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CONTENTS

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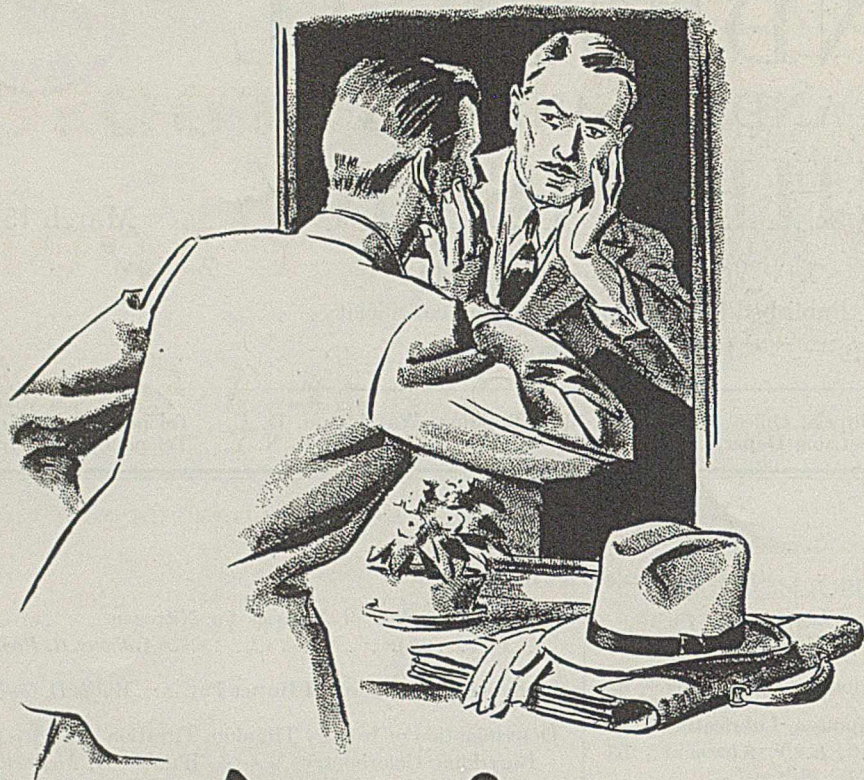
Surface-Tension Measurements of Viscous Liquids <i>A. H. Pfund and E. W. Greenfield</i>	81	Semi-Micromethod of Analysis for Nitrogen <i>Anthony R. Ronzio</i>	122
A New Buret for Potentiometric Titrations . . . <i>L. S. Keyser</i>	82	Studying the Hardness of Butter Fat . . . <i>Willis D. Gallup</i>	123
Laboratory Service Testing of Automotive Lubricating Greases <i>E. N. Klemgard</i>	83	Determination of Iron by Titanium Titration and by α, α' - Bipyridine Colorimetry <i>William D. McFarlane</i>	124
Determination of Starch in Plant Tissues <i>George W. Pucher and Hubert Bradford Vickery</i>	92	Direct Titration of Sulfates <i>R. T. Sheen and H. L. Kahler</i>	127
Determination of Zinc in Soils <i>Hugh M. Boggs and A. O. Alben</i>	97	Determination of Sulfate <i>John E. Ricci</i>	130
Recovering Chloroform from Used Dithizone Solutions <i>Donald A. Biddle</i>	99	Gravimetric Determination of Selenium in Alloy Steel <i>Louis Silverman</i>	132
Measuring the Susceptibility of Asphalts to Temperature Changes . . . <i>A. Holmes, J. O. Collins, and W. C. Child</i>	100	Detection of Rhenium in the Sodium Carbonate Bead <i>Herman Yagoda</i>	133
Control of High Lights in Reading Microbalance Swings <i>Paul H. M.-P. Brinton</i>	104	Rotenone Determination by Colorimetric Methods <i>H. D. Rogers and J. A. Calamari</i>	135
Determination of Gaseous Olefins or Hydrogen by Catalytic Hydrogenation <i>Wallace A. McMillan, Howard A. Cole, and A. V. Ritchie</i>	105	Determination of Iron in Sea Water <i>Norris W. Rakestraw, Henry E. Mahnecke, and Eliot F. Beach</i>	136
Fluidity and Hygroscopic Properties of Shellac <i>R. V. Townend and W. R. Clayton</i>	108	Determination of Reducing Sugars and Sucrose in Plant Materials <i>W. Z. Hassid</i>	138
Determination of Selenium in 18-8 Stainless Steels <i>George G. Marvin with Walter C. Schumb</i>	109	The Assay of the Platinum Metals <i>F. E. Beamish and J. J. Russell</i>	141
An Efficient Laboratory Extraction Apparatus <i>Frederick C. Oppen</i>	110	A Thermionic Titrimeter without Batteries <i>Hobart H. Willard and O. B. Hager, Jr.</i>	144
A Rapid and Efficient Mixer <i>D. H. Nelson</i>	111	A Continuous-Reading Electron-Tube Conductance Meter <i>R. L. Garman</i>	146
The Determination of Rhenium. II <i>Loren C. Hurd and Bernard J. Babler</i>	112	When Is a Desiccator? <i>Harold Simmons Booth and Lucille McIntyre</i>	148
Separation of Stannic Oxide from Various Oxides by Igni- tion with Ammonium Iodide <i>Earle R. Caley and M. Gilbert Burford</i>	114	A Versatile Low-Temperature Thermostat . . . <i>G. B. Heisig</i>	149
The Ignition of Silicic Acid <i>Knut A. Krieger and Hiram S. Lukens</i>	118	Improved Apparatus for Isolation of Fluorine <i>W. K. Gilkey, H. L. Rohs, and H. V. Hansen</i>	150
Determining Copper in the Presence of Interfering Elements <i>H. W. Foote and John E. Vance</i>	119	Improved Micromanometer <i>Harry W. Smith, Jr.</i>	151
A New Buret for Alkali Titrations <i>L. S. Keyser</i>	121	Device for Determining Rate of Siphoning in Metal Ex- traction Systems <i>R. S. Asbury</i>	152

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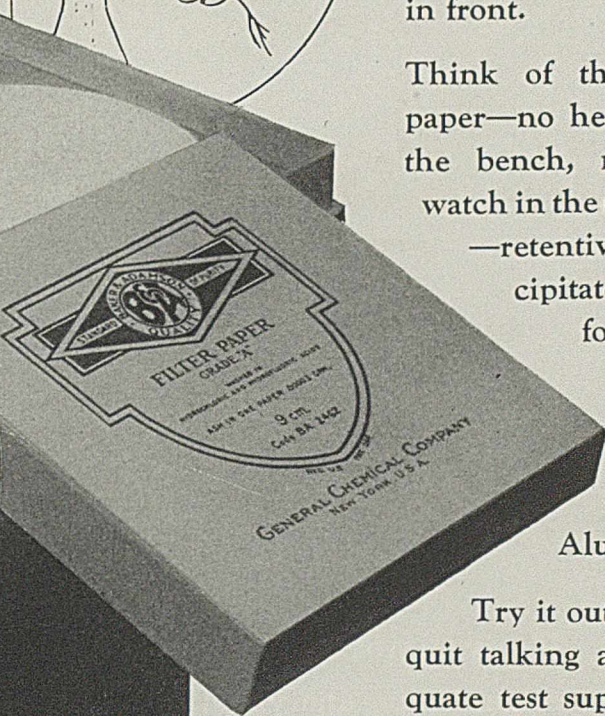
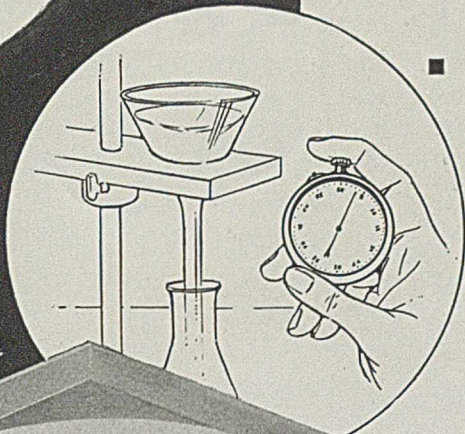
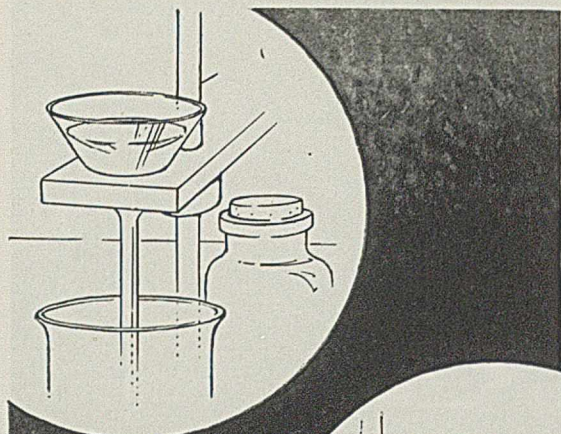
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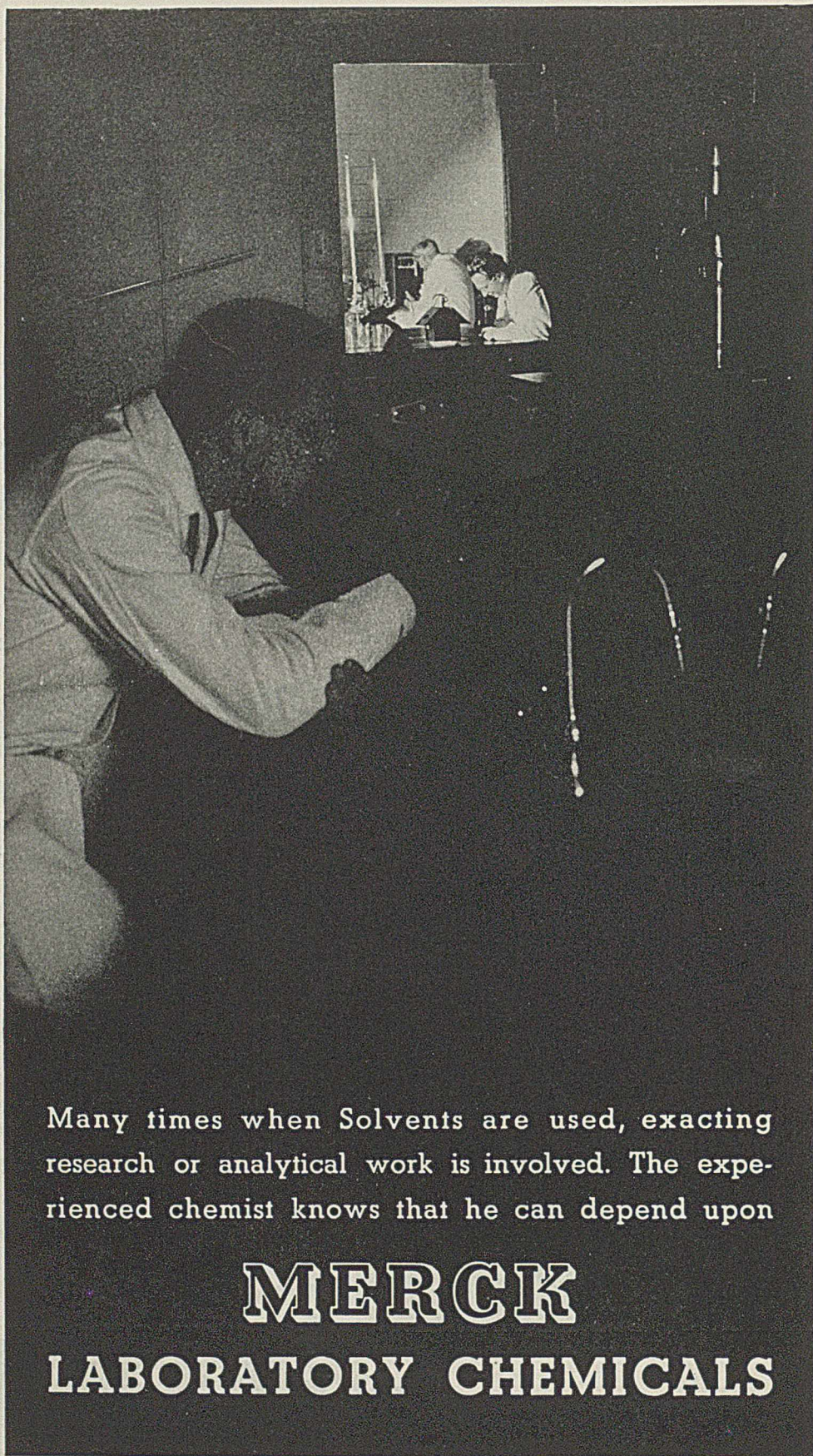
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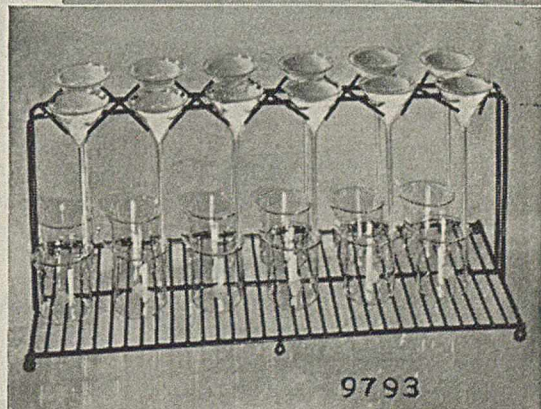
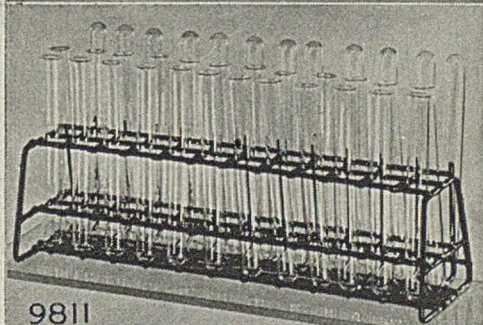
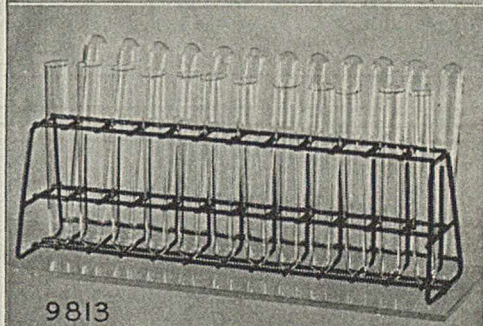
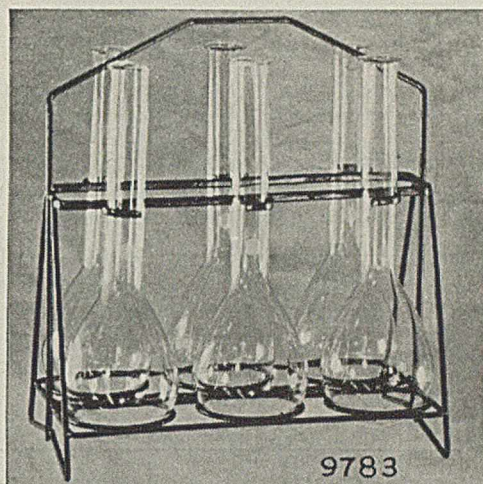
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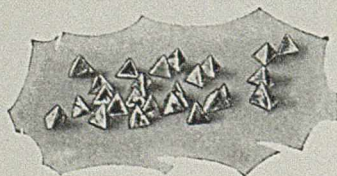
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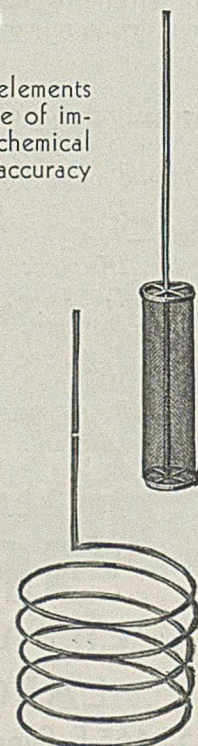
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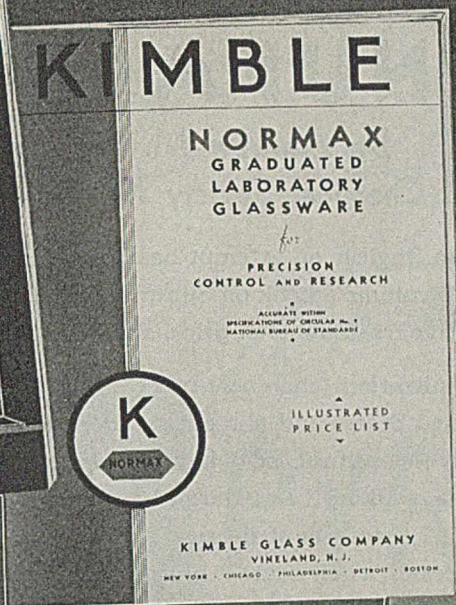
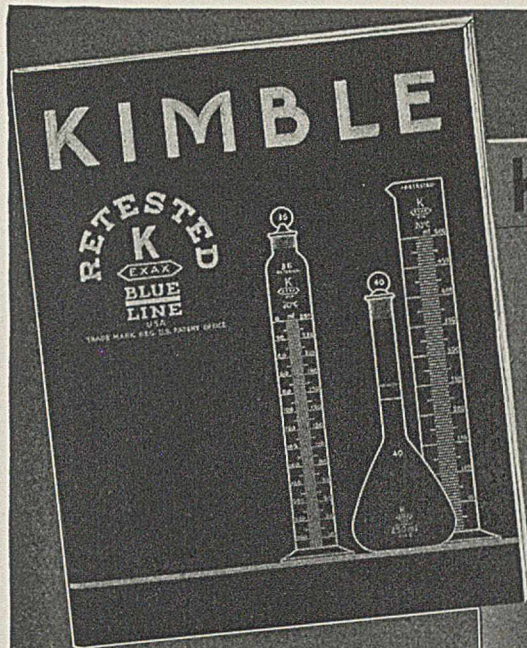
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SULFURIC ACID MANUFACTURE

by Andrew M. Fairlie

American Chemical Society Monograph No. 69

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Describing both the nitration (chamber) processes and the contact processes as practiced in the United States and abroad, it deals with many developments of prime importance to the sulfuric acid industry which have been evolved and placed on a practical working basis during the last ten years—flash roasting processes, liquid-cooled chambers of the new Mills-Packard and Gaillard-Parrish types, new tower processes, a new contact process, new sulfur burners, sulfur spray nozzles for molten sulfur, sulfur-fired steam boilers, new vanadium and platinum catalysts, the expansion of the use of vanadium-mass, self-contained heat-exchange converters, etc.

There is no previous book in any language that describes all of these recent developments with an array of up-to-date details, pertaining to equipment and methods of operation used in modern manufacturing practice.

CONTENTS

Preface.
Introduction.
Historical
Chemistry and Theory Relating to Sulfuric Acid Manufacture.
Construction Materials.
Production Materials.
Burners, Roasters and Furnaces.
Burner- or Furnace-gas.
Nitration Processes—Methods of Nitration.
Glover Tower.
Lead Chambers and Chamber Substitutes.
Recovery of Nitrogen Oxides.
Auxiliary Equipment of a Nitration-process Plant.
Complete Plant Design—Operation of a Nitration-process Plant.
Purification and Concentration of Sulfuric Acid.
Contact or Catalytic Processes. General Discussion.
The Composition of Burner- or Furnace-gas. Cleansing, Cooling and Drying the Gas.
Blowers; Preheaters; Heat-exchangers; Converters.
Catalysts.
Comparison of Platinum and Vanadium Catalysts.
SO₂-gas Coolers; SO₂ Absorbers; Oleum Manufacture; Miscellaneous Contact-process Equipment.
Complete Contact Plant. Operation. Methods of Control of Process.
Special Types of Contact Plant; Individual Installations.
Mixing and Shipping Sulfuric Acid; Hazards and Safety Measures; Costs and Cost-accounting; To Buy or To Build? Choice of Process; Trends in the Industry.
APPENDIXES.

Emphasis is laid on the value of the following tables included in the Appendixes.

- I. Hydrometers.
- II. Sulfuric Acid Tables of the Manufacturing Chemists Association of the United States.
- III. Sulfuric Acid Temperature Correction Tables.
- IV. Sulfuric Acid Conversion Factors.
- V. Sulfur Dioxide Percentage Tables.
- VI. Nitrosity of Nitrous Vitriol or Sulfuric Acid.
- VII. Boiling Points of Sulfuric Acid Solutions.
- VIII. Properties of Saturated Steam.
- IX. Tables Giving the Composition and Weight of Sulfuric Acid Solutions, from 1.02 to 100 per cent H₂SO₄.
- X. Fuming Sulfuric Acid Tables.
- XI. Table for Finding Conversion Percentage.
- XII. Brick Shapes, Illustrated, with Sizes.
- XIII. Lead Pipe and Sheet Lead, Sizes and Weights.
- XIV. General Conversion Factors (9 pages of them) for Converting Quantities of a Given Unit into Equivalent Quantities of a Different Unit.
- XV. Nomographs.

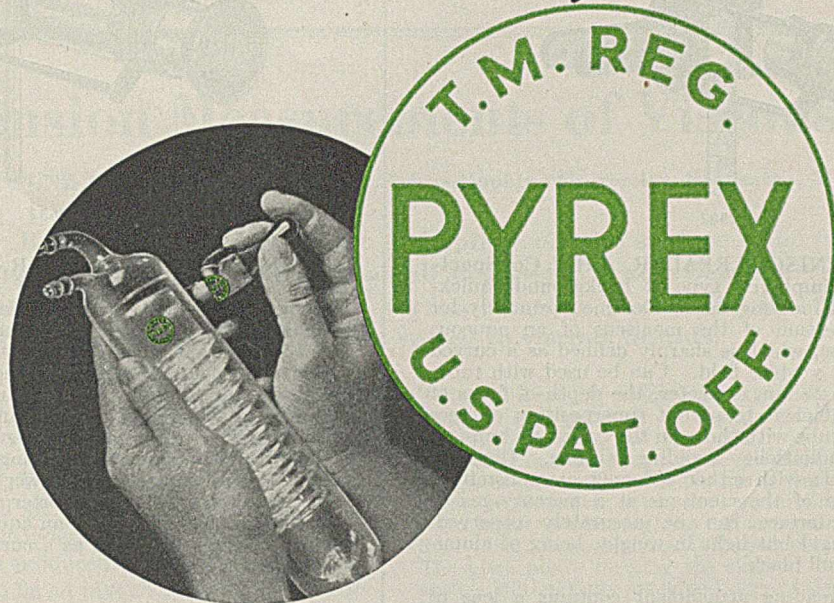
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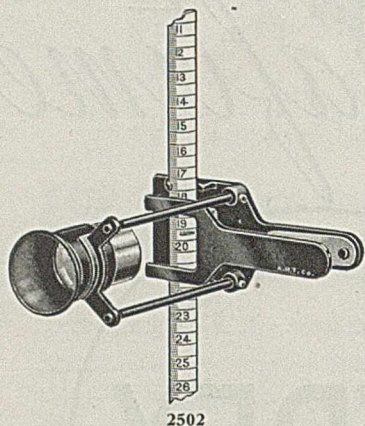
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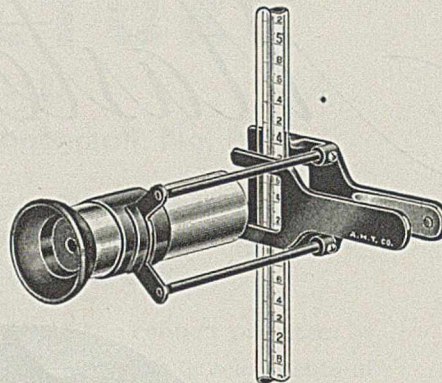


2502-A
Thermometer Reading Attachment



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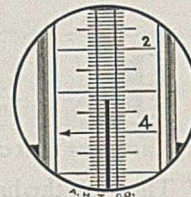
9632

THERMOMETER READER, A.H.T. Co. Specification. With improved type of background and quick-acting clamp exactly as furnished with No. 2502 Burette Meniscus Reader, but with a higher power magnifying lens so mounted that reflections from the surface of the outside tube of an enclosed scale thermometer such, for example, as a Beckmann thermometer, are reduced to a minimum. This greatly increases the ease and accuracy of reading a thermometer scale graduated in small intervals.

The Burette Meniscus Reading Attachment contains a lens of lower magnifying power and of different depth of focus, mounted in a shorter tube, for observing the position of the meniscus of an aqueous liquid in a burette, which is sharply defined as a curved black line against a white field.



9633
Burette Meniscus Reading Attachment



Field of view in Beckmann Thermometer graduated in 0.01°

9632. Thermometer Reader, A.H.T. Co. Specification, as above described, without Burette Meniscus Reading Attachment..... 10.00
Code Word..... *Ovjiv*
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HARRISON E. HOWE, EDITOR

Surface-Tension Measurements of Viscous Liquids

A. H. PFUND AND E. W. GREENFIELD, Johns Hopkins University, Baltimore, Md.

By allowing a small air jet to impinge on the surface of a liquid, there is produced a small depression whose depth is an inverse function of the surface tension of the liquid. This procedure is particularly suited to viscous liquids.

THE usual methods for surface-tension measurements fail when applied to highly viscous fluids. The following method, developed by one of the authors (A. H. P.) in 1932 and tested by the other (E. W. G.) in 1934 is based upon the observation that if a small air jet be allowed to impinge on the surface of a liquid, an indentation or depression of the type shown in Figure 1 is produced. The depth of this depression has been found to be an inverse function of the surface tension. The method is at its best when applied to liquids which are nonvolatile, viscous, and transparent.

The general arrangement of the apparatus is shown in Figure 2, where *A* is a glass tube drawn down to a bore of about 0.8 mm. at its lower end which is separated by about 3 mm. from the liquid surface, *C*. While there is nothing critical about the dimensions of the cell, *B*, the thickness of the fluid layer in the direction *LM* was chosen as 10 mm. The depth of the depression is 1 to 2 mm. since instability sets in when the depth is made considerably greater. Measurements of the depth of the depression are carried out with a short-focus Gaertner telescope, *M*, supplied with a micrometer eyepiece reading to 0.01 mm. Illumination is effected by means of the small lamp, *L*, which is replaced by an arc lamp when the liquids are nearly black. Light coming over the top of the liquid is cut out by the opaque shield, *S*. Since it is necessary that the distance between the end of the glass tube, *A*, and the liquid surface be kept constant—a condition difficult to realize by attempting to fill the cell always to the same level—an arrangement of the type shown in Figure 3 was adopted.

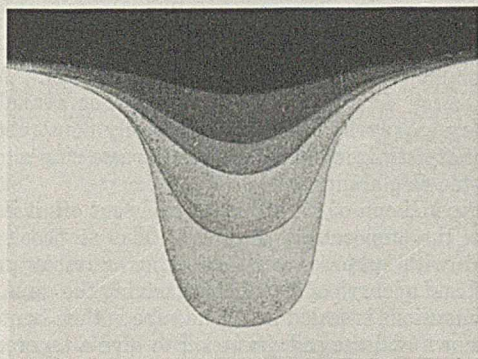


FIGURE 1. FORM OF DEPRESSION WITH SUCCESSIVE INCREMENTS OF AIR PRESSURE

Here the cell, *B*, which fits neatly between the blocks, *DD*, is mounted on a plate, *E*, to which a hinge, *H*, is attached at one end and a screw, *F*, at the other. By means of this screw it is possible to raise or lower the cell bodily and thus to bring the image of the undisturbed surface into coincidence with the telescope cross hair, set to the zero reading of the micrometer.

To facilitate cleaning, the cell is made out of a brass block, 10 mm. thick, from which a U-shaped portion has been removed. The glass plates forming the sides of the cell are simply held against the carefully machined sides of the brass block with small clamps (not shown).

