion of various mixtures of naphthalene and thianaphthene are given in Table VII, and they are represented by:

$$\Delta H \text{ calories per gram} = 22.231 - 12.850\,N^3 \quad (2)$$

where N is the mole fraction of naphthalene in the total mixture. The heat of fusion of pure naphthalene calculated by extrapolating this equation to $N = 1$ was 35.08 cal. per gram or 4496 cal. per mole.

APPLICATION OF RESULTS

A naphthalene sample was investigated with a Beckman IR-3 spectrophotometer, which identified the impurity as thianaphthene, at a concentration of 1.24 mole %. The freezing point of the sample (79.798° C.) was determined by the Rossini method (*3*), using 2 grams of Molecular Sieve per 50 grams of sample. The freezing point depression was only 0.489° C.; hence, the impurity concentration was 0.885 mole % using the standard cryoscopic melting point equation (*5*). Because thianaphthene forms solid solutions with naphthalene, the following equation for solid solutions was used to calculate the correct mole per cent of impurity.

$$100\,X_2'' = \frac{1.811\,(t_o - t_f)}{(1 - K)} \quad (3)$$

where t_o = 80.287° C., melting point of pure naphthalene
t_f = 79.798° C., melting point of experimental sample
1.811 = 100 × cryoscopic constant of naphthalene (*6*)
K = equilibrium distribution constant of thianaphthene between the solid and liquid phases at 79.798° C.

The value of K at 79.798° C. obtained from a sensitive plot, was 0.2896. Substituting this value for K into Equation 3, and assuming thianaphthene the only impurity, the mole per cent of thianaphthene was 1.25. The thianaphthene concentration value of 1.24 mole % was obtained by the infrared technique.

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Colorimetric Determination of Ethylene Oxide by Conversion to Formaldehyde

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▶A sensitive colorimetric method for ethylene oxide has been used for determination of oxide residues in certain spices fumigated with this substance. Ethylene oxide is hydrolyzed to ethylene glycol, then reacts with sodium periodate to yield formaldehyde, which is determined colorimetrically with sodium chromotropate in concentrated sulfuric acid. An evolution procedure removes ethylene oxide from interfering substances that react with periodate ion. Data are shown for the determination of ethylene oxide in nutmeg and paprika.

During an investigation of residual amounts of ethylene oxide in fumigated foods, the need for a sensitive method, free of interferences, arose. The Lubatti method (*4*) is limited because it is a titrimetric procedure and requires a very large sample for determinations in the parts per million range. Its limitations for the determination of low concentrations of ethylene oxide in air were recently discussed by Hollingsworth and Waling (*3*). Apparently the only colorimetric method for epoxides that has been reported in the literature is the lepidine method of Gunther and coworkers (*2*). This is sensitive but requires stringent control of reaction conditions for good reproducibility, and with most substances the color reaction will not occur unless ethylene oxide is removed.

The method reported is based upon the commonly known fact that ethylene oxide is hydrolyzed to ethylene glycol in the presence of mineral acid at elevated temperatures. Persinger and Dunn (*5*) of this laboratory showed that this reaction could be used for determination of certain epoxides. Ethylene and propylene oxide were hydrolyzed at steam bath temperature with aqueous hydrochloric acid. Although some chlorohydrin formation may have occurred, subsequent quantitative reaction of the products with periodic acid was obtained. The decrease in periodate ion, measured spectrophotometrically, was shown to be a measure of the epoxide originally present. In the method reported here ethylene oxide is hydrolyzed to ethylene glycol in the presence of a trace of sulfuric acid, and the glycol is determined colorimetrically by a modification of the method of Speck and Forist (*6*). Ethylene glycol reacts with sodium periodate to form 2 moles of formaldehyde. The excess periodate is reduced by sodium sulfite and the formaldehyde is determined colorimetrically with sodium chromotropate in concentrated sulfuric acid.

After this paper was prepared for publication, a method was presented by Brokke, Kiigemagi, and Terriere (*1*) for the determination of Aramite residues, which determines ethylene oxide colorimetrically. Ethylene oxide is hydrolyzed to ethylene glycol, cleaved to formaldehyde, and subsequently determined colorimetrically by a phenylhydrazine reaction.

DEVELOPMENT OF METHOD

The rate of hydrolysis of ethylene oxide to ethylene glycol at 98° ± 2° C. is shown graphically in Figure 1. For this study the ethylene glycol formed in the reaction was determined by a modification of the method of Speck and Forist (*6*) given in the procedure. The absorbance is plotted as a function of the hydrolysis time. The curve reaches a maximum in approximately 40 minutes and indicates quantitative reaction. To ensure reproducible results, hydrolysis conditions of 60 minutes at 98° ± 2° C. have been selected as optimum. A calibration curve obtained for ethylene oxide at a wave length of 570 mμ, using these hydrolysis conditions, showed that the system follows Beer's law. This direct procedure for ethylene oxide can be used in the absence of interfering substances. When interferences are present, ethylene oxide must be physically separated from these substances before reaction. Because of its volatility, ethylene oxide can be readily separated from most interfering substances by evolution from boiling water (*2*).

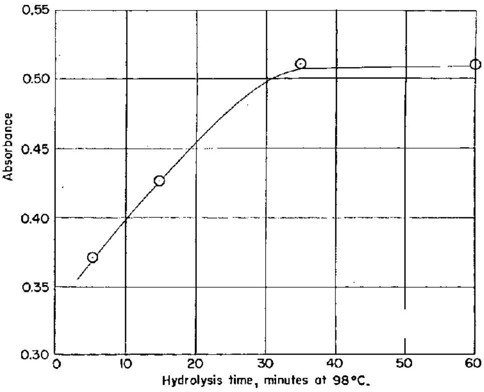

Figure 1. Rate of hydrolysis of ethylene oxide to ethylene glycol

0.351 mg. of ethylene oxide in presence of 1.0 ml. of 0.5N sulfuric acid

Using the equipment shown in Figure 2, the efficiency of the evolution process was investigated; the results are shown in Figures 3 and 4. Figure 3 shows the effect of the rate of air flow upon the recovery of ethylene oxide from boiling water at a fixed evolution time of 30 minutes. The maximum recovery of 86% is obtained at 10 ml. per minute. Figure 4 shows the effect of the time of evolution, from boiling water, upon the efficiency of the recovery process at a fixed flow rate of 10 ml. per minute. In this case the maximum recovery is also 86% and occurs in approximately 30 minutes during the evolution. The procedure given below is based upon the optimum reaction conditions indicated by these experiments.

APPARATUS AND REAGENTS

Beckman Model B spectrophotometer with 1-cm. cells or similar equipment.

Evolution equipment shown in Figure 2.

Flowmeter capable of measuring 10 ml. of air flow per minute.

Sulfuric acid, 0.5N aqueous solution.

Sulfuric acid, concentrated (95%).

Sodium hydroxide, 0.5N aqueous solution.

Sodium chromotropate (sodium 1,8-dihydroxynaphthalene - 3,6 - disulfonate), practical grade, Eastman Organic Chemicals.

Hydroxylamine hydrochloride, 0.5N aqueous solution.

Triethanolamine, 0.5N aqueous solution.

Sodium sulfite, 5.5% solution, prepared fresh each week from reagent grade material.

Sodium periodate, 0.1M aqueous solution, prepared from reagent grade sodium metaperiodate.

CALIBRATION CURVE

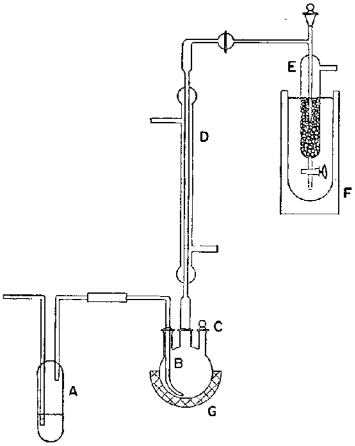

Figure 2. Apparatus for evolution of ethylene oxide

A. Scrubber, 250 ml., containing hydroxylamine hydrochloride and triethanolamine
B. Ebullator with capillary tip
C. Distillation flask, 1 liter
D. Water condenser
E. Scrubber, 50 ml., containing glass beads with capillary tip ebullator
F. Dewar flask containing ice-water slurry
G. Glas-Col heating mantle

Put approximately 50 ml. of distilled water in a 100-ml. volumetric flask. Tare the flask, introduce approximately 1.5 grams of ethylene oxide, and swirl to mix the contents thoroughly. When the ethylene oxide is dissolved record the total weight of the flask and contents, and calculate the net weight of the ethylene oxide. Dilute the contents of the flask to the mark with additional distilled water and mix thoroughly. Transfer a 10-ml. aliquot of this dilution to a 1000-ml. volumetric flask containing approximately 200 ml. of distilled water, dilute to the mark, and mix. For the analysis of samples by the evolution procedure given below, transfer 1-, 3-, and 5-ml. aliquots of the second dilution to the distillation flask. For the analysis of samples using the direct procedure, transfer the aliquots directly to pressure bottles containing

20 ml. of distilled water. Measure the absorbance of each standard following the procedure described below.

PROCEDURE

Assemble the equipment as shown in Figure 2, using silicone grease exclusively for all joints in order to prevent possible reaction of ethylene oxide with the lubricants. Place 25 ml. of 0.5*N* hydroxylamine hydrochloride and 25 ml. of 0.5*N* triethanolamine in scrubber *A* and mix. Prepare this mixture fresh at least weekly. This scrubber can be omitted if the laboratory air supply does not contain interfering aldehydes.

By means of a graduated cylinder transfer 200 ml. of distilled water to the 1-liter distillation flask, *C*. For samples that foam considerably, use a larger flask. Into the distillation flask introduce an amount of sample that contains no more than 0.7 mg. of ethylene oxide. Stopper the flask and thoroughly mix the contents. By means of a graduated cylinder introduce 20 ml. of distilled water, previously cooled to approximately 5° C., into scrubber *E* (Figure 2). Connect the scrubber to the reflux condenser by means of the ball and socket joint. Immerse the scrubber in the Dewar flask, *F*, containing ice-water slurry. Adjust the air flow to 10 ml. per minute by means of a suitable flowmeter. Connect scrubber *A* to the ebullator, *B*, in the distillation flask by rubber tubing. Make sure the system is completely air-tight. Turn on the condenser water. The temperature of this water should be above 10° C. Commence heating the distillation flask and allow the contents to reflux for 30 minutes. Disconnect the heat source, remove the Dewar flask, and rinse the drain tube of the scrubber with distilled water. Drain the contents of the scrubber into a heat-resistant pressure bottle. Rinse the scrubber three times, using a minimum amount of distilled water. Drain after each rinse, collecting the rinsings in the pressure bottle. Prepare a blank by adding distilled water to a second heat-resistant pressure bottle, filling to the same level as the sample bottle. For samples that do not contain interfering substances, the evolution procedure can be omitted and the samples introduced directly into the pressure bottles at this point.

By means of a suitable pipet transfer 1.0 ml. of 0.5*N* sulfuric acid to each bottle. Stopper the pressure bottles, protecting the rubber gaskets on the stoppers by polyethylene film. Enclose the bottles securely in fabric bags and place as close together as possible in a steam bath for 60 minutes at 98° ± 2° C. Remove the bottles from the bath and allow to cool to room temperature. When the bottles have cooled, loosen the bags, uncap the bottles carefully to release any pressure, and remove the bags. Quantitatively transfer the contents of each bottle to a 100-ml. glass-stoppered graduated cylinder. Pipet 1.0 ml. of 0.5*N* sodium hydroxide to each graduate, stopper, and mix. Pipet 2.0 ml. of 0.1*N* sodium periodate to each graduate, stopper and mix, and allow to react for 15 minutes at room temperature. Pipet 2.0 ml. of 5.5% sodium sulfite into each graduate, dilute to the 100-ml. mark with distilled water, stopper, and mix.

Transfer 10-ml. aliquots of each dilution to 100-ml. glass-stoppered graduated cylinders. Add approximately 0.05 gram of sodium chromotropate to each cylinder and shake to effect solution. The reagent does not have to be weighed each time, but should be carefully estimated to ensure a sufficient amount. Dilute the contents of each cylinder to the 50-ml. mark with concentrated sulfuric acid and allow the normal heat rise to occur. The sulfuric acid is best dispensed from an acid buret. By means of a 20-ml. pipet or capillary glass tubing connected to a nitrogen source and immersed in the acid solution, ebullate vigorously with nitrogen for approximately 10 minutes. Allow the contents of each cylinder to cool to room temperature. Measure the absorbance of the sample against the blank at 570 mμ, using 1-cm. cells. The colors developed are stable for at least 48 hours (*6*). Read the concentration of ethylene oxide from the calibration curve.

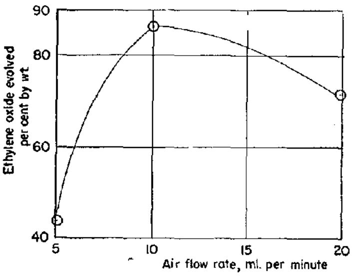

Figure 3. Effect of air flow rate on recovery of ethylene oxide from water

Evolution time, 30 minutes

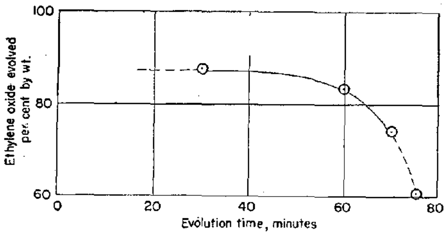

Figure 4. Effect of evolution time on recovery of ethylene oxide from water

Air flow rate, 10 ml. per minute

DISCUSSION AND RESULTS

Direct hydrolysis of ethylene oxide to ethylene glycol and subsequent reaction with sodium periodate to formaldehyde give the theoretical yield. When ethylene oxide is evolved from boiling water, only 86% of the oxide is recovered. It was found, by analysis of the water after evolution, that approximately 14% of the ethylene oxide originally present was hydrolyzed during evolution to ethylene glycol. Because of this factor a separate calibration curve is required when the evolution procedure is used.

The method reported has been used for the determination of ethylene oxide residues in spices fumigated with this material. The data shown in Table I were obtained on samples of unfumigated nutmeg, to which had been added

Table I. Determination of Known Concentrations of Ethylene Oxide in Nutmeg

Sample Size, G.	Ethylene Oxide, P.P.M. Added	Ethylene Oxide, P.P.M. Found	Recovery, %
5.0	136.0	136.5	100.2
5.0	81.6	82.4	100.9
10.0	68.6	69.3	102.0
10.0	40.8	42.3	103.5
20.0	33.0	32.2	97.6
20.0	19.8	19.2	97.2
20.0	13.2	13.6	103.0
20.0	6.6	7.6	116.0
20.0	2.5	1.8	72.0
20.0	1.2	0.8	67.0

Table II. Determination of Ethylene Oxide in Nutmeg

Sample[a]	Absorbance	Ethylene Oxide, P.P.M.
Untreated	0.018	0.5
	0.006	0.1
	0.008	0.2
	−0.023	−0.7
	−0.015	−0.5
	0.015	0.5
	Av.	0.2 ± 0.4
Fumigated	0.043	1.7
	0.048	1.7
	0.052	2.0
	0.056	2.2
	Av.	1.9 ± 0.2

[a] 20-gram samples.

Table III. Determination of Ethylene Oxide in Paprika

Sample[a]	Av. Absorbance	Ethylene Oxide, P.P.M. Added	Ethylene Oxide, P.P.M. Found[b]	Recovery, %
Untreated	0.006	...	0.12 ± 0.1 (2)	...
	0.022	1.3	0.7 (1)	54.0
	0.060	2.6	2.2 (1)	85.0
Fumigated	0.211	...	8.3 ± 1.1 (4)	...
	0.104	...	4.1 ± 0.0 (2)	...
	0.211	...	8.3 ± 0.4 (2)	...
	0.145	...	5.6 ± 0.6 (2)	...

[a] 20-gram samples.

[b] Figures in parenthesis represent number of determinations.

known amounts of ethylene oxide as an aqueous dilution. These data were obtained by the evolution procedure, and therefore a calibration curve based on this procedure was used.

Essentially complete recovery is obtained for concentrations of ethylene oxide over the range of 6 to 136 p.p.m. The results are independent of sample size, indicating no interferences from materials present in the nutmeg. When a 20-gram sample is used, the lower limit of detection by the method is approximately 1.0 p.p.m. This limit can be extended by using larger sample sizes.

Table II shows the analysis of treated and untreated nutmeg. For the untreated nutmeg the apparent ethylene oxide content is 0.12 ± 0.4 p.p.m. This is below the lower limit of detection by this method and is not significant. For the sample fumigated with ethylene oxide the residual oxide was 1.9 ± 0.2 p.p.m.

Table III shows the analysis of samples of fumigated and untreated paprika. In this case the interference obtained is also below the lower limit of detection by the method. The ethylene oxide found in these spices represents only the free ethylene oxide. Any combined ethylene oxide formed by reaction in the fumigation process is not determined. With all the spices investigated, no appreciable interference was obtained when the evolution procedure was used.

SCOPE

The lepidine method of Gunther and coworkers (*2*) cannot be used for the determination of ethylene oxide in admixture with most substances without prior separation. The method presented here can be used directly, if materials that react with periodate to form formaldehyde are absent. The direct method should be generally applicable to the determination of most 1,2-epoxides. Substances that react with periodate ion and other interferences were discussed by Speck and Forist (*6*). In general, these substances interfere in the determination of 1,2-epoxides by the direct method presented here.

The only compounds that interfere in the evolution procedure are other volatile epoxides such as propylene oxide. The evolution procedure should be directly applicable to the determination of this compound in the presence of interfering substances. If the scrubbing technique given in the procedure is used, the method should be directly applicable to the determination of low concentrations of 1,2-epoxides in air.

ACKNOWLEDGMENT

The samples of paprika used in this investigation were obtained from the R. T. French Co., Rochester, N. Y., and the nutmeg samples from McCormick and Co., Baltimore, Md.

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Thermolysis of Thorium Precipitates

Salts of Organic Acids

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▶ The thermal decomposition of the thorium precipitates with stearic, pyrogallic, m-hydroxybenzoic, m-cresoxyacetic, benzoic, 2,4-dichlorophenoxyacetic, phenylacetic, cinnamic, and o-aminobenzoic acids, and mercaptothiazole were studied on the thermobalance. In general, the precipitates decomposed at fairly low temperatures. The least stable began to lose weight at 35° C., while the most stable exhibited no weight loss below 285° C. The oxide levels were obtained in the temperature range from 450° to 675° C.

In an attempt to separate thorium from uranium and the rare earth elements, a large number of organic acids have been proposed as the precipitating agents. These organic acids form insoluble salts with thorium but not with the other elements, which allows a separation to be made. Many of these salts are sufficiently insoluble to be proposed for the gravimetric determination of thorium. Generally, however, the precipitated compounds are basic salts of variable composition and are ignited and weighed as thorium oxide. The temperature limits for the ignition to thorium oxide are in most cases unknown.

The thermal decomposition of the precipitated compounds is being studied on the thermobalance, to determine the exact temperature limits of the thorium salt, intermediate compounds (if any), and minimum oxide temperatures.

The precipitates examined have all been prepared previously: the thorium salts of stearic, pyrogallic, *m*-hydroxybenzoic (*3*), *m*-cresoxyacetic (*8*), benzoic (*9*, *12*), 2,4-dichlorophenoxyacetic (*2*), phenylacetic (*1*, *6*), cinnamic (*4*, *10*, *11*), and *o*-aminobenzoic (anthranilic acid) (*5*) acids, and mercaptobenzothiazole (*7*).

EXPERIMENTAL

Reagents. Thorium nitrate tetrahydrate was obtained from the Lindsay Chemical Co., West Chicago, Ill. *m*-Cresoxyacetic acid was obtained from Purkis, Williams, Ltd., London, England. The other organic acids were obtained from Eastman Organic Chemicals, Rochester 3, N. Y.

All other reagents were of C.P. quality.

Thermobalance. The thermobalance used has been described (*13*). The heating rates on all samples were 4.5° per minute, to a maximum temperature limit of about 900° C. The weight of the sample was recorded to ±0.1 mg., and the temperature was recorded to ±1° C.

Preparation of Precipitates. The thorium precipitates were prepared according to procedures described (*1*–*12*). In general, an aqueous solution of the organic acid was added to a boiling hot solution containing about 0.2 gram of thorium nitrate in 150 ml. of water. The final pH was adjusted by addition of 2*N* ammonium hydroxide. In certain cases, 1 to 5 grams of ammonium chloride or ammonium acetate was added to aid in coagulation of the precipitates. All the precipitates were formed in the pH range of 3 to 5. After digestion, they were filtered into sintered porcelain crucibles, washed according to directions in the literature, and dried at room temperature for at least 24 hours before thermal decomposition on the thermobalance. In many cases, the precipitates were gelatinous and exceedingly difficult to filter and wash.

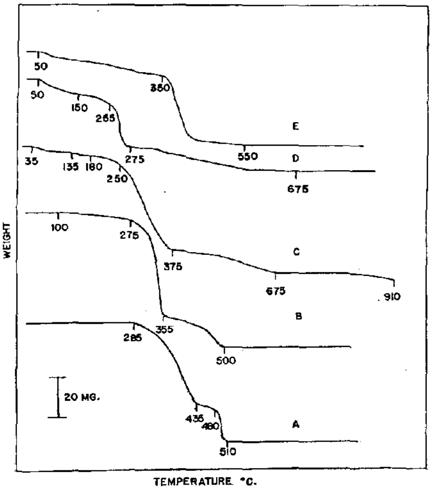

Figure 1. Thermolysis of thorium precipitates

A. Benzoate
B. Phenylacetate
C. Mercaptobenzothiazole
D. Pyrogallate
E. *m*-Hydroxybenzoate

DISCUSSION

Thermal decomposition curves are shown in Figures 1 and 2. In general, the first weight loss occurred below 150° C. After various stages of decomposition, the oxide levels of ThO_2 were obtained in the 450° to 675° C. range. The oxide level appeared above 675° C. only in the case of the thorium mercaptobenzothiazole precipitate, where it was not obtained even at 910° C., the upper limit of the thermobalance. The sample weights, oxide level weights, and minimum oxide level temperatures are given in Table I.

Thorium Benzoate. This was the most stable of all the thorium compounds examined. The formula of the precipitated compound corresponded to that of the normal salt, $Th(C_6H_5CO_2)_4$. The first weight loss was observed at 285° C. Beyond this, the compound decomposed

Table I. Minimum Oxide Level Temperature Limits and Composition Data for Thorium Precipitates

Precipitate	Temp., ° C.[a]	Sample Weight, Mg.	Oxide Weight, Mg. Found	Oxide Weight, Mg. Theor.	Formula Found
1. Thorium benzoate	510	93.8	34.9	34.6	$Th(C_6H_5CO_2)_4$
2. Thorium phenylacetate	500	99.3	33.3	33.9	$Th(C_6H_5CH_2CO_2)_4$
3. Thorium mercaptobenzothiazole	>910	96.3	28.4	28.4	$Th(C_7H_4NS_2)_4$
4. Thorium pyrogallate	675	94.9	49.4	48.9	$Th(OH)_2(C_6H_3O_3)_2$
5. Thorium stearate	450	96.8	31.6	30.7	$Th(OH)_2(HOC_6H_4CO_2)_2$
6. Thorium *m*-hydroxybenzoate	550	99.8	53.8	52.3	$Th(OH)_2(HOC_6H_4CO_2)_2$
7. Thorium cinnamate	490	88.7	32.6	33.9	$Th(OH)(C_6H_5C_2H_2CO_3)_3$
8. Thorium *m*-cresoxyacetate	500	85.4	40.8	37.9	$Th(OH)_2(CH_3C_6H_4OCH_2\text{-}CO_2)_2$
9. Thorium *o*-aminobenzoate	450	93.1	52.9	58.6	$Th(OH)_3(NH_2C_6H_4CO_2)$
10. Thorium 2,4-dichlorophenoxyacetate	475	88.9	27.9	25.8	$Th(OH)(Cl_2C_6H_3OCH_2\text{-}CO_2)_3$

[a] Heating rate 4.5° per minute.

rapidly. A sharp change of slope was observed in the decomposition curve at 435° C., but a constant weight level did not appear. Instead, further decomposition occurred to give the oxide level beginning at 510° C.

Thorium Phenylacetate. The precipitated compound, contrary to Datta and Banerjee (*2*), corresponded to the formula for the normal salt, $Th(C_6H_5CH_2CO_2)_4$. Previous investigators had assigned the formulas $Th(OH)(C_6H_5CH_2CO_2)_3.3H_2O$ (*6*) and $Th(OH)(C_6H_5CH_2CO_2)_3$ (*1*). Because of this variable composition, the precipitates were ignited and weighed as ThO_2.

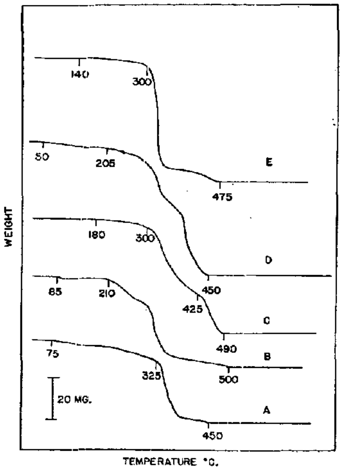

Figure 2. Thermolysis of thorium precipitates

A. *o*-Aminobenzoate
B. Cresoxyacetate
C. Cinnamate
D. Stearate
E. 2,4-Dichlorophenoxyacetate

The thermal decomposition curve showed that the compound began to lose weight at 100° C. The weight loss was slow at first but became rapid beyond 275° C., giving a break in the curve at 355° C. Beyond this temperature, further decomposition took place to give the oxide level beginning at 500° C.

Thorium Mercaptobenzothiazole Precipitate. The precipitated compound corresponded to the formula given by Spacu and Pirtea (*7*), $Th(C_7H_4NS_2)_4$ (calculated from the weight of ThO_2 in the thermobalance pan at 910° C.). The precipitate began to lose weight at 35° C., slowly at first but more rapidly beyond 180° C. Several intermediate breaks were found in the curve, one at 375° C. and another at 675° C. It was thought that the oxide level was reached at 675° C., but on further heating additional weight was lost. The curve was still descending at 910° C.

The original investigators recommended drying the precipitate at 105° to 110° C., but the thermolysis curve indicates that a constant weight level was not found in this temperature range. However, the absence of a level may be due to the more rapid heating rate during this investigation.

Thorium Pyrogallate. The precipitated compound corresponded to the formula for the basic salt, $Th(OH)_2(C_6H_3O_3)_2$. The precipitate began to decompose slowly above 50° C. Beyond 150° C., the rate of decomposition increased to give the oxide level beginning at 675° C.

Thorium *m*-Hydroxybenzoate. The precipitated compound corresponded closely to the formula for the basic salt, $Th(OH)_2(HOC_6H_4CO_2)_2$. The thermolysis curve showed that the first weight loss occurred at 50° C. Weight loss was slow at first but increased rapidly above 350° C. to give the oxide level beginning at 550° C. It has been stated that *m*-hydroxybenzoic acid will qualitatively separate thorium from cerium(III) (*3*).

Thorium *o*-Aminobenzoate (Anthranilate). The precipitated compound corresponded to some formula intermediate between $Th(OH)_2(H_2NC_6H_4CO_2)_2$ and $Th(OH)_3(H_2NC_6H_4CO_2)_2$. The latter formula is given in Table I. Murthy and Raghava Rao (*5*) assigned the formula, $Th(OH)_2(H_2NC_6H_4(CO_2)_2$, to the precipitated compound. The first weight loss occurred at 75° C. Although the rate of weight loss was slow at first, it increased rapidly beyond 325° C. to give the oxide level beginning at 450° C.

Thorium *m*-Cresoxyacetate. The precipitated compound corresponded approximately to the formula for the basic salt, $Th(OH)_2(CH_3C_6H_4OCH_2CO_2)_2$. Previous workers (*8*) stated that the precipitate was of a variable composition, but mainly $Th(OH)(CH_3C_6H_4OCH_2CO_2)_3.3H_2O$. After a slight weight loss at 85° C., a constant weight level appeared, which extended to about 210° C. Beyond this temperature, the compound decomposed rapidly to give the oxide level beginning at 500° C.

Thorium Cinnamate. The precipitated compound corresponded closely to the formula for the basic salt, $Th(OH)(C_6H_5C_2H_2CO_2)_3$. The precipitate was stable up to 180° C., where it began to decompose slowly. The rate of decomposition increased rapidly beyond 300° C. to give the oxide level beginning at 490° C. Previous investigators (*11*) stated that the composition of the precipitate was variable and thus ignited it to the oxide at an unspecified temperature. This organic acid has been successfully used for the separation of thorium from the rare earths and other metals in monazite sands.

Thorium Stearate. The precipitated compound corresponded closely to the formula for the basic salt, $Th(OH)_2(C_{17}H_{35}CO_2)_2$. It began to lose weight beginning at 50° C. Beyond 205° C., the rate of decomposition increased rapidly to give the oxide level beginning at 450° C. Determination of thorium with this organic acid is said to be more accurate than with *m*-nitrobenzoic acid (*3*).

Thorium 2,4-Dichlorophenoxyacetate. The precipitated compound corresponded closely to the formula for the basic salt, $Th(OH)(Cl_2C_6H_3OCH_2CO_2)_3$. The thermolysis curve showed that the precipitate began to lose weight slowly beginning at 140° C. Beyond 300° C., the rate of decomposition increased rapidly to give the oxide level beginning at 475° C. Previous investigators (*2*) found this reagent satisfactory in separating thorium from a large number of other metal ions.

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Absorptiometric Determination of Lead in Rubber Products and Compounding Materials

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▶A semimicro ultraviolet absorptiometric method that is rapid and sensitive has been developed for the quantitative determination of lead in rubber products and trace amounts of lead in rubber-grade zinc oxide. The ash of rubber products, or the inorganic material as is, is dissolved in a minimum amount of concentrated hydrochloric acid, then made up to contain a 50% excess of the acid. The absorbance is measured at 250, 270, and 289 mμ to calculate lead content. The interference of iron and most other cations is eliminated mathematically as background absorbance. Copper content must be less than about one tenth of the lead present.

THE USE OF litharge (PbO) as an inorganic accelerator of vulcanization of rubber products is no longer as important as it was prior to the discovery of organic accelerators (*3*). However, the use of lead in some form is still prevalent in a limited number of products (*2, 4*). Table I illustrates applications of inorganic and organic lead compounds in rubber products. Lead compounds are still used primarily to activate or accelerate vulcanization, but metallic lead has found application as a filler in balance dough because of its great density.

An analysis for type of accelerator in an unknown rubber product (*6*) would not be complete in some cases without a check for lead. The ASTM procedure for the chemical analysis of rubber products includes a conventional macro scale gravimetric method, where lead is determined as lead sulfate (*1*).

A sensitive absorptiometric procedure has been developed for microdetermination of sulfur in rubber products as lead sulfate (*5*). A similar technique is here adapted to the rapid determination of lead as a minor—e.g., 0.1 to 5%—component in rubber products on a micro scale. Lead may be determined in rubber-grade lead compounds as a control test by the same micro method.

The basis of this test is the absorbance of lead in 50% hydrochloric acid, in which it has a sharp symmetrical maximum at 270 mμ (Figure 1).

METHOD

Equipment. Beckman Model DU spectrophotometer with 1.00-cm. quartz cells.

Borosilicate glass beakers, 5 ml., for dry ashing or test tubes, 16 × 100 mm., for wet ashing.

Glass-stoppered graduated cylinder, 10 ml.

Reagents. Hydrochloric acid, 50% by volume. Make an exact 1 to 1 dilution of reagent grade concentrated hydrochloric acid (37%).

Instrument Calibration. Refer to the calibration procedure outlined by Kress (*5*).

Procedure. Homogenize the sample in a rubber mill, then weight a 1- to 10-mg. sample, or more if less than 1% lead is expected. Ash in a 5-ml. beaker at 550° C. for about 10 minutes, then in the front of a high-temperature muffle (900° C.) for 1 or 2 minutes until ashing is complete. [Alternately, wet ash with 3 to 5 drops of perchloric acid and about 1 ml. of concentrated nitric acid in small test tubes (*5*)].

Cool the beaker, then dissolve the ash in about 2 ml. of 50% hydrochloric acid, stirring with a glass rod if necessary. Transfer to a 10-ml. glass-stoppered cylinder using 50% acid wash. Dilute to volume with 50% acid and mix well. If wet ashing is used, pipet 10 ml. of 50% acid into the test tube and mix.

Measure the absorbance at 250, 270, and 289 mμ, using a blank of 50% acid. If absorbance is above 1.8, dilute with 50% acid as needed. Include all dilutions in calculating sample concentration, *c*.

Substitute appropriate absorbance values in the equation below to determine lead content of the sample.

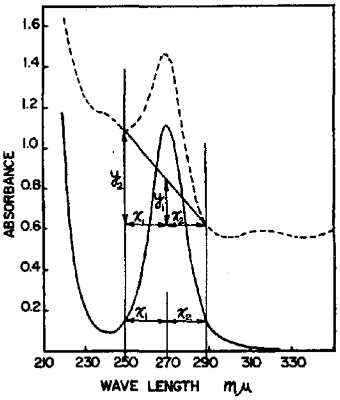

Figure 1. Interference of ferric iron in 50% hydrochloric acid

--- 500 mg. of zinc oxide with lead and iron impurity
— 0.2 mg. of lead alone

Table I. Applications of Lead in Rubber Compounding

Compounding Ingredient	% Lead Content (Theory)	Typical Application	% Lead Residue Expected in Ash
Inorganic			
Litharge (PbO)	93	1 to 3% as activator for carbamate accelerators in natural rubber wire insulation	1 to 3
Red lead (Pb_3O_4)	91	3 to 5% as activator for oxime accelerators in synthetic butyl tubes	3 to 5
Metallic lead	100	Filler in tire balance dough to add weight	50
Organic			
Methyl ledate (lead dimethyl dithiocarbamate)	46	0.2% to 0.6% as accelerator for natural rubber electrical wire insulation	0.1 to 0.3
SPDX (lead phenyldimethyldithiocarbamate complex)	34	0.1 to 0.4% as accelerator for natural and GR-S synthetic rubber stocks	0.03 to 0.15

Table II. Determination of Lead in Rubber Products

Product	Theoretical Form and %	Methods of Analysis			
				Absorptiometric	
		Electrolytic	Gravimetric	Wet ash	Dry ash
Tire balance dough No. 1		47.9	...	...	47.3
	Metallic lead, unknown	46.7			
		48.7			
		Av. 48.0 ± 0.7			
Tire balance dough No. 2	Metallic	...	47.1	52.9	50.6
	Lead, unknown		50.8	52.8	50.1
			Av. 49.0 ± 1.8	52.8 ± 0.1	50.4 ± 0.3
Butyl stock No. 1 (production)	Pb_3O_4[a], 5.10	...	...	...	5.28
					5.42
					Av. 5.35
Butyl stock No. 2 (three different production samples, a, b, c)	Pb_3O_4, 5.10	...	...	a 5.55	4.17
				b 5.23	4.52
				c 5.49	4.00
Control stock No. 3	Pb_3O_4, 5.10	...	...	5.11[b]	4.34

[a] Reported as Pb_3O_4 corrected for rubber-grade pigment purity of 95% as Pb_3O_4 by analysis.

[b] Higher recovery by wet ashing makes this method preferred, but dry ashing is usually satisfactory if care is taken to dissolve all of the ash residue.

$$\Delta A^{S}_{270} = (A_{270} - A_{289}) - \left(\frac{A_{250} - A_{289}}{2}\right) \qquad (1)$$

$$\%\ \text{lead} = \frac{\Delta A^{S}_{270} \times 100}{\Delta a^{Pb}_{270} \times c(\text{mg./ml.})} \qquad (2)$$

The data of Table II illustrate the precision of the absorptiometric determination of lead in rubber products. Agreement with both electrolytic and gravimetric methods is good. With the absorptiometric method, there is no danger of loss through solubility of the lead sulfate, as with the gravimetric procedure.

RUBBER COMPOUNDING MATERIALS

In the manufacture of white rubber products, it is undesirable to have lead compounds present, because they form lead sulfide with sulfur added for vulcanization and cause a brown discoloration. Consequently, it is necessary to control the lead content of zinc oxide, which is a common ingredient in tire white sidewall stocks.

The lead content of rubber-grade zinc oxide is usually below 0.2%. The electrolytic procedure used, which normally requires a large sample—e.g., 20 grams—is not believed to be accurate at lead concentrations below about 0.01%. There is some danger of occlusion of zinc, and the weight of lead recovered is often only 1 or 2 mg., which cannot be weighed accurately enough with normal macro-sized electrodes when lead content is critical.

The absorptiometric method offers an unusually rapid procedure which is of acceptable accuracy for traces of lead as low as 0.001% in zinc oxide.

Lead in Zinc Oxide. The sample size of zinc oxide is determined by the normal lead content as follows:

Normal Lead Sulfate Content, %	Approx. Sample Weight, Grams (G. ZnO/10 Ml.)
Below 0.004	1 to 2
0.03	0.4
0.1	0.1
1	0.01

The weights given are close to the maximum allowable in 10 ml. of 50% acid without further dilution.

Weigh an appropriate amount of the zinc oxide and transfer to the 10-ml. cylinder. Add just enough concentrated hydrochloric acid to dissolve the sample with vigorous shaking. Add the last of the acid drop by drop.

Dilute to 5.0 ml. with distilled water, then to 10.0 ml. with concentrated hydrochloric acid. Mix well and measure the absorbance at 250, 270, and 289 mμ. Thereafter, follow the procedure for determination of lead in rubber products. The results are usually multiplied by 1.46 to convert to lead sulfate.

EXPERIMENTAL WORK

Acid Concentration. The wave length and intensity of maximum absorbance of the lead chloride complex depend on the acid concentration (*5*, *8*). Where the lead content is about 1% or higher, as in the ash of rubber products or the analysis of lead compounds, the small amount of ash or the micro-sized sample can often be most conveniently dissolved directly in 50% hydrochloric acid. However, for traces of lead in zinc oxide, the large amount of sample to be dissolved greatly reduces the free or excess hydrochloric acid concentration.

Lead sulfate determined in rubber-grade zinc oxide by direct solution in 50% hydrochloric acid may run as low as 70% of the true values, as determined with 50% free hydrochloric acid solvent or by electrolysis (Table III). The absorbance curves of Figure 2 show why this is so. Apparently the zinc chloride formed has no direct effect on the lead absorbance, but it lowers the total absorbance indirectly by reducing the excess acid concentration. Consequently, all samples for determination of trace amounts of lead should first be just dissolved in the minimum amount of concentrated or 50% acid before diluting to a 50% excess by volume.

Major Interferences. Absorbance in hydrochloric acid is not specific for lead. Other heavy metals, particularly mercury and bismuth, also absorb selectively, but their absorbance

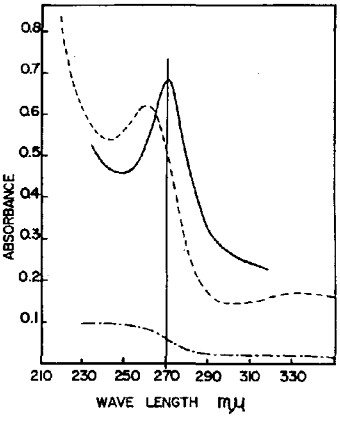

Figure 2. Effect of excess acid on absorbance maximum

Zinc oxide solution containing 0.01% lead sulfate impurity

--- In 50% acid, equivalent to 20% excess by volume

— In 70% acid, equivalent to 50% excess by volume

Zinc oxide solution containing no lead by electrolysis

-.- In 50% acid

in the 250- to 280-mμ region is low and nonselective. As minor components, they would not cause any appreciable interference that would not be corrected for as background absorbance by the calculation developed to eliminate iron interference. This is also true for the lighter elements: vanadium, chromium, tin, and antimony, which show interfering absorbance. Of these six elements, only antimony (as the sulfide) and bismuth (as a carbamate accelerator complex) have found any use in rubber compounding.

The chlorides of calcium, magnesium, aluminum, and zinc, which are the most common elements in the ash of rubber products besides iron, have essentially no absorbance in the ultraviolet above 230 mμ. Of trace elements that may be present in rubber products, such as copper, manganese, cobalt, and nickel, the chloride of copper is the only one that absorbs appreciably above 240 mμ (Figures 3 and 4).

IRON. If iron interference is excessive, a liquid-liquid extraction of the 50% hydrochloric acid solution with ethyl ether removes the greater part of the iron without extracting lead chloride. Another chemical method for removing iron interference, when present in concentrations comparable to the lead content, is use of titanous chloride to reduce the iron to the ferrous state (*8*).

Normally, the iron content should be lower than lead for best results, but it can be tolerated to the extent of about twice the lead content. As ferric chloride has an intense yellow coloration in hydrochloric acid, absence of more than a light yellow coloration indicates that iron interference is not excessive.

When inorganic lead compounds are added to rubber products, the lead content is usually so much greater than the trace of iron present that absorbance of iron is almost negligible. For rubber-grade zinc oxides the iron content is usually of the same order of, or less than, the lead content. Therefore, in rubber chemistry analyses where lead is present, the absorbance curve in 50% hydrochloric acid is usually one of combined iron and lead absorbance, with the lead maximum at 270 mμ distinct and usually dominant.

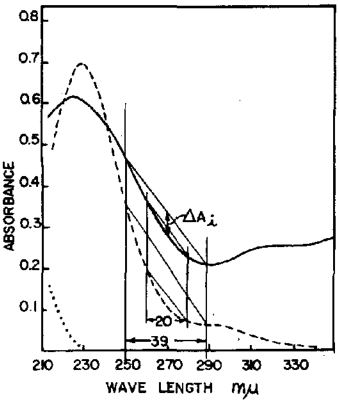

Figure 3. Negative background interference in 50% hydrochloric acid

— 5.0 p.p.m. of ferric iron
.... 50.0 p.p.m. of manganese
---- Antimony

Figure 1 illustrates the combined absorbance of lead and iron in a rubber-grade zinc oxide. Absorbance will be similar for the ash of rubber products whose iron content approaches that of lead. Iron absorbance between 250 and 289 mμ is essentially linear with a small negative curvature (Figure 3), and can be eliminated mathematically by considering it to be a linear background absorbance. A suitable equation for elimination of iron absorbance was derived as follows.

In Figure 1 the lead absorbance maximum is symmetrical. In the absence of iron, absorbance at 289 mμ is essentially identical to that at 250 mμ. The distances between these two wave lengths of equal absorbance and the wave length of the maximum (270 mμ) are 20 and 19 mμ. To simplify the calculations of background absorbance, they are considered equidistant (20 mμ) from the wave length of the maximum, and also of equal absorbance.

Interference due to intensity of background absorbance may be eliminated by basing calculations on difference in absorbance between 270 and 289 mμ. Interference due to increase in background absorbance between 289 mμ and 270 mμ may be eliminated by determining the change in absorbance of the background over this range.

In Figure 1, x_1 is assumed equal to x_2. Then, by similar triangles, interference due to the increase of the background absorbance between 289 mμ and 270 mμ (y_1) is equal to $\frac{1}{2}\,y_2$ or to $\frac{1}{2}(A_{250} - A_{289})$. Combining these terms, the corrected differential absorbance at 270 mμ due to lead in the sample, after both intensity and increase in intensity of iron absorbance have been subtracted mathematically, will be given by the Equation 1. Per cent lead in the sample may then be calculated from the ratio of the specific absorbance difference for the sample to that obtained for a lead standard (*5*).

$$\%\ \text{Lead} = \frac{\Delta a^{S}_{270} \times 100}{\Delta a^{\text{Pb}}_{270}} = \frac{\Delta A^{s}_{270} \times 100}{\Delta a^{\text{Pb}}_{270} \times c}$$

$$\%\ \text{Lead} = \frac{(A^{s}_{270} - A^{s}_{289}) - \left(\dfrac{A^{s}_{250} - A^{s}_{289}}{2}\right)}{\Delta a^{\text{Pb}}_{270} \times c} \times 100 \qquad (3)$$

where

A = measured absorbance at single specified wave length

a = absorptivity at single wave length

For 1-cm. cell, $a = A/c$

ΔA^{s}_{270} = differential absorbance (so defined for convenience). As defined mathematically in the text, it represents an absorbance difference of the sample between 270 and 289 mμ after correction for the slope of interfering background absorbance.

^{s} = sample absorbance

$\Delta a^{\text{Pb}}_{270}$ = difference in absorptivity between 270 and 289 mμ for lead alone in 50% hydrochloric acid. The value should be approximately 50 but varies somewhat with different instruments.

c = concentration of sample in grams per liter or mg. per milliliter at dilution at which absorbance is measured

COPPER. Copper promotes deterioration of natural rubber products and is

Table III. Absorptiometric vs. Electrolytic Determination of Lead Sulfate in Commercial Rubber-Grade Zinc Oxide

% Lead Sulfate by Electrolysis	% Lead Sulfate by Direct Soln. in 50% HCl	% Lead Sulfate Found by Adding Excess of 50% HCl after Soln.		
		Found	Av.	Mean dev.
2.27 2.35 Av. 2.31	...	2.20 2.32 2.22 2.32	2.26	±0.06
0.58	0.53	0.56 0.57	0.56	±0.01
0.10 0.11 Av. 0.105	...	0.132 0.127	0.130	±0.002
0.099 0.100 Av. 0.10	...	0.098	0.098	...
0.04	0.026	0.036 0.036	0.036	0.00
...	1.92	2.44	...	...
Zinc Oxide, C.P. 0.0002 to none (Unreliable at this concentration)	...	0.0004 0.0002	0.0003	±0.0001

carefully controlled by actual analysis of the raw materials going into the final product. The normal rubber product contains copper at concentrations below 0.002%, which does not interfere with the determination of lead when lead is added as a compounding material.

Most rubber-grade zinc oxides, with normal lead content below 0.2% as lead sulfate, have lead contents ranging from 10 to 200 times the copper content. With an occasional sample the lead-copper ratio may fall to 6 or rise to over 500. Only with the purest grades of nearly lead-free zinc oxides will the copper content approach that of lead.

The ultimate limit and accuracy of determination of lead in purer grades of zinc oxides and other materials depends on whether the copper content is well below that of lead. Figure 4 shows that possible interference due to copper will be below 2% of the lead content as long as copper concentration is below about one tenth of the lead present. If much copper is present, the absorbance at 289 mμ will be greater than at 250 mμ. With iron and most other interfering materials, the absorbance at 250 mμ will normally be higher than at 289 mμ. Therefore, if absorbance at 289 mμ is significantly greater than at 250 mμ, copper interference may be expected, and the method should not be used without some modification to eliminate copper interference. A possibility is the estimation of copper in lead by the ratio of the absorbance at 270 mμ to that at 289 mμ, followed by correction for the interference of this amount of copper.

The specific absorbance of copper at 270 mμ is about the same as that of lead, but its maximum is so broad that absorbance at 289 mμ is about 7 times that of lead. Because of this, the interference of copper with the lead determination is greatly reduced when the absorbance difference method ($A_{270} - A_{289}$) is used to determine lead absorbance of a sample. For lead $\Delta a^{Pb}_{270-289}$ is about 50, while for copper, $\Delta a^{Cu}_{270-289}$ is only about 8.4 (Figure 4). Therefore, even pure copper calculated on the absorbance difference method would amount to only 17% as lead. When the copper to lead ratio is less than 1 to 10, the copper interference will be below 1.7% of the lead present. Copper content of zinc oxide for use in rubber products is below 0.003%. This maximum figure would calculate as only 0.0005% lead.

It is helpful to remember that copper chloride in 50% hydrochloric acid has a rather strong yellow color if present at concentrations much above 10 p.p.m. The ether extraction for ferric chloride removal will not affect this copper chloride coloration.

Choice of Wave Length Interval. The wave lengths of 250 and 289 mμ were arbitrarily placed near the lead absorption curve minimum to retain good sensitivity. An even narrower wave length interval might be chosen to make the background correction more accurate, because the assumption of a linear background holds more closely as the interval is reduced.

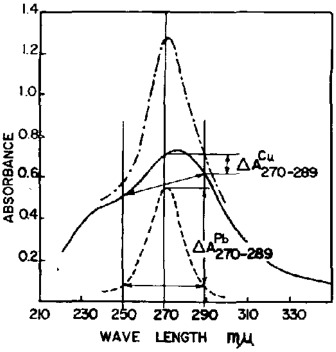

Figure 4. Positive background interference in 50% hydrochloric acid

— 25 p.p.m. of copper
--- 20 p.p.m. of lead
-.- Sum of copper and lead absorbance

The effect of narrowing the wave length interval to reduce interference from elements that absorb rather strongly, but nonselectively, over the 250- to 289-mμ interval is shown in Figure 3 for the antimony curve. The absorbance of antimony, vanadium, chromium, tin, and molybdenum, all reported to interfere with lead absorbance at 270 mμ (*8*), is essentially nonselective (no maximum) over this spectral region. Through the 250- to 289-mμ interval, each element exhibits a negative curvature resembling that of iron (ΔA_i in Figure 3) but varying in slope and depression from the essentially linear and shallow slope of vanadium to the sharp drop and distinct depression of antimony absorbance. Of the elements mentioned, antimony would cause the greatest interference, but all would tend to lower apparent lead content if present in appreciable amounts as background interference. Incidentally, this negative absorbance would also be assurance that no lead would be found where none was present, in the absence of positive copper interference.

As the wave length interval is narrowed through 39, 30, and 20 mμ, the Δa value for lead falls from 50 to 43 to 28, respectively. The drop from an absorptivity of 50 to 28 reduces the sensitivity for lead determination by about 44%. Calculations have shown that, by narrowing the interval to 20 mμ the relative interference of all the above elements with negative sloping curves is reduced to about half its value at the 40-mμ interval.

The intensity of absorbance of interfering elements at 270 mμ in 50% acid is comparable to lead for only iron and copper. The absorptivity value of antimony is about 50% that of lead, while the intensity of vanadium, chromium, mercury, bismuth, thallium, and tin absorbances is less than 8% of lead at 270 mμ. Consequently, as long as the concentration of interfering elements (other than copper and iron) is less than the lead present, interference due to negative curvature of background absorbance may be considered negligible. Of course, the closer the background absorbance approaches linearity, or the lower the concentration of nonlinear interference, the more accurate this calculation will be.

Though background of possible elemental interference has been shown to be negative, the absorbance of indeterminate materials in commercial products (as dirt in zinc oxide) tends to make background absorbance approach linearity more closely than is indicated in the curve of pure iron and antimony in Figure 3.

Therefore, the choice of a wide (39 mμ) wave length interval to obtain high sensitivity is believed justified here, when traces of lead in zinc oxide and in the ash of rubber products are being determined. In other applications the optimum conditions for interference elimination may be calculated.

OTHER APPLICATIONS

The rapid micromethod for determining lead should prove satisfactory for many materials other than rubber compounding chemicals. Its possible application to determination of trace amounts of lead in reagent grade sodium, calcium, magnesium, zinc, cobalt, nickel, and manganese compounds appears promising. It should prove sensitive enough to determine lead in toxicological studies on biological specimens, or for lead compounds in petroleum products.

In rubber chemistry, the use of absorptiometric analysis with 50% hydrochloric acid should prove ideal for determining antimony when antimony sulfide is used in rubber products (*7*). It would also be an excellent method for determining bismuth when the thiocarbamate salt of bismuth (Bismate) is used as an accelerator (*2*). The elements that might interfere with the determination of antimony and bismuth, such as mercury, chromium, vanadium, and thallium, are never used in rubber products.

The 50% acid should also prove of value in many applications as a screening reagent in qualitative analysis for several of the heavier metallic cations, once the more common iron is removed by ether extraction of the acid solution.

ADVANTAGES

The main advantages of the absorptiometric method over conventional electrolytic and gravimetric procedures are its improved simplicity, speed, sensitivity, and accuracy. Lead may be determined down to about 1 p.p.m., the lower limit depending on the amount of background interference.

ACKNOWLEDGMENT

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Potentiometric Method for Determination of Carbonyl Sulfide in Petroleum Gases

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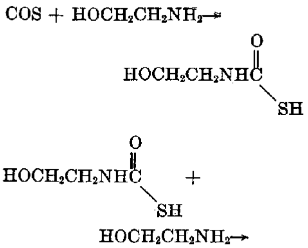
▶ Carbonyl sulfide in petroleum gases can be determined potentiometrically after absorption in alcoholic monoethanolamine solution by titrating it with standard silver nitrate solution. Mercaptans and hydrogen sulfide are first removed from the gas stream by absorption in alcoholic caustic solution. Concentration as low as 2 mg. per cubic meter of gas may be conveniently determined.

DETERMINATION of sulfur compounds in refinery gas streams is of considerable importance in the petroleum and petrochemical industries. Sulfur constituents such as hydrogen sulfide, mercaptans, carbonyl sulfide, and free sulfur may act, in certain processes, as catalyst poisoning agents and corrosive agents. A potentiometric method has been developed for the determination of carbonyl sulfide in gases in concentrations as low as 2 mg. per cubic meter.

Soloveichik (*10*) determined carbonyl sulfide in soil gases colorimetrically by absorbing the gas in alcoholic potassium hydroxide and converting the carbonyl sulfide to hydrogen sulfide. Avdeeva (*1*) described a method of determining carbonyl sulfide and carbon disulfide by absorption in selective reagents, oxidation, and measurement as the barium sulfate precipitate. A method of determining carbon disulfide and carbonyl sulfide in gases by adsorption in piperidine-chlorobenzene or alcoholic potassium hydroxide and resolution of the proportion colorimetrically or iodometrically was reported by Riesz and Wohlberg (*9*). Field and Oldach (*3*, *4*) used a catalytic method to convert organic sulfur to hydrogen sulfide which is absorbed in caustic, converted to a bismuth sulfide suspension, and read photometrically. They also developed a procedure for the determination and identification of sulfur compounds in gas mixtures based on differences in solubility in an inert solvent (*7*). Hakewill and Rueck (*5*) absorbed carbonyl sulfide in alcoholic potassium hydroxide and determined the amount iodometrically. The use of selective absorbents for analyzing manufactured gas for sulfur compounds is described by MacHattie and McNiven (*6*). Thiophene, carbonyl sulfide, and carbon disulfide in producer gas have been determined (*2*) by treating a gas sample with a piperidine–ethyl alcohol reagent and measuring in the ultraviolet region. Rapoport (*8*) used a series of absorbents and a combustion technique for the determination of carbon disulfide, carbonyl sulfide, and thiophene.

