INDUSTRIAL AND ENGINEERING CHEMISTRY

POLITECHNIKI
ŚLĄSKIEJ

ANALYTICAL EDITION

HARRISON E. HOWE, EDITOR ● ISSUED FEBRUARY 16, 1942 ● VOL. 14, NO. 2 ● CONSECUTIVE NO. 4

Research with Polarograph . . . . . Otto H. Müller 99

Determination of Aniline Point of Dark Petroleum Oils . . . . Bruce B. Carr and M. S. Agruss 105

Determination of Free Sulfur in Lubricating Oil . . Harry Levin and Ervin Stehr 107

Mercury Cathode Method for Determining Small Amounts of Titanium and Similar Metals in Alloys . . . . M. H. Steinmetz 109

Determination of Lead in Sugars and Sugar Products . . . . Thos. D. Gray 110

Determination of Zinc in Rubber Compounds . . . Willard P. Tyler 114

Continuous Liquid Extractor for Large Volumes of Solution . . . . Ralph Hossfeld 118

Rapid Turbidimetric Method for Determination of Sulfates . Joseph F. Treon and W. E. Crutchfield, Jr. 119

Ceric Sulfate in Determination of Iron Using Molybdisilicic (Silicomolybdic) Acid Method . . Albert C. Titus and Claude W. Sill 121

Determination of Phosphorus in Lubricating Oil . . Harry Levin, F. P. Farrell, and A. J. Millendorf 122

Determination of Moisture in Sugar Products: Corn Sugar "70" or "80"; Refiners' Sirup, Final Molasses (Blackstrap), and Hydrol . . . . J. E. Cleland and W. R. Fetzer 124

Determining Liquid and Vapor Densities in Closed Systems . . . . G. H. Wagner, Grant C. Bailey, and W. G. Eversole 129

Heats of Wetting for Evaluation of Gas-Adsorbing Coconut Carbons . . . . Hosmer W. Stone and Raymond O. Clinton 131

Turbidimetric Determination of Polymerized Hydrocarbons in Solution . . . . Bassett Ferguson, Jr., and Mark D. Snyder 135

Polarographic Determination of Nitrates in Blood and Urine . . . Eugene W. Scott and Karl Bambach 136

Determination of Combined Nitrogen in Steel . . . . H. F. Beeghly 137

Volumetric Determination of Sulfur in Coal and Coke . . . . S. S. Tomkins 141

Determination of Copper Reduced by Sugars . . . Albert H. Best, A. Harding Peterson, and Harold M. Sell 145

Content of *l*-Pimaric Acid in Pine Oleoresin . . . . Elmer E. Fleck and Samuel Palkin 146

Colorimetric Determination of Silver with 2-Thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine . . . John H. Yoe and Lyle G. Overholser 148

Rapid Estimation of Bromides in Presence of Chlorides . . . . Marvin Lane 149

Determination of Sulfur . . . . William Rieman III and George Hagen 150

Conductometric Assay of Inorganic Salt in Presence of Wetting Agents . . . . J. H. Percy and C. J. Arrowsmith 151

Improved Sublimation Apparatus . . . O. A. Nelson 153

Assay of Benzaldehyde . . . . Marcelle Schubert and Janet G. Dinkelspiel 154

Colorimetric Determination of Phosphorus in Biological Materials . . . . Ruth Adele Koenig and C. R. Johnson 155

Estimation of Bromides in Presence of Other Halides . P. L. Kapur, M. R. Verma, and B. D. Khosla 157

Adjustable Safety Shield . . . . Arthur Furst 158

Modified Noyons Thermic Diaferometer for Respiratory Gas Analysis . . . . Thorne M. Carpenter and Vladimir S. Coropatchinsky 159

Pressure Regulating and Indicating Apparatus for Vacuum Systems . . . . Bassett Ferguson, Jr. 164

Continuous Washing Apparatus for Solutions in Organic Solvents . . . . A. L. LeRosen 165

Determination of Solubilities of Gases at High Temperatures and High Pressures by Rotating Bomb . V. N. Ipatieff and G. S. Monroe 166

Determination of Critical Temperatures by Rotating Bomb . . . . V. N. Ipatieff and G. S. Monroe 171

Glass Electrode Measurements of pH of Chromic Acid Solutions . . . . Winslow H. Hartford 174

Molecular Still Heads . . . . A. J. Bailey 177

Special Slide Rule for Calcium Carbonate Equilibrium Problems in Corrosion Control of Water Supplies . . . . A. Adler Hirsch 178

Improved Methoxyl Apparatus . . . . . A. J. Bailey 181

MICROCHEMISTRY:

Colorimetric Determination of Phosphorus in Soils . . . . Mildred S. Sherman 182

Semimicropycnometer for Heavy Water . . . . . B. J. Fontana and Melvin Calvin 185

Polarograph Reading Directly in Percentage . . . B. P. Caldwell and Solomon Reznek 187

Micromethod for Identification of Volatile Liquids Sidney W. Benson 189

Apparatus for Microevaporations . . . . L. T. Kurtz 191

MODERN LABORATORIES:

Socony-Vacuum's New Engineering Building . . C. H. Schlesman 192

The American Chemical Society assumes no responsibility for the statements and opinions advanced by contributors to its publications.

26,800 copies of this issue printed.

Copyright 1942 by American Chemical Society.

Publication Office: Easton, Penna.

Editorial Office: 1155 16th Street, N. W., Washington, D. C.
Telephone: Republic 5301. Cable: Jiechem (Washington)

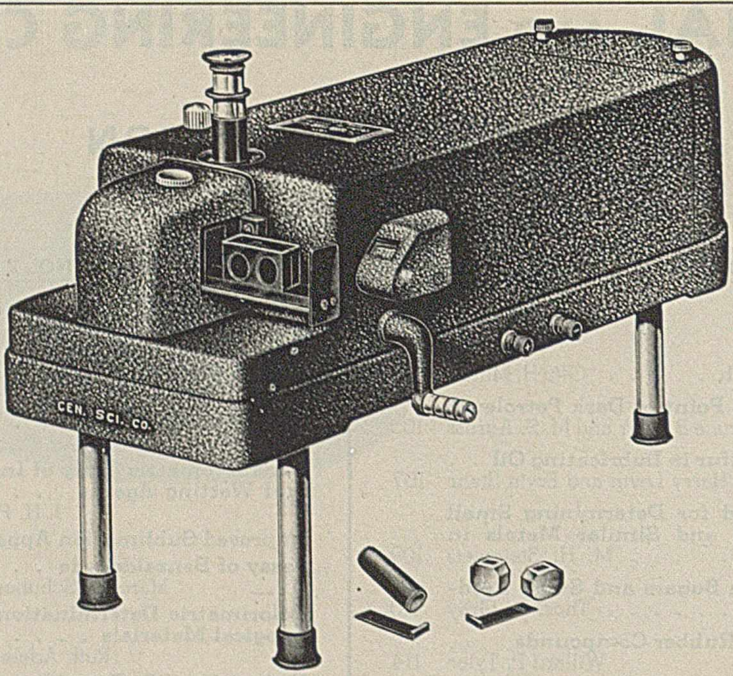
Advertising Department: 332 West 42nd Street, New York, N. Y.
Telephone: Bryant 9-4430

Published by the American Chemical Society, Publication Office, 20th & Northampton Sts., Easton, Penna. Entered as second-class matter at the Post Office at Easton, Penna., under the Act of March 3, 1879, as 24 times a year. Industrial Edition monthly on the 1st; Analytical Edition monthly on the 15th. Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

Annual subscription rate, Industrial Edition and Analytical Edition sold only as a unit, members $3.00, others $4.00. Foreign postage to countries not in the Pan American Union, $2.25; Canadian postage, $0.75.

Single copies: Industrial Edition, $0.75; Analytical Edition, $0.50. Special rates to members.

No claims can be allowed for copies of journals lost in the mails unless such claims are received within 60 days of the date of issue, and no claims will be allowed for issues lost as a result of insufficient notice of change of address. (Ten days' advance notice required.) "Missing from files" cannot be accepted as the reason for honoring a claim. Address claims to Charles L. Parsons, Business Manager, 1155 16th Street, N. W., Washington, D. C., U. S. A.



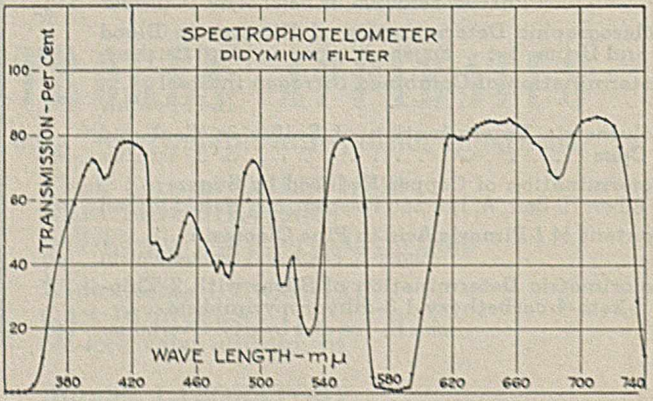
Cenco-Sheard

"Spectrophotelometer"

12315 "SPECTROPHOTELOMETER," Cenco-Sheard, a precision photoelectric spectrophotometer for research in spectral transmission of solid and liquid media and for routine precision clinical and chemical analysis. The range of the instrument is from approximately 325 mμ to 750 mμ, the lower limit depending upon the characteristics of the light source used for illumination.

(Write for full particulars.)

Complete with two slit plates for 2.5, 5, 10, and 20 mμ bands, two glass light filters and two absorption cells, but without illuminator, bench, transformer, condensing lens or galvanometer........................Each $375.00



Transmission curve made with the "Spectrophotelometer" showing high resolving power

Subject to 10% Federal Excise Tax.

CENTRAL SCIENTIFIC COMPANY

CHICAGO
1700 Irving Pk. Road
Lakeview
Station

SCIENTIFIC INSTRUMENTS

TRADE MARK CENCO REG. U.S. PAT. OFF.

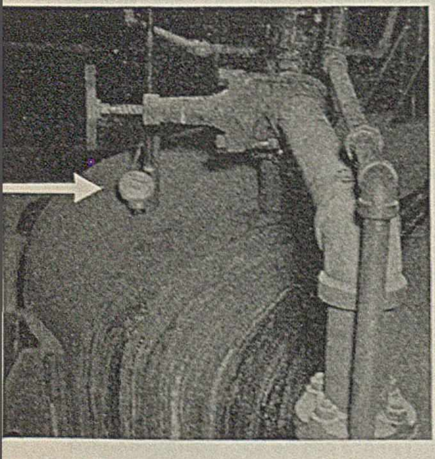
LABORATORY APPARATUS

BOSTON
79 Amherst St.
Cambridge A
Station

New York • Boston • CHICAGO • Toronto • San Francisco

Kettle Operation Guided By Micromax Pyrometers In Reichhold Plant

The operator of a processing kettle for plastic resins in the Elizabeth, N. J., plant of Reichhold Chemicals, Inc., has just paused at the Micromax Pyrometer to see how closely he is controlling the temperature within the kettle.



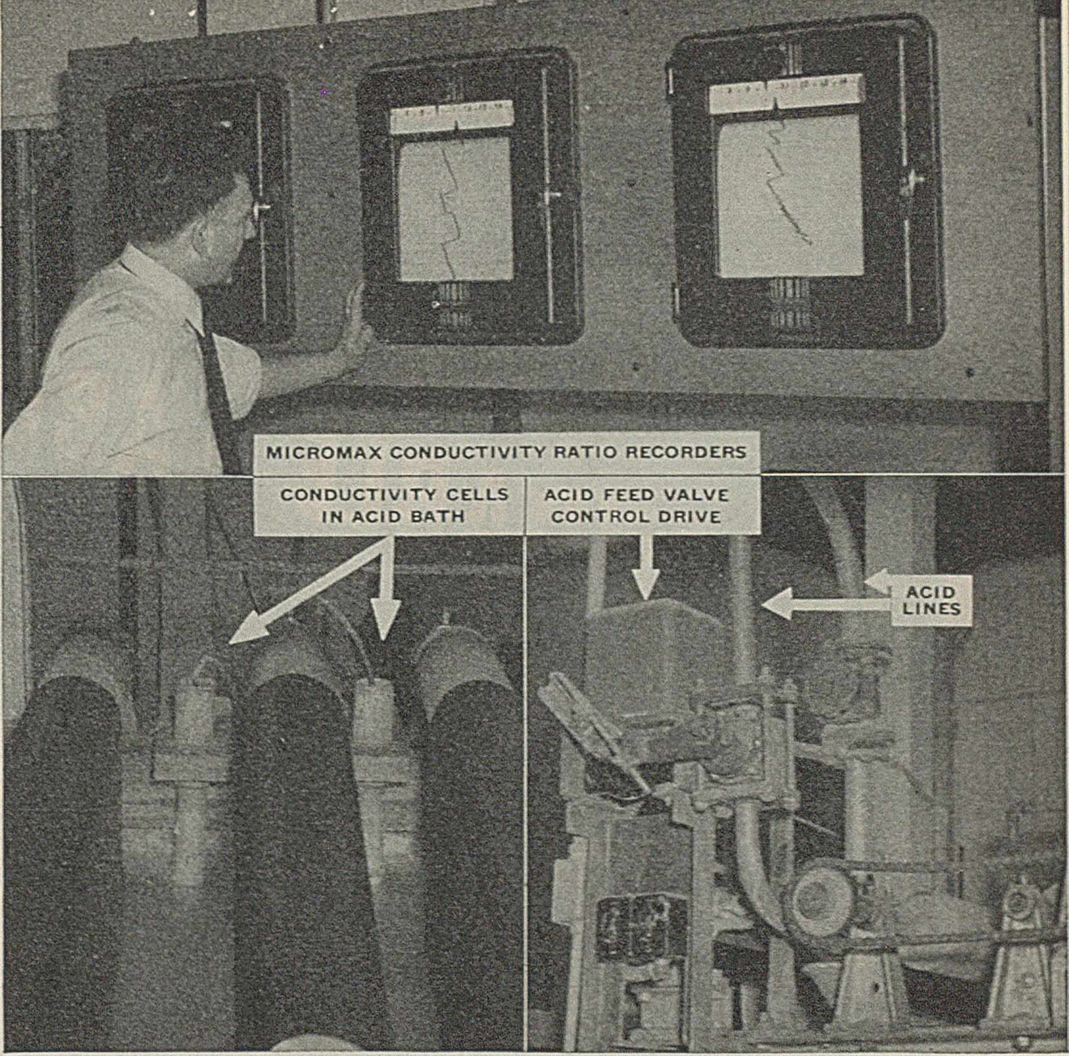
Portion of head of resinkettle. Arrow indicates the simple, strong, easily-opened head of the L&N Thermocouple which is detecting temperature of resin.

This comparatively low temperature must be recorded both accurately and promptly, because the kettle man's job requires him to change the temperature from time to time according to a prearranged cycle, and the limits of this cycle are extremely close. Micromax is particularly well suited to this service, because the operator can either read its bold scale from a distance or can consult its clear record when a close-up is desired.

Appealing, too, to many users is the fact that Micromax is a machine rather than a motorized instrument. Its firm, rigid construction and crisp, powerful way of operating are principal reasons for its widespread use, for recording and controlling temperatures as detected by electrical resistance thermometers, thermocouples or our own "Rayotube" radiation detectors.

Micromax Pyrometers are made in 5 models and hundreds of ranges. Particulars are given in our catalogs; outline your problem and we will send the appropriate publication.

Jrl Ad EN-0600B(14)


MICROMAX CONDUCTIVITY RATIO RECORDERS
CONDUCTIVITY CELLS IN ACID BATH
ACID FEED VALVE CONTROL DRIVE
ACID LINES

SIX BENEFITS GAINED By This Micromax Control of Acid Bath

Half a dozen specific benefits came to the men of Botany Worsted Mills when they changed from manual control to Micromax Automatic Conductivity Control of the Company's "carbonizing" baths. These baths apply H_2SO_4 for oxidation of vegetable matter in wool; the nominal strength of the bath is about 3° Be. Principal benefits of automatic control are:

1) Bath strength is more uniform than the best human operator could maintain. 2) Less acid is used. 3) Color is more "level". 4) Production proceeds with greater smoothness. 5) The process is recorded for the benefit of the operator. 6) Any effect of carbonizing on other processes can be studied accurately and objectively, by consulting the records.

The Micromax equipment used on this process is standard and, with changes in the instrument range and in the type of conductivity cell, is widely applicable to the recording and often the control of solutions in many process industries. If you have a problem along these lines, please consult us.

LEEDS & NORTHRUP COMPANY, 4920 STENTON AVE., PHILA., PA.

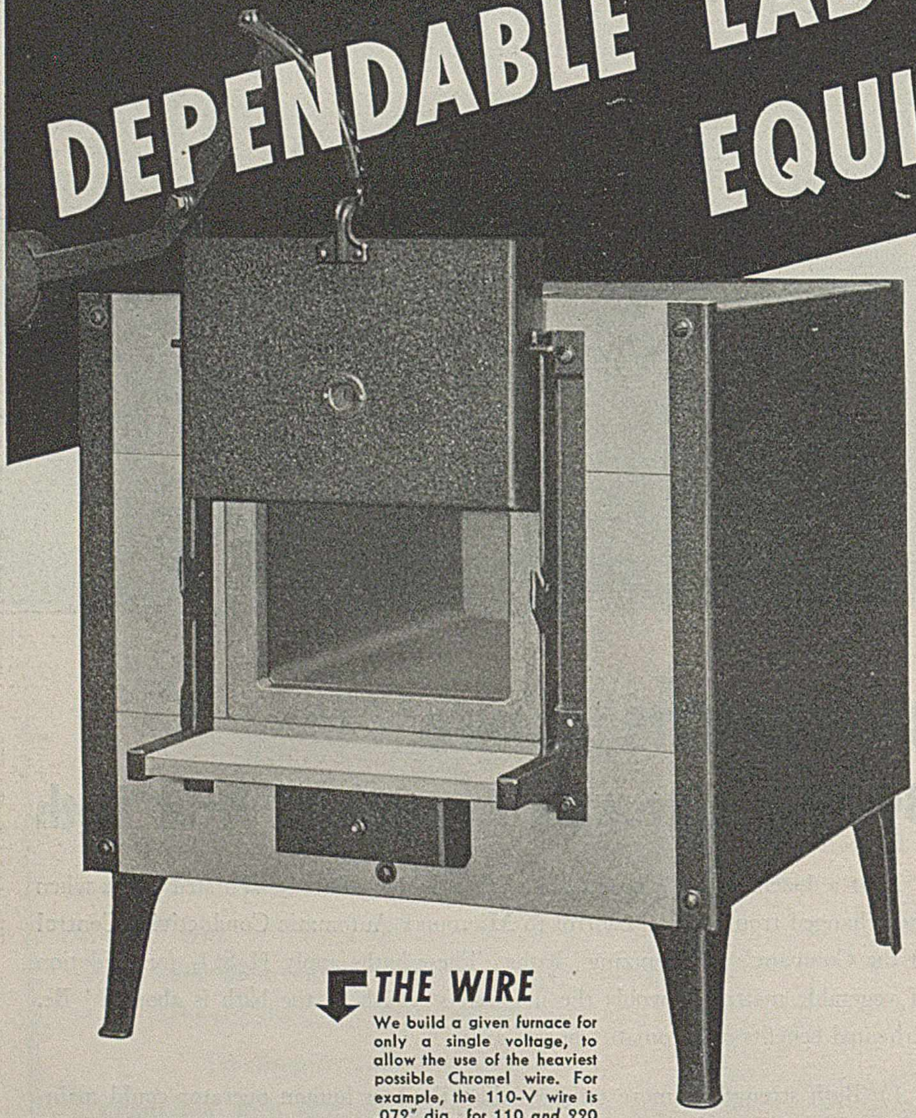
LEEDS & NORTHRUP

MEASURING INSTRUMENTS · TELEMETERS · AUTOMATIC CONTROLS · HEAT-TREATING FURNACES

HIGH SPEED PRODUCTION SCHEDULES

CALL FOR

DEPENDABLE LABORATORY EQUIPMENT

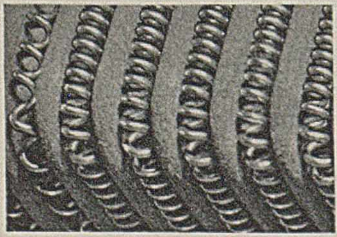


Hoskins electric laboratory furnaces deliver the goods, month in and out. Their Chromel Units are durable—almost beyond belief. We don't invite you to abuse these furnaces, but if you must force them through an emergency, you'll see what a good factor of safety has been built into them. Hoskins Furnaces *are* dependable. Write to your dealer or us. . . . Hoskins Manufacturing Company, Detroit, Mich.

- ● When the unit wears out, all you need to buy is the Chromel wire itself, which comes as a coil.
- ● You install the Chromel wire merely by wrapping it around the grooved muffle.
- ● This furnace can be had, equipped with a small inexpensive pyrometer and couple.
- ● The sliding door saves heat. To remove a crucible you don't need to open the door all the way.
- ● The turns of the Chromel coil are "condensed" to compensate for heat losses at the door.
- ● These furnaces are available as muffle, carbon combustion and small crucible types, good for 1850-2000° F.

THE WIRE

We build a given furnace for only a single voltage, to allow the use of the heaviest possible Chromel wire. For example, the 110-V wire is .072" dia., for 110 *and* 220 it would be .045".



INSULATION

The insulation is 4½" thick all around. The furnace is well made in all respects. We don't build a "cheap" furnace, because a cheap furnace can't be good. Hoskins Furnaces are cheaper in the long run.

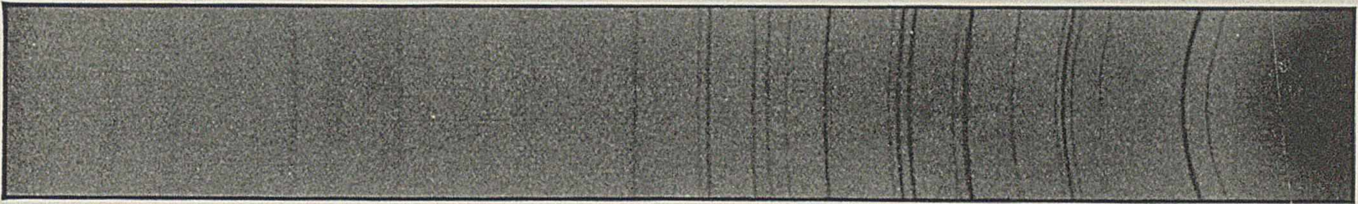
HOSKINS PRODUCTS

ELECTRIC HEAT TREATING FURNACES • • HEATING ELEMENT ALLOYS • • THERMOCOUPLE AND LEAD WIRE • • PYROMETERS • • WELDING WIRE • • HEAT RESISTANT CASTINGS • • ENAMELING FIXTURES • • SPARK PLUG ELECTRODE WIRE • • SPECIAL ALLOYS OF NICKEL • • PROTECTION TUBES

HEATING ELEMENT WIRE
Chromel
NICKEL-CHROMIUM

Pattern A

Lines That Solved A Difficult Problem



Pattern B

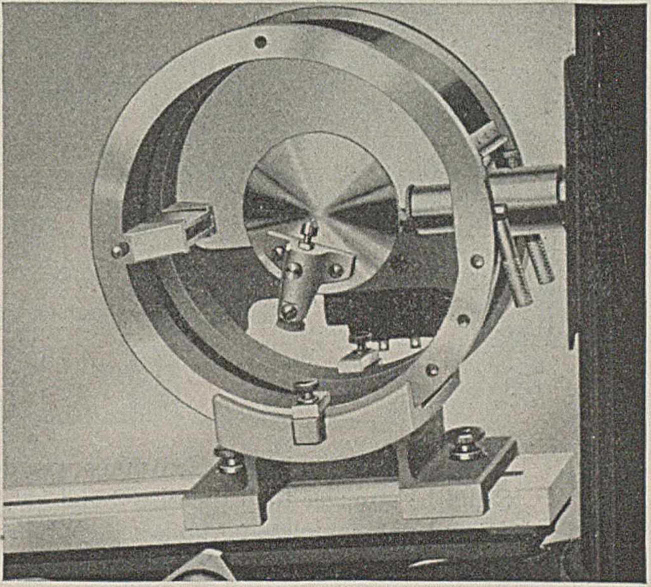
G-E XRD Unit successfully analyzes two different chemical compounds which have identical chemical formulae

House paint and welding rods may seem as far apart as the poles, yet the production of each is dependent upon the use of titanium oxide compounds. However, since these compounds may assume two very different crystalline forms, rutile and anatase, this problem had to be solved:

Rutile and anatase have identical chemical formulae, TiO_2—yet when used as a coating for welding rods or as a catylitic agent in speeding up chemical reaction, they have entirely different behaviors. Obviously, then, in order to insure a completely satisfactory finished product, it is necessary, when preparing the pure oxides of titanium, to know the concentration of each of the forms in the oxide so that precise control of quality can be established.

When conventional methods of analysis failed to find the answer, x-ray diffraction solved it easily and quickly. With the G-E XRD Unit's Powder Camera it is possible to make a diffraction photograph of the powdered sample which will readily differentiate between the two oxides. Pattern (A) established that the sample was pure rutile, while Pattern (B) was established as pure anatase.

If you employ the oxides of titanium in your manufacturing processes, the G-E X-Ray Diffraction Unit will prove an invaluable aid in differentiating between these two common forms. Modern, progressive analytical laboratories have been quick to recognize the G-E XRD Unit as a dependable "problem solver." Why not do as they did? Use the convenient coupon to request full information about the G-E XRD Unit and its application to your problems. The services of our X-Ray Diffraction Laboratory are yours for the asking; address your request to Department R42.



The G-E XRD Powder Camera is constructed especially for the routine application of the important and widely used "powder" diffraction method of analysis to any sort of material.

CLIP, SIGN, and MAIL, TODAY

Please send me complete information about the G-E XRD X-Ray Diffraction Unit.

Name____

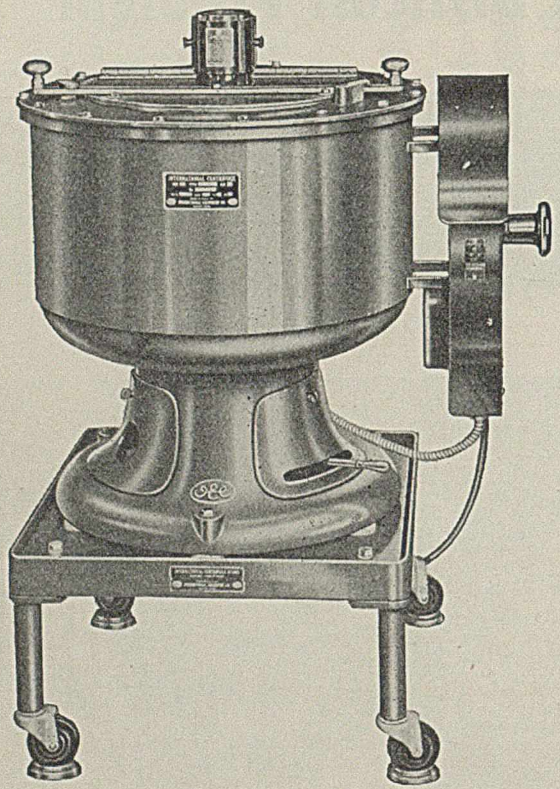
Position______________________________________

(Please attach to, or write on, your company letterhead)

GENERAL ELECTRIC
X-RAY CORPORATION
2012 JACKSON BLVD. CHICAGO, ILL., U. S. A.

NEW BLOOD PLASMA CENTRIFUGE

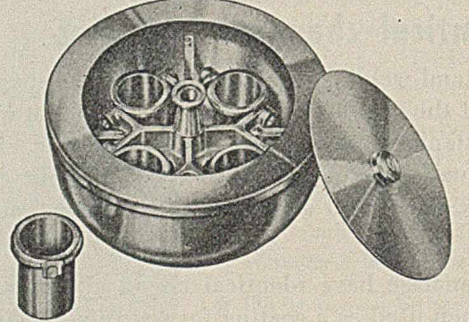
INTERNATIONAL MODEL BP



Designed Especially For The 600 ml. and 650 ml. Bottles

SPEED 2500 R.P.M.

Windshielded Head To Minimize Heating of Blood



The New Model BP Centrifuge was designed to provide an intermediate model which would be stronger than the Size 2 and yet less expensive than the Size 3. The centrifuge is shipped as a complete portable self-contained unit, wired and ready to plug into any lighting circuit.

To insure adequate protection when swinging the large 600 and 650 ml. bottles an extra large shaft has been provided as well as a heavy all welded steel boiler plate guard with bar lock cover. The centrifuge is powered with a specially designed motor and is equipped with an indicating tachometer and 50 step speed control rheostat.

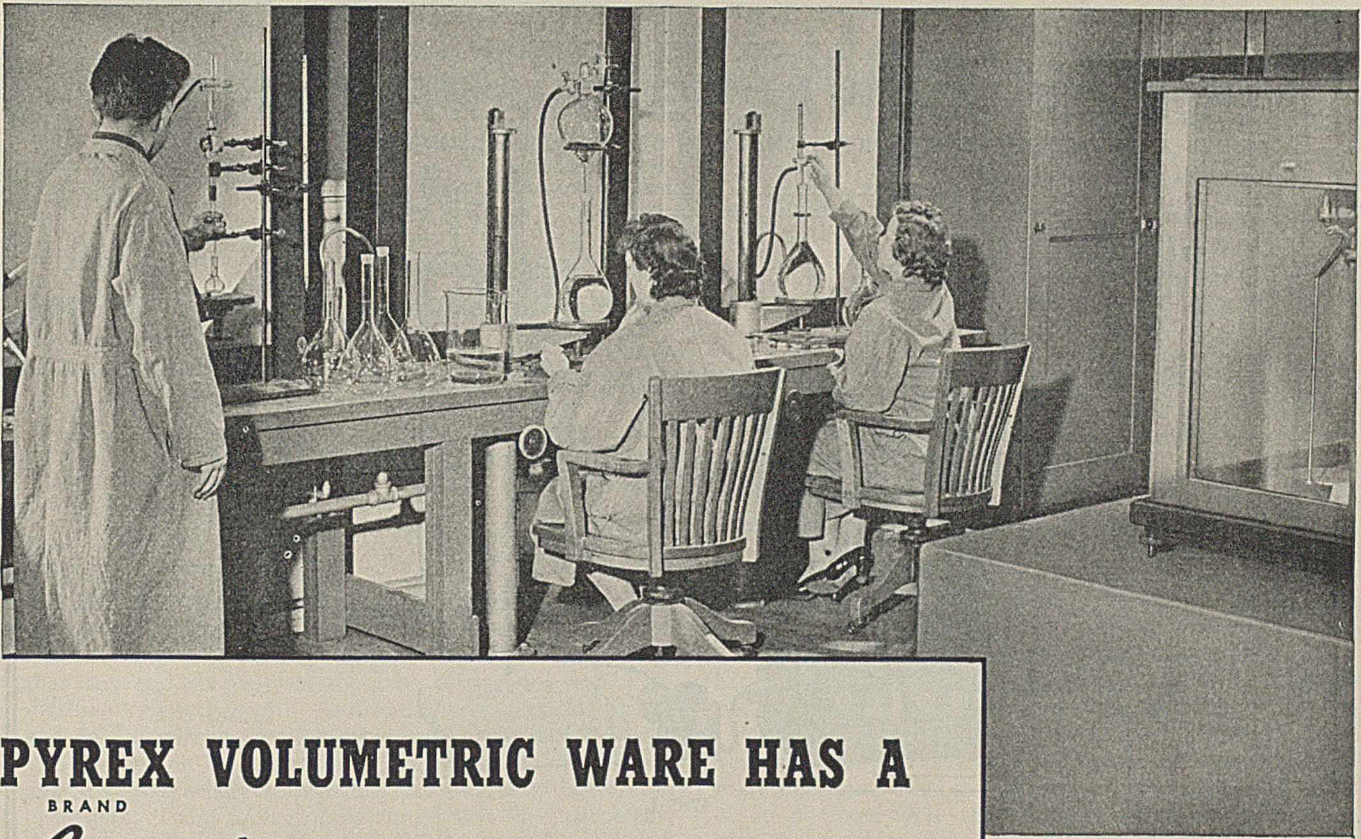
The four place head shown above will accommodate the Cutter 650 ml. Saftifuge bottles, the Baxter 600 ml. Centrivac bottles and the T. C. Wheaton 550 ml. blood bottles, as well as the proposed Corning and Fenwal 650 ml. refillable blood plasma bottles. The head and cups are entirely wind-shielded by enclosure in a bowl and cover of spun aluminum which provide a dead air space in which the bottles swing, thus reducing air friction and minimizing heating of the blood.

Send for Descriptive Literature

INTERNATIONAL EQUIPMENT CO.

352 WESTERN AVENUE BOSTON, MASS.

Makers of Fine Centrifuges for More than Forty Years



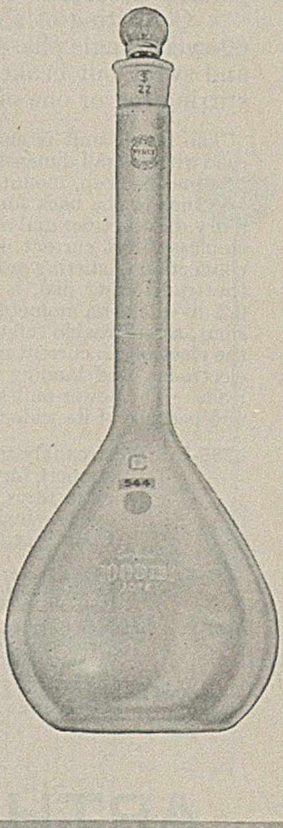
PYREX BRAND VOLUMETRIC WARE HAS A *Control Laboratory* ALL ITS OWN

In addition to its general Research Laboratories, Corning also maintains a specialized Volumetric Control Laboratory.

Here skilled technicians maintain the accuracy of all calibrating instruments, check and double check calibrations on all catalog items and supervise the marking of volumetric ware made special to order.

All volumetric standards are in accordance with U. S. Bureau of Standards' recommendations. Standard "Pyrex" Volumetric Ware is held within twice the tolerance, while Corning Certified "Pyrex" Ware is held to within the tolerances and specifications prescribed by the Bureau.

Sturdy, accurate, made of *balanced* glass, "Pyrex" Volumetric Ware is recommended for all general purposes where a glass of high chemical stability is required. For work necessitating extreme accuracy, Corning Certified "Pyrex" Ware should be specified. Both are available through your regular source of supply.



T.M. REG. PYREX U.S. PAT. OFF.

CORNING
means
Research in Glass

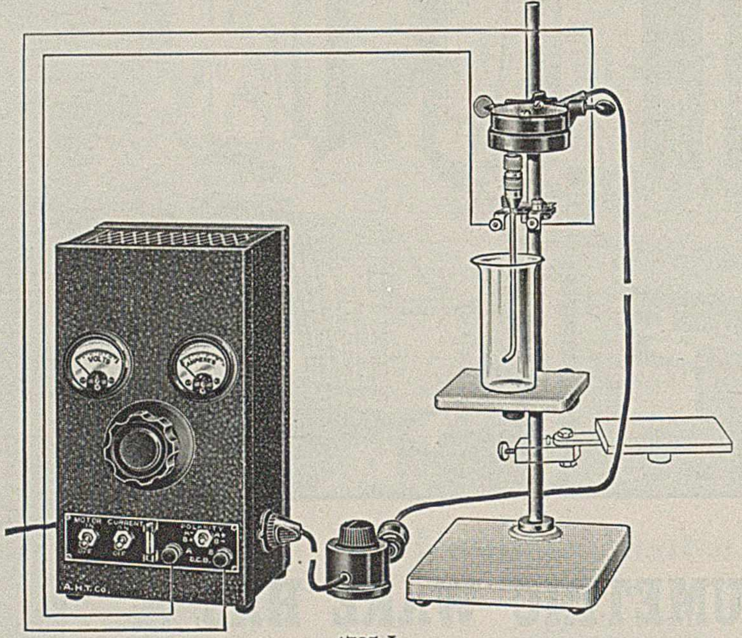
TRADE MARK VYCOR REG. U.S. PAT. OFF.

PYREX BRAND LABORATORY WARE
"PYREX" and "VYCOR" are registered trade-marks and indicate manufacture by
CORNING GLASS WORKS • CORNING, NEW YORK

A.H.T. CO. SPECIFICATION

ELECTROANALYSIS APPARATUS

FOR THE QUANTITATIVE ANALYSIS OF METALS, ALLOYS OR MATTES



4785-L

ELECTROANALYSIS APPARATUS, Single Unit, A.H.T. Co. Specification, for the quantitative analysis of metals, alloys or mattes. An assembly which provides maximum flexibility and greatest possible protection from acid fumes for the electrical control parts.

Consisting of a power unit for supplying controlled low voltage direct current, from a 110-volt, 60-cycle, single phase, alternating current circuit, connected with a separate electrode support with base and swing-out beaker shelf of Coors porcelain, and variable speed electric stirrer for rotating a glass stirring rod or one of the electrodes.

The power unit is enclosed in a ventilated sheet metal case with overall dimensions 12 inches high × 7 inches wide × 6 inches deep, mounted on rubber feet and with slotted openings in the back for hanging on the wall. It contains a dry disk rectifier and a variable transformer for delivering stepless direct current up to 5 amperes, and an outlet for connection to stirring motor. On the front face are mounted the transformer dial, a voltmeter, range 0 to 10 volts in 0.2 divisions, an ammeter, range 0 to 5 amperes in 0.1 divisions, a replaceable safety fuse and switches for the stirrer, the electrolytic current and for changing the polarity of the electrodes, and binding posts for connecting the electrode leads. The power unit is suitable for macro determinations and because of its wide range of control, is also suitable for micro tests when used with cells of the Clarke-Hermance type.

The electrode support consists of an acid-proof Coors porcelain base $8^1/_2 \times 6^1/_2$ inches with $20 \times {}^1/_2$-inch rod of aluminum alloy with "Alumilite" finish; beaker shelf of Coors porcelain on swinging arm; non-corrosive electrode clamp with adjustable aluminum binding posts and clamp holder; and electric stirrer consisting of brushless, shaded pole motor totally enclosed in acid-resisting housing with aluminum supporting rod and with rheostat, and two aluminum chucks, one attached to the motor for holding the special glass stirring rod which rotates inside a platinum electrode, and a smaller chuck for insertion in the motor chuck to take electrode stems up to B&S gauge-16 wire when rotating electrode is used.

4785-L. **Electroanalysis Apparatus,** as above described, complete as shown in illustration, with power unit and electrode support for stationary or rotating electrodes, insulated lead wires with terminals, Pyrex beaker 180 ml, two extra fuses, cord and plug, and directions for operation but without platinum electrodes. For 110 volts, 60 cycles, single phase, a. c. 98.75
Code Word .... *Exulk*

4785-N. **Electrolytic Power Unit,** only, as supplied with above. Complete with two extra fuses, cord and plug, but without connecting cords for electrodes or electrode support. For 110 volts, 60 cycles, single phase a. c. 70.00
Code Word .... *Exumi*

4785-P. **Electrode Support,** only, as supplied with above. Complete with Coors porcelain base and swingout beaker shelf, non-corrosive electrode clamp, clamp holder and stirring motor with two chucks, glass stirring rod and rheostat, but without platinum electrodes, beaker or connecting leads 28.25
Code Word .... *Exunf*

NOTE—No. 8307 and 8308 Platinum Electrodes, as listed on page 660 of our catalogue, are suitable for use with above. We also offer a special anode, weight 8.5 grams, and two special electrodes, 6.5 and 8 grams respectively, for the same purpose.

More detailed information sent upon request.

ARTHUR H. THOMAS COMPANY

RETAIL—WHOLESALE—EXPORT

LABORATORY APPARATUS AND REAGENTS

WEST WASHINGTON SQUARE, PHILADELPHIA, U.S.A.
Cable Address, "Balance," Philadelphia

INDUSTRIAL AND ENGINEERING CHEMISTRY

ANALYTICAL EDITION

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY ● HARRISON E. HOWE, EDITOR

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

Research with the Polarograph

OTTO H. MÜLLER, Department of Anatomy, Cornell University Medical College, New York, N. Y.

LIKE many new analytical tools, the polarograph has been ballyhooed at times and belittled at others. The enthusiasm of early workers was misinterpreted as suggesting that any and all analyses could be carried out with this machine by any layman. As a result, there was skepticism and an unfavorable reaction when actual tests revealed that the polarograph had a definitely limited field of application and that a specially trained chemist was essential for its operation. Today it is generally agreed that this instrument is of unquestionable value, and this paper will serve to demonstrate some of its uses.

Polarography

EQUIPMENT. To simplify studies with the dropping mercury electrode, the polarograph was designed by Heyrovský and Shikata in 1925 (*22*) for plotting current-voltage curves automatically. As is shown in Figure 1, it consists of a potentiometric wheel, *P*, driven by a motor, *M*, and geared to a camera, *C*, in a fixed ratio for recording deflections of the galvanometer, *G*. (For simplicity, only this type of polarograph is discussed here. However, several other instruments for use with the dropping mercury electrode are produced by American manufacturers and sold under various trade names.) The current-voltage curves obtained with it (polarograms) are of value only if they indicate specifically the processes going on at one of the electrodes. It is therefore essential to have an electrolytic cell with one large nonpolarizable and one small easily polarizable electrode. A large calomel electrode and the dropping mercury electrode are undoubtedly the best combination meeting these requirements. (Other easily polarized electrodes can also be used under proper conditions, but they lack the advantage of an easily reproducible fresh surface and are seldom free from the effects of previous polarization.)

PRINCIPLES. Using such a cell it is possible to obtain with the polarograph what its name implies—that is, a graph showing the polarization of the small electrode with increasing applied voltage. The presence of any depolarizer at the electrode surface is indicated on such a graph by a flow of current. Under suitable, well-defined conditions, the depolarizer can reach the electrode only by simple diffusion, so that the current will be limited by the quantity of depolarizer which can diffuse to the electrode surface in unit time. This so-called "diffusion current" is proportional to the concentration of the depolarizer and serves for quantitative analysis (*25*). The potential at which the depolarization occurs is an indication of the nature of the depolarizer and serves for qualitative analysis (*20*). If more than one depolarizer acts over a given range of the applied voltage, a complex polarogram with several current increases at different potentials (waves) will be obtained, permitting the simultaneous qualitative and quantitative analysis of a number of substances. An example of such a curve in which optimum conditions prevail is shown in Figure 2.

Heyrovský and collaborators have made a systematic investigation of the factors which govern the polarographic wave and have been able to give a theoretical explanation of the observed facts, thus changing polarography from an empirical into an exact method. For details, the reader is referred to the original literature (*18*, *20*, *21*, *25*) or to review papers (*27*, *38*, *39*, *52*) and monographs (*19*, *24*, *28*, *42*).

Theoretically, every substance can be analyzed polarographically if it is electroreducible or -oxidizable within the potential range of the electrode. The maximal range of the

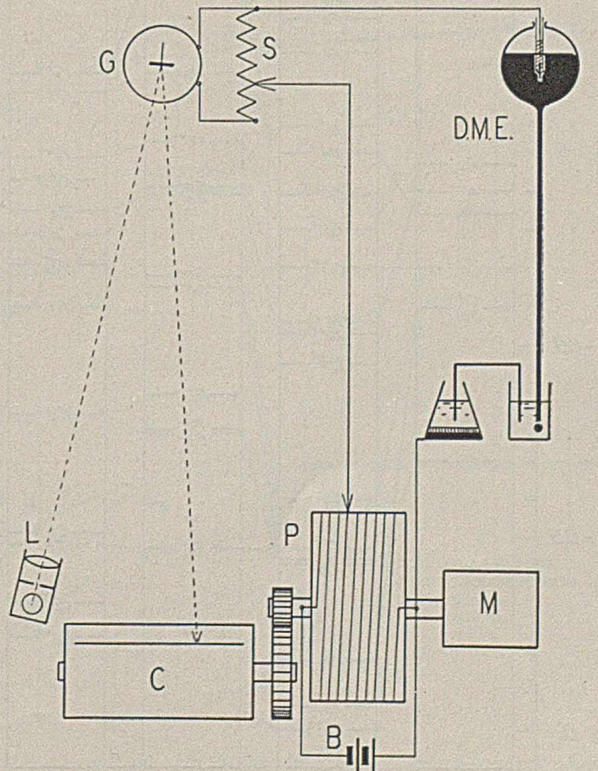


FIGURE 1. DIAGRAM OF POLAROGRAPH AND ELECTROLYTIC CELL

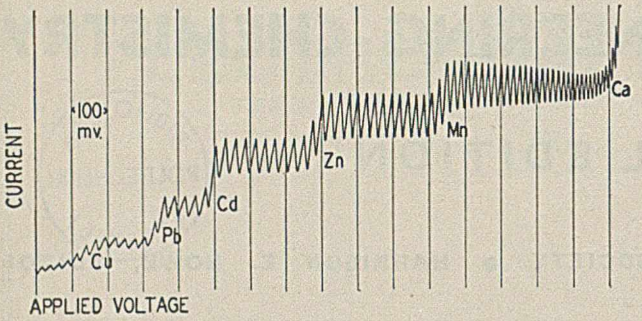


Figure 2. Polarogram Demonstrating Simultaneous Analysis of Copper, Lead, Cadmium, Zinc, and Manganese in a Solution of Calcium Chloride

dropping mercury electrode is from $E_{S.C.E.}$ + 0.6 to −2.6 volts, but in most solutions it is much smaller. If there is a great number of different electroactive substances in solution, the analysis becomes difficult, since some of them may have characteristic potentials (half-wave potentials, *20*) that overlap or come so close together that the resolution of individual waves becomes impossible. Such coincidences may sometimes be overcome by altering the pH of the medium in which the reaction is carried out, or by changing the reactants into complexes, from which they deposit at potentials far enough apart so that each wave can be measured separately. Figure 3 shows a chart of inorganic reduction potentials in different media (*42*). It may be seen that wave coincidences can be overcome in a good number of cases. If this is not possible, or if an ion with a more positive reduction potential is present in excess, recourse must be taken to ordinary chemical methods to bring about a preliminary separation. This is the case in most practical analyses which require a careful combination of electrochemical and general analytical procedures executed by a well-trained chemist. However, some analyses with the dropping mercury electrode, although possible, become so complicated that it is best to use a different method. These points are well demonstrated by the procedure for the analysis of brass (*24*) which is shown in Table I. Copper, zinc, nickel, lead, iron, and tin are all polarographically determinable. However, for simplicity, the procedure is divided into one gravimetric and three polarographic analyses in different media.

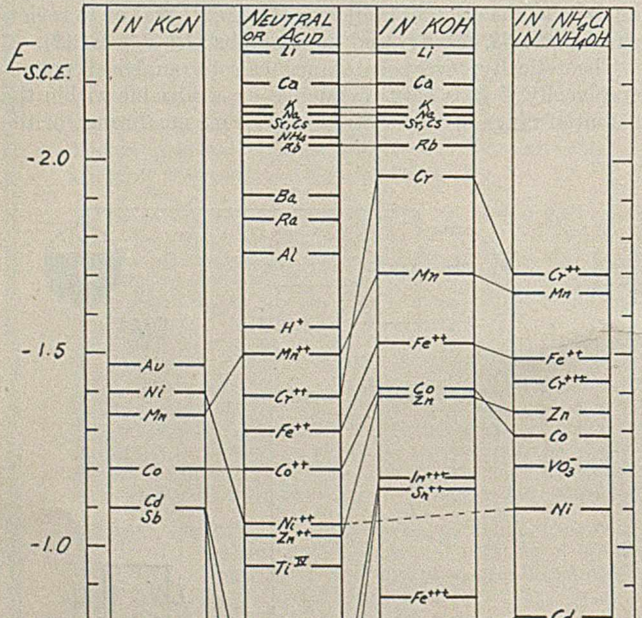


Figure 3. Table of Half-Wave Potentials of Metal Ions (*42*)

There are but few procedures published in as much detail as the one just mentioned, and even these should be used with reservation by either novice or expert. With rare exceptions, therefore, every contemplated polarographic analysis presents its own problem, for which the investigator must develop his own technique. This consists largely of finding supporting electrolytes or *Grundlösungen* which bring about the necessary separation of wave coincidences, so that every polarographic wave is significant and measurable. The reliability of each procedure must be tested by the construction of calibration curves under identical conditions at which the analysis is to be carried out. A clear understanding of the fundamental principles is obviously essential. A person trained in physical chemistry should be able to acquire a good deal of experience in a relatively short time by carrying out the series of experiments described in the *Journal of Chemical Education* (*42*). For these no polarograph is needed and the necessary equipment should be available in most laboratories. Once a particular procedure has been fully developed, the analyses can be carried out by anyone with some training in chemical analysis—for instance, classes of medical students have been able to make polarometric oxygen and chloride determinations with but a few minutes of instruction. It is well, however, to have expert advice available, since experience has shown that, even in the simplest analyses, irregularities of unforeseen origin are bound to occur.

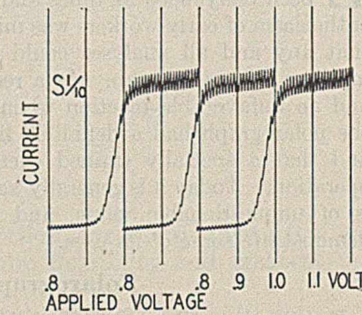


Figure 4. Polarographic Zinc Waves Repeated Three Times

Table I. Brass Analysis

(Determination of Cu, Zn, Ni, Pb, Fe, and Sn according to Hohn, *24*)

Dissolve 0.5 gram of sample in concentrated HNO_3, evaporate to dryness; heat with 5 cc. of concentrated HNO_3, add water, and filter

SnO_2 Determine gravimetrically	Cu, Zn, Ni, Pb, Fe Add 15 cc. of concentrated NH_3 and 5 cc. of 2 *N* $(NH_4)_2CO_3$ and filter	
	Pb, Fe Dissolve in hot 2 *N* HNO_3, make up to fixed volume. Determine polarographically in slightly acid NH_4Cl solution	Cu, Zn, Ni Make up to fixed volume. Determine polarographically (*a*) in NH_3 + NH_4Cl solution to get Cu and sum of Zn + Ni (*b*) in KCN + Na_2SO_3 solution to get Ni only

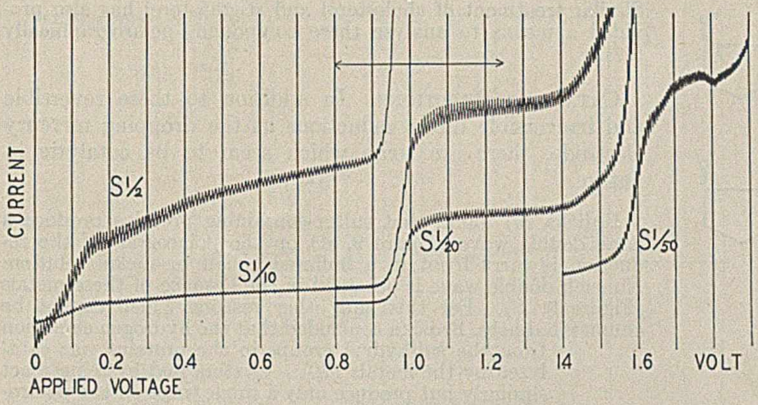


Figure 5. A Step in Analysis of a Magnesium Alloy

Looking for components of solution by recording curves at different sensitivities of galvanometer. Accidentally, middle (zinc) wave of curve *S* 1/10 was repeated over voltage increment indicated.

Sensitivity and Accuracy. The polarographic method is applicable over a concentration range of 10^{-6} to 10^{-2} molar; for best results, however, a 10^{-4} to 10^{-3} molar solution is desirable. In the latter case, an accuracy of ±1 per cent can be reached by repeating polarograms of the same solution several times (Figure 4) and averaging the individual measurements of the diffusion current. This can easily be done if the volume of the solution is 1 cc. or more, because the quantity of material electrolyzed is so small that the body of the solution remains unaltered and subsequent polarograms are identical. This is clearly demonstrated in the middle curve of Figure 5, where part of the curve was accidentally repeated, causing merely a thickening of the lines drawn. When smaller volumes of solution are analyzed, special precautions are necessary, since the quantity of material which is removed by electrolysis and also the end products formed become significant under these conditions. Furthermore, a residual current, which is inherent in the method, becomes appreciable in dilute solutions and necessitates a correction of the observed small currents. In general, therefore, the accuracy and sensitivity of the method are as follows: in practice, 1 cc. of a 10^{-5} *M* solution or 1 microgram of material (if its molecular weight is 100) can be analyzed with an accuracy of ±1 to 3 per cent. Under extreme conditions, 0.01 cc. of a 10^{-6} *M* solution or 0.001 microgram of material (if its molecular weight is 100) can be analyzed, but the error is about ±100 per cent.

Scope. The scope of the polarographic method includes a large variety of inorganic and organic ions and compounds. Analyses have been made of practically all metallic ions, of many anions which form complexes or precipitate with mercury, and of a number of complex anions such as bromate and nitrate ions. Even dissolved gases—e. g., oxygen, sulfur dioxide, and cyanogen—have been determined. In the organic field an ever-increasing number of compounds has been found suitable for polarographic analysis. Besides the group of known reversible oxidation-reduction systems, a great many compounds have been studied which are irreversibly reduced or oxidized at the dropping mercury electrode. In almost all these reactions, the pH of the solution has an influence on the reduction potential. For this reason and because reactions at the electrode can either produce or use up hydrogen ions (*39*, *41*), adequate buffering of the solution becomes essential in organic analyses.

Reversible Reactions. The ideal example of a reversible reaction at the dropping mercury electrode is given by quinhydrone and its components (*45*). In a well-buffered solution, the curve due to the reduction of quinone (Figure 6, *a*) will have the same characteristic half-wave potential (corrected for *IR*) as the curve due to the oxidation of hydroquinone (Figure 6, *c*). This potential is also obtained if quinhydrone is studied (Figure 6, *b*). Here one half of the curve represents an oxidation of hydroquinone at the mercury anode, while the other half represents a reduction of the quinone at the mercury electrode which is now cathode. Generalizing, one can say that an oxidation-reduction system is reversible in a thermodynamic sense whenever identical polarographic half-wave potentials are obtained in the reduction of the oxidant and oxidation of the reductant (*39*). These reversible reductions and oxidations are best for obtaining a clear understanding of the polarographic wave and will be discussed further herein.

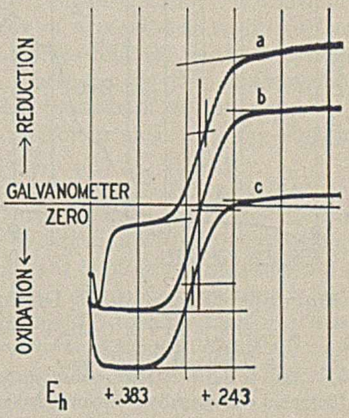


Figure 6. Polarogram of Solution Buffered at pH 6.67

a quinone, *b* quinhydrone, and *c* hydroquinone (*45*)

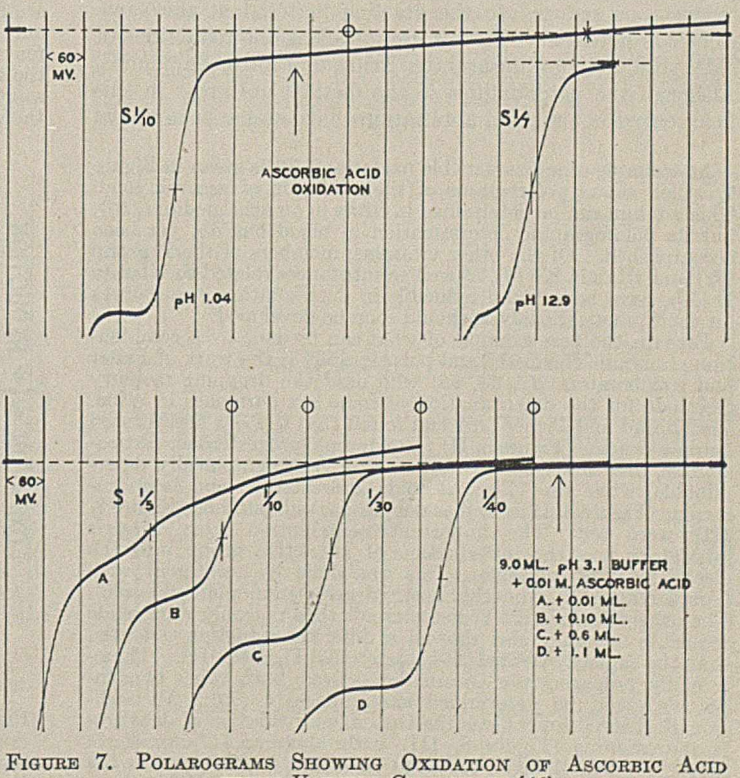


Figure 7. Polarograms Showing Oxidation of Ascorbic Acid under Varying Conditions (*46*)

For each curve, potential corresponding to that of calomel half-cell—i. e., when applied voltage is zero—is indicated by a circle

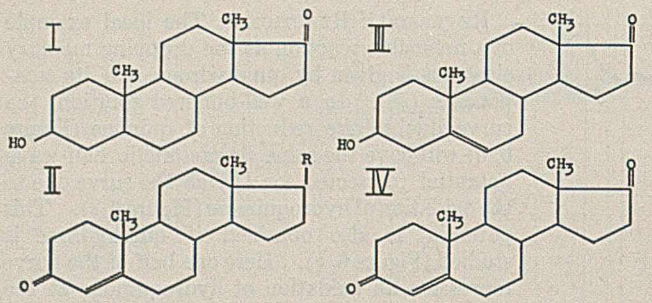


FIGURE 8

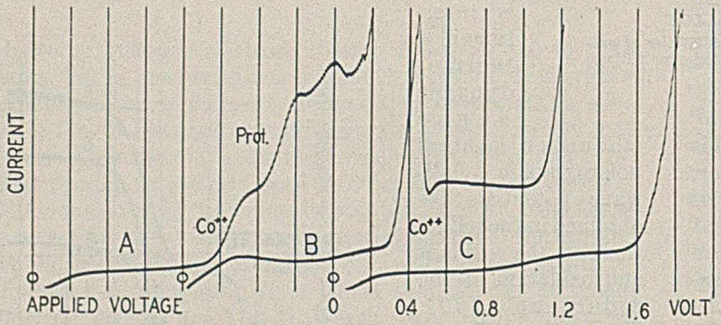


FIGURE 9. POLAROGRAMS DEMONSTRATING BRDIČKA'S REACTION (*9*)

A. 2 cc. of 8×10^{-3} *M* $CoCl_2$ + 1 cc. of 1 *N* NH_4Cl + 6 cc. of H_2O + 1 cc. of 1 *N* NH_4OH + 0.1 cc. of human blood plasma
B. Like *A* but without plasma
C. Like *A* but with H_2O instead of $CoCl_2$

Potential corresponding to calomel half-cell (applied voltage zero) indicated by circle

IRREVERSIBLE REACTIONS. By far the majority of organic analyses involve reactions which are not strictly reversible—that is, reactions in which the end products cannot be reoxidized or reduced to the starting material at the same electrode potential. To this group belong the reductions of aldehydes, ketones, unsaturated acids, and nitro compounds. Although the potentialities of the method are great in this field, only few practical applications have so far been made.

An example of an irreversible oxidation (*46*) is given in Figure 7, which shows polarograms of the oxidation of ascorbic acid. This vitamin can be determined in fruits in an acid medium (*26*), but its polarographic determination in blood has not yet been accomplished. Of the other vitamins, members of the B group (*32*) and vitamin K (*16*), as well as substances related to vitamin E (*50*), have been found reducible in pure solution; procedures for their practical analysis should soon be developed.

Perhaps the best example of what can be done by a combination of organic chemistry and polarography is the work of Fieser and collaborators (*17, 58, 59*) who used the dropping mercury electrode for the determination of some sex hormones in urine. Eisenbrand and Picher (*15*) had found that the α-β unsaturated ketonic steroids (Figure 8, II) testosterone, progesterone, corticosterone, and desoxycorticosterone were polarographically determinable, while the 17-ketosteroids androsterone and isoandrosterone (Figure 8, I) as well as dehydroisoandrosterone (Figure 8, III) were not. The important contribution from Fieser's laboratory was the introduction of an active group into the electro-inactive molecule. This was done by treatment with Girard reagent *T* (trimethyl acethydrazide ammonium chloride). The otherwise inactive 17-ketosteroids thus not only were made reducible but they also showed a different reduction potential than the similarly treated Δ^4-ketosteroids (Figure 8, II). Therefore, by preparing the Girard derivatives, both types of compounds could be determined simultaneously (*59*). An additional accomplishment was the Oppenauer oxidation of dehydroisoandrosterone (Figure 8, III) with aluminum-*t*-butoxide in acetone, which changed the position of the double bond in the rings and oxidized the hydroxyl group at position 3 to form Δ^4-androstenedione-3,17 (Figure 8, IV). The Girard derivative of this compound showed two waves, as might be expected. Similar treatment of cholesterol and stigmasterol has also provided a means to analyze these compounds polarographically (*17*).

CATALYTIC REACTIONS. In addition to these reversible and irreversible direct reductions at the dropping mercury electrode, there are some which seem to be catalytic in nature.

Brdička (*9*) found that sulfur-containing proteins produce a large double wave (Figure 9, *A*) on the polarogram if the reduction is carried out in a buffered cobalt or nickel solution. No such double wave is obtained in the absence of these metals (Figure 9, *C*). For this and other reasons which cannot be enumerated here, Brdička concluded that the hydrogen evolution from the sulfhydryl groups in the proteins was catalyzed by the metals (*10*). Cystine and cysteine react similarly but produce only a single wave on the polarogram (*11*). When a number of blood proteins from different individuals were studied, the interesting observation was made that serum from cancer patients produced a protein double wave that was definitely smaller than that resulting from the serum of normal individuals (*12*). This seemed to offer possibilities for the diagnosis of cancer and stimulated research on the subject (*7, 8, 13, 55*). Unfortunately, other diseases—e. g., pneumonia (*14*) and arthritis (*36*)—were found to have a similar effect, so that the test is not specific for cancer. Much promising work, however, is still in progress and even now valuable information is being obtained on the course of disease.

THEORETICAL APPLICATIONS. Aside from the foregoing practical applications, there are numerous theoretical problems in which the polarograph has been of service.

To get a clear picture of the happenings at the electrode-solution interface, let us again consider the polarogram of quinhydrone in a well-buffered solution (Figure 10, *A*). Since the electrode-reaction is reversible in this case, the polarographic wave will be practically identical with the familiar electrometric titration curve (Figure 10, *B*). In both, the midpoint of the curve gives us E_0, the characterizing potential of the oxidation-reduction system, yet the conditions responsible for these curves are fundamentally different. The polarographic wave indicates only the condition of the electrode-solution interface. The current of electrons flowing from or to the electrode corresponds to the titrating agent added to this interface while the body of the solution remains unchanged. In the electrometric titrations, the whole of the solution is altered and the electrode serves only

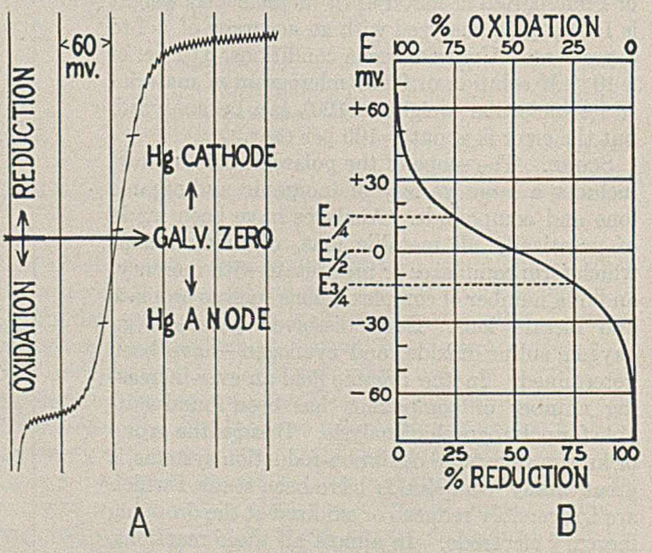


FIGURE 10. (*A*) POLAROGRAM OF QUINHYDRONE IN BUFFERED SOLUTION, REPRESENTING DIRECT TITRATION OF ELECTRODE-SOLUTION INTERFACE, WHILE BODY OF SOLUTION REMAINS PRACTICALLY UNCHANGED. (*B*) TYPICAL POTENTIOMETRIC OXIDATIVE OR REDUCTIVE TITRATION CURVE, REPRESENTING CHANGES THROUGHOUT BODY OF SOLUTION (*39*)

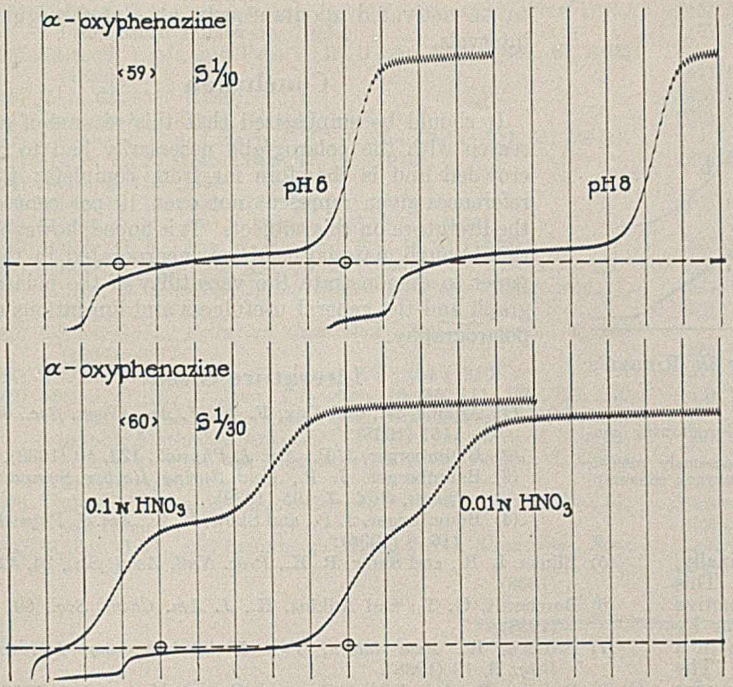


FIGURE 11. POLAROGRAMS OF α-OXYPHENAZINE

In McIlvaine buffers of pH 6 and 8, and in 0.1 and 0.01 N HNO_3 solutions (*37*). Potential corresponding to calomel half-cell (applied voltage zero) indicated by circle

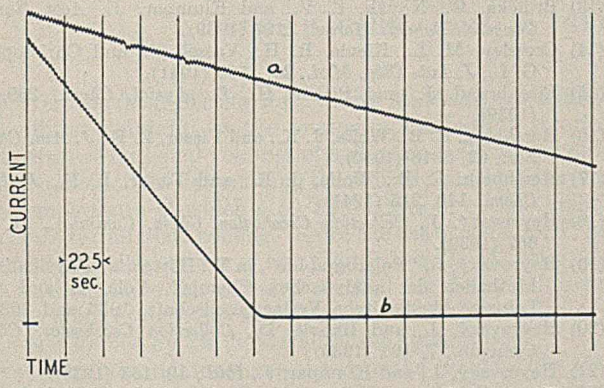


FIGURE 12. POLAROGRAPHIC RECORD OF CURRENT-TIME CURVES

Rates of oxygen consumption of yeast cells, (*a*) in absence of substrate, (*b*) in presence of glucose (*42*)

to demonstrate this change. The information gained in both cases is identical (*39*). Speed, ease of operation, and the absence of a need for a suitable titrating agent are advantages of the polarographic method, while higher accuracy and familiarity with the procedure speak for the electrometric titrations.

A good example of such studies is given in Figure 11, which shows the reduction of α-oxyphenazine (*37*), one of the semiquinone-forming compounds investigated by Michaelis (*35*). It is reduced in two steps in very acid solutions, while in more alkaline solutions the reduction proceeds in a single step. By means of the polarograph these studies have been extended (*37*) to measurements in the overvoltage range of potential and to irreversible systems. In the inorganic field similar investigations have been carried out with numerous complex metal ions (*31*).

There are many other theoretical polarographic problems in which the reductions are not reversible. To these belong studies on the effect of substitutions in an organic molecule upon its reduction potential (*1*, *48*, *49*, *56*); rate studies such as the inversion of sucrose (*23*), or the tautomerization of an optically active azomethine (*6*); studies in keto-enol tautomerism and the polymerization of pyruvic acid (*43*); and studies of the effectiveness of buffers (*41*).

Polarometry

KINETIC STUDIES. All polarographic analyses require enough time to draw the curve and to evaluate the result. To save time, modifications of the technique have been developed wherein the currents obtained at a constant applied voltage are observed and recorded. This is possible whenever the reduction produces a wave with an extended plateau (*42*)—for instance, the oxygen concentration in a solution (*54*) has been determined by applying a fixed voltage of $E_{S.C.E.}$ −0.5 volt and noting the corresponding galvanometer deflections (*3*, *5*, *57*). Also, changes in oxygen concentration with time have been recorded by means of the polarograph. Figure 12 shows the rate of oxygen consumption of a yeast suspension (*a*) in the absence of substrate and (*b*) in the presence of glucose (*42*). These curves demonstrate the well-known fact that the rate of oxygen consumption of yeast is of zero order until very low oxygen pressures are reached.

TITRATIONS. The foregoing studies suggest reactions in which an analyzable component of the solution is altered by titration with a precipitating agent, while the current is observed at a constant applied voltage. Such titrations have been called polarometric titrations (*33*) to show their relationship to the polarographic method. [Kolthoff and Pan (*29*) have proposed the term "amperometric" to describe these titrations. As will be apparent from what is said below, their term fails to be specific, since it is also applicable to other unrelated methods in which current is measured.] Four main types are known at present and their respective titration curves are shown in Figure 13.

In *A*, the electroactive substance is removed from solution by precipitation with an inactive substance—e. g., lead titrated with sulfate ion (*30*, *34*, *51*). In *B*, to an inactive substance an electroactive precipitating agent is added—e. g., sulfate titrated with barium ion (*34*). In *C*, both the component of the solution and the precipitant are reducible at the given applied voltage—e. g., lead titrated with dichromate ion (*29*, *47*). The end points

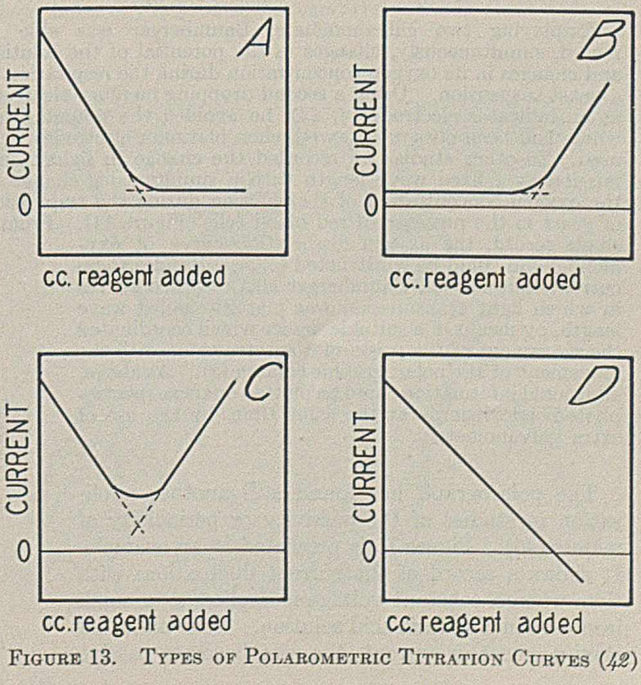


FIGURE 13. TYPES OF POLAROMETRIC TITRATION CURVES (*42*)

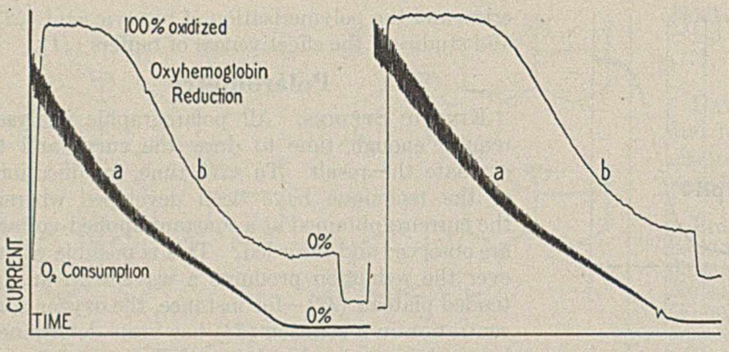


FIGURE 14. CHANGES DURING RESPIRATION OF YEAST IN RINGER'S SOLUTION (*3*)

In presence of glucose and defibrinated monkey blood.
a. Current-time curve obtained with dropping mercury electrode, showing consumption of oxygen
b. Current-time curve obtained with photocell and taken simultaneously with *a*, showing reduction of oxyhemoglobin accompanying change in oxygen consumption

of these titrations are usually obtained by extrapolation. Finally, in *D*, the titrating agent produces a reversal of current. This type of curve may be obtained either by an oxidative-reductive titration—e. g., titanium titrated with ferric ion (*53*)—or by precipitation of a polarographically determinable anion with a suitable cation—e. g., chloride titrated with silver ion (*42*). The end point in this case is reached when the current becomes zero (corrected for any residual current)—i. e., where the straight titration curve intersects the galvanometer zero line. These polarometric titrations are fast and accurate but have limitations similar to conductivity measurements.

Amperometry

Attention should also be called to some other, little known applications of the polarograph, in all of which it serves as a convenient device for the automatic recording of currents. These currents may be due to chemical reductions or oxidations as in polarography and polarometry, they may be created by the action of light on a photocell as in spectrophotometry or colorimetry, or they may be the sufficiently amplified very small currents flowing through vacuum tubes as used in potentiometry. Since current is measured in all of these studies, they can justly be grouped together as "amperometric". Examples of these techniques can be found in a paper by Baumberger (*3*).

Employing two galvanometers, Baumberger was able to record, simultaneously, changes in the potential of the solution and changes in its oxygen concentration during the respiration of a yeast suspension. Using a second dropping mercury electrode as an indicator electrode (*4*, *44*), he avoided the potential lag which had been always observed when platinum electrodes were used. In other studies he recorded the change in light transmission at a fixed wave length with a simultaneous change in the oxygen concentration of the solution during the respiration of yeast in the presence of red blood cells (Figure 14). From a single record, the oxygen dissociation curve of oxyhemoglobin could be constructed (*2*, *3*). Besides these current-time curves, Baumberger also recorded curves in which light transmission was plotted against wave length, by means of a suitable device which coordinated the movement of the prism of a spectrometer with the movement of the polarographic camera (*3*). As above, additional information could be plotted on these spectrophotometric records at the same time, by the use of extra galvanometers.

The polarograph has found still another application in studies of the passivity or periodicity of metals (*40*). Figure 15 is presented as an example. It shows a record of the current fluctuations with time when a constant voltage is applied to a small iron wire in a sulfuric acid solution. After an initial slow decrease in current, the wire becomes passive to be activated spontaneously at almost regular intervals.

Conclusion

It should be emphasized that this résumé of research with the polarograph necessarily had to be crowded and is therefore far from complete; the references given represent not even 10 per cent of the literature on this subject. It is hoped, however, that enough material has been incorporated in this paper to demonstrate the versatility of the polarograph and the general usefulness and limitations of polarography.

Literature Cited

(1) Adkins, H., and Cox, F. W., *J. Am. Chem. Soc.*, 60, 1151 (1938).
(2) Baumberger, J. P., *Am. J. Physiol.*, 123, 10 (1938).
(3) Baumberger, J. P., *Cold Spring Harbor Symposia Quant. Biol.*, 7, 195 (1939).
(4) Baumberger, J. P., and Skow, R. K., *Am. J. Physiol.*, 116, 8 (1936).
(5) Blinks, L. R., and Skow, R. K., *Proc. Natl. Acad. Sci.*, 24, 420 (1938).
(6) Borcherdt, G. T., and Adkins, H., *J. Am. Chem. Soc.*, 60, 3 (1938).
(7) Brdička, R., *Acta intern. Ver. Krebsbekämpfung, Louvain, Belg.*, 3, 13 (1938).
(8) Brdička, R., *Acta Radiol. Cancerol. Bohem. Morav.*, 2, 7 (1939).
(9) Brdička, R., *Collection Czechoslov. Chem. Commun.*, 5, 112 (1933).
(10) *Ibid.*, 5, 148 (1933).
(11) *Ibid.*, 5, 238 (1933).
(12) Brdička, R., *Nature*, 139, 330, 1020 (1937).
(13) Brdička, R., Novák, F. V., and Klumpar, J., *Acta Radiol. Cancerol. Bohem. Morav.*, 2, 27 (1939).
(14) Crossley, M. L., Kienle, R. H., Vassel, V., and Christopher, G. L., *J. Lab. Clin. Med.*, 26, 1500 (1941).
(15) Eisenbrand, J., and Picher, H., *Z. physiol. Chem.*, 260, 83 (1939).
(16) Hershberg, E. B., Wolfe, J. K., and Fieser, L. F., *J. Am. Chem. Soc.*, 62, 3516 (1940).
(17) Hershberg, E. B., Wolfe, J. K., and Fieser, L. F., *J. Biol. Chem.*, 140, 215 (1941).
(18) Heyrovský, J., *Collection Czechoslov. Chem. Commun.*, 11, 98, 667 (1939).
(19) Heyrovský, J., "Polarographie", in W. Böttger's "Physikalische Methoden der analytischen Chemie", Vols. II and III, Leipzig, Akademische Verlagsgesellschaft, 1936 and 1939.
(20) Heyrovský, J., and Ilkovič, D., *Collection Czechoslov. Chem. Commun.*, 7, 198 (1935).
(21) Heyrovský, J., and Klumpar, J., *Ibid.*, 10, 153 (1938).
(22) Heyrovský, J., and Shikata, M., *Rec. trav. chim.*, 44, 496 (1925).
(23) Heyrovský, J., and Smoleř, I., *Collection Czechoslov. Chem. Commun.*, 4, 521 (1932).
(24) Hohn, H., "Chemische Analysen mit dem Polarographen" in E. Zintl's "Anleitungen für die chemische Laboratoriumspraxis", Vol. III, Berlin, Julius Springer, 1937.
(25) Ilkovič, D., *Collection Czechoslov. Chem. Commun.*, 6, 498 (1934).
(26) Kodíček, E., and Wenig, K., *Nature*, 142, 35 (1938).
(27) Kolthoff, I. M., and Lingane, J. J., *Chem. Rev.*, 24, 1 (1939).

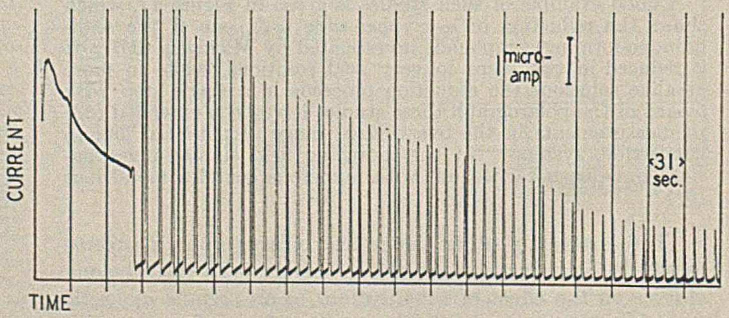


FIGURE 15. POLAROGRAPHIC CURRENT-TIME CURVE

Showing periodicity of a small iron wire in 1 *N* H_2SO_4 at constant applied voltage of $E_h = +0.50$ volt (*40*)

(28) Kolthoff, I. M., and Lingane, J. J., "Polarography", New York, Interscience Publishers, 1941.
(29) Kolthoff, I. M., and Pan, Y. D., *J. Am. Chem. Soc.*, 61, 3402 (1939).
(30) *Ibid.*, 62, 3332 (1940).
(31) Lingane, J. J., *Chem. Rev.*, 29, 1 (1941).
(32) Lingane, J. J., and Davis, O. L., *J. Biol. Chem.*, 137, 567 (1941).
(33) Majer, V., *Z. Elektrochem.*, 42, 120 (1936).
(34) *Ibid.*, 42, 123 (1936).
(35) Michaelis, L., *Chem. Rev.*, 16, 243 (1935).
(36) Müller, O. H., *Am. J. Physiol.*, 133, P393 (1941).
(37) Müller, O. H., *Ann. N. Y. Acad. Sci.*, 40, 91 (1940).
(38) Müller, O. H., *Chem. Rev.*, 24, 95 (1939).
(39) Müller, O. H., *Cold Spring Harbor Symposia Quant. Biol.*, 7, 59 (1939).
(40) Müller, O. H., *Collection Czechoslov. Chem. Commun.*, 6, 269 (1934).
(41) Müller, O. H., *J. Am. Chem. Soc.*, 62, 2434 (1940).
(42) Müller, O. H., *J. Chem. Education*, 18, 65, 111, 172, 227, 320 (1941). These papers have been combined in "The Polarographic Method of Analysis", No. 2 in the series of "Contributions to Chemical Education", Easton, Penna., *J. Chem. Education*, 1941.
(43) Müller, O. H., and Baumberger, J. P., *J. Am. Chem. Soc.*, 61, 590 (1939).
(44) Müller, O. H., and Baumberger, J. P., *Trans. Electrochem. Soc.*, 71, 169 (1937).
(45) *Ibid.*, 71, 181 (1937).
(46) Müller, O. H., and Phillips, R. A., *Am. J. Physiol.*, 129, P426 (1940).
(47) Neuberger, A., *Z. anal. Chem.*, 116, 1 (1939).
(48) Semerano, G., and Chisini, A., *Gazz. chim. ital.*, 63, 802 (1933).
(49) Shikata, M., and Tachi, I., *Collection Czechoslov. Chem. Commun.*, 10, 368 (1938).
(50) Smith, L. I., Kolthoff, I. M., Wawzonek, S., and Ruoff, P. M., *J. Am. Chem. Soc.*, 63, 1018 (1941).
(51) Spalenka, M., *Collection Czechoslov. Chem. Commun.*, 11, 146 (1939).
(52) Stackelberg, M. v., *Z. Elektrochem.*, 45, 466 (1939).
(53) Strubl, R., *Collection Czechoslov. Chem. Commun.*, 10, 475 (1938).
(54) Vítek, V., *Ibid.*, 7, 537 (1935).
(55) Waldschmidt-Leitz, E., and Mayer, K., *Z. physiol. Chem.*, 261, 1 (1939).
(56) Winkel, A., and Proske, G., *Ber.*, 69, 693, 1917 (1936).
(57) Winzler, R. J., *J. Cellular Comp. Physiol.*, 17, 263 (1941).
(58) Wolfe, J. K., Fieser, L. F., and Friedgood, H. B., *J. Am. Chem. Soc.*, 63, 582 (1941).
(59) Wolfe, J. K., Hershberg, E. B., and Fieser, L. F., *J. Biol. Chem.*, 136, 653 (1940).

PRESENTED before the Divisions of Agricultural and Food Chemistry, Biological Chemistry, and Medicinal Chemistry, Symposium on New Analytical Tools for Biological and Food Research, at the 102nd Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J.

Determination of the Aniline Point of Dark Petroleum Oils

BRUCE B. CARR AND M. S. AGRUSS, The Pure Oil Company, Chicago, Ill.

THE American Society for Testing Materials has defined aniline point (*1*) as the minimum equilibrium solution temperature for equal volumes of aniline and oil and has published a method for determining the aniline point by observing the temperature at which a 50/50 mixture of oil and aniline becomes turbid upon cooling. Since the use of the A. S. T. M. method is limited to oils of less than 8 A. S. T. M. color (*1*), the authors have developed a method for determining the aniline point of dark oils based on the visual observation of a thin film formed on the glass wall of the apparatus.

Previous investigators have observed the clouding of a thin film of aniline and oil and have made use of this principle to determine approximate aniline points. The method described by the Institution of Petroleum Technologists (*3*) suggests that the aniline point of dark oils can usually be determined with suitable illumination or by observation of the thin film of the mixture which is washed up on the sides of the tube during stirring. Donn (*2*) utilized the sharp break in the viscosity temperature curve to indicate the aniline point, but resorted to an approximate method for dark oils in which a drop of the hot solution was observed under a microscope. VanWijk and Boelhouwer (*5*) and Matteson, Zeitfuchs, and Eldredge (*4*) make use of the variation in transparency to infrared radiation.

Description of Apparatus

The apparatus shown in Figure 1 consists essentially of a double jacketed Pyrex test tube having a triple-junction copper-constantan thermocouple cemented to the inner wall of the tube. The aniline-oil mixture is stirred by swinging the apparatus back and forth over a small arc in such a manner that the contents run from one end of the tube to the other, alternately covering and exposing the thermocouple attached to the wall of the tube. This stirring action may be accomplished in a number of ways; the authors clamped the apparatus to a vertical arm which is pivoted at its lower end. The arm is moved back and forth about 25 times per minute by a slow-speed motor geared down to this speed. A small 7-watt light and shield are clamped on the arm to illuminate the film, and the apparatus is heated by a Bunsen burner which is also clamped on the oscillating arm. The temperature may be measured by any type of millivoltmeter or potentiometer which is calibrated to 0.1 millivolt in the range of 0 to 15 millivolts. An instrument calibrated to 0.01 millivolt should be used if greater than 0.5° F. accuracy is desired.