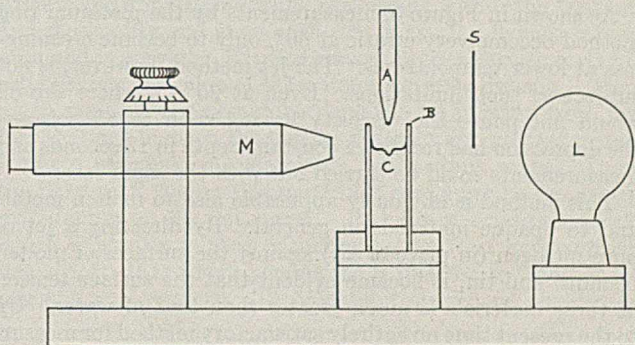


FIGURE 2. ARRANGEMENT OF APPARATUS

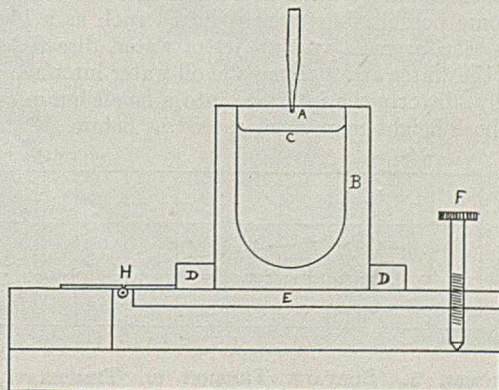


FIGURE 3. ARRANGEMENT FOR MAINTAINING CONSTANT SEPARATION BETWEEN JET ORIFICE AND LIQUID SURFACE

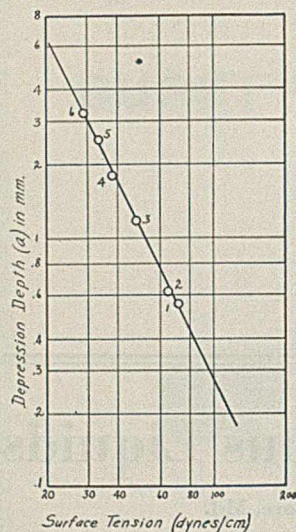


FIGURE 4. CALIBRATION CURVE, LIQUIDS OF KNOWN SURFACE TENSION

1, Water. 2, Glycerol. 3, Glycerol. 4, Dibutyl phthalate. 5, Oil 104. 6, Oil 108.

An advantage of the air-jet method over other methods is brought out in a study of temperature-surface tension relationships in oils used for the impregnation of cables. The specific case chosen for the sake of illustration relates to a mineral oil designated as No. 100/100. At 100° C. this oil had a viscosity of 0.5 poise and was therefore fluid; at 60° C., however, the viscosity has risen to 4 poises and the oil was thick. Surface-tension measurements made by the air-jet method and by the "Jolly balance platinum ring" method are in excellent agreement at temperatures above 60° C.

As shown in Figure 5, measurements by the platinum ring method become very erratic at 60°, only to become meaningless at lower temperatures. The jet method, however, is not subject to such limitations. Even at 25° C. where the oil would not pour—the viscosity having risen to 85 poises—the depression had reached a constant depth in 12 seconds and measurements could be carried out with the same ease.

This method is obviously applicable also to molten metals and to opaque materials in general. By directing a jet of pure nitrogen (in place of air) against the surfaces of molten bismuth and tin, it became evident that the surface tension of these materials is much greater than that of water. Up to the present time no entirely satisfactory method for measuring the depth of the depression has been found.

Another possible application of a modified jet method lies in the measurement of interfacial tension of water in contact with some nonmiscible, viscous liquid such as a heavy oil. In this case, a small, vertical jet of water, directed upward within the water and striking the oil-water interface perpendicularly, distorts the interface into a small hump or elevation whose height may be measured as before. Calibration

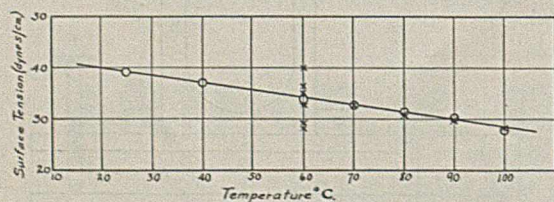


FIGURE 5. SURFACE TENSION vs. TEMPERATURE (MINERAL OIL 106)

xx Platinum ring-Jolly balance method
oo Air-jet method

For the sake of brevity, no description of the apparatus used in the production and maintenance of constant air pressure will be given. A pressure of about 2.4 cm. of water was found best. Calibration was effected by means of the known surface tensions of pure liquids—water, glycerol, glycol, dibutyl phthalate, and several mineral oils—no corrections being applied for density differences. The calibration curve obtained is shown in Figure 4, where the data are plotted on double logarithmic paper. The equation of this curve is

$$\gamma = Ka^{-1/2}$$

where γ is the surface tension, K a constant, and a the depth of the depression.

may be effected through the use of liquids having higher fluidity and a known interfacial tension with water. In the absence of such information it is always possible to make measurements by creating electrically excited ripples (I) at the interface between water and nonmiscible liquids of high fluidity.

In connection with the preceding work it was noticed that air jets are extremely sensitive to short sound waves. If an air jet of the previously described type be directed vertically downward on a water surface—the separation between orifice and surface being 7.5 cm. and the pressure equal to 7.5 cm. of water—the depression immediately disappears as soon as a hissing sound is produced or if keys be rattled. There is a critical jet velocity and separation at which the sensitiveness is greatest. The behavior of the jet is therefore similar to that of the well-known "sensitive flame." The sensitive jet is well adapted for lecture-room demonstration: It is merely necessary to use a vertical projection lantern and to send the light through a flat-bottomed glass dish containing water. By focusing the water surface on the screen, it is found that a black spot appears where the water surface is deformed. This spot disappears immediately upon the production of short sound waves.

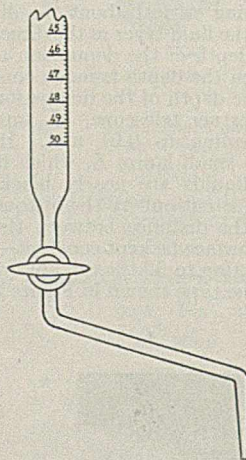
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(1) Pfund, A. H., *Phys. Rev.*, **32**, 326 (1911).

RECEIVED November 1, 1935. Presented at the meeting of the Committee on Insulation (National Research Council) at Urbana, Ill., 1934.

A New Buret for Potentiometric Titrations

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THE burets which are commonly used for potentiometric titrations are usually the ordinary straight type or those which have the faucet type of stopcock. In many titrations where a stirrer, electrodes, and other apparatus are necessary in or above the titrating receptacle, it has been found convenient to use the buret herewith illustrated. It has the advantage of allowing control of the stopcock at a comfortable distance from the encumbering mechanism over the reaction vessel. Although the buret is not available from

laboratory supply houses, it can be easily constructed from the ordinary straight buret by anyone possessing a minimum of glass-blowing ability.

The tapered end of the stopcock tip is cut off at its base as far from the stopcock as possible. The stopcock is then wrapped with asbestos cord or other suitable protection afforded and a length of glass tubing having the same approximate dimensions is sealed on. The tube is then bent into the shape shown and the end drawn off to give a tapered point.

RECEIVED December 31, 1935.

Laboratory Service Testing of Automotive Lubricating Greases

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GREASE manufacturers in the United States produce annually nearly 300,000,000 pounds of lubricating grease, which is sold for approximately \$18,000,000. Of this total amount, 150,000,000 pounds of special grease, about 50 per cent, are consumed in automotive units. As in other industries, grease manufacturers are intently alert to new developments in mechanical engineering, particularly in the automotive field. This is only natural, since roughly one-half of the total amount of grease produced is consumed by the motorist.

Special service tests for automobile lubricating oils and gasoline have been more or less standardized, but the service testing of lubricating greases has been largely a matter of special technic developed as occasion necessitated by the grease manufacturer, automobile manufacturer, institution, or consumer. Because casual observation of service results in equipment on the road often leads to erroneous results and comparisons, laboratory service tests are frequently used to secure more precise data from which definite conclusions may

The importance and necessity of developing service tests of value in formulating improved automotive greases are emphasized in view of the grease industry's desire to meet more adequately the demands of modern cars, high-speed driving, and the consequent more severe lubrication conditions. Laboratory service tests have been devised which permit comparisons of service properties to be ascertained more quickly, economically, and precisely than in more laborious road tests. Road tests are, however, considered necessary for final evaluation of service properties.

color of the grease, odor, customer appeal, attractive appearance, and type of container, but performance must not be ignored. The discriminating purchasing agent, chemist, and engineer are frequently interested in knowing just how good a given lubricating grease is and how it performs in service.

Pressure-Gun Grease

Many of the cars on the road are equipped with some form of plain bushing shackle. In some cases, needle bearings

have been fitted into the king pins, and the development of "knee-action" front wheels has brought about modifications in steering mechanism bearings. However, the chief problem regarding the quality of pressure-gun greases is their ability to "stay in place." For this reason service tests for determining the retention characteristics of such greases have been developed by grease manufacturers and are of interest.

As with most lubricating grease problems, the viscosity of the mineral oil content, the consistency of the grease while being applied and while performing within the bearing, and the quality and amount of soap may all influence results obtained in service. For this reason, precise service tests for establishing the value of these items are very difficult. That much research remains to be done can be inferred from the fact that one finds on the market different gun greases manufactured with calcium, aluminum, and sodium soaps. Thus, the "experts," who in this particular case must be the grease manufacturers, do not agree. Perhaps a condition exists which is similar to that occurring in the food and clothing industries: that which pleases one is rejected by another for psychological reasons. Technically it should be possible to

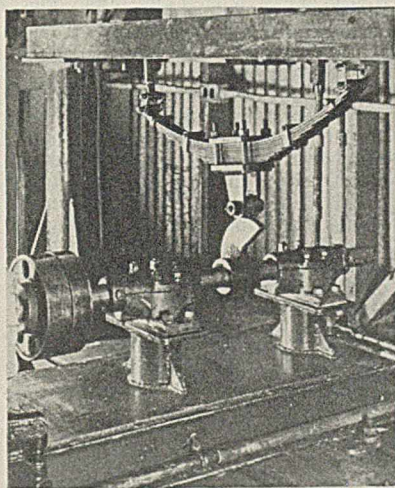


FIGURE 1. APPARATUS FOR DETERMINING RETENTION PROPERTIES OF PRESSURE-GUN GREASES IN SPRING SHACKLES

that under a given set of conditions one grease is superior to another. The time-honored tests for melting point, penetration, and per cent of water, soap, and ash, while of greatest value as control tests to secure uniform quality, leave too much to the investigator's imagination in predicting service performance. Carefully performed laboratory service tests are believed to be invaluable as indicators, pointing the direction in which definite improvements in automotive greases may be made.

Salesmanship must necessarily take into consideration

be drawn. In some cases, a series of greases differing only slightly in their usual properties must be studied to determine their relative service value. Road tests for thousands of miles might be needed to reveal practical differences, but accelerated laboratory service tests can be devised which enable definite comparisons to be made in a few hours.

Obviously, service tests may be used for proving

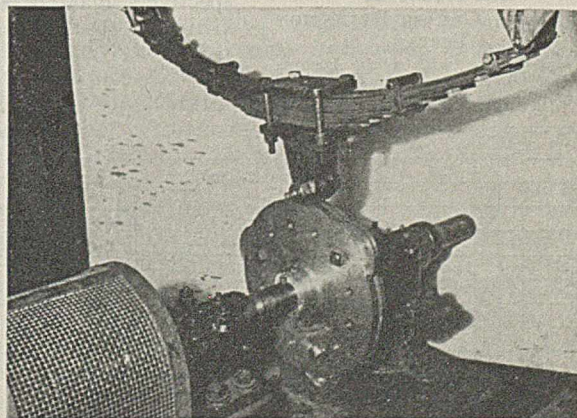


FIGURE 2. MODIFIED APPARATUS FOR DETERMINING RETENTION PROPERTIES

Produces more rapid vibration than device shown in Figure 1

TABLE I. PHYSICAL AND CHEMICAL TESTS ON COMMERCIAL PRESSURE-GUN LUBRICANTS

Lubricant Designation	Penetration at 77° F.		Dropping Point Ubbelohde	Kind of Soap	Ash %	S. U. Viscosity of Mineral Oil Content at 100° F.	Texture	Flow of Grease through Saybolt Universal Viscosity Tube		
	Unworked	Worked						35° F. G./min.	77° F. G./min.	100° F. G./min.
355 Al 400	...	385	89	Aluminum	..	400	Smooth	0.5	9.7	..
375 Ca 301	362	375	97	Calcium	1.04	301	Smooth
340 Ca 319	347	340	90	Calcium	1.06	319	Smooth
370 Ca 350	375	370	90	Calcium	..	350	Smooth
314 Ca 868	315	314	96	Calcium	1.61	868	Smooth
336 Ca 335	323	336	...	Calcium	..	335	Stringy	0.3	2.0	15.1
318 Ca 460	320	318	...	Calcium	1.34	460	Smooth	0.7	11.0	25.2
345 Ca 310	342	345	...	Calcium	1.7 max.	310	Smooth	1.4	19.8	..
354 Ca 315	354	354	...	Calcium	1.7 max.	315	Smooth	2.0	22.8	..
335 Al 290	325	335	...	Aluminum	..	290	Smooth	0.3	7.9	37.0
321 Ca 3000 (blown saponifiable oil)	316	321	90	Calcium	..	3000	Stringy	...	1.1	..
319 Ca 35 (latex)	309	319	88	Calcium	..	35	Stringy	...	0.2	..
227 Ca 300	207	227	92	Calcium	..	300
318 Ca 500 (polyisobutylene)	...	318	95	Calcium	..	500
305 Ca 310 (milled)	305	305	91	Calcium	..	310	...	0.5	4.4	..
285 Ca 500 (latex)	...	285	95	Calcium	..	500	...	0.2	2.2	..
282 Ca 425	...	282	...	Calcium	..	425	...	0.3	5.0	..
350 Na 3100	...	350	135	Sodium	..	3100	...	Trace	1.1	..
450 Na 2500	...	450	...	Sodium	..	2500
390 Al 3000	...	390	101	Aluminum	..	3000	...	Trace
400 Al 1000 (app.)	...	400	...	Aluminum	..	1000
350 Al 1000 (app.)	...	350	...	Aluminum	..	1000
Oil 2000/100° F.	2000

determine which of two greases is best adapted to service in a given chassis bearing under given service conditions. However, the term "given service conditions" is a limitation which greatly restricts our general problem, and atmospheric temperatures, rain, dust, ice, wear, and design are variables which stand in the way of simplified service testing. The following method of testing has been worked out with a view to including the more normal types of operating conditions and thus forms the basis of opinions on retentivity as related to oil viscosity, consistency, type of soap base, and quantity of soap.

TESTING PRESSURE-GUN GREASES FOR RETENTIVITY. Either plain pin or screw-type shackle bolts have been adopted for the testing of pressure-gun greases in the apparatus shown in Figures 1 and 2 because they present the most important current shackle bolt lubrication problems. A model A Ford front spring with shackles and a Buick series 33-50 rear spring shackle, representing characteristic plain pin and screw-type shackle bolts, respectively, make it possible to study retentivity.

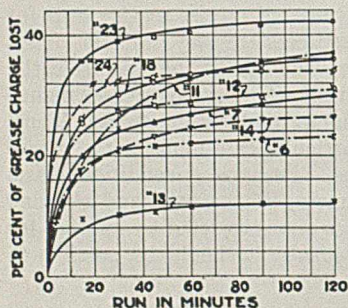


FIGURE 3. GREASE RETENTION TESTS

Front spring with plain bushing shackles on chassis lubricant tester. Charge, 2.80 to 2.90 grams of grease.

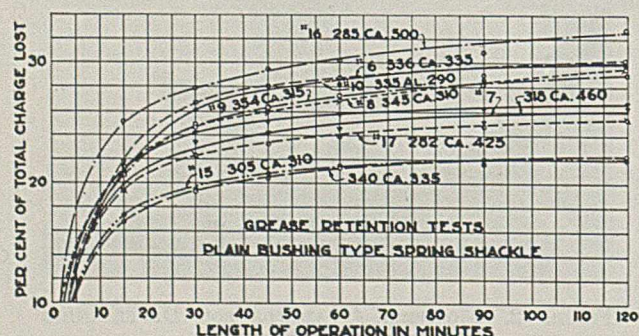


FIGURE 4

The actuating cam shown in Figure 1 was driven by a 3-horsepower electric motor through a 30 to 1 reduction gear. This mechanism imparts a 2.5-cm. (1-inch) deflection to the spring 60 times per minute. The cam is so designed that after maximum lift it leaves the roller follower and the spring returns freely to normal position. The deflection may also be obtained by means of a suitably designed cam as in Figure 2.

Before each test the spring shackles were completely disassembled and washed thoroughly with benzene, care being taken to remove all the old grease from the grease ducts and fittings. After thorough drying, the shackles and bolts were assembled, making certain that all interchangeable parts were replaced in the positions from which they were taken.

A small screw-type grease gun was filled with the grease to be tested and weighed on a balance to the nearest 0.05 gram. Each shackle was charged with grease until it showed signs of being forced out at the ends of the shackle bolt bushings. The filling gun was then reweighed and a small pad of cotton was used to wipe off the excess grease. The increase in weight of the cotton, subtracted from the loss of weight of the gun, gave the weight of grease charged to the shackle. The clearance between shackle and bushing was maintained at approximately 0.02 cm. (0.008 inch).

One form of grease-retention test consisted of taking a set of six readings during a 2-hour test period, the first four being taken at the end of 15-minute periods and the last two at the end of 0.5-hour periods. The readings were obtained by shutting the motor down and wiping the edges of the shackle bolts and bushings thoroughly with a weighed wad of cotton, and then measuring the increase of weight of the cotton.

An examination of Figures 3, 4, and 5 reveals that neither the kind of soap base, the viscosity of the oil content, the penetration value, nor slight variations in soap content alone

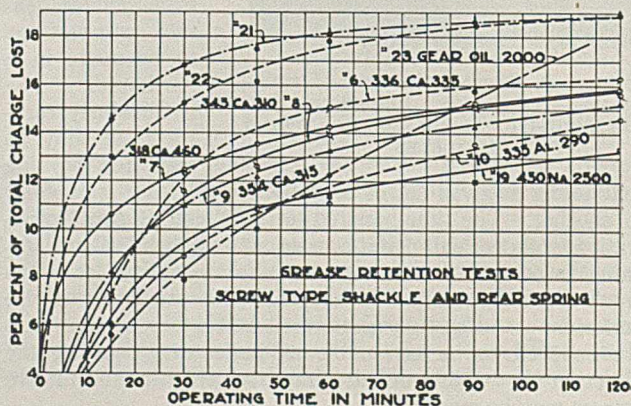


FIGURE 5

make one product better than another. Probably the combination of these factors and the modifying agents present which influence adhesion, aëration, and stability of the grease while in the shackles are the important items in determining the retentivity of a pressure-gun grease.

Grease 305 Ca 310 (Figure 4) shows a loss of 22 per cent in the 2-hour retention test (first number indicates worked penetration; second, soap base symbol; third, Saybolt Universal viscosity of oil content at 37.78° C., 100° F.). Grease 354 Ca 315 is similar with regard to penetration, type of soap, and mineral oil viscosity, but shows a loss of 28.8 per cent. A possible explanation of this difference is that the first grease has been milled to stabilize it, thus increasing its retentivity. It therefore may be concluded that the usual tests for penetration, soap base within certain limits, and oil viscosity do not accurately indicate the degree of retention which may be expected from a given pressure-gun grease. It also follows that further research towards establishing a correlation between retention, pressure viscosity, and stability of the grease film within the bearing are greatly needed.

RETENTIVITY OF PRESSURE-GUN GREASES IN PRESENCE OF WATER. In order to obtain information as to whether or not an aluminum stearate-base grease was more resistant to the action of rain water than a lime-base grease, the retention tester discussed above and shown in Figure 1 was equipped with a water-spray apparatus.

Alterations made in equipment consisted in the addition of a device for spraying water upon the shackles, and the building of a small tank about the apparatus to collect the water sprayed upon the shackles. The spray apparatus consists of two atomizers dipping into a tray of water. The two atomizers are operated by air under pressure, the intensity of the air jet being controlled through the use of an air valve and a pressure gage. The spray apparatus was placed in position so that a fine spray of water could be thrown up on the shackles.

Modifications of this device have undoubtedly been devised by others for splashing, dripping, or spraying water onto the shackles. The device as used is a simple method of obtaining a gentle washing action analogous to what might be met in service in stormy weather. The rebound of spray from the side of the tank and other parts of the apparatus results in water contacting the shackles from every direction from which water might come in actual service. The test conditions can also be fairly well reproduced by controlling the air pressure and the level of the water in the tray.

TABLE II. RETENTION OF GREASE

(Lubricant tester as shown in Figures 1 and 2, plain shackles, 2-hour test period, fine spray of water)

Kind of soap	Grease 335 Al 283	Grease 354 Ca 327	
	Aluminum	Aluminum	Calcium
Per cent of soap	10.2	7.9	
Worked penetration	335	354	
Oil viscosity, S. U. at 100° F.	283	327	
Charge of grease, grams	2.81	2.81	2.88
Total water spray on shackles, liters	12.50	12.15	12.20
Water wiped from bearing surfaces and grooves, grams	0.141	0.235	0.302
Grease wiped from bearing surfaces and grooves, grams	0.160	0.149	0.179
Grease obtained by pressure-benzene treatment	1.241	1.320	1.302
Total grease retained, grams	1.401	1.469	1.481
Per cent retention	50	52	51

The spring, shackle bolts, and the crossbar from which the spring and shackles were suspended were assembled outside the tank which surrounds the lift cam. An excess of grease was forced through the Zerk fittings of the apparatus and measurements made as previously described.

A 2-hour test period was selected. This was consistent with previous tests carried out in the absence of water, in which the length of the test period was 2 hours. Except for

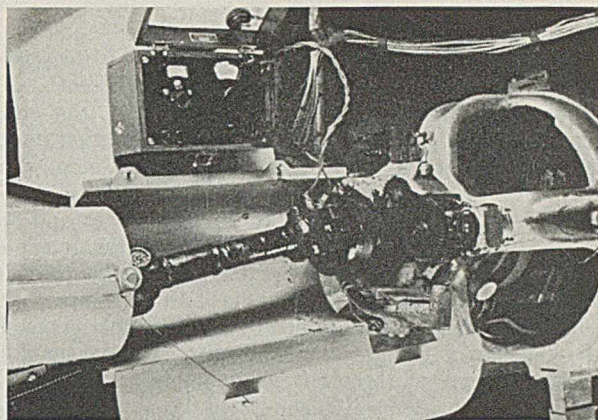


FIGURE 6. UNIVERSAL JOINT GREASE SERVICE TESTER, VIEWED FROM ABOVE

Electric dynamometer at right for absorbing power transmitted. Note method for determining temperatures within joints by means of thermocouples and shield for accumulating grease thrown from joint.

the spray playing on the shackles, the conditions of the test were identical with those of tests carried out on a dry basis. It was not possible to carry out observations on the amount of grease leaving the shackles at 15-minute or 0.5-hour intervals so as to obtain a retention-time curve.

The problem of recovering the grease from the water sprayed on the shackles was given consideration. However, this seemed impractical since the surfaces of the interior of the tank were large and the surfaces of the springs were irregular and likely to retain a certain amount of grease in crevices. The removal and measurement of the grease retained on the bearing was resorted to since the surface areas were smaller and easier to work with.

The results shown in Table II were obtained in the test.

The results on the two greases are in fairly close agreement, except in the amount of water removed from the shackles. However, these water figures are not very reliable, since losses are bound to occur through evaporation of water and probably also the loss of droplets of water from the shackles in removing shackle bolts. Neither grease showed any evidence of emulsification in the shackles as the result of the entrance of water.

The comparison between these two greases seems to be a fair basis for comparison of calcium- and aluminum-base chassis lubricants under wet conditions, since the oil viscosities, consistencies, and soap contents of the two greases were similar.

A complete investigation of the effect of water on shackle lubrication would of course include an investigation of screw-type shackles as well as plain shackles, and also the effect of different methods of bringing water in contact with the shackles. The effect of high-pressure washing should be of special interest in this regard. The effect of oil viscosity, soap content, and glycerol content on retention under wet conditions might also be investigated. However, since the results so far obtained show so little difference in the behavior of calcium- and aluminum-base greases in the presence of water, it is doubtful if much information of value would be obtained by further work on a comparison of aluminum- and calcium-base greases, although a comparison with sodium-base grease would no doubt be of interest.

Ordinarily, it is considered that temperature conditions met with in pressure-gun grease service are so low that high melting point soda-base greases are unnecessary. Since speeds and load are low, extreme pressure agents in most cases appear to be unnecessary.

Universal Joint Grease

Figure 6 shows a view of an apparatus used for service testing of universal joint greases. It consists essentially of two joints connected by an intermediate shaft, the entire assembly being driven by a 30-horsepower induction motor. Tests may be carried out at a speed of 3590 r. p. m. which corresponds to an approximate road speed of 80 miles per hour. The load transmitted was 20 horsepower and was absorbed by means of a 35-horsepower Sprague dynamometer. Conditions conducive to accelerated wear were provided for by operating the joints at an angle of 10°. Temperatures within the bearings were obtained by means of thermocouples and retention of the grease was studied and measured by collecting the grease thrown from the joints.

PENETRATION. Table III shows that very little relation exists between penetration and the temperatures attained within universal joints. Sample 4 has a fairly low unworked penetration value of 205, and the temperature rise within the universal joint was 19.5° C. (35° F.). Universal joint grease 7 was much softer, having an unworked penetration value of 325, yet the temperature rise was 27.8° C. (50° F.). Universal joint grease 6 is somewhat heavier than 7, but the lower penetration value of 275 apparently did not cause any significant difference in the bearing operating temperature which remained at 50° above atmospheric. It is therefore concluded that from the standpoint of service the penetration of a

universal joint grease is not of paramount importance. It is fully realized that consistency and viscosity must be taken into consideration in dispensing greases at low temperatures. A range of 300 to 330 worked penetration should be satisfactory for purposes of manufacturing control.

PERCENTAGE OF WATER. Most commercial universal joint greases contain less than one per cent of water, and while it appears that the moisture content has no direct bearing on efficacy of lubrication, it is felt that a good grease should not contain more than 1.5 per cent of water. At very low temperatures, greases containing no glycerol and much water might be found objectionable.

MELTING POINT. Inasmuch as the service tests indicate no definite advantages for No. 5 and No. 7 high melting point greases, particularly from the standpoint of bearing temperatures and wear, the point is not especially important if service characteristics alone are taken into consideration. If a high melting point were indicative of good grease retention, we should expect No. 5 and No. 7 to be considerably less subject to leakage. An examination of Table III will indicate that the opposite of this is true. We therefore conclude that, from the standpoint of service, melting point specifications are not essential providing the greases are well-made products having soda-soap bases.

FREE ALKALI. The analysis indicates that grease 5 has a free acid content of 0.42 per cent. However, the corrosion test (copper strip, 3 hours at 100° C., 212° F.) was satisfactory

TABLE III. RESULTS OF SERVICE TESTS MADE WITH A SPICER UNIVERSAL JOINT
(Type G, plain bearing joint)

Sample	Max. Op. Temp. above Housing ° F.	Fe ₂ O ₃ in Universal Joint after Test Gram	Throw-Off 30 Hours ^a Grams	Pressure Viscosity ^b G./min.	Viscosity of Oil, Saybolt Seconds at 100° F.	Soap %	Penetration Cone at 77° F. ^c	MacMichael No. 24 Wire at 95° F. ^c
1	30 ¹	0.157 ³	65.0 ⁶	869 ⁵	657 ⁷	14.1	299	180
2	31 ²	0.198 ⁴	62.5 ⁵	949 ⁶	1062 ⁸	11.4	345	100
3	34 ³	0.133 ²	60.0 ³	544 ¹	247 ⁹ Fur.	8.2	304	160
4	35 ⁴	0.245 ¹	67.0 ⁷	602 ⁴	745 ¹⁰ Fur.	14.2	204	Not detd.
5	38 ⁵	Trace ⁵	58.8 ²	342 ²	1986 ³	7.8	310	Not detd.
6	50 ⁷	0.117 ²	54.5 ¹	230 ¹	295 ²	18.5	275	Not detd.
7	50 ⁷	0.143 ⁴	61.8 ⁴	602 ⁴	2072 ⁴	7.8	325	Not detd.