The method reported here consists of the passage of the sample gas through two scrubbers, the first of which removes hydrogen sulfide and mercaptans by absorption in 30% caustic and the second of which absorbs carbonyl sulfide in alcoholic monoethanolamine.

The contents of the monoethanolamine scrubber are titrated with silver nitrate solution in acidic alcoholic titration solvent, using the potential difference between a glass reference electrode and a silver sulfide electrode to indicate the end point. The precipitates from several titrations were filtered from the solutions, washed, and dried in a desiccator. They were then weighed, dissolved in nitric acid, and analyzed for silver content by potentiometric titration with potassium iodide. The results showed a silver content of approximately 86%, which corresponds closely to that of silver sulfide. The titration of the contents of the monoethanolamine scrubber requires 2 moles of silver nitrate per mole of carbonyl sulfide. The following equations are postulated as a possible explanation of the stoichiometry. Equation 4 describes the over-all reaction.



$$COS + HOCH_2CH_2NH_2 \rightarrow HOCH_2CH_2NHC(=O)SH \quad (1)$$

$$HOCH_2CH_2NHC(=O)SH + HOCH_2CH_2NH_2 \rightarrow H_2S + (HOCH_2CH_2NH)_2C{=}O \quad (2)$$

$$H_2S + 2AgNO_3 \rightarrow Ag_2S + 2HNO_3 \quad (3)$$

$$COS + 2HOCH_2CH_2NH_2 + 2AgNO_3 \rightarrow Ag_2S + (HOCH_2CH_2NH)_2C{=}O + 2HNO_3 \quad (4)$$

APPARATUS AND REAGENTS

Absorbers. Gas washing bottles,

125-ml., with coarse-porosity, sintered-glass disks.

Gas meter, wet type, having a measuring capacity of about 3 liters per revolution and a cumulative register up to about 300 liters. The meter was equipped with a thermometer and water manometer for measuring the gas temperature and pressure, respectively.

Flow control valve. A stainless steel, $^1/_8$-inch needle valve, for samples taken from the liquid state. An arrangement was supplied for heating the valve.

Titrometer. Precision Dual A.C. Titrometer equipped with a glass reference electrode, a silver sulfide indicating electrode, and a 10-ml. buret graduated in 0.05 ml.

Acidic titration solvent. Sodium acetate trihydrate, 2.7 grams, was dissolved in 20 ml. of oxygen-free water and 975 ml. of anhydrous ethyl alcohol, and 4.6 ml. of glacial acetic acid was added. Refined isopropyl alcohol, which has been passed through a small column of activated alumina, or Formula 2B denatured alcohol (a mixture of absolute ethyl alcohol and 5% by volume of benzene) may be substituted for the anhydrous ethyl alcohol. The solution was purged with a rapid stream of nitrogen for 10 to 15 minutes each day prior to use to remove dissolved oxygen.

Ammonium hydroxide, concentrated.

Carbonyl sulfide, Matheson Co., 97% as determined by mass spectrometry.

Monoethanolamine, Eastman Kodak White Label, 5% solution in ethyl alcohol.

Nitrogen, Linde, H. P. dry, containing less than 0.1% oxygen.

Silver nitrate solution. Silver nitrate, 17 grams, was dissolved in 100 ml. of distilled water and diluted to 1 liter with 92% isopropyl alcohol (prepared from refined, peroxide-free alcohol and distilled water). A 0.01*N* solution was prepared by exact dilution of the alcoholic 0.1*N* solution with refined 92% isopropyl alcohol. The silver nitrate solutions were standardized against standard 0.1*N* potassium iodide.

Sodium hydroxide solution, 30% aqueous. This was purged with nitrogen for 10 to 15 minutes each day prior to use to remove dissolved oxygen.

PROCEDURE

Connect the gas absorbers in series as shown in Figure 1. Connect the outlet tube of the second absorber to the wet test meter. Connect the inlet tube of the first absorber to the flow control valve on the sample line and to the rate control valve from the nitrogen line so that either the sample or nitrogen may be passed through the absorbers. Make all connections as short as possible with glass tubing joined either by ground-glass joints or short lengths of Tygon tubing.

Place 20 ml. of 30% aqueous sodium hydroxide in the first scrubber and 20 ml. of 5% alcoholic monoethanolamine in the second scrubber, which should be completely masked with black tape. Flush the assembled apparatus with 25 liters of nitrogen.

Pass sufficient gaseous sample through the absorbers to afford a titration of 2 to 10 ml. of 0.01*N* silver nitrate (usually 8 to 12 liters). The gas sample should pass through the absorbers at a rate of 150 to 180 ml. per minute. Record the meter reading, the temperature, and the barometric pressure. Flush the absorbers with 5 to 10 liters of nitrogen and disconnect them.

Quantitatively transfer the monoethanolamine solution from the second absorber into a 250-ml., tall-form titration beaker. Dilute to 125 ml. with acidic titration solvent and titrate potentiometrically, using the glass-silver sulfide electrode system.

Select the end point at the bottom of the straight line portion of the break in the titration curve (Figure 2). The end point potential should be approximately +50 mv. Unpublished work (*11*) on the titration of pure halides and mercaptans with silver ion has shown empirically that the stoichiometric point is at the end of the steepest portion of the titration curve. In the present application, the end points have been taken in this manner, although the difference from the conventional inflection point is within experimental error. If the titration falls appreciably outside the 2- to 10-ml. range, use a larger sample or an aliquot of the scrubber solution.

Calculate the gas volume at standard conditions by means of the following equation:

$$V = V_o \times \frac{273}{273 + T} \times \frac{P - p}{760}$$

where V_o = observed volume of gas, liters
P = barometric pressure, mm. of mercury
p = vapor pressure of water at temperature T

Calculate the carbonyl sulfide content of the sample using the following equation:

$$\text{carbonyl sulfide, mg. per cubic meter} = \frac{AN\ 30{,}000}{V}$$

where A = volume of silver nitrate, ml.
N = normality of silver nitrate
V = volume of sample, standard conditions

EXPERIMENTAL

A number of synthetic and refinery gas samples were tested for carbonyl sulfide using this method. Synthetic samples were prepared by injecting known amounts of carbonyl sulfide into a stream of propane at a point before the caustic prescrubber. Table I compares the results obtained on several samples with those obtained using the mass spectrometer or a lamp combustion method.

Carbon disulfide, mercaptans, and hydrogen sulfide would interfere with the titration, as they form titratable complexes with monoethanolamine. However, hydrogen sulfide, mercaptans, sulfur dioxide, and carbon dioxide are absorbed in the 30% aqueous caustic solution. Carbon disulfide is usually present in such small amounts that it does not constitute a major interference.

Hydrolysis of carbonyl sulfide in the 30% caustic solution may become

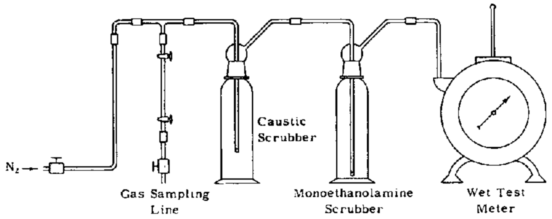


Figure 1. Apparatus for absorption of carbonyl sulfide

Table I. Comparison of Methods for Determination of Carbonyl Sulfide[a]

	Carbonyl Sulfide, Calcd. as Sulfur, Wt. %		
Sample	Lamp method for total sulfur	Potentiometric titration method	Mass spectrometer
Depropanizer tops		0.0059	0.0053, 0.0055
Untreated propane		0.0045, 0.0050	0.0040, 0.0055
Treated propane		0.0005, 0.0005	0.0005, 0.0005
Untreated propane		0.0068	0.0073
Untreated propane		0.0059	0.0062
Untreated propane		0.0051	0.0046
Blend of COS in C_8	0.280	0.255	
Blend of COS in C_7	0.055	0.068	
	0.066	0.066	
	0.057	0.058	

[a] Comparison data from Taylor (*12*).

Table II. Analysis of Synthetic Samples

Experiment	COS, Mg. Added	COS, Mg. Found	Recovery, %	Remarks[a]
A	17.9	17.0	95	MEA[b] scrubber
		0.5	3	Caustic scrubber
B	22.2	20.6	93	MEA scrubber
		0.7	3	Caustic scrubber
C	17.9	16.7	93	No caustic scrubber
D	17.8	16.4	92	Scrubber at 0° C.
E	17.8	16.7	93	Scrubber at 35° C.
F	22.2	20.5	92	Isopropyl alcohol as titration solvent
G	22.2	21.5	97	Solution titrated after 2 hours in dark
H	22.2	12.6	57	Solution titrated after 2 hours in light
I	22.2	1.5	7	Solution titrated after 8 hours in light
J	22.2	18.0	81	Scrubber exposed to sunlight during run
K	193	170	88	1st MEA scrubber
			2	2nd MEA scrubber

[a] Conditions of determination are same as given under procedure unless otherwise specified.
[b] Monoethanolamine.

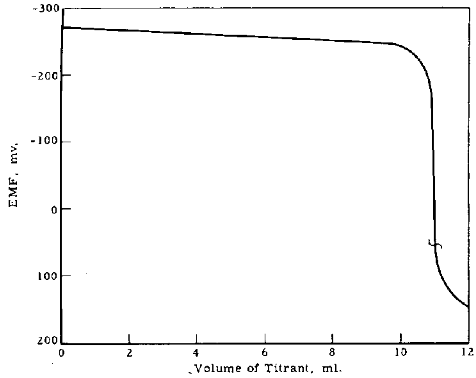


Figure 2. Typical titration curve

appreciable if certain precautions are not taken. Satisfactory results were obtained using a flow rate between 150 and 180 ml. per minute and a coarse-porosity, sintered-glass disk immersed about 0.5 inch in the caustic solution. Titrations of the caustic scrubber from determinations of synthetic samples of carbonyl sulfide in propane indicate that between 1 to 3% of the carbonyl sulfide is hydrolyzed in the caustic scrubber solution. (Table II, *A* and *B*).

Light appears to be the most serious factor affecting recovery of the carbonyl sulfide. Successive determinations were made allowing the monoethanolamine scrubber solution to stand for different periods of time before titrating (Table II, *G*, *H*, and *I*). Recoveries of up to 97% were obtained on solutions which were placed in the dark for several hours before titration. Upon standing in normal room light for 2 hours, only 57% of the normal titration was obtained, and on standing 8 hours in the light, recovery dropped to 7%. This effect was verified by allowing sunlight to fall on the monoethanolamine scrubber during a run and titrating immediately after completion of the run. Recovery of the carbonyl sulfide dropped to 81%. For this reason the monoethanolamine scrubber should be completely masked with black tape and the solution should be titrated immediately on completion of the run.

The acidity of the titration solvent was varied by omitting the acetic acid, the sodium acetate, or both. The composition of the titration solvent made the recovery of carbonyl sulfide vary by several per cent, giving somewhat higher results when the acetic acid was omitted and lower results when the sodium acetate was omitted.

Variation of the temperature of the absorber or titration solution did not affect the results measurably over a range from 0° to 35° C. There was some indication of incomplete absorption of the carbonyl sulfide, amounting to about 2%, with larger sample sizes (Table II, *K*). This was determined by placing two monoethanolamine scrubbers in series.

A variety of other amines (5% solutions in alcohol) and a 5% alcoholic potassium hydroxide solution were tried in place of monoethanolamine in the carbonyl sulfide scrubber. The other amines studied were triethanolamine, diethanolamine, *n*-butyldiethanolamine, ethylamine, and di-*n*-amylamine. Alcoholic potassium hydroxide gave a poor titration curve and low recoveries. The other amines were unsatisfactory from the standpoint of reaction rate, stability, or reproducibility. These amines may give more suitable results by the proper adjustment of the acidity of the titration medium. Di-*n*-amylamine proved satisfactory when the apparent pH was controlled at 10.6 in the beginning of the titration. However, the results obtained were one half those obtained using monoethanolamine. The following equation was postulated for the reaction of carbonyl sulfide with di-*n*-amylamine and silver nitrate:

$$(C_5H_{11})_2NH + COS + AgNO_3 \rightarrow (C_5H_{11})_2NCOSAg + HNO_3 \quad (5)$$

ACKNOWLEDGMENT

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Determination of Boron in Fluoride Salts

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▶Trace amounts of boron in fluoride salts can be determined after the salts are dissolved at room temperature in a solution of aluminum chloride and hydrochloric acid and then diluted with an equal volume of ethyl alcohol. A reproducible fraction of the boron is extracted when the aqueous solution is equilibrated with an equal volume of ethyl ether for 5 minutes. The boron in the ether phase is determined spectrophotometrically with carminic acid. The partition coefficient of boron, C_o/C_a, is 0.59 ± 0.02 when the concentration of hydrochloric acid is 4*M* and that of aluminum chloride is 2*M*. This coefficient is independent of temperature between 13° and 28° C. The method was applied successfully to the determination of as little as 10 γ of boron. The coefficient of variation for samples that contain 200 γ of boron is 3%.

ORDINARILY, two conditions are requisite for the determination of trace amounts of boron in a fluoride salt: The salt must be dissolved in such a manner that the formation of extremely volatile boron trifluoride is obviated; free fluoride must be eliminated because it decolorizes most of the boron–organic dye chromophores that are commonly used in the measurement of microquantities of boron. In particular, anthraquinone derivatives (*1*,*4*), which represent a class of colorimetric reagents for boron, are readily decolorized by fluoride. No specific methods for the separation of traces of boron from fluoride have been reported previously.

Usually fluoride is removed from solutions as the volatile hydrofluoric acid or, if silica is present, as silicon tetrafluoride or hydrofluosilicic acid (*5*) by the application of heat. Such methods, however, cannot be applied to samples that contain boron because considerable amounts of this material are lost if acidic solutions of the samples are evaporated.

Separation of boron from undesired constituents of a solution as volatile methyl borate is probably the most common method of effecting isolation as well as separation of boron. This method is time-consuming and subject to considerable error through incompleteness of the separation. Also, some of the fluoride will almost certainly be carried over during distillation of methyl borate.

The authors have observed that a large variety of fluoride salts and mixtures thereof can be dissolved at room temperature in acidic solutions that contain aluminum salts. The mechanism of this dissolution can best be explained by the greater stability of the aluminum fluoride complexes. For example, the stability of monofluoro complexes of various metals has been reported to decrease in the following order: thorium, aluminum, beryllium, zirconium, iron(III), and hydrogen ion (*6*).

Although this procedure afforded a possible means of dissolving the fluoride salts without loss of boron, it does not provide a separation of boron. Glaze and Finn (*2*,*3*) reported a method to separate boron from other constituents of glass, which consisted of fusing the glass with sodium carbonate, dissolving the melt, diluting the sample solution with ethyl alcohol, and extracting boron from the aqueous phase into ether. The final determination of boron in the ether phase was performed volumetrically on a macro scale. The principle of this extraction is based on the distribution of boric oxide (or ethyl borate) between the ethereal and acid-alcohol phases. The partition coefficient of boron

$$k = \frac{\text{concentration in organic phase}}{\text{concentration in aqueous phase}} = \frac{C_o}{C_a}$$

is dependent on temperature and concentration of alcohol, but independent of boron concentration. Glaze and Finn (*2*,*3*) found the partition coefficient of boron to be $0.417 - 0.00232t$ when sulfuric acid was used and $0.668 - 0.0469\sqrt{t}$ when hydrochloric acid was used. Inasmuch as the carminic acid method (*4*) for the determination of boron has been satisfactory, this method was chosen for the colorimetric determination of boron.

APPARATUS AND REAGENTS

Beaker, 250-ml., Corning 7280 or Vycor 7800 glass.

Crucible, 50-ml., Vycor 7900 glass.

Cylinder, 25-ml., fabricated from clear plastic, graduated to 0.5 ml.

Flask, Erlenmeyer, 300-ml., Corning 7280 glass.

Foil, aluminum.

Stirring rod, fabricated from strip of Teflon.

Beckman Model DU spectrophotometer with matching 1-cm silica cells.

Use distilled water in preparing all reagent solutions.

Aluminum chloride hexahydrate, reagent grade.

Ethyl alcohol, absolute.

Boron standard solutions. Dissolve 881 mg. of sodium tetraborate decahydrate, in 100 ml. of water in a polyethylene bottle to prepare a solution that contains 1000 γ of boron per ml.

Carminic acid solution, 0.093 % w./v. in sulfuric acid. The carminic acid was obtained from National Aniline Division of Allied Chemical and Dye Corp. Dissolve 138 mg. in 150 ml. of 18*M* sulfuric acid in a 300-ml. Erlenmeyer flask (boron-free glass).

Diethyl ether, anhydrous.

PROCEDURE

Transfer a weighed amount of finely ground fluoride salt that contains less than 500 γ of boron to a 300-ml. Erlenmeyer flask, then add 15 grams of aluminum chloride hexahydrate, 20 ml. of water, and 10 ml. of 12*M* hydrochloric acid. Place a Teflon-covered stirring bar in the flask and cover with a cap of aluminum foil. Stir the sample magnetically until it is completely dissolved. Add 30 ml. of ethyl alcohol and 60 ml. of ether to the flask. Cool, if necessary, to room temperature and then manually shake for 5 minutes. Allow the mixture to stand until the phases have separated completely. Pipet 25 ml. of the ether phase to a 250-ml. beaker that contains approximately 5 ml. of water. Heat the ether-water mixture slowly on a steam bath until the liquid volume is approximately 2 to 4 ml. Transfer the cooled sample solution to a 25-ml. graduated plastic cylinder.

Wash out the beaker twice with 2 to 3 ml. of water, then transfer the washings to the cylinder. Dilute the solution in the cylinder to 10 ml. with water and mix thoroughly. Transfer a 2-ml. test portion of this sample (or a 1-ml. test portion and 1 ml. of water) to a 50-ml. Vycor crucible, then add 2 drops of 12*M* hydrochloric acid and 10 ml. of 18*M* sulfuric acid to the crucible. Cool the crucible to room temperature. Add 10 ml. of carminic acid solution and stir the contents of the crucible with the Teflon stirring rod for 1 minute. Allow the sample to stand for 45 minutes for the color to develop completely. Stir the solution for 15 seconds and transfer a portion to a 1-cm silica cell. Measure the absorbance of the sample at 585 mμ *vs.* a reagent blank that contains

Table I. Partition Coefficient of Boron in Ether and Hydrochloric Acid–Aluminum Chloride–Ethyl Alcohol Solutions at Various Temperatures

Conditions: HCl, $4M$
Aqueous-alcohol ratio, 1 to 1
Aqueous-alcohol volume, 60 ml.
Ether volume, 60 ml.

Temperature, ° C.	B Present, γ	V_a, Ml.	V_o, Ml.	B_t, γ	k
13	456	81.0	38.5	13.4	0.616
	242	77.0	41.0	7.04	0.586
	242	78.0	40.0	6.76	0.567
19	242	80.0	39.0	6.92	0.587
	242	79.0	39.0	6.92	0.580
	225	81.5	38.0	6.36	0.593
24	242	78.0	41.0	7.15	0.615
25	248	78.5	42.5	7.21	0.608
26	242	77.0	41.0	7.21	0.608
27	242	77.0	41.0	7.09	0.597
	248	77.5	42.0	7.32	0.608
	248	78.0	41.5	6.81	0.555
	225	78.5	41.5	6.31	0.573
28	242	75.5	43.5	7.15	0.608
				Av.	0.593 ± 0.02

2 ml. of water, 2 drops of $12M$ hydrochloric acid, 10 ml. of $18M$ sulfuric acid, and 10 ml. of carminic acid solution. Compare the absorbance reading with a calibration curve prepared from the standard boron solution.

Calculations.

$$k = C_o/C_a$$

$$C_o = \frac{10}{2} \times \frac{B_t}{25} = B_t/5$$

$$B = C_oV_o + C_a/V_a = C_o(V_o + V_a/k)$$

$$= B_t/5\ (V_o + V_a/k)$$

$$B = B_t/5\ (V_o + V_a/0.593)$$

$$\text{or } B = 12B_t/k' = 34.58\ B_t$$

$$\text{where } k' = \frac{10}{2} \times \frac{60}{25} \times B_t/B$$

Nomenclature.

B = boron added, γ
B_t = boron in test portion, γ
B_{25} = boron in 25-ml. aliquot of ether phase, γ
B_o = boron in ether phase, γ
B_a = boron in aqueous phase, γ
V_o = volume of organic phase after equilibration, ml.
V_a = volume of aqueous phase after equilibration, ml.
C_o = boron in organic phase after equilibration, γ/ml.
C_a = boron in aqueous phase after equilibration, γ/ml.
k = C_o/C_a
k' = empirical factor expressing ratio of quantity of boron in ether to total boron

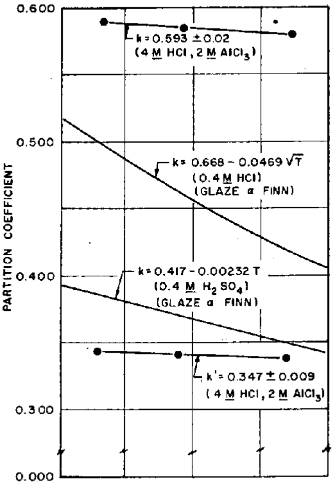

Figure 1. Effect of temperature on partition coefficient of boron

DETERMINATION OF PARTITION COEFFICIENT

The effect of aluminum chloride upon the partition coefficient of boron in hydrochloric acid was investigated at several temperatures. Test solutions were prepared by dissolving 15 grams of aluminum chloride hexahydrate in 15 ml. of water in a 300-ml. Erlenmeyer flask and adding 10 ml. of $12M$ hydrochloric acid. After 5 ml. of a boron solution and 30 ml. of absolute ethyl alcohol were added, the solution was thoroughly mixed. Then 60 ml. of anhydrous ether was added and the flask was capped with aluminum foil. The solution was cooled until its temperature was 3° to 4° C. below the desired test temperature. After this the flask was shaken manually in a gentle, swirling manner for 5 minutes and allowed to stand until the two phases were clear. The temperature of the mixture was then recorded. A 25-ml. aliquot of the ether phase was immediately pipetted into a 250-ml. beaker that contained 5 to 10 ml. of water. The remaining mixture in the flask was decanted into a 100-ml. graduated cylinder and allowed to stand until the phases were separated and clear, following which the volumes of the phases were measured and recorded. The aliquot of the ether phase was evaporated on a steam bath until all of the ether was removed. Boron was determined by the procedure given above

The partition coefficient, k, of boron was then calculated. The results of these tests are reported in Table I.

The conditions in Table I were taken as representative of those which would be required to determine the boron content of a sample that contained about 1 gram of fluoride. Fifteen grams of aluminum chloride hexahydrate is equivalent to 0.06 mole of aluminum. Inasmuch as 1 gram of fluoride is equivalent to approximately 0.05 mole of fluoride ion, the mole ratio of aluminum and fluoride (about 1) was considered sufficiently large to ensure quantitative complexing of the fluoride. The volume of the aqueous phase was arbitrarily taken as 30 ml. so that it would be sufficiently large to permit complete solution of the aluminum chloride hexahydrate and the fluoride salt. Evaporation of larger volumes was not desirable because of the high volatility of boron in acid solutions. The hydrochloric acid molarity is based entirely on the amount of acid added, and does not include that derived from the solution of aluminum chloride hexahydrate. As Glaze and Finn reported the partition coefficient of boron to be at a maximum when water–ethyl alcohol and aqueous-ether ratios are unity, these conditions were incorporated into the procedure. Likewise, the minimum equilibration time of 5 minutes reported by Glaze and Finn to yield a constant value for k was used in these tests.

The results in Table I show that the partition coefficient can be determined with a coefficient of variation of 3%. This precison is considered to be satisfactory for the over-all method, especially because all liquid volumes (except aliquots) were measured in plastic cylinders to eliminate boron contamination from Pyrex volumetric flasks. Inasmuch as the average value for k was determined using all the data, the precision of the results proves that k is independent of temperature between 13° and 28° C.

The volumes of the aqueous and organic phases, although not exactly reproducible at a specified temperature, do not vary significantly with temperature. These small fluctuations in volumes are considered to be the result of evaporation, variable increase in volume of the aqueous phase during dissolution of aluminum chloride hexahydrate, and lack of precision of volume measurement in graduated cylinders. Inasmuch as k is calculated from concentrations which are based on V_o and V_a, the variations in these volumes cause small errors in calculations.

Calculations that are based on the concentration of boron in ether could be subject to considerable error due to the high volatility of ether and consequent increase of the boron concentration. The precision of k indicates that the loss of ether by evaporation is insignificant in comparison to the change in ether volume through dissolution of ether in the aqueous phase. To facilitate the use of this extraction technique as an analytical method, an empirical factor, k', has been defined to simplify calculations and to eliminate the measurement of the phase volumes after equilibration.

$$B_t \times 5 = B_{25}$$

$$B_{25} \times \frac{60}{25} = B'_o$$

$$\frac{B'_o}{B} = k'$$

This factor is also constant ($\bar{x}_k{}' = 0.347 \pm 0.009$) between 13° and 23° C. with a coefficient of variation of 3%.

EFFECT OF ACID CONCENTRATION ON PARTITION COEFFICIENT

A series of tests was made to determine the effect of hydrochloric acid concentration in the aqueous phase on the partition coefficient. All of the conditions described in the above tests were duplicated with the exception of the molarity of hydrochloric acid. To achieve various acid concentrations and yet maintain a constant aqueous volume of 30 ml., calculated volumes of water and 12M hydrochloric acid were mixed to yield the desired concentration. The results of these tests are presented in Table II.

Table II. Effect of Acid Concentration on the Partition Coefficient

(250 mg. of boron taken)

HCl, M	Av. Value, $\bar{x}$	
	k	k'
0	0.687	0.414
0.4	0.754	0.439
2.0	0.704	0.410
3.0	0.678	0.388
5.0	0.599	0.345
6.0	0.629	0.349

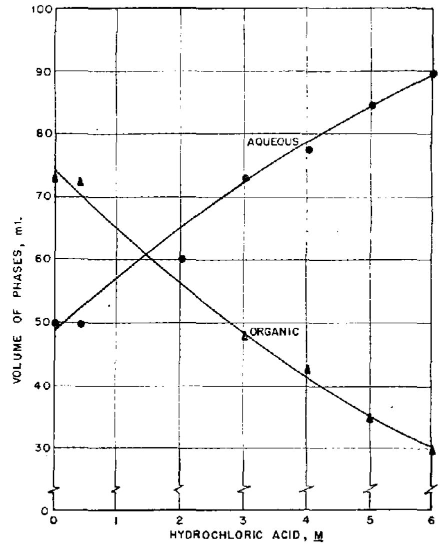

Figure 2. Effect of concentration of hydrochloric acid on volume of phases

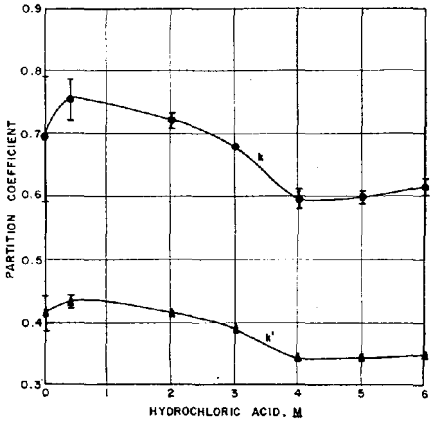

Figure 3. Variation of partition coefficient of boron with concentration of hydrochloric acid

A comparison of the results in Tables I and II reveals that the values of k and k' remain constant when the acid concentration is increased from 4M to 6M, and increase when the acid concentration is decreased below 4M. The anomalous value of "zero molar" hydrochloric acid is postulated to be due to the imprecision of the results in this system wherein the concentration of acid is dependent on the hydrolysis of aluminum chloride hexahydrate. The standard deviations of the values of k and k' in zero molar systems are 0.1 and 0.03, respectively, and approximately three times the deviations in more acidic media.

BORON SEPARATION BY ETHER EXTRACTION

To determine the effectiveness of the procedure, test solutions were prepared as for the determination of the partition coefficient. Various weights of hydrofluoric acid, sodium fluoride, and a mixture of sodium fluoride and zirconium fluoride were added to this solution. The mixtures were stirred in 300-ml. Erlenmeyer flasks until the solid samples were dissolved, after which 30 ml. of ethyl alcohol was added; then the samples were extracted with ether as described above. The results of these tests (Table III) reveal that the boron content of such standard samples can be determined quantitatively within the limit of error imposed by the precision with which k and k' are established. The only observable effect of increasing hydrofluoric acid concentration is an accompanying increase of solubility of ether in the aqueous phase. This effect is in line with the

Table III. Determination of Boron in Standard Samples of Fluoride Salts

B present, 247.5
$k = 0.593$
$k' = 0.347$

					Boron Calcd. from			
					k		k'	
Compound	Weight, Gram	V_a, Ml.	V_o, Ml.	B_t, γ	γ	% recovery	γ	% recovery
HF	0.25	78.0	41.0	7.3	252	102	252	102
	0.50	83.0	37.0	7.2	255	103	249	101
	1.00	87.0	36.0	6.9	252	102	239	97
NaF	1.0	78.5	43.0	7.2	253	102	249	101
	1.0	78.5	42.5	7.2	252	102	249	101
$NaF\text{-}ZrF_4$	1.0	...	...	6.0	...	...	207	107[a]
	1.0	...	...	5.85	...	...	202	105[a]

[a] 193.2 γ of boron present.

Table IV. Determination of Boron in Mixtures of Fluoride Salt[a]

($k' = 0.347$)

Sample, Grams	B Found, P.P.M.	Sample, Grams	B Found, P.P.M.
1.001	50	1.001	15
1.089	50	1.007	10
1.010	50	1.022	15
0.982	50	1.001	15
1.002	50	0.105	75
1.001	40	0.117	90
1.054	70	0.996	90
1.047	80	1.010	90

[a] Duplicate determinations in eight different samples.

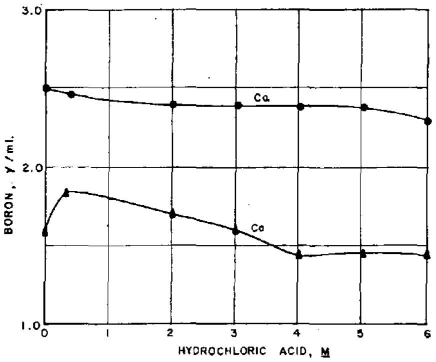

Figure 4. Effect of concentration of hydrochloric acid on concentration of boron in aqueous and organic phases

change in solubility of ether which is caused by an increase in hydrogen ions.

RESULTS

The procedure was applied to the determination of boron in mixtures of alkali metal and zirconium fluorides in which the boron content was presumed to be very low. The results are given in Table IV.

The results of these determinations exhibit a reproducibility that is considered excellent for such low concentrations of boron. Unfortunately, the precision of the results is limited by the measurement of very small absorbances, but it can be increased by using cells with long light paths and small volumes. This limitation can be overcome only to the extent to which the size of the sample or test portion can be increased. The weight of fluoride salt that can be analyzed by the above method is limited by the solubility of the salt in 30 ml. of hydrochloric acid.

DISCUSSION

The results in Tables I and II reveal two striking variations from the data reported by Glaze and Finn: The value for k for a specific acid concentration is constant over a temperature range of 13° to 28° C.; the magnitude of k is considerably higher than that reported in the literature. These differences are illustrated graphically in Figure 1. Both of these effects are thought to be due to the high ionic strength of the hydrochloric acid–aluminum chloride solutions. Glaze and Finn report that the solubility of boric oxide in water is decreased by the addition of sodium chloride, and the effect of temperature on k is diminished by the addition of sodium carbonate to the aqueous solution prior to extraction.

The relationship of k' to Henry's partition law has not been fully investigated. This factor was derived by assuming that the concentration of boron in the aliquot of the ether phase was proportional to the concentration of boron in the initial volume of ether (60 ml.); therefore, k' is the fraction of boron that is extracted into 60 ml. of ether. The constancy of this ratio was observed before the significance of the changes in volumes during equilibration was resolved. This empirical factor is essentially independent of small volume changes. The obvious utilitarian value of such a factor made it desirable to investigate the effects of various conditions on k' as well as k.

Variations in acid concentration have a definite effect on the final volumes of the two phases after equilibration (Figure 2). This effect could be attributed to the hydrogen ion concentration or ionic strength of the mixtures. The data in Table III reveal that the volume change that occurs in 4M hydrochloric acid is much larger after 1 gram of hydrofluoric acid has been added than that which is found for the corresponding addition of 1 gram of sodium fluoride. This indicates that the mutual solubility of the ether and acid-alcohol phases is dependent on the hydrogen ion concentration of the latter phase. The partition coefficient, k, is a ratio of concentrations and is dependent on phase volumes. The variation of k and k' with acid concentration is shown is Figure 3. Figure 4 shows that change in concentration of hydrochloric acid appears to have little effect on the concentration of boron in the final aqueous phase, while the effect on the concentration of boron in the final ether phase is not constant but roughly parallels the k' curve of Figure 3. These data indicate that k and k' are determined by the concentration of boron in the ether phase, and this concentration varies with hydrogen ion concentration.

Acid concentrations less than 4M are unsatisfactory for two reasons: k and k' are altered by small variations in acidity, and fluoride salts are not dissolved as readily in these weaker acids as in 4M acid. Substitution of 5- or 6M acid for 4M has the advantage of stabilizing k and k' against small changes in acid concentration, but decreases the solubility of aluminum chloride hexahydrate to such a degree that relatively long periods of time are consumed in dissolving 15 grams of aluminum chloride hexahydrate in 30 ml. of acid. A hydrochloric acid concentration of $4M$ was found to be the most satisfactory.

The application of k' to the calculation of the boron content of samples eliminates measurement of the phase volumes and the subsequent lengthy mathematical treatment involved when k is used. Therefore, k' has been used to calculate the boron content of the samples listed in Table IV and is recommended for all calculations that are used with this method.

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Determination of Traces of Isocyanate in Urethane-Based Polymers

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▶ Control of the unreacted isocyanate groups in urethane-based polymers is required to yield products of reproducible properties. Qualitative and quantitative methods for determining traces (<0.5%) of isocyanate groups in these products have been developed. For the quantitative determination, the residual isocyanate is allowed to react with an excess of *n*-butylamine and the unreacted amine determined colorimetrically with malachite green. In a rapid qualitative test, a colorless secondary amine derived from malachite green reacts with isocyanate to form a colored product. Both methods are new and extremely sensitive.

Unreacted isocyanate groups in urethane-based polymers can result in products of varied properties. As no available analytical method was sensitive enough to detect or determine residual isocyanate at the levels found in these materials, it was necessary to develop new methods specifically for these products.

In the most commonly used chemical methods of determining isocyanates (*3*) an excess of *n*-butylamine is added to an isocyanate and the unreacted *n*-butylamine titrated acidimetrically with sulfuric acid. The method is highly satisfactory for gross amounts of isocyanate, but of limited usefulness at low isocyanate concentration. The isocyanate group shows an absorption band in the infrared spectrum, but the band is not of sufficient intensity to allow the determination of traces of isocyanate.

This paper describes qualitative and quantitative methods of detecting and determining traces of isocyanate in urethane-based polymers. In the quantitative method, residual isocyanate is allowed to react with an excess of standard solution of *n*-butylamine in tetrahydrofuran and the unreacted *n*-butylamine is determined colorimetrically by malachite green, with which it forms a colorless derivative. The rapid qualitative method depends upon the reaction of isocyanate groups with the colorless secondary amine derived from malachite green and *n*-butylamine to form a product of the characteristic color of malachite green.

The colorimetric application of the reaction of *n*-butylamine with malachite green is based upon the work of Kulberg and Mustafin (*2*), in which they reported the colorimetric determination of piperidine in pyridine by reaction with malachite green. The quantitative determination of piperidine is based upon the decrease of the light absorption of a malachite green solution as the concentration of piperidine increases. Diltey and Wizinger (*1*) observed in 1926 that some triphenylmethane dyes yielded a colorless complex with piperidine.

REAGENTS AND APPARATUS

Tetrahydrofuran, sodium-dried and distilled (available from Electrochemicals Department, E. I. du Pont de Nemours & Co.) The peroxide content at the time of use, in terms of active oxygen, must be less than 5 p.p.m.

Pyridine, reagent grade (Mallinckrodt Chemical Co.). It must contain 0.05 to 0.15% water to control the color intensity of the pyridine–malachite green solution.

Standard Solution of *n*-Butylamine in Tetrahydrofuran. Purify *n*-butylamine by distillation from solid potassium hydroxide; collect the fraction boiling between 76° and 78° C. If the standard solution is to be used within 2 days, add 30 ml. of dried and distilled tetrahydrofuran to a 50-ml. volumetric flask, weigh 5 drops of *n*-butylamine from a tared Lunge bottle into the flask, and record loss in weight of the bottle (approximately 0.1 gram). Dilute to 50-ml. volume with tetrahydrofuran. Take a 10-ml. aliquot of this solution and dilute to 250-ml. volume with tetrahydrofuran. The concentration of *n*-butylamine in the final solution should be near 1.2 μmoles per ml. of tetrahydrofuran.

A standard solution stable for a month or more can be prepared as follows:

Add 0.25 gram of *n*-butylamine to 1 gallon of dried distilled tetrahydrofuran. Let the solution stand for at least 3 days before use. Transfer 25.00 ml. (pipet) of the solution to a 50-ml. Erlenmeyer flask and titrate with $0.01N$ hydrochloric acid to a bromophenol blue end point. The concentration should fall in the range of 1.0 to 1.2 μmoles of *n*-butylamine per ml. If it is below this range, add more *n*-butylamine to the *n*-butylamine–tetrahydrofuran solution (1 drop of *n*-butylamine per gallon is roughly equivalent to 0.07 μmole per ml.). Allow the solution to

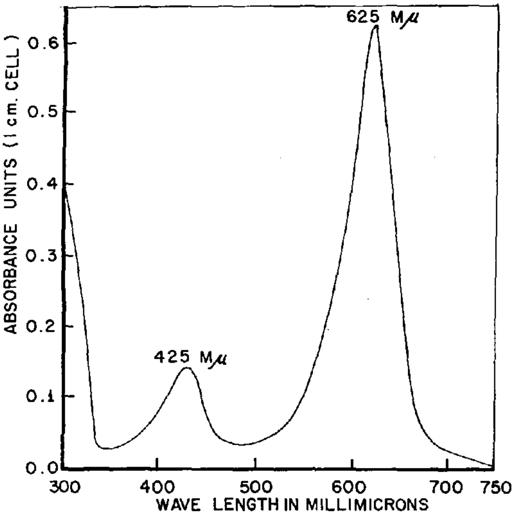

Figure 1. Absorption spectrum of malachite green in pyridine-tetrahydrofuran solution

stand at least 1 hour after mixing and restandardize as above. If concentration is above the range, add more tetrahydrofuran and allow the solution to stand 3 days before standardizing again.

Malachite Green in Pyridine. Recrystallize malachite green [oxalate salt, $(C_{23}H_{25}N_2.C_2HO_4)_2.H_2C_2O_4$], Du Pont Victoria Green small crystals or equivalent] from hot water and dry in air for several days. Weigh 0.45 gram of recrystallized malachite green into 450 grams of pyridine containing 0.05 to 0.15% water. This solution should contain sufficient reagent to give a transmittance of 25 to 35% when 5 ml. of the solution is mixed with 5 ml. of tetrahydrofuran. Occasionally, variations in the amount of impurities present in the pyridine cause the reagent to fail to meet this specification and more malachite green or pyridine must be added. The solution must stand 24 hours after preparation or readjustment before use.

n-Butylamine–Malachite Green Derivative [4,4'-(α-Butylaminobenzylidine) bis-(*N*,*N*'-dimethylaniline)]. Prepare the *n*-butylamine–malachite green derivative by weighing approximately 20 grams of malachite green (Du Pont Victoria Green small crystals) into a 250-ml. beaker and add sufficient *n*-butylamine to discharge all the color. Avoid a large excess of *n*-butylamine by adding it dropwise and stirring after each increment. Transfer the white pasty solid formed to a Soxhlet extractor thimble and extract with diethyl ether overnight. Discard the residue remaining in the thimble (*n*-butylamine oxalic acid salt). Evaporate the ether solution to approximately 50 ml. in a 250-ml. Erlenmeyer flask and chill in ice to bring down white crystals. Remove the ether with a filter stick from the crystals in the flask and add 25 ml. of cold ether to wash the product. Chill the solution in ice and again remove ether with a filter stick. Transfer the flask containing the crystals to a vacuum desiccator and evacuate to 1 mm. for 2 hours. Keep the final product tightly stoppered and store in a brown glass bottle. The material may assume a slight greenish color after standing several weeks, but this is not noticeable when the test reagent is prepared. Theory for 4,4'-(α-butylaminobenzylidine)bis-(*N*,*N*'-dimethylaniline): $C_{27}H_{35}N_3$, C 80.8%, H 8.73%, N 10.4%. Found, C, 80.5%, H 8.79%, N, 10.0%. Observed melting point 111.2° C.

Cumene. Eastman white label cumene (isopropylbenzene) may be used as received.

Heavy Mineral Oil, Nujol (registered trademark), Stanco, Inc., Linden, N. J.

Isocyanate Test Reagent. Dissolve 0.20 gram of *n*-butylamine–malachite green derivative in 50 ml. of cumene. When the solid has dissolved, add 50 ml. of mineral oil and mix thoroughly. The reagent should be colorless or slightly green at this point. Place 0.5 to 1.0 ml. of fresh reagent in small vials. Prepare a fresh master batch of reagent from the solid derivative once every 2 weeks.

Photelometer, Cenco-Sheard-Sanford, or equivalent, 610-mμ filter.

Matched Absorption Cells, 1-cm.

PROCEDURE

Quantitative Analysis. Calibration. Pipet the following 5-ml. mixtures of tetrahydrofuran and standard *n*-butylamine into the 1-cm. cell and to each add 5 ml. of solution of malachite green in pyridine:

Tetrahydrofuran, Ml.	Standard Butylamine, Ml.
5	0
4	1
3	2
2	3
1	4
0	5

Mix the solution in the cell with a thin glass rod until it appears homogeneous. A melting point tube serves the purpose well. Do not place the solution in the light path of the Photelometer until the reading is made. At the end of 3 minutes, ±5 seconds, from the time malachite green solution began to be added to the cell, read the per cent transmittance compared to a blank of a mixture of 5 ml. of tetrahydrofuran and 5 ml. of pyridine.

Make a plot of per cent transmittance *vs.* concentration in micromoles of butylamine per 5 ml. (Figures 1 and 2).

Determination. Weigh a sample of polymer into the 25-ml. glass-stoppered flask (use 0.05 gram for 0.4 to 1.0% isocyanate and 0.10 gram for 0 to 0.4% isocyanate). From a buret or pipet, add 15.0 ml. of standard butylamine solution to the flask and shake mechanically for the following periods of time, depending on the speed or accuracy required.

—NCO Recovery as Function of Shaking Time

Time of Shaking, Hr.	Approximate Fraction of —NCO Recovery
0.5	0.62
1.5	0.82
3–4	1.00

Withdraw 5 ml. of the unreacted butylamine solution from the 25-ml. flask using a 5-ml. pipet with the tip wrapped like a swab with a thin layer of glass wool. Remove the glass wool and pipet the 5-ml. portion into the 1-cm. absorption cell. Pipet 5 ml. of malachite green solution into the cell and mix. At the end of 3 minutes, ±5 seconds, from the time the malachite green solution began to be added to the cell, read the per cent transmittance compared to a blank of a mixture of 5 ml. of tetrahydrofuran and 5 ml. of pyridine. From the plot of concentration *vs.* per cent transmittance, determine the concentration of unreacted butylamine expressed as micromoles per 5 ml. of tetrahydrofuran. Determine the difference between the initial and final *n*-butylamine concentrations and multiply this difference by 3 to obtain the change in *n*-butylamine concentration of the 15-ml. aliquot.

Qualitative Detection. At the moment the polymer is to be tested, open the vial and cut a small piece of polymer from the large sample in such a way that the small piece is not touched with the hands. Insert the small piece into the vial, cap tightly, and label. If isocyanate is present, a green color will develop in 20 to 30 seconds. If no isocyanate is present, no color will develop.

DISCUSSION AND RESULTS

The accuracy of the quantitative method was verified by determination of the per cent isocyanate in weighed samples of pure 3,3′-diisocyanato-4,4′-dimethylcarbanilide and toluene-2,4-diisocyanate alone and in the presence of a typical urethane-based polymer.

The 95% confidence limits for the average of a duplicate determination for the determination of less than 0.600% free isocyanate in a cured elastomer was ±0.033%, calculated on the basis of quadruplicate determinations of four samples by two analysts on two different days.

Recovery of —NCO from Standard Sample

(Toluene-2,4-diisocyanate)

Theory, Mole	Found, Mole	% Recovery
0.40×10^{-6}	0.43×10^{-6}	107
1.50×10^{-6}	1.60×10^{-6}	107
1.99×10^{-6}	2.30×10^{-6}	115
0.56×10^{-6}	0.62×10^{-6}	110

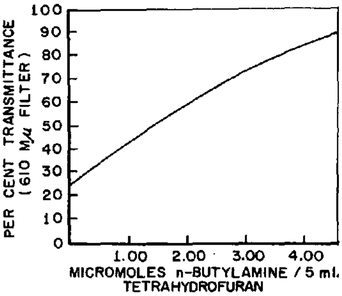

Figure 2. Calibration curve for decolorization of malachite green with *n*-butylamine

5 ml. of 0.1 % malachite green in pyridine

At the level of 0.5 μmole of butylamine per ml. of solution a variation of ±1% in the transmittance reading corresponded to a ±8% change in per cent recovery. The precision of the photometric equipment is estimated to be about ±1% and therefore the per cent recovery values were in the expected range.

Water, weak amines, ureas, and urethanes did not interfere with the quantitative method. Strong and weak tertiary amines and amines that might be present in urethane-based polymers, such as *o*-toluidine, *p*-toluidine, and *m*-toluenediamine, which have ionization constants less than 1×10^{-6}, did not react with malachite green.

n-Butylamine concentration in tetrahydrofuran diminished upon long standing. This has been tentatively attributed to the reaction of peroxides formed in tetrahydrofuran (or peroxide decomposition products) with *n*-butylamine.

The qualitative isocyanate test reagent will detect less than 0.005 mmole of isocyanate per gram of sample. Polymer samples, if correctly formulated, showed no change in color after standing at least 6 days.

The qualitative isocyanate test reagent was not sensitive to oxygen or carbon dioxide. Addition of approximately 5% water generated color. The reagent also generated color if allowed to stand 3 to 5 minutes in the atmosphere, owing to solvent evaporation or atmospheric moisture. Strong mineral acids such as sulfuric acid formed the colored basic dye from the qualitative test reagent. Weaker acids, such as acetic, formic, and hydrofluoric, did not form a color. Free mineral acids are not normally present in urethane polymers.

The reagent became sluggish as it aged and therefore should be freshly prepared before use. Contamination with strong amines causes the reagent to become less sensitive.

The equation for the malachite green-*n*-butylamine reaction was determined to be as follows:

$$(C_{23}H_{25}N_2 . C_2HO_4)_2 . H_2C_2O_4 + 8\ n\text{-}C_4H_9NH_2 \rightarrow 2\ C_{23}H_{25}N_2NHC_4H_9 + 3\ (C_4H_9NH_2)_2 . H_2C_2O_4$$

The product, $C_{23}H_{25}N_2NHC_4H_9$, was colorless and upon reaction with isocyanate formed a colored product.

The chemistry of the malachite green-*n*-butylamine reaction used in the quantitative method was generally applicable to other basic dyes (crystal violet, brilliant green, methyl violet) and other strong primary and secondary amines (ionization constant greater than 1×10^{-6}) (anhydrous ammonia, methylamine, dimethylamine, benzylamine). It is possible that by modification of the dye structure a selective method of determining amines of other base strengths could be developed. No work of this nature has been attempted at this laboratory.

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Determination of Acetone in Aqueous and Benzene Solution by Messinger's Iodoform Method

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▶ The accuracy of Messinger's iodoform method for the determination of acetone in aqueous and benzene solution has been investigated. For aliquots of aqueous solutions containing between 7 and 41 mg. of acetone the method indicates 102.1 ± 0.2% of the true acetone content; for benzene solutions, 99.9 ± 1.1% of the true content, when special precautions are taken. Critical accounts of the factors affecting the accurate determination of acetone in aqueous and aromatic hydrocarbon solution are given.

THE ANALYSIS of dilute solutions of acetone in water and benzene became necessary in connection with other work on liquid-liquid extraction, involving the benzene-acetone-water system.

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Because of the ease and simplicity of the analytical procedure, the hydroxylamine hydrochloride method (*6*, *8*) appeared suitable for acetone determination in both liquids. Investigation of eight aqueous solutions containing between 140 and 250 mg. of acetone showed that the content could be determined with a standard error of ±2.2% or 95% confidence level error of ±5.2%. The analysis of eight solutions containing between 16 and 37 mg. of acetone in benzene by the same method led to a standard error of ±2.9% and a 95% confidence limit error of ±6.9%. The chief source of error in the hydroxylamine hydrochloride method, even with the more concentrated aqueous solutions, derives from the color matching of the acid-base indicators at pH 4.0. The large standard errors are attributed to the slow color change with both screened methyl orange and bromophenol blue indicators, which appears to be due to the buffering of the solution by the oxime hydrolysis.

The hydroxylamine hydrochloride method, although possibly suitable for large concentrations of acetone, fails in solutions containing less than 250 mg. of acetone and has been abandoned by the authors in favor of the Messinger iodoform method (*4*, *6*, *9*, *10*).

The Messinger method of determining acetone in solution depends upon the reaction of an alkaline solution of acetone with an excess of iodine to form iodoform, according to the equation

$$CH_3COCH_3 + 3I_2 + 4NaOH = CHI_3 + 3NaI + CH_3COONa + 3H_2O \quad (1)$$

At the completion of the reaction, the unreacted iodine excess is liberated from the alkaline solution with acid and estimated with sodium thiosulfate. In the work described it was found possible to analyze solutions containing between 7 and 41 mg. of acetone in water and benzene with standard errors of ±0.2 and ±1.1%, respectively, on a single determination.

MATERIALS

British Drug Houses AnalaR acetone, dried with barium oxide, was distilled over fresh barium oxide through a 2-foot column, packed with Nichrome wire rings 5 mm. in diameter, using a 20 to 1 reflux ratio. Fractional distillation took place at atmospheric pressure, and a magnetically controlled still head was used, protected from atmospheric moisture by desiccant tubes. The acetone taken for all experiments was the middle fraction of samples which had been refluxed overnight over barium oxide and had a normal boiling point of 56.1° ± 0.1°C.

The benzene was BDH crystallizable grade taken without further purification, and the water was laboratory once-distilled water. No particular precautions were taken with the two solvents; as in the liquid-liquid extraction process, less pure grades of benzene and water were to be used.

ACETONE DETERMINATION IN AQUEOUS SOLUTION

Procedure. Standard solutions of acetone in water were prepared by breaking thin-walled glass capsules of known weight and acetone content in a weighed quantity of water. Pipets were used to transfer different volumes of the standard solutions, the accurate size of the aliquot being determined by weight.

Aliquots of standard acetone solutions were added to tared 150-ml. glass-stoppered flasks containing 5 ml. of 5*N* sodium hydroxide solution and the flasks were reweighed to obtain the acetone content. Then 50 ml. of approximately 0.1*N* iodine solution were added, and the flasks were thoroughly shaken and allowed to stand for at least 10 minutes. Blanks, prepared in the same way without acetone, were given similar treatment. After completion of the reaction, 5.25 ml. of 5*N* sulfuric acid or its equivalent were added and the flasks were vigorously shaken to liberate all the excess iodine, which was titrated with standard sodium thiosulfate, using starch at the end point. The difference of the blank and acetone solution thiosulfate titers gave the iodine used in the iodoform reaction.

Experimental Data and Discussion. Table I shows five sample results from 20 determinations on aqueous solution containing between 7 and 41 mg. of acetone. Three standard acetone solutions—A, B, and C—containing 0.9821, 1.748, and 2.794 mg. of acetone per gram of solution, were prepared independently and weighed aliquots were taken for analysis.

From the average of 20 determinations it is found that the Messinger iodoform method, performed under the conditions specified, indicates 102.10% of the true acetone content, with a standard error of ±0.20% and a 95% confidence limit error of ±0.42% on a single determination.

The deviation in the final column from the theoretical value of 100.00% indicates that the reaction of acetone with iodine is predominantly that shown in Equation 1, accompanied by a small amount of side reaction requiring more than three molecules of iodine per molecule of acetone. The consistency of the results over a sixfold acetone concentration range indicates that systematic errors have been eliminated by standardization of conditions, and that the side reaction is reproducible under these conditions.

During preliminary investigation undertaken to determine the experimental conditions under which the iodoform method would give reproducible results of the desired accuracy, a number of features were examined experimentally. Aliquots of standard iodine solutions which had been dissolved in alkali to give colorless solutions containing iodide, hypoiodite, and iodate ions did not regenerate all the original iodine content on the addition of acid. Because the Messinger method utilizes this same reliberation of iodine from alkaline solution by acid, it was important to examine whether the loss of iodine was a constant value, proportional to the iodine content of the solution, or dependent on the quantity of acid used for the reliberation. Investigation showed that a slight excess of acid was necessary for the reproducible reliberation of iodine and that stoichiometric neutralization produced low and variable regenerations.

The quantitative loss of iodine due to the consecutive alkaline and acidic conditions was assessed using 20- and 50-ml. samples of standard iodine solution, which on direct titration required 12.36 and 30.90 ml. of thiosulfate, and, after treatment with 5 ml. of 5*N* sodium hydroxide and then with 5.25 ml. of 5*N* sulfuric acid, required 12.26 and 30.80 ml. of thiosulfate, respectively. Identical losses were found with solutions treated with acid and then left for 3 hours before titration with thiosulfate solution. As the iodine losses are constant over a twofold change of concentration, blanks are run with each acetone determination to allow for this reneutralization error.