The inner tube (Figure 2) is 15 mm. in outside diameter and 125 mm. long (not including the standard-taper ground-glass joint which is sealed to the top of the tube to hold the glass stopper). The triple thermocouple junctions are brought into the tube through two small holes which are located about 90 mm. from the bottom of the tube. The junctions are separated to cover more of the tube surface and cemented in place with air-

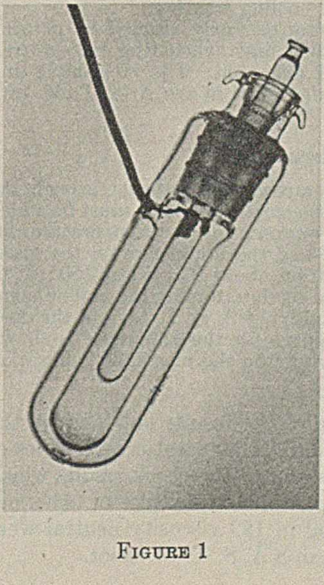


FIGURE 1

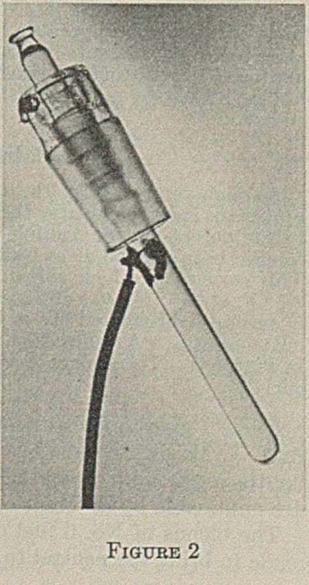


FIGURE 2

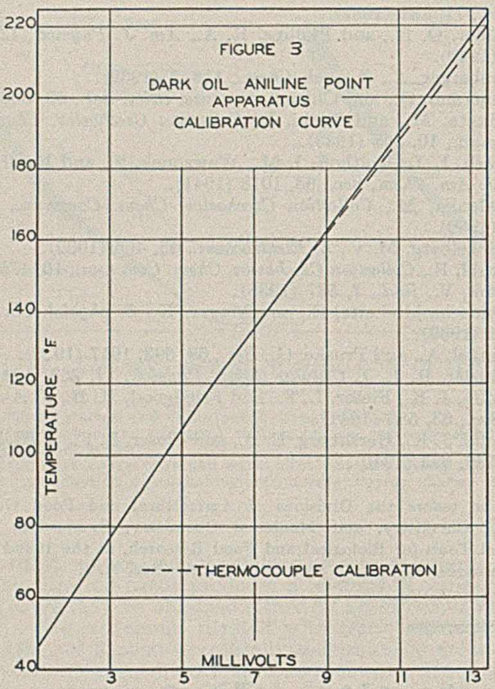


Figure 3

drying Insalute cement. The inner tube is supported in the jacket by means of a second ground-glass standard-taper joint.

The outer jacket is a double-walled tube 6 cm. in outside diameter and 19.5 cm. long, the inner surface of which is ground at the top to form half of the ground-glass joint which supports the inner tube. The jacket is vented near the top. A short section of glass tubing (not shown in the photograph) should be attached to the outer jacket just below the clamp to aid in blowing cold air through the jacket if this is necessary. A clamp is provided to hold the apparatus on the stirring mechanism.

Operation

Three cubic centimeters each of oil and aniline are pipetted into the inner test tube; the glass stopper is inserted and fastened by means of a rubber band. The apparatus is then clamped in a nearly horizontal position and the flame and stirring device are started. As the mixture is heated the inner tube should be vented at least every 50° F. The aniline point is taken as the temperature at which a cloudy film first appears on the glass wall surrounding the thermocouple junctions as the mixture is cooled from above its solution temperature. The rate of cooling should be controlled as specified in the A. S. T. M. procedure; however, when using a millivoltmeter, which may be read instantly, instead of a potentiometer the rate of cooling was found to have very little effect. The apparatus may be easily cleaned by pouring a suitable solvent into the tube and evacuating into a trap through a glass tube of small diameter. The oil sample and aniline should be prepared as described in the A. S. T. M. procedure.

Calibration

At high temperature, the temperature gradient through the apparatus becomes so large that a small correction must be added to the potentiometer reading, representing the temperature difference between the glass wall and the liquid film on the glass. This correction, which varies from about 0.5° F. at 150° F. to 2.5° F. at 215° F., was obtained by determining the aniline point of several light-colored oils in both the A. S. T. M. and the dark oil apparatus. A calibration curve for the apparatus is shown in Figure 3. The broken curve is the thermocouple calibration curve.

Table I gives a comparison of the results obtained by the A. S. T. M. method and the dark oil apparatus on a series of light-colored samples, and also shows the check results which are obtainable by different operators on samples of black oil.

The blends of No. 6 fuel oil in 180 viscosity neutral were made to bring the neutral to an 8 A. S. T. M. color.

Precision

The precision of this test is limited mainly by the precision with which the potentiometer can be read, since the potentiometer reading at which the film around the thermocouple becomes cloudy is highly reproducible. Duplicate determinations by different operators check within 0.5° F. The accuracy of the test depends largely on the thermocouple calibrations or the overall calibrations of the apparatus. The authors used constant-temperature (±0.025° F.) viscosity baths to ensure accurate calibrations; however, a periodic check should be made on the calibration. If the apparatus is carefully calibrated and corrected as shown in Figure 3 an accuracy of ±0.5° F. should be easily attainable.

Table I. Comparative Results

Material	A. S. T. M. Aniline Point ° F.	Dark Oil Method ° F.
Kerosene	120	120.3
Kerosene	161	161.2
Kerosene distillate	168	168.0
Kerosene distillate	159	158.7
Cracked gasoline	97	97.0
No. 3 furnace oil	150	149.5
85 viscosity neutral	203	203.0
180 viscosity neutral	216	216.3
Blend fuel oil in neutral	209	209.2
Blend fuel oil in neutral	212	212.0
No. 6 fuel oil (black), operator 1	...	168.7
No. 6 fuel oil (black), operator 2	...	168.8
Still bottoms (black)	...	150.4
Black oil	...	146.0
700 E. P. gas oil (8 plus N. P. A. color)	...	118.0
20 gravity bottoms (Sweet Lake crude—black)		
Operator 1	...	221.0
Operator 2	...	221.2
Operator 3	...	221.3
28 gravity topped crude (Roscommon crude—black)		
Operator 1	...	178.6
Operator 2	...	178.7
Operator 3	...	178.2

Discussion

The simplicity in design and construction of the apparatus makes it available at very little cost to any laboratory which is equipped with the necessary millivoltmeter or potentiometer. In ease of operation and time consumed the method is comparable with the proposed A. S. T. M. method for light-colored samples. The method is applicable to black stocks such as No. 6 fuel oil and most still bottoms; however, in the case of heavy tars the film may not be translucent even after 50 per cent dilution with aniline. If the solution temperature is below room temperature the aniline point may be determined by blowing cold dry air through the outer jacket, or by a method (*4*) involving the use of a standard diluent having an aniline point around 140° F. The aniline point of a 50/50 per cent by volume mixture of sample and diluent is determined, the aniline point of the sample then being obtained from a curve showing the relation between aniline points of oils and oil diluent blends. The aniline point of very black samples could presumably be determined in the same manner.

Literature Cited

(1) Am. Soc. Testing Materials, "Standards on Petroleum Products and Lubricants", Appendix 2, p. 14, Sept. 1940.
(2) Donn, Leon, Ind. Eng. Chem., Anal. Ed., 9, 202 (1937).
(3) Inst. Petroleum Tech., "Standard Methods for Testing Petroleum and Its Products", 3rd ed., Serial Designation F. O. 23, 1935.
(4) Matteson, Robert, Zeitfuchs, E. H., and Eldredge, K. R., Ind. Eng. Chem., Anal. Ed., 13, 394 (1941).
(5) VanWijk, W. R., and Boelhouwer, J. W. M., *J. Inst. Petroleum Tech.*, 24, 598 (1938).

Presented before the Division of Petroleum Chemistry at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J.

Determination of Free Sulfur in Lubricating Oil

HARRY LEVIN AND ERVIN STEHR, The Texas Company, Beacon, N. Y.

THE increasing use of sulfurized fatty and mineral oils in lubricating oil has made important a method for determining free sulfur in such products.

In the sulfurization of fatty and mineral oils by direct reaction with elementary sulfur at elevated temperatures, control of the final free sulfur content is important because for some products, such as certain cutting and extreme pressure oils, a relatively high free sulfur content is desired, whereas for others, such as automotive oils, complete absence of free sulfur is commonly required. In those cases where presence of free sulfur has been considered desirable, the benefits have been variously attributed to cooling effect, increasing film strength, and antiwelding properties.

Various means have been used to determine sulfur in related products. Garner and Evans (*2*) describe a method for determining free sulfur in gasoline, involving refluxing the fuel with copper-bronze powder, solution of the metal and its sulfides in bromine water, oxidation to sulfate, and final recovery of the sulfur as barium sulfate. These authors also review the considerable previously published literature on what has been variously called free sulfur, active sulfur, corrosive sulfur, and loosely bound sulfur in gasoline and other light petroleum products. These generally involve the following steps:

> Fixation of the sulfur as metallic sulfide by heating or agitating with a metal, usually sodium, mercury, copper, or an alloy.
>
> Either determination of the increase in weight of the metal (calculated to sulfur), oxidation of the sulfide and final weighing of barium sulfate, or conversion of the sulfur to thiosulfate or hydrogen sulfide and its determination iodometrically.

An adaptation of the doctor test (alkaline plumbite solution) has been applied by Wirth and Strong (*5*), and Comay (*1*) has reduced the free sulfur of light petroleum distillates directly with nascent hydrogen.

Very little literature exists on the determination of free sulfur in heavier petroleum products such as lubricating oil. Sivertsev and Meerzon (*4*) shake the sample of oil with mercury, filter, treat the sulfide with hydrochloric acid and use hydrogen to sweep the hydrogen sulfide into cadmium chloride solution, filter the cadmium sulfide, and complete the determination iodometrically. Garner describes the difficulties of filtering the sulfides of mercury, particularly when free sulfur is high. Another disadvantage to the use of mercury is the lack of ready evidence of completion of sulfur removal. A purchaser's specification has been encountered which contains a method for active sulfur based on digesting the oil with copper powder at 149° C., filtering to remove copper and its sulfides, and determining total sulfur (bomb method) in the oil before and after this treatment. The present authors' experiments have shown that this treatment may cause a reduction of several per cent in the sulfur content of an oil though it actually contains no free sulfur.

Hardman and Barbehenn (*3*) determine free sulfur in rubber by extracting the sample with boiling acetone in the presence of copper, liberating hydrogen sulfide from the metallic sulfide by digesting with concentrated hydrochloric acid, and absorbing the hydrogen sulfide in ammoniacal cadmium chloride where it is determined iodometrically after acidification. This method is in many respects similar to some that had been applied to gasoline and discussed by Garner and Evans. Hardman and Barbehenn discuss previously published methods for determining free sulfur in rubber and most of these indicate a similarity to the problem as applied to gasoline.

Of the various methods to which reference is made, the principle of that employed by Hardman and Barbehenn for rubber seemed, and subsequently proved, most promising for free sulfur in oil. Their solvent had to be modified to ensure complete solution of oil samples and the apparatus and technique modified to ensure complete recovery of the large amount of free sulfur found in some products. Loss of sulfide had been reported by others (*2*) working with somewhat related methods on gasoline.

The following detailed method has proved satisfactory for determining free sulfur in pure petroleum lubricating oils, in such oils blended with fatty oils or sulfurized fatty or unsaponifiable oils, as well as in sulfurized fatty or sulfurized unsaponifiable oils themselves.

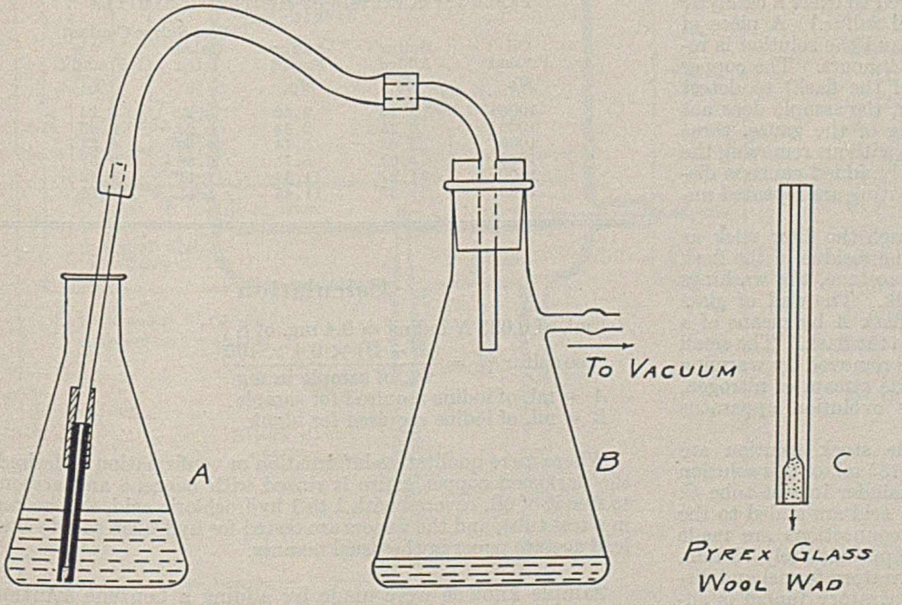


FIGURE 1. APPARATUS FOR REMOVING SOLVENT

Apparatus

Apparatus for removing solvent is shown in Figure 1. The filter stick, *C*, shown in place in *A*, is 70 to 80 mm. long and 2 mm. in bore, expanded to 6 mm. for a distance of 10 mm., the enlarged head being packed with fine glass wool.

Apparatus for liberating and determining hydrogen sulfide (Figure 2) includes a buret provided with rubber stopper at the bottom for tight fit in neck of flask *B*.

Reagents

Copper gauze, 40-mesh, cut into pieces 2.5 cm. (1 inch) square and folded double. These strips are reduced by heating in a flame to redness and promptly dropping into a test tube containing methyl alcohol. The strips, after rinsing with acetone, are stored under benzene until used.

Cadmium chloride stock solution, 36 grams of $CdCl_2.2^1/_2H_2O$ dissolved in 300 ml. of water, to which a mixture of 800

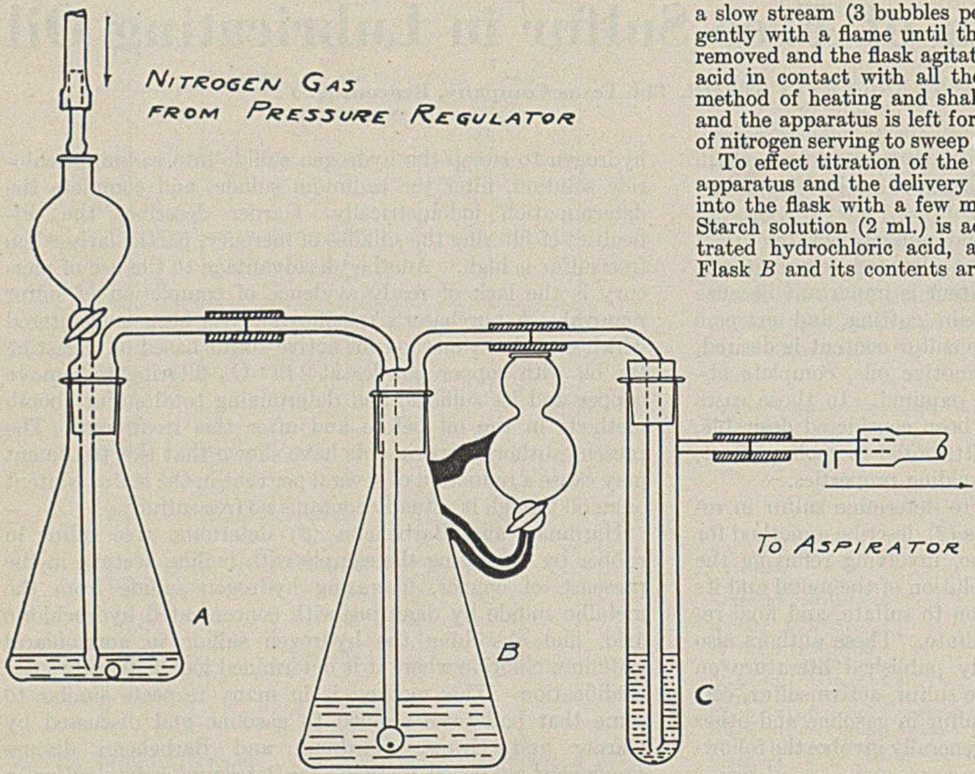


Figure 2. Apparatus for Liberating and Determining Hydrogen Sulfide

A. 300-cc. Erlenmeyer flask equipped with 60-cc. separatory funnel through ground-glass stopper
B. Special flask (ground-glass joint) for absorption and titration. Attached 25-cc. separatory funnel is joined at its lower end to flask by 2-mm. (inside diameter) glass tubing
C. Test tube (trap)

ml. of water and 1200 ml. of concentrated ammonium hydroxide is added.

Standard iodine solution, 0.025 *N;* 1 per cent aqueous starch solution; nitrogen (low purity); acetone, c. p., free of uncombined sulfur; and benzene, c. p., free of uncombined sulfur.

Procedure

The sample is weighed into a 300-cc. flask (*A*, Figure 1), the amount taken depending upon the free sulfur content; 1 gram is usually satisfactory. Fifty milliliters of c. p. benzene are added, with agitation to dissolve the sample, and 100 ml. of c. p. acetone are added. (The use of acetone, employed by Hardman and Barbehenn, was retained because it appeared to exert a catalytic effect in the reaction between copper and sulfur.) A piece of prepared copper gauze is put in the flask and the solution is refluxed under a water-cooled condenser for 2 hours. The copper is then inspected (through the bottom of the flask) to detect discoloration. If there is no discoloration, the sample does not contain free sulfur. If there is darkening of the gauze, three additional clean pieces of gauze are added (without removing the first) and heating is repeated. If the newly added gauze is discolored, the addition of fresh gauze and heating are repeated until newly added copper is not discolored.

The liquid in the flask is removed through the filter stick as illustrated in Figure 1, and discarded. The residue in the flask is washed successively with benzene and acetone, the washings being removed through the same filter stick. The wad of glass wool is pushed from the filter stick into flask *A* by means of a stiff iron wire and the filter stick is added to the flask. The small amount of solvent adhering to the flask is removed by warming on a steam bath while introducing a gentle stream of nitrogen, and the flask is then connected to the evolution apparatus (Figure 2, *A*).

Thirty milliliters of cadmium chloride stock solution are diluted with distilled water to 160 ml. and 135 ml. of this solution are placed in flask *B* (Figure 2), the remainder in test tube *C*. After 30 ml. of concentrated hydrochloric acid are added to the separatory funnel over flask *A* and all connections are made secure, nitrogen gas under low pressure (approximately 75 mm. of mercury) is allowed to pass into the separatory funnel and displace the acid. The stopcock of this separatory funnel is adjusted so that the gas continues to pass through the apparatus in a slow stream (3 bubbles per second). Flask *A* is then heated gently with a flame until the acid begins to boil. The flame is removed and the flask agitated for about 0.5 minute to bring the acid in contact with all the copper sulfide in the flask. This method of heating and shaking is repeated three or four times and the apparatus is left for 10 minutes, the continuous passage of nitrogen serving to sweep out the hydrogen sulfide.

To effect titration of the sulfide, flask *B* is removed from the apparatus and the delivery tube, attached to its neck, is rinsed into the flask with a few milliliters of dilute hydrochloric acid. Starch solution (2 ml.) is added, followed by 30 ml. of concentrated hydrochloric acid, and the flask is quickly stoppered. Flask *B* and its contents are cooled by tap water, the stopcock of the attached separatory funnel being opened momentarily to equalize pressure, and 20 ml. of dilute cadmium chloride solution (stock solution diluted with one volume of water) are added to the separatory funnel. The stopper on flask *B* is removed and a buret, with a rubber stopper attached to its tip, is promptly inserted to make a tight connection at the neck of the flask. The stopcock of the separatory funnel is then opened and standard iodine solution is added from the buret while the flask is agitated. The gas displaced by the iodine solution passes through the separatory funnel where hydrogen sulfide is trapped.

When the solution in the flask turns blue, the addition of iodine is discontinued and the stopper attached to the buret is loosened to permit the solution from the separatory funnel to enter the flask; the additional liberation of hydrogen sulfide commonly discharges the blue color. The stopper of the buret is again tightly inserted into the flask and the solution in test tube *C* is introduced into the separatory funnel of flask *B*. The titration is continued to the blue end point and the separatory funnel is drained as before. Finally the test tube is rinsed with dilute hydrochloric acid and water, the rinsings are added to flask *B* through the separatory funnel, and iodine reagent is added dropwise to the usual blue end point.

A blank test is run on the reagents and its titer is subtracted from that of the sample.

Table I. Analysis of Synthetic Samples

Oil Present	Sulfur Added	Sulfur Found	Free Sulfur Content Calculated	Free Sulfur Content Found
Mg.	*Mg.*	*Mg.*	%	%
1000	2.25	2.40	0.22	0.24
1000	2.25	2.35	0.22	0.23
1000	5.63	5.74	0.56	0.57
1000	5.63	5.71	0.56	0.57
1000	11.27	11.34	1.11	1.12
1000	11.27	11.45	1.11	1.13

Calculation

1 ml. of 0.025 N iodine $\Bumpeq$ 0.4 mg. of S

$$\text{Free sulfur }\% = \frac{(A - B) \times 0.4 \times 100}{\text{wt. of sample in mg.}}$$

A = ml. of iodine required for sample
B = ml. of iodine required for blank

Where mere qualitative information or confirmation is desired, the darkened copper gauze is rinsed with benzene and acetone to free it of oil, covered with 1 to 1 hydrochloric acid, and heated in a test tube, and the vapors are tested for hydrogen sulfide with lead acetate paper in the usual manner.

Sample knowns were made by adding a benzene solution of elementary sulfur to 1 gram of oil known to be free of un-

Table II. Analyses of Commercial Products

Sample	Total Sulfur (Bomb Method) %	Free Sulfur (Proposed Method) %
Topped Mexican crude[a]	4.0	0.00
Venezuela crude[a]	2.0	0.00
Special naphthenic Diesel lubricating oil SAE 30[a]	2.18	0.00
Special naphthenic Diesel lubricating oil SAE 40[a]	1.90	0.00
Special naphthenic motor oil[a]	2.42	0.00
Special cutting oil A	3.08	0.97–1.01
Special cutting oil B	2.06	1.09–1.11
Sulfurized gear oil A	1.30	0.56–0.58
Sulfurized gear oil B	2.25	1.27–1.33
Sulfurized mineral oil	1.03	0.52–0.56
Sulfurized fatty oil	10.01	0.00

[a] These products are possessed of their high total sulfur content, naturally.

combined sulfur. The results of typical analyses are given in Table I.

A variety of commercial petroleum products of relatively high total sulfur content were analyzed and consistent results for free sulfur obtained. Typical of these are the results in Table II.

The method has been used for over two years and proved suitable for routine testing. As little as 0.001 per cent of free sulfur has been determined with it. Investigation of the utility of the method for oils containing added soaps, halogenated materials, etc., has not been completed. However, tests made with mineral oils containing either 5 per cent of lead naphthenate, 5 per cent of lead linoleate, unsaturated acids (5 per cent oleic acid), unsaturated hydrocarbons (30 per cent pine oil), or large amounts of oxidized oils from engine tests or laboratory oxidation tests (contain peroxides) showed no significant interference by these substances.

Acknowledgment

The authors acknowledge their appreciation of the assistance of F. C. Gast, L. Donn, and Karl Uhrig in the development and testing of this method.

Literature Cited

(1) Comay, S., Ind. Eng. Chem., Anal. Ed., 8, 460 (1936).
(2) Garner, F. H., and Evans, E. B., *J. Inst. Petroleum Tech.*, 71, 451 (1931).
(3) Hardman, A. F., and Barbehenn, H. E., Ind. Eng. Chem., Anal. Ed., 7, 103 (1935).
(4) Sivertsev, A. P., and Meerzon, E. A., *Zavodskaya Lab.*, 9, 528 (1940).
(5) Wirth, C., and Strong, J. R., Ind. Eng. Chem., Anal. Ed., 8, 344 (1936).

Presented before the Division of Petroleum Chemistry at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J.

Mercury Cathode Method for Determining Small Amounts of Titanium and Similar Metals in Alloys

M. H. STEINMETZ
Schenectady Works Laboratory, General Electric Company,
Schenectady, N. Y.

THE mercury cathode method of analysis as described by Lundell, Hoffman, and Bright (*1*, *2*) has been used in this laboratory for many years. When using an average size cell and charge (0.5 gram) it takes overnight (14 hours) before all the amalgam-forming elements are deposited in the mercury.

To shorten time, when only small amounts or traces of titanium, aluminum, magnesium, or vanadium are present, a larger cell (Figure 1) has been used whereby a larger charge (5.0 gram) may be used and time shortened to 5 hours. For the larger cell, 2 to 3 amperes and 10 volts are used, as contrasted with the smaller cell using 1 ampere and 5 volts. In some cases where amounts of titanium, etc., are very small, two or three 5-gram charges are run through the cell, the electrolyzed solutions are combined, and analysis is carried out by usual methods.

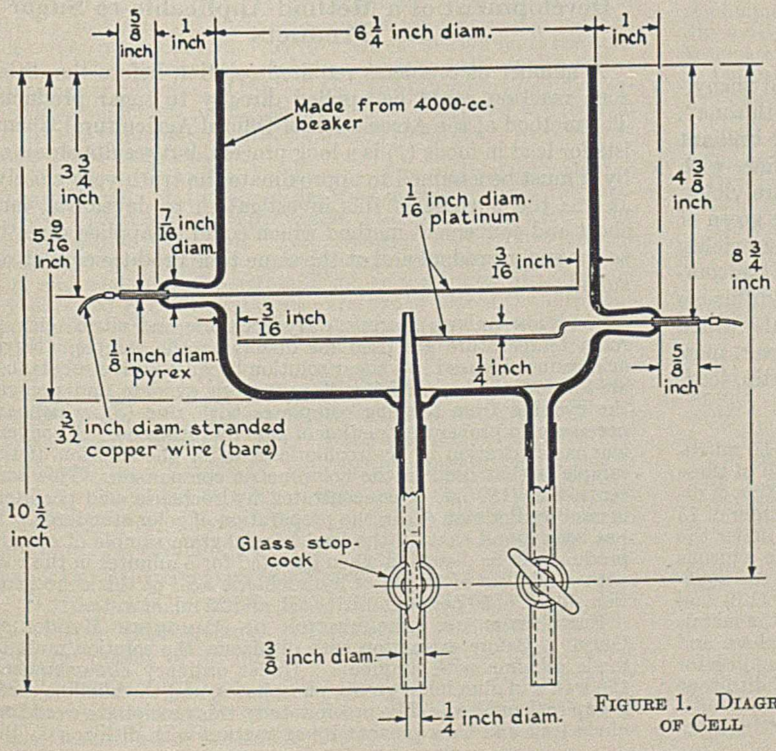


Figure 1. Diagram of Cell

Literature Cited

(1) Lundell, G. E. F., and Hoffman, J. I., "Outlines of Methods of Chemical Analysis", p. 94, New York, John Wiley & Sons, 1938.
(2) Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., "Chemical Analysis of Iron and Steel", p. 47, New York, John Wiley & Sons, 1931.

Determination of Lead in Sugars and Sugar Products

An Adaptation of the Diphenylthiocarbazone Reaction

THOS. D. GRAY[1], Western Sugar Refinery, San Francisco, Calif.

A VERY short and convenient dithizone method for the determination of lead in sugars and sugar products has been developed. This is accomplished without ashing the sugar product, without the use of a centrifuge for separating the aqueous and chloroform layers, and without the use of a shaking machine for dissolving and extracting samples. Only one concentration of dithizone is necessary for the whole procedure, including final colorimetric comparison and qualitative tests on water and reagents.

With the exception of lead nitrate, which should be recrystallized prior to use in preparation of standard lead solution, the reagents, including Eastman Kodak Company reagent grade dithizone, need no purification, as the blank is sufficiently low for ordinary testing. For analytical research, however, dithizone and other reagents may be purified according to methods of the Association of Official Agricultural Chemists (*1*, *2*).

The simple, inexpensive equipment required consists of a few burets, separatory funnels, Nessler tubes, Pyrex flasks and bottles, a vacuum pipet for taking aliquots of chloroform solutions, and a Pyrex still for making lead-free water.

A discussion of the theory of the diphenylthiocarbazone reaction and its application, as well as a detailed description of the procedure, is presented in this paper.

Many discussions of the dithizone reaction may be found in the literature. Particularly interesting are those relating to the examination of pharmaceutical chemicals (*6*), biological materials (*5*), soils (*7*), maple sirup (*8*), and foods (*1*); to experimental methods used in the study of the role of heavy metals in plant nutrition (*10*); and to a method used in delicate control of lead in cancer research (*9*).

Diphenylthiocarbazone Reaction

Diphenylthiocarbazone is phenylazothioformic acid phenylhydrazide, abbreviated in the literature to "dithizone". This highly colored organic compound produces a brilliant green color when dissolved in chloroform and combines with twelve or more metals, forming complexes which are violet, yellow, or red. These colors, when mixed with the green of uncombined dithizone, are changed to shades of green, violet, blue, and red, depending upon the concentration of the complexes formed and the concentration of the unused dithizone in the chloroform solution. The principal metals which form these complexes with dithizone are copper, silver, mercury, gold, zinc, cobalt, nickel, cadmium, stannous tin, lead, bismuth, and thallium.

Suppose a dilute solution (50 to 100 ml., containing 50 micrograms or less) of the chlorides or nitrates of any or all of these metals is placed in a separatory funnel and a dilute solution of dithizone in chloroform (10 ml. of a concentration of the order of 15 mg. per liter) is added. Dithizone is not specific, but under the proper conditions of hydrogen-ion concentration in the aqueous phase, these metals may be separated into groups. If the aqueous phase is made alkaline with ammonia (pH 8.0 to 11.0) and the separatory funnel is shaken vigorously, a group of the metals will pass from the aqueous phase to the chloroform phase and form colored complexes with the dithizone. After standing for a few minutes, the layers will separate and the colored dithizone layer can be drawn off into a suitable vessel. If another portion of the dithizone is added and the separatory funnel is shaken again, more metals are extracted, but this extract does not contain as high a proportion of colored complexes as the first. This process of extractive enrichment may be repeated until the dithizone layer remains pure green, an indication that all the metals which form complexes at that pH have been extracted.

If, in addition to making the aqueous phase alkaline (pH 8.0 to 11.0), we add potassium cyanide, complexes of all the metals of the alkaline group except lead, stannous tin, bismuth, and thallium will be formed with the potassium cyanide. These complexes will not react with dithizone. If the solution is then subjected to extractive enrichment with dithizone, the combined extracts will contain only lead, stannous tin, bismuth, and thallium.

The acid solution of these metals can be adjusted to the optimum pH at which bismuth and stannous tin react with dithizone and the dithizone extraction repeated for their removal. The remaining metals in the group are thallium and lead. Thallium is rare and its presence in ordinary work is unlikely (*3*). The solution containing lead can then be readjusted to pH 8.0 to 11.0, potassium cyanide added, and the lead isolated as a dithizone complex by extractive enrichment, as before.

The lead in the combined dithizone extracts is transferred to dilute acid of definite volume and concentration by shaking in a separatory funnel. The dithizone is drawn off and discarded. The acid-aqueous layer is adjusted to a definite hydrogen-ion concentration and is a mixture of ammonia, citric acid, and potassium cyanide of definite volume and concentration added for the purpose of forming fixation or competitive complexes, as before. Dithizone of a definite volume and concentration is then added, the mixture is shaken vigorously, and the dithizone is drawn off into a Nessler tube. A set of standards is prepared by using the technique described above, with known quantities of a standard lead solution. The standards are arranged in order in Nessler tubes and the lead content of the unknown is determined by matching its color with a standard.

Development of a Method Applicable to Sugar Products

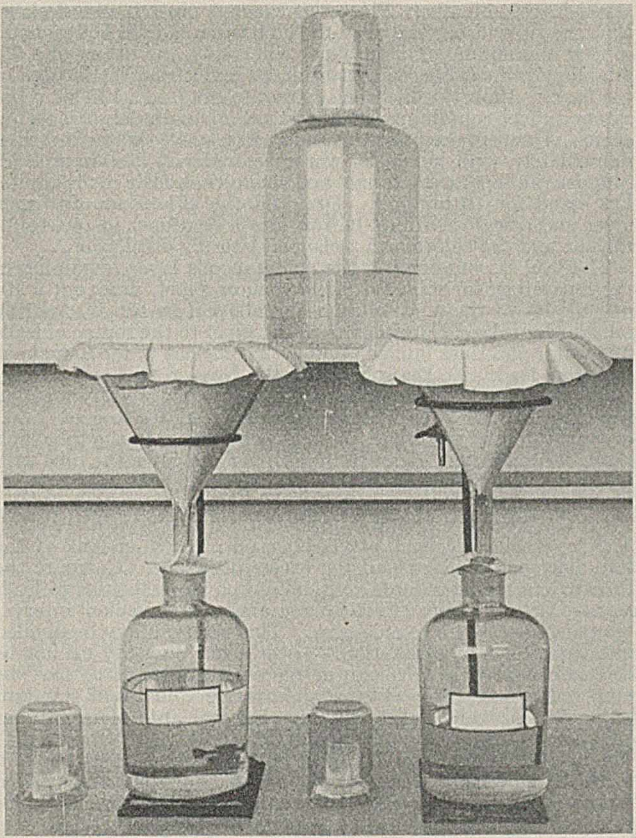
A number of problems required solution before the dithizone reaction could be applied directly to sugar products. The method of the Association of Official Agricultural Chemists for lead in foods (*1*) is a long process, but results obtained by it must be assumed to approximate the truth very closely. It was the purpose of this investigation to develop a very short and convenient method which could be applied directly to the sugar product and at the same time produce correct results.

SOLUTION OF THE SAMPLE. Hydrochloric and citric acids at room temperature are used for dissolving the sample. Nitric acid cannot be used in a sugar solution because active substances are formed which combine with potassium cyanide and prevent the cyanide from forming complexes with zinc (*8*), which are necessary to prevent extraction of zinc by dithizone. A convenient concentration of hydrochloric acid for the solution of the sample is that used in the colorimetric comparison. This concentration (180 ml. of concentrated hydrochloric acid per liter) is used by Perlman (*8*) in the preparation of color standards. It has been found that all the lead in a 10-gram sample of a sugar product will be dissolved when agitated for 5 minutes in the cold with a mixture of 15 ml. of hydrochloric acid of this concentration, 10 ml. of 50 per cent citric acid, and 25 ml. of water.

PREVENTION OF PRECIPITATION OF AMMONIUM HYDROXIDE GROUP. Before extraction with dithizone, the solution must be made alkaline with ammonia. Under ordinary circumstances, the iron and aluminum group, phosphates, and the alkaline earth group (calcium) would be precipitated; this precipitate would occlude lead and thus prevent its extraction with dithizone. Be-

---

[1] Present address, 1248 Capuchino Ave., Burlingame, Calif.



Equipment for Preparation of Lead-Free Water

cause dithizone reacts only with metals in solution, the solution must be perfectly clear after it is made alkaline with ammonia. The 10 ml. of citric acid added with the hydrochloric acid for the solution of the substance accomplishes this.

Optimum pH. The optimum pH for dithizone extraction of lead from a sugar solution was found to be 9.5.

Ammonium Hydroxide Required for pH Adjustment. From 10 to 13 ml. of concentrated ammonium hydroxide are required for pH adjustment, depending upon the concentrations of the hydrochloric and citric acids and of the ammonium hydroxide. The presence of the 5- to 10- gram sample normally has little effect. The concentrations of the acids approximate the values given under "Solution of the Sample" and the ammonium hydroxide loses ammonia upon standing. The amount of ammonium hydroxide required for adjusting the pH to 9.5 must, therefore, be determined periodically.

Potassium Cyanide Required. For normal samples of sugar products, in the quantities used in this analysis, the presence of 1 gram of potassium cyanide is sufficient for the formation of competitive complexes. These complexes are formed with all the metals of the alkaline group except lead, bismuth, stannous tin, and thallium. Therefore, 5 ml. of a solution of potassium cyanide (20 grams per 100 ml.) are added before the dithizone extraction. The extract can contain only lead, bismuth, stannous tin, and thallium.

Bismuth, Stannous Tin, and Thallium. Tests made on sugar products by the method of the Association of Official Agricultural Chemists (*4*) show the absence of bismuth and stannous tin. Stannic tin is present in minute quantities in sugar products but it will not react with dithizone under the conditions given above. Thallium is rare and its presence in ordinary work is unlikely (*3*). Under the conditions outlined, the dithizone extract will contain lead only.

Dithizone Concentration and Volume. When employing the usual technique for extracting a solute from a solution by means of an immiscible solvent, a partition of the solute between the two solvents nearly always exists and this makes it necessary to extract the solution many times with small quantities of the immiscible solvent to make the separation complete (*7*). This process is called "extractive enrichment". The chloroform layer settles out perfectly after each successive extraction when there is no sugar present in the aqueous layer. When sugar is present, and the solution has been agitated with a small volume of dithizone, the use of a centrifuge is necessary for breaking up the emulsion and separating the layers. It often requires 30 minutes' centrifuging to accomplish this. Extractive enrichment under these conditions would be very impractical, if not impossible. The problem becomes one of completely extracting the lead from a sugar solution under any conditions.

A technique has been devised in which this is accomplished with a single dithizone extraction and without the use of a centrifuge for separating the aqueous and chloroform layers. A large volume of dilute dithizone is used to extract a small quantity of lead from a comparatively small volume of solution; 15 micrograms or less of lead, in the presence of 10 grams of sugar in 75 ml. of solution, under the proper conditions of hydrogen-ion concentration, etc., will be completely extracted when shaken with 125 ml. of a chloroform solution of dithizone of a concentration of 7.5 mg. per liter.

Separation of Aqueous and Chloroform Layers. The extraction is made in a 500-ml. volumetric flask. The layers separate upon standing for 10 minutes. Centrifuging is not necessary.

Taking an Aliquot from the Chloroform-Dithizone Layer. A 75-ml. aliquot is taken from the dithizone layer on the bottom of the flask by connecting the pipet to a source of vacuum. The vacuum pipet is described in detail below.

Preparation of Reagents

Lead-Free Water. Redistill ordinary distilled water in an all-Pyrex glass still, or dissolve 4 grams of disodium phosphate in 12 liters of ordinary distilled water in a large Pyrex bottle, add 4 grams of calcium carbonate, and stir thoroughly. Let it settle overnight, and filter into 4-liter bottles with standard taper stoppers. The filter papers should be perfectly clean and about 45 cm. (15 inches) in diameter, and should cover the funnels. Test each bottle of prepared water for lead.

The author is indebted to P. R. Stout of the University of California for this method of preparing lead-free water.

Hydrochloric Acid Reagent. To 180 ml. of hydrochloric acid in a liter flask, add 300 to 400 ml. of lead-free water, cool to room temperature, and make up to 1 liter with lead-free water.

Citric Acid Reagent. Heat 500 grams of citric acid in a minimum quantity of lead-free water in a beaker. After it has dissolved, cool and make up to 1 liter with lead-free water in a volumetric flask.

Ammonium Hydroxide Reagent, concentrated ammonium hydroxide, 28 per cent.

Potassium Cyanide Reagent. Dissolve 100 grams of potassium cyanide in lead-free water and make up to 500 ml. in a volumetric flask.

Dithizone Reagent. Dissolve 7.5 mg. of diphenylthiocarbazone in 1 liter of chloroform.

Ammonia-Cyanide-Citrate Reagent. Dissolve 10 grams of citric acid in lead-free water, add 500 ml. of ammonium hydroxide, dissolve 20 grams of potassium cyanide in lead-free water, and add it to the ammoniacal solution in a volumetric flask. Make up to 1 liter with lead-free water.

Lead Nitrate Stock Solution. Recrystallize from 5 to 10 grams of lead nitrate by evaporating an aqueous solution on the water bath. Filter and dry the crystals at 100° to constant weight. Preserve the product in a small, tightly capped reagent bottle. Weigh very accurately 3.197 grams of the purified salt, dissolve it in dilute nitric acid (0.1 to 1.0 per cent), and make up to 1 liter with lead-free water in an accurately calibrated volumetric flask; 1 ml. of this solution will contain 0.002 gram of lead.

Standard Lead Solution. Using accurately calibrated volumetric equipment, dilute 1.5 ml. of lead nitrate stock solution to 2000 ml. with hydrochloric acid reagent; 1 ml. of this solution will contain 1.5 micrograms of lead. This solution is used in the preparation of color standards.

Apparatus Required

The vacuum pipet consists simply of a convenient means of making and breaking connection between a vacuum line and a pipet, and of making and breaking connection between a source of lead-free water and the pipet. The connections must be made of material which will cause no lead contamination in the pipet, as shown by a negative test for lead made on water which has passed through the connections and the pipet. By means of suitable clamps, two pipets, 75-ml. and 10-ml., are held rigidly in place at the proper distance above a sink to allow 500-ml. volumetric flasks and 125-ml. separatory funnels to be held under the tips.

Volumetric flasks, 500 ml., are required. The 500-ml. graduation marks are not used in the lead determinations. The neck of each flask must be of such length that the tip of a 75-ml. pipet will be 3 to 4 mm. from the bottom of the flask when taking an aliquot from the chloroform layer.

Separatory funnels, Nessler tubes, an all-Pyrex glass still, Pyrex bottles (one 12-liter and several of 4-liter capacity), and two or more 25 cm. (10-inch) glass funnels are also used. The Pyrex bottles and funnels are used in the preparation of lead-free water when an all-Pyrex glass still is not available.

Isolation and Determination of Lead

Weigh 5.5 to 10.0 grams of the sugar product in a 50-ml. Pyrex beaker, and measure 25 ml. of lead-free water into another 50-ml. beaker from a buret of large capacity. By transferring water portionwise from this beaker to the one containing the sample, wash the sugar or sirup into a 500-ml. Pyrex volumetric flask, and add 15 ml. of hydrochloric acid reagent and 10 ml. of citric acid reagent, accurately measured from burets. Rotate the flask for 5 minutes, and add the quantity of concentrated ammonium hydroxide (28 per cent) necessary for adjusting the pH to 9.5, determined periodically as described later.

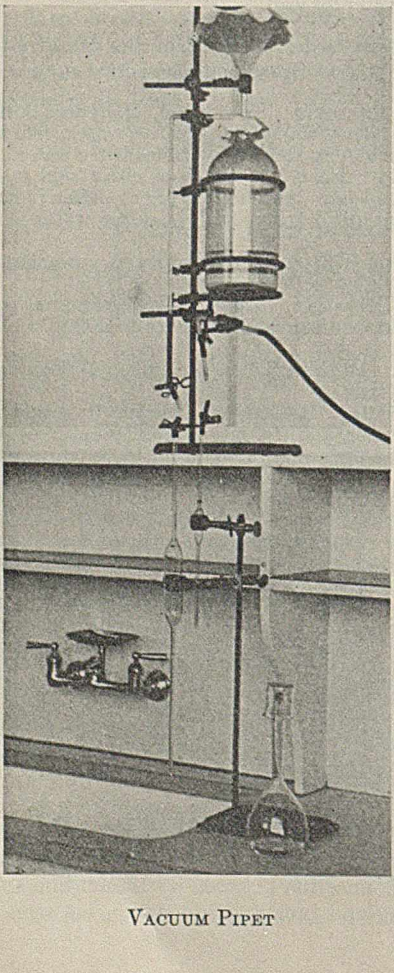
Place the flask in a cooling bath and allow it to remain for 5 minutes, agitating the contents occasionally while cooling. Remove it from the bath and add immediately 5 ml. of potassium cyanide solution and 125 ml. of dithizone. Without stoppering the flask, agitate the contents vigorously for 2 minutes, and let it stand for 10 minutes. Place the vacuum pipet in the flask so that the tip will be very close to the bottom, adjust the vacuum so that a minimum of disturbance will result, and draw out a 75-ml. aliquot of the chloroform-dithizone layer from the bottom of the flask. Allow the dithizone extract to run into a 125-ml. separatory funnel containing exactly 11 ml. of hydrochloric acid reagent. Connect the pipet to a source of lead-free water and rinse immediately with sufficient water to make it free from lead. Stopper the separatory funnel and shake vigorously for 1 minute. Let stand for 10 minutes. Draw off the chloroform-dithizone layer and discard; it may be run into a container for waste dithizone and the chloroform reclaimed later by distillation.

The lead is contained in the acid-aqueous layer remaining in the separatory funnel. With the vacuum pipet, draw out a 10-ml. aliquot of the acid solution and allow it to run into a 100-ml. Nessler tube. Connect the 10-ml. pipet to the source of lead-free water and rinse immediately with sufficient water to make it free from lead. To the solution in the Nessler tube add exactly 10 ml. of ammonia-cyanide-citrate reagent, mix well by rotating the tube, and allow it to stand for a few minutes to cool. Add exactly 10 ml. of dithizone, place a cork stopper in the tube, and shake for 1 minute. Remove the stopper and cover the tube with a 50-ml. beaker. Rinse the stopper with 200 ml., or more, of lead-free water.

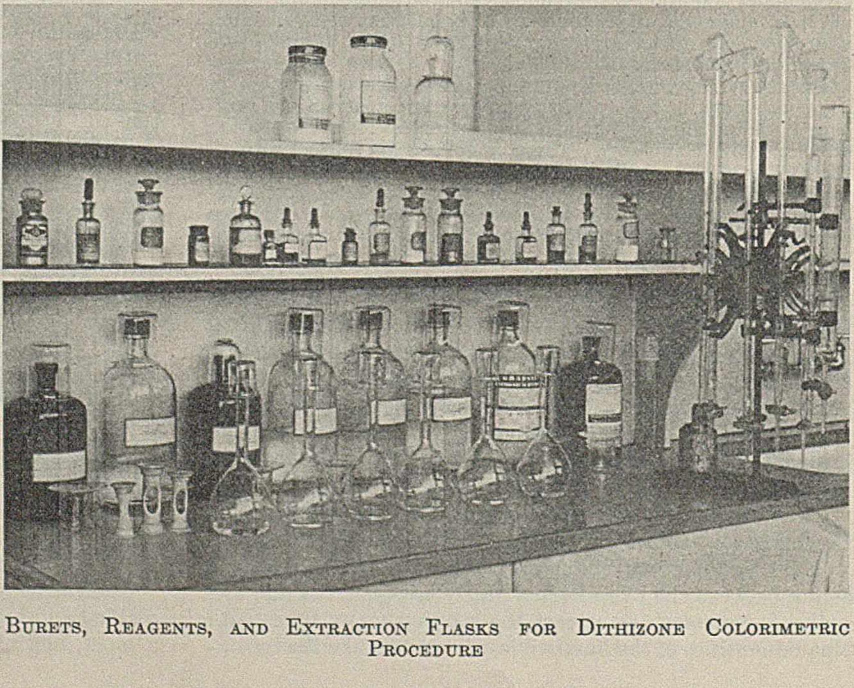
Let the Nessler tube stand until the dithizone layer has settled. This layer will be colored green, blue, purple, red, or pink by the lead-dithizone complex and the excess dithizone. Compare the tube to a set of standards containing known quantities of lead, arranged in order from 0 to 15 micrograms. A convenient interval between them is 1.5 micrograms. This interval may be divided into three parts by estimation. If the exact quantity cannot be determined in this way, one or more extra standards may be prepared by measuring out the appropriate volumes of standard lead solution, which fall within this interval, into Nessler tubes and proceeding as directed under "Preparation of Standards". The lead content of extracts must be kept within the range of 0 to 15 micrograms by adjusting the quantity of the sample taken for extraction. If the color of an extract is found to match the standard which represents 15 micrograms of lead (the highest in this range), it is advisable to repeat the determination, using a smaller sample. The extract of the smaller sample will match a standard having a smaller lead content and all possibility of exceeding the range, without detection, will have been eliminated.

Make a blank determination on water and reagents, following the procedure given above, but substituting from 5 to 10 ml. of water for the sample of the sugar product.

Having determined the number of micrograms of lead contained in the extract, deduct the quantity found in the blank and calculate to parts per million in the sample. For example: The sample weighed into the volumetric flask was 9.52 grams. In the colorimetric procedure it was found that, after deducting the equivalent in milliliters of standard lead solution found in the



Vacuum Pipet



Burets, Reagents, and Extraction Flasks for Dithizone Colorimetric Procedure blank determination, the sample contained the quantity of lead which is equivalent to 3.0 ml. of that solution:

$$3.0 \times 1.5 = 4.5 \text{ micrograms} = 0.0000045 \text{ gram of lead}$$

Two aliquots were taken during the analysis. Considering these ratios, the weight of the sample represented in the final colorimetric comparison was

$$\frac{75}{125} \times \frac{10}{11} \times 9.52 = 5.19 \text{ grams}$$

Then the sample contains

$$\frac{0.0000045 \times 1{,}000{,}000}{5.19} = 0.86 \text{ or } 0.9 \text{ part per million of lead}$$

Lead is eliminated from glassware by rinsing about six times with lead-free water, occasionally using dilute nitric acid before using water. Allow a small quantity of the water from the last rinsing to remain in each vessel. Pour the water from a dozen or more vessels into a large separatory funnel and make a qualitative test for lead. The hands of the operator may be immersed in 0.1 per cent nitric acid and rinsed with lead-free water as a precautionary measure. Rinse cork stoppers used in Nessler tubes with about 200 ml. of lead-free water immediately after use, and cover with beakers after rinsing. Before using new cork stoppers, shake them in a bottle with dithizone and dilute ammonia.

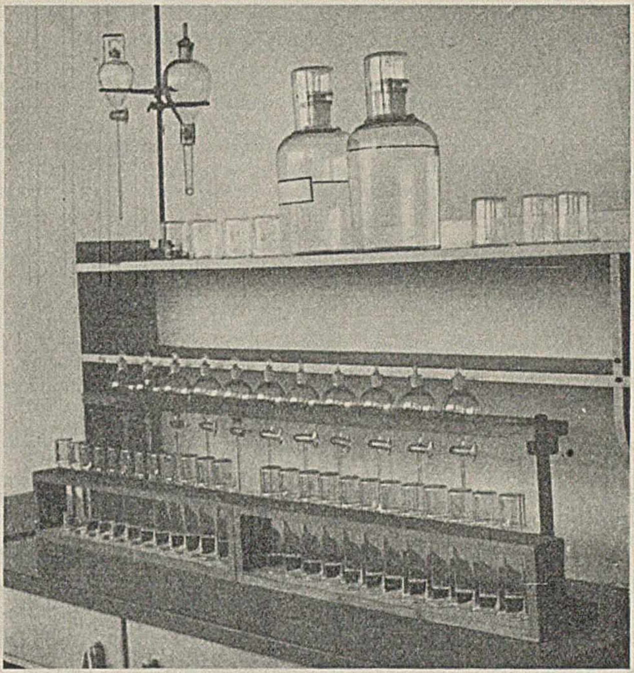
Dithizone extractions are made in three different types of containers—separatory funnels, Nessler tubes, and 500-ml. flasks. The usual technique of agitation for separatory funnels must be varied for extractions made in Nessler tubes and flasks. The appearance of the emulsion in a separatory funnel is noted while shaking dithizone with hydrochloric acid reagent, and Nessler tubes and 500-ml. flasks are agitated in a manner which will cause this same appearance of completeness in the emulsion. Nessler tubes will require a more gentle agitation and flasks will require a more vigorous shaking than separatory funnels to produce this result. Regardless of the type of vessel, the agitation should never be more vigorous than necessary to produce this appearance of completeness in the emulsion. The quantity of nonsugars should be kept to a minimum in the first extraction by using smaller samples for the analysis of products of very low purity. If the layers in a Nessler tube do not separate, the entire contents of the tube may be filtered into another tube through a pledget of cotton in a small funnel, and the clear filtrate compared with the standards. Permanence in the emulsion will rarely occur under the conditions outlined above. Filtration will not impair the accuracy of the test if the apparatus has been rinsed until free from lead.

Determination of Quantity of Ammonium Hydroxide Required for Adjustment of pH for Dithizone Extraction

Mix 30 to 35 ml. of lead-free water with exactly 15 ml. of hydrochloric acid reagent and exactly 10 ml. of citric acid reagent in a 100-ml. beaker. Add 9 ml. of concentrated ammonium hydroxide, cool in a water bath to about 20°, add 5 ml. of potassium cyanide solution, and determine the pH with a pH meter. Add ammonium hydroxide in quantities of about 1 ml. until the pH is 9.5. Note the number of milliliters required. Make this determination periodically, whenever new reagents (hydrochloric acid, citric acid, or potassium cyanide) are prepared, or a new bottle of ammonium hydroxide is used.

When determining lead in samples of sugar products whose composition is abnormal (old samples, damaged samples, sirups which have been subjected to some special treatment for experimental purposes, etc.) this procedure must be modified and a determination made for each abnormal sample.

Dissolve 5 to 10 grams of the sample in 25 ml. of lead-free water in a 100-ml. beaker, add exactly 15 ml. of hydrochloric acid reagent and exactly 10 ml. of citric acid reagent, and proceed as before.



SEPARATORY FUNNELS AND NESSLER TUBES FOR DITHIZONE COLORIMETRIC PROCEDURE

Preparation of Standards

Arrange eleven Nessler tubes in a row and measure into them accurately, by means of calibrated burets, the following quantities of standard lead solution (1 ml. contains 0.0000015 gram of lead) and hydrochloric acid reagent:

Nessler tube number	1	2	3	4	5	6	7	8	9	10	11
Standard lead solution, ml.	0	1	2	3	4	5	6	7	8	9	10
Hydrochloric acid reagent, ml.	10	9	8	7	6	5	4	3	2	1	0

After mixing the contents by rotating the tubes, add exactly 10 ml. of ammonia-cyanide-citrate reagent to each tube. Mix well and allow them to stand until cool. Then add 10 ml. of dithizone, place cork stoppers in the tubes, and shake them for 1 minute. Remove the stoppers and cover with 50-ml. beakers. Wash each stopper with at least 200 ml. of lead-free water. Allow the Nessler tubes to stand until the dithizone layers have settled.

These layers will exhibit various shades from green in the first tube to pink in the last one, with intermediate blues, purples, and reds, depending upon the proportions of lead-dithizone complex and uncombined dithizone. The colors represent quantities of lead in the range of 0 to 15 micrograms and are arranged at intervals of 1.5 micrograms.

Qualitative Test for Lead

WATER. Add 2 drops of citric acid to 30 to 50 ml. of water in a separatory funnel, make alkaline with ammonia, and then add 1 ml. of potassium cyanide. Mix well and add about 5 ml. of dithizone. Shake the separatory funnel vigorously and allow the layers to separate. A pink color in the chloroform layer shows the presence of lead. A green color or a mixed color containing green and red indicates that the excess dithizone has not been transferred from the chloroform phase to the aqueous phase. Add more water and ammonia or run the chloroform layer into another separatory funnel containing water and ammonia and potassium cyanide. In either instance, shake the separatory funnel vigorously and allow the layers to separate. A water-white chloroform layer is a negative test and a pink color in this layer is a positive test for lead.

CHLOROFORM (new or reclaimed). To 50 ml. of chloroform in a separatory funnel add about 15 ml. of lead-free water, 2 drops of citric acid, and sufficient ammonia to make the aqueous phase alkaline. Add 1 ml. of potassium cyanide and about 10 ml. of dithizone, and shake vigorously. A pink color in the chloroform layer indicates the presence of lead. If a green color, due to ex-

Table I. Comparative Results

(A. Method of Association of Official Agricultural Chemists for lead in foods. B. Dithizone colorimetric procedure for lead in sugars and sugar products, described in this paper.)

Sample	Lead Found A	Lead Found B
	P. p. m.	*P. p. m.*
1	0.5	0.5
2	0.6	0.5
3	1.2	1.4
4	1.3	0.9
5	1.7	1.7
6	1.8	1.7
7	1.8	1.8
8	1.9	2.05
9	2.2	2.1
10	2.3	2.0
11	3.0	2.3
12	3.5	3.5
13	3.95	4.0
14	5.2	5.0

cess dithizone, is also present in the chloroform layer, remove it as in testing water.

Other Reagents. About 20 ml. of the reagent are treated in the same manner as a sample of water, when attempting to locate a source of contamination in quantitative or qualitative determinations. In the dithizone colorimetric procedure the combined contamination of all the reagents simply appears as a minute quantity of lead in the blank determination and, unless the blank becomes higher than usual, it is not necessary to make qualitative tests on individual reagents.

Results obtained with this method (Table I) agree with those obtained with the method of the Association of Official Agricultural Chemists for lead in foods (*1*). The accuracy of results obtained with the new procedure depends, to a very great extent, upon ability to match colors, upon ability and willingness to dispense exact quantities of solutions from burets, and upon the exclusive use of glassware which has been found by qualitative tests to be free from lead.

Literature Cited

(1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, p. 394 (1940).
(2) *Ibid.*, p. 396.
(3) *Ibid.*, p. 404.
(4) *Ibid.*, p. 405.
(5) Bambach, Karl, Ind. Eng. Chem., Anal. Ed., 11, 400 (1939).
(6) *Ibid.*, 12, 63 (1940).
(7) Hibbard, P. L., *Ibid.*, 10, 615 (1938).
(8) Perlman, J. L., *Ibid.*, 10, 134 (1938).
(9) Smith, F. L., Commonwealth of Pennsylvania, *Safe Practice Bull.* 52, Part 2, Lead Poisoning (Feb., 1940).
(10) Stout and Arnon, *Am. J. Botany*, 26, 144–9 (1939).

Presented before the Division of Sugar Chemistry and Technology at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J.

Determination of Zinc in Rubber Compounds

A New Internal Indicator Method

WILLARD P. TYLER
General Chemical Laboratories, The B. F. Goodrich Co., Akron, Ohio

A SURVEY of the chemical literature reveals very little information regarding the determination of zinc in rubber compositions. Some of the earlier standard procedures involve the use of the gravimetric sulfide method, but the only direct references to the use of ferrocyanide as a volumetric precipitant with an external indicator applied to the analysis of rubber compounds are those of the A. S. T. M. (*1*) and Casazza (*3*). The A. S. T. M. method is used in the rubber industry with various modifications, and, in the absence of evidence to the contrary, is assumed to be the only volumetric method in general use for the determination of zinc.

The difficulty of manipulation and the low degree of accuracy of the external indicator procedure led to the consideration of a new method for this determination. The principal internal indicator methods for the determination of zinc have been considered by Kolthoff and Furman (*7*). One method employs ferrocyanide as precipitant and ferrous iron as an indicator and the other, based on the work of Cone and Cady (*4*) supplemented by that of Kolthoff (*6*), utilizes the ferricyanide-ferrocyanide oxidation-reduction system in equilibrium with precipitated zinc potassium ferrocyanide, using diphenylamine or diphenylbenzidine as indicator. With the latter method as a basis the experimental work for the development of a procedure suitable for the analysis of all types of rubber compounds was undertaken.

Experimental

With some modifications the diphenylbenzidine indicator method proved satisfactory in the presence of the ions usually found in an acid solution of the ash obtained from rubber compounds. It was also successful with rubber compounds of certain simple types, if the ash was treated in such a manner as to remove all oxidizing agents, reducing agents, and iron, if chlorides were present in only small quantities, and if there were no more than 10 grams of ammonium salts present in the solution to be titrated.

However, when this method was applied to the analysis of rubber stocks containing clay or other silicates, the zinc found was from 10 to 30 per cent low. This observation apparently has not been reported in the literature. Investigation of this phenomenon revealed that it occurs with any method of analysis which involves ashing as a preliminary step because of a reaction between zinc oxide and silicates which occurs even at the lowest possible ashing temperature. The reaction product is not decomposed by ordinary acid treatment and even prolonged acid digestion gives results 5 to 10 per cent low. The presence of lead oxide also causes low and inconsistent results, but the reasons for this effect have not been investigated yet.

Because of these phenomena it became necessary to resort either to fusion or to wet oxidation (digestion) in order to find a generally applicable method for the preliminary destruction of the sample. The latter method is the more practical. Concentrated nitric acid, bromine, and fuming nitric acid used successively will oxidize most of the organic material in a rubber compound. The best reagent for oxidizing the carbon black and organic matter remaining in the residue is perchloric acid, and when its addition is preceded by the above oxidizing agents this reagent is safe to use. Unfortunately, even small quantities of perchlorates had a detrimental effect on the color change and position of the end point when diphenylamine or diphenylbenzidine was used as indicator. Since no way of overcoming this effect was found, it became necessary to discontinue the use of these indicators in connection with wet-oxidation methods of determination.

Because of these facts it was necessary to devise a new method suitable for determining the zinc after wet oxidation of the sample. Gravimetric methods were discarded as being impractical. Precipitation methods, such as precipitation with anthranilic acid or 8-hydroxyquinoline followed by volumetric determination of the precipitate, were discarded as being time-consuming and none too accurate in solutions containing as many ions and added salts as are inevitably present. The problem centered on finding a suitable indicator to be used with the ferricyanide-ferrocyanide system in the manner of diphenylbenzidine.

Only indicators from stock which were thought to possess oxidation potentials in the neighborhood of +0.75 volt were tried. The results obtained indicated that the potential of a suitable indicator must be no higher than +0.75 volt and probably not much lower. The compounds which proved to be unsatisfactory in color development or in reproducibility of end point were *p*-phenetidine, benzidine acetate, *N*-phenylanthranilic acid, *p*-aminodiphenylamine, 2,4-diaminodiphenylamine, diphenylcarbazide, and two *p*-phenylenediamine derivatives. All these indicators were tried under varying conditions of temperature and acidity, both by direct and back-titration. *p*-Anisidine showed promise as an indicator but proved to give very high results. *o*-Tolidine gave satisfactory results but the color change, yellow through yellow-green to blue-green, was not sharp enough to ensure accuracy without considerable experience.

Schulek and Rózsa (*10*) described a new multiform indicator, *p*-ethoxychrysoidine, which presumably had the properties desired for this purpose, although the literature does not describe this use for it. A sample of this dye was prepared as described below and it was found to be an excellent indicator under at least two sets of conditions applicable to the analysis of rubber compounds.

Tananaev and Georgobiani (*11*) reported the use of "blue ethyl acidic RR(B)", 2-(*p*-ethylaminophenylazo)-1,8-dihydroxynaphthalene-3,5-disulfonic acid sodium salt, as an indicator for lead titration with ferrocyanide and suggested its use for the determination of other metals. According to Rowe's Colour Index (*9*), Ethyl Acid Blue RR(B) is dye No. 59, which is the sodium salt of *p*-dimethylaminobenzeneazo-1,8-dihydroxynaphthalene-4-sulfonic acid. This was available from Eimer & Amend, New York, as Azo Acid Blue B, originally obtained from G. Grubler and Co., Leipzig. This dye was not received until the work described below was completed, but it was then tried as a substitute indicator. The end point was not quite so sharp as with *p*-ethoxychrysoidine and results were somewhat erratic, but further work on conditions of operation might prove it to be a satisfactory indicator.

As a result of the experimental work two methods of analysis were devised and tested. Method I is the more general and is, with slight modification, applicable to all rubber compounds, vulcanized and unvulcanized, and to latices. Method II is applicable only to rubber stocks and latices free of lead, silicates, or other fusible ash, and containing but small amounts of acid-insoluble fillers.

Method I. Wet-Oxidation Method

Reagents and Solutions. *Indicator.* *p*-Ethoxychrysoidine (*p*-ethoxyphenylazo-*m*-phenylenediamine), 0.2 per cent in sulfuric acid (sp. gr. 1.84, diluted 1 to 1 with water). The indicator is prepared by coupling diazotized *p*-phenetidine hydrochloride with *m*-phenylenediamine. An analogous preparation for chrysoidine is described by Houben-Weyl (*5*). Recrystallization of the dye is unnecessary. Store the solution in the dark.

Standard Potassium Ferrocyanide Solution. Approximately 0.04 *M* solution of reagent grade potassium ferrocyanide trihydrate. If available, highly purified crystals may be used as a primary standard but the solution is not stable (cf. standardization).

Standard Zinc Chloride Solution. Zinc solution (0.06 *M*) made from zinc of known purity dissolved in hydrochloric acid, or impure zinc compound dissolved in acid and standardized against potassium ferrocyanide (cf. standardization).

Potassium Ferricyanide. One per cent of the reagent grade crystals dissolved in water. This solution is stable only if kept in the dark.

Nitric Acid–Bromine Mixture, reagent grade nitric acid (sp. gr. 1.42) saturated with bromine. Free bromine must be present.

Perchloric Acid, reagent grade, 60 or 72 per cent acid.

Sulfuric Acid, reagent grade (sp. gr. 1.84) diluted 1 to 1.

Ammonium Hydroxide, reagent grade (sp. gr. 0.90).

Wash Solution, 25 grams of ammonium sulfate and 10 ml. of ammonium hydroxide per liter.

Fuming Nitric Acid. The red fuming type is preferred. Reagent grade.

Procedure A (for vulcanized rubber compounds only). Place the ground sample of rubber (0.5 to 2.0 grams) in a 400- to 500-ml. wide-mouthed flask. Add 15 ml. of nitric acid–bromine mixture, cover the flask, and let stand for 10 minutes or longer. Add 10 ml. of red fuming nitric acid, replace the cover, and place on a steam plate or bath until the rubber is disintegrated. Transfer to an electric hot plate or a burner, remove the cover, and evaporate to 10 to 15 ml. Cool partially, add 10 ml. of perchloric acid, and evaporate until all carbon and organic material are destroyed.

(*Caution.* To ensure safety to the operator, the operations involving the oxidation of organic matter with perchloric acid should be done behind a safety screen. The evaporation of perchloric acid to fumes should be done under a hood whose flue is free from condensed organic vapors, organic dust, and carbon or soot.)

This operation requires a temperature of about 200° C. Continue evaporation to about 5 ml. Dense white fumes should be evolved and the hot solution may be a pale yellow color but should become colorless on cooling unless much iron is present. If lead is present add 3 ml. of sulfuric acid and evaporate until dense fumes again appear.

Dilute to 50 ml., boil for a minute, cool, neutralize with ammonium hydroxide, add 5 ml. in excess, and boil for one minute. Filter hot and wash with four 25-ml. portions of hot wash solution. For greater accuracy when there is a large flocculent precipitate, wash only twice with 20-ml. portions of wash solution, wash the precipitate into the original flask, add 5 ml. of sulfuric acid, digest, precipitate as before, filter, and wash the precipitate with four 20-ml. portions of wash solution. Evaporate the combined filtrates to 100 to 125 ml., making sure in every case that nearly all of the ammonia is boiled off to prevent the formation of excess ammonium salts. Add 5 ml. of sulfuric acid and titrate in the manner described below. The temperature must be 90° C. at the start of the titration and should not fall below 70° C.

Add 4 to 6 drops of indicator and 4 to 7 drops of ferricyanide solution, the latter always in amounts equal to or greater than the former. Shake until the red color changes to yellow and titrate with standard ferrocyanide solution until a strong salmon-pink color persists. Back-titrate with standard zinc solution to a pale green color. Continue "back and forth" titration (as few times as possible) until a few drops of zinc solution cause the color to fade through a neutral shade to a very pale apple green. The last few drops must be added slowly, with shaking between drops, since the precipitation equilibrium is reached slowly. Because of the equilibrium conditions the zinc must always be added last. When only small quantities of zinc are present the indicator may not fade readily upon addition of ferrocyanide. This may be remedied by adding several milliliters of zinc solution first.

Standardization. If the zinc solution is a primary standard, standardize the ferrocyanide with it according to the method just described, using a hot solution containing the zinc, 5 ml. of sulfuric acid, and 5 grams of ammonium sulfate per 100 ml. of solution. If the zinc solution is not standard, standardize the ferrocyanide with 0.1 *N* potassium permanganate according to the method of Kolthoff and Furman (*8*). This method specifies that about 1 gram of ferrocyanide in 120 ml. of 1 *N* sulfuric acid be titrated with permanganate and that a fresh, approximately 1 per cent ferricyanide solution be used for color comparison at the end point. The ferrocyanide solution may also be standardized against permanganate or ceric sulfate using *o*-phenanthroline-ferrous complex (ferroin) as indicator. The zinc solution may then be standardized against the ferrocyanide solution.

PROCEDURE B (for latices and unvulcanized rubber stocks). Because of the difficulty of destroying unvulcanized rubber readily with nitric acid–bromine mixture to such an extent that the use of perchloric acid is safe, the following modification of Procedure A is necessary.

Add 20 ml. of nitric acid–bromine mixture to the sample of latex or thinly sheeted unvulcanized rubber compound and warm until vigorous reaction starts, keeping the flask covered. If overnight digestion is convenient, add 20 ml. of red fuming nitric acid after the first reaction has subsided, cover the flask, and allow it to stand overnight on a steam plate or bath. After this treatment perchloric acid may be added and the evaporation safely continued as in Procedure A. If the determination must be completed without interruption, add 10 ml. of red fuming nitric acid after the first reaction has subsided, heat gently until the rubber is disintegrated, and evaporate nearly to dryness. Add 10 ml. of red fuming nitric acid and 10 ml. of perchloric acid and evaporate as in Procedure A. Whichever method of digestion is used, complete the determination according to Procedure A. The actual rubber content of samples should not exceed 2 grams. Do not evaporate or coagulate latices before the oxidation.

Method II. Ashing Method

This method may be used for unvulcanized and vulcanized compounds and latices which contain no clay or lead, and have a comparatively low acid-insoluble ash.

REAGENTS. Same as in Method I where specified with the addition of reagent grade hydrochloric acid (sp. gr. 1.2), saturated bromine water, and 1 per cent diphenylbenzidine in concentrated sulfuric acid.

PROCEDURE A (*p*-ethoxychrysoidine as indicator). Ash a sample of from 0.5 to 2.0 grams of rubber in a crucible in an overnight ashing muffle furnace which is capable of slowly ashing the sample without combustion at a maximum temperature of 550° C. Ashing may be accomplished over a burner if the sample is not allowed to flame.

Treat the ash with 5 ml. of hydrochloric acid and 5 ml. of sulfuric acid, warm if necessary to free the precipitate from the crucible, and transfer to a beaker. Dilute to 50 ml., boil to dissolve all the ash possible, add 5 ml. of bromine water, cool, neutralize with ammonium hydroxide, and continue the preparation of the solution and the determination exactly as in Method I, Procedure A, except that the solution must be boiled for at least 10 minutes after acidification before titration.

PROCEDURE B (diphenylbenzidine as indicator). Up to the point of adding the indicator, follow Method II, Procedure A, exactly. In place of *p*-ethoxychrysoidine add 4 drops of diphenylbenzidine and 4 to 5 drops of ferricyanide solution. If a deep blue color does not develop, add sulfuric acid in 2-ml. portions until it does appear on shaking. Titrate with ferrocyanide solution until the blue fades markedly to a gray-green, stop titrating, and shake with the addition of small portions of sulfuric acid until a deep purple color appears; then continue dropwise titration to a yellow-green color. Back-titration is permissible but the ferrocyanide must be added last.

Discussion of Methods

INDICATORS. The use of *p*-ethoxychrysoidine may require some experience in determining the best ratios of indicator to ferricyanide. When there was much variation in this ratio from that specified in the procedure the accuracy was affected to a small extent, because the equilibrium between the ions from the precipitate, the ferrocyanide ions from reduced ferricyanide, and the excess ferrocyanide ions necessary to reduce the indicator is sensitive to variations in the quantities of indicator and ferricyanide. Because of this equilibrium and because of the greater sharpness of the end-point color change, the titration must be finished with the zinc solution.

Since the diphenylbenzidine method checked well with electrometric titration and also with the *p*-ethoxychrysoidine method in standardization titrations, Method II, Procedure B, may be used as a standard to check experimental work with *p*-ethoxychrysoidine. However, the author found that *p*-ethoxychrysoidine end points were better than those obtained with diphenylbenzidine because the latter indicator fades during titration and it is frequently difficult to bring the color back sufficiently to obtain a sharp end point.

In standardization with diphenylbenzidine indicator, 5 grams of ammonium sulfate and 5 ml. of sulfuric acid per 100 ml. of solution must be present. More sulfuric acid usually must be added during titration as is noted in Method II, Procedure B.

Neither indicator works well with less than 10 mg. of zinc but standard zinc solution may be added to the reaction mixture as soon as there is evidence of too little zinc in the solution.

The use of ferricyanide incorporated in the standard ferrocyanide solution as advocated by Kolthoff and Furman (*7*) was not satisfactory with either indicator.

INTERFERENCES. Oxidizing and reducing agents which will affect the ferricyanide-ferrocyanide system or the indicator will interfere with both methods, but all such substances are removed by the preliminary treatments. Manganese and copper will interfere, but they are not usually found in rubber compounds except those containing certain organic copper rubber dyes. Any other metals which form precipitates with ferrocyanide in strong acid solution will interfere, with the exception of lead which is successfully removed by Method I but not by Method II. Results of trial determinations of mixtures containing lead indicate that there should be no more than a slight positive error when using Method I, even if some lead sulfate is present at the time of titration. About 5 grams of chloride ion can be present in Method I and about 3 grams in Method II without impairing the end-point colors. Ammonium sulfate must be present for quantitative precipitation, but amounts greater than 10 grams tend to diminish the intensity of the end-point colors.

Iron must be removed if present to an extent great enough to cause a very noticeable blue color when ferrocyanide is added. A very small trace of iron appears to sharpen the end-point colors but most rubber compounds contain too much iron to leave in the solution. A number of substances which form complex ions with ferric iron were employed in an attempt to eliminate the removal of iron. Tartrate, citrate, oxalate, fluoride, phosphate, and pyrophosphate were without effect, although the last was cited by Aruina (*2*) as being effective for this purpose.

APPLICATIONS. In addition to being applicable to practically all rubber stocks and latices, the method will probably be equally effective with synthetic rubber mixtures which do not contain appreciable quantities of saturated hydrocarbons. Organic zinc compounds can be readily determined by either method. Inorganic zinc compounds can be determined by titration of an acid solution of the material using either indicator if interfering ions are removed. Application to alloys would be more difficult because of the necessity of removing interfering ions present and added during prior treatment. The removal of interfering ions by precipitation with hydrogen sulfide is not recommended because drastic treatment, such as evaporation with perchloric acid, would be necessary to remove the excess hydrogen sulfide, traces of which are very injurious to the determination. The determination of smaller quantities of zinc by means of a more dilute ferrocyanide solution, a larger sample, or both, is now being investigated.

Discussion of Results

The precision and accuracy of the titrations of standard zinc solution were tested by a series of comparisons of the *p*-ethoxychrysoidine method with the diphenylbenzidine method and with electrometric titration. The diphenylbenzidine end point coincided with that obtained with electrometric

Table I. Results of a Study of the Methods

Sample No.	% Zinc Oxide Present	% Zinc Oxide Found, Average	Precision, Average % Deviation from Mean, ±	Accuracy, % Deviation of Mean from True Value
External Indicator Method, Uranyl Acetate on Spot Plate				
1^a	4.20	4.59	1.3	+ 9.3
2^a	4.17	3.52	6.0	−15.6
3^a	4.65	3.40	3.0	−27.0
4^a	21.10	19.50	2.5	− 7.6
Method II, Procedure B, Using Diphenylbenzidine				
1^a	4.20	4.08	1.0	− 2.8
2^a	4.17	3.12	4.0	−25.0
2^b	4.17	3.30	9.0	−21.0
3^a	4.65	3.82	2.3	−18.0
3^b	4.65	3.90	2.5	−16.0
4^a	21.10	20.75	0.96	− 1.7
4^b	21.10	20.90	0.38	− 0.95
Method II, Procedure A, Using *p*-Ethoxychrysoidine				
1^a	4.20	4.16	0.40	− 1.0
4^b	21.10	21.03	0.10	− 0.3
6^b	2.75	2.44	3.50	−12.7
Method I, Procedure A				
1^a	4.20	4.17	0.54	− 0.7
2^a	4.17	4.18	0.70	+ 0.2
2^b	4.17	4.22	0.20	+ 1.2
3^a	4.65	4.45	0.75	− 4.3
3^b	4.65	4.52	0.70	− 2.9
4^a	21.10	20.70	0.50	− 1.9
4^b	21.10	21.10	0.10	0.0
5^b	2.30	2.28	0.44	− 0.9
6^a	2.75	2.74	0.91	− 0.3

[a] One precipitation of ammonia-insoluble material.
[b] Two precipitations of ammonia-insoluble material.

titration within ±0.2 per cent. The precision obtained in five successive titrations using diphenylbenzidine was ±0.2 per cent average deviation from the mean. The average of twenty successive *p*-ethoxychrysoidine titrations was the same as that of the diphenylbenzidine titrations and a precision of ±0.2 per cent was obtained with a maximum deviation of ±0.5 per cent. In this last series of titrations the ratio of indicator to ferricyanide was varied through all combinations of from 4 to 6 drops of indicator and from 4 to 7 drops of ferricyanide in which the ferricyanide was present in amounts equal to or greater than the indicator. When ratios outside these limits were used the values obtained were more erratic but still had a precision within ±0.5 per cent.

Table I shows the results of analysis of especially prepared rubber compounds by the uranyl acetate indicator method (*1*) by Methods II-B, II-A, and I-A. The experimental compounds were carefully weighed and mixed in 500- and 1000-gram batches. The quantities of zinc oxide added and the batch weights were carefully checked. The purity of the zinc oxide used was 100 ± 0.2 per cent, as determined by analysis according to a simplified form of Method I-A. The compounds were vulcanized in the form of sheets, 6 × 8 × 0.1 inch, and samples from various parts of the sheets were ground together for analysis. The experimental compounds contained the following principal fillers:

1. 21% carbon black
2. 21% whiting, 21% clay, and 10.5% titanium dioxide
3. 23% barytes and 23% clay
4. 21% whiting, 10.5% magnesium carbonate, and 2.5% ferric oxide
5. 31% barytes and 18.5% clay
6. 16.5% carbon black and 11% litharge

The results tabulated in Table I show very clearly the effect of ashing on the accuracy of zinc determinations in rubber compounds containing clay or lead. The data leave little choice between the accuracy and precision of Methods I and II, providing lead and clay are absent. The poor results obtained with the external indicator method are difficult to explain and may not be typical of the method, although difficulty has frequently been encountered in this laboratory with regard to obtaining the same type of end point in the determination as in the standardization. The amount of reagent used for a blank with the external indicator method is large and inconsistent.

In order to test Method I further, results obtained in routine analysis in the laboratory over a period of several months were examined for precision. Only those determinations in which two or more analyses were run were considered in compiling the averages. Eighteen samples, varying from 1.2 to 6.1 per cent in zinc oxide content, were analyzed with a precision (average percentage deviation from the mean) of ±1.14 per cent and a maximum single deviation from the mean of 2.60 per cent. Seven other samples containing from 14.0 to 45.0 per cent zinc oxide were analyzed with a precision of ±0.31 per cent and a maximum single deviation from the mean of 0.85 per cent.

A test of Method I, Procedure B, was made involving eight successive determinations of zinc oxide in a latex mix. The average value was 1.97 ± 0.9 per cent. This is satisfactory precision when it is considered that obtaining a homogeneous sample of a latex mix as heavily compounded as the one used in these tests is not always easy. It was found that, ordinarily, not more than two samples could be taken from a latex mix without thoroughly remixing the batch to maintain homogeneity.

To summarize the interpretation of the data obtained in testing these procedures: Any of the internal indicator methods described is capable of accuracy and precision sufficient for most analyses for research in rubber technology and is also well suited to the speed required in control analyses without appreciable loss of accuracy. Each method, however, must be used only under the conditions most favorable to its success.

A comparison of the merits of the methods by analysts in this laboratory resulted in a general preference for Method I over the external indicator method. No comparisons with Method II were made by the analysts, but the author's experience has been that the titration using *p*-ethoxychrysoidine as indicator with either method is more rapid than the titration using diphenylbenzidine. The back-titration necessary when *p*-ethoxychrysoidine is used is of advantage when small or unknown quantities of zinc are present, and there is no uncertainty concerning the approach of the end point as there frequently is with diphenylbenzidine. With diphenylbenzidine, the return of the purple color prior to final titration to an end point is frequently slow and the speed of color return appears to be a function of the proximity to the end point when titration is interrupted and to the quantity of sulfuric acid in the solution.

Summary

Two internal indicator volumetric methods for the determination of zinc in rubber compounds have been devised and investigated. The first method is a wet-oxidation method employing nitric acid, bromine, and perchloric acid as oxidants, and *p*-ethoxychrysoidine, a new oxidation-reduction indicator for this use, as indicator. It is of general application to all types of rubber compounds. The second method, less generally applicable to rubber compounds, utilizes either the new indicator or the well-known indicator, diphenylbenzidine. This method depends on ashing of the sample, and cannot be used for the analysis of zinc in rubber compounds containing lead or silicates, since it has been found that no method in which the sample is ashed will yield accurate results if these materials are present. Both methods use potassium ferrocyanide as the volumetric precipitant and potassium ferricyanide as an integral part of the indicator system. Both methods are applicable to other organic and

inorganic zinc-containing materials. The first method appears to have a slight advantage in ease of manipulation, total time of determination, and range of applicability. There is little choice between the methods or indicators as regards precision, accuracy, or the actual time used by the analyst for a determination, providing each method and indicator is used only under the proper conditions. Both methods are superior to the external indicator method using uranyl acetate, the method now in common use in rubber laboratories.

Acknowledgment

The author wishes to thank V. E. Wellman, director of this laboratory, for his constructive criticism and aid in preparing this paper, and J. A. Freese, R. A. Emmett, H. M. Zimmerman, L. V. Rogers, and J. Snyder for their assistance in testing the methods under routine laboratory conditions.

Literature Cited

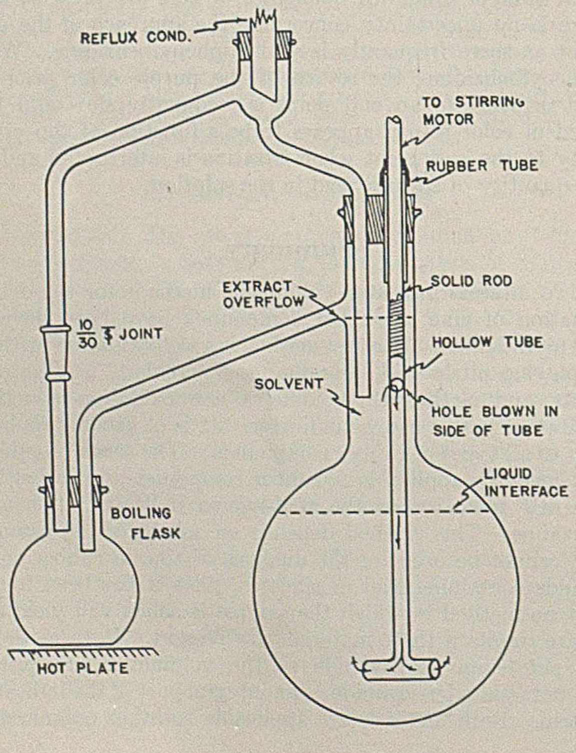
(1) Am. Soc. Testing Materials, "Tentative Methods of Testing Hard Rubber Products", Designation D530-39T.
(2) Aruina, A. S., *Zavodskaya Lab.*, 8, 565 (1939).
(3) Casazza, E., *Rubber Chem. Tech.*, 13, 181 (1940).
(4) Cone, W. H., and Cady, L. C., *J. Am. Chem. Soc.*, 49, 356 (1927).
(5) Houben-Weyl, "Die Methoden der organischen Chemie", 2nd ed., Vol. 4, p. 686, Leipzig, Thieme, 1924.
(6) Kolthoff, I. M., *Chem. Weekblad*, 24, 203 (1927).
(7) Kolthoff, I. M., and Furman, N. H., "Volumetric Analysis", Vol. II, pp. 251–7, New York, John Wiley & Sons, 1929.
(8) *Ibid.*, p. 287.
(9) Rowe, F. M., "Colour Index", 1st ed., Bradford, Yorkshire, Society of Dyers and Colourists, 1924.
(10) Schulek, E., and Rózsa, P., *Z. anal. Chem.*, 115, 185 (1939).
(11) Tananaev, I., and Georgobiani, M. Ya., *J. Applied Chem.* (U. S. S. R.), 9, 1725 (1936).

PRESENTED before the Division of Rubber Chemistry at the 101st Meeting of the AMERICAN CHEMICAL SOCIETY, St. Louis, Mo.

Continuous Liquid Extractor for Large Volumes of Solution

RALPH HOSSFELD
Division of Agricultural Biochemistry, University of Minnesota, St. Paul, Minn.

THE need for prolonged extraction of comparatively large quantities of solutions with an immiscible solvent of lesser specific gravity usually leads to the use of a continuous liquid-liquid extraction device similar to that described by Marshall (*1*), in which the solvent is made to bubble up through the solution by means of a long funnel tube leading from a reflux condenser. The solvent together with the extracted material is then returned through a suitable overflow to the boiling flask. Although having the advantage of simplicity in construction and operation, such an apparatus is necessarily inefficient because of limited contact of the solvent with the material to be extracted. Furthermore, it cannot be used conveniently with solutions, such as neutralized cook liquors from wood-pulping studies, that contain finely divided solids which occlude a part of the extractable material and settle out.



The apparatus described herein obviates the above difficulties by providing vigorous agitation and continuously recirculated dispersion of the solvent from the solvent layer through the lower layer being extracted. By so doing, the concentration of extractives in the solvent layer is maintained near the limit of distribution between the two phases. This concentrated extract is continuously replaced by fresh reflux from the boiling flask. The principle is that of a centrifugal pump, the rotor being the hollow T-stirrer (*2*) indicated in the diagram. The solvent is drawn from the solvent layer through a hole well up the stem of the stirrer, and flows down the stem of the T, from which, in a finely divided state, it is thrown into the solution by centrifugal force.

For complete extraction of a 2-liter batch of neutralized wood-cook liquor, the usual type of extractor required from 4 to 6 days, whereas the present apparatus required from 10 to 12 hours.

The diagram is self-explanatory. Pyrex glass was used throughout in the construction. The extraction flask is a distilling flask of from 2- to 5-liter capacity as required. The bearing for the stirrer is a short section of glass tubing of such size as will fit the stem snugly and is sealed at the outer end by means of a short section of well-lubricated rubber tubing.

The extraction flask is filled to within about 200 ml. of the side arm with the solution to be extracted, the remaining volume being occupied by the solvent. If the solution contains suspended solids which are preferentially wetted by the solvent, a small cotton plug placed in the entrance of the overflow tube serves well as a filter.

Should an emulsion form during operation, it may be suppressed by varying the speed of the stirrer: the more stable the emulsion, the slower the speed permissible to maintain the level of the emulsion slightly below the intake hole of the stirrer. The optimum speed for good circulation with a minimum of moderately stable emulsion was found to be about 500 r. p. m. when using a 3-cm. tip on a stirrer of 7-mm. bore.

Literature Cited

(1) Marshall, F. C. B., *Chem. News*, 143, 235–6 (1931).
(2) Woodburn, H. M., IND. ENG. CHEM., ANAL. ED., 13, 356 (1941).