Exponents indicate relative standing.

^a 100-gram initial charge.

^b 30 lb. per sq. inch at 140° F.

^c Unworked.

TABLE IV. ANALYTICAL DATA ON COMMERCIAL UNIVERSAL JOINT GREASES

Grease No.	1	2	3	4	5	6	7	8	9
Physical Properties:									
Appearance	Granular and dark green	Stringy and dark green	Stringy and dark green	Stringy and dark green	Stringy and dark green	Stringy and dark green	Stringy and dark green	Stringy and dark green	Dark green Brown
Odor	Sweet	Soapy	Soapy	Soapy	Soapy	Soapy	Soapy	Soapy	Soapy
Melting point, ° C., Gillette	72	59	49	86	50	80	62	66	Liquid
Melting point, ° C., Ubbelohde	130	82	151	167	143	126	153	143	Liquid
Channel test, ° F.	25	15	30	80	15	30	20	25	10
Penetration at 77° F., unworked	205	310	275	325	310	...
Penetration at 77° F., worked	320	325	330
MacMichael, viscosity No. 24 wire at 95° F.	180	100	160
Corrosion, copper strip, 3 hrs. at 212° F.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.
Bleeding test, 1 hr. at 175° F.	No sep.	No sep.	No sep.	No sep.	No sep.	No sep.	No sep.	No sep.	...
Separation test at 220° F.	None	None	None	None	None	...
Separation test at 250° F.	None	None	None	...	Slight
Composition, per cent by weight:									
Soap	14.1	11.4	8.2	14.2	7.8	18.5	7.8	7.9	8.0
Moisture	0.70	0.65	0.1	0.60	0.7	1.5	0.55	0.45	0.6
Oil	85.0	86.0	91.0	86.0	90.7	80.3	91.0	92.5	91.6
Free alkali (or acid) (oleic acid) (NaOH)	0.35	Neutral	0.42	0.42	0.7
Asphaltic material	0.03	0.01	0.2	...	0.09
Sulfur	0.14	0.37	0.26	0.06	0.24	0.04	0.07	0.43	0.01
Ash:	0.49	0.82	0.96	0.34	0.89	0.32	0.36	0.64	0.45
Per cent by weight	2.61	2.09	1.50	2.59	1.44	3.68	1.61	1.47	0.89
Analysis, per cent of ash:									
Na ₂ CO ₃	95.4	92.2	87.2	87.4	82.1	95.2	82.8	87.6	...
Na ₂ SO ₄	4.3	5.5	11.5	9.0	12.2	4.1	8.6	10.9	...
Fe ₂ O ₃	1.0	1.1
Al ₂ O ₃	2.9
CaO	0.4	...	0.5	...	2.0	0.2	2.3	0.9	95.0
Acid-insoluble and Fe ₂ O ₃	0.9	1.1	0.8	4.0	0.9	...
Mineral oil:									
Viscosity, S. U. at 100° F.	657	1062	247 Fur.	745 Fur.	1986	295 Fur.	2072	1060	2810
Viscosity, S. U. at 210° F.	65	66	109.6	156	102	153	111	66.0	128
Gravity, ° A. P. I.	22.4	17.4	19.7	20.9	20.3	23.7	20.8	17.4	19.0
Flash, ° F.	400	395	415	465	405	515	335	365	405

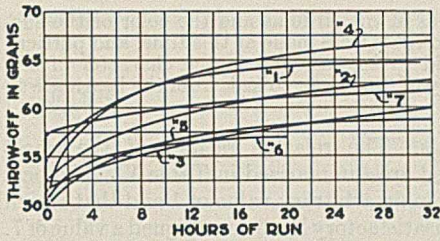


FIGURE 7. REJECTION OF LUBRICANT BY SPICER PLAIN BEARING UNIVERSAL JOINT, TYPE G

Speed 3590 r. p. m., 10° angularity between faces. Original charge 100 grams of lubricant

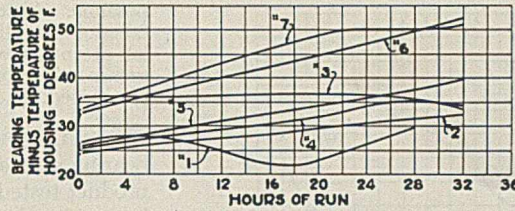


FIGURE 8. TEMPERATURE INCREASE IN SPICER TYPE G UNIVERSAL JOINT

Speed 3590 r. p. m., 20 h. p., 10° angularity

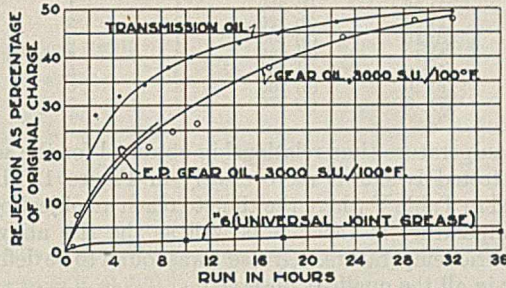


FIGURE 9. REJECTION OF LUBRICANT FROM SPICER NEEDLE-BEARING UNIVERSAL JOINT, TYPE KRL

Speed 3590 r. p. m., load 20 h. p. Universal joint charged with lubricant to 7.5 grams

be observed from Table III that universal joint grease 5, containing only 7.8 per cent of soap, lost 58.8 per cent in 30 hours of operation, as compared with 54.5 per cent for No. 6, containing 18.5 per cent of soap. This difference in retention properties is not proportional to the difference in soap percentages.

Again, universal joint grease 1, a nationally advertised product which was found to be lost from the joint to a greater extent than any of the other products tested, contains only 4.4 per cent less soap than No. 6 which had the best retention properties. Therefore, the necessity for specifying the ash or soap content is not at all apparent when considering service results. It is obvious that in order to conform to definite penetration ranges an adequate soap content must be utilized by the grease manufacturer. The fact that the ash content may vary within fairly wide limits does not appear to have a serious effect on service results.

CORROSION. None of the commercial universal joint greases investigated failed to meet the copper-strip corrosion test.

MINERAL OIL. What has been said above with regard to soap content can also be applied to the percentage of mineral oil used for compounding universal joint lubrications. Slight variations in soap content and consequently oil content are not reflected in the service results.

TESTS WITH NEEDLE-BEARING UNIVERSAL JOINTS. Gear oils and semi-fluid gear greases of the types recommended by the manufacturers of the needle-bearing trunnion universal joints are rejected at a rate some ten times greater than that of a grease such as No. 6, while the operating temperatures are substantially the same in each case. At the end of 32 hours' testing, with each of the lubricants used, the rejection curve showed that little further rejection was probable, and that ample lubricant remained in the bearings.

Lubrication failure for needle joints appears possible only through careless assembly or damage to the cork seals, regardless of mileage run.

During the test period which exceeded 10,000 miles the wear on the bearings was negligible. The fine-lapped finish of the bearing pins did not acquire a full polish during this time.

Figure 9 presents the performance of the greases tested in a clear form, showing especially the low throw-off of universal joint grease 6 with its satisfactory operating temperature.

and, since wear in the service test was exceedingly low for this product, it must be concluded that the free acid content of even this amount is not a serious disadvantage. While these service tests have not been carried out with the particular view of ascertaining the practical significance of free alkali and free acid, the results obtained are such that no particular service disadvantages could be predicted on the basis of these qualities. Therefore the free alkali and free acid specifications appear to have no very useful purpose with regard to service.

FILLERS. It is the writer's belief that no grease recommended for universal joint lubrication should contain any appreciable quantity of filler, as inert solid materials would greatly accelerate wear.

ASH. The ash content is some indication as to the percentage of soap present in the grease. Since the soap content does not correlate at all well with retention properties, it cannot alone be taken as an indication of serviceability. It will

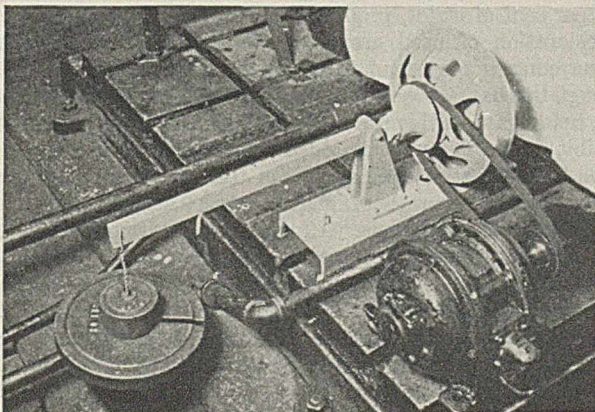


FIGURE 10. GENERAL ARRANGEMENT OF LABORATORY APPARATUS FOR MAKING SERVICE TESTS ON WHEEL BEARING GREASES

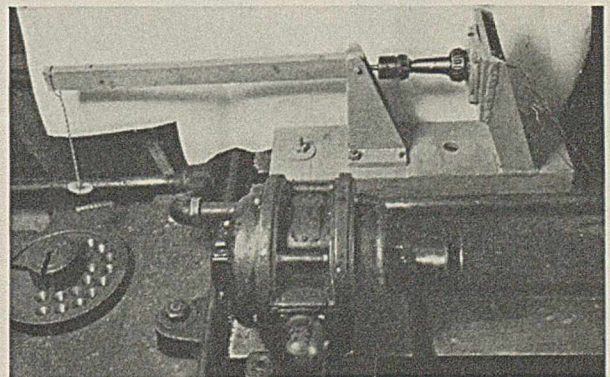


FIGURE 11. WHEEL BEARING GREASE TESTER SHOWN IN FIGURE 10

Disassembled to show method of applying axial load by means of the weight and lever system. Note thermocouple leads to bearing.

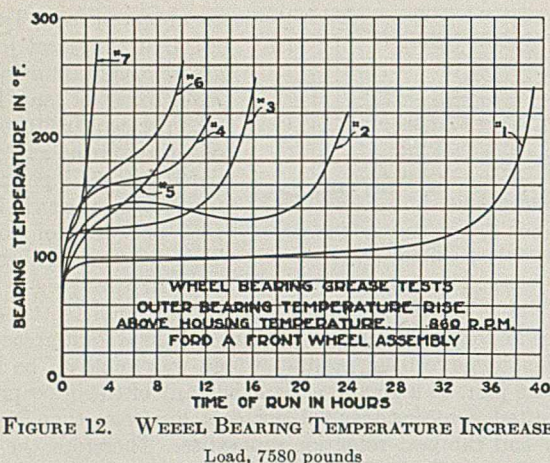


FIGURE 12. WHEEL BEARING TEMPERATURE INCREASES

Load, 7580 pounds

Because the performance of universal joint grease 6 was so satisfactory in service tests, it is concluded that a grease is preferable to an oil.

Wheel Bearing Greases

A service testing device which has been utilized successfully consisted of a front wheel hub and spindle assembly from a model A Ford car. The arrangement of this spindle and the mechanism employed for loading the bearings in an axial direction are shown completely in Figure 10. An axial load of 1336 pounds is produced by a weight of 30 pounds at the end of the lever arm. This is equivalent to producing a total radial load of 7580 pounds on the bearing. Obviously, this load of 7580 pounds is greatly in excess of the normal load which a Ford front axle is required to carry, although shock loads may be even higher. The hub is operated by means of a 0.5-horsepower motor producing a speed of 860 r. p. m. This is equivalent to a road speed of approximately 80 miles per hour. Both the loading and speed are considerably in excess of normal conditions for a car operating on the road. This, however, was considered necessary in order to produce accelerated tests.

Thermocouples were placed under the inner race of both spindle bearings and enabled fairly accurate temperatures to be obtained with the bearings in service. The entire wheel bearing grease tester was enclosed in a thin metal housing in order to avoid sudden fluctuations in temperature due to drafts. New outer bearing cones and races were used for each test run. After thoroughly cleaning the bearings with aviation gasoline, they were carefully packed with 10 grams of the sample of grease to be tested, the grease being kneaded into the spaces between the Timken tapered rollers and their separator. Later tests indicate that one of the patent bearing packers would accomplish accurate results.

Temperature readings for the bearings were made hourly and at the same time the housing and atmospheric temperatures were recorded. Following these hourly temperature readings, the driving motor was stopped and the apparatus disassembled for inspection. Care was taken to disturb the grease as little as

possible. Observations of the oil films and the color of the surfaces of the rollers and races were made at this time, and particular attention was paid to any changes in the character of the grease. The tendency of the grease to leak from the bearing was also noted.

RESULTS OF TESTS. The relative ratings of the wheel bearing greases tested are summarized in Table V. The best product tested is given an arbitrary value of 1 and that which is considered most unsatisfactory has been assigned a value of 7.

TABLE V. TEST OF WHEEL BEARING GREASES

Grease	Time to Reach High Temperatures Hours	Temperature Rise ° F.	Appearance of Roller Bearing	Retention of Grease	Final Rating
1	(1) 39	(1) 250	1	1	1
2	(2) 24	(2) 220	3	2	2
3	(3) 16	(3) 250	1	3	3
4	(4) 12	(5) 220	6	4	4
5	(5) 9	(4) 200	3	5	5
6	(6) 10	(6) 260	3	6	6
7	(7) 3	(7) 275	7	7	7

The temperature-time relationship obtained for the several greases tested is shown more clearly in Figure 12 than is indicated in Table V where the time to reach an objectionably high temperature is variable as well as the rise above the atmospheric temperature. Grease 1 was found to be definitely superior in all the qualities observed.

The analyses of the wheel bearing greases tested are shown in Table VI. The following brief comments deal with the laboratory tests made on the greases investigated and discuss the formulas and usual chemical laboratory tests.

PENETRATION. Grease manufacturers are not in general agreement as to whether worked or unworked penetration values should be established. Table VI shows wheel bearing greases having variations in unworked penetrations ranging from 155 for grease 8 to 240 for grease 9. The worked penetration values range from 197 to 316. Information from other sources indicates that the consistency of commercial wheel bearing greases may vary from a worked penetration value of 170 to values as high as 300. It is realized that worked penetration values are more significant from the standpoint of service than corresponding unworked penetrations. For a satisfactory grease there should be no objection to establishing a worked penetration range of 210 to 240.

PERCENTAGE OF WATER. In general, the water content of wheel bearing grease at present used throughout the country will vary from a trace to as much as 1.8 per cent. The effect of these variations in water content has not been conclusively demonstrated in the service tests which the author has conducted. It is felt that the presence of appreciable quantities of water is of little significance and it has been found that the experimental grease, containing as much as 1.1 per cent of water, produces no objectionable corrosion or discoloration of used grease or bearing surfaces. A high water content may tend to increase corrosion and wear, although this has not been definitely proved. In order to reduce the tendencies in this direction, 0.1 per cent of a material to inhibit corrosion has been added to grease 1. Practical tests have shown that in the presence of this ingredient the water content may reach rather high percentages without detrimental effects to the bearings. A maximum water content of 1.5 per cent is a good working value.

MELTING POINT. It will be observed from Table VI that Ubbelohde dropping points vary from 100° C. for grease 7 to 200+° C. for grease 4. A study of dropping points in connection with service results and retention in wheel bearings has not conclusively demonstrated that a minimum specification as high as 180° C. is definitely necessary. In view of the fact that field and laboratory service tests have not resulted in noticeable leakage when operating on wheel bearing grease 1 having an Ubbelohde dropping point of 145° C., a minimum

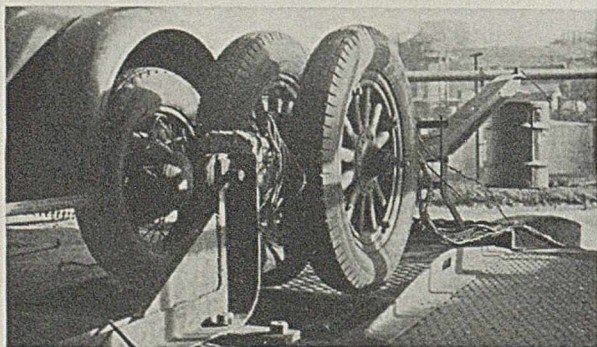


FIGURE 13. CHASSIS DYNAMOMETER ATTACHMENT FOR MAKING WHEEL BEARING GREASE TESTS IN LOADED FRONT WHEELS

Heat supplied by electric resistance coils to simulate conditions of braking

TABLE VI. ANALYTICAL RESULTS ON WHEEL BEARING GREASES

Grease No.	1	2	3	4	5	6	7	8	9	10
Physical tests:										
Appearance	Bright black Spongy	Brown Slt. Stringy	Green black Stringy	Green brown Stringy	Light brown Stringy	Bright green	Gray brown	Dark green Granular Stringy	Dirty brown Soft Stringy	Brown Granular Stringy
Odor	E. P. base	Fatty	Soapy	Soapy	Soapy	Soapy	Soapy	Soapy	Soapy and like nitrobenzene	Sweet-pungent
Dropping point, ° C.										
Gillette	145	150	100+	80	100+	...	97
Ubbelohde	162	162	162	200+	133	162	100	133	129	139
Unworked penetration at 77° F.	232	236	164	204	199	198	159	155	240	189
Worked penetration at 77° F.	None	None	None	225	280	236	197	None	316	310
Separation test at 250° F.	O.K.	O.K.	O.K.	None	None	None	None	None	None	None
Corrosion, 3 hrs. at 210° F.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.
Composition, per cent by weight:										
Water	1.4	...	1.4	0.1	1.75	0.45	1.8	1.0	1.8	1.1
Oil	80.3	83.5	79.0	78.5	72.0	79.5	81.0	73.0
Soap	19.9	16.4	19.0	18.8	23.5	18.4	17.2	22.0
Free alkali as NaOH	0.04	Neutral	0.19	0.12	0.02	0.18	0.05 as Ca(OH) ₂	0.13	...	0.11
Free acid as oleic	0.07	...
Ash:										
Per cent by weight	2.86	...	4.14	3.20	3.41	4.02	2.60	3.90	2.95	4.30
Analysis, per cent of ash:										
Na ₂ CO ₃	89.8	93.3	97.2	89.6	...	95.7	96.9	94.1
Na ₂ SO ₄	7.0	3.4	2.0	8.5	...	2.8	3.4	3.9
R ₂ O ₃	2.2	1.0	0.2	1.5	1.6	1.3	Ca ₂ SO ₄	Na ₂ SO ₄
CaO	1.0	0.2	0.4	0.3	96.2
Mineral oil:										
Viscosity, S. U. at 100° F.	348 Fur.	1254	330	282	355	803	1867	1440
Viscosity, S. U. at 210° F.	179 app.	...	66.1	76.0	50.3	72.2	52.1	63.7	90.4	81.8
Gravity, ° A. P. I.	22.2	21.1	23.9	25.4	22.1	20.9	19.6	20.2

TABLE VII. PERFORMANCE CHARACTERISTICS OF STEERING GEAR LUBRICANTS

Lubricant	Mechanical Efficiency		% Efficient, 150° F.		Timken Wear ^a Mg.	Timken Film Strength ^b O. K.	Film Strength ^b Failed	Heat Stability Separation at 220° F.	Retention ^c %
	Buick gear, -40° F. Stat.	Dyn.	Stat.	Dyn.					
1	24.0	13.0	75.0	77.0	34.4	8,575	11,430	Jells	4.8
2	31.0	16.0	73.5	76.0	24.9	7,140	10,000	Jells	3.0
3	0 Solid	...	80.0	79.5	31.2	14,280	17,140	Becomes hard	1.15
4	71.0	55.0	76.5	79.7	...	14,280	17,140	O.K.	9.2
5	27.0	8.0	73.5	77.5	9.8	22,860	25,700	O.K.	8.9
6	62.0	36.0	76.2	78.0	8.2	17,140	18,570	O.K.	3.5
7	68.0	62.0	70.0	76.5	..	14,280	17,140	Oil separates	5.65
8	68.0	15.0	73.5	76.0	..	2,900	5,714	Oil separates	3.8

^a 6 hours at 100 feet per minute, 40,000 lb. per sq. inch.
^b 400 feet per minute, lb. per sq. inch.
^c Per cent of charge lost.

Ubbelohde dropping point of 135° C. (275° F.) appears to be justifiable.

PERCENTAGE OF FREE ALKALI AND FREE ACID. There should be no objection to a maximum free alkali value of 0.6 per cent and a maximum free acid value of 0.3 per cent, but many bearing manufacturers specify much closer ranges. It is felt, however, that there should be no difficulty in maintaining wheel bearing greases at a point much nearer to neutral than is indicated by these rather wide ranges. From the standpoint of service, however, there are no indications that products having extreme values within these ranges will be objectionable under actual service conditions.

PERCENTAGE OF FILLERS. It is generally agreed that any good wheel bearing grease should contain no appreciable quantities of inert fillers, as these materials will act as lapping compounds and cause increased wear.

PERCENTAGE OF ASH. Reference to Table VI reveals that the soap contents of the wheel bearing greases investigated vary from 16.4 to 23.5 per cent. The best service results were obtained with grease 1, having a soap content of 19.5 per cent. In general, the ash values are proportional to the percentage of soap. However, appreciable deviations in the ash content are not considered as having any particular influence on the serviceability of the grease. It is therefore apparent that a maximum ash content of 5 per cent could be readily met by most grease manufacturers and there is no need for meeting rigid specifications established at appreciably lower values. From the standpoint of control and uniformity, however, complying with the above suggested worked penetration

ranges would serve in a better manner than making ash tests on all batches of wheel bearing grease.

CORROSION. None of the greases investigated was found to be unsatisfactory when subjected to the 3-hour copper strip corrosion test carried out at 100° C. (212° F.). While it might appear that there is no necessity for including a specification of this kind in view of the general high quality of greases in this respect, it is felt that, since wheel bearing greases

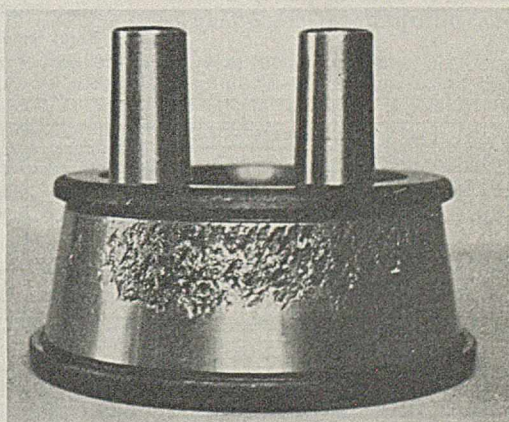


FIGURE 14. INNER RACE OF TAPERED ROLLER-TYPE WHEEL BEARING

Showing results of overloading and improper lubrication

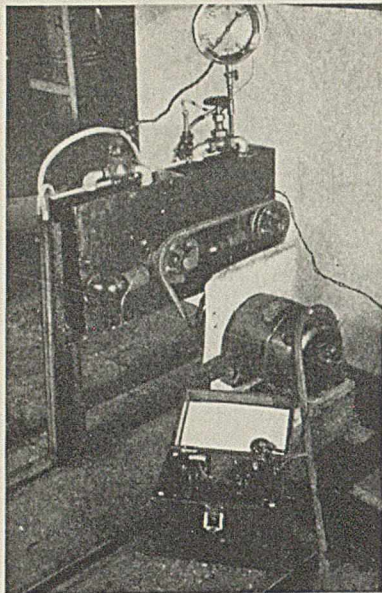


FIGURE 15. LABORATORY APPARATUS FOR DETERMINING SERVICE CHARACTERISTICS OF AUTOMOTIVE WATER-PUMP GREASES

Temperature of cooling fluid, rate of flow, and discharge pressure of pumps are easily controlled.

discussed under the heading of "Percentage of Ash." Wheel bearing grease 7 has been prepared with a calcium base and in service tests has been given a rating of 7, and from all considerations was the most objectionable product investigated. Not emphasized in Table V is the fact that leakage for grease 7 was many times that of any of the other greases tested. It is significant that all of the other greases were manufactured with soda-soap bases.

Water-Pump Grease

A laboratory service testing device, making use of Chevrolet or other makes of water pumps, is shown in Figure 15. By selection of a motor pulley of suitable size, pumpshaft speeds may be

may contain sulfurized materials and other "extreme pressure" bases, the corrosion test is of importance. There is some evidence from the field that soda-soap base wheel bearing greases are corrosive when a small amount of water gains entrance to a bearing. For this reason, the addition to soda-soap greases of traces of compounds which inhibit corrosion seems justified.

SOAP. The question of soap content has been dis-

attained of 500 to 2000 r. p. m. Water at temperatures up to 100° C. (212° F.) or various antifreeze mixtures which may have a detrimental effect on the lubricating film are placed in the rectangular metal boxes on the sides of which the pumps are mounted. Practical tests and comparisons of the abilities of greases to resist the displacing action of the various solutions can be made.

Prolonged tests with various makes of pump packing, in which the packing gland is kept abnormally tight, yield results bearing on the characteristics of grease and packing most desirable for preventing shaft scoring. With this device it is also possible to gain information as to the quantity of grease which may find its way into the cooling system and retard heat transfer. The investigation with this equipment has not yet been completed.

Steering Gear Grease

Eight steering gear lubricants were subjected to a series of tests to determine their qualities in four essential respects: efficiency, wear, stability, and retention. The efficiency and retention tests were applied over a temperature range from -40° to 82.22° C. (-40° to 180° F.).

The tests were mostly of a conventional nature, but attention is drawn to the separation test at 104.44° C. (220° F.) which is regarded as being significant. The aluminum-soap greases (No. 1, No. 2, and No. 3) heated to this temperature either jell or solidify, and the calcium-soap lubricants (No. 7 and No. 8) separate and do not recombine on cooling. The sodium-soap lubricants (No. 15, No. 18, and No. 6) are heat-stable. The test temperature of 220° F., while appreciably higher than temperatures which have been observed in service, is not unreasonably so and has been employed to cover extreme cases.