Haughton (*6*) showed that the Messinger iodoform method was dependent on the rate of addition of the iodine solution to the alkaline acetone, and that slow dropwise additions gave more consistent results and indicated higher percentages of the true acetone contents.

Table I. Determination of Acetone in Aqueous Solution

Acetone Taken, Mg.	Acetone Soln.	NaS_2O_3 Titer, Ml. Blank	NaS_2O_3 Titer, Ml. Back[a]	$Na_2S_3O_3$ Normality	Acetone Estd. by Eq. 1, Mg.	Acetone Found, %
7.227	A	32.09	25.24	0.1114	7.387	102.2
13.49	C	41.50	28.70	0.1111	13.77	102.1
17.87	C	41.29	24.40	0.1114	18.21	101.9
30.32	B	41.19	12.35	0.1106	30.88	101.8
41.20	C	41.29	2.39	0.1114	41.95	101.8
					Mean of 20	102.10 ± 0.20

[a] Iodine remaining after iodoform reaction with aqueous acetone.

Table II. Determination of Acetone in Benzene Solution

Acetone Taken, Mg.	Acetone Soln.	$Na_2S_2O_3$ Blank	Titer, Ml. Back	$Na_2S_2O_3$ Normality	Acetone Estd. by Eq. 1, Mg.	Acetone, Found, %
7.801	B′	45.74	38.29	0.1097	7.911	101.4
13.71	D′	45.77	32.88	0.1097	13.69	99.8
15.19	C′	45.74	31.92	0.1097	14.68	96.6
19.79	D′	45.98	27.15	0.1096	19.98	100.9
31.14	A′	45.81	17.01	0.1097	30.58	98.2
					Mean of 22	99.89 ± 1.11

To examine this effect under the authors' experimental conditions two pipets were used, the first giving a normal fast delivery and drainage of 50 ml. in 50 seconds and the second giving a continuous slow delivery of 50 ml. in 300 seconds. Tests were conducted on standard solutions containing 16.523 and 23.233 mg. of acetone: The fast addition of iodine to the two solutions indicated 102.07 and 101.75% of the true acetone contents, whereas the slow addition indicated 100.51 and 99.53% of the true values. These results differ from those of Haughton, probably because of the different methods of effecting the slow addition. In view of the greater analytical convenience, the fast delivery was used in all subsequent experiments.

Because the Messinger method utilizes a reaction complicated by side reactions, it is necessary for highest precision to calibrate with known acetone solutions, using conditions under which it is subsequently to be performed. Although the effect of variation of all conditions has not been studied, experience has indicated that the following factors are important: concentration of alkaline solution, concentration and rate of addition of iodine solution to alkaline acetone solution, length of time allowed for iodoform reaction, quantity of acid used to liberate iodine from alkaline solution, and in benzene solutions, temperature and absence of light.

ACETONE DETERMINATION IN BENZENE SOLUTION

The determination of acetone in benzene by the Messinger method is further complicated by the photooxidation of iodoform in benzene solution (*1-3, 7*), which produces free iodine. Gross and Schwarz (*5*) suggested an opaque titrating vessel with a clear space to observe the end point, kept in a closed box when not viewed. In this investigation black felt bags with a small window covered by a flap were used to protect the titrating flasks from light. Following the procedure for aqueous solutions with the flasks protected from light, determination of acetone in benzene at room temperature (approximately 25° C.) gave low and inconsistent results: A considerable improvement was obtained by cooling the flasks in ice water during the iodoform stage of the analysis. The reason for this improvement is not completely clear, although lower temperatures give a more favorable distribution coefficient with higher concentrations of acetone in the aqueous phase where the iodoform reaction takes place.

Procedure. Standard solutions of acetone in benzene, prepared as for aqueous solutions, were weighed into tared 150-ml. flasks containing 5 ml. of $5N$ sodium hydroxide. To these flasks, protected from light by felt bags, 50 ml. of approximately $0.1N$ iodine solution were added, and the contents were shaken, transferred to a light-free sink containing ice water, and allowed to react for at least 30 minutes with occasional vigorous shaking. Blanks containing the same volume of benzene without acetone were treated in the same manner. After reaction, the flasks were removed, dried, replaced in the felt bags, and treated with 5.25 ml. of $5N$ sulfuric acid to liberate the iodine excess, which was titrated with standard thiosulfate solution, the flap of the bag being opened only momentarily to check the progress of the titration. The end point was determined in the aqueous phase, using 2 ml. of starch as indicator, and the solution was vigorously shaken to remove the last traces of iodine from the benzene layer. The weight of acetone estimated was obtained, using Equation 1, from the difference of the iodine in the blanks and in the solutions after iodoform reaction.

Experimental Data. Five specimen results of the determination of between 8 and 31 mg. of acetone from 22 benzene solutions are shown in Table II. The samples were obtained by weighing aliquots of four independently prepared acetone standard solutions in benzene—A′, B′, C′, and D′—containing 3.553, 1.781, 3.465, and 3.265 mg. of acetone per gram of solution, respectively.

Statistical analysis of the results in benzene shows that the Messinger method, performed under the conditions described, indicates 99.89% of the true acetone content, with a standard error of ±1.11% or a 95% confidence limit error of ±2.30% on a single determination. A number of low results were obtained, but there was no reason to neglect these in the statistical analysis; they were probably due to some unnoticed photooxidation. No significance is to be attributed to the nearly 100.00% estimation of acetone present in the benzene, which is probably due to cancellation of errors. Using a less pure Iscor entrainer benzene, the mean of ten estimations indicated 101.4% of the true acetone content, with a similar standard error. The larger standard errors observed for the determination of acetone in benzene solutions can be adequately explained by the nonquantitative extraction of acetone from the benzene layer, the photooxidation of iodoform, and the less distinct and less easily observed end point.

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Determination of Acetyl in Pectin and in Acetylated Carbohydrate Polymers

Hydroxamic Acid Reaction

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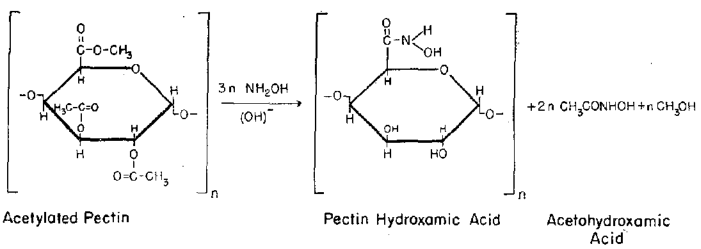
▶The reaction of the ester groups in pectin with alkaline hydroxylamine at room temperature produces hydroxamic acids. Pectin hydroxamic acid forms with ferric ions an insoluble complex and acetohydroxamic acid, produced from secondary acetyl groups of pectin, forms a soluble red complex. These reactions, applied to pectic substances, serve as the basis for a specific and rapid colorimetric method for the determination of up to 450 γ of acetyl per sample, with an accuracy within about ±2%. These reactions apply also to the quantitative determination of acetyl in acetylated carbohydrate polymers.



Some controversy exists about the presence of acetyl in some pectic substances but it seems now to be generally accepted that pectin from sugar beets (*20*) and from some fruits (*17*) may contain about 4% acetyl. A chemical characterization of pectic substances from a particular source material requires a determination of acetyl as well as the determination of the methoxyl content and molecular weight.

Several methods have been described for the determination of acetyl esters in pectin (*9, 15, 19*); however, no single method is both rapid and specific, yet sensitive enough to determine micro amounts of acetyl in milligram quantities of pectic substances.

The reaction between esters and hydroxylamine to produce hydroxamic acids has been applied successfully for the analyses of many types of esters (*2, 4, 8, 10–14, 24*), lactones (*1*), amides, (*2, 3, 21*), anhydrides (*5, 7*), and nitriles (*23*). The reaction of the ester groups of pectin with hydroxylamine at room temperature produces hydroxamic acids. Pectin hydroxamic acid forms with ferric iron an insoluble red complex (*18*), whereas the acetohydroxamic acid produced from secondary acetyl groups forms a soluble red iron complex. The present work describes the colorimetric determination of 2 to 10 micromoles (86 to 430 γ) of acetyl per milliliter of test solution in about 20 minutes with an accuracy within about ±2%. The variables and limitations of the method indicate that it satisfies the requirements for a specific, sensitive, and rapid colorimetric procedure for acetyl in pectic substances and acetylated carbohydrate polymers.

REAGENTS

Sodium Hydroxide. Dissolve 9.4 grams of reagent grade sodium hydroxide in 100 ml. of water.

Hydroxylamine Hydrochloride. Dissolve 3.75 grams of hydroxylamine hydrochloride in 100 ml. of water.

Ferric Perchlorate. Dissolve 1.93 grams of ferric chloride ($FeCl_3.6H_2O$) in 5 ml. of concentrated hydrochloric acid, add 5 ml. of 70% perchloric acid, and evaporate the solution almost to dryness. [Smith (*22*) states that "absolute ethyl alcohol may be mixed at ordinary temperatures with 72.5% perchloric acid without the least necessary apprehension." Nevertheless normal precautions should be used in mixing, handling, and storing perchloric acid-containing reagents.] Dilute to 100 ml. with water for use as a stock solution. This solution, when stored in the refrigerator, is stable for at least 1 month. Add 8.3 ml. of 70% perchloric acid to 60 ml. of the stock ferric perchlorate solution. Cool in ice and make to 500 ml. with chilled reagent grade absolute methanol. This solution is stable for at least 1 week at room temperature.

Acid Methanol Solution. Chill 35.2 ml. of 70% perchloric acid and make to 500 ml. with chilled reagent grade absolute methanol.

Glucose Pentaacetate Standard. Weigh 108.9 mg. of pure crystalline β-D-glucose pentaacetate, dissolve by heating gently in about 5 ml. of ethyl alcohol, and make to 100 ml. with water. Take 2-, 4-, 5-, and 7-ml. aliquots of this solution and make to 50 ml. with water. Five-milliliter aliquots of these diluted aqueous solutions represent 120, 240, 300, and 420 γ of acetyl. Prepare a blank using 5 ml. of water in place of the standard solution. Use this blank to set the colorimeter at 100% transmittance. Prepare a standard curve by plotting the galvanometer readings obtained against the micrograms of acetyl on semilog one-cycle paper. Use the standard, which is linear from 0 to 500 γ of acetyl per test, to obtain the concentration of acetyl in the samples.

METHOD

Pectic Substances. Pipet accurately 2 ml. of a freshly prepared 1 to 1 mixture of sodium hydroxide and hydroxylamine solution into a 25-ml. volumetric flask. To this mixture add with agitation 5.0 ml. of the sample solution estimated to contain between 100 to 450 γ of acetyl.

After 5 minutes or longer, add 5 ml. of acid methanol solution and mix the solution thoroughly, and then make to volume with the ferric perchlorate solution, adding it in small increments, with thorough mixing after each addition. After 5 minutes remove the precipitated pectin hydroxamic acid–ferric complex by filtering the solution through a Whatman No. 12 filter paper directly into a colorimeter tube. Determine the intensity of the color, using a wave length of 520 mμ. Prepare a sample blank by adding to 5 ml. of sample in a 25-ml. volumetric flask, 1 ml. of the sodium hydroxide solution. Mix thoroughly and allow to stand 2 to 3 minutes; then add 1 ml. of the hydroxylamine hydrochloride solution and proceed as outlined above. Determine the amount of acetyl in the sample from the standard curve.

Acetylated Carbohydrate Polymers. Weigh a sample of acetylated carbohydrate polymer estimated to contain 2 to 11 mg. of acetyl into a 100-ml. beaker. Add a stirring bar and while stirring on a magnetic stirrer add 25.0 ml. of hydroxylamine solution. Add 25.0 ml. of the sodium hydroxide solution dropwise while stirring for 15 minutes. Continue stirring until the carbohydrate polymer is dissolved. Pipet accurately 2 ml. of the solution into a 25-ml. volumetric flask. Add 5 ml. each of water and acid-methanol and mix thoroughly. Make to volume with the ferric perchlorate solution, taking care to add it in small increments and to mix thoroughly after each addition. After 5 minutes, determine the color as previously described.

Variables and Limitations. The reaction of pectin acetate with alkaline hydroxylamine is shown below. The analytical possibilities of the hydroxamic acids were introduced by Feigl, Anger, and Frehden (*6*, *7*), and since that time an extensive literature on various aspects of the hydroxamic acid-ferric ion reaction was accumulated.

The alkaline hydroxylamine solution of Thompson (*24*) was employed and the other reagents, with minor changes, are those of Goddu, LeBlanc, and Wright (*8*). The 66% methanol reaction mixture aids in the precipitation of the insoluble pectin hydroxamic acid–ferric complex, in which condition it is removed from the solution prior to the colorimetric determination of the soluble ferric acetohydroxamic acid complex. Although pectic acid has no methyl ester groups to react with hydroxylamine, its ferric salt is insoluble and is removed from the solution.

The reaction time of 5 minutes with the alkaline hydroxylamine is in excess of that required for the carbohydrate acetates that were tested and these results are in agreement with the findings of Hestrin (*10*). The sample was added to the hydroxylamine to ensure the presence of an excess of the reagent at all times. Formation of hydroxamic acids at a reduced rate was found even in acidic conditions and it was not advisable to prepare a blank by adding reagents in a reverse order. Sodium hydroxide, added initially, de-esterified the material so completely that no esters were available for hydroxamic acid formation. A blank prepared in this manner was included with each sample and used to adjust the colorimeter to 100% transmittance. Alcoholic solutions of acid and ferric perchlorate were used to ensure complete precipitation of the pectin hydroxamic acid–ferric complex formed during the reaction. Poor precision was obtained unless the acid solution was added separately and prior to the addition of the ferric perchlorate. The maximum color intensity of the ferric acetohydroxamic acid complex was reached after 5 minutes and remained unchanged for at least 2 hours. The absorption maximum of this complex, determined with the Cary recording spectrophotometer, was 520 mμ and is in agreement with values reported by others (*11*, *24*). An Evelyn colorimeter (520-mμ filter) was used for the color readings and in accordance with Beer's law, the color density was directly proportional to the concentration in the range up to 420 γ of acetyl per 5 ml. of test sample. The intensity of the color was found to be insensitive to temperature in the range of 20° to 30° C.

The success of the proposed procedure depends upon the complete precipitation of ferric pectate and pectin hydroxamic acid–ferric complex and its removal from the solution. Precipitation of polygalacturonide hydroxamic acids under these conditions depends in part upon their molecular weights and degree of substitution. Polygalacturonide hydroxamic acids having a degree of polymerization of 10 (molecular weight, 2000) are soluble in the reaction medium. Naturally occurring pectic substances have much higher molecular weights and an order of a degree of polymerization of 100 and above; hence, no naturally occurring polygalacturonide esters are likely to be encountered that would fail to precipitate under these reaction conditions.

The soluble ferric acetohydroxamic acid complex was not adsorbed or selectively removed from the reaction mixture by filtration under the conditions described for removing the insoluble material.

The reaction conditions and the colorimetric procedure outlined in the proposed method were employed to determine the extent of conversion of glucose pentaacetate to acetohydroxamic acid. Compared with a sample of crystalline acetohydroxamic acid as a standard, the reaction with β-D-glucose pentaacetate proceeded to an extent of 86%. This value is in agreement with that reported by Thompson (*24*), who used different reaction conditions. Sorbitol hexaacetate, araban diacetate, starch triacetate, and mannogalactan triacetate react with the alkaline hydroxylamine to an extent of 86% as in the case with the β-D-glucose pentaacetate. The reaction of acetyl esters of carbohydrates with hydroxylamine in the proposed method apparently proceeds to the same extent regardless of the nature of the carbohydrate moiety. Although acetohydroxamic acid is a stable crystalline compound, it seemed preferable to use a standard curve prepared with crystalline β-D-glucose pentaacetate so that no further corrections were required.

RESULTS

Various pectins were analyzed by the proposed methods and compared with the distillation method of Pippen and coworkers (*19*) and the results are given in Table I.

Table I. Values Obtained by Proposed Colorimetric and Distillation Method

Source of Pectin	Acetyl, % Colorimetric	Acetyl, % Distillation (*19*)
Raspberry	0.25	0.53
	0.24	0.53
Apricot	1.36	2.09
	1.36	2.09
Citrus	0.23	0.32
	0.25	0.36
Strawberry	1.47	1.92
	1.38	1.89
Cherry	0.18	...
	0.17	...
Sugar beet	2.50	2.82
	2.50	2.76
Synthetic pectin acetate	4.80	5.45
	4.80	5.36

Comparison of the colorimetric and distillation values for all of these samples analyzed shows that the distillation procedure gives results higher than the colorimetric method. The percentage difference between the methods varies from 11 to 55%. This indicates that the difference is real and due perhaps to the presence of volatile acids incorporated during the isolation of the pectin or possibly formed during the preliminary saponification procedure before distillation (*16*). The differences are not consistent and cannot be accounted for by assuming a lower degree of conversion of the pectin acetate to acetohydroxamic acid than for the standard. Such conditions would result in a fairly constant difference between the two methods. Duplicate acetyl analysis of the pectin samples determined by the colorimetric method shows good precision and in view of the known deleterious effects of alkali and other recognized deficiencies of available methods for the analysis of acetyl in pectin, the colorimetric method seems to give reliable results for naturally occurring acetyl in the range up to 450 γ per test.

Analysis of the β-D-glucose pentaacetate standard, arabinose tetraacetate, and sorbitol hexaacetate by direct saponification and by the proposed method are in good agreement and gave calculated values for these pure compounds.

Determination of acetyl in acetylated carbohydrate polymers is shown in Table II. The acetates of guar mannogalactan, araban, starch, and pectin gave results in good agreement with those obtained by saponification.

Table II. Determination of Acetyl in Acetylated Carbohydrate Polymers

	Acetyl, %		
Acetate	Colorimetric	Saponification	Calcd.
Glucose penta-	57.6 55.7 57.0	56.5	55.1
Guar tri-	47.5 45.2 46.9	47.3	44.8
Araban di-	41.3	41.7	39.8
Starch tri-	43.9	43.9	44.8
Pectin di-	37.3 35.3 36.6	[a]	33.1[b]

[a] Contains carbomethoxyl groups which saponify under same conditions as acetyl.

[b] Calculated on basis of 100% anhydrouronic acid.

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Complexometric Titrations Using Azoxine Indicators

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▶7 - (1 - naphthylazo) - 8 - quinolinol-5-sulfonic acid and several related compounds are valuable as metal ion indicators in complexometric titrations. Cadmium, cobalt, copper, lead, nickel, rare earths, thorium, yttrium, and zinc can be accurately titrated in acid solution with 0.05M (ethylenedinitrilo)tetraacetate. In many cases a small amount of copper must be present in order for the indicator to function properly. Calcium and magnesium do not interfere if the pH is 5.5 or less. With citrate as a masking agent, zinc and other divalent metals can be titrated in the presence of uranium(VI), thorium, or zirconium. The use of tartrate, fluoride, iodide, or thiourea as masking agents in certain cases also increases the selectivity of the method.

Compounds which form highly colored metal complexes are widely used as indicators for complexometric titrations of metal ions with (ethylenedinitrilo)tetraacetic acid (EDTA). Eriochrome Black T was the first such indicator to gain great popularity. It has been widely used for the titration of calcium and magnesium with EDTA, as well as for the direct titration of zinc, manganese, cadmium, and lead. It cannot be used for direct titration of metals such as copper, cobalt, and nickel because these metals react irreversibly with the indicator. Slight traces of iron and copper interfere with other titrations in which Eriochrome Black T is employed as the indicator.

Other indicators have been proposed for use in the titration of certain of the divalent metals. Murexide is reasonably good for copper and calcium, but is poor for zinc, cobalt, and the like. Pyridylazonaphthol (*1*) serves as an indicator for some titrations. Its chief disadvantage is its slow reaction in acid solution. Pyrocatechol Violet has been proposed as an indicator (*6*), but it does not seem to give a good color change for titration of divalent metals. Zincon (*5*) has been suggested as an indicator for EDTA titrations but information regarding its use is thus far sketchy. Aluminum (and probably several other metal ions) can be determined in an acidic water-acetone solution by adding excess EDTA and back titrating with zinc using dithizone indicator (*7*). This procedure works well if the pH is carefully controlled.

This paper is concerned with the analytical applications of a new class of metal ion indicators, the 7-(arylazo)-8-quinolinol-5-sulfonic acids, which will be called the azoxines for convenience. These indicators give sharp, easily detectable end points in the titration of a large number of metal ions. The titrations are carried out in moderately acid solution where calcium and magnesium do not titrate or interfere. Most of the titrations can be carried out in the presence of complexing anions such as tartrate, citrate, and sulfosalicylate. Finally, titrations using azoxine indicators lend themselves well to the use of masking agents to increase the selectivity of EDTA titrations.

PREPARATION AND PROPERTIES OF AZOXINES

The azoxine indicators were prepared by coupling a diazotized amine with 8-quinolinol-5-sulfonic acid. The product is purified by recrystallization from dimethylformamide and water.

Place 0.1 mole of the appropriate amine ground to a medium powder in a 1-liter beaker and add 50 ml. of water, 30 ml. of concentrated hydrochloric acid, and approximately 50 grams of crushed ice. When the amine solution has cooled to less than 10° C., add slowly a solution of 9 grams of sodium nitrite in 30 ml. of water through a funnel whose tip extends below the surface of the amine solution. Test for completeness of diazotization with starch-iodide paper.

While the mixture is still cold add 200 ml. of 1.2*M* sodium hydroxide. This should make the solution slightly basic (pH 8 to 10). Add with stirring 22.5 grams (0.1 mole) of lump-free 8-quinolinol-5-sulfonic acid. Stir 10 minutes and filter.

Dissolve the solid product in the minimum amount of warm (50° C.) dimethylformamide. Filter to remove any insoluble residue and add water to the filtrate equal to 2 or 3 times the volume of dimethylformamide used. Filter 3 or 4 hours later and dry in a vacuum desiccator.

The phenyl-, *p*-chlorophenyl-, *p*-nitrophenyl-, and 1-naphthylazoxines were prepared by this procedure. In dilute, acidic solution the phenyl derivative is orange-rose, the *p*-chlorophenyl is golden orange, the *p*-nitrophenyl is yellow-rose, and the naphthyl is rose-violet. These become gradually more yellow as the pH is raised, until at pH 8 they are almost clear yellow. The *p*-nitrophenylazoxine is an exception, becoming an intense rose-violet color in alkaline solution. All of these compounds form clear yellow complexes with copper(II), zinc, and several other metals. The absorption spectra for both free and complexed naphthylazoxine is given in Figure 1. Because in weak acid solution the color contrast between the free indicator and the metal complex is greatest in the case of naphthylazoxine, this compound was chosen as the most satisfactory indicator for visual titrations.

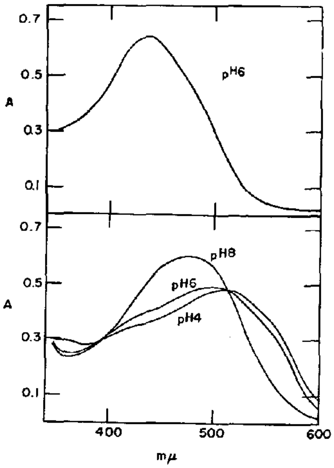

Figure 1. Absorption spectra

Upper curve. Complex of copper naphthylazoxine ($2 \times 10^{-4} M$)
Lower curves. Naphthylazoxine ($2 \times 10^{-5} M$)

REAGENTS AND APPARATUS

0.05*M* EDTA. Prepare an aqueous solution from the reagent grade disodium or diammonium salt of (ethylenenitrilo)tetraacetic acid. Standardize by titrating zinc nitrate (pure zinc metal as primary standard) at pH 8 to 10 with Eriochrome Black T indicator. Alternatively standardize by titrating cupric nitrate (electrolytic copper metal as primary standard) by the procedure given below.

Naphthylazoxine. Prepare a 1% solution in dimethylformamide.

0.005*M* Cupric Nitrate. Prepare an aqueous solution from reagent grade cupric nitrate.

PROCEDURE

Take a sample containing 0.15 to 0.40 mmole of the metal ion to be titrated and adjust the volume to 50 to 75 ml. If a masking agent is needed, add 5 to 10 ml. of 0.1*M* solution for each 0.1 mmole of ion to be masked. Consult Table I for information regarding the suggested buffer and pH to be used. Add the buffer and check the pH of the solution with a pH meter. If it is not in the correct range, adjust the pH further with dilute ammonia or perchloric acid. Add 0.5 ml. of naphthylazoxine indicator, and titrate with 0.05*M* EDTA until the indicator changes to its full red color. Add 1.00 ml. of 0.005*M* cupric nitrate and titrate to the sharpest color change from yellow or yellow-orange to red. Run a blank on each batch of 0.005*M* cupric nitrate and subtract this from the buret reading.

If cobalt, lead, or zinc is titrated and the pH is in the range from 6.0 to 6.5, the addition of 0.005*M* cupric nitrate may be eliminated. If this is done, take the end point as the point when the indicator attains its maximum red color.

TITRATIONS WITH COPPER(II) ADDED

When 0.05*M* EDTA is used with naphthylazoxine indicator, the titration for zinc gives a sharp end point from yellow to red between pH 5.5 and 6.5; copper is titrated sharply if the pH is in the approximate range from 3.5 to 6.5. Cobalt and lead also give fairly sharp end points in weak acid solution. Most other metals form only a weak azoxine complex and give a gradual color change in the vicinity of the stoichiometric point. In such cases the determination can usually be carried out successfully if a small, measured quantity of copper(II) is added near the end of the titration.

A specific example of this is the titration of lanthanum. Lanthanum reacts with naphthylazoxine but the complex formed is weak, so that the end point color change is gradual and begins too soon. This is illustrated on the theoretical curve for titration of lanthanum at pH 6 with EDTA (Figure 2). By adding a small amount of copper(II), which forms a rather strong complex with naphthylazoxine, a sharp color change occurs when the sum of copper (II) and lanthanum has been titrated. This is shown by the curve in Figure 2 in which pCu is plotted against milliliters of EDTA.

As copper(II) forms a stronger EDTA complex ($\log K = 18.8$) than lanthanum ($\log K = 15.5$), it might seem at first that the cupric azoxine complex would be broken by EDTA before all of the lanthanum is titrated. However, the

Table I. Suggested Conditions for Titration

Ion(s) Titrated	pH Range	Buffer
Cd^{++}, Co^{++}, Cu^{++}, Pb^{++}, Ni^{++}, rare earths, Y^{+++}, Zn^{++}	5.5 to 6.5	Ammonium acetate (~2g.) or pyridine (5 to 10 drops)
Cu^{++} (alone)	4.0	Formate
Mn^{++}	6.5 to 7.0	Pyridine (10 drops)
Fe^{+++}, Th^{+4}	3.0 to 3.5	Chloroacetate
Cd^{++}, Co^{++}, Cu^{++}, Pb^{++}, Ni^{++}, Zn^{++} in presence of citrate or tartrate	6.0 to 6.5	Ammonium acetate (~2g.) or pyridine (5 to 10 drops)

Table II. Titration of Metal Ions with 0.05M EDTA and Naphthylazoxine Indicator

Ion	Theoretical	Actual[a]	Difference	pH at End Point
Cd^{++}	9.87	9.85	−0.02	5.4
		9.85	−0.02	5.5
Co^{++}	9.14	9.14	0.00	5.0
		9.13[b]	−0.01	5.6
		9.13	−0.01	5.6
Cu^{++}	9.01	9.02	+0.01	3.6
		9.00	−0.01	3.6
		9.00	−0.01	3.6
La^{+++}	9.27	9.27	0.00	6.4
		9.24	−0.03	5.6
		9.28	+0.01	6.3
Ni^{++}	9.23	9.22	−0.01	5.2
		9.23	0.00	5.2
		9.25	+0.02	5.9
Th^{+4}	4.33	4.34	+0.01	3.2
		4.34	+0.01	3.2
		4.33	0.00	3.4
Y^{+++}	9.79	9.82	+0.03	5.4
		9.85	+0.06	5.4
		9.81	+0.02	5.2
Yb^{+++}	9.77	9.78	+0.01	5.2
		9.77	0.00	5.2
		9.77	0.00	5.2
Zn^{++}	9.11	0.09	−0.02	5.2
		9.08	−0.03	5.3
		9.10[b]	−0.01	6.1

[a] 1 ml. of 0.005*M* copper(II) added except where noted.
[b] No copper added.

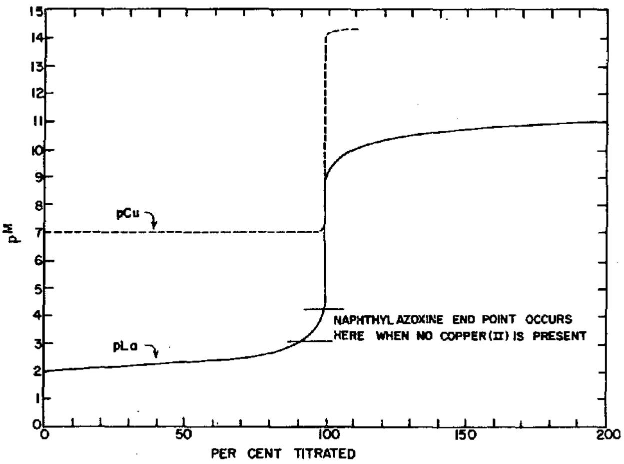

Figure 2. Theoretical curve for titration of lanthanum

driving force of a complex formation reaction can be estimated from the difference in formation constants of the complexes involved. The reaction of interest in the present case is the conversion of copper(II) azoxine (CuIn) to copper(II) EDTA.

$$\text{CuIn} + \text{EDTA} \rightleftharpoons \text{Cu EDTA} + \text{In} \quad (1)$$

Taking the formation constant reported for copper(II) 8-quinolinol-5-sulfonic acid (*4*) as an estimate of the constant for the related compound, naphthylazoxine, the constant for Reaction 1 may be approximated.

$$K = \frac{K_{\text{EDTA}}}{K_{\text{in}}} = \frac{10^{18.8}}{10^{11.5}} = 10^{7.3}$$

The reaction of lanthanum with EDTA may be considered to be merely

$$\text{La}^{+++} + \text{EDTA} \rightleftharpoons \text{La EDTA} \quad (2)$$

because the copper(II) forms a complex with naphthylazoxine sufficiently stable so that none of the indicator may be considered as being available to the lanthanum. The formation constant for Reaction 2 is, therefore, $10^{15.5}$ compared to $10^{7.3}$ for Reaction 1.

This is more qualitative than quantitative. An acid solution makes an important difference in the strength of all complexes and this was not taken into account. Also, incorporation of the hydrolysis constants for lanthanum in Reaction 2 would make some difference at the slightly acid pH of the titration.

TITRATION OF SINGLE METAL IONS

The following metals can be titrated directly with EDTA at pH 5.5 to 6.5 using naphthylazoxine indicator with copper(II) added: cadmium, cobalt, copper(II), lead, nickel, rare earths, yttrium, and zinc. At this pH aluminum, iron(III), thorium, and zirconium react irreversibly with the indicator. At pH 3.0 to 3.5, however, thorium and iron(III) can be titrated directly if a small amount of copper is added. The EDTA complexes of magnesium and the alkaline earths are too weak to be titrated in acid solution.

The precision and accuracy were studied by titrating portions of carefully standardized metal ion solutions (Table II). The solutions taken for analysis were standardized as follows: cadmium by EDTA titration using Eriochrome Black T indicator; cobalt by titration of the acid formed on passing the cobalt perchlorate solution through a hydrogen-form cation exchange column; copper, nickel, and zinc solutions by using the pure metal as a primary standard; thorium by EDTA titration using Alizarin Red S indicator (*2*); lanthanum by EDTA titration using Thorin indicator (*3*).

INTERFERENCE STUDY

Magnesium forms a rather weak complex with EDTA (log $K = 8.7$) and does not interfere in titrations where the pH is 6.0 or below. Calcium represents a near-borderline case (log K of EDTA complex $= 10.7$) but does not interfere provided the pH of the titration is not greater than 5.5. Manganese (II) (log $K = 13.8$) interferes in all titrations carried out at pH 5.5 to 6.5, but can be quantitatively titrated with other divalent metals if the pH is in the range from 6.5 to 7.0. All divalent metals forming EDTA complexes having a log K greater than about 13 interfere in the titration of thorium at pH

3.0 to 3.5. Copper may be quantitatively titrated together with thorium.

In titrations with azoxine indicators at pH 5.5 to 6.5, no end point can be obtained if macro amounts of aluminum, iron(III), thorium, or zirconium are present. However, as shown by the data in Table III, traces of these ions will not interfere with the end point. This is of practical significance, especially in EDTA titrations following separations, because it permits the use of separations that sometimes leave traces of the tri- or quadrivalent metals.

The effect of inorganic anions and organic chelating agents was studied by titrating zinc in the presence of an approximately equimolar concentration of the added ion or compound. These titrations were carried out at pH 6.4 ± 0.2 (acetate buffer) without added copper. The results, summarized in Table IV, indicate that, at least in this particular titration, a wide variety of chelating ions can be tolerated. It should also be mentioned that sulfate, acetate, chloroacetate, and the like do not interfere in the naphthylazoxine method for thorium, as is the case with the Alizarin Red and other indicator methods.

Table III. Cation Interference Study

Ion Titrated	Ion Added, 0.05*M*		Ml. 0.05*M* EDTA			pH at End Point
		Ml.	Theoretical	Actual	Diff.	
Cd^{++}	Mg^{++}	6.0	5.12	5.13	+0.01	5.5
Cd^{++}	Ca^{++}	6.0	5.12	5.12	0.00	4.9
Cd^{++}	Ca^{++}	6.0	5.12	5.29	+0.27	5.6
Co^{++}	Mg^{++}	6.0	4.73	4.72	−0.01	5.6
Co^{++}	Ca^{++}	6.0	4.73	4.73	0.00	5.6
Mn^{++}	Mg^{++}	5.0	5.18	5.20	+0.02	5.8
Mn^{++}	Ca^{++}	5.0	5.18	fails	...	5.7
Ni^{++}	Mg^{++}	5.0	4.69	4.66	−0.03	5.7
Ni^{++}	Ca^{++}	5.0	4.69	fails	...	5.6
Zn^{++}	Mg^{++}	6.0	5.09	5.08	−0.01	5.6
Zn^{++}	Ca^{++}	6.0	5.09	5.10	+0.01	4.9
Zn^{++}	Al^{+++}	0.05	5.19	5.19	0.00	6.4
Zn^{++}	Fe^{+++}	0.05	5.19	5.19	0.00	6.4
Zn^{++}	Th^{+4}	0.05	5.19[a]	5.23	+0.04	6.4
Zn^{++}	Zr^{+4}	0.05	6.33	6.33	0.00	6.4

[a] Theoretical EDTA is 5.24 ml. if thorium is also titrated.

Table IV. Effect of Anions and Chelating Agents

Conditions: 5.00 ml. of 0.05360*M* zinc nitrate titrated with 0.0518*M* EDTA, pH 6.4 ± 0.2, naphthylazoxine indicator, no copper(II) added

Ion Added	Ratio of Ion Added to Zn	Dev. from Theory Ml. EDTA	Remarks
F^-	2 to 1	0.00	
Br^-	2 to 1	+0.02	
I^-	2 to 1	0.00	
SO_4^{--}	2 to 1	+0.01	
PO_4^{---}	2 to 1	0.00	Must titrate slowly
CN^-	2 to 1	0.00	End point orange but sharp
SCN^-	2 to 1	0.00	
Ascorbic acid	20 to 1	+0.01	
2,3-Dimercapto-1-propanol	5 to 1	...	Fails
Citric acid	20 to 1	0.00	Excellent
Ethylenediamine	2 to 1	0.00	
Iminodiacetic acid	2 to 1	0.00	Fair, long orange range
Malonic acid	2 to 1	0.00	Excellent
Oxalic acid	2 to 1	0.00	
Tartaric acid	20 to 1	0.00	

USE OF MASKING AGENTS

The selectivity of EDTA titrations using azoxine indicators can be greatly improved through the use of masking agents. One important example is the titration of metal ions in the presence of uranium(VI) using tartrate or citrate to complex the latter. If present in very high concentration, the yellow color of the uranyl complex prevents satisfactory visual observation of an end point, but it should still be possible to detect the end point photometrically.

Citrate will mask thorium and zirconium (but not aluminum or rare earths) and permit the titration of zinc and the like with EDTA. This is quite striking because the log *K* for zinc EDTA is 16.6 and for thorium EDTA is 23.2. It is also of important practical value. For example, a mixture of thorium and zinc can be analyzed by titrating the zinc with EDTA (naphthylazoxine indicator) using citrate to mask the thorium; the thorium is determined in the presence of zinc by an EDTA titration at pH 2.5 (Alizarin Red S indicator).

Several metals do not complex readily with EDTA, but will interfere unless they are kept in solution by means of a suitable complexing agent. Antimony is taken care of by the addition of tartrate, and interference by beryllium niobium, and tantalum is prevented by the addition of fluoride.

Table V. Titrations Using Masking Agents

Conditions: Ratio of ion masked to ion titrated, 1 to 1. Titration with 0.05*M* EDTA, naphthylazoxine indicator, no copper(II) added

Ion Titrated	Ion Masked	Masking Agent	pH at End Point	Ml. EDTA		
				Theoretical	Actual	Diff.
Cd^{++}	UO_2^{++}	Tartrate	5.6	9.86	9.85	−0.01
Co^{++}	UO_2^{++}	Tartrate	5.8	9.14	9.17	+0.03
Ni^{++}	UO_2^{++}	Tartrate	5.9	9.23	9.24	+0.01
Yb^{+++}	UO_2^{++}	Tartrate	5.3	9.10	9.12	+0.02
Zn^{++}	Ag^{+}	Chloride	6.4	5.19	5.19	0.00
Zn^{++}	Al^{+++}	Citrate	6.4	5.19	fails	....
Zn^{++}	Be^{++}	Fluoride	6.4	5.19	5.19	0.00
Zn^{++}	Cu^{++}	Thiourea	6.4	5.19	5.19	0.00
Zn^{++}	Hg^{++}	Iodide	6.4	5.19	5.20	+0.01
Zn^{++}	Nb^{+5}	Fluoride	6.4	5.19	5.19	0.00
Zn^{++}	Sb^{+++}	Tartrate	6.4	5.19	5.19	0.00
Zn^{++}	Sn^{++}	Citrate	6.4	5.19	5.19	0.00
Zn^{++}	Sn^{+4}	Citrate	6.4	5.19	fails	...
Zn^{++}	Ti^{+4}	Fluoride	6.4	5.19	5.19	0.00
Zn^{++}	Th^{+4}	Citrate	6.4	5.19	5.19	0.00
Zn^{++}	UO_2^{++}	Tartrate	6.0	9.10	9.12	+0.02
Zn^{++}	Zr^{+4}	Citrate	6.4	5.19	5.19	0.00

Several other masking possibilities have been demonstrated. Zinc can be titrated in the presence of copper by adding thiourea to complex the latter. Iodide serves as an almost specific masking agent for mercury(II). Copper can be titrated at pH 3.0 to 3.5 without interference from aluminum if fluoride is added. This titration fails at higher pH values. Data for these and other titrations *using masking agents* are presented in Table V.

DISCUSSION

In order to obtain rapid equilibrium near the end point in titrations where some copper must be present, the copper should be added near the end point. The titration of thorium is an exception; here the equilibrium is rapid even when the copper is added at the start of the titration. In titrations where a masking agent such as citrate is present, it is advisable to delay adding the naphthylazoxine indicator until a few tenths of a milliliter before the expected end point.

When determining metals that form weak azoxine complexes (rare earths, for example), zinc can be added instead of copper in order to obtain a sharp end point. Zinc gives better results than copper for titrations to be carried out in the presence of calcium, but the addition of copper affords a greater toleration for chelating agents.

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Determination of Monomeric Epsilon-Caprolactam and Moisture in 6 Nylon

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▶ A rapid procedure for the simultaneous determination of ε-caprolactam monomer and moisture in 6 nylon flake and yarn is described. They are separated from the sample by vacuum extraction at 200° C., the monomer and part of the moisture being condensed in a water-ice cold trap. The monomer is determined by refractive index in an aqueous dilution of the condensate, while moisture is obtained by difference. The procedure requires less than 3 hours as compared to the 24-hour water-extraction procedure for the determination of total water-extractable material and, when used in conjunction with the water-extraction procedure, it furnishes an estimate of the dimer content plus any low molecular weight, water-soluble, linear molecules present in the polymer.

IN THE polymerization of ε-caprolactam (hereafter referred to as monomer) to 6 nylon (a polycaproamide produced by polymerization of ε-caprolactam), it is important to be able to determine the amount of unpolymerized lactam remaining in the polymer. Hanford and Joyce (*1*) employ a 30-minute vacuum extraction at 180° C. to determine monomer in the polymer. The monomer is condensed on a dry ice–acetone cold finger, dissolved in acetone, recovered by evaporation of the acetone, and finally dried and weighed. Van Velden and coworkers (*3*) have determined, separately, monomer, ring compounds, and short linear molecules in 6 nylon. Hot methanolic extraction up to 36 hours is followed by evaporation and careful drying. Monomer is determined by sublimation and weighing. The ring compounds and short linear molecules left after sublimation of the monomer are separated by a strongly basic ion exchange resin.

The amount of water-soluble material in 6 nylon can be determined by Soxhlet extraction for 16 hours in the case of 1/8-inch flake or 8 hours in the case of yarn. This procedure is based on the loss in weight of the sample and involves careful drying of Soxhlet thimbles and of the extracted sample. An independent sample moisture analysis is required to allow results to be expressed on a dry sample basis. These steps are subject to considerable error and require about 24 hours. Furthermore, an estimate of monomer plus dimer (dimer, as used in this paper, is a mixture of cyclic dimer, trimer, etc.) and water-soluble linear molecules is obtained, whereas results for monomer alone are often desirable.

This paper presents a vacuum extraction technique which is rapid, accurate, and specific for monomer in the presence of 6 nylon, dimer, and moisture. The extraction is carried out at 200° C., and the monomer is condensed in a cold trap, dissolved in water, and determined by refractive index measurement. Since the total sample weight loss represents monomer plus moisture, the latter is obtained by difference.

APPARATUS

The glassware is constructed of Pyrex chemical glass No. 7740 and is illustrated in a schematic assembly in Figure 1. The sample tube is 180 mm. long over-all and 25 mm. in outside diameter with a 35/25 socket joint. The glass bridge is constructed of tubing 20 mm. in outside diameter with 35/20 and 28/15 ball joints. The trap is 32 mm. in outside diameter and 255 mm. long over-all; outside diameters for the central tube, the side arm, and the nipple are 20, 11, and 15 mm., respectively, and the socket joints are 28/15 and 18/9. The bottom end of the central tube of the cold trap is displaced toward one wall to allow easier entry of water into the tube when dissolving the monomer and when shaking and mixing the solution. The No. 28 and No. 35

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pinch clamps (Catalog No. 3241, Arthur H. Thomas Co., Philadelphia, Pa.) have all possible excess metal removed to allow good contact between the glass joints and the special 115-volt, 180-watt, Glas-Col mantles (Glas-Col Apparatus Co., Inc., Terre Haute, Ind.). These mantles contain iron-constantan thermocouples to indicate the temperature of the glass bridges.

The following numbers refer to the main heating unit (Figure 2). An aluminum block, 10 × 28 × 12 inches, 6, is insulated with 2 inches of Johns-Manville marine sheathing (Johns-Manville Co., Philadelphia, Pa.), and contains 16 holes, 1 inch in diameter and 5-$^3/_4$ inches in depth. The block is heated by ten 800-watt Chromalox rods (Edwin L. Wiegand Co., Pittsburgh, Pa.) which are grouped by pairs into three base-heat and two control-heat circuits, 7; a Tagliabue Celectray indicating potentiometer controller, 8 (C. J. Tagliabue Corp., Newark, N. J.), connected to an iron-constantan thermocouple, which is placed in the middle of the block, controls the temperature of the block at 200° ± 5° C.

On each of the long sides of the block are mounted an 8-position vacuum manifold, 3, and an electrical manifold containing eight 115-volt receptacles and eight iron-constantan thermocouple-lead receptacles, 4. The receptacles and vacuum positions are aligned with the holes in the block. The 115-volt receptacles are divided into groups of four, each group being connected in parallel to one 115-volt, 7.5-ampere variable transformer, 10 (Catalog No. 9708-G, Arthur H. Thomas Co., Philadelphia, Pa.). The thermocouple receptacles are connected through a 16-position switching arrangement to a pyrometer, 2, made especially for heating mantles (Catalog No. 11-472-60, Fisher Scientific Co., Pittsburgh, Pa.).

Sixteen 16-ounce Dewar flasks serve as the cold trap containers, 5. Two Cenco Megavac pumps, 9 (Catalog No. 92015, Central Scientific Co., Chicago, Ill.), connected in parallel, maintain vacuum in the manifold, and the actual pressure in the manifold and the glass equipment is determined by a 240-mm. Bennert closed-tube mercury manometer (Catalog No. 6365, Arthur H. Thomas Co., Philadelphia, Pa.) graduated to 0.1 mm., 1.

Table I. Refractive Indices of Aqueous Monomeric ε-Caprolactam Solutions (25.0° C.)

n_D	Grams/5.00 Ml. Soln.
1.3323	0.000
1.3350	0.088
1.3400	0.248
1.3450	0.406
1.3500	0.563
1.3550	0.717
1.3600	0.871
1.3650	1.025
1.3700	1.184
1.3750	1.340
1.3800	1.495
1.3850	1.649
1.3900	1.804
1.3950	1.959
1.4000	2.112

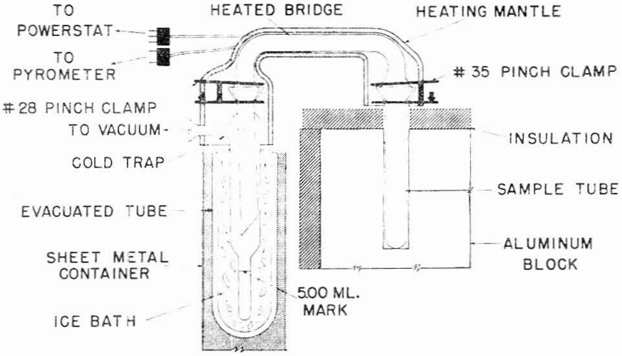

Figure 1. Vacuum extraction apparatus assembly

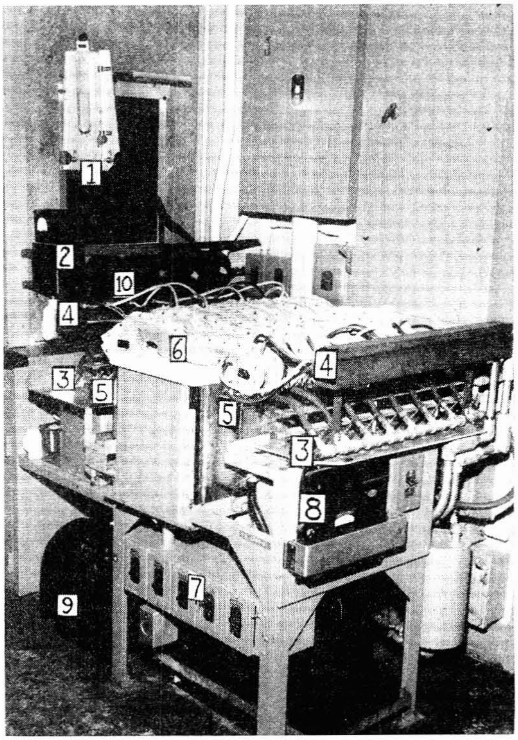

Figure 2. Extraction equipment

Refractive index readings are made on a Bausch & Lomb Abbe-type refractometer (Bausch & Lomb Optical Co., Rochester, N. Y.). The prism temperature is controlled at 25.0° ± 0.1° C. by a water bath (Precision Scientific Co., Chicago, Ill.) containing a centrifugal pump and a cooling jacket through which flows 68° F. water; the bath temperature is controlled by a Magna-Set thermoregulator (Precision Thermometer & Instrument Co., Philadelphia, Pa.). The refractometer is calibrated at the lower end of the scale with atmosphere-equilibrated distilled water and at the upper end with a standard glass.

SAMPLING

All flake samples must be ground to pass an $^1/_8$-inch screen and all yarn samples must be free of finish oils which are volatile under the conditions of the analysis. A sample size of 10 to 15 grams is used for all flakes and yarns containing less than 5% monomer,

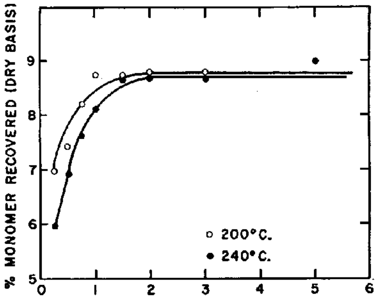

Figure 3. Vacuum extraction of 6 nylon flake

Ten-gram sample of $^1/_8$-inch flake, 5 mm. Hg pressure, 225° C. bridge temp.

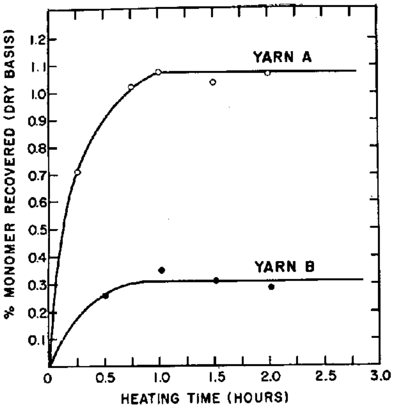

Figure 4. Vacuum extraction of 6 nylon yarn

Ten-gram sample, 5 mm. Hg pressure, 200° C. sample temp., 225° C. bridge temp.

while 5-gram samples are employed for materials containing more than 5% monomer.

PROCEDURE

Prepare a calibration curve or table relating grams of monomer per 5.00 ml. aqueous solution to refractive index. Typical data taken from such a linear plot are shown in Table I.

Weigh an empty, rubber-stoppered, dry sample tube on an analytical balance, place the proper amount of sample in the tube, restopper, and reweigh. Place a dry, cold trap in the wet-ice bath and connect the trap to the proper vacuum manifold position by the 18/9 joint, using a No. 18 pinch clamp.

Connect a bridge, contained in the special Glas-Col mantle, to the sample tube using a No. 35 pinch clamp and place the tube in the proper hole in the block, swinging the 28/15 ball over the corresponding cold trap socket; quickly secure the bridge to the trap with a No. 28 pinch clamp. Fold the mantle flaps snugly around the joints and clamps.

Slowly open the vacuum connection on the manifold and allow the pressure to descend to less than 20 mm. of mercury. Connect the 115-volt and thermocouple plugs to the proper receptacles and turn the proper variable transformer to give a mantle temperature of 225° ± 15° C.

Allow flake samples to heat for 2 hours, and yarn samples for 1 hour, at a system pressure of less than 20 mm. of mercury, a bridge temperature of 225° ± 15° C., and a block temperature of 200° ± 5° C. Higher pressures indicate air entering the system, causing incomplete removal of monomer. Low bridge temperatures may cause condensation of monomer in the bridge. High bridge temperatures may cause polymerization of the monomer.

At the end of the extraction period, close the vacuum valve, turn off the variable transformer, and disconnect the cold trap from the vacuum system. Disconnect the bridge from the cold trap and stopper both cold trap openings with plugs made from the appropriate ball joints. Disconnect the bridge from the sample tube and quickly stopper the tube with the proper rubber stopper. Place the tube in a desiccator to cool.

Examine the bridge carefully. The presence of condensed monomer in the bridge invalidates the analysis.

Remove the top plug from the cold trap and add about 1 ml. of warm, distilled water with a medicine dropper to wet the monomer. Let the tube stand about 10 minutes and wash the remaining monomer into the calibrated nipple with distilled water. When all of the monomer is dissolved, add additional water until the volume of the solution in the nipple is exactly 5.00 ml. Replace the top plug, shake the trap to mix the solution thoroughly, remove the side plug, and pour the solution into a small beaker. Take three independent refractive index readings at 25.0° ± 0.1° C., approaching the end point from each side, and determine the average. In a similar manner, determine the average refractive index of the distilled water; if this differs from 1.3323, correct all sample refractive indices to the 1.3323 basis. Convert the average sample refractive index to grams of monomer using a calibration plot or table relating grams of monomer per 5.00 ml. solution to refractive index.

When the stoppered sample tube is cool, remove it from the desiccator and reweigh.

Calculations.

$$\%\ \text{moisture} = \frac{(A - C - D) \times 100}{A - B}$$

% monomer (dry basis) =

$$\frac{D \times 100}{A - B} \times \frac{100}{100 - \%\ \text{moisture}}$$

where

A = weight of stoppered test tube plus sample, grams
B = weight of stoppered test tube, grams
C = weight of stoppered test tube plus dry extracted sample, grams
D = weight of monomer extracted, grams

RESULTS AND DISCUSSION

The relationship between refractive index (sodium D light) at 25° C. and grams of monomer per 5 ml. of aqueous solution is linear. Typical data taken from such a plot are shown in Table I. Assuming that an Abbe refractometer reading is accurate and precise to ±0.0001 unit, these data indicate that the amount of monomer in 5 ml. of aqueous solution can be determined to ±0.003 gram or to ±0.03% absolute for a 10-gram polymer sample.

A study was made of the effects of variations in flake particle size, sample temperature, bridge temperature, and system pressure upon the vacuum extraction of monomer and moisture from 6 nylon polymer. Experimental equipment was generally similar to that described under Apparatus, but differed from it in these specific points: The connecting bridges and ball and socket joints were wrapped with flexible heating tape (prior to the design and fabrication of the special Glas-Col mantles); iron-constantan thermocouples connected to a potentiometer were used to measure the temperature of the bridges; and a manostat was included in the vacuum system to maintain constant pressure throughout the extraction.

Effect of Flake Particle Size. For a given set of experimental conditions, the extraction rate was inversely proportional to the size of the flake particles. A nominal flake size of $^1/_8$-inch was adopted as standard because of the possibility of smaller particles being sucked from the test tube into the bridge and cold trap when vacuum was applied to the system.