PAPER No. 1919, Scientific Journal Series, Minnesota Agricultural Experiment Station.

Rapid Turbidimetric Method for Determination of Sulfates

JOSEPH F. TREON AND W. E. CRUTCHFIELD, JR.
Kettering Laboratory of Applied Physiology, College of Medicine, University of Cincinnati, Cincinnati, Ohio

SINCE benzene, phenols, and various other cyclic compounds alter the ratio of inorganic to ethereal (organic) sulfates in urine, it seemed desirable to obtain a rapid method for the determination of this ratio. Gravimetric methods have been used largely for this purpose but they are time-consuming. A nephelometric method for determination of inorganic sulfates in biological fluids has also been reported recently by Medes and Stavers (*2*).

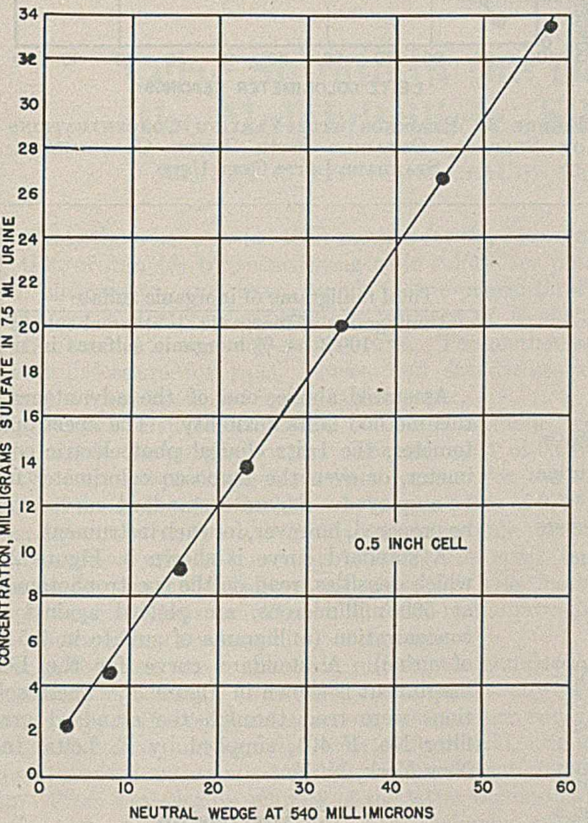


FIGURE 1. DIFFERENCES BETWEEN WEDGE READINGS FOR SAMPLES WITH VARYING CONCENTRATIONS OF SULFATE AND BLANKS. 0.5-INCH CELL USED

The authors first devised a colorimetric method (*4*), based on precipitation of the sulfate with benzidine and coupling of the benzidine with chromotropic acid to yield Dianil Blue R (colour index No. 390, *3*). Since it proved to be somewhat tedious, however, the simpler and shorter photometric method here reported was developed.

The advantages in this method over gravimetric methods are: (1) the speed of determination is increased; (2) a small aliquot may be used; (3) for the final measurement of the sulfates there is a choice of several instruments—namely, the neutral wedge photometer, the spectrophotometer, and the Leitz clinical photoelectric colorimeter.

Procedure

DETERMINATION OF INORGANIC SULFATES IN URINE. The urine is collected, the total volume is measured, and 7.5 ml. are pipetted into a small Büchner funnel equipped with Whatman No. 12 paper, and filtered by suction. As soon as the filtration is complete, the paper is washed three times with 15 to 20 ml. of distilled water. Three drops of alcoholic methyl red are added to the filtrate, which is made faintly alkaline with approximately *N* sodium hydroxide and then the acidity is regulated by making it just acid with hydrochloric acid (1 part of concentrated hydrochloric acid plus 4 parts of water). An excess of 1 ml. of hydrochloric acid (1 + 4) is added and the solution is diluted to 250 ml. with distilled water in a volumetric flask and shaken.

In order to eliminate any slight variation caused by the color of the urine, just enough solution is withdrawn for a blank (about 1.5 ml.) and read in a 1.25-cm. (0.5-inch) precision cell on the neutral wedge photometer, with a 540-millimicron filter (Aminco No. 54). To the remaining solution in the 250-ml. volumetric flask is added 1 gram of 20- to 30-mesh barium chloride. (This may be prepared from reagent-grade barium chloride, or obtained already screened from the Parr Instrument Company, Moline, Ill.) As a matter of convenience, a scoop may be made which will deliver 1 gram. The solution is shaken well, placed in the same cell, and read immediately on the neutral wedge photometer at 540 millimicrons. This reading is converted to the amount (in milligrams) of sulfate in 7.5 ml. of urine by reading from the standard curve (Figure 1).

HYDROLYSIS OF ETHEREAL SULFATES AND DETERMINATION OF TOTAL INORGANIC AND ETHEREAL SULFATE. A 7.5-ml. sample of urine is pipetted into a 150-ml. Erlenmeyer flask containing 2 ml. of water and 7.5 ml. of hydrochloric acid (1 + 4), and a cold-finger condenser is inserted into the top of the flask. The solution is boiled for 20 to 30 minutes, then cooled. Three drops of alcoholic methyl red are added to the sample. It is made just alkaline with approximately *N* sodium hydroxide and is filtered by suction through a Whatman No. 12 paper in a small Büchner funnel. The paper is washed three times with 15 to 20 ml. of distilled water. The filtrate is made just acid with hydrochloric acid (1 + 4). An excess of 1 ml. of hydrochloric acid (1 + 4) is added, and the solution is diluted to 250 ml. with distilled water

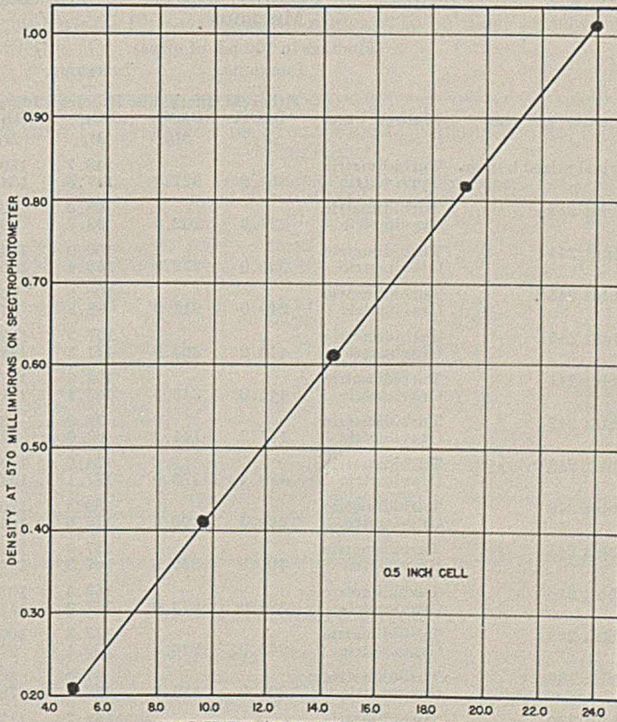


FIGURE 2. SPECTROPHOTOMETRIC DENSITY READINGS WITH VARYING CONCENTRATIONS OF SULFATE. 0.5-INCH CELL USED

in a volumetric flask and shaken, after which the procedure for the determination of inorganic sulfates is followed.

Preparation of Standard Curve. The standard curve is prepared from a series of readings on known amounts of sulfate in "synthetic urine" solutions prepared as described by Cholak (*1*), and containing approximately 5 mg. of sulfate per milliliter. The exact amount of sulfate is determined either by direct weighing of anhydrous sodium sulfate (Merck reagent) or by titrating diluted sulfuric acid (sulfate equivalent to acid) against standard alkali.

To 7.5 ml. of synthetic urine is added 1 ml. of the standard sulfate solution described above. In a similar manner solutions are made with 0.0, 2.0, 3.0, 4.0, 5.0, and 6.0 ml. of standard sulfate. They are made just alkaline to alcoholic methyl red with approximately *N* sodium hydroxide, and then just acid with hydrochloric acid (1 + 4), after which an excess of 1 ml. of hydrochloric acid (1 + 4) is added. The solutions are washed thoroughly into 250-ml. volumetric flasks, diluted to the mark, and shaken. The procedure is continued as described for determination of inorganic sulfates in urine.

The differences between the wedge readings for samples and blanks are plotted against the concentration (milligrams of sulfate in 7.5 ml. of urine) to give a standard curve (Figure 1).

Calculation of Per Cent of Inorganic Sulfates in Urine. The amount of inorganic sulfates in the entire sample is calculated as follows:

$$\text{Milligrams of sulfate as read from curve} \times \frac{\text{total volume of urine}}{7.5} = \text{quantity of inorganic sulfates (in milligrams)}$$

Inorganic plus ethereal sulfates in the entire sample:

$$\text{Milligrams of sulfate as read from curve} \times \frac{\text{total volume of urine}}{7.5} = \text{quantity of inorganic plus ethereal sulfates (in milligrams)}$$

Per cent of inorganic sulfates in urine:

$$\frac{\text{Milligrams of inorganic sulfate as read from curve}}{\text{Milligrams of inorganic + ethereal sulfate as read from curve}} \times 100\% = \%\ \text{inorganic sulfates in urine}$$

or

$$\frac{\text{Total milligrams of inorganic sulfate}}{\text{Total milligrams of inorganic + ethereal sulfate}} \times 100\% = \%\ \text{inorganic sulfates in urine}$$

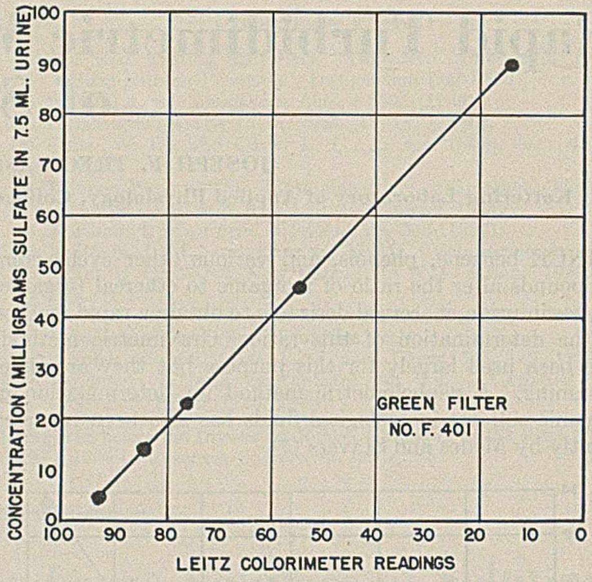


Figure 3. Readings with Varying Concentrations of Sulfate, Obtained with Leitz Colorimeter. Standard Leitz Cell Used

As stated above, one of the advantages of this method is its flexibility. The spectrophotometer, the Leitz clinical photoelectric colorimeter, or even the Duboscq colorimeter may be employed. Separate standard curves must be prepared, however, for each instrument.

A standard curve is shown in Figure 2 in which densities, read on the spectrophotometer at 560 millimicrons, are plotted against the concentration (milligrams of sulfate in 7.5 ml. of urine). A standard curve for the Leitz instrument is shown in Figure 3. These solutions were read through the standard green filter No. F 401, supplied by E. Leitz, Inc., New York, N. Y.

Discussion

After the solution has been made just acid, the same results are obtained if 0.5 or 1.0 ml. of hydrochloric acid (1 + 4) is added in excess.

The wave length of the filter is not of particular importance since no selective color is being measured; however, wave lengths have been selected to which the eye is sensitive.

If aqueous barium chloride is used instead of 20- to 30-mesh crystalline barium chloride, the suspension is not lasting and very low and inconsistent results are obtained.

The results on urine samples obtained by the gravimetric method were compared with those obtained by the photometric method, the spectrophotometer being employed to measure densities (Table I). Figures for amounts and ratios were calculated on a basis of 100 ml. of normal urines. Although in some instances the amounts are not in good agreement, the ratios are:

Table I. Comparison of Spectrophotometric and Gravimetric Methods

(Findings in 100 ml. of urine)

Source of Urine	Method Used	Inorganic + Ethereal $BaOS_4$ *Mg.*	Inorganic $BaSO_4$ *Mg.*	Inorganic + Ethereal SO_4^{--} *Mg.*	Inorganic SO_4^{--} *Mg.*	Inorganic SO_4^{--} %
Normal mixed human	Turbidimetric			148.7	139.3	93.6
	Gravimetric	356.8	327.2	147.8	134.7	91.1
Rabbit 243	Turbidimetric			98.0	89.3	91.1
	Gravimetric	227.6	202.6	93.7	83.4	91.5
Rabbit 244	Turbidimetric			156.0	134.6	86.3
	Gravimetric	385.0	332.0	158.4	136.3	86.0
Rabbit 245	Turbidimetric			106.6	95.3	89.3
	Gravimetric	240.0	212.0	98.8	87.0	88.0
Rabbit 246	Turbidimetric			157.3	153.3	97.4
	Gravimetric	416.0	363.0	171.2	149.4	87.0
Rabbit 241	Turbidimetric			192.0	157.3	81.9
	Gravimetric	445.0	343.5	183.1	141.1	77.2
Rabbit 242	Turbidimetric			78.0	73.3	94.0
	Gravimetric	155.2	141.2	63.9	57.7	92.0
Rabbit 248	Turbidimetric			174.0	157.3	90.4
	Gravimetric	430.4	378.0	177.1	155.6	87.9
Rabbit 249	Turbidimetric			189.3	170.6	90.1
	Gravimetric	429.2	400.4	176.6	164.7	93.3
Rabbit 245	Turbidimetric			157.3	134.6	85.6
	Gravimetric	406.5	350.5	167.3	144.0	86.0
Rabbit 246	Turbidimetric			133.3	108.0	81.0
	Gravimetric	309.0	273.0	127.2	112.3	88.0
Rabbit 268	Turbidimetric			117.3	106.6	90.9
	Gravimetric	265.0	236.5	109.1	97.3	89.0
Rabbit 269	Turbidimetric			91.9	86.0	93.6
	Gravimetric	208.0	189.5	85.6	78.0	91.0
Rabbit 270	Turbidimetric			132.7	117.3	88.4
	Gravimetric	274.0	243.2	112.8	100.1	88.7
Rabbit 271	Turbidimetric			212.0	200.0	94.3
	Gravimetric	599.2	561.2	246.5	230.5	93.6

SENSITIVITY. A difference of 0.25° in the spectrophotometric readings corresponds to about 0.25 mg. of sulfate in 7.5 ml. of urine. In the case of the neutral wedge photometer, a difference of 1 unit (1 mm.) corresponds to about 0.33 mg. of sulfate in 7.5 ml. of urine. Both instruments are calibrated for slightly finer divisions, but the readings given above may be duplicated without difficulty. Although determinations may be made over a greater range with the Leitz instrument, the sensitivity is little more than 1 mg. of sulfate in 7.5 ml. of urine for a difference of 1 unit.

PRACTICAL APPLICATION. The method works well in practice. The urine sulfates of rabbits treated with cyclic compounds were determined by the photometric method and the proportion of the inorganic sulfates was found to have fallen to 10 per cent or less. Upon cessation of the treatment, the inorganic sulfates returned to a normal of 85 to 95 per cent.

The presence of proteins does not interfere measurably with the method, since a solution containing 15 mg. of sulfate and 0.125 ml. of monkey blood serum yielded 15 mg. of sulfate.

Acknowledgment

The writers are indebted to W. Deichmann for carrying out the gravimetric sulfate determinations.

Literature Cited

(1) Cholak, J., IND. ENG. CHEM., ANAL. ED., 7, 287 (1935).

(2) Medes, Grace, and Stavers, Elizabeth, *J. Lab. Clin. Med.*, 25, 624 (1940).

(3) Society of Dyers and Colourists, "Colour Index", 1st ed., p. 99, Bradford, England, 1924.

(4) Treon, J. F., and Crutchfield, W. E., Jr., in preparation.

Ceric Sulfate in the Determination of Iron Using the Molybdisilicic (Silicomolybdic) Acid Method

ALBERT C. TITUS AND CLAUDE W. SILL, University of Utah, Salt Lake City, Utah

THE authors have varied their method for the determination of iron (*3*) by substituting ceric sulfate for potassium dichromate, and have found that *o*-phenanthroline ferrous ion indicator is satisfactory in place of *N*-phenylanthranilic acid in the ceric sulfate runs. The method and general procedure for runs, blanks, and standardizations follow the ideas presented in the earlier paper.

The "stock ferric chloride" and "stock dichromate" were those used in the previous paper. The normality of 0.09733 for the former was taken from that paper. For the normality of the dichromate 0.10058 was used in place of 0.10073 being obtained from pure dichromate from volume ratios of the respective solutions used in titrating the stock ferric chloride by the molybdisilicic acid method. This method of substitution allows cancellation of errors in the procedure and blanks, giving an "absolute" normality.

From the dichromate the ceric sulfate was standardized by another substitution procedure, cancelling out any slight errors (*1*, *4*). The oxidizing solutions were in turn run into potassium iodide and acidified with sulfuric acid, and the iodine liberated was titrated with a sodium thiosulfate solution. From the relative volumes of the latter the normality of the ceric sulfate was obtained, after making a suitable correction for acidity differences.

The ceric sulfate was also standardized against sublimed arsenic trioxide, using osmium tetroxide catalyst and *o*-phenanthroline ferrous indicator. This method gave a normality of 0.09664 for the ceric sulfate, which is somewhat lower than the values of 0.09704 and 0.09697 obtained by the molybdisilicic (suggested by M. B. Mellon as a name preferable to silicomolybdic) acid method at the end and beginning of the work, using the stock ferric chloride whose stated normality was shown in the preceding paper to be absolute and so independent of the method used there. However, the thiosulfate method gave 0.09682 for the ceric sulfate normality. It appears that after application of the blanks the molybdisilicic acid method with ceric sulfate gives slightly too low results for iron, since the volume of ceric sulfate used seemed to be as much as 3 parts in a thousand too low, giving too high a normality above.

In Table I are comparisons of the volumes of ceric sulfate used for the titration of iron, with different indicator combinations. Unless otherwise noted, each figure represents the average of four runs from which no run varies by over 0.02 ml. In untabulated cases the blanks were positive but not over 0.02 ml. It will be noted that nonapplication of the blanks resulted in much better agreement than did application. The blanks for the molybdisilicic acid method and the volumes tabulated are those used in calculating the normalities given above. Had the blanks not been applied for the runs at the beginning of the work the normality would have been 0.09684 in place of 0.09697, a better agreement with the other methods. There is some question as to the real significance of the blanks, especially since their application in the earlier paper resulted in slightly low values for iron as compared with the value by weight. The use of *o*-phenanthroline ferrous indicator appears to be most satisfactory (Table I).

TABLE I. TITRATION OF STOCK FERRIC CHLORIDE WITH CERIC SULFATE[a]

Method	Ceric Sulfate per 45.00 Ml. of $FeCl_3$ *Ml.*	Applied Experimental Blank *Ml.*	Corrected Volume *Ml.*
Molybdisilicic acid, *N*-phenylanthranilic acid (first runs)	45.23 45.23	−0.06 −0.07	45.17 45.16
Same (at end of work)	45.22 45.21	−0.08 −0.08	45.14 45.13
Mercuric chloride[b], *o*-phenanthroline, cold	45.23 45.22	Less than −0.02	... ...
Molybdisilicic acid, *o*-phenanthroline (same directions as with *N*-phenylanthranilic acid)	45.23[c] 45.20	−0.02 −0.02	45.21 45.18

[a] 32 ml. of 1 to 1 H_2SO_4 added in all runs, in addition to equivalent of 8 ml. present in added ceric sulfate volume.

[b] No trouble (*2*) experienced with adsorption of indicator on calomel with small excess of stannous chloride used.

[c] Three runs only.

Literature Cited

(1) Furman and Wallace, *J. Am. Chem. Soc.*, 53, 1283 (1931).

(2) Lang (private communication cited), Oesper, "Newer Methods of Volumetric Analysis", p. 191, New York, Van Nostrand Co., 1938.

(3) Titus and Sill, IND. ENG. CHEM., ANAL. ED., 13, 416 (1941).

(4) Vosburgh, *J. Am. Chem. Soc.*, 44, 2130 (1922).

CONTRIBUTION 68 from the Chemical Laboratories of the University of Utah.

Determination of Phosphorus in Lubricating Oil

HARRY LEVIN, F. P. FARRELL, AND A. J. MILLENDORF
The Texas Company, Beacon, N. Y.

THE increasing use of lubricating oil additives of the organically combined phosphorus type emphasizes the need of a method for phosphorus determination. These additives, which are predominantly organic phosphates (*3*, *12*), phosphites (*13*), and phosphatides (*14*), are employed to improve the service behavior of the lubricating mineral oil with respect to oxidation stability, sludge formation, corrosiveness, and varnishing of engine parts.

Although it is occasionally desirable to know the precise nature of the phosphorus-type additive, this entails the usual lengthy and complex organic analysis which is rendered more difficult by the small amount present in lubricating oil. With samples of this kind one is generally content with detection and determination of the phosphorus, so that the quantity of additive can be calculated when its nature is known.

Of the methods available in the literature for determining phosphorus, the colorimetric and solid volumetric appeared most worthy of investigation because of their speed and simplicity.

The colorimetric methods of Denigès (*2*) and Fiske and Subbarow (*6*) for inorganic phosphorus compounds have been extended by Goodloe (*8*) to the photometric determination of added phosphorus in oils. This author ignites a gram of sample with a like amount of zinc oxide and after appropriate solution of the residue in dilute sulfuric acid, addition of molybdate, and reduction by stannous chloride, measures the intensity of the blue reduced molybdenum solution with an electric colorimeter whose scale is calibrated in terms of phosphorus. The present authors found that this procedure requires a considerable experience and is unreliable on used oils (for which its author, however, had not proposed it), since oils through use may accumulate impurities which, though not phosphorus, also reduce molybdenum. This lack of specificity gave preference to precipitation methods in which phosphorus is a constituent of the precipitate which, unlike the colorimetric method, serves at once for qualitative as well as quantitative determination.

Formation of yellow ammonium phosphomolybdate has long been used for the detection and determination of phosphorus in inorganic materials. Goetz (*4*, *7*, *10*) extended its application to steel by centrifuging the solution and precipitate and estimated the phosphorus from the volume of precipitate. This method appeared attractive because it involves apparatus commonly found in petroleum laboratories, and is the second step in the method finally adopted and used successfully in the authors' laboratories for three years. Recently Piercy, Plant, and Rogers (*11*) described a method for phosphorus in linseed oil and employed a similar centrifuging operation. To convert the phosphorus of the linseed oil to inorganic water-soluble form, these authors ignite 2 grams of oil in a standard Parr oxygen bomb. Though this, in the opinion of the present authors, is a dangerously large sample for ignition in such a bomb [the A. S. T. M. (*1*) recommendation for bomb sulfur being 0.6 to 0.8 gram], it is still much too small for the application of the centrifugal method to many commercial mineral lubricating oils because of their low concentration of phosphorus additives. For the same reason the classical Carius (*16*) method is unsuitable.

In the present method the phosphorus is converted to inorganic soluble form by ignition with sodium naphthenate which is soluble in oil and basic in nature. Ignition with oil-insoluble materials, such as potassium nitrate and potassium hydroxide (*5*) and calcium carbonate (*9*) recommended for other substances, yielded low and unreliable results when applied to lubricating oils, probably owing to loss of organic phosphorus because of lack of sufficiently intimate admixture of the oil and the reacting agent which is insoluble in it. The use of the relatively oil-insoluble sodium stearate likewise yielded low results.

Apparatus

An International Size 2 centrifuge, with special centrifuge tube (Figure 1), equipped with a capillary stem having a capacity of about 0.25 cc. The capillary has an inside diameter of approximately 2 mm., an inside length of about 4 cm., and seven graduations at each 0.030 cc. with subdivisions of five equal spaces.

No. 3 porcelain dishes.

Reagents

Ammonium molybdate prepared (*15*) by dissolving 90 grams of pure ammonium molybdate in 100 ml. of 6 *N* ammonium hydroxide plus sufficient water to effect solution, adding 240 grams of ammonium nitrate, and diluting to 1 liter.

Nitric acid, approximately 5 *N*.

Sodium naphthenate.

Procedure

NEW OILS. Into a No. 3 porcelain dish weigh 5 to 50 grams of sample (depending upon phosphorus content and limited by calibrated stem of centrifuge tube. This range of weight is satisfactory for samples containing 0.001 to 0.100 per cent of phosphorus. Samples of higher concentration have been analyzed by this method modified to use appropriately smaller samples) and approximately 2.5 grams of sodium naphthenate, and dilute to approximately 50 grams with ordinary phosphorus-free mineral oil.

Heat to 150° to 160° C. and keep at that temperature for not less than 2 minutes while stirring with a thermometer. Wipe the bulb of the thermometer with a piece of filter paper and add it to the dish. Ignite and burn until volatile matter is gone and a small amount of carbon is left.

Allow the dish to cool, add 20 ml. of 5 *N* nitric acid, boil gently for 5 minutes to convert pyrophosphates to orthophosphates, and filter into a 100-cc. special centrifuge tube (Figure 1). Wash the dish, sediment, and filter paper with 5 successive small washings of hot water, taking care not to use too much liquid, as the final volume must be 100 ml.

Bring the contents of the centrifuge tube to 50° to 55° C. by placing it in a water bath at that temperature, add 10 ml. of

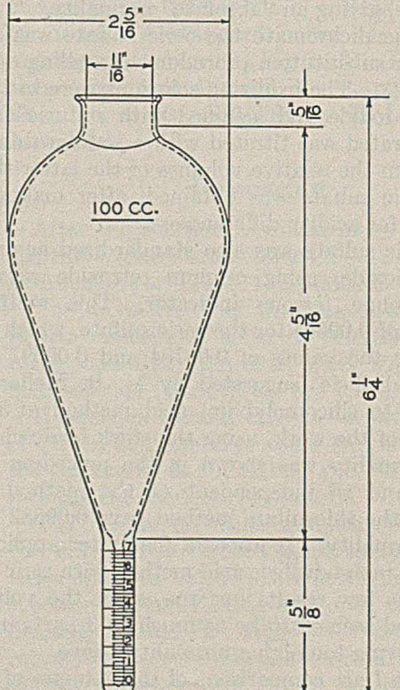


FIGURE 1. CENTRIFUGE TUBE

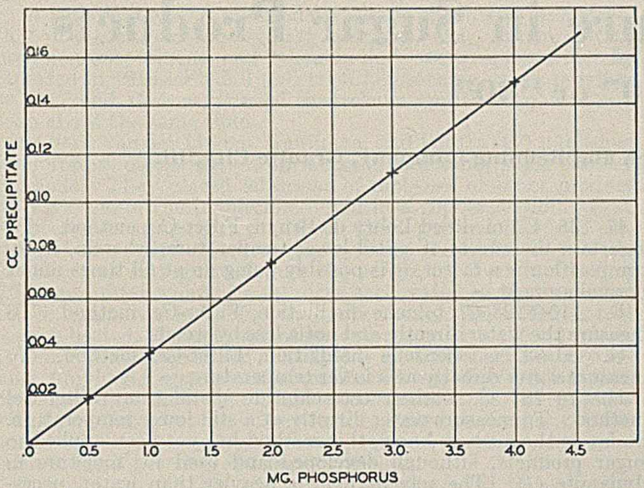


FIGURE 2. GRAPH FOR CALCULATION OF PHOSPHORUS CONTENT

ammonium molybdate reagent, and stir for 5 to 10 minutes. Permit to cool and adjust the volume to 100 ml. by adding water.

Centrifuge for 10 minutes at 2000 r. p. m. If the volume of precipitate is difficult to read, owing to uneven surface, stir the surface with a fine, clean platinum wire, recentrifuge the tube for 1 to 2 minutes, and read the volume.

Determine the amount of phosphorus by reference to Figure 2, which was prepared from tests on known solutions of lecithin in oil and confirmed by direct precipitation of standard solutions of disodium phosphate.

USED OILS. Through use, lubricating oils commonly become contaminated with metals, salts, and soaps of lead, copper, aluminum, iron, and tin. To determine the organically combined phosphorus still present in solution in the oil, a sample is clarified by centrifuging.

Some soluble heavy metal (lead, etc.) salts or soaps in solution in the oil used for phosphorus determination would cause high results, due to formation of insoluble heavy metal molybdates. Therefore, the ash resulting from burning the clarified used oil with sodium naphthenate is treated in the following manner:

Carefully add approximately 10 ml. of concentrated hydrochloric acid to the ash, covering the dish with a watch glass to prevent loss through spattering. After washing spattered material from the watch glass into the dish, evaporate the solution to dryness on a steam bath and add 20 ml. of 0.3 *N* hydrochloric acid. Warm the acid solution and saturate with hydrogen sulfide to precipitate the copper, lead, and tin. Eliminate the excess of hydrogen sulfide by heating the solution and then filter through paper (Whatman No. 44) and wash thoroughly with approximately 50 ml. of hot water. Evaporate the combined filtrate to dryness, add 20 ml. of 5 *N* nitric acid, and filter the solution into the special centrifuge tube. The presence of soluble iron and aluminum salts does not interfere. The procedure from this point is identical with that used for the determination of phosphorus in new oil.

When this method was applied to mineral lubricating oils to which known amounts of organic phosphorus compounds (additives) had been added, the results shown in Tables I and II were obtained, from which the accuracy and the precision of the method can be seen. The additives contained 2 to 10 per cent of combined phosphorus.

The last three samples (Table I) contain many times the phosphorus found in modified lubricating oils. Though good results were obtained, the method is not particularly recommended for products so high in phosphorus, because very small samples must be used.

Experience indicates that approximately 1 hour of a man's applied time and 2 hours of elapsed time are required for a single sample tested in duplicate. The method is very suitable for routine mass testing.

The qualitative value of the test is indicated by the fact that samples (25 grams) containing 0.00003 per cent of organically combined phosphorus consistently gave a precipitate though it was too little for quantitative purposes. Samples containing 0.00001 per cent of phosphorus did not consistently give a precipitate but the solution always was yellow compared to a blank test.

Summary

A simple accurate method for determining organically combined phosphorus in lubricating oil involves ignition of the sample with sodium naphthenate which serves to bind the phosphorus in inorganic water-soluble form. The water solution of the phosphate is reacted to form ammonium phosphomolybdate, which is centrifuged, and the phosphorus is calculated from the volume of precipitate.

The method has been used for over three years, during which it has been applied satisfactorily to new and used lubricating oils containing phosphorus organically combined as phosphate, phosphite, and phosphatide.

TABLE I. DETERMINATION OF PHOSPHORUS IN OILS

Sample	Phosphorus Present	Phosphorus Found	Sample	Phosphorus Present	Phosphorus Found
	%	%		%	%
1	0.001	0.001	10	0.025	0.025
2	0.002	0.002	11	0.025	0.025
3	0.003	0.003	12	0.025	0.024–0.024
4	0.005	0.005	13	0.050	0.048–0.048
5	0.010	0.010	14	0.050	0.049–0.051
6	0.010	0.010	15	0.092	0.093
7	0.011	0.011	16	3.00	2.98
8	0.011	0.012	17	4.00	3.98
9	0.022	0.023	18	5.00	5.00

TABLE II. DETERMINATION OF ADDITIVE (PHOSPHORUS TYPE)

Sample	Additive Present	Additive Found	Sample	Additive Present	Additive Found
	%	%		%	%
1	0.06	0.06	8	0.21	0.21
2	0.09	0.09	9	0.25	0.25
3	0.10	0.10	10	0.25	0.25
4	0.10	0.10	11	0.50	0.52
5	0.10	0.10	12	0.50	0.53
6	0.10	0.10	13	1.00	1.03
7	0.10	0.12			

Acknowledgment

The authors express their appreciation for the assistance of A. E. Burch and W. W. Johnson, who made many of the determinations.

Literature Cited

(1) American Society for Testing Materials, Standards on Petroleum Products and Lubricants, p. 238, Sept., 1940.
(2) Denigès, G., *Mikrochemie* (Pregl Festschr.), 27–45 (1929).
(3) du Pont de Nemours & Co., E. I., French Patent 790,666 (1935).
(4) Eggertz, V., *J. prakt. Chem.*, 79, 496 (1860).
(5) Elek, A., *J. Am. Chem. Soc.*, 50, 1213–14 (1928).
(6) Fiske and Subbarow, *J. Biol. Chem.*, 66, 375–400 (1925).
(7) Goetz, G. W., and Wedding, H., *Stahl u. Eisen*, 7, 118 (1887).
(8) Goodloe, IND. ENG. CHEM., ANAL. ED., 9, 527–9 (1937).
(9) Howk, B. W., with DeTurk, E. E., *Ibid.*, 4, 111 (1932).
(10) Lundell, Hoffman, and Bright, "Chemical Analysis of Iron and Steel", p. 226, New York, John Wiley & Sons, 1931.
(11) Piercy, Plant, and Rogers, IND. ENG. CHEM., ANAL. ED., 12, 165 (1940).
(12) Standard Oil Development Co., British Patent 465,825 (1937).
(13) Texas Co., assignee of Ashburn, H. V., Conary, R., and Stutsman, P., U. S. Patent 2,226,543 (Dec. 31, 1940).
(14) Texas Co., Hall, F. W., and Towne, C. C., Serial No. 223,487, co-pending application of U. S. Patent 2,221,162 (Nov. 12, 1940).
(15) Treadwell and Hall, "Analytical Chemistry", 7th ed., Vol. 2, p. 382, New York, John Wiley & Sons, 1930.
(16) *Ibid.*, 8th ed., Vol. 2, p. 303, 1935.

PRESENTED before the Division of Petroleum Chemistry at the 102nd Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J.

Determination of Moisture in Sugar Products

Corn Sugar "70" or "80"

J. E. CLELAND AND W. R. FETZER, Union Starch and Refining Company, Granite City, Ill.

THE first paper of this series (*17*) dealt with moisture determination in corn sirup and corn sugar by the filter paper method. An average analysis of confectioners' corn sirup was given, since all manufacturers produce a product with essentially the same composition. However, the composition of crude corn sugar varies considerably, not only in dextrose equivalent (reducing sugars as dextrose, dry substance basis), but in residual constituents, such as acidity, protein, and ash, which are also present in greater amounts in corn sugar than in corn sirup. The composition of these crude sugars can be expressed best by tabulation of the range of values for the critical tests usually made on them (dry basis):

Reducing sugars as dextrose	82 to 92
Residual acidity as hydrochloric acid	0.02 to 0.04
Crude protein	0.06 to 0.15
Ash	0.8 to 1.5

The crude sugars, either chipped or in billet form, are generally sold in two grades: "70" corn sugar, containing not less than 70 per cent reducing sugars as dextrose, and "80" corn sugar, containing not less than 80 per cent reducing sugars as dextrose.

Although the filter paper method has been found satisfactory for numerous samples analyzed, occasional samples show apparent instability at 100° C. in vacuum. This is manifested by a tendency to lose weight very slowly, at a rate which would be neglected normally, but which would not be called a drying "plateau" as exhibited by corn sirup. This condition calls for an arbitrary definition of constancy, which is not regarded as a satisfactory basis for true moisture. Such a corn sugar has been the subject of many drying techniques, in an attempt to establish a method applicable to all corn sugars.

The following test made on an "80" sugar is an example of this slow "creep" or failure to reach a definite moisture plateau. The procedure was the Filter-Cel method (*9*) carried out at 100° C. in a Weber oven with a pressure of 1 mm. or less.

Elapsed Time	Sample Weight		Moisture	
Hours	*Grams*	*Grams*	%	%
4	20.5235	21.6140	50.00	50.02
19			50.16	50.15
24			50.18	50.18
29			50.27	50.27
73			50.85	50.87

Constancy of weight normally would be stated to occur in the period from 19 to 24 hours and such deviation usually would be passed over. However, there is no question that decomposition occurs later. This casts a shadow of doubt over the assumption that constancy occurs earlier, as a very slow decomposition might be taking place.

In order to eliminate any shadow of doubt, a series of tests was employed as follows:

A. 100° C., air oven, Filter-Cel method. To ascertain whether the vacuum was removing a possible volatile constituent.

B. 100° C., vacuum oven, Filter-Cel method. Short intervals of drying to see if constancy could be attained within reasonable limits.

C. 100° C., vacuum oven, Filter-Cel method. Extended period of drying to estimate the amount of decomposition.

D. 80° C., vacuum, Filter-Cel method. To find the effect of a lower temperature.

E. 38° C., modified Lobry de Bruyn, Filter-Cel method. To ascertain the effects of a still lower temperature, wherein, if decomposition is a factor, it is possibly going on at all times under normal storage.

F. 110–112° C., toluene distillation, Filter-Cel method. To measure the water directly and not a loss by weight.

G. 80–82° C., benzene distillation, Filter-Cel method. To measure water directly at a lower temperature.

H. 76–78° C., carbon tetrachloride distillation, Filter-Cel method. To measure water directly at a still lower temperature. So far as the authors know, this method has not been applied to sugar products, although developed and used for moisture in dynamite (*1*). The solvent here is heavier than water, necessitating a different type of trap. This type of trap offers mechanical disadvantages for similar development of the new bulb types of traps which have been successfully employed with benzene and toluene.

The data obtained on corn sugar for tests mentioned above appear in Table I.

With the exception of the benzene and carbon tetrachloride distillation methods, all have been described in previous papers of this series. Since the determination of true moisture in corn sugar has been obtained in part by correlation of distillation methods to gravimetric methods, a review of the development of the former will be given.

Historical

The literature on moisture determination reveals that a great deal of attention has been devoted to distillation methods. A large number of organic liquids, covering a wide range of boiling points and densities, have been proposed and used with many materials. For general purposes, the most useful ones appear to have been benzene and its homologs, toluene and xylene. Others extensively used are carbon tetrachloride and the lighter fractions of petroleum.

Hoffmann (*24*) in 1908 presented an interesting résumé of work on distillation up to that time. Attention was called to the fact that a German patent was granted in 1901 on a process for the determination of water in solids and liquids by distillation. The substance to be examined was either distilled with a liquid immiscible with water but with a higher boiling point or heated with such a liquid and then distilled with another liquid, likewise immiscible with water but with lower boiling point. In either case, the water collected in the distillation was measured. The method was originally designed for analysis of cereals and cereal products, and employed such liquids as petroleum fractions and toluene. It was quickly varied to make application to other substances by Gray (*23*), to other foods by Thorner (*41*), to cellulose products by Schwalbe (*36*), and to lignite by Gräfe (*22*). These investigators used a wide range of liquids immiscible with water.

Hoffmann presented data on hops, showing that the distillation process with turpentine and toluene gave results which very closely agreed with those obtained by older methods of drying *in vacuo* with phosphorus pentoxide or in drying chambers at 80° C. The author stated that for any substance in which water is to be determined, at least one of the ten variations of the method mentioned in the article will be found suitable.

Marcusson (*28*) worked with oils, fats, soaps, etc. (in 1905), and used xylene or benzene as his immiscible liquids. Testoni (*40*) made determinations on molasses by distillation in 1904.

Schwalbe (*36*) in 1908 reported the application of the distillation method to plant materials. "In examination of dense materials, it is important to select for the liquid of high boiling point one such that the tension of the aqueous vapor above 100° may be great enough to enable the bubbles of steam to overcome the resistance of passing through the mass." Many workers appear to have taken this view also, but it is not necessarily true with adequate dispersion.

In 1910 Sadtler (*35*) reported on the use of benzene for distillation of water from cheese, egg albumen, etc. Folpmers (*20*) used benzene, toluene, and xylene in his work on spices which he reported in 1916. Sindall (*39*) tried kerosene on spices previous to 1917 and Besson (*4*) used "petroleum spirit" on cheese and soap about the same time.

In 1917, van der Linden, Kauffman, and Leistra (*27*) published their results of distillation on molasses and other sugar factory products. They placed 50 grams of molasses or other product with 350 cc. of the immiscible liquid in a copper distilling flask connected to an upright condenser, the lower end of which discharged into a 250-cc. measuring cylinder graduated to 0.05 cc. Heating was so regulated that 100 cc. passed over in the first 0.75 hour, after which the rate was accelerated so that a second 100 cc. came over in the fourth quarter hour. When 200 cc. had been collected, the determination was assumed to be complete.

These workers observed that xylene gave very satisfactory results, provided a certain rate of distillation was observed, but that prolonged heating would cause decomposition of the product with formation of water. They further stated that other volatile immiscible liquids, such as benzene, toluene, kerosene, and mixtures of these gave less satisfactory results.

It would appear that the earlier workers failed to make the liquids of lower boiling point work satisfactorily on viscous materials because of apparatus limitations and no sample dispersion. The Dean and Stark (*12*) "distilling receiver tube" had not been developed nor had the improvements in dispersion due to Rice (*33*) and Fetzer, Evans, and Longenecker (*19*) made their appearance.

The development of the Dean and Stark device, which permits continuous refluxing and separation of the water, was a great forward step, as it provided means of removing the last traces of water efficiently. In 1925, Bidwell and Sterling (*5*) improved the design for precise work and their well-known "traps" are now standard equipment.

Norman (*32*) presented work on fats, oils, soaps, etc., in 1925 and drew attention to a special still head provided with a built-in reflux condenser of simple design to permit continuous refluxing. Accurate results were claimed and the use of benzene instead of xylene was recommended.

Yamada and Koshitaka (*43*) modified Norman's apparatus and recommended it for water determination of crude camphor in 1927. It was claimed that adhesion of condensed water on the wall of the still head can be completely avoided by a special still head with built-in reflux condenser having an inverted part at its end. The use of toluene or xylene was recommended instead of benzene for camphor.

In 1926, Dedlow and Smith (*13*) found that xylene distillation caused decomposition when applied to meat extract and successfully modified the method by conducting the distillation with xylene under vacuum. This is an interesting variation and gives a flexibility which should prove useful for many products, although it is a little complicated for routine work.

In 1936, Alexander (*1*) reported on an interesting variation in which a volatile liquid heavier than water—i. e., carbon tetrachloride—was used with a special tube adapted to the reverse of usual conditions. The paper stated that the method has long been in use in laboratories of the Hercules Powder Company for routine moisture determinations on dynamite. This liquid has some advantages, notably nonflammability. It has been investigated in this laboratory on corn sirup and corn sugar and results are reported below.

In 1929, Rice (*33*) contributed much to the successful operation of the distillation method for sugar products by placing Filter-Cel in the distillation flask and running the sirup in on top. This very useful technique was further developed in 1935 by Fetzer, Evans, and Longenecker (*19*) to apply to extremely viscous materials, such as high-gravity corn sirup. Trusler (*42*) in 1940 presented a very interesting study which reported on the use of benzene, toluene, and xylene with soaps.

The literature reveals that the method has been applied to mineral, vegetable, and animal oils, fats, sulfonated oils, camphor, tars, meat extract, cheese, eggs, cereals and cereal products, cellulose products, spices, hops, coal, fruits, sugar refinery products, corn products, tobacco, and many others, with varying degrees of success. Many ingenious improvements have been made and development has carried it to rather high precision but it appears to be ignored or neglected frequently under conditions where it might be of great use.

Among other contributions to the subject of moisture determination by distillation are:

Blythe (*6*), sulfonated oils; Barber (*3*), sulfonated oils by 100° oven, paraffin, benzene, toluene, gasoline, and xylene; Bakker and Stunhauer (*2*), foods and spices; Boller (*7*), determination of water with hydrocarbons; Cone and Davis (*10*), tobacco; Calderwood and Piechowski (*8*), technique; do Couto (*11*), oils and tar; Dohmer (*15*), case-hardening materials; Drefahl (*16*), wood preservatives; Fuchs (*21*), benzene method for mineral oils; Feder (*18*), methods proposed for sausages; Holtappel (*25*), foods with xylene; Jones and McLachlan (*26*), moisture by the toluene method; Myhill (*31*), coals with benzene, toluene, and xylene; Michel (*30*), foods; Marcusson (*28*, *29*), lubricating greases (among earliest papers); Sindall (*38*, *39*), distillation method recommended for spices; Rogers (*34*), leather with toluene; Schwalbe (*37*), further work on cellulose products; and DeLoureiro (*14*), improvements in technique.

Table I. Data on Corn Sugar

Test	Sample Weight		Elapsed Time	Moisture	
	Grams	*Grams*	*Hours*	%	%
A	10.8855	11.8616	16	49.58	49.61
			60	49.80	49.82
			84	49.90	49.91
			129	50.12	50.11
B	11.7250	10.4780	2	47.76	48.51
			4	49.53	49.55
			6	49.62	49.64
			8	49.65	49.67
			12	49.65	49.67
C	15.7759	13.9630	15	49.63	49.63
			60	49.85	49.96
D	14.0200	15.2040	15	49.63	49.65
			22	49.64	49.66
			37	49.65	49.67
			52	49.65	49.67
E	13.2823		100	49.50	
			300	49.60	
			500	49.62	
			600	49.64	
			700	49.64	
F	46.5593	46.5225	10	49.62	49.63
			15	49.63	49.64
			22	49.67	49.76
			52	50.41	50.40
G	35.6202	36.8530	12	49.66	49.68
			18	49.66	49.68
			50	49.66	49.68
			70	49.66	49.68
H	The common sample of sugar used for the above tests could not be used for carbon tetrachloride distillation, as the apparatus available was the standard Hercules distillation traps of 6-ml. capacity. Accordingly a heavier gravity of sugar was used. In the employment of dispersion for carbon tetrachloride distillation, the technique must be altered from that followed for benzene and toluene. The amount of Filter-Cel must be reduced, as the mass requires more space because of more vigorous agitation of carbon tetrachloride. In calibration of the traps, the amount of water recovered is never the full volume added. The blank is high, amounting to +0.14 ml. for the apparatus employed. Otherwise, the procedure followed was that of Alexander (*1*). With the common sugar products tested, water recovery was more rapid and completed in less time as compared to benzene distillation. The data obtained were:				

80° C. Vacuum Oven		Carbon Tetrachloride Distillation	
%	%	%	%
20.19	20.21	20.18	20.23

The method may be said to suffer from two faults. One would seem to be inadequate appreciation of the importance of dispersion of viscous materials and the second, a tube design which limits size of samples in precise work.

Experimental

For this test, a corn sugar sirup, 90.7 per cent dextrose equivalent, was made, 26.45° Bé. (Bé. = Bé. 140°/60° F. + 1.00), adjusted to pH 5, carefully divided into samples in 120-ml. (4-ounce) bottles, fitted with screw caps lined with wax paper. These were placed in the refrigerator for subsequent analysis, one bottle being used for each analysis.

The moisture traps of the usual Bidwell and Sterling design have a capacity of 5 ml. in 0.1 ml. The outside diameter is approximately 10 mm. in order to obtain relatively large intervals for each 0.1-ml. division—essentially a microburet.

Larger traps (10-ml.) are obtained by increasing the diameter of the trap but with attendant sacrifice of precision in reading the meniscus; 10-ml. traps are the largest type practical for the usual apparatus. The small traps limit the test to materials containing comparatively small amounts of water, whereas it is de-

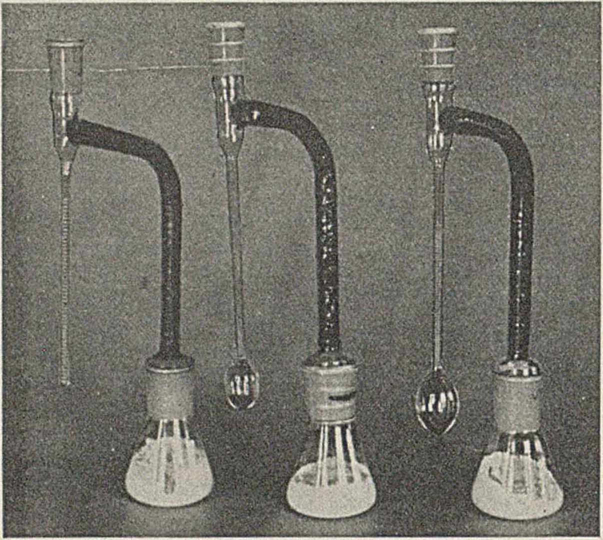


Figure 1. Moisture Traps

sirable in the interest of experimental precision to use large samples. Materials such as sirups, containing relatively large percentages of water, require a small amount of sample for 5- and 10-ml. traps, with a corresponding decrease in precision.

The usual 5-ml. traps were altered to include an ovoid bulb at the bottom (Figure 1). The bulbs chosen for sirup work were 15-, 20-, and 30-ml., blown on the usual 5-ml. (in 0.1-ml.) receivers, giving a total trap capacity of 20, 25, and 35 ml.

These traps have been used with a great deal of success. In order to enable the water to run freely into the bulb, special precautions must be observed in cleaning them: Scour with a cleanser powder (Dutch Cleanser), employing hot water and a small tube brush. Close the bottom opening and fill the trap with warm bichromate–sulfuric acid cleaning solution. Allow to stand a few hours, rinse well with distilled water, fill trap with 2 per cent sodium or potassium hydroxide solution (*14*), and allow to stand for a short period. Rinse thoroughly, drain, and dry by means of a radiant infrared lamp, which has been found more successful than an alcohol or ether wash.

Benzene Distillation

Benzene distillation presents a mixing problem when applied to a Filter-Cel sirup mass, particularly in the case of viscous corn sirup, where mixing must be thorough if the water is to be removed quickly and completely. The azeotropic binary mixture of benzene and water starts to boil around 69° C. It is therefore necessary to guard against evaporation during incorporation of Filter-Cel and sirup. This was accomplished by slipping a length of Gooch filter rubber tubing over the neck of the flask, then passing the stirring rod through and wiring the tubing to the stirring rod. The rubber tubing provides a flexible joint for stirring the Filter-Cel sirup mass and no vapor is lost from the flask.

In this work, all the traps were calibrated by distillation of weighed quantities of water as in an actual determination.

Apparatus. Distillation flask, 250-ml. standard flask (*9*), used throughout this work for distillation and vacuum oven work.

Benzene, Mallinckrodt, analytical reagent grade.

Filter-Cel, prepared as previously described (*9*).

Procedure. Approximately 30 grams of prepared Filter-Cel are run into a distillation flask, and brought to a constant weight in a vacuum oven (usually 4 hours). The sample is run on top of the Filter-Cel and reweighed for sample weight, then incorporated with the Filter-Cel. Then 100 ml. of benzene are run into the flask, which is fitted with rubber closure (described above), and Filter-Cel, sample, and benzene are thoroughly worked into a homogeneous mass. The flask is connected with the trap and condenser, and distillation is started gradually—2 drops per second. Ninety per cent of the water is removed within an hour, after which the rate of distillation is increased to 4 drops a second. After constancy has been attained, the trap water is brought to 20° C. and read. Large traps require considerable care in this operation, as do pycnometers, and the technique is much the same.

The data indicate that on a corn sugar which does admit of decomposition with prolonged heating, a value equal to or deviating by very little can be obtained by the Filter-Cel method, provided the time element is 8 to 12 hours from the air oven at 100° C., vacuum oven at 100° C., and toluene distillation. Vacuum oven at 80° C., Lobry de Bruyn at 38° C., and benzene and carbon tetrachloride distillations—all Filter-Cel methods—yield drying plateaus which are maintained for periods that extend beyond any anticipated moisture test and weight constancy can be regarded as true moisture.

The distillation methods as applied to sirups cannot be relied upon unless the material is dispersed over a large surface. Direct use of the solvents without dispersion will lead to erroneous results, either through failure to obtain the release of all the moisture, or by decomposition, which may be initiated in the mass by a delayed elimination of the water.

In order to complete the picture of moisture methods as applied to hydrolytic products of starch, a sample of corn sirup was rerun to include the benzene–Filter-Cel distillation, with results as follows:

° *C.*			A %		B %	
			(1)	(2)	(1)	(2)
100	Vacuum oven	Filter-Cel method	19.11	19.11	31.99	3.197
38	Lobry de Bruyn	Filter-Cel method	19.10	...	...	...
110–112	Toluene distillation	Filter-Cel method	19.12	19.11	...	...
80– 82	Benzene distillation	Filter-Cel method	19.09	19.10	...	...
76– 78	Carbon tetrachloride distillation	Filter-Cel method	...	...	31.96	31.97

Conclusions

Three methods have been recommended for determination of true moisture of crude corn sugar:

80° C. vacuum oven, Filter-Cel method.
38° C. Lobry de Bruyn, Filter-Cel method.
80–82° C. benzene distillation, Filter-Cel method.

The increased capacity of the type of receiver tube designed for this work permits much greater precision because of larger sample weights employed. The authors consider this practically essential in a research which aims at true moisture.

Dispersion is greatly facilitated by dilution and the use of large samples, where the purpose of the work is to determine stability of soluble materials such as viscous sugar sirups.

The 80° C. vacuum oven, Filter-Cel method, has been adopted for determination of moisture in "80" corn sugars by the Technical Advisory Committee of the Corn Industries Research Foundation.

The so-called "70" sugars are often difficult by oven methods and in these cases the value of benzene distillation is stressed. Some tanners' sugars ("70") decompose fairly rapidly at 100° C. and stubbornly retain lost traces of moisture at 80° C. In these cases a vacuum oven temperature of 90° C. is recommended as results at this level are most reproducible and check benzene distillation or the modified Lobry de Bruyn method at 38° C.

Stability of corn sugar on drying is dependent upon the pH of the material. Maximum stability is attained between pH 4.5 and 5.5. Precautions also should be observed in moisture tests on tanners' corn sugar. These bleached sugars often contain as high as 1500 p. p. m. of sulfur dioxide and are subject to "creep" in drying. Ash content is also often a factor in the stability of the corn sugar in drying. The above data have been obtained on standard hydrolytic products of starch with normal ash contents.

Literature Cited

(1) Alexander, H. B., Ind. Eng. Chem., Anal. Ed., 8, 314 (1936).
(2) Bakker, C., and Stunhauer, A. J., *Chem. Weekblad*, 19, 285 (1922).
(3) Barber, C. F., *J. Soc. Leather Trades' Chem.*, 3, 206 (1919).

(4) Besson, A. A., *Schweiz. Apoth. Ztg.*, 55, 69 (1917).
(5) Bidwell, G. L., and Sterling, W. F., Ind. Eng. Chem., 17, 147 (1925).
(6) Blythe, J. R., *J. Soc. Leather Trades' Chem.*, 3, 101 (1919).
(7) Boller, W. H., *Chem.-Ztg.*, 52, 721 (1928).
(8) Calderwood, H. N., and Piechowski, R. J., Ind. Eng. Chem., Anal. Ed., 9, 520 (1937).
(9) Cleland, J. E., and Fetzer, W. R., *Ibid.*, 13, 858 (1941).
(10) Cone, R. M., and Davis, L. H., *Ibid.*, 9, 219 (1937).
(11) Couto, A. V. do, *Chimica Industria* (Italy), 3, 462 (1928).
(12) Dean, E. W., and Stark, D. D., J. Ind. Eng. Chem., 12, 486 (1920).
(13) Dedlow, C., and Smith, D. T., *Ibid.*, 18, 858 (1926).
(14) DeLoureiro, J. A., *J. Assoc. Official Agr. Chem.*, 21, 645 (1938).
(15) Dohmer, P. W., *Z. angew. Chem.*, 51, 725 (1927).
(16) Drefahl, L. C., *et al.*, *Proc. Am. Wood Preservers' Assoc.*, 1926, 38–77.
(17) Evans, J. W., and Fetzer, W. R., Ind. Eng. Chem., Anal. Ed., 13, 855 (1941).
(18) Feder, E., *Z. Nahr. Genussm.*, 37, 265–78 (1919).
(19) Fetzer, W. R., Evans, J. W., and Longenecker, J. B., Ind. Eng. Chem., Anal. Ed., 5, 81 (1933).
(20) Folpmers, T., *Chem. Weekblad*, 13, 14 (1916).
(21) Fuchs, F. C., *Eng. Mining J.*, 106, 357 (1918).
(22) Gräfe, E., *Braunkohle*, 5, 581 (1906).
(23) Gray, C. A., *Z. angew. Chem.*, 21, 890 (1908).
(24) Hoffmann, J. F., *Ibid.*, 21, 2095 (1908).
(25) Holtappel, K. J., *Pharm. Tijdschr. Nederland. Indië*, 3, 247-61 (1927).
(26) Jones, J. M., and McLachlan, T., *Analyst*, 52, 383–7(1927).
(27) Linden, T. van der, Kauffman, M., and Leistra, F., *Arch. Suikerind.*, 25, 951 (1917); *Analyst*, 43, 221 (1918).
(28) Marcusson, J., *Mitt. kgl. Materialprüfungsamt Gross-Lichterfelde West*, 22, 48 (1904); *Z. angew. Chem.*, 18, 754 (1905).
(29) Marcusson, J., *Mitt. kgl. Materialprüfungsamt Gross-Lichterfelde West*, 23, 58 (1905).
(30) Michel, Franz, *Chem.-Ztg.*, 37, 353 (1913).
(31) Myhill, A. R., *Gas. J.*, 150, 21 (1920).
(32) Norman, W., *Z. angew. Chem.*, 38, 380 (1925).
(33) Rice, E. W., Ind. Eng. Chem., 21, 31 (1929).
(34) Rogers, Bur. Chem., *Bull.* 137, 172 (1910).
(35) Sadtler, S. S., J. Ind. Eng. Chem., 2, 66 (1910).
(36) Schwalbe, C. G., *Z. angew. Chem.*, 21, 2311 (1908).
(37) *Ibid.*, (I) 32, 125 (1919).
(38) Sindall, H. E., *J. Assoc. Official Agr. Chem.*, (2) 2, 197 (1917).
(39) *Ibid.*, 3, 427–8 (1920).
(40) Testoni, G., *Staz. sper. agrar. ital.*, 37, 366; *Chem.-Zentr.* (2), 75, 562 (1904).
(41) Thorner, W., *Z. angew. Chem.*, 21, 148 (1908).
(42) Trusler, R. B., Ind. Eng. Chem., Anal. Ed., 12, 509 (1940).
(43) Yamada, S., and Koshitaka, T., *J. Soc. Chem. Ind.* (Japan), 30, 356 (1927).

Refiners' Sirup, Final Molasses (Blackstrap), and Hydrol

The success of the new moisture methods, previously described for the hydrolytic products of starch (*1–4*), caused the investigation to be extended to more troublesome sugar refinery products, such as refiners' sirup, blackstrap molasses, and hydrol, the molasses from the manufacture of dextrose. It is impossible, of course, to cover the complete range of such products, and those used for testing were considered typical. It is recognized that a more thoroughly exhausted blackstrap or material which had been subjected to inimical manufacturing conditions might not be comparable to the materials studied.

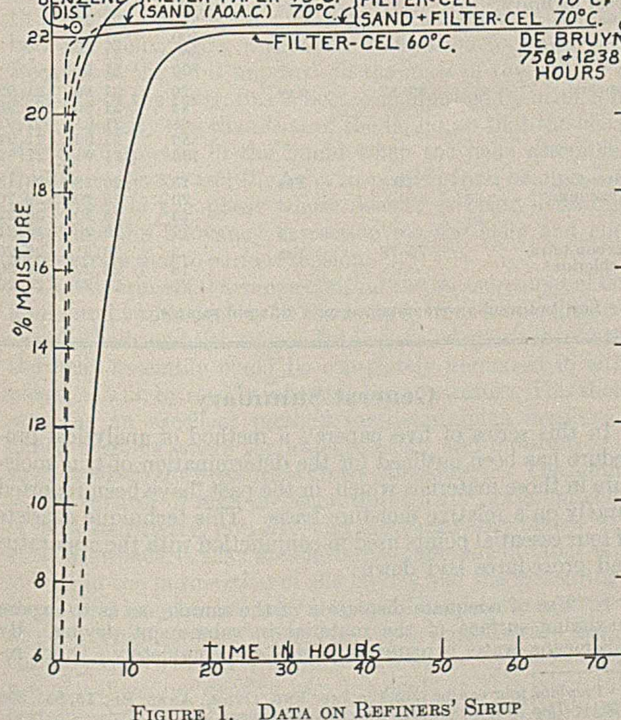


Figure 1. Data on Refiners' Sirup

The methods used have previously been discussed in detail (*1–4*). The A. O. A. C. sand method was used for comparison but altered in order to make it more workable. The moisture dish was aluminum with a tight-fitting cover. After the first weighing of the dried sample, the dish was closed tightly with the cover, inverted, and in order to loosen the sand, the bottom was tapped sharply with a spatula handle. Then the contents of the dish were shaken to assure a free-flowing material with a maximum exposure of surface. Constant weight was defined as a change of 1 mg. or less per 3-hour heating interval.

Refiners' Sirup

The sample used has the following analysis based on dry substance:

	%
Sucrose	44.20
Invert	47.10
Ash	2.70
Organic nonsugars	6.00

The data obtained are given in Table I and Figure 1.

At 70° C. in vacuum, the Filter-Cel method attained constancy. This value was checked by the following methods: filter paper, A. O. A. C., A. O. A. C. modified, A. O. A. C. sand and Filter-Cel mixture, modified Lobry de Bruyn Filter-Cel method, 38° C., and benzene Filter-Cel distillation. Data at 100° C., the Filter-Cel method in vacuum, and toluene distillation show evidence of decomposition.

Final Molasses (Blackstrap)

The molasses used in this test had the following analysis, dry-substance basis:

	%
Sucrose	44.08
Invert	22.62
Ash	12.93
Organic nonsugars	16.37

The data obtained appear in Table II and Figure 2.

Since the toluene distillation and 100° C. Filter-Cel method in vacuum gave decomposition on refiners' sirup, they were not tried on blackstrap, which is more susceptible to decomposition. The benzene distillation–Filter-Cel method; 70° C.

Table I. Data on Refiners' Sirup

Method	Temperature ° C.	Constancy	Time Hours	Moisture %	Moisture %
A. O. A. C. sand, vacuum	70	Doubtful	10	22.32	22.31
			14	22.30	22.32
			18	22.32	22.35
Filter paper, vacuum	70	Yes	8	22.32	22.31
			12	22.32	22.31
Filter-Cel, vacuum	60	No	70	22.22	22.23
Filter-Cel, vacuum	70	Yes	20	22.32	22.31
			25	22.33	22.34
			35	22.33	22.34
Filter-Cel plus sand, vacuum	70	Yes	15	22.30	22.32
			30	22.34	22.34
			39	22.34	22.35
Benzene	80–82	Yes	12	22.25	22.26
			20	22.29	22.31
			30	22.29	22.31
Lobry de Bruyn, vacuum	38	Yes	758	22.27	22.29
			1238	22.27	22.29
Filter-Cel, vacuum	100	No	8	22.92	23.04
			13	23.38	23.38
			18	23.66	23.71
Toluene	110–112	No	6	23.35	23.37
Filter-Cel, vacuum[a]	70	Yes	15	22.25	22.25
			21	22.25	22.26
			29	22.25	22.26
Carbon tetrachloride[a]	76–78	Yes	3	22.21	22.24
			18	22.21	22.24
			30	22.21	22.24

[a] The last two results were obtained months later and samples had lost some water during storage.

Table II. Data on Blackstrap Molasses

Method	Temperature ° C.	Constancy	Time Hours	Moisture %	Moisture %
A. O. A. C. sand, vacuum	70	Yes[a]	20	28.50	28.51
			23	28.52	28.55
			26	28.52	28.55
Filter-Cel, vacuum	70	Yes[a]	21	28.57	28.57
			24	28.57	28.57
			27	28.57	28.57
Lobry de Bruyn	38	Yes	800	28.57	28.54
			900	28.57	28.54
Benzene	80–82	Yes	3	28.55	28.57
			18	28.55	28.57
Filter-Cel, vacuum	70	Yes	6	27.58	27.59
			12	27.60	27.60
			18	27.60	27.60
Carbon tetrachloride	76–78	Yes	3	27.62	27.61
			18	27.63	27.62

[a] Constancy was obtained by employing 3-hour heating intervals. Tests employing louger heating intervals failed to achieve constancy with final values exceeding Lobry de Bruyn values.

Filter-Cel vacuum; A. O. A. C. modified sand; and Lobry de Bruyn–Filter-Cel method at 38° C. all checked, indicating that the value obtained was probably the true moisture of the sample.

Hydrol

The hydrol which was tested had the following composition, dry-substance basis:

	%
Reducing sugars as dextrose	73.1
Dextrose (Sichert-Bleyer)	59.0
Ash	7.25
Crude protein	0.37

The data obtained are given in Table III. Again, close agreement was obtained. However, sufficient samples of hydrol have not been analyzed to state whether the moisture can be determined in all hydrol by the benzene–Filter-Cel method or by the 70° C. vacuum oven–Filter-Cel method.

Conclusions

Various moisture methods for determination of moisture in sugar by-products have been compared.

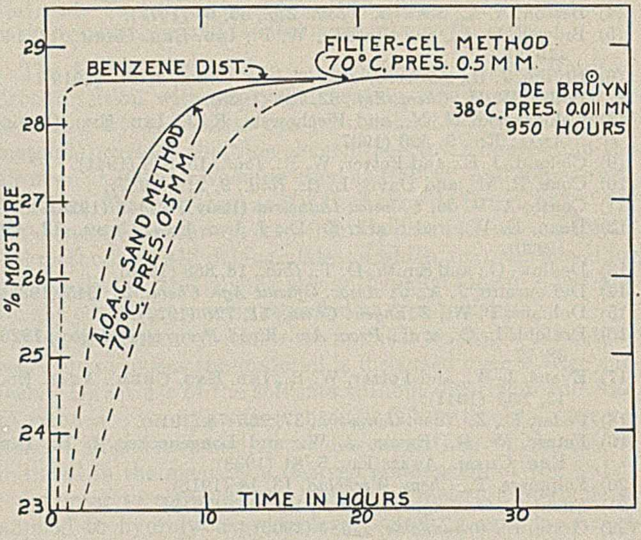


Figure 2. Blackstrap Molasses

For determination of moisture, the 70° C. vacuum oven–Filter-Cel and the benzene distillation–Filter-Cel methods are recommended, except in possible cases where constancy cannot be attained by these. Recourse is had then to calibration by means of the modified Lobry de Bruyn–Filter-Cel method at 38° C.

The A. O. A. C. sand method, as modified, can be forced to give results comparable to those obtained by the other methods. It is not recommended by the authors, as much attention must be devoted to manipulation and a series of results may vary widely.

Table III. Data on Hydrol

Method	Temperature ° C.	Constancy	Time Hours	Moisture %	Moisture %
Filter-Cel, vacuum	70	Yes	15	21.90	21.88
			20	21.96	21.94
			25	21.98	21.96
			30	21.98	21.96
Lobry de Bruyn, vacuum	38	Yes	100	21.60	...
			300	21.75	...
			500	21.90	...
			600	21.91	...
			700	21.91	...
Benzene	80–82	Yes	20	21.89	21.92
			44	21.90	21.93
			68	21.91	21.93
			80	21.92	21.94
			100	21.94	21.92
Filter-Cel, vacuum[a]	70	Yes	15	26.18	26.18
			20	26.20	26.20
			25	26.20	26.22
			30	26.20	26.21
Carbon tetrachloride[a]	76–78	Yes	3	26.21	26.20
			18	26.22	26.20
			24	26.23	26.20

[a] Last two results were obtained on a different sample.

General Summary

In this series of five papers[1], a method of analytical procedure has been outlined for the determination of true moisture in those materials which, in the past, have been reported largely on a relative moisture basis. This technique consists of four essential points used in conjunction with the apparatus and procedures laid down:

1. Use of adequate dispersion of the sample, so as to expose maximum surface of the material in subsequent drying. By this means, water is removed quickly and completely. Quick re-

---

[1] Previous four can be found in Ind. Eng. Chem., Anal. Ed., 13, 855, 858 (1941); *Ibid.*, 14, 27 (1942); and this issue, page 124.

moval decreases the possibility of decomposition by reducing the material to the dry state in the minimum of time. Complete removal precludes the possibility of "slow creep", or inability to obtain constancy, which is defined as decomposition, loss of volatiles, etc.

2. Use of the modified Lobry de Bruyn technique of drying at 38° C., high vacuum, and extended time to obtain moisture and corresponding dry substance. Under these conditions, the temperature does not exceed that of normal storage conditions, and if decomposition is a factor, it may be expected to be present under storage conditions.

3. Use of the vacuum oven at 60° C. upwards, to determine a temperature constancy curve, whose final values correlate those obtained by the low-temperature drying method of 2. This technique involves high drying temperatures, high vacuum, and relatively short time. By it, the temperature limitations of the material are determined for this common laboratory drying practice.

4. Use of distillation methods to determine actual water. This procedure gives a range of temperature from 76° (carbon tetrachloride) to 140° C. (xylene), atmospheric pressure, and time limits which may be shorter than corresponding vacuum oven or, in any event, shorter than the modified Lobry de Bruyn technique. By distillation methods, the effect of vacuum in the removal of volatiles or other possible decomposition of the material should be substantially decreased if not entirely eliminated from the results. Thus, a drying curve should be obtained whose final values equal those of the Lobry de Bruyn or vacuum oven methods. If no correlation can be obtained, volatiles or decomposition may be considered a factor. In any event, a closer relative moisture value will be obtained.

Attention should be called to the interchanging features of the apparatus described. With use of standard taper joints, it is possible to oven-dry a sample and check the same sample further by distillation, or vice versa. Thus, it is often desirable, for example, to test a distillation sample upon completion by means of various oven temperatures for stability, etc.

The methods described in this series of papers have been tested and approved by various laboratories of the corn products industry through the Technical Advisory Committee of the Corn Industries Research Foundation, which have been most thorough in their criticism.

Literature Cited

(1) Cleland, J. E., and Fetzer, W. R., Ind. Eng. Chem., Anal. Ed., 13, 858 (1941).
(2) *Ibid.*, 14, 27 (1942).
(3) *Ibid.*, 14, 124 (1942).
(4) Evans, J. W., and Fetzer, W. R., *Ibid.*, 13, 855 (1941).

Determining Liquid and Vapor Densities in Closed Systems

A Precise Method

G. H. WAGNER, GRANT C. BAILEY, AND W. G. EVERSOLE
State University of Iowa, Iowa City, Iowa

THE method proposed here for measuring densities makes use of a quartz bob suspended from a quartz helix. If the helix and bob are suspended in a homogeneous medium, the system will be buoyed up according to Archimedes' principle, causing a change in the length of the helix. Thus the length of the helix can be related to density by a calibration in a series of media of known density. Actually, it is possible to measure both liquid and vapor densities with the same bob and helix, using a separate calibration for each phase. Because of the limit imposed on the mass of the bob by the strength of the helix, this is best accomplished by using a bob with a density less than that of the liquid, so that the helix is stretched upward in the liquid when the helix assembly is totally immersed and the helix suspended from below. Total immersion in the phase whose density is being determined simplifies the buoyancy correction for the helix and eliminates errors due to surface tension.

The experimental arrangement for the measurement of both liquid and vapor density in the same system would then consist of a helix and bob suspended in a sealed glass tube, so that the helix assembly could be completely immersed in either phase, at will, by merely inverting the apparatus. This should serve as an excellent method for determining densities in closed systems where the absence of air and moisture is desired or where the pressure is above atmospheric. The method is also capable of high precision through the optimum choice of helix sensitivity, bob size, and measuring instrument. The chief drawback is that a considerable amount of labor is involved in the purification of the liquids and the measuring of the several lengths necessary for the calibration for each phase at each temperature; moreover, vapor densities are not accurately known over a wide range. However, by the extensive use of helices for density measurements in this laboratory, certain properties of quartz helices and methods of calibration have evolved which make the calibration much less laborious without sacrificing precision of measurement.

Theory and Method of Calibration

RELATIVE DENSITIES. The length to which a helix extends under the influence of gravity is a function of the temperature, T, and density, ρ, of the medium in which it is suspended, such that any change in length, ΔL, may be written

$$\Delta L = \left(\frac{\partial L}{\partial T}\right)_{\rho} \Delta T + \left(\frac{\partial L}{\partial \rho}\right)_{T} \Delta \rho \qquad (1)$$

The temperature and density coefficients of the helices used in this laboratory have been found to be constant over a 25° or greater temperature range, and over a considerable range of length, so that Equation 1 may be written for this range

$$\Delta L = a \Delta T + b \Delta \rho \qquad (2)$$

For an unloaded quartz helix, 4 × 0.9 cm., made from a fiber of 0.2-mm. diameter and consisting of 63 turns, $\left(\frac{\partial L}{\partial \rho}\right)_{T}$ is approximately 0.15 cm.^{4} per gram. A 1-cc. quartz bob suspended from the helix increases this value to approximately 5 cm.^{4} per gram. This sensitivity can be increased indefinitely (with a corresponding decrease in the range of densities which can be measured) by increasing the volume of the bob, and using a bob density only slightly different from that of the medium in order to avoid overloading the helix. By such means it is easily possible to measure small changes in density with a precision which cannot be justified by the possible precision of temperature control. Under normal load ($\simeq$ 1.1 gram in air) a helix of the dimensions given above will extend to approximately 9.0 cm. It should stretch to from 12 to 20 cm. before breaking. The temperature coefficient, a, is of a much lower order of magnitude than the density coefficient, b, but it must be taken into account for precise work at different temperatures.

By measuring the length of the helix at different temperatures in media of known density, a and b can be found by solving the simultaneous equations resulting from Equation 2.

Equation 2 can be put into the useful form

$$\rho = \rho_s + \frac{a\,(T_s^0 - T^0) - (L_s - L)}{b} \tag{2b}$$

Here L_s is the length of the helix in the standard medium of density, ρ_s, at the standard temperature, T_s^0, and L is the length in a medium of density ρ at a temperature T^0. Equation 2b expresses density in terms of the density of a standard medium and is applicable to both liquid and vapor density measurements, once a and b are known.

Absolute Densities. For the vapor, the calibration can be made practically independent of standard densities. The density coefficient, b, may be written

$$b = \left(\frac{\partial L}{\partial M}\right)_T \left(\frac{\partial M}{\partial \rho}\right)_T \tag{3}$$

M is the apparent effective mass of the helix and bob as indicated by the length of the helix.

As with sorption balances (*2*), $\left(\frac{\partial L}{\partial M}\right)_T$ can be determined from the changes in length caused by the addition of small weights to a platinum bucket which is suspended from the helix in a medium of constant density and temperature. In this calibration the bob is removed and the calibration is extended over the range of length where $\frac{\partial L}{\partial M}$ is constant. The mass and volume of the bob should be such that all density measurements are made in this constant range.

$$\left(\frac{\partial M}{\partial \rho}\right)_T = \left(\frac{\partial M_b}{\partial \rho}\right)_T + \left(\frac{\partial M_s}{\partial \rho}\right)_T \tag{4}$$

M_b and M_s are, respectively, the apparent effective mass of the bob and the spring and V_b and V_s are the corresponding volumes.

$$M_b = V_b\,(\rho_b - \rho) \tag{5}$$

where ρ_b and ρ are the densities of the bob and the medium, and

$$\left(\frac{\partial M_b}{\partial \rho}\right)_T = -\,V_b \tag{6}$$

This is the actual volume of the bob and its value can be determined by weighing in liquids of known density.

On the other hand $\left(\frac{\partial M_s}{\partial \rho}\right)_T$ is not the negative of the actual volume of the spring. The reason for this is that the apparent effective mass is obtained from L by means of a calibration which is made in terms of weights suspended from the lower end of the spring. The mass of the spring is not located at the lower end but is distributed over the entire length. If there are n turns in a perfect helix, any given element of mass located at turn t will stretch only the t turns which are above it, and the elongation produced will be only t/n times as great as was produced by the same mass in the calibration. If σ_s is the volume of quartz fiber in one turn of the helix, and ρ_s is the density of quartz, the element of mass is $\sigma_s\,(\rho_s - \rho)\,dt$ and the apparent effective mass of the spring is

$$M_s = \int_0^n (t/n)\,(\rho_s - \rho)\sigma_s\,dt = (\rho_s - \rho)\sigma_s\,(n/2) \tag{7}$$

and therefore

$$\left(\frac{\partial M_s}{\partial \rho}\right)_T = -\,\sigma_s\,n/2 = -\,V_s \tag{8}$$

This is one half of the actual volume of the helix. Thus V_s for a perfect helix may be determined from the weight of the helix and the density of fused quartz. It will be noticed that the factor $^1/_2$ will cause only one suspension end to be included in V_s. This is exactly what is desired, since the mass of the lower suspension end acts on all n turns, while the upper suspension end acts on none of the parts of the spring which is being measured. Although the helices used in this laboratory are slightly tapered, V_s as determined by this simple calculation has been found to agree within ±0.002 cc. with the value V_s ($\simeq$ 0.025 cc.) determined experimentally. This corresponds to a 10 per cent error in the apparent effective volume of the helix, but introduces an error of only $0.2/V_b$ per cent in the measured density.

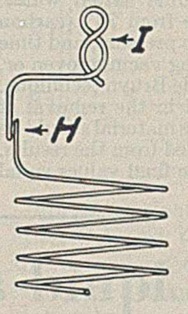


Figure 1

V_s is determined experimentally from length measurements on the unloaded helix in media of known density, and from Equations 3 and 4 is equal to $-\,b/\left(\frac{\partial L}{\partial M}\right)_T$ when the bob is absent. The value of $\left(\frac{\partial L}{\partial M}\right)_T$ for the unloaded helix must be determined by measuring the change in length caused by the addition of a small weight to the unloaded helix. This is necessary because the elongation per gram is different for small loads than for normal loads. A 0.02- to 0.03-gram piece of quartz fiber with a small hook for suspending from the suspension point of the helix (see Figure 1) makes a satisfactory weight. Any but a perfect helix will give two different values for V_s, depending on which end of the helix is up.

Combining Equations 2b, 3, 4, 6, and 8 and using the length of the helix loaded with bob in vacuum, L_s^0, at temperature T_s^0 as standard, we obtain for the density

$$\rho = \frac{a(T_s^0 - T^0) - (L_s^0 - L)}{-\left(\frac{\partial L}{\partial M}\right)_T (V_b + V_s)} \tag{9}$$

Vapor or liquid densities calculated to the fourth significant figure from Equation 9 may be considered absolute, since the standard liquid densities necessary for determining V_b and V_s are known with this accuracy.

The size and density of the bob used will depend on the density of the material to be measured and the elastic properties of the helix. When helix and bob are to be used for both liquid and vapor density measurements, a bob density which is about the average of the densities of the two phases is preferred. This permits the use of a bob of larger volume, with correspondingly increased precision of measurement, without exceeding the load limit of the helix in either phase. The bob is blown in an oxyhydrogen flame from a quartz tube which has a diameter and wall thickness calculated to give the desired bob volume and weight, so that the extension in both phases falls within the constant range of $\left(\frac{\partial L}{\partial M}\right)_T$.

Precision

The validity of this method of calibration has been checked for both liquid and vapor. Using a helix of the dimensions given above, a bob having a volume of about 1.35 cc. and weight (in vacuum) of about 1 gram, and a measuring microscope (*3*) which could be read to 0.00006 cm., the density values for water from 10° to 35° C. were checked to 0.00003 gram per cc., using water at 25° C. as the standard liquid. With the same helix and bob assembly, vapor densities of sulfur dioxide in equilibrium with its solutions at 15°, 20°, and 25° C. checked with the densities calculated from vapor pressure data to 0.00001 gram per cc., using the saturated vapor of pure sulfur dioxide as standard. Numerical data are reported in another paper (*4*).

For the precision with which these measurements were carried out, it was necessary to devise suspension points for both helix and bob so that the helix was never distorted when suspended, but hung freely. Precise indices which were out of the axis of the tube were also necessary for proper focusing. The cross point in a figure-eight loop of the helix fiber (*I*, Figure 1) was used to suspend the helix from a loop of 0.1-mm. (0.004-inch) platinum wire and likewise to suspend the bob from the helix. The indices (*H*, Figure 1) consisted of 0.5-mm. loops in the helix fiber at either end of the helix. They had sufficient curvature to permit the most accurate setting of the microscope cross hair at their outer edge and were in good enough alignment so that no change in the focus of the microscope was necessary when reading the two ends.

It is generally recognized that quartz helices exhibit no hysteresis after once being annealed. Quartz is also not easily corroded and has a very low thermal coefficient of volumetric expansion, 1.2×10^{-6} per ° C. For a 2-cc. quartz bob, and a change in temperature of 15°, the volumetric expansion amounts to 0.000036 cc. This is negligible for ordinary vapor density measurements but appreciable for precise measurements of liquid density, and will account for the small divergence which the authors have found in water. However, this effect can be eliminated by making the necessary correction for the change in the volume of the bob.

The volume of a hollow quartz bob of substantial wall thickness is also not greatly affected by pressures of the order of 4 atmospheres (approximate vapor pressure of sulfur dioxide at 25°). If the bob is sealed off at atmospheric pressure, the effect of 4 atmospheres is reduced to that of 3 atmospheres. Using Bridgman's (*1*) value for the compressibility of mineral quartz, the change in the volume of a 1-cc. bob would be 0.27×10^{-5} cc. per atmosphere. The error resulting from this cause can be reduced if necessary by determining the approximate compressibility of the bob before it is sealed off.

It is believed that this method will be found useful for the precise measurement of densities in many systems which are not accessible to measurements by the usual methods.

Literature Cited

(1) Bridgman, P. W., *Am. J. Sci.*, 15, 287 (1928).

(2) McBain, J. W., and Bakr, A. M., *J. Am. Chem. Soc.*, 48, 690 (1926).

(3) Wagner, G. H., Bailey, G. C., and Eversole, W. G., Ind. Eng. Chem., Anal. Ed., 13, 658 (1941).

(4) Wagner, G. H., Bailey, G. C., and Eversole, W. G., *J. Phys. Chem.*, 45, 1388 (1941).

Heats of Wetting for the Evaluation of Gas-Adsorbing Coconut Carbons

HOSMER W. STONE AND RAYMOND O. CLINTON, University of California, Los Angeles, Calif.

THE use of heat of wetting as a means of evaluating gas-adsorbing carbons has been suggested by several authors in recent years (*1*, *7*), and restricted semianalytical methods have been developed by Macy (*8*) and Burstin and Winkler (*4*). This method has the distinct advantages, in comparison with other methods, of extreme rapidity and satisfactory accuracy, and by suitable correlation affords data as to other analytical characteristics of the carbon, as is shown below.

A large number of methods for evaluating the gas-adsorbing qualities of carbons have appeared in the literature, most of which have been critically discussed by Chaney, Ray, and St. John (*5*), and by Berl and Herbert (*3*). The majority of these methods are time-consuming and not overly indicative of the value of a carbon for a particular purpose. As has been pointed out by Chaney, Ray, and St. John (*5*), the most reliable analytical data pertaining to gas-adsorbing carbons are:

1. SERVICE TIME. Time required for the break-through of a vapor under standard conditions.
2. ADSORPTION VALUE. The weight of a vapor adsorbed by a carbon under conditions of saturation.
3. RETENTIVITY VALUE. The weight of vapor held by a carbon through secondary valence bonds, under standard conditions.

All these data are more or less arbitrary, yet under suitable conditions they afford the most reliable evidence obtainable at present as to the gas-adsorbing characteristics of a given carbon. The chief criticism of these methods arises from the lack of definition of terms and of precise descriptions of the techniques which have appeared in the literature. It is only by a rigorous standardization of the analytical procedures that quantitative results can be achieved and duplicated. Toward this end, the authors have sought to standardize their methods as thoroughly as possible.

Macy (*8*) and later Bell and Philip (*2*) have shown the existence of a quantitative relation between the heat of wetting and the retentivity value of a specific carbon, but the possibility of a quantitative relation between adsorption value and heat of wetting has been a matter of considerable dispute. Burstin and Winkler (*4*) first suggested such a relation, but, unfortunately, their data were insufficient to warrant such a conclusion. Macy (*8*), as the result of the analysis of a large number of different carbons, found several rather large discrepancies, and, therefore, stated that no correlation between adsorption value and heat of wetting could exist. Other authors have either been undecided (*2*) or have confirmed in a degree (*3*) the data of Burstin and Winkler.

No correlation of heat of wetting with the service time of a carbon has been found in the literature.

In view of evidence which has been obtained by the authors, a definite relation between the heat of wetting of a carbon as determined under certain conditions as stated and the other analytical characteristics listed is postulated. This relation, however, is limited to specific types of carbon—that is, to carbons which have a common raw material source. While the present paper concerns itself with gas-adsorbing carbons derived from coconut, since this is the most efficient and most common type in use at present, nevertheless the procedure, with suitable modification, should be applicable to other common-source carbons.

The question of the effect of varying the method of activation on the correlation of these characteristics of common-source material carbons has been raised. Of the thirteen coconut carbons used in this work, five are known to have been activated by the same method. The other eight carbons were commercial carbons from various sources, whose method of activation was not known. Two of these latter carbons were prepared by high-temperature steam treatment

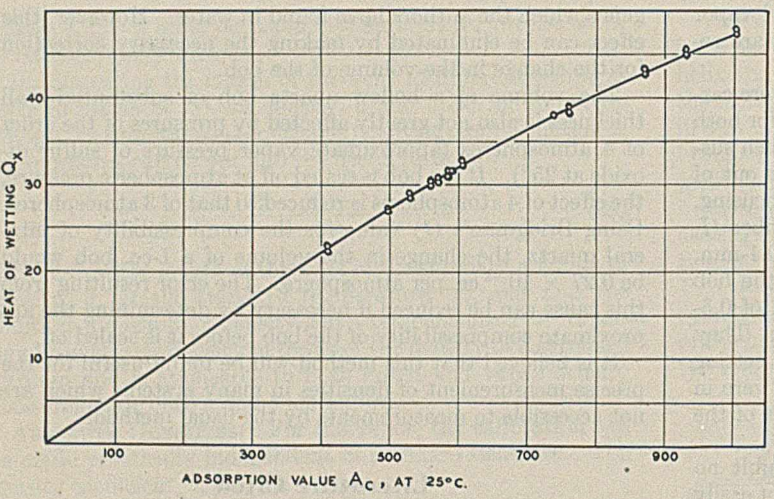


Figure 1. Relation between Adsorption Value for Carbon Tetrachloride and Heat of Wetting in *m*-Xylene

of a spent carbon which had been used to remove hydrocarbons from carbon dioxide. The temperatures of stripping were 425° and 535° C. The stripped carbons possessed a higher degree of activation than the original source carbon.

Pearce and McKinley (*9*) found the relation between adsorption value and the heat of adsorption (vapor phase) to be given by the expression:

$$Q = mX^n$$

where Q is the heat evolved in calories per gram of carbon, X is the milliliters of a given vapor adsorbed, and m and n are constants, depending upon the vapor used. Burstin and Winkler (*4*) found the following equation:

$$A_b = 19\, Q_b$$

where A_b is the adsorption value in milligrams of benzene adsorbed per gram of carbon, and Q_b is the heat of wetting for benzene in calories per gram of carbon. Both equations were derived from the analysis of a very limited number of carbons, and, therefore, their general applicability is slight.