EFFICIENCY. A steering gear lubricant tester was constructed, as shown in Figure 16, in such a way that two gears could be held at controlled temperatures and the ratio of steering wheel effort to steering arm torque could be determined. The gears tested were a Saginaw worm and roller type made for Buick cars and representative of steering gears used by General Motors for 1934, and a Gemmer worm and sector type as used on the 1934 Ford. Gears of these types are estimated to be on 30 and 62 per cent, respectively, of 1932-34 cars. Large inspection

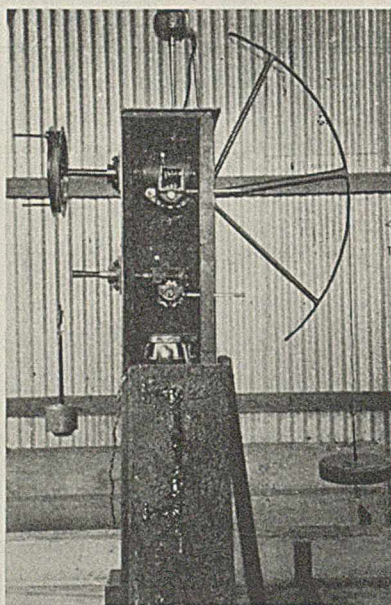


FIGURE 16. APPARATUS FOR DETERMINING STATIC AND DYNAMIC EFFICIENCIES OF STEERING GEARS

Front removed to show arrangement of gears

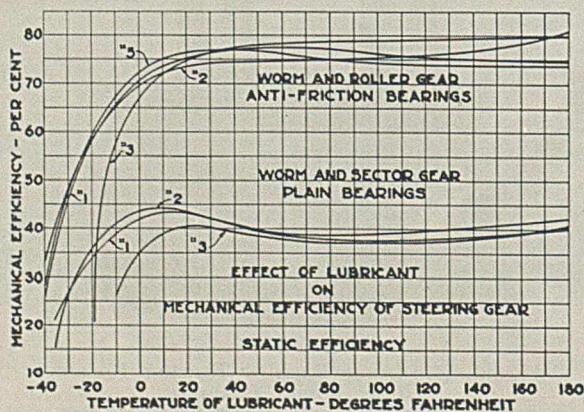


FIGURE 17

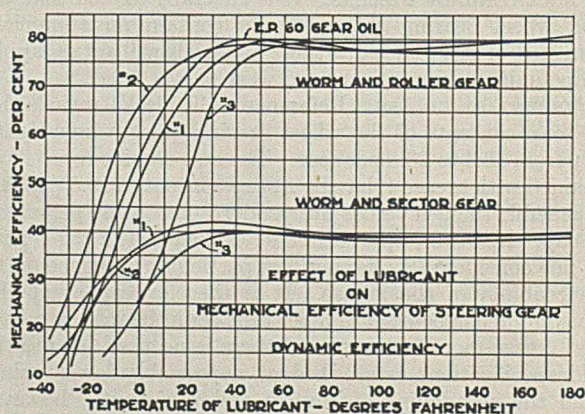


FIGURE 18

TABLE VIII. ANALYTICAL DATA: STEERING GEAR LUBRICANTS

Sample No.	1	2	3	5	6	7	8	9
Physical tests:								
Appearance	Green brown Stringy	Black viscous Liquid	Black Semi-solid	Black Liquid	Brown stringy Semi-solid	Light brown Semi-solid	Brown Semi-solid	Dark green Brown
Odor	Pine tar	Sharp-soapy	Soapy	Pungent	E. P. base	E. P. base-soapy	Fatty	Sharp-soapy
Dropping point								
Gillette, ° C.	36	Room temp.	76	Liquid	Room temp.	42	50	Liquid
Ubbelohde, ° C.	48	78	92	Liquid	126	78	81	Liquid
Pour point, ° F.	50	60	Above 120	- 5	5	Too heavy	Too heavy	30
Channel test, ° F.	0	10	10	-10	Below 0	0	0	10
MacMichael, 1-cm. bob, 60 r. p. m.	No. 26 wire 140 at 75° F.	No. 26 wire 65 at 70° F.	No. 24 wire 126 at 80° F.	No. 26 wire 33 at 76° F.	No. 26 wire 56 at 80° F.	No. 26 wire 55 at 70° F.	No. 26 wire 143 at 70° F.	No. 26 wire 93 at 80° F.
Corrosion, copper 3 hr., 212° F.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.
Bleeding test, 175° F., 1 hr.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.
Separation test, 220° F.	Jells	Jells	Becomes hard like axle grease	No separation	No separation	Grease breaks down	Separates	Slight separation
Composition, per cent by weight:								
Soap	10.2	7.3	8.7	4.6	2.9	5.6	7.1	8.0
Moisture	0.1	0.1	0.2	0.15	0.1	0.4	0.2	0.6
Oil	85.9	92.2	79.8	93.5	97.1	92.5	90.0	91.6
Free alkali or fatty acid	4.1 oleic	3.6 oleic	11.2 oleic	Pb present	0.01 NaOH	0.14 oleic	0.21 oleic	0.7 oleic
Asphaltic material	2.0	0.3	2.0	0.32	Trace	0.01
Sulfur	0.33	0.50	0.83	2.00	1.86	2.47	0.40	0.45
Ash:								
Ash, %	3.08	0.77	1.78	3.3	0.35	0.77	0.86	0.89
Analysis, %	14.0 Na ₂ CO ₃ 69.3 PbO 13.8 PbSO ₄	77.2 Al ₂ O ₃ 21.6 Na ₂ CO ₃	80.1 Al ₂ O ₃ 7.3 Al ₂ SO ₄ 6.9 Na ₂ CO ₃	90.0 PbO 0.9 Acid-ins.	90.0 Na ₂ CO ₃	62.2 CaO 9.8 Al ₂ (SO ₄) ₂	91.6 CaO 6.4 Na ₂ CO ₃ 2.8 Fe ₂ O ₃	80.5 CaO 19.6 CaSO ₄ 3.7 Fe ₂ O ₃
Mineral oil:								
Color	Green black	Black	Black	..	3-Red	Red-blue	8	Brown-black
Viscosity, S. U. at 100° F.	1667	2000	3270	2640	314	548	379	2810
Viscosity, S. U. at 210° F.	89.4	118	164	135	49	53.9	51.4	128
Gravity, ° A. P. I.	20.5	21.9	19.7	16.8	23.2	20.2	22.5	19.0
Flash, ° F.	405	285	390	345	375	320	370	405

Sample No.	10	11	12	13	14	15	16	17
Physical tests:								
Appearance	Green brown Liquid	Black Liquid	Black Green	Black Brown	Green Semi-solid	Dark green Brown	Black	Green Semi-solid
Odor	Sweet soapy	Phenol-like	Sour	Faintly soapy	Slightly soapy	Pine tar	Nitrobenzene	Sweet
Dropping point								
Gillette, ° C.	Liquid	Room temp.	Liquid	Liquid	54	Liquid	Liquid	Room temp.
Ubbelohde, ° C.	Liquid	Liquid	Liquid	Liquid	84	Liquid	Liquid	64
Pour point, ° F.	30	50	60	- 5	100	15	-0	20
Channel test, ° F.	15	..	40	-10	25	5	-5	0
MacMichael, 1 cm. bob, 60 r. p. m.	No. 26 wire 180 at 80° F.	No. 26 wire 50 at 70° F.	No. 26 wire 100 at 80° F.	No. 26 wire 15 at 80° F.	No. 26 wire 154 at 70° F.	No. 26 wire 14 at 80° F.	No. 26 wire 14 at 80° F.	No. 26 wire 113 at 70° F.
Corrosion, copper 3 hr., 212° F.	..	O.K.	O.K.	Not O.K.	O.K.	O.K.	O.K.	O.K.
Bleeding test, 175° F., 1 hr.	..	O.K.	O.K.	O.K.
Separation test, 220° F.	Solidifies	No separation	Solidifies	No separation	No separation	No separation	No separation	No separation
Composition, per cent by weight:								
Soap	6.6	1.2	6.3	3.5	5.5	3.7	3.1	5.2
Moisture	0.2	0.05	0.2	0.1	0.2	None	Trace	0.1
Oil	92.2	98.3	90.5	95.5	84.0	95.6	97.0	92.0
Free alkali or fatty acid	Al ₂ O ₃ pres.	0.6 oleic	0.56 oleic	Lead present	0.03 NaOH	0.35 oleic	0.21 oleic	1.1 oleic
Asphaltic material	0.03	0.1	0.2	0.5	..	0.2	0.1	..
Sulfur	0.28	0.95	0.99	2.33	0.37	2.37	5.76	2.47
Ash:								
Ash, %	0.86	0.04	0.08	0.37	1.02	0.03	0.005	0.97
Analysis, %	85.6 Al ₂ O ₃ 8.4 Al ₂ (SO ₄) ₃	No analysis	No analysis	34.2 PbO 51.3 PbSO ₄	80.0 Na ₂ CO ₃ 9.6 Na ₂ SO ₄ 2.5 Fe ₂ O ₃	No analysis	No analysis	59.6 Na ₂ CO ₃ 38.4 Na ₂ SO ₄ 2.2 Fe ₂ O ₃
Mineral oil:								
Color	Green red	Brown black	Green	Black	Green black	Green black	..	Dark green
Viscosity, S. U. at 100° F.	2298	4520	4560	1267	3930	1305	..	1097
Viscosity, S. U. at 210° F.	120	230	218	92	177	87	..	65.4
Gravity, ° A. P. I.	21.8	21.6	23.7	18.6	23.2	20.7	..	17.5
Flash, ° F.	420	390	530	390	490	415	..	410

holes were made in the casings of the gears for convenience in changing lubricants and were closed by plates. Thermometers were inserted directly into the lubricant by means of packing nuts. The gears were set to factory adjustments at the beginning of the series of tests and were not subsequently altered.

Temperatures down to -40° F. were secured by carbon dioxide snow condensed in a chamois-skin bag formed around the gear housing, and those up to 180° F. were secured by means of a hot plate and a fan for circulating the warm air in the cabinet. Observations on actual cars with atmospheric temperature ranges up to 105° F. showed that temperatures in steering gears in service seldom exceed 160° F.

The efficiency tests were conducted by hanging a 50-pound weight from the quadrant representing 1350 inch-pounds, or a condition intermediate between turning the wheels while stationary and turning at 10 miles per hour. This was regarded as typical of the effort applied when parking in a crowded street. It was then determined what weight needed to be added to the input pulley to secure the first movement of the steering arm (static efficiency) and also to secure a rate of movement of 10° in 5 seconds (dynamic efficiency). Static efficiency measurements were made in the middle of the worm only and dynamic

efficiency measurements were made in three positions. The steering arm moves through about 90° in the case of both gears and dynamic efficiency tests were run in the central position and 15° on either side of this.

Preliminary experiments showed that tests made in this manner gave the same average results as tests at 10° intervals over the whole range. The dynamic and static efficiencies were found to be nearly equal at all temperatures where the lubricant was fluid, but at low temperatures the dynamic efficiency was much lower than the static—that is, initial movement of the gears was secured with less effort than was necessary for a continuous movement of 2° per second. This corresponds to about 36° per second on the steering wheel or moderately rapid turning.

The results obtained are shown in Figures 17 and 18.

RETENTION. Observations were made on the retention characteristics of the lubricants by collecting the leakage at high temperatures from 15.56° C. (60° F.) upwards. Some of

this leakage was due to the method of mounting the gears, and the figures are much higher than would be found in practice. However, the relative figures show what may be expected with gears in poor mechanical condition.

FILM STRENGTH AND WEAR TESTS. Film strength determinations were made on the Timken machine at rubbing speeds of 400 and 100 feet per minute, and wear tests, also on the Timken machine, were carried out for a duration of 6 hours at 40,000 pounds' pressure and a speed of 100 feet per minute. The 40,000 pounds' pressure is at first sight above the film strength pressure at 100 feet per minute for some of the lubricants, but these pressures are nominal, assuming line contact, and actual unit pressures after a run-in period will be considerably less than this. No actual failures of lubrication occurred during the wear tests.

Table VII summarizes the significant performance characteristics of the most important of the lubricants tested.

Lubricant 6 is exceeded in dynamic efficiency at low temperatures only by No. 7, which is unsatisfactory from the point of view of heat stability, and by No. 4 which is consider-

ably inferior from the point of view of retention. Its wear characteristics were good and its retention was exceeded only by No. 3, which gave a poor efficiency at low temperatures and unsatisfactory heat stability.

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Determination of Starch in Plant Tissues

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OF THE various methods that have been proposed to determine the starch content of plant tissues, only those which depend upon the estimation of the sugar produced by hydrolysis of the starch with dilute acid or with enzymes have received much attention in recent years. Sullivan (15) has recently reviewed and discussed the whole problem of starch determination, and has pointed out the unreliability of most methods that have been suggested. Denny (5) has carefully compared the results with several procedures, and has shown that hydrolysis of prepared tissue with takadiastase, even under the best conditions, may lead to serious error owing to the inclusion of substances other than starch which are hydrolyzed by this enzyme preparation with the production of sugar. He has therefore emphasized the desirability of extracting the starch from the tissue with some suitable solvent as a step preliminary to its isolation and subsequent hydrolysis to sugar.

Even this procedure, in the authors' experience, may not entirely eliminate contaminating sugar-yielding substances, and it has, accordingly, seemed desirable to base the estimation of starch in plant tissues upon a more specific reaction for this substance—namely, the well-known color reaction with iodine. A procedure of this kind was described in 1895 by Dennstedt and Voigtländer (4), but was found unreliable by Littleton (8) and by Witte (17). Occasional references to the application of the iodine-starch reaction for quantitative purposes are to be found in the literature (9), but no satisfactory analytical development appears to have been made.¹

The method described in the present paper is designed to be applied to samples of dry plant tissue.

The powdered material is prepared for analysis by thorough extraction with 75 per cent alcohol, and is then ground either by hand or in a special ball mill to an extremely fine powder. The starch is extracted from a suitable sample either by 21 per cent hydrochloric acid at 20° to 22° C. (Rask's method, 11) or by concentrated calcium chloride solution at 100° C., the solvents being applied repeatedly until no further starch is removed. The starch is then precipitated at the correct acid reaction and salt

concentration by means of iodine-potassium iodide reagent, the precipitate is decomposed with alcoholic alkali, and the starch is isolated as such. It is then dissolved in water with the aid of acetic acid, and a definite excess of iodine is added as potassium iodide-iodate mixture. The starch-iodine compound remains in colloidal solution under these conditions, and the intensity of the light transmitted through an S-61 (red) filter is read in a Zeiss Pulfrich spectrophotometer against a control solution containing the reagents alone. The quantity of starch present is calculated from a calibration curve prepared by subjecting known quantities of highly purified potato starch to the same procedure.

The method gives results that can be duplicated within 10 per cent on quantities of the order 0.1 to 0.2 mg. and within 3 per cent on quantities between 1 and 3 mg. of starch.

Reagents

Calcium chloride solution: 216 grams of Baker's c. p. anhydrous calcium chloride dissolved in 250 ml. of water. The hot solution is filtered through asbestos and is kept in a warm place; concentration approximately 46 per cent by weight.

Hydrochloric acid (Rask's acid): 247 ml. of concentrated hydrochloric acid diluted to 500 ml.; concentration approximately 21 per cent.

Hydrochloric acid 2.3 N: 100 ml. of concentrated hydrochloric acid diluted to 500 ml.

Acetic acid 2 N: 57 ml. of glacial acetic acid diluted to 500 ml.

Sodium hydroxide 10 N: 420 grams of sodium hydroxide diluted to 1000 ml.

Alcoholic sodium hydroxide 0.25 N: 25 ml. of 5 N sodium hydroxide, 320 ml. of 95 per cent alcohol diluted to 500 ml.

Sodium chloride 20 per cent: 20 grams of pure sodium chloride diluted to 100 ml.

Iodine-potassium iodide: 30 grams of iodine and 50 grams of potassium iodide diluted to 250 ml.

Potassium iodide 10 per cent: prepared in small quantities and discarded when it becomes yellow.

Magnesium carbonate: c. p. grade containing very little free alkali.

Thymol blue 0.04 per cent: prepared according to Clark (3).

Potassium iodate 0.01 N: 0.1783 gram of pure potassium iodate diluted to 500 ml.

Of these reagents, the potassium iodate alone needs to be prepared with quantitative accuracy.

Preparation of Tissue

Green plant tissue is rapidly dried in a ventilated oven, provided with a fan and baffles to circulate the air over the tissue,

¹ The paper of Sullivan (16) which describes a method based upon precipitation with iodine and subsequent hydrolysis of the starch to sugar, came to hand after this manuscript had been submitted for publication.

at 70° to 80° C., and is then ground to pass a 50- to 60-mesh sieve. Weighed samples of from 2 to 5 grams are continuously extracted in paper thimbles with 75 per cent alcohol for at least 6 hours, the residues are dried and weighed, and are then ground in a mortar or, preferably, in a small ball mill until the powder will pass through fine silk bolting cloth.

A convenient ball mill can be readily improvised from quarter-pint cream bottles closed by rubber stoppers. A cylindrical block of wood that contains four evenly spaced holes bored parallel to the axis, and of such size as to accommodate the bottles snugly, is mounted on an axle constructed of 0.6-cm (0.25-inch) pipe attached firmly to the block and carefully centered. The axle is set in bearings held by clamps, and the cylinder is rotated by a belt from a laboratory motor around the cylinder or suitable pulley attached to the axle. About 45 0.6-cm. (0.25-inch) steel ball bearings are added to each bottle with the sample, and the mill is rotated at 120 revolutions per minute for about 8 hours.

Extraction of Starch

HYDROCHLORIC ACID METHOD OF RASK. It is convenient to carry out the extraction of four samples simultaneously; 0.200-gram samples of the ground tissue are weighed into 25 × 200 mm. heavy-walled Pyrex test tubes, and 1.5 grams of sharp sand, 5 cc. of water, and a stout glass stirring rod are added to each. The tubes are placed in a boiling water bath for 15 minutes to gelatinize the starch, the contents being vigorously triturated from time to time with the rod. The tubes are cooled to 10° C. and 5 ml. of concentrated hydrochloric acid are slowly added, the temperature being kept below 22° C. The contents are then ground with the rod over a period of about 10 minutes, each tube being treated for about 0.5 minute at a time and kept in a water bath at 20° C. during the intervals. The rods are then rinsed off with a few drops of Rask's acid and the tubes are centrifuged for 1 minute. The supernatant fluid is decanted into 25 × 200 mm. test tubes calibrated at 50 ml., allowing sufficient time for drainage, and the lips are rinsed with a little water; these tubes are kept in a water bath at 10° to 15° C.

The centrifuged residues are next ground with the rods for about 0.5 minute each, and 3 ml. of Rask's acid are added, the alternate grinding of each tube being continued as before for 5 to 7 minutes. The tubes are then centrifuged and the residues are extracted twice more in the same manner, the successive extracts being collected in the graduated test tubes. A few drops of the fourth extract are tested with a drop of 0.01 *N* iodine solution, and if a definite blue color is observed a fifth extract is made. Finally the residues are washed by grinding once with 10 ml. of water.

The combined extracts are made to 50 ml. with water and are then kept in a refrigerator until the next step in the analysis is undertaken; they are stable under these conditions for at least 72 hours.

CALCIUM CHLORIDE METHOD. Samples of 0.200 gram of tissue are weighed out into test tubes as before and 0.05 gram of magnesium carbonate, 1.5 grams of sharp sand, 5 ml. of water, and a stirring rod are added to each. The tubes are heated with occasional trituration in a boiling water bath for 15 minutes and 7 ml. of the concentrated calcium chloride reagent, previously heated in the same bath, are added. The four tubes are then ground successively, while in the boiling water bath, for 0.5 minute each over a period of about 10 minutes. The rods are rinsed

with a few drops of water, the tubes are centrifuged, and the extracts are collected in 25 × 200 mm. test tubes graduated at 50 ml. The residues are ground for 0.5 minute each, are returned to the boiling water bath, and 3 ml. of water and 5 ml. of hot calcium chloride solution are added to each. The alternate grinding is continued for about 8 minutes, when the tubes are again centrifuged. Two more successive extracts are made in the same manner. A few drops of the fourth extract are acidified with dilute hydrochloric acid and tested with a drop of 0.01 *N* iodine solution; if a blue color is obtained a fifth extraction with calcium chloride is made. The residues are finally washed by being stirred with 5 ml. of water and centrifuged. The combined extracts are made to 50 ml. volume and are kept in the refrigerator.

Precipitation of Starch Iodide

The proper size of aliquot of the starch extract to be taken for analysis can readily be determined after a little experience by removing 0.2 ml. and testing with a drop of 0.01 *N* iodine solution. If a light blue color is obtained, 10 ml. of the extract should be used; if an intense blue, 5 ml. or less. Calcium chloride extracts must, of course, be acidified before testing.

The aliquots are transferred to Gradwohl-Blavais sugar tubes and are diluted to 10 ml.; 2 drops of 0.04 per cent thymol blue and a slim stirring rod with an enlarged end are placed in each.

HYDROCHLORIC ACID EXTRACTS. The tubes are cooled to 10° C. in a bath and 10 *N* sodium hydroxide is added drop by drop with constant stirring to a faint blue color, then 2.3 *N* hydrochloric acid to a yellow color and 1 ml. in excess. The temperature must not be allowed to rise above 25° C. If the aliquot is less than 5 ml., 2 ml. of 20 per cent sodium chloride are added and finally the starch is precipitated by the addition of 0.5 ml. of concentrated calcium chloride

and 6 to 10 drops of iodine-potassium iodide reagent. The calcium chloride is necessary in order to produce a precipitate which, on decomposition with alcoholic sodium hydroxide, will yield a granular precipitate of starch—without it this precipitate is gummy.

CALCIUM CHLORIDE EXTRACTS. If the aliquots are smaller than 5 ml., 1 ml. of calcium chloride is introduced. The acidity is adjusted as already described, 2 ml. of 20 per cent sodium chloride are added, and the starch is precipitated with 6 to 10 drops of iodine-potassium iodide.

The subsequent procedure is identical for both acid and calcium chloride extracts. The tubes are allowed to stand for 10 minutes and are then lightly stoppered or covered with glass bulbs and immersed in a boiling water bath for 15 minutes. After being cooled to room temperature, any precipitate floating on the surface is broken up with a small rod and the tubes are centrifuged. It is usually impossible to decant the supernatant fluid from these precipitates. The best method is to draw it off with a long thin capillary tube attached to a suction flask and source of vacuum with light-walled rubber tubing so that the rate of flow can be instantly controlled. By this means floating particles are usually caught on the walls of the tube and the fluid may

Starch is extracted from plant tissues either by hot concentrated calcium chloride solution or by cold 21 per cent hydrochloric acid, and is precipitated from the extract by means of iodine at the correct acidity and salt concentration. The iodine precipitate is decomposed with alcoholic alkali, and the starch is isolated as such, dissolved in dilute acetic acid, and converted again to the iodine compound under conditions in which it remains in colloidal solution. The light transmission is read in a Pulfrich spectrophotometer and the quantity of starch present is calculated from a calibration curve constructed from observations on pure potato starch.

The method has been applied to a number of plant tissues. The results, in general, are lower than those obtained by calculation of the starch from the sugar reduction obtained after hydrolysis, but are believed to be more trustworthy. It has been found that, in many cases, sugar-yielding substances contaminate the isolated starch and give rise to interference.

The method is highly specific and gives results duplicable within 3 per cent on quantities of starch between 1 and 3 mg. in the aliquot analyzed and within 10 per cent on quantities as small as 0.1 mg.

be removed to less than 1 ml. As a rule floating particles consist of sublimed iodine, and their loss does not affect the analysis. The precipitates are washed twice successively with 2-ml. portions of 60 per cent alcohol, the precipitate being mixed with the wash fluid by gentle shaking of the tube which is then thoroughly centrifuged. Spattering of the precipitate on the walls of the tube must be avoided.

Decomposition of Starch Iodide

To the packed precipitates, 2 ml. of alcoholic sodium hydroxide are added and the precipitates are triturated with glass rods until nearly colorless. The rods are then washed with 60 per cent alcohol, and the decomposition is completed by heating the tubes in a bath at 70° to 80° C. for 5 minutes with gentle agitation. The tubes are cooled and centrifuged, the fluid is decanted from the starch, and this is washed twice with 2 ml. of 60 per cent alcohol. After the last washing the tubes are inverted and allowed to drain thoroughly.

Estimation of the Starch

The starch precipitates are treated with 5 ml. of water and are heated with frequent shaking for 5 minutes in a boiling water bath. After being cooled, 0.5 ml. of 2 *N* acetic acid is added, and the contents of the tubes are thoroughly mixed and centrifuged. The fluids are decanted into 25 × 200 mm. test tubes, calibrated at 20 and 50 ml., immersed in a water bath at 15° C. The residues are washed by being agitated with 3 ml. of water, and are centrifuged.

The solutions of starch are treated with 2 ml. of 2 *N* acetic acid, 0.5 ml. of 10 per cent potassium iodide, and 5 ml. of 0.01 *N* potassium iodate, all being exactly measured. Two compensating solutions are simultaneously prepared that contain 8 ml. of water, 2.5 ml. of 2 *N* acetic acid, 0.5 ml. of 10 per cent potassium iodide, and 5 ml. of potassium iodate. The two compensating solutions are diluted to 20 and 50 ml., respectively. The unknowns are diluted to either 20 or 50 ml., depending on the intensity of color developed, and are allowed to stand, after being thoroughly mixed, for 5 minutes. The extinction coefficient of each solution is then determined in the Pulfrich spectrophotometer using the compensating solution of the same volume on the control side of the instrument, and the equivalent of starch is calculated from the calibration curve. The quantity found is referred to the 0.200-mg. sample of prepared tissue and this in turn corrected for the loss in weight during the preparation of the original dried tissue for the starch analysis.

It will be found that the 50-ml. dilution should be used for quantities in excess of 0.5 mg. of starch, the 20-ml. dilution for smaller amounts. Cells should be selected of such length that the readings fall between 20 and 80 per cent transmission.

Reference Standard and Calibration of Instrument

In order to obtain from the extinction coefficient the actual quantity of starch present, it is necessary to calibrate the instrument in terms of a reference standard of pure starch. For this purpose, a high grade of potato starch was selected. This was thoroughly extracted with a mixture of ether and alcohol and with water, and was then dried in the air. Analyses of two different lots so treated gave moisture contents of 11.36 and 4.78 per cent, ash contents of 0.29 and 0.30 per cent, and no nitrogen. The two specimens therefore contained 88.4 and 94.9 per cent of starch. Calculation of the starch content by means of the factor 0.93 from the sugar reduction after hydrolysis with 0.7 *N* hydrochloric acid for 2.5 hours gave 87.4 and 94.4 per cent. The values obtained for the organic solids were therefore taken to represent the starch content of these samples with sufficient accuracy. Both were used in the preparation of the calibration curve.

Standard solutions of starch in hydrochloric acid were obtained by treating the equivalent of 0.050 gram of dry starch as already described for the extraction of starch from tissue. To prepare solutions in calcium chloride, the equivalent of 0.050 gram of starch, 0.05 gram of magnesium carbonate, and 5 ml. of water were heated in a boiling water bath for 15 minutes and 15 ml. of calcium chloride solution were added. A few drops of caprylic alcohol and a few angular quartz pebbles were introduced and the solution was boiled under reflux for 2 hours. The solution was then diluted with 15 ml. of water, transferred to a 25 × 200 mm. test tube calibrated at 50 ml., diluted to the mark, and centrifuged.

Aliquots of these solutions that contained 0.1 to 3.0 mg. of starch were then carried through the procedure already described, with particular attention to the addition of salts previous to the precipitation with iodine. Determinations were also made on solutions in calcium chloride that were heated for longer times both at 100° C. and at the boiling point. Furthermore, the precipitation with iodine was carried out in the cold and at 100° C., in the presence of acetic acid and also of hydrochloric acid, and finally the readings of the color were made at various temperatures from 15° to 28° C. All results were duplicable within 5 per cent in spite of these variations. The data were found to yield satisfactorily straight lines between the limits 0.1 and 0.6 mg. of starch read at 20-ml. volume, and between the limits 0.2 and 3.0 mg. of starch at 50-ml. volume. Accordingly, all the data were assembled and the best straight lines for the two volumes were obtained by the method of least squares. The data for these lines are shown in Table I.

TABLE I. CALIBRATION DATA FOR STARCH DETERMINATION
(Filter S-61; 1-cm. cell)

Starch Mg.	Volume Ml.	Extinction Coefficient
0.100	20	0.069
0.200	20	0.133
0.500	20	0.343
0.200	50	0.053
0.500	50	0.138
1.00	50	0.278
2.00	50	0.559
3.00	50	0.840

Comparison of Colorimetric with Hydrolytic Method on Pure Starch

Samples of standard starch solution both in calcium chloride and in hydrochloric acid were carried through the procedure described up to the isolation of the starch precipitate, save that the iodine precipitates were not heated but were allowed to stand at room temperature for 30 minutes.

The precipitated starch was treated with 2 ml. of 0.7 *N* hydrochloric acid and the tubes, covered with glass bulbs, were heated in a boiling water bath for 2.5 hours. After completion of the hydrolysis, the solutions were cooled and neutralized to phenol red with 0.5 *N* sodium hydroxide. They were then diluted to 10, 15, or 20 ml., depending on the quantity of starch present, and aliquots were analyzed for reducing sugar by the Shaffer and Somogyi (14) method (copper reagent No. 50 containing 1 gram of potassium iodide).