Effect of Sample Tube Temperature. The sample temperature had to be chosen so that all monomer present in the sample could be removed in a reasonable length of time with no appreciable addition or loss of monomer due to sample degradation or polymerization. A sample temperature of 200° C. was adopted because earlier, independent polymerization studies had indicated that the rates of monomer and polymer formation at this temperature were negligible. All the monomer could be extracted from $^1/_8$-inch flake in less than 2 hours (Figure 3) and from yarn in less than 1 hour (Figure 4); at 200° C. the sample does not become molten, eliminating the safety hazard of the shattering of the glass sample tube as the sample cools to room temperature.

Effect of Bridge Temperature. The bridge temperature must be maintained at a level high enough to prevent monomer condensation on the bridge walls and low enough to prevent polymerization. A series of vacuum extractions was performed on several portions of one polymer sample and on each successive run the temperature of the bridge was raised until consistent results were obtained. Experimental conditions were: 10-gram samples of $^1/_8$-inch flake, sample tube temperature of 200° C., system pressure of 5 mm. of mercury, and 2 hours' heating time. Table II illustrates that bridge temperatures in the range 210° to 225° C. are adequate and that the sample may be presumed to contain about 8.89% extractable monomer.

Effect of System Pressure. Because variations in pressure may occur during the vacuum extraction process, it was necessary to determine the highest permissible system pressure consistent with rapid and quantitative removal of the monomer from the sample. Ten-gram samples of $^1/_8$-inch flake and sample and bridge temperatures of 200° and 225° C. respectively, were used. Monomer present was 8.89%. The data in Table III indicate that, at 1 and 7 mm. of mercury pressure, complete extractions were obtained after 1.5 hours, while at 20-mm. mercury pressure about 2 hours were required.

Consequently, a 2-hour extraction period at a system pressure of 20 mm. of mercury, or less, was adopted for flake polymer samples. Pressures greater than 20 mm. were not investigated, since at these pressures, the flow of monomer vapor through the bridge to the cold trap is too slow.

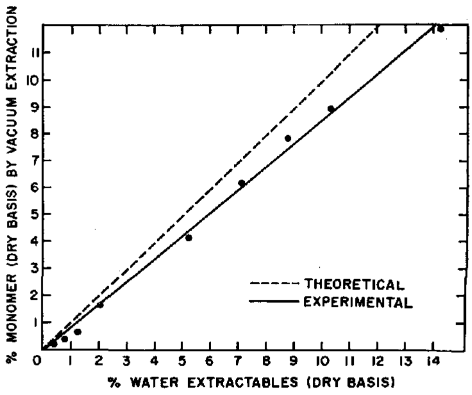

Figure 5. Comparison of vacuum- and water-extraction methods

Table II. Vacuum Extraction of 6 Nylon

Bridge Temp., ° C.	Monomer Recovered, %
132	8.50
168	8.70
210	8.89
225	8.89

Table III. Vacuum Extraction of 6 Nylon Polymer

Pressure, Mm. Hg	Heating Time		
	1 hr.	1.5 hr.	2 hr.
1	8.46	8.87	8.90
7	..	9.11	8.83
20	8.05	8.59	8.98

Comparison of Water- and Vacuum-Extraction Methods. Samples were analyzed by water-extraction and vacuum-extraction methods. The data in Figure 5 clearly indicate that the vacuum-extraction method gives lower results than the water-extraction method. It was postulated that water extracts monomer, dimer, and water-soluble linear molecules from 6 nylon polymer, while the vacuum-extraction method removes only the monomer.

To determine the validity of the foregoing postulate, the following experiments were performed:

A. A series of four 6 nylon flake samples was analyzed by the vacuum-extraction technique. The vacuum-extracted residues were subjected to extraction by water. The water extract was analyzed for the amount of monomer solids present by evaporating the water, and heating at 100° C. under full vacuum, a procedure which removes any water or monomer present. The melting point of the residue was about 280° C. indicating that the residue was largely dimer (*2*). The results, summarized in Table IV, showed that essentially all of the monomer was extracted by vacuum extraction.

Table IV. Difference between Vacuum- and Water-Extraction Methods

Sample No.	Original Vacuum Extraction, %	% Water Extractables in Vacuum-Extracted Residue	
		Sample weight loss (dimer + monomer, if present)	Recovered from water extract (dimer only)
16-7E	2.40	1.74	1.79
16-8E	4.15	2.02	1.84
16-9E	15.67	2.21	2.15
16-10E	11.90	1.59	1.42

B. Further proof that dimer is not extracted by the vacuum-extraction method was obtained by placing a known amount of purified dimer in a sample tube and vacuum-extracting it for 2 hours at 200° C. and at 1 mm. of mercury pressure. This procedure did not remove any detectable amount of dimer from the sample tube, as determined by weight loss of the sample tube, and no condensed material was found in the cold trap.

Because vacuum extraction will not extract dimer from polymer samples, whereas water extraction does, the difference in results obtained by the two procedures on a given sample indicates the amount of dimer, plus any water-soluble, linear molecules present in the sample.

PRECISION

A statistical study was carried out on 16 analyses on each of two flakes of different monomer and moisture contents. In the higher range, an average of 7.99% monomer and 1.70% moisture was obtained with standard deviations of 0.26 and 0.25%, respectively. For a polymer of low monomer and moisture content, an average of 0.53% monomer and 0.47% moisture was found with standard deviations of 0.03 and 0.06%, respectively.

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Applications of Anion Exchange Resins to Determination of Boron

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▶The behavior of boric acid and of several known interferences has been investigated using both weak and strong base anion exchange resins. A simple, rapid chromatographic technique employs chloride ion as an elution indicator, applicable to the concentration and separation of boron from dilute solutions of low total salt content. Boron is separated from most of the known titrimetric interferences by a mixed bed ion exchange column. The procedure is rapid, requires no special treatment of the sample prior to the exchange process, and compares favorably with existing techniques. However, it cannot be recommended for separation of boron prior to colorimetric determination.

SEVERAL rapid and accurate procedures are available for the determination of boron, but there is no single method of suitable accuracy which can be applied to a variety of sample types without the prior separation of boron from its determinative interferences. Separative techniques which have been employed include ion exchange, precipitation, extraction, distillation, paper chromatography, and electrolytic procedures. Of these, only the distillation of boric acid as the methyl ester and the ion exchange procedures have shown general applicability. However, the methylborate distillation technique is time-consuming and tedious, and gives slightly low boron recovery even when multiple distillations are carried out.

The utilization of ion exchange resins for the separation of boron has been confined, with one exception (*8*), to the separation of boron from cationic interference by retaining the cations on a strong acid cation exchange resin while the boric acid and other anions pass into the effluent. Such procedures are not applicable to samples for titrimetric determination which contain reasonable concentrations of anionic interferences whether these are of the buffering or complexing nature. Also, cations forming anionic complexes might not be removed by the cation exchange resin. A strong acid effluent is obtained which, on neutralization, produces a high ionic strength medium and thereby decreases the accuracy of a titrimetric process involving the use of color indicators.

STRONG BASE RESINS

Ion Exchange Chromatography. Two general methods use strong base resins to separate boron from its interferences. The first of these removes all anions from the sample and quantitatively elutes them in order of their increasing affinity for the resin. The second uses the resin in an anionic form such that the boric acid from the sample solution is not held by the resin, while the interferences are retained.

Schutz (*8*) reports the use of strong base anion exchange resins for the quantitative separation of boron. He uses the resin Amberlite IRA-400 in the formate form to separate boric and phosphoric acids in the determination of boron in fertilizers. The phosphoric acid is retained by the resin while the boric acid is washed into the effluent by distilled water. Samples are of low total salt content and relatively large resin bed capacity. Positive errors of 0.1 to 0.4 mg. of boron are obtained on 1-gram samples containing 25 to 40 mg. of boron.

Prior to the above publication, similar separations had been attempted in this laboratory using the chloride and the nitrate forms of the same resin. The results obtained are accurate to about ±0.2 mg. of boron, but serious contamination of the boron-containing effluent is noted. Less accurate results were obtained as the total foreign ion concentration increased.

Preliminary studies of the behavior of boric acid and the common anionic

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interferences, phosphate, arsenite, and arsenate, produce the following order of elution from strong base resins in the hydroxide form: borate, chloride, nitrate, arsenite, phosphate, and arsenate. Borate appears to be weakly held by the resin, chloride ion somewhat more strongly, and the succeeding ions were retained strongly. The presence of chloride ion, silver chloride, silver nitrate, or mixtures of these, does not interfere with the titrimetric determination of boron. It thus appears feasible to use chloride ion to indicate the complete elution of borate from the column. By placing acidified silver nitrate in the receiving flask, and adding a small amount of chloride ion to the sample, it would be possible to elute with a relatively concentrated reagent until a very definite chloride test appeared in the receiver. At this point all of the borate and none of the more strongly retained ions would have been eluted. Such a procedure would allow the collection of a single eluent fraction as the sample, and would keep the total volume of eluent reasonably low.

WEAK BASE RESINS

Mixed Resin Bed Separations. As the name implies, weak base exchange resins contain ionizable groups having weakly basic properties. The extent of absorption of a weak acid by such a resin is largely dependent upon the ionization constant of the weak acid (*4*). Because of the great affinity of resins of this type for the hydroxyl ion, it is possible to separate very weak acids from stronger acids by the hydrolysis of the resin salts formed by the anions of the former.

Weak base resins will not retain such acids as boric, silicic, or carbonic (*7*). If boric acid can be quantitatively recovered from a bed of a weak base resin, a simple and rapid method of separation of boric acid from all other anions except those of extremely weak acids is available. Further, this resin could be mixed with a strong acid cation exchange resin to give a mixed resin bed which would simultaneously remove cations and most anions without the necessity for an elution procedure. By using the cation exchanger in the free acid form and the anion exchanger in the free base form, the sample could be deionized. The effluent from such an ideal ion exchange column would contain only the boric acid and such other weak acids as would not be retained by the resin.

A single mixed resin bed has three distinct advantages (*5*). It increases the efficiency of both of the component resins over that achieved with either alone; a mixed resin bed has a sharp break-through point for ionic solids which allows a more complete utilization of the resin bed capacity; and the quality of the effluent is, within reasonable limits, independent of the concentration of ionic solids in the sample.

The technique has been used widely for the treatment of water, and for the deionization of analytical samples, but apparently no analytical separations of weak acids by this means have been reported.

EXPERIMENTAL

Reagents. Standard boric acid solutions were prepared by dissolving weighed amounts of anhydrous boric oxide in water to give a concentration of approximately 1.0 mg. of boron per milliliter. The boric oxide was prepared by fusion of reagent grade boric acid in a platinum dish. All other reagents were prepared by solution of the appropriate reagent grade chemical.

Carbonate-free sodium hydroxide solutions were prepared from saturated sodium hydroxide solution and were standardized by potentiometric titration of aliquots of the standard boric acid solution using the procedure described by Martin and Hayes (*3*). This procedure was also used for the determination of the boron in the samples eluted from the ion exchange columns. The method involves the adjustment of sample and complexing agent (invert sugar) to a pH of 6.90, mixing of the two, and a titration with $0.02N$ carbonate-free sodium hydroxide of the complex acid formed to restore the pH of 6.90. As shown by Hollander and Rieman (*1*), there is a small error in this type of titration. The accuracy which may be expected is indicated in Table I. A degree of familiarity with the procedure is required before highly precise results are obtained. Plus or minus 0.03 mg. of boron was selected as a safe limit of accuracy in the titration.

Table I. Standardization of Sodium Hydroxide Solutions

Solution No.	No. of Replicates	Titer, Mg. B/Ml.	Std. Dev., Mg. B/Ml.
1	6	0.2520	0.014
2	5	0.2838	0.011
3	5	0.2332	0.004
4	6	0.2681	0.008
5	6	0.2431	0.010

Resins. Strong Base Resin, Amberlite IRA-400.

Weak Base Resins, Amberlite IR-4B, Amberlite IR-45, DeAcidite, Nalcite WBR.

Strong Acid Resin, Nalcite HCR (Dowex 50), 8% cross linkage, 50 to 100 mesh.

The resins were obtained from the manufacturer in the fully regenerated free acid or base forms. The resins were air-dried, crushed in a mortar, screened to the appropriate mesh size, and washed free of fines. Used resins were regenerated or converted into other ionic forms by using $1N$ solutions of the appropriate acid or base and rinsing with distilled water until the rinse water was approximately neutral to methyl orange or phenolphthalein indicator.

Ion Exchange Column. The ion exchange columns consisted of borosilicate glass tubing of varied diameter and length equipped with three-way stopcocks at the bottom. One outlet was used to collect the effluent and the other was permanently connected by rubber tubing to an elevated distilled water reservoir. A 1-inch-thick, glass-wool plug was used to support the resin. The columns were filled by adding approximately 40 ml. of resin as a slurry to the column containing about 1 inch of water above the plug. The column was drained to about the resin level, and the bed was then raised by adding water from the reservoir. This settled the resin and removed trapped air. The stopcock controlled flow rates.

Samples, rinse, and eluent solutions were admitted from a 250-ml. separatory funnel connected to the top of the column by a rubber stopper. The funnel created an air lock in the column by which the liquid level was maintained at least 1 inch above the resin bed. In this manner the sample was admitted at the flow rate determined by the column stopcock, and the stopcock of the funnel was left open.

Columns about 60 cm. in length and 11 mm. in inner diameter were used for determinations. Columns of 22-mm. inner diameter were generally used for regeneration.

ION EXCHANGE CHROMATOGRAPHY

Borate was separated from several anionic interferences such as phosphate, arsenite, and arsenate by addition of chloride ion to the sample solution before admitting it to an ion exchange column containing a strong base resin in the free base form. Elution from the column was continued until a positive test for chloride ion was noted in the receiving flask. While it was possible to effect successful separations, such a method appears to have limited application.

MIXED RESIN BED SEPARATIONS

Evaluation of Resins. Some weak base resins such as Amberlite IR-4B and DeAcidite retained small amounts of boric acid and quantitative recovery of the borate either by washing or by elution with sodium chloride solution was impossible. The resin Amberlite IR-45 did not exhibit this behavior and was used in subsequent work.

The cation exchange resin chosen was Nalcite HCR (Dowex 50). This type of resin was shown by Martin and Hayes (*3*) and by Kramer (*2*) to provide a good separation of borate from reasonably large quantities of 15 different cations.

Procedure. The resins in their fully regenerated form were crushed, screened to 40 to 60 mesh, washed free of fines, and combined on the basis of equivalent exchange capacity using the capacity ratings of the manufacturer. Successive portions of boric acid were passed through 50 ml. of the mixed resin at a constant flow rate of 2.8 ml. per minute. The resin was rinsed with distilled water until 250 ml. of effluent had been obtained, and 100-ml. aliquots were titrated by the above method. The more significant results are shown in Table II.

Table II. Evaluation of Resins

Mg. of Boron Recovered[a]

IR-45–Nalcite HCR	Nalcite WBR–Nalcite HCR
3.93	3.94
3.93	3.95
3.94	
3.94	

(3.93 mg. of B as H_3BO_3, 10 mg. of P as KH_2PO_4, and 10 mg. of As as AsO_3^{---} present)

IR-45–Nalcite HCR	Nalcite WBR–Nalcite HCR
3.93	3.96
3.93	3.94

Separations from Known Interferences

No.	Sample[a]	Mg. B Found
1	120 mg. of Fe as $Fe_2(SO_4)_3$ in 10 ml. 1*N* HCl	3.92
2	As above plus 10 mg. of P as PO_4^{---} and 10 mg. of As as AsO_3^{---}	3.94
3	118 mg. of Sn as $SnCl_4$ plus HCl to prevent hydrolysis	3.95
4	10 ml. of 0.1*M* $KMnO_4$ in 1*M* H_2SO_4	3.92
5	10 ml. of 0.1*M* $K_2Cr_2O_7$ in 1*M* H_2SO_4	3.91
6	40.2 mg. of Mo as MoO_4^{--}	3.92
7	1 meq. of $NaHCO_2$	3.94
8	10 meq. of $NaHCO_2$	3.93
9	5 meq. of $NaC_2H_3O_2$	3.94
10	10 meq. of $NaC_2H_3O_2$	3.89
11	0.5 meq. of $Na_2C_2O_4$	3.93
12	5 meq. of $Na_2C_2O_4$	3.93
13	10 ml. of 0.1*M* KF	3.65[b] 2.98[c] 3.91[d]

[a] 3.93 mg. of B as H_3BO_3 present.
[b] Sample titrated directly without separation.
[c] Sample passed through ion exchange bed before titration.
[d] Boron added after KF soln. passed through ion exchange column.

For further evaluation of IR-45–Nalcite HCR, it was assumed that ions removed by the cation exchanger alone would also be removed by the resin when used in a mixed bed. Hence, only those interferences noted by workers who used cation exchange resins to separate boron and anionic interferences were studied. The results shown in Table II were obtained with fresh resin for each sample.

In utilizing a mixed resin bed there was some question regarding the behavior of cations which form insoluble hydroxides as the pH of the solution rises, due to the neutralization of excess acidity by the exchange process. Samples 1 and 2 (Table II), containing iron, gave no difficulties. Spot tests on the effluent indicated the absence of iron, sulfate, and phosphate. Only a trace of chloride was present, and the pH was found to be 5.6. The stannic chloride sample produced a thin gelatinous layer on the upper surface of the resin bed, with marked reduction of the flow rate. Agitation of the upper few milliliters of the resin bed dispersed the precipitate and normal flow was restored. No turbidity or interference in the titration was noted in the effluent sample. Shaking small amounts of stannic chloride in a test tube with a portion of the mixed resin resulted in the appearance and then disappearance of a turbidity, indicating that ion exchange rather than a physical retention by the resin bed had taken place. Kramer (*2*) suggested that tin be removed prior to a cation separation by plating it out on metallic zinc. It seems probable that samples known to contain large amounts of tin could be satisfactorily handled by a combined batch and column operation.

Permanganate, dichromate, and molybdate attacked some cation exchange resins in the free acid form (*6*). Molybdate was reduced in part to molybdenum blues, which passed into the effluent and prohibited the use of color indicators for the boric acid titration. However, molybdate was reported to be retained by weak base resins in the chloride form (*9*). Permanganate and dichromate attacked the resin, but this had no evident effect on the separation or boric acid recovery. The molybdate did not seem to attack the resin, and no molybdenum blues appeared in the effluent.

Anions of weak organic acids, such as formate, acetate, and oxalate, interfered in the boric acid titration because of their buffering effect. Samples such as 8, 10, and 12 (Table II) could not be titrated with reasonable accuracy without the separation of boric acid from these anions. The potentiometric titration will tolerate small amounts of these anions. No buffering was noted with samples 7 to 12 after passage through the ion exchange column.

Boric acid could not be separated from fluoride ion using this technique. The fluoride interfered by forming fluoboric acids of sufficiently acidic character to be retained by the anion exchange resin. The resin bed retained free fluoride ion, but apparently did not decompose the fluoboric acids, as indicated by the data for sample 13 in Table II.

The passage of an acidic sample through the mixed resin bed liberated small bubbles of carbon dioxide from the anion exchange resin. (The latter was always found to contain some carbonate.) These carbon dioxide pockets are small and disappear as the resin is rinsed with water, and have no apparent adverse effects on the separation or recovery of boric acid. The small gas pockets did not alter the flow rates appreciably, but indicated the amount of resin that had been exhausted, because the bubbles appeared as far down the column as the free acids had reached. No leakage of ions was noted unless the bubbles reached the bottom of the column; in such cases insufficient resin had been used and the sample was discarded.

The resin pairs differed in color and in density and could be separated readily for regeneration. One batch of resin showed an appreciable blank after several regenerations; therefore, it is recommended that they be discarded after use, or else rigidly checked after each regeneration.

There was sufficient surface attraction between the two resins in the fully regenerated forms to keep the mixture homogeneous if a 60- to 100-mesh size was used. When larger particle sizes were used, the resins tended to separate. Smaller sizes decreased the flow rates markedly.

Practical Applications. To compare the proposed mixed bed ion exchange separation technique with existing separation methods, the analysis of a glass and of a synthetic steel was undertaken. These represent fairly difficult types of samples, for which comparable data have been published using other methods.

PROCEDURE A. DETERMINATION OF BORON IN GLASS. National Bureau of Standards glass No. 93 (12.76% boron oxide) and silica samples were ignited at 500° C. for 1 hour. Samples of 0.2 to 0.3 gram were fused in a platinum crucible with approximately six times the sample weight of potassium carbonate; the melt was taken up in a minimum of hot water and transferred to a 250-ml. separatory funnel containing 30 to 40 ml. of mixed, 60 to 100 mesh, IR-45 and Nalcite HCR resins in the free base and acid forms, respectively. The funnel was swirled and contents allowed to settle until no further sign of carbon dioxide evolution was apparent. The resin solution mixture was transferred to a glass column 11 mm. in inner diameter, which already contained about 20 ml. of the mixed resin. The separatory funnel was connected to the top of the column, rinsed with several small portions of distilled water, and then filled with distilled water. Rinsing was continued at a rate of 2.5 ml. per minute until a total effluent of 250 ml. was collected in a volumetric flask. Aliquots of 100 ml. were then taken for the determination of the boric acid.

For a blank determination, samples of Mallinckrodt analytical grade $SiO_2 . xH_2O$, 100-mesh, were given the same treatment as the glass samples. A known amount of boric acid was added just after the melt was transferred to the separatory funnel. The average error caused by loss of boric acid was added to the amount of boron found in the glass analyses. The results are tabulated in Table III.

Table III. Determination of Blank in Analysis of Glass Samples

Wt. of SiO_2, Gram	Mg. of Boron		
	Added	Found	Not recovered
0.2695	10.47	10.39	0.08
	10.47	10.32	0.15
0.1697	10.47	10.41	0.06
	10.47	10.40	0.07
0.2367	10.47	10.33	0.14
	10.47	10.35	0.12
		Average	0.10

Table IV. Analysis of Glass Sample

Wt. of Glass, Gram	Mg. of Boron			% B_2O_3 (Corrected for Blank)
	Present	Found	Not recovered	
0.2022	8.02	7.90	0.12	12.74
		7.91	0.11	
0.1529	6.07	5.94	0.13	12.70
		5.91	0.16	
0.2029	8.02	7.89	0.13	12.68
0.3137	12.44	12.20	0.24	12.69
		Average		12.70

Table V. Comparison of Separation Procedures

	% B_2O_3
NBS certificate of analysis	12.76
Precipitation of SiO_2 (*1*)[a]	12.51
Precipitation of SiO_2 by cation exchange (*2*)[a]	12.44
Extraction (*10*)[a]	12.72
Mixed bed ion exchange	12.70

[a] Denotes literature reference.

Table VI. Analysis of Synthetic Steel Samples

Wt. of Steel, Gram	Mg. As Added as AsO_3^{---}	Mg. P Added as KH_2PO_4	Mg. B Added as H_3BO_3	Mg. B Found
0.2538	...	...	0.983	0.94[a]
0.2538	...	...	0.983	0.97
0.2538	...	...	0.983	0.97
0.2538	5	5	0.983	0.97
0.2538	5	5	0.983	1.00
0.2538	10	10	9.83	9.83[a]

[a] Results obtained on 100- to 250-ml. aliquots of effluent.

The average blank correction applied is not exactly correct, in that the ratio of silica to boron varies from blank to sample, and the same blank was applied to all weights of sample. However the magnitude of this variation is about the same as the probable error in the determination of the blank. The precision obtained with varied weights of sample indicated that this assumption is reasonable.

The addition of the carbonate melt to the resin in the separatory funnel was necessary so that the solution could be neutralized, and carbon dioxide evolved, before the sample was admitted to the column. This prevented complete disruption of the resin bed by the formation of large amounts of carbon dioxide in the column. Such action results in a relatively slow neutralization of the carbonate by the resin and closely approximates a homogeneous precipitation of the silica, thereby reducing possible loss of boron by coprecipitation.

Some boron is lost, as is indicated by the silica blank data. By correcting for this loss, good agreement was reached with the value of 12.76% boron oxide given by the National Bureau of Standards (Table IV).

Colloidal silica appeared in the effluent, but caused no interference in the potentiometric titration. Some difficulty was encountered due to the accumulation of silica on the top of the resin bed, but was easily overcome by occasional stirring of the upper few milliliters of the resin.

Results obtained with the procedure are reproducible and should provide accuracy to at least ±0.10 mg. of boron for glass samples.

The other methods of separation which have been applied to the analysis of National Bureau of Standards glass No. 93 include methylborate distillation, precipitation of interferences, cation exchange, and liquid-liquid extraction. Comparative data are given in Table V.

The mixed bed ion exchange procedure appears to give satisfactory results with less manipulative skill and time consumption than many of the other published methods. A single analysis can be performed in approximately 3 hours after the solution of the sample, and the analyst's attention is only required for approximately half of this time.

PROCEDURE B. ANALYSIS OF SYNTHETIC STEELS. Synthetic standards were prepared using National Bureau of Standards steel 55a; 6.3444 grams were dissolved in 80 ml. of 1 to 1 hydrochloric acid with gentle heating. Two milliliters of 30% hydrogen peroxide were added after the steel had dissolved, to destroy carbonaceous material. The solution was boiled for 10 minutes, cooled, and diluted to 250 ml. Known amounts of boric acid and interferences were added to 10-ml. aliquots (which contained 0.2538 gram of steel). These samples were passed through approximately 50 ml. of the mixed resin at a flow rate of 2.5 ml. per minute. The column was rinsed with distilled water at the same rate until 250 ml. of effluent were collected. Either an aliquot or the entire sample was analyzed for boron by the titrimetric procedure mentioned above. The results are given in Table VI.

All results obtained were within the experimental error of the titration step. The same results might be expected with the cation exchange method, if the samples do not contain phosphorus or arsenic.

Colorimetric Determination of Boron. Attempts were made to employ various colorimetric methods to the determination of the boron content of the effluent from the mixed bed ion exchange columns. The results were somewhat high, and the method cannot be recommended at the present time for the determination of microgram quantities of boron. The magnitude of the error, averaging about plus 3 to 5 γ of boron on samples containing 21 γ, indicates that the recovery of boron is quantitative to well within the accuracy which might be expected of a titrimetric procedure.

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Quantitative Determination of Organic Nitrogen in Water, Sewage, and Industrial Wastes

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▶A modified Kjeldahl method gives 98.4% recovery of organic nitrogen with a standard deviation from the average of 0.235%. Such recovery is 7% higher than that obtained with the copper oxide–Kjeldahl method. The method is simpler to perform, requires less time, is more precise and accurate than other methods; it can handle the usual interfering substances, carbohydrates and lipides. Ammonia can be separated and recovered from organic nitrogen. No appreciable loss of organic nitrogen results from the presence of nitrates and nitrites.

SULFURIC acid with various catalysts will digest organic material and convert nitrogen to ammonium acid sulfate. After ammonia is made alkaline and distilled, it is collected in either boric or sulfuric acid and titrated.

The selection of a proper catalyst for the Kjeldahl method has been the subject of many investigations and reports. Willits, Ogg, and coworkers (*3, 5, 6*) have shown that mercury is much superior to copper, and they have also condemned the use of selenium as a catalyst (*3, 4*). These authors, as well as McKenzie and Wallace (*2*), have conclusively shown that the mercury catalyst, concentration of potassium sulfate, temperature, and time of digestion are the important factors. McKenzie and Wallace have proposed a method for the microdetermination of organic nitrogen that gives excellent results with a much shorter digestion time than is required by present methods.

The following data are presented to determine the feasibility of a new method for the determination of organic nitrogen in routine analysis of water, sewage, and industrial wastes.

REAGENTS AND EQUIPMENT

Sulfuric acid, analytical reagent grade, 36N.

Potassium sulfate, analytical reagent grade.

Mercuric sulfate solution. Dissolve 8 grams of red mercuric oxide and dilute to 100 ml. with 6N sulfuric acid.

Mixed indicator. Mix two volumes of 0.2% methyl red in 95% ethyl alcohol with one volume of 0.2% methylene blue in 95% ethyl alcohol.

Indicating boric acid. Dilute 20 grams of boric acid and 10 ml. of mixed indicator to 1000 ml. with ammonia-free distilled water.

Potassium acid iodate solution, 0.02N, 0.7998 gram of potassium acid iodate (analytical reagent grade) per 1000 ml. of solution.

Standard amino acid solution. Dissolve 0.5365 gram of glycine, 0.8368 gram of DL-valine, 0.5365 gram of DL-alanine, and 0.7295 gram of 1-tryptophan in 500 ml. of ammonia-free distilled water. Dissolve 0.8583 gram of 1-cystine in 50 ml. of 0.1N sodium hydroxide. Mix the two solutions and dilute to 1 liter. This standard nitrogen solution contains 0.5 mg. of nitrogen per ml.

Sulfuric acid solution, 0.02N, 1 ml. = 0.2802 mg. of nitrogen.

Copper sulfate solution, 10% by weight of copper sulfate, analytical reagent grade.

Sodium hydroxide–sodium thiosulfate solution. Dissolve 500 grams of sodium hydroxide and 25 grams of sodium thiosulfate pentahydrate in distilled water and dilute to 1 liter.

Sulfuric acid–mercuric sulfate–potassium sulfate solution. Dissolve 125 grams of potassium sulfate in 800 ml. of distilled water and 400 ml. of 36N sulfuric acid. Add 50 ml. of mercuric sulfate solution and dilute to 2000 ml.

Sodium hydroxide solution. Dilute 500 grams of sodium hydroxide, analytical reagent grade, to 1 liter.

Phosphate buffer solution, 0.5M. Dilute 14.3 grams of monobasic potassium phosphate, (analytical reagent grade) and 68.8 grams of dibasic potassium phosphate (analytical reagent grade) to 1 liter with distilled water.

Standard ammonium chloride solution. Dilute 1.9107 grams of chemically pure ammonium chloride to 1 liter. This solution contains 0.5 mg. nitrogen per ml.

A six-unit Precision macro-Kjeldahl apparatus was used for the Kjeldahl determinations. Titrations were performed using two 50-ml. Normax burets certified by the National Bureau of Standards.

EXPERIMENTAL PROCEDURES

McKenzie and Wallace Kjeldahl Method. Samples of the standard

Table I. Recovery Tests on Standard Amino Acid Solution,[a] McKenzie-Wallace Method

Potassium Acid Iodate Titrant[b]		Sulfuric Acid Titrant[c]	
Nitrogen recovered, %	Dev. from av.	Nitrogen recovered, %	Dev. from av.
98.40	0.07	96.96	1.17
98.80	0.33	97.20	0.93
99.36	0.89	98.40	0.27
98.00	0.47	99.84	1.71
99.52	1.05	99.28	1.15
99.36	0.89	100.16	1.03
98.16	0.31	95.04	3.09
98.96	1.51	Av. 98.13	1.33
98.80	0.33		
98.96	0.49		
98.08	0.39		
97.28	1.19		
Av. 98.47	0.66		

[a] 12.50 mg. nitrogen applied.

[b] Std. dev. $\sigma = \sqrt{\frac{\Sigma d^2}{n-1}} = \sqrt{\frac{7.315}{11}} = \sqrt{0.665} = 0.815.$

Accuracy = 98.47 ± 0.815%.

Std. dev. of av. $= \sigma\bar{x} = \frac{\sigma}{\sqrt{n}}, 98.47 \pm \frac{0.815}{\sqrt{12}} = 98.47 \pm 0.235\%.$

[c] Accuracy = 98.13 ± 1.68%; std. dev. of av. = 98.13 ± 0.63%.

Table II. Recovery Tests on Standard Amino Acid Solution[a]

Copper Oxide–Kjeldahl Method[b]		Modified Kjeldahl Method[c]	
Nitrogen recovered, %	Dev. from av.	Nitrogen recovered, %	Dev. from av.
91.84	0.71	98.16	0.57
93.44	2.31	97.76	0.97
90.72	0.41	99.28	0.55
88.48	2.65	99.28	0.55
93.04	1.91	98.88	0.15
91.20	0.07	96.48	2.25
91.68	0.55	98.64	0.09
90.08	1.05	98.64	0.09
89.44	1.69	99.36	0.63
91.36	0.23	99.84	0.11
Av. 91.13	1.16	99.20	0.47
		99.28	0.55
		Av. 98.73	0.582

[a] 12.50 mg. nitrogen added.
[b] Accuracy = 91.13 ± 1.53%; std. dev. of av. = 91.13 ± 0.484%.
[c] Accuracy = 98.73 ± 0.719%; std. dev. of av. = 98.73 ± 0.265%.

Table III. Comparison of Methods by Nitrogen Determination of Primary Effluent

Copper Oxide–Kjeldahl		Modified Kjeldahl	
Mg. nitrogen	Dev. from av.	Mg. nitrogen	Dev. from av.
6.674	0.034	6.882	0.003
6.596	0.044	6.881	0.002
6.599	0.041	6.862	0.017
6.637	0.003	6.874	0.005
6.550	0.010	6.893	0.014
6.781	0.141	6.885	0.006
Av. 6.640	0.0455	6.879	0.0078
7.358	0.240	7.565	0.047
6.672	0.046	7.468	0.050
7.146	0.028	7.497	0.021
7.295	0.177	7.543	0.025
Av. 7.118	0.123	7.518	0.036

Table IV. Nitrogen Recovery in Presence of Interfering Substances[a]

Primary Effluent, Mg. Nitrogen		Nitrogen Recovered,[c] %	Dev. from Av.
	+ added nitrogen[b]		
8.070	10.474	96.16	2.09
7.997	10.493	99.84	1.59
8.010	10.516	100.24	1.99
8.114	10.508	95.76	2.49
8.095	10.501	96.24	2.01
8.135	10.576	97.64	0.61
7.983	10.503	100.80	2.55
7.999	10.462	98.52	0.27
8.029	10.493	98.56	0.31
8.046	10.515	98.76	0.51
		Av. 98.25	1.44

[a] 0.5 gram each of sucrose and fat added.
[b] 2.50 mg. nitrogen added.
[c] Accuracy = 98.25 ± 1.776%; std. dev. of av. = 98.25 ± 0.571%.

Table V. Recovery of Ammonia in Presence of Organic Nitrogen[a]

Organic Nitrogen Recovered[b]		Ammonia Recovered[c]	
%	Dev. from av.	%	Dev. from av.
98.80	0.04	99.20	0.11
98.40	0.36	98.80	0.29
98.30	0.46	99.40	0.31
99.10	0.34	99.30	0.21
99.20	0.44	99.00	0.09
99.00	0.24	98.50	0.59
98.20	0.56	99.80	0.71
98.40	0.36	98.90	0.19
97.60	1.16	99.50	0.41
99.60	0.84	99.50	0.41
Av. 98.76	0.48	99.09	0.33

[a] 10 mg. each of organic nitrogen and ammonia added.
[b] Accuracy = 98.76 ± 0.596%; std. dev. of av. = 98.76 ± 0.179%.
[c] Accuracy = 99.09 ± 0.404%; std. dev. of av. = 99.09 ± 0.121%.

amino acid solution were diluted to 250 ml. with ammonia-free distilled water in 650-ml. Kjeldahl flasks. One milliliter of mercuric sulfate reagent, 5 grams of potassium sulfate, and 10 ml. of 36N sulfuric acid were added to each flask. These samples were digested for 20 to 30 minutes beyond the fuming point, along with a reagent blank for each run. After digestion, 250 ml. of ammonia-free distilled water and 50 ml. of sodium hydroxide–sodium thiosulfate reagent were added to the samples, which were then distilled into 50.0 ml. of indicating boric acid solution. Two hundred-milliliter aliquots were collected and titrated with 0.02N potassium iodate solution to a lilac end point.

Samples of the standard amino acid solution were treated as above, except that the distillates were titrated with 0.02N sulfuric acid. Results are shown in Table I.

Copper Oxide–Kjeldahl Method (*1*). Samples of the standard amino acid solution were again diluted to 250 ml. with ammonia-free distilled water; 10 ml. of 36N sulfuric acid and 1 ml. of copper sulfate reagent were added. These samples were then digested for 30 minutes beyond the fuming point. After the addition of 25 ml. of sodium hydroxide solution and boiling saddles, they were distilled into indicating boric acid solution. The distillates were titrated with 0.02N sulfuric acid. Results are shown in Table II.

Modified Kjeldahl–Mercuric Sulfate Method. Samples of the standard amino acid solution were diluted to 200 ml. and to each was added 50 ml. of the sulfuric acid–mercuric sulfate–potassium sulfate solution. These samples were digested for 20 minutes beyond the fuming point. After the addition of 50 ml. of the sodium hydroxide–sodium thiosulfate solution, the samples were distilled into 50.0 ml. of the indicating boric acid solution. The distillate was titrated with 0.02N sulfuric acid. These results are also shown in Table II.

Nitrogen determinations for samples of sewage primary effluent were run by the modified method and on aliquots of the same primary effluent samples using the copper oxide–Kjeldahl method (Table III).

To determine whether carbohydrates and lipides normally present in small quantities in sewage will interfere with the modified Kjeldahl method, nitrogen determinations were made on 20 samples of primary effluent. Nothing was added to 10 of the samples. To the other 10 samples were added 5 ml. of the standard amino acid solution, 0.5 gram of sucrose, 0.5 gram of Swift shortening, and 50 ml. of the sulfuric acid–mercuric sulfate–potassium sulfate reagent along with 10 ml. of 36N sulfuric acid. All samples were examined in the usual manner. Results are shown in Table IV.

Free ammonia was determined by adding 20 ml. of standard ammonium chloride solution to 200 ml. of ammonia-free distilled water. Twenty milliliters of standard amino acid solution, previously neutralized with 1N sulfuric acid, were also added. The resulting solution was adjusted to pH 7.4 with 0.1N sodium hydroxide, and 25 ml. of phosphate buffer were added. The ammonia was distilled, collected, and titrated with 0.02N sulfuric acid. After removal of the free ammonia, organic nitrogen was determined (Table V).

The interference of nitrates with the Kjeldahl method was investigated by adding 5 p.p.m. of nitrate to samples of the standard amino acid. Ten milliliters of ethyl alcohol were added to five samples, and the rest were used as

Table VI. Recovery of Organic Nitrogen in Presence of Nitrates

Ethyl Alcohol Added, Ml.	Organic Nitrogen Recovered, %
0	98.35
	98.02
	99.34
	97.80
	98.02
5	99.04
	97.95
	99.36
	98.74
	98.94

controls. Results are shown in Table VI.

RESULTS AND CONCLUSIONS

An average of 98.47% recovery of nitrogen was obtained with the modified method. Recovery tests from amino acids are not entirely satisfactory because samples of 100% purity are difficult to obtain and the hygroscopic properties of these compounds are marked.

Although the expanded McKenzie-Wallace micromethod gives slightly more precise results than other methods tested, the ease and simplicity of a procedure in routine work must be considered. The potassium acid iodate solution can be made more accurately than sulfuric acid, but the high purity is expensive. Sulfuric acid can be standardized against reagent grade sodium carbonate and stored for several years without appreciable change in normality. Although high purity of reagents is desirable, it is not mandatory if reagent blanks are examined along with the samples.

The mixed indicator usually gives a much sharper end point than methyl red alone. The boric acid solution used to absorb the ammonia is about 0.05M so that the pH at the end point is well within the range of the mixed indicator.

The modified Kjeldahl method, using sulfuric acid in place of potassium acid iodate, is preferred by the authors over other methods. The usual interferences in this method cause a pyrolytic loss of nitrogen due to the high acid-salt ratio which results. To determine to what extent this occurred, samples of primary effluent were examined in comparison with duplicate samples to which had been added sucrose, fat, and amino acid nitrogen. Results given in Table IV indicate that with excess sulfuric acid added there is not enough interference to be significant. There is, however, a greater spread in the per cent recovery, partially because it was calculated on the relatively small quantity of amino acid nitrogen that was added to the primary effluent. The modified Kjeldahl method has further merit in that there is no bumping during distillation. This permits the solution to be distilled at a faster rate.

The effect of nitrates in concentrations usually found in water and sewage on the determination of organic nitrogen was insignificant. Less than 0.5% loss resulted.

The modified Kjeldahl–mercuric sulfate method has been successfully used in the Sanitary Engineering Research Laboratory of the University of Florida as a routine procedure for 11 months.

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Automatic Recording Thermobalance

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▶ An automatic recording thermobalance was constructed from standard laboratory equipment at a minimum of expense, to plot pyrolysis curves. The unbalance is detected by a photoelectric null-point detector and is restored by an electromagnetic restoring device. The balance recorded weight changes over the ranges of 50, 100, and 200 mg. with an accuracy within ±0.3, ±0.4, and ±0.8 mg., respectively. The sensitivity was 0.3 mg. The balance required 10 minutes to register a full range weight change. Construction details and a discussion of the thermobalance are given.

A THERMOBALANCE measures the changes in weight of a substance as it is heated. Several systems for automatically recording changes in weight have been described (*2*).

Duval has shown (*1*) how the curves of weight *vs.* temperature (pyrolysis curves) can be used to study the composition of many substances. Because the recording thermobalance used by Duval was not commercially available at the time of this work, an automatic recording thermobalance was constructed from standard laboratory equipment at a minimum expense. Weight changes were detected by a photoelectric cell and measured with an electromagnetic restoring device. The temperature of the furnace, surrounding the material being studied, was increased linearly with time and the weight was plotted as a function of time. The resulting curves of weight *vs.* temperature were used to study the composition of hydrated aluminum oxide samples. This report presents the construction details and a discussion of this thermobalance.

The automatic recording thermobalance consists of four main systems:

1. The thermo system for holding and heating the sample.
2. The balance system for weighing the sample.
3. The automatic or control system to compensate the balance for changes of sample weight.
4. The recording system for recording the force needed to compensate the balance, and thus the weight change of the sample.

The complete apparatus is shown in Figures 1, 2, and 3.

THERMO SYSTEM

The thermo system (Figure 4) consists of a vertically mounted electric tube furnace, a quartz rod which supports the sample within the furnace,

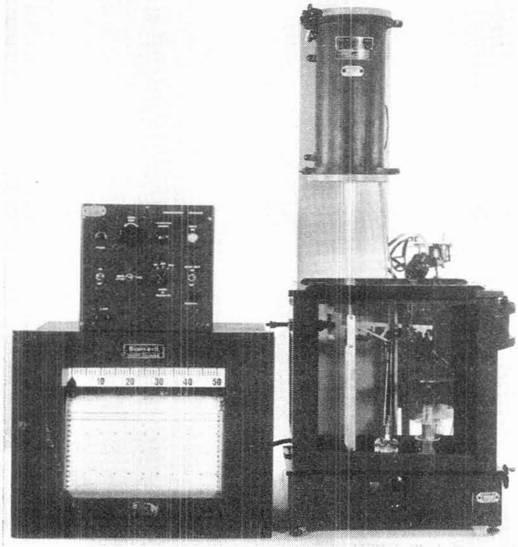

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Figure 1. Thermobalance

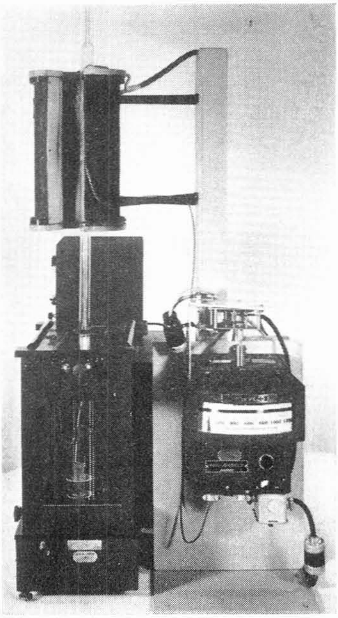


Figure 2. Side view of thermobalance

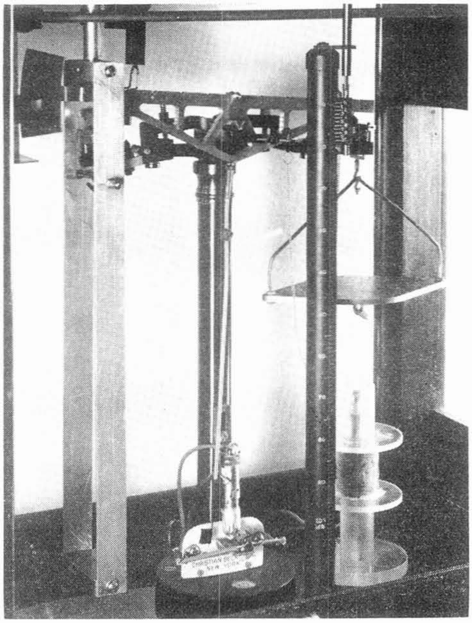


Figure 3. Balance modifications

and a controller for controlling the temperature of the furnace.

A Wheelco 0° to 1200° C. temperature controller (Wheelco Instruments Co., Chicago, Ill.), with a one-revolution-per-day clock motor driving the set point, was used to increase the temperature of the furnace at a constant rate. A limit switch on the controller shuts off the power to the power outlets and thus the entire apparatus when the heating cycle is completed.

BALANCE SYSTEM

The balance system (Figures 3 and 5) consists of a modified analytical balance. The hot convection currents from the furnace are kept out of the balance by placing the balance below the furnace. This arrangement is the same as that used by Duval.

The quartz rod, upon which the sample is placed in the furnace, is supported by a yoke and counterbalance (Figure 6). The sample carrier is suspended from beneath the left knife-edge of the balance in place of the balance pan. The quartz sample rod extends up through a hole cut in the balance case and into the furnace. The right balance pan is replaced by a short brass pan, beneath which is suspended a bar magnet (Figure 7). The weight of the pan is adjusted to counterbalance the sample carrier on the other side of the balance. The sample carrier, counterbalance, and magnet load the balance to about half capacity, permitting a maximum sample of about 100 grams.

The bar magnet is suspended within a hollow "work" coil. The action of the coil upon the magnet is used to return the balance to its original null position following a change in weight of the sample.

Deflection of the balance pointer is detected by a photoelectric cell arrangement (Figure 8). A black paper flag is glued to the balance pointer. A 6-volt lamp and a cadmium sulfide miniature photocell are arranged on opposite sides of the flag. The lamp is masked with aluminum foil and the front of the photocell is masked with black tape. A narrow slit is cut in each mask so that a narrow beam of light strikes the photocell slit when the pointer flag is

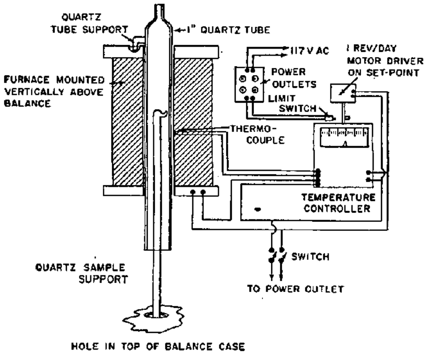


Figure 4. Thermo system

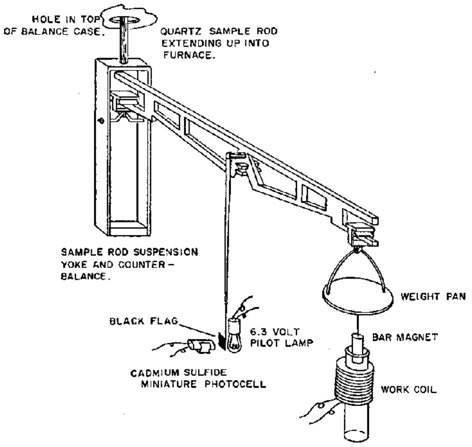


Figure 5. Balance modifications

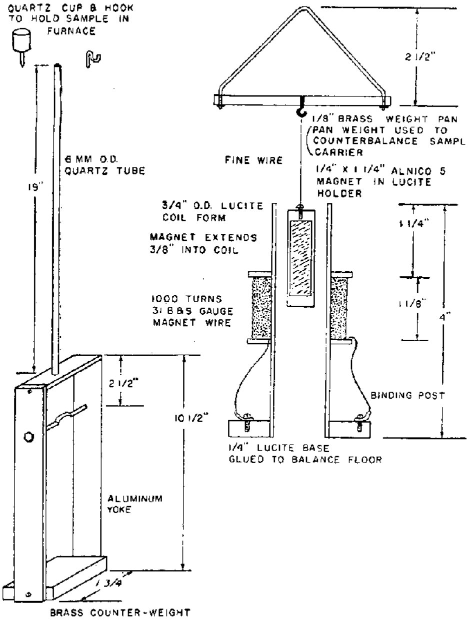


Figure 6. Sample carrier

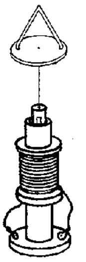


Figure 7. Weigh pan and magnetic balancer

not interposed. A state of balance is indicated when the flag interrupts the light beam to the photocell sufficiently to open a relay in the control system.

AUTOMATIC CONTROL SYSTEM

The automatic or control system is shown above the recorder in Figure 1 and a schematic diagram is given in Figure 9. The control system responds to a signal from the photocell (indicating a decrease in sample weight) by increasing the current in the work coil to compensate for the decrease in weight. An output signal, proportional to the amount of compensation and thus to the change in weight, is fed from the control unit to the recording system. The values and dimensions given are for three operating ranges: 50-, 100-, and 200-mg. weight change (corresponding to positions *A*, *B*, and *C*, respectively, of switch SW_1 in Figure 9).

A 1-r.p.m. clock motor, *M*, is connected by a rubber belt to the 1000-ohm, 10-turn Helipot, R_{10}. The belt must fit loosely to allow manual resetting of the Helipot. The 10,000-ohm relay, L_3, is operated by a thyratron, V_3, connected to the photocell, Cl_1. Potentiometer R_{11} adjusts the sensitivity of the relay circuit. The ganged rotary switch, SW_1-SW_2, is used to select the range of operation. The 200-ohm Helipot, R_8, is a calibration adjustment. The photocell, Cl_1, source lamp, W_2, and work coil, L_2, are the components located in the balance case and are connected to the control unit by a multiconductor cable.

The control system performs as follows:

A loss of sample weight causes the balance pointer to be deflected from between lamp W_2 and photocell Cl_1.

The increased light striking Cl_1 increases the current through it.

The increased current in Cl_1 causes thyratron V_3 to become conductive.

Current through V_3 energizes relay L_3, closing contacts SW_5 and SW_6.

Clock motor *M* turns the 1000-ohm potentiometer, R_{10}, increasing the current to the work coil, L_2.

With increasing current, the repulsion between L_2 and the bar magnet suspended within it reduces the effective weight of the magnet and the balance returns to the null position.

When the balance has returned to the null position, the flag on the pointer again reduces the amount of light entering CL_1, reducing the current to V_3, which then becomes nonconducting. Relay L_3 is de-energized, preventing any further increase in current in L_2.

The current in the work coil is measured by the recording system in terms of the voltage drop across R_8 and R_5, R_6, or R_7.

A critically damped balance and a rate of coil current increase that is slower than the balance response are necessary to prevent overshooting of the null position. Overdamping of the balance slows its response, while underdamping causes overshooting of the null position.

RECORDING SYSTEM

A standard chart-type 0- to 50-mv. potentiometer recorder (Brown ElectroniK, Minneapolis-Honeywell Regulator Co., Philadelphia, Pa.) is used to record the output signal from the control system. An output signal of 0 to 50 mv. is obtained for each operating range: 0 to 50, 0 to 100, and 0 to 200 mg. The recorder has a linear scale in units of milligrams.

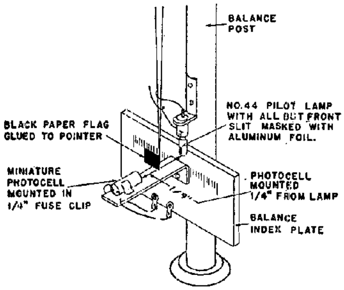


Figure 8. Photoelectric cell

When the balance is fully returned to null position, following a loss of sample weight, the force acting between the bar magnet and the work coil must be equal to the weight loss of the sample. For a magnet of given strength at a given point in a given coil the force is

$$F = k_1 I = W$$

where

W = weight loss
F = force
I = current in the coil
k_1 = constant of proportionality

The current through the range resistor (R_5, R_6, or R_7) and the calibration adjustment, R_8, is equal to I, and the voltage drop across this resistance (the output signal) is given by Ohm's law

$$V = IR$$

where V = voltage drop
R = resistance

or because R is fixed for any given range,

$$V = k_2 I$$

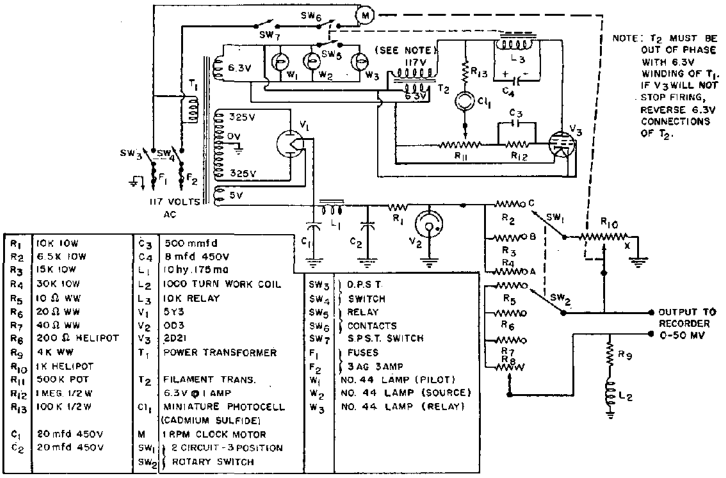
where k_2 = constant.

Combining this equation with the force equation, we obtain

$$V = \frac{k_2}{k_1} W = KW$$

where K = constant.

Therefore the deflection of the recorder pen is directly proportional to the weight loss of the sample.