Previous workers (*2, 4, 8*) have determined the heat of wetting of carbon by benzene, and compared these data with the adsorption value for benzene. The present writers have found the use of *m*-xylene for the determination of heats of wetting to offer several advantages—notably, a decreased volatility, a constant specific heat over the temperature range used, and approximately 50 per cent higher values for the heat of wetting. Because of the difficulties inherent in the use of the accelerated chloropicrin service time method, it was found desirable to use the accelerated carbon tetrachloride service time method (*6*) with suitable modifications. The use of this latter method makes possible a saving of time, since the service time and adsorption value determinations may be made successively.

Results of the analysis of thirteen samples of coconut carbons have led to the following empirical relations:

$$\begin{aligned} A_c^{25} &= 17.9\, Q_x + 5.8 \times 10^{-6}\, (Q_x)^{4.43} \\ S_c^{20} &= 1.34\, Q_x \\ S_c^{25} &= 1.16\, Q_x \\ R_c &= 9.38\, Q_x \end{aligned}$$

In the above equations:

A_c^{25} = adsorption value for carbon tetrachloride (*4*) in mg. adsorbed per gram of carbon at 25° C.
S_c^{20} and S_c^{25} = service times for chloropicrin in minutes at 20° and 25° C., respectively
R_C = retentivity value for carbon tetrachloride in mg. retained per gram of carbon
Q_x = heat of wetting in *m*-xylene, in calories evolved per gram of carbon

Throughout this article, except as otherwise indicated, "chloropicrin service time" refers to the chloropicrin service time value as calculated from the carbon tetrachloride service time through the use of an integer factor. This factor has appeared in the literature with a value of 3.0 (*6*), but as the authors have used a 15.0-cm. column length of carbon in the service time determinations instead of 10.0 cm., the value of 2.0 has been used in the present work.

The results of the analyses are presented graphically in Figures 1, 2, and 3, and summarized in Table I.

Experimental

Service Time and Adsorption Value. For the determination of these values, modifications of the methods of Chaney and of Fieldner (*5, 8*) are used. The apparatus is shown in Figure 4. The carbon tetrachloride is dried and redistilled before use, reserving the fraction boiling at 76–77.5° C.

Table I. Analyses of Coconut Carbons

AD	A_c^{25}	R_c	S^{20}	S_c^{25}	Q_x
0.52	528	268	38.5	33.4	28.6
0.49	589	300	42.6	37.0	31.7
0.54	497	252	36.8	31.6	27.1
0.52	571	291	41.0	35.8	30.7
0.52	605	302	43.2	37.4	32.3
0.48	736	362	51.0	44.0	38.1
0.43	930	421	61.2	53.0	45.2
0.53	562	293	40.4	35.0	30.3
0.54	410	214	30.4	26.5	22.7
0.48	586	291	42.0	36.4	31.5
0.45	758	363	52.6	45.4	38.9
0.44	872	405	58.0	50.2	43.1
0.38	1004	454	64.2	55.4	47.5

AD = apparent density of 8- to 14-mesh carbon in grams per ml. Values for Q_x represent average of from 5 to 10 determinations, with a maximum deviation from the mean of 0.2 calorie.

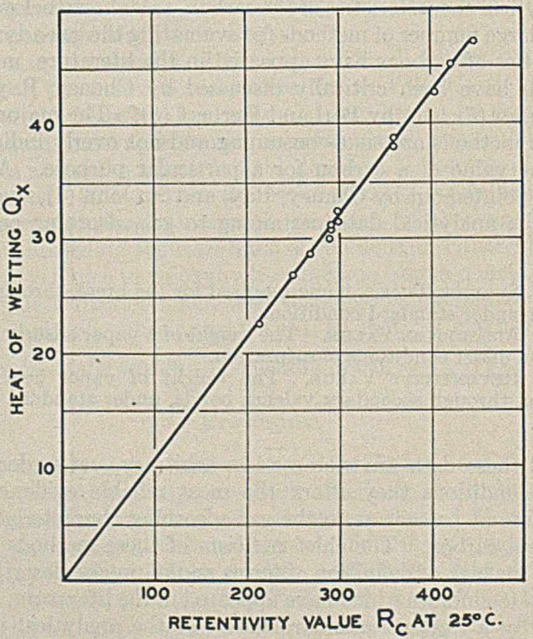


Figure 2. Relation between Retentivity Value for Carbon Tetrachloride and Heat of Wetting in *m*-Xylene

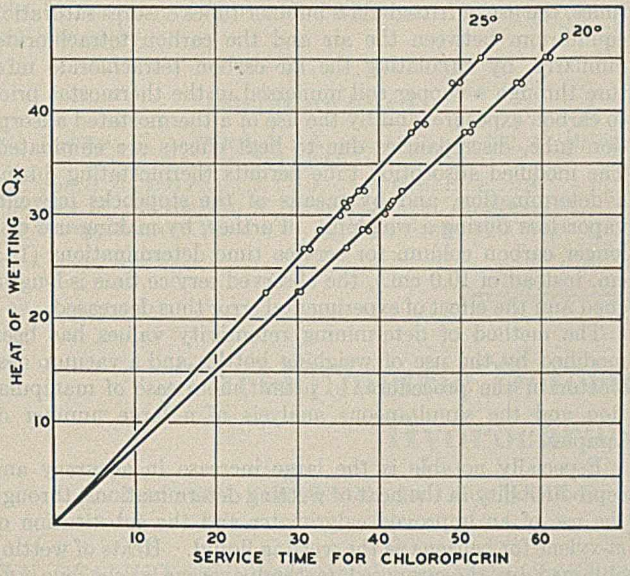


FIGURE 3. RELATION BETWEEN SERVICE TIMES AT 20° AND 25° AND HEAT OF WETTING IN *m*-XYLENE

A composite sample of the carbon is screened to 8- to 14-mesh on standard screens, dried 4 hours at 140° to 150° C., and cooled in a desiccator. A volume of the dried carbon (about 25 ml.), sufficient to give a tamped column length of 15.0 cm. in the adsorption tube, is transferred to the adsorption tube and the tube and contents are weighed to 1 mg. The carbon is then tamped by tapping lightly on a level wooden surface until no further diminution in volume is noted, at which point the column of carbon in the adsorption tube should measure exactly 15.0 cm. in length. This column length of 15.0 cm. should be reproducible upon inverting the adsorption tube and retamping the carbon. A simple method of achieving this result involves the use of a flat-bottomed test tube 1.3 cm. in inside diameter, and calibrated at 15.0 cm., for the measurement of the carbon before insertion into the adsorption tube. The adsorption tube is placed in position in the thermostat, which is controlled at 25.0°. Sufficient time is then allowed (about 30 minutes) for the carbon to reach temperature equilibrium with the thermostat.

An air-flow rate of 650 ml. per minute (490 ml. per minute, per sq. cm. of cross-sectional area of the carbon) is established through the apparatus, with the three-way stopcock turned so as to vent the carbon tetrachloride-saturated air to a hood. The stopcock is then turned to allow the carbon tetrachloride–air mixture to pass through the adsorption tube, the initial starting time is noted, and any necessary flow-rate adjustments are quickly made.

The first appearance of a greenish tinge in the burner flame (which is adjusted to a height of about 7.5 cm., 3 inches) is taken as the breakdown point, and the elapsed time recorded as "accelerated carbon tetrachloride service time". The adsorption tube-to-burner connection is then broken and the effluent carbon tetrachloride–air mixtures vented to a hood.

Passage of the carbon tetrachloride–air mixture is continued, with weighings of the adsorption tube each half hour, until no further gain in weight is evident (3 to 5 hours). The gain of carbon tetrachloride in milligrams per gram of carbon is recorded as the adsorption value.

The "accelerated carbon tetrachloride service time" as determined above is multiplied by 2.0 (*6*) to convert to the approximate corresponding "chloropicrin service time".

Precautions must be taken to ensure a constant 0° C. temperature of the carbon tetrachloride in the cooling bath, as well as a constant air-flow rate throughout the determination, since small variations in these factors will introduce relatively large errors.

RETENTIVITY VALUES. These values are determined by a modification of Macy's method (*8*).

A 3- to 4-gram sample of the saturated carbon from the adsorption value determination is transferred quickly from the adsorption tube to a glass-stoppered weighing bottle and weighed. The glass stopper is removed and the weighing bottle is placed in a vacuum desiccator lubricated with de Khotinsky cement which is in turn placed in an oven maintained at 90° to 100° C. The desiccator is connected to a vacuum pump and the carbons are evacuated at 2-mm. pressure, with periodical weighings, until the weight loss amounts to not more than 15 mg. over a period of 0.5 hour. The retentivity value is determined by graphing the percentage weight of vapor retained against time, and extending the portion of the curve representing low rate of vapor loss, which is approximately a straight line, back to the retentivity axis, as is shown in Figure 5.

The retentivity values may also be determined by evacuation at lower temperatures if wished, with achievement of comparable results. Lowering the temperature greatly extends the amount of time required to complete a determination, however—for example, evacuation at 25° requires 90 to 100 hours for the attainment of retentivity values, while at 100° 3 to 5 hours are required, as shown in Figure 5.

HEATS OF WETTING. A cylindrical silvered Dewar flask, 10 cm. high by 3.0 cm. in inside diameter, is used as a calorimeter. A 15° to 45° thermometer, graduated in tenths or twentieths of a degree is supported above the Dewar flask in such a manner that the thermometer bulb is about 5 mm. above the bottom of the flask. The thermometer is calibrated for 40-mm. immersion.

The heat capacity of the assembly is determined by the heat of neutralization of sodium hydroxide and hydrochloric acid using the value $H_N \cong 13{,}895$ calories at 20° (*10*). The authors' calorimeter, of the type outlined, had a heat capacity of 5.0 calories per degree.

A 25.00-ml. portion of dry *m*-xylene (boiling point 137–9°) is pipetted into the calorimeter, and the temperature of the cal-

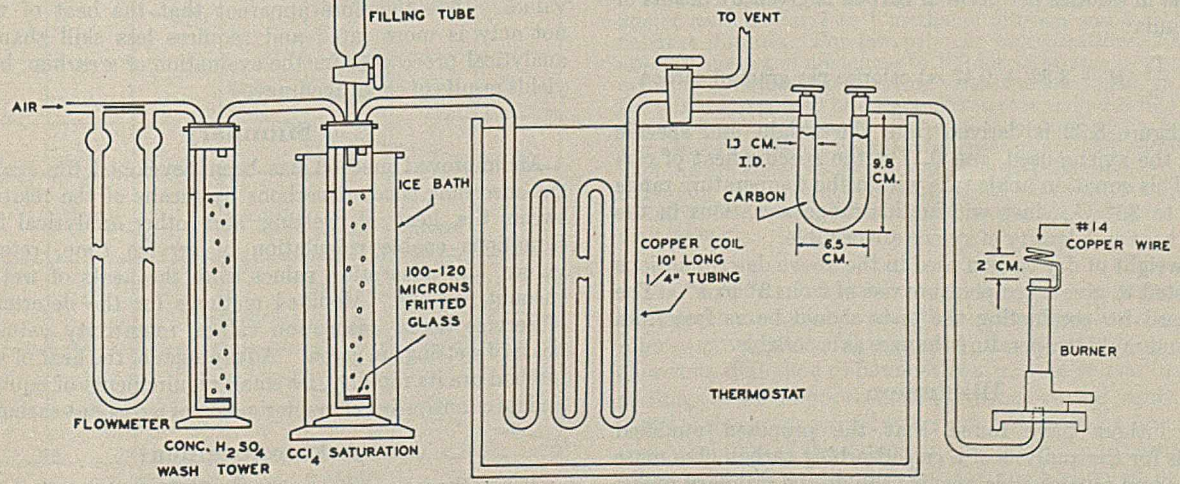


FIGURE 4. APPARATUS FOR DETERMINATION OF ADSORPTION VALUES AND SERVICE TIMES

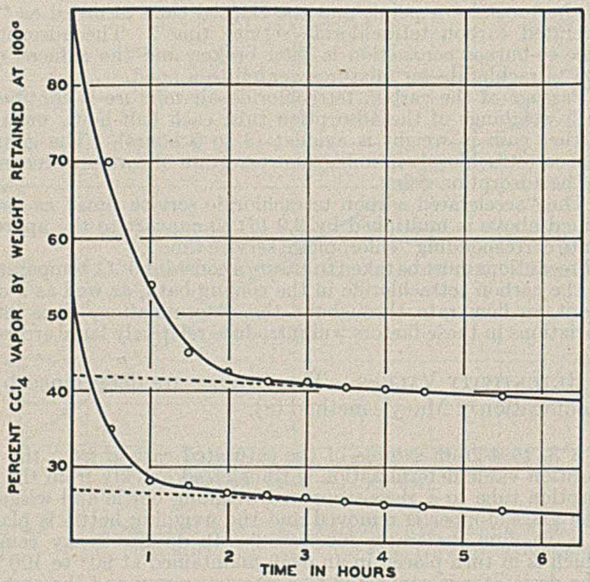


Figure 5. Graphical Method for Determination of Retentivities

orimeter and contents is adjusted to a predetermined value, identical with that of the carbon sample to be tested, by means of small test tubes containing hot or cold water. This temperature is then recorded to within 0.02° as "initial xylene temperature".

A sample of the carbon to be tested (previously screened to 8- to 14-mesh and dried 8 hours at 140°) is weighed to the nearest milligram and added rapidly to the calorimeter. The contents of the calorimeter are mixed by a gentle rotation of the thermometer until a maximum temperature is reached. This temperature is read to within 0.02° and recorded as "final temperature".

Unused *m*-xylene may be recovered by transferring the contents of the calorimeter, at the conclusion of the run, to a No. 5 Whatman filter. The calorimeter should be wiped dry with a clean, lintless cloth between each run.

The temperature of the carbon should be known with an accuracy of 0.3° C. prior to its addition to the calorimeter. If it differs from the initial xylene temperature by more than 0.3°, the calculation of the initial mixing temperature of the carbon-xylene mixture from the known initial xylene temperature and the temperature of the carbon is then made, and this value subtracted from the final temperature and recorded as T_r, the temperature rise. From the known heat capacity of the calorimeter, H, and the weight of carbon used, m, the corresponding heat of wetting, Q_x, of the carbon for *m*-xylene in calories per gram of carbon is given by means of the formula:

$$Q_x = \frac{T_r}{m}(H + 8.32 + 0.17\,m) \text{ calories per gram of carbon}$$

The figure 8.32 is derived from the weight and specific heat of the xylene used, and 0.17 is the specific heat of carbon. This equation holds true within the temperature range of 18° to 35° C., since within this range variations in the specific heat and density of xylene are neglible.

The weight of dry carbon used in the above determinations is adjusted to give a temperature rise of from 3° to 4°. The room used for conducting the tests should be as free from drafts and rapid temperature changes as is possible.

Discussion

The authors have found that the proposed modified methods for the analysis of a gas-adsorbing carbon give more accurate and reproducible results than do the standard procedures. In the determination of adsorption values and service times, the use of fritted-glass bubbler tubes ensures saturation equilibrium between the air and the carbon tetrachloride. Similarly, by circulating the air-carbon tetrachloride mixture through a copper coil immersed in the thermostat prior to carbon exposure, and by the use of a thermostated adsorption tube, discrepancies due to heat effects are eliminated. The modified adsorption tube permits thermostating during a determination, and by means of the stopcocks prevents vapor loss during a weighing. Further, by making use of a longer carbon column for service time determinations (15.0 cm. instead of 10.0 cm.), the observed service time is lengthened and the effect of experimental error thus decreased.

The method of determining retentivity values has been modified by the use of weighing bottles and a vacuum desiccator in the procedure, to permit more ease of manipulation and the simultaneous analysis of a large number of samples.

Especially notable is the large increase in accuracy and reproducibility in the heat of wetting determinations, through the use of an improved calorimeter and the substitution of *m*-xylene for benzene as the wetting liquid. Heats of wetting obtained by the proposed method average about one and one-half times as large as those obtained by the standard Chemical Warfare Service method, on the same carbon. The comparison of these *m*-xylene heats of wetting with the corresponding service times, retentivity values, and adsorption values, as derived from the proposed procedures, leads to straight-line or smooth-curve functions. This statement, however, does not hold true for the standard methods of analysis when compared with the heats of wetting as determined according to C. W. S. specifications.

Using the modified procedures, duplication of results can be achieved in the determination of retentivity and adsorption values to within ±0.5 per cent. Constancy of service time values is dependent not only upon the temperature of the carbon tetrachloride saturation tower, and of the thermostat, but upon gas-flow rate per unit cross-sectional area of carbon and other factors such as the packing of the carbon and the observance of the first trace of carbon tetrachloride break-through. For this reason, some slight skill is required to duplicate results to within ±0.25 minute. The heats of wetting are readily duplicable to within 0.3 calorie. In accord with the proposed method of analysis for calculating service times, adsorption values, and retentivity values from the corresponding heats of wetting in *m*-xylene, the average mean deviation in the heats of wetting—namely, 0.2 calorie—will lead to a maximum error in the calculated values of the other analytical characteristics of ±0.25-minute service time, and less than ±5 mg. in adsorption and retentivity values. It is therefore apparent that the heat of wetting not only is more rapid and requires less skill than other analytical procedures for the evaluation of a carbon, but also yields results of equal accuracy.

Summary

An improved method has been developed for evaluating gas-adsorbing coconut carbons by means of the relation between the heat of wetting and other analytical factors. Equations enable calculation of service time, retentivity values, and adsorption values from the heats of wetting of coconut carbons. Modified methods for the determination of service times, adsorption values, retentivity values, and heats of wetting are given. Advantages of the heat of wetting method are its rapidity, its small requirements of equipment, and its quantitative characterization of a coconut carbon.

Acknowledgment

The authors are indebted to A. B. Ray of the Carbide and Carbon Chemicals Corporation for supplying six of the car-

bons used in this work, and for supplying certain data regarding these carbons.

Literature Cited

(1) Andress, K., and Berl, E., *Z. physik. Chem.*, 122, 81 (1926); *Z. angew. Chem.*, 35, 722 (1922).
(2) Bell, S. H., and Philip, J. C., *J. Chem. Soc.*, 1934, 1164.
(3) Berl, E., and Herbert, W., *Z. angew. Chem.*, 43, 904 (1930).
(4) Burstin, H., and Winkler, J., *Przemysl Chem.*, 13, 114 (1929).
(5) Chaney, N. K., Ray, A. B., and St. John, A., Ind. Eng. Chem., 15, 1244 (1923).
(6) Fieldner, A. C., Oberfell, G. G., Teague, M. C., and Lawrence, J. N., *Ibid.*, 11, 524 (1919).
(7) Herbst, H., *Kolloid Z.*, 38, 314 (1926).
(8) Macy, R., *J. Phys. Chem.*, 35, 1397 (1931).
(9) Pearce, J. N., and McKinley, L., *Ibid.*, 32, 360 (1928).
(10) Richards, T. W., and Rowe, A. W., *J. Am. Chem. Soc.*, 44, 684 (1922).

Presented before the Division of Analytical and Micro Chemistry at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J.

Turbidimetric Determination of Polymerized Hydrocarbons in Solution

BASSETT FERGUSON, Jr., and MARK D. SNYDER, Ugite Sales Corporation, Chester, Penna.

IN DEALING with unsaturated hydrocarbons subject to polymerization it is frequently necessary to determine the polymer content in a solution of the monomer. As the polymer is usually relatively high boiling, the monomer may be flash-distilled under vacuum and the residue weighed and considered polymer. This method is more or less inaccurate, especially for small quantities of polymer.

Some users of these materials have empirical specifications for maximum polymer content based on the insolubility of the polymer in methanol or petroleum naphtha. If a given dilution of the sample with one of these solvents does not produce a distinct cloud of precipitate, the polymer content may be assumed to be below the predetermined value. No mention has been found in the literature, however, of extending this principle to give an accurate analytical method.

To obtain a rapid and accurate analytical method for the analysis of polystyrene in solution of styrene and other aromatics, the dilutions for maximum sensitivity of the sample with methanol and petroleum naphtha were determined. It was found that two parts of absolute methanol added to one part of sample will give a distinct cloud when 0.0005 per cent of polymer is present in the original sample, and nine parts of Atlantic Refining Co.'s No. 44 naphtha added to one part of sample will give a distinct cloud when 0.005 per cent of polymer is present.

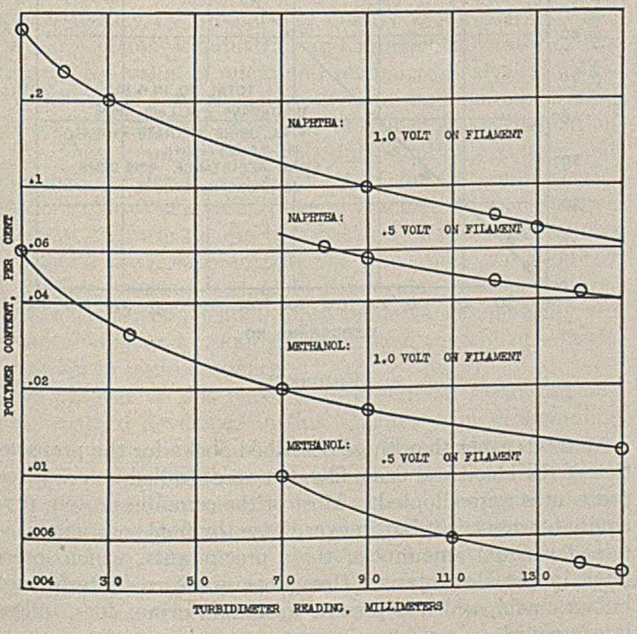


Figure 1

Furthermore, at these dilutions the effect on the polymer solubility of small changes in temperature is small. Analyses are normally performed at a room temperature of 20° to 25° C., but it was found that differences in results are negligible between 15° and 30° C.

Using these optimum dilutions, a set of standards was made up covering the range of 0.0005 to 0.3 per cent polymer directly. Higher polymer contents could be measured by first diluting the sample 10 to 1 or 100 to 1 with xylene. As had been feared, however, the standards containing the higher polymer concentrations deteriorated in a few weeks' time, owing to the settling of the precipitated polymer.

Some means of measuring the turbidity was then sought. Measurement of the height of a column of the liquid through which fine print could be read (as used in the kauri-butanol test) was tried, but great differences were found between different operators' ability to distinguish the fine print through the turbid liquid.

A Burgess-Parr sulfur turbidimeter (Arthur H. Thomas Co. catalog No. 9334) proved to be a satisfactory instrument for the measurement. A column of liquid is placed above an incandescent filament of standard (adjustable) intensity and a movable tube dipping into the liquid indicates the point of extinction of the filament by the turbid liquid.

Figure 1 shows per cent of polymer corresponding to turbidimeter readings for 2 to 1 methanol dilution and 9 to 1 No. 44 naphtha dilution. For low polymer concentrations, 200 ml. of absolute methanol are added to 100 ml. of sample in a stoppered cylinder and mixed by inverting several times. After 15 minutes the mixture is poured into the turbidimeter and a reading is taken using 0.5 or 1 volt on the filament, depending on the turbidity. For somewhat higher polymer concentrations, 180 ml. of No. 44 naphtha are added to 20 ml. of sample and the same procedure is followed. For polymer concentrations above the scale, 10 to 1 or 100 to 1 dilutions of the original sample with toluene or xylene may be used.

The turbidity increases during the first few minutes after adding the methanol or naphtha, but approaches a maximum after approximately 10 minutes. The 15-minute period was chosen so that time differences of a minute or two in making readings make no appreciable difference on the result.

A number of other polymers are known to be precipitated from a solution of the monomer by methanol and certain other solvents and it is believed that this method could be readily adapted to polymer analysis in such cases.

Polarographic Determination of Nitrates in Blood and Urine

EUGENE W. SCOTT AND KARL BAMBACH
Kettering Laboratory of Applied Physiology, College of Medicine, University of Cincinnati, Cincinnati, Ohio

COLORIMETRIC methods have been used successfully for the determination of small amounts of nitrate in water and food extracts, but in the authors' experience the application of these methods to biological materials such as blood and urine has not been satisfactory. Whelan's method (*4*) was also tried, but the difficulty of preventing atmospheric oxidation of the reagent, diphenylbenzidine, rendered this procedure unsuitable. The use of the polarograph for the determination of nitrates has been reported by Tokuoka (*3*) and has been recently discussed by Kolthoff and Lingane (*2*). After a suitable procedure was developed for the removal of proteins and interfering substances, this method was used for blood and urine filtrates, with only slight modifications.

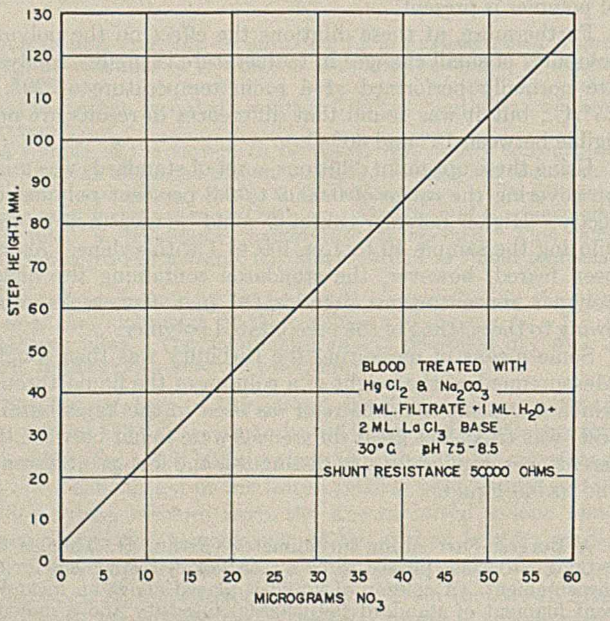


FIGURE 1

The apparatus employed is a Leeds & Northrup Electro-Chemograph, equipped with a Micromax recorder and the dropping mercury electrode and electrolysis cell which were supplied with the instrument. Galvanometer sensitivity ranges of 0 to 80 and 0 to 8 microamperes are used. The estimations are made graphically by comparing the step height obtained with the samples to those obtained by adding known amounts of nitrate to blood and urine filtrates which previously showed no nitrate step. The standard charts prepared in this way are shown in Figures 1 and 2.

The blood filtrates are prepared by mixing 0.5 ml. of fresh blood with 3.5 ml. of water, and adding 0.5 ml. of mercuric chloride solution (5 grams per 100 ml.) and 0.5 ml. of sodium carbonate solution (1 gram per 100 ml.). After filtering, 2 ml. of the filtrate are acidified with 1 ml. of 0.4 *N* hydrochloric acid, heated to boiling, cooled, and made alkaline with 1 ml. of 1 *N* sodium hydroxide. One milliliter of this solution, which is equivalent to 0.05 ml. of blood, is placed in the electrolysis cell and mixed with 1 ml. of water and 2 ml. of 0.1 *N* lanthanum chloride, and nitrogen is bubbled through the solution for 5 minutes. The current set up by electrolyzing this solution at 30° over a range of 1.0 to 1.8 volts is recorded and the height of the nitrate step is measured from this chart. The method of measurement was that employed by Cholak and Bambach (*1*). The step height in the case of urine samples was slightly higher (3 to 5 per cent) for a given amount of nitrate. Separate standard curves were therefore used for urine and for blood.

The urine filtrate is prepared by mixing 0.5 ml. of fresh urine with 0.5 ml. of mercuric chloride solution (5 grams per 100 ml.) and 5.0 ml. of saturated barium hydroxide solution, diluting to 10 ml. with water, and filtering. One milliliter of this filtrate is used in the electrolysis cell under the conditions described above for the final blood filtrate.

The lanthanum chloride solution is prepared by dissolving lanthanum oxide (obtained by ignition of the acetate) in a slight excess of hydrochloric acid. A large excess of acid is avoided, since it has to be neutralized by the filtrate used. The nitrate step appears only in neutral or alkaline solutions. The half-wave potential of the nitrate step is 1.33 to 1.39 volts in the case of blood filtrates, and 1.47 to 1.53 volts in the case of urine filtrates, when referred to the standard calomel electrode. The difference in half-wave potential was probably due to a difference in supporting electrolytes.

When the higher sensitivity of the galvanometer is used, it is possible to determine as little as 0.5 microgram of nitrate in 1 ml. of the electrolysis mixture, which is equivalent to 40 micrograms of nitrate per milliliter of blood. The full sensitivity of the instrument cannot be employed because of the salts and other substances present in the filtrates. With pure solutions of nitrate it should be possible to determine as little as 0.1 microgram in 1 ml.

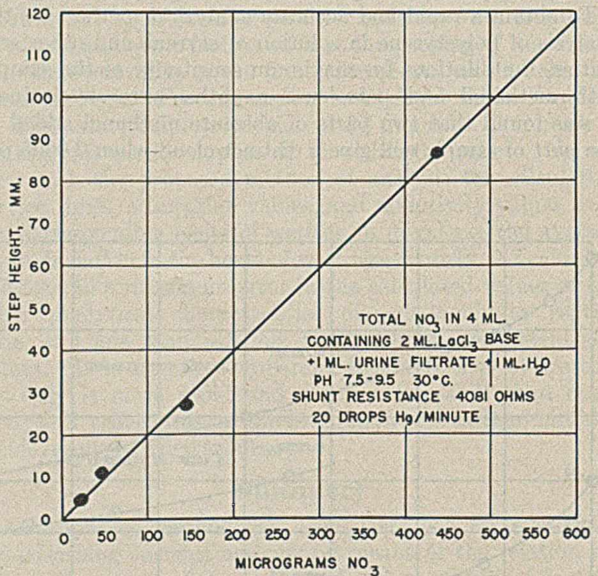


FIGURE 2

Methods other than those described above for the preparation of the blood and urine filtrates were studied before these procedures were adopted. Most of the common protein precipitants were tried, but in every case the final solutions contained residual amounts of these precipitants, which interfered in the electrolysis. Urea does not cause interference but uric acid, which is present in human urine, does, unless it is removed.

The method of polarographic determination here reported has so far been applied only to rabbit blood and urine. The appearance and increased concentration of nitrate in both fluids after the oral or intravenous ingestion of certain aliphatic nitro compounds were successfully followed with this procedure.

Results obtained will be reported elsewhere.

Literature Cited

(1) Cholak, J., and Bambach, K., Ind. Eng. Chem., Anal. Ed. 13, 583 (1941).
(2) Kolthoff, I. M., and Lingane, J. J., "Polarography", p. 314, New York, Interscience Publishers, 1941.
(3) Tokuoka, M., *Collection Czechoslov. Chem. Commun.*, 4, 444 (1932).
(4) Whelan, M., *J. Biol. Chem.*, 86, 189 (1930).

Determination of Combined Nitrogen in Steel

A Rapid Method

H. F. BEEGHLY
Research and Development Division, Jones & Laughlin Steel Corporation, Pittsburgh, Penna.

A rapid method for determining combined nitrogen in steel utilizes a micro-Kjeldahl steam-distillation unit and a photoelectric spectrophotometer in conjunction with the well-known Nessler color reaction. The method is accurate and can be used for micro-, semimicro-, or macrosamples. The procedure is suitable for investigational work and has been in use for routine determinations for approximately one year with appreciable economy of labor and time. It is applicable to all steels containing acid- or alkali-soluble nitrogen compounds and may be modified to accommodate materials containing nitrogen in a difficultly soluble form.

NITROGEN is believed by many investigators to exercise a considerable influence on the physical properties of steel. The large number of determinations necessary for control purposes and to provide data for statistical studies make it essential to have an analytical method which, without sacrifice of accuracy, will reduce to the minimum the time and labor of a single nitrogen determination.

The Allen and the vacuum fusion methods are the most commonly used for determining nitrogen in steel. Neither is sufficiently rapid to use for control purposes nor to care adequately for the large numbers of routine determinations made necessary by present-day quality requirements. The experience of many industrial and research laboratories has indicated the value of micro and semimicro analytical methods where rapid accurate determinations are required. Using a micro-Kjeldahl unit designed to utilize steam-distillation in removing ammonia from alkaline solution, Klinger and Koch (*5*) developed a micromethod for determining the nitrogen content of steel surfaces. The method was sensitive and gave accurate results but, because of the large volume of reagents used, substantially the same time was required for a single determination as in the regular macroprocedure. Most of the micro-Kjeldahl units available commercially are not suitable for determining the nitrogen content of a series of samples in rapid sequence.

The purpose of this paper is to describe a rapid and accurate method developed in this laboratory for determining combined nitrogen in carbon steel. The method utilizes a standard micro-Kjeldahl unit which is suitable for rapid determinations either singly or in series. The ammonia in the distillate is determined by means of the color reaction introduced by Nessler. A photoelectric spectrophotometer is used to measure the intensity of the ammonia-Nessler color complex. The procedure may be applied to steels for which the usual macromethods are suitable and is also suitable for small quantities of material for which macroprocedures are not applicable. Modifications of the method are necessary for pig irons and alloy steels containing nitrogen compounds not readily soluble in acid or alkali.

The chemical reactions for the microprocedure are essentially the same as for the macroprocedure, except that the

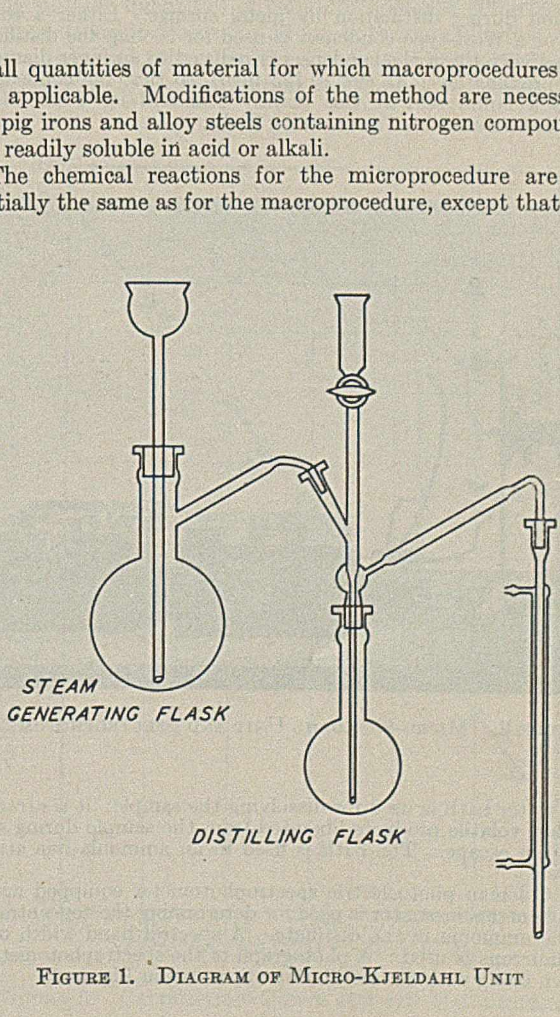


Figure 1. Diagram of Micro-Kjeldahl Unit

reagents are used in a more concentrated form. Nessler's reagent is used in place of standard solutions of acid and alkali.

Reagents

Hydrochloric acid, one part of acid, specific gravity 1.19, added to one part of ammonia-free water.

Sodium hydroxide, 600 grams dissolved quickly in 1 liter of ammonia-free water.

Nessler's reagent (*1*). Fifty grams of potassium iodide are dissolved in a minimum volume of cold water (approximately 35 ml.). A saturated solution of mercuric chloride is added slowly until the first slight precipitate of red mercuric iodide persists, and 400 ml. of a clarified 9 *N* solution of alkali (potassium or sodium hydroxide) are then added. The solution is diluted to 1 liter with ammonia-free water and allowed to clarify; the clear supernatant liquid is removed and used. The reagent does not deteriorate and can be stored indefinitely.

Standard ammonium chloride, 3.818 grams dissolved in water to make 1 liter of stock solution. Ten milliliters of this stock are diluted to 1 liter to give a solution, 1 ml. of which contains 0.01 mg. of ammonia nitrogen.

All reagents used are of C. P. grade. Solutions are prepared in an ammonia-free atmosphere and stored in carefully stoppered Pyrex bottles. When rubber stoppers are used they are first boiled for 30 minutes in a 10 per cent solution of sodium hydroxide and rinsed with ammonia-free water.

Apparatus

The micro-Kjeldahl apparatus illustrated in Figure 1 is simple in construction and is designed so that it can be attached to a single ring stand. It is built of Pyrex glass with all individual parts connected by standard-taper ground-glass joints. The steam-generating flask has a capacity of 500 ml. The distilling flasks generally used have a capacity of 50 ml. but other sizes are available and may be used when necessary; they are held in position during distillation by metal springs. Either a coiled tube or a West-type condenser is used for cooling the distillate; the delivery tip of the condenser is reduced to an inner diameter of approximately 0.31 cm. (0.125 inch), so that the condensate forms a liquid seal at this point. Standard low-form 50-ml. Nessler tubes are used as receiving flasks.

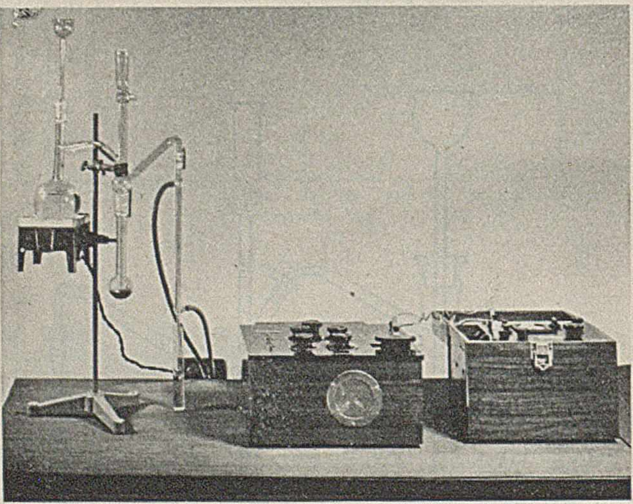


FIGURE 2. MICRO-KJELDAHL UNIT AND SPECTROPHOTOMETER

A water bath is used for dissolving the sample; it is arranged so that volatile products liberated from the sample during solution can escape. The bath is used in an ammonia-free atmosphere.

A Coleman photoelectric spectrophotometer equipped with a double monochromator is used for determining the concentration of the ammonia in the distillate. A spectral band width of 30 millimicrons is used. A photograph of the spectrophotometer is shown along with the distillation apparatus in Figure 2.

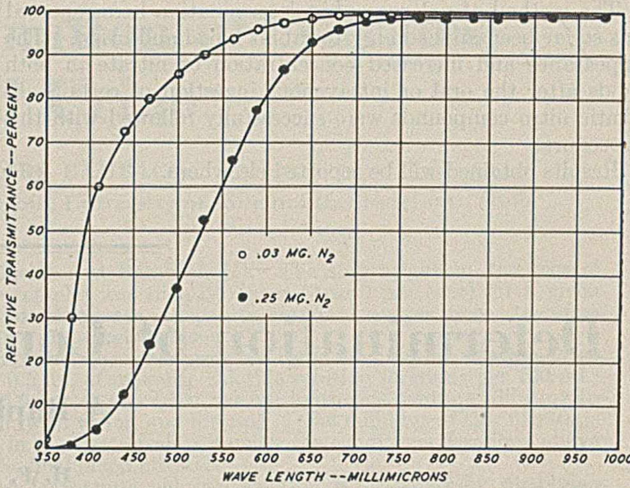


FIGURE 3. SPECTRAL TRANSMITTANCE CURVES FOR AMMONIA-NESSLER COLOR COMPLEX

Procedure

A weighed sample is placed in a 50-ml. distillation flask and covered with acid, and the flask and its contents are heated in a water bath until the sample dissolves. In general a 500-mg. sample is used with 10 ml. of hydrochloric acid as solvent. The quantities of sample and solvent may be varied, when necessary.

While the sample is dissolving, the steam-generating flask of the micro unit is filled with ammonia-free water. Heat is applied so that the steam generated passes through a distilling flask and into the condenser. Fifty-milliliter portions of the distillate are collected and tested with Nessler's reagent. When this test shows that the apparatus is free from ammonia the generating flask is refilled. The temperature is then maintained at slightly below the boiling point until a sample is ready for distillation. Then the temperature is increased sufficiently to cause a steady evolution of steam; an excess of sodium hydroxide (10 ml. are sufficient for 10 ml. of hydrochloric acid) is added from a buret to a dissolved sample in such a manner that the acid solution and the alkali remain in two separate layers. The flask containing the sample and the excess of strong alkali is connected to the micro unit in place of the empty distilling flask, without interrupting the steam generation. The steam passing from the generator into the distillation flask liberates and carries ammonia and steam into the condenser where the steam condenses. The solution is collected in a clean 50-ml. Nessler tube. The complete distillation requires about 5 minutes for a sample. The apparatus is then ready for the substitution and distillation of a second sample immediately. No delay is necessary for rinsing distillation flasks or transferring the sample to the apparatus. The capacity of the steam generator shown in Figure 2 is sufficient to distill the ammonia from a series of 6 samples without refilling.

The distillates are diluted to 50 ml. with ammonia-free water and 1 ml. of Nessler's reagent is added to each; the intensity of the resulting color is measured with the photoelectric spectrophotometer. The transmittance readings are then converted to per cent nitrogen by means of a standard conversion curve.

Precautions

A blank is determined on the reagents in exactly the same manner as for the steel except for omission of the sample. With carefully prepared reagents the blank correction is usually negligible; nevertheless the determination of a reagent blank should be made a daily practice.

The composition of the reagents should be reproduced closely from batch to batch. Each time a fresh stock of Nessler solution is used the calibration of the instrument should be checked. The most reliable and convenient means of checking or establishing the calibration curve is to dilute known quantities of standard ammonium chloride (or sulfate) to a volume of 50 ml., nesslerize directly, and determine the transmittance at the desired wave length.

The efficiency of the distillation procedure should be checked independently at least once each 8 hours by running a steel of known nitrogen content. In this manner possible errors in the determination are likely to be detected. Steels such as 55-a, 15-c, or 101-a certified by the National Bureau of Standards are suitable for this purpose.

After addition of the Nessler solution to the distillate the color develops rapidly and the intensity remains relatively constant for an hour. A minimum interval of 5 minutes between addition of Nessler reagent and the spectrophotometric reading is adequate. Readings should usually be completed on a series of samples within 30 minutes after addition of Nessler reagent to the first sample.

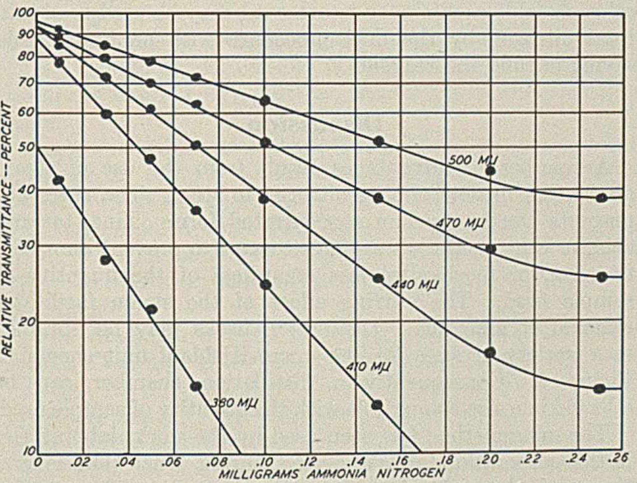


Figure 4. Transmittance of Ammonia-Nessler Complex at Different Wave Lengths

Consistently reliable results cannot be obtained unless the apparatus, including all distillation flasks and receiving flasks, is free from traces of ammonia. For this reason it is preferable to use a stock of clean Nessler tubes as receiving flasks and then nesslerize the distillate in them rather than to collect the distillate in a volumetric flask and transfer the solution to another flask. Such an arrangement also effects a worthwhile saving in time.

The size of sample may be varied as desired. In general, it is preferable to choose a sample of such size that it will contain from 0.02 to 0.12 mg. of ammonia nitrogen. By using a sample of either 500 or 250 mg. of steel this nitrogen content usually will be obtained. Sample solutions and distillates must be protected from possible contamination by atmospheric ammonia. The temperature of the distillate should be maintained constant, as near 25° C. as practicable.

Experimental

The spectral transmittance of the ammonia-Nessler complex was determined with the Coleman spectrophotometer, using a spectral band 30 millimicrons wide and distilled water as a reference standard. Two typical curves are shown in Figure 3. The transmittance of the ammonia-Nessler complex decreases sharply as the wave length is decreased below 650 millimicrons. It will be observed that the spectral region between approximately 390 and 500 millimicrons is the region giving a maximum difference in transmittance for a given difference in concentration. Wave lengths outside this region can be used for quantitative work only with considerable sacrifice of sensitivity. A band 30 millimicrons wide with a mean wave length of 410 millimicrons was chosen for a major portion of the work reported here because it gave a suitable sensitivity over a fairly wide concentration range.

Different solutions containing the same quantities of ammonium chloride were nesslerized and transmittance readings taken for three different concentrations. The maximum deviations from the mean transmittance values was 0.5, 0.3, and 0.2 per cent, respectively, for concentrations of 0.01, 0.03, and 0.05 mg. of ammonia nitrogen. These values indicated that the intensity of the ammonia Nessler complex could be reproduced consistently enough to permit the method to be used for determining nitrogen in steel by the micromethod.

Curves were constructed from the data obtained by measuring the transmittance of solutions prepared by adding 1 ml. of Nessler's reagent directly to 50 ml. of solutions containing different known quantities of ammonium chloride. The relationship between the logarithm of transmittance and the ammonia concentration is shown by the curves in Figure 4, which indicate that the ammonia-Nessler complex conforms to Beer's law up to a concentration of approximately 0.16 mg. Known quantities of ammonium chloride were placed in clean digestion flasks, 10 ml. each of hydrochloric acid and alkali were added, and the ammonia was recovered by a 5-minute distillation. The distillate was diluted to 50 ml., 1 ml. of Nessler's reagent added, and the transmittance determined after the color had developed. The agreement between the results of these experiments indicated that a 5-minute distillation was adequate for complete recovery of the ammonia.

A conversion curve was constructed for the instrument by using suitable quantities of carefully prepared standard ammonium chloride diluted to 50 ml. with ammonia-free water and nesslerized directly. Two points were sufficient to establish accurately the position and slope of the curve. The

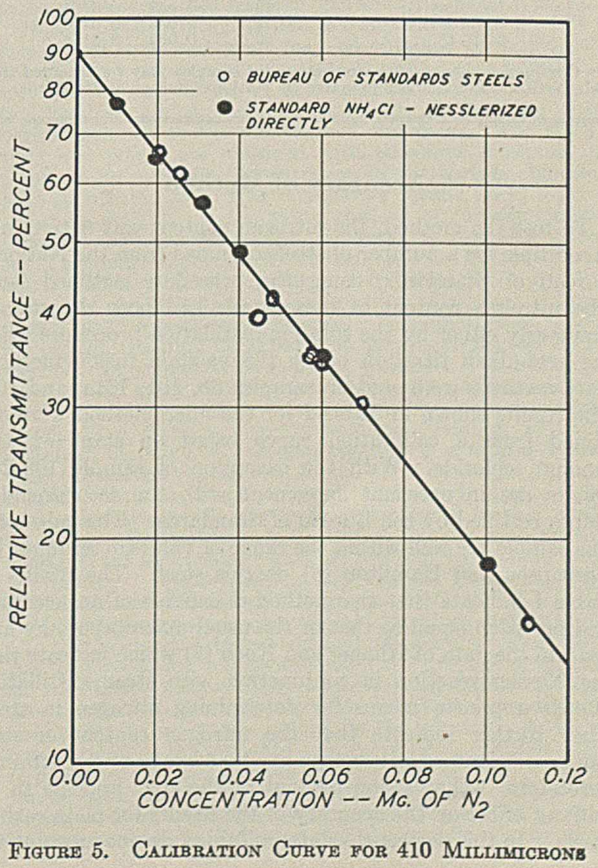


Figure 5. Calibration Curve for 410 Millimicrons

curve shown in Figure 5 was prepared in this manner for a wave length of 410 millimicrons. The transmittance values obtained on steels supplied by the National Bureau of Standards are also shown in Figure 5; they are the averages of the values shown in Table I. The nitrogen values are those supplied by the National Bureau of Standards. The curve in Figure 5 indicates that a suitable calibration curve for nitrogen in steel can be established by direct nesslerization of a pure solution of ammonium chloride.

TABLE I. DETERMINATION OF COMBINED NITROGEN IN BUREAU OF STANDARDS STEELS

Standard Sample No.	Type of Steel	Wt. of Sample	Transmittance at 410 Mμ	Nitrogen Found		Nitrogen Present[a]
		Mg.		Mg.	%	%
55a	Open hearth iron, 0.01% C	500	64.5	0.021	0.0042	0.004
			68.0	0.018	0.0036	
			63.7	0.021	0.0042	
			64.7	0.021	0.0042	
			66.5	0.019	0.0038	
			63.6	0.021	0.0042	
15c	Basic open hearth steel, 0.1% C	500	61.4	0.024	0.0048	0.005
			61.0	0.024	0.0048	
			61.4	0.024	0.0048	
			59.0	0.026	0.0052	
8b	Acid Bessemer steel, 0.1% C	500	34.7	0.060	0.0120	0.0120
			31.7	0.066	0.0132	
			35.7	0.058	0.0116	
			36.0	0.058	0.0116	
10b	Acid Bessemer steel, 0.4% C	500	34.6	0.060	0.0120	0.0114
			34.8	0.060	0.0120	
22	Acid Bessemer steel, 0.6% C	500	40.6	0.050	0.0100	0.0095
			41.0	0.050	0.0100	
			42.5	0.047	0.0094	
23	Acid Bessemer steel, 0.8% C	500	34.3	0.061	0.0122	0.0116
			35.7	0.059	0.0118	
101	Stainless steel 18–8, 0.06% C	250	32.0	0.065	0.026	0.028
			29.8	0.070	0.028	
			28.9	0.072	0.029	
101a	Stainless steel 18–8, 0.05% C	250	15.6	0.111	0.044	0.044
			15.0	0.113	0.045	
			15.7	0.110	0.044	
106	Nitriding steel Nitralloy G, Cr-Mo-Al, 0.3% C	500	39.3	0.052	0.0104	0.009
			39.5	0.052	0.0104	
			39.0	0.053	0.0106	
			39.3	0.052	0.0104	

[a] Complete analyses of current standard samples may be obtained from their certificates of analysis prepared by National Bureau of Standards.

Accuracy of Method

To test the method, the nitrogen content was determined in multiple for a number of steels obtained from the National Bureau of Standards, using the procedure outlined here. The nitrogen content of these steels had been determined previously either by the solution-distillation procedure using the acid-alkali titration or by the vacuum fusion method. Both methods were used on samples 8b, 101, 101a, and 106. The results shown in Table I for the micromethod were obtained from a calibration curve based on standard ammonium chloride. With the exception of sample 106 the results are in excellent agreement with the recommended values certified by the Bureau of Standards. The values for this sample are well within the range of values determined by Thompson and Hamilton (*6*) on this steel. The results in Table I indicate that the method is capable of an accuracy and precision equal to that of the usual macroprocedure and confirm the data of Klinger and Koch (*5*) which indicate that the Nessler reaction in conjunction with steam-distillation affords a precise means for determining nitrogen in steel. They further indicate that the nitrogen content of steel can be determined with a rapidity that has not been attained heretofore. The carbon content of the steel appears to be without effect on the accuracy of the results for plain carbon steels. In this respect the data in Table I do not substantiate the conclusions of Tschischewski (*7*) and of Jordan and Swindells (*4*) that use of Nessler solution with high-carbon steels produces low results.

Samples 101, 101a, and 106 are low in carbon but contain appreciable quantities of chromium, nickel, molybdenum, and aluminum. Results indicate that the nitrogen in these steels is determined with essentially the same accuracy as in plain carbon steels. However, for pig irons or for materials high in such elements as silicon, titanium, vanadium, tungsten, or columbium or for materials containing these elements in combination with carbon and nitrogen, the routine procedure will not give accurate results for total nitrogen. In the macroanalysis of such steels special digestion treatments involving the use of hydrofluoric (*2*), sulfuric (*3*, *8*), perchloric (*3*), or phosphoric acids (*8*) have been developed. These, or other suitable preliminary treatments, may be used to obtain total nitrogen by the microprocedure with an appreciable saving in time and reagents.

Discussion

A number of advantages result from the use of steam distillation in determining nitrogen in steel. The necessary reagents can be used in concentrated form. Zinc, tartaric acid, or other materials are unnecessary to prevent bumping, foaming, or mechanical loss regardless of the quantity of sample used. The stirring effect of the steam facilitates removal of ammonia. Distillation flasks may be obtained in a variety of sizes for the micro-Kjeldahl unit shown in Figure 2. Consequently a distillation chamber can be selected in a size compatible with the quantity of sample used.

The micromethod has been used by the works laboratories in this corporation for over a year, during which time several thousand determinations have been made. The routine procedure has been applied mainly to low-carbon Bessemer and open hearth steels but has been applied successfully to high-carbon steels and, in modified form, to pig irons. The routine method appears capable of an accuracy substantially the same as that of the usual solution distillation or vacuum fusion procedure and permits an appreciable saving in labor and reagents. The technique of the method can be mastered by relatively inexperienced operators. The procedure is somewhat more exacting than that for direct distillation methods, but, in general, consistent results can be obtained with less difficulty.

Acknowledgment

The writer is indebted to H. W. Graham and H. K. Work, whose interest in nitrogen in steel made this work possible. In addition he acknowledges his debt to H. E. Slocum and his associates in the Aliquippa and Pittsburgh Works for their cooperation in establishing the method for use in the mill laboratories. To G. E. F. Lundell and his associates at the National Bureau of Standards, he is indebted for their cooperation in supplying steels of known nitrogen content.

Literature Cited

(1) Am. Public Health Assoc., "Standard Methods of Water Analysis", 7th ed., p. 14, 1933.
(2) Cunningham, T. R., and Hammer, H. L., IND. ENG. CHEM., ANAL. ED., 11, 303–4 (1939).
(3) Johnson, C. M., *Iron Age*, 134, No. 4, 10–15 (1934).
(4) Jordan, L., and Swindells, F. W., Natl. Bur. Standards, *Sci. Paper* 457 (1922).
(5) Klinger, P., and Koch, W., *Arch. Eisenhüttenw.*, 10, 463–8 (1937).
(6) Thompson, J. G., and Hamilton, E. H., *Bur. Standards J. Research*, 9, 593–5 (1932); *Research Paper* 494.
(7) Tschischewski, N., *J. Iron Steel Inst.*, 92, No. 2, 47–106 (1915).
(8) U. S. Steel Corp. Chemists, "Sampling and Analysis of Carbon and Alloy Steels", pp. 292–8, 1938.

Volumetric Determination of Sulfur in Coal and Coke

S. S. TOMKINS, Consolidated Edison Company of New York, Inc., New York, N. Y.

THE present accepted standard method (*1*) for the determination of sulfur in coal and coke specifies its oxidation and the recovery of the sulfur compounds in the form of soluble sulfates, followed by gravimetric determination as barium sulfate. The conversion of the sulfur compounds into sulfates is accomplished by combustion of the coal in an oxygen bomb, ignition with Eschka mixture, or fusion with sodium peroxide. The soluble sulfates are recovered in the bomb washings or by leaching the Eschka and peroxide residues. Complete conversion of the sulfur compounds to sulfate is ensured by a further wet-oxidation with bromine water.

Some fuel laboratories have found the gravimetric determination as barium sulfate time-consuming and costly, especially where a large number of coal samples are tested daily, and have studied volumetric methods using internal indicators. The methods receiving most consideration employ either tetrahydroxyquinone (*4*, *5*, *6*) or sodium rhodizonate (*4*) as indicator.

The American Society for Testing Materials Committee D5 on Coal and Coke has sponsored during the past year, through its Subcommittee I on Methods of Testing, a coöperative study of the comparative accuracy and reproducibility of the standard method of sulfur determination and of volumetric methods using tetrahydroxyquinone and sodium rhodizonate as indicators. Samples of four coals ranging in sulfur content from approximately 0.6 to 3.3 per cent were collected from large commercial deliveries, air-dried, reduced, and ground to pass through a 250-micron (No. 60) sieve in accordance with the standard A. S. T. M. methods (*1*, *3*). Representative portions of each coal were distributed among the following eight laboratories cooperating in the study:

Commercial Testing and Engineering Company, Chicago, Ill.
Consolidated Edison Company of New York, Inc., New York, N. Y.
Fuel Engineering Company of New York, New York, N. Y.
State of Illinois, State Geological Survey Division, Urbana, Ill.
The Koppers Coal Company, Pittsburgh, Penna.
The Textor Laboratories, Cleveland, Ohio
United States Department of Interior, Bureau of Mines Central Experiment Station, Pittsburgh, Penna.
Western Electric Company, Kearny, N. J.

Experimental

The coal samples were oxidized in an oxygen bomb or by the Eschka method. Separate portions of each sample were used for each determination.

Gravimetric determinations (*1*) were made on the bomb washings by seven of the cooperating laboratories and on the leachings from the Eschka mixture by all eight laboratories. Volumetric determinations using tetrahydroxyquinone as internal indicator were made by the seven laboratories, and six of the laboratories used sodium rhodizonate as indicator.

A total of 380 individual determinations was made.

The procedures employed in the volumetric methods were as follows:

TETRAHYDROXYQUINONE AS INDICATOR. *Reagents.* Sodium carbonate solution, 18.3 grams per liter. Methyl orange indicator, 0.1 per cent aqueous solution. Bromine water, saturated solution. Phenolphthalein indicator, 0.5 per cent solution in 50 per cent by volume neutral isopropyl alcohol. Approximately 0.02 *N* sodium hydroxide solution. Approximately 0.02 *N* hydrochloric acid solution. Hydrochloric acid solution, 50 per cent by volume concentrated hydrochloric acid, 50 per cent by volume water. Isopropyl alcohol, 99 per cent, ethyl alcohol, 95 per cent, or denatured alcohol, formulas 30 or 3A. Tetrahydroxyquinone indicator. Barium chloride solution gravimetrically standardized, 1 ml. equivalent to 0.0005 gram of sulfur.

Procedure. Bomb-Washing Method. Weigh approximately 1 gram of the coal or coke sample into the capsule in which it is to be burned. Samples which are likely to be blown out of the capsule should be briquetted. Place the capsule in the bomb and proceed as outlined in Section 21 (*1*) finally collecting the bomb washings in a 250-ml. beaker. Titrate the bomb washings with the sodium carbonate solution using methyl orange indicator. Heat the solution and filter. Proceed as indicated below under Eschka method.

Eschka Method. Proceed as outlined in Sections 17 to 20, inclusive (*1*), finally collecting the Eschka leachings of about 250 ml. in a beaker.

Make the bomb washings or Eschka leachings slightly acid with 1 to 1 hydrochloric acid and add 2 ml. of bromine water. Evaporate to about 75 ml. or less and cool to below 35° C. Add 2 or 3 drops of phenolphthalein indicator and then add carefully approximately 0.02 *N* sodium hydroxide until solution is faintly pink. Transfer the solution to a 100-ml. volumetric flask and dilute to 100 ml. with distilled water. Pipet a 25-ml. aliquot into a 125-ml. Erlenmeyer flask and neutralize by adding carefully approximately 0.02 *N* hydrochloric acid until the pink color just disappears. Add 25 ml. of isopropyl alcohol and about 0.4 to 0.5 gram of tetrahydroxyquinone indicator. Swirl the flask until the indicator is dissolved and titrate slowly with standard barium chloride solution, continually swirling the flask until a permanent rose color is imparted to the mixture.

Calculation. The barium chloride solution gives a blank titration of 0.1 ml. and this value should be deducted. The per cent of sulfur in the sample equals (ml. of barium chloride chloride solution − 0.1) × 0.2. When the Eschka method is used, a further correction must be applied either by running a blank or preferably by determining a known amount of sulfate added to a solution of the reagents after these have been put through the prescribed series of operations (*1*, Section 20, *f*).

Notes. The titration is best accomplished over a white surface. A sharper end point may be obtained by adding about 1.0 ml. of a 1 per cent silver nitrate solution to the titration mixture after about 2.0 ml. of the standard barium chloride solution has been added, and then continuing the titration with the barium chloride to the rose colored end point. The most distinct end points are obtained with titrations requiring up to about 15 ml. and the concentration of the barium chloride has been so selected as to give satisfactory results up to 3 per cent sulfur by weight. If the sulfur content of the sample should exceed 3 per cent by weight, it would be desirable either to select a smaller aliquot such as 10 ml. or to use a stronger barium chloride solution (1 ml. equivalent to 0.001 gram of sulfur).

SODIUM RHODIZONATE AS INDICATOR. *Reagents.* Approximately 0.02 *N* sodium hydroxide. Phenolphthalein indicator, 0.5 per cent solution in 50 per cent by volume neutral isopropyl alcohol. Barium chloride solution, either 0.1 *N* or 1 ml. equivalent to 0.001 gram of sulfur, gravimetrically standardized. Ammonium sulfate solution, either 0.1 *N* or 1 ml. equivalent to standardized barium chloride solution. Sodium rhodizonate indicator, prepared by grinding together in a mortar 1 part by weight of sodium rhodizonate to 400 parts by weight ammonium chloride until thoroughly mixed. Isopropyl alcohol, 99 per cent, ethyl alcohol, 95 per cent, or denatured alcohol, formulas 30 or 3A. Hydrochloric acid solution, 50 per cent by volume concentrated hydrochloric acid, 50 per cent by volume water.

Procedure. Bomb-Washing and Eschka Methods. Proceed as outlined under Tetrahydroxyquinone Method.

Make the bomb washings or Eschka leachings slightly acid with 1 to 1 hydrochloric acid and add 2 ml. of bromine water. Evaporate to about 35-ml. volume and add 2 or 3 drops of phenolphthalein indicator. Add carefully approximately 0.02 *N* sodium hydroxide until solution is faintly pink. Add a volume of isopropyl alcohol equivalent to the volume of the solution. Add a measured amount of the standard barium chloride solution sufficient to precipitate the sulfate plus an excess of 3 to 5 ml. This excess can be estimated readily with a little experience. After allowing a minute or two for completion of the reaction, add 0.2 gram of the sodium rhodizonate indicator and thoroughly mix by swirling.

TABLE I. DETERMINATION OF SULFUR IN COAL

(Comparison between A. S. T. M. standard gravimetric methods and selected volumetric methods)

Laboratory	A. S. T. M. Gravimetric Methods D-271-40				Volumetric Methods				Average
	Bomb Washings		Eschka		Tetrahydroxyquinone		Sodium Rhodizonate		
	Determination	Max. diff.	Determination	Max. diff.	Determination	Max. diff.	Determination	Max. diff.	
	Per cent by weight				Per cent by weight				
				Sulfur Found in Coal A					
A	1.17		1.20		1.24		1.22		
	1.18	0.06	1.18	0.05	1.20	0.04	1.25		
	1.21		1.23		1.24		1.26		
	1.23		1.21		1.20		1.26	0.04	
							1.26		
							1.25		
							1.25		
Av.	1.20		1.21		1.22		1.25		1.22
B	1.15		1.22		1.20		1.23		
	1.20	0.05	1.21	0.01	1.18	0.06	1.24	0.10	
	1.19		1.22		1.24		1.14		
Av.	1.18		1.22		1.21		1.20		1.21
C	1.18		1.28		1.26		1.17		
	1.28	0.10	1.31	0.03	1.26	0.00	1.25	0.16	
	1.23		1.30		1.26		1.33		
Av.	1.23		1.30		1.26		1.25		1.26
D	1.25		1.23		1.24		1.20		
	1.26	0.02	1.18	0.05	1.22	0.04	1.21	0.03	
	1.24		1.20		1.20		1.23		
Av.	1.25		1.20		1.22		1.21		1.22
E	1.18		1.31		1.18		1.15		
	1.24	0.06	1.22	0.09	1.21	0.08	1.22		
	1.22		1.22		1.26		1.26		
			1.24				1.30	0.16	
							1.31		
							1.13		
							1.22		
Av.	1.22		1.25		1.22		1.23		1.23
F	1.14		1.39		1.18		..		
	1.15	0.06	1.36	0.03	1.15	0.07	..	..	
	1.20		1.37		1.22		..		
Av.	1.16		1.37		1.18		..		1.24
G	..		1.20		..		1.21		
	..	..	1.26	0.06	..	..	1.23	0.03	
	..		1.26		..		1.24		
Av.	..		1.24		..		1.23		1.24
H	1.23		1.24		1.32		..		
	1.20	0.03	1.22	0.08	1.30	0.04	..	..	
	1.23		1.30		1.28		..		
Av.	1.22		1.25		1.28		..		1.25
No. of tests	22		26		22		26		
Grand av.	1.21		1.26		1.23		1.23		1.23
Max. diff. between determinations		0.14		0.21		0.17		0.30	

Laboratory	A. S. T. M. Gravimetric Methods D271-40				Volumetric Methods				Average
	Bomb Washings		Eschka		Tetrahydroxyquinone		Sodium Rhodizonate		
	Determination	Max. diff.	Determination	Max. diff.	Determination	Max. diff.	Determination	Max. diff.	
	Per cent by weight				Per cent by weight				
				Sulfur Found in Coal B					
A	1.64		1.68		1.65		1.67		
	1.64	0.04	1.70	0.02	1.70	0.05	1.66	0.04	
	1.64		1.68		1.68		1.70		
	1.68		1.69		1.66		1.69		
Av.	1.65		1.69		1.67		1.68		1.67
B	1.66		1.64		1.66		1.65		
	1.66	0.07	1.64	0.01	1.69	0.06	1.62	0.03	
	1.73		1.65		1.63		1.65		
Av.	1.68		1.64		1.66		1.64		1.66
C	1.68		1.61		1.60		1.61		
	1.58	0.10	1.61	0.01	1.69	0.09	1.58	0.03	
	1.60		1.62		1.62		1.61		
Av.	1.62		1.61		1.64		1.60		1.62
D	1.54		1.68		1.55		1.54		
	1.55	0.01	1.66	0.02	1.54	0.04	1.56	0.04	
	1.54		1.66		1.58		1.52		
Av.	1.54		1.67		1.56		1.54		1.58
E	1.65		1.64		1.56		1.66		
	1.64	0.02	1.67		1.60	0.04	1.56		
	1.63		1.60	0.08	1.59		1.72		
			1.66			1.71		0.14	
			1.68				1.61		
							1.58		
							1.60		
Av.	1.64		1.65		1.58		1.63		1.63
F	1.60		1.70		1.60		..		
	1.62	0.02	1.73	0.03	1.63	0.03	..	..	
	1.61		1.73		1.66		..		
Av.	1.61		1.72		1.63		..		1.65
G	..		1.69		..		1.63		
	..	..	1.70	0.02	..	..	1.72	0.09	
	..		1.68		..		1.68		
Av.	..		1.69				1.68		1.69
H	1.61		1.67		1.64		..		
	1.64	0.03	1.68	0.01	1.66	0.08	..	..	
	1.61		1.67		1.72		..		
Av.	1.62		1.67		1.67		..		1.65
No. of tests	22		27		22		23		
Grand av.	1.62		1.67		1.63		1.63		1.64
Max. diff. between determinations		0.19		0.13		0.18		0.20	

TABLE II. DETERMINATION OF SULFUR IN COAL

(Comparison between A. S. T. M. standard gravimetric methods and selected volumetric methods)

	A. S. T. M. Gravimetric Methods D271-40				Volumetric Methods				
	Bomb Washings		Eschka		Tetrahydroxyquinone		Sodium Rhodizonate		
Laboratory	Determination	Max. diff.	Determination	Max. diff.	Determination	Max. diff.	Determination	Max. diff.	Average
	Per cent by weight				Per cent by weight				
	Sulfur Found in Coal C								
A	0.69 0.68 0.71 0.71	0.03	0.71 0.71 0.70 0.71	0.01	0.68 0.66 0.68 0.70 0.72 0.70	0.06	0.67 0.69 0.74 0.74	0.07	
Av.	0.70		0.71		0.70		0.71		0.71
B	0.73 0.74 0.73	0.01	0.69 0.67 0.68	0.01	0.69 0.66 0.74	0.08	0.79 0.71 0.73	0.08	
Av.	0.73		0.68		0.70		0.74		0.71
C	0.70 0.68 0.70	0.02	0.66 0.65 0.69	0.04	0.74 0.76 0.71	0.05	0.68 0.65 0.66	0.02	
Av.	0.69		0.67		0.74		0.66		0.69
D	0.63 0.64 0.66	0.03	0.67 0.65 0.66	0.02	0.66 0.68 0.65	0.03	0.65 0.70 0.69	0.05	
Av.	0.64		0.66		0.66		0.68		0.66
E	0.74 0.69 0.71	0.05	0.70 0.69 0.66 0.71 0.69	0.05	0.66 0.68 0.68	0.02	0.68 0.70 0.70 0.63 0.64 0.60	0.10	
Av.	0.71		0.69		0.67		0.66		0.68
F	0.68 0.71 0.66	0.05	0.73 0.74 0.73	0.01	0.70 0.66 0.66	0.04	.. .. ..	..	
Av.	0.68		0.73		0.67		..		0.69
G	.. .. ..	..	0.71 0.71 0.69	0.02	.. .. ..	..	0.66 0.72 0.64	0.08	
Av.	..		0.70		..		0.67		0.69
H	0.67 0.70 0.69	0.03	0.70 0.65 0.68	0.05	0.78 0.80 0.78	0.02	.. .. ..	..	
Av.	0.69		0.67		0.79		..		0.72
No. of tests	22		27		24		22		
Grand av.	0.69		0.69		0.70		0.69		0.69
Max. diff. between determinations		0.11		0.09		0.15		0.19	

	A. S. T. M. Gravimetric Methods D271-40				Volumetric Methods				
	Bomb Washings		Eschka		Tetrahydroxyquinone		Sodium Rhodizonate		
Laboratory	Determination	Max. diff.	Determination	Max. diff.	Determination	Max. diff.	Determination	Max. diff.	Average
	Per cent by weight				Per cent by weight				
	Sulfur Found in Coal D								
A	3.16 3.12 3.22 3.24	0.12	3.26 3.26 3.20 3.24	0.06	3.15 3.15 3.20 3.15	0.05	3.18 3.14 3.12 3.14 3.25 3.23	0.13	
Av.	3.19		3.24		3.16		3.19		3.20
B	3.18 3.18 3.24	0.06	3.20 3.20 3.20	0.00	3.11 3.18 3.19	0.08	3.14 3.13 3.27	0.06	
Av.	3.20		3.20		3.16		3.18		3.19
C	3.20 3.21 3.29	0.09	3.37 3.36 3.38	0.02	3.17 3.16 3.19	0.03	3.02 3.07 3.04	0.02	
Av.	3.23		3.37		3.18		3.04		3.21
D	3.14 3.17 3.16	0.03	3.16 3.22 3.23	0.07	3.09 3.10 3.06	0.04	3.12 3.11 3.08	0.04	
Av.	3.16		3.20		3.08		3.10		3.14
E	3.13 3.15 3.20	0.07	3.20 3.19 3.18 3.27 3.24	0.09	3.14 3.18 3.13	0.05	3.18 3.20 3.22 3.14 3.09 3.10 3.10	0.12	
Av.	3.16		3.22		3.15		3.15		3.17
F	3.06 3.12 3.13	0.07	3.27 3.31 3.29	0.04	3.26 3.21 3.18	0.08	.. .. ..	..	
Av.	3.10		3.29		3.22		..		3.20
G	.. .. ..	..	3.27 3.24 3.23	0.04	.. .. ..	..	3.22 3.18 3.12	0.10	
Av.	..		3.25		..		3.17		3.21
H	3.16 3.21 ..	0.05	3.25 3.26 3.26	0.01	3.18 3.18 3.16	0.02	.. .. ..	..	
Av.	3.19		3.26		3.17		..		3.21
No. of tests	21		27		22		25		
Grand av.	3.18		3.25		3.16		3.14		3.18
Max. diff. between determinations		0.23		0.22		0.20		0.25	

Table III. Summary

Coal	Over-all Average Sulfur, % by Wt.	Maximum Differences between Over-all Averages and Averages Reported by Each Laboratory: A. S. T. M. Gravimetric Methods, Bomb washing	Eschka	T. H. Q.	Sodium rhodizonate	Permissible A. S. T. M. Difference between Different Laboratories
A	1.23	0.07	0.14	0.05	0.04	0.10
B	1.64	0.10	0.08	0.08	0.10	0.10
C	0.69	0.05	0.04	0.10	0.05	0.10
D	3.18	0.08	0.19	0.10	0.14	0.20

Table IV. Summary

	A. S. T. M. Gravimetric Methods				Volumetric Methods				Permissible A. S. T. M. Difference between Determinations by Same Laboratory
	Bomb Washing		Eschka		T. H. Q.		Sodium Rhodizonate		
Coal	Max. diff. between detns.	No. of labs. exceeding A. S. T. M. permissible difference	Max. diff. between detns.	No. of labs. exceeding A. S. T. M. permissible difference	Max. diff. between detns.	No. of labs. exceeding A. S. T. M. permissible difference	Max. diff. between detns.	No. of labs. exceeding A. S. T. M. permissible difference	
A	0.10	4	0.09	3	0.07	3	0.16	3	0.05
B	0.10	2	0.08	1	0.09	3	0.14	2	0.05
C	0.05	0	0.05	0	0.08	2	0.10	4	0.05
D	0.12	1	0.09	0	0.08	0	0.13	2	0.10

At this point the solution should have acquired a distinct red color, indicating an excess of barium chloride. If the color is not red, add more of the standard barium chloride solution and another portion of the indicator. It is important that the indicator be added after the reaction is complete and that an excess of barium chloride be present.

Titrate the excess barium chloride with standard ammonium sulfate solution, adding about one drop per second with constant swirling until there is a slight fading of the original red to a light pink. Continue the titration at a rate of 5 to 7 drops per minute until one drop produces a light orange tint. Allow to stand a minute or two. A change to a pronounced canary yellow indicates the end point; if this does not occur, one more drop is usually sufficient. Direct titration to the yellow color invariably means an overrun end point introducing a significant error.

Calculation. Ml. of $BaCl_2$ solution − ml. $(NH_4)_2SO_4$ solution × factor in grams of *S* per ml. × 100 = % by wt. of *S*.

When using the Eschka method, the additional correction previously referred to must be applied.

Discussion of Results

The results obtained are presented in Tables I and II.

The maximum differences between the over-all average sulfur content of each coal and the averages reported by each laboratory for each method are summarized in Table III.

These data show that the average results reported by all the laboratories for all the methods are well within the permissible A. S. T. M. differences for different laboratories established for the present gravimetric methods, with the single exception in the case of the Eschka determination for Coal A. This rather large difference was caused by one laboratory obtaining abnormally high results on this coal by the Eschka gravimetric method as compared with the results of the other laboratories, and hence is not considered significant. Eliminating the average of this laboratory, the maximum difference would be reduced from 0.14 to 0.07.

The maximum differences between individual determinations reported by any laboratory for each coal and method, and the number of laboratories reporting maximum differences between individual determinations which exceed the permissible A. S. T. M. differences for the same laboratory, are summarized in Table IV.

Table V summarizes the average sulfur contents by the several laboratories and presents the standard deviation and probable error. The standard deviation has been calculated in accordance with the A. S. T. M. method (*2*) and measures the spread or dispersion of the individual determinations about the mean value. The standard deviation, σ, is the square root of the average of the squares of the individual results from their arithmetical average. It is used to determine the fraction of the total number of tests falling within certain limits—namely, 68.3 per cent of all determinations should fall within the band, mean ± σ. The larger the value of the standard deviation, the greater the spread about the mean value. The probable error, *r*, by definition is the value of the limit from the average within which 50 per cent of the results will fall and is indicated to be 0.6745 × σ. Since the average standard deviations are relatively of the same order of magnitude, the average sulfur contents as determined by any of these methods will check each other closely, and will be within the present A. S. T. M. permissible differences between determinations. Also the variation of successive determinations about the mean value will be about the same for each of the methods.

On the basis of the results reported herewith, it is concluded that the volumetric methods using either tetrahydroxyquinone or sodium rhodizonate as indicators will yield results of the same degree of reproducibility and accuracy as the present standard gravimetric method.

Comments received from the several cooperating laboratories did not indicate any serious difficulties in carrying

Table V. Comparison of Results, Standard Deviations, and Probable Errors by Various Methods

	A. S. T. M. Gravimetric		Volumetric		
Method	Bomb washings	Eschka	T. H. Q.	Sodium rhodizonate	Average
Coal A					
No. of tests	22	26	22	26	96
Average sulfur content, % by wt.	1.21	1.26	1.23	1.23	1.23
Standard deviation, σ	0.045	0.063	0.038	0.044	0.040
Probable error, *r*	0.030	0.043	0.026	0.030	0.032
Coal B					
No. of tests	22	27	22	23	94
Average sulfur content, % by wt.	1.62	1.67	1.63	1.63	1.64
Standard deviation, σ	0.045	0.048	0.061	0.061	0.054
Probable error, *r*	0.030	0.032	0.041	0.041	0.036
Coal C					
No. of tests	22	27	24	22	95
Average sulfur content, % by wt.	0.69	0.69	0.70	0.69	0.69
Standard deviation, σ	0.030	0.029	0.044	0.061	0.041
Probable error, *r*	0.020	0.019	0.030	0.041	0.028
Coal D					
No. of tests	21	27	22	25	95
Average sulfur content, % by wt.	3.18	3.25	3.16	3.14	3.18
Standard deviation, σ	0.063	0.025	0.036	0.088	0.053
Probable error, *r*	0.042	0.017	0.025	0.059	0.036
Coals A, B, and C					
Average standard deviation, σ	0.040	0.046	0.048	0.055	0.047
Average probable error, *r*	0.027	0.031	0.032	0.037	0.032

out the procedures, even though analysts unfamiliar with these volumetric methods were employed. The principal difficulty in applying the methods seems to have been in determining the sodium rhodizonate end point. However, two laboratories apparently solved this problem by doubling the amount of indicator.

The principal merit of the volumetric methods is the saving in time and cost in laboratories testing a considerable number of samples each day. Laboratories determining calorific value can use the oxygen bomb calorimeter and a volumetric determination of the sulfur in the bomb washings to considerable advantage. The saving in time by use of the volumetric methods instead of the present standard gravimetric method is not appreciable in laboratories making an occasional determination.

As a result of this study, the subcommittee is recommending the tetrahydroxyquinone and sodium rhodizonate methods for adoption as A. S. T. M. tentative standards as alternatives to the present standard gravimetric method.

Acknowledgment

The writer wishes to express his appreciation to W. A. Selvig, U. S. Bureau of Mines Pittsburgh Experiment Station, C. A. Lunn, C. F. Stolzenbach, and A. C. Vogel, Consolidated Edison Company of New York, Inc., and to the cooperating laboratories for their fine contributions to this work.

Literature Cited

(1) Am. Soc. Testing Materials, "Laboratory Sampling and Analysis of Coal and Coke", Designation D271-40.
(2) Am. Soc. Testing Materials, Committee E-1 "Manual on the Presentation of Data".
(3) Am. Soc. Testing Materials, "Method of Sampling Coals", Designation D492-40 T.
(4) Brunjes, H. L., and Manning, M. J., Ind. Eng. Chem., Anal. Ed., 12, 718–20 (1940).
(5) Schroeder, W. C., *Ibid.*, 5, 403–6 (1933).
(6) Sheen, R. T., and Kahler, H. L., *Ibid.*, 8, 127–30 (1936).

Presented before the Division of Gas and Fuel Chemistry at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J.

Determination of Copper Reduced by Sugars

Use of Ceric Sulfate as a Volumetric Reagent

ALBERT H. BEST, A. HARDING PETERSON, AND HAROLD M. SELL
Division of Fruit and Vegetable Crops and Diseases, Bureau of Plant Industry,
U. S. Department of Agriculture, Gainesville, Fla.

IN PHYSIOLOGICAL studies on the tung tree a reliable method was desired for the determination of reducing sugars in various tissues. Several methods (*3*, *8*, *10*) are reported in the literature on the use of ceric sulfate in the determination of reducing sugars, but none involves the determination of cuprous oxide through the reduction of ferric ammonium sulfate with subsequent titration of the ferrous ion with ceric sulfate. The volumetric permanganate method (*1*) is reliable and has been employed in the determination of reducing sugar in plant tissue. However, the authors have found that ceric sulfate can be substituted for potassium permanganate in this method with the following advantages: It gives a sharper end point with *o*-phenanthroline ferrous complex indicator (*11*); the solution of this salt is exceedingly stable (*2*); the reduced form (cerous ion) is colorless, offering no interference with indicators; and there is only one change in valence, Ce^{IV} to Ce^{III}, and hence no intermediate products are possible.

Table I. Determination of Reducing Sugars

(Expressed in milligrams of dextrose)

Munson-Walker	Volumetric Permanganate	Shaffer-Hartman	Volumetric Ceric Sulfate
	50 Ml. of Dextrose[a]		
49.5	49.5	49.9	49.6
49.3	49.6	50.1	49.8
49.8	50.0	49.8	49.6
49.5	49.5	49.7	49.9
49.9	49.3	49.9	50.0
49.7	50.0	50.0	49.7
50.0	49.5	50.2	49.9
49.5	49.3	49.5	50.0
49.2	49.6	49.6	50.0
49.5	49.7	50.0	49.6
Av. 49.6	49.6	49.9	49.8
	50 Ml. of Diluted Extract of Tung Leaves		
49.6	50.5	50.5	50.4
49.6	50.1	50.3	50.7
49.7	50.4	50.3	50.4
49.5	50.3	50.3	50.5
49.6	50.8	50.6	50.7
49.7	50.4	50.7	50.3
49.4	50.1	50.3	50.4
50.0	50.5	50.7	50.3
49.9	50.1	50.5	50.7
49.8	50.2	50.7	50.3
Av. 49.7	50.3	50.5	50.5
	25 Ml. of Dextrose and 25 Ml. of Diluted Extract of Tung Leaves		
48.8	49.2	50.1	49.7
49.7	49.8	50.6	49.9
50.0	49.4	50.8	49.8
49.4	49.9	50.2	49.9
48.9	48.8	50.3	49.6
48.9	49.1	50.3	49.4
49.3	49.8	49.9	49.4
49.2	49.0	50.1	49.4
48.8	48.8	50.6	49.4
49.8	49.9	50.2	49.9
Av. 49.3	49.4	50.3	49.6

[a] Dextrose solution contained 1 mg. of dextrose per ml.

Experimental

The methods of preparation of tung tissue and the analytical procedure used for the precipitation of cuprous oxide are similar to those of the Association of Official Agricultural Chemists (*1*) with the exception of a few changes to facilitate certain operations.

In the clarification of the aqueous sugar solution, which is obtained from the alcoholic extract of tung tissue, the flocculent precipitate formed by the addition of saturated lead acetate is removed by centrifugation rather than by the tedious process of filtration. The cuprous oxide is precipitated as directed in the Munson-Walker procedure (*1*, *5*), except that an electric heater is substituted for a Bunsen burner.

The cuprous oxide is dissolved in ferric ammonium sulfate as in the volumetric permanganate method (*1*), with the exception that 50 ml. of hot ferric ammonium sulfate are used instead of 10 ml. of cold solution. Great care must be exercised to ensure complete solution (*4*); otherwise erratic results will be obtained. The solution is made to a final volume of approximately 150 ml. and then titrated at once at a temperature between 50° and 60° C. with 0.05 *N* ceric sulfate (*7*). One drop of *o*-phenanthroline ferrous complex indicator is added at the beginning of the titration and another near the end point. The color change is from orange to a light green. Solutions having a high temperature cause the indicator to fade (*9*).

Results

The volumetric ceric sulfate method compared with the volumetric permanganate (*1*), Munson-Walker (*1*, *5*), and Shaffer-Hartman (*6*) methods gave essentially the same results on a known dextrose solution, an aqueous extract of tung leaves, and a mixture of the extract and a known dextrose solution (Table I). It is evident that ceric sulfate can be used successfully in this procedure.

Literature Cited

(1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 5th ed., pp. 125, 138–9, 500 (1940).
(2) Furman, H., *J. Am. Chem. Soc.*, 50, 755–64 (1928).
(3) Hassid, W. Z., Ind. Eng. Chem., Anal. Ed., 9, 228–9 (1937).
(4) Kraybill, H. R., Youden, W. J., and Sullivan, J. T., *J. Assoc. Official Agr. Chem.*, 19, 125 (1936).
(5) Munson, L. S., and Walker, P. H., *J. Am. Chem. Soc.*, 28, 663–86 (1906).
(6) Shaffer, P. A., and Hartman, A. F., *J. Biol. Chem.*, 45, 349–64 (1921).
(7) Smith, G. F., "Ceric Sulfate", Vol. 1, 4th ed., pp. 31, 52, Columbus, Ohio, G. Frederick Smith Chemical Co., 1940.
(8) Stegman, R. A., and Englis, D. T., *Trans. Illinois State Acad. Sci.*, 27, 75–6 (1934).
(9) Sullivan, J. T., *J. Assoc. Official Agr. Chem.*, 18, 382–6 (1935).
(10) Vanossi, R., and Ferramola, R., *Anales soc. cient. Argentina*, 121, 59–73 (1936).
(11) Walden, G. H., Hammett, L. P., and Chapman, R. P., *J. Am. Chem. Soc.*, 55, 2649–54 (1933).

Content of *l*-Pimaric Acid in Pine Oleoresin

Improved Methods for Its Determination

ELMER E. FLECK AND SAMUEL PALKIN
Bureau of Agricultural Chemistry and Engineering, United States Department of Agriculture, Washington, D. C.

THE *l*-pimaric acid content of pine oleoresin has been a matter of considerable speculation for a long time.

Dupont (*4*) advanced a theoretical basis for predicting the amount of individual resin acids present in pine oleoresin. He estimated the amounts of these acids present by observation of the optical rotation of mixtures (*2*) and by isomerization of the *l*-pimaric acid present with mineral acid (*3*). This type of analysis was further developed by Sandermann (*6*) for *l*-pimaric acid present in oleoresin by change in optical rotation when this acid of $[\alpha]_D$ −280° is isomerized with mineral acid to *l*-abietic acid $[\alpha]_D$ −104°. The method is subject to the objection that, in addition to *l*-pimaric acid, other unidentified acidic constituents are also isomerized, under the condition of this determination, to *l*-abietic acid.