In addition, samples of dry starch were hydrolyzed directly, and also after having been dissolved in calcium chloride and precipitated with alcohol, or simply dissolved in hydrochloric acid. The glucose values are summarized in Table II.

TABLE II. YIELD OF GLUCOSE FROM POTATO STARCH

	Glucose %	No. of Determinations	Factor
Direct analysis of starch	106.8 ± 1.0	8	0.936
Solution of starch (CaCl ₂ or HCl)	99.2 ± 2.0	7	1.008
Solution of starch in either solvent precipitated with iodine	99.2 ± 2.0	14	1.008

Starch on direct analysis yields 106.8 per cent of glucose, but, after having been dissolved in either of the two solvents, yields 99.2 per cent and the yield is unchanged by precipitation with iodine. It is clear therefore that the empirical factor 0.93, long in use to convert glucose yield into starch, does not apply if the starch has been taken up in either of these solvents. This factor is based upon the experiments of a number of early investigators (6, 10).

The factor 1.01 calculated from the present experiments on starch solutions suggests that there may have been incomplete solution of the sugar-yielding material, but tests of the trace

of residue left after solution of the starch in the solvent showed that it gave no blue color with iodine and can therefore not be what is ordinarily understood as starch. Inasmuch as the present method to determine starch depends on the blue coloration, it is necessary to define starch for our purposes in terms of this reaction, and to correlate the results of the colorimetric method with the glucose yielded by starch after the starch has been treated with solvents.

The yield of glucose from starch that has been precipitated by iodine varies materially according to the temperature and acidity at which the precipitation is made, although neither factor has much effect upon the color value. Data that illustrate these points are shown in Table III. Equal samples of starch solutions were precipitated with iodine at room temperature and one sample was then heated to 100° C. as described. The acidity at which the precipitations were conducted was also varied. Examination of the data shows that the colorimetric values were not affected by heating at any of the acidities tested. The glucose values were, however, seriously reduced if the iodine precipitate was heated in the presence of mineral acid.

TABLE III. COMPARISON OF COLORIMETRIC AND SUGAR METHODS ON RECOVERY OF PURE STARCH

(After iodine precipitation at room temperature and at 100° C.)

Acid per 15 ml. of Neutralized Starch Solution	Starch, Colorimetric		Starch from Sugar Titration, Glucose X 1.01	
	Room temperature		Room temperature	
	100° C.	100° C.	100° C.	100° C.
	Mg.	Mg.	Mg.	Mg.
Acetic acid 5.0 N, 0.3 to 0.5 ml.	0.095	0.099	0.092	0.097
	2.03	2.02	1.98	1.96
	2.00	2.03	2.00	2.00
	2.02	2.00	1.97	1.98
Hydrochloric acid 2.3 N, 0.5 ml.	2.04	1.68
	2.04	2.00	1.98	1.32
	2.00	1.97	2.00	1.20
	1.03	1.00
Hydrochloric acid 2.3 N, 2.0 ml.	1.00	1.05
	1.01	1.02
	0.098	0.093
	0.095	0.104
Hydrochloric acid 2.3 N, 2.6 ml.	2.00	1.22
	1.99	1.01

It might be inferred from these data that precipitation in the presence of acetic acid in the cold is preferable to the procedure here recommended. As will be shown below, however, in the practical application of the method to plant tissues, the precipitation of interfering substances is to a large extent avoided by the technic the authors have adopted.

Starch Determination in Plant Tissue

BEHAVIOR OF CALCIUM CHLORIDE EXTRACTS. A solution of pure starch in concentrated calcium chloride is not stable at room temperature for more than 48 hours, the amount of starch precipitable by iodine slowly diminishing. Dilution with 10 volumes of water gives a solution which is even less stable, notable losses of starch frequently being observed within 24 hours.

Losses of starch also occur during the process of extracting starch from plant tissues with hot calcium chloride unless steps are taken to control the acidity. The calcium chloride solutions the authors have used were faintly alkaline to phenolphthalein. After being heated with plant tissue, they rapidly became more acid and marked losses of starch occurred if the reaction was allowed to drop below pH 6.0.

Table IV shows the effect upon the apparent starch content when samples of leaf tissue are heated with calcium chloride alone and together with calcium or magnesium carbonate. The extracts were made by heating 0.5 gram of dry tissue at 100° C. for 17 hours with 5 ml. of water and 10 ml. of calcium chloride; from 0.1 to 0.2 gram of the carbonates was used in addition where mentioned. The extracts were diluted to 50 ml. and the reaction was determined at the quinhydrone

electrode; starch analyses were then carried out on suitable aliquots.

TABLE IV. EFFECT ON RECOVERY OF STARCH OF HEATING TISSUE WITH CALCIUM CHLORIDE AT DIFFERENT REACTIONS

(Extractions at 100° C. for 17 hours)

Tissue Used	Reaction of Final CaCl ₂ Solution	Starch %
	pH	
Tobacco leaf E	3.06	0.00
Tobacco leaf E + CaCO ₃	4.99	0.58
Tobacco leaf E + 2.0 per cent of starch	3.06	0.00
Tobacco leaf E + MgCO ₃	6.93	1.88
Tobacco leaf E + 2.0 per cent of starch + MgCO ₃	6.94	4.00
Tobacco leaf H	3.10	0.00
Tobacco leaf H + MgCO ₃	7.32	0.14
Tomato leaf	4.45	0.30
Tomato leaf + CaCO ₃	4.90	0.61
Tomato leaf + MgCO ₃	6.96	2.17

Complete loss of starch took place if the reaction was not controlled. Calcium carbonate in the quantity used was ineffective in maintaining a relatively neutral solution and serious loss of starch occurred. Magnesium carbonate, however, preserved a neutral solution and permitted complete recovery of the starch.

Although an unusually long period of heating was employed in these experiments in order to magnify the results, appreciable loss may occur from tobacco leaf tissues during extraction of starch as described above, unless magnesium carbonate is added. The losses were small, however, with salvia or alfalfa leaf tissue.

The authors have recommended extraction with calcium chloride at 100° C. rather than at the boiling point of the concentrated solution (113° C.). A careful comparison of starch values obtained by successive extractions at the boiling point and at 100° C. showed that somewhat lower results were obtained at the higher temperature. Data that illustrate this and also give a comparison with cold hydrochloric acid extraction are shown in Table V.

TABLE V. COMPARISON OF EXTRACTION OF STARCH BY BOILING CALCIUM CHLORIDE SOLUTION, BY CALCIUM CHLORIDE AT 100° C., AND BY HYDROCHLORIC ACID

Tissue Used	CaCl ₂ 113°-114° C.	CaCl ₂ 100° C.	HCl 20° C.
	%	%	%
Tobacco leaf E	1.55	1.65	1.60
Tomato leaf	1.43	1.43	1.45
Tomato stem A	9.95	10.65	10.60
Tobacco stem H	0.73	0.76	0.78
Tobacco stem K	4.23	4.70	4.63
Tobacco stem J	1.73	1.81	1.88
Tobacco stem I	1.60	1.65	1.68

It is clear that the cold hydrochloric acid extraction method is to be preferred to extraction with calcium chloride at the boiling point. The stability of hydrochloric acid extracts for considerable periods of time (5), provided they are stored in a refrigerator, is also a point in favor of this method of extraction and for most purposes the authors prefer it.

ILLUSTRATIVE DATA. Tables VI and VII show data that illustrate the close reproducibility of starch determinations in various plant tissues, and the accuracy with which starch can be recovered when added to a starch-free tissue. It will be noted that 0.2 mg. of starch in the aliquots actually analyzed was recovered with an accuracy of ± 10 per cent, but that a somewhat larger quantity can be determined within ± 2 per cent. It is accordingly desirable to select aliquots with attention to this point.

Table VIII gives a comparison of starch determined by the colorimetric method with values determined by the reducing power of the starch after isolation as described and subsequent hydrolysis with acid. The discrepancy between the two methods is especially high for tissues of low starch content and suggests that substances other than starch which yield sugar

TABLE VI. DUPLICABILITY OF COLORIMETRIC DETERMINATION OF STARCH IN PLANT TISSUE

Tissue Analyzed	Starch in CaCl ₂ Extract		Starch in HCl Extract	
	%		%	
Tomato stem	10.90	10.90	10.90	10.90
	10.80	10.80	10.80	10.80
Rhubarb rhizome	32.00	32.94	32.94	32.94
	32.50	33.20	33.20	33.20
Rhubarb leaf	...	0.35	0.35	0.35
	...	0.38	0.38	0.38
Tobacco leaf E	1.50	1.38	1.38	1.38
	1.44	1.44	1.44	1.44
Tobacco leaf F	...	0.67	0.67	0.67
	...	0.63	0.63	0.63
Tobacco leaf B	...	5.50	5.50	5.50
	...	5.35	5.35	5.35
Tobacco leaf D	...	6.00	6.00	6.00
	...	5.85	5.85	5.85
Tobacco leaf J	...	6.15	6.15	6.15
	...	1.42	1.42	1.42
Tobacco stem K	...	1.38	1.38	1.38
	...	4.60	4.60	4.60
Beet root	...	4.70	4.70	4.70
	...	4.75	4.75	4.75
Alfalfa stem	...	0.16	0.16	0.16
	...	0.15	0.15	0.15
...	...	7.45	7.45	7.45
...	...	7.50	7.50	7.50

TABLE VII. RECOVERY OF STARCH ADDED TO STARCH-FREE BEET LEAF TISSUE

(0.200-gram samples of tissue)			
Starch Added	Starch in Aliquot Used	Starch Found	Recovery
9.40	1.88	9.70	103
		9.60	102
		9.50	101
		9.35	99.6
		9.30	99
1.00	0.20	1.00	100
		1.05	105
		1.07	107
		1.07	107
		0.90	90

on hydrolysis are precipitated. That this is the case was demonstrated by further extraction of the tissues after the starch had been removed and by extraction of starch-free tissues. In all cases, substances which gave reduction values and actual fermentable sugar were so obtained. Clearly, therefore, the high sugar titration values are due to contamination of the extracts with hydrolyzable substances other than starch.

The sugar titration values of the calcium chloride extracts agree in range with the hydrochloric acid extracts, provided the precipitation of the starch iodide is made at pH 1. Precipitation at pH 3 leads to higher values, and Table IX gives actual data that illustrate the magnitude of the discrepancies that may occur. The beet and rhubarb tissues were all low in true starch, but the extracts gave unusually large precipitates with iodine at pH 3, which in turn yielded much sugar on hydrolysis. Much less of this material was usually obtained at pH 1 in the cold.

It is clearly impossible to interpret the sugar titration values of the substances precipitated by iodine as being entirely due to starch. The colorimetric values, however, are identical regardless of the method of extraction or precipitation.

LOWER LIMIT OF ACCURACY OF THE METHOD. Extracts of starch from plant tissue prepared by either method frequently contain other substances that are either precipitated by iodine or adsorbed on the starch precipitate. These substances may give rise to a turbidity in the solution of free starch later obtained that interferes with the reading of the spectrophotometer. The amount of these extraneous substances varies with the tissue analyzed, but, in all cases the authors have encountered, can be minimized by heating the solution to 100° C. after the addition of the iodine reagent to the extract previously acidified to approximately pH 1.

In order to obtain an idea of the magnitude of the interference that may occur, analyses of starch-free beet leaf tissue were carried out. The extracts from this tissue gave no blue color with iodine, but yielded a small white flocculent precipitate under the conditions of the analysis. If the precipitation was made in acetic acid solution at pH 3, this precipitate was much larger and yielded a solution in water that showed a marked Tyndall effect in the spectrophotometer. On the other hand, if the precipitation was carried out at 100° C. at pH 1, the precipitate was very small and yielded a solution that was apparently clear. When diluted to 20 ml. and observed in a 3-cm. cell in the spectrophotometer, extinction coefficients of 0.032 and 0.010 were obtained, respectively. Both readings are beyond the lower limit of accuracy of the starch calibration curve of the instrument and therefore have little significance. Nevertheless the results illustrate the superiority of the iodine precipitation at pH 1, and also serve as a blank on the method when applied to the analysis of tissues very low in starch. The value 0.01 for the extinction coefficient has been repeatedly found for tissues that gave no qualitative evidence of the presence of starch. Consequently when attempts are made to estimate quantities of 0.1 mg. or less of starch, it would seem advisable to deduct 0.01 from the extinction coefficient observed to allow for this blank.

The calibration curve is constructed on the basis of 0.200 gram of tissue, the extract from which is made to 50 ml., and of this 10 ml. at most are subsequently diluted to 20 ml. The limit of the calibration is 0.1 mg. of starch; consequently the lower limit of the method is a starch concentration of 0.25 per cent of the prepared tissue. If it is desired to determine smaller proportions, a larger sample of tissue must be employed. As much as 0.5 gram can be satisfactorily extracted by the technic described.

Tissues that contain high proportions of starch are most conveniently dealt with by reducing the size of sample se-

TABLE VIII. COMPARISON OF COLORIMETRIC METHOD FOR STARCH WITH SUGAR TITRATION VALUES

	Colorimetric Starch in Tissues	Sugar Titration Values		
		CaCl ₂ extract	HCl extract precipitation at pH 3	HCl extract precipitation at pH 1
	%	%	%	%
Alfalfa stem 39	7.50	...	9.14	9.51
Alfalfa stem 40	5.85	6.54
Tomato stem C	9.50	10.50
Tomato stem B	10.60	11.70	12.54	...
Tomato stem A	10.90	12.34	13.02	12.00
Tomato stem residues ^a	0.48	...	0.92	0.75
	0.18	...	0.39	...
	0.20	...	0.40	0.30
	0.25	...	0.55	...
	0.15	0.37	1.77	0.41
Beet root	0.05	0.21	0.89	0.15
Beet top	0.41	0.82	2.20	0.77
Rhubarb leaf	1.41	1.48	2.18	1.50
Tobacco leaf E	5.50	6.20
Tobacco leaf B	0.63	0.85
Tobacco leaf F	0.78	...	1.13	...
Tobacco stem H	1.68	1.80	2.37	1.75
Tobacco stem I	1.88	...	2.23	...
Tobacco stem J	4.63	5.00	5.19	5.08
Tobacco stem K	31.88	40.02	43.00	39.1

^a Tissue first extracted by refluxing with CaCl₂ + MgCO₃ for 2 hours. Residue washed and then extracted in usual way with HCl.

TABLE IX. COMPARISON OF COLORIMETRIC METHOD AND SUGAR TITRATION UNDER DIFFERENT CONDITIONS

Tissue Analyzed	Colorimetric Starch	Sugar Titration Values		
		CaCl ₂ extract	HCl extract precipitation at pH 3	HCl extract precipitation at pH 1 in cold
	%	%	%	%
Alfalfa leaf	7.45	...	9.14	9.51
Beet top	0.00	0.18	0.89	0.15
Beet root	0.16	0.37	1.77	0.41
Rhubarb leaf	0.35	0.82	2.20	0.77
Tobacco leaf B	5.50	6.20
Tobacco leaf F	0.63	1.85
Tobacco stem K	4.70	...	5.19	5.18

lected. For tissues with 30 per cent or more, it is advisable to employ 0.100 gram or even less.

Action of Takadiastase on Starch Extracts

The purity of the starch extracts from plant tissues can be readily tested by observations of the effect of takadiastase upon them.

An aliquot of the extract that contains less than 3 mg. of starch is neutralized with sodium hydroxide and acidified with a slight excess of acetic acid; 0.5 ml. of calcium chloride and 2 ml. of a 0.1 per cent solution of takadiastase (takadiastase undiluted 900 per cent, Parke, Davis and Co.) in water are added. The solution is warmed at 50° to 52° C. for 30 minutes with occasional stirring, is cooled and acidified with 2 ml. of dilute hydrochloric acid, and a few drops of iodine-potassium iodide reagent are added. If the precipitate produced is blue, the analytical procedure may be completed as already described. If no blue precipitate is formed, it is obvious that the extract contained no substance other than starch that reacts with iodine to give a blue color.

A careful investigation of the authors' standard preparations of potato starch showed them to be free from such contaminants; this confirms the statements of Ling and Nanji (?). In addition, tests on a number of preparations of leaf tissue revealed no case in which the amount of blue precipitate obtained after digestion of the extract with takadiastase gave readings at the spectrophotometer that could be regarded as significant.

Discussion

The colorimetric method employs three distinct steps, each of which contributes markedly to the specificity for starch. The preliminary dilute alcohol extraction of the tissue removes compounds such as glucosides and alkaloids, some of which yield insoluble colored compounds with iodine (1, 2). The precipitation of the starch with iodine eliminates a large group of polysaccharides which may be present in the starch extract but which are not precipitated by iodine. The utilization of the highly specific blue color of the iodine-starch complex for the quantitative measurement eliminates unknown carbohydrate compounds which may have been precipitated by the iodine or adsorbed on the starch precipitate. When formed in the presence of a large definite excess of iodine, this color is reproducible and stable. In addition, the use of the light filter which transmits a band of light of wave

length most strongly absorbed by the iodine-starch complex further contributes to the over-all specificity of the method.

The only source of interference that may be anticipated is from substances of the amylohemiacellulose type described by Schulze (13), Schryver and Thomas (12), and Ling and Nanji (?), which occur in certain starch-bearing seeds, in fruits, leaves, and stem tissues. These substances give an intense blue, or blue-violet, color with iodine, but differ from true starch in that they are not digested by takadiastase.

The present method of determining starch is essentially a comparison between starch isolated from the tissue under analysis and potato starch taken as standard. The authors have found no evidence of the presence of amylohemiacellulose in the standard starch they have used, nor in the tissues they have employed in their tests of the method. Obviously, however, tests should be made for such compounds before applying the colorimetric method in new cases. On the other hand, however, such information as is available in the literature indicates that the relative proportion of these compounds is usually very small, so that serious errors will seldom be encountered.

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Determination of Zinc in Soils

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MANY methods for the determination of small amounts of zinc in various materials have appeared in recent years. A review of those appearing prior to 1932 is given by Todd and Elvehjem (15). Since that time methods for the determination of zinc have been reported by Hibbard (?) and others (10, 12). Most of these are unsatisfactory for soil probably because of the large amounts and number of interfering substances present in them. Procedures involving the precipitation of iron and aluminum from the solution before the zinc is precipitated (1, 13) seem to be unsatisfactory because these bulky precipitates retain zinc, and it is difficult to remove all the iron.

In the work reported in this paper on the determination of zinc in soils, variations of several methods are used, including a modification of Hibbard's method for the determination of zinc in plant material in which the zinc is precipitated by

hydrogen sulfide from a properly buffered solution, after a preliminary precipitation with hydrogen sulfide to remove certain impurities. An acid concentration higher than that recommended by Hibbard was found necessary, probably because of the large mass of soluble salts resulting from a soil fusion. The zinc is determined with Nessler tubes by a method adapted to amounts found in soils.

Turbidimetric Determination of Zinc

Several methods (3, 6, 11, 16) have been used in the determination of small amounts of zinc, such as ferrocyanide turbidity, ferrocyanide titration, iodometric titration, polarigraph, and indirectly a colorimetric phosphate method. The ferrocyanide turbidity method has been used by the greatest number of investigators and was adopted for this work.

That the degree of opalescence produced by zinc in a potassium ferrocyanide solution is dependent on time, salt con-

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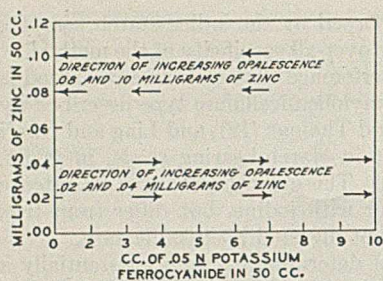


FIGURE 1. CHANGE IN OPALESCENCE WITH VARIOUS AMOUNTS OF POTASSIUM FERROCYANIDE AND ZINC

amounts of zinc from 0.02 to 0.1 mg. in 50 cc. of solution is given in this paper.

The potassium ferrocyanide used by the various workers varied from 0.1738 to 0.00264 gram per 50 cc. A comparison of opalescence was made using from 0.02 to 0.1 mg. of zinc and from 1 to 10 cc. of 0.05 *N* potassium ferrocyanide in 50 cc. Fifteen cubic centimeters of *N* hydrochloric acid were used in all these tests. The readings of the various amounts of zinc and potassium ferrocyanide are depicted on a parallelogram shown in Figure 1.

For each amount of zinc the opalescence varied with each amount of potassium ferrocyanide. With 0.10 and 0.08 mg. of zinc, opalescence was greatest with 1 cc. of the 0.05 *N* potassium ferrocyanide and least with 10 cc. With 0.02 and 0.04 mg. of zinc, the opalescence produced was reverse order, being greatest with 10 cc. of the 0.05 *N* potassium ferrocyanide and practically none with 1 cc. With amounts of zinc from 0.02 to 0.1 mg. and 15 cc. of *N* hydrochloric acid in 50 cc. it would seem about 5 cc. of 0.05 *N* potassium ferrocyanide should be used.

The effects of acid on the opalescence of zinc in amounts from 0.02 to 0.1 mg. in potassium ferrocyanide solution are shown in Figures 2 and 3.

The readings from which Figures 2 and 3 were made are approximate, because the same amount and shade of opalescence are reproduced only by identical conditions in all respects. Three milligrams of zinc with 3 cc. of *N* hydrochloric acid were taken as a standard for the readings in both figures. Figure 2 shows that with 0.02, 0.03, and 0.04 mg. of zinc there is opalescence with 3 cc. of *N* hydrochloric acid. The opalescence increases up to 9 cc. with 0.02 and 0.03 mg. and up to 12 cc. with 0.04 mg. of *N* hydrochloric acid and zinc, respectively. After maximum opalescence is reached the opalescence decreases with increasing amounts of acid until between 18 and 24 cc. of *N* hydrochloric acid there is no opalescence.

Figure 3 shows the apparent amounts of zinc as judged by opalescence produced with 3, 9, 12, and 15 cc. of *N* hydrochloric acid on from 0.03 to 0.12 mg. of zinc. Three cubic centimeters of *N* hydrochloric acid show the least opalescence for the various amounts of zinc and the least difference between the various amounts of zinc. Fifteen cubic centimeters of *N* hydrochloric acid have the greatest opalescence and the greatest differences between the various amounts of

centration, kind of acid, strength of acid, and the potassium ferrocyanide-zinc ratio has been pointed out by several investigators (2, 5, 14). The degree of dependence of opalescence on the potassium ferrocyanide-zinc ratio and amount of hydrochloric acid for

zinc. Figure 2 has shown a disappearance of opalescence with more than 15 cc. of *N* hydrochloric acid with very small amounts of zinc. From these results it would seem that 15 cc. of *N* hydrochloric acid are about right to use in 50 cc. of solution with zinc ranging from 0.03 to 0.1 mg.

The zinc as separated was free of contaminating salts except for the small amount of sulfide in combination with the zinc. Several investigators add salts of various kinds to increase the opalescence. Added salts were found to impart a greenish tinge to the opalescence and seemed to hasten its breaking down, and for that reason are not used in this method. The clearest opalescence was secured by using acid alone. Maximum opalescence is attained in about 3 minutes and persists for 15.

Analytical Procedure

The soil sample is first fused with potassium pyrosulfate and the fusion disintegrated in a hot dilute hydrochloric acid solution (13). The silica is removed by filtration and the filtrate and washing are evaporated to a fairly small volume. The acidity of this solution is fixed at 0.4 *N* and the interfering members of the first hydrogen sulfide group in qualitative analysis are removed with hydrogen sulfide. The solution is buffered, a filter aid added, and the pH fixed at about 3.5 (neutral gray color to bromophenol blue or bromochlorophenol blue). The zinc is then precipitated with hydrogen sulfide and filtered. After thorough washing it is dissolved off the paper with 1 *N* hydrochloric acid. The acid solution containing the zinc is made up to a definite volume and the zinc determined with Nessler tubes on an aliquot by the ferrocyanide method.

REAGENTS AND PRECAUTIONS. Only iron, nickel, or monel metal screens and grinding equipment should be used in the preparation of the sample, avoiding all brass. Zinc-free glassware must be used. Pyrex ware is satisfactory.

The buffer solution (9) for zinc precipitation consists of 650 grams of ammonium sulfate, 500 grams of citric acid, 200 cc. of 90 per cent formic acid, and 500 cc. of concentrated ammonium hydroxide in 2.5 liters. The 3.2 pH buffer solution consists of 37 cc. of 0.1 *N* hydrochloric acid and 2.5508 grams of potassium acid phthalate in 250 cc. of solution (4). The indicator solution is prepared by dissolving 1 gram of bromochlorophenol blue or bromophenol blue in 28.5 cc. of 0.1 *N* hydroxide and diluting to 2.5 liters with water.

FUSION. Two 5-gram portions of soil are fused in 50-cc. platinum crucibles, each with 12 to 20 grams of potassium pyrosulfate (8). If the soil is mixed with half or less of pyrosulfate and the remainder added in one or more portions as the fusion progresses, boiling over will be practically prevented. The amount of potassium pyrosulfate needed is largely determined by the quan-

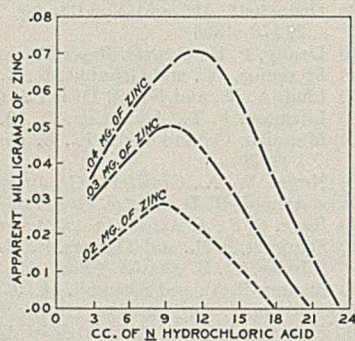


FIGURE 2. EFFECT OF AMOUNT OF HYDROCHLORIC ACID ON OPALESCENCE OF SMALL AMOUNTS OF ZINC

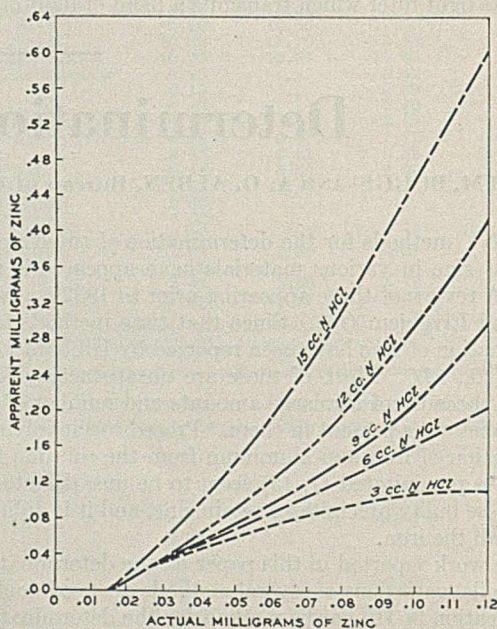


FIGURE 3. EFFECT OF AMOUNT OF HYDROCHLORIC ACID ON OPALESCENCE OF ZINC IN POTASSIUM FERROCYANIDE SOLUTION

tity of calcium and organic matter in the sample, more being required as these components increase. The fusions can usually be made almost completely with the lid off, covering only toward the end.

SEPARATION OF IMPURITIES. The fusions are cooled and placed one at a time in a 400-cc. beaker containing 250 cc. of water and 10 cc. of hydrochloric acid. After they have loosened and the crucibles and lids have been removed and washed, the solution is evaporated to about 100 cc. on a hot plate. If much calcium is present, the solution must be kept heated almost to the point where bumping will occur in order to disintegrate the fusion. If the fusion is allowed to cool gradually before being placed in the acid solution for disintegration, it will come free from the crucible much more readily than if the fusion is placed in the solution hot or its cooling hurried unduly. The solution is filtered on a Büchner funnel, removing the silica and a good part of the gypsum. The precipitate is washed several times with cold distilled water. The filtrate and washings are evaporated to 100 to 150 cc.