R_1	10K 10W	C_3	500 mmfd	SW_3	D.P.S.T.
R_2	6.5K 10W	C_4	8 mfd 450V	SW_4	SWITCH
R_3	15K 10W	L_1	10 hy .175 ma	SW_5	RELAY
R_4	30K 10W	L_2	1000 TURN WORK COIL	SW_6	CONTACTS
R_5	10 Ω WW	L_3	10K RELAY	SW_7	S.P.S.T. SWITCH
R_6	20 Ω WW	V_1	5Y3	F_1	FUSES
R_7	40 Ω WW	V_2	OD3	F_2	3 AG 3 AMP
R_8	200 Ω HELIPOT	V_3	2D21	W_1	NO. 44 LAMP (PILOT)
R_9	4K WW	T_1	POWER TRANSFORMER	W_2	NO. 44 LAMP (SOURCE)
R_{10}	1K HELIPOT			W_3	NO. 44 LAMP (RELAY)
R_{11}	500K POT	T_2	FILAMENT TRANS.		
R_{12}	1 MEG. 1/2 W		6.3V @ 1 AMP		
R_{13}	100K 1/2 W	Cl_1	MINIATURE PHOTOCELL (CADMIUM SULFIDE)		
C_1	20 mfd 450V	M	1 RPM CLOCK MOTOR		
C_2	20 mfd 450V	SW_1 SW_2	2 CIRCUIT - 3 POSITION ROTARY SWITCH		

Figure 9. Control unit

Because the recorder chart is driven at a constant speed and the furnace temperature increases at a constant rate, the distance the chart has traveled is proportional to the change of temperature. With the equipment used, the temperature changed from 20° to 600° C. in 14 hours and 20 minutes and the recorder chart speed was 2 inches per hour. An inch on the chart therefore corresponded to 19.8° C.

CALIBRATION AND OPERATION

The thermobalance is calibrated in the following manner:

The recorder and control system are turned on. The furnace and controller are off.

With the 1000-ohm Helipot, R_{10}, set at zero coil current (position X in Figure 9) and with SW_7 open, the desired operating range—50 mg., for example—is selected on the range switch, SW_1-SW_2.

With the pointer flag deflected from between the light source, W_2, and Cl_1, the sensitivity is adjusted with R_{11} to where lamp W_3 is on (indicating that relay contacts SW_5-SW_6 are closed).

The balance is adjusted by means of weights and rider (or chain) until the pointer flag sufficiently reduces the light beam to the photocell to just turn off W_3 (indicating relay contacts SW_5-SW_6 are open).

A weight corresponding to the desired range (50 mg.) is added to the weight pan and SW_7 is closed.

When the balance is fully returned to the null position and W_3 is again off, the calibration adjustment, R_8, is adjusted to give a reading on the recorder of the added weight (50 mg. in this case).

The balance is now calibrated for the desired operating range and no further calibration is necessary unless the range is changed. It is, however, desirable to check the calibration occasionally.

When a sample is placed on the sample rod in the furnace, the balance must be adjusted by means of weights until W_3 is off (with SW_7 open and R_{10} set at zero current). SW_7 is then closed and the furnace is turned on. The operation then proceeds automatically until the entire unit is shut off by the limit switch on the temperature controller.

THERMOBALANCE CHARACTERISTICS

The thermobalance described in this report has a sensitivity of 0.3 mg. and is accurate to ±0.3, ±0.4, and ±0.8 mg. on the 50-, 100-, and 200-mg. range, respectively. It requires 10 minutes to record a full range weight change.

The thermobalance used by Duval (*1*) measured the displacement of the balance to obtain the change in weight of the sample, but the authors preferred to measure the force necessary to return the balance to the null position. Because the balance and the recorder are both null-type instruments, this thermobalance has a constant sensitivity and is not affected by changes in the line voltage.

For stability, the only components that must remain constant are the magnet, work coil, and range resistors. Use of an Alnico 5 magnet, a rigid work coil, and wire-wound resistors gives a very stable system.

The force between the coil and magnet must be repulsion rather than attraction in order to obtain stable operation. When the magnet is repelled by the coil, an equilibrium position exists. Any displacement from the equilibrium position increases or decreases the force in a manner which returns the magnet to the equilibrium position. The control system alters the current in the coil, to bring the equilibrium position into coincidence with the original null position. If an attractive force exists between the coil and magnet, no equilibrium position exists, as any motion of the magnet brings it into a field that acts to increase the displacement.

The repulsive force must be small compared to the weight of the magnet in order to keep the suspended magnet centered in the coil. If the force is large, the magnet will "cock" with the coil. Fastening the magnet rigidly to the balance beam would solve this alignment problem and permit much larger forces and, consequently, larger changes of weight.

This thermobalance was designed to follow weight loss only. Weight increases, as well as decreases, could be followed with the balance by the use of a reversible motor drive on the potentiometer. The motor-driven potentiometer would merely be reversed by the action of the light beam on the photocell. The current in the work coil would then be constantly changing and a small oscillation to either side of the rest point would be recorded.

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Automatic Recording Balance

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▶This automatic recording balance, designed and constructed for use in thermogravimetric and related studies, is an electronically controlled null-point instrument using a linear variable differential transformer as the sensing element. No closely regulated voltage sources or batteries are required for the automatic balance or weight recording. The recording circuit is a servo-system requiring no recalibration. Data obtained with this instrument, when correlated with differential thermal analysis and high temperature x-ray data, are useful in deducing the nature of solid state reactions.

SEVERAL investigators have constructed automatic balances to follow weight changes in thermogravimetric and other studies and have used a considerable variety of methods. Most of the automatic balances are equipped to record weight changes photographically or by pen and ink. A treatise on thermogravimetric analysis has been prepared by Duval (*5*).

In general, the balances may be classed in two principal groups: those which measure the deflection of the balance caused by a change in sample weight (*1, 3, 4*) and those which operate at or near the null point by exerting a force (*2, 13*) or at the null point by adding or removing weight (*6, 8–10*). The sensing elements in either case are usually optical or electronic. One type of sensing element, used in at least two deflection-measuring balances (*3, 12*) is the linear variable differential transformer. This device consists of a hollow cylinder on which are wound three coils, a primary and two secondary windings. When the magnetic permeability within the cylinder is symmetric about a mid-point, an alternating current in the primary induces alternating currents in the secondaries, which are equal in magnitude but out of phase by 180°. When a permeable core is introduced into the cylinder so that it is symmetric with respect to the midpoint of the cylinder, no voltage difference is detectable at the secondary terminals. If, however, the core is moved along the axis of the cylinder, the induced alternating current in one of the secondaries exceeds that in the other. This unbalance signal may be measured or used to effect a return to a control point. As the secondary voltages are 180° out of phase, the unbalance signal may be used to indicate direction as well as degree of displacement. In the work cited (*3, 12*) the output from the transformer was taken as a measure of the weight.

DESIGN OF AUTOMATIC BALANCE

The automatic recording balance described is designed to operate at null balance—i.e., any deflection of the balance caused by a gain or loss in weight is detected and the balance chain is moved automatically, so that more or less of its weight is supported by the balance beam. The position of the chain is continuously recorded on a strip-chart recording potentiometer.

The balance assembly includes an analytical balance, a linear variable differential transformer, an amplifier and motor, and a gear assembly fitted with a slip clutch (Figure 1). The linear variable differential transformer is supported from the center post of the balance, so that the core, suspended from the right-hand pan hook, is at the midpoint of the transformer when the balance is at the null point. The converter (chopper) of the amplifier was removed. The alternating current ordinarily used to drive the converter supplies the primary of the transformer. The signal from the secondary windings of the transformer is fed into the amplifier at the converter socket. The 27-r.p.m. motor associated with the amplifier is connected, through a 200 to 1 reduction worm gear and a slip clutch, to a drum from which the balance chain is controlled. A magnetic damper prevents oscillation of the balance.

The voltage divider on the primary of the transformer is used to decrease the voltage input to a point at which solenoid action is not troublesome. The voltage divider on secondary No. 2 and the potentiometer on secondary No. 1 are added so that the outputs of the two secondaries can be matched (zero signal) when the balance is at the null point. This eliminates tedious mechanical adjustment of the core position.

Recording Circuit. To obtain a means of continuously recording the position of the balance chain, a precision potentiometer is driven by the same shaft that turns the balance chain drum. The drive mechanism is designed so that the potentiometer turns through 340 to 350° as the chain position is moved from 0 to 100 mg. The ordinary slide-wire of the recording potentiometer is disconnected. An auxiliary slide-wire, mounted on the same shaft, is supplied with the same potential that feeds the potentiometer on the balance. The difference signal taken from the moving contracts is fed into the recorder amplifier (Figure 2) so that the amplifier and motor drive the slide-wire until a zero difference signal is obtained. As the recorder pen is driven by the same shaft, a continuous pen-and-ink indication and record of the balance chain position are obtained. After the two potentiometers are properly matched in position and voltage

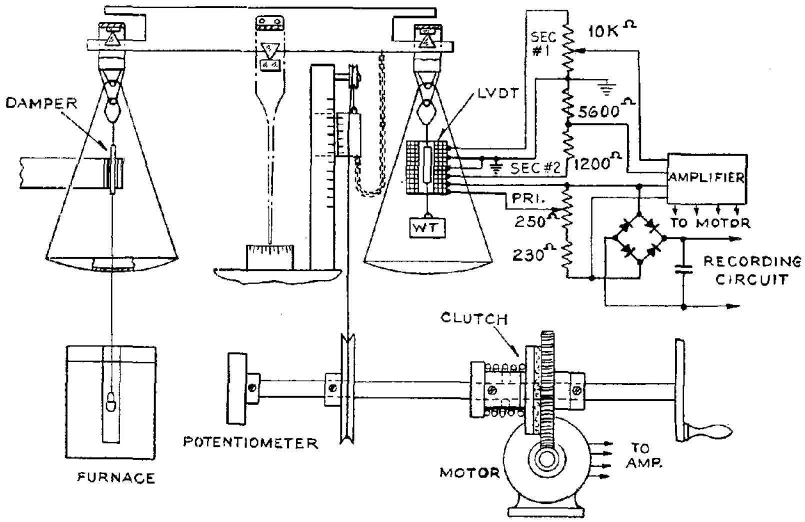

Figure 1. Outline drawing of automatic recording balance

The commercial parts listed are satisfactory:
LVDT, Schaevitz Engineering, Camden, N. J., Model 060S-L
Amplifier, Minneapolis Honeywell Regulator Co., Model 41-R-77-7, with motor 76750-3
Potentiometer, Helipot Division, Beckman Instruments, Inc., Model LR1KL15LT
Slide-wire (Figure 2), Leeds & Northrup Co., retransmitting slidewire, 5-inch, 1000-ohm, with contact
Slip clutch, Pic Design Corp., Lynbrook, L. I., N. Y., Model R3-3
Gear strain must be desired to fit the balance selected.

drops across the potentiometers are adjusted, no calibration is necessary.

Thermobalance. To use this automatic recording balance as a thermobalance (its principal use), the sample to be studied is suspended in a furnace by an articulate platinum wire hung from the magnetic damper (Figure 1). For temperatures above 700° C., some radiation shielding is desirable between the furnace and the balance.

GENERAL FEATURES

The balance is designed and is now used for weight changes up to 0.1000 gram. This is the range dictated by the design of the commercial balance—i.e., ordinary analytical balances are designed so that any weight of less than 0.1 gram is added by means of a chain, one end of which is suspended from the balance beam, the other from a movable support associated with a scale for reading the position of the chain. Repeated manual displacement of the chain position and observation of the position after automatic rebalancing show that the reproducibility of the automatic balance is within ±0.0001 gram.

The automatic recording balance was designed to provide an accuracy within ±0.0002 gram. The principal limitations on this accuracy are the potentiometer, the slide-wire, and the recorder. The potentiometer has a rated precision of not greater than 0.2% deviation from linearity. This deviation is its limitation, as it has over 1000 turns, each turn otherwise representing a maximum possible error of less than 0.0001 gram. Recording potentiometers are, in general, accurate to 0.25%, however, in this servo-system a much higher difference signal (per unit displacement) is available, so that the accuracy should be better. Repeated addition and removal of 0.0100-, 0.0200-, and 0.0500-gram weights to one or the other balance pan and observation of the pen position after automatic rebalancing indicate that the desired accuracy has been attained.

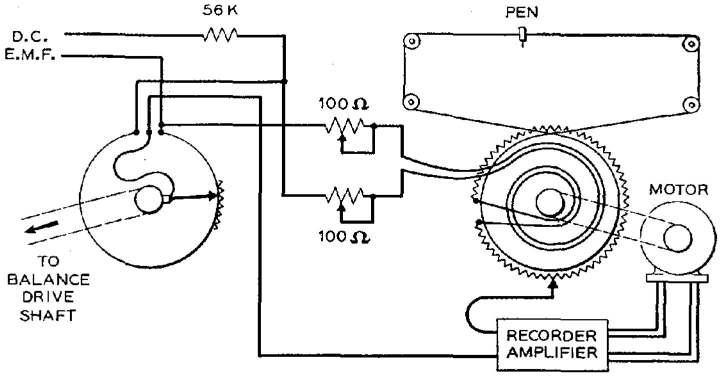

Figure 2. Recording circuit for balance

The fixed range of the apparatus is not normally a disadvantage. For nearly

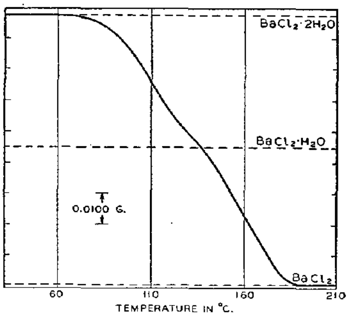

Figure 3. Thermal decomposition of barium chloride dihydrate

all purposes, the sample weight may be selected such that a change in weight of no more than 0.100 gram is expected. If, for some reason, the sample size is fixed, the range may be changed by changing the weight of the chain or the point of suspension on the beam. By either method, if the range is increased the limit of accuracy will be determined by the recording system accuracy—about 0.2%. If the range is decreased, the limit of accuracy will be that of the balance—about 0.0001 gram.

A Leeds & Northrup two-pen recorder associated with a differential thermal analysis apparatus (*7*) is used with this balance. The controls associated with the same apparatus program the heating and cooling of the furnace. Heating rates of 10°, 6°, and 0.5° C. per minute may be used with a temperature range of 0° to 1500° C. to give a continuous record of temperature as well as weight. The furnace is a platinum-wound vertical furnace fitted with a water jacket for controlled or rapid cooling. It is designed to dissipate about 1800 watts at 1500° C.

The four adjustable potentiometers are of the screw-driver-adjust type to avoid accidental displacement after the proper settings have been found.

OPERATION OF BALANCE

To use the apparatus as a thermogravimetric balance, the sample is placed in the platinum sample cup and weighed, the final portion of the weighing being done automatically, and weights are added to the left-hand pan to bring the chain near the end of the scale. The recorder-controller is then turned on and the controller set for the desired heating rate and temperature limit. The temperature-measuring circuit is standardized and the heating cycle started. When the furnace has reached the desired temperature limit, the system is switched off, the balance beam is locked, the strip chart recording is removed from the recorder, and the weight loss is noted at the temperatures of interest.

EXPERIMENTAL RESULTS

A few weight-loss studies were performed on known stable hydrates simply to test the apparatus. A typical record is shown in Figure 3. Barium chloride forms a crystalline dihydrate which is stable at room temperature. Upon heating, it loses this water of crystallization. This is not a rapid process, as the water within the crystal must diffuse to the surface or rupture the crystal in order to escape. The record shows the course of the dehydration as the furnace temperature is increased at the rate of 6° C. per minute. The inflection indicates that a monohydrate is formed. A similar effect was found by Orosco (*11*). The sample weighed 588.0 mg. The loss in weight on heating was 86.7 mg. The weight loss calculated from the formula weights is 86.8 mg.

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Adiabatic Calorimeter for Determination of Cryoscopic Data

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▶ A precision adiabatic calorimeter for determining cryoscopic data of compounds melting in the range −175° to +140° C. is described. Advantages of this apparatus include rugged construction with high precision and moderate operating time. The melting point, heat of fusion, and cryoscopic constants of phenol, 3,5-xylenol, p-α-cumylphenol, quinoline, 2,4,6-collidine, ε-caprolactam, maleic anhydride, di-α-cumyl peroxide, and naphthalene are presented. Data on the Raoult's law behavior of systems involving these compounds and probable impurities permit sound routine evaluation of purity when the impurities follow Raoult's law.

Melting point, heat of fusion, and cryoscopic constants are primarily used for establishing the purity of spectroscopic standards. These quantities are absolute physical constants and depend only on the accuracy of the experimental measurement.

The theory and application of calorimetry for the absolute determination of purity were originally reported by Johnston and Giauque (*5*). Other workers have applied this method to systems where the impurity is liquid-soluble and solid-insoluble (*2, 8–10*). Detection of a liquid-soluble, solid-soluble impurity has been described (*1, 8*) and recently a method of treating calorimetric data when a dilute impurity forms solid solutions with the major component has been developed (*7*).

This paper describes an adiabatic calorimeter that operates in the temperature range from −175° to +140° C. It has been in continuous operation for over 2 years, so apparently this apparatus is more rugged and versatile than the usual high precision calorimeter. The precision is sufficient to justify its use for determining the necessary fundamental properties of new compounds for the evaluation of their purity.

APPARATUS AND PROCEDURE

The design of this calorimeter (Figure 1) follows that of other precision adiabatic calorimeters (*2, 9, 10*). It was constructed from nickel parts soldered together with pure silver. It consisted of a nickel tube 2 inches long and 1.52 inches in inside diameter, machined to a wall thickness of 0.02 inch; the top and bottom were of 0.02-inch nickel sheet; a filling tube, 1, has an inside diameter of 0.25 inch, a wall thickness of 0.01 inch, and a length of 2.7 inches. The thermometer and heater wells, 4 and 5, were nickel tubes 0.235 inch in inside diameter, 1-$^9/_{16}$ inches long, with a wall thickness of $^1/_{32}$ inch, and closed on the inner end with 0.02-inch nickel sheet. Thirty 5-mil nickel conduction vanes, 3, perforated at random with $^1/_8$-inch holes and provided with one central and two radial $^1/_4$-inch holes (to slip over the thermometer and heater wells) were forced into the calorimeter with a die to obtain good thermal contact between the walls and the thermometer and heater wells. The vanes were separated by nickel spacer strips bent in a zigzag shape with the ends joined to form an irregular circle. A radiation cap, 8, ($^1/_{32}$-inch copper, 1.630 inches in inside diameter and 1 inch long) was fastened to the calorimeter by means of three studs, 7. It had a $^1/_8$-inch hole, 9, drilled on the cylindrical wall near the bottom which served as a lead exit. The exterior surfaces of the calorimeter, 2.7-inch length of filling tube, and radiation cap were electrolytically plated with gold. The total volume of the calorimeter plus 2.70 inches of the filling tube was 42.92 ml. The volume of the calorimeter alone was 40.75 ml.

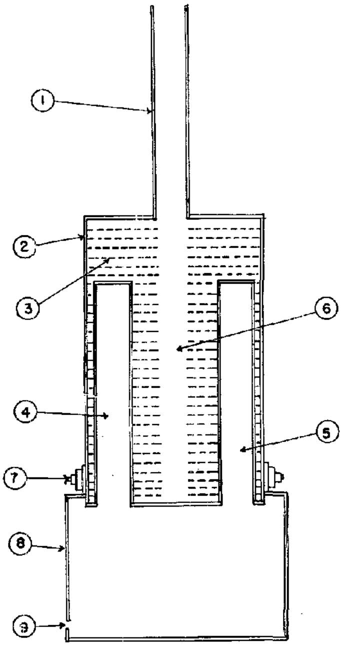

Figure 1. Calorimeter

1. Nickel filling tube
2. Nickel calorimeter
3. Randomly drilled nickel conduction vanes
4. Resistance heater well
5. Platinum resistance thermometer well
6. Central hole drilled in each vane for removal or introduction of sample with hypodermic syringe
7. Studs to fasten radiation shield
8. Copper radiation shield covering thermometer and heater
9. Lead exit for heater and thermometer

A Leeds & Northrup helium-filled, platinum resistance thermometer and a Leeds & Northrup Mueller bridge were used to measure temperature. The thermometer was held in the thermometer well of the calorimeter by soft solder. The four platinum leads from the thermometer were soldered to four Brown & Sharpe No. 36 double glass-covered wires. These leads passed through the $^1/_8$-inch hole, 9, in the radiation cap and were wound around the cap four times before terminating.

The calorimeter heater consisted of 49 ohms of B&S No. 36 glass-covered Manganin wire wrapped bifilarly on a 2-inch long, $^3/_{16}$-inch outside diameter copper tube. The ends of the Manganin heater wire were soldered to two short lengths of similar wire and wound further around the tube until about three turns of the copper lead wire were included in the windings. The heater wires were cemented onto the tube with silicone resin 98 (General Electric Co.). The heater leads were connected to two B&S No. 36 double glass-covered copper wires which passed through the lead exit hole, 9. The heater leads were wound four times around the radiation cap with the thermometer leads. These wires were cemented to the radiation shield with silicone resin. One of the two heater current leads was tapped near the radiation shield. The other heater current lead was tapped near the side shield. These taps serve as heater potential leads and automatically correct for leakage to the shield of 50% of the heat generated in the heater current leads. The seven leads coming from the radiation cap were approximately 3 inches long and had small copper lugs soldered to their ends.

Figure 2 is a schematic drawing of the shields and calorimeter assembly. The adiabatic shield, 3, was made in three parts, separately heated for better control. The side shield was a 4-inch long brass tube with an outside diameter of 2-$^3/_4$ inches and wall thickness of $^1/_{16}$ inch. Six spiral grooves were machined in the outside of the side shield. Lengths of B&S No. 36 double glass-covered copper lead wires which connected with all wires to the calorimeter (thermometer, heater, and difference thermocouples), were wound in these grooves and cemented with silicone resin. These lead wires entered the shield through copper conductors which were supported by mica washers mounted over holes in bottom of the side shield. Sauereisen cement was used for securing the mica washers and lead-in studs. The copper lead-in studs were connected to screw terminals inside the shield where junctions were made with the lugs on the leads from the calorimeter thermometer, heater, and difference thermocouples. The other ends of the lead wires (cemented in the grooves in the side shield) were soldered to mica terminal strips mounted on the outside of the side shield. The lead wires connecting the electrical components of the calorimeter to the outside were soldered to these mica terminal strips on the side shield.

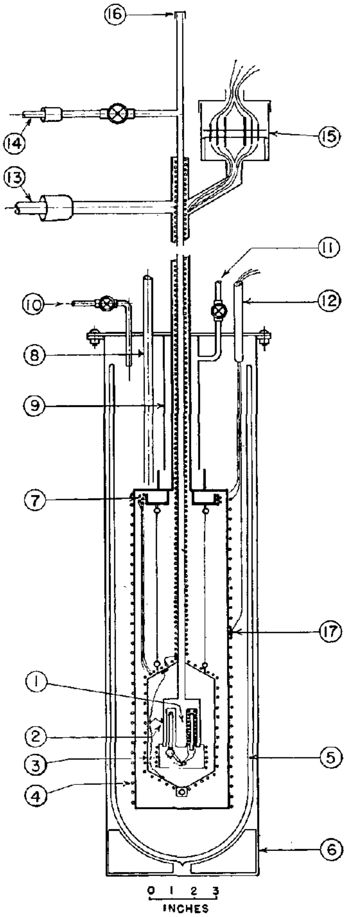

Figure 2. Calorimeter assembly

1. Calorimeter
2. Difference thermocouple (schematic)
3. Copper adiabatic shield
4. Cryostat can with heating element
5. Glass Dewar for liquid nitrogen refrigerant
6. Copper Dewar case
7. Copper ring having leads baked on with silicone resin to equilibrate them to temperature of cryostat can
8. Liquid refrigerant entrant tube
9. Jacket over cryostat pumping tube
10. Gas escape tube from Dewar case (safety vent)
11. Cold gas escape tube from pumping tube jacket
12. Heater and thermocouple exit tube from cryostat
13. Exit from cryostat pumping tube
14. Exit from calorimeter filling line
15. Calorimeter and shield lead exit cup
16. Nickel cap for calorimeter filling line
17. Cryostat can, copper-constantan thermocouple

All lead wires were wound around the copper equilibration ring, 7, before they emerged from the apparatus through the lead exit cup, 15.

The side shield heater consisted of 400 ohms of B&S No. 30 glass-covered Manganin wire, bifilarly wound over the lead wires in the grooves and cemented with silicone resin. The conical top and bottom shields were provided with heaters each consisting of 150 ohms of the Manganin wire, bifilarly wound and cemented onto the external surface.

Four copper-constantan difference thermocouples, 2, were provided for reading the differences in temperature between the calorimeter and side shield, between the side shield and the top and bottom shields, and between the filling tube and the top shield. The temperature difference between calorimeter and side shield was indicated continuously on a Leeds & Northrup H. S.-type galvanometer. A separate galvanometer was provided for reading the temperature differences between either the top or the bottom shield and the side shield, or between the top shield and the filling tube. The side shield was also provided with a thermocouple.

The filling tube, 14 and 16, had five heaters connected in series and tapped so that each heater could be used individually. The heaters consisted of approximately 35 ohms each of B&S No. 30 glass-covered Manganin wire. Difference thermocouples were provided to read the temperature differences between the top shield and the tube at the heater taps. The most frequently used couple was at the tube bottom. This difference thermocouple was read along with the top and bottom shield thermocouple during operation. A constantan lead was brought from the difference thermocouple to an ice bath for measurement of the temperature.

The cryostat can, 4, enclosed the calorimeter shield assembly and was made of $^1/_{16}$-inch copper. It was provided with a heater consisting of 70 ohms of B&S No. 30 glass-covered silicone impregnated copper wire wound bifilarly along its entire length. The lid of the cryostat can was made of Monel to facilitate soldering. It supported the copper lead equilibrating ring, 7, and the calorimeter shield assembly.

The cryostat can was placed inside of a glass Dewar flask, 5, which served to contain liquid nitrogen refrigerant for low-temperature operation, and to insulate the system for high-temperature operation. The glass Dewar, 5, was inserted in a large copper container, 6, for protection against mechanical injury. Liquid nitrogen refrigerant was introduced through tube 8. Exit tube 11 allowed cold nitrogen gas from the liquid nitrogen refrigerant to cool the cryostat pumping tube when all other exit tubes were closed. Exit tube 12 carried the leads for the cryostat can heater and thermocouple and was sealed with Apiezon wax.

Separate and independent control circuits for manual operation were provided for the side, top, and bottom shields and the tube heaters. The control circuits were supplied from a regulated 10-ampere direct current power supply. A three-position, double-pole, double-throw switch was used in each control circuit to turn the heater current on, or to increase the current by 10%. A coarse and fine rheostat provided a current variation from 0 to 500 ma. for each circuit.

Table I. Evaluation of Calorimeter Accuracy

n-Heptane	No. of Detns.	Av. Dev.[b]	Temp. Range, ° C.
Heat of fusion	3	±0.10%	......
Triple point	5	0.0004° C.	......
Purity	1	0.005 mole %	......
Heat capacity	16	±0.15%	−135 to −48
Benzoic acid[a]			
Heat of fusion	2	±0.13%	......
Triple point	4	0.003° C.	......
Heat capacity	11	±0.16%	26 to 115
	3	±0.29%	125 to 135

[a] Purity was not checked as sample reacted with nickel oxide present in calorimeters.

[b] Deviation from values reported by Calorimetry Conference for *n*-heptane and National Bureau of Standards (*3*) for benzoic acid.

The control circuit for the cryostat can heater was a voltage divider consisting of a series of electric light bulbs with taps for intermediate voltages. A 50-ohm, 300-watt potentiometer was placed in series with the cryostat can heater for fine control. By controlling the cryostat can temperature, it was always possible to operate the calorimeter at zero-temperature drift with the shields balanced. This method of operation appears to be superior to the method which utilizes an off-balanced shield to minimize the drift.

The calorimeter heater current was supplied by a stabilized bank of ten Edison cells. A four-pole, double-throw Leeds & Northrup thumb switch was used to turn off simultaneously the heater current and a Standard Electric timer (Model S.W.-1). A tuning, fork-type, frequency standard (American Time Products Co.) delivered 60-cycle alternating current to the timer which was accurate to 9 p.p.m. (based on a 3-day comparison with time signals broadcast by Station WWV, Washington, D. C.). The heater current was measured by the voltage drop across a 0.100000-ohm Leeds & Northrup standard resistor on a White double potentiometer. The heater potential was divided by a Leeds & Northrup No. 7591 volt box and also read on the White double potentiometer. A Leeds & Northrup Wenner potentiometer was used for thermocouple readings.

OPERATION

The operation of adiabatic calorimeters has been described in varying degrees of detail (*2*, *8*, *9*). The present apparatus was operated manually, requiring about 2 working days and two operators for the evaluation of one compound, plus 1 to 2 days for calculation.

Introduction and removal of the sample were relatively simple. Low-boiling samples were vacuum distilled into the apparatus. High-boiling liquids or high-melting solids were introduced with a 50-ml. hypodermic syringe (heated with an infrared lamp, if necessary) provided with a $^1/_8$-inch diameter nickel tube long enough to extend to the bottom of the calorimeter. The usual charge was about 30 grams of sample.

PERFORMANCE

The performance of this calorimeter and the operating procedure were tested by comparing the data on *n*-heptane and benzoic acid, Calorimetry Conference heat capacity standards. Table I compares the results obtained in the apparatus with published results. The heat capacity data of benzoic acid in the premelting region was calculated with no correction for the impurities which may be present, due to reaction of the benzoic acid with the calorimeter metal.

MATERIALS

PHENOL. U.S.P. phenol (Barrett Division, Allied Chemical & Dye Corp.) was fractionally distilled through a 25 mm. × 3 foot Podbielniak column, rejecting the initial 10% and the final 20% cuts. This sample was redistilled before using to remove traces of water.

3,5-XYLENOL, commercial grade, was purified by selective sulfonation (*6*) and final recrystallizations from a petroleum solvent.

p-α-CUMYLPHENOL. Prepared in the laboratory from phenol and α-methylstyrene in the presence of an acid catalyst, and purified by recrystallizations from heptane.

QUINOLINE. Refined quinoline (Barrett Division, Allied Chemical & Dye Corp.) was further purified by repeated precipitation of the phosphoric acid addition compound from methanol, followed by washing the crystallization mass three times with methanol after filtration, drying at 55° C. (overnight), and liberating the final quinoline with aqueous sodium hydroxide. The wet quinoline was distilled, with rejection of the 10% forecut and 20% final cut, to remove water. The sample used for the calorimetric determination was vacuum distilled to remove last traces of water.

ε-CAPROLACTAM. The ε-caprolactam (Lot 106, CF 298), obtained from the National Aniline Division, Allied Chemical & Dye Corp., was treated with Molecular Sieve, 4A pellets (Linde Air Products Co.) to remove water before using.

2,4,6-COLLIDINE. Commercial grade was fractionally distilled through a 25 mm. × 3 ft. Podbielniak column; the heart cut of this distillation was used for the sample. This material was distilled three times, with rejection of 5 to 10% of fore- and aftercuts, to remove water. The final three distillations and operations necessary for transferring the sample to the apparatus were carried out in a nitrogen atmosphere.

MALEIC ANHYDRIDE. The maleic anhydride (National Aniline Division, Allied Chemical & Dye Corp.) was purified by fractional distillation in a 3-foot 1-inch vacuum-jacketed column packed with glass helices.

DI-α-CUMYL PEROXIDE, laboratory preparation, identified by an infrared spectrum. Handling of the sample was minimized because of the danger of explosion.

NAPHTHALENE. Refined liquid naphthalene (Barrett Division, Allied Chemical & Dye Corp.) was purified by slow freezing in an insulated Dewar flask and discarding the central core. This procedure was repeated four times in successively smaller Dewar flasks.

RESULTS

The melting points, heats of fusion, and cryoscopic constants obtained with the present calorimeter on some organic compounds are listed in Table II.

To evaluate the applicability of the freezing or melting point as a measure of purity of routine samples, studies were made of the freezing point depression produced by the addition of some compounds known to be present as impurities in commercial products. Table III lists freezing point depression data obtained with the Rossini freezing point technique (*4*) on some of the materials listed in Table II. The last column lists the ratio of the first cryoscopic constant, calculated from $\frac{X_2}{\Delta t}$ (the ratio of the added mole fractions of impurity to the freezing point depression produced) to the first cryoscopic constant, $\frac{\Delta H_f}{RT_o^2}$, calculated from the calorimetric data. An ideal solute should give a ratio of 1 ± 0.02 for the value when the concentration of the impurity is 5 mole %, or less. Table III shows that water deviates from ideal behavior in phenol and in ε-caprolactam. Both quinoline and thianaphthene deviate from ideal behavior when present in naphthalene; water usually deviates from ideal solution laws in hygroscopic materials. Molecular Sieve, 4A powder (Linde Air Products Co.) has been used to remove water from samples of this type.

Table II. Melting Points, Heats of Fusion, and Cryoscopic Constants

Material	M. P., ° C.[a] (1 Atm., N_2 Sat.) of 100.00 Mole % Material	Heat of Fusion[c], Cal./Mole	Cryoscopic Constants, Deg.$^{-1}$	
			$\frac{\Delta H_f}{RT_o^2}$	$\frac{1}{T_o} - \frac{(\Delta C_p)_m^*}{2\Delta H_f}$
Phenol	40.982 ± 0.004	2898 (I)	0.01427	0
3,5-Xylenol	63.441 ± 0.026	4164 (F)	0.01850	0.002
p-α-Cumylphenol	73.252 ± 0.018	5181 (F)	0.02173	0
Quinoline	−15.220 ± 0.023	2563 (F)	0.01940	0.003
2,4,6-Collidine	−44.192 ± 0.014	2279 (F)	0.02188	0.002
ε-Caprolactam	69.207 ± 0.009	3856 (I)	0.01655	0.0007
Maleic anhydride	52.850 ± 0.009	3262 (I)	0.01545	0.002
Di-α-cumyl peroxide	39.204 ± 0.065	6725 (F)	0.03469	0.001
Naphthalene	80.287 ± 0.019[b]	4496 (I)	0.01811	0.002

[a] Deviations are arbitrarily 10% of m. p. depression ($t_0 - t_m$), calculated from slope of least squares line of equilibrium temp. *vs.* reciprocal fraction melted.

[b] Solid solutions treatment (*7*).

[c] An integral heat of fusion (I) is usually more accurate than a fractional heat of fusion (F).

Table III. Solute Behavior of Various Systems

Impurity	$100X_2$, Mole % Impurity Added	Δt, ° C., Freezing Point Depression	$\frac{X_2}{\Delta t}$	$\frac{RT_o^2}{\Delta H_f} \cdot \frac{X_2}{\Delta t}$
	Phenol Systems			
Cumene	1.0864	0.7640	0.01422	0.9965
Acetophenone	0.8423	0.5989	0.01406	0.9853
	1.9239	1.3824	0.01392	0.9755
Mesityl oxide	0.9572	0.6868	0.01394	0.9769
Benzaldehyde	0.9270	0.8560	0.01413	0.9902
α-Methylstyrene	0.8442	0.6093	0.01386	0.9713
Above impurities combined	2.0820	1.5382	0.01354	0.95
Water	0.7724	0.4850	0.01592	1.116
	2.0192	1.1609	0.01739	1.219
	ε-Caprolactam Systems			
Cyclohexanone	0.9418	0.568	0.01658	0.9982
	2.5538	1.543	0.01655	1.0000
Cyclohexanone oxime	0.9782	0.579	0.01689	0.9799
	1.9530	1.220	0.01601	1.0337
Octahydrophenazine	0.5023	0.308	0.01631	1.0147
	1.0170	0.628	0.01619	1.0222
Above impurities combined	2.8952	1.715	0.01688	0.9805
Water	1.199	0.583	0.02057	0.8046
	3.2650	1.907	0.01712	0.9667
	Naphthalene Systems			
Quinoline	1.128	0.515	0.0219	0.826
	1.971	0.892	0.0221	0.819
Thianaphthene	5.56	2.397	0.0232	0.780

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Improved Instrument for High-Frequency Conductometric Titration

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▶ The purpose of this work was to develop an instrumental method for the detection of end points in titrations involving colloidal electrolytes. Operating at a fixed frequency, an amplitude-stabilized oscillator in conjunction with a specially shaped conductance cell produces a practically linear response over a range of an order of magnitude of conductance. Use of three oscillator frequencies with two cells allows titration of solutions with conductances between 4×10^{-4} and $6.5 \times 10^{-2}N$ potassium chloride in the "linear" response range of the instrument. A nonlinear but useful response is produced down to conductances as low as that of $3 \times 10^{-5}N$ potassium chloride and as high as that of 1N. The device permits rapid titration in colloidal systems, even though the conductance change so produced is only a few per cent of the total conductance of the solution.

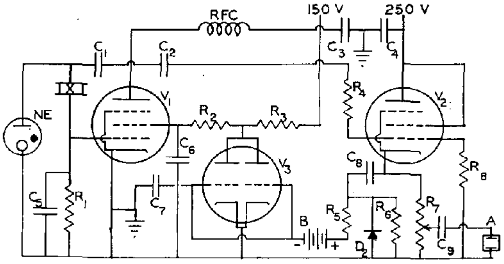

Figure 1. High-frequency source

A. Two-pronged socket
B. $22\frac{1}{2}$-volt battery, Burgess U-15
C_1, C_2, C_5, C_8. 0.001 mfd.
C_3, C_4. 0.05 mfd.
C_6, C_7. 0.01 mfd.
C_9. 0.002-mfd. mica
D_2. Germanium diode 1N58 A
NE. Neon bulb NE-2.
R_1. 51 kilo-ohms
R_2. 10 kilo-ohms.
R_3. 39 kilo-ohms, 2 watts
R_4. 4.7 kilo-ohms
R_5, R_6. 100 kilo-ohms
R_7. 2-kilo-ohm potentiometer
R_8. 470 kilo-ohms
RFC. Radio-frequency choke, 15 mh.
V_1, V_2. 6AQ5 beam power amplifier tube
V_3. 12AT7 dual triode
X. Crystal socket for crystal holders with $\frac{1}{2}$-inch spaced pins, 0.093-inch diameter (for Type FT-243 and FT-241-A holders)
Mounted crystals, approximately 0.1, 1.0, and 3.0 mc.
One $2 \times 4 \times 10$ inch chassis
One $2 \times 5 \times 4$ inch chassis
Cabinet to hold meter, switches, potentiometer, and shunt resistors. Can also contain power supply
Power supply, regulated at 250 and 150 volts, 40 ma.
Connecting cable, shielded 5-conductor with appropriate terminals and sockets
Battery, 6 volts

ALTHOUGH the simple response of a conventional 1000-cycle bridge to changes in conductance is especially desirable in titrating colloidal electrolytes, the necessity of having electrodes in contact with the solution makes it very inconvenient to use this type of instrument. External electrodes, which eliminate many of these inconveniences, require a high-frequency device, and the possibility of constructing an inexpensive high-frequency unit with a linear response to conductance was explored. As indicated by Hall and coworkers (*3*), the response of a high-frequency cell to changes in conductance can at best only approach that of a conventional conductance cell. To make the high-frequency cell response as nearly as possible like that of the conventional cell, it is necessary to minimize capacitance effects within the cell by proper cell design.

An instrument by Blake (*1*) measures the admittance of a conductance tube, but it has a nonlinear response over the conductance range of the solutions studied. To shift the response range, the conductance cell was modified by inserting capillary sections between the electrodes. The amplitude stability of the crystal oscillator was improved by a clamp tube circuit operated by the signal from the cathode follower stage. The latter serves to isolate the oscillator from the load and provides a low impedance signal source for the conductance cell.

A standard constant input–impedance multiplier circuit is used with the meter. The conventional bucking current arrangement permits taking advantage of the maximum meter deflection in the course of a titration by canceling out current carried by ions not involved in the titration reaction.

DESCRIPTION OF APPARATUS

The high-frequency source (Figure 1) consists of a Pierce oscillator with a neon bulb connected as a limiter in the crystal circuit to prevent possible damage to the crystal. Frequency is changed by plugging in the appropriate crystal. Interchangeable mounted

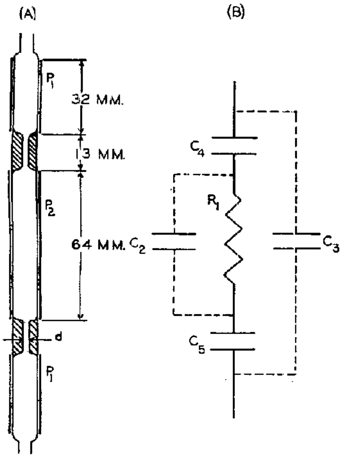

Figure 2. Cell and equivalent circuit

C_2. Capacitance across solution
C_3. External electrode capacitance
C_4, C_5. Individual electrodes to solution capacitances
d. Capillary diameter
P_1. Output electrode
P_2. Input electrode
R_1. Resistance of cell due to solution

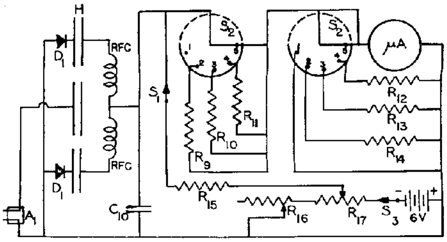

Figure 3. Cell and meter circuits

A_1. Two-pronged plug
C_{10}. 0.001 mfd.
D_1. Germanium diode 1N35
H. Conductance cell holder
μA. 25-µa. meter
R_9. $^7/_8\, R_M$
R_{10}. $^3/_4\, R_M$
R_{11}. $^1/_2\, R_M$
R_{12}. R_M
R_{13}. $^1/_3 R_M$
R_{14}. $^1/_7\, R_M$
where R_M is meter resistance (values best determined experimentally)
R_{15}. 22 kilo-ohms
R_{16}. 10 kilo-ohm wire-wound potentiometer, 4-watt
R_{17}. 600-ohm wire-wound potentiometer
S_1. Single-pole single-throw switch
S_2. Double-pole 5-position, nonshorting switch
S_3. Double-pole single-throw switch (second pole used for power supply)

quartz crystals of a type formerly used in military transmitters are used for the 1000- and 3000-kc. frequencies and a secondary frequency standard type is used for 100 kc. The signal at the cathode of the cathode follower stage is rectified and applied to the grids of the dual triode, which has both sections connected in parallel. This acts as a clamp tube to maintain a constant signal output by reducing the screen grid voltage of the oscillator tube when the amplitude of the oscillation exceeds a value determined by battery *B*. The high-frequency source is built on a 5 × 2 × 4 inch chassis mounted on the conduction cell housing.

The conductance cell is made of three sections of thin-walled borosilicate glass tubing 7 mm. in diameter, which are sealed to two sections of capillary tubing about 12 mm. long. The capillary in cell *A* has an inside bore of 1.61 mm. and that in cell *B* a diameter of 0.66 mm. Each electrode is 0.005-inch copper foil wrapped around the 7-mm. tubing, soldered together, and cemented in place. The end sections extend about 4 inches beyond the electrodes. A diagram of a typical cell is shown in Figure 2, *A*. To facilitate changing conductance cells, modified $^1/_4$-inch fuse mounting clips are used to make electrical contact with the electrode and to provide mechanical support for the cell. The cell and associated germanium rectifiers and chokes are mounted in a 10 × 2 × 4 inch chassis.

The indicating meter and power supply are housed in a 8 × 8 × 8 inch cabinet. A conventional voltage-regulated power supply capable of delivering up to 40 ma. at 250 and 150 volts is used. Connections from the

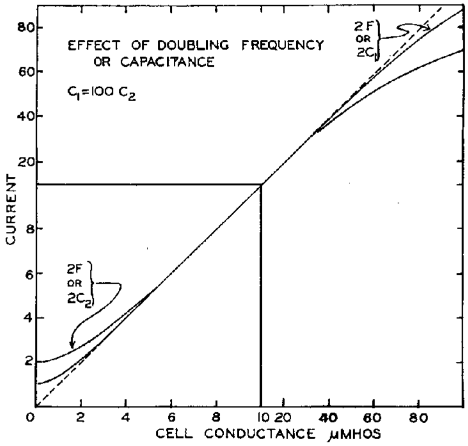

Figure 4. Theoretical response of cell

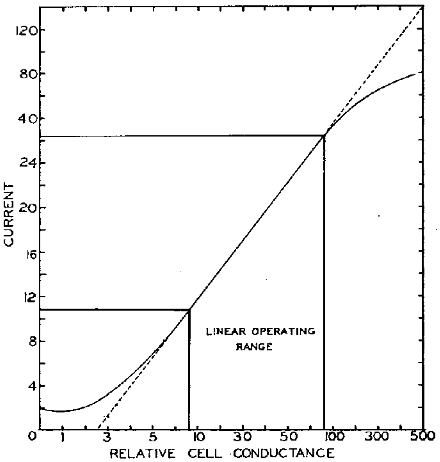

Figure 5. Response of cell A at 1 mc.

power supply to the oscillator and from the meter to the conductance cell are made of a multiwire shielded cable terminating in an octal plug and socket. The meter is a $4^1/_2$-inch rectangular model with a 25-μa. movement accurate to ±2%. Experimentally determined shunts are used to produce meter ranges of 50, 100, and 200 μa. with a constant input impedance maintained by appropriate series resistors. A bucking current may be supplied to the meter circuit by means of a 6-volt battery and the associated resistor-potentiometer network. This feature is especially useful in performing titrations in solutions which contain high concentrations of ions not involved in the titration reaction.

PRINCIPLE AND METHOD OF OPERATION

The output stage of the oscillator applies a signal of constant frequency and amplitude to the middle electrode of the cell. The path through the cell to ground includes capacitance between the electrode and the solution, electrolytic conductance within the solution, and capacitive coupling from the solution to the other electrodes where rectification to direct current is accomplished by germanium diodes. Change in the electrolytic conductance of the solution produces a corresponding change in the current through the diodes and is observed on a microammeter.

A frequency of 1 mc. in conjunction with a cell *A* is suitable for most titrations. The solution to be titrated is drawn into the lower end of the conductance cell by a Sigmamotor pump and returned to the titration vessel, thermostated at room temperature. The oscillator output and bucking current are selected to produce a nearly full scale meter deflection in the 50- or 25-μa. range during a titration. Meter deflection is plotted against volume of titrant as is done with data obtained by an ordinary conductance bridge. The time required for an ordinary titration, including cleaning the cell for the next titration, is less than 10 minutes.

THEORETICAL CONSIDERATIONS

The electrical equivalent circuit of the conductance cell is shown in Figure 2, *B*.

Electrodes P_1 (Figure 2, *A*) are considered as a single electrode. Because the interelectrode capacity, C_3, is constant and both the frequency and amplitude are fixed, the portion of signal passed by C_3 is constant and need not be considered in a titration apparatus. C_4 and C_5 can be treated as a single capacitance, C_1, located at C_4. This simplified circuit can be further reduced to a series equivalent circuit consisting of a series resistance, R_s, and series capacitance, C_s, the values of which can be calculated from equations referred to by Reilley and McCurdy (*5*) in their excellent discussion of high-frequency measurements. The current, *I*, passing through the series circuit may be calculated from the equation (*2*)

$$I = \frac{E}{\sqrt{R_s^2 + X_s^2}}$$

where *E* is the applied signal voltage and X_s is the reactance of C_s (*2*). X_s becomes small for large values of C_1 and small values of C_2; thus the current becomes almost entirely a function of R_s over a wide range of values of the latter. Small values of C_2 make R_s nearly equal to R_1, except at very high values of R_1. As C_2 decreases and R_1 increases as the diameter of the section of the cell between the electrodes decreases, these parameters may be adjusted to some extent. By suitable selection of C_1 and C_2 the current becomes very nearly proportional to the solution conductance over a considerable range of the latter.

The theoretical curve for a cell in which $C_1 = 100\ C_2$, $E = 1$, and C_1, C_2 and the frequency have fixed values is shown in Figure 4. The relatively linear portion of the curve in the region of the inflection point becomes longer as the ratio of C_1 to C_2 increases. As the curve illustrates, increasing C_1 extends the upper portion of the curve, thus improving the high conductance response. Decreasing C_2 extends the low conductance response. Changing the frequency has the same effect as a proportional change in both C_1 and C_2.

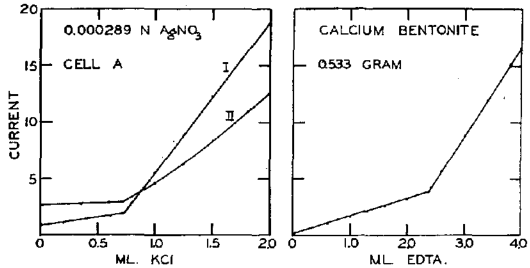

Figure 6. Frequency effect (*left*) and titration of colloidal system (*right*)

Table I. Linear Ranges of Experimental Cells

Cell	Capillary Diameter, Mm.	Frequency, Mc.	Linear Range (Molarity of KCl)
A	1.614	0.1	4×10^{-4} to 5×10^{-3}
		1.0	7×10^{-4} to 7×10^{-3}
B	0.664	1.0	3.5×10^{-3} to 3.5×10^{-2}
		3.0	6×10^{-3} to 6.5×10^{-2}

EXPERIMENTAL RESULTS

The experimental curve for cell *A* at a frequency of 1 mc. is shown in Figure 5. The conductance values approximate $1 \times 10^{-4}M$ potassium chloride concentrations. The current scale is in arbitrary units. Cell *B* was constructed with thinner walls and capillary sections of smaller diameter, thus shifting the response to higher specific conductances. Its response shows the same general features as cell *A*. The practically linear response ranges of these cells at various frequencies are shown in Table I. In addition, at 0.1 mc., cell *A* gives a nonlinear but unambiguous response to conductance as low as that of 3×10^{-5} *M* potassium chloride. For cell *B* at 3 mc., a useful response is obtained up to the conductance of 1*M* potassium chloride.

Figure 6 shows the effect of frequency on the shape of a typical titration curve. Curve I illustrates the titration of a solution whose conductance is within the linear operating range of cell *A* at 0.1 mc. The same solution at 1.0 mc. has a conductance which moves the titration curve below the linear range shown in Figure 5. A solution whose conductance places it above the linear section of the response curve produces a titration curve that is convex upward.

Figure 6 (right) is the titration curve for a suspension of calcium bentonite buffered at pH 8.5 with potassium hydroxide and boric acid. The titrant is 0.107*N* dipotassium dihydrogen (ethylenedinitrilo)tetraacetate (EDTA). The curves show excellent reproducibility and provide data from which the base exchange capacity of calcium bentonite may be calculated. The values thus obtained agree with those determined by conventional ammonium acetate methods (*4*).

ACKNOWLEDGMENT

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construction of the electronic equipment.

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Selective Precipitation of Thorium Iodate from a Tartaric Acid–Hydrogen Peroxide Medium

Application to Rapid Spectrophotometric Determination of Thorium in Silicate Rocks and in Ores

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▶This paper presents a selective iodate separation of thorium from nitric acid medium containing *d*-tartaric acid and hydrogen peroxide. The catalytic decomposition of hydrogen peroxide is prevented by the use of 8-quinolinol. A few micrograms of thorium are separated sufficiently clean from 30 mg. of such oxides as cerium, zirconium, titanium, niobium, tantalum, scandium, or iron with one iodate precipitation to allow an accurate determination of thorium with the thoron–mesotartaric acid spectrophotometric method. The method is successful for the determination of 0.001% or more of thorium dioxide in silicate rocks and for 0.01% or more in black sand, monazite, thorite, thorianite, eschynite, euxenite, and zircon.

The precipitation of thorium iodate from nitric acid medium (*4*) is a generally reliable and widely used method for the separation of thorium. Lead, mercury, tin, niobium, tantalum, tungsten, cerium(IV), uranium(IV), zirconium, titanium, silver, and to a smaller extent scandium, bismuth, and iron(III) also precipitate from this medium. A clean separation of thorium iodate is obtained from the rare earth elements by reprecipitation. A dense, less contaminated, and easily filterable precipitate is obtained from homogeneous solution (*6*). Tillu and Athavale (*7*) used oxalic acid to prevent the precipitation of 20 mg. each of titanium and bismuth and 40 mg. of zirconium. The procedure was not applied to the determination of small amounts of thorium. Kronstadt and Eberle (*3*) used mercury as a carrier for the precipitation of 20 γ or more of thorium.

The present investigation concerns the separation of thorium iodate from nitric acid medium containing hydrogen peroxide, *d*-tartaric acid, and 8-quinolinol. Tartaric acid minimizes the coprecipitation of zirconium, tungsten, scandium, and bismuth. Hydrogen peroxide minimizes the precipitation of titanium, niobium, and tantalum; 8-quinolinol prevents the catalytic decomposition of hydrogen peroxide, which is especially serious in the presence of cerium. Although less than 10% of the iron added is precipitated, the mixed carrier of mercury and iron used is more effective than mercury alone for the precipitation of microgram amounts of thorium. This separation procedure combined with the recently developed (*2*) spectrophotometric determination of thorium with the thoron–mesotartaric acid system is applied successfully to the determination of 0.001% or more of thorium dioxide in silicate rocks and 0.01% or more in black sand, monazite, thorite, thorianite, eschynite, euxenite, and zircon.

REAGENTS AND APPARATUS

All chemicals used are reagent grade.

Ferric nitrate (carrier solution), 1 ml. equivalent to 2 mg. of Fe_2O_3. Dissolve 0.875 gram of ferric nitrate hexahydrate in 100 ml. of (1 plus 99) nitric acid.

Potassium hydroxide (precipitating solution), 50% by weight aqueous.

Potassium hydroxide (wash solution). Dilute 2 ml. of 50% potassium hydroxide solution to 500 ml. with water.

Ammonium nitrate (wash solution), 1% aqueous.

8-Quinolinol. Dissolve 0.5 gram of reagent in 100 ml. of (1 plus 99) nitric acid.

Hydrogen peroxide solution, 3%. Dilute 10 ml. of 30% hydrogen peroxide to 100 ml. with water.

d-Tartaric acid solution. Dissolve 600 grams of tartaric acid in sufficient water to make 1 liter of solution. Filter through a dry paper and do not wash.

Potassium iodate solution, 6% aqueous. Filter through a dry paper and do not wash.

Mercuric nitrate (carrier solution), 1 ml. equivalent to 1 mg. of HgO. Dissolve 1.58 grams of mercuric nitrate monohydrate in 10 ml. of (1 plus 1) nitric acid and dilute with water to a liter.

Iodate wash solution. Mix 60 ml. of nitric acid, 6 ml. of 30% hydrogen peroxide, and 200 ml. of 6% potassium iodate solution with enough water to make a liter of solution.

PROCEDURE

The preparation of the solution for analysis should present no problems, except occasionally for a niobium and tantalum ore. Although the medium for the precipitation of thorium will keep niobium and tantalum in solution, there may be a problem in preparing the solution of the sample in this medium without prior hydrolysis of niobium and tantalum. Two alternative procedures are given. The first procedure is the simplest but may fail on high-grade tantalates containing very little titanium. The second procedure is of general applicability.