The recent discovery that *l*-pimaric acid readily forms a Diels-Alder addition compound in the cold with maleic anhydride (*1*, *7*) has provided a new basis for analytical determinations of *l*-pimaric acid and possibly other conjugated double bond acids that might be present. The mild conditions of this reaction and the technique for quantitative removal of the addition product, without altering the other unstable acids present in the complex, make possible a new approach to the problem of the "sapinic acids". Sandermann (*5*) used this reaction with maleic anhydride to replace the isomerization of *l*-pimaric acid with mineral acid. The change in optical rotation was observed and used as a basis for calculating the amount of *l*-pimaric acid present.

Another method developed by Sandermann (*5*, *6*) also made use of the addition product of maleic anhydride with *l*-pimaric acid, but depended upon acidimetric titration and not rotation measurements. In this method a known weight of resin acids was reacted with an excess of maleic anhydride, the excess maleic anhydride was then extracted, and the resin acids plus the *l*-pimaric acid addition product was titrated with alkali. The per cent of *l*-pimaric acid present was calculated from the increased alkali needed to neutralize the reaction product over that needed for the original acids.

In the present work this maleic anhydride procedure was modified so that a known amount of maleic anhydride was added to a known amount of resin acid mixture in *n*-pentane solution. After reaction had taken place the excess maleic anhydride was extracted quantitatively and the aqueous extract titrated with alkali. Since the addition compound of *l*-pimaric acid is not soluble in water, this makes possible the determination of the amount of maleic anhydride reacted and from that the per cent of *l*-pimaric acid can be calculated.

While no reaction between maleic anhydride and gum turpentine constituents is to be expected at room temperatures, nevertheless to eliminate the possibility of abnormal behavior blank determinations with turpentine were made. These showed that the reaction of maleic anhydride with turpentine at a temperature around 20° C. for a period of 4 hours was smaller than the limits of experimental error. This makes possible the determination of *l*-pimaric acid present in pine oleoresin without the necessity of first extracting the acidic portion of the oleoresin from the turpentine.

In this method any unknown compound, present in the oleoresin, that reacts with maleic anhydride at room temperature will give too high a value for the *l*-pimaric acid content of oleoresin.

A new method for the determination of *l*-pimaric acid makes use of the insolubility of the *l*-pimaric acid addition product of maleic anhydride in *n*-pentane. At 20° C. the solubility of this addition product was found to be 0.03 gram in 100 cc. of *n*-pentane.

For analysis the pine oleoresin was dissolved in *n*-pentane and filtered free from dirt, chips, and water. The concentration of the acidic constituents was determined by titration with alkali and then a known volume of *n*-pentane solution was reacted with an excess of maleic anhydride in acetone solution. The addition product crystallized from solution and was filtered off, washed, dried, and weighed. This addition product was found to be of high purity. All samples melted above 220° C. The purified material melts at 226–229° C. (*7*).

The completeness of the removal of this addition compound from *n*-pentane solution is illustrated by the reaction of pure *l*-pimaric acid with maleic anhydride. Thus, of a 3-gram sample of *l*-pimaric acid, less than 0.05 gram of noncrystalline material was removed from the mother liquor after the addition compound had been removed by filtration.

The quantitative nature of this reaction at room temperature was not disturbed by the presence of other nonreacting resin acids and turpentine. This was shown by addition of pure *l*-pimaric acid to an *n*-pentane solution of oleoresin to increase the *l*-pimaric acid content from 32.7 to 35.9 per cent. *l*-Pimaric acid found in the fortified oleoresin was 36.2 per cent.

The solubility of the addition product is increased somewhat by the small amount of acetone added and also by the resin acids of unknown identity that are present in the oleoresin.

These factors would produce too low a value for *l*-pimaric acid of pine oleoresin.

These two methods for the analysis of pine oleoresin were applied to a series of longleaf oleoresin samples collected during the season of 1940 near Olustee, Fla. The samples were stored at −5° C. and all determinations were made at the end of the turpentining season.

These results (Table I) are in fair agreement with those reported by Sandermann (*5*) and show that *l*-pimaric acid does not account for the major portion of the primary acids present in pine oleoresin. The straight-line decrease of *l*-pimaric acid content of longleaf oleoresin with the season indicates that the controlling factor in the decrease of *l*-pimaric acid is the length of the face on the tree over which the oleoresin flows, exposed to the air, to reach the cup. Evidently *l*-pimaric acid is not appreciably isomerized by rise in temperature during the hot part of the season, as is indicated by Sandermann (*5*). If temperature were a governing factor, the *l*-pimaric acid content of oleoresin should reach a minimum at midsummer and rise again with the cooler weather of fall.

TABLE I. *l*-PIMARIC ACID PRESENT IN RESIN ACID FRACTION OF PINE OLEORESIN

	l-Pimaric Acid	
Month, 1940	Volumetric method, %	Gravimetric method, %
April	38.4	36.0
	38.7	
June	36.3	34.2
	36.6	33.7
August	35.4	32.4
	35.1	31.7
November	33.2	31.3
	33.7	30.5

Quantitative Reaction of *l*-Pimaric Acid with Maleic Anhydride

A solution of 3.00 grams of *l*-pimaric acid, $[\alpha]^{20}_{D}$ −274° (2 per cent absolute alcohol), in 150 cc. of *n*-pentane was stirred while a solution of 1.3 grams of maleic anhydride in 10 cc. of absolute ether was added. Stirring was continued for 2 hours, during which time the addition compound crystallized from solution. It was removed by filtration and the filtrate was extracted with water until the aqueous extracts reacted neutral to Congo red. The *n*-pentane was then distilled and the noncrystalline residue weighed less than 0.05 gram.

Description of Methods

Approximately 100 grams of well-mixed pine gum were dissolved in 200 cc. of *n*-pentane, and the mixture was filtered through a fluted filter paper into a glass-stoppered flask. This filtration removed dirt, chips, and water found in the pine oleoresin.

To determine the total resin acid content of this solution 10 cc. were pipetted into 25 cc. of an alcohol-benzene mixture (500 cc. of alcohol, 500 cc. of benzene, and 0.2 gram of phenolphthalein). This solution was then titrated with 0.5 *N* alcoholic potassium hydroxide.

VOLUMETRIC DETERMINATION OF *l*-PIMARIC ACID. Twenty-five cubic centimeters of the above standardized *n*-pentane solution of pine oleoresin were placed in an iodine flask, and to it were added 20 cc. of standardized 10 per cent maleic anhydride in acetone solution. The flask was shaken and then allowed to stand at 20° C. for 4 hours.

At the end of this time the contents of the flask were transferred into a separatory funnel with the aid of 50 cc. of benzene. The maleic anhydride was then extracted as maleic acid with three 100-cc. portions of water. These aqueous extracts were united in a second separatory funnel and then extracted with 25 cc. of benzene. The aqueous layer was drawn off into the titration beaker and the benzene extract was washed by shaking with 15 cc. of additional water. This wash was also added to the titration beaker. The amount of maleic acid in the aqueous extracts was determined by titration with aqueous 0.5 *N* sodium hydroxide, using phenolphthalein as an indicator. The difference between the amount of maleic anhydride originally added and that accounted for in the aqueous extracts represents the amount of maleic anhydride reacted with *l*-pimaric acid.

The per cent of *l*-pimaric acid present in the acidic portion of the pine oleoresin was calculated by the formula:

$$\%\ l\text{-pimaric acid} = \frac{a \times 3.082 \times 100}{b}$$

where *a* equals the weight in grams of maleic anhydride reacted with *l*-pimaric acid, and *b* equals the weight in grams of resin acids present in the 25 cc. of *n*-pentane solution used.

GRAVIMETRIC DETERMINATION OF *l*-PIMARIC ACID. Two hundred cubic centimeters of the standardized *n*-pentane solution of pine oleoresin were placed in a three-necked distilling flask fitted with a thermometer and a stirrer. The stirrer was connected into the stoppered reaction flask through a bearing which was not gas-tight.

The *n*-pentane solution was stirred and a solution of 7 grams of maleic anhydride in 4 cc. of acetone was added rapidly. Stirring was continued for 2.5 hours. During the first half hour the temperature of the reaction mixture increased and cooling with water was necessary to hold the temperature at 30° C.

At the end of the first hour crystallization had taken place and at the end of 2 hours the reaction was packed in ice and stirring was continued for a half hour longer. The crystalline material was then filtered into a Büchner funnel using mild suction. A portion of the filtrate was used to make the transfer as quantitative as possible. Suction was then cut off entirely, 25 cc. of *n*-pentane were added to the filter cake, and the cake was puddled to ensure efficient washing. The *n*-pentane wash was drawn off slowly with very mild suction. The crystalline material was transferred to a weighed crystallizing dish and dried in vacuum at 100° C. for 2 hours and then weighed.

The per cent of *l*-pimaric acid present in the acids of pine oleoresin was calculated by the formula:

$$\%\ l\text{-pimaric acid} = \frac{c \times 0.755 \times 100}{d}$$

where *c* equals the weight in grams of the dried addition product of *l*-pimaric acid and maleic anhydride and *d* equals the weight in grams of the resin acids present in the 200 cc. of *n*-pentane solution used.

The amount of maleic anhydride added was adjusted so as to have approximately 1 gram excess at the end of the reaction. Larger excess was avoided in order to keep to a minimum the amount of acetone added. A large excess also causes maleic anhydride to crystallize from the reaction mixture.

DETERMINATION OF *l*-PIMARIC ACID ADDED TO PINE OLEORESIN. A solution of 200 grams of longleaf pine oleoresin in 400 cc. of *n*-pentane was filtered as outlined above. This solution was titrated with alcoholic potassium hydroxide to determine the concentration of resin acids present.

A solution of 6 grams of maleic anhydride in 3 cc. of acetone was then reacted with 200 cc. of the *n*-pentane solution which contained 44.10 grams of resin acids. The dried addition product weighed 19.10 grams, which corresponds to 32.7 per cent of *l*-pimaric acid present in the acidic portion of the oleoresin.

To a second 200-cc. portion of the standardized resin acid solution were added 2.20 grams of pure *l*-pimaric acid. A solution of 7 grams of maleic anhydride in 4 cc. of acetone was added as outlined above. The dried addition product weighed 22.20 grams, which corresponds to 36.2 per cent of *l*-pimaric acid.

Based on the control run and the amount of pure *l*-pimaric acid added, the calculated value should be 35.9 per cent.

Summary

Determination of the *l*-pimaric acid content of longleaf pine oleoresin throughout the turpentining season showed a constant decrease in *l*-pimaric acid content with the progress of the season. The progressive change in *l*-pimaric acid content was followed by means of a volumetric and a gravimetric method based on the Diels-Alder reaction with maleic anhydride.

Literature Cited

(1) Bacon and Ruzicka, *Chemistry & Industry*, 1936, 546
(2) Dupont, *Bull. chim. soc.*, (4) 29, 726 (1921).
(3) *Ibid.*, p. 734.
(4) Dupont, *Compt. rend.*, 178, 1560 (1924).
(5) Sandermann, *Ber.*, 71, 2005 (1938).
(6) Sandermann, *Bull. inst. pin*, (3) 31, 137 (1937).
(7) Wienhaus and Sandermann, *Ber.*, 69, 2202 (1936).

Colorimetric Determination of Silver with 2-Thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine

JOHN H. YOE AND LYLE G. OVERHOLSER, University of Virginia, Charlottesville, Va.

SHEPPARD and Brigham (*3*) reported the preparation of a compound to which they assigned the name 2-thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine and which gave reactions with a number of metallic ions. The reaction with silver was observed to be especially sensitive and selective in nitric acid solution. Further studies by the present authors have shown that the compound gives the following reactions in neutral solution in addition to those reported (*3*): Co^{++}, Mn^{++}, Ni^{++}, pink colors; Hg^{++}, pink precipitate; Tl^{+}, blue precipitate. In nitric acid solution Au^{+++} and Hg_2^{++} give pink precipitates and Pd^{++} a slight red precipitate. In the nitric acid–sodium acetate buffer used for the determination of silver, the following reactions were observed: Ag^{+}, purple color and precipitate; Au^{+++} and Pd^{++}, orange color and precipitate; Hg_2^{++} and Hg^{++}, pink color and precipitate.

Schoonover (*2*) described a method for the colorimetric determination of silver using *p*-dimethylaminobenzalrhodanine and noted that adsorption of silver on glassware may introduce appreciable error at low silver concentrations. The authors have found that the purple colored compound given by silver with 2-thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine is also applicable to the colorimetric determination of small amounts of silver. A comparison of these silver reagents under the conditions recommended in this paper showed that their sensitivity is approximately the same, that solutions of the silver compound of 2-thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine are more stable, especially at higher silver concentrations, and that the colors given by *p*-dimethylaminobenzalrhodanine with gold and palladium are more intense than those given by the former reagent.

The effect of a number of factors on the reaction of silver with 2-thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine has been studied and is reported in this paper. Results of a study of the colorimetric determination of silver with this reagent are also given.

Reagents

All reagents used were of the highest purity obtainable and were further purified, if necessary, to remove any chloride present.

2-Thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine. One sample was obtained from the Eastman Kodak Company and another was prepared in this laboratory. A solution containing 0.01 per cent of the reagent in acetone was used. The solution has a dark orange color when first prepared but slowly changes to a yellow color. The freshly prepared solution is slightly more sensitive and for this reason fresh solutions should be prepared at least once a week.

Silver. A solution containing 1 mg. of silver per ml. was prepared from silver nitrate and was diluted to the desired concentration.

Sodium acetate–nitric acid buffer was prepared by adding 320 ml. of 1 *M* nitric acid to 200 ml. of 1 *M* sodium acetate and diluting to 1 liter with water. The buffer had a pH of 1.1 as prepared but on diluting 10 times with water the pH changed to 2.0.

Gelatin. A 0.2 per cent aqueous solution was used.

Experimental

The reagent has a pink color in basic solution, orange in neutral solution, and yellow in acid solution. The intensity of the yellow color is only slightly affected by the pH, the intensity being nearly the same in 0.01 or 2 *M* nitric acid.

The intensity of the colored silver compound, as well as the rate of its development, is markedly influenced by the pH. The reaction rate is greatest and the color development most intense in approximately neutral solutions having a low electrolyte concentration. The reaction rate decreases with decreasing pH and the color formed may vary from purple to blue, depending on the pH. Despite the decreased reaction rate, a buffer with a low pH was used because less interference and a greater stability of the color resulted. Even at the low pH, however, the reproducibility and stability of the color are unsatisfactory for colorimetry, unless a small amount of gelatin is present to stabilize the colloidal suspension of the silver compound. Under the conditions recommended, 40 to 50 minutes are required for the development of maximum color intensity. The color is not sufficiently stable to permit the use of a set of standards over an extended period of time. Consequently, the unknowns and standards should be prepared at as nearly the same time as possible and the comparison should be completed within an hour.

All experiments were performed at room temperature, except for several at 50° C. to determine the temperature effect. The sensitivity was less at 50°, undoubtedly because of an adsorption of silver by the glassware.

General Procedure

Transfer the silver solution to a 100-ml. volumetric flask, add 10 ml. of the sodium acetate–nitric acid buffer and 0.5 ml. of the gelatin solution, and dilute almost to the mark with water. Add 0.6 ml. of the reagent, make up to the mark with water, and mix thoroughly. Color comparison may be made 30 to 40 minutes after addition of the reagent, either in 50-ml. Nessler tubes (220 mm.) or in 100-ml. tubes (160 mm.) in a roulette comparator (*4*). Using a volume of 100 ml., the following increments in the series of standards were used: 0 to 6 micrograms, 2 micrograms; 7 to 30 micrograms, 1 microgram. With a volume of 50 ml.: 0 to 7 micrograms, 1 microgram; 8 to 12 micrograms, 0.5 microgram; 13 to 16 micrograms, 1 microgram.

The method may be applied to smaller volumes, using smaller amounts of the reagents and suitable standards. Precautions must be taken, however, at very low silver concentrations to

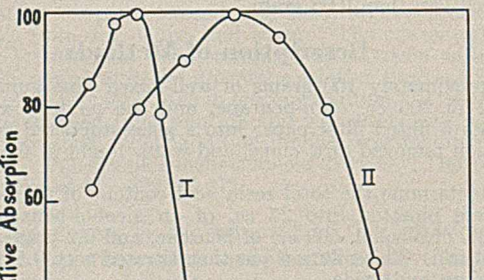


FIGURE 1. RELATIVE ABSORPTION OF 2-THIO-5-KETO-4-CARBETHOXY-1,3-DIHYDROPYRIMIDINE AND ITS SILVER COMPOUND

I. Reagent. II. Silver compound

avoid error due to adsorption of silver by the glassware. All vessels must be either Pyrex or fused silica. If Pyrex is used, heating must be avoided. Pyrex test tubes are satisfactory for making the color comparisons.

Interference

As previously noted, a number of ions give reactions with the reagent in neutral or very weakly acid solutions but fail to react in a stronger nitric acid solution. In addition to the observations on the spot plate, the possible interference of a number of ions was determined under the conditions recommended in the general procedure, using a silver concentration of 20 micrograms. Mercurous and mercuric mercury interfere and must be absent. The following colored ions interfere only if present at concentrations exceeding that required to produce the color due to the ion itself. The limiting concentrations are: Co^{++}, 0.5 mg.; Cu^{++}, 1 mg.; Fe^{+++}, 2 mg.; Ni^{++}, 1.5 mg. The following ions are without effect at a concentration of 10 mg.: Cd^{++}, Mn^{++}, Pb^{++}, and Zn^{++}.

The limiting concentrations are: nitric acid, 0.10; sodium nitrate, 3; sodium sulfate, 0.1; ammonium nitrate, 0.5 millimoles. Larger amounts of nitric acid or sodium nitrate cause a decrease in color intensity. Sulfate and ammonium ions have the reverse effect—i. e., they increase the color intensity.

Sensitivity

On the spot plate using 0.05 ml. of silver solution, 0.05 ml. of buffer, and 0.03 ml. of reagent, the minimum concentration of silver detectable is 5 p. p. m. (0.25 microgram); in aqueous solution the minimum is 3 p. p. m. (0.15 microgram).

The sensitivity at the various silver concentrations using 50-ml. Nessler tubes (220 mm.) is as follows: 0 to 2 micrograms, 2 micrograms; 3 to 7 micrograms, 1 microgram; 8 to 12 micrograms, 0.5 microgram; 13 to 16 micrograms, 1 microgram. The sensitivity falls off sharply above 15 micrograms, and the amount of silver should not exceed this value for 50-ml. volumes.

With the roulette comparator using 100-ml. tubes (160 mm.) the sensitivity is: 0 to 6 micrograms, 3 micrograms; 7 to 30 micrograms, 1 microgram. Above 25 micrograms the sensitivity decreases and little increase in the intensity occurs above 30 micrograms. The most sensitive range is from 15 to 20 micrograms.

Although the reaction is sensitive to about 1 part in 30,000,000 (3 micrograms) at the lowest silver concentrations, a sensitivity of 1 part in 100,000,000 (1 microgram) may be attained by working in the most sensitive range.

Relative Absorption Curves

The relative absorption curves for the reagent and for the silver compound obtained from measurements with a photoelectric spectrophotometer (*1*) are given in Figure 1. Curve I, the reagent curve, was obtained for a solution prepared from 10 ml. of buffer, plus 0.5 ml. of gelatin, plus 1 ml. of reagent, plus water to make 100 ml. Curve II, the compound curve, was obtained for a solution prepared as above, using 120 micrograms of silver and 1.2 ml. of reagent. At 500 mμ the absorption by the reagent is very slight, whereas that of the compound is approximately at the maximum, a condition favorable for the elimination of absorption due to excess reagent, without sacrificing the sensitivity. The reaction, however, is not especially suitable for spectrophotometric studies because of the slow reaction rate and the limited stability of the colored solutions.

Literature Cited

(1) Barton and Yoe, Ind. Eng. Chem., Anal. Ed., 12, 166 (1940).
(2) Schoonover, *J. Research Natl. Bur. Standards*, 15, 377 (1935).
(3) Sheppard and Brigham, *J. Am. Chem. Soc.*, 58, 1046 (1936).
(4) Yoe and Crumpler, Ind. Eng. Chem., Anal. Ed., 7, 78 (1935).

This investigation was supported partly by a grant-in-aid from the Carnegie Corporation of New York. It is one of a projected series based upon studies of organic reagents in inorganic analysis, conducted as a cooperative effort in which ten institutions are participating under the direction of John H. Yoe. Those cooperating with the University of Virginia are: Hampden-Sydney, Mary Baldwin, Randolph-Macon (Ashland), Virginia Military Institute, Virginia Polytechnic Institute, Washington and Lee, William and Mary, University of North Carolina, and Tulane University.

Rapid Estimation of Bromides in the Presence of Chlorides

MARVIN LANE
The Permutit Company, Birmingham, N. J.

DURING the course of work in this laboratory, it became necessary to find a rapid method for the determination of low concentrations of bromides in the presence of equivalent or excess amounts of chlorides. Since none of the available methods proved suitable, a method for higher bromide concentrations (*1*, *2*) was simplified and adapted for low concentrations by the use of a photoelectric colorimeter. The method is based upon the liberation of free bromine by the addition of chlorine water and measurement of the developed color directly in the aqueous solution. Previous methods require extraction of the liberated bromine by carbon tetrachloride.

Apparatus. The photoelectric colorimeter was a Klett-Summerson Model 900-3, in which was used a KS-42 filter (transmission range 400 to 465 millimicrons). (This instrument is available from the Klett Manufacturing Company, 179 East 87th St., New York, N. Y.) A buret was mounted in position to discharge into the colorimeter cell.

Procedure. Fifty milliliters of bromide-containing solution were treated with 10 ml. of 1 to 1 sulfuric acid, and the whole was diluted to 75 ml. and mixed thoroughly. About 50 ml. were placed in the colorimeter cell and the indicator was adjusted to read zero. Saturated chlorine water was then added dropwise, stirring the cell contents well after each addition and observing the scale reading. The maximum scale reading was used for reading the bromide concentration from the calibration curve.

Data from which the calibration curve was plotted are given in the following table:

Colorimeter Scale Reading	Bromide Concentration *Milliequivalents/l.*
17	0.02
70	0.80
85	1.0
139	1.6
174	2.0

In order to obtain reproducible results, it was essential to measure the maximum developed color. Under these conditions, blindfold tests consistently gave results within 0.02 milliequivalents per liter in the range 0.02 to 2.0 milliequivalents per liter of bromide concentration, in the presence of chloride concentrations ranging from an equivalent concentration to 1000 times the bromide concentration. Higher concentrations may be measured by diluting an aliquot to bring the concentration within the above range. Obviously, the presence of iodides or color will interfere with this determination.

Literature Cited

(1) Snell and Snell, "Colorimetric Methods of Analysis", 2nd ed., Vol. 1, p. 544, New York, D. Van Nostrand Co., 1936.
(2) Sweeney and Winthrow, J. Ind. Eng Chem., 9, 674 (1917).

Determination of Sulfur

Accuracy and Precision of Several Methods

WILLIAM RIEMAN III AND GEORGE HAGEN, Rutgers University, New Brunswick, N. J.

IT IS well known that the gravimetric determination of sulfur as barium sulfate is subject to rather large errors, due chiefly to coprecipitation. Many methods for the precipitation, filtration, and drying of the barium sulfate have been recommended. The author of each method generally gives experimental data on the determination of sulfur in a pure compound, such as sodium or potassium sulfate, to indicate the accuracy of the method. Frequently data are also included for the analysis of a mixture of the alkali sulfate with about an equal quantity of some other salt, such as sodium chloride or nitrate. But data for the determination of known amounts of sulfate in the presence of much larger quantities of other salts are exceedingly scarce in the literature.

TABLE I. IMPORTANT FEATURES OF VARIOUS METHODS

Method	Na_2SO_4 Taken	HCl Taken	Total Volume	Excess $BaCl_2$	Order of Mixing	Time of Mixing	Digestion	Temperature of Drying
	Millimoles	*Millimoles*	*Ml.*	*Millimoles*		*Min.*	*Hours*	*° C.*
K and S	2.1	12	350	2.9	Usual	4	1	800
F and T	3.5	3	450	1.5	Usual	8	12	115
F and T (modified)	3.5	3	450	1.5	Usual	8	21	130
P and N	3.5	18	350	0.5	Reverse	4	1	800
H and W	7.5	27	550	1.5	Usual	Fast	1	800

This paper describes the results of determinations of sulfur (*2*) in known mixtures of sodium sulfate and sodium chloride by several well-known methods. Sodium chloride was chosen as the foreign salt because it is often present in solution when barium sulfate is precipitated for the determination of sulfur. The fusion of inorganic substances with sodium carbonate and subsequent acidification with hydrochloric acid introduce quantities of sodium chloride much larger than the sulfur that may be in the sample. The sodium peroxide bomb method for the determination of sulfur in organic substances also introduces large quantities of sodium chloride—for example, when 0.5 gram of sodium benzene sulfonate is oxidized by 14 grams of sodium peroxide, the resultant mixture after acidification contains 130 moles of sodium chloride for each mole of sodium sulfate.

The following methods were investigated: The method of Kolthoff and Sandell (*4*) was tested because it is typical of those found in most textbooks of quantitative analysis. The procedure of Fales and Thompson (*1*) was investigated because of the unusual treatment of the precipitate—drying at 110° to 120° C. instead of the customary ignition. This method was found to be very inconvenient because of the digestion period of 12 hours; therefore, a modification with a digestion period of 21 hours was also investigated. Fales and Thompson found that nitrate ion introduced less error in their method than chloride ion. In the determination of sulfur following a fusion with either sodium carbonate or sodium peroxide, the nitrate ion can be introduced as easily as the chloride by using nitric acid for the acidification. Therefore the modified method of Fales and Thompson was also tested in the presence of sodium nitrate instead of sodium chloride. The method of Popoff and Neuman (*6*) was investigated because it has been found better than the usual methods. Hintz and Weber (*3*) claimed an unusual accuracy for their method in the presence of a large quantity of sodium chloride. The method of Njegovan and Marjanovic (*5*) was also tested and discarded because difficulty was experienced in filtering the very fine-grained precipitate.

Reagents

Reagent grade sodium sulfate was purified by recrystallization and dried at 110° C. No further loss was incurred by heating to a dull red heat. The sodium chloride was purified by treating the saturated solution with hydrogen chloride. In some cases, reagent grade sodium chloride was used without purification; then appropriate blank corrections were applied to the results. The other compounds were of reagent grade.

Procedure

An appropriate quantity of pure sodium sulfate was taken, either by direct weighing or by weighing a standard solution with a weight buret, and to it were added known quantities of pure sodium chloride (or nitrate). The mixture was then analyzed for sulfur according to the procedure under investigation. Blank corrections were applied in all cases.

The important features of the various methods are listed in Table I.

Results

Table II gives the relative errors of the methods tested. The values for no foreign salt and for the maximum quantity of foreign salt are the mean of four determinations. The other values generally represent single determinations.

The precision of the methods is indicated by the relative mean deviation of the values with no foreign salt and with the maximum quantity of foreign salt (Table III).

Discussion

Table II reveals that the method of Hintz and Weber is by far the most accurate when the entire range of ratios of sodium chloride to sodium sulfate is considered. It is un-

TABLE II. RELATIVE ERRORS OF METHODS

Method	Molar Ratio of NaCl (or $NaNO_3$) to Na_2SO_4										
	0	1	2	5	10	20	40	60	110	190	309
	Parts per thousand										
K and S	−3	−8	−8	−9	−11	− 9	−12	−16	−17	−16	..
F and T	−2	...	...	...	..	..	..	−12	−13	..	−12
F and T (modified)	−5	−6	−6	−7	− 8	−10	..	−13	−15	..	−15
F and T ($NaNO_3$)	−5	+2	+1	+2	+ 4	+ 6	..	+12	+ 9	+13	+14
P and N	+3	+3	+4	+4	+ 4	+ 3	+ 4	+ 7	+ 9	..	..
H and W	+2	+2	+1	+4	+ 4	+ 3	+ 3	+ 4	+ 4	+ 4	..

TABLE III. PRECISION OF METHODS

Method	Relative Mean Deviation	
	No foreign salt	Maximum foreign salt
	Parts per thousand	
K and S	1.5	1.3
F and T	0.1	0.2
F and T (modified)	0.5	1.4
F and T ($NaNO_3$)	0.5	0.2
P and N	0.3	1.1
H and W	0.3	0.6

fortunate that this method is used so little and that it is not mentioned in the textbooks of analytical chemistry, particularly because it is the quickest and easiest of all. The method of Popoff and Neuman stands second in accuracy.

Four determinations are not enough to establish the precision of a method, but they give a valuable clue regarding the reproducibility of results. In this respect, the original method of Fales and Thompson is by far the best, with Hintz and Weber's procedure second.

It is interesting to consider the causes of the errors. When barium chloride is added slowly to sodium sulfate, the crystals of the precipitate grow in an excess of sulfate ions. Thus they acquire a negative charge and attract the sodium ions, which are then buried beneath the surface of the crystals by deposition of barium sulfate. This coprecipitation of sodium accounts for the low results in the method of Kolthoff and Sandell.

This negative error is partly compensated by incomplete drying in the method of Fales and Thompson. Nitrate ion is extensively coprecipitated by barium sulfate and introduces a positive error. This accounts for the increasing positive errors with addition of sodium nitrate in the method of Fales and Thompson.

The procedure of Popoff and Neuman decreases the coprecipitation of sodium by the reverse precipitation. This method of precipitation, however, increases the usually small coprecipitation of chloride ion until it becomes the major error. This introduces a positive error.

When the precipitant is added all at once, as recommended by Hintz and Weber, the growth of the crystals occurs chiefly after the addition of the precipitant when there is a comparatively small excess of barium ion. Thus neither the positive error due to the coprecipitation of chloride ion nor the negative error due to the coprecipitation of sodium ion is great, and the method yields good results. It might be expected that the rapid precipitation would produce very fine-grained barium sulfate, but no difficulty was experienced in this filtration. Perhaps the rather high acidity of the method accounts for the filterability by increasing the solubility slightly.

Literature Cited

(1) Fales and Thompson, Ind. Eng. Chem., Anal. Ed., 11, 206 (1939).
(2) Hagen, George, master's thesis, Rutgers University, 1941.
(3) Hintz and Weber, *Z. anal. Chem.*, 31, 714 (1906).
(4) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis", p. 319, New York, Macmillan Co., 1935.
(5) Njegovan and Marjanovic, *Z. anal. Chem.*, 73, 271 (1928).
(6) Popoff and Neuman, Ind. Eng. Chem., Anal. Ed., 2, 45 (1930).

Conductometric Assay of Inorganic Salt in the Presence of Wetting Agents

J. H. PERCY AND C. J. ARROWSMITH, Colgate-Palmolive-Peet Company, Jersey City, N. J.

A method is described for the rapid assay of active ingredient in commercial wetting agents by a conductometric method. It is not necessary for the chemical nature of the material to be known so long as a small amount of material free of inorganic salt can be isolated for the calibration curve. The method may be applied wherever the components of a mixture have materially different specific conductivities in solution.

DAWSON (*5*) suggested that electrical conductivity of aqueous solutions might be used as a physical constant for evaluation of mixtures with the help of a calibration curve, just as specific gravity, refractive index, or viscosity is used. Relatively few applications of this principle have been made, most analyses by conductometric means having been carried out by titration methods (*3*, *6*).

References have been made to the use of conductivity for controlling the purity of a liquid such as distilled water (*1*, *7*), evaluating the concentration of sulfuric acid (*2*), or determining the concentration of a single electrolyte in aqueous solution (*4*). Šandera (*8*) determined the composition of a mixture of organic liquids by determining the conductivity of a saturated solution of a suitable electrolyte in the mixture. However, no use has apparently been made of the method in the rather frequently occurring problem of determining the composition of a mixture of two water-soluble materials which have different specific conductivities in aqueous solution.

It is known that at concentrations below the point where appreciable errors are introduced by concentration effects, electrical conductivity is an additive property, so that when a mixture of two water-soluble solids is dissolved in water and diluted to a fixed concentration, the conductivity is a straight-line function of composition by weight in the original mixture. It is possible to apply this relationship very generally. For example, it may be employed in connection with a second constant, such as refractive index or analytical composition with respect to a single element, for the evaluation of three-component systems.

This principle has here been applied to the rapid assay of sulfonated and sulfated surface-active agents for inorganic salt and active ingredient content. In this case the surface-active compounds are organic sulfonates or sulfates of high molecular weight which have specific conductivity in water solution approximately one seventh to one tenth that of sodium sulfate; in general, commercial products contain mixtures of several or many related compounds as active ingredients.

The method gives results which compare favorably with those obtained by solvent means or by precipitation of the usual analytical precipitates in the presence of the surface-active material, and can be carried out in very much shorter time.

Experimental

The measuring bridge used was Model RC-1 of Industrial Instruments, Inc., Jersey City, N. J., a 60-cycle alternating current bridge using a cathode ray tube as null-point indicator. The cell was of the dip type, with a constant of 1.108.

Variations in pH within reasonable limits made little or no difference in the results obtained. The materials examined had normal pH values in dilute solution of 7.0, 6.5, and 5.5, respectively. In all three cases a variation of one full pH unit from the normal in the very dilute solution used gave no detectable error.

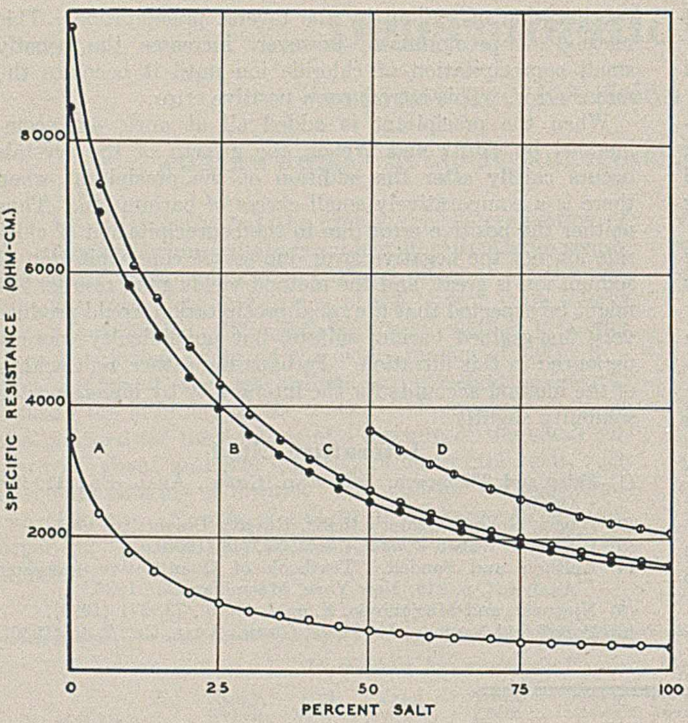


FIGURE 1. SPECIFIC RESISTANCE *vs.* PER CENT SODIUM SULFATE IN DRY SOLID

(Curves *A* and *D* were determined by A. C. Bell.)

A. Sodium sulfate and sodium salt of sulfated coconut oil monoglyceride, 0.20% solution
B. Sodium sulfate and sodium salt of commercial sodium lauryl sulfate, 0.04% solution
C. Sodium sulfate and sodium salt of mixed alkyl aromatic sulfonic acids, 0.04% solution
D. Sodium sulfate and sodium salt of sulfated coconut oil monoglyceride, 0.03% solution

SALT-FREE MATERIALS. In preparing the calibration curve, inorganic salt-free active ingredient was used. Three methods of preparation were employed.

When the inorganic material present was insoluble in hot alcohol—e. g., sodium sulfite or sodium sulfate—two extraction methods were used. In the first method, the oven-dried material was extracted in a Soxhlet extractor with absolute ethanol and the extract dried in a vacuum oven at 100° C. In the second method, a concentrated aqueous solution of a small amount of the material was extracted twice with butanol. The extracts were combined and diluted with several volumes of butanol; then the solvent was fractionally distilled off to remove water until the boiling point was constant (116°) and the solution was filtered hot to remove the salt which crystallized during the distillation. Evaporation of the filtrate gave material free of inorganic salt.

The material was not considered salt-free unless a qualitative test for sulfate ion was negative.

In cases not reported here, when the inorganic salts were soluble in alcohol, dialysis has been used for isolation of the active ingredient.

With all methods care was taken that no fractionation of the organic material occurred during the separation; more soluble fractions will in general have higher specific conductivity.

CALIBRATION CURVE. With salt-free material obtained by the methods described above, the calibration curve was made by the following method: Exactly 200 ml. of 0.040 per cent solution of salt-free material in distilled water were prepared and the conductivity was read. (In all determinations distilled water having a specific resistance of more than 300,000 ohm-cm. was used.) Without removing the electrodes, 10.53 ml. of a 0.040 per cent solution of sodium sulfate were added from a buret and the mixture was gently agitated with the electrodes until a constant reading was obtained on the bridge. This gave the point of the calibration curve for 5 per cent (10.53/210.53) salt content. More salt solution was added and the procedure was continued down to the 50 per cent point. For the other half of the calibration curve the procedure was reversed, with salt solution in the beaker and salt-free active ingredient solution added from the buret. For each point the temperature was read with an accuracy of 0.2° and the reading was corrected to 25° by the formula

$$R_{25} = R_t + 0.02\,(t - 25)\,R_t$$

R_t and R_{25} being the observed and corrected resistances, respectively.

When several conductivity cells are used for the work, the values should also be corrected for cell constant before the calibration curve is drawn.

Calibration curves for three typical materials are shown. Curves are plotted in Figure 1 for specific resistance *vs.* composition and in Figure 2 for specific conductivity *vs.* composition. Since the latter is an additive property, the curves for conductivity are straight lines. Each point represents a single determination, and the deviations from the straight line in the conductivity curves are a measure of the error of the method.

Points are reproducible to 1 per cent salt content or better, and the maximum error is probably less than 2 per cent salt content.

If another concentration than 0.040 per cent is used, it should be so chosen that the range of composition most often dealt with gives specific resistances of 2000 to 5000 ohm-cm. These are low enough to eliminate errors due to variations in the distilled

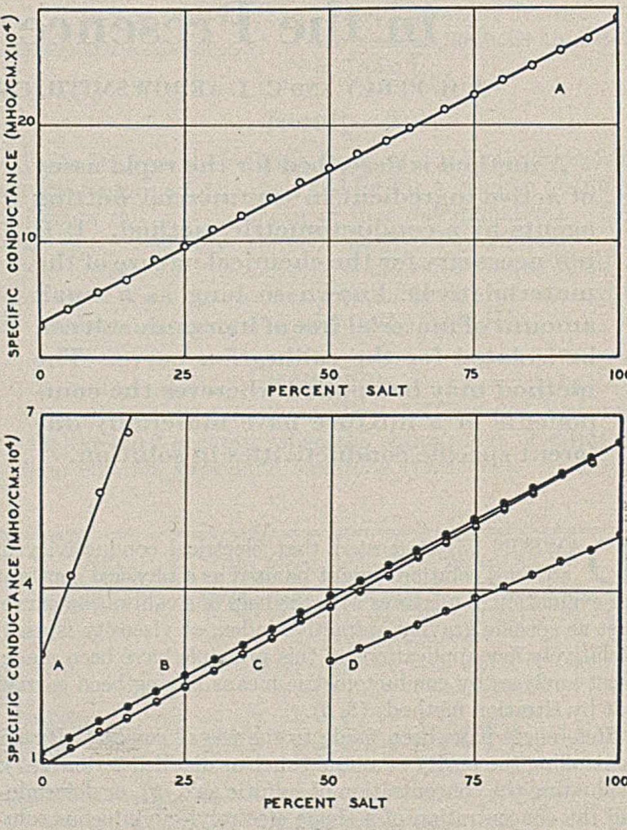


FIGURE 2. SPECIFIC CONDUCTIVITY *vs.* PER CENT SODIUM SULFATE IN DRY SOLID

(Curves *A* and *D* were determined by A. C. Bell.)

A. Sodium sulfate and sodium salt of sulfated coconut oil monoglyceride, 0.20% solution
B. Sodium sulfate and sodium salt of commercial sodium lauryl sulfate, 0.04% solution
C. Sodium sulfate and sodium salt of mixed alkyl aromatic sulfonic acids, 0.04% solution
D. Sodium sulfate and sodium salt of sulfated coconut oil monoglyceride, 0.03% solution

water and high enough to avoid errors due to polarization of electrodes.

Analytical Procedure

In operation, a sample of the material was dried in a vacuum oven, and a solution of 0.040 per cent concentration made up in distilled water. The solution was allowed to stand 15 minutes to reach thermal equilibrium, and was then transferred to a short specific gravity cylinder large enough to hold the dipping electrode. The solution was agitated gently with the electrode, which was inserted to a fixed mark, and the bridge was balanced. The temperature of the solution was read and the specific resistance corrected to 25° by the formula given above, and for cell constant when necessary.

To ensure clean electrodes, it was found better to make another reading on a fresh sample of the solution and accept the values only if the two readings agreed within 1 per cent.

The salt content was read directly from the calibration curve.

Any nonvolatile water-insoluble material that is present will affect the result by decreasing the apparent amount of salt present. This may be corrected for by determining the amount of water-insoluble material by a suitable method (ether extraction for fatty material, filtration of aqueous solution for solids), and correcting for this in making up the solution for conductivity reading, so that the concentration is 0.040 per cent with respect to soluble inorganic salt plus soluble active ingredient. The result is then obtained as per cent salt on a moisture-free and water-insoluble–free basis.

It is undoubtedly possible to apply this procedure when more than one inorganic salt is present. In the particular case of sodium sulfite–sodium sulfate mixtures, when the sodium sulfite is present in variable small percentages, little error is introduced by considering the sulfite present as sodium sulfate, since the specific conductivities of the pure salts are almost equal. In other cases it would probably be necessary to determine the concentration ratios of the inorganic salts present by some other means and use a calibration curve for the mixture actually worked with.

Literature Cited

(1) Archbutt, *Analyst*, 37, 538–43 (1912).
(2) Bishop, to General Chemical Co., U. S. Patent 933,015 (1909).
(3) Callan and Horrobin, *J. Soc. Chem. Ind.*, 47, 329T (1928).
(4) Coster, Ind. Eng. Chem., 25, 980 (1933).
(5) Dawson, *J. Soc. Dyers Colourists*, 35, 123 (1919).
(6) Grant, *Ind. Chemist*, 10, 350–4, 391–5 (1934).
(7) Kendall, *J. Am. Chem. Soc.*, 38, 2460 (1916).
(8) Šandera, K., *Chimie & industrie*, Special No., 231–4 (1933).

An Improved Sublimation Apparatus

O. A. NELSON
Bureau of Entomology and Plant Quarantine,
U. S. Department of Agriculture, Washington, D. C.

PROBABLY the most common type of sublimation apparatus to be found in chemical laboratories consists of two test tubes, one within the other. The substance to be sublimed is placed in the larger test tube, which is then heated in a bath or with a free flame, while the inner tube, which functions as a condenser for the sublimate, is kept cold with running water. The capacity of such an apparatus is very limited, as only a small quantity of substance will adhere to the surface of the condenser, or will drop off when the inner tube is removed.

The apparatus shown in Figure 1, *A*, has been found to give excellent results with a number of compounds. The condenser may be a straight tube or made with a bell-shaped lower end, as shown. Heating the end of this tube with a soft brushy flame to the softening point of the glass and applying a gentle suction to the other end produce an even convex or cuplike surface.

The most important feature of this apparatus is a screen to catch any crystals of the sublimate that may break away from the condenser. This screen is supported by three glass rods fused into the edge of the condenser cup and bent inward at right angles (*B*). If a bath is used for heating, the surface of the liquid should be at about the level of the screen or a trifle above, to prevent sublimation on the screen and clogging of the meshes. The screen must be resistant to action by the sublimate, and of such mesh as to retain all crystals that may fall on it. A 40-mesh German-silver screen was used in this laboratory. For sublimation under vacuum, a tube may be sealed into the side of the outer jacket, as shown in Figure 1, or run through the rubber stopper supporting the condenser. Cooling water may be run in and out of the condenser through a two-hole stopper at the top, instead of through the one-hole stopper and side tube as shown in the diagram.

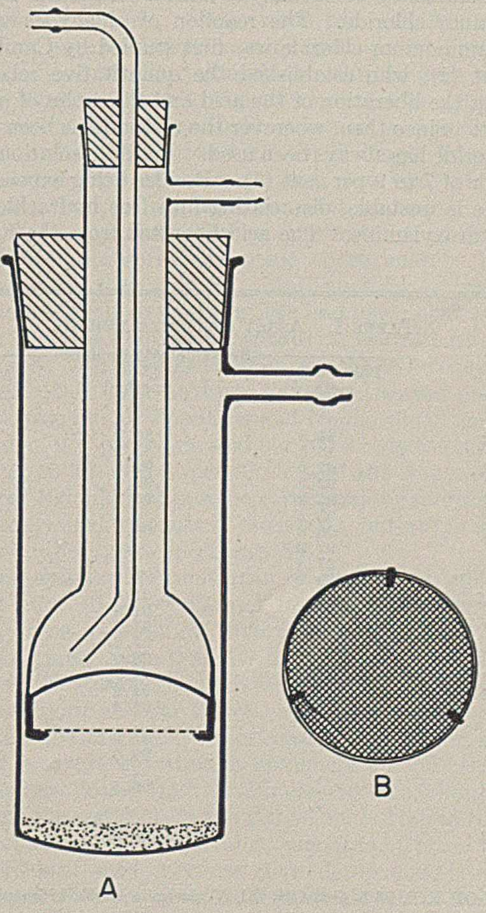


Figure 1. Sublimation Apparatus

Assay of Benzaldehyde

Use of Hydroxylammonium Sulfate and Aqueous Sodium Hydroxide

MARCELLE SCHUBERT AND JANET G. DINKELSPIEL, Research Laboratory, Benzol Products Co., Newark, N. J.

THE strength of benzaldehyde, either pure or in solution, can be estimated with varying degrees of accuracy by several methods. The official methods of the Association of Official Agricultural Chemists (*1*) recommend determining the benzaldehyde as the phenylhydrazone. Though this method gives the most reliable and constant results, it is time-consuming, and the phenylhydrazine must be freshly distilled (though if stored in the refrigerator it will keep for about 3 weeks); the precipitate must stand overnight, the filtration requires considerable time, and *in vacuo* at 70° C. the precipitate requires 3 hours to dry. Furthermore phenylhydrazine can cause a very disagreeable allergy, resulting in swelling and intense itching of the fingers or other parts, and eventual peeling of the skin.

The bisulfite method originally proposed by Ripper (*8*) has been discussed by Kolthoff (*5*, *6*) and Donnally (*3*). Benzaldehyde is added to a known excess of sodium bisulfite, and the sodium bisulfite not used in forming the benzaldehyde addition compound is titrated with standard iodine solution. This method is not, in the authors' experience or according to the literature, satisfactory even for pure material. It is awkward and inconvenient, and the authors have found it to be decidedly unreliable.

The third method, recommended by the United States Pharmacopoeia (*9*), involves the titration of the hydrochloric acid liberated by benzaldehyde from a solution of hydroxylammonium chloride. The reaction of aldehydes with hydroxylammonium chloride was first studied by Cambier and Brochet (*2*), who established the quantitative relationship between the liberation of the acid and the moles of aldehyde present. Since then, wherever the method has been applied, the chloride has always been used. In dilute solution there is an error of 7 to 9 per cent (*7*). Besides being expensive, the chloride is unstable, dissociating into free hydrochloric acid and hydroxylamine. The acid liberated from the hydroxylammonium chloride by benzaldehyde is titrated using alcoholic potassium hydroxide with bromophenol blue as indicator (*4*, *9*). It was claimed (*4*) that unless the alkali was added drop by drop, results would be low.

TABLE I. ASSAY OF BENZALDEHYDE

Batch No.	Benzaldehyde Found: Pharmacopoeia method[a]	A. O. A. C. method	Authors' method
	%	%	%
242	84.3	86.0	..
	85.8	85.8	..
243	92.6	92.6	..
	92.2	92.6	..
244	95.0	95.3	..
	95.5	..	..
233	98.3	99.1	..
	97.0	..	..
	97.3	..	..
	99.2	..	..
PL12	..	91.5	91.8
	..	91.8	92.1
	..	91.7	92.2
PL13	..	97.8	97.6
	..	98.0	98.1
	..	97.7	97.5
151	..	94.2	94.2
	..	94.4	93.8
	..	..	94.0
152	..	95.9	95.5
	..	96.0	95.8
	..	..	96.0
153	..	96.5	96.5
	..	..	96.3
	..	..	96.5
154	..	96.4	96.6
	..	96.5	96.4
	..	..	96.3

[a] $NH_2OH.HCl$, 96% C_2H_5OH, 0.1 *N* alcoholic KOH, bromophenol blue.

The authors first compared the results obtained by the phenylhydrazone and the hydroxylammonium salt methods and found that they checked. Next preliminary experiments using aqueous sodium hydroxide instead of alcoholic potassium hydroxide showed that the aqueous alkali was entirely satisfactory. They then found that it was not necessary to add the alkali drop by drop. Finally, as a result of the search for a better indicator, they found that tetrabromophenol blue gave an end point much more quickly perceived, although it does not affect the extreme deviation in the results.

Two years ago the Commercial Solvents Corporation put hydroxylammonium sulfate on the market, and as this salt is stable and cheap, the authors immediately decided to test its usefulness in the assay of benzaldehyde. The hydroxylammonium sulfate as furnished by the Commercial Solvents Corporation is entirely satisfactory, and can be used without further purification, though it may be necessary to filter the solution to make it brilliantly clear. If it is desired to recrystallize the reagent, boiling in 50 per cent methyl alcohol with a little Darco G60 gives excellent results. The authors' experiments may be summarized as follows (see Table I):

Hydroxylammonium sulfate can be used in place of the unstable and expensive chloride.

Aqueous sodium hydroxide can be used in place of alcoholic potassium hydroxide.

The sodium hydroxide can be run in rapidly to within 2 to 3 cc. of the end point in less than one minute. A single titration, after sufficient practice in catching the end point, requires only 1.75 minutes.

Tetrabromophenol blue gives an end point more quickly perceived than in the case of bromophenol blue (*9*), though the error is about the same.

The extreme deviation in the results obtained depends largely on how frequently such titrations are run. When run daily, the extreme variation may be, on an average, only 0.2 to 0.3 per cent, while weekly titrations immediately raise the error to as much as 0.6 to 0.7 per cent. The extreme deviation has thus been reduced from 1 to 1.5 per cent (alcoholic potassium hydroxide and bromophenol blue) to a maximum of 0.6 to 0.7 per cent.

Procedure

Solutions required: 1.25 per cent hydroxylammonium sulfate in 50 per cent methyl alcohol, 0.1 *N* standard aqueous sodium hydroxide, and 0.1 per cent tetrabromophenol blue in 50 per cent methyl alcohol.

The 50 per cent methanolic solution of hydroxylammonium sulfate is acid and must be neutralized. For six batches of benzaldehyde which are assayed in triplicate, 600 ml. of solution are made. Three milliliters of tetrabromophenol blue indicator are added, turning the solution a clear green. About 12 to 15 ml. of 0.1 *N* sodium hydroxide are required to change the color to blue. Since the indicator is dichroic, the color in bulk is different from that of a small quantity; therefore alkali is added until the color of a 30-ml. sample poured into a 75-ml. Erlenmeyer-shaped flask is a clear pale blue. The solution should be neutralized immediately before use, because if it stands for more than 2 hours, sufficient acid is liberated by hydrolysis of the hydroxylammonium sulfate to change the color of the indicator and so make the results of the benzaldehyde assay high.

A 5-ml. Lunge weighing pipet is used to measure out the sample. In order further to reduce the danger of oxidation, the pipet is filled nearly full. The taper is fine enough so that about 10 drops give 0.2 gram. The weight of the pipet after weighing out the first sample can safely be used as the weight of the pipet before the next sample, and so on, without introducing an appreciable error. The benzaldehyde is dropped into a 75-ml. Erlenmeyer-shaped glass-stoppered flask containing 30 ml. of neutralized hydroxylammonium sulfate solution, and the flask is gently swirled. Samples lower than 90 per cent benzaldehyde usually go into solution with difficulty.

Titration

Standard 0.1 *N* sodium hydroxide is run rapidly into the solution until within about 2 to 3 ml. of the end point, then a few drops at a time until the color is green-blue, and finally dropwise until the color is again the clear, pale blue. The absence of direct sunlight is desirable. This part of the assay is almost exclusively responsible for any error.

The results obtained will be more truly representative if the samples are kept in glass-stoppered Pyrex bottles whose lips can be thoroughly cleaned.

The benzaldehyde content is calculated from the expression

$$\frac{\text{Ml. of } 0.1000\ N\ \text{NaOH} \times 0.0106}{\text{weight of sample}} \times 100 = \%\ \text{benzaldehyde}$$

Acknowledgment

The authors gratefully acknowledge the cooperation of the Commercial Solvents Corporation in furnishing samples of hydroxylammonium sulfate.

Literature Cited

(1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 4th ed., p. 314, 1935.
(2) Cambier, R., and Brochet, A., *Compt. rend.*, 120, 449 (1895).
(3) Donnally, L. H., Ind. Eng. Chem., Anal. Ed., 5, 91–2 (1933).
(4) *Givaudanian*, p. 4 (May, 1939).
(5) Kolthoff, I. M., and Furman, N. H., "Volumetric Analysis", 1st ed., Vol. II, pp. 450–2, New York, John Wiley & Sons, 1929.
(6) Kolthoff, I. M., and Rosenblum, C., "Acid-Base Indicators", 1st English ed. (tr. from 4th German ed.), p. 123, New York, Macmillan Co., 1937.
(7) Neuberg, C., and Gottschalk, A., *Biochem. Z.*, 146, 167 (1924).
(8) Ripper, *Monatsh.*, 22, 1079 (1900).
(9) U. S. Pharmacopoeia XI, p. 247 (1936).

Colorimetric Determination of Phosphorus in Biological Materials

RUTH ADELE KOENIG AND C. R. JOHNSON, University of Texas, Austin, Texas

MISSON'S (*3*) method for the estimation of phosphorus has recently been adapted to the determination of this element in iron, steel, and iron ores (*4*, *5*). During use of the method in food analyses in this laboratory, the fact became evident that its range, sensitivity, and precision could be increased considerably in this application, where limiting interferences are rare. For this purpose the effect of time on the development of the yellow phosphovanadiomolybdate at various concentrations has been studied, the optimum acid concentration has been found, the range over which Beer's law holds precisely has been determined at three wave lengths of light, and spectrophotometric calibration data have been obtained with nine series of standard solutions. The results of these experiments have been condensed in a convenient procedure for the rapid and precise determination of phosphorus in foods and other biological materials, and this procedure has been tested by comparison with official gravimetric methods.

Apparatus and Reagents

A Coleman Model 10-S spectrophotometer was used to measure transmittance values. The spectral band width was 30 mμ. Matched square cuvettes were used to hold the reference liquids and test solutions. The dark current adjustment was frequently checked during the measurements, which were made at temperatures between 25° and 30° C.

Two independently prepared sets of reagents were used. 15 *N* nitric acid, 6 *N* hydrochloric acid, 9 *N* perchloric acid, and 4 *N* aqua ammonia were purified by distillation methods. Standard potassium dihydrogen phosphate solution containing 0.1000 mg. of phosphorus per ml. was made by dissolving 0.4393 gram of twice recrystallized and vacuum-dried material in distilled water and making to 1 liter. Another standard solution containing 0.1000 mg. of phosphorus per ml. was made by dissolving 1.351 grams of silver phosphate (*2*) in 5 ml. of 15 *N* nitric acid and diluting to 1 liter. Ammonium vanadate solutions were made by dissolving 2.345 grams of vacuum-desiccated ammonium metavanadate in 500 ml. of hot water, adding 10 ml. of 15 *N* nitric acid, and diluting to 1 liter. One sample of this salt was prepared by double recrystallization of reagent grade material with centrifugal draining; the other was a sample of atomic weight purity. One ammonium molybdate solution was prepared as described by Willard and Center (*5*), using vacuum-dried molybdic acid purified by precipitation with 6 *N* hydrochloric acid, followed by two crystallizations from water, with centrifugal draining. A second solution of this reagent was a 10 per cent solution of ammonium molybdate shown to be free of phosphate and chloride by blank tests; this was used with the systems containing silver. Fresh molybdate solutions were prepared frequently, as required.

Summary of Calibration Experiments

In obtaining calibration data, opportunity was taken to study the effect of various factors on the precision and accuracy of the method. Thus, while test solutions for the calibrations were made by the same method described below for the analyses, standard phosphate solutions were used instead of digested samples, various concentrations and mixtures of nitric and perchloric acid were tried, and each system was kept under observation for a much longer time. Different combinations of solutions from the two sets of reagents were used, to eliminate constant errors.

In Table I are given the median transmittances from about 1200 calibration observations made approximately 30 minutes after color development. Mathematical treatment of the data as a whole showed that the best agreement with the medians in Table I for all phosphate concentrations studied was obtained with systems containing 5 ml. of 9 *N* perchloric or 3 ml. of 15 *N* nitric acid per 100 ml. Delayed precipitation took place in all standards and blanks which contained only 2 ml. of 9 *N* perchloric acid per 100 ml., in the standards containing 10 ml. of 9 *N* perchloric acid and 5 mg. of phosphorus per 100 ml., and in some corresponding solutions containing equivalent amounts of nitric acid, but not in systems with intermediate acid concentrations.

In such systems transmittance readings were sufficiently constant after 10 to 30 minutes for precise measurements: transmittances were almost invariably lower after 12 to 24 hours, but rarely more than 1.0 unit lower. The minimum drop in transmittance occurred in systems containing 5 ml. of 9 *N* perchloric acid per 100 ml. On two counts, therefore, this is the optimum acid concentration. However, neither time nor acid concentration is extremely critical: transmittance readings taken from 10 minutes to many hours after making up the test solutions to 100 ml. with 2 ml. to 10 ml. of 9 *N* perchloric acid or equivalent amounts of nitric acid or nitric-perchloric acid mixtures give approximately correct results, even when precipitation of molybdic acid or the yellow complex is eventually to occur.

No significant differences due to interchange of reagents were observed during the calibrations. The order of addition of vanadate and molybdate should not be reversed.

Readings taken with water as the reference liquid were a little more reproducible than those made with blanks, but water should be used as the reference liquid only when all the developing reagents are free from phosphate and the solutions to be analyzed are colorless.

TABLE I. CONCENTRATION-TRANSMITTANCE DATA FOR PHOSPHORUS DETERMINATIONS

Phosphorus	Transmittance at Various Wave Lengths					
	Blank Reference			Water Reference		
	430 mμ	450 mμ	470 mμ	430 mμ	450 mμ	470 mμ
Mg./100 ml.	%	%	%	%	%	%
0.200	77.1	84.0	88.6	72.9	81.6	87.6
0.500	53.0	66.0	76.0	50.4	64.3	75.2
1.000	28.6	44.2	58.7	27.1	43.0	57.8
1.800	10.7	23.5	38.8	10.1	22.8	38.2
2.50	[5.1]	13.5	27.2	[4.8]	13.1	26.6
3.50	...	[6.6]	16.4	...	[6.3]	16.1
5.00	...	...	[8.2]	...	...	[8.1]

Graphical representation of the data in Table I shows that Beer's law is followed very closely except for the bracketed values, which were not used in the final reduction of results. The 4 per cent deviation of these values is probably due to an instrumental error; it is undesirable to use transmittances lower than 10 per cent in precise analyses.

Analytical Procedure

The following procedure is designed for the determination of phosphorus in aliquot portions of the solution obtained by ashing a 10-gram sample of material by successive treatment with 60 ml. (and, if necessary, additional 30-ml. portions) of 15 *N* nitric acid and 24 ml. of 9 *N* perchloric acid, according to the method of Gerritz (*1*).

PROCEDURE. When ashing is complete, evaporate the solution to about 50 ml., filter through a Munroe or Pyrex filtering crucible to remove silica, dilute, boil for at least 30 minutes, cool, and make up to exactly 250 ml. Most of this solution may be reserved for the determination of calcium and iron.

To analyze a colorless solution for phosphate pipet a 10.00-ml. or other suitable aliquot portion into a 100-ml. volumetric flask, add 5 ml. of 9 *N* perchloric acid or 3 ml. of 15 *N* nitric acid, and bring the volume to 70 ml. Add 10.0 ml. of ammonium vanadate solution, gradually mix in 10.0 ml. of ammonium molybdate solution, and dilute to exactly 100 ml. After 30 minutes make duplicate transmittance readings with two portions of the solutions, at the optimum wave length. If the reagents are free from phosphate use water as a reference liquid; otherwise use a blank containing the reagents. Calculate the result of the analysis from the median transmittance by appropriate substitution in Equation 1 below, or by use of a graph derived from this equation.

In analyzing colored solutions—e. g., the light yellow or yellow-green solutions derived from many foods—use as a reference liquid a system containing the same aliquot portion of colored liquid as the test solution, with all the reagents except the ammonium molybdate, which in this case must be free from phosphate.

For convenience in calculating results with maximum precision the data in Table I have been reduced by the method of least squares to equations of the form:

$$\text{Mg. of P per 100 ml. of test solution} = \frac{a \log_{10} T + b}{l} \qquad (1)$$

in which T is the percentage transmittance relative to the reference liquid, and l is the thickness of the solution in centimeters. Values of the constants a and b for the various conditions studied are given in Table II. In the present calibrations l was 1.308 cm., and the data in Table II apply to cases in which matched square cuvettes of about this size are used (*4*). The actual value of l should in any case be determined with a micrometer and calipers. Under the conditions specified, Equation 1 yields results correct to between 0.4 and 2 per cent over the range from 0.2 to 4.5 mg. of phosphorus per 100 ml. of final test solution.

Applications and Tests of Method

The procedure described above has been used in the analysis of some 80 different materials, including vegetables, meats, flour, milk, eggs, fruits, grasses, berries, vinegar, yeast, gelatin, agar, condiments, urine, feces, baking powders, wine, beer, fertilizers, oils, pharmaceuticals, chemical reagents, and about 40 food concentrates. In view of the small mineral content of most of these substances, few interferences were expected; the fact that results obtained at all three wave lengths were generally in good agreement and independent of aliquot size may be taken as evidence of the absence of serious interferences. Of course, one wave length usually provides a result of maximum precision, depending on the size and phosphate content of the aliquot. The optimum conditions may be selected by the analyst, who may use the lowest wave length to obtain sensitivity, the highest to obtain range, or more than one for confirmatory purposes.

TABLE II. CONSTANTS FOR CONCENTRATION-TRANSMITTANCE EQUATIONS

	Wave Length		
	Mμ	*a*	*b*
Blank reference	430	−2.442	4.867
	450	−3.789	7.55
	470	−5.89	11.72
Water reference	430	−2.437	4.802
	450	−3.783	7.49
	470	−5.85	11.62

In addition to the various checks on the procedure provided by the use of two primary standard materials in the calibrations, an additional check was made by comparison of the method with A. O. A. C. official gravimetric methods, for representative materials. The results in Table III are typical, and further confirm the soundness of the method. The precision and accuracy of the spectrophotometric analyses are satisfactory, considering that they require only a fraction of the time needed for the gravimetric determinations.

TABLE III. SUMMARY OF TYPICAL RESULTS

Material[a]	Spectrophotometric Method			Official Method	
	430 mμ	450 mμ	470 mμ		
	Mg. P per 10 grams of material				
Apple vinegar	0.430	0.436	0.432	...	
Dried grass 1	7.3	...	...	7.$_0$	(volumetric)
Dried grass 2	18.2	18.2	17.6	17.$_9$	
Kelp concentrate	25.7	26.1	26.3	27.8	
Tomato concentrate	27.7	28.1	28.5	28.3	
Milk powder	...	70.3	70.0	70.2	
Spinach concentrate	...	72.5	70.8	70.6	
Liver concentrate	189	195	193	193	
Baking powder 1	303	309	310	303	
Baking powder 2	324	320	318	314	
Baking powder 3	841	839	834	828	
Fertilizer	560	550	544	5$_{20}$	(not official)
$FePO_4.2H_2O$ (1 g. per liter)	164$_6$	165$_0$	165$_2$	[1658]	(theoretical)

[a] All samples were dried before analysis by 12 to 24 hours of vacuum desiccation, except vinegar and ferric phosphate, which also were not ashed.

The authors are indebted to the Division of Chemistry of the Texas Agricultural Experiment Station for analyzed grass samples, to California Vegetable Concentrates, Inc., for the food concentrates, and to W. C. Craig for many gravimetric analyses.

Literature Cited

(1) Gerritz, H. W., IND. ENG. CHEM., ANAL. ED., 7, 167 (1935).
(2) Johnson, C. R., and Nunn, L. G., Jr., *J. Chem. Education*, 17, 528 (1940).
(3) Misson, G., *Chem.-Ztg.*, 32, 633 (1908).
(4) Murray, W. M., Jr., and Ashley, S. E. Q., IND. ENG. CHEM., ANAL. ED., 10, 1 (1938).
(5) Willard, H. H., and Center, E. J., *Ibid.*, 13, 81 (1941).

Estimation of Bromides in the Presence of Other Halides

P. L. KAPUR, M. R. VERMA, AND B. D. KHOSLA, University Chemical Laboratories, Lahore, India

ESTIMATION of bromides in the presence of other halides is a problem of importance and a number of papers on the subject have been published.

Bromides in Presence of Chlorides

Most of the published methods can be classified under two general heads: (1) those depending upon the choice of certain oxidizing agents by which bromine alone is liberated and distilled off, the chloride remaining in the residue as chloride, after which bromine collected is determined iodometrically, gravimetrically as silver bromide, or colorimetrically by means of fluorescein solution or fuchsin–sulfuric acid reagent; and (2) those depending upon the quantitative oxidation of bromides to bromates either by chlorine water in the presence of sodium bicarbonate (*11*) or by the addition of the theoretical amount of hypochlorite in the presence of borate buffer and sodium chloride to half saturation (*5*, *8*). If chloride be present a small amount of chlorate is invariably formed and this must be allowed for by using controls subjected to the same procedure from the start; if iodide be present, it is quantitatively oxidized to iodate and then the apparent bromide figure includes the iodide.

TABLE I. DETERMINATION OF BROMIDES

KBr Solution Taken	$Na_2S_2O_3$ Required, $I_2 = 2Br$	Strength of $Na_2S_2O_3$	Weight of KBr in 100 Ml. Found	Weight of KBr in 100 Ml. Present
Ml.	*Ml.*		*Gram*	*Gram*
2.0	12.45	0.001602	0.996	1.0000
1.0	16.95	0.0005902	1.000	1.0000
5.0	42.35	0.0005902	0.4997	0.5000
1.0	16.65	0.0001200	0.1990	0.2000
1.0	8.25	0.0001200	0.0990	0.1000

To effect oxidation Baubigny and Rivals (*1*) used a mixture of copper sulfate and potassium permanganate, Clausmann (*3*) used a mixture of chromic and sulfuric acids, Baughman and Skinner (*2*) used chromic acid in concentrated solutions, Meloche and Willard (*7*) used potassium permanganate and hydrochloric acid, and Edwards, Nanji, and Parkes (*6*) used potassium permanganate and dilute phosphoric acid. These methods require distilling the bromide mixture with the oxidizing agent and collecting the liberated bromine in a vessel containing potassium iodide solutions, when an equivalent amount of iodine is liberated which can be estimated volumetrically by titrating against standard thiosulfate solution. There are other methods where bromine produced by oxidizing agents is extracted with carbon tetrachloride (*9*, *10*), which is separated and shaken with potassium iodide. Iodine thus liberated is determined volumetrically. Denoël (*4*) has recently described an extraction method for the estimation of bromides in the presence of chlorides, using potassium bromate as the oxidizing agent.

TABLE II. BLANK EXPERIMENTS WITH SODIUM CHLORIDE ALONE

Sodium Chloride Present	Sodium Thiosulfate Used
Mg.	*Ml.*
25	Nil
50	Nil
75	Nil
100	0.03
150	0.18

In the present investigation the authors used mixtures of nitric and chromic acids as oxidizing agents and removed the liberated bromine by shaking the mixtures with carbon tetrachloride.

TABLE III. DETERMINATION OF BROMIDES IN PRESENCE OF CHLORIDE

KBr Solution Taken	NaCl Added	$Na_2S_2O_3$ Required, $I_2 = 2Br$	KBr in 100 Ml. of Solution Found	KBr in 100 Ml. of Solution Present
Ml.	*Gram*	*Ml.*	*Grams*	*Grams*
2.0	0.025	11.12	1.0008	1.0004
2.0	0.050	11.12	1.0008	1.0004
2.0	0.075	11.12	1.0008	1.0004
2.0	0.100	11.15	1.0035	1.0004
2.0	0.125	11.20	1.0080	1.0004
2.0	0.150	11.30	1.0170	1.0004

Strength of $Na_2S_2O_3$ used, 1 ml. = 0.0018 gram of KBr

REAGENTS. A 1 per cent stock solution of potassium bromide was made from analytical reagent potassium bromide. Different volumes of this solution were taken to estimate the bromide content.

Carbon tetrachloride available in the stores was purified according to the standard methods (*12*).

Nitric acid and chromic acid were extra pure Merck quality.

PROCEDURE. A known volume of potassium bromide solution was mixed with an excess of 10 per cent chromic acid and an equal volume of concentrated nitric acid in a 100-ml. separating funnel. The mixture was shaken with 10 ml. of carbon tetrachloride. The lower layer of carbon tetrachloride containing the liberated bromine was separated. To ensure complete removal of bromine, the solution was further shaken a number of times with successive 5-ml. portions of carbon tetrachloride and the latter was separated. It was found that chromic acid dissolves to a small extent in carbon tetrachloride and interferes later on with the estimations. Therefore, carbon tetrachloride extractions were shaken with water to remove any chromic acid present. To safeguard against any loss of bromine, the water layer was again shaken with a fresh 5-ml. portion of carbon tetrachloride and this extraction added to the rest of the extractions. To the carbon tetrachloride extractions in a glass-stoppered Erlenmeyer flask potassium iodide was added and the equivalent amount of iodine liberated was titrated against standard sodium thiosulfate. The end point is indicated by the disappearance of violet color from the carbon tetrachloride.

TABLE IV. EFFECT OF IODIDES

Potassium Iodide Present	Sodium Thiosulfate Used
Mg.	
25	Nil
30	Nil
40	Nil
75	Nil

In Table I are given the results obtained on a specimen of pure potassium bromide, showing experimental results in very good agreement with the calculated ones. In all these cases 10 ml. of 10 per cent chromic acid and 10 ml. of nitric acid were used for oxidation. Carbon tetrachloride extraction was done four times.

As may be seen from Table I, very small amounts of bromides, like 0.001 gram in 1.0 ml. of 0.1 per cent solution, can be easily and accurately estimated.

A preliminary series of blank determinations was carried out to ascertain the effect of chromic acid–nitric acid mixture on varying concentrations of chloride. The figures in Table II show that no iodine is liberated from carbon tetrachloride extractions on the addition of potassium iodide when the concentration of chloride is not very high.

In Table III are recorded results of determination of potassium bromide in the presence of varying quantities of sodium chloride.

It is clear that if the amount of chloride present be not large, the amount of bromide found is almost theoretical. High results in the presence of much chloride have been noted by other investigators (*9*).

Bromides in Presence of Iodides

The interference of iodides in the oxidation method of determining bromides is overcome by oxidizing the iodide to iodate (*7*). The authors have observed that the method described above, when slightly modified, overcomes the interference of iodides, as they are completely oxidized to iodates by the excess of nitric acid–chromic acid mixture.

TABLE V. DETERMINATION OF BROMIDES IN PRESENCE OF IODIDE

KBr Solution Taken	KI Added	$Na_2S_2O_3$ Required, $I_2 = 2Br$	KBr in 100 Ml. of Solution	
			Found	Present
Ml.	*Gram*	*Ml.*	*Grams*	*Grams*
2.0	0.0150	15.20	1.00016	1.0002
2.0	0.0300	15.20	1.00016	1.0002
2.0	0.0450	15.20	1.00016	1.0002
2.0	0.0600	15.20	1.00016	1.0002
2.0	0.0750	15.20	1.00016	1.0002

Strength of $Na_2S_2O_3$ used, 1 ml. = 0.001316 gram of KBr

PROCEDURE. To the mixture of halides 25 per cent instead of 10 per cent chromic acid was added with nitric acid, thus ensuring complete conversion of iodides to iodate. The rest of the procedure was as described above.

Preliminary experiments were carried out with potassium iodide alone and it was found (Table IV) that no iodine is detected in the carbon tetrachloride extractions.

In Table V are given the results of determination of potassium bromide in the presence of varying concentrations of potassium iodide. The results are self-explanatory.

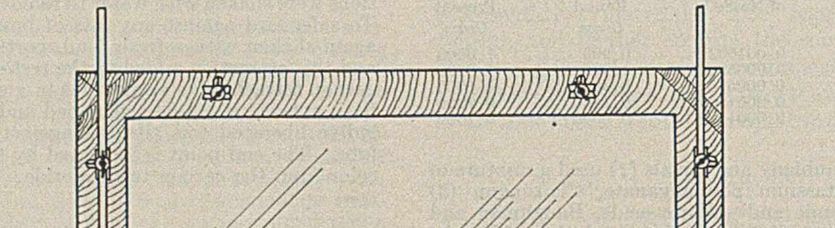
It is evident that the method described can be used safely with great accuracy for the determination of bromides in the presence of iodides and chlorides, provided the chlorides are not present in large amount as in saline waters, "potash salts", etc.

Literature Cited

(1) Baubigny and Rivals, *Compt. rend.*, 124, 859 (1897).
(2) Baughman, W. F., and Skinner, W. W., J. IND. ENG. CHEM., 11, 954 (1919).
(3) Clausmann, *Bull. soc. chem.*, 9 (4), 188 (1911).
(4) Denoël, A., *J. pharm. Belg.*, 22, 179 (1940).
(5) Dixon, T. F., *Biochem. J.*, 28, 48 (1934).
(6) Edwards, F. W., Nanji, H. R., and Parkes, E. B., *Analyst*, 61, 743 (1936).
(7) Meloche, C. C., and Willard, H. H., J. IND. ENG. CHEM., 14, 422 (1922).
(8) Meulen, J. H. van der, *Chem. Weekblad*, 28, 82 (1931).
(9) Sutton, F., "Systematic Handbook of Volumetric Analysis", London, J. S. A. Churchill, 1935.
(10) Swift, E. H., "System of Chemical Analysis", New York, Prentice Hall, 1939.
(11) Szabo, Z., *Z. anal. Chem.*, 84, 24 (1931).
(12) Weissberger, Proskaner, "Organic Solvents", Oxford, Clarendon Press, 1935.

An Adjustable Safety Shield

ARTHUR FURST, San Francisco Junior College, San Francisco, Calif.



THE adjustable safety shield here described was developed by the writer to overcome the limitations to the arrangement of apparatus when a conventional safety shield is used.

The conventional shield consists of either safety glass or wire-encased glass set close to the base legs and rigidly attached to them. Protection is afforded at the very bottom where there is no real need, while at the same time the shield protects only a restricted area. The height of the shield is the limiting height of the apparatus. If the arrangement must be modified, the dimensions of the safety shield are a hampering factor. Unless an assortment of shield sizes is kept, only a limited number and types of arrangements can be used.

To give more leeway to the assembling of apparatus and still maintain complete protection, an adjustable, portable safety shield was constructed, using the safety glass from an old automobile wind wing. It was tested by shattering a liter beaker against it from a distance of 4 feet. The glass was enframed in 2 by 4 inch wood, and cushioned by strips of cloth. Into two holes bored in each side were forced the shaft ends of some broken rings. These served to clamp the shield to the ring stands which had been removed from the original iron stands and fastened to large wooden blocks.

This shield can easily be made higher or lower, and used either vertically or horizontally. Ultimate freedom and flexibility in setting up apparatus are achieved.

A Modified Noyons Thermic Diaferometer for Respiratory Gas Analysis

THORNE M. CARPENTER AND VLADIMIR S. COROPATCHINSKY
Nutrition Laboratory, Carnegie Institution of Washington, Boston, Mass.

A modification of the thermic diaferometer of Noyons is described, the general principle of which is the analysis of the carbon dioxide content and oxygen deficit of respiratory chamber gases based on measurements of the deflections of a sensitive galvanometer, which indicates the changes in resistance of platinum wires caused by a difference in the cooling powers of the gases surrounding the wires. The apparatus has been standardized by analyses with diluted respiratory air in comparison with atmospheric air, and constants have been established for the equivalent percentages of carbon dioxide and oxygen deficit in samples of respiratory chamber air per millimeter deflection of the galvanometer. The accuracy of functioning of the apparatus has been demonstrated by alcohol control tests. Forty-six consecutive tests on five days gave an average respiratory quotient of 0.662 with a standard deviation of ±0.0084. The standard deviation of the quotients from the theoretical alcohol quotient of 0.667 was ±0.0097.

IN 1937 Noyons (*1*) published the description of an apparatus for gas analysis, the principle of which was dependence upon measurement of the changes in resistance of platinum wires in two arms of a Wheatstone bridge caused by differences in the cooling powers of the gases surrounding the wires. In August, 1938, one of the authors (T. M. C.) saw the apparatus demonstrated at the Sixteenth International Physiological Congress in Zurich, Switzerland, and was able to obtain measurements and details with regard to its construction.

A schematic diagram indicating the general principle of the apparatus is shown in Figure 1, and photographs of the assembled apparatus are reproduced in Figures 2 and 3. The apparatus consists of two parallel pathways for two continuous streams of air, which are driven either through absorbents for both carbon dioxide and water vapor or through an absorbent for water vapor alone. After passing through the absorbents, portions of the two streams of air are aspirated by means of a constant-level hydrostatic pump through chambers containing resistance wires which form two arms of a Wheatstone bridge system. The changes in cooling power of the gas passing through the system are measured by the deflections of a delicate galvanometer.

The streams of air enter the apparatus through *A*1 or *A*2 (Figure 1), and the direction of either air current can be determined by stopcocks *B*1 and *B*2. The air, aspirated from the outside, is driven through the absorption system by pumps *P*1 and *P*2, and the rate of flow is controlled by needle valves *N*1 and *N*2. When it is desired to pass the air along the system without removing its carbon dioxide content, stopcocks *D*1 and *D*2 are closed and stopcocks *C*1 and *C*2 are turned in such a direction that the air passes directly to the absorbing vessels, *E*1 and *E*2, where the water vapor is removed. To remove carbon dioxide as well as water vapor, stopcocks *C*1 and *C*2 are closed and *D*1 and *D*2 are opened, which permits the air to pass through two parallel sets of tubes *F*1 and *F*2, containing the carbon dioxide absorbent. After leaving the carbon dioxide absorbing system, the gas in the original Noyons apparatus

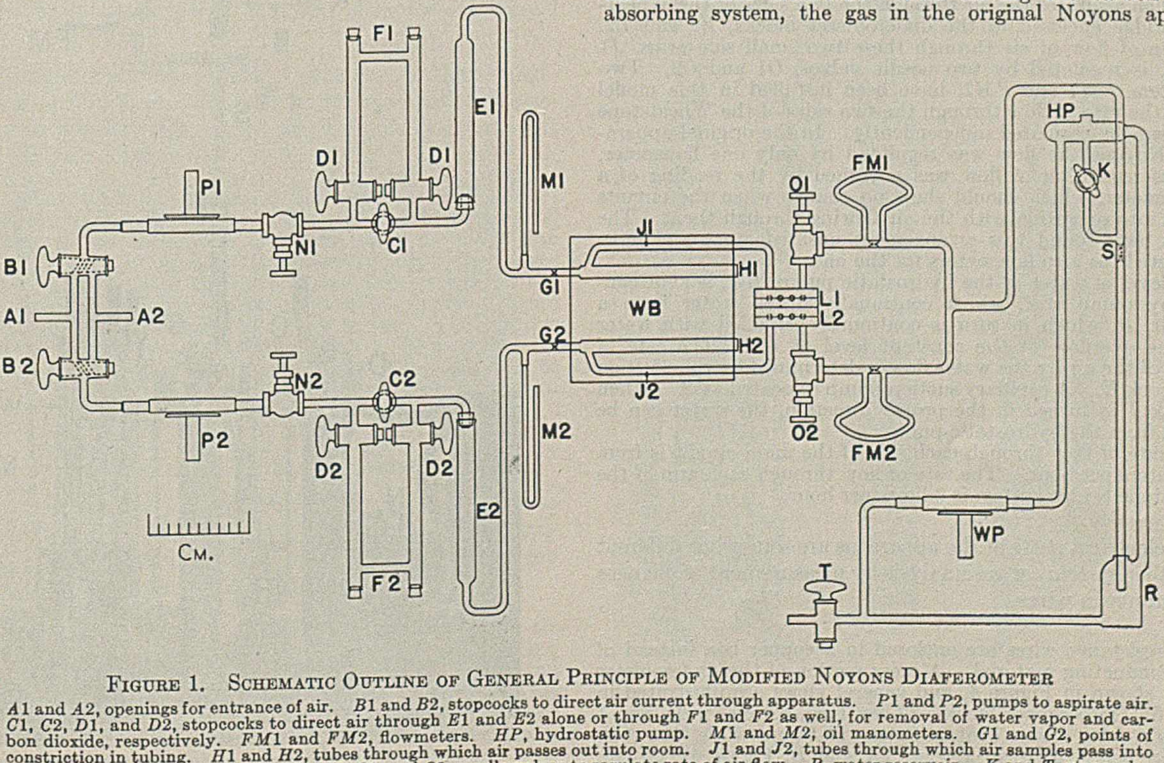


FIGURE 1. SCHEMATIC OUTLINE OF GENERAL PRINCIPLE OF MODIFIED NOYONS DIAFEROMETER

*A*1 and *A*2, openings for entrance of air. *B*1 and *B*2, stopcocks to direct air current through apparatus. *P*1 and *P*2, pumps to aspirate air. *C*1, *C*2, *D*1, and *D*2, stopcocks to direct air through *E*1 and *E*2 alone or through *F*1 and *F*2 as well, for removal of water vapor and carbon dioxide, respectively. *FM*1 and *FM*2, flowmeters. *HP*, hydrostatic pump. *M*1 and *M*2, oil manometers. *G*1 and *G*2, points of constriction in tubing. *H*1 and *H*2, tubes through which air passes out into room. *J*1 and *J*2, tubes through which air samples pass into diaferometer blocks *L*1 and *L*2. *N*1, *N*2, *O*1, and *O*2, needle valves to regulate rate of air flow. *R*, water reservoir. *K* and *T*, stopcocks. *S*, capillary suction pump. *WB*, water bath. *WP*, water pump.

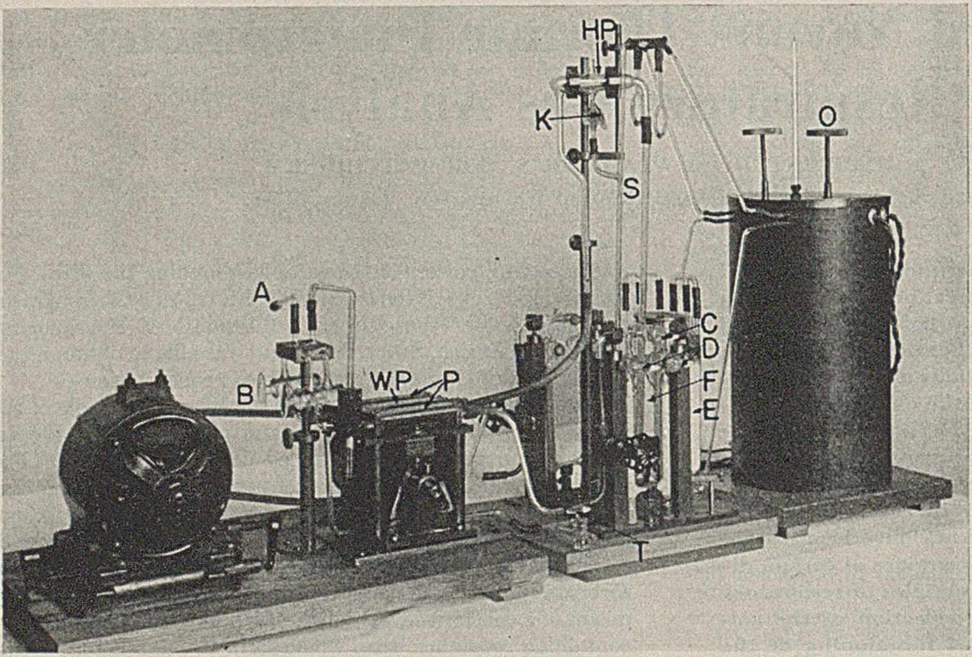


Figure 2. General View of Modified Noyons Diaferometer

passed through a saturator, but the authors found it more satisfactory to remove the water vapor completely.*

Containers $E1$ and $E2$ hold 12 grams of Dehydrite each, and the two parallel sets of tubes, $F1$ and $F2$, hold 15 grams of Ascarite each. These amounts serve for thirty analyses.

The rate of flow of the air through the continuing circuit is regulated by oil manometers $M1$ and $M2$. To have pressure at this point, a constriction is made in the tubing leading to the outside air at points $G1$ and $G2$. After leaving these points, the excess air passes out freely through the parallel tubes, $H1$ and $H2$, to the outside air. These two tubes are immersed in a cylindrical glass water bath, *WB*.

From these two main air streams samples are drawn for analysis through tubes $J1$ and $J2$ by means of a hydrostatic pump, *HP*, which aspirates the air through the two sides of the Wheatstone bridge enclosed in the diaferometer blocks, $L1$ and $L2$. The rate of flow of air through these two small side arms, $J1$ and $J2$, is regulated by two needle valves, $O1$ and $O2$. Two flowmeters, $FM1$ and $FM2$, have been installed in this model so that the rate of flow through the two sides of the Wheatstone bridge can be regulated independently. In the original apparatus of Noyons the flow was regulated by only one flowmeter, and this regulation of flow was governed by the reading of a galvanometer, which should show no change when the circuits are put into operation with the air flowing through them. The authors have found this arrangement unsatisfactory and have substituted the two flowmeters for the one.

The level of water in the hydrostatic pump, *HP*, is kept constant by pump *WP*, which continually draws water from a reservoir, *R*, which in turn is continually supplied with water from the overflow at the constant level at *HP*. The rate of suction of the air by the water flow is determined by the position of stopcock *K*. A capillary suction pump is located at *S*. When stopcock *T* is turned in the proper direction, the water can be drained from the hydrostatic pump.