The acidity of the solution is now fixed at 0.4 N by adding the proper amount of 5 N sodium hydroxide. This is determined by titrating 1 cc. of the unknown solution in a 100-cc. beaker, with 1 cc. of bromophenol blue indicator solution to the same color as an identical volume of pH 3.2 buffer solution with 1 cc. of bromophenol blue indicator. It is convenient to have ready for comparison 100-cc. beakers containing, respectively, 10, 15, and 20 cc. of the buffer solution with 1 cc. of the indicator solution. From this result and the volume of solution the amount of 5 N sodium hydroxide required to bring the solution to 0.4 N acidity can be calculated.

After the normality is fixed, hydrogen sulfide is passed rapidly into the cold solution (10) for 15 minutes, the solution is filtered, and the precipitate washed with a 0.4 N hydrochloric acid solution, saturated with hydrogen sulfide. The precipitate is discarded.

SEPARATION OF ZINC. To the filtrate, approximately 250 cc., are added 25 cc. of buffer solution and 2.5 cc. of bromophenol blue indicator solution. The solution is titrated to a gray color, or slightly beyond, with 5 N sodium hydroxide. One cubic centimeter of 5 per cent talc suspension is then added and the zinc precipitated by passing a rapid stream of hydrogen sulfide for 30 minutes.

The precipitate is filtered and the filter carefully washed with hydrogen sulfide water containing 4 cc. of 90 per cent formic acid per liter. This washing frees the filter of iron. At least four washings are necessary and finally the precipitate and tips of the funnels are washed once with distilled water. The zinc sulfide on the paper is then dissolved by washing the filter with 30 cc. of 1 N hydrochloric acid into a 100-cc. volumetric flask and made to volume by washing the paper repeatedly with distilled water.

DETERMINATION OF ZINC. Aliquots of 10 to 25 cc. of the solution from separation of the zinc are placed in 50-cc. Nessler tubes. The acidity is increased until each one has 15 cc. of N hydrochloric acid, water is added to make 45 cc., and finally 5 cc. of the 0.05 N potassium ferrocyanide are added. The whole is mixed thoroughly and then compared with a set of standards made up in a similar manner. If talc filter acid and water are saturated with hydrogen sulfide and filtered, and the hydrochloric acid used afterward for the standards is run through this filter, the standards will have the same shade of color as the unknowns, a considerable aid in quick reaching of the unknowns. Comparison of unknowns with standards is best made by placing the Nessler tubes over fine print as suggested by Birekner (2).

Application and Results

The method was checked by adding 1 mg. of zinc to an acid and a neutral soil at various steps in the process, and the added zinc recovered. The results are shown in Table I.

TABLE I. RECOVERY OF ADDED ZINC FROM AN ACID AND NEUTRAL SOIL

Stage in Method When Zinc Was Added	Zinc Added Mg.	Inherent Zinc in Soil Sample Mg.	Total Zinc Recovered Mg.
Monroe silt loam, virgin soil, 3 to 6 inches, pH 4.68			
Zinc applied in solution before fusion	1.00	0.40	1.40
Zinc added dry before fusion	1.00	0.40	1.40
Zinc added in solution before fusion	1.00	0.40	1.40
Fused very hard	1.00	0.40	1.40
Yaholla fine sandy loam, 24 to 36 inches, pH 7.00			
Zinc added before silica filtered	1.00	0.22	1.20+
Zinc added after silica filtered	1.00	0.22	1.20+

The zinc content of six soils ranging in reaction from pH 4.25 to 8.40 as determined by this method is given in Table II. This table shows considerable variation in the zinc content of soil profiles. The lowest amount of zinc in any horizon is 0.04 mg. per 10-gram sample and the highest amount is 0.83 mg. Rosette of pecans has been found to be associated with deficiencies of available zinc in soils and a discussion of this relationship will be presented in another publication.

TABLE II. ZINC CONTENT OF TYPICAL SOILS (Amount per 10 grams)

Depths	Yaholla Fine Sandy Loam	Uvalde Silty Clay Loam	Frio Silty Clay Loam	Acadia Very Fine Sandy Loam	Catalpa Silty Clay Loam	Ochlocknee Fine Sandy Loam
Inches	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
0-3	0.73	0.23
3-6	0.83	0.25
6-12	0.63	0.53	0.53	0.04
	0.63	0.38	0.53	0.09	0.73	0.25
<i>Feet</i>						
1-2	0.53	0.38	0.53	0.17	0.83	0.23
2-3	0.43	0.43	0.63	0.21	0.83	0.33
3-4	0.43	0.38	0.63	0.19	0.83	0.38
4-5	0.43	0.33	0.63	0.29	0.83	0.33
5-6	0.43	0.43	0.63	0.31	0.83	0.33
6-7	0.43
7-8	0.53
8-9	0.63
9-10	0.68
10-11	0.73
11-12	0.78

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Recovering Chloroform from Used Dithizone Solutions

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CHLOROFORM from used dithizone solutions can be economically recovered by first removing any aqueous layer, then washing until colorless with commercial sulfuric acid equal to 5 or 10 per cent of its volume, treating with lime, distilling in the presence of some of the excess lime, and finally adding alcohol (1.0 to 1.5 per cent by volume). The sulfuric acid removes the organic impurities, while the lime neutralizes the excess acid or any acid resulting from the decomposition of the chloroform during distillation, and the alcohol acts as a preservative. The product meets the tests of the U. S. Pharmacopeia and is suitable for further use with dithizone or in other procedures.

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Measuring the Susceptibility of Asphalts to Temperature Changes

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PRIOR to the introduction of modern distillation methods into the petroleum industry, the sources of petroleum asphalts were comparatively few. Subsequently, however, the increased use of vacuum pipe stills, as well as other improvements in refining methods, opened a considerably broader field, resulting in the production of asphalts from sources which previously could not be processed for that purpose in existing equipment without some decomposition. Modern methods have also made possible the manufacture of a larger number of asphalt grades than were formerly produced.

Asphalts, in general, are classified in several groups according to their use as binders and paving asphalts for the construction of roads, saturants and roofing asphalts for the roofing trade, as well as innumerable specialty products for many other uses. Each classification is subdivided into numerous grades depending upon their consistency, which is usually designated by one or more of the standardized tests, such as softening point, penetration, and viscosity. The ring and ball softening point is defined as that temperature at which a sample of asphalt, molded in a ring of standard size and upon which a 0.94-cm. (0.375-inch) steel ball has been set, sags under the weight of the ball to a depth of 2.5 cm. (1 inch) when suspended in a fluid, either water or glycerol, heated at a definite rate of 5° C. (9° F.) per minute. The penetration is defined as the depth, measured in one-hundredths of a centimeter, to which a standard-size needle penetrates the asphalt under definite conditions of temperature, weight, and time. Because of the nature of asphalts, these methods are necessarily fixed, arbitrary, and closely defined, in order that comparable results may be obtained. The viscosity may be determined in numerous ways by means of efflux-type or torsion-type viscometers.

While these tests *per se* serve to define the physical characteristics of an asphalt under specified conditions, they do not, individually or collectively, give a clear picture as to the behavior over the wider range of conditions encountered in actual service.

Recently, there has been an increasing demand from the asphalt consumer for some simple method by which the behavior of an asphalt under service conditions can be definitely

The need for some suitable means of expressing the change in consistency of asphalts over the wide range of temperature usually encountered in actual service is demonstrated. While no single factor has been developed which will adequately serve to measure the temperature susceptibility over the entire desired range of conditions, three methods are suggested which can be used in conjunction with one another for this purpose. The softening point-penetration index indicates the susceptibility over a narrow range of normal atmospheric temperatures, the ratio of the penetration at 25° C. (77° F.) to the penetration at 0° C. (32° F.) at subnormal, and the fluidity index at elevated temperatures.

indicate numerically the consistency changes of an asphalt at normal, subnormal, and elevated temperatures. It should be borne in mind, however, that asphalts have other characteristics just as important which do not come within the scope of this paper.

Review of Some Present Methods

In dealing with asphalts, the term "susceptibility" is generally employed to indicate the tendency of this material to change in consistency with changes in temperature. A product that changes consistency rapidly with temperature is spoken of as possessing a high susceptibility, and one which

changes slowly with temperature has a low susceptibility.

If an asphalt which is highly susceptible is used as a filler in block pavements, either wood or stone, the heat under normal summer conditions will cause the asphalt to soften almost to the point of being fluid. This will ooze out of the joint onto the blocks, rendering them sticky. An asphalt with low susceptibility will not soften to any such degree under the same conditions and although expansion will take place, the bitumen will remain in a more or less solid, nonsticky condition. In an asphalt macadam road, other conditions being equal, a highly susceptible asphalt tends to lower road stability and cause displacement under the action of heavy traffic in hot weather, because the asphalt will soften to a greater degree and hence lose more of its bonding power than one of low susceptibility. On the other hand, it is sometimes desirable to have an asphalt which becomes fluid rapidly as the temperature is raised. In the manufacture of some impregnated products a highly susceptible asphalt, in this case one which becomes fluid more rapidly at elevated temperatures than one of low susceptibility, tends to impregnate the material to a greater extent than the less susceptible bitumen, under the same conditions.

Thus, susceptibility of an asphalt is a property which manifests itself readily and is easily recognizable in all fields where asphalt is employed. The existing methods of measuring this property are not entirely suitable, either because of the limited range of consistencies over which they may be calculated or because they require the use of special apparatus and methods of testing not readily available nor widely in use.

SUSCEPTIBILITY FACTOR. Two methods of expressing the susceptibility factor which have been used for a number of years are calculated from the following formulas:

$$\text{Susceptibility factor} = \frac{\text{penetration at } 46.1^{\circ} \text{ C. per 50 grams per 5 seconds} - \text{penetration at } 0^{\circ} \text{ C. per 200 grams per 60 seconds}}{\text{penetration at } 25^{\circ} \text{ C. per 100 grams per 5 seconds}} \quad (1)$$

$$\text{Susceptibility factor} = \frac{\text{penetration at } 37.8^{\circ} \text{ C. per 100 grams per 5 seconds}}{\text{penetration at } 25^{\circ} \text{ C. per 100 grams per 5 seconds}} \quad (2)$$

measured. In an attempt to meet one phase of this condition, the available asphalt data obtained from various crude sources were reviewed with the result that factors were evolved which

Method 1 has gradually been almost entirely supplanted by method 2, which was originally given in the paving asphalt specifications for one of our large cities. Application of the

data to these two methods indicates that, while they give results in the same order of magnitude, they are not always in agreement. It was also observed that no calculations could be made on asphalts softer than 70 to 75 penetration at 25° C. (77° F.) because the values of penetration at 37.8° C. (100° F.) and 46.1° C. (115° F.) were indeterminate, owing to the limitations of the penetration test. The limit of penetration is approximately 350, corresponding to the depth of the asphalt container specified by the test. For a given source of asphalt, the factors varied over a rather wide range, depending upon the consistency.

A third type of factor has been suggested by Abraham (1).

$$\text{Susceptibility factor} = \frac{\text{hardness at } 0^{\circ} \text{ C.} - \text{hardness at } 46.1^{\circ} \text{ C.}}{\text{softening point (Kramer-Sarnow)}^{\circ} \text{ C.}} \quad (3)$$

Since the hardness, defined as the cube root of the number of grams which must be applied to a circular flat surface 1 sq. cm. in area to cause it to displace the substance at a speed of 1 cm. per minute, is determined by a special apparatus not in general use, this method has little practical value. The Kramer-Sarnow softening point differs from the more common ring and ball method in that the former is obtained by placing 5 grams of mercury on a plug of asphalt formed in a glass tube of definite size. The Kramer-Sarnow softening point is the temperature at which the mercury drops through the tube.

The Kramer-Sarnow softening point is usually 8° to 14° C. lower than the ring and ball softening point.

FLUIDITY FACTOR. The correlation of the viscosity of an asphalt and its penetration forms the basis for the calculation of a "fluidity factor" (4) which is used in some sections of the country for describing the change in consistency of an asphalt with temperature. The formula in this case becomes:

$$\text{Fluidity factor} = \left(\frac{\text{Furol viscosity at } 135^{\circ} \text{ C.} - \text{penetration at } 25^{\circ} \text{ C. per } 100 \text{ grams per } 5 \text{ seconds}}{\text{penetration at } 25^{\circ} \text{ C. per } 100 \text{ grams per } 5 \text{ seconds}} \right) \quad (4)$$

As pointed out by Zapata (4), this factor is of particular value over the range of paving grades, although it does not remain constant for asphalts from a given source but varies with the consistency. An asphalt of 122 penetration at 25° C. per 100 grams per 5 seconds and Furol viscosity at 135° C. (275° F.) of 222 seconds shows a factor of 122 by this method, whereas a product from the same source of 29 penetration at 25° C. (77° F.) and 799 Furol viscosity at 135° C. (275° F.) shows a value of 223.

FLOAT TEST INDEX. Another method known as the float test index, which has been used in one of the midwestern state specifications for paving asphalts, is calculated as follows:

$$\text{Float test index} = \sqrt{F \times P} \quad (5)$$

where F is the float test in seconds at 80° C. (176° F.) and P the penetration at 25° C. per 100 grams per 5 seconds.

The float test is a consistency test in which asphalt is poured into a standardized mold or collar. After cooling the sample for the designated time, the collar is screwed into the bottom of the aluminum float or saucer and the assembly floated in a water bath at the desired temperature. As the plug of asphalt is warmed by the water, it becomes fluid and is forced upward and out of the collar. The time in seconds between placing the apparatus on the water and when the water breaks through the material, causing the float to sink, is taken as the float test of the material.

The lack of specific data on the float test at 80° C. (176° F.) precludes a detailed discussion on this factor, although it would appear that this method would be more or less limited to those asphalts in the paving range of consistencies—i. e., from 30 to 95 penetration at 25° C. (77° F.).

HOEPFNER-METZGER VISCOSITY LAW. The Hoepfner-Metzger viscosity law of normal tars and asphalts (3) has also been suggested as a means of determining the susceptibility of asphalts. The so-called Hoepfner-Metzger "rigid point" of asphalts and Ubbelohde drop-point form the basis of this system. Any tests which measure the viscosity of an asphalt can be correlated by means of this law. As in the case of some other factors, it requires tests employing special apparatus and methods not in general use in this country, thus limiting the wide application of such a system.

Evolution of Suggested Methods

Before discussing the new methods evolved, a few comments should be made on the familiar viscosity index system for evaluating lubricating oils as developed by Dean and Davis (2), since two of the proposed factors may be described as being essentially indexes similar to this system. Briefly, the Dean and Davis system consists in obtaining the Saybolt Universal viscosities of two series of oils, each derived from an extreme type of crude, at the standard temperatures of 37.8° C. (100° F.) and 98.9° C. (210° F.). From these basic figures, a general relationship between the viscosity at 37.8° C. (100° F.) and at 98.9° C. (210° F.) was formulated for each series. From these equations a system of so-called viscosity indexes was developed which indicates the viscosity-temperature coefficients of any oil on a scale in which the series of oils (Texas-Coastal) having a high temperature coefficient are designated as 0 and those with a low coefficient (Pennsylvania) as 100.

The usefulness and widespread adoption of this method for evaluating the viscosity-temperature characteristics or susceptibility, as it might be called, of lubricating oils is general knowledge.

We are interested at present in one of the important characteristics of asphalts—namely, the degree of hardening or softening which takes place, or in other words, the susceptibility over the temperature range more or less governed by climatic conditions. At these temperatures, asphalts of particular interest are those with measurable penetrations. These considerations would suggest that a factor used for indicating susceptibility should include both the softening point and penetration at 25° C. (77° F.).

The statement should probably be made at this point that no single factor or method has been developed in the present investigation, which will adequately serve to measure the susceptibility over the entire desired range of consistency and temperature. Three methods will be described, however, which can be used in conjunction with one another to give a fairly complete picture of the susceptibility characteristics of an asphalt.

SOFTENING POINT-PENETRATION INDEX. From the correlation of data from a large number of crude sources, a general relationship has been found to exist between the softening point and penetration for straight reduced asphalts—i. e., those produced by steam and/or vacuum distillation, from any given source. This relationship, which gives a straight line on log-log coordinate paper, may be expressed by the equation:

$$\text{Log } M = a \text{ log } P + \text{log } k \quad (6)$$

$$\text{or} \quad M = kP^a \quad (7)$$

where M is the ring and ball softening point, in ° F., P the penetration, and a and k are constants depending upon the source of the asphalt and the temperatures at which the penetration is taken. While this relationship gives no indication, by itself, of the change in consistency of any one asphalt with

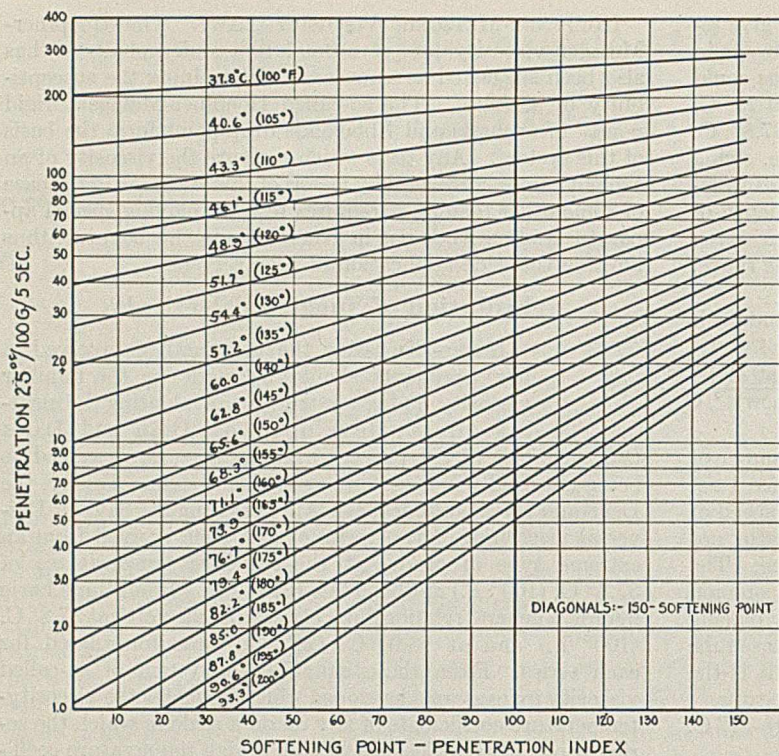


FIGURE 1

temperature, experience has shown in a general way that the higher the penetration of an asphalt at 25° C. (77° F.) for a given softening point, the less susceptible is that asphalt to temperature changes.

An attempt to express this general relationship numerically resulted in the development of the so-called softening point-penetration index. From the data obtained on two series of asphalts from sources of extreme types, a chart (Figure 1) was constructed. Basic figures used for developing the arbitrary scales were obtained from accurate tests on vacuum-pipe still reduced asphalts from Heavy Mexican and petroleum tar. Asphalts from Heavy Mexican crude were arbitrarily chosen as 100 on the index scale as representing products having a low consistency-temperature coefficient, while those from petroleum tar were selected as the other extreme—that is, as 0 on the scale, representing asphalts with a high consistency-temperature coefficient. These two extremes correspond to the use of Pennsylvania and Texas-Coastal oils, respectively, as extremes in the Dean and Davis lubricating oil viscosity index system. In this discussion, petroleum tar is to be considered as the residue from the cracking of virgin gas oil under high temperature and pressure. As in the viscosity index system, the sources of asphalts selected as standards do not represent either the lowest or highest known susceptibilities.

In Figure 1, the ordinate represents the penetration at 25° C. per 100 grams per 5 seconds, those for Mexican asphalt being on the right and for petroleum tar products on the left of the 0 to 100 scale. The abscissa represents the index number, which may be extended above 100 or below 0, and the diagonal lines indicate constant or iso-softening point. Thus, for example, the straight line shown for 54.4° C. (130° F.) softening point was drawn between 19.5 penetration at 25° C. (77° F.) at 0 index, the penetration of a petroleum tar asphalt of this softening point, and 57 penetration at 25° C. (77° F.), the corresponding value at 100 index for Mexican asphalt. As an example of the use of this chart, it is desired to determine the softening point-penetration index of an asphalt having a softening point of 54.4° C. (130° F.) and 40 penetration at 25° C. per 100 grams per 5 seconds. The penetration is read from the ordinate scale on the left, followed horizontally to the right until it intersects the 54.4° C. (130° F.)

iso-softening point line. At this point, the index number is read vertically downward from the abscissa scale giving a value of 67.

This index may be applied to oxidized asphalts as well as straight reduced grades. The former are made by air-blowing or refining a straight reduced crude residuum usually of soft consistency which is commonly referred to as the base. It is known that the greater the extent of oxidation, the lower is the susceptibility of an asphalt. In other words, the higher the softening point of an oxidized asphalt blown from a given base, the higher is its index. Likewise, for a given softening point, the softer the consistency of the oxidizing base, the higher is the index.

Table I gives the values of this index for asphalts from various sources over the relatively narrow range of paving asphalts from 30 to 95 penetration at 25° C. (77° F.) as well as for the whole range from 0 to 200 penetration at 25° C. (77° F.).

Mexican and petroleum tar asphalts have obviously a 100 and 0 index, respectively, over the entire range since they are the assumed standards. The asphalts from the remaining sources vary somewhat, particularly over the wide range, since the softer asphalts from any given source usually display a higher index.

From the values in Table I, it appears that the softening point-penetration index affords a ready means of classifying asphalts as to their susceptibility characteristics at what the authors chose to call normal temperatures—i. e., 25° C. (77° F.).

TABLE I. NUMERICAL MAGNITUDE OF SOFTENING POINT-PENETRATION INDEX

Asphalts ^a	Range of Values for Softening Point-Penetration Index	
	Paving range, 30-90 penetration at 25° C.	Whole range, 0-200 penetration at 25° C.
Mexican	100	100
Venezuelan	85-88	78-90
Colombian	67-77	67-100
Heavy Smackover	82-94	72-110
West Texas	59-62	52-90
Headton	70-76	70-80
Midcontinent	59-65	52-75
Van Zandt	68-75	68-110
California (Kern River)	14-27	4-58
East Venezuelan	10-27	5-65
Petroleum tar	0	0

^a Straight reduced asphalts. Penetration range, penetration 25° C. per 100 grams per 5 seconds.

SUSCEPTIBILITY AT SUBNORMAL TEMPERATURES. It was previously shown that methods 1 and 2 for determining the susceptibility factor of an asphalt were limited to asphalts with a maximum penetration of 70 to 75 at 25° C. (77° F.). Another method which has been used from time to time in practice and which extends the range of asphalts consists in calculating the ratio of penetration at 25° C. per 100 grams per 5 seconds and penetration at 0° C. per 200 grams per 60 seconds. Thus, at subnormal temperatures, the susceptibility becomes:

$$\text{Susceptibility factor} = \frac{\text{penetration at 25° C. per 100 grams per 5 seconds}}{\text{penetration at 0° C. per 200 grams per 60 seconds}} \quad (8)$$

This method not only extends the range over which a factor can be obtained but also indicates the behavior of an asphalt

over the temperature range from 25° to 0° C. (77° to 32° F.). The characteristics of an asphalt, as the temperature is lowered, are just as important, if not more so, than at higher temperatures because it is at the lower temperatures that asphalts fail by cracking and thus lose their protective or bonding properties. From these considerations, this method possesses distinct advantages over methods 1 and 2. The available data for various sources were calculated by method 8 and shown in Table II.

In this case, Mexican asphalts showed a fairly constant factor of 3.3, whereas the petroleum tar asphalts varied over the wide range shown. The smaller the ratio of the two penetrations, the lower is the susceptibility of the asphalt over this temperature range.

TABLE II. NUMERICAL MAGNITUDE OF THE SUSCEPTIBILITY FACTOR AT SUBNORMAL TEMPERATURES

(Susceptibility factor = $\frac{\text{penetration at 25° C. per 100 grams per 5 seconds}}{\text{penetration at 0° C. per 200 grams per 60 seconds}}$)

Asphalts ^a	Range of Susceptibility Factor Values	
	Paving range, 30-90 penetration at 25° C.	Whole range, 0-200 penetration at 25° C.
Mexican	3.3	3.3
Venezuelan	3.4-3.8	3.3-4.5
Colombian	3.5-5.0	3.3-5.5
Heavy Smackover	2.71-3.50	2.5-5.0
West Texas	4.6-5.8	4.2-9.0
Healdton	5.4-6.6	5.2-9.0
Midcontinent	3.7-4.8	3.4-7.0
Van Zandt	3.2-4.2	1.8-7.0
California (Kern River)	12.5-13.3	12.5-13.3
East Venezuelan	4.4-5.2	3.8-10.0
Petroleum tar	7.0-17.0	7.0-17.0

^a Straight reduced asphalts. Penetration range, penetration at 25° C. per 100 grams per 5 seconds.

FLUIDITY INDEX. In order to determine the susceptibility at elevated temperatures, the so-called fluidity index was developed in essentially the same manner as the softening point-penetration index, but using the penetration at 25° C. per 100 grams per 5 seconds and Furol viscosity at 135° C. (275° F.) as the required inspections. Experience has shown that the higher the softening point-penetration relationship an asphalt possessed, the less susceptible it was to changes in temperature. To carry this one step further, it has been generally found that of two asphalts with the same penetration at 25° C. (77° F.) that product which shows the higher viscosity at a given temperature is less susceptible than the material with the lower viscosity. Hence, the penetration can be linked with viscosity to give an indication of changes in consistency at more or less elevated temperatures.

In constructing the fluidity index chart (Figure 2), the same two series of asphalts were used as in the softening point-penetration index—that is, Heavy Mexican asphalts were arbitrarily taken as 100 and petroleum tar asphalts as 0 in the index scale. The ordinate in this case represents the Furol viscosity at 135° C. (275° F.), the abscissa the fluidity index, and the diagonal lines indicate constant penetration at 25° C. (77° F.).

By applying a large number of data to this index, results such as given in Table III are obtained.

The viscosity at 135° C. (275° F.) was chosen because it was found that data could be obtained at this temperature over the important range of consistencies from 200 to 25 penetration at 25° C. (77° F.). While higher temperatures may be employed, the differences between asphalts from various

sources are not as marked and for softer asphalts the limit of accuracy of the Furol viscometer enters the picture. Similarly, at low temperatures, the viscosities on the harder asphalts are unduly high with the accompanying sacrifice of accuracy. This index can also be applied to oxidized asphalts since, for a given penetration, the rise in viscosity is dependent upon the extent of oxidation. As in the case of the softening point-penetration index, the softer the base from which an oxidized asphalt is blown, the higher will be its index.

TABLE III. NUMERICAL MAGNITUDE OF THE FLUIDITY INDEX

Asphalts	Range of Fluidity Index Values	
	Paving range, 30-95 penetration at 25° C.	Whole range, 0-200 penetration at 25° C.
Mexican	100	100
Venezuelan	85-87	76-87
Colombian	79-81	77-81
Midcontinent	83-86	83-86
Van Zandt	77-79	77-79
California (Kern River)	45	...
California (Kern River oxidized)	54-60	...
West Texas (straight reduced)	69-71	69-71
West Texas oxidized (41-50 penetration at 25° C.)	84	...
Petroleum tar	0	0

Discussion of Results

The present study has indicated the improbability of finding a single factor or index which will cover a wide range of consistencies and adequately serve to measure the susceptibility of an asphalt over the entire range from subnormal atmospheric temperatures to elevated temperatures. It does not necessarily follow that an asphalt which shows a high softening point-penetration index value will also display a low susceptibility factor at low temperatures and a high fluidity factor at elevated temperatures.

Table IV represents a comparison of some of the data to illustrate this feature.