Procedure 1 (Ores and Silicate Rocks). Mix 0.0500 gram of a finely ground representative sample of the ore with 2 grams of sodium peroxide in a platinum crucible. For a silicate rock, use 0.3 gram of rock and 3 to 5 grams of sodium peroxide or potassium carbonate. Sinter the sodium peroxide mixture (covered) in a small furnace, at 460° ± 20° C. for 1 hour (fuse if potassium carbonate is used). A true sinter with no attack on the platinum will be obtained if the sodium peroxide is fresh and dry.

Place the crucible and melt in a 150-ml. beaker containing 30 to 100 ml. of water. Cover the beaker immediately with a watch glass; the dissolution reaction may be vigorous. Digest the solution on a steam bath for 15 minutes. Acidify with (1 plus 1) nitric acid, adding about 2 ml. in excess. Observe whether the sample is completely decomposed. The results of this observation determine whether additional steps are required later.

Add 1 ml. of ferric nitrate carrier solution. Add 1 or 2 drops of 30% hydrogen peroxide and then 50% potassium hydroxide solution to neutrality. Add 5 ml. excess for each 50 ml. of solution. Digest on the steam bath for about 15 minutes. Filter on a fast filter paper and wash the precipitate several times with potassium hydroxide wash solution. Drain the precipitate thoroughly by placing the palm of the hand over the funnel and pressing down.

If incomplete decomposition of the sample was indicated above, wash the precipitate several times with ammonium nitrate wash solution. Disregard any cloudiness that may form in the filtrate. Reject filtrate. Ignite the precipitate in a small platinum or porcelain crucible and fuse with a small amount of potassium pyrosulfate. Leach the melt with 30 ml. of (3 plus 97) nitric acid solution. Add several drops of 30% hydrogen peroxide and then neutralize with 50% potassium hydroxide solution, adding 5-ml. excess for each 50 ml. of solution. Digest the precipitate on the steam bath for 15 minutes. Filter on a fast filter paper and wash with potassium hydroxide wash solution. Omit the foregoing steps, if complete decomposition was obtained.

Pipet 5 ml. of water and 1 ml. of 8-quinolinol into a 100-ml. beaker and place under the funnel. Dissolve the hydroxide precipitate as follows: Add 1 ml. of 3% hydrogen peroxide over the precipitate, being careful to make the peroxide come in contact with all portions of the precipitate. When the hydrogen peroxide has drained, add 2 ml. of hot (1 plus 1) nitric acid slowly and dropwise to allow the acid to dissolve as much precipitate as possible. After the acid drains, add 5 ml. of hot water, playing the water over all surfaces of the filter paper. Repeat the sequence of peroxide, acid, and water twice more. Drain the funnel. Add all reagents and water with pipets to ensure proper concentrations for the subsequent iodate separation. Add 0.1 ml. of potassium iodate solution and 5 ml. of *d*-tartaric acid solution. The solution is now ready for the iodate separation.

Procedure 2 (Ores). Follow Procedure 1 through the first precipitation with potassium hydroxide (end of third paragraph). After washing with potassium hydroxide, wash the precipitate several times with ammonium nitrate wash solution. Ignite the precipitate in a small porcelain or platinum crucible and fuse with no more than 0.5 gram of potassium pyrosulfate until a clear melt is obtained. If sulfur trioxide is lost completely before sample is completely dissolved, cool the melt and add one drop of sulfuric acid to convert the sulfate to bisulfate. Heat gently and increase heat until a clear melt is obtained. Cool.

Transfer the crucible to a 100-ml. beaker containing 15 ml. of water, 6 ml. of (1 plus 1) nitric acid, 5 ml. of *d*-tartaric acid solution, 1 ml. of 8-quinolinol, 0.1 ml. of potassium iodate solution, and 3 ml. of 3% hydrogen peroxide solution, all added with pipets. Allow the melt to dissolve in the cold by stirring the solution. Remove crucible and rinse inside and outside with exactly 5 ml. of water from a pipet, adding the rinses to the beaker. The solution is now ready for the iodate separation.

Iodate Separation. Add slowly from pipets, first 10 ml. of potassium iodate and then 5 ml. of the mercury carrier solution, stirring the solution during each addition. Place the beaker in an ice bath and allow to stand for 45 minutes.

Stir in a small amount of paper pulp and filter on a slow (No. 42 Whatman or equivalent) 7-cm. filter paper. Wash the precipitate thoroughly six to eight times with ice-cold iodate wash solution (25 to 35 ml.). Wash further if the sample is known to contain large amounts of titanium, niobium, or tantalum. Disregard any cloudiness or small precipitate that sometimes forms in the filtrate. This is due to post precipitation of mercury.

Drain the precipitate and stem of funnel by pressing funnel with hand. Also drain the last drop from the beaker in which the precipitation was made. Remove beaker containing the filtrate and substitute the beaker in which the iodate precipitation was made. Dissolve the precipitate from the filter with alternate additions of 5 ml. each of hot (1 plus 1) hydrochloric acid and 5 ml. of hot water. Repeat the cycle twice more. Drain the paper and funnel stem.

Add 1 ml. of perchloric acid to the solution and evaporate the solution on a steam bath until it is colorless and fumes of perchloric acid appear. Place the beaker on a sand bath (170° to 190° C.) until the perchloric acid is completely evaporated (about 30 minutes). Cool. Careful heating at sand-bath temperature is necessary to prevent the formation of an insoluble form of any zirconium that might be present. Add 2 ml. of (1 plus 1) hydrochloric acid and evaporate the solution on the steam bath until dry. Cool. The sample is now ready for the spectrophotometric determination of thorium (*2*).

Ordinarily, 2 to 60 γ of thorium dioxide are determined in the spectrophotometric procedure. If more than these amounts of thorium are present, an aliquot of the solution should be taken. The proper size of aliquot is estimated by comparing the size of the iodate precipitate obtained prior to the addition of the mercury carrier against thorium standards similarly precipitated.

The blank correction for each batch of reagents is obtained by carrying about five water samples through the iodate separation and spectrophotometric determination and averaging the results. Ordinarily, the blank correction amounts to an absorbance of about 0.005.

EXPERIMENTAL DATA

The conditions adopted for the iodate separation require a total volume of solution of 50 ml. containing 3 ml. of nitric acid, 3 grams of *d*-tartaric acid, 0.3 ml. of 30% hydrogen peroxide, 2 mg. of ferric oxide (added as the nitrate), 5 mg. of mercuric oxide (added as the nitrate), 5 mg. of 8-quinolinol, and 0.6 gram of potassium iodate. These conditions permit the presence of at least 500 mg. of potassium pyrosulfate without loss of thorium through formation of sulfate complexes.

Effect of Variables. Iodate and Nitric Acid Concentration. The solubility of thorium iodate increases with increase in acidity or decrease in iodate concentration. The ideal balance should allow complete precipitation of thorium and yet minimize the coprecipitation of foreign ions. The recommended combination of acidity and iodate concentration is one of many fulfilling these objectives. The sensitivity of the recommended system to changes is best illustrated by the fact that if more than the recommended amount of nitric acid is present, 2 ml. of excess iodate solution are required for each milliliter of excess nitric acid to precipitate the thorium completely. At the 500-γ level of thorium dioxide, an increase of either 1 ml. of nitric acid or a decrease of 2 ml. of 6% potassium iodate results in a 7% loss of thorium.

Mercury Carrier. Greater amounts than recommended result in increased coprecipitation of foreign ions; stoichiometric amounts of halides–to form, for example $HgCl_2$—completely prevent precipitation of mercuric iodate; thus halides must be absent.

Hydrogen Peroxide. Only slightly more than the stoichiometric amounts required to form the peroxy compounds of niobium, tantalum, and titanium are required. Amounts much greater than recommended cause the precipitation of a peroxy compound of zirconium, especially when 10 mg. or more of zirconium are present. No more than 0.5 ml. of 30% hydrogen peroxide should be used, preferably less.

8-QUINOLINOL. The concentration of 8-quinolinol is less critical than that of any of the other reagents. Although 5 mg. are recommended, 0.5 to 50 mg. may be used.

d-TARTARIC ACID. Tartaric acid delays the precipitation of thorium iodate. However, the concentration can be increased by a factor of 50% over the recommended amount without affecting the recovery of thorium, if the recommended 45 minutes are allowed before filtering. A few drops of potassium iodate are added before the tartaric acid to prevent the reduction of iron which would otherwise take place in the presence of peroxide and absence of iodate.

Table I illustrates the results obtained on the recovery of 2.44 to 1950 γ of thorium dioxide in the presence of 30 mg. each of the oxides of zirconium, cerium(III), titanium, niobium, tantalum, iron(III), or scandium; 50 mg. of iron(III) oxide, and 15 mg. of tantalum oxide—each element tested separately. Also shown are the recoveries of the same amount of thorium in the presence of a mixture of 5 mg. each of the oxides of zirconium, cerium, titanium, niobium, tantalum, iron(III), and scandium. As no more than a 50-mg. sample of thorium ores containing these constituents is used for analysis, the experiments provide a good basis for the applicability of the separation procedure to the determination of thorium in such ores. The recoveries shown are satisfactory. Rare earth elements other than cerium were not tested because cerium is most likely to coprecipitate; the yttrium earth iodates are appreciably more soluble than the cerium earth iodates and substantial amounts of yttrium earths may be present without interference in the spectrophotometric determination of thorium. Other ions that form insoluble iodates were not tested. Some (lead, bismuth, and mercury) can be tolerated in large amounts in the spectrophotometric determination; others (tungsten and bismuth) are soluble in the proposed tartaric acid medium; still others are separated during preparation of the sample solution—for example, tungsten and tin are separated as the soluble tungstate and stannate in the sodium hydroxide precipitation. The remaining tin is removed as insoluble metastannic acid by fuming with perchloric acid in the last stages of the analysis.

The excellent recoveries shown in Table I should not be interpreted as proof that thorium was completely separated from the elements tested. The determination of thorium was made spectrometrically by a method that tolerates the presence of several milligrams of zirconium and iron(II), and 20 to several hundred micrograms of the other elements without interference (*2*). Occlusion tests showed that the amount of zirconium occluded varied from 0.2 to 2 mg. of zirconium dioxide, depending on the size of the thorium iodate precipitate and the amounts of zirconium tested (for thorium the range tested was 2 γ to 2 mg. of ThO_2, for zirconium 2 to 30 mg. of ZrO_2). Occlusion was highest for highest thorium. Similarly, the amounts of iron occluded varied from 200 γ to 1.6 mg. of Fe_2O_3. For microgram amounts of thorium, less than 200 γ of ceric oxide were occluded when 30 mg. were added and less than 20 γ of titanium dioxide from 30 mg. of titanium oxide tested. The amounts of niobium and tantalum occluded were estimated to be less than 200 γ of each. These elements are further separated during the perchloric acid fuming. No tests were made on the extent of scandium occlusion.

Table I. Recoveries of Thorium in Presence of Various Elements

Elements Tested, Mg. (as Oxides)	ThO_2 Added, γ					
	2.44	6.10	24.38	48.75	390.0	1950
	ThO_2 Found, γ					
Blank	2.18	5.91	24.4	47.5	386	1950
30 ZrO_2	2.50	6.02	24.3	47.9	393	1940
30 Ce_2O_3	2.25	5.85	24.5	48.2	396	1920
30 TiO_2	2.48	6.35	23.9	47.8	389	1940
30 Nb_2O_5	2.37	5.95	25.2	47.6	394	1960
30 Ta_2O_5	2.13	6.37	23.7	46.5	387	1920
15 Ta_2O_5	2.30	6.05	23.6	47.2	..	..
50 Fe_2O_3	2.36	6.62	24.8	49.4	394	1960
30 Fe_2O_3	2.60	6.08	24.3	48.9	389	1940
30 Sc_2O_3	2.80	6.20	23.9	48.1	388	1920
Mixture of 5 mg. each of oxides of Zr, Ce, Ti, Nb, Ta, Fe, Sc	2.66	6.13	25.3	48.6	397	1950

TEST OF PROCEDURES

Several representative ores were analyzed according to the procedures outlined. The results are compared in Table II with those obtained by careful gravimetric analysis using standard methods. The zircon samples were analyzed according to the spectrophotometric procedure of Cuttitta (*1*). The method for silicate rocks was tested on a standard diabase W-1 (*5*) containing about 0.0003% of thorium dioxide, to which known amounts of thorium were added. Two unspiked samples were included and the average absorbance obtained for these blanks was subtracted from the absorbances given by the spiked samples. The results are given in Table III in terms of the per cent of thorium dioxide that would be present if only the spike were considered.

The silicate rock procedure also was tested on three counting standards obtained from the AEC New Brunswick laboratory, as mixtures of a stand-

Table II. Test of Procedure on Ores

Sample	ThO_2, % Other method	ThO_2, % New method
Black sand 1	4.00	4.05
Black sand 2	2.13	2.16
Monazite 1[a]	9.65[b]	9.84
Monazite 2	4.24	4.26
Zircon 1	0.065	0.065
Zircon 2	0.15	0.15
Polycrase euxenite	5.47	5.44
Eschynite	6.28	6.27, 6.22
Thorite	1.94	2.16
Thorianite	1.72	1.77

[a] New Brunswick AEC standard monazite.

[b] Certificate value.

Table III. Test of Procedure on Silicate Rock

ThO_2, % Added	ThO_2, % Found
0.00081	0.00095
0.0020	0.0021
0.0049	0.0048
0.0081	0.0079
0.0097	0.0097
0.019	0.019

Table IV. Test of Silicate Rock Procedure on Monazite-Dunite Mixtures

ThO_2, % Present	ThO_2, % Found
0.0011	0.0014
0.011	0.012
0.023	0.022
0.057	0.055
0.11	0.11
1.14	1.10

ard monazite in a dunite base (Table IV). A sodium peroxide sinter was used to decompose the samples.

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Paper Chromatography of 3,5-Dinitrobenzoates of Alcohols

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▶ The separation and identification of the 3,5-dinitrobenzoates of some primary, aliphatic alcohols in the range C_1 to C_{12} are described.

THE 3,5-dinitrobenzoates are very commonly used for the identification of alcohols. The separation of these derivatives by paper chromatography however, has been little investigated. Rice, Keller, and Kirchner (*4*) used a 20% aqueous dioxane solution among other solvents, for the separation of the 3,5-dinitrobenzoates of some alcohols, but stated that a mixture of methyl, ethyl, propyl, and butyl 3,5-dinitrobenzoates showed only two spots on development. One spot had an R_f value of 0.75 for the methyl 3,5-dinitrobenzoate, and the other large spot, with its center at an R_f of about 0.9, was believed to represent a mixture of ethyl, propyl, and butyl 3,5-dinitrobenzoates.

A better separation was obtained by Meigh (*2*), who used the two-phase system methanol-*n*-heptane. However, the high volatility of the solvents is a disadvantage of this method.

By adapting the two-phase system dimethylformamide-Decalin(decahydronaphthalene), first used by Horner and Kirmse (*1*) for the paper chromatography of the 2,4-dinitrophenylhydrazones of aldehydes and ketones, the authors obtained a very satisfactory separation and identification of the 3,5-dinitrobenzoates of some primary, aliphatic alcohols in the range C_1 to C_{12}.

At an earlier stage and with excellent results, the authors had adapted the method of Horner and Kirmse (*1*) for a great variety of 2,4-dinitrophenylhydrazones of aldehydes and ketones. It had been their experience, in working with the 2,4-dinitrophenylhydrazones, that an important factor in obtaining good results was the saturation of the atmosphere in the chromatograph chamber with the vapors of the stationary phase (dimethylformamide) as well as with those of the mobile phase (Decalin). This also seemed to be the case in the separation of the 3,5-dinitrobenzoates of the alcohols as described in detail below.

EXPERIMENTAL

Schleicher & Schüll chromatographic paper No. 2043b was immersed in a 50% solution of *N,N*-dimethylformamide (Merck) in acetone, followed by drying at room temperature for a short time to evaporate the acetone. The 3,5-dinitrobenzoate samples in chloroform solution (1 mg. per ml.) were applied to the dimethylformamide-impregnated paper in the normal way by means of a micropipet in quantities of 10 to 100 γ. Thereafter the paper sheet was placed in the chromatograph developing chamber for about 12 hours for saturation at 25° C. (without filling the trough with the mobile phase).

The correct saturation of the atmosphere in the developing chamber proved to be of great importance to the results obtained. In a 38 × 30 × 54 cm. chamber both the side walls were covered with filter paper sheets (about 25 × 45 cm.) kept moist with dimethylformamide previously saturated with Decalin. Two crystallizing dishes filled with the mobile phase were placed on the bottom of the chamber.

After having been kept for about 12 hours at 25° C. in a chromatograph chamber, the atmosphere of which had been saturated with both phases as described above, the trough was filled with the mobile phase, Decalin (Merck) previously saturated with dimethylformamide, and the chromatogram was developed, using the descending technique. The mobile phase traveled about 35 cm. in 7 hours. The finished chromatogram was dried at 60° to 70° C.

In spite of the fact that the 3,5-dinitrobenzoates of the alcohols examined are colorless, it was unnecessary to spray the chromatograms with 1-naphthylamine, as described by Rice, Keller, and Kirchner (*4*), or to use the procedure of Meigh (*2*) with Rhodamine 6 GBN in order to reveal the spots. Simply hanging the dried sheets in the daylight for 1 to 2 hours or irradiating them under an ultraviolet lamp for 10 to 15 minutes resulted in the formation of distinct violet spots. About 5 to 10 γ of a 3,5-dinitrobenzoate were easily detectable in this manner. A very satisfactory method for the examination of a chromatogram was to place it on a support consisting of another filter paper sheet, which had been made strongly yellow fluorescent by immersing it in an 0.1% alcoholic solution of fluorescein made alkaline with a 10% aqueous potassium hydroxide solution, and examine the chromatogram under ultraviolet light. As an ultraviolet source, a Philips mercury vapor lamp, HPW 125 W, was used, which produced light mainly in the region of 3655 A. The ultraviolet lamp was placed about 40 to 50 cm. in front of

Table I. R_f Values of 3,5-Dinitrobenzoates of Some Aliphatic Alcohols (C_1 — C_{12})

Compound	R_f
Methanol	0.21
Ethyl alcohol	0.40
1-Propanol	0.50
2-Propanol	0.52
Sorbic alcohol	0.55
1-Butanol	0.64
1-Hexene-3-ol	0.69
1-Pentanol	0.72
1-Hexene-2-ol	0.73
1-Hexanol	0.79
1-Nonenol	0.86
Lauric alcohol	0.92

the chromatogram, which was placed directly on the fluorescent support. This procedure made possible the detection of less than 5 γ of 3,5-dinitrobenzoates as dark spots. Traces of a derivative could be recognized as a dark shadow on the fluorescent support.

RESULTS

Table I shows the R_f values of a typical satisfactory separation of the 3,5-dinitrobenzoates of some common primary, aliphatic alcohols obtained in a run of 35 cm. at 25° C. according to the procedure given above. The R_f values should not be taken as absolute. In a two-phase solvent system, as used here, with one polar phase impregnated on the paper and one less polar organic solvent as mobile phase, it is practically impossible to obtain completely reproducible R_f values, as the amount of the stationary phase fixed on the paper may easily be variable, even if care is taken to impregnate the paper sheets as uniformly as possible. The humidity of the air during the preparation of the papers is also an important factor, influencing strongly the R_f values of such two-phase systems, as stated by Neher and Wettstein (*3*).

A mixture of the 3,5-dinitrobenzoates of 1-pentanol and 1-hexene-3-ol showed only one spot on developing. Such is the case also with a mixture of 1-hexene-3-ol and 1-hexene-2-ol. However, 1-pentanol and 1-hexanol could be separated clearly and a mixture of 1-hexene-2-ol and hexanol also separated nicely into two well defined spots, in spite of the close R_f values. All substances were tested with a quantity of 10 γ each. A difference in R_f value of about ±0.06 seemed to be necessary to obtain a clear separation.

ACKNOWLEDGMENT

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Determination of Vanadium in Titanium Tetrachloride and Titanium Alloys—Correction

In the article on "Determination of Vanadium in Titanium Tetrachloride and Titanium Alloys" [Owens, W. H., Norton, C. L., Curtis, J. A., ANAL. CHEM. **29,** 243 (1957)] the first sentence under Procedures in the third column should read: "Pipet a 2-ml. aliquot of titanium tetrachloride into a clean, dry 250-ml. beaker." In Table IV, first column, "Control," and "$NiSO_4 . 6H_2O$" should both be dropped one line to correspond with the first figures in the second and third columns. On page 244, second column, the third line above Interfering Elements should read "from Table III."

Improved Dumas Method for Molecular Weight Determination

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▶ Careful constriction of the neck and tip of an improved bulb makes possible endless re-use of the same bulb for determining molecular weights of liquids boiling between 105° and 200° C. by the Dumas method. With adequate precautions, titration of the available acidity of compounds such as triethylgermanium bromide or acetic acid can replace weighing.

NUMEROUS limitations beset the traditional Dumas method of determining the molecular weight of a liquid. Excessive time is required in the determination. Actual sealing of the bulb is difficult and often causes some decomposition of the compound; sealing can be hazardous with flammable compound. It is necessary to calibrate the bulb after sealing it; thus each determination requires a new bulb.

Three main improvements have been developed on the Dumas method for molecular weights. Vaporization of a liquid of boiling point above 105° and under 200° C. under atmospheric pressure, followed by condensation and then weighing, in an unsealed bulb, yields the satisfactory molecular weight of 120.2 ± 0.7 for chlorobenzene. In an unsealed bulb, vaporization of a liquid—of boiling point above 105° and under 200°—under atmospheric pressure, followed by condensation and then by titration of the available acidity, yields the satisfactory molecular weight of 249.8 ± 2.1 for triethylgermanium bromide. Carbon dioxide displaces air, and a molecular weight of 44.35 ± 0.07 for carbon dioxide results.

Molecular weights here are calculated from the perfect gas law, $PV = wRT/M$ and are 1 to 7% higher than the corresponding formula weights because of absorption of the gaseous compound on the glass surface of the container and deviation from ideality. High values persist in all gas methods using simple equipment, but disappear in the elaborate method of limiting density in a system with a counterpoise and a gas density balance.

METHOD WITH UNSEALED BULB

The altered design of the Dumas bulb resembles equipment used in obtaining molecular weights of 149 and 151 for phosphorus(III) dichloroisocyanate, which has the formula weight of 144 (*2*). Constriction of the neck and tip of the bulb structurally minimizes diffusion of the gaseous compound out of the bulb into the room after all the liquid compound has vaporized and all the vapors have reached the temperature of the liquid bath. Immersion of the bulb in the hot liquid bath for only 2.5 to 3.0 minutes functionally minimizes diffusion of the gaseous compound out of the bulb into the room. In almost all instances the bulb may be re-used.

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Table I. Molecular Weights

Compound	Formula Wt.	Mol. Wt., Weighing	Average	Mol. Wt., Titration	Average
$(C_2H_5)_3GeBr$	239.7	242.8, 246.0, 246.0	244.8 ± 1.6	250.9, 252.4, 244.9, 251.3, 249.5	249.8 ± 2.1
$(C_2H_5)_3GeOCOCH_3$	218.8	231.3, 224.2, 225.8, 232.0	228.3 ± 3.3	219.5, 220.1, 222.8, 218.1	220.1 ± 1.3
$(CH_3)_2Si(OCOCF_3)_2$	284.2	289.5, 291.9, 292.7	291.4 ± 1.1	......	.....
Cl_2	70.92	73.2, 73.2, 73.4	73.3 ± 0.1	71.6, 72.4, 72.4, 72.3	72.2 ± 0.3
CO_2	44.01	44.42, 44.25, 44.39	44.35 ± 0.07	......	.....
$C_6H_5CH_3$	92.13	92.9, 94.5, 93.7, 95.1	94.0 ± 0.7	......	.....
C_6H_5Cl	112.56	119.6, 120.1, 119.6, 121.5	120.2 ± 0.7	......	.....
$C_6H_4(CH_3)_2$ (*o*)	106.16	113.1, 110.2, 111.3, 111.0	111.4 ± 0.9	......	.....
$C_6H_5OCH_3$	108.13	113.0, 113.5, 115.4, 114.4	114.1 ± 0.8	......	.....
CH_3COOH (234° C.)	60.05	......	.....	62.0, 61.6, 62.2, 61.6	61.8 ± 0.3
CH_3COOH (213° C.)	60.05	......	.....	63.9, 63.7, 64.7, 63.3	63.9 ± 0.4
CH_3COOH (193° C.)	60.05	......	.....	67.5, 66.8, 66.6, 66.6	66.9 ± 0.3
CH_3COOH (182° C.)	60.05	......	.....	69.9, 70.0, 69.6, 69.9	69.9 ± 0.1
CH_3COOH (165.5° C.)	60.05	......	.....	74.5, 74.7, 74.7, 75.1	74.8 ± 0.2

Description of Bulbs. All the modified bulbs used for moderate-boiling liquids—boiling point above 105° and under 200°—have flat bottoms and range in size from 2.7 to 100 ml.; observed operational difficulties render a bulb of approximately 1.5 ml. the smallest ordinarily useful. Figure 1 shows the 4.511-ml. bulb used with acetic acid, which has the following special dimensions: upper neck tapering from 2.0 mm. to 1.0 mm. in inside diameter at the tip at *A*; two tiny glass "ears" at *C*, for fastening platinum wire beneath, with a loop for holding. A 2.700-ml. bulb, for organometallic compounds, resembles the 4.511-ml. bulb in general proportions. A 24.32-ml. bulb, used with neutral organic compounds, has a comparable construction, with upper neck tapering from 3.5 to 1.5 mm. in inside diameter at the tip.

MODERATE-BOILING LIQUIDS

Weighing. Complete vaporization of the liquid compound requires a liquid bath temperature 50° above the boiling point of the compound, such as toluene, chlorobenzene, *o*-xylene, anisole, triethylgermanium bromide (*7*), triethylgermanium acetate (*4*), or dimethylbis - (trifluoroacetoxy)silane (*5*). Equilibrium conditions require approximately 2.5 minutes of immersion of the bulb in the liquid bath, while longer immersion promotes secondary gaseous diffusion, with low results.

Procedure. Introduce the liquid into the weighed bulb, using a syringe and a transfer micropipet constructed from borosilicate glass tubing 4 mm. in outside diameter—for the compounds in Table I take 0.6 ml. for the 24.32-ml. bulb, 0.3 ml. for the 4.511-ml. bulb, and 0.15 ml. for the 2.700-ml. bulb. Place a 19-mm. length of hemocytometer rubber tubing on the neck to permit deep immersion to the glass ears. Immerse bulb in bath at constant temperature for 2.5 to 3.0 minutes; next insert a glass rod into the rubber tubing to close; then withdraw the bulb and cool the bulb rapidly with cold water to condense the compound. Wash the outside of the bulb completely; it is easy to remove a water-soluble compound such as glycerol, if previously used in the hot liquid bath. Remove the rubber tubing and glass rod; dry the bulb and then reweigh. An alternative procedure is to remove the bulb from the liquid bath, without any rubber tubing, instantly place the tip of an index finger over the tip of the bulb, then cool the bulb in water, dry, and reweigh. Calculate the molecular weight from the equation $PV = \frac{wRT}{M}$.

Titration. The method suggested for obtaining molecular weights of acidic or basic compounds by titration and without weighing is an extension of the earlier method with a self-filling micropipet and a liquid (*1*, *3*).

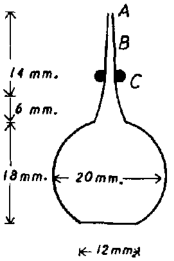

Figure 1. Dumas bulb

A. Tip
B. Narrowing
C. Ears

Procedure. Follow the method of weighing for moderate-boiling liquids, but instead of weighing the condensed liquid, first introduce 0.1 ml. of phenolphthalein solution with a micropipet of extremely small diameter, and then slowly titrate the available acidity, using 0.0300*M* sodium hydroxide in ethyl alcohol in a 10-ml. buret with a special adapter. This adapter, made from borosilicate glass tubing 4 mm. in outside diameter, has the following dimensions: 70-mm. length; 10 mm. of tubing 4 mm. in outside diameter, flared at the end; 50-mm. length of 0.6-mm. average outside diameter and 0.25-mm. average inside diameter. A 14-mm. length of hemocytometer rubber tubing connects the glass adapter and the delivery tip of the 10-ml. buret. Rotate the glass bulb extremely slowly and carefully with the fingers during the slow titration.

Table I lists the temperatures of the liquid bath used with acetic acid, which has considerable association at temperatures only slightly above its boiling point of 118°. These molecular weights for acetic acid are in general agreement with values obtained by Johnson and Nash (*6*).

PERMANENT GASES

Weighing (**Titration**). Carbon dioxide and chlorine both displace air satisfactorily. Relatively simple apparatus serves for the determination of the molecular weight of carbon dioxide (well suited for an undergraduate experiment in physical chemistry). Although toxic, chlorine offers the possibility of titration in addition to weighing.

Procedure. Fill a 125-ml. Erlenmeyer flask almost completely with powdered solid carbon dioxide; insert a one-hole rubber stopper through which a long borosilicate glass tube 4 mm. in outside diameter fits flush. This tube has two 90° bends, with constriction on one side to an average of thin-walled capillary 1 mm. in outside diameter and 180 mm. long. The capillary side of the U-tube reaches the bottom of a 102.85-ml. round-bottomed flask with a 2-mm. straight-bore stopcock; the molecular weight flask is 165 mm. long, exclusive of 46 mm. of the length above and outside the stopcock; much of the length is tubing 8 mm. in outside diameter.

First weigh the evacuated round-bottomed flask. Next pass gaseous carbon dioxide through the flask for 15 minutes to expel all the air, warming the Erlenmeyer flask with one hand. Remove the long capillary from the molecular weight unit and close the stopcock immediately; let the bulb stand 15 minutes to reach room temperature; then quickly reopen and reclose the stopcock; next evacuate the region outside the closed stopcock and let air replace the carbon dioxide in this zone; finally reweigh the molecular weight unit to obtain the weight of carbon dioxide.

Similarly, use a long capillary to pass chlorine gas from a cylinder through the molecular weight flask (Table I).

Table I also lists the titration of chlorine in a 15-ml. round-bottomed flask with both parts of a 10/30 standard-taper ground joint and also a 2-mm. straight-bore stopcock. Displace the air with chlorine, shake with excess potassium iodide solution, and then titrate the liberated iodine with standard sodium thiosulfate solution.

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Colorimetric Estimation of Milligram Quantities of Inorganic Azides

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▶The azide is acidified and the resulting hydrazoic acid is distilled into an acidified ferric nitrate solution. The reddish brown color due to formation of ferric azide is suitable for quantitative measurement at 460 mμ. The color obeys Beer's law over the range of concentration investigated—i.e., 0.5 to 4 mg. of azide ion per 50 ml. of colored solution. The method is applicable to the determination of lead azide in primer mixtures, except those containing thiocyanates. It is not recommended for purity determinations.

Conventional methods for the quantitative estimation of inorganic azides have usually been restricted to determining purity of lead azide. The azide is oxidized by a cerium(IV) salt with subsequent measurement of the volume of nitrogen gas evolved or by titration of an excess of a measured volume of a standard cerium(IV) salt solution with ferrous perchlorate (*1*, *3*). Because these methods are not wholly satisfactory for the determination of milligram quantities of azides, either alone or in the presence of other substances, the method described herein was developed.

The formation of red ferric azide when hydrazoic acid reacts with ferric chloride, is the basis of the qualitative test described by Feigl (*2*). An attempt to apply this test to quantitative measurement was unsuccessful because of the instability of the ferric chloride. However, use of ferric nitrate proved satisfactory in connection with a simple distillation of the hydrazoic acid formed when an azide solution is acidified.

It was felt that the method would be particularly useful for determination of lead azide in the presence of other materials and when only small samples are available for analysis, as in some primer mixtures. Synthetic primer mixtures were prepared and analyzed with favorable results.

The method was also employed successfully in this laboratory to investigate the rate and extent of formation of copper azide on small strips of copper foil, which had been exposed to hydrazoic acid vapor (*5*).

APPARATUS

Very simple distillation equipment is employed. A 10-ml. micro round-bottomed flask with a neck about 4 cm. long is fitted with a one-hole rubber stopper. The latter supports a glass tube drawn out until a very small orifice (approximately 0.4 mm. in inside diameter) is obtained on the receiver end. The tube is bent to extend nearly to the bottom of a 50-ml. volumetric flask.

Absorption measurements are made with a Beckman Model DU spectrophotometer using 1-cm. Corex cells.

REAGENTS

All reagents were reagent grade chemicals.

An acidified ferric nitrate solution is prepared by dissolving 2.000 grams of ferric nitrate in about 50 ml. of water, and adding 5 ml. of concentrated nitric acid which is relatively free of nitrogen dioxide as determined by observation. This is filtered and the filtrate is diluted to 1 liter.

A standard azide solution is prepared from sodium azide (Fisher Scientific Co., Cat. S-227).

PREPARATION OF STANDARD CURVE

Sodium azide solution (1 ml. equal to 1 mg. of azide ion) is used in preparing the standard samples containing up to 4.0 mg. of azide ion. The standard solution placed in the distilling flask is diluted to about 5 ml. with distilled water. Two or three glass beads are used to help prevent bumping. Twenty milliliters of the ferric nitrate solution are pipetted into a 50-ml. volumetric flask and the stopper assembly is made ready for immediate connection after the addition of 0.6 ml. of 1 to 4 sulfuric acid to the contents of the distilling flask. The orifice of the glass tube is placed well below the surface of the ferric nitrate solution in the receiver. The receiver is cooled in an ice bath and the distillation is continued for 3.5 minutes after first appearance of the reddish brown ferric azide color. The solution is adjusted in the receiver to approximately 25° C., diluted to the mark with water, and again adjusted to 25° ± 1° C. The transmittance is immediately measured at 460 mμ against a reference solution made by diluting 20 ml. of the ferric nitrate solution to 50 ml.

PROCEDURE FOR PRIMER MIXTURES

Place a sample containing 0.5 to 4.0 mg. of N_3 in the distilling flask, add glass beads and distilled water until the flask is about half filled. Add 2 drops of a 2% solution of sodium hydroxide and 0.3 ml. of a 30% hydrogen peroxide solution, and then boil the mixture gently for 1 minute to remove the excess hydrogen peroxide. Cool the flask and contents to 25° C. or below and proceed as indicated under preparation of standard curve.

DISCUSSION AND RESULTS

The absorption maximum is broad and measurement is made at 460 mμ. The intensity of the color varies with pH, but this variable is satisfactorily controlled by the distillation technique so long as no acid distills over. For this reason sulfuric acid is used to displace the azide ion. The color is stable for at least an hour if the volumetric receiver is full and stoppered to prevent

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Table I. Determination of Azide Ion in Synthetic Primer Mixtures

Azide Ion Present, Mg.	Azide (N_3) Found, Mg.	Relative Error, %
0.50	0.46	−8.0
1.00	1.04	+4.0
1.00	1.01	+1.0
2.00	2.01	+0.5
3.50	3.40	−2.9
3.60	3.49	−3.1
4.00	3.88	−3.0
	Mean	−1.6
	Standard deviation	3.9

Table II. Determinations of N_3 in Lead Azide, Purity 92.05%

Azide (N_3) Calcd., Mg.	Azide (N_3) Found, Mg.	Purity Found, %	Relative Error, %
2.64	2.66	92.7	+0.8
2.38	2.42	93.5	+1.7
1.81	1.74	88.7	−3.9
2.84	2.67	86.6	−6.0
3.16	3.20	93.3	+1.3
1.49	1.50	92.5	+0.7
1.80	1.85	94.6	+2.8
2.77	2.64	87.9	−4.7
1.68	1.79	98.0	+6.5
3.68	3.55	88.7	−3.5
	Mean	91.6	−0.4
	Standard deviation	3.6	3.9

undue exposure to air. Ricca (*4*) has shown that aeration causes appreciable fading of the color and suggests that this is due to the loss of hydrazoic acid. He has also presented evidence that the color is due not to undissociated ferric azide but to the complex ion $Fe(N_3)^{++}$.

Interference from sulfites, thiosulfates, and sulfides is avoided by preliminary oxidation of the alkaline sample with hydrogen peroxide (*2*). Cyanates and thiocyanates, however, interfere and render the method ineffective. Nitric acid batch variations may tend to shift the standard curve slightly and it is advisable to prepare a new standard curve when new ferric nitrate solution is prepared. The necessity for preparing a new curve with each batch of reagent is found in the reaction.

$$N_3^- + NO_2^- + 2H^+ \rightarrow H_2O + N_2 + N_2O$$

The use of ferric sulfate in sulfuric acid to eliminate this difficulty was unsatisfactory, as color development with a sulfate reagent was poor. Azide ion gave, in equivalent concentration, a 57% *T* in a nitric acid reagent and 86% *T* in the sulfuric acid media.

Samples of synthetic primer mixtures were prepared, using 10 mg. of antimony trisulfide (stibnite), 10 mg. of potassium chlorate (both approximate weights), and accurately measured amounts of sodium azide solution of known concentration. Table I indicates results for determinations on such mixtures.

Table II shows azide ion values found from analyses of military grade lead azide, the purity of which was 92.05% by the Navy titration method (*3*).

While the relative errors shown are not considered excessive with small amounts of azide, they are too large to permit the use of the method for purity determinations. This is clearly illustrated by the purities calculated from the results and also shown in Table II.

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(2) Feigl, F., "Spot Tests, Inorganic Applications," 4th ed., Vol. 1, p. 268, Elsevier, New York, 1954.
(3) Military Specification, **MIL-L-3055**, Sept. 30, 1949.
(4) Ricca, B., *Gazz. chim. ital.* **75**, 71 (1945).
(5) U. S. Naval Ammunition Depot, Crane, Confidential Rept. **QE/C 56-40.**

RECEIVED for review August 27, 1956. Accepted December 13, 1956. The opinions and assertions contained in this article are the private ones of the authors and are not to be construed as reflecting the views of the Navy Department.

CORRESPONDENCE

Determination of Potassium as the Metaperiodate

SIR: After publication of "Determination of Potassium as the Metaperiodate" [ANAL. CHEM. **28,** 2011–5 (1956)] our attention was called to "Determination of Potassium in Soap and Mixed Caustic Lye" by W. T. Miller and J. T. R. Andrews [*J. Am. Oil Chemists' Soc.* **26,** 309–12 (1949)]. These authors report increased accuracy and sensitivity of the Willard and Boyle periodate procedure for potassium through (1) hand stirring during precipitation of the potassium periodate, (2) totally reducing the periodate to iodine, and (3) titrating the iodine with sodium thiosulfate solution. Because our own paper deals in part with these points, we wish to call this paper to the attention of those interested in this procedure.

RALPH E. JENTOFT
REX J. ROBINSON

CRYSTALLOGRAPHIC DATA

154. Yttrium Trifluoride, YF_3, Orthorhombic Form

155. Samarium Trifluoride, SmF_3, Orthorhombic Form

156. Ytterbium Trifluoride, YbF_3, Orthorhombic Form

EUGENE STARITZKY and L. B. ASPREY, The University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M.

THE trifluorides of yttrium, samarium, and ytterbium were precipitated with hydrofluoric acid from aqueous solutions of corresponding chlorides. The precipitates were oven-dried at 110° C., dried under vacuum at 1000° C., and then heated under argon to about 100° C. above their melting point.

The yttrium oxide used as starting material for this preparation is believed to be about 99% pure. The samarium was purified by E. I. Onstott of this laboratory by an electrolytic process (*1*). It contained 0.07% neodymium and 0.003% europium (determined spectrophotometrically). No other rare earth elements were detectable spectrographically in the ytterbium oxide used, which was purified by ion exchange methods.

The structure of these orthorhombic trifluorides, belonging to the space group $Pnma - D_{2h}^{16}$ with a unit cell containing four formula units, has been determined by Zalkin and Templeton (*2*). They reported the following unit cell dimensions:

	YF_3	SmF_3	YbF_3
a_0, A.	6.353	6.669	6.216
b_0, A.	6.850	7.059	6.786
c_0, A.	4.393	4.405	4.434
Volume per formula unit, A.^{3}	47.79	51.84	46.76
Density (x-ray), grams per cc.	5.069	6.643	8.168

The powder x-ray diffraction pattern of yttrium fluoride is given on ASTM cards 5-0546, 5-0547, of samarium fluoride on card 5-0517, and of ytterbium fluoride on cards 5-0551, 5-0552.

The density of the trifluorides crystallized from melts was determined with a Berman microbalance as 6.61 grams per cc. for the samarium salt; 8.17 grams per cc. for the ytterbium compound.

CRYSTAL MORPHOLOGY. The trifluorides crystallized from their melts as aggregates of coarse anhedrons characterized by prominent {010} cleavage and twinned polysynthetically on {101} (Figure 1).

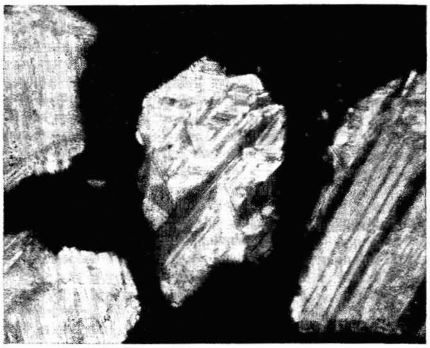


Figure 1. Cleavage fragments of orthorhombic samarium trifluoride showing repeated twinning

Crossed polarized light

OPTICAL PROPERTIES.

	YF_3	SmF_3	YbF_3
Refractive indices (5893 A.)			
n_X	1.536	1.577	1.569
n_Y	1.553	1.597	1.580
n_Z	1.569	1.608	1.599
Geometric mean	1.552_6	1.594	1.582_6
Molecular refraction, cc.	9.21	10.60	9.41
Optic axial angle, 2*V*	85°	72°	78°

Optic Orientation. $X = c$; $Y = b$; $Z = a$.

Extinction Angles. Extinctions on {010} cleavage plates are symmetric with respect to the trace of the composition plane {101}. The angle between the *Z*-directions in adjacent twin lamellae is 67° for samarium trifluoride, 71° for ytterbium fluoride.

Color. Samarium trifluoride is pink; yttrium and ytterbium fluorides are colorless.

LITERATURE CITED

(1) Onstott, E. I., *J. Am. Chem. Soc.* **77**, 2129–32 (1955).
(2) Zalkin, A., Templeton, D. H., *Ibid.*, **75**, 2453–8 (1953).

WORK done under auspices of Atomic Energy Commission. Crystallographic data for publication in this section should be sent to W. C. McCrone, 500 East 33rd St., Chicago 16, Ill.

157. Lanthanum Trifluoride, LaF_3

158. Neodymium Trifluoride, NdF_3

EUGENE STARITZKY and L. B. ASPREY, The University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M.

LANTHANUM and neodymium fluorides were precipitated with hydrofluoric acid from aqueous solutions of corresponding chlorides. The precipitates were heated to 400° C. in an atmosphere of gaseous hydrogen fluoride, heated under vacuum to about 1000° C., and then melted under argon at about 1400° C. The fluorides crystallized from their melts as coarse-grained anhedral aggregates.

The lanthanum source material used was purified by ion exchange methods. Spectrographic analysis indicated the presence of 0.02% calcium and 0.005% magnesium; no rare earth elements were detected. Spectrographic analysis of the neodymium salt indicated the presence of 0.1% magnesium, 0.01% calcium, 0.03% iron, and 0.2% cerium. No other rare earth elements were detected.

Oftedal (*2*) proposed a structure for hexagonal rare earth fluorides belonging to the space group $P6_3/mcm - D_{6h}^3$ with a cell containing six formula units. Cell dimensions reported by Oftedal (*1*) for lanthanum fluoride are, after converting from *kX* to Angstrom units, $a_0 = 7.117 \pm 0.007$ A., $c_0 = 7.344 \pm 0.007$ A.; for neodymium fluoride corresponding figures are $a_0 = 7.035 \pm 0.007$ A., $c_0 = 7.210 \pm 0.007$ A.

X-RAY DIFFRACTION DATA.

	LaF_3	NdF_3
Cell dimensions		
a_0, A.	7.186 ± 0.001	7.030 ± 0.001
c_0, A.	7.352 ± 0.001	7.200 ± 0.001
c_0/a_0	1.023	1.024
Volume per formula unit, A.^{3}	54.80	51.36
Formula weight	195.92	201.27
Density, grams per cc.	5.936	6.506

The above cell dimensions were determined by linear extrapolation against the function $(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ to the zero value of that func-

Table I. Partial Powder X-Ray Diffraction Patterns of Lanthanum Trifluoride and Neodymium Trifluoride

	Lanthanum Fluoride		Neodymium Fluoride		
hk·l	*d*, A., calcd.	*d*, A., obsd.[a]	*d*, A., calcd.	*d*, A., obsd.[a]	*I*[b]
00·2	3.676	3.66	3.600	3.58	50
11·0	3.593	3.58	3.515	3.49	15
11·1	3.228	3.21	3.159	3.14	95
20·0	3.112	...	3.044	3.03	< 5
11·2	2.570	2.562	2.515	2.515	10
20·2	2.375	...	2.324	2.310	< 5
12·1	2.240	2.236	2.192	2.189	5
30·0	2.074	2.070	2.029	2.022	65
11·3	2.025	2.020	1.982	1.974	100
00·4	1.838	1.834	1.800	1.795	15
30·2	1.807	1.803	1.768	1.764	50
22·1	1.745	1.741	1.707	1.703	35
11·4	1.636	1.632	1.602	1.600	10
22·2	1.614	1.610	1.579	1.577	5
22·3	1.4489	1.446	1.4180	1.415	30
30·4	1.3757	1.374	1.3466	1.343	25
11·5	1.3609	1.358	1.3325	1.331	15
41·1	1.3354	1.334	1.3065	1.305	30
22·4	1.2847	1.283	1.2575	1.255	< 5
41·2	1.2739	1.273	1.2464	1.245	10
00·6	1.2253	1.224	1.2000	1.199	10
33·0	1.1977	1.197	1.1717	1.171	15
41·3	1.1878	1.187	1.1623	1.161	30
11·6	1.1597	1.159	1.1356	1.134	10

More than 20 additional lines were measured in each pattern.

[a] Philips 114.6-mm.-diameter powder camera, Straumanis mounting; $\lambda(\mathrm{Cu}K\alpha) = 1.5418$ A.

[b] Relative peak intensities above background from densitometer measurements. Intensities of lanthanum trifluoride pattern were not significantly different.

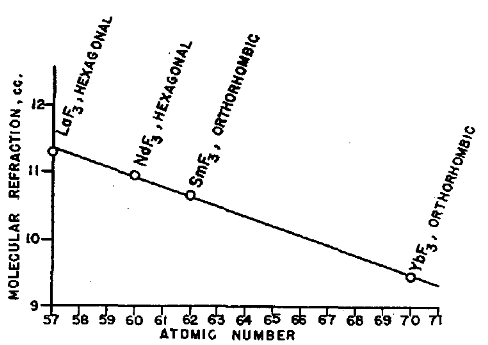


Figure 1. Molecular refraction of some rare earth trifluorides

Table II. Absorption Spectrum of Neodymium Trifluoride

(Band maxima in mμ and relative intensities as viewed with a Zeiss microspectrometer eyepiece)

Parallel to *O*	Parallel to *E*
...	667 medium
...	628 very weak
595 very weak	595 weak
582 medium strong	586 weak
578 very strong	578 very strong
570 medium strong	571 strong 569 medium
...	532 weak
524 medium	524 weak
521 strong	521 very strong
518 medium strong	...
512 weak	513 medium weak
505 medium weak	509 weak
470 weak	470 weak

tion of a_0 and c_0 values calculated from several groups of diffraction lines in restricted angular ranges In all some 30 α_1 and α_2 lines in the angular range 40° to 84° were used in each case.

OPTICAL PROPERTIES.

Uniaxial negative.

	LaF_3	NdF_3
Refractive indices (5893 A.)		
n_O	1.603	1.628
n_E	1.597	1.621
Geometric mean	1.601	1.6257
Lorentz-Lorenz refraction, cc.	11.31	10.95
Color	Colorless	Brown

The above figures for molecular refraction have been plotted as a function of the atomic number of the metal on Figure 1, together with corresponding data for the orthorhombic trifluorides of samarium and ytterbium. This property of trifluorides of lanthanide elements appears to be approximated by a linear function of the atomic number, not markedly affected by structural differences.

LITERATURE CITED

(1) Oftedal, I., *Z. phys. Chem.* (B) 5, 272–91 (1929).
(2) *Ibid.*, (B) 13, 190–200 (1931).

WORK done under auspices of Atomic Energy Commission. Crystallographic data for publication in this section should be sent to W. C. McCrone, 500 East 33rd St., Chicago 16, Ill.

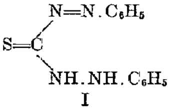
MEETING REPORTS

Society for Analytical Chemistry

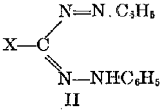
A MEETING of the Society for Analytical Chemistry was held November 7 in London, at which the following paper was presented and discussed.

Structure of Dithizone and Its Metal Complexes. H. M. N. H. IRVING, Inorganic Chemistry Laboratories, South Parks Road, Oxford.

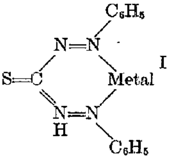
Diphenylthiocarbazone (dithizone, I and II, X = SH) was first prepared by Emil Fischer in 1878, but it was not introduced into analysis until 30 years ago. About this time, and on the basis of exiguous experimental evidence, structural formulas were ascribed to a number of the metal dithizonates, and Helmuth Fischer postulated that the imino-hydrogen of I could be replaced to form the so-called keto complexes—e.g., III—and that the hydrogen of the thiol form, II, X = SH, could in certain circumstances be removed also to give enol complexes—e.g., IV.



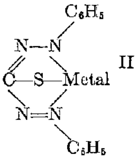
I



II



III



IV

The experimental investigation of dithizone and its metal complexes is complicated by the fact that the reagent is very sparingly soluble in water ($\sim 3 \times 10^{-7}$ M). Its intensely colored metal complexes need never be isolated in analytical procedures, for their amount is ascertainable by absorptiometry in organic solutions, which normally contain less than 20 γ of metal at a concentration of $\sim 10^{-5}$ M. However, it has proved possible to show that dithizone (in the thiol form, II, X = SH) is a weak acid, with pK = 4.5, that shows no signs of losing a second proton up to pH 14. The empirical formulas of a number of metal dithizonates have been established by a variety of techniques and the physical chemistry of their solvent extraction has been thoroughly worked out.

Recent work suggests that the two forms of dithizone, I and II, X = SH, coexist in solution, the position of equilibrium depending upon the solvent used, but not upon time, concentration, or illumination. Chloroform-soluble metal complexes have been prepared from triphenylformazan, II, X = C_6H_5, apparently by replacing an imino hydrogen, thus lending some support to Helmuth Fischer's formulation of keto complexes, III. However, *S*-methyldithizone, II, X = SCH_3, has been prepared by unambiguous syntheses and does not form metal complexes analogous to those of dithizone, suggesting that the presence of an acidic thiol hydrogen is essential. Solid red *S*-methyldithizone dissolves in organic solvents to give red solutions that rapidly turn yellow-brown in consequence of a complicated sequence of cis-trans and/or syn-anti isomerization, which can be reversed by suitable irradiation. Similar photochemical isomerizations have been noted with certain alkylformazans and arylformazans, II, X = alkyl or aryl, but not with chloroformazyl or formazan itself, II, X = Cl or H. The change in color from yellow to royal blue that occurs when solutions of mercury dithizonate are suitably irradiated may arise from a similar isomerization.

Some tentative formulations were proposed for some of the metal dithizonates, and the implications of the possible structural isomerism were discussed in relation to their use in analysis.

On October 25 the Midlands Section met in Nottingham.

Recent Advances in Ion Exchange Resins. D. K. HALE, Chemical Research Laboratory, Teddington.

The properties and methods of application of conventional ion exchange resins were outlined. New ion exchange materials were described, including chelating resins, ion exchange membranes, and ion exchange papers. Recent developments of electron exchange resins were described, including new ion exchange techniques, such as gradient elution and ion exclusion.

On December 5 a meeting on the subject of trade effluents was held in London.

Determination of Metallic Contaminants. N. T. WILKINSON, Research Department, Alkali Division, Imperial Chemical Industries, Ltd., Northwich.

This paper dealt with the work of the Joint A.B.C.M./S.A.C. Committee on Methods for the Analysis of Trade Effluents (Panel 2, Metallic Contaminants). Special points of interest were mentioned regarding methods published in *The Analyst*. Methods under consideration were discussed in more detail.

Analytical Problems Concerned with Oil and Grease in Effluents and River Waters. J. G. SHERRATT, Public Analyst's Laboratory, Warrington.

Some of the objectionable consequences of oil pollution of surface waters and discharge of oily liquids into public sewers were briefly considered, and special problems inherent in sampling and analysis of oil-containing effluents were discussed. Methods were suggested whereby some of the difficulties may be overcome.

Trade Effluents Analysis. Oxygen Demand. C. J. REGAN, formerly Chemist-in-Chief, London County Council.

As the ultimate purification of a trade effluent is usually the result of biochemical oxidation, its oxygen demand is generally the most important analytical characteristic.

Apart from the theoretical calculation of the ultimate oxygen demand (U.O.D.), which can be made from the contents of organic carbon and of ammoniacal and organic nitrogen, three methods of assessing the oxygen demand of a trade effluent were briefly mentioned: (1) absorption from acid permanganate, permanganate value; (2) absorption from boiling acid dichromate, dichromate value; and (3) biochemical oxygen demand (B.O.D).

Comments were made regarding the results obtained by these techniques and the particular usefulness of dichromate value in trade effluents received special mention. The need for care in interpretation of the results was stressed.

The North of England Section met in Liverpool on December 8.

Some Applications of the Weisz Ring Oven. W. I. STEPHEN, Birmingham University.

A novel microchemical technique, called the ring-oven technique, which has recently been described by Weisz, employs only simple readily constructed apparatus for the quantitative separation of ions in a single drop of solution. The qualitative analysis of mixtures of several common cations can readily be carried out on extremely small amounts of material (1 to 2γ in 1 μl. of solution).