The rate of flow through each side of the main circuit is from 4 to 5 liters per hour. The rate of flow through each arm of the Wheatstone bridge system is 3 liters per hour.

The electrical parts of the apparatus are somewhat different from other systems of gas analysis by measurement of changes in resistance in wires.

The resistance wires are enclosed in a copper box instead of in nonconducting material. A cross section of the diaferometer itself is shown in Figure 4, and general views are illustrated in Figure 5. Two copper blocks, 22 cm. long, 6.4 cm. wide, and 1 cm. thick, form a case containing the platinum wires. In each block are semicylindrical grooves (*A* and *B*, Figure 4), 20 cm. long and 2.4 mm. deep. Holes *C* and *D*, 4.4 mm. in diameter, are made through the block to connect one end of each groove with the air current. Two other grooves, *F* and *G*, 2.4 mm. deep, run the entire length of the block and carry the platinum resistance wires, which are fastened into terminals *K* and *L* at one end of the block and terminals *M* and *N* at the other end. Springs of No. 40 Manganin wire, $S1$ and $S2$, keep the platinum wires at the right tension so that they will not sag. The outside connections are insulated from the blocks. The electric current passing through the two platinum wires in each set of blocks is 56 milliamperes.

Two such blocks, when placed with the grooved sides facing one another, form one container for one arm of the Wheatstone bridge system. To permit the stream of air to pass from opening *D* and groove *B* across the wires in grooves *G* and *F* to groove *A* and out through opening *C*, the two copper blocks are separated at all points around the outside edge by a layer of aluminum foil, 0.4 mm. thick. The blocks and foil are made air-tight by shellac and held together by machine screws at various points. An end cross section of the blocks, separated, is shown in the lower part of

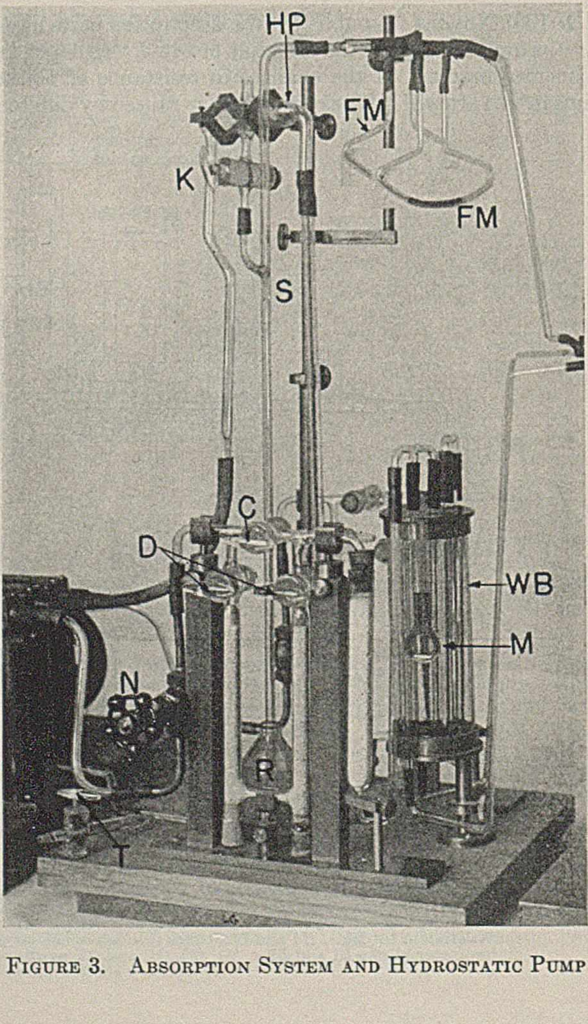


Figure 3. Absorption System and Hydrostatic Pump

Figure 4. Two sets of such blocks are placed together, back to back, and form the two arms of the Wheatstone bridge. This is placed in a thermostat, a copper box of double walls forming a case of about 1400 cc., which is filled with water. As the thermostat can be maintained at constant temperature, the Wheatstone bridge is protected against external thermic influences.

A diagram of the electric circuits for the Wheatstone bridge system is shown in Figure 6.

The two arms of the bridge, *A* and *B* (the resistance of one side of which is changed by the gas of unknown composition), contain the platinum wires, 19.5 cm. in length and 0.02 mm. in diameter, and each arm has a resistance of 120 ohms. The other two arms, *C* and *D*, are fixed resistances, each of 200 ohms. Final adjustment of the bridge is made by a small (0.1-ohm) slide-wire rheostat, *E*. At *F* there are three 6-volt storage batteries connected in series, at *H* there is a resistance box for regulating the amperage, and at *J* a Weston standard, portable milliammeter, Model 1, having a range of 1500 milliamperes and 150 scale divisions.

The galvanometer, *G*, is a Moll type made by Kipp, sensitive to 1.22×10^{-6} volt, and it gives a deflection of 1 mm. (equivalent to 5.7×10^{-9} ampere) at 1 meter scale distance. *LM* is a double-pole, double-throw, vacuum mercury switch which is used when the air currents through the two sets of absorbers are reversed. The full width of the galvanometer scale, which is 50 cm. in length, may thus be used with the zero setting at the same end in both sets of readings. The distance from the galvanometer mirror to the scale is 440 cm. The shunt used with the galvanometer is 40.1 ohms for oxygen and 3.9 ohms for carbon dioxide.

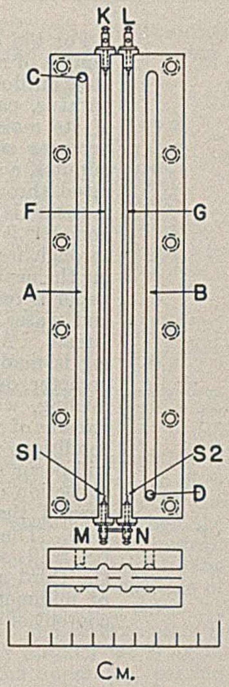


FIGURE 4. CROSS SECTION OF DIAFEROMETER

D and *C*, openings for entrance and exit of air by grooves *B* and *A* and *G* and *F*. *K*, *L*, *M*, and *N*, terminals to which platinum wires in *G* and *F* are fastened. *S1* and *S2*, springs to prevent wires from sagging.

A drawing of the pump, three of which are in the arrangement, is shown in Figure 7. This pump operates on the eccentric principle, driving a plunger which regularly closes a soft piece of rubber tubing.

The rubber tubing, *RT*, is shown in the upper part of the drawing connected to the ingoing valve, *V1*, and the outgoing valve, *V2*. These valves alternately close and open as the piston plunger, *P*, presses up against the rubber tubing. The valves are simple cylinders with lightly movable flaps placed on the ends, which are cut off at an angle. In the lower part of Figure 7 the pump is shown without the rubber tubing. The pump is driven by a 0.125-horsepower motor, with a 9-cm. pulley attached to the shaft of the pump and a 4-cm. pulley attached to the motor. The speed of the motor is cut down by resistance to about 600 revolutions per minute.

Standardization of the Apparatus

After the apparatus was constructed, the first problem was its standardization, to determine the deflection of the galvanometer per definite unit of carbon dioxide and of oxygen deficit in the gas passing through the system.

To determine the deflection for carbon dioxide, expired air diluted with atmospheric air was passed through one side of the system without absorption of the carbon dioxide, and on the other side the carbon dioxide was removed from it. This caused a deflection of the galvanometer, and from the number of millimeters' deflection and the known percentage of carbon dioxide in the air sample (as determined by the Carpenter gas-analysis apparatus), the percentage of carbon dioxide per millimeter deflection of the galvanometer could be calculated. The apparatus is so sensitive (a 500-mm. deflection on the galvanometer scale corresponds to a change in resistance of 0.012 ohm) that its sensitivity had to be cut down by shunting the galvanometer, in order to have a readable length of deflection of the galvanometer for the amount of carbon dioxide ordinarily occurring in respiration chamber air.

The standardization for the oxygen value was made by passing atmospheric air through potassium pyrogallate to remove a portion of its oxygen content and then collecting it in a gasometer. Through one side of the apparatus atmospheric air, freed from carbon dioxide, was passed and through the other side the air from the gasometer, freed from carbon dioxide. This gave a difference in the composition of the air in the two sides of the apparatus with respect to the oxygen content, and from the deflection of the galvanometer it was possible to standardize the apparatus for the oxygen measurement. In all these standardizations a comparison of the composition of the gases was made by the Carpenter gas-analysis apparatus.

A large number of standardizations were made, particularly of the value for oxygen per millimeter deflection of the galvanometer. It was necessary, first, to determine the regularity of these values, for it was evident that if the value changed with time, the apparatus would not be serviceable. In the course of these standardizations the authors tried on two occasions a mixture of carbon dioxide, oxygen, and nitrogen made from compressed gases in cylinders. However, this was found unsatisfactory, because apparently in making the mixture of these gases some one of the rare gases, which have a high cooling power, was increased in amount above that which would occur in normal atmospheric air.

Alcohol Control Tests

After the apparatus was once standardized for carbon dioxide and oxygen with diluted expired air, the next logical step, according to the experience in the Nutrition Laboratory, was to determine whether the values for carbon dioxide con-

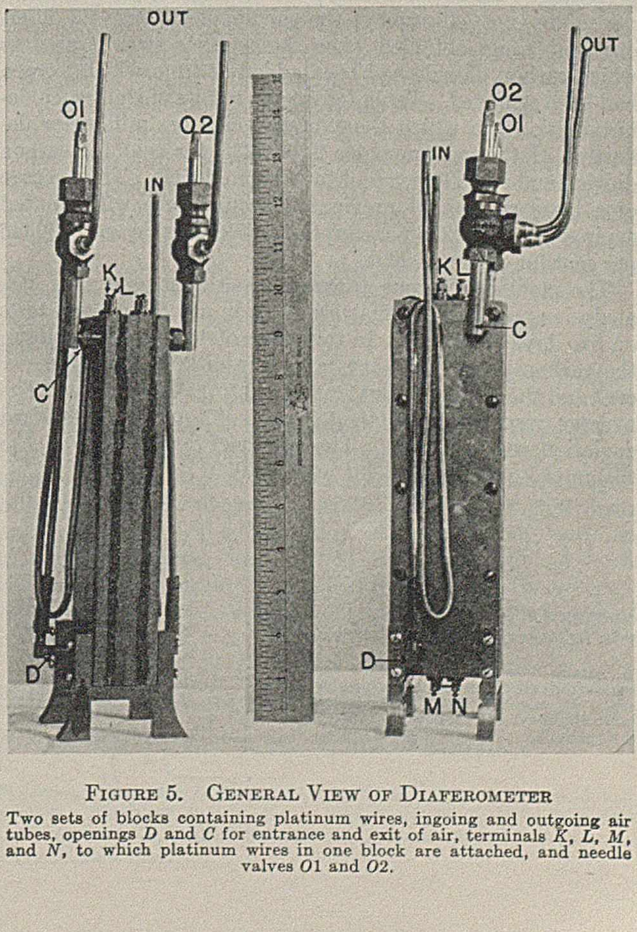


FIGURE 5. GENERAL VIEW OF DIAFEROMETER

Two sets of blocks containing platinum wires, ingoing and outgoing air tubes, openings *D* and *C* for entrance and exit of air, terminals *K*, *L*, *M*, and *N*, to which platinum wires in one block are attached, and needle valves *O1* and *O2*.

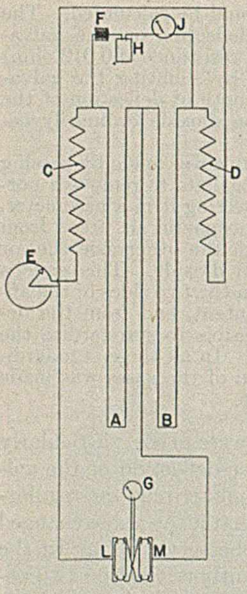


Figure 6. Diagram of Electric Circuit for Wheatstone Bridge System

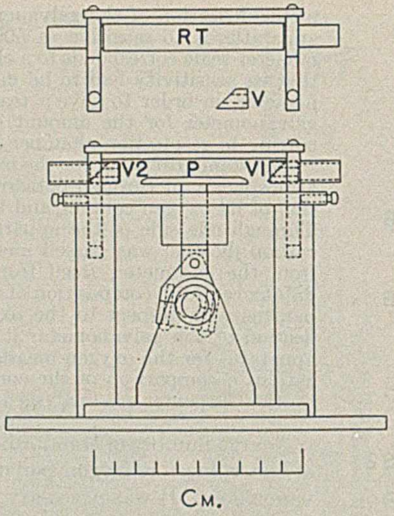


Figure 7. Pump for Aspiration of Air through Apparatus

tent and oxygen deficit per millimeter deflection of the galvanometer would be the same if ethyl alcohol were burned in a stream of atmospheric air. For this purpose the usual arrangement of apparatus was used (Figure 8), in which air passed over an alcohol lamp containing a small flame. At first, comparisons were made of the Carpenter gas-analysis apparatus and the modified Noyons apparatus to make sure that there was not present any gas, either unburned or foreign, which would contaminate the mixture so that it could not be read with the modified Noyons apparatus. In these tests the percentage values for carbon dioxide content and oxygen deficit per millimeter deflection of the galvanometer were no different from those obtained when atmospheric air was used to which carbon dioxide had been added or from which oxygen had been removed. Table I gives the results of eight such determinations, in which the average value per millimeter deflection of the galvanometer is 0.00238 per cent for carbon dioxide and 0.00336 per cent for oxygen deficit. The average of a large number of previous determinations with diluted expired air is 0.00238 per cent for carbon dioxide and 0.00335 per cent for oxygen deficit.

The modified Noyons apparatus was then used as a gas-analysis apparatus for analysis of air in alcohol control tests on five days (Table II). In this series of 46 consecutive tests, the carbon dioxide content ranged from 0.591 to 0.848 per cent and the oxygen deficit from 0.843 to 1.299 per cent. The average respiratory quotient was 0.662 and the standard deviation was ±0.0084. The standard deviation from the theoretical quotient of 0.667 was ±0.0097.

Procedure

For the determination of the carbon dioxide in a sample of respiratory chamber air, the first step is to have outdoor air flow through both sides of the apparatus, passing through the Dehydrite for removal of its moisture content. When the galvanometer becomes steady, which usually requires about 30 minutes, a sample of respiratory chamber air is aspirated through both sides of the apparatus, and its moisture is also removed. The position of the galvanometer is read after the sample has been flowing through for 4 minutes (reading 1, Table III). During the next 3 minutes carbon dioxide as well as water vapor is removed from one of the two streams of air and water vapor alone is removed from the other stream. At the end of these 3 minutes a second reading is made, to show the magnitude of the galvanometer deflection. Immediately after this second reading, water vapor alone is removed from both streams of air. At the end of 1.5 minutes under these conditions the largest deflection of the galvanometer will occur and should be recorded (reading 3). The deflection of the galvanometer will then move back toward the initial position and in 2.5 minutes will stop. The position of the galvanometer should then be read again (No. 4). The difference between the third and the fourth reading indicates, in terms of millimeters' deflection of the galvanometer, the content of carbon dioxide in the air sample.

Table I. Constants of Modified Noyons Apparatus

(Obtained by comparison of volumetric gas analysis with diaferometer readings in alcohol control tests)

	Galvanometer Reading		Volumetric Gas Analysis		Value per Mm. Deflection	
Date, 1941	CO_2	O_2 deficit	CO_2	O_2 deficit	CO_2	O_2 deficit
	Mm.	*Mm.*	%	%	%	%
June 10	375	311	0.891	1.041	0.00238	0.00335
June 10	378	312	0.899	1.044	0.00238	0.00335
June 11	378	315	0.902	1.055	0.00239	0.00335
June 11	386	309	0.918	1.035	0.00238	0.00335
June 16	354	290	0.840	0.971	0.00237	0.00335
June 18	343	284	0.803	0.950	0.00234	0.00334
June 19	376	309	0.893	1.040	0.00238	0.00337
June 19	355	288	0.853	0.981	0.00240	0.00341
				Av.	0.00238	0.00336

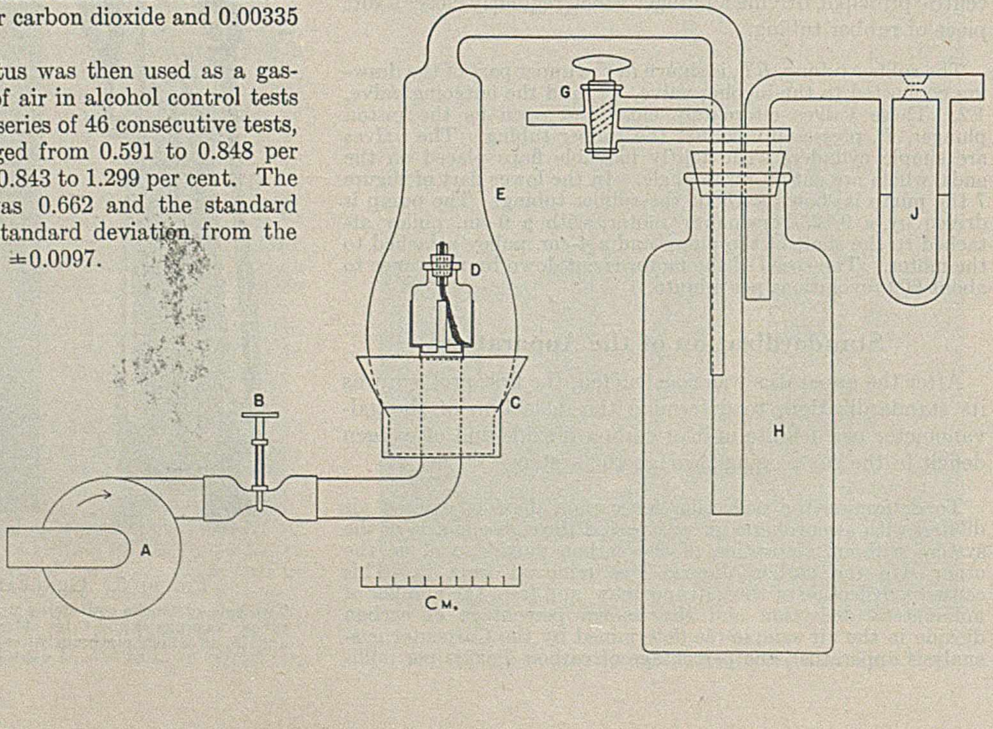


Figure 8. Arrangement for Alcohol Control Tests

A, rotary blower. *B*, pinchcock for regulating rate of flow of air. *C*, water seal. *D*, alcohol lamp. *E*, Pyrex lamp chimney. *G*, stopcock for drawing sample. *H*, mixing chamber. *J*, flowmeter.

Table II. Respiratory Quotients (CO_2/O_2) of Burning Ethyl Alcohol Obtained with Modified Noyons Diaferometer

(June–July, 1941)

June 25	June 26	June 30	July 1	July 2
0.638	0.654	0.649	0.677	0.659
0.657	0.667	0.653	0.664	0.663
0.649	0.664	0.657	0.677	0.661
0.657	0.668	0.657	0.657	0.668
0.662	0.663	0.660	0.683	0.657
0.666	0.661	0.662	0.661	0.664
0.673	0.646	0.659	0.670	0.668
0.672	0.668	...	0.657	0.655
...	0.655	...	0.675	...
...	0.664	...	0.668	...
...	0.664	...	0.668	...
...	...	...	0.667	...
Av. 0.659	0.661	0.657	0.669	0.662

For the determination of the oxygen deficit in a sample of respiratory chamber air, outdoor air is also allowed to flow through both sides of the apparatus, but in this case both the carbon dioxide and the water vapor are absorbed. When the galvanometer becomes steady (usually in about 30 minutes), the position of the galvanometer is read. Then for 4 minutes the sample of respiratory chamber air is passed through one side of the system, while outdoor air passes through the other side. At the end of the 4 minutes, the deflection of the galvanometer is read (reading 2). Immediately thereafter outdoor air is again allowed to flow through both sides of the apparatus, passing through both absorption systems. At the end of 2 minutes the largest deflection of the galvanometer will occur and should be recorded (reading 3). The deflection of the galvanometer will then move back towards the initial position and in 4 minutes will stop. The position of the galvanometer should then again be read (reading 4). The difference between the third and fourth readings represents the difference between the content of oxygen in the sample of respiratory chamber air (carbon dioxide–free) and the content of oxygen in carbon dioxide–free outdoor air, this difference being expressed in terms of millimeters' deflection of the galvanometer.

The initial reading of the galvanometer, both for the carbon dioxide and for the oxygen determination, is made only to see that the galvanometer is steady. The preliminary 30-minute period at the start, when the apparatus is brought into equilibrium, is necessary only at the beginning of a series of analyses on any one day and need not be repeated before each analysis in the series.

Table III. Analysis of a Prepared Sample of Diluted Expired Air Made with Diaferometer, June 17, 1941

Diaferometer Determinations

Reading No.	Carbon Dioxide			Oxygen		
		Galvanometer Deflection Total	Galvanometer Deflection Difference		Galvanometer Deflection Total	Galvanometer Deflection Difference
	Min.	*Mm.*	*Mm.*	*Min.*	*Mm.*	*Mm.*
Left side						
1	0	440		0	420	
2	3	205		4	311	
3	4.5	204		6	300	
4	7	439	235	10	424	124
Right side						
1	0	388		0	378	
2	3	158		4	280	
3	4	155		6	246	
4	7	388	233	10	370	124
		Av.	234			124

Standardization by Comparison with Volumetric Gas Analysis, Gas Analysis of Air Sample

	Reading	Difference	H_2O	True Reading
Vol.	99.925	....	0.204	99.721
CO_2	99.370	0.555	...	....
O_2	79.012	20.358	...	....
H_2O	78.808	0.204	...	....

CO_2 in 100 volumes of air sample (0.555 ÷ 99.721)	0.557
O_2 in CO_2-free outdoor air [20.940 ÷ (100 − 0.03)]	20.946
O_2 in CO_2-free air sample [20.358 ÷ (99.721 − 0.555)]	20.529
O_2 deficit (20.946 − 20.529)	0.417
CO_2 per 1-mm. galvanometer deflection (0.557 ÷ 234), %	0.00238
O_2 deficit per 1-mm. galvanometer deflection (0.417 ÷ 124), %	0.00336

Theoretically, the third reading of the galvanometer deflection (in the carbon dioxide and oxygen determinations) should be made under the same conditions as the second reading as regards the composition of the air streams passing through the two sides of the diaferometer. The interval of time between these two readings is so short, however, that actually the respective compositions of the air streams in *L*1 and *L*2 (Figure 1) at the time of the third reading are still the same as at the time of the second reading. The total time required for an analysis can, therefore, be shortened by making the described changes in the air streams at the end of the second reading instead of waiting until the end of the third reading. The second reading is not absolutely necessary but is desirable as a check on the third.

Usually there is a difference of about 2 to 3 mm. between the initial reading and the fourth reading. The total time required for the analysis of an air sample for both carbon dioxide and oxygen is approximately 17 minutes, and the total volume of sample required for the complete analysis is 1 liter.

Precautions in Use of Apparatus

The strength of the electric current passing through the diaferometer should be checked frequently, to make sure that it has remained unchanged.

The manometers showing the rates of flow of the sampling streams that pass through the diaferometer should be checked frequently, as otherwise incorrect readings will be obtained.

It is necessary to have clean water in the hydrostatic pump, in order for the aspiration of air to be uniform.

A check on the completeness of absorption of either carbon dioxide or water vapor or both can be obtained by reversing the currents of air and at the same time reversing the galvanometer. The same reading should be obtained for carbon dioxide and similarly for oxygen, irrespective of whether the right or the left side of the apparatus is used (Table III).

After the apparatus has been thoroughly standardized by comparison with volumetric gas analysis, it is no longer necessary to standardize it in this way, but alcohol control tests made regularly will demonstrate the accuracy of functioning of the apparatus, provided the ratio of carbon dioxide increase to oxygen deficit in the burning of alcohol is within 0.01 of the theoretical ratio of 0.667. If the apparatus gives this ratio, neither the value for carbon dioxide nor that for oxygen deficit has been changed.

The apparatus is designed primarily for analysis of respiratory chamber air. It could be adapted for analysis of expired air, if the shunts in the galvanometer system were changed to decrease the sensitivity or if the reading scale were brought closer to the galvanometer. It cannot be used for the analysis of gases from any respiratory system in which foreign gases are present that do not exist in atmospheric air, such as methane, hydrogen, and carbon monoxide. When such respiratory systems are used, these foreign gases must be removed from the air samples before analysis with the modified Noyons apparatus.

Literature Cited

(1) Noyons, A. K. M., *Ann. physiol.*, 13, 909 (1937).

Presented before the Divisions of Agricultural and Food, Biological, and Medicinal Chemistry, Symposium on New Analytical Tools for Biological and Food Research, at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J.

Pressure Regulating and Indicating Apparatus for Vacuum Systems

BASSETT FERGUSON, JR., Ugite Sales Corporation, Chester, Penna.

FOR many laboratory vacuum systems the automatically controlled air leak is the simplest and most satisfactory method of pressure control. Figure 1 illustrates such an apparatus which has been evolved to eliminate many of the objections to earlier designs of this type of control. This device has proved to be inexpensive, easy to operate and maintain, and capable of an accuracy of ±0.2 mm. for pressures of 5 to 760 mm.

With the apparatus set up as shown, stopcock *C* is opened, switch *M* is closed, and mercury is admitted through valve *D* (by means of a leveling bottle) until the mercury just makes contact at *E*, closing the electrical circuit. *D* is then closed and *M* is opened. The system is evacuated to the desired pressure at which point *C* and *M* are closed. Bulb *A* maintains the desired pressure and as the vacuum source tends to decrease the system pressure the mercury will rise in the right-hand arm of the U-tube, making contact at *E* and activating electromagnet *G*, thus opening capillary leak *H*.

The capacity of bulb *B* and the resistance offered by capillary *N* cushion the effect of this leak on the mercury, and capillary *I* prevents setting up a harmonic surging of the mercury. When sufficient air has entered *H* to increase the system pressure to that of *A*, the contact at *E* is broken and the spring flap on *G* closes *H*.

A needle valve in the line to the vacuum source may be used to adjust the frequency of this cycle; six to twelve cycles per minute are satisfactory. When increasing system pressure, or when bringing it to atmospheric pressure after use, it is customary to open stopcock *C*. If this is neglected, however, the mercury is forced into bulb *A* as the pressure is equalized, but it then falls back into position in the tube without further adjustment.

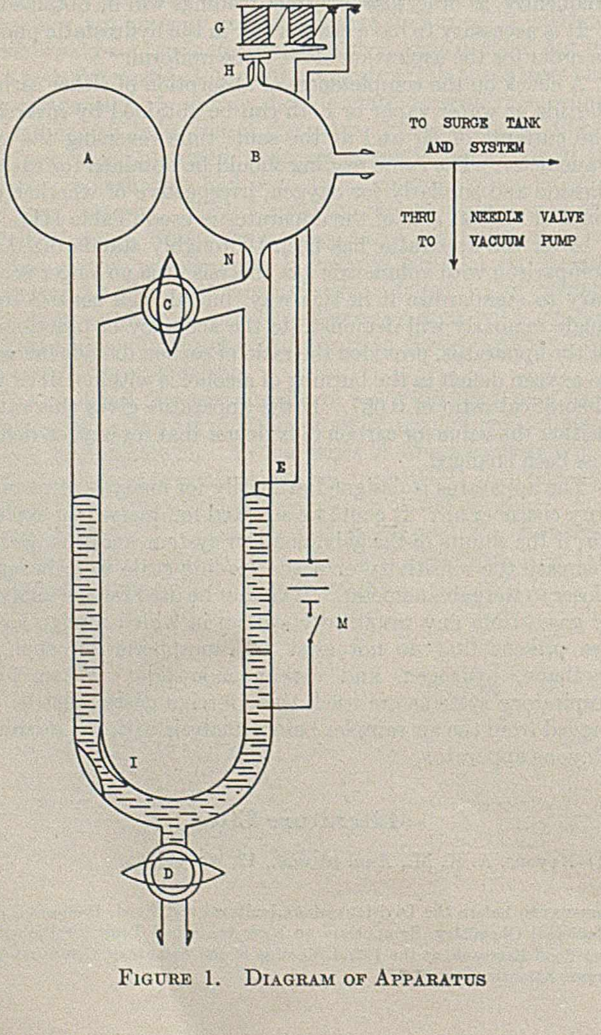


FIGURE 1. DIAGRAM OF APPARATUS

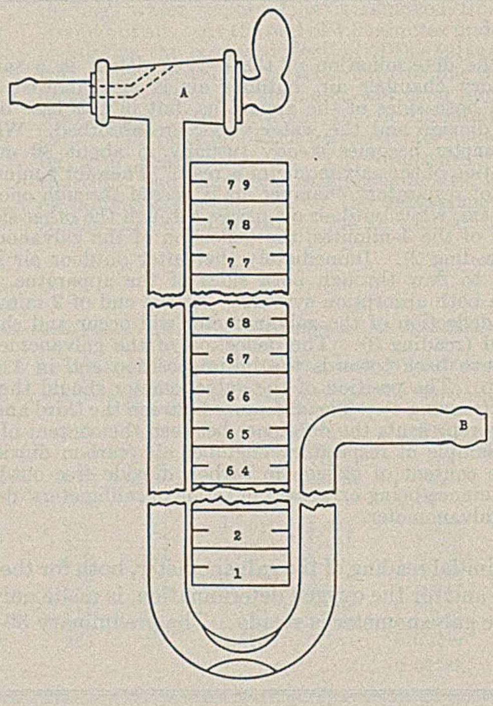


FIGURE 2. CLOSED-END MANOMETER

Oxidation of the mercury by the sparking at *E* may be decreased by floating a small quantity of oil on the mercury. White Russian mineral oil may be used after shaking with mercury to remove sulfides and filtering. The U-tube may be cleaned readily by draining the mercury from stopcock *D* and rinsing, by use of a leveling bottle, with dilute nitric acid, water, and acetone successively.

The glassware is furnished to Ugite Sales Corporation specification by Ace Glass, Inc., Vineland, N. J. The electromagnet is an ordinary twin-coil buzzer, obtainable at any electrical supply shop. It is then wired directly to the coils instead of through the make-and-break buzzer as furnished. Dry cells or a direct current source is used. The device may be mounted on a board for convenience in handling.

A closed-end manometer has several advantages over the open-end type for use in vacuum systems. It is independent of atmospheric pressure and obviates the necessity for continual barometric readings and corrections. It is read more easily and accurately, since under increasing vacuum its legs approach a common height, while the reverse is true of the open-end type.

The disadvantages of the closed-end manometer are mainly the difficulties encountered in filling the manometer properly, and in removing the mercury and cleaning the manometer.

Figure 2 illustrates a design for a closed-end manometer which overcomes these troubles. Stopcock *A* may be opened and after sufficient mercury has been admitted through *B*, *A* is attached to a source of vacuum, exhausting the air above the mercury in the left-hand column. The closed arm of the manometer may be heated with a Bunsen burner to drive off air adsorbed to the surface of the glass and dispersed in the mercury. Now a slight air pressure is applied at *B*, forcing the mercury up into stopcock *A*. When the left-hand column is completely filled with mercury, *A* is closed. The manometer may be checked against the barometer to determine the success of the filling operation. It should agree with the barometer within 1 mm. at 760 mm., which amounts to a much smaller error at reduced pressure—(e. g., 0.05 mm. at 40 mm.).

For cleaning, the entire plug of stopcock *A* is removed, and dilute nitric acid, water, and acetone, consecutively, are circulated through the tube.

A constriction at the bottom of the tube cushions pressure changes. A sliding wooden scale may be used to simplify reading the differential heights of the two columns. This glassware is made to Ugite Sales Corporation specifications by Ace Glass, Inc., Vineland, N. J.

Continuous Washing Apparatus for Solutions in Organic Solvents

A. L. LeROSEN, California Institute of Technology, Pasadena, Calif.

OFTEN it is necessary to wash petroleum ether, benzene, chloroform, etc., solutions free from a water-soluble solvent, alkali, or acid. If many solutions must be washed the operations are tedious and time-consuming, but these difficulties may be eliminated by the device shown in Figure 1. A constant air space is maintained in a separatory funnel while a stream of water is passed through the solvent.

To operate, water is added to the solvent mixture. After this first wash water is drained off as usual, the washing tube is inserted with pinchclamp open. The water is then turned on at a suitable rate and when the upper layer has reached the washing tube outlet, the pinchclamp is closed and the stopcock is opened. The closed air space maintains a constant level, so that the quantities of water entering and leaving are always equal. This washing is continued as long as necessary—e. g., 5 to 10 minutes for ligroin plus alcohol in a 500-cc. funnel. Then the bottom stopcock is closed, the pinchclamp is opened, the washing tube is rinsed with some pure solvent, and the water stream is stopped. This procedure has given satisfactory results with volumes of solvent from a few cubic centimeters up to 8 liters. The setup used in this laboratory, a series of 8 units, is shown in Figure 3.

For liquids heavier than water the washing tube is slightly modified (Figure 2) and reaches near the bottom of the separatory funnel. The water flows out at the top through a glass tube. The stopcock remains closed until the washed solvent is drawn off. No air pocket is present in this case.

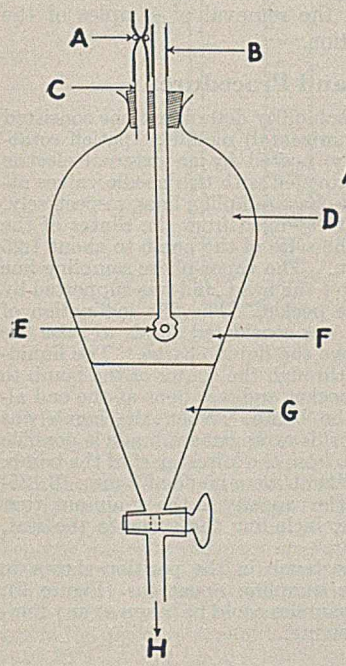


FIGURE 1 (*Left*). WASHING APPARATUS
A pinchclamp, *B* water inlet, *C* air adjustment tube, *D* constant air space, *E* washing tube outlet, *F* solution, *G* water, *H* outlet to drain

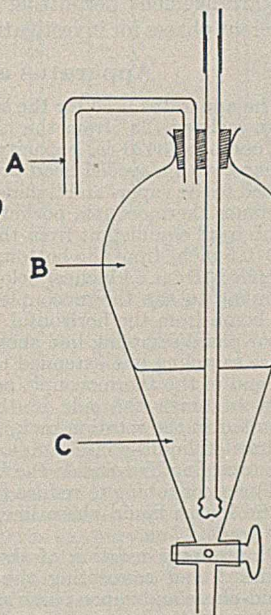


FIGURE 2 (*Right*). MODIFIED APPARATUS
A water outlet, *B* water, *C* solution

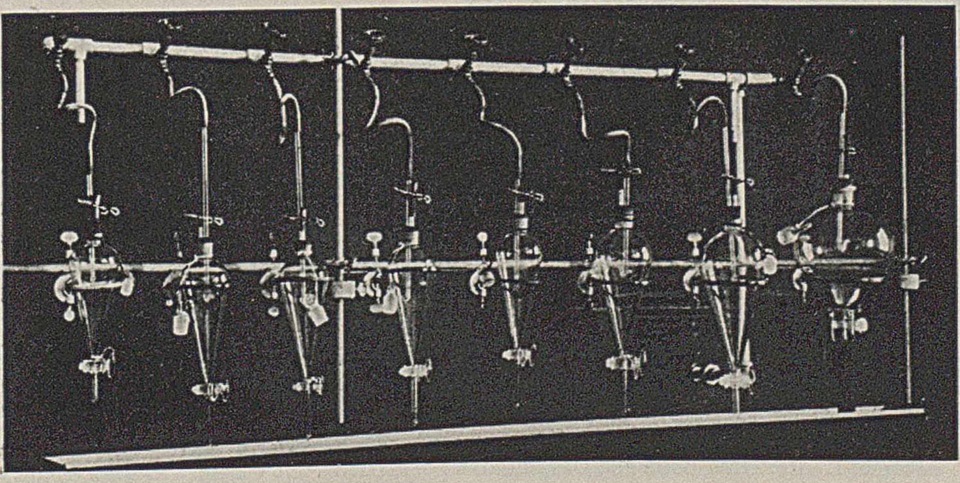


FIGURE 3

GATES and Crellin Laboratories of Chemistry, California Institute of Technology, Contribution 849.

Determination of Solubilities of Gases at High Temperatures and High Pressures by the Rotating Bomb

V. N. IPATIEFF AND G. S. MONROE, Universal Oil Products Co., Riverside, Ill.

VERY little information can be found in the literature concerning the solubility of gases in liquids at high temperatures and high pressures.

The first work in this direction was carried out by V. V. Ipatieff, Jr., in 1930 when he employed the rotating bomb for this purpose (*1*, *2*). (This preliminary investigation was made in June, 1930, in the Institute of High Pressures, Leningrad. It was mentioned by V. N. Ipatieff at the meeting of the Scientific Technical Department before his departure from Russia.)

Since the literature contains data about the solubility of methane in some hydrocarbons at temperatures not higher than about 100° C., the authors decided to make experiments to determine the solubility of the gas in benzene over a temperature range approaching the critical.

For this purpose it was necessary to modify the rotating bomb, adding sampling lines by means of which either liquid-phase or vapor-phase samples could be taken. This change made it possible not only to determine solubilities but also to establish phase conditions within the bomb in the determination of the critical temperatures of individual substances and two-component systems to be described in a later paper.

The apparatus can be improved for the more accurate measurement of temperature and pressure. The authors recommend this type of apparatus not only for the determination of solubilities at high temperatures and high pressures but also for the study of reactions involving heterogeneous systems, the arrangement permitting the removal of samples of the different phases for investigation.

Apparatus and Procedure

The apparatus used for the solubility determinations consisted of an inclined (28° from the horizontal) modified Ipatieff rotating bomb of 3420-cc. capacity, heated by an external electric furnace, with a special head provided with two needle valves attached to the vapor- and liquid-phase sampling lines, respectively. An inner thermocouple pocket extended from the center of the bomb head equidistant from the sides of the bomb to about 1.25 cm. (0.5 inch) from the bottom. The vapor-phase sampling line extended 10 cm. (4 inches) below the head, and was supported by clamping to the thermocouple pocket. The 28° inclination of the bomb from the horizontal was considered ample to raise the vapor-phase sampling line above the liquid charge. The liquid-phase sampling line extended through the center of the bomb to the end of the thermocouple pocket and was bent at the end almost to touch the side of the bomb. When the bomb was mounted in the rotation rack, this arrangement made it possible to draw off liquid-phase sample from the lowest part of the bomb. The sampling lines inside the bomb were made of 3-mm. (0.125-inch) copper tubing to reduce the capacity to the minimum, that of the longer liquid-phase line, including the valve to the seat, being only 1.7 cc.

On stopping rotation of the bomb in the position shown in Figure 1 and connecting the sampling apparatus (Figure 2), liquid-phase and vapor-phase samples could be taken at any temperature and corresponding pressure.

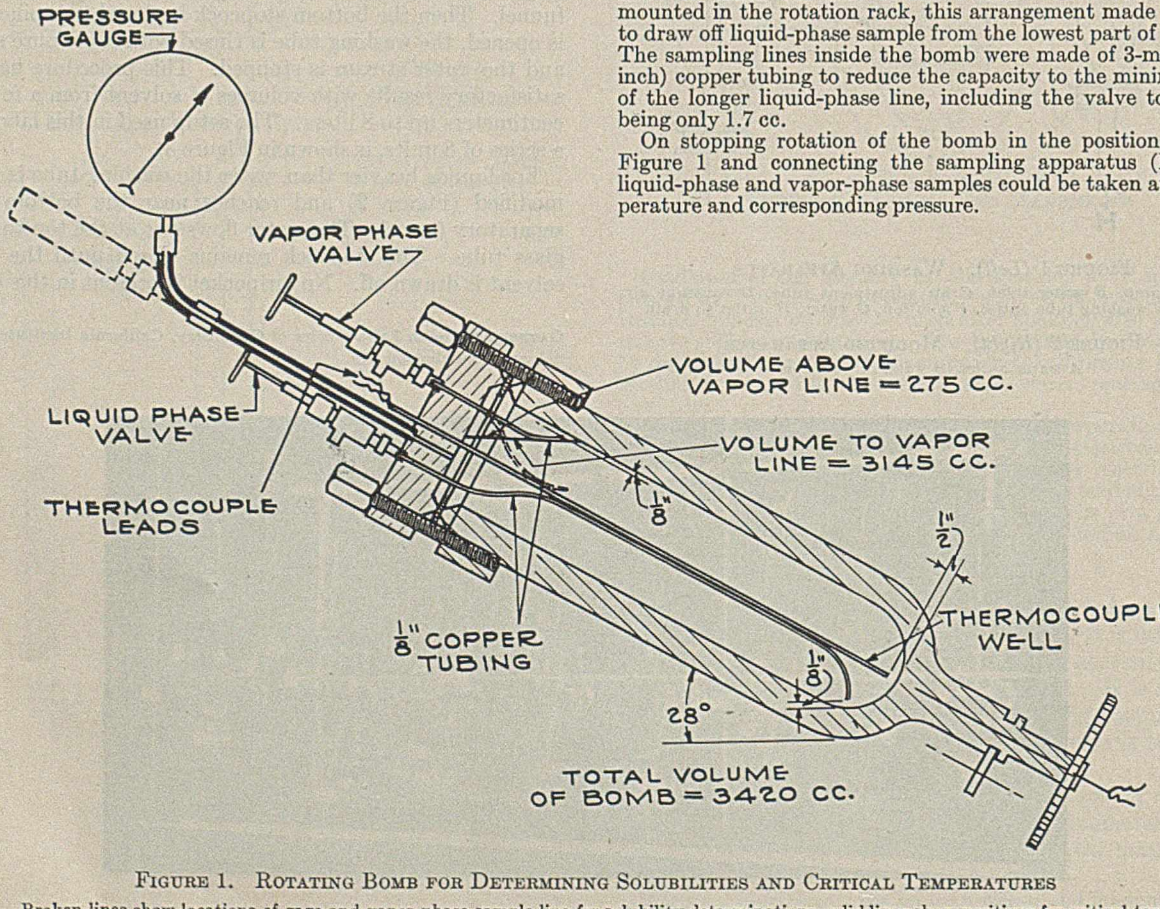


FIGURE 1. ROTATING BOMB FOR DETERMINING SOLUBILITIES AND CRITICAL TEMPERATURES

Broken lines show locations of gage and vapor-phase sample line for solubility determinations, solid lines show positions for critical temperature determinations.

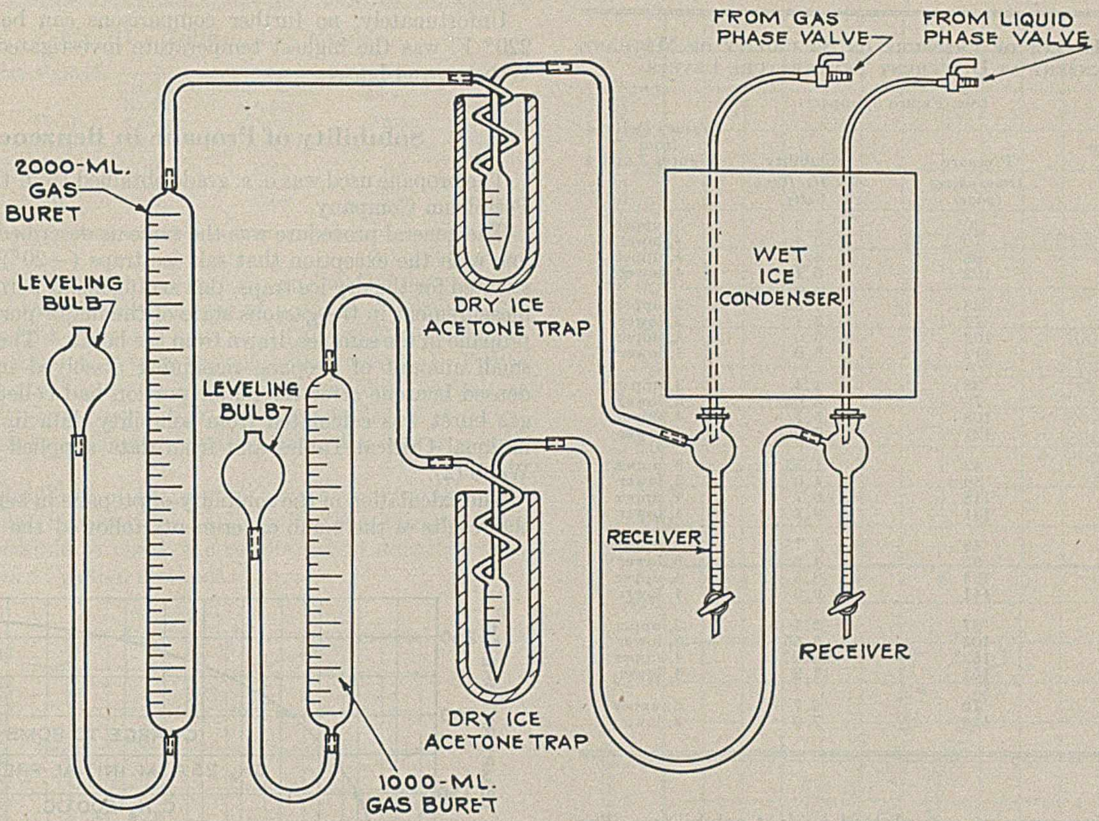


Figure 2. Sampling Apparatus for Determining Solubilities

The sampling device used for both liquid-phase and vapor-phase samples consisted of a wet ice condenser with a calibrated receiver (10-cc. capacity) which condensed most of the benzene from the methane. The outlet of the receiver led to a graduated dry ice trap (10-cc. capacity) to condense any benzene escaping previous condensation. The methane thus stripped free from benzene was collected over salt water in gas burets of 1000-cc. and 2000-cc. capacity for the liquid-phase and vapor-phase samples, respectively. After sampling, the cooling baths were removed from the traps and the contents of the same, together with the gas in the gas burets, allowed to reach room temperature equilibrium by standing 1.5 to 2 hours before reading the volumes.

The purges were made with a similar but smaller apparatus consisting of a wet ice trap connecting to a gas buret of about 500-cc. capacity.

Procedure for Solubility Determinations. The solubility bomb was evacuated to high vacuum and the benzene (1200 to 1500 cc.) was charged from a graduated cylinder by suction. Methane was then charged into the bomb to the desired pressure (25, 50, 75, and 80 atmospheres, initial in the experiments described). The bomb was placed in the rotation rack and heated to the desired temperature level. After rotation for 0.5 hour, which was considered sufficient to establish equilibrium, the sampling lines were purged, about 50 cc. of gas being taken from the vapor-phase line and a sufficient amount of sample taken from the liquid-phase line to give about 1.7 cc. of condensate, which was the capacity of the liquid-phase sampling line. The bomb was again rotated for a few minutes to ascertain whether the temperature of the bomb had changed during the purging operation.

The liquid-phase and vapor-phase samples required for the solubility determinations were then taken, about 7 to 9 cc. of benzene condensate for the liquid-phase sample and about 700 to 1000 cc. of gas for the vapor-phase sample. From the data thus obtained the composition of the vapor and liquid phases could be calculated and the solubility of methane in benzene determined from the composition of the liquid phase. The solubility of the methane in the benzene separating in the traps was ignored, since according to the Bunsen absorption coefficient the amount dissolved would be less than experimental error. It was necessary to determine the composition of the sample from the vapor-phase sample cock as well as that from the liquid-phase cock in order to establish the existence of a one-phase or two-phase condition within the bomb.

In making the solubility determinations, because of the relatively large amount of benzene in the bomb, usually 1200 to 1500 cc., compared with the small amount drawn from the bomb during the sampling operation, it was not necessary to charge the bomb for each determination. The bomb was discharged, cleaned, and recharged only when a change in the initial pressure was made.

Solubility determinations were made for each pressure level (25, 50, 75, and 80 atmospheres initial) at various temperatures, and the data thus obtained reduced by means of curves to isobars and isotherms as indicated in the tables.

Solubility of Methane in Benzene

The benzene used in these experiments was Baker's c. p., thiophene-free, n_{D}^{20} − 1.5012.

The methane used was obtained from the Carbide and Carbon Chemicals Corporation, Charleston, W. Va., and had the following Goeckel analysis:

Carbon dioxide	0.0
Olefins	0.0
Oxygen	0.0
Carbon monoxide	0.0
Hydrogen	0.0
Nitrogen	4.0
Paraffins	96.0
Index	1.01

In determining the effect of pressure on the solubility of gas in liquid (methane in benzene) the ideal procedure would be to hold the temperature constant when the pressure was varied for isotherm values, or to hold the pressure constant and vary the temperature for isobar determinations.

It is evident that such a procedure cannot be followed when the rotating bomb is used, since pressure and temperature change simultaneously. This condition necessitates recourse to the type of curves in which temperature and the corresponding pressures are plotted against solubility. The effect of pressure change on solubility at various temperature levels or the effect of temperature change on solubility at different pressures can readily be determined from special curves (Figures 3 and 4). The values given in Tables I and II and Figure 5 were obtained in this way.

Sage, Webster, and Lacey (*3*) have plotted the bubble point pressure *vs.* mass per cent methane for 100° to 220° F. isotherms for the methane-benzene system. If we compare these results with the bomb results we see that the agreement for the two methods is good.

Table I. Effect of Pressure on Solubility of Methane in Benzene at Different Temperature Levels

(See Figure 5, upper)

Temperature Level	Pressure	Solubility	Values Derived from Figures 3 and 4
° *C.*	*Atmospheres (gage)*	*G.* CH_4*/100 g.* C_6H_6	
100	30	1.3	3, upper
100	70	3.4	3, lower
100	98	4.8	4, upper
100	102	5.1	4, lower
125	33	1.35	3, upper
125	72	3.4	3, lower
125	102	5.0	4, upper
125	112	6.0	4, lower
150	38	1.4	3, upper
150	79	3.65	3, lower
150	108	5.7	4, upper
150	121	7.0	4, lower
175	42	1.55	3, upper
175	86	4.0	3, lower
175	118	6.7	4, upper
175	131	8.2	4, lower
200	49	1.75	3, upper
200	95	4.6	3, lower
200	133	8.5	4, upper
200	141	9.6	4, lower
225	57	2.1	3, upper
225	103	5.55	3, lower
225	152?	13.2?	4, upper
225	152	11.9	4, lower
250	70	2.7	3, upper
250	116	7.9	3, lower

Table II. Effect of Temperature on Solubility of Methane in Benzene at Different Pressure Levels

(See Figure 5, lower)

Pressure Level	Temperature	Solubility	Values Derived from Figures 3 and 4
Atmospheres (gage)	° *C.*	*G.* CH_4*/100 g.* C_6H_6	
90	...	...	3
90	185	4.2	4
90	...	...	5
90	65	4.0	6
100	...	...	3
100	215	5.1	4
100	120	5.0	5
100	120	4.9	6
110	...	...	3
110	240	6.5	4
110	155	5.9	5
110	122	5.9	6
120	...	...	3
120	252	9.0	4
120	177	6.9	5
120	147	6.9	6
130	...	...	3
130	...	...	4
130	195	8.1	5
130	172	8.1	6
140	...	...	3
140	...	...	4
140	208	9.6	5
140	198	9.5	6

Unfortunately, no further comparisons can be made, as 220° F. was the highest temperature investigated by Sage, Webster, and Lacey.

Solubility of Propane in Benzene

The propane used was c. p. grade obtained from the Phillips Petroleum Company.

The general procedure was the same as described for methane with the exception that salt ice traps (−20°) were substituted for the dry ice traps, this arrangement permitting the measurement in the gaseous state of the major portion of the propane in the samples drawn from the bomb. The relatively small amount of propane remaining dissolved in the condensed benzene after the major portion had collected in the gas buret was calculated from solubility data in the International Critical Tables and from data supplied by G. M. Webb (*4*).

The calculation of the solubility of propane in benzene from the results of the bomb experiments followed the same plan

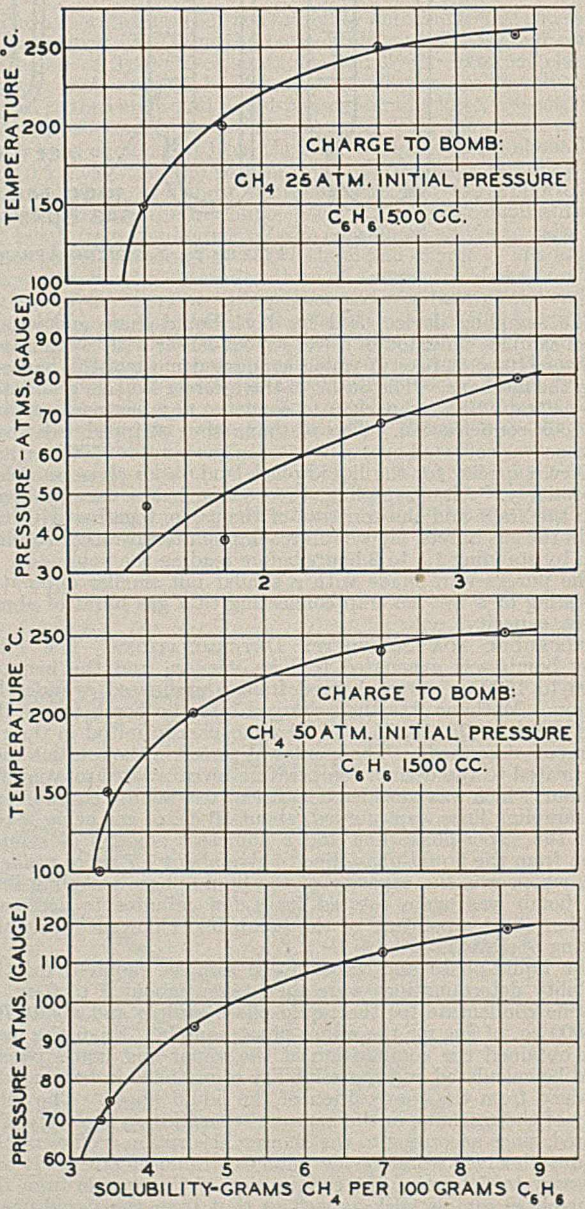


Figure 3. Effect of Pressure and Temperature on Solubility of Methane in Benzene

Table III. Comparative Values

Bomb Method: Total pressure absolute	Bomb Method: Temp.	Bomb Method: CH_4 in liquid phase	Sage, Webster, and Lacey: Bubble point pressure absolute	Sage, Webster, and Lacey: Temp.	Sage, Webster, and Lacey: CH_4
Lb./sq. in.	*° F.*	*Wt. %*	*Lb./sq. in.*	*° F.*	*Wt. %*
1065	216	3.3	1065	220	3.2
1455	217	4.6	1455	220	4.5
1605	216	5.2	1605	220	5.0

as outlined for methane in benzene. In the case, however, of propane only two concentrations of propane in benzene (7.7 and 19.9 weight per cent) were used (Figure 6). This gave only two points for plotting the solubility curves. In Figure 7 the corresponding two points on the solubility curves are joined by straight broken lines. While the degree of curvature is not shown, the general direction of the curves is indicated.

As no solubilities of propane in benzene under high pressures and high temperatures could be found in the literature, it was impossible to check the results herein described with those obtained by other methods.

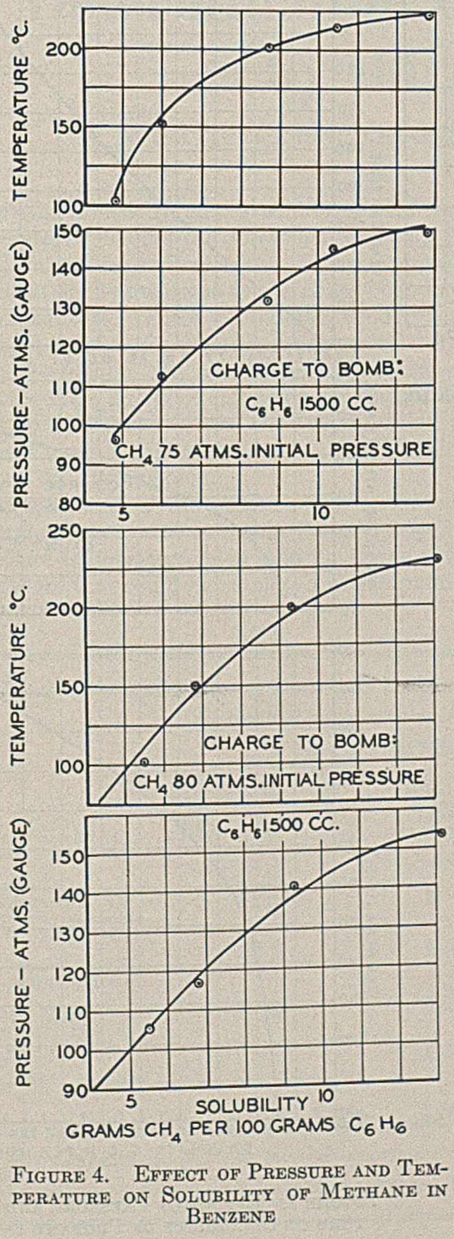


Figure 4. Effect of Pressure and Temperature on Solubility of Methane in Benzene

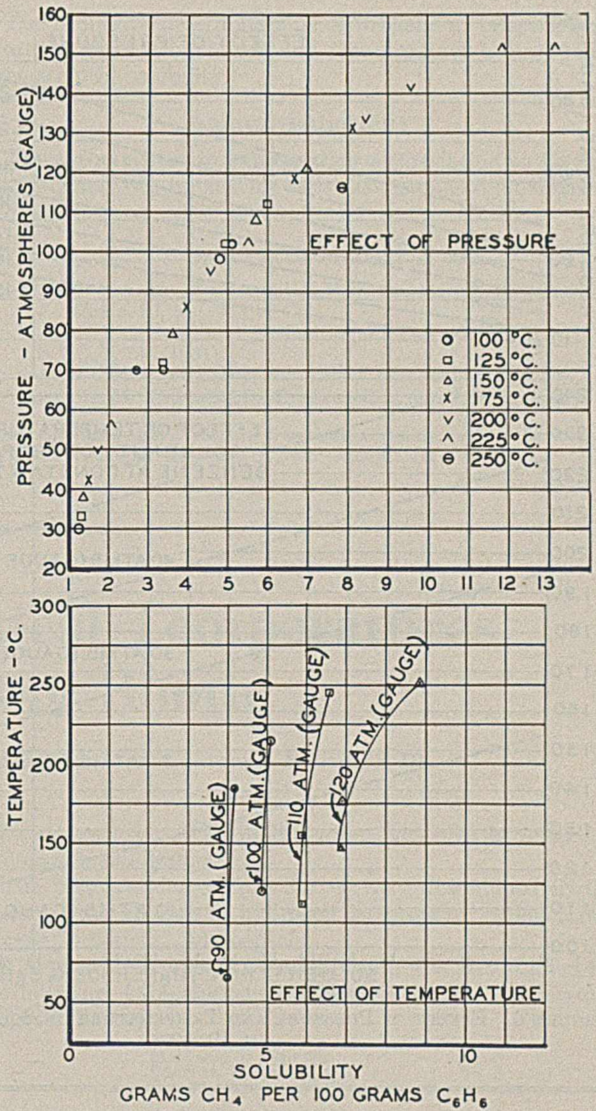


Figure 5. Effect of Pressure and Temperature on Solubility of Methane in Benzene

Solubility of Sulfur Dioxide in Benzene

The procedure for determining the solubility of sulfur dioxide in benzene at 26° C. under pressures from 1.2 to 2.7 atmospheres (absolute) was essentially the same as previously described, the determinations being made with the bomb at

Table IV. Effect of Pressure on Solubility of Propane in Benzene at Different Temperature Levels

Temperature Level	Pressure	Solubility	Values Derived from Figure 7
° C.	*Atmospheres (gage)*	*G. C_3H_8/100 g. C_6H_6*	
150	10.0	7.41	Upper
150	20.0	22.25	Lower
160	12.0	7.54	Upper
160	23.5	22.36	Lower
170	14.5	7.66	Upper
170	27.5	22.50	Lower
180	17.0	7.77	Upper
180	32.0	22.70	Lower
190	20.0	7.87	Upper
190	37.5	22.95	Lower
200	23.0	7.97	Upper
200	42.5	23.24	Lower
210	27.0	8.07	Upper
210	48.0	23.56	Lower

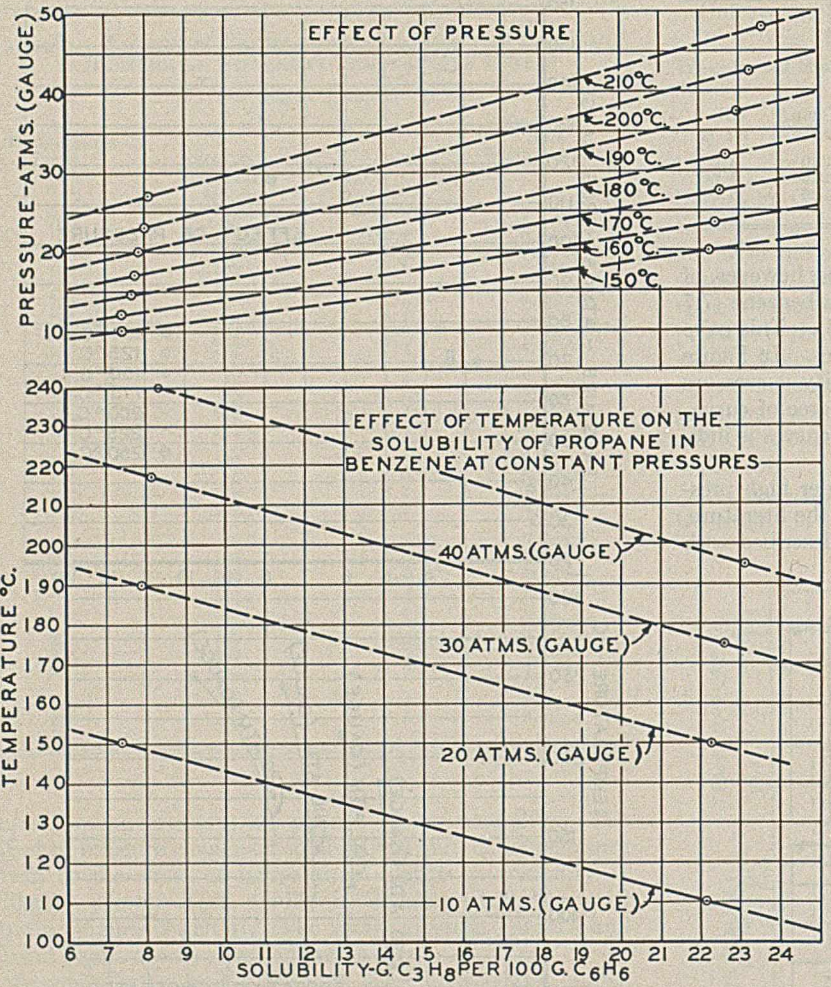


Figure 6. Effect of Pressure and Temperature on Solubility of Propane in Benzene

Table V. Effect of Temperature on Solubility of Propane in Benzene at Different Pressure Levels

Pressure Level	Temperature	Solubility	Values Derived from Figure 7
Atmospheres (gage)	*° C.*	*G. C_3H_8/100 g. C_6H_6*	
10	150	7.41	Upper
10	110	22.12	Lower
20	190	7.88	Upper
20	150	22.26	Lower
30	217	8.13	Upper
30	175	22.60	Lower
40	242	8.32	Upper
40	195	23.08	Lower

room temperature and the sulfur dioxide being added to the bomb until the desired pressure was reached after the benzene had been charged.

The liquid-phase samples were collected in a dry ice–acetone trap provided with a ground-glass joint for attachment to a modified Podbielniak fractionating column. The sulfur dioxide was removed from the sample by fractionation, collecting the evolved sulfur dioxide in a gas buret over mercury. When the vapor had reached 80° C., the distillation was stopped and the apparatus after reaching room temperature was purged with a stream of air to remove any sulfur dioxide remaining in the apparatus. The purge was added to gas previously obtained during the distillation and the amount of sulfur dioxide determined by absorption in potassium hydroxide solution. The residue remaining in the trap after distillation was weighed as benzene.

The results obtained with benzene and sulfur dioxide are given in Table VI.

• • •

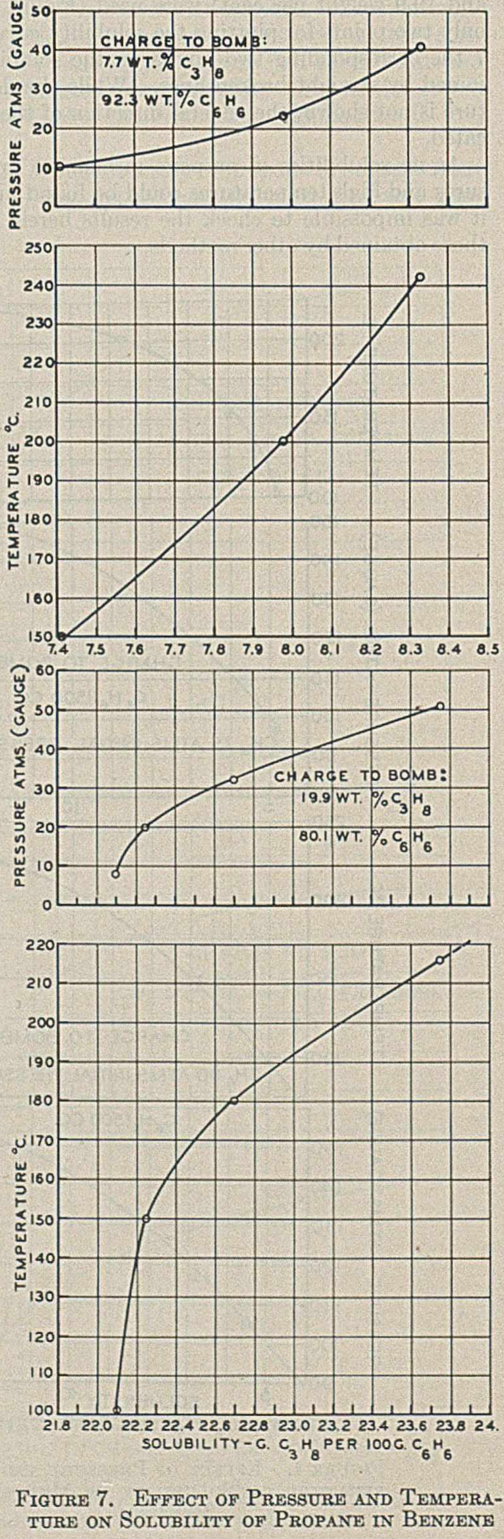


Figure 7. Effect of Pressure and Temperature on Solubility of Propane in Benzene

Table VI. Solubility of Sulfur Dioxide in Benzene

Temperature of Bomb ° C.	Total Pressure *Atmospheres (abs.)*	Solubility *G. SO_2 dioxide/100 g. C_6H_6*
26	1.20	24.7
26	1.75	37.6
27	2.40	84.8
25	2.65	125.5

Conclusions

The results obtained show that the modified rotating bomb can be used to determine the solubility of gases at high pressures and high temperatures approaching the critical.

The method applied to the determination of the solubility of methane in benzene indicates that pressure is the principal factor affecting the solubility. The effect of temperature is minor, becoming more noticeable at higher pressures.

The solubility determinations of propane in benzene indicate that both temperature and pressure have a marked influence on the solubility.

Acknowledgment

The authors wish to express their appreciation to Charles Rohlfing and Lee Fischer for assistance rendered on these experiments.

Literature Cited

(1) Ipatieff, V. V., Jr., Feodorovitch, V. P., and Levine, I. M., *Oil Gas J.*, 32, No. 20, 14 (1933).
(2) Ipatieff, V. V., Jr., and Tichomroff, V. T., *J. Gen. Chem.* (U. S. S. R.), 1, 736 (1931).
(3) Sage, Webster, and Lacey, Ind. Eng. Chem., 28, 1047 (1936).
(4) Webb, G. M., Universal Oil Products Co., unpublished data.

Presented before the Division of Petroleum Chemistry at the 102nd Meeting of the American Chemical Society ,Atlantic City, N. J.

Determination of Critical Temperatures by the Rotating Bomb

V. N. IPATIEFF and G. S. MONROE, Universal Oil Products Company, Riverside, Ill.

THE methods usually employed in determining critical temperatures involve the determination of the pressure-volume relation along various isotherms or the appearance or disappearance of the meniscus at the phase boundary at the critical temperature. These procedures, though capable of giving a high degree of accuracy, require special apparatus and skillful technique. In cases where an accuracy of only ±2° C. is required, a method involving less elaborate apparatus would be desirable. It was with this in mind that the authors developed a method for determining critical temperatures by the rotating bomb.

A study was made of the pressure-temperature curves of various pure substances to ascertain if any change occurred in the pressure-temperature relation in the region of the critical temperature that could be employed in determining critical temperatures. The investigation was also extended to two-component systems.

The pressure-temperature curves were determined in the presence and absence of hydrogen for propane, cyclohexane, hexane "practical", and benzene.

The pressure-temperature relationship was also studied for the following two-component systems over the temperature ranges indicated:

Methane, 27 mole %
Benzene, 73 mole %
Temperature range, 62° to 261° C.

Benzene, 70 mole %
Propane, 30 mole %
Temperature range, 94° to 256° C.

Hexane "practical", 32 weight %
Benzene, 68 weight %
Temperature range, 150° to 288° C.

Table I. Comparison of Points of Discontinuity on Pressure-Temperature Curves of Pure Substances

(Determined by the rotating bomb with critical temperatures obtained from literature)

Substance	Propane	Propane + H_2	Hexane "Practical"	Hexane "Practical" + H_2	Cyclohexane	Cyclohexane + H_2	Benzene			Benzene + H_2		
Amount charged, cc.	2000	2200	1400	1400	1800	1800	700	1300	1500	700	1300	1500
Temperature of break, ° C.	96–98	96–98	226–229	234–239	276–281	277–280	283–290[a]	286–289	285–288.5	288–290.5	288.5–289.5	286–288
Critical temp. (literature), ° C.	96.9	96.9	234.8[b]	234.8[b]	281	281	288.6	288.6	288.6	288.6	288.6	288.6
Test samples:												
Above break temp., ° C.	...	101	...	235	...	283	...	...	...	...	292	294
Liquid-phase sampling cock, cc. liquid/100 cc. gas	...	7.7	...	5.4	...	8.6	...	...	...	...	5.2	6.2
Vapor - phase sampling cock, cc. liquid/100 cc. gas	...	7.8	...	5.5	...	8.7	...	...	...	...	5.1	5.9
Below break temp., ° C.	...	88	...	228	...	270	...	...	...	...	288	282
Liquid - phase sampling cock, cc. liquid/100 cc. gas	...	10.5	...	8.9	...	9.1[c]	...	...	...	...	5.1	8.7
Vapor - phase sampling cock, cc. liquid/100 cc. gas	...	2.2	...	0.5	...	9.2[c]	...	...	...	...	1.4	0.4
Curve	1-A	1-B	2-A	2-B	3-A	3-B	4-A	4-B	4-C	5-A	5-B	5-C

[a] Determination of additional points on pressure-temperature curve between 283° and 290° would reduce range of discontinuity.
[b] *n*-Hexane.
[c] Apparently with amount of cyclohexane charged (1800 cc.), liquid level was still above vapor-phase sample line.

Apparatus and Procedure

The Ipatieff rotating bomb used for the determination of the solubility of methane in benzene was also used in this work, modified as follows:

The vapor-phase sampling line was bent outward to within 0.31 cm. (0.125 inch) of the bomb wall. This gave the bomb a capacity of 3145 cc. up to the vapor-sampling line or 92 per cent of the total capacity of the bomb (3420 cc.). This change made possible the study of two-phase systems over a greater range of temperature than by the previous arrangement by which solubilities were determined (*1*).

The gage was mounted at approximately 120° to the axis of rotation of the bomb. This made it possible to stop the rotation of the bomb momentarily and read the gage in a vertical position, thus giving greater accuracy in the pressure readings.

In studying the pressure-temperature relationship with pure substances the procedure was essentially as follows:

The bomb was evacuated and the charge drawn into the bomb by the vacuum from a graduated cylinder until the desired amount of liquid was charged. In case of propane the bomb was evacuated and the propane charged from a graduated pressure charger.

When hydrogen was used, the bomb was charged with the substance to be investigated according to the procedure outlined above and enough hydrogen added to increase the gage pressure about 10 atmospheres. With hydrogen present, it was possible to determine when a two-phase or one-phase condition existed in the bomb by comparing the ratio of the liquid to gas from the samples taken from the vapor-phase and liquid-phase sample lines.

In studying the two-component systems the procedure for charging was as follows:

In case of benzene-methane, the benzene and methane were charged as described above when hydrogen was used with pure substances.

When the propane-benzene system was studied, the benzene was charged to the bomb after evacuation, and propane was charged from a pressure charger in the desired amount.

The hexane-benzene was mixed in the desired proportions outside the bomb, and charged to the bomb after evacuation.

The heat input to the heating furnace was controlled to raise the temperature approximately 1° C. per minute.

The procedure for drawing samples when the bomb charge consisted of two-component systems has been previously outlined (*1*).

In studying the compositions of samples from the hexane-benzene system, the weight per cents of the two constituents were determined by refractive index curves, the compositions of sam-

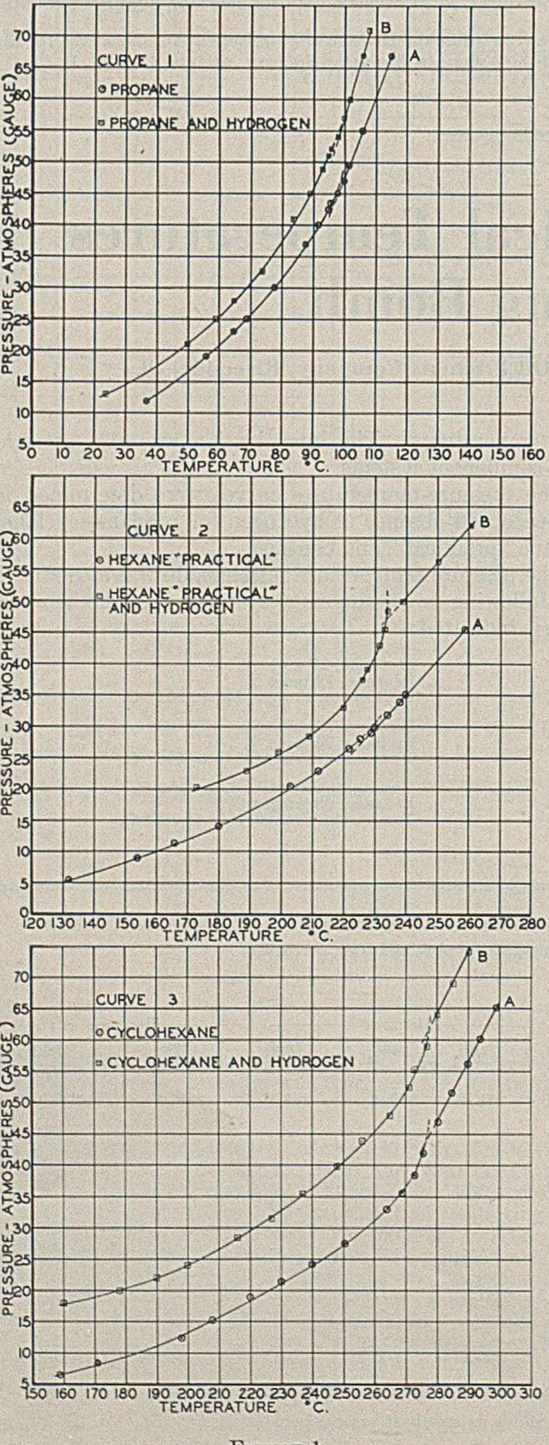


FIGURE 1

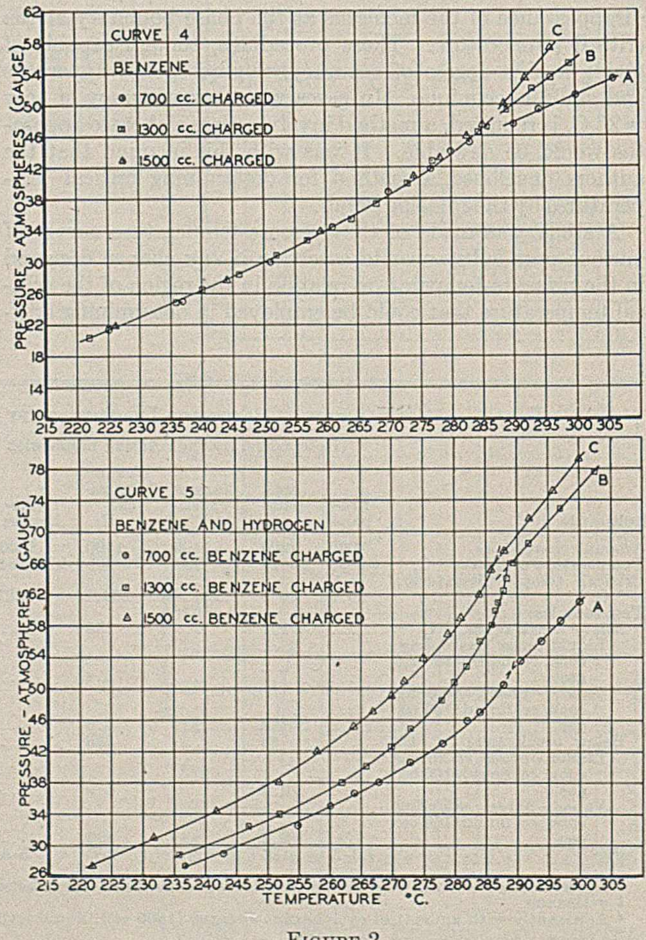


FIGURE 2

ples from the other systems investigated being determined by the ratio of liquid to gas.

Pressure-Temperature Relation of Pure Substances. Table I and Figures 1 and 2 summarize the results obtained with pure substances alone and in the presence of a small amount of hydrogen (10 atmospheres, initial). In all experiments the pressure-temperature curves became discontinuous in the region of the critical temperature, the part below the critical temperature being curved and the section above the critical temperature being practically straight. Variations over a relatively wide range in the amount of material charged did not noticeably affect the temperature of break on the curve.

In case of propane (curves 1-A and 1-B), the break in both curves occurred over a range of 96° to 98° C., the hydrogen having no noticeable effect on the temperature of the break in the curve. Bomb samples drawn from the vapor-phase and liquid-phase sampling lines when hydrogen was used showed that at a temperature of 100–101° C. the bomb charge was a single phase, the hydrogen content of the two samples being the same. When samples were taken at 88° C., the hydrogen content indicated the existence of two phases in the bomb.

Curves 2-A and 2-B, using hexane "practical" from petroleum, showed the characteristic breaks in the pressure-temperature curves at 226–229° and 234–239° C., respectively. The hydrogen content of samples drawn (curve 2-B) indicated the presence of a single-phase region at 235° C. and a two-phase region below 228° C. The critical temperature for *n*-hexane is 234.8° C. Closer agreement with the critical temperature of *n*-hexane cannot be expected, as the sample used probably had hexane isomers.

The experiments with cyclohexane (curve 3-A) and with hydrogen (curve 3-B) gave points of discontinuity on the pressure-temperature curves at 276–281° C. The critical temperature for cyclohexane according to the literature is 281° C. The presence of hydrogen did not noticeably displace the break on the curves. In this case samples drawn from the bomb when runs were made with hydrogen did not indicate a two-phase region below the critical temperature. This may be due to the possibility that the level of the liquid phase was above the vapor-phase draw-off line and samples of liquid phase were obtained from both sampling cocks. This suggests the difficulty of obtaining satisfactory samples when working in the region of the critical if the liquid level of the charge in the bomb is high. However, the presence of hydrogen was beneficial in that the temperature of the break on the curve was more clearly defined.

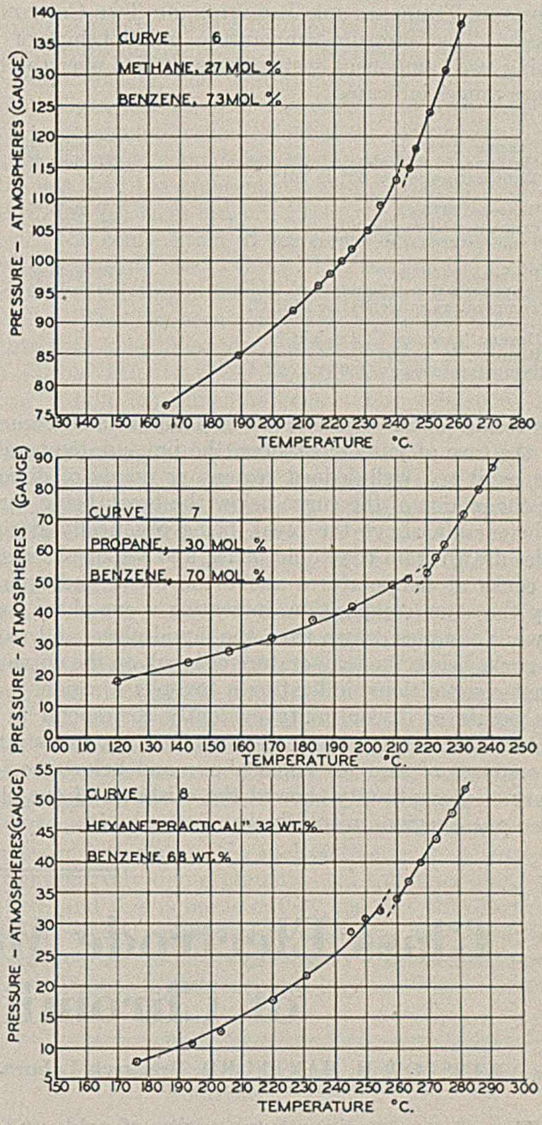


Figure 3

Table II. Summary of Determination of Critical Temperatures of Two-Component Systems by the Rotating Bomb

System			
Benzene, mole %	73	70	68 wt. %
Methane, mole %	27	..	..
Propane, mole %	..	30	..
Hexane "practical", weight %	..	..	32
Amount charged, liquid, cc.			
Benzene	1600	1415	..
Benzene + hexane "practical"	..	..	1500
Methane, atmospheres (initial)	55	..	..
Propane	..	600	..
Temperature of break, ° C.	240–244	214–220	255–260
Test samples:			
Above break temperature at, ° C.	246	222	266
Liquid-phase sample cock, cc. liquid/100 cc. gas	1.0	0.9	68.5 wt. % C_6H_6 31.5 wt. % C_6H_{14}
Vapor-phase sample cock, cc. liquid/100 cc. gas	1.0	0.9	68.5 wt. % C_6H_6 31.5 wt. % C_6H_{14}
Below break temperature at, ° C.	238	216	256
Liquid-phase sample cock, cc. liquid/100 cc. gas	1.1	1.0	69.5 wt. % C_6H_6 30.5 wt. % C_6H_{14}
Vapor-phase sample cock, cc. liquid/100 cc. gas	0.1	0.4	66.0 wt. % C_6H_6 34.0 wt. % C_6H_{14}
Curve	6	7	8

The results of determinations of the critical temperature of benzene in the absence of hydrogen (curves 4-A, B, and C) and in the presence of hydrogen (curves 5-A, B, and C) were on the whole satisfactory. The hydrogen did not noticeably displace the break on the pressure-temperature curve. The critical as determined by the break on the pressure-temperature curve (in the presence and absence of hydrogen) ranged from 286° to 291° C. (critical temperature of benzene according to the literature is 288.6° C.). In the case of benzene, samples drawn from the bomb, when runs were made with hydrogen, indicated a two-phase region below the break on the temperature-pressure curve and a one-phase condition above the break.

In the case of benzene the presence of hydrogen again gave a sharper break on the pressure-temperature curve at the critical than did runs made in the absence of hydrogen.

In the runs with benzene, variations in the amount charged (700 to 1500 cc.) produced no noticeable effect in the temperature of break on the curve.

Pressure-Temperature Relation of Two-Component Systems. The pressure-temperature relationship of the following two-component systems was studied over the temperature ranges indicated:

Benzene, 1600 cc. (73 mole %)
Methane, 55 atmosphere initial (gage) (27 mole %)
Temperature range, 62° to 261° C.

Benzene, 1415 cc. (70 mole %)
Propane, 610 cc. (liquid) (30 mole %)
Temperature range, 100° to 250° C.

Benzene, 1440 cc. (70 mole %)
Propane, 605 cc. (liquid) (30 mole %)
Temperature range, 94° to 256° C.

Hexane "practical", 32 weight %
Benzene, 68 weight %
Temperature range, 150° to 288° C.

The results obtained are given in Table II and Figure 3. As in the case of pure substances, the pressure-temperature curves exhibited well-defined regions or points of discontinuity, the section of the curve below the break being curved and the section above the break being practically straight. Samples drawn from the liquid-phase and vapor-phase sampling cocks at temperatures above the break had approximately the same composition, indicating a one-phase condition, while samples drawn from the liquid-phase and vapor-phase cocks below the temperature of break on the curve had different compositions, indicating a two-phase region.

The points of discontinuity evidently correspond to the critical temperatures of the two-component systems studied, since analyses of samples taken above and below the temperature of discontinuity showed the existence of one-phase and two-phase regions, respectively.

Conclusions

The results obtained with pure substances in either the presence or absence of hydrogen indicate that the critical temperatures may be determined with a fair degree of accuracy and by determining a sufficient number of points in the range of discontinuity the accuracy should be ±2° C.

The amount of material charged to the bomb may vary from 20 to 50 per cent of the total capacity of the bomb without any appreciable shift in the temperature of discontinuity.

It is probable that a bomb of smaller size (200 to 300-cc. capacity) might serve equally well if no samples are removed. The smaller bomb could be easily rotated in a liquid heating bath and the temperature determined with greater accuracy than in case of the larger bomb used in these experiments.

The pressure-temperature curves of two-component systems exhibited points of discontinuity similar to those shown by individual substances, and the critical temperatures of the systems probably lie within the break on the curves. Up to the present time, however, check determinations have not been made on two-component systems of known critical temperatures.