For example, Colombian 53 penetration asphalt shows a lower softening point-penetration index than a 55 penetration

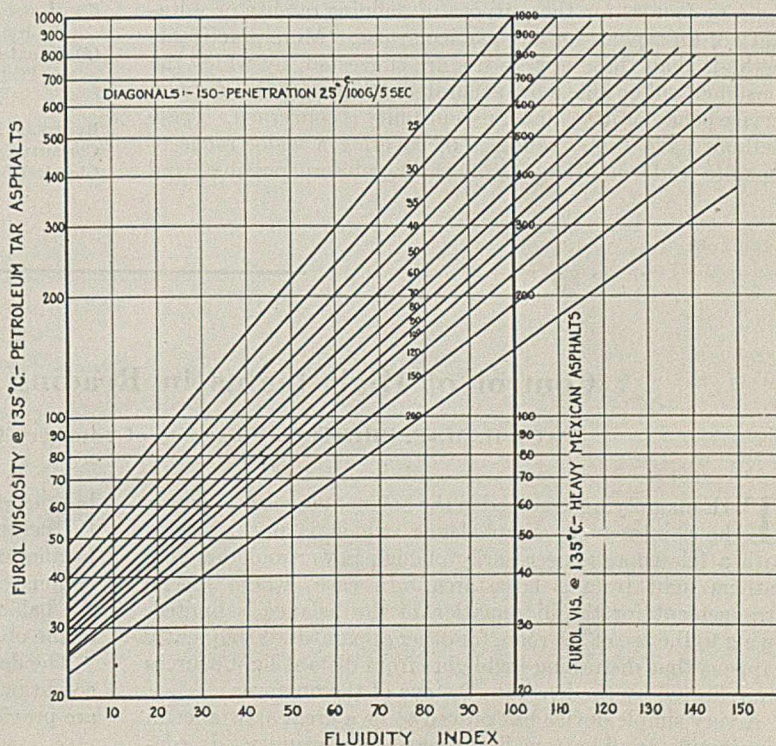


FIGURE 2

Healdton asphalt—i. e., 70 as compared with 73, respectively—although the subnormal temperature susceptibility for the latter is considerably higher than for the former asphalt. In other words, while the Healdton asphalt is not as susceptible at normal temperatures as the Colombian grade, the latter does not harden as rapidly as the temperature is lowered. A similar example can be shown with respect to the fluidity index. West Texas asphalt with 50 penetration at 25° C. has the same softening point-penetration index as a Midcontinent asphalt of the same consistency, although at elevated temperatures, as measured by the fluidity index, the Midcontinent asphalt has a higher index than the former. In this case also, the low temperature susceptibility is lower for the Midcontinent than for the West Texas product.

TABLE IV. CHANGES IN SUSCEPTIBILITY CHARACTERISTICS BETWEEN LOW AND ELEVATED TEMPERATURES

Source and Grade	Softening Point-Penetration Index	Susceptibility Factor ^a	Fluidity Index
Colombian, 53 penetration at 25° C.	70	3.83	81
Healdton, 55 penetration at 25° C.	73	6.11	..
Midcontinent, 50 penetration at 25° C.	63	3.92	85
West Texas, 50 penetration at 25° C.	63	5.88	70

^a Penetration at 25° C.
Penetration at 0° C.

Thus, any theoretical consideration or comparison of asphalts must take into account these differences in behavior. In practice, certain uses demand a highly susceptible asphalt at elevated temperatures while, in other cases, the low-temperature characteristics are more important.

In applying the proposed methods of measuring susceptibility as an aid in choosing the proper asphalt for a given service, the fact should be borne in mind that susceptibility is by no means the sole criterion upon which the quality of an asphalt is based. Other properties, such as resistance to weathering, water absorption, or resistance to acid and alkali, for example, are usually just as important as susceptibility.

In the presentation of the results of this study, no attempts have been made to establish definite limits to any of the indexes or factors for the purpose of defining quality or suitability of an asphalt for any particular use. More practicable methods than those now in use are suggested, by which the consumer will be able more accurately to correlate his data on service behavior in so far as susceptibility is concerned. These methods have the advantages of covering a wider range of asphalts and conditions than was heretofore possible, and

employing apparatus and tests which are commonly used and hence familiar to those in asphalt work. The correlation between service behavior and the susceptibility as determined by the suggested methods should then serve as a guide for future decisions on the suitability of an asphalt for a given purpose. At the present time, the lack of reliable actual service data prevents the authors from giving any specific examples of this correlation in any one field.

In addition, it is hoped that the present contribution will serve as a basis for further thought and experimentation on the subject of susceptibility, which will undoubtedly result in a still greater appreciation of this characteristic of asphalts.

Conclusions

No single factor has thus far been evolved which will adequately express the temperature susceptibility of an asphalt over the wide range of temperatures encountered in the commercial application of asphalts.

Present methods are not entirely suitable, because they are too limited in the range of consistencies over which they can be determined or require the use of apparatus and testing methods not commonly used or recognized as standards.

A combination of factors or indexes is suggested by which a definite measure of the temperature susceptibility characteristics of a wide range of asphalts can be determined. The softening point-penetration index indicates this characteristic over a narrow range of normal atmospheric temperatures, the ratio of penetration at 25° C. to penetration at 0° C. at subnormal and the fluidity index at elevated temperatures.

These methods are equally applicable to straight reduced and oxidized asphalts and are easily determined by means of tests which are in common use.

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RECEIVED May 11, 1935. Presented before the Division of Petroleum Chemistry, Symposium on Asphalt, at the 89th Meeting of the American Chemical Society, New York, N. Y., April 22 to 26, 1935.

Control of High Lights in Reading Microbalance Swings

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THE magnifying lens used in the balance case for observing the pointer of a microbalance, which is not provided with a telescope, is necessarily of high power and therefore gathers light from a large area. In cases where special arrangement for the illumination of the balance is limited, owing to the use of the room for other apparatus, it frequently happens that disturbing highlights from distant light sources are reflected by the lens into the eye of the observer.

A very simple device has proved to be a great assistance in overcoming trouble from ill-arranged light sources. It consists of a 10- or 12-inch square of dark cardboard (preferably,

but not necessarily, dull black), with a 1-inch circular hole in the center. By holding this card in the hand between the balance case and the observer the highlights are almost totally eliminated, the necessity of closing one eye is removed, and the balance is, in a measure, protected from the hot breath of the observer.

The device serves equally well in correcting faulty lighting conditions for ordinary analytical or assay balances which are provided with a magnifying lens in the balance case.

RECEIVED December 13, 1935.

Determination of Gaseous Olefins or Hydrogen by Catalytic Hydrogenation

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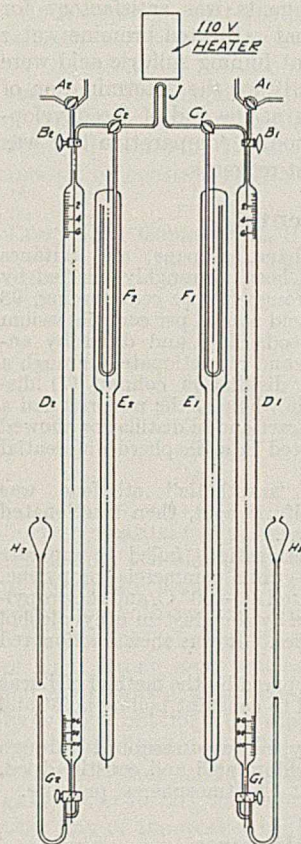


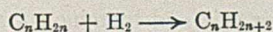
FIGURE 1. DIAGRAM OF APPARATUS

nearing saturation, or with changes in temperature. In addition, reagents for the determination of olefins are corrosive and volatile, necessitating unusual precautions and auxiliary reagents.

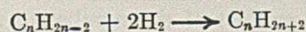
Proposed Method

A new method for the quantitative determination of gaseous olefins by catalytic hydrogenation, which has been developed in this laboratory and used for the past three years, gives consistent reproducible results accurate to a few tenths of a per cent in a time comparable with that of any liquid reagent method.

It requires only that a measured volume of hydrogen be mixed with a known quantity of olefin-containing gas and the mixture passed over a suitable catalyst at room temperature and substantially atmospheric pressure. The resulting contraction in volume is a direct measure of the amount of olefin present according to the reaction:



Thus, one volume of olefin reacts with one volume of hydrogen to form one volume of paraffin, and the change in volume on hydrogenation is from two volumes to one. In the case of acetylene or diolefins, the contraction is twice the volume present according to the reaction:



EXISTING methods for the analysis of olefinic gases may properly be divided into two classes: those using sulfuric acid, and those using bromine, but both depending on the reagent to react selectively with the olefins, leaving untouched any paraffins or cyclics present. For accurate work this is an admitted impossibility, even when the gaseous mixtures are separated by low-temperature fractional distillation and the resulting fractions are analyzed separately. Corrections must still be applied, which are at best rather doubtful, since these so-called selective reagents possess, in common with all absorption media, the undesirable ability to take up varying amounts of substances, other than the one they are being applied to absorb, and then to regenerate a portion of the dissolved constituents when used with another gas of different composition, when

Suitable corrections must be applied if present with olefins. The only two compounds likely to be found are acetylene and butadienes, and these can be determined separately by saturated potassium mercuric iodide (3) and maleic anhydride (11), respectively.

Typical results on synthetic samples of propylene in propane are shown in Table I.

TABLE I. ANALYSIS OF PROPANE-PROPYLENE MIXTURES

Run No.	Propylene %	Difference from True Per Cent
Sample 1 as synthesized	10.5	...
1	10.4	-0.1
2	10.4	-0.1
3	10.4	-0.1
4	10.7	+0.2
5	10.5	...
6	10.6	+0.1
Sample 2 as synthesized	50.5	...
1	50.8	+0.1
2	50.4	-0.1
3	50.5	...
4	50.5	...
5	50.5	...
6	50.3	-0.2
7	50.5	...

During the development of the method, similar consistent quantitative check runs were made using ethylene, propylene, individual and mixed butylenes, hydrogen, and acetylene. With only a few exceptions out of the hundreds of runs made, the results were not more in error than the possible accuracy of measurement of 0.05 ml. of gas.

Apparatus

The apparatus used, as shown schematically in Figure 1, consists of two complete Bureau of Standards (8) water-jacketed buret and compensator assemblies with a catalyst tube mounted between them. A heater is provided for catalyst preparation and regeneration.

The catalyst is prepared by melting about 4.0 grams of c. p. nickel nitrate hexahydrate in its own water of crystallization in a 50-cc. porcelain evaporating dish. Shredded long-fiber asbestos, which has previously been digested with hot nitric acid, washed, dried, and ignited, is then added until all the solution is absorbed. Any excess solution is pressed out with a porcelain spatula and drained from the evaporating dish. The nickel-saturated asbestos is then lightly calcined with a soft Bunsen flame until part of it appears black and the remainder greenish yellow. After cooling, the mass is broken up into small pieces and added to a U-shaped catalyst tube of 8.0-mm. Pyrex glass to a depth of about 6.5 cm. on each side. Both ends are plugged loosely with ignited asbestos or glass wool and the glass tube is indented before the plugs to keep them in place.

The tube is then heated to not over 310° C. while slowly drawing laboratory air through it with the vacuum line. This is continued until no further brown fumes are evolved and the whole mass becomes entirely black.

The catalyst tube is cooled, connected to the apparatus, and flushed with hydrogen. It is then heated in a current of hydrogen to not over 325° C. for several hours and finally allowed to cool with the hydrogen still passing over it. The catalyst should be protected against air at all times to avoid poisoning.

When poisoned it should be flushed with hydrogen and reheated in that atmosphere to 325° C. When cooled the activity will be restored.

Procedure

It is assumed that the catalyst tube, J, has been activated as described above and that the manifold from B₁ to B₂ is filled

with hydrogen to protect it. Accordingly, with the mercury in the leveling bulbs and burets at the same level, the gases in manometers F_1 and F_2 are drawn into their respective burets, the contents of which are then discarded to the atmosphere.

Connection is then made from A_2 (left-hand buret) to a cylinder of pure hydrogen through a suitable reducing valve. After thorough purging through A_2 , the cock is opened to the buret and 70.0 or 80.0 ml. of hydrogen are drawn into D_2 . Cock A_2 is again closed, C_1 is opened to J , F_1 , and B_1 , and B_2 is carefully opened, allowing the hydrogen to level manometer F_1 by filling it until the mercury almost touches the electrical contact, then reversing G_2 to slow down the rate until contact is shown by the right light flashing; at which point G_2 is quickly closed and then C_1 is closed to F_1 but opened to J and B_1 . Manometer F_2 is ordinarily left filled with mercury. After C_1 is closed to F_1 , the remaining hydrogen is flushed out the tail of cock B_1 . B_2 is then reversed and mercury brought to A_2 as before.

The apparatus is now ready for an analysis. Pure hydrogen is again added through A_2 until about 50.0 ml. are taken, although the amount of hydrogen required depends on the sample. Preferably about twice as much hydrogen is taken as is required; acetylene and diolefins, of course, require twice as much hydrogen as olefins. A_2 is then closed and B_2 opened to the manifold. With the levels in H_2 and D_2 approximately equal, C_1 is opened toward B_2 , F_1 , and J , and the mercury in F_1 brought to the contact point by adjusting H_2 . The balance is always obtained by allowing the mercury to flow upward toward the platinum point—never the reverse. At that point, G_2 is quickly closed and the reading taken for "hydrogen added."

Approximately 50.0 ml. of sample are taken into D_1 in a similar manner, except that C_1 is opened toward B_1 before B_1 is reversed. After F_1 is set, G_1 is quickly closed and the amount of "sample" noted.

With C_1 opened, the mercury in F_1 is pulled up until it just touches the cock, which is then closed to the manometer. This step is important and should not be neglected. With G_1 and G_2 opened full, the hydrogen in D_2 is passed into D_1 and the gases are thoroughly mixed by alternately raising and lowering H_2 and H_1 from three to five times.

Both cocks are then partially closed so that the speed is reduced to about 2.0 minutes per pass each way. After five complete passes, the mercury in buret D_1 is raised to cock B_1 , which is then closed. H_2 and D_2 are approximately balanced, and C_1 is carefully opened under a little pressure to the manifold and B_1 . The mercury level is set to the point in F_1 , the level is read in D_2 , and the contraction noted.

Successively, two additional complete passes over the catalyst are made and the contraction is again noted until the volumes remain constant.

In the case of olefins or hydrogen, the loss in volume is a direct measure of the amount present. In the case of acetylene or diolefins, the shrinkage is twice the amount present.

After each analysis, tube J should be flushed with hydrogen and the manifold isolated to protect the catalyst against poisoning by air.

For the determination of hydrogen in fixed gas cuts or "total unsaturation" in gases containing relatively large amounts of carbon monoxide, it is necessary to heat the catalyst to 180° C. and pass the hydrogenation mixture over it at that temperature. Operation in such cases is exactly as at room temperature except for heating the catalyst and allowing time for cooling before the contraction is noted. At the end of such determinations, it is necessary to purge the catalyst with hydrogen and heat it to 310° C. before using again at room temperature. Such regenerations take about 10 minutes and do not impair the activity of the catalyst. If used only at 180° C., activation between runs is not necessary. The presence of hydrogen or olefins in the original gas does not affect the determination but does reduce the amount of auxiliary gas necessary to be added.

Oxygen, if present, must be removed or determined since it is also hydrogenated and hence must be considered in the subsequent calculations.

Comparison of Methods

During preliminary work on the problem, a complete test was made of the usual reagents for the determination of both total and individual olefins. Sulfuric acid in varying strengths

and containing various recommended catalysts (4, 5, 10) bromine and bromine water, silver nitrate, dichromates, permanganate, chromic acid, cuprous sulfate, β -naphthol, and several other reagents were tested but the results were not satisfactory. Absorption was either incomplete or the reagent also attacked the paraffins. In some cases, corrections, when applied, yielded good results for individual olefins but poor results for mixtures. The conclusion of the tests was that none of the present liquid reagents was satisfactory for reliable quantitative work but that saturated bromine water in 2 to 1 dilution, and 30 per cent fuming sulfuric acid were probably the two best, particularly for the determination of total unsaturation. Accordingly, at the end of the development of the hydrogenation method, a comparative test was made between it and the two best reagents.

Experimental

PARAFFINS. The paraffins, ethane, propane, and butanes were commercial gases which had been thoroughly purified by successive chemical scrubbing through 30 per cent fuming, 98 per cent, and 79 per cent sulfuric acid and 54 per cent potassium hydroxide, then passed through soda lime and dried by anhydrous. They were fractionated and refractionated through a special precision low-temperature distillation column (?) discarding both end fractions until the whole of the material had a constant boiling point and the end fractions on distillation showed the same vapor pressure when tested in a Shepherd differential manometer.

ETHYLENE. Ohio Chemical "anesthetic" ethylene was scrubbed through 90 per cent sulfuric acid, then fractionated and treated the same as the paraffins.

PROPYLENE. After several fractionations failed to separate a small amount of propane impurity from commercial propylene, the redistilled mixture was brominated at -50° C. and the propylene regenerated from the dibromide by zinc dust in ethyl alcohol after fractionation of the dibromides. It was then fractionated the same as ethylene.

BUTYLENE. α -Butylene was prepared by the method of Lucas and Dillon (6), then refractionated to constant boiling point and vapor pressure.

ACETYLENE. Commercial acetylene was scrubbed through water, cuprous chloride solution, dilute acid and caustic, dried, and refractionated several times at 1.5 atmospheres' pressure.

Synthetic Mixtures

For the comparative test, nine synthetic mixtures of accurately known composition were made in a calibrated and carefully evacuated all-glass system by blending by condensation, ethylene with ethane, propylene with propane, α -butylene with isobutane, and acetylene with ethane. These samples were representative of the corresponding cuts made in low-temperature fractional distillation. Each mixture was then analyzed successively by each of the three methods.

TABLE II. COMPARATIVE TESTS

Sample No.	True Per Cent	Proposed Hydrogenation Method	Sulfuric Acid Method	Bromine Method
		%	%	%
1E	5.4	5.2	9.0	7.3
1P	6.5	6.5	7.8	7.3
2E	6.6	6.4	9.3	7.1
1B	46.9	47.1	54.5	47.5
2P	48.6	48.9	48.6	48.8
2B	49.8	49.9	47.9	50.9
3E	69.3	69.6	68.0	66.8
3P	73.2	73.2	73.8	74.0
1A	40.8	40.6	41.0	40.0

Both the sulfuric acid and bromine runs were made in six pass cycles followed by three passes into caustic for both, and one pass into alkaline pyrogallol for the bromine runs. A U. S. Steel Corporation (1) apparatus with Francis auto-bubblers was used for all reagents.

Results on the reagent methods were calculated, except for 1B and 2B by the sulfuric acid method (Table II), by subtracting the product of the number of cycles times the

constant contraction from the total absorption, multiplying by 100, and dividing by the sample volume. Both the butylene mixtures (1B and 2B) showed no constant contraction in acid but continued to react until the samples could no longer be measured. Corrections for these samples were calculated by the method of Sullivan (9). The corrected results are shown in Table II. Catalytic hydrogenations were made as described, no corrections being necessary.

It is apparent that the hydrogenation method gives consistently the best results even when corrections are applied for the secondary reaction and solubility effects of the liquid reagents. The magnitude of the corrections and the number of passes to constant contraction are shown in Table III. The acid values for 1B and 2B are based on 12 passes only, and not on constant contractions.

TABLE III. CORRECTIONS BASED ON CONSTANT CONTRACTIONS

Sample No.	Acid		Bromine	
	Passes	Correction Ml.	Passes	Correction Ml.
1E	30	- 8.0	36	-2.4
1P	36	-15.0	24	-3.4
1B	12	-15.5	36	-0.9
2E	36	- 4.8	36	-1.2
2P	24	- 6.4	30	-2.5
2B	12	-13.7	30	-2.0
3E	24	- 3.2	36	-2.4
3P	36	- 4.8	30	-1.0
1A	18	- 2.1	48	-4.0

Even a casual comparison of Table III shows that the corrections for low olefin concentrations may exceed the amount of unsaturate present and that without applying some such correction both reagents are worthless for exact work.

In the light of work by some other investigators, the use of such strong acid was admittedly a doubtful procedure, but the results with it were no worse than those which would have been obtained for ethylene if some other weaker acid had been substituted. The choice of 30 per cent fuming acid was made after careful tests on mixed olefinic gases where it gave better results, after corrections were applied as outlined, than any of the weaker acids and in less time. For the individual cuts, weaker acids reacted less with the paraffins but the results were little, if any, more satisfactory. The "selective" absorption of individual olefins from a mixture by increasing acid concentrations was totally unsatisfactory, as has been found by other investigators (2).

TABLE IV. DETERMINATION IN SYNTHETIC MIXTURES

	Mixture I		Mixture II	
	Synthesized	Found	Synthesized	Found
Carbon dioxide, %	3.2	..	5.0	..
Oxygen, %	0.4	..	None	..
Carbon monoxide, %	6.3	..	26.0	..
Hydrogen, %	41.7	41.8	12.4	12.4
Ethane, %	48.4	..	56.6	..
Hydrogen sulfide, grains per 100 cu. ft.	13.0	..	10.0	..

In spite of the increase in accuracy by the hydrogenation method, it requires only about the same time as the reagent methods. Five 4-minute cycles over the catalyst are almost always sufficient for completely hydrogenating 50.0 ml. of olefins, which is the largest sample usually taken, and only three volume readings are necessary in the whole analysis.

The absorption methods, though requiring less time per pass, take more time because of the larger number of passes necessary to constant contraction and the large number of volume readings. For control work, rapid determinations can be made in 12 minutes on as little as 10 cc. of gas with an accuracy comparable with usual reagent methods.

The method is equally applicable to the determination of hydrogen in refinery and manufactured gas. In such cases the catalyst should be used at 180° to 195° C., at which temperature it is active in the presence of any amounts of carbon monoxide, and any pure olefin is added instead of hydrogen. This is shown in Table IV for two synthetic mixtures of gas similar to manufactured gases encountered in practice.

Application

The method is now being used in this and other laboratories for the determination of total unsaturation and of hydrogen, and in conjunction with low-temperature fractionation to give a complete analysis of refinery and cracked gases. In spite of rough usage and exposure to gases containing sulfur compounds up to approximately 60 grains per 100 cubic feet, calculated as hydrogen sulfide, no catalyst failures have occurred in over 3 years. Typical check results on two routine plant gases separated by fractional distillation and then hydrogenated are shown in Table V.

TABLE V. CHECK RESULTS ON PLANT GASES

	Reformed Gas		Absorption Gas	
	%	%	%	%
Oxygen	0.1	0.1	None	None
Carbon dioxide	None	None	None	None
Carbon monoxide	None	None	None	None
Hydrogen	11.5	11.3	6.3	6.3
Methane	20.5	20.7	45.5	45.5
Ethylene	16.9	16.8	3.1	3.0
Ethane	8.6	8.8	24.5	24.6
Acetylene	1.2	1.1	None	None
Propylene	20.9	20.9	5.0	5.0
Propane	16.8	16.8	12.6	12.6
Isobutane	0.2	0.2	0.6	0.5
Iso + 1-butene	1.8	1.7	0.4	0.6
N-Butane	0.5	0.5	0.8	0.7
2-Butenes	1.0	1.1	0.3	0.3
Butadiene	None	None	Trace	Trace
Pentanes and heavier	None	None	0.9	0.9
Total unsaturation (on original sample)	42.8	42.8	9.1	9.0

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Fluidity and Hygroscopic Properties of Shellac

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WHENEVER shellac is to be used as a thermoplastic material, its degree of fluidity when heated is an important consideration, and may also furnish information about the age or past history of the resin. When shellac is heated, it gradually loses water with a corresponding loss of its plastic properties. This same change takes place, though much more slowly, at ordinary temperatures. It has been shown that the thermoplasticity can be restored by heating polymerized shellac with water under pressure (5); however, in this case certainly some secondary reactions take place as well as a hydration, since the iodine number is increased.

To measure the fluidity under heat, three methods have been used, two of which are today in regular commercial use. In the so-called Victor test (3) the sample is not subjected to any previous conditioning, but is tested in its normal state, being merely ground to 20-mesh. For the Westinghouse or Metropolitan-Vickers test (4), the sample is placed in a desiccator over calcium chloride for 48 hours before testing. Recently Committee D-9 of the American Society for Testing Materials has been working on a modification of the V-tube method (1), which recommends that the sample be conditioned by heating for 16 hours in a well-ventilated oven at $41^{\circ} \pm 2^{\circ}$ C. The results obtained by different laboratories with the three methods have not checked each other particularly well.

Some time ago it was of interest to the authors to measure the hygroscopic property of shellac and note the effect on flow. Experiments were carried out on several shellacs, and the following series, obtained in using an ordinary superfine grade, is typical:

After grinding to 30-mesh, about 5-gram samples were spread out in thin layers in desiccators of constant humidity, held at room temperature (about 27° C., 80° F.). The humidity regulators were concentrated sulfuric acid (0.0 per cent humidity), 45.8° B \acute{e} . sulfuric acid (25.0 per cent humidity), 36.5° B \acute{e} . sulfuric acid (50.0 per cent humidity), saturated ammonium chloride solution (79.3 per cent humidity), and water (100 per cent humidity).

The samples were weighed daily until they came to constant weight, which occurred in about 5 days. Weighings were continued for several days more in order to get check readings, after which the samples were transferred to an ordinary concentrated sulfuric acid desiccator and dried to constant weight. Finally the weights of the containers were taken.

It took considerable time for a sample to come to equilibrium in the moist atmosphere. However, particularly in the case of the two high humidities, changes took place with sufficient rapidity, whenever the sample was removed to balance, to make accurate weighing difficult. The results

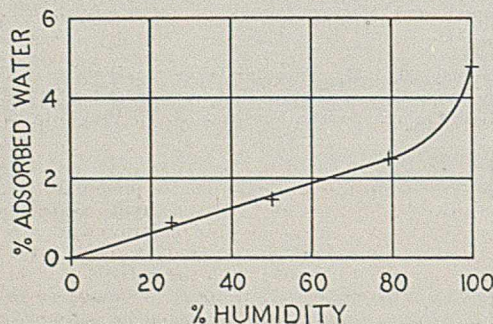


FIGURE 1

obtained have been plotted in Figure 1. It is of interest that when the sample which had been dried over concentrated sulfuric acid was removed to an ordinary drying oven for 24 hours and held at 41° C., it picked up 0.37 per cent moisture.

The equilibrium moisture in the experiments described above is believed to represent merely adsorbed water attracted by the free hydroxyl groups of the shellac. Gardner (2) has shown that shellac varnish films are permeable to water vapor, and also absorbent to moisture. These films were formed by the evaporation of a solvent, and might conceivably be in a different physical condition from lac in its native state—that is, the secretion of the lac insect—or in the manufactured condition, as shellac. In this latter case, also, the progressive adsorption of moisture with increasing humidity found in the authors' experiments is in accordance with the assumption of a relatively porous structure.

Samples duplicating those described above were prepared and tested for Victor flow, after coming to equilibrium at the humidities mentioned. In this test the measure of fluidity is the distance in millimeters which the molten shellac flows down an incline of 15° to the horizontal in exactly 12 minutes at a temperature of 100° C. The flow of the original sample was 48 mm. The results obtained are given in Table I, which shows the very great effect of a small amount of adsorbed water on the fluidity, as measured by the Victor method. Attempts to bring back the fluidity of a "dead" lac—that is, one which possessed zero flow under ordinary conditions—by exposing it to the action of a high humid atmosphere were unsuccessful.

TABLE I. VICTOR FLOW TEST

Humidity %	Absorbed Moisture %	Flow Mm.
0.0	0.00	19
25.0	0.89	28.5
50.0	1.46	46
79.3	2.48	65
100.0	4.79	103

Summary

These experiments show the marked hygroscopic nature of shellac and the need for specifying exactly the conditions of preparation of the sample in any method for determining the fluidity. It is recommended that the sample be conditioned previous to testing by exposure to 50 per cent relative humidity at room temperature, for three reasons: (1) In manufacturing operations shellac is used under ordinary atmospheric conditions which would average near this figure; (2) at this humidity equilibrium appears to be much more quickly established than at the higher or lower points; and (3) in weighing the sample less trouble is experienced than in the case of shellac conditioned at either high or low humidity. If the sample is prepared as described, at least 2 days should be allowed for the moisture content to come to equilibrium before testing for flow.