By a simple extension of the principles of the ring-oven technique, rapid analyses on a semiquantitative basis can be carried out for several common metals with accuracies of the order of ±5%.

A combination of the techniques of electrographic analysis and the ring-oven method has led to the development of ring electrography, which is applied to rapid qualitative and semiquantitative testing of several alloys of simple composition.

The Midlands Section met in Nottingham on December 11.

Aspects of the Application of Chromatography to the Quantitative Analysis of Inorganic Substances. F. H. POLLARD, Bristol University.

The paper considered problems involved in obtaining chromatographic separations of mixtures of inorganic substances suitable for subsequent quantitative analysis. Use of paper strips, cellulose columns, and ion exchange resins for chromatographic separations. Recent work on the alkaline earths, valency states of iron, etc., determination of small percentages of metals associated with lead and similar topics, and work on the oxy acids of sulfur.

At a meeting of the Midlands Section held January 10 at The University, Birmingham, the following paper was presented and discussed.

Analytical Chemistry of Some Newer Insecticides and Herbicides. K. GARDNER, Fisons Pest Control, Ltd., Cambridge.

The number of chemicals proposed for use as pesticides has increased very rapidly since the last war. Apart from the complex problems associated with the analysis of pesticide residues on and in vegetable matter, the determination of the active ingredient content in the technical product is often made difficult by closely related impurities. A large majority of recently developed insecticides and herbicides are based on chlorinated hydrocarbons and organophosphorus compounds. The analytical chemistry of some of these technical materials was discussed: insecticides demeton, dimefox, and malathion and the herbicides CMU and sodium trichloroacetate.

At a meeting of the North of England Section on January 26, in Manchester, recent advances in the analysis of fertilizers were discussed by H. N. Wilson, I.C.I., Ltd., Billingham.

The present methods of analyzing fertilizers for nitrogen, phosphate, and potash were reviewed, with emphasis on recent developments, and references to colorimetric or physical methods which, in the lecturer's experience, have proved valuable in recent years.

At a meeting of the Western Section on February 22 at Bristol, a lecture on the oxygen demand of trade effluents with respect to river pollution was given by C. J. Regan.

The formulation of standard methods of analysis for aqueous liquids of different degrees of impurity was first considered. The importance of the oxygen demand was emphasized, particularly in regard to trade effluents and river pollution. Here it is essentially a biochemical question, as the ultimate purification of organic matter is a biological process.

Apart from theoretical calculation of the ultimate oxygen demand, from a knowledge of the organically combined elements present, three methods of assessing the oxygen demand of a trade effluent were described: absorption from acid potassium permanganate, absorption from acid boiling potassium dichromate, and biochemical oxygen demand. These are tests recommended by the panel of the Joint Committee of the Association of British Chemical Manufacturers and Society for Analytical Chemistry, now sitting.

Modified Hershberg Melting Point Apparatus

Helmut E. Drechsel, Smith, Kline & French Laboratories, Philadelphia, Pa.

NUMEROUS methods and types of apparatus are available for determining melting points of organic compounds. One of the most popular is the capillary tube method employing an apparatus designed by Hershberg [IND. ENG. CHEM., ANAL. ED. **8**, 312 (1936)], or some modification of it. In most cases the bath liquid is heated with a small gas flame or an insulated electric heater applied to the outer surface of the apparatus. Not only is an open flame a hazard in the laboratory, but by using it or an external electric heater, it is difficult to attain a desirably slow and constant rise in bath temperature when approaching the melting point. The factors influencing the reproducibility of a melting point are well known (Weissberger, A., ed., "Technique of Organic Chemistry," Vol. I, "Physical Methods of Organic Chemistry," Pt. I, 2nd ed., pp. 49 ff., Interscience, New York, 1949). A modified Hershberg apparatus reduces these factors to a minimum, and allows the corrected melting point of a substance to be read directly from the thermometer calibrated in the apparatus.

The apparatus (Figure 1) consists of a U-shaped tube with a connecting tube between the two arms. The larger arm is twice the diameter of the smaller and is filled with approximately 175 ml. of silicone oil (silicone fluid, General Electric and Dow Corning). The smaller arm contains an agitator of the spiral or corkscrew propeller type with a clearance of 1 mm. between the blades and the walls of the tube. This permits thorough agitation without a vortex or bubbles in the oil, which decrease visibility when the melting point is being read.

An unsheathed heating coil of Nichrome wire is located in the bottom of the U. Acceleration of heating is constant, depending on the voltage input supplied through a variable transformer. Figure 2 shows the voltage and time needed to obtain various temperatures. In normal use a setting of 10- to 55-volt input will give a temperature range of 45° to 320° C.

A holder for melting point capillaries is held in the larger arm of the U by a ground joint. A small glass sleeve or bushing is used in place of the conventional glass rings for keeping the melting-point capillaries in place. These tube-guides are sturdy and prevent the tubes from vibrating while the agitator is running. One thermometer covers the range 0° to 350° C. The thermometer is made from top quality material and is completely annealed to relieve all strains, thus ensuring repeated accurate temperature readings. The immersion and emergent stem corrections are eliminated by calibration of the thermometer blank every 50° of the scale from 0° to 300° in the apparatus and under actual operating conditions. For convenience, two immersion rings engraved on the thermometer stem designate maximum and minimum immersion attained through expansion of the silicone oil during heating. Calibration points on the thermometer are established with a series of National Bureau of Standards certified registered thermometers, and are checked at various points on the scale with certified U. S. Pharmacopoeia reference melting point compounds (Table I).

In the initial temperature tests four thermometers were made to cover the ranges 30° to 110°, 110° to 190°, 190° to 270°, and 270° to 350° in 0.5° divisions. For calibration the blank thermometer was placed in the thermometer holder and the standard was fixed in the larger arm of the U-tube, so that the depth of immersion was the same in each instance. The position of the immersion ring was marked on the blank thermometer. The bath was then heated to the desired calibration point—e.g., 30°—as determined by the corrected temperature of the standard thermometer and the height of the mercury column in the blank, measured in millimeters. Four reference points were thus established on each blank, from which the scale for each thermometer was engraved.

The finished thermometers were checked against USP reference melting point compounds (Table I).

These four thermometers were then used as standards, with the temperature

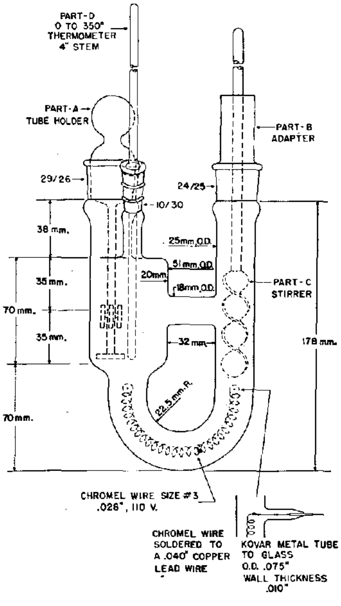


Figure 1. Melting point apparatus

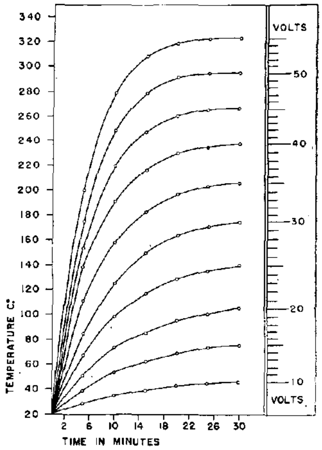


Figure 2. Chart of voltage input from transformer, in relation to temperature rise per minute for Drechsel melting point apparatus

Table I. Check of Calibrated Thermometers

Substance	USP M.P., ° C.	Thermometer No.	M.P. Found, ° C.	Δ
Vanillin	81 – 83	1	81 – 83	0
Acetanilide	114 –116	2	114 –116	0
Acetophenetidin	134 –136	2	133.5–136	0
Sulfanilamide	164.5–166.5	2	163.5–165.5	+1
Sulfapyridine	190 –193	3	190 –192	0
Caffeine	235 –237.5	3	235 –236	0
Oxanilide	250	3	249.5–250	+0.5
Anthraquinone	286 subl.	4	284 –284.5	+1.5

correction applied as found in Table I, to calibrate all additional melting point apparatus thermometers. A thermometer with a range of 0° to 350° C. in 1° divisions calibrated every 50° of the range was then used in the actual apparatus.

Constructional Details. Figure 1 shows the assembled melting point apparatus with all parts in place.

The Kovar metal to glass seal is made with the following Corning glasses: No. 774 (Pyrex) to 3320 (Uranium) to 772 (Nonex) to 7052 (Kovar sealing glass). The Chromel wire is silver-soldered to a 0.40-inch copper lead, and the copper lead wire is soldered into the Kovar metal tube, also with silver solder. The leads connecting the apparatus and the variable transformer are made from a braided 0.40-inch copper wire covered with plastic insulation tubing to give flexibility, and a suitable electric plug is attached to fit the variable transformer.

A is the melting point capillary tube holder with four small guides to support the capillary tubes. The 19-mm. disk at the bottom was cut from a section of borosilicate glass rod 19 mm. in diameter. The two air holes in the tube holder are important, as they relieve the pressure in the apparatus as the silicon oil expands.

B is the adapter for the spiral stirrer; this serves as a guide for the stirrer. Enough clearance should be present between the adapter and stirrer shaft to permit a pressure release as the silicone oil is heated.

C is the stirrer with the spiral blade. The blade is made from a section of $^{1}/_{8}$-inch thick borosilicate plate glass cut 20 mm. in width. When the spiral is fabricated it will narrow about 2 mm. to a finished product of 18 mm. in width. It is important that the spiral be fabricated so as to circulate the silicone oil in a counterclockwise direction, so that the silicone oil is pulled through the agitator and down through the test chamber.

D is the test thermometer.

Figure 2, a voltage input chart, shows voltage required in relation to a temperature rise per minute.

A patent on this apparatus has been applied for; the apparatus is manufactured by Kontes Glass Co., Vineland, N. J.

Device for Orienting Small Crystals under the Microscope

Betty J. Steinbach[1] and Thomas R. P. Gibb, Jr., Tufts University, Medford, Mass.

The optical characterization of small crystals is greatly expedited by a device which permits a single crystal or fragment to be oriented in various ways under the polarizing microscope, particularly when the crystal has a preferred habit or cleavage—for example, boric acid—or only a single small crystal is available. The novice finds it much easier to visualize the optic directions and to measure optical properties with the aid of such a device, as the crystal may easily be turned to show centered or at least recognizable interference figures.

The axial rotation stage (available from Kenneth A. Dawson Co., Belmont, Mass.) was developed in the hope of satisfying the need for a crystal-orienting device intermediate between makeshifts of limited applicability (*2*) and the intricate universal stage of Federov (*1*). The device described permits orientation on three axes of rotation, allowing continuous examination of interference figures and usually measurement of all indices of refraction. Rotation about one of these axes is limited to 20° or 30°, depending on the objective used. Nevertheless, this limited rotation is a desirable feature, as it frequently eliminates the need for precise alignment of the crystal with the shaft. It is particularly desirable as a means of obtaining centered figures.

In the construction of the stage (Figure 1) the following specifications are essential. The center of rotation of the yoke, *F*, must be slightly more than the thickness of a microscope slide above the top of the supporting plate *A*, as the crystal must be at the center of rotation of the yoke and must also be immersed in an index of refraction liquid. The liquid is contained by capillary attraction in a cell which consists of two small pieces of microscope slide about 0.5 × 0.3 cm. cemented to a slide about 2 mm. apart and covered by a fragment of a cover glass. If the center of rotation of the yoke is too high, the crystals may not be close enough to the condenser to give a good interference figure.

A segment, *G*, of a protractor is mounted on the base beside the yoke which carries a pointer, *H*. A second segment, *J*, is mounted on an extension of the yoke. The pointer, *I*, on the shaft is mounted on a sleeve and may be positioned by means of the setscrew. *J* need cover only 180° because, if the pointer is properly set, both melatopes and both bisectrices of an interference figure can be brought to the cross hair without going off the scale. If the 180° scale is used, the side extension of the yoke need not be as long as illustrated, as it need not extend beyond the edge of the microscope stage. Brass stock $^{1}/_{8}$ inch thick was used for the base, *B*, and yoke; the axle was made of $^{1}/_{16}$-inch drill rod, machined down to 0.030 inch at the tip.

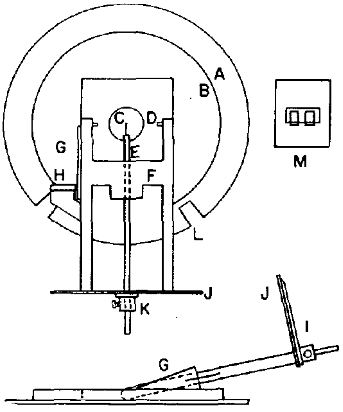


Figure 1. Top and side views of rotation device and glass cell

A. Base plate *B*. Base
C. Crystal mounted on shaft above circular aperture in base plate
D. Pivots (setscrews with conical end)
E. Shaft *F*. Yoke
G. Segment of protractor
H and *I*. Pointers *J*. Protractor
K. Sleeve with set screw attached to pointer *I*
L. Slots to accommodate stage clips
M. Cell

A similar instrument, lacking the third axis of rotation, has been described by Wood and Ayliffe (*3*), who also describe a method for mounting crystals in a preferred orientation by means of a goniometer. This is seldom necessary with the device described here. Small crystals are simply "picked up" from a flat surface by the tip of the shaft, which is previously touched to a tiny drop of Pliobond cement.

The authors acknowledge the assistance of Andrew Levesque, who constructed the device and contributed materially to its design.

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Excerpted from a thesis submitted in partial fulfillment of the requirements for the B.S. degree at Tufts University. Contribution 237 from Department of Chemistry, Tufts University.

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[1] Present address, Massachusetts Institute of Technology, Cambridge, Mass.

Small Dry Box for Sampling

E. C. Fiebig, E. L. Spencer, and R. N. McCoy, Shell Development Co., Emeryville, Calif.

Most analytical laboratories are periodically called upon to analyze air- or water-sensitive materials. Standard commercial dry boxes generally consist of large boxlike structures fitted with various accessories and are intended for a variety of operations which are conducted by means of rubber gloves attached to the box. They are expensive, require an excessive amount of laboratory space, and consume large volumes of inert gas for purging, and the gloves make delicate handling operations difficult. In addition, they are difficult to clean if a noxious material is spilled. Franklin and Voltz [Anal. Chem. **27,** 865 (1955)] recently described a small low-cost plastic bag which overcomes most of these disadvantages. For the limited purpose of sampling materials for analysis the authors have devised a small, compact dry box based upon use of an inverted 150-mm. glass funnel. All operations are conducted through an open 16 × 50 mm. slot cut in the side of the funnel. The entrance of significant amounts of air or water vapor is prevented by a continuous outflow of inert gas through the same slot.

The dry box is illustrated in Figure 1. The funnel, *A*, is a common glass funnel which has had a slot cut in the side by drilling two holes and making connecting cuts between them with a Carborundum cutting wheel.

The hollow stainless steel base, *B*, has twelve 0.03-inch holes drilled in a 5-inch-diameter circle to facilitate purging with inert gas. It is fitted with two rubber and two threaded feet (to enable the entire box to be tilted), a gas inlet fitting, *C*, and four small metal blocks glued to the top in such a manner that the funnel can be slid from front to rear without uncovering any of the holes.

The sample vial holder, *D*, is solid metal and is held from sliding by two short metal pins set in the base. The front face is beveled at an angle of 45° to enable the sample to be seen clearly. An oversize hole (0.75 inch for 2-dram vials) is drilled almost through the block from the front at an angle of 20° from the horizontal to hold sample vials. This angle is such that liquid in nearly empty vials is accessible while nearly full vials do not overflow.

A sheet metal table, *E*, is fitted over the sample vial holder as shown. The clips hold horizontal-type weighing bottles which contain boats or other open sample containers during weighing and handling operations outside the dry box. The front space on the table provides a working area when the sample is being transferred to boats or other sample containers.

The cap remover, *F*, has metal fingers which grip the vial cap by spring tension as shown. A screw-type pinch clamp is placed on the rubber tubing, *G*, at point *H* and used for proportioning the gas flow between the top and bottom of the dry box.

In use, the funnel is removed and the sample vial is placed in the block and wedged securely in place with a rubber wedge. Appropriate sample receivers are placed on the table and the funnel is replaced. Inert gas is passed into the box at a rate of about 5 liters per minute. After 2 minutes of purging, the cap remover is inserted through the slot and slipped over the vial cap, and the cap is unscrewed and placed to one side inside the dry box. The entire dry box is tilted, if necessary, to make the contents of the vial accessible, and the desired quantity of sample is transferred by reaching through the slot with a spatula, eye dropper, hypodermic syringe, or other sampling aid. Liquid samples can be sucked into glass bulbs having capillary stems by inserting the stem into the sample while the bulb is outside the dry box where it can be heated and cooled. Sampling equipment such as eye droppers and bulbs which contain air must always be filled with inert gas before use. Boats or other open sample containers are placed inside a suitable container which is closed before the dry box is opened.

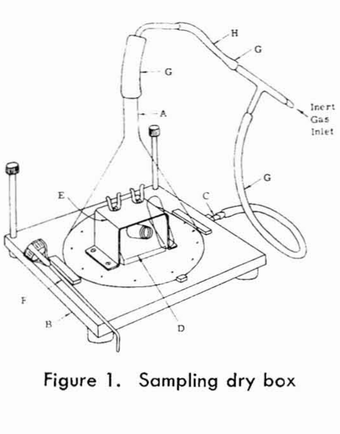

Figure 1. Sampling dry box

The prototype model of this box was constructed by using wooden blocks and a perforated section of copper tubing for the bottom inert gas distribution system. However, the wooden blocks absorbed spilled materials and could not be readily cleaned. The recommended design can be subjected to drastic cleaning measures if necessary. Other materials, such as plastics, could also be used for most of the parts involved. While plastics might absorb or be attacked by spilled materials, the initial cost might be low enough to permit damaged parts to be discarded.

Satisfactory use of this box requires some coordination with the "sample makers" to ensure that the sample is furnished in a suitable container. The authors have found that coworkers making sensitive materials are usually aware of the sampling problem and will cooperate.

Experience in routine use has shown that the dry box is convenient, useful, efficient, and easily stored. Hygroscopic, water- and oxygen-sensitive, and even pyrophoric organic boron compounds prepared by Buls, Davis, and Thomas [*J. Am. Chem. Soc.* **79,** 337 (1957)] have been sampled in it and successfully analyzed. Commercial purified nitrogen (99.9%) was sufficiently dry and inert to be used as the purge gas without further treatment.

Device for Monitoring Absorbance of Column Eluates in a Spectrophotometer

J. B. Stark, Roy Teranishi, and G. F. Bailey, Western Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture, Albany 10, Calif.

A device for continuous or manual monitoring of chromatographic-column eluates offers certain advantages in circuit simplicity and ease of operation over others previously described (*1*). Automatic monitoring avoids circuit complexity by the use of commercially available automatic recycling timing devices of the type used to control reflux ratio in distillation columns. The ease of operation is illustrated by the routine manual determination of absorbance at any set wave length for 50 samples in about 30 minutes. When desired, the spectrum can be scanned on a sample before proceeding to the next.

In Figure 1 the machined aluminum plate, *A*, $6\frac{5}{8} \times 5\frac{7}{8} \times \frac{3}{8}$ inches, serves as a lid and cell holder to cover the sample compartment. The lower edge of the plate is milled $\frac{9}{16}$ inch in and $\frac{3}{16}$ inch deep (Figure 2). The wooden block, *B*, fastened to the metal plate with screws, positions the cell in the path of the light beam. The 2-cm. path cell, *C*, is made from a Teflon plug 2.15 cm. in diameter with a 4-mm.

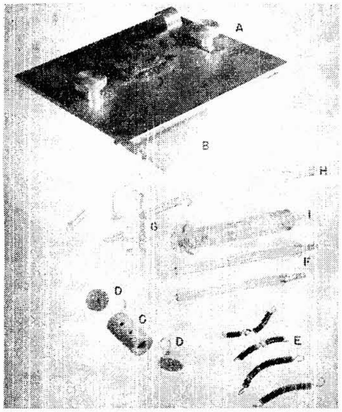

Figure 1. Disassembled monitoring device

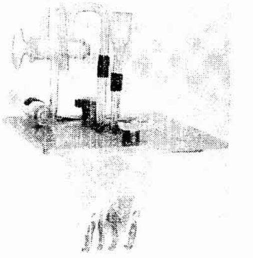

Figure 2. Assembled monitoring device

clear aperture (*2*). The ends are threaded to hold the quartz disks, *D*, 11 mm. in diameter and 2 mm. thick. The cell is held to block *B* with two springs, *E*. The holes in the top of the cell are tapered to fit a 5/20 standard-taper inner joint. The inlet and outlet tubes, *F*, of the cell are made of 2-mm. capillary tubing joined to a 5/20 inner joint. The tip of the ground joint is cut off so that it will not extend into the light beam through the cell. The tubes are positioned and held in the cell with the aid of two springs, *E*, attached to the ears on the tubes as shown in Figure 2. The tubes are aligned in the plate by means of screws and washers as shown in Figure 1. The stopcock is 2-mm. bore. The funnel has a capacity of 5 to 10 ml., and the syringe a capacity of 10 ml.

CONTINUOUS MONITORING

To operate the device for continuously monitoring a column effluent, the funnel stopcock and syringe shown in Figure 2 are removed. The outlet of the column is attached to a tube, *F*, entering the Teflon cell. An outlet tube leading to a fraction cutter or other collector is attached to the other tube *F*. Filling the cell with alcohol aids in preventing air-bubble formation. Another Teflon cell can be used for a reference cell or a standard cell 2 cm. in diameter can be used in conjunction with a metal disk diaphragm having a 4-mm. aperture.

The tendency of the pen to dig through the paper at slow chart speeds is eliminated by recording intermittently in a manner that consists of a closure of the "master" switch for a short period at predetermined intervals. The "power," "slit," "pen," "chart," and "lamp" switches remain on during the entire column run, while contact from the master switch is made by a program timer of the general class used for reflux ratio control. The most usual operating conditions were 7 seconds of recording at 6-minute intervals, with a chart speed of 1 inch per minute. Under these conditions continuous column operation has been satisfactorily maintained for 5 days. The spectrophotometer timer and fraction collector were usually synchronized to give three observations per time-controlled fraction with a column flow rate of 1 ml. per minute.

MANUAL OPERATION

For manual operation, the switches are connected to operate in the regular manner. The apparatus is assembled as shown in Figure 2. The sample is loaded into the funnel and at the same time drawn through the cell with the syringe. A solution with an absorbance of 2 can be washed out completely with 4 to 5 ml. of solvent or replaced by the same volume of new solution.

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Mention of products by commercial name does not imply recommendation by the Department of Agriculture over others of a similar nature not mentioned.

Warburg Manometer Flask for Increased Sensitivity in Ethylene Determinations

Harlan K. Pratt, University of California, Davis, Calif., and Curt W. Greiner, Greiner Glassblowing Laboratory, 3604 East Medford St., Los Angeles 63, Calif.

An improved flask has been designed for the manometric determination of ethylene by the method of Young, Pratt, and Biale (*3*). In this strictly chemical determination, the flask volume is critical only in its effect on the accuracy of the physical measurement. By using flasks with the smallest possible gas space above a given volume of liquid, sensitivity is increased because the amount of gas released in an analysis gives a larger pressure reading in the constant-volume, variable-pressure manometric system.

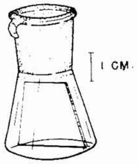

Figure 1. Manometer flask

The flask here depicted (Greiner Catalog No. 23-500) is conical, with a 17/20 standard-taper ground joint, and with a glass partition dividing the body of the flask into two equal compartments. Each side of the flask will accommodate 3 ml. of sample or reagent. The hooks are placed so that shaking is in a plane at a right angle to the partition; if shaking is parallel to the partition, premature mixing is likely. Total volumes of the flasks average about 10 ml., and the vessel constants of one set averaged 0.66, compared to 1.80 for the two-chamber vessels previously used or to standard 15-ml. Warburg vessels.

Warburg manometers can be read to the nearest 0.5 mm. Assuming that the total available volume of one sample of mercuric perchlorate solution is 20 ml., and 3-ml. aliquots are taken for analysis (*3*), a minimum of 120 μl. of ethylene could be determined with the standard vessels, or 44 μl. with the type described (allowing ±5% as satisfactory accuracy).

Further increase in sensitivity might be obtained using the hydraulic leverage principle recently described by Burk and Hobby (*1*). The special flask of Stanley and Tracewell (*2*) does not appear to meet the desired standard of high fluid volume coupled with low gas volume.

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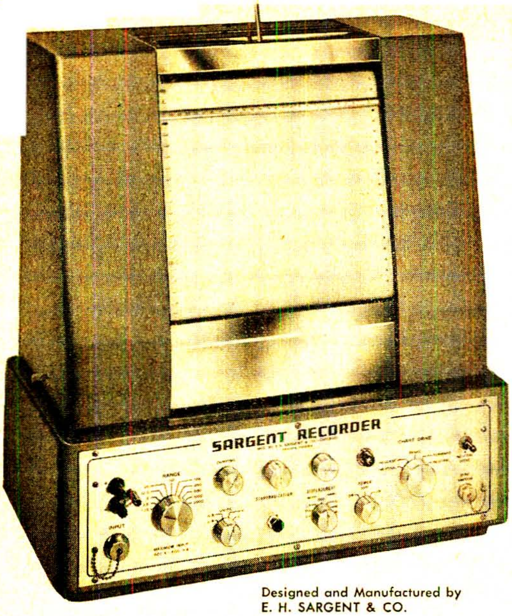

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Balances. Circle 10A for complete file on modern Mettler balances cited as being based on the principle of weighing by substitution. Mettler Instrument Corp., Hightstown, N. J. **10A**

Balances. Bulletin available on Troemner precision balance Model W-33. Capacity: 120 gm. Sensitivity: 2 mg. Sensitivity reciprocal: 6.5 mg. Henry Troemner, Inc., 911 Arch St., Phila. 7, Pa. **29A-4**

Balances. Brochure available providing complete information on company's triple beam balance. Capacity: 311 gram. Sensitivity: 1 centigram. Balance has a preweigher to speed results. Ohaus Scale Corp., 1050 Commerce Ave., Union, N. J. **32A**

Balances. Catalog available on company's balances and weights. Weights are of rhodium plated bronze, brunton metal, or stainless steel. Classes M, S and S-1. Wm. Ainsworth & Sons, Inc., 2151 Lawrence St., Denver 5, Colo. **35A**

Balances. Complete information available on company's 23 Torsion balances with no knife edges and 17 Christian Becker analytical balances. The Torsion Balance Co., Clifton, N. J. **51A**

Blenders. New catalog available on twin-shell blenders. Yoke model is cited as being ideal for small scale batch blending. Yoke arrangement fits standard 4 or 8 quart blender frame, permits two different blends at once. The Patterson-Kelley Co., Inc., 2340 Hanson St., East Stroudsburg, Pa. **28A**

Blenders. Specifications and applications data available on the gallon-sized Waring commercial "Blendor" cited as being ideal for pilot and experimental runs. Unit has multi-speed $1^1/_2$ h.p. motor, $7^1/_2$ foot 3 conductor ground cord, stainless steel container. Waring Products Corp., 25 West 43rd St., N. Y. 36, N. Y. **69A-2**

Carbon Determinators. 16-page catalog illustrates company's carbon determinator cited as providing an accurate 2-minute carbon analysis. Harry W. Dietert Co., 9330 Roselawn, Detroit 4, Mich. **22A**

Cells, Glass Absorption. Circle 89A-4 for complete information on Klett glass absorption cells. Klett Manufacturing Co., 177 East 87th St., N. Y., N. Y. **89A-4**

Centrifuges. Bulletin available on company's new high-speed angle centrifuge, a fully enclosed table model with speeds up to 17,000 r.p.m., forces up to 34,390 G and capacity of 400 ml. Instrumentation includes electric tachometer, ammeter, automatic timer, and autotransformer. International Equipment Co., 1284 Soldiers Field Rd., Boston 35, Mass. **44A**

Centrifuges. Bulletin available on superspeed refrigerated centrifuge with dual automatic temperature and holding control. 16,000 rpm (32,700 × G). Capacities: From 400 ml. or less at superspeed, to 2,000 ml. at lower speeds. Ivan Sorvall, Inc., Norwalk, Conn. **68A-1**

Chromatographs. 8-page bulletin available on the Fisher-Gulf "Partitioner" for gas-liquid partition chromatography. Completely automatic, it is cited as providing fast, precise quantitative and qualitative analyses of volatile materials. Fisher Scientific Co., 100 Fisher Bldg., Pittsburgh 19, Pa. **48A**

Chromatographs. Bulletin available on company's "Kromo-Tog" for gas and vapor phase chromatography in plant or laboratory. Model K-2 accommodates two separate columns. Burrell Corp., 2223 Fifth Ave., Pittsburgh 19, Pa. **75A-1**

Chromatographs. Descriptive folder and details available on chromatograph cited as being ideal for school or industry, research or control. Boiling range: 20°–400° C. Temperate increase rate: 2° C./min. Temperature maintained within 1° C. Uses 1.1 sq. ft. bench space. Wilkens Instrument & Research, Inc., Acheson Bldg., Berkeley 4, Calif. **90A-1**

Chromatography Cells. Circle 86A-4 for catalog on "Gow-Mac" gas chromatography cells. Catalog contains information on thermal conductivity cells for 225° C. operation, temperature regulated cell for operation at room temperature or 200° C. and power supply and control unit. Gow-Mac Instrument Co., 100 Kings Rd., Madison, N. J. **86A-4**

Colorimeters. Catalog available on company's "Spectronic 20" colorimeter cited as providing accurate readings at any wavelength in the 340 mμ-950 mμ range. Instant-acting meter gives exact percent transmission or optical density. Band pass: 20 mμ. Bausch & Lomb Optical Co., 60916 St. Paul St., Rochester 2, N. Y. **4th Cover**

Combustion Apparatus. Detailed information available on company's Van Slyke-Folch micro combustion apparatus. Uses magnetic stirring. For rapid quantitative microdetermination of carbon in organic compounds by a wet combustion method. Arthur H. Thomas Co., Vine St. at Third, Phila. 5, Pa. **78A**

Comparators. Handbook, "Modern pH and Chlorine Control," available. Gives theory and application of pH control; illustrates and describes full

(Continued on page 64 A)

Product Capsules

Taylor line. Contains information on comparators used to maintain uniform pH, chlorine levels in processing. W. A. Taylor and Co., 7306 York Rd., Baltimore 4, Md. **29A-1**

Crucibles. Coors crucibles are available in a complete variety of sizes and styles and are resistant to chemical attack and thermal shock. Complete information available. Coors Porcelain Co., Golden, Colo. **86A-2**

Densitometers. Bulletin available on company's photoelectric instrument for the rapid and convenient evaluation of strips and sheets of filter paper in partition chromatography and paper electrophoresis. Photovolt Corp., 95 Madison Ave., N. Y. 16, N. Y. **53A-2**

Drying and Calcining Equipment. Circle 88A for bulletin "Research and Pilot Plant Equipment for Drying and Calcining." Contains information on gas fired rotary continuous combination calciner and cooler that heats to 2000° F. and cools to between 150–200° F. 3′ 6″ wide, 9′ 6″ long, 4′ high. The C. O. Bartlett & Snow Co., 6210 Harvard Ave., Cleveland 5, Ohio. **88A**

Electrometers. Circle 74A for bulletin on the Curtiss-Wright dynamic capacitor electrometer. Provides direct readings as low as 10^{-16} ampere. Drift: less than ± 1 mv per day. Accuracy: $\pm 2\%$. Electronics Div., Curtiss-Wright Corp., Carlstadt, N. J. **74A**

Electrophoresis Apparatus. Folder available on the Spinco Model CP continuous-flow curtain electrophoresis unit that prepares volumes of pure fractions from any mixture which can be separated by paper electrophoresis. Spinco Div., Beckman Instruments, Inc., Stanford Park, Palo Alto, Calif. **80A**

Fluorometers. Bulletin available on instrument used to determine the optimum wavelength for activating organic compounds and the optimum wavelength for measuring their emitted fluorescence spectra. For manual operation, for recording or for oscilloscope presentation. Farrand Optical Co., Inc., Bronx Blvd. & E. 238th St., N. Y. 70, N. Y. **56A-2**

Fluorometers. Klett fluorometers are designed for the rapid and accurate determination of thiamin, riboflavin, and other substances which fluoresce in solution. Klett Manufacturing Co., 179 East 87th St., N. Y., N. Y. **39A-3**

Fluorometers. Bulletin available on line-operated multiplier fluorescence meter possessing high-sensitivity for measurement of low concentrations. Photovolt Corp., 95 Madison Ave., N. Y. 15, N. Y. **53A-3**

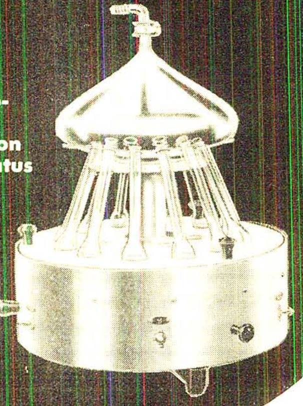
(Continued on page 66 A)

AMINCO now manufactures

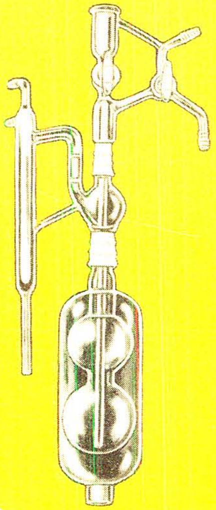
A FAMILY of INSTRUMENTS for Kjeldahl Determinations of Nitrogen

Step 1—Digestion

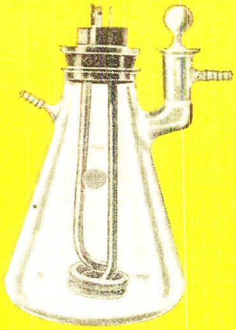
Aminco-Koegel Digestion Apparatus



Step 2—Distillation



Aminco-Koegel Distillation Equipment



New Bulletins. 2271 and 2286 (yours upon request), outline the details for Kjeldahl determinations of nitrogen using Aminco's new family of instruments.
Step 1: Samples are initially processed on a 12-unit rotary digestion rack, noted for its even, bump-free heating. Step 2: The digested samples are then transferred to a distillation apparatus where ammonia is quantitatively distilled into an absorbing solution. (Various interchangeable components are available in distillation apparatus.) The distillate is then ready for the final step in the Kjeldahl procedure. Step 3: Titration, which is rapidly, accurately and mechanically accomplished by the new Menisco-matic Buret. The Buret is fitted with a counter which provides direct digital readings of total ml delivered in titrametric analyses.

Digestion Apparatus, Cat. No. 4-1860, without flasks or fume hood as shown above. Accommodates 12 flasks up to 100 ml capacity each **$207**

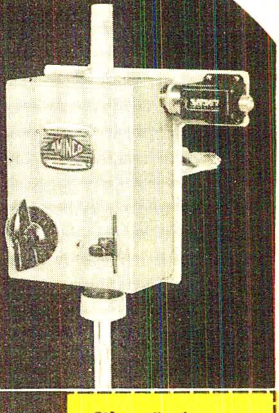
Distillation Flask No. 4-1870, and Distillation Apparatus, Cat. No. 4-1865, consists of distillation head and condenser, short entrance tube, and steam generator assembly, as shown at top right **$126**

Steam Generator Assembly, Cat. No. 4-1880, two liter, Pyrex. Complete with heater and line cord **$48.75**

Glassware Stand, Cat. No. 4-1886, holds digestion and distillation flasks. Useful when filling and draining flasks after washing. May be rotated through 360° **$29.75**

Step 3—Titration

Aminco-Koegel Menisco-matic Buret



4-1890 Menisco-matic Buret, complete with Standard Pyrex Reservoir $275

AMINCO

AMERICAN INSTRUMENT COMPANY, INC.

Silver Spring, Maryland

In Metropolitan Washington, D. C.

For further information, circle numbers 65 A-1, 65 A-2, 65 A-3, 65 A-4 on Readers' Service Card, page 77 A

Product Capsules

Freeze-Drying Apparatus. Circle 38A for details on company's new "Centri-Freeze" cited as being a complete freeze-drying laboratory on wheels. Stainless steel cart is 40" long, 28" wide, and 35" high. Lucite vacuum drum is 17" high, 12" in diameter. Arthur S. LaPine and Co., 6001 So. Knox Ave., Chicago 29, Ill. **38A**

Funnels, Separatory. Company's funnels are heavy walled yet have little thermal stress because they are made of Pyrex glass. Seals between bulb and stopcock, and stopcock and outlet tubing are re-enforced. Tip is fire-polished. Corning Glass Works, 72-4 Crystal St., Corning, N. Y. **34A**

Furnaces. Complete data available on furnace for general lab work and process control. Chamber size: 4" × 3¾" or 9". Variable temperature control from 350° F. to 1800° F. Welded steel construction, embedded element plates. Thermo Electric Manufacturing Co., 478 Huff St., Dubuque, Iowa **90A-2**

Furnaces. Bulletin available on laboratory muffle furnace with temperature range to 2300° F. All temperature control and indicating devices are located in the furnace pyramid base. Hevi Duty Electric Co., Milwaukee 1, Wis. **41A-2**

Furnaces. Bulletin available on company's compact laboratory box furnaces cited as being ideal for heat treating small parts, ash determinations, fusions, ignitions, assaying, and dry precipitates. Laboratory Equipment Div., Lindberg Engineering Co., 2440 W. Hubbard St., Chicago 12, Ill. **86A-1**

Furnaces. Bulletin available on company's tube type laboratory furnace cited as being ideal for annealing, brazing, heat treatment, hardening, sintering, reducing metal powders, silver soldering, and nitriding. Laboratory Equipment Div., Lindberg Engineering Co., 2440 W. Hubbard St., Chicago 12, Ill. **89A-3**

Glass Apparatus. Circle 67A for copy of special apparatus catalog, "Custom Made Laboratory Glassware." Contains hundreds of special pieces of laboratory glassware. Corning Glass Works, 69-4 Crystal St., Corning, N. Y. **67A**

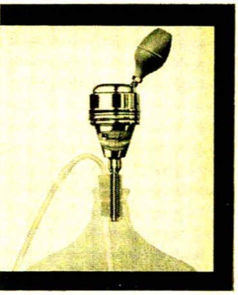
Heating Tapes. Company's new flexible electrothermal pipe heaters are waterproof and acid and alkali resistant. Available in 12.5', 25' or 50' lengths. Consistant temperatures up to 100° C. E. Machlett & Son, 220 East 23rd St., N. Y. 10, N. Y. **91A-1**

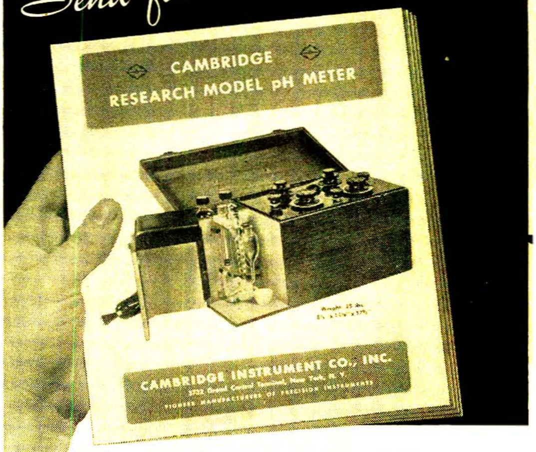
Laboratory Apparatus. Circle 69A-1 for catalog on company's scientific instruments and apparatus. Catalog includes information on weighing funnels, polyethylene wash bottles, and filter bells. New York Laboratory Supply Co., Inc., 76 Varick St., N. Y. 13, N. Y. **69A-1**

Laboratory Furniture. Circle 24A-1 for copy of "Steelab." Contains hundreds of ideas for laboratory furniture layouts. Circle 24A-2 for copy of "Fume Hoods," a complete fume control prospectus. Laboratory Furniture Co., Inc., Mineola, L. I., N. Y. **24A-1, 2**

Laboratory Furniture. Brochure available on "Moduline" unitized steel furniture cited as being flexible in function and arrangement, permanent in its all-welded construction, and economical in initial cost and upkeep. Aloe Scientific, Div. of A. S. Aloe Co., 5655 Kingsbury, St. Louis 12, Mo. **56A-1**

(Continued on page 67 A)





Laboratory Instruments. Circle indicated numbers for complete information on the following: new vapor fractometer that separates and analyzes fuel gas components in less than one hour, 42A-1; model 21 infrared spectrophotometer, 42A-2; the "Spectracord 4000" spectrophotometer, 42A-3; and a quarterly publication, "Instrument News," 42A-4. Instrument Div., Perkin-Elmer Corp., 800 Main Ave., Norwalk, Conn. **42A-1 to 4**

Melting Point Apparatus. Details available on company's micro cold stage for micro fusion studies over the range −100° C. to +70° C. Thomas-McCrone thermometer reading model. Arthur H. Thomas Co., Vine St. at 3rd, Phila., Pa. **54A-1**

Mercury Cleaners. Catalog available. Includes information on motor-driven oxifier that separates by air oxidation the dissolved base metals from the body of contaminated mercury. 2 to 4 hrs. per 25-lb. batch. Bethlehem Apparatus Co., 810 Front St., Hellertown, Pa. **66A-1**

Mercury Ejectors. Circle 52A-2 for bulletin on Leybold mercury ejectors and diffusion pumps. Circle 52A-1 for bulletin on Apiezon oil distillates for high vacuum work. James G. Biddle Co., 1316 Arch St., Phila. 7, Pa. **52A-1, 2**

Mercury Vapor Detectors. Information available on portable, ultraviolet photometer that measures toxic mercury vapors. Weight: 7 lbs. Size: 13″ × 8$^1/_2$″ × 4$^1/_2$″. Harold Kruger Instruments, Box 164, San Gabriel, Calif. **86A-3**

Metallographic Equipment. 16-page bulletin available that catalogs the apparatus and instruments needed for metallographic analysis. Circle 83A for copy. Fisher Scientific Co., 100 Fisher Bldg., Pittsburgh 19, Pa. **83A**

Mixers. Illustrated laboratory mixer bulletin available. Contains information on electric or air driven units, single or variable speeds, explosion-proof motors, accessories. Circle 33A for copy. Mixing Equipment Co., Inc., 160-d Mt. Read Blvd., Rochester 11, N. Y. **33A**

Nephelometers. 64-page manual, "Coleman Tools for Science," available. Contains information on company's complete line of nephelometers. Dept. A, Coleman Instruments, Inc., Maywood, Ill. **85A-1**

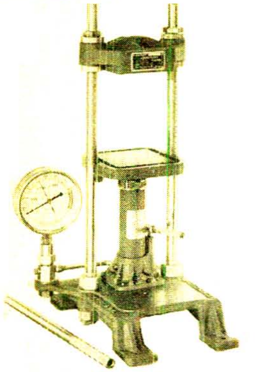
Nuclear Instruments. Catalog available. Contains full information on company's complete line of nuclear instruments, including complete proportional counting system and proportional counter converter. Nuclear Measurements Corp., 2460 N. Arlington Ave., Indianapolis 18, Ind. **75A-2**

Oil & Catalyst Testing Equipment. Catalog available. Contains information on company's complete line of apparatus for analysis, by the rapid combustion method, of sulfur in oil, oil additives, coal, coke and many other hydrocarbons. Laboratory Equipment Corp., 3004 Hilltop Rd., St. Joseph, Mich.

Ovens. Bulletin available on company's new rectangular oven. Hydraulic-type thermostat provides precise control of temperatures from 60° to 250°. Design insures constant, thorough circulation, company states. Central Scientific Co., 1708 Irving Park Rd., Chicago 13, Ill. **20A**

pH Meters. Detailed information available on the following Beckman pH meters: pocket, "Zeromatic," model N-1, model GS, model G, and model N-2. Harshaw Scientific, 1945 East 97th St., Cleveland 6, Ohio **16A**

(*Continued on page 68A*)



Product Capsules

pH Meters. Bulletin available on company's fully stabilized line-operated pH meter for plant and laboratory use. Compact, simple in construction. Photovolt Corp., 95 Madison Ave., N. Y. 16, N. Y. **53A-1**

pH Meters. Circle 65A-1 for data file on the Beckman pocket pH meter, a completely portable, battery operated, accurate instrument. Circle 65A-2 for data file on the Beckman "Zeromatic" pH meter. Instrument is drift-free and features push-button control and mirror-backed scale. Scientific Instruments Div., Beckman Instruments, Inc., 2500 Fullerton Rd., Fullerton, Calif. **65A-1, 2**

Phototubes, Multiplier. DuMont multiplier phototubes are available in a wide selection of sizes and electrical characteristics. Circle 12A for complete information. Industrial Tube Sales, Allen B. DuMont Laboratories, Inc., 2 Main Ave., Passaic, N. J. **12A**

Phototubes, Multiplier. Circle 87A for catalog, "RCA Photosensitive Devices and Cathode-Ray Tubes." Tube Div., Radio Corp. of America, Harrison, N. J. **87A**

Polarographs. Company's cathode ray "Polarotrace" is cited as providing speedy, direct or derivative operation; greater resolution due to formation of peaked polarograms; polarograms reproduced every seven seconds; accurate determinations at concentrations of fractions of a microgram per millilitre. Southern Instruments Computer Div., Camberley, Surrey, England **70A**

Polyethylene Ware. Brochure available on company's range of polyethylene ware. Contains information on wide mouth bottles, filtering flasks, connectors, and stoppers. Ace Glass Inc., Vineland, N. J. **26A**

Presses, Hydraulic. Bulletin available on press used for making KBr pellets for infrared spectroscopic analysis. 20-ton capacity. Bench mounted, hand operated. Loomis Engineering & Manufacturing Co., 133 So. 14th St., Newark 7, N. J. **18A**

Presses, Pellet. Specifications available on company's hand operated pellet press that develops approximately 2000 lb. compressive force to produce pellets up to 1/2" thick. Parr Instrument Co., Moline, Ill. **73A-1**

Publications. Subscription information available on "Analytical Abstracts" and "The Analyst." Both are British publications. The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1, England **39A-1**

Pumps. Single-stage vacuum distillation pump provides guaranteed vacuum .02 mm (20 microns) and free air capacity 33.4 liters per min. Efficient in long, continuous service, company states. W. M. Welch Scientific Co., 1515 Sedgwick St., Chicago 10, Ill. **41A-1**

Refractometers. Detailed literature available on the Abbe refractometer. Range of measurements: nd 1.3 to nd 1.71 and sugar percentage scale 0% to 95%. For liquids and solids by transmitted and reflected light. Carl Zeiss, Inc., 485 Fifth Ave., N. Y. 17, N. Y. **61A-2**

Refractometers. Bulletin available on company's automatic, recording chromatographic refractometer that features an exclusive range-extension system. Phoenix Precision Instrument Co., 3805 N. 5th St., Phila. 40, Pa. **66A-2**

Scalers, Electronic. Catalog available providing details and prices on the following electronic instruments: utility scaler, ampliscaler, autoscaler, "1000" scaler, superscaler, and research scaler. Tracerlab, Inc., 1601 Trapelo Rd., Waltham 54, Mass. **30A**

Spectrographs. Complete information available on Bausch & Lomb spectrographs. ARL "Quantometers," "Quantographs," and other advanced optical and x-ray emission equipment. Applied Research Laboratories, 3721 Park Pl., Glendale 8, Calif. **71A**

Spectrometers, N-M-R. Circle 14A for latest "Radio Frequency Spectroscopy Bulletin." Full technical information on both N-M-R and E-P-R spectroscopy and the complete "N-M-R at Work" series will be included. Instrument Div., Varian Associates, Palo Alto 4, Calif. **14A**

Spectrophotometers. Complete information on Coleman spectrophotometers available. The diffraction grating creates a true undistorted spectrum. The fixed (35 mμ) band-pass allows valid use of calibration curves, is constant at all wavelengths. Coleman Instruments, Inc., Maywood, Ill. **7A**

Spectrophotometers. Data file available on the Beckman DK-2 automatic recording spectrophotometer cited as providing speed and precision in chemical research involving analysis in the ultraviolet, visible and near infrared ranges. Scientific Instruments Div., Beckman Instruments, Inc., 2500 Fullerton, Calif. **3A-1**

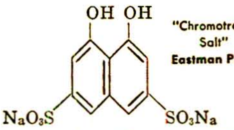
Spectrophotometers. Bulletin available on the Cary Model 11 recording spectrophotometer. Designed for applications in the ultraviolet and visible ranges, the instrument is cited as being

(Continued on page 71A)

...AMONG SOME 3500 ORGANICS

Eastman P230

Sometimes we tire of the sport of baiting born salesmen by admitting out loud we know no uses for many of the compounds we sell. Then we can turn to something like chromotropic acid, for which we know enough uses to bring the average back up.



"Chromotropic Salt" Eastman P230

4,5-Dihydroxy-2,7-naphthalenedisulfonic Acid Disodium Salt

Do you want to determine titanium? Buy **Eastman P230** and see *Anal. Chim. Acta*, *6*, 7. Also Volume I of Feigl's *Spot Tests* and Volume I of Welcher's *Organic Analytical Reagents.*

Hexoses? Buy **Eastman P230** and see *Anal. Chem.*, *25*, 771.

Chromium? Buy **Eastman P230** and see Welcher.

Formaldehyde and formic acid? Send for our abstract and *then* buy **Eastman P230.**

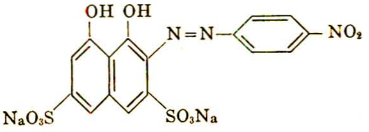
Silver? Buy **Eastman P230** and see Welcher and Feigl.

Serine? Buy **Eastman P230** and send for our abstract. (A molecule of formaldehyde splits off for each molecule of serine converted to glycine.)

Methanol? Buy **Eastman P230** and see *J. Assn. Off. Agri. Chem.*, August '51.

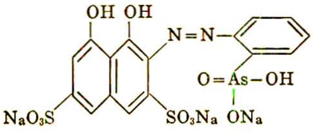
Mercury? Buy **Eastman P230** and see Welcher.

You can also buy **Eastman P230** and couple it with diazotized *p-Nitroaniline* (Eastman 179) to



with which you can spot-test for borates, according to Feigl. Unless you need the exercise, that would be a little quixotic because you can buy the reagent as *4,5-Dihydroxy-3-(p-nitrophenylazo)-2,7-naphthalenedisulfonic Acid Disodium Salt* (Eastman 4411).

East of the Oder, meanwhile, they have been busy diazotizing *o-Arsanilic Acid* and coupling it with chromotropic acid (doubtless using exotic brands instead of Eastman 6747 and **Eastman P230**, respectively) to get



which democrat or monarchist can purchase as *3-(2-Arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic Acid Trisodium Salt* (Eastman 7302, with the name slurred to "Arsenazo"). If he reads and believes scientific Russian, he may buy it for the determination of beryllium, rare earths (as a group), and aluminum in Al-Ni-Cr and Al-Mg alloys. (We'll supply the references, if asked.)

And still the roll of analytical uses for **P230** unfolds in wild profusion. Coupled with diazotized *Sulfanilic Acid* (Eastman 238), it makes

available as *4,5-Dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalenedisulfonic Acid Trisodium Salt* (Eastman 7309, referred to by aficionados as "SPADNS"). It is an indicator for 1) the titration of thorium, 2) the complexometric titration of zirconium, 3) the titrimetric determination of micrograms of fluoride ions. (Abstract on request.)

If those aren't enough uses, perhaps you'd better buy something else.

A scoop for radicals

"I have in my hand a little bottle which contains some dry, dark violet prisms of **a free radical,**" you will casually remark to acquaintances and students suspected of being unfamiliar with *J.A.C.S.*, *72*, 1051; *J. Org. Chem.*, *17*, 1437; or *J. Chem. Soc. 1954*, 3574 and *1956*, 1127. It will be diphenylpicrylhydrazyl. You will have made it by treating *1,1-Diphenyl-2-picrylhydrazine* (Eastman 7365) with lead peroxide. It will keep on the shelf for a while but not long enough for us to have relieved you of the preparation chore. Being reasonably inert to molecular oxygen, it will make a very fine scavenger with which to scoop other, less long-lived free radicals out of a reaction. As your insight will at once tell you, it will inhibit polymerization, abstract hydrogen from certain molecules, and be paramagnetic because of its unpaired electron.

News, real news

The radio and TV newscasters have apparently failed to grasp the importance of this (very few of them being biochemists), but word has very recently been received that DL-*Methoxyphenylacetic Acid* is **a selective precipitant for sodium** in the presence of large amounts of K^+, Ru^+, NH_4^+, Mg^{++}, Cl^-, NO_3^-, PO_4^{---}, SO_4^{--}, and up to 30 mg per ml of Li^+. And we gladly sell it as Eastman 7361, even providing an abstract if you like.