Acknowledgment

The authors are indebted to Lee Fischer and Charles Rohlfing for valuable assistance rendered during the course of the experiments.

Literature Cited

(1) Ipatieff, V. N., and Monroe, G. S., Ind. Eng. Chem., Anal. Ed., 14, 166 (1942).

Presented before the Division of Petroleum Chemistry at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J.

Glass Electrode Measurements of the pH of Chromic Acid Solutions

WINSLOW H. HARTFORD, Research Laboratories, Mutual Chemical Co. of America, Baltimore, Md.

The effect of temperature, purity of acid, and water on the pH of aqueous chromic acid solutions has been measured and shown to be negligible, except for a slight variation with temperature in dilute solutions.

A considerable variation in the readings obtained at pH below 2 with different types of measuring instruments exists. It increases as the pH of the solution decreases, and may amount to 0.2 pH at pH 0. A large portion of this discrepancy results from various liquid junction potentials, while a residual portion cannot at present be explained.

Calculations show that the correct pH value is probably not far from that obtained with certain of the instruments used. All instruments are self-consistent and may be used for control purposes, if standardized against known solutions.

THE pH of chromic acid solutions has been measured by means of the glass electrode by Thompson (*17*), Buzzard and Wilson (*2*), and Neuss and Rieman (*15*), and by means of the hydrogen electrode in fairly dilute solution by Britton (*1*). (The term "chromic acid" is used in this paper to apply to both solid chromium trioxide and its aqueous solutions.) It is only under unusual circumstances that the latter method is satisfactory, and with the development of modern equipment for glass electrode measurements, the glass electrode is practically universally used for such determinations, and has become of industrial importance in the control of baths for the anodic oxidation of aluminum (*2*). It is the purpose of this paper to show the effect of varying apparatus and conditions on the pH readings obtained with chromic acid solutions, and to present certain calculations which corroborate data obtained with one type of apparatus.

Apparatus

The equipment used for these measurements consisted of six commercial-type instruments of three different makes with various types of electrode assemblies, as shown in Table I. All instruments were provided with a temperature compensator and used a saturated calomel electrode as reference half-cell, except Nos. 2A and 5A, in which a silver–silver chloride reference electrode was substituted.

No difference was discernible between setups 1 and 2 and these were used unless otherwise specified.

Materials

The material used in most of the work was technical flake chromic acid, analyzing 99.8 per cent chromium trioxide, 0.03 per cent sulfate, and 0.017 per cent chromic oxide. Chromium trioxide was determined by electrometric titration according to the method of Kelley (*9*), sulfate gravimetrically as barium sulfate after reduction of the hexavalent chromium by alcohol and hydrochloric acid, and chromic oxide by cerimetry according to

Table I. Types of Electrode Assemblies Used

No.	Instrument	Glass Electrode	Liquid Junction
1	A-1	Quinhydrone-HCl[a]	Small ground-glass, with pinhole
2	A-1	Sealed[a]	Small ground-glass, with pinhole
2A	A-1	Sealed	Small ground-glass, with pinhole
3	A-1	Sealed[a]	Fiber diaphragm
4	A-1	Sealed	Capillary junction
5	A-1	Sealed	Broad junction
5A	A-1	Sealed	Broad junction
6	A-2	Sealed	Small ground-glass, as above
7	A-2	Sealed	Fiber diaphragm
8	A-2	Sealed	Broad junction
9	A-2	Sealed	Flowing junction
10	B-1	Sealed	Broad junction
11	B-2	Sealed	Broad junction
12	B-3	Sealed	Fiber junction
13	B-3	Sealed	Large ground-glass
14	C	Quinhydrone-HCl, 30 meg.	Capillary junction
15	C	Quinhydrone-HCl, 30 meg.	Large ground-glass
16	C	Quinhydrone-HCl, 3 meg.	Capillary junction
17	C	Quinhydrone-HCl, 3 meg.	Large ground-glass

[a] Several glass electrodes used.

a modification of the method of Willard and Young (*20*). For some experiments a special grade of c. p. chromium trioxide, prepared by washing specially selected c. p. material with distilled water, was used. It tested 99.9 per cent chromium trioxide, 0.0005 per cent sulfate, and 0.008 per cent chromic oxide. As reference standard for the pH measurements, Bureau of Standards potassium acid phthalate, 0.0500 *M*, was used. This solution had a pH of 4.00 at 25° C., and varies therefrom by about ±0.008 pH at 19° or 31° C., according to the data supplied with the sample (*14*). Secondary pH standards were sodium acetate–acetic acid buffers, 0.1 *N* hydrochloric acid solutions, and hydrochloric acid–potassium chloride buffers. The meter was checked at least once each day. Determinations were frequently performed on separate days on identical samples, and results were reproducible within 0.02 pH.

Effect of Varied Conditions

Temperature. Solutions were tested at 19°, 25°, and 31° C. (Table II). It will be noted that the effect of raising temperature is to cause a slight decrease in pH, this effect is, however, nearly negligible except at low concentrations of chromium trioxide.

Water. Measurements of solutions of equal concentration in Baltimore city water and in laboratory distilled water showed no discernible difference. Slight corrections should be made in the case of waters of high alkali or calcium bicarbonate content.

Purity of Chromium Trioxide. The technical grade and c. p. material described above were tested with the following results:

Mole of CrO_3/Liter	pH, Technical Grade, 27° C.	pH, c. p. Grade, 27° C.
0.9695	0.10	0.10
0.1939	0.80	0.80
0.0485	1.39	1.39

The small amount of impurities present in technical chromium trioxide has no effect on the pH of solutions.

Effect of Variation in Measuring Equipment

The effect of various pH cells and instruments for effecting the measurements was next studied, with the results shown in Table III.

The wide variations observed obviously require explanation. Several sources of inaccuracy are inherent in commercial glass-electrode instruments, and these will be discussed.

Errors Due to High Acidity and Concentration of Solutions. MacInnes and Belcher (*13*) and Dole (*5*) have observed erroneous results from glass electrodes in highly acid solutions, especially at pH below 0, and in solutions of high electrolyte content. The generally accepted explanation is that the effect is due to the fact that the hydrated proton, $(H_3O)^+$, is transferred through the glass membrane, and that the low activity of the water in these solutions is responsible for the discrepancy. While no definite figures are available for the activity of the water in the chromic acid solutions under consideration, the concentration and pH are such that only slight indication of the effect would be expected. Approximate calculations indicate that the correction at 1.0 *M* chromium trioxide should be of the order of 0.012 pH, which is less than the experimental error. Hubbard, Hamilton, and Finn (*8*) have indicated that the "acid error" may vary with the composition of the electrode; however, commercial instruments use Corning 015 glass for the electrode and any errors existing in the measurement would be common to all cells. This has been confirmed by the fact that measurements with assemblies identical except for the glass electrodes (Table III, 1, 2, 3; 14, 16; 15, 17) gave results identical within experimental error. The electrodes used gave normal readings in 0.1 *M* hydrochloric acid, and did not show the error reported by Hubbard, Hamilton, and Finn (*8*).

The same considerations which render pH measurements on chromic acid solutions feasible up to 1 *M* make it necessary to state that any values which may be obtained in more concentrated solutions—e. g., plating baths—are of value for comparison only.

Errors Due to Action of Chromic Acid on Glass Electrode. Watson (*19*) and Kerridge (*10*) have observed that glass electrodes cleaned in a mixture of chromic and sulfuric acids are not suitable for immediate use in the measurement of pH, and Dole (*4*) has observed increase in weight of glass cleaned in this manner, caused by adsorption of chromic acid. Laboratory cleaning solutions normally contain large quantities of sulfuric acid and might be expected to be dehydrating in action, with resultant change in the properties of the glass. No such action is to be expected from the relatively dilute chromic acid solutions under consideration, and this is borne out by the fact that electrodes with which several samples of chromic acid have been measured give accurate readings immediately when checked against a buffer. Tubbs (*18*) has reported high readings in the field

Table II. pH Readings of Chromic Acid Solutions with Equipment 1 and 2

CrO_3	pH		
Mole/l.	19° C.	25° C.	31° C.
1.00	0.11	0.10	0.08
0.80	0.21	..	..
0.60	0.31	..	..
0.50	..	0.40	0.39
0.40	0.51	..	..
0.20	0.77	0.79	0.78
0.10	..	1.09	1.07
0.05	1.40	1.39	1.37
0.04	1.51	..	..
0.03	1.61	..	..
0.02	1.82	1.80	1.77
0.01	..	2.08	2.06

Table III. Effect of Variations in Measuring Equipment

Apparatus No. (from Table I)	Mole of CrO_3 per Liter:			
	1.00	0.50	0.20	0.10
	pH at 25° C.			
1	0.10	0.40	0.79	1.09
2	0.10	0.40	0.79	1.09
2A	0.12	..	..	..
3	0.11	0.41	0.79	1.09
4	0.13	..	..	..
5	0.20	..	..	..
5A	0.18	..	..	..
6	0.14	..	..	..
7	0.14	..	..	..
8	0.20	..	..	..
9	0.20	..	..	..
10	0.27	..	..	..
11	0.30	..	..	..
12	0.21	..	..	..
13	0.25	0.53	0.89	1.18
14	0.20	0.47	0.84	1.13
15	0.26	..	..	..
16	0.24	..	..	..
17	0.25	..	..	..

with an electrode kept immersed in chromic acid instead of distilled water between readings, but such high readings may be due to diffusion in the liquid junction rather than any action on the glass.

SLIDE-WIRE INACCURACIES. Dole (*3*) has reported work by Blair indicating that errors exist in the slide-wire of a commercial pH electrometer, although another electrometer studied by Lanford and Kiehl (*11*) showed little difference when checked against the Type K potentiometer. Repeated checks with standard solutions of hydrochloric acid at a pH of 1.08, where a variation in the observed pH of chromic acid of 0.04 to 0.09 pH (see Table III, column 5) was noted with different electrode assemblies, indicate that a definite effect exists under conditions where both acid errors and slide-wire inaccuracies are completely balanced out. While it is possible that the variation of 0.2 pH noted at pH 0.10 might be due to slide-wire inaccuracies, it seems unlikely that slide-wire errors would amount to as much as 10 per cent over the range pH 0 to 1, or that the error would be nearly identical for all instruments of the same make.

LIQUID JUNCTION. Examination of the data in Table III indicates that the type of liquid junction is an important factor in determining the value obtained for the pH of chromic acid solutions. Algebraic analysis of the results indicates that approximately half the discrepancy is due to variations in the method of forming the liquid junction, while half is due to some factor at present unknown. The data show further that those liquid junctions possessing the broadest surface of contact give the highest readings. The increase in pH appears to be connected with diffusion in the broad junction, since calomel electrodes of the sleeve type in which diffusion has accidentally taken place invariably give readings of higher pH.

The excellent check results obtained with all instruments on other solutions of low pH indicate that the variations observed are peculiar to the liquid junction between chromic acid and saturated potassium chloride. Extensive work on junction potentials (*6*, *7*, *16*) has shown that the ground-glass sleeve or fiber-type junction is normally the least reproducible of liquid junctions; the author has found in the data given above that all junctions studied were reproducible within experimental error, but that diffusion effects appear to introduce a drift toward high pH in the broad types of junction. In this particular case, it would seem that the broad types of junction are more subject to error. This is confirmed in some degree by the calculations given below.

Theoretical

Neuss and Rieman (*15*), in connection with their measurements of the ionization of chromic acid, determined values for the ionization constants in a cell designed to eliminate liquid junction errors, and calculated the variation of the constants with the ionic strength, according to the Debye-Hückel theory. From their data, at 25° C.:

$$K_1' = \frac{[\mathrm{H^+}][\mathrm{HCrO_4^-}]}{[\mathrm{H_2CrO_4}]} = 0.18 \text{ at } \mu = 0.16$$

where $$\mathrm{p}K_1' = 1.05 - \frac{\sqrt{\mu}}{1 + 0.7\sqrt{\mu}}$$

and $$\frac{(\mathrm{HCrO_4^-})^2}{(\mathrm{Cr_2O_7})^{--}} = 0.023,\ \frac{[\mathrm{HCrO_4^-}]^2}{[\mathrm{Cr_2O_7}]^{--}} = K'$$

where $$\mathrm{p}K' = 1.64 + \frac{\sqrt{\mu}}{1 + 0.7\sqrt{\mu}}$$

(Concentrations are here denoted by brackets, activities by parentheses.)

Finally, $$\mathrm{pH} = -\log\,(\mathrm{H^+}) = -\,(\log[\mathrm{H^+}] + \log\gamma)$$

where $\log\gamma$ is derived from values given by Scatchard (*16*) or MacInnes (*12*). If the chromic acid molality $= M$, and $M - [\mathrm{H^+}] = y$, since $[\mathrm{H^+}] = [\mathrm{HCrO_4^-}] + 2[\mathrm{Cr_2O_7}]^{--}$, on elimination of $[\mathrm{HCrO_4^-}]$ and $[\mathrm{Cr_2O_7}]^{--}$:

$$y = \frac{K'[\mathrm{H^+}]}{4K_1'}\left(\sqrt{1 + \frac{8[\mathrm{H^+}]}{K'}} - 1\right)$$

whence:

$[\mathrm{H^+}]$	μ	K_1'	K'	$\gamma\mathrm{H^+}$	y	M	$(\mathrm{H^+})$	pH
0.01	0.0118	0.116	0.0178	0.921	0.000514	0.01051	0.00921	2.04
0.02	0.0248	0.123	0.0166	0.888	0.00153	0.02153	0.01776	1.75
0.04	0.0518	0.140	0.0145	0.870	0.00395	0.04395	0.0348	1.46
0.08	0.107	0.164	0.0123	0.848	0.00942	0.08942	0.0678	1.17
0.10	0.136	0.175	0.0117	0.842	0.0122	0.1122	0.0842	1.07
0.20	0.279	0.216	0.0093	0.838	0.0261	0.2261	0.1676	0.78
0.40	0.579	0.277	0.0074	0.863	0.0528	0.4528	0.3452	0.49

Plotting M against pH gives a curve which is in best agreement (±0.04 pH) with the data determined with instrument A with small junctions up to 0.2 M, which represents the highest concentration at which the equations are valid. However, any of the assemblies employed in this work give self-consistent results, and no false e. m. f.'s are developed by the action of the chromic acid up to 1 M on the glass electrode in any case, as shown by the reproducibility of readings with standard buffer at all times. Because of the acid error, the possible action of chromic acid on the glass electrode, the increase in liquid junction errors, the lack of any theoretical check on the measurements, and the fact that many commercial meters do not read below pH 0 or −0.5, it did not seem feasible to obtain pH values for higher concentrations of chromic acid.

Acknowledgments

The author wishes to express his thanks to the following who have made pH measurements on chromic acid solutions: A. O. Beckman, National Technical Laboratories, Pasadena, Calif.; F. R. McCrumb, W. A. Taylor & Co., Baltimore, Md.; and Mutual Chemical Co. of America, Jersey City, N. J. He is much indebted to William Rieman III of Rutgers University for his assistance in the calculations of pH.

Literature Cited

(1) Britton, H. T. S., *J. Chem. Soc.*, **125**, 1572 (1924).
(2) Buzzard, R. W., and Wilson, J. H., Natl. Bur. Standards, *Research Paper* 961 (1937).
(3) Dole, M., "Glass Electrode", p. 36, New York, John Wiley & Sons, 1941.
(4) *Ibid.*, p. 82.
(5) Dole, M., *J. Am. Chem. Soc.*, **54**, 3095 (1932).
(6) Ferguson, A. L., Van Lente, K., and Hitchens, R., *Ibid.*, **54**, 1285 (1932).
(7) Guggenheim, E. A., *Ibid.*, **52**, 1315 (1930).
(8) Hubbard, D., Hamilton, E. H., and Finn, A. N., *J. Research, Natl. Bur. Standards*, **22**, 339 (1939).
(9) Kelley and Co-workers, J. IND. ENG. CHEM., **9**, 780 (1917).
(10) Kerridge, P. M. T., *J. Sci. Instruments*, **3**, 404 (1926).
(11) Lanford, O. E., and Kiehl, S. J., *J. Phys. Chem.*, **45**, 300 (1941).
(12) MacInnes, D., *J. Am. Chem. Soc.*, **41**, 1086 (1919).
(13) MacInnes, D., and Belcher, D., *Ibid.*, **53**, 3315 (1931).
(14) Natl. Bur. Standards, "Supplementary Certificate of Standard Sample 84a (for Use as a pH Standard)", (Jan. 30, 1940).
(15) Neuss, J. D., and Rieman, W., *J. Am. Chem. Soc.*, **56**, 2238 (1934).
(16) Scatchard, G., *Ibid.*, **47**, 696 (1925).
(17) Thompson, M. S., *J. Research, Natl. Bur. Standards*, **9**, 833 (1932).
(18) Tubbs, L. G., private communication.
(19) Watson, F. J., *Chem. Eng. Mining Rev.*, **20**, 59 (1927).
(20) Willard, H. A., and Young, P., *J. Am. Chem. Soc.*, **50**, 1322, 1379 (1928); *Trans. Electrochem. Soc.* (preprint), **67** (1935).

Molecular Still Heads

A. J. BAILEY
University of Washington, Seattle, Wash.

MANY devices for molecular distillation have been developed and made available to chemists in general through publication. Morton (*3*) reviewed a number of the types most useful in the laboratory, Detwiler and Markley (*2*) cited over a hundred publications, and others are readily found in the literature.

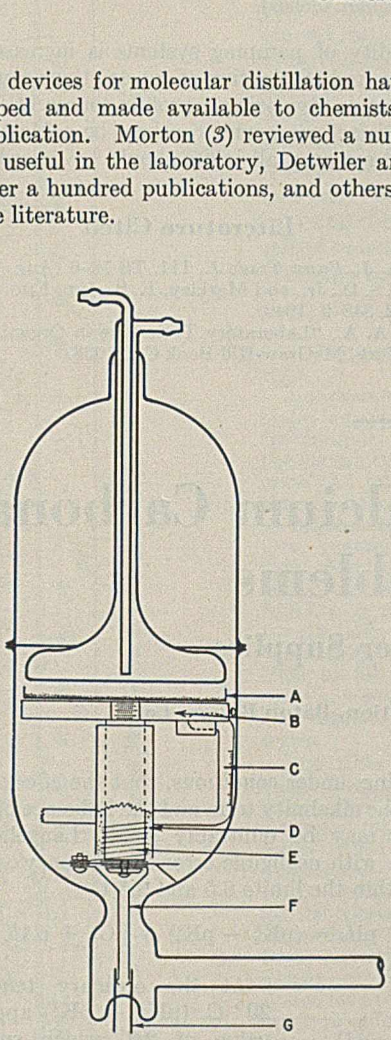


FIGURE 1. MOLECULAR STILL

A, lead sample pan; *B*, brass hot plate; *C*, thermometer; *D*, glass wool insulation; *E*, No. 30 Nichrome wire (20 ohms) insulated above and below by glass wool and wrapped on a brass bar; *F*, spring bronze contacts insulated by mica washers; *G*, tungsten wires sealed in

Experience in this laboratory has shown that the use of standard glass parts contributes greatly to the economy of construction, rigidity, and mechanical strength of the still, and interchangeability and general serviceability of the device. Several designs are of sufficient value to justify more general use.

Figure 1 shows one type of molecular still made from two standard Pyrex microbell jars. The parts are inexpensive, and the simple and rugged construction contributes to rapid and safe manipulation. The design shown includes improvements indicated by many months of continuous operation, and is free from the usual vagaries such as temperamental heater, thermal control, and measuring devices, and erratic and undependable vacuum seals.

A feature of early designs which caused endless trouble was the material which insulated the heating element. Materials such as mica and glazed or unglazed porcelain were unsatisfactory because of the large quantities of gas given off when heated. Glass wool taken from a bat in the general laboratory supply and wrapped around the heater proved admirably effective as insulation. The various glass tapes, cloths, and sleeves supplied by the Owens-Corning Fiberglas Corporation, Toledo, Ohio, permit easy application. An input to the heater of about 20 watts sufficed for temperatures up to 300° C. The most satisfactory wax for completing the vacuum seal between the two bell jars was picein; it was equally effective whether built up as a dam on the outside of the joint or allowed to form a layer between the opposite joint faces, although it was usually easier to make a successful seal at the first attempt by the latter method. The condenser effectively cooled the wax seal so that the vapor pressure of the wax did not interfere. The details of construction are apparent in Figure 1.

While several types of vacuum systems were employed, best results were obtained by using a simple, short-coupled vacuum line. The still was coupled to a freezing trap which was attached to the mercury pump. A McLeod gage was also connected directly to the mercury pump. Between the mercury pump and the mechanical forepump a three-way stopcock was inserted. The third outlet led to the high-vacuum side of the mercury pump, thus making it possible to by-pass the mercury pump completely to prevent contaminating the mercury. On the low-vacuum side of the mercury pump, a liter flask was connected to serve as a reservoir. It was then possible to reduce the running time of the mechanical pump to two or three brief periods in 24 hours. Using the molecular still and vacuum system as described, a two-stage Kurth mercury pump and Cenco Hyvac fore-pump reduced the reading of the McLeod gage to 10^{-6} mm. of mercury in about an hour if the heater was not energized, and to the same level in about 2 hours with the heater and sample at 200° C. The combination of McLeod gage and freezing trap records the pressure of permanent gases only and these not in the distillation gap. The total pressure of temporarily uncondensable molecules in the gap during distillation was probably higher than 10^{-6}. The effectiveness of this still was demonstrated by successfully distilling lignin for the first time (*1*) and it has proved to be dependable, sturdy, and simple to operate.

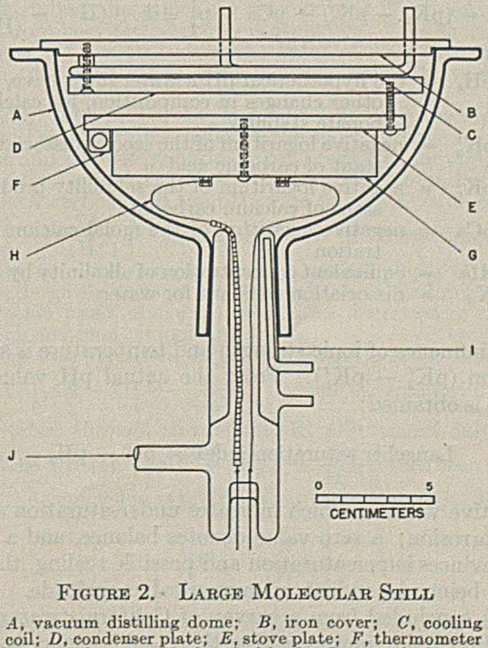


FIGURE 2. LARGE MOLECULAR STILL

A, vacuum distilling dome; *B*, iron cover; *C*, cooling coil; *D*, condenser plate; *E*, stove plate; *F*, thermometer well; *G*, heater; *H*, electrical lead; *I*, water jacket for tapered joint; *J*, vacuum line

Large Molecular Still

For larger capacity, a still of somewhat similar design was developed (Figure 2).

The central unit of construction was a standard Pyrex vacuum distilling dome (Catalog No. 3480) which contained the heater, hot plate, condenser, and thermometer. The heater was an inexpensive commercial hot plate 11.25 cm. (4.5 inches) in diameter and was fastened to a circular brass plate 13.75 cm. (5.5 inches) in diameter and 0.625 cm. (0.25 inch) thick: these two constituted the stove. It was suspended by three machine screws from the condenser, and the length of the screws permitted varying the stove-condenser distance. The condenser consisted of a circular brass plate 15 cm. (6 inches) in diameter and 0.625 cm. (0.25 inch) thick with a copper cooling coil soldered to the upper surface, and fastened rigidly to the iron cover. The electrical connections were made by wires, one threaded through magnesium oxide beads, soldered to a nickel bead fused to the tungsten wires sealed through the glass. An internal condenser was attached to the male ground joint to maintain the vapor pressure of the wax on the joint at a safe value. Picein wax was used to seal both the cover joint and the tapered joint. The thermometers for both stills were made from the broken stems of regular thermometers, with bulbs of proper size blown, and stems curved to fit the walls of the stills. Glass plates were used to cover both stove and condenser when direct contact with metal was undesirable. This still had a heating surface of over 150 sq. cm. (23 square inches) and a condensing surface of over 180 sq. cm. (28 square inches).

The rapidity of pumping systems is increased by large, short tubing, and elimination of constrictions caused by stopcocks, the latter also being a prolific source of leaks in high vacua. Satisfactory service can best be achieved by an all-glass, sealed system; all joints should be regarded with suspicion.

Literature Cited

(1) Bailey, A. J., *Paper Trade J.*, 111, TS 73–6 (Aug. 15, 1940).
(2) Detwiler, S. D., Jr., and Markley, K. S., Ind. Eng. Chem., Anal. Ed., 12, 348–9 (1940).
(3) Morton, A. A., "Laboratory Technique in Organic Chemistry", New York, McGraw-Hill Book Co., 1938.

A Special Slide Rule for Calcium Carbonate Equilibrium Problems

In Corrosion Control of Water Supplies

A. ADLER HIRSCH, State Department of Education, Baton Rouge, La.

PROTECTION of distribution systems against corrosion by means of a calcium carbonate film was first proposed by Tillmans (*4*), but a comprehensive theoretical formulation of conditions for deposition in the system CO_2—HCO_3^-—CO_3^{--}—Ca^{++} was evolved recently by Langelier (*7*). His complete equation involves pH, titratable alkalinity as calcium carbonate, calcium concentration, ionic strength, and temperature:

$$pH_s = (pK'_2 - pK'_s) + pCa + p\left[Alk + (H^+) - \frac{K_w}{(H^+)}\right] + \log\left[1 + \frac{2K'_2}{H_s^+}\right] \quad (1)$$

where pH_s = the hypothetical pH a water must have, without other changes in composition, for calcium carbonate stability
pK'_2 = negative logarithm of the second dissociation constant of carbonic acid
pK'_s = negative logarithm of the solubility product constant of calcium carbonate
pCa = negative logarithm of the molal calcium concentration
Alk = equivalent concentration of alkalinity by titration
K_w = dissociation constant for water

The influence of ionic strength and temperature is shown in the term $(pK'_2 - pK'_s)$. From the actual pH value of the sample is obtained:

$$\text{Langelier saturation index} = pH - pH_s \quad (2)$$

a negative value of which indicates undersaturation and possible corrosion; a zero value denotes balance, and a positive value evinces supersaturation and possible scaling, the actual effects being dependent on numerical magnitude. DeMartini (*2*) concluded from a survey of California waters that a saturation index more positive than −0.5 generally implied freedom from serious corrosion.

By showing, under conditions, that the effect of (H^+) and (OH^-) on the alkalinity term and the influence of the final log parenthesis may be omittably small, Langelier simplified Equation 1 with negligible error for ordinary waters whose pH_s lies within the limits 6.5 and 9.5 to

$$pH_s = (pK'_2 - pK'_s) + pCa + pAlk \quad (3)$$

At the ordinary temperature of 20° C. $(pK'_2 - pK')$ approximates a value of 2.3, which substituted in Equation 3 gives a short form:

$$pH_s = 2.3 + pCa + pAlk \quad (4)$$

A further simplification of the Langelier formula is ultimately possible in certain restricted cases where, in the absence of a calcium determination, it may be assumed that the calcium and alkalinity values are proportional. If calcium and alkalinity are taken as equivalent, Equation 4 becomes

$$pH_s = 2.6 + 2pAlk \quad (5)$$

which resembles in form the empirical equation of Baylis' experimentally established calcium carbonate equilibrium curve (*1*) and is equivalent to Strohecker's short formula (*9*).

To facilitate further the calculation of pH_s Hoover and Riehl (*6*) prepared a nomogram to solve Equation 3 graphically. Their drawing provides for temperature and salinity influences but omits corrections for the final log term of Equation 1 and the effect of (H^+) and (OH^-) ions.

The slide rule described below was designed primarily to provide immediate and easy solution to the full Langelier formulation with suitable provisions for all corrections; its application in solving the simplifications, Equations 3 and 4, is especially rapid and effortless.

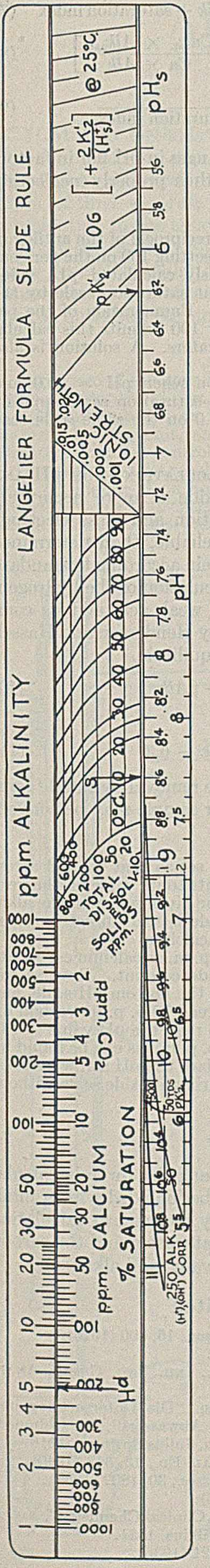

LANGELIER FORMULA SLIDE RULE
p.p.m. ALKALINITY
LOG $\left[1+\frac{2K'_2}{(H_s^+)}\right]$ @ 25°C
pH_s
pK'_2
IONIC STRENGTH
TOTAL DISSOLVED SOLIDS P.P.M.
0°C. 10 20 30 40 50 60 70 80 90
pH
ppm. CO_2
ppm. CALCIUM
% SATURATION
250 ALK. 50 ALK. 10 ALK.
(H+), (OH-) CORR.

Figure 1. Arrangement of Scales on Slide Rule

This special slide rule enables mechanical calculation of (1) the full Langelier equation and its contractions; (2) degree of calcium carbonate saturation; and (3) dissolved carbon dioxide from pH and alkalinity values, or vice versa. Incidentally, ordinary multiplication and division may be performed by using the logarithmically divided calcium and alkalinity scales.

Description

Arrangement of the scales is shown in Figure 1. On the upper stock is ruled the alkalinity scale, which gives the p*Alk* value for the alkalinity in p. p. m. as calcium carbonate figures marked. Although total dissolved solid correction factors extend only to 800 p. p. m., the scales for alkalinity and for calcium are ruled to an even 1000 to fill out the log cycle and enable their use as regular logarithmic scales.

The slide carries pCa values for calcium content. The semilog graph labeled "total dissolved solids", with temperature parameters, gives the $(pK'_2 - pK'_s)$ term. Data for its construction were taken from the Hoover-Riehl nomograph; hence proper provision is included for a corrected temperature effect (*6*). An accompanying scale of ionic strength is provided for use in cases where this fundamental information is known. The log $\left[1 + \frac{2K'_2}{(H_s^+)}\right]$ correction is supplied by gage lines on the right-hand end of the slide.

The top edge of the crowded bottom stock is ruled arithmetically to give pH_s; the lower edge is divided likewise but enumerated in the opposite direction to allow calculation of carbon dioxide from actual pH. In the region of $pH_s = 10.2$ is located an arc for use in conjunction with the log term correction gage lines; this short curve shows the variation of pK'_2 with total dissolved solids at 25° C. Correction for (H^+) and (OH^-) ions is provided by the graph plotted for alkalinity levels of 10, 50, and 250 p. p. m.

Applications

Langelier Formula Calculations. *Simple Form, Equation 4.* Method. Set the calcium figure on the slide opposite the alkalinity value on the top scale. The position of arrow *S*, located within the total solids plot, at a $(pK'_2 - pK'_s)$ value of 2.3, points directly to the pH_s value on the inside edge of the bottom stock.

Computation may be best illustrated by a specific example, using the following analysis:

	P. p. m.		P. p. m.
Na	18	Mg	6
Cl	16	Ca	15
Alkalinity as $CaCO_3$	33	SO_4	44
Total dissolved solids (by analysis), p. p. m.	132		
pH	10.0		

To find pH_s set 15 on the calcium scale opposite 33 on the alkalinity scale, and read at the point of arrow *S* that $pH_s = 8.9$. Since the actual pH is 10.0, the saturation index is $^+1.1$, indicating a tendency to scale.

Simple Form with Temperature and Total Dissolved Solids. Correction, Equation 3. Method. The alkalinity and calcium settings remain as before, but the position of $(pK'_2 - pK'_s)$ is now obtained from the total dissolved solids–temperature graph. Total dissolved solids is the quantity obtained by summation of the ions and not the result of evaporation; this quantity may also be obtained from electrical conductivity, using the formula of Gustafson and Behrman (*3*). In the graph 40 p. p. m. total dissolved solids is taken equivalent to 0.001 ionic strength, as suggested by Langelier, who showed that many natural waters contain equal equivalent concentrations of monovalent and divalent ions. The graph may also be employed in terms of ionic strength; this is preferable for treated waters, especially zeolite effluent using the sodium cycle, wherein the relation between equivalent concentrations of the two valence types is altered considerably. A special stoichiometric slide rule (*5*) facilitates the calculation of ionic strength from the analytical statement.

This type of calculation will suffice to establish pH_s for most waters. The plot lucidly demonstrates that temperature influence on pH_s is dominant compared to the total dissolved solids effect; a wide variation from 50 to 400 p. p. m. dissolved solids is needed to produce practically the same shift of pH_s as a drop of only 10° C. below usual room temperature.

Solution with Correction for Log $\left[1 + \frac{2K'_2}{(H_s^+)}\right]$. The gage lines to the right of the slide are designed to follow Langelier's tabulated values of log $\left[1 + \frac{2K'_2}{(H_s^+)}\right]$ in terms of the difference $(pK'_2 - pK'_s)$. pK'_2 in turn depends on temperature and solids content, but for simplicity its values are given only at 25° C. as its variation with ordinary temperatures is negligible. The short vertical curve near $pH_s = 10.2$ gives the value of pK'_2 from 1 to 800 p. p. m. dissolved solids, within which range its variation is limited.

Method. The pK'_2 arrow, located in the gage line area, is set opposite the proper pK'_2 value on the short vertical arc and the gage line opposite the preliminary pH_s, corrected for temperature and dissolved solids, is followed to its top edge and then projected back vertically to the pH_s scale to give a value corrected for log $\left[1 + \frac{2K'_2}{(H_s^+)}\right]$. Below $pH_s = 8.9$ this correction becomes negligible, as noted from the nearly vertical slopes of the gage lines for large differences between pK'_2 and preliminary pH_s. On the other hand, above $pH'_s = 8.9$, consideration of this term becomes increasingly important.

Solution with Correction for (H^+) *and* (OH^-) *Ions.* Previously the term $p\left[Alk + (H^+) - \frac{K_w}{(H^+)}\right]$, which for equilibrium conditions reached through theoretical (H) adjustment only should properly be written $p\left[Alk + (H_s^+) - \frac{K_w}{(H_s^+)}\right]$, has been assumed to have the same value as p*Alk*. However, a plot of the difference

$$p\left[Alk + (H^+) - \frac{K_w}{(H^+)}\right] - pAlk$$

in Figure 2 shows a correction, $\Delta\, pH_s$, exceeding 0.05, applicable within the shaded zone. This correction is significant for waters of low alkalinity and mineralization, especially in calcium. On

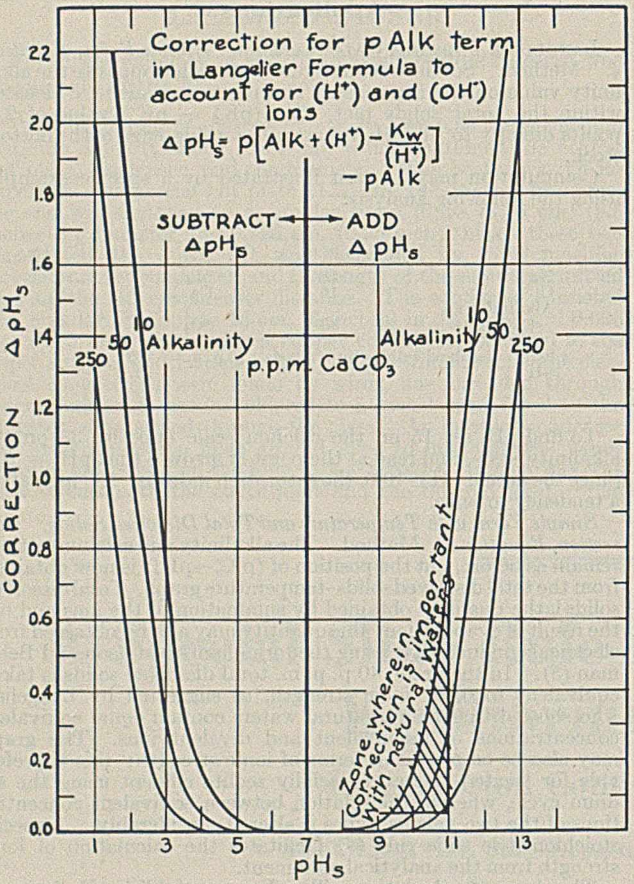


FIGURE 2

the acid side this correction is without practical importance but is drawn in Figure 2 merely to show symmetry. These three curves are reproduced on the bottom of the slide rule to enable this final correction for those cases above about $pH_s = 9.5$ where needed.

Method. The ordinate from the edge of the stock at the uncorrected pH_s value vertically downward to the alkalinity parameter, interpolated if necessary, is noted and the correction read from the auxiliary scale of ordinates near $pH_s = 9.1$. This increment is added to the preliminary value of pH_s preferably before making the preceding log term correction, as the rate of variation of the latter with respect to initial pH_s is the larger. Adjustment of corrections by iteration may be disregarded.

Problem. Using the previous lime-softened water analysis, find pH_s at a temperature of 10° C. with all corrections included. Set 15 on the calcium scale opposite 33 on the alkalinity scale as before. Move the glass index to a point in the total dissolved solids–temperature plot corresponding to 132 p. p. m. total solids and 10° C. temperature. Under the hairline, the preliminary value of pH_s corrected for temperature and solids is 9.09. To correct for the log term, set the pK_2' arrow opposite the 132 p. p. m. solids point on the pK_2' arc. Project $pH_s = 9.09$ along the gage line direction to the upper edge of the slide, then drop this point vertically to the pH_s scale to read $pH_s = 9.14$. No final correction for (H^+) and (OH^-) is necessary, as the intersection of the hairline at $pH_s = 9.14$ with the interpolated location of the 33 p. p. m. alkalinity parameter is at zero.

DEGREE OF CALCIUM CARBONATE SATURATION. It is evident from Equation 3 that a corrosive water may be balanced if the calcium and/or the alkalinity is increased so that the log of their product is augmented to the extent of the saturation index. The saturation index represents the deficit in the product of calcium by alkalinity ions. Rewriting Equation 3 using logs

$$pH_s = (pK_2' - pK_s') - (\log Ca + \log Alk) \qquad (6)$$

Since balance is attained when $pH - pH_s = 0$, this condition will be established by making

$$\log Ca_{sat.} + \log Alk_{sat.} = \log Ca + \log Alk + \text{saturation index} \qquad (7)$$

whence

$$\text{Saturation index} = \log\left[\frac{Ca_{sat.} \times Alk_{sat.}}{Ca \times Alk}\right] \qquad (8)$$

or

$$\frac{Ca \times Alk}{Ca_{sat.} \times Alk_{sat.}} = \frac{1}{\log^{-1}\text{saturation index}} \qquad (9)$$

This procedure presupposes no changes in pH nor in factors affecting the term $(pK_2' - pK_s')$, thus properly neglecting any slight elevation in salinity.

Method. It is sufficient to find the reciprocal of the antilog of the saturation index. This is done by setting 100 on the per cent saturation scale opposite the previously calculated pH_s value and noting the reading on the per cent saturation scale by the actual pH, also along the pH_s scale. Enumeration of the per cent saturation scale above and below 100 permits this calculation for both scaling and corrosive waters. A solution is also possible using the slide in reverse.

Problem. Find per cent saturation when $pH = 10.0$ and $pH_s = 9.14$. Set 100 on the per cent saturation scale opposite 9.14 on the pH_s scale and opposite 10.0 on the same scale read the hairline at 700 per cent saturation.

DISSOLVED CARBON DIOXIDE CALCULATION FROM pH AND ALKALINITY VALUES. Carbon dioxide is more accurately calculated from the alkalinity titration and glass electrode readings, both of which are very reliable, than determined by direct titration with phenolphthalein according to standard methods. This simple mass law calculation of the hydrogen-ion concentration of a mixture of a weak acid and its completely dissociated salt was applied by Henderson and Hasselback (*8*) in 1908 to blood chemistry equilibria.

$$pH = pK + pCO_2 - pAlk \qquad (10)$$

since $pK = 6.3$ in distilled water

$$pCO_2 = pH + pAlk - 6.3 \qquad (11)$$

The extent to which carbon dioxide removal by simple aeration raises the pH value of a water sample may be conveniently calculated by this method.

Method. The slide is reversed and set so that the pH arrow (located to allow for the constant) points to its value on the very bottom scale. The hairline is set at the given value on the alkalinity scale and p. p. m. carbon dioxide is read directly underneath on the scale normally devoted to calcium.

Problem. Given alkalinity = 95 p. p. m. as calcium carbonate and $pH = 6.5$, find the carbon dioxide content. Reverse the slide, set the pH arrow opposite 6.5 on the bottom pH scale, and across from 95 on the alkalinity scale read 70 p. p. m. carbon dioxide on the carbon dioxide scale. To raise the pH value to 7.0, carbon dioxide must be reduced to 26 p. p. m., as can be found by shifting the slide toward the right to place the pH arrow over 7.0 on the bottom scale and reading the carbon dioxide scale without shifting the hairline.

Summary

This special slide rule expedites Langelier formula calculations and enables all corrections to be included with a minimum of effort. It also permits easy mechanical calculation of the degree of calcium carbonate saturation and the carbon dioxide content from the actual pH value and alkalinity.

Literature Cited

(1) Baylis, J. R., *J. Am. Water Works Assoc.*, **15**, 600 (1926).
(2) DeMartini, F. E., *Ibid.*, **30**, 85 (1939).
(3) Gustafson, H., and Behrman, A. S., IND. ENG. CHEM., ANAL. ED., **11**, 355 (1939).
(4) Heyer, von, Tillmans, and Heublein, "Die Untersuchung und Beurteilung des Wassers und des Abwassers", W. Ohlmuller and O. Spitta, 4th ed., p. 40, Berlin, Julius Springer, 1910.
(5) Hirsch, A. A., IND. ENG. CHEM., ANAL. ED., **12**, 542 (1940).
(6) Hoover, C P., *J. Am. Water Works Assoc.*, **30**, 1802 (1938).
(7) Langelier, W. F., *Ibid.*, **28**, 1500 (1936).
(8) Peters and Van Slyke, "Quantitative Clinical Chemistry", Vol. I, p. 874, Baltimore, Williams and Wilkins, 1931.
(9) Strohecker, R., *Z. anal. Chem.*, **107**, 321 (1936).

An Improved Methoxyl Apparatus

A. J. BAILEY, University of Washington, Seattle, Wash.

COMMON methods of methoxyl assay employ a cumbersome and complex apparatus. The standard method of the Technical Association of the Pulp and Paper Industry (*3*) uses three separate pieces of apparatus for maintaining temperature in the assay system, while that of Peniston and Hibbert (*2*) employs four separate units; other methods require generally similar equipment. The proposed apparatus represents a simplification in apparatus with greatly improved operating characteristics.

Apparatus

A diagram of the apparatus is shown in Figure 1. The apparatus was patterned, in part, after the standard T. A. P. P. I. apparatus (*3*), but embodies an internal electrical heater rather than an external heating unit, and the absorption system is simplified. Greatly simplified control is one of the major advantages.

OPERATION. Best results were obtained by heating the glycerol bath (*I*, Figure 1) on a small adjustable, thermostatically controlled hot plate (Central Scientific Co., Catalog No. 16,627), which maintained the bath at 130° C. with almost no change for hours on end. The heater immersed in the jacket was connected to the alternating current line through a fixed resistance of such size as to maintain the jacket temperature at 55°. With the trap and absorption tubes filled, the sample was introduced, and the apparatus was closed and lowered into the glycerol bath. Introduction of a slow stream of carbon dioxide completed the necessary adjustments. This apparatus was in full-day operation for several weeks at a time; once adjusted, virtually no further adjustments were required and supervision was necessary only at hourly intervals to change absorption tubes and scrubbing liquid and to introduce a new sample and, if necessary, new hydriodic acid and phenol.

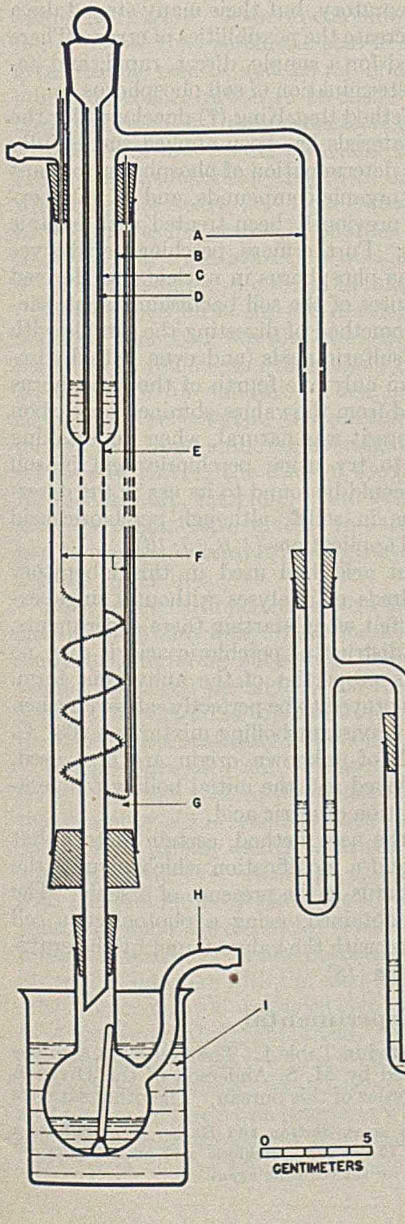


FIGURE 1
METHOXYL APPARATUS
Drawn to scale

A, 7 mm.; *B*, 22 mm.; *C*, 8 mm.; *D*, 5 mm.; and *E*, 10 mm. in outside diameter.

F, electrical leads, approximately 4 feet of No. 26 Nichrome wire; *G*, water jacket at 55° C.; *H*, CO_2 inlet; *I*, glycerol bath at 130°.

Over-all length of water jacket was 60 cm., outside diameter 38 mm.; a thermometer was suspended inside. Glycerol bath was maintained at constant temperature by thermostatically controlled heater.

It was found desirable to add samples in a small glass boat and to use an antibump tube as shown. Three or four samples were hydrolyzed with 15 ml. of hydriodic acid (specific gravity 1.7) before the flask was replaced with a new flask and fresh reagent. The addition of phenol was not necessary, but contributed to a shorter time and smoother reaction.

As Clark (*1*) and Peniston and Hibbert (*2*) noted, the apparatus and reagents must be heated before use to free the system completely of methoxyl. All grades of phenol used in this laboratory have given positive tests for methoxyl. A convenient method of testing for completion of removal of methoxyl is to use an absorption tube containing alcoholic silver nitrate. In addition to the causes of error recorded by Peniston and Hibbert necessitating a blank determination, a prolific source of blank correction was found to be the instability of potassium iodide solution. Even short standing caused a faintly yellow solution (formation of free iodine) and consequent large blank correction.

Variations in Method

This apparatus was used with equal success in the Zeisel (*5*), Vieböck and Schwappach (*4*), and Peniston and Hibbert (*2*) methods and gave an accuracy identical to that obtained by the older apparatus. It should give identical accuracy in Clark's (*1*) and similar methods. In the Peniston and Hibbert method the addition of phenol to the flask was not essential and carbon dioxide was used directly from a tank. A phosphorus suspension and a 5 per cent cadmium sulfate–5 per cent sodium thiosulfate solution gave identical results as a scrubbing medium. With the size of sample ordinarily used in the Zeisel method, the silver nitrate absorbing solution and subsequent gravimetric determination gave lower accuracy than the bromine–potassium acetate–glacial acetic acid absorbing solution (*2*) and subsequent volumetric determination of the iodine. The latter method possesses great advantages in simplified procedure, high inherent accuracy, freedom from interference, rapidity, and ability to use extremely small samples.

This apparatus has been in successful use in the author's laboratory for several years in the analysis of methoxy phenols and lignin preparations, and has been used by Irwin A. Pearl of this laboratory in recent months with similar success and satisfaction. The method employing the volumetric determination of iodine, substantially as described by Peniston and Hibbert but modified as above, has been found to be most accurate and convenient. It consistently gave values that varied less than 0.1 per cent from the theoretical with 3- to 7-mg. samples of vanillin; in general, accuracy was similar to that reported by Peniston and Hibbert.

Literature Cited

(1) Clark, E. P., *J. Assoc. Official Agr. Chem.*, 15, 136–40 (1932).
(2) Peniston, Q. P., and Hibbert, H., *Paper Trade J.*, 109, 46–8 (Oct. 26, 1939).
(3) Technical Assoc. of Pulp and Paper Ind., "Methoxyl Groups in Wood", *T. A. P. P. I. Standard* T2m (1934).
(4) Vieböck, F., and Schwappach, A., *Ber.*, 63, 2818–23 (1930).
(5) Zeisel, S., *Monatsh.*, 6, 989 (1885); 7, 406 (1886).

CONTRIBUTION from the Department of Chemistry and Chemical Engineering and Lignin and Cellulose Research Laboratories.

MICROCHEMISTRY

Colorimetric Determination of Phosphorus in Soils

Provision for Eliminating the Interference of Arsenic

MILDRED S. SHERMAN, Bureau of Plant Industry, U. S. Department of Agriculture, Beltsville Research Center, Beltsville, Md.

A colorimetric method that is both rapid and accurate has been developed for the determination of phosphorus in soils. The soil is digested with 60 per cent perchloric acid which quickly destroys the organic matter and converts the phosphorus present to the inorganic form. A final boiling temperature of 203° C. is, no doubt, responsible for the complete extraction of the soil phosphorus. Sixty per cent perchloric acid is not a hazardous reagent and has been used for over two years in hundreds of analyses without a single explosion.

An aliquot of the perchloric acid solution of the soil is treated with ammonium molybdate and 1,2,4-aminonaphtholsulfonic acid. The depth of the blue color formed is measured in a photoelectric colorimeter and the phosphorus value calculated from the calibration curve of the instrument. The effect of variations in acidity, time, and temperature upon the development of this color is discussed.

Arsenates also give a blue color with the reagents used in this method. A slight modification, however, permits the determination of phosphorus in the presence of arsenic: An excess of sodium bisulfite in the presence of perchloric acid at room temperature reduces any arsenates to arsenites which do not interfere.

The values for the determination of phosphorus in thirteen soil samples of varying iron and organic matter content are presented and are shown to be in close accord with those obtained by the conventional gravimetric method of W. O. Robinson.

The working time for six determinations is 3 hours.

THE standard procedures for the determination of phosphorus in soils are the official method (*2*), in which the sample is digested with magnesium nitrate followed by a volumetric determination of the yellow ammonium phosphate, and the Robinson method (*13*), in which the sample is digested with hydrofluoric acid followed by a gravimetric determination of the magnesium pyrophosphate. Both methods give satisfactory results and demand only the equipment found in any general laboratory, but their many steps take a good deal of time and increase the possibilities of error. There seemed to be a real need for a simple, direct, rapid, and accurate method for the determination of soil phosphorus.

The perchloric acid method that King (*7*) developed for the analysis of biological materials has been applied successfully in this laboratory to the determination of phosphorus in plant materials, in crystalline organic compounds, and in water extracts of soils that had previously been treated with organic or inorganic phosphates. Furthermore, perchloric acid gives theoretical values for the phosphorus in nucleic acid derived from yeast or from cultures of the soil bacterium, Azotobacter. The ordinary micromethod of digesting the sample with a mixture of nitric and sulfuric acids (and even with hydrogen peroxide) had shown only one fourth of the phosphorus which would be expected from the values obtained for carbon and hydrogen. Therefore it was natural, when undertaking some Neubauer tests, to try using perchloric acid in soil analysis. No reference could be found to its use in the determination of phosphorus in soils[a], although perchloric acid has had many analytical applications (*4, 6, 15, 16*).

Since the 60 per cent acid had used in this laboratory for 18 months in hundreds of analyses without a single explosion, no anxiety was felt when starting these experiments. The somewhat general distrust of perchloric acid is due, no doubt, to the hazardous properties of the anhydrous form. The 60 per cent acid has proved to be perfectly safe even when it becomes a 72 per cent constant-boiling mixture at 203° C. Nevertheless, when soils of unknown origin are first used, a screen should be employed and the initial boiling temperature lowered by the addition of nitric acid.

This paper presents the new method, certain factors that influence its accuracy, and a modification which permits the determination of phosphorus in the presence of arsenic. The analytical results thus obtained, using a photoelectric cell colorimeter, are compared with the values found by the gravimetric method of Robinson (*13*).

Experimental

The soils studied are listed in Table I. The first eight samples were very kindly furnished by M. S. Anderson of the Division of Soil Chemistry and Physics of this bureau. The other samples were described in previous reports (*5, 11*). The soils were air-dried and rolled; the stones and stems held on a 10-mesh sieve were discarded, and the entire sample was ground to pass a 100-mesh sieve according to the directions of Robinson. Thirty-five mesh is fine enough for the perchloric acid method, but since it was to be checked by Robinson's method, his directions were followed explicitly.

---

[a] While this paper was in press, Shelton and Harper (*14*) published a method which uses 4 ml. of 72 per cent perchloric acid on a 2-gram soil sample and hydrazine sulfate for the reducing agent.

Extraction of Soil Phosphorus. The soil is boiled with 60 per cent perchloric acid which quickly destroys the organic matter and converts the phosphorus present to the inorganic form. This digestion is usually complete in 40 minutes. The final boiling temperature of 203° C. is responsible, no doubt, for the complete extraction of the soil phosphorus. An aliquot of this solution can then be treated with ammonium molybdate and reduced to give a blue color that is proportional to the phosphorus present.

Conditions Affecting Color Development. King used a Duboscq colorimeter and 1.2 ml. of 60 per cent perchloric acid in a 15-ml. volume to "contain almost the same 'total acidity' as the sulfuric acid used by Martland and Robison" (*8*). With a photoelectric cell colorimeter, however, it was soon evident that variations in acidity, temperature, and time affected the development of the blue color.

If too little acid is present when the reducing agent is added, some of the excess ammonium molybdate is reduced and the results are too high. If too much acid is present, the reduction of the phosphomolybdate is inhibited and the phosphorus values will be low. Experiment showed that the use of 2 to 4 ml. of 60 per cent perchloric acid in a final volume of 25 ml. gives reliable results, and 2.5 ml. of acid were adopted as the minimum concentration to be used. This acidity range was later confirmed by Rae and Eastcott (*12*).

A series of low results coincided with a sudden cold spell (14° C. on the laboratory bench). Investigation showed that with reagents below 20° C. the readings were low; above 29° C. the results gradually became too high; and from 33° to 50° C. they were erratic. A working temperature of 25° ± 4° C. was therefore adopted as the standard procedure.

The time required for the development of the maximum depth of blue color was also studied. After the reagents are made up to volume and thoroughly mixed, the color deepens gradually for 15 minutes. Then for 5 minutes very little change can be noted in the colorimeter. A slight increase follows and upon standing overnight a fine blue precipitate settles out, leaving the color of the liquid much less intense. All readings are, therefore, made between 15 and 25 minutes after the reagents are mixed. In determining the phosphorus in a series of solutions, it is very easy to make the readings at exactly 15 minutes.

Since boiling with perchloric acid displaces nitric and hydrochloric acids and dehydrates the silica (*17*), no exhaustive study of interfering substances was made. Solutions containing hydrogen peroxide or nitric acid, however, must be boiled with perchloric to obtain the correct values even when the phosphorus is already in the inorganic form.

The presence of 5 mg. of iron in the 25-ml. final volume gives a greenish cast to the blue color but it does not affect the reliability of the readings when using a red filter. Smaller aliquots are usually taken when this greenish tinge becomes apparent to the eye. Although titanium and vanadium react with ammonium molybdate, the high acid concentration prevents any such interference. Should magnesium chloride be present in solutions digested according to the official method, it does not interfere with the color formation.

Stannous chloride was tried but was discarded in favor of 1,2,4-aminonaphtholsulfonic acid. Although smaller amounts of phosphorus (0.003 mg.) may be detected in the optimum range of the instrument when using stannous chloride, as little as 2 p. p. m. of ferric iron interferes with the reaction, whereas the phosphorus values are still accurate in the presence of 200 p. p. m. of iron when using the sulfonic acid reagent and perchloric acid. Then, too, extremely slight variations in the size of the stannous chloride drops cause decided differences in the readings of the instrument.

Reagents (phosphorus-free). Perchloric acid, 60 per cent.

Ammonium molybdate, 5 grams mixed with 100 ml. of distilled water, allowed to stand overnight, then filtered into a dark-glass bottle.

1,2,4-Aminonaphtholsulfonic acid, recrystallized according to Fiske and Subbarow (*3*, p. 388). A 0.125-gram sample of this reagent is mixed with 44 ml. of 15 per cent sodium hydrogen sulfite solution in a dark, glass-stoppered bottle. A 20 per cent solution of sodium sulfite is then added drop by drop until the solution is clear. This should require 5 to 7 ml.

The reagents and the distilled water used in making the solutions to volume are kept at 25° ± 4° C. Fresh solutions are prepared at least every two weeks.

Calibration of the Photometer. The depth of the blue color is measured in a V-type Aminco photometer, equipped with red filters, calibrated by using various dilutions of two different standard solutions of recrystallized monopotassium phosphate. The readings were checked at several points with phosphates of known purity. W. Edwards Deming of this bureau made a statistical analysis of the resulting curve which showed the optimum range of the instrument to be between 0.015 and 0.1 mg. of phosphorus in 25 ml., although 0.0025 mg. of phosphorus gives a visible blue. This consideration governed the size of the soil sample and the final dilution after the digestion with perchloric acid. Thus for a soil of low phosphorus content, such as Norfolk sandy loam, a 5-gram sample and a final volume of 100 ml. are necessary for a color intensity falling within the range of the instrument. For the Barnes loam, however, a 2-gram sample in 200 ml. is adequate. The same conditions of acid concentration, temperature of reagent solutions, and age of the blue complex which had been adopted for this method, were observed in calibrating the photometer. Frequent checks on the calibration curve have shown no change in two years.

Analytical Procedure. The prepared soil sample of 2 to 5 grams is weighed into a 300-ml. Erlenmeyer flask, mixed with 30 ml. of 60 per cent perchloric acid, and digested in a hood until the dark color due to the organic matter disappears. Heating is continued 20 minutes longer to be sure that all the phosphorus is converted to the inorganic form. At this stage heavy white fumes of perchloric acid appear and the insoluble material becomes like white sand. An additional 1 to 2 ml. of perchloric acid may be used to wash down any black particles that stick to the sides of the flask; occasionally the flask is shaken. The total time on the hot plate averages 40 minutes.

When the sample is sufficiently cool to avoid spattering, it is diluted with distilled water and filtered into an appropriate-sized volumetric flask. The residue is carefully washed to bring the volume to the mark. The equivalent of about 20 ml. of 60 per cent perchloric acid was found in this diluted volume. If the aliquot used thus contains 0.5 ml. or more of perchloric acid, due allowance therefor is made when adding acid to develop the blue color.

After thorough mixing, an aliquot of 1 to 15 ml. is pipetted into a 25-ml. volumetric flask, perchloric acid is added to total 2.5 ml., and the volume is diluted with distilled water to about 20 ml. The flask is shaken after each addition. Then 0.8 ml. of the sulfonic acid reagent is added and finally 2 ml. of ammonium molybdate. The volume is adjusted to 25 ml., mixed well, and the color measured in the photometer when the solution is 15 minutes old. There is no apparent turbidity if the sulfonic and molybdate reagents are added when the volume is near the final dilution.

The zero setting of the instrument is adjusted for the blank of the reagents just before each series of readings by following a procedure and time interval identical with those used for the unknowns. This compensates for the age of reagents and differences in time of preparations for carrying out the color reaction. The phosphorus present is then quickly calculated from the calibration chart of the instrument. The results of the phosphorus determinations by this method are shown in the last column of Table I.

For preliminary trials, Erlenmeyer flasks graduated at 200 and 250 ml. were used and the sample was diluted therein without filtering off the sandy residue. After thorough mixing on a me-

TABLE I. PHOSPHORUS CONTENTS OF SOILS DETERMINED BY GRAVIMETRIC AND COLORIMETRIC METHODS

Sample No.	Kind and Location of Soil	Horizon	Depth	Gravimetric			
				P_2O_5 as $Mg_2P_2O_7$	P_2O_5 in residue[a]	P_2O_5 in $Mg_2P_2O_7$ + residue	P O_5, Colorimetric
			Inches	%	%	%	%
C-2929	Barnes loam, Labolt, S. D.	A	0– 9	0.150	0.024	0.174	0.173
				0.147	0.033	0.180	0.174
C-2930	Barnes loam, Labolt, S. D.	B_1	9–17	0.097	0.009	0.106	0.102
				0.097	0.007	0.104	0.102
C-2916	Carrington loam, Buchanan County, Iowa	A_1	0– 3	0.115	0.015	0.130	0.133
				0.126	0.006	0.132	0.133
C-2917	Carrington loam, Buchanan County, Iowa	A_2	3–13	0.112	0.008	0.120	0.119
				0.115	0.006	0.121	0.118
C-3871	Kirvin fine sandy loam, Tyler, Texas	A	0–12	0.044	0.011	0.055	0.053
				0.046	0.010	0.056	0.053
C-3872	Kirvin fine sandy loam, Tyler, Texas	B	12–24	0.079	0.005	0.084	0.077
				0.078	0.005	0.083	0.076
C-3174	Russell silt loam, Morgan County, Ind.	A	0– 2	0.087	0.005	0.092	0.085
				0.090	0.004	0.094	0.086
C-3175	Russell silt loam, Morgan County, Ind.	B	2– 8	0.047	0.005	0.052	0.053
				0.045	0.005	0.050	0.052
C-1600	Cecil clay loam, Abbeville County, S. C.	B	3– 8	0.044	0.007	0.051	0.047
				0.046	0.005	0.051	0.046
C-1671	Chester loam, Rockville, Md.	A_2	2–10	0.105	0.003	0.108	0.107
				0.103	0.005	0.108	0.106
C-1672 and 3	Chester loam, Rockville, Md.	B	10–32	0.080	0.0004	0.080	0.079
				0.081	0.0008	0.082	0.078
	Las Vegas, Clark County, Nev.	A	. . .	0.062	0.009	0.071	0.070
				0.066	0.010	0.076	0.071
C-1601	Norfolk sandy loam, Edgefield County, S. C.	A	0–14	0.021	0.000	0.021	0.021
				0.021	0.000	0.021	0.020

[a] Determined colorimetrically.

chanical shaker, the needed aliquot was filtered off. This saved considerable time in working out such details as the amount of acid, length of heating, and particle size necessary. Even with such differences in technique, in all the sixty-seven preliminary determinations, the maximum variation from the finally accepted value was only 0.013 per cent of phosphorus pentoxide.

In this study an accuracy of 0.001 per cent was desired and all factors, therefore, were carefully controlled. A working curve for the instrument can, however, be quickly prepared with as few as eight points if an accuracy of 0.01 per cent is all that is demanded. In this case, the reagent solutions need not be made up so often, since the zero setting of the colorimeter compensates for their cloudiness. The method can also be adapted for use in a visual colorimeter.

The same samples of soil were analyzed by Robinson's method, in which the sample is digested with hydrofluoric acid after destroying the organic matter with nitric acid and by igniting with a Bunsen burner. The phosphorus is precipitated from a nitric acid-solution by ammonium molybdate, redissolved and precipitated as magnesium ammonium phosphate, ignited, and weighed on a Kuhlmann balance as magnesium pyrophosphate. The results of this method are given in the fifth column of Table I.

Details inherent in the gravimetric method would tend to make its results lower than those of a colorimetric method. However, the unusual difference between the two methods in the values for the Barnes loam A sample led to a few qualitative tests for phosphorus in the residues discarded after the hydrofluoric acid digestion. In all preliminary trials, the colorimetric tests showed phosphorus present in the residue.

Since the qualitative tests were all positive, each of the residues from the hydrofluoric acid treatment was boiled with 25 ml. of perchloric acid and the phosphorus therein was determined colorimetrically. The results are shown in column 6. It is also evident from column 7 that the sum of phosphorus found in the magnesium ammonium phosphate precipitate and that left in the residue from the nitric acid extraction is in close accord with the phosphorus values obtained colorimetrically.

The residues from several perchloric acid digestions were also tested for possible phosphorus inclusions in the silicates present in the soil.

The following samples were weighed in duplicate: 2 grams of Barnes loam A, 2 grams of Carrington loam A_1, 2.5 grams of Chester loam A, 3 grams of Cecil clay loam B, and 4 grams of Kirvin fine sandy loam B. The samples were digested in 30 ml. of perchloric acid in the usual manner and the residue was washed until acid-free. The filter paper containing the residue was then placed in a platinum dish, and Robinson's hydrofluoric acid procedure followed. After the nitric acid had been expelled by boiling with perchloric acid, the phosphorus was determined colorimetrically on the total sample. The Barnes loam residue contained 0.005 per cent of phosphorus pentoxide, but the residues from the other four soils gave negative results. Where there are strong reasons to suspect that the soil phosphorus is present in some unusual form which might be unaffected by digestion with perchloric acid, a preliminary sodium carbonate fusion is recommended.

The perchloric acid method was also tried on Bureau of Standards standard phosphate rock samples to determine the magnitude of dilution errors. A Kuhlmann balance and certified glassware were used, and the results were corrected for moisture determined by the technique previously described (*9*). The Tennessee phosphate rock No. 56a results corresponded to 99.15 per cent of the certificate value (32.90 per cent phosphorus pentoxide) and the Florida land pebble rock No. 120, to 97.84 per cent of the certificate value (35.20 per cent phosphorus pentoxide). Both samples were soluble in perchloric acid at room temperature and six determinations were made in 90 minutes.

DETERMINATION IN PRESENCE OF ARSENIC. Arsenic is known to react with ammonium molybdate to form an arsenomolybdate which also gives a blue complex upon reduction. Digestion of the soil with perchloric acid converts any spray residues to the pentavalent form, causing an interference that has an additive effect upon the phosphorus values. Since preliminary comparisons showed that the colorimetric method gave higher results than the gravimetric, it seemed advisable to look for possible interference from arsenic in the samples tested.

Pett (*10*) has pointed out that arsenites, in contrast to arsenates, do not give a blue color with the phosphorus reagents and he has developed a method which permits the determination of phosphorus in the presence of arsenic. Using sodium bisulfite and sulfuric acid, he found that a 60-minute reduction period at 50° C. was necessary to complete the reaction. But the effect of heat upon the intensity of the blue color had been observed since early in 1939—for example, 1 ml. of a standard monopotassium phosphate solution gives an instrument reading of 40.5 at a room temperature of about 23° C. But if the standard is diluted and warmed to 50° C. in the presence of perchloric acid prior to the color development, the instrument readings will range from 40.5 to 191.0, depending upon the amount of acid added. These observations were later corroborated by Allen (*1*) and these factors were taken into consideration in the calibration of the colorimeter and in the development of the procedure.

Preliminary tests on potassium arsenate showed that heat was unnecessary to effect the reduction of the arsenite form if perchloric acid were used and details of this substitution were worked out. Pett's findings for the necessary concentration of sodium bisulfite for this reaction were verified. One-tenth gram was ineffective, but 0.4 gram was adequate and his concentration was adopted.

The time necessary to reduce the arsenates completely is dependent upon their concentration when using sodium bisulfite and perchloric acid at room temperature. Amounts below 0.02 mg. of arsenic are reduced in less than 30 minutes, whereas 0.1 mg. of arsenic must stand 4 to 5 hours. There is no harm in letting the solutions stand overnight if the reagent blank for setting the photometer is allowed to stand in a volumetric flask for the same length of time.

The blank for 2.5 ml. of perchloric acid in 15 ml. of water increases according to the time it stands in the flask. The presence of 0.4 gram of sodium bisulfite is inconsequential in this connection. But when the molybdate and sulfonic acid reagents are added to a dilute acid solution that has stood for two days in a volumetric flask, a milky-blue tinge appears. It is imperative, therefore, that the reagent blank be prepared and determined for the same time interval as that used for the sample.

Since the straight colorimetric readings had been made on these samples, and it was known that none of them was high enough to approach a combined value of 0.1 mg. of arsenic, a 3-hour reducing period was adopted to be sure that all the arsenic which might be present was in the arsenite form.

PROCEDURE FOR ELIMINATION OF ARSENATES. An aliquot of the perchloric acid extract of the soil is placed in a 25-ml. volumetric flask and enough acid is added to bring its concentration up to 2.5 ml. An appropriate-sized glass scoop is used to add 0.4 gram of solid sodium bisulfite. Since the bisulfite does not affect the blank, such a measurement is close enough. The neck of the flask is washed with water and the volume brought to 20 ml. The flask is shaken a little to dissolve the solid, and then is allowed to stand on the bench for 3 hours. A blank is prepared at the same time and in the same manner. After standing, the procedure for the development of the blue color is continued as described above. If a lower second reading is obtained, it indicates that arsenic is present in the sample and that the lower reading is the true value for the phosphorus.

The values obtained with this modification agreed with those of the straight determination and proved conclusively that no arsenic was present in the soils used in this study.

The perchloric acid method was also run on six samples of soil that were very kindly supplied by R. D. Chisholm of the Moorestown, N. J., laboratory of the Bureau of Entomology and Plant Quarantine. These soils had been treated with lead arsenate for the control of Japanese beetles and contained 0.017 to 0.059 per cent of arsenic. After the arsenates had been converted to arsenites by the procedure just described, the phosphorus was easily determined. The instrument used, however, gives only arbitrary readings not simply related to transmission values and has no spectral dispersion. It would be necessary, therefore, to measure true spectral transmissions in order to determine arsenic in the presence of phosphorus.

Acknowledgment

The writer wishes to thank Franklin E. Allison for his many helpful suggestions and S. B. Hendricks, M. S. Anderson, W. O. Robinson, W. L. Hill, E. J. Jones, H. G. Byers, and L. A. Pinck for their constructive criticism of the manuscript.

The author is indebted to K. D. Jacob of this bureau for supplying various phosphates which were used as checks upon the method, and to his staff for making several volumetric phosphorus determinations that were used to check the preliminary trials of the method.

Literature Cited

(1) Allen, R. J. L., *Biochem. J.*, 34, 858 (1940).
(2) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 4th ed., p. 12 (1935).
(3) Fiske, C., and Subbarow, Y., *J. Biol. Chem.*, 66, 375 (1925).
(4) Gieseking, J. E., Snider, H. J., and Getz, C. A., IND. ENG. CHEM., ANAL. ED., 7, 185 (1935).
(5) Hilbert, G. E., Pinck, L. A., Sherman, M. S., and Tremearne, T. H., *Soil Sci.*, 46, 409 (1938); see p. 411.
(6) Kahane, Ernest, "L'Action de l'Acide Perchlorique sur les Matières Organiques", p. 124, Paris, Hermann et Cie, 1934.
(7) King, E. J., *Biochem. J.*, 26, 292 (1932).
(8) Martland, M., and Robison, R., *Ibid.*, 20, 847 (1926).
(9) Milner, R. T., and Sherman, M. S., IND. ENG. CHEM., ANAL. ED., 8, 427 (1936).
(10) Pett, L. B., *Biochem. J.*, 27, 1672 (1933).
(11) Pinck, L. A., Sherman, M. S., and Allison, F. E., *Soil Sci.*, 51, 351 (1941).
(12) Rae, J. J., and Eastcott, E. V., *J. Biol. Chem.*, 129, 255 (1939); see p. 257.
(13) Robinson, W. O., U. S. Dept. Agr., *Circ.*, 139, 13 (Oct., 1930).
(14) Shelton, W. R. and Harper, Horace J., *Iowa State Coll. J. Sci.*, 15, 403 (1935).
(15) Smith, G. Frederick, Chemical Co., "Perchloric Acid", (Nov., 1934); "Mixed Perchloric, Sulfuric, and Phosphoric Acids and Their Applications in Analysis" (1935).
(16) Volk, G. W., and Jones, Randall., *Soil Sci. Soc. Amer. Proc.* 2, 197 (1937).
(17) Willard, H. H., and Cake, W. E., *J. Am. Chem. Soc.*, 42, 2208 (1920).

PRESENTED before the Division of Analytical and Micro Chemistry at the 102nd Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J.

Semimicropycnometer for Heavy Water

B. J. FONTANA AND MELVIN CALVIN
University of California, Berkeley, Calif.

IN THE course of investigating some exchange reactions, small samples (about 1 cc.) of heavy water were manipulated and purified by distillation in a high-vacuum line. A simple and convenient pycnometer was devised which took advantage of the use of the high-vacuum line for filling it. The densities determined by means of this pycnometer are reproducible to 1 to 2 parts per 10,000, without thermostatic control. The results can be calculated for any temperature between 15° and 40° C. within this limit of error, provided the difference between the temperature of the actual determination and the temperature at which the density value is desired is not greater than 5°. For the usual determination of d_4^{25} or d_4^{20} the pycnometer is then conveniently weighed at room temperature.

TABLE I. TYPICAL PYCNOMETER CALIBRATION

(Weight of pycnometer, 3.4616 grams)

Weight of Water W	Temperature ° C.	D/W^a	Deviation from Mean $\times 10^{-4}$
0.7935	20.9	1.2578	+1.5
0.7937	21.2	1.2574	−2.5
0.7935	20.7	1.2578	+1.5
0.7936	21.1	1.2576	−0.5
	Av.	1.25765	±1.5

[a] D = density of water at temperature of determination; D/W then is reciprocal of volume of pycnometer.

The method employed by Gilfillan and Polanyi (*3*) in filling their flotation micropycnometer suggested the construction of an ordinary weight pycnometer which could be filled by the same method. Their micropycnometer was evacuated and the sample allowed to draw up into the pycnometer upon re-admitting air to the system. The authors' pycnometer is illustrated in Figure 1, *a*. Sizes of from 0.5- to 1-cc. capacity made from ordinary Pyrex tubing have been constructed and used.

The pycnometer is lowered into the removable tube, Figure 1, *b*, with the ground tip resting at the bottom of the bulb. The tube is inserted in a vertical position at a suitable place in the high-vacuum line. When the sample has been suitably purified, it is frozen (carbon dioxide or liquid air), and the system, including the pycnometer arm, is evacuated to 10^{-5} mm. or better for 15 to 30 minutes. Such a high degree of evacuation is necessary to

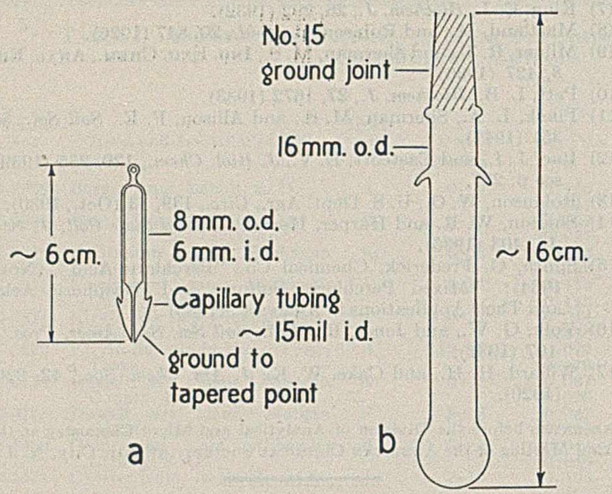


FIGURE 1. DIAGRAM OF PYCNOMETER AND VACUUM LINE ATTACHMENT

prevent the formation of an air bubble when the sample is introduced into the pycnometer. The sample is then thawed and distilled over into the pycnometer arm at room temperature by immersing the arm in a cooling bath (carbon dioxide or liquid air). The sample is again melted and air is carefully allowed to re-enter the evacuated system. The sample should rise into and completely fill the pycnometer with no visible air bubble at the top of the bulb. Not more than 0.05- to 0.1-cc. excess of water over the capacity of the pycnometer is required by this method. If a very small air bubble appears, it will usually dissolve if the pycnometer is allowed to stand, with tip still immersed, for an hour or more. The weight of the dissolved air is negligible. When the pycnometer is removed from the tube and suspended on the balance pan the sample should preferably be about 5° to 10° below room temperature.

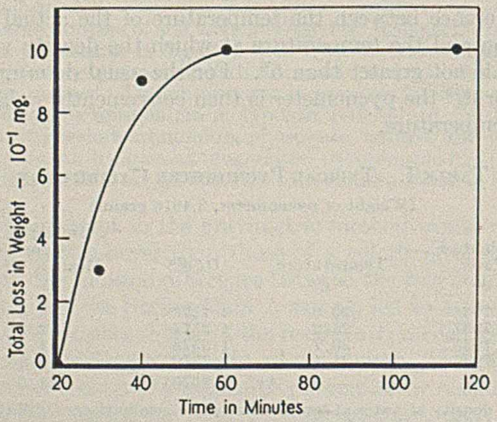


FIGURE 2. TYPICAL PYCNOMETER WEIGHING

The pycnometer is carefully wiped and then suspended with ground tip up. The balance case is then closed (thermometer in balance case) and the pycnometer is allowed to stand for about one hour before weighing. As the sample warms up to room temperature the water expands through the capillary tip and evaporates at the tip as fast as it appears. Constant weight is reached in less than an hour and is maintained for a long period after. This is illustrated in Figure 2, where a typical example of a series of weighings of a filled pycnometer is given, starting 20 minutes after the sample was put into the balance case.

To empty, the pycnometer is replaced in its tube with the tip resting on a small metal coil a short distance above the bottom of the bulb. The sample usually will not pump out directly upon evacuating, but the water slowly evaporates along the capillary until a small bubble appears at the top of the capillary. On readmitting air to the system and tapping the pycnometer, the air bubble will rise to the top of the bulb; evacuating now readily expels the sample.

The pycnometer may be cleaned with chromic acid cleaning solution by alternately filling and expelling, with the use of an ordinary water aspirator.

The reproducibility of the density determinations is illustrated by the typical calibration results tabulated in Table I for a pycnometer of about 0.8-cc. capacity, with four separate samples of ordinary water. The average deviation from the mean is seen to be slightly greater than 1 part in 10,000.

In order to calculate the composition of the sample of heavy water, using the formula determined by Longsworth (*6*, *9*), the density at 25° C. is required. The density at 25° C. (or at any other temperature, t_2, between 15° and 40°) can be readily calculated from the determined density at temperature t_1. The difference in density, $d_2 - d_1$, at the respective temperatures, t_2 and t_1, is obtained for ordinary water from any suitable tables (*4*). This difference is added to the observed value of the density to give the desired density.

TABLE II. VARIATION OF DIFFERENCE IN DENSITY OF D_2O AND H_2O WITH TEMPERATURE[a]

t° C.	5	10	15	20	25	30	35	40
$\Delta(\Delta d_4^t) \times 10^{-4}$	..	+7.0	+4.9	+2.6	+1.2	−0.8	−2.7	−2.6

[a] The recent data of Chang and Chien (*1*, *8*) indicate that these values are very probably in error. The effect of the new data is to make $\Delta(\Delta d)$ slightly larger (approximately 1.5×10^{-4} part larger) in the intervals of 15–20° C. and 20–25° C. only. The newer data, of course, should be used to estimate corrections as suggested herein.

That this transformation can ordinarily be done with negligible error is seen from the data of Lewis and MacDonald (*5*) as recalculated by Farkas (*2*). Table II lists the differences between the difference in density of heavy water and water at various temperatures calculated from the data of Farkas (*2*). The difference in density between ordinary water and pure deuterium oxide is seen to vary by less than 4 parts per thousand from the 25° C. value over the range from 15° to 40° C.—that is, in this range the largest error possible in a density value so transformed would be 4 parts in 10,000 when interpolating from a value at 15° to one at 25° C. Ordinarily the error will be much less than this—for example, transforming densities over the 5° ranges from 20° to 25° or 25° to 30° results in an error of 1 to 2 parts in 10,000. In more dilute solutions of deuterium oxide these errors should be of the same order of magnitude or less. For greater accuracy throughout the whole range of temperatures given, the data of Farkas (*2*) may be used to estimate small corrections for the transformations. The nonlinearity of density with mole fraction (*7*) must, however, be borne in mind when making estimates of the corrections for mixtures of deuterium oxide and water.

Though especially suited to the determination of the density of heavy water, this pycnometer might be used for other pure liquids or volatile mixtures. In such cases, however, temperature control would probably be desirable.

Literature Cited

(1) Chang, T. L., and Chien, T. Y., *J. Am. Chem. Soc.*, 63, 1709 (1941).
(2) Farkas, "Light and Heavy Hydrogen", p. 173, Cambridge University Press, 1935.
(3) Gilfillan and Polanyi, *Z. physik. Chem.*, 166A, 254 (1933).
(4) Handbook of Chemistry and Physics, 24th ed., p. 1648, Cleveland, Chemical Rubber Publishing Co., 1940.
(5) Lewis and MacDonald, *J. Am. Chem. Soc.*, 55, 3057 (1933).
(6) Longsworth, *Ibid.*, 59, 1483 (1937).
(7) Luten, *Phys. Rev.*, 45, 161 (1934).
(8) Stokland, Ronaess, and Tronstad, *Trans. Faraday Soc.*, 35, 312 (1939).
(9) Swift, *J. Am. Chem. Soc.*, 61, 198 (1939).

CONTRIBUTION from the Radiation Laboratory and the Department of Chemistry. Work supported by funds from the foundation of the late A. B. Miller.

A Polarograph Reading Directly in Percentage

Analysis of Lead Arsenate

B. P. CALDWELL AND SOLOMON REZNEK[1]
Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

When the conditions can be established so as to obtain a polarographic "wave" or "step" such that the upper and lower levels are essentially parallel to the voltage axis and to each other, a manually operated polarograph may be so manipulated as to read directly in terms of percentage. A polarograph capable of being so operated was constructed. A continuously variable shunt, with coarse and fine adjustments, is required in place of the usual stepwise shunt. The apparatus consists of three inexpensive radio-type potentiometers, a voltmeter, and a wall-type galvanometer with lamp and scale, together with battery and dropping mercury electrode.

The technique of using a manually operated polarograph so as to give direct percentage readings is described and an application to the analysis of commercial lead arsenate insecticides is given.

WHILE automatic polarographs (*1*) are convenient and even essential for many types of work, the basic principles of polarography may often be usefully applied by means of relatively simple manually operated devices. These, on the other hand, may range from the precision research instrument of Kolthoff and Lingane (*4*) to the very simple arrangements of Müller (*7*) or of Petering and Daniels (*9*).

Neither the automatic nor the manually operated polarographs are designed to read directly in terms of percentage of a given substance. Quantitative determinations are based on (1) the measurement of the wave height of the full wave, as obtained automatically or plotted from manual readings, (2) the increase in current between two voltage settings selected after an examination of the full wave, the "increment" method, or (3) the proportional increase in wave height caused by the addition of a known concentration of a particular substance to a solution containing an unknown concentration of the substance, the "internal standard" method. Since the observed wave heights depend, among other things, on the constants of the galvanometer used, each of these methods requires a calibration curve, a series of standards, or a calculation of some sort to determine the concentration from the wave height.

While Kolthoff and Lingane (*5*) describe a shunt circuit which allows the observed diffusion current to be read directly in microamperes, it is believed that a circuit designed to read directly in terms of percentage of a given substance would further simplify routine analyses.

To use such a circuit it is assumed, as in the increment method, that the diffusion current is directly proportional to the concentration and that the wave form is reasonably close to the ideal—i. e., the two levels are parallel to one another and cover an appreciable voltage interval.

The stepwise construction of the Ayrton shunt usually employed precludes exact adjustment of the galvanometer beam to a predetermined point on the scale. On the other hand, if the shunt consists of a continuously variable resistance, the galvanometer scale should be susceptible of being set to read directly in terms of percentage. The instrument described was so constructed.

The application to the analysis of lead arsenate insecticides is intended merely as an illustration of the technique of using the instrument. Normally, the lead content of such a product is determined more precisely by chemical methods. In this application the polarographic method serves as a rapid sorting-out method. The chief usefulness in the method would lie in the determination of relatively minor constituents, present in the order of 1 per cent or less, with a precision equal, in such cases, to most chemical methods.

Apparatus

The shunt (arranged in an Ayrton connection, so that the total resistance across the galvanometer is constant) consists of two General Radio Company potentiometers arranged in tandem (Figure 1). A fixed resistance is inserted in the galvanometer circuit to bring the total resistance up to the critical damping resistance of the galvanometer employed.

A third General Radio Company potentiometer serves to deliver any desired potential from a battery, which may consist of dry cells or a 4- or 6-volt storage battery. The applied potential, as indicated by the Weston Model 301 voltmeter, *V*, may be adjusted to 0.02 volt, which is sufficiently close for most applications.

In more precise instruments the voltage is determined by a potentiometer balanced against a standard cell. While a low-resistance voltmeter (most cheaper types) may show some deviation from the true reading, this is immaterial in practical work, since standards and unknowns are electrolyzed at the same dial (voltage) settings.

The galvanometer was a Leeds & Northrup 2239 D type, with a period of 28 seconds, a sensitivity of 2×10^{-9} ampere per mm. per meter, and a critical damping resistance of 11,500 ohms.

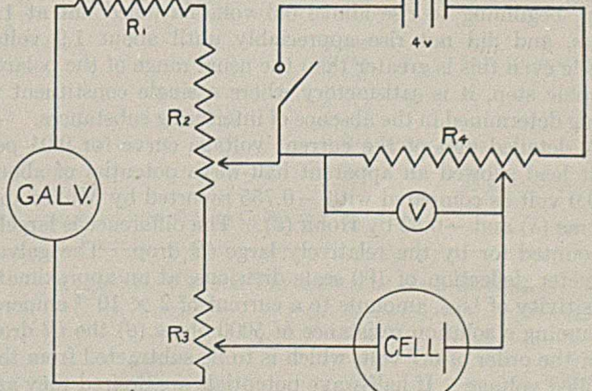


FIGURE 1. DIAGRAM OF CIRCUIT

R_1.	9000-ohm fixed resistance
R_2.	2000-ohm Model 314-A General Radio Co. potentiometer
R_3.	20-ohm Model 214-A General Radio Co. potentiometer
R_4.	50-ohm Model 214-A General Radio Co. potentiometer

---

[1] Present address, U. S. Food and Drug Administration, Philadelphia, Penna.