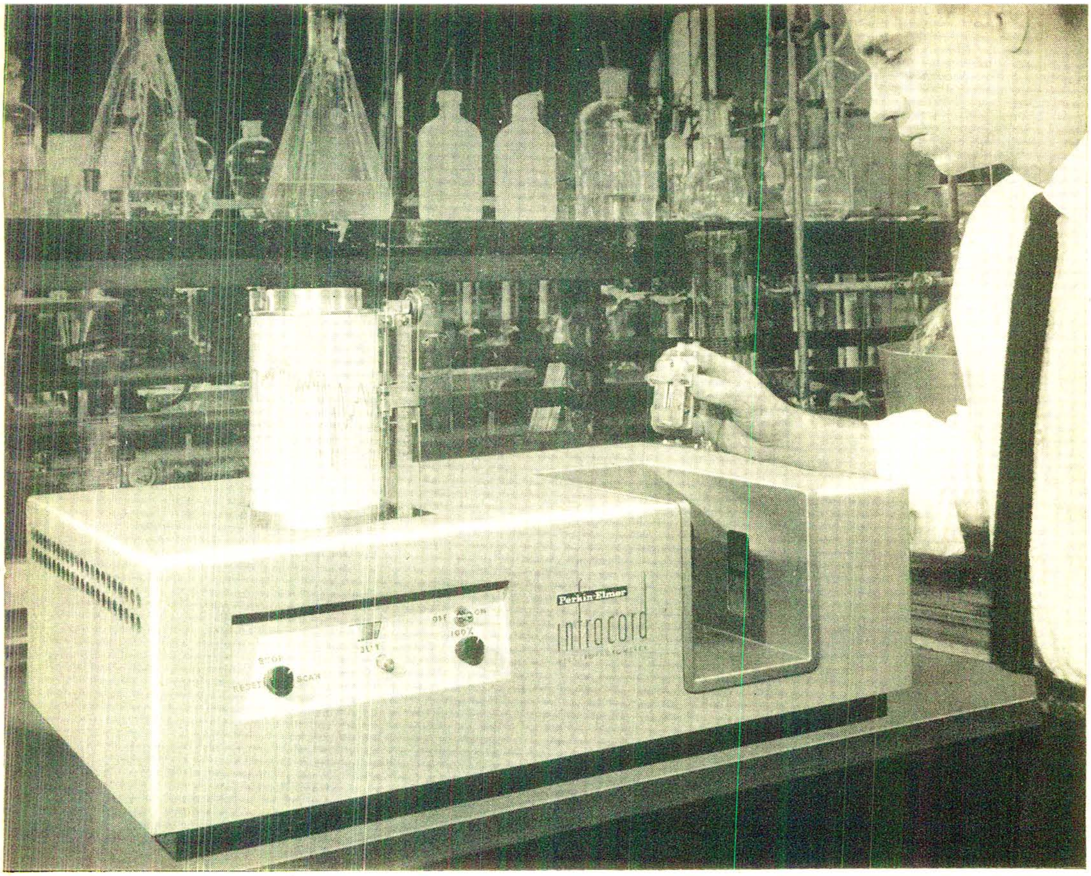
Any or all of these abstracts and/or organics come from *Distillation Products Industries*, Eastman Organic Chemicals Department, Rochester 3, N. Y. (There are more. Some 3500 organics in our Eastman Organic Chemicals List No. 40. If you haven't a copy, let us know.)

DPi

Eastman Organic Chemicals

Also...vitamins A and E in bulk...distilled monoglycerides

Distillation Products Industries *is a division of* **Eastman Kodak Company**



a new low cost infrared instrument for the organic chemical laboratory:

THE INFRACORD* DOUBLE BEAM SPECTROPHOTOMETER

The new Infracord Spectrophotometer puts infrared analysis and its advantages within the reach of every laboratory. The result of a 4-year development program by Perkin-Elmer, the Infracord embodies the latest advances in optical, electronic, and mechanical design. A highly efficient *double beam* optical null system, previously available in only the most expensive spectrophotometers, provides the speed, energy, short path length and resolution so necessary for good qualitative and quantitative analysis.

Designed to meet the rapidly expanding use of infrared and analytical techniques, the Infracord is as simple to operate as an analytical balance.

Rugged and compact, the Infracord as an everyday tool for the chemist gives him a fast answer and a permanent record of his work—at the bench. It handles the spectroscopist's routine work. Write for complete information.

*T.M.

NOTE THESE FEATURES:

- double beam measuring system
- atmospheric and solvent compensation
- differential analysis
- linear wavelength vs. transmittance recording
- broad line of sampling accessories
- single unit construction
- requires only 120 volt, 60 cycle power source
- 2.5 to 15 microns in 12 minutes
- instant wavelength reset
- direct recording on notebook size paper
- reproducible performance

PRICE: $3850.00 f.o.b. Norwalk, Connecticut
(in U. S. and Canada only)

INSTRUMENT DIVISION
Perkin-Elmer *Corporation*
NORWALK, CONNECTICUT

For further information, circle number 70 A on Readers' Service Card, page 77 A

accurate, rugged, dependable, and economical. Applied Physics Corp., 362 W. Colorado St., Pasadena 1, Calif. **50A**

Spectrophotometers, Infrared. Complete information available on the Model 21 double beam recording infrared spectrophotometer. Wavelength range is from 800 millimicrons to 15.5 microns covering the near infrared and fundamental regions of the spectrum. Perkin-Elmer Corp., Norwalk, Conn. **43A**

Stirrers. Circle 47A-1 for details on company's power stirrer. Two speeds: two 1/4″ shafts turn in opposite directions at 300 or 600 r.p.m. at high torque. Circle 47A-2 for information on stainless steel hinged blade type paddle stirrers. Wilkens-Anderson Co., 4525 W. Division St., Chicago 51, Ill. **47A-1, 2**

Stirrers. Bulletin available on company's continuous duty stirrers for highly viscous materials. Transmission provides constant torque at any speed in the range 0 to 500 r.p.m. Uses hollow spindle. Eberbach Corp., Ann Arbor, Mich. **61A-1**

Stirrers. Circle 68A-2 for information on company's explosion proof laboratory stirrers powered by air and used for stirring all types of solvents, laquers, paints, oils, synthetics, fine and heavy chemicals. Arrow Engineering Co., Inc., 200 Central Ave., Hillside, N. J. **68A-2**

Stopcocks. New catalog available. Illustrates products featuring the "Lab-Crest" stopcock and includes prices and specifications. Fischer & Porter Co., 1547 County Line Rd., Hatboro, Pa. **23A**

Thermometers. Company's thermometers are cited as being individually retested before shipping to insure accuracy. The colored substance used to fill the lines and numbers of the graduated scale is unaffected by organic materials and acids (except hydrofluoric). Kimble Glass Co., Toledo 1, Ohio **3rd Cover**

Thermometers, Electronic Resistance. Informative bulletin available on instrument that covers a range from −100° C. to 900° C., with 0.1° C. sensitivity and digital reading of temperature directly. The Emil Greiner Co., 20-26 N. Moore St., N. Y. 13, N. Y. **40A**

Titration Apparatus. Full information available on company's automatic electrometric titration apparatus using the second derivative method of H. V. Malmstadt. For use in all titrations

(*Continued on page 72 A*)

Product Capsules

usually classified as potentiometric. Push-button start, automatic shutoff. E. H. Sargent & Co., 4647 W. Foster Ave., Chicago 30, Ill.

Tubing, Plastic. Company's translucent polyethylene or transparent vinyl tubing is cited as being chemically inert, non-toxic, light in weight, strong, resilient, and economical. Complete information available. American Agile Corp., 5461 Dunham Rd., Maple Heights, Ohio **79A**

Tubing, Plastic. Tygon flexible plastic tubing is cited as being glass clear, chemically inert, tough, and easy to handle. Available in more than 60 sizes. U. S. Stoneware, Akron 9, Ohio **82A**

Viscosimeters. Circle 89A-1 for bulletin on the Hoeppler viscosimeter that operates on the falling ball principle. Circle 89A-2 for bulletin on the Ubbelohde viscosimeter that operates on the principle of the suspended level. Fish-Schurman Corp., 72 Portman Rd., New Rochelle, N. Y. **89A-1, 2**

Voltage Regulators. Bulletin available on the "Stabiline" automatic voltage regulator cited as providing constant voltage regardless of line or load changes. Obtainable in three types: instantaneous electronic, electro mechanical, and tubeless magnetic. The Superior Electric Co., 1004 Bradley Ave., Bristol, Conn. **25A**

Warburg Apparatus. Bulletin available on the rectangular and the rotary models of Aminco's Warburg instruments. Both models maintain temperature constancy within ±.02° C. Rotary model features 360° rotatable manometer carriage. Rectangular model features two independent shaking racks. American Instrument Co., Inc., Silver Spring, Md. **27A**

X-Ray Equipment. Company's x-ray diffraction unit, x-ray diffractometer, x-ray spectrograph or the "Autrometer" are cited as assisting in obtaining extensive or prefixed elemental data with rapidity, accuracy and reproducibility on samples regardless of their free or combined state. Complete details available. Instruments Div., Philips Electronics, Inc., 750 So. Fulton Ave., Mt. Vernon, N. Y. **62A**

X-Ray Equipment. Catalog available on the Hilger micro-focus x-ray unit that features an extra-fine, high intensity focal spot. For all diffraction studies. Cited as being ideal for large lattice structures. Jarrell-Ash Co., 32 Farwell St., Newtonville 60, Mass. **73A-2**

(Continued on page 74 A)

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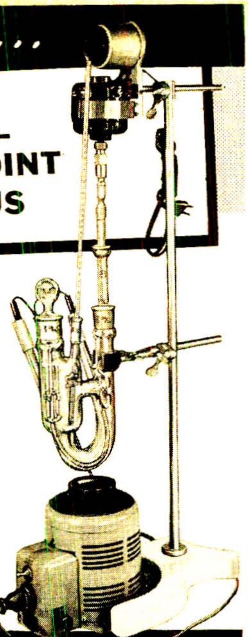

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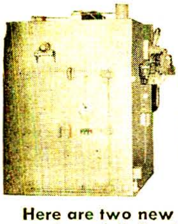


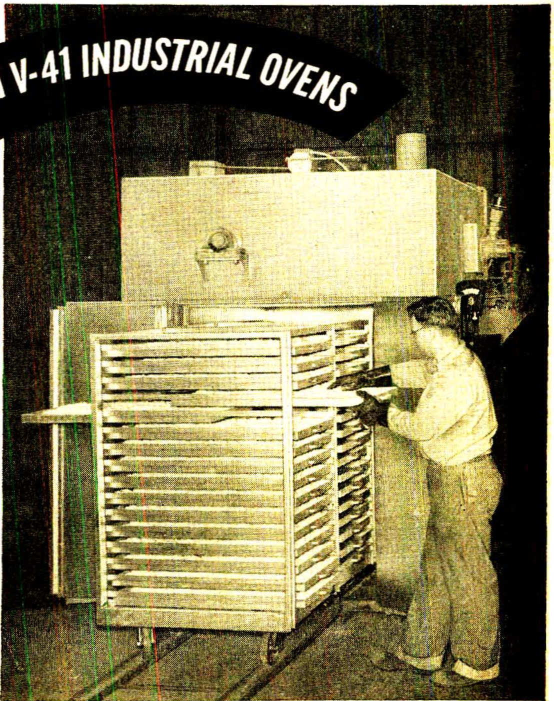
Here are two new ovens, proven in the field, that were developed especially for chemical dehydration and other processes that require larger air volume than normally found in standard ovens. Built-in exhaust fans can be regulated to control the flow of air and will operate automatically at pre-set times.

THE DESPATCH V-39, a truck-loading, batch type oven, has proven itself in the chemical drying field. At Diamond Alkali Company's Painesville, Ohio plant they're reducing the moisture content of chromium chemicals from 15% to no more than 4% and holding it there. A 2-hour bake at 500°F does the job thoroughly!

Investigate the Despatch V-39 or V-41—you'll discover that they offer the large volume horizontal airflow that maintains exceptional temperature uniformity. They're double walled, with insulated construction that means top economy and have Micromatic control systems to hold temperatures within close limits.

Floor length doors make it possible to roll loads directly into the V-39's 60 cu. ft. chamber or the big V-41's 101 cu. ft. oven. Both have 500°F ratings with gas, electric or steam heaters (heavy duty models rated at 650°F.) Automatic safety switches and circuits protect the operator and the product at all times.

For complete technical details write for Bulletin 100—it describes the complete line of laboratory and production ovens made by Despatch.



Trayloaded truck of chromium chemicals is readied for drying at Diamond Alkali Co. Tracks guide heavily loaded trucks into the V-39 oven—protect oven's interior.

DESPATCH OVEN CO. Established in 1902

DESPATCH OVEN COMPANY
341 Despatch Building, Minneapolis 14, Minn.

For further information, circle number 73 A-3 on Readers' Service Card, page 77 A

Product Capsules

CHEMICALS AND MATERIALS

Adsorbents. A hard, porous, white granular synthetic adsorbent, produced in a variety of mesh classifications, Florisil is cited as being used in the most difficult separations of organic compounds. Floridin Co., Box 989, Tallahassee, Fla. **64A**

Chemicals, Reagent. New catalog available. A reference guide, it lists more than 1300 "Baker Analyzed" reagents and other high-purity laboratory chemicals. Has new listings important in new procedures. J. T. Baker Chemical Co., Phillipsburg, N. J. **37A**

Chemicals, Reagent. Mallinckrodt analytical reagents are cited as being of uniform purity and packaged in space-saving, easy-to-handle "Stormor" bottles. Complete line includes over 400 reagents. Mallinckrodt Chemical Works, St. Louis 7, Mo. **60A**

Filter Papers. Circle 19A-2 for analysis kit sampler with large assortment of 11 cm circles in wide selection of grades. Several quantitative papers included in sampler also are available in sheets or strips for chromatography and electrophoresis. Carl Schleicher & Schuell Co., Keene, N. H. **19A-2**

Laboratory Chemicals. Circle indicated numbers for complete information on the following Baker & Adamson laboratory chemicals: inorganic reagents, 8A-1; "CP" acids, 8A-2; radiochemicals, 8A-3; rare earths, 8A-4; biological-grade chemicals, 8A-5; organic chemicals, 8A-6; and biological stains & indicators, 8A-7. General Chemical Div., Allied Chemical & Dye Corp., 40 Rector St., N. Y. 6, N. Y. **8A-1 to 7**

Lithium Dispersions. Specifications, information for preparing dispersions including handling instructions, prices and product data on lithium metal available. Lithium Corporation of America, Inc., 2525 Rand Tower, Minneapolis 2, Minn. **2nd Cover**

Neopentyl Glycol. Reactive, compact, symmetrical neopentyl glycol represents an ideal polyol for the production of polyester resins and plasticizers. It exceeds other commercial glycols in providing resistance to high temperatures, discoloration, and hydrolysis. Circle 31A for samples and full information. Eastman Chemical Products, Inc., Kingsport, Tenn. **31A**

Organic Chemicals. Company states that it is the only one to package pure organics under an inert atmosphere of Argon to protect purity. Matheson, Coleman & Bell, Norwood, Ohio **85A-2**

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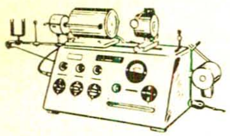

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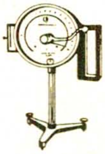

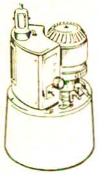

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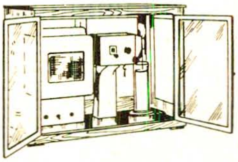

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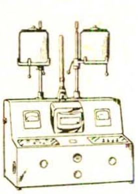

For complete technical information and prices contact

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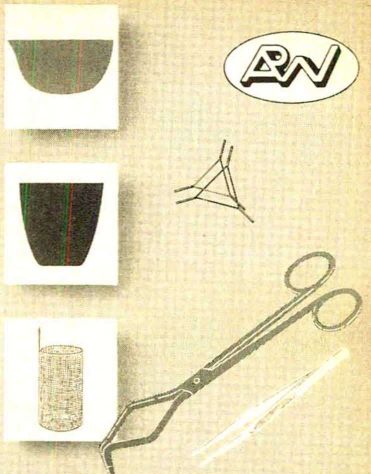

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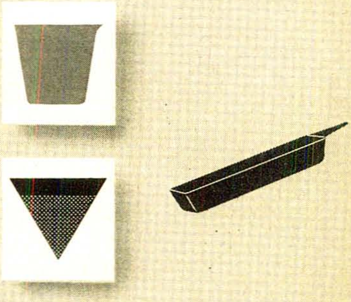

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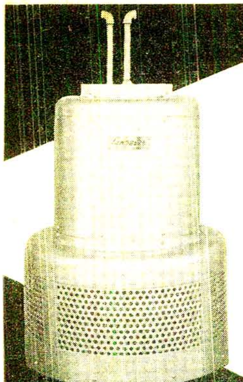
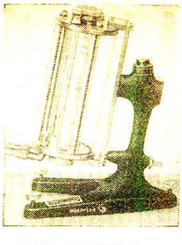
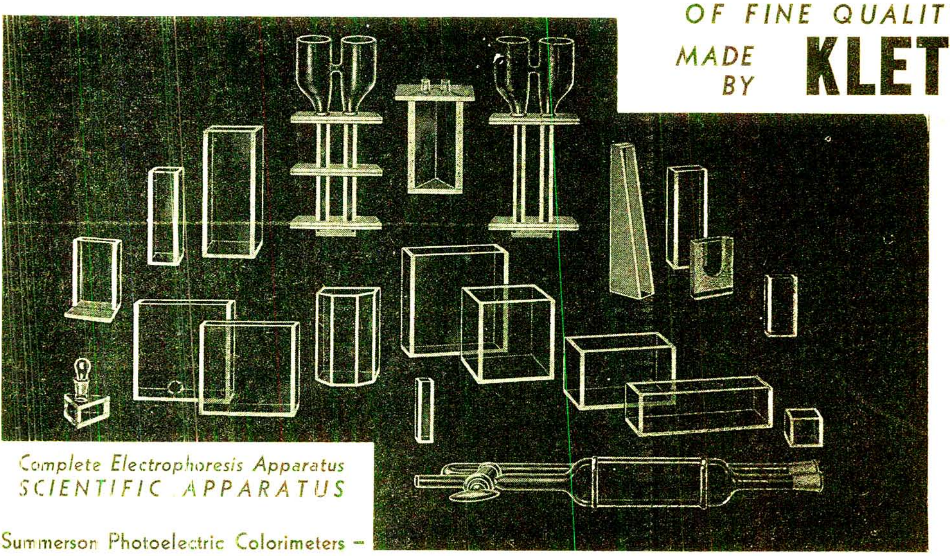



TIME





ANALYTICAL CHEMISTRY

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ANALYTICAL CHEMISTRY

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May 1957—Valid through October 1957

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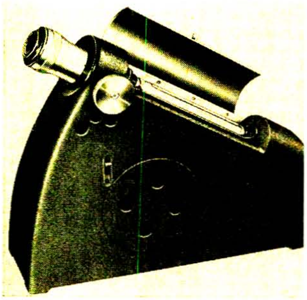

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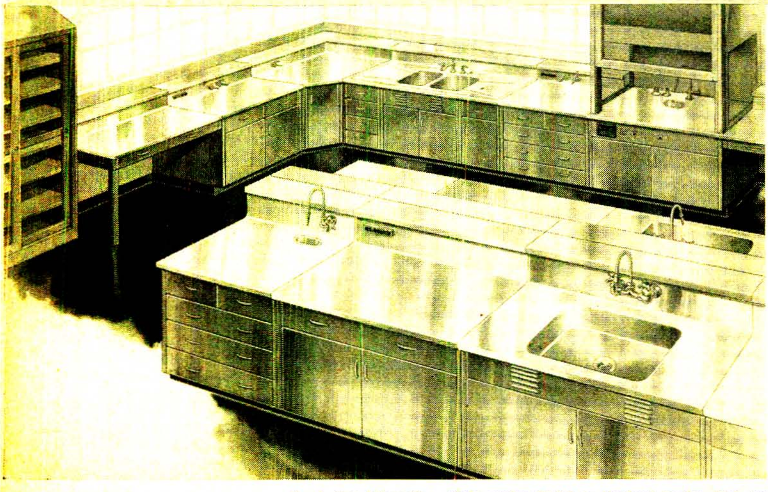

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Pittsburgh Conference Exhibit Features New Instrumentation

Pittsburgh, Pa. This city was host to scores of analytical chemists and spectroscopists March 3 to 8, when the Analytical Chemistry Group, Pittsburgh Section, ACS, and the Spectroscopy Society of Pittsburgh held their eighth annual joint conference. The Exposition of Modern Laboratory Equipment, presented in conjunction with the conference, displayed many recent advances in modern instrumentation for the analyst.

These well-attended events emphasized several new trends in instrumentation through the media of papers given and equipment shown. One of these trends was simplification of instrumentation, some of which has been made possible through such electronic developments as printed circuits, multiple purpose electronic tubes, and transistors. Low-cost, limited range instruments (infrared spectrophotometers, flame photometers, and mass spectrometers) have also made their appearance in the field as a further trend. The combined techniques of mass spectroscopy with chromatography, and ultraviolet with chromatography, received a certain amount of attention.

The following instruments are typical of recent developments.

Process Control Equipment

Applied Research Laboratories demonstrated its Quantrol, a new two-channel, x-ray fluorescence analyzer designed for process control applications. This unit is reported to be the first of its type to be commercially available for monitoring inorganic elements in inorganic or organic streams.

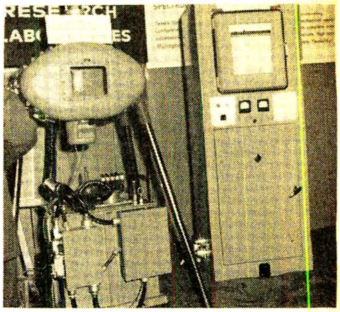
Consisting of a spectrometer, x-ray power supply, and ratio recording console, the Quantrol has many potential industrial applications. The company reports that gaging applications, such as measurement of tin and zinc plating weights, have been completely developed. Other uses, like the measurement of concentration of various elements in ore concentrates, are now under way. Still other applications, among them the measurement of copper or bromine in solutions, are being studied for specific chemical process problems. **1**

Double-Beam Infrared Spectrophotometer

Baird-Atomic exhibited its recently announced KM-1 infrared spectrophotometer, shown here with the 80 × 100 mm. prism mounted on top of the instrument. This prism is the heart of the double-beam, recording instrument. The KM-1 features high-quality infrared absorption analyses in the medium price range, as well as further expandability with use of supplementary accessory equipment. **2**

New Apparatus for Radiation Applications

New models of two nuclear instruments were also shown at the Pittsburgh



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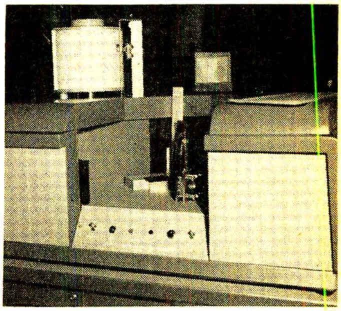

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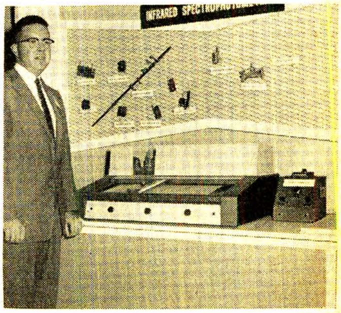

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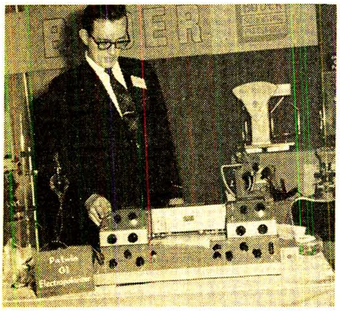

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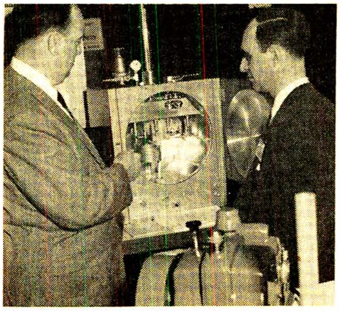

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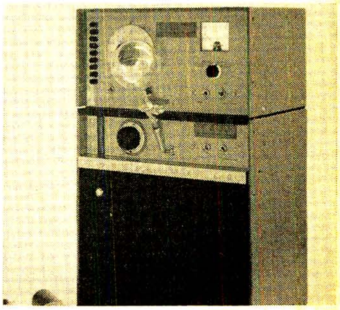

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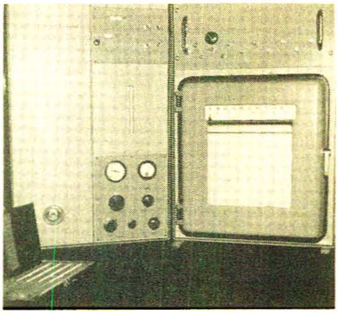


See item 13

Conference by Baird-Atomic, Inc. The radiation survey meter, Model 414, can be used for monitoring radiation in hot laboratories and at reactor installations. The company reports that the instrument, which incorporates a new one-tube circuit design for reliability and long battery life, can detect and measure x-ray, gamma, and beta radiation.

The non-overloading linear amplifier, Model 215, is recommended by Baird-Atomic for pulse height analysis of x-rays in the presence of high energy gamma rays because it is designed to amplify small pulses in the presence of much larger overload pulses. **3**

Infrared Family Expanded

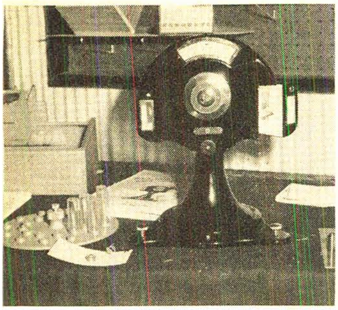
A new addition to its growing family of infrared instruments was introduced at Pittsburgh by Beckman Instruments, Inc. This latest member, shown on page 81 A by E. P. Evans of Beckman, is the IR-5 infrared spectrophotometer, a low-cost, double-beam instrument, selling for less than \$5000. It is a null-type single monochromator instrument, featuring a horizontal type X-Y recorder, hermetically sealed optics, and both single and double beam operation. Fixed operating parameters simplify operation. According to the company, the instrument has a minimum of controls and produces reliable spectra with a scanning time of 16 minutes for the 2 to 16 micron region. **4**

Power Supply for Spectrophotometer

Beckman Instruments also announced a new power supply for use with the DU spectrophotometer. The power supply is said to eliminate the need for the storage battery and the dry cell batteries while providing all the power needed to operate the DU spectrophotometer. It also furnishes power for the DU hydrogen lamp and makes the power supply unit of the ultraviolet accessory set unnecessary. **5**

Electropolarizing Instrument

Boder Instruments exhibited the new Patwin recording electropolarizer, demonstrated by J. G. Waltz, company representative. This low cost instrument features the following: an initial polarizing bridge which can be set with 4.5 inch, 1% voltmeter or standard cell; a span voltage bridge



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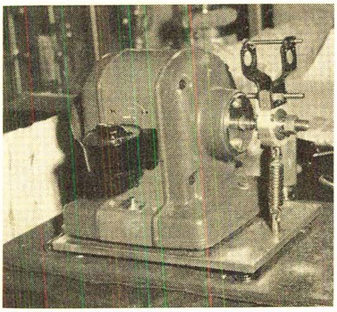

See item 16

which can be set with 4.5 inch, 1% voltmeter, standard cell, or standardized against the initial voltage; a 10-turn, 0.1% potentiometer driven by a synchronous motor for applying voltage to the cell; and switches for damping, for stopping the chart and bridge motor, and for setting run or standby. **6**

Vapor Phase Analyzer

J. F. Green (left) of Central Scientific Co. demonstrates the company's new vapor phase analyzer to C. J. Hess of Bethlehem Steel Co. Designed for use in gas chromatography, the instrument contains a detector cell, which is a diffusion type thermal conductivity cell with the time constant of less than one second. The cell is said to be very stable with negligible drift.

A packed 10-foot column is furnished with the analyzer and provision is made for use of two columns in series. The company reports that column pressure is continuously adjustable from 0–30 psig. Several controls permit adjustment of bridge balance, sensitivity, temperature range, and temperature control. A recorder can be directly connected to the analyzer for increased practicability. **7**

Low-Cost Mass Spectrometer

Consolidated Electrodynamics Corp. introduced at Pittsburgh its new Type 21-611 mass spectrometer. This is a low-cost, small-size instrument (smallest mass spectrometer in existence, says the company), developed for medical, industrial, and university application. Only eight vacuum tubes are used, all types of traps are eliminated, and printed circuits are utilized wherever feasible.

The control unit can be operated remotely, permitting use of the 21-611 in process stream applications. In addition, the company reports the mass spectrometer will displace Orsat gas analysis methods. It is said to be capable of accurately analyzing extremely small amounts of gases, gaseous mixtures, or volatile liquids, with its overall mass range extending from 2 to 80. Simplified operation permits use by untrained personnel. **8**

Moisture Monitor

Another instrument exhibited by Consolidated Electrodynamics was its portable, low-cost moisture monitor (Type 26-301). Capable of measuring minute quantities of moisture present in gaseous mixtures, the instrument is suitable for a wide variety of applications, says the company. The moisture monitor incorporates an electrolytic cell, and is equipped with an adjustable flow regulator and meter calibrated in p.p.m. Readings from 0 to 1000 p.p.m. can be obtained by means of a 5-step attenuator. CEC says this versatile instrument is equally adaptable to the analytical laboratory or the process plant. **9**

Controlled Environment Oven

A new controlled humidity and temperature oven, manufactured by the Electric Hotpack Co., Inc., made its first appearance at the Pittsburgh Conference. This mechanically convected oven was developed for laboratory, pilot plant, and industrial testing of chemicals, plastics, metals, etc., to the accuracy of government specifications, says the company. Its range covers room temperature to 100° ± $^1/_2$° C., and 20% to 100% RH within 5% RH. Features include: stainless steel construction; hermetically sealed-in triple-paned viewing window; a built-in water filter; and a continuous supply of conditioned water furnished to the wet bulb reservoir with sight glass to indicate water level. **10**

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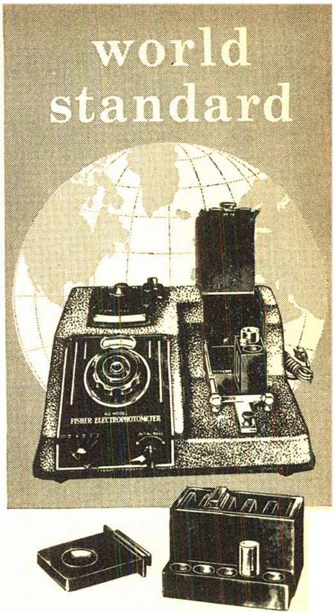

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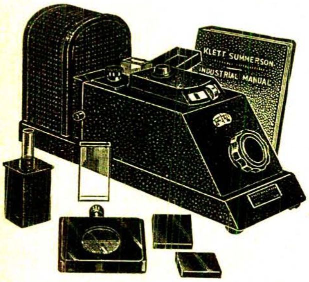

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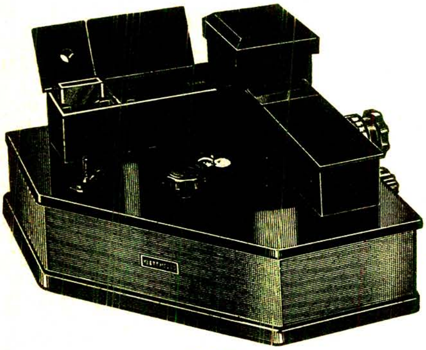

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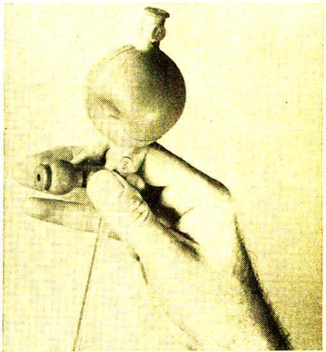

This amazing new instrument is now standard equipment in government, medical and industrial laboratories throughout the nation. Offers more precise measurement (to 0.01 cc), more complete control, and avoids all the risks of mouth pipetting. Holds set level indefinitely, fits any pipette, operates easily with one hand. Order a supply of PROPIPETTES now, $6.90 each.

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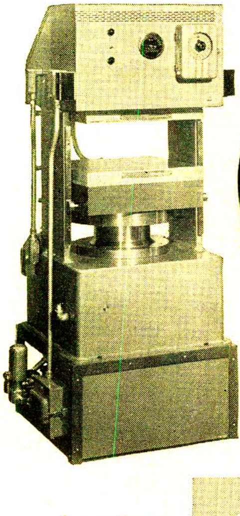

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NaCl Crystals

E. C. Stewart of Harshaw Scientific shows a sample of the largest single NaCl crystals ever made. Dimensions are 12 inches in diameter, 12 inches high, and weighing 75 pounds. These crystals are cut up to make window blanks for infrared transmission and prisms for infrared spectroscopy. **11**

Insulated Containers

Harshaw Scientific also exhibited the new VirTis insul-steel containers. These containers have stainless steel lining, polyurethane foam insulation, and an exterior surface of mylar film. They are said to be unbreakable and serve over the temperature range of −328° F. to +225° F. for liquefied gases. **12**

Control Programmer

The Perkin-Elmer Corp. displayed for the first time a new control programmer for use with their vapor fractometer. The new instrument is reported to make possible semi-automatic operation for the vapor fractometer. It should prove particularly useful in research problems of a semi-continuous nature, says the company. **13**

New Recorder Commercially Available

A commercial model of its recorder, whose prototype was first shown at the National Chemical Exposition in Cleveland, was exhibited by E. H. Sargent & Co. This equipment is the vertical bench type, with the chart at the top and base and control panel below. Several chart drive speeds are possible by interchanging two gears on the end of the chassis; multiple ranges are also available with selection by panel switch. The company claims an accuracy of 0.1% or 20 microvolts, whichever is greater, for this recorder. **14**

Precision Balances

Spex Industries, Inc. exhibited two models (250 mg. and 500 mg.) of its Sauter Ultra-Matic precision balance, said to be ideal for the spectrographer. According to the company, these balances are capable of accurately weighing small quantities of materials in a matter of seconds.

No weights are required for these spring type balances. A single knob controls the weighing operation. The

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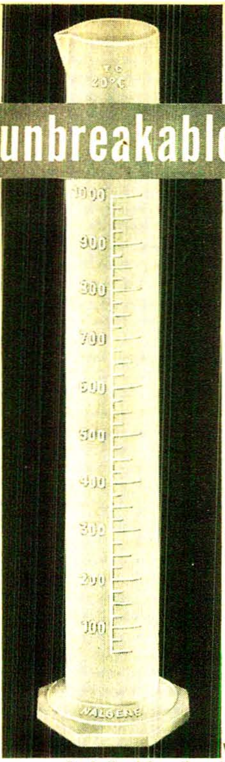

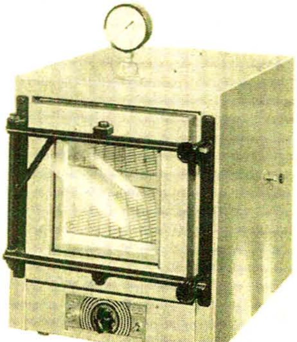

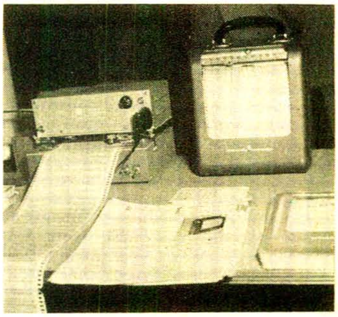

See item 17

use of special alloys is reported to eliminate errors due to magnetic forces or temperature variations. Range extensions permit weighings up to 1250 mg. capacity with the 250 mg. model, and up to 2500 mg. capacity with the 500 mg. balance. Spex emphasizes that these balances are also fitted with a weighing pan designed to hold the plastic vials used in the Wig-L-Bug electric mortar described below. **15**

Electric Mortar

Mixing and grinding are faster, cheaper, and simpler with its new Wig-L-Bug, says Spex Industries. This electric mortar is a compact instrument which uses plastic and metal vials for the mixing and grinding operation. A single vial can be used for weighing, mixing, and storing, thus saving space. The company says the action of the Wig-L-Bug is reciprocating in the form of a figure 8; the ball pestle is swung through a $6^{1}/_{2}°$ arc at 3200 r.p.m., striking the ends of the vial about 2000 times in 10 seconds. **16**

Strip-Chart Potentiometer Recorder

Varian Associates exhibited its new Model G-11 strip-chart recorder (right), a companion for the previously available Model G-10 (left). The company reports the G-11 is a remarkably versatile, minimum-size instrument, selling at a moderate price. It features unitized, interchangeable input circuits; adjustable span; and a weight of less than 15 pounds.

Among its specifications, the basic G-11 is said to have a one-second balancing time, single chart speed. It is fitted with a Type A-1 input chassis having mercury cell reference, and operates from 115 volts, 60 c.p.s. Various accessories are available, including spare chart drive-motor assemblies for various speeds. **17**

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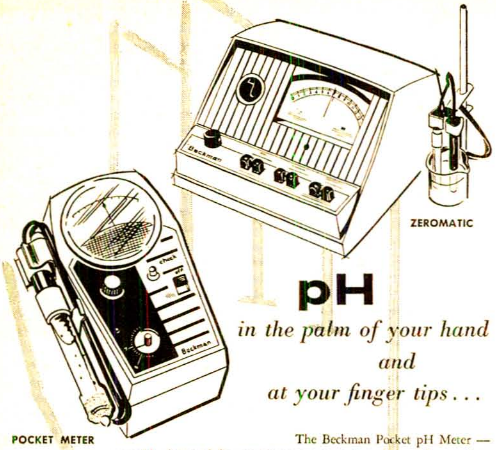
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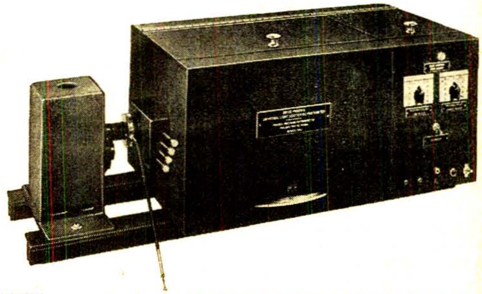

Thirteen Additions to Organic Chemicals Line

Distillation Products Industries, a division of Eastman Kodak Co., announces 13 chemicals newly available from the company.

Among these organic chemicals is 2-*p*-dimethylaminostyryl - 1,3,3 - trimethyl-3*H*-pseudoindolium iodide, a reagent for the determination of sulfur dioxide or smog in air.

Another addition to the list is 3,3′-dimethylnaphthidine. The company says this reagent is useful in the determination of chlorine in water, as an oxidation-reduction indicator, as an indicator for the determination of gallium, and also as an indicator for titration of zinc, cadmium, calcium, and indium.

4,5 - Dihydroxy - 3 - (*p* - sulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt is a third new Eastman organic chemical. According to the company, recent literature reports this compound may be used as an indicator in complexometric titration of zirconium, for the titration of thorium, and for the titrimetric determination of microgram amounts of fluoride ion.

The fourth added chemical is *N*-phenylbenzohydroxamic acid, which is reported useful in the gravimetric determination of copper, iron, aluminum, and titanium; the colorimetric determination of vanadium; and as a reagent for tin.

The remaining additions to Eastman's list of organic chemicals include the following:

2-Amino-2-(hydroxymethyl)-1,3-propanediol
tert-Butyl ethyl ether
tert-Butyl methyl ether
o-Dibromobenzene
5,7-Diiodo-8-quinolinol
Diphenyl phthalate
9-Methylanthracene
1-Methylquinolinium chloride
5-Nitro-2-benzimidazolethiol **18**

Laboratory Quantities of Four Complexing Agents Available

Fisher Scientific Co. is now offering the following compounds in laboratory amounts:

(Tetra) sodium ethylenediamine tetraacetate, known for forming stable, soluble compounds with most metallic ions, is available as a liquid in a technical grade. This compound is considered a versatile complexing agent, one gram of the solution chelating a minimum of 67 mg. of calcium carbonate at pH 11, says the company.

(Tetra) potassium ethylenediamine tetraacetate is offered for the first time anywhere in laboratory quantities, claims Fisher. Recommended particularly for reactions where the sodium ion is undesirable, as in determination of barium or strontium, it can also be used in complexing reactions where the sodium salt would be used. This compound is available in a purified grade.

Ethylenediamine tetraacetic acid, offered in dry powder form in a reagent grade, is said to be especially effective for the inactivation of polyvalent metal ions. Fisher says it is also used as a raw material for the preparation of various derivatives, including metal chelates, salts, and esters.

Calcium disodium ethylenediamine tetraacetate, widely used as a stabilizer in the drug and pharmaceutical industries, is available as a solution in approximately 25% concentration. This compound is offered in a purified grade. **19**

List of Radioactive Compounds Expanded

Three additions to its list of over 160 radioactive carbon-14 compounds are announced by the Nuclear-Chicago Corp. These are: gramine-C-14, DL-tryptophan-3-C-14, and D-mannose.

Gramine-C-14 is said to be of value in chemical, biological, and pharmacological research. This radioactive alkaloid is useful in the preparation of tagged tryptophan and in the study of tryptophan chemistry and physiology.

DL-tryptophan-3-C-14 is a radioactive amino acid which will be useful in the study of amino acid formation and metabolism and in the study of biological systems, says the company.

Uniformly labelled D-mannose, the newest addition to Nuclear-Chicago's list of labelled sugars, is available at the activity of 20 millicuries per millimole. The company feels it will be useful in metabolism, photosynthesis, and physiological studies of sugar systems. **20**

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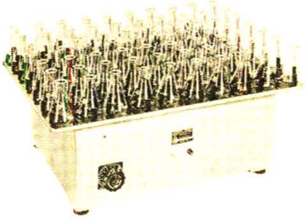

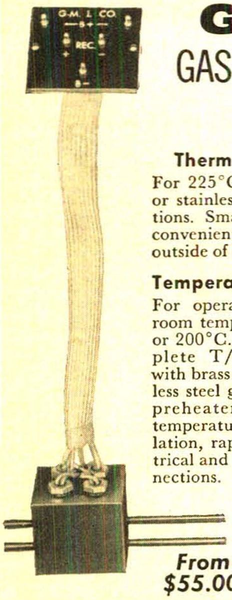
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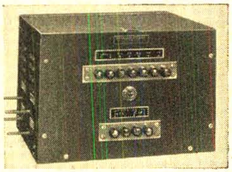

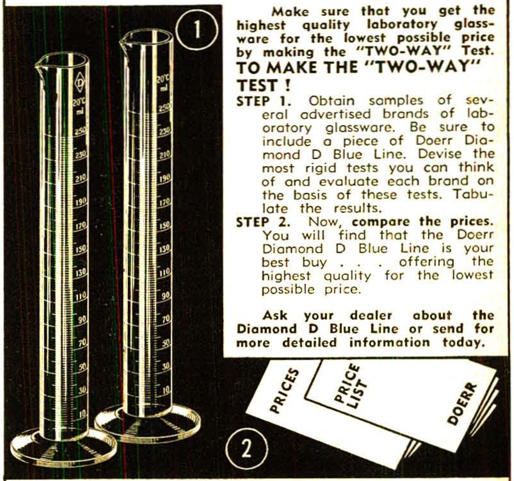
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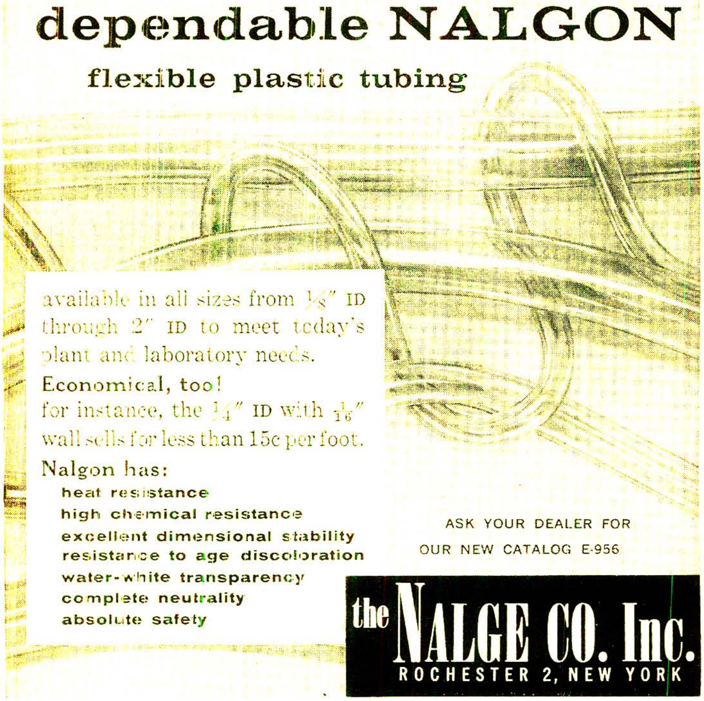

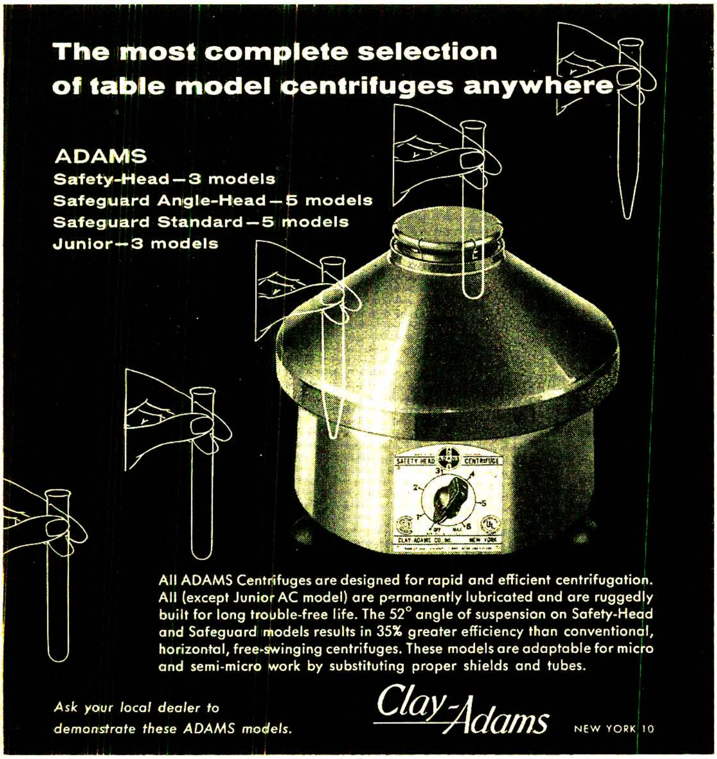

MANUFACTURERS' LITERATURE

Centrifuges. Four-page illustrated folder describes Servall superspeed SS-1 angle centrifuge, with details on its latest development which is a sealed rotor cover. Ivan Sorvall, Inc. **21**

Magnetic Separator. Bulletin provides data on design, capacity, and applications of electromagnetic separator developed expressly for laboratory use. Carpco Mfg., Inc. (*Bull. MB-103*). **22**

Recorder. Six-page bulletin contains specifications and features of new two-channel rectilinear galvanometer recorder, which records two functions rectilinearly on two scales on a single chart. Texas Instruments Inc. (*Bull. No. R-502*) **23**

Spectrographic Equipment. Illustrated manual of 32 pages covers company line of spectrographic equipment and describes new program designed to aid firms in selecting proper equipment for their needs. Bausch & Lomb Optical Co. (*D-277*) **24**

Scientific Apparatus and Methods. Forty-two page booklet features articles on several scientific methods and includes catalog section describing new apparatus available. E. H. Sargent & Co. (*Vol. 9, No. 1*) **25**

Silicones. Illustrated catalog discusses more than 115 applications for silicones including uses in rubber products, water repellents, lubricants, and others. General Electric Co. (*CDS-97*) **26**

Bath Coolers. Data sheet gives performance data and description of portable cooler for laboratory water baths. Arthur S. LaPine & Co. **27**

Specific Gravity Apparatus. Leaflet describes device for specific gravity measurements in the laboratory. Instrument supports interchangeable hydrometer vessels in vertical position on a swinging arm. Royco Instruments. **28**

Freeze-Drying Units. New 18-page catalog contains material on freeze-drying equipment and accessories, including histological, biological, infrared, and rotor-freeze units. Will Corp. **29**

Electrochromatography. Brochure describes operation of electrochromatography set and its use for paper-strip electrophoresis and one- and two-dimensional paper chromatography. Microchemical Specialties Co. (*EC-301*) **30**

Laboratory Apparatus. Ten-page catalog contains descriptions of equipment, apparatus, and furniture for the laboratory, including crystal lattice models, pH meters, balances, ovens, and bath coolers. Arthur S. LaPine & Co. (*Review No. 7*) **31**

Technical Glassware. Illustrated catalog of 234 pages gives descriptions and prices of 11,130 items of laboratory and scientific glassware. Kontes Glass Co. (*Cat. TG-15*) **32**

Analytical Instruments. New 16-page catalog provides information on company line of infrared and ultraviolet spectrophotometers, monochromators, flame photometers, vapor fractometers, as well as accessories available. Perkin-Elmer Corp. **33**

Chemicals. Brochure lists available fine chemicals and their prices. Includes several new compounds. Mann Fine Chemicals, Inc. **34**

Radioactivity Measuring Instruments. Two-color, 64-page catalog illustrates and describes full line of nuclear instruments, including scaling units, ratemeters, gamma-ray spectrometer systems, Geiger and scintillation detectors, as well as lead shields, personnel protection devices, and gamma and beta sources. Nuclear-Chicago Corp. (*Cat. Q*) **35**

Drying and Calcining Equipment. Eight-page bulletin gives data on dryers and calciners for research and pilot plant uses. C. O. Bartlett & Snow Co. (*Bull. No. 117*) **36**

Spectrochemical Analysis. New 28-page illustrated brochure provides informative data on spectrochemical analysis, outlining methods, instruments, and typical analytical problems. Also includes bibliography of pertinent reference handbooks. Jarrell-Ash Co. (*CH401*) **37**

Labeled Compounds. Twenty-four page catalog and price list includes newly available carbon, tritium, and deuterium labeled compounds, as well as descriptions of self-luminous sources. New England Nuclear Corp. **38**

Photoelectric and Electronic Measuring Instruments. Four-page bulletin features pH meters, colorimeters, photometers, and densitometers among company's line of measuring instruments. Photovolt Corp. **39**

Teflon Tubing. Two-page bulletin describes Teflon thin-walled tubing, with emphasis on its electrical properties and wide range of applications. Haveg Industries, Inc. (*Bull. T-200*) **40**

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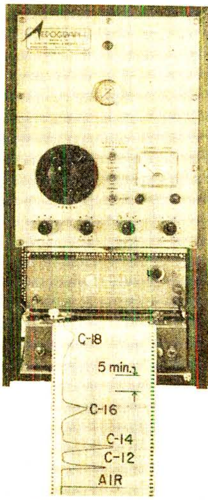

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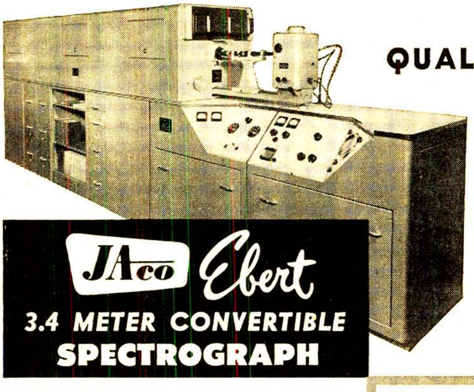

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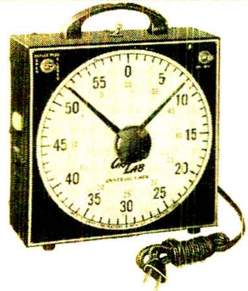

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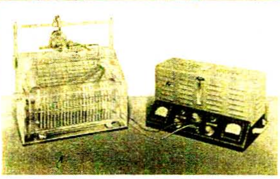

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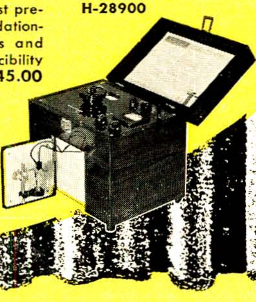

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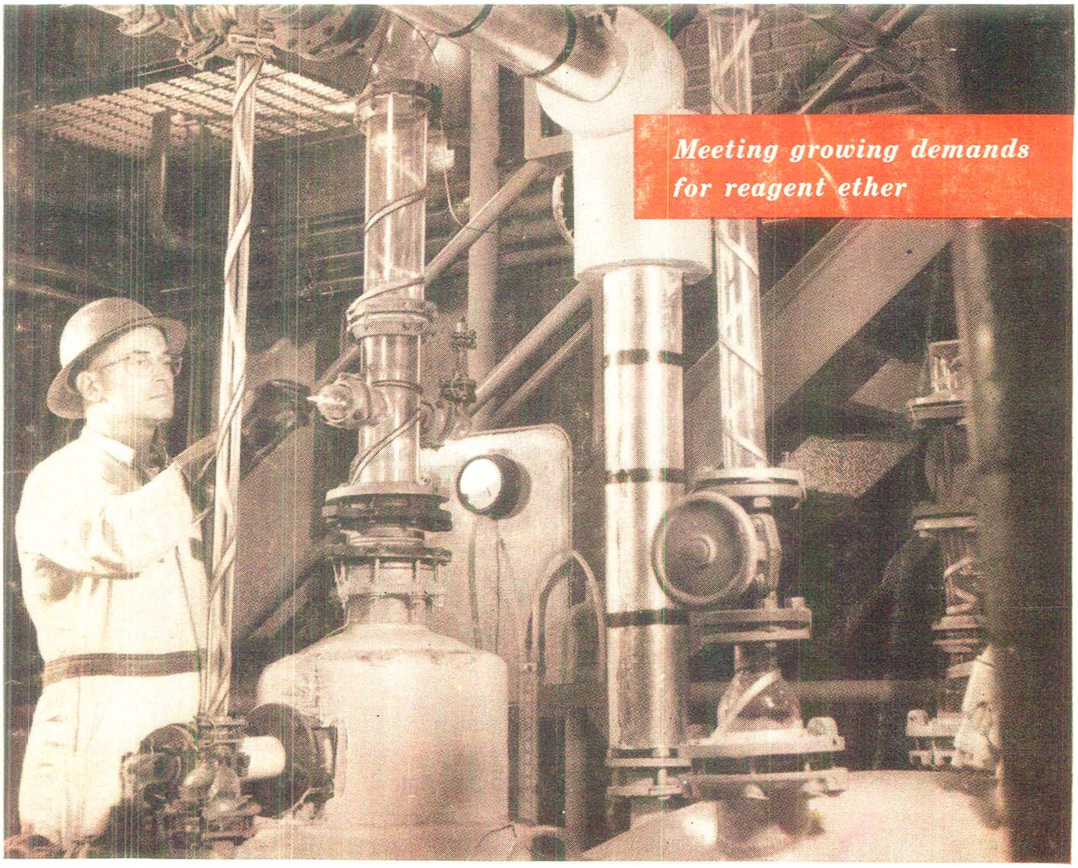

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