Table I. Calibration of Galvanometer Scale in Terms of Percentage

Voltmeter Reading	Scale Readings					
	Blank[a]	0.01% Pb	0.01% Pb[b]	0.015% Pb	0.020% Pb	0.025% Pb
Volts						
0.4	−0.8	...	...	...	...	...
0.5	0.0	0.0	0.0	0.0	0.0	0.0
0.6[c]	0.0	0.0	0.0	0.2	0.2	0.5
1.1	2.2	86.0	...	...	...	...
1.2	2.8	93.5	...	...	...	...
1.3	3.5	98.2	102.5	148.5	198	244
1.4	4.0	100.2	104.0	153.5	201	248
1.5	4.5	101.1	105.3	155.1	205	251
1.6	6.1	103.5	106.7	157.0	208	255
1.7	12	108.0	110.2	158.8	211	259

[a] 20 cc. of foundation solution diluted to 50 cc.
[b] Solution set to read 104.0 at 1.4 volts to allow for blank.
[c] Readings between 0.6 and 1.1 volts omitted to condense table.

With a fixed resistance of 9000 ohms, the total resistance of the shunt circuit was 11,020 ohms, thus leaving the galvanometer slightly overdamped. The galvanometer was used with a Leeds & Northrup lamp and scale, No. 2100.

A small (10- to 15-cc.) beaker was used as the electrolysis cell. No attempt was made to protect the contents from air, since the sulfite present was sufficient to take care of any oxygen diffusing into the solution for a considerable period. A large calomel electrode of a simple type (*3*) served as an anode; the dropping mercury cathode consisted of a 10-cm. piece of "marine barometer" tubing (Corning) attached to a 60-cm. length of heavy-walled rubber tubing previously washed with alkali, acid, and water to remove talc and surface sulfur. With the particular capillary and head of mercury used, the drop rate in distilled water, under zero voltage, was 4.0 seconds.

An on-off single-pole snap switch serves to disconnect the battery.

Procedure

To employ the instrument so that a reading is obtained directly in terms of percentage, the following procedure is employed:

The approximate range of concentrations at which a most nearly ideal step is obtained must first be ascertained. At too low concentrations the residual current, due to traces of oxygen, impurities, "condenser current", etc. (*4*), approaches the diffusion current of the ion being determined. At too high concentrations the characteristics of the curve become such as to make it less useful for quantitative comparisons. The slope becomes flatter, so that the step occupies too great a voltage range and the upper plateau is no longer parallel to the lower.

In the present case, for example, it was found that concentrations of lead up to about 0.01 per cent were suitable. The step, beginning to rise above 0.6 volt, flattened out at 1.4 volts, and did not rise appreciably until about 1.9 volts. While even this is greater than the usual range of the polarographic step, it is satisfactory where a single constituent is being determined in the absence of interfering substances.

A detailed plot of the current voltage curve for 0.01 per cent lead showed an apparent half-wave potential of about −0.9 volt as compared with −0.755 reported by Müller and Petras (*8*) and −0.82 by Hohn (*2*). The difference is largely accounted for by the relatively large *iR* drop. The galvanometer deflection of 100 scale divisions, at an approximate sensitivity of $^1/_{100}$, amounts to a current of 2×10^{-5} ampere. Assuming a solution resistance of 5000 ohms (*6*) the *iR* drop is of the order of 0.1 volt, which is to be subtracted from the applied voltage. If half-wave potentials are desired they are determined from the voltmeter readings by making correction for *iR* drop, and anode potential, if necessary. In actual analysis the voltmeter readings are convenient dial settings to indicate that the same applied voltage has been used for standard and unknown.

At lead concentrations around 0.01 per cent it is necessary to remove dissolved oxygen, normally present in solution to the extent of about 8 p. p. m. This was conveniently accomplished by the use of sodium sulfite and by working in alkaline solution to prevent precipitation of lead sulfite. Alkali, sulfite, and Methocel (Dow brand of methyl cellulose, grade M-361, here used as a "maximum" suppressor) were incorporated in the foundation solution. By using the same dilution of this solution throughout, the composition was kept constant except for the concentration of the material being determined. Temperature control was not found necessary, other than to allow the solutions, previously made to volume in volumetric flasks, to stand at room temperature in the vicinity of the polarograph together with the standards. As a reading takes but a few minutes by the method described, the samples and standards may all be run within a time interval during which the room temperature is not likely to change appreciably. If a change of more than 0.5° C. is anticipated, some sort of bath for temperature control may be necessary.

Samples (0.500 gram) are dissolved in 50 cc. of 5 per cent sodium hydroxide with the aid of heat if necessary, and made to 500 cc. To a 5-cc. aliquot are added 20 cc. of foundation solution (10 cc. of 5 per cent sodium hydroxide, 2.5 cc. of 1 per cent Methocel, and 2.5 cc. of 10 per cent sodium sulfite made to 20 cc.) and the sample is made to 50 cc. The final dilution thus contains 0.01 per cent of sample, 1 per cent of sodium hydroxide, 0.05 per cent of Methocel, and 0.5 per cent of sodium sulfite. The proportions of the constituents of the foundation solution may be allowed to vary somewhat, but the volume of solution added to sample and standard must be accurately measured (pipetted), so that the concentrations are the same in samples and standards. The foundation solution is stable except for the sulfite, which should be prepared daily.

Five to 10 cc. of a standard containing 0.01 per cent of lead, prepared by addition of foundation solution to a suitable volume of a standard lead nitrate solution, are poured into the beaker serving as electrolysis cell, the galvanometer scale is set at 0 with the voltmeter reading 0.5 volt, and the coarse and fine shunts are manipulated so that the 0.01 per cent solution gives a reading of approximately 100 on the scale at a voltage setting of 1.4 volts. The standard solution is removed, the cathode and agar-salt bridge are connected to the anode washed with water, and a beaker containing foundation solution, diluted in the same manner (20 to 50 cc.) is introduced. With the shunt settings as before, the displacement of the galvanometer due to the residual current in the range 0.5 to 1.4 volts is determined. The 0.01 per cent lead standard is re-introduced, after rinsing the electrodes by immersion in a beaker containing the solution to be measured, the galvanometer is set at 0 at 0.5 volt as before, and the voltmeter is again set at 1.4 volts. The fine adjustment is then manipulated so that the reading at 1.4 volts is 100, plus the correction due to the residual current (Table I, column 4). Subsequent readings are then directly in terms of percentage, after subtracting the scale divisions equivalent to the residual current.

Table II. Lead Content of Lead Arsenate Insecticides

Sample	Pb Content by Chemical Analysis[a]	Scale Readings				Pb Content from Scale Reading[b]
		0.5 volt	1.3 volts	1.4 volts	1.5 volts	
23	70.1	0.0	74.2	74.8	75.1	70.8
25	59.8	0.0	64.0	64.3	64.9	60.3
33	59.6	0.0	63.5	64.0	64.2	60.0
72	59.4	0.0	62.0	63.2	63.8	59.2
93	58.5	0.0	60.9	61.3	61.7	57.3

[a] Gravimetric chromate method.
[b] From scale reading at 1.4 volts by subtracting 4.0 units to correct for residual current.

With shunt settings undisturbed, the sample solutions were measured with the results shown in Table II. The samples consisted of lead arsenate and basic lead arsenate insecticides, previously analyzed for lead content by chemical assay by W. J. Kirby, Insecticide Division, Agricultural Marketing Service. After subtracting the blank (4 scale divisions at 1.4 volts) the readings are compared in terms of lead content with the chemical analysis.

The zero setting is checked at the end of each reading to compensate for galvanometer drift. Another variation to be allowed for is the oscillation of the galvanometer beam due to the changing size of the mercury drops. With a long-period galvanometer this amounts to about one scale division under the above conditions, but the amplitude of swing is very constant and it is satisfactory to take either the maximum, the minimum, or the middle of the swing for each reading, so long as a consistent practice is followed.

It is seen (Table I) that after setting the shunt so that the reading at 1.4 volts in column 4 represents 0.01 per cent of lead, after subtracting the blank, the subsequent readings at the same voltage are directly in terms of percentage up to concentrations of about 0.025 per cent when the proportionality between wave height and concentration begins to fall off. Within this range the precision is within 2.5 per cent and somewhat better than this at the lower concentrations.

Literature Cited

(1) Heyrovský, J., *Phil. Mag.*, 45, 303 (1923).

(2) Hohn, H., "Chemische Analysen mit dem Polarographen", Berlin, Julius Springer, 1937.

(3) Kolthoff, I. M., "pH and Electro-Titrations", p. 94, New York, John Wiley & Sons, 1931.

(4) Kolthoff, I. M., and Lingane, J. J., *Chem. Rev.*, 24, 1 (1939).

(5) Kolthoff, I. M., and Lingane, J. J., "Polarography", New York, Interscience Publishers, 1941.

(6) Müller, O. H., *Chem. Rev.*, 24, 67 (1939).

(7) Müller, O. H., *J. Chem. Education*, 18, 111 (1941).

(8) Müller, R. H., and Petras, J. F., *J. Am. Chem. Soc.*, 60, 2990 (1938).

(9) Petering, H. G., and Daniels, F., *Ibid.*, 60, 2796 (1938).

PRESENTED before the Division of Analytical and Micro Chemistry at the 102nd Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J. From a dissertation submitted by S. Reznek to the graduate faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of doctor of philosophy, June, 1940.

Micromethod for Identification of Volatile Liquids

Vapor Pressure, Boiling Point, and Olefin Content of Cyclobutane and *cis*-2-Butene

SIDNEY W. BENSON, Mallinckrodt Chemical Laboratories, Harvard University, Cambridge, Mass.

A PREVIOUS paper described a micromethod for identifying hydrocarbons by their physical properties (*1*), using the vapor pressure of the material as one of the properties for identification. In the apparatus vapor pressure measurements were limited to a small range of vapor pressures, from 1.0 to 30.0 mm. of mercury, because of the small size of the sample. Since then an apparatus has been devised to measure vapor pressures up to the boiling point on samples as small as 3 cc. of gas at normal temperature and pressure. This apparatus has been incorporated into the previous system, with some minor changes. As a further aid in the identification of liquids, an adaptation has been made of a bromination titration to determine the olefin content.

Apparatus

The vapor pressure apparatus constitutes the only essentially new addition. The assembly is shown in Figure 1. A capillary manometer is connected to a bulb through capillary tubing, all of 2-mm. diameter. The total volume is estimated at 1.8 cc., so that at the boiling point a gas sample of 3 cc. at N. T. P. would be only 60 per cent in the vapor state. The manometer has the left end joined to a three-way stopcock, so that it can be pumped out with a vacuum pump and the absolute pressure read directly, or it can be opened to the air and the pressure read against the barometric pressure. This method enables one to use a manometer of only half the barometric length, and still cover a range of from 0 to 1000 mm.

The manometer is connected to the system through a three-way stopcock and a Toepler pump. The sample can be distilled into bulb C_1 (Figure 1), using liquid nitrogen, or it can be pumped into the bulb with the Toepler pump. Once it is in the bulb the leveling bulb is raised so that the mercury acts as a cut-off to keep the system free of stopcock grease in which the hydrocarbons dissolve at the higher pressures. Measurements made on *cis*-2-butene using the stopcock showed that as much as 8 per cent of the hydrocarbon dissolved in the stopcock grease in the course of a determination.

Dewar flasks containing freezing mixtures at various temperatures are placed around bulb C_1 containing the sample and the vapor pressure is read. Because of the small volume of the system, equilibrium is established very quickly, usually in 5 to 7 minutes, and it is possible to make a complete set of readings up to the boiling point in about 45 minutes.

Freezing mixtures used were absolute methyl alcohol (−96° C.), solid carbon dioxide in acetone (−78.5° C.), chloroform (−67° C.), *m*-xylene (−55° C.), cyclohexanone (−45° C.), mercury (−38.9° C.), carbon tetrachloride (−22° C.), ice-salt (−10° C.), ice (0.0° C.), benzene (5.5° C.), ethylene bromide (10.0° C.), and water from 10° C. to room temperature. These baths keep their temperatures to within 3° C. over a period of a

TABLE I. DENSITIES AND MOLECULAR WEIGHTS

Compound	Temperature ° *C.*	Density *G./cc.*	Molecular Weight
Ethylene	−78.5	0.540	28.0
	−96.0	0.560	28.0 (theoretical)
	−80.0	0.534 (*8*)	...
Cyclobutane	−78.5	0.802	55.6
	−67.0	0.788	56.0 (theoretical)
	−46.0	0.761	...
	−37.0	0.731	...
	−26.0	0.715	...
	0.0	0.698	...
	0.0	0.703 (*4*)	...
cis-2-Butene	−78.5	0.724	56.0
	−78.5	0.711[a]	56.0 (theoretical)

[a] Extrapolated from data of Coffin and Maass (*3*).

TABLE II. VAPOR PRESSURES OF *cis*-2-BUTENE

t ° *C.*	*P* (Author) *Mm.*	*P* (Kistiakowsky) *Mm.*	Deviation %
−78.5	6.9	6.5	+ 6.2
−66.6	16.1	20.1	−20.0
−48.0	60.9	62.0	− 1.8
−38.9	107.5	106.8	+ 0.7
−22.5	234	251	− 6.8
−11.0	413	420	− 1.7
0.0	659	658	+ 0.2
2.7	730	730	0.0
3.5	752	751	+ 0.1
5.5	813	816	− 0.3

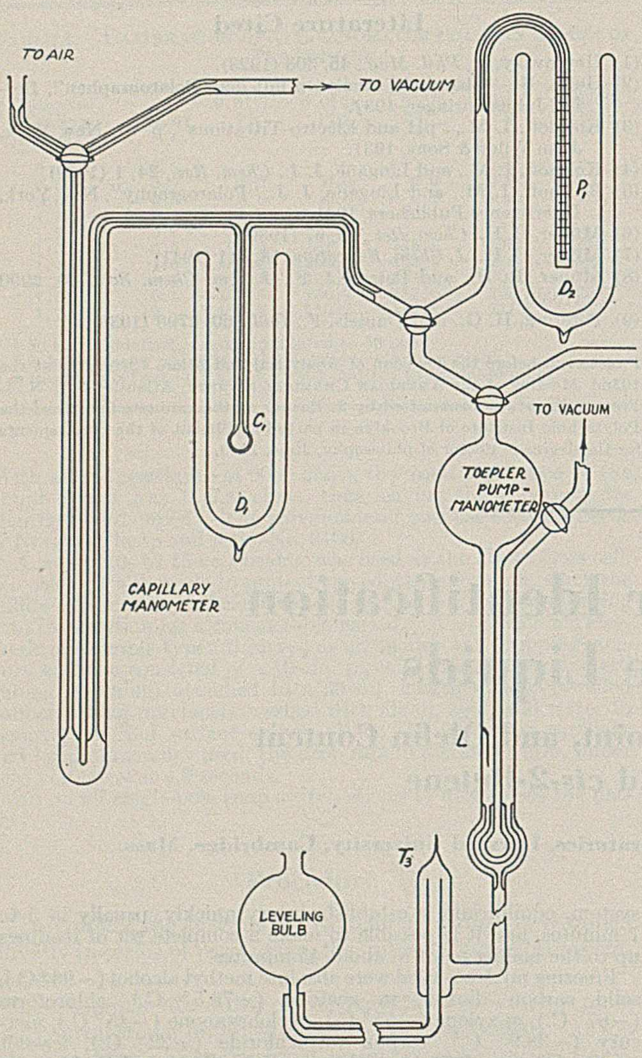


Figure 1. Analytical Apparatus

C_1. Bulb
D_1, D_2. Dewar flasks
P_1. Micropycnometer
L. Constant volume indicator
T_3. Trap

half hour, larger drifts being due to impurities. The temperature was read with an alcohol thermometer calibrated before each run with solid carbon dioxide in acetone (−78.5° C.), melting mercury (−38.9° C.), and ice (0.0° C.) and a linear interpolation used between these points. Above 0.0° C. a mercury thermometer was used, calibrated at the ice point.

Pressures were read, starting at the lower temperatures and going up to the boiling point. Each pressure reading was taken from both sides of the temperature to ensure the establishment of equilibrium. Although no measurements were made above room temperature, the system is adaptable to use at higher temperatures by wrapping it in a Nichrome spiral heating element.

Materials

cis-2-Butene was obtained from G. B. Kistiakowsky, who used it in his determinations of the heat of hydrogenation of olefins (*5*). It was distilled into the system under vacuum, using a magnetic break-off, and put through two isothermal bulb-to-bulb distillations.

Ethylene and cyclobutane were obtained together with carbon monoxide from the photochemical decomposition of cyclopentanone and separated by fractional distillation through a series of traps. The separations were complete in the case of carbon monoxide and there was about a 1 per cent contamination of the cyclobutane fraction with ethylene. This was removed by further fractionation. Microcombustions were made on the gases to determine their purity, using the apparatus described by Blacet and Leighton (*2*), and showed the samples to be 99.5 per cent pure. Further evidence of the purity was obtained from the molecular weight determinations.

As a final check on the identity of the cyclobutane, microtitrations were carried out using a modification of the method described by Uhlig and Levin (*9*).

Densities and Molecular Weights

The densities and molecular weights were measured by the method described in the first paper (*1*). Several determinations were made on different samples (Table I).

Vapor Pressures

As a check on the accuracy of the vapor pressure apparatus, measurements were made on pure *cis*-2-butene. The vapor pressures obtained are shown in Table II, together with the values of Kistiakowsky (*5*). The boiling point as measured here was 3.8° C. The boiling point determined by Kistiakowsky was 3.7° C., while the boiling point as determined by Roper (*6*) is 3.5° C., all at 760 mm. of mercury. The data obtained by Roper, Kistiakowsky, and the author have been plotted in Figure 2, and the best straight line has been drawn through the points. The data of Roper lie closest to this line. The points at lowest temperatures fall off from the curve most, because of the large relative error in these low vapor pressure readings.

Table III. Vapor Pressure of Cyclobutane

P Mm.	T ° K.	$1/T \times 10^3$	log P	P Calculated[a]	Deviation %
5.8	194.6	5.139	0.763	5.2	+11.5
50.5	227.6	4.394	1.703	50.3	+ 0.4
55.2	229.1	4.365	1.715	55.0	+ 0.4
73.8	234.2	4.270	1.868	73.4	+ 0.5
160	250.2	3.997	2.204	165	− 3.1
255	260.2	3.843	2.407	270	− 5.5
474	273.1	3.662	2.675	469	+ 1.0
583	278.6	3.589	2.766	586	− 0.6
706	283.5	3.527	2.849	708	− 0.3
765	285.8	3.499	2.883	771	− 0.8
832	288.1	3.471	2.920	840	− 1.0

[a] Determined from experimental curve.

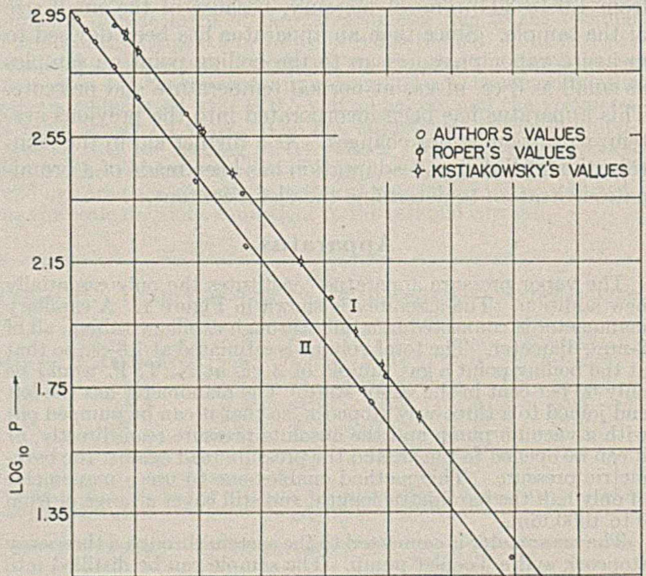


Figure 2. Vapor Pressure Measurements
Curve I. *cis*-2-Butene. Curve II. Cyclobutane

The data for cyclobutane have been assembled in Table III and plotted in Figure 2. As can be seen, they lie very close to a straight line.

The general equation for the vapor pressure–temperature dependence is given by the Clausius-Clapeyron equation:

$$\log P = -\frac{a}{T} + b$$

Table IV. Clausius-Clapeyron Constants and Heats of Vaporization

Compound	a	b	$H_{\text{vap.}} \left(\frac{\text{Kcal.}}{\text{Mole}}\right)$
Cyclobutane	1324.5	7.5215	6.054
cis-2-Butene	1320.7	7.6630	6.037
			5.900 (*6*)
			5.810 (*5*)

In Table IV are given the experimentally determined constants for cyclobutane and *cis*-2-butene, as well as the heats of vaporization. These constants are good to about 1 per cent.

Titration

A direct adaptation of the method of Uhlig and Levin (*9*) was used. Previous attempts had been made using the method of Lewis and Bradstreet (*7*) but the results were not better than 5 to 9 per cent.

A solution of bromine in c. p. glacial acetic acid was made, containing 0.045 millimole of bromine per cubic centimeter (0.045 molar). It was stored in the dark in a brown, glass-stoppered bottle. It was used in a calibrated, 10-cc. buret graduated in 0.05 cc. The concentration of the bromine solution changed very little from day to day, never more than one part in a thousand, but it was nevertheless daily restandardized with a 0.1 molar standard solution of sodium thiosulfate.

The titrations were carried out in a 25-cc. glass-stoppered, Erlenmeyer flask. A small sealed bulb was dipped into liquid air, so that the sample was frozen out in the bottom. The end was cut off, and the tube and contents were quickly dropped into the precooled flask, containing 5 cc. of chloroform. The flask was swirled for a few seconds in an ice-salt bath at −10° C. and the contents were titrated. The total time of titration was about 5 minutes. The end point was distinct when a blue-white lamp was used for illumination and the flask held against a white background. Various samples of olefinic hydrocarbons brominated immediately, while the cyclobutane and samples of cyclohexane and cyclopentane showed no bromination at all, even after 30 minutes at −10° C. The cooling was found necessary, not in order to slow down the bromination of the olefins, but to lower the vapor pressure of the hydrocarbons and prevent losses. The results of the brominations are given in Table V.

Table V. Bromination Experiments

Compound	Sample *Millimoles*	Olefin Found *Millimole*	Olefin Present *Millimole*
Chloroform	50.00	0.000	0.000
Cyclohexane	0.560	0.002	0.000
Cyclopentane	0.493	0.002	0.000
Cyclobutane	0.413	0.003	0.000
Cyclopentene	0.330	0.326	0.330
Cycloheptene	0.340	0.337	0.340
cis-2-Butene	0.534	0.529	0.534
2-Pentene	0.335	0.330	0.335

Literature Cited

(1) Benson, Ind. Eng. Chem., Anal. Ed., 13, 502 (1941).
(2) Blacet and Leighton, *Ibid.*, 3, 276 (1931).
(3) Coffin and Maass, *Trans. Roy. Soc. Canada*, 21, 33 (1938).
(4) Egloff, "Physical Constants of Hydrocarbons", Vol. II, p. 164, New York, Reinhold Publishing Corp., 1940.
(5) Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.*, 57, 876 (1935).
(6) Lamb and Roper, *Ibid.*, 62, 806 (1940).
(7) Lewis and Bradstreet, Ind. Eng. Chem., Anal. Ed., 12, 387 (1940).
(8) Maass and Wright, *J. Am. Chem. Soc.*, 43, 1098 (1921).
(9) Uhlig and Levin, Ind. Eng. Chem., Anal. Ed., 13, 90 (1941).

Apparatus for Microevaporations

L. T. KURTZ
University of Illinois, Urbana, Ill.

IN MICROPROCEDURES, it is frequently necessary to evaporate small quantities of solution. It is desirable to carry out these evaporations in the original tube or cone, but boiling is out of the question, since the formation of bubbles ejects the solution from the cone. Evaporation on a steam bath is slow because of condensation on the sides of the tube and the absence of convective currents above the solution. The usual procedure, which calls for transferring the solution to a watch glass or slide by means of a capillary pipet, is undesirable since it involves the loss of some of the material.

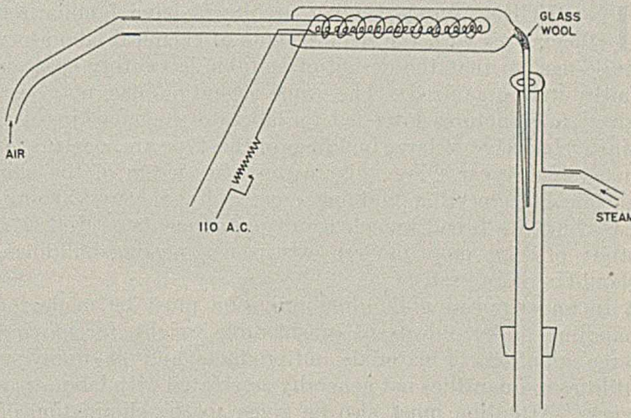


Figure 1. Diagram of Apparatus

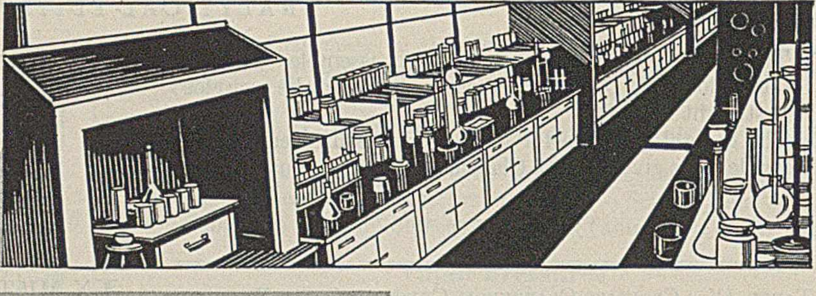
The desired evaporation can be carried out by blowing a blast of hot air on the surface of the solution, which at the same time is being heated in a steam jacket. An air current from an atomizer bulb or compressed air connection is passed through a heater which is made by enclosing a coil of 80 cm. of 20 mil (No. 24 B. and S. gage) Nichrome wire in a piece of Pyrex tubing, about 15 mm. in diameter and 15 cm. long (Figure 1). Since permanent seals cannot be made around Nichrome wire, the leads are brought out through small holes in the side of the tube. The coil is connected to the 110-volt current through a resistance of 25 to 30 ohms, which may take the form of a slide-wire resistance or electric glow cones. The hot air is introduced into the microcone by an extension of the heater tube which is drawn to a bore of about 1.5 mm. This extension contains a wad of glass wool to catch tiny pieces of oxide which may be given off from the Nichrome wire after prolonged heating. The heater unit is clamped above the steam jacket, which in turn is clamped loosely in a vertical position. The microcone, containing the solution to be evaporated, is placed in the steam jacket which is raised until the delivery tube is just above the surface of the liquid. For convenience in adjusting the steam jacket, a one-hole cork is slipped on it to serve as a handle. The steam should move rapidly through the jacket, so that the sides of the microcone will not be fogged by condensate.

This device has been found very efficient; a volume of 0.3 ml. may be evaporated in 2 or 3 minutes.

Acknowledgment

The writer wishes to acknowledge technical assistance from R. W. Waggener and P. A. Roth, as well as criticisms of this paper by J. H. Reedy.

MODERN LABORATORIES



Socony-Vacuum's New Engineering Building

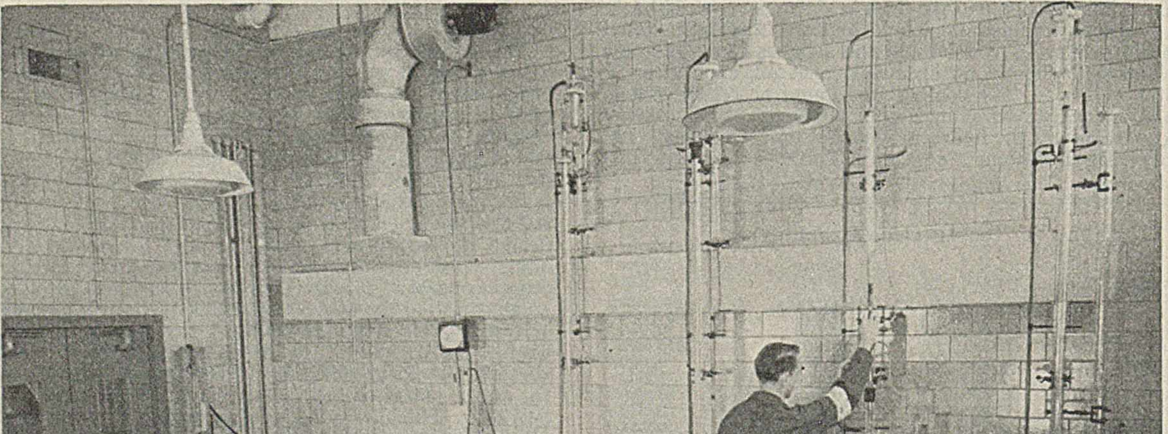
C. H. SCHLESMAN, Socony-Vacuum Oil Company, Paulsboro, N. J.

IN RECENT years leading architects have familiarized themselves with the requirements of chemical laboratory buildings, so that the design of suitable laboratory space is fairly well organized. The same attention has not been given to structures intended for laboratory engineering use, since relatively few large buildings of this type are constructed in a single year. For this reason, the design of the new chemical engineering building erected by Socony-Vacuum, based upon a broad knowledge of requirements as well as a study of some more modern existing engineering buildings, should be of interest.

In an engineering building provision must be made for handling bulky objects of considerable weight, for moving large quantities of materials and products, and for supplying utilities in quantities not generally associated with laboratory work. Attention must also be given to the elimination of accident hazards, which are intensified by the need for working during 24 hours of each day.

In designing the building, safety was considered of paramount importance, flexibility of layout and adaptation to future needs being next in importance. The lowest practicable operating cost was sought, recognizing that a substantial part of the operating personnel would consist of experienced chemical engineers and other skilled research technicians. The appearance of laboratory buildings should be as attractive as possible without increasing the capital investment unduly, since customers and field men are frequent visitors.

A flat-roof structure of steel construction with a high central bay to provide the necessary head room was selected, as this would provide an unobstructed floor area for engineering work. By limiting the clear roof span to 28 feet, it was possible to avoid the use of deep roof trusses which create



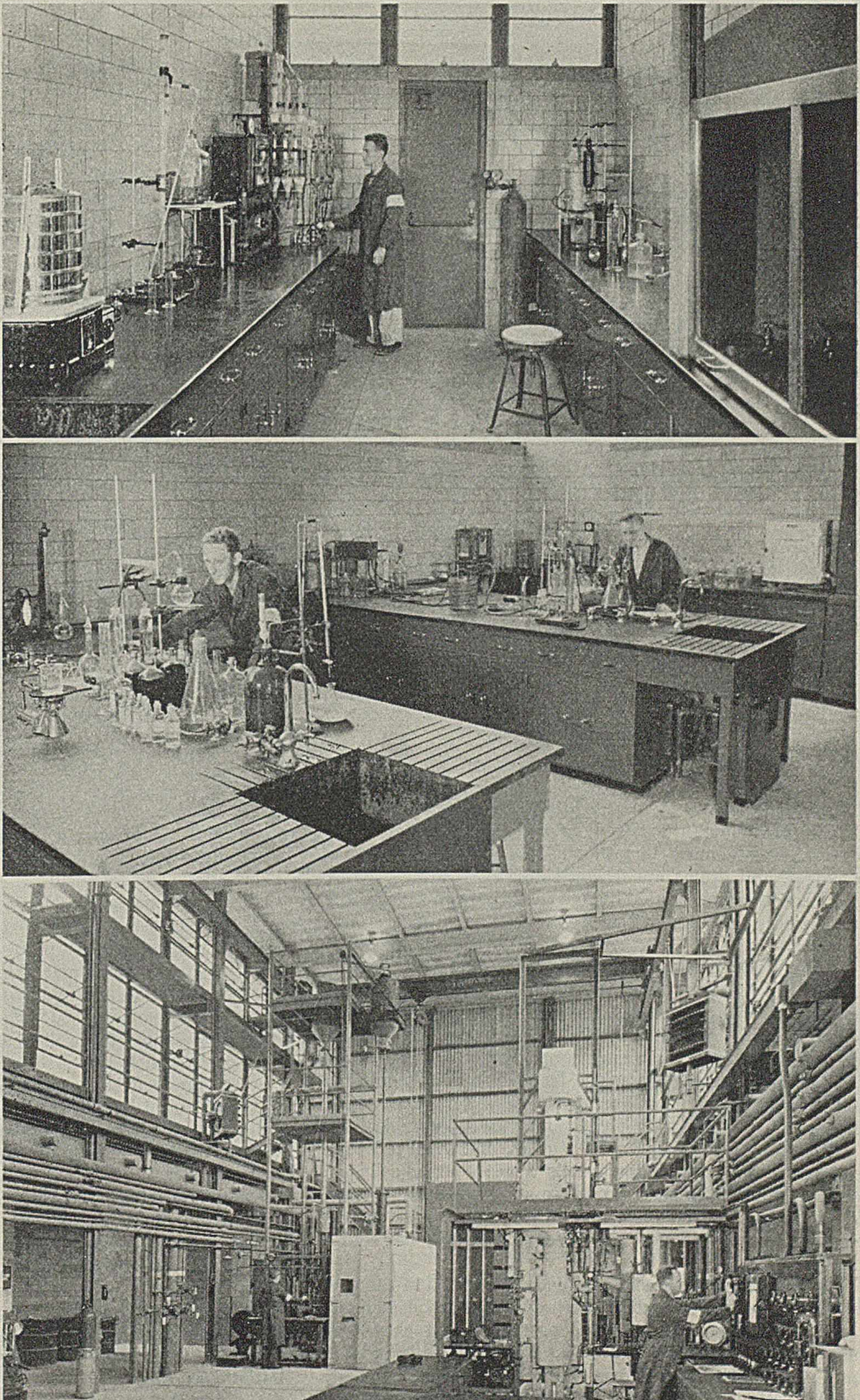
Distillation Room

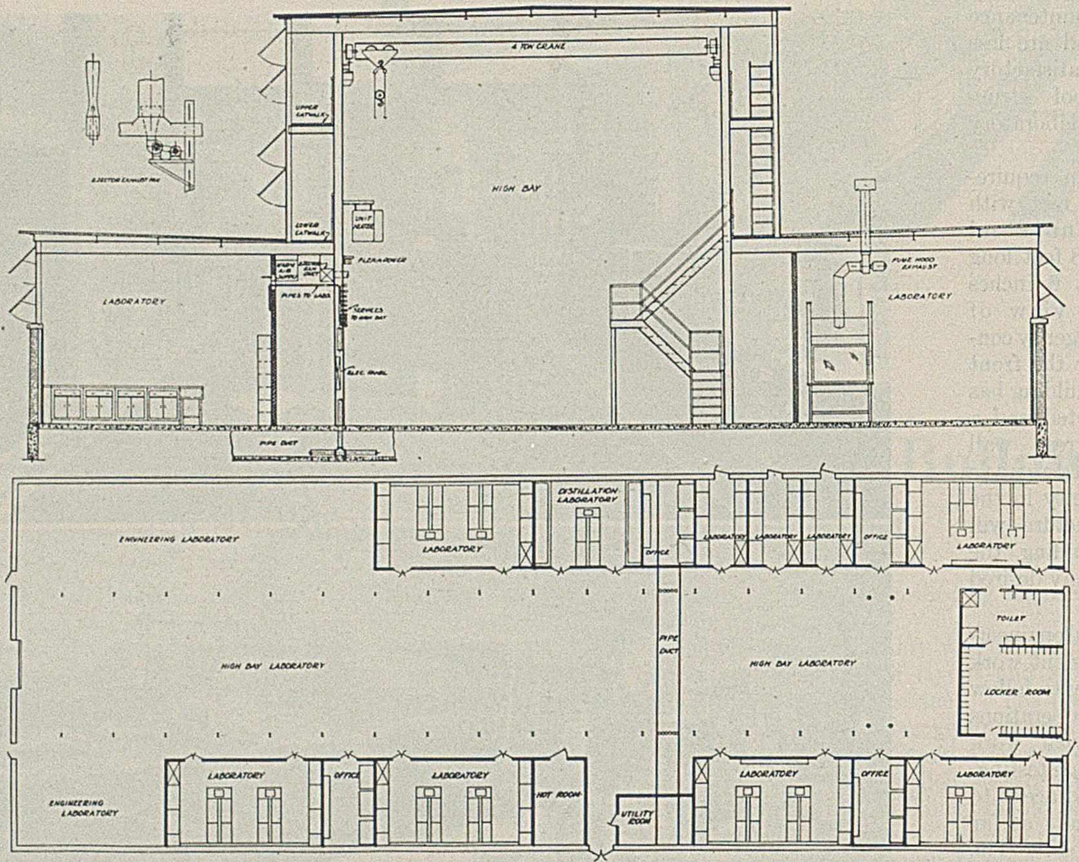
difficult maintenance problems and are less flexible and satisfactory than flat-roof structures for laboratory buildings.

The design requirements were met with a brick and steel structure 208 feet long and 78 feet 6 inches wide. In view of present emergency conditions, only the front half of the building has been completed and a temporary rear wall placed. Adequate utility capacity in the present structure will permit extending the building to any desired length.

In chemical engineering development work it is necessary to follow pilot-plant operations with analytical work and small-scale testing, carried on adjacent to the actual units as far as practicable. The necessity of erecting bubble towers and similar structures dictated head room under the crane of about 30 feet, while laboratory work in some engineering operations required only 13 feet of head room. This led to the construction of the step type of structure, which appears to offer several very definite advantages, since test work can be located adjacent to the unit while utilities can conveniently be supplied from headers placed on the columns. Experience with laboratory construction indicated that windows below a 7-foot level are a liability in an engineering building, as they interfere with the use of walls for the support of apparatus.

In a building as large as this the routing of material, utilities, and foot traffic assumes great importance. The personnel enter the building through two small front entrances.


(*Above*) Small Laboratory (*Center*) Large Laboratory
(*Below*) High Bay Engineering Laboratory


EJECTOR EXHAUST FAN
4 TON CRANE
UPPER CATWALK
LOWER CATWALK
UNIT HEATER
HIGH BAY
FLEXA POWER
PIPES TO LABS
SERVICES TO HIGH BAY
ELEC. PANEL
LABORATORY
PIPE DUCT
FUME HOOD EXHAUST
LABORATORY
ENGINEERING LABORATORY
LABORATORY
DISTILLATION LABORATORY
OFFICE
LABORATORY
LABORATORY
LABORATORY
OFFICE
LABORATORY
HIGH BAY LABORATORY
PIPE DUCT
HIGH BAY LABORATORY
TOILET
LOCKER ROOM
ENGINEERING LABORATORY
LABORATORY
OFFICE
LABORATORY
HOT ROOM
UTILITY ROOM
LABORATORY
OFFICE
LABORATORY

(*Above*) Cross Section of Engineering Laboratory; (*below*) Floor Plan

Shower and locker rooms are adjacent to the entrances. Within the building the movement of personnel is channelized by two well defined longitudinal aisles. Samples, small packages, and drums are received at a door in the center, which is not ordinarily used by foot traffic. Heavy trucks and bulky pieces of equipment can be brought in through a large door in the rear.

Steam, compressed air, water, and electrical services enter the building and pass directly across it by means of an underfloor pipe trench. Branches rise along the line of the main columns to a utility rack running the length of the building on each side of the main engineering bay. Laterals to the various laboratories and to the large chemical engineering units run overhead. All large electrical power loads are fed from a Flexa power system located along the utility rack.

All lighting loads, laboratory benches, and small units are fed from small distributor panels spaced periodically on columns, which also serve to locate safety equipment, such as gas masks, fire blankets, fire extinguishers, heating and vent controls, telephones, and other general purpose equipment.

Tall chemical engineering equipment is erected in the central bay. Floor drain outlets are provided at frequent intervals. Flue outlets are located along the utility racks. The flues connect to two vertical stacks which normally provide draft. A motor-driven blower forces a powerful jet of air through a throat in the stack if it is desired to augment the draft. This eliminates the corrosion and explosion hazard difficulties encountered where the stack gases pass through the blower, and avoids back pressure when the blower is not in use.

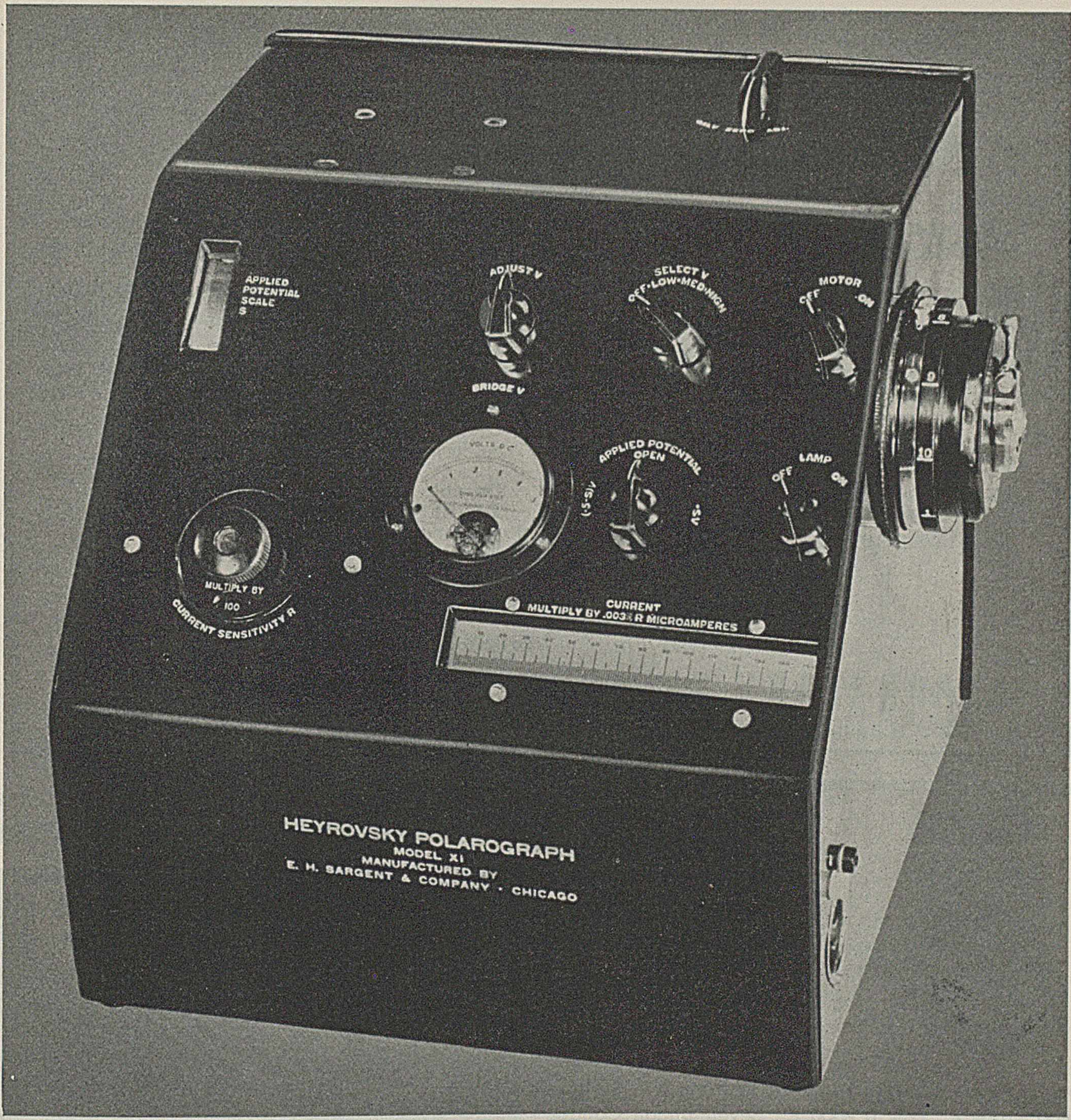
As bubble towers and similar engineering equipment may rise 30 feet from the floor line, catwalks have been provided along each side of the bay at the 15 and 22 foot levels. These catwalks connect by platforms and stairs with the various units, provide secure operating platforms, and also provide for escape of the personnel in case of an emergency. Along each side of the chemical engineering bay space has been provided at the rear for small-scale operations which can be carried out in normal head room.

The main aisles also serve the laboratories. Laboratory doors have always been a problem. Doors provide means for isolating areas in the event of fire or when toxic gases are being handled, but are otherwise best left open. A happy solution has been reached by providing double doors which fold back against the wall in the aisle and are held in this position by fusible links. The doors may be released at any time and are small enough to avoid obstructing the aisles.

The chemical laboratories are of a conventional design, a buff glazed tile being employed for the walls to reduce maintenance expense. Metal furniture was chosen, since wooden furniture sometimes gives trouble in this climate, and metal drawers are better able to carry the heavy loads imposed upon them in an engineering laboratory. Alberene stone has been found ideal in petroleum work for table tops; it can be cut, patched, and refinished as required with a minimum of loss.

Fireproof construction has been used throughout, an explosion venting type of window has been specified, and provision has been made for fog-type automatic sprinklers in hazardous areas.

Considerable experience is required before an accurate appraisal of the value of a new structure can be made. However, a building of the present design seems ideally suited to the needs of a rapidly growing chemical engineering organization. The structure is expected to show a low maintenance cost and make production efficiency possible without departing from the high standards of safety requirements which are common in the petroleum industry.


APPLIED POTENTIAL SCALE S
ADJUST V
BRIDGE V
SELECT V
OFF·LOW·MED·HIGH
MOTOR
OFF ON
VOLTS D.C.
APPLIED POTENTIAL
OPEN
LAMP
OFF ON
MULTIPLY BY
100
CURRENT SENSITIVITY R
CURRENT
MULTIPLY BY .003 R MICROAMPERES
HEYROVSKY POLAROGRAPH
MODEL XI
MANUFACTURED BY
E. H. SARGENT & COMPANY · CHICAGO

The application of the polarographic method of analysis expands steadily. Some of the analyses being made with the Heyrovsky Polarographs now in use include the analysis of brass; of steel and iron; of lead, magnesium, nickel, and zinc alloys; of metallic impurities in aluminum; of lead and zinc in paints; of major constituents in plating solutions; and the differentiation of waters. Accuracy; rapidity; the possibility of detecting and identifying minute quantities and of making simultaneous determinations of several components; small sample requirement; preservation of sample; and permanent photographic recording of every analysis are some of the reasons why the Heyrovsky Polarograph is becoming so widely accepted.

The procedures established thus far by no means define the field of polarography — the perfected instrumental system of the Heyrovsky Polarograph creates unlimited possibilities for analytical and research applications.

A bibliography of more than 700 papers dealing with the polarographic method of analysis and a booklet discussing the Polarograph and polarographic analysis are available without charge on request.

E. H. SARGENT & CO.

SCIENTIFIC LABORATORY SUPPLIES

155-165 EAST SUPERIOR STREET, CHICAGO, ILLINOIS

Available to You . . .

This Well-Known Apparatus and Equipment

★ ★ ★

Better **KJELDAHL NITROGEN APPARATUS**

Unparalleled system of fume disposal (Patented). Not available in any other apparatus.

Radically Improved GOLDFISCH EXTRACTION APPARATUS
147 users evidence its efficiency and value.

Minimum Frothing CRUDE FIBER CONDENSERS
No metal parts in contact with solution. No rubber hose connections.

Self-Cleaning LABCONCO ELECTRIC WHEAT GRINDER
Over 150 now in use.

Flask Formed GOLDFISCH ELECTRIC HEATERS
Individually tested for uniform heat.

Wide Range LABCONCO GAS BURNERS
Set-lock valve adjustment.

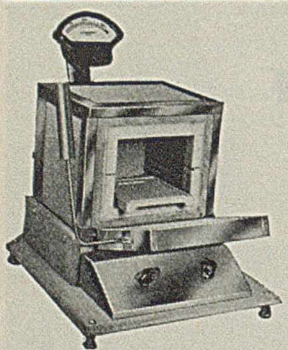
Durable LABORATORY TABLES and CARTS
Acid and fire resisting.

Detailed specifications and full information will be sent on request without any obligation on your part.

Manufactured and Sold Direct to the User By

LABORATORY CONSTRUCTION COMPANY, INC.

1113-1115 Holmes Street Kansas City, Missouri, U. S. A.



HUPPERT LABORATORY FURNACES

•

"a furnace for every laboratory need"

•

MODEL ILLUSTRATED

$74.25

COMPLETE

Three heat ranges, High 1000°–1800°F., Medium 500°–1000°F., Low 0°–500°F. Seven Button Control Switch in each heat range furnishes any desired temperature and maintains that temperature as long as you want it. Makes duplication of results certain.

Large Muffle: 4½ x 4½ x 3⅝ inches. Outside dimensions of Furnace: 12″ wide, 14″ long, 11½″ high. Shipping weight 32 lbs. Operates on 110 Volts, A. C., or D. C.

Huppert Furnaces are ruggedly built for heavy duty service, with stainless steel housing and with no exposed contacts. Prices range from $24.75 to $157.50 with standard heat ranges up to 2500°F. (Special voltages, dimensions and temperature ranges to order.)

WRITE FOR FREE CATALOG

K. H. HUPPERT

156 W. Walton Place Chicago, Ill.

AMERICAN QUALITY – *Worldwide standard*

CHEMICAL AND SCIENTIFIC PORCELAIN WARE

COORS PORCELAIN COMPANY

GOLDEN, COLORADO

KANSAS CITY, MO.
A. J. Griner Company

MINNEAPOLIS, MINN.
Geo. T. Walker & Co.

DALLAS, TEXAS
Greene Bros., Inc.

NEW YORK, N. Y.
E. Machlett & Son

BOSTON, MASS.
Howe & French, Inc.

PITTSBURGH, PA.
Burrell Technical Supply Co.

ANN ARBOR, MICH.
Eberbach & Son Co.

RICHMOND, VA.
Phipps & Bird, Inc.

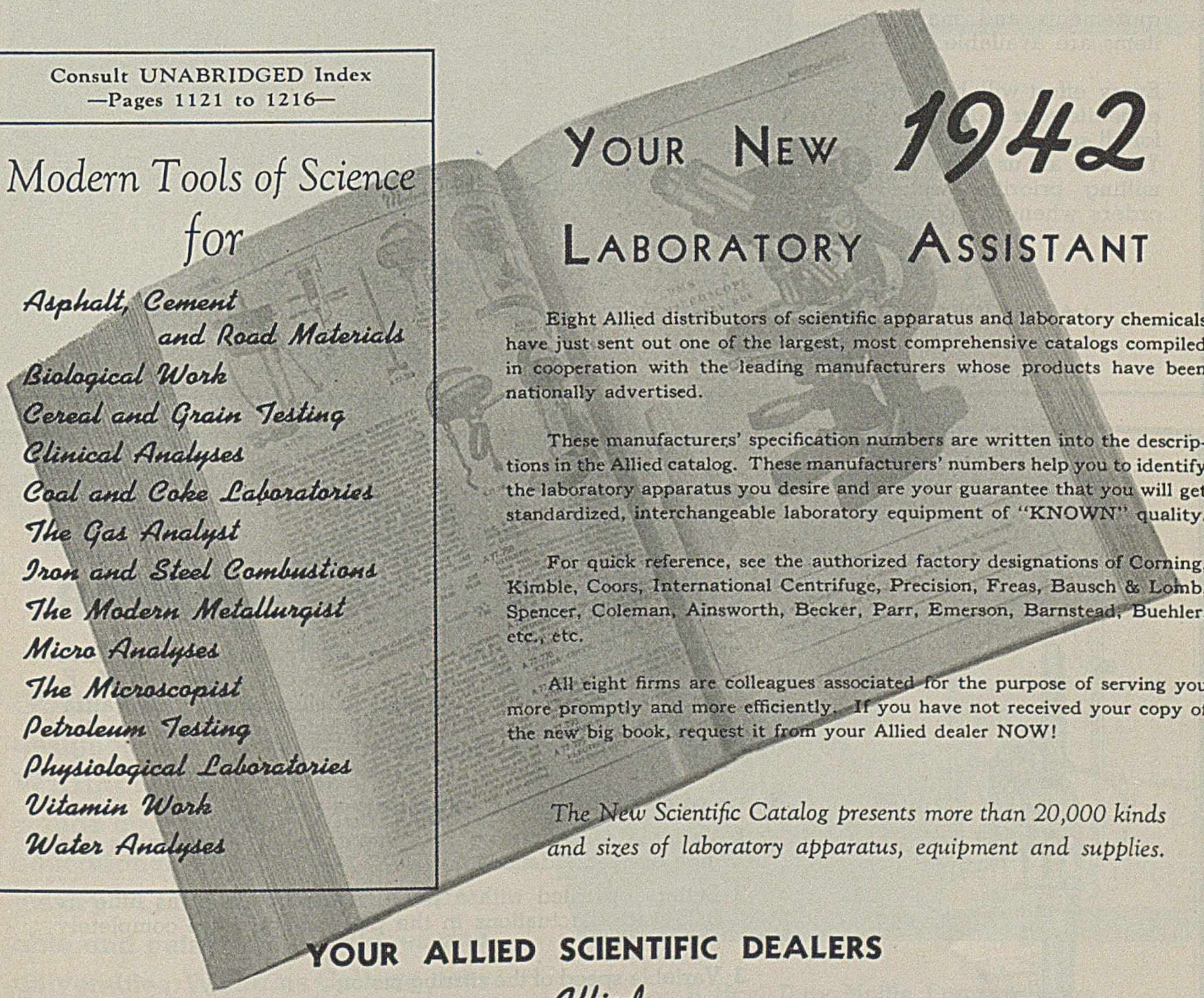
Nation-Wide Facilities

Allied for Your Defense

Consult UNABRIDGED Index
—Pages 1121 to 1216—

Modern Tools of Science for

Asphalt, Cement and Road Materials
Biological Work
Cereal and Grain Testing
Clinical Analyses
Coal and Coke Laboratories
The Gas Analyst
Iron and Steel Combustions
The Modern Metallurgist
Micro Analyses
The Microscopist
Petroleum Testing
Physiological Laboratories
Vitamin Work
Water Analyses



YOUR NEW 1942 LABORATORY ASSISTANT

Eight Allied distributors of scientific apparatus and laboratory chemicals have just sent out one of the largest, most comprehensive catalogs compiled in cooperation with the leading manufacturers whose products have been nationally advertised.

These manufacturers' specification numbers are written into the descriptions in the Allied catalog. These manufacturers' numbers help you to identify the laboratory apparatus you desire and are your guarantee that you will get standardized, interchangeable laboratory equipment of "KNOWN" quality.

For quick reference, see the authorized factory designations of Corning, Kimble, Coors, International Centrifuge, Precision, Freas, Bausch & Lomb, Spencer, Coleman, Ainsworth, Becker, Parr, Emerson, Barnstead, Buehler, etc., etc.

All eight firms are colleagues associated for the purpose of serving you more promptly and more efficiently. If you have not received your copy of the new big book, request it from your Allied dealer NOW!

The New Scientific Catalog presents more than 20,000 kinds and sizes of laboratory apparatus, equipment and supplies.

YOUR ALLIED SCIENTIFIC DEALERS

Allied

BURRELL TECH. SUPPLY CO.
Pittsburgh, Pa.
EBERBACH & SON CO.
Ann Arbor, Mich.
GREENE BROS., INC.
Dallas, Texas
A. J. GRINER COMPANY
Kansas City, Mo.

HOWE & FRENCH, INC.
Boston, Mass.
E. MACHLETT & SON
New York, N. Y.
PHIPPS & BIRD, INC.
Richmond, Va.
GEO. T. WALKER & CO.
Minneapolis, Minn.

Allied

Our Modern, New Home

to better serve the laboratories of industry

Through many modern facilities which our new building affords, we are in a position to cooperate advantageously with the laboratories of vital industries — in their all out effort to meet the needs of our government.

Stocks of all essential laboratory items have been increased to meet current requirements and many new items are available.

Every effort will be made to expedite your orders promptly for all supplies and materials. You can aid us in this by submitting priorities with your orders whenever possible.

THE CHEMICAL RUBBER COMPANY
LABORATORY SUPPLIES & EQUIPMENT

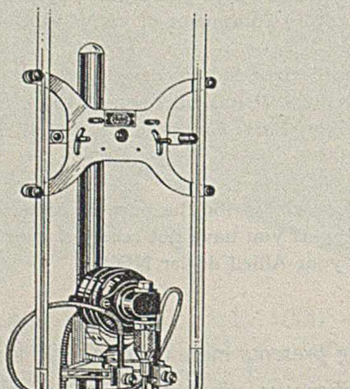
80,000 sq. feet of floor space

★ *Send for Supplement "D" showing new equipment*

THE CHEMICAL RUBBER CO.

LABORATORY SUPPLIES — SCIENTIFIC EQUIPMENT — HANDBOOK OF CHEMISTRY AND PHYSICS

2310 Superior Ave. — Cleveland, Ohio



Leitz "G & D" Electro-Titrator
Made in U.S.A.

Leitz

"G & D" ELECTRO-TITRATOR

A universal Electro-Titrator using a highly stable and sensitive voltmeter circuit designed by Dr. R. L. Garman and Dr. M. E. Droz for determinations of end-points in electrometric neutralization titrations (including pH determinations), oxidation-reduction titrations, and precipitation titrations.

Some of its outstanding advantages are:

1 Variable sensitivity up to a maximum of 40 millivolts per inch of needle deflection;

2 Battery operated with a power consumption of as little as 0.25 watt; fluctuations in the power supply are completely eliminated;

3 Variable speed of the stirring motor;

4 A clearly visible meter with a scale, 3⅛" long, permits continuous reading of the voltage changes throughout the entire progress of the titration.

Pamphlet No. 1283 Upon Request

E. LEITZ, INC.

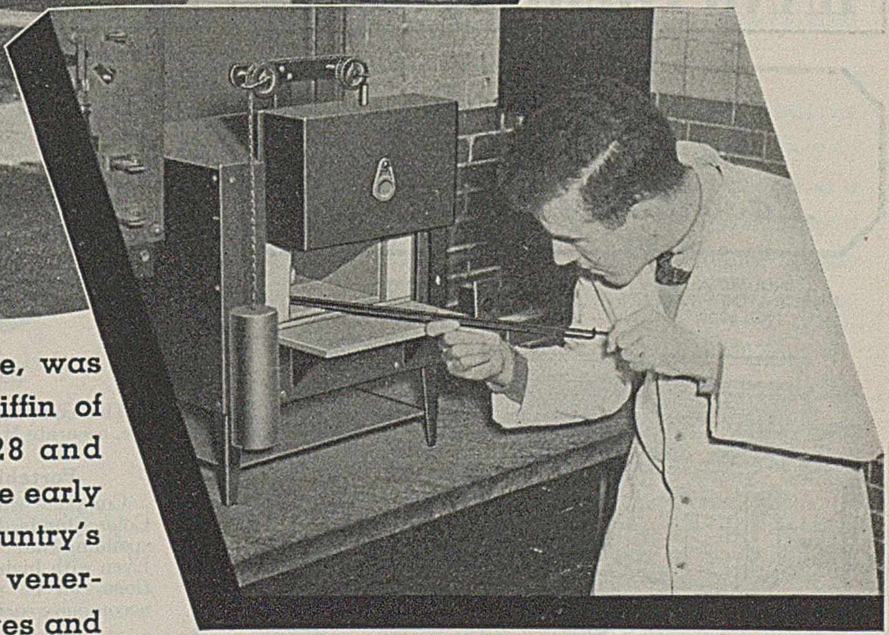
730 Fifth Ave., New York, N. Y.

Branch Offices: Chicago, Washington, D. C.

Williams College

and **HEVI DUTY**

FURNACES



Griffin Hall, pictured above, was designed by President Griffin of Williams College in 1828 and stands as a monument to the early educational efforts in our country's history — Like many of the venerable and outstanding colleges and universities, Williams College uses Hevi Duty Laboratory Furnaces for chemical study and analysis.

A Hevi Duty Muffle Furnace in the Thompson Chemical Laboratory at Williams College.

Send for Hevi Duty Laboratory Furnace Bulletins

HEVI DUTY ELECTRIC COMPANY

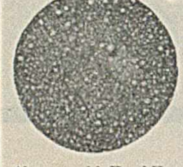
HEAT TREATING FURNACES HEVI DUTY ELECTRIC EXCLUSIVELY

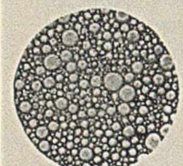
MILWAUKEE, WISCONSIN

Now! A Laboratory-Size HOMOGENIZER!

. . . *Save Time and Materials*

For liquid batches of 1 to 10 oz. Merely pour mixture into bowl and press hand-lever. Homogenizes instantly—each stroke of hand-lever ejects a jet of completely emulsified liquid. Provides permanent suspension for emulsions—no failures, if ingredient ratio is sound. In photos at left, note fine degree of dispersion secured (above) compared to coarseness of same mixture emulsified with mortar and pestle (below).





Above—with Hand Homogenizer
Below—with mortar and pestle

Hundreds of laboratories use the Hand Homogenizer because it saves time, avoids material waste. Portable, easy to operate and clean, strongly built of molded aluminum, with stainless steel piston. 10½ in. high, 12 oz. bowl. Only $6.50 complete—order direct or from your laboratory supply house (satisfaction guaranteed)—or write for further details.

International Emulsifiers, Inc.
Dept. C-19, 2409 Surrey Court, Chicago, Ill.

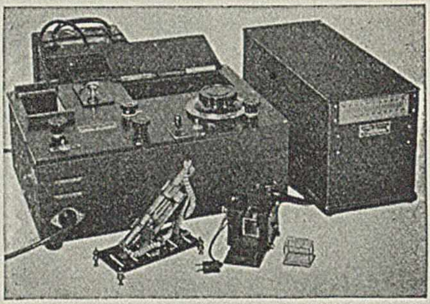
International HAND HOMOGENIZER

LUMETRON

Photoelectric COLORIMETER and FLUORESCENCE METER

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

TRANSMISSION
FLUORESCENCE
TURBIDITY
U. V. ABSORPTION



Mod. 402EF for determination of Vit. B_1 and B_2

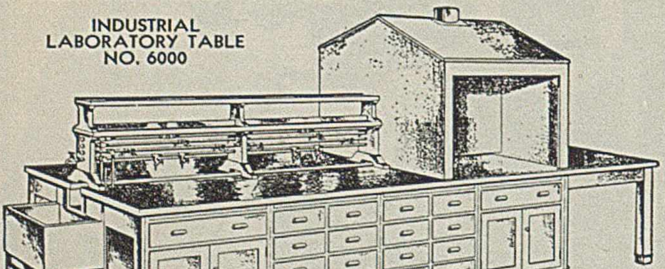
Also

Portable Colorimeters	Electronic Photometer for Vit. A
Reflection Meters	Electronic Small-Spot Photometer
Barrier-Layer Photocells	Electronic Interval Timers

PHOTOVOLT CORP.
95 Madison Ave. New York City

QUALITY
Laboratory Furniture

INDUSTRIAL LABORATORY TABLE NO. 6000



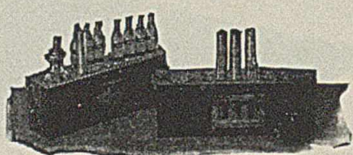
HALF A CENTURY OF LEADERSHIP ASSURES YOUR SATISFACTION

Yes, for more than half a century, Peterson Laboratory Furniture has been giving outstanding satisfaction. Every user of laboratory furniture should have a copy of Peterson's complete catalog handy. Our staff of experts will, upon request, gladly assist in the planning of more efficient laboratory arrangement. There is no charge for this service.

Send today for Peterson's Furniture Catalog, containing much valuable information regarding the efficient and economical installation of laboratory furniture. It is free.

LEONARD PETERSON & CO., INC.
1224-34 Fullerton Ave. Chicago, U.S.A.

LAMOTTE CHEMICAL CONTROL SERVICE



LaMotte Block Comparator

This compact LaMotte Outfit greatly facilitates simple, accurate Hydrogen Ion Measurements.

Portable—Convenient—Inexpensive

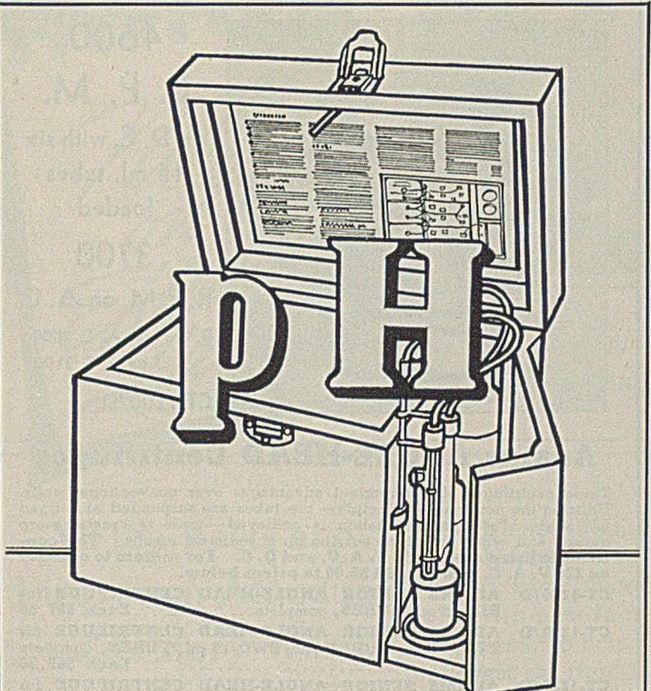
Complete with any one set of LaMotte Permanent Color Standards, together with a supply of the corresponding indicator solution and marked test tubes. Even with highly colored or turbid solutions determinations can be made with accuracy. Full instructions accompany each unit.

Complete, f. o. b. Baltimore, $12.50

LaMotte Range Finding Indicator Solutions

For use in determining approximate pH values of unknown solutions as a guide to the selection of the proper single range indicator for accurate pH determination. In 50, 100 and 500 cc. containers. Complete information on request.

LAMOTTE
CHEMICAL PRODUCTS CO.
Originators of Practical Application of pH Control
Dept. F Towson, Baltimore, Md.



COLORIMETRIC

or

ELECTROMETRIC

The importance of pH is recognized in practically all types of research and control work involving aqueous solutions.

Whatever method of measurement is employed—colorimetric or electrometric—we can supply the necessary equipment promptly and completely.

A letter of inquiry outlining your pH problem will bring helpful information.

Pages 480 to 492 of our Catalog 5 are devoted to Colorimetric and Electrometric pH equipment.

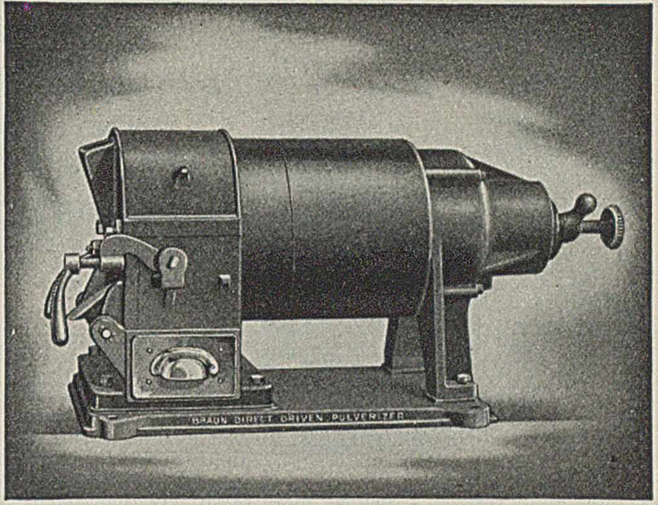
LABORATORY APPARATUS
CATALOG 5
WILL CORPORATION

WILL CORPORATION
ROCHESTER, N. Y.

Office and Warehouses

Will Corporation, 596 Broadway, New York City
Buffalo Apparatus Corp., Buffalo, N. Y.

LABORATORY APPARATUS AND CHEMICALS



Braun Direct-Driven Pulverizer

TO MEET YOUR NEED FOR GREATER SPEED

The answer to many critical production problems is more efficient machinery. The Braun Direct-Driven Pulverizer is the most up-to-the-minute laboratory grinder available for a wide variety of applications. It has a definite place in busy laboratories where samples are being tested almost continuously, day-in and day-out.

Ready to run at the touch of a finger, it reduces samples at a truly astonishing rate. It is easy to operate, economical to maintain and requires a minimum of attention. It is ball bearing equipped throughout and is permanently lubricated at the factory, so that no further lubrication is ever required.

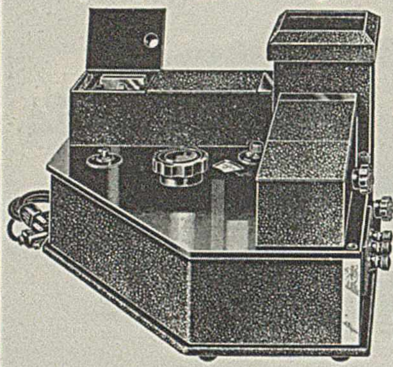
The pulverizer is entirely self-contained. The motor is built in—no belts, gears, shafting or pulleys are needed. It conserves valuable space—takes up less than two by three feet.

Cut down bottleneck conditions in your laboratory with this efficient, speedy, economical pulverizer. Write Dept. I-2 today for Bulletin C-135 which gives complete details.

BRAUN
CORPORATION

2260 East Fifteenth Street BRAUN **Los Angeles, California**
San Francisco, Calif. *Seattle, Washington*
BRAUN-KNECHT-HEIMANN-CO. SCIENTIFIC SUPPLIES CO.

A. DAIGGER
offers
The Klett Fluorimeter



FOR
ASSAYING RIBOFLAVIN AND THIAMIN
QUICK • INEXPENSIVE
CONVENIENT

The fluorimetric system of vitamin assay enables thiamin determination to be made quicker, less expensively, and more sensitively than previous biological methods. A great advantage of the fluorimetric system over photometric methods is that the degree of turbidity sufficient to nullify a photometric determination may not interfere with this new method. The apparatus needed consists only of three units—fluorimeter, galvanometer, and transformer. No other accessories are required to ensure satisfactory operation.

No. 2070 Klett Fluorimeter complete with 2 cuvettes, 2 lamp filters, 2 photocell filters, wooden box for dates, 6 filters, operates on 110–120 Volts 60 cycles alternating current.
Without galvanometer....$225.00
No. 2071 Klett Fluorimeter-Colorimeter complete with 2 cuvettes, 2 lamp filters, 2 photocell filters (for use with fluorimeter) wooden box for 6 filters, test tube holder, variable slit, 2 graduated test tubes, and incandescent lamp, operates on 110–120 Volts 60 cycles alternating current.
Without galvanometer....$285.00
No. 3402 Galvanometer, Rubicon 3402 HH and transformer for galvanometer lamp........$55.00
Filters................$2.75 each

WRITE FOR ILLUSTRATED FOLDER
A. DAIGGER & CO. 159 W. Kinzie St., Chicago
Laboratory Supplies and Chemicals

4600
R. P. M.
on D. C. with six
15 ml. tubes
loaded
3700
R. P. M. on A. C.
R. C. F. on A. C. 2000
on D. C. 3100
CT-1200/D

Adams ANGLE-HEAD Centrifuges

These centrifuges offer important advantages over conventional units. Utilizing the new angle principle—the tubes are suspended at a fixed 52° angle. Faster sedimentation is achieved—mass is created more quickly and, when at rest, no stirring up of sediment results. **The centrifuges listed are for 110 V. A. C. and D. C. For motors to operate on 220 V. A. C. or D. C. add $2.00 to prices below.**

CT-1200/D **ADAMS SENIOR ANGLE-HEAD CENTRIFUGE** for **SIX** 15 ml. **TUBES,** complete..............**Each $67.50**
CT-1210/D **ADAMS SENIOR ANGLE-HEAD CENTRIFUGE** for **TWO** 50 ml. **TUBES** and **TWO** 15 ml. **TUBES,** complete ....**Each $67.50**
CT-1220/D **ADAMS SENIOR ANGLE-HEAD CENTRIFUGE** for **FOUR** 50 ml. **TUBES,** complete............**Each $69.50**

Seven heads shown in our catalog No. 111 IC are interchangeable on the same Centrifuge. If you have not already received a copy, write for one on your letterhead, please.

CLAY-ADAMS CO INC.
44 EAST 23rd STREET, NEW YORK, N. Y.

THE SAFER, BETTER WAY . . . .
WITH A
***Caulfield* PIPETTOR**

ACCURATE
SANITARY
MODERN
●
Fits any size of pipette . . . .
Draws up any desired amount . . . .
Discharges accurately . . . .

The CAULFIELD PIPETTOR is enthusiastically endorsed by leading colleges, institutions and industrial laboratories. Its simplicity, accuracy, clear visibility and ease of operation make its use the ideal pipetting technique for every laboratory.

Write for descriptive folder and prices

SCHAAR & COMPANY
Complete Laboratory Equipment
754 WEST LEXINGTON ST., CHICAGO

The Spencer Colorimeter

- Simplifies Technique
- Improves Accuracy
- Saves Time

The Spencer Direct Result Colorimeter presents many important advantages over other present day instruments.

(1) Direct reading of the percentage of the unknown. (2) Inclined eyepiece for comfort. (3) Simple, accurate adjustment of artificial illumination. (4) Tilted plungers which dissipate air bubbles as they are immersed. (5) Cups which are easily taken apart for cleaning, with no necessity to check the zero adjustment. (6) Reverse position of instrument affords convenience in placing or removing cups. (7) A beautiful, easy to clean, modern design that combines strength and practicability.

Write Dept. B-48
for complete
descriptive literature

Spencer Lens Company
BUFFALO, NEW YORK
Scientific Instrument Division of
AMERICAN OPTICAL COMPANY
Sales Offices: New York, Chicago, San Francisco, Washington, Boston, Los Angeles, Dallas, Columbus, St. Louis, Philadelphia, Atlanta

Notes on the Efficient Laboratory

Prepared in cooperation with the technical and research staff of NORTON COMPANY, Worcester, Mass.

All the Facts and Figures on Alundum Laboratory Ware... Complete Specifying Data... List Prices...

NOW IN THIS FREE CATALOG...

JUST OUT! The new catalog entitled "Norton Refractory Laboratory Ware" is freely available for your laboratory, as an aid and convenience in purchasing. Write for it, addressing Norton Company, Worcester, Mass., and ask for Form 793A.

Rarely, if ever, have ten concise pages contained more useful information for the man who wishes to keep his laboratory at the peak of efficiency in spite of rush conditions.

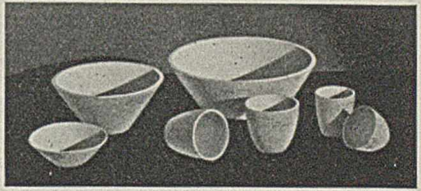
Norton's new catalog of laboratory ware places at your finger-tips *complete facts, specifications, prices,* to help you select and purchase the right type of porous medium for your specific purposes.

Permeability, porosity, pore size, pressure loss, uniformity, strengths and capacities are fully indicated, together with the list price of each article, in stock and special sizes.

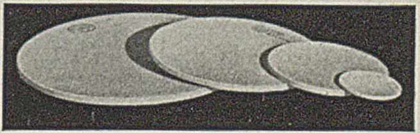
You Can Ignite in the Device You Use to Filter

The purity, resistance to acids and most other liquors, and extreme refractoriness of ALUNDUM (Al_2O_3) material fits it ideally for laboratory filtering devices. Unharmed by the substances being filtered, the devices can also be ignited to constant weight after each filtration.

FILTER CONES fitting perfectly into ordinary 60° funnel, for organic and inorganic filtrations and determinations, and for Invert Sugar, present large filtering area for rapid removal of solid particles from liquids. Furnished (with stand free on request) in three standard mixes: RA 320 (dense), RA 321 (medium), RA 322 (coarse), in four diameters, with capacity from 20 c.c. to 250 c.c.



FILTER DISHES for washing and drying crystals, rewashing precipitates — CRUCIBLES for fine (Barium Sulphate) and coarse (Silver Chloride) precipitates, also for Mn, Pb, Sn determinations. Dishes and crucibles supplied in RA 84 (dense), RA 360 (medium), RA 98 (coarse) mixes — crucibles also in RA 766 (extra coarse) for crude fibre determinations. Dishes of four diameters, capacities from 50 c.c. to 400 c.c.; crucibles, 25 c.c. and 35 c.c.



FILTER DISCS for small amounts of suspended matter, such as lead sulphate suspended in concentrated sulphuric acid, finely divided carbon in gasolene, excess sodium bismuthate in Mn determinations. Also used as refractory filters to obtain dust-free samples of hot flue gases. Look for RA 98 and RA 225 in free catalog, "Norton Refractory Laboratory Ware."

NORTON RESEARCH
INGREDIENT NUMBER ONE IN FUSED ALUMINA LABORATORY WARE

NORTON LABORATORY WARE
Distributed by the following:
Central Scientific Co., Chicago and Other Cities
Eimer and Amend, New York City
Fisher Scientific Co., Pittsburgh
Arthur H. Thomas Co., Philadelphia
E. H. Sargent & Co., Chicago
Braun Corp., Los Angeles
Braun, Knecht, Heiman, San Francisco
Or simply order through your favorite Laboratory Supply House

ANHYDROUS
ALUMINUM CHLORIDE
IN
ORGANIC CHEMISTRY

by

CHARLES ALLEN THOMAS
Central Research Director, *Monsanto Chemical Company*
In Collaboration with
Mary Baluk Moshier, Herbert E. Morris, and R. W. Moshier
Thomas and Hochwalt Laboratories, Monsanto Chemical Company

American Chemical Society Monograph No. 87

THIS volume has been eagerly awaited for some time by all those concerned with the catalysis and isomerization of organic compounds. The reactions of aluminum chloride with hundreds of compounds are discussed in detail; and a feature of the book is the presentation of the exact changes which occur in structure. A résumé of the work of Friedel and Crafts, who did the pioneer work in this field, is included. This is indeed a monumental compilation which will be invaluable to research workers in the fields of petroleum, plastics, rubber, synthetic coatings, flotation agents, dyes, fats and waxes, cleansing and dry-cleaning agents, perfumes and textiles.

Chapters

Introduction
Historical Sketch of Charles Friedel and James Mason Crafts
Physical Properties of Anhydrous Aluminum Chloride
Mechanism of Reactions Catalyzed by Anhydrous Aluminum Chloride
Friedel-Crafts Syntheses.
Part I. Reactions of Aromatic Hydrocarbons with Halogenated Compounds other than Acyl Halides
Friedel-Crafts Syntheses
Part II. Ketone Syntheses
Friedel-Crafts Reactions.
Part III. Ring Closure with Evolution of Hydrogen Halide
Addition Reactions. Part I
Addition Reactions.
Part II. Syntheses of Keto-Acids from Dicarboxylic Acid Anhydrides
Aldehyde Syntheses
Aromatic Halogenation
Dehydrating Condensations
Dehydrogenating Condensations and Reduction Phenomena
Miscellaneous Condensations
Aromatic Rearrangements and Migrations
Effect of Anhydrous Aluminum Chloride on Aromatic Compounds
Anhydrous Aluminum Chloride in Aliphatic Chemistry
Polymerization
Anhydrous Aluminum Chloride in the Petroleum Industry
Preparation, Manufacture, and Purification of Anhydrous Aluminum Chloride
Notes of Application of Anhydrous Aluminum Chloride
Author Index, Subject Index

972 Pages Illustrated Price $15.00

REINHOLD PUBLISHING CORPORATION, 330 West 42nd Street, New York, U. S. A.

ANALYTICAL LABORATORY
MERCK
MERCK

A GUARANTY OF QUALITY

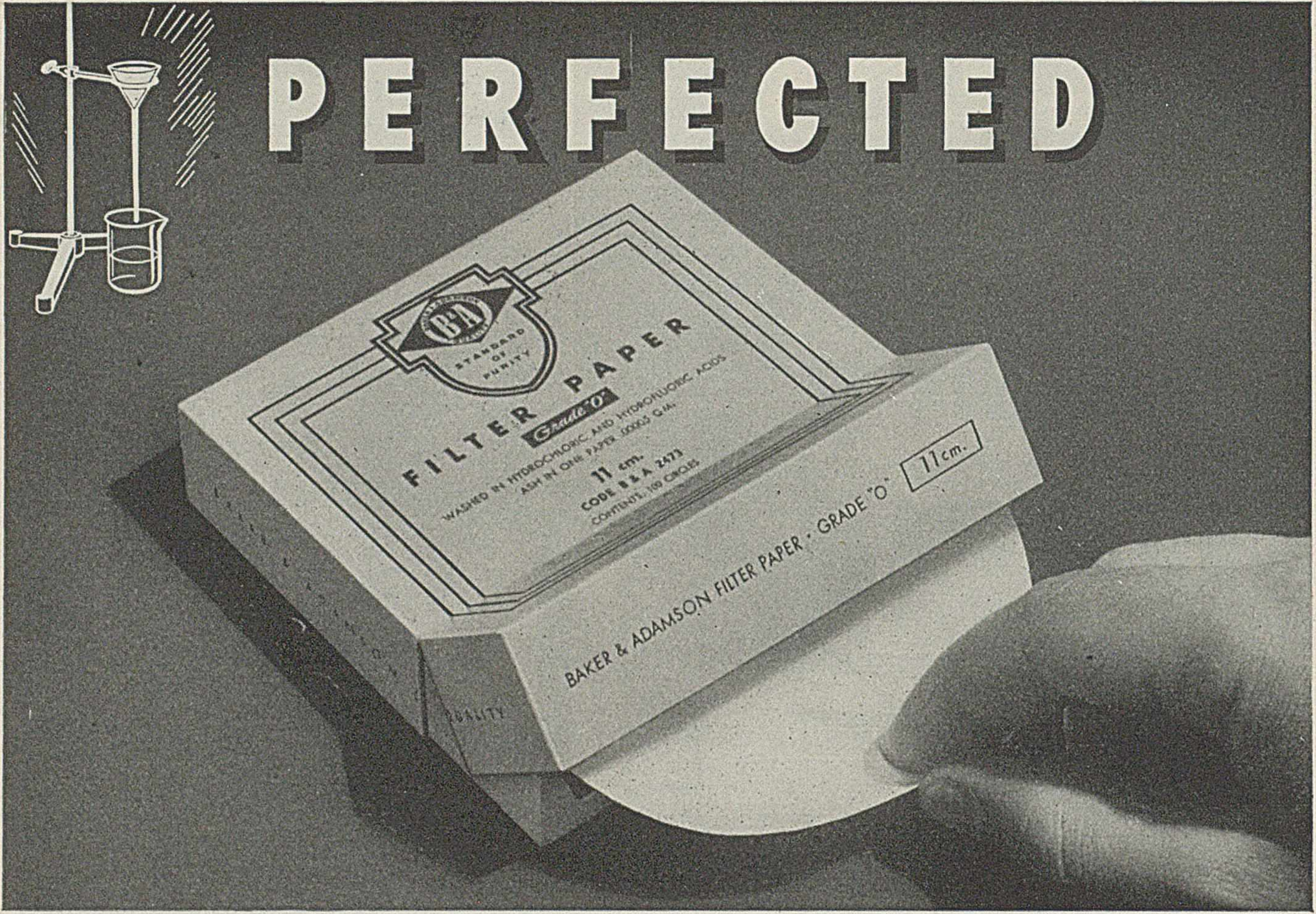
Chemical experience of many years has enabled Merck & Co. Inc. to plan, design and equip the new Merck Analytical Laboratories, wherein rigid and constant control is exercised over more than 1,500 products bearing the Merck label. The wide range of precision, analytical and testing facilities includes not only chemical methods, but physical and optical procedures as well. Because of these modern control facilities, thousands of industrial chemists, students, and research workers use Merck Laboratory Chemicals with complete confidence in their purity and uniformity.

A PLEDGE OF SERVICE

Although the Merck factories are now operating on a 24-hour day, 7-day week schedule in order to supply the needs of our armed forces and civilian population, it may not always be possible to supply you immediately with your complete requirements of Merck Chemicals. But in spite of the difficulties which confront us, we shall continue to do everything possible to serve our customers to the limit of our ability. In facing the vital emergency job that lies ahead, it is our hope that we may continue to have the understanding cooperation of our customers, which has helped us immeasurably in our efforts to serve them.

MERCK & CO. Inc. *Manufacturing Chemists* **RAHWAY, N. J.**

New York · Philadelphia · St. Louis · ***In Canada:*** **MERCK & CO. Ltd., Montreal and Toronto**


PERFECTED
B&A
STANDARD OF PURITY
FILTER PAPER
Grade "O"
WASHED IN HYDROCHLORIC AND HYDROFLUORIC ACIDS
11 cm.
BAKER & ADAMSON FILTER PAPER · GRADE "O"
11cm.

A *NEW* Quantitative Filter Paper

Made Entirely of Domestic Raw Materials

Baker & Adamson *Announces the Commercial Availability of Grade "O" Domestic Quantitative Filter Paper.*

High in retention . . . low in ash content and entirely American made, Grade "O" fills an ever increasing need for a reliable, domestic quantitative paper.

Grade "O" is an "ashless," double acid washed paper, treated under the most careful laboratory supervision. Unusually uniform in weight and thickness, B & A Grade "O" is especially designed for use in the most exacting types of work.

The development of a successful domestic quantitative paper is but another example of the contributions of General Chemical Company and its Baker & Adamson Division towards an American self-sufficiency in chemical materials. Among similar, recent contributions is the development of a domestic source for Potassium Cyanide, Potassium Cyanate and other chemicals.

B&A
FINE CHEMICALS AND LABORATORY REAGENTS

SETTING THE PACE IN CHEMICAL PURITY SINCE 1882

BAKER & ADAMSON

Reagent Chemicals AND C.P. Acids

Division of GENERAL CHEMICAL COMPANY, 40 Rector St., New York

Sales Offices: Atlanta • Baltimore • Boston • Bridgeport (Conn.) • Buffalo • Charlotte (N. C.) • Chicago • Cleveland Denver • Detroit • Houston • Kansas City • Milwaukee • Minneapolis • Newark (N. J.) • New York • Philadelphia • Pittsburgh • Providence (R. I.) • St. Louis • Utica (N. Y.)
Pacific Coast Sales Offices: San Francisco • Los Angeles • *Pacific Northwest Sales Offices:* Wenatchee (Wash.) • Yakima (Wash.) • *In Canada:* The Nichols Chemical Company, Limited • Montreal • Toronto • Vancouver