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Determination of Selenium in 18-8 Stainless Steels

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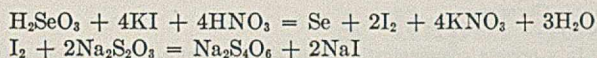
THE method used by the Carpenter Steel Company for the determination of selenium in 18-8 type steels has been the only available method. It depends upon solution of the steel in aqua regia, addition of perchloric acid, and evaporation to fumes to dehydrate silica. Solution of the perchlorates and chromic acid in water is followed by filtration to remove silica. Hydrochloric acid is added to bring the concentration to about 30 per cent, followed by addition of concentrated hydrochloric acid saturated with sulfur dioxide gas. After being allowed to settle for 3 hours at an elevated temperature, the precipitated selenium is filtered upon a tared Gooch crucible, washed, dried, and weighed. The crucible is then heated to redness, the selenium volatilized, the crucible reweighed, and the loss in weight represents the selenium present.

The manufacturer's analysis of the sample of steel used throughout this work was as follows:

C	Mn	P	S	Si	Cr	Ni	Se
0.11	0.83	0.137	0.009	0.50	18.29	8.99	0.218

The percentage of selenium was independently checked by an analysis carried out according to the directions furnished by the Carpenter Steel Company. The value is too high, in the light of further work, apparently because of certain positive errors which seem to be inherent in this method. Communication with industrial laboratories also showed that considerable difficulty was being experienced in getting satisfactory results in selenium determination.

The method developed in this laboratory depends upon solution of the steel in perchloric acid, catching the small amount of selenium which is evolved as hydrogen selenide, filtration of the solution to obtain the precipitate of selenium plus silica, and solution of the selenium in nitric acid, followed by the volumetric determination of selenium iodometrically, according to the equations:



The apparatus used consists of a 250-cc. Erlenmeyer flask with a one-hole rubber stopper carrying a 7.5-cm. (3-inch) drying tube, with the stem elongated and bent so that the tube is in a horizontal position.

The selenious acid used was prepared from pure sublimed SeO_2 and the concentration determined gravimetrically by precipitation of selenium with strong hydrochloric acid and sulfur dioxide. The thiosulfate used was approximately 0.01 *N*. The selenium titer of the thiosulfate solution was obtained by direct titration of this standard solution of selenious acid. Bureau of Standards sample No. 101, used for checking certain results, has the following analysis:

C	Mn	P	S	Si	Cu	Ni	Cr
0.061	0.554	0.011	0.013	0.763	0.056	8.44	17.56

Analytical reagent perchloric acid containing approximately 60 per cent of perchloric acid was used.

Procedure

Weigh a 5.00-gram sample of steel into a 250-cc. Erlenmeyer flask. Add a mixture of 50 cc. of 60 per cent perchloric acid and 30 cc. of water. (Somewhat less perchloric acid might be used to effect solution.) Insert the one-hole rubber stopper and drying tube. In the large end of the drying tube, place a pad of glass wool about 2.5 cm. (1 inch) long, lightly packed, and upon it pour 4 or 5 drops of concentrated nitric acid. Heat the

flask and contents to 80° to 85° C., remove from heat, and allow solution to proceed. At the end of about 2 minutes, remove the drying tube with the glass wool from the flask; solution of the steel will proceed without loss of any selenium as hydrogen selenide. Remove the glass wool, containing about 1 mg. of precipitated selenium, from the tube, place in a beaker, and wash out the tube with concentrated nitric acid into the beaker. To this nitric acid solution add the precipitate obtained by filtration of the main solution. Filter the main solution through a pad of asbestos with the aid of suction, and wash with warm water. Digest the pad of asbestos plus the dark-colored precipitate and the glass wool with about 40 cc. of concentrated nitric acid and evaporate the solution to a volume of about 10 to 15 cc. Make the solution slightly alkaline with ammonium hydroxide to precipitate small amounts of iron, filter, and wash the residue with hot water. The amount of iron is so small that the selenium carried down may be neglected. Make the clear filtrate just acid with nitric acid and add an excess of 10 cc. of concentrated nitric acid. Heat the solution to about 60°, add 3 grams of urea to eliminate small amounts of nitrous acid, and cool the solution to room temperature, to allow an iodometric titration. Bring the volume of the solution to 400 cc., add 3 grams of potassium iodide, allow to stand 1 or 2 minutes, and titrate the liberated iodine with thiosulfate, using starch as an indicator. The end point should last several minutes.

Experimental Data

Because it was impossible to obtain a standard sample of steel containing selenium, it became necessary to examine carefully the gas evolved, the precipitates formed, and the main solution, in order to determine the percentage of selenium present. When hydrogen selenide is passed over glass wool containing a few drops of nitric acid, it is oxidized to red selenium, which is readily visible. This test is sufficiently sensitive to detect the hydrogen selenide evolved when 0.1 gram of selenium steel (0.19 per cent of selenium) is mixed with 5.0 grams of Bureau of Standards steel No. 101; thus the method will detect 0.2 mg. of selenium.

Using this test, it is evident that hydrogen selenide is evolved when a selenium steel is treated with dilute perchloric acid, but this evolution lasts for only a few minutes while the steel starts to go into solution. Once the steel is reacting vigorously the hydrogen selenide ceases to be evolved. With concentrated perchloric acid (approximately 60 per cent) no hydrogen selenide is evolved. The reason for this experimental fact has not yet been established.

In order to test whether the glass wool moistened with nitric acid caught all the hydrogen selenide, the following method was used:

Two bubble tubes, each containing 25 cc. of concentrated nitric acid, were connected to an Erlenmeyer flask containing the selenium steel and dilute perchloric acid. The evolved gas was bubbled successively through the tubes until the steel was completely dissolved. An examination of the two nitric acid solutions showed that the first tube caught all the selenium; none was found in the second tube. Therefore, the tube of glass wool plus nitric acid was inserted in the neck of the flask and connected to a bubble tube of nitric acid. After solution of a 5.0-gram sample of selenium steel with this arrangement, no selenium was found in the nitric acid of the bubble tube, proving that the glass wool plus nitric acid caught the hydrogen selenide which was evolved.

The tube containing the glass wool, nitric acid, and red selenium was added to the remaining selenium in the precipitate. Approximately 1 mg. of selenium was evolved as hydrogen selenide when the recommended concentrations of perchloric acid are used.

The solution, containing a dark red to black precipitate of selenium together with about four-fifths of the silica, was filtered on a pad of asbestos, supported by about 1.3 cm. (0.5 inch) of wool felt and a perforated porcelain plate, using the tall-form straight-sided Gooch funnel. After filtering and washing three or four times with warm water, a glass rod was pushed up through the

stem of the funnel against the porcelain plate and the entire pad forced to the top so that the asbestos layer plus the precipitate could be removed easily. The asbestos pad thoroughly cleaned the sides of the funnel, as it moved up. The asbestos pad was added to the glass wool and the entire mass treated with concentrated nitric acid, as described above.

After filtering out the precipitate, it was necessary to examine the filtrate for selenium. To this filtrate, a volume of about 100 cc., were added 125 cc. of concentrated hydrochloric acid which had been saturated with sulfur dioxide. The solution was allowed to stand for 2 hours; upon filtering no selenium was found. Therefore, to this solution was added a definite quantity of selenious acid, equivalent to 1.14 mg. of selenium. After standing 2 hours, the solution was filtered and the amount of selenium obtained checked with the amount added, showing that the solution was initially in the proper condition for the precipitation of selenium.

Samples of Bureau Standards steel No. 101 were dissolved in 50 cc. of perchloric acid plus 30 cc. of water and a definite amount of selenium (1.14 mg.) was added in the form of selenious acid. Upon precipitation with hydrochloric acid and sulfur dioxide the correct amount of selenium was found present, showing the accuracy of the iodometric method.

Using the method as outlined on the manufacturer's sample (reported as 0.218 per cent of selenium) the following representative values were obtained: 0.190, 0.191, 0.191, 0.188, 0.193, 0.192, 0.193, 0.188, 0.189, and 0.190 per cent of selenium. These percentages all reduce to 0.19 per cent when two significant figures are reported, as is customary in steel analyses.

The manufacturer's sample was diluted with an equal quantity of Bureau of Standards sample No. 101. An analysis of this diluted sample by the recommended procedure gave values of 0.094 and 0.094 per cent of selenium.

Since experiments showed that no hydrogen selenide was evolved by 60 per cent perchloric acid, a sample of selenium steel was dissolved in this strength of acid, by heating to about 85° C. After complete solution of the steel, 125 cc. of concentrated hydrochloric acid saturated with sulfur dioxide were added. After standing for 2 hours the precipitate was filtered, washed, dissolved in nitric acid, and carried through the volumetric procedure as described, to give 0.190 and 0.191 per cent of selenium. These results indicate an alternate procedure for the determination of selenium and furnish a check upon the procedure given.

The method of the Carpenter Steel Company was employed on samples of selenium steel and carried to the point where the precipitated selenium was filtered upon a Gooch crucible. At this point, the precipitate was carried through the volu-

metric procedure and 0.190, 0.193, and 0.194 per cent of selenium were obtained, furnishing additional corroboration of the procedure given.

As for interfering constituents, Bureau of Standards steel No. 101 was carried through the recommended procedure and gave a blank result. It might be expected that a small amount of copper could remain in the insoluble residue and then react with hydriodic acid to yield iodine, but the fact that negative results were obtained in the blank experiment was considered sufficient proof that selenium alone was measured by this volumetric method.

For routine work, the procedure could be materially shortened by eliminating the use of the glass wool and applying a correction factor of about 0.5 mg. for the selenium which is evolved as hydrogen selenide. Also the precipitation and elimination of small amounts of iron by ammonium hydroxide could possibly be eliminated in routine steel analyses.

Conclusion

The procedure given is fairly rapid. A series of 5 samples was analyzed simultaneously in 1.5 hours. The accuracy has been checked by two procedures, and seems adequate. The values are lower than those obtained by the original method of the Carpenter Steel Company, but an examination of the gravimetric method, for such small amounts of precipitate, led to the conclusion that it yields slightly high results.¹

Acknowledgment

The need for a method for the determination of selenium in 18-8 type steels was first suggested by G. E. F. Lundell of the Bureau of Standards to L. F. Hamilton of the Analytical Division of the Department of Chemistry of this institute, at the latter's request. The authors undertook the investigation after communicating with Berton H. DeLong, metallurgist for the Carpenter Steel Company, Reading, Pa., manufacturers of the type of steel to be investigated. Mr. DeLong very kindly furnished the material for analysis and generously offered to cooperate in every way possible.

RECEIVED October 22, 1935. Publication 51, Research Laboratory of Inorganic Chemistry.

¹ In a private communication from the Carpenter Steel Company, it is stated that "our figure of 0.218 per cent of selenium is from a routine heat analysis obtained in our control laboratory;" hence deviations in results of the magnitude observed are only to be expected.

An Efficient Laboratory Extraction Apparatus

FREDERICK C. OPPEN, University of Wisconsin, Madison, Wis.

A SERIES of studies in this laboratory upon the constituents of various seeds has frequently met the problem of efficient extraction of large quantities of material. Metal apparatus was ruled out in order to avoid the possibility of contamination; various glass makeshifts proved leaky and inefficient. With low-boiling solvents such as acetone, petroleum ether, ethyl ether, etc., these difficulties became acute. Accordingly, a modified Soxhlet-type extractor (illustrated) was developed which can be duplicated at moderate expense from parts readily available. This model has been in use for the past year, and has given very satisfactory results. It is described here in the hope that it may prove helpful to others having similar problems.

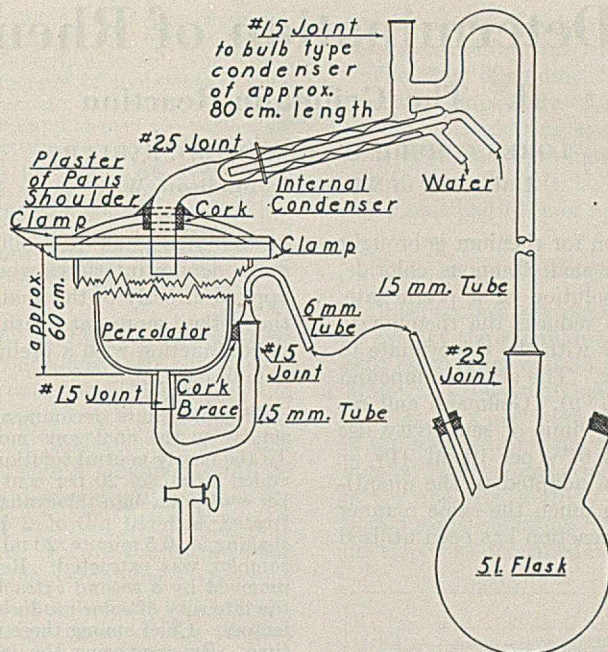
The extractor is made from a 7-liter Oldberg, or cylindrical, percolator and has a capacity of about 3 kg. of seeds. A percolator with a ground upper surface is selected, together with a small desiccator lid of the same diameter, and these are re-ground to a good fit. Next a large hole for the cork is cut in the lid, preferably with a cylindrical copper tool in a slow-speed drill press, using a rough grade of grinding compound. The main novel feature is an internal condenser which cools and liquefies nearly all vapors before they pass into the percolator, thus reducing loss at the ground interface between the percolator and its cover. In operation, this interface is rendered more nearly solvent-tight by clamping it at two diametral points with large laboratory clamps as indicated. A second advantage gained from the use of an internal condenser is that uniform conditions of cold solvent extraction are maintained, often of value where sensitive crude materials are involved. The bulk of vapors is

condensed as in the usual Soxhlet extractor by the large Allihn-type reflux condenser (not shown).

The numerous potential leaks in such a set-up are avoided by substituting ground-glass joints for corks wherever possible. The joint connecting the siphon tube to the bottom of the percolator is ground in carefully by hand, first using discarded glass stoppers of suitable size and taper until a minimum of grinding is necessary to adapt the standard taper joint. The three corks do not cause trouble if they are of fine grain and coated with collodion.

A narrow cloth bag containing the material to be extracted occupies about four-fifths of the volume of the percolator but must not be allowed to pack the interior completely, if siphoning is to be effective. A channel is provided by inverting an 80-mm. evaporating dish over the bottom opening and placing several 10- to 15-mm. tubes along the full length of the side of the bag. These may be bent to conform to the curve of the percolator. The siphon tube extends only a small distance above the top of the bag, and must not be larger than 6 mm. in diameter if it is to fill properly. Sometimes the column fails to break completely after siphoning has stopped, causing the liquid to trickle over slowly. This prevents thorough extraction of the upper portion of material, and is caused by surface tension at the exit end of the siphon tube. It may be remedied by grinding off this end at a 45° angle.

The apparatus may be adapted to smaller charges than the maximum by inverting beakers or bottles within the percolator to occupy the excess space. It is most conveniently



wherever there is liquid or hot vapor is important in this design, whose details may be varied to suit individual convenience.

Acknowledgment

The writer wishes to thank R. A. Willihnganz for his cooperation in designing and constructing this extractor.

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RECEIVED November 25, 1935.

A Rapid and Efficient Mixer

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IT IS frequently a time-consuming and tedious process to prepare for analysis samples of emulsions and plastics. The horizontal spiral-bit type of mixer has been successfully used in this laboratory and offers some distinct advantages over other methods of preparing such samples.

It is very easily assembled by attaching a spiral bit to the horizontal shaft of an electric motor, which should have a speed of 1725 r. p. m. and be rated at not less than 0.1 horsepower. A drill chuck obtained from any hardware store for approximately \$2 is mounted directly on the shaft. The diameter of the motor shaft must be specified in ordering the chuck. The spiral bit may be obtained from any hardware store for approximately 75 cents by specifying a 0.75-inch, solid-center, spiral bit. Before using this bit it is necessary to remove the tip, or worm, and the two cutters. The bit is then placed in the chuck. When the motor runs, the bit is turned in the opposite direction from that used when bor-

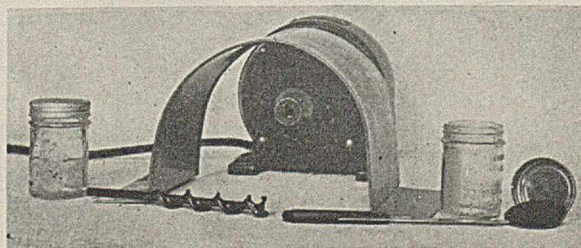
ing. This motion throws the sample into the bottom of the sample jar which is slipped over the bit. The jar is held in the hand and moved around to facilitate mixing. When the sample jar is withdrawn some particles of the sample may fly off, and are conveniently caught by a piece of tin shaped in a half-circle and placed on the bench over the bit.

The author's experience in using this mixer for preparing butter samples indicates the following precautions which must be observed:

Use a thick-walled glass sample jar with a screw cap, straight sides, flat bottom, and a capacity of approximately twice the volume of the sample.

Mix the sample for at least 3 full minutes. Since the butter can be mixed at temperatures from 12° to 25° C., the usual time required for properly tempering the sample can be eliminated.

Avoid partial separation of the sample due to melting around the edges of the sample jar.



RECEIVED December 10, 1935

The Determination of Rhenium

II. The Geilmann Reaction

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THE Geilmann (2) color reaction for rhenium is brought about by adding hydrochloric acid, stannous chloride, and potassium thiocyanate to a solution of a perrhenate. The stannous chloride presumably reduces the rhenium to the hexavalent state where it reacts with the thiocyanate to yield an intensely colored complex. The actual compound formed is said to be $\text{ReO}(\text{CNS})_4$ (1, 9). Geilmann and co-workers have found that the lower limit of sensitivity lies somewhere in the neighborhood of 0.5γ per 10 ml. ($1\gamma = 0.001$ mg.). The reaction has been adapted to the quantitative determination of rhenium in much the same manner as the corresponding molybdenum reaction has been utilized

in the Maag and McCollum (7) determination. Although molybdenum interferes when the Geilmann determination is applied directly to the analysis of minerals and concentrates, the method represents, with slight modification and when used in conjunction with a preliminary separation, the best available to date.

The procedure recommended by the original authors and similar to the analogous molybdenum method was as follows: To the nearly neutral solution of rhenium as the perrhenate were added 10 ml. of 20 per cent hydrochloric acid and 2 ml. of 10 per cent potassium thiocyanate. This was diluted to 50 ml. and treated with 10 ml. of 2 per cent stannous chloride. After shaking for 0.5 minute, 20 ml. of ether were added and the yellow complex was extracted. Residual traces of the complex were removed by a second extraction. It was early recognized that the intensity of color produced was dependent upon a number of factors. Chief among these were concentrations of reagents and time. By comparing the intensities of colors produced under varying conditions with the color of an aged ether extract of the complex, they were able to establish optimum concentrations and to arrive at what seemed to be the proper time interval between the addition of stannous chloride and extraction with ether. The reaction was apparently stopped by the addition of the extractor.

During the course of a series of analyses made in this laboratory (4) it became evident that the development of the color depended not only upon the concentration of the reagents but upon the amount of rhenium present. Likewise it was suspected that the reaction was not stopped by the addition of the extractor but continued in the nonaqueous solution at a greatly reduced rate.

The research herein reported was conducted in an effort to ascertain the magnitude and character of the color changes taking place during the course of the reaction and to establish if possible concentrations and time factors more favorable to analytical applications. The Eastman universal colorimeter, an instrument which has been previously described (5, 6) and used (3) in a research of this type, was used to follow color changes.

Experimental

Solutions used were similar to those of Geilmann, Wrigge, and Weibke (2). Potassium perrhenate solutions containing 10γ

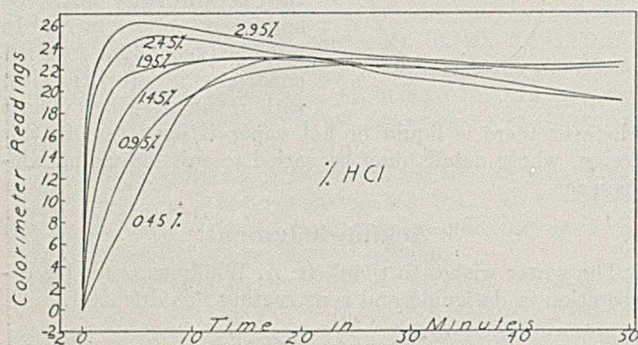


FIGURE 1

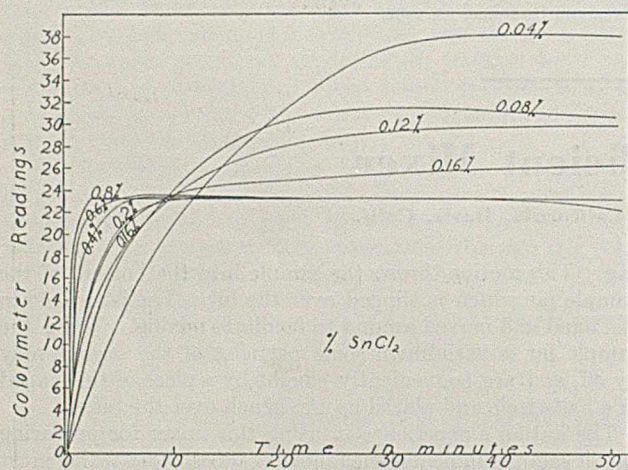


FIGURE 2

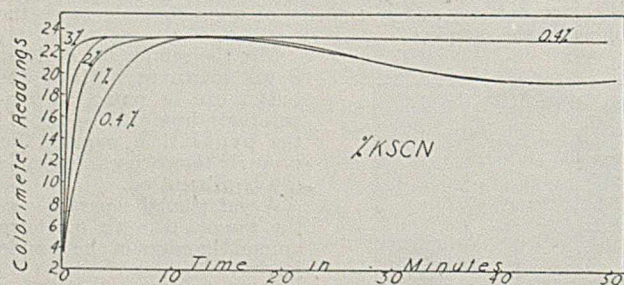


FIGURE 3

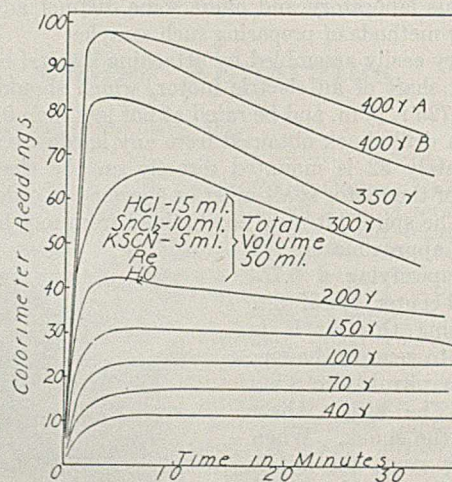


FIGURE 4

per ml. served as a source of rhenium. The procedure followed throughout was to run into the sample tube of the colorimeter a known amount of standard perrhenate solution. In a beaker were placed the desired amounts of hydrochloric acid, stannous chloride, potassium thiocyanate, and enough water so that the total volume of this solution and that of the perrhenate would equal 50 ml. The reagent mixture was then quickly mixed with the perrhenate solution and placed in the colorimeter. The time of mixing was taken as the zero time in all cases. The color changes were followed by the -blue wedge. When working with deeply colored solutions it was sometimes found necessary to make slight corrections with other wedges. All concentrations reported are on the weight basis.

Figure 1 illustrates the effect of varying the hydrochloric acid concentration in solutions containing 0.40 per cent of stannous chloride, 1.0 per cent of potassium thiocyanate, and 100 γ of rhenium. The percentage of acid includes that contained in the stannous chloride solution. In low acid concentrations the color did not reach a maximum until 20 minutes had elapsed. In the neighborhood of 2 per cent the color maximum was reached in 5 minutes, but fading took place over a period of 30 minutes. Figure 2 illustrates the effect of stannous chloride in a system containing 2.0 per cent of hydrochloric acid, 1.0 per cent of potassium thiocyanate, and 100 γ of rhenium. Low concentrations of the reagent developed the color slowly, but it is to be noted that at the end of 35 minutes the color with 0.04 per cent of stannous chloride was almost twice as intense as in a 0.8 per cent solution. In the latter concentration, however, the color maximum was quickly reached and remained practically constant over an appreciable period.

Figure 3 illustrates the variation produced by changing the potassium thiocyanate concentration in solutions containing 2.0 per cent of hydrochloric acid, 0.4 per cent of stannous chloride, and 100 γ of rhenium. Concentrations above 0.4 per cent produced a maximum color at the end of 5 minutes, whereas amounts in excess of 1 per cent promoted fading after 15 or 20 minutes. In Figure 4 are represented color concentrations produced by varying amounts of rhenium reduced in solutions containing 2.0 per cent of hydrochloric acid, 0.40 per cent of stannous chloride, and 1 per cent of potassium thiocyanate. Significant is the fading encountered in concentrations of rhenium much above 200 γ . Under the conditions of the experiment it would appear that 7 minutes is the optimum time interval before extraction. In the 400 γ region there is illustrated a phenomenon which has often been encountered in these laboratories and which may introduce serious error into a determination. Curves A and B represent the behavior of solutions containing exactly the same concentrations of reagents, the difference being that the solution represented by B was shaken vigorously for 1 minute before being placed in the colorimeter. Violent and prolonged agitation does not appear to shift the maximum but does promote more rapid fading of the color. In Figure 5 are plotted colorimeter scale readings against rhenium concentrations. Colors were developed in solutions containing 2.0 per cent of hydrochloric acid, 0.4 per cent of stannous chloride,

and 1 per cent of potassium thiocyanate. The time interval before extraction was 7 minutes.

The effect of stannic chloride was studied because in actual practice samples are often encountered which contain small amounts of oxidizing agents. These would oxidize the stannous chloride to produce significant concentrations of tetra-valent tin. Stannic chloride in concentrations as high as 2 per cent had little or no effect.

Nonaqueous Extractors

Butyl acetate, cyclohexanol, and ethyl ether have been used to extract the rhenium thiocyanate. The mixture of 65 per cent ethyl ether and 35 per cent petroleum ether as used by Malowan (8) for molybdenum extracts rhenium incompletely.

Because it had been suspected that nonaqueous solutions of the complex were not stable over a period of hours and that standards for comparison had best be prepared at the time of the analysis, a study was made of the behavior of these nonaqueous solutions. The color of 150 γ of rhenium was developed as described in the preceding paragraph, 7 minutes

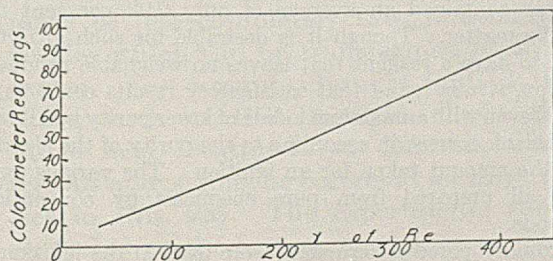


FIGURE 5

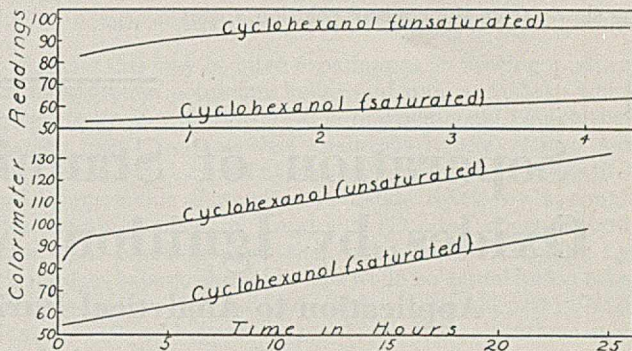


FIGURE 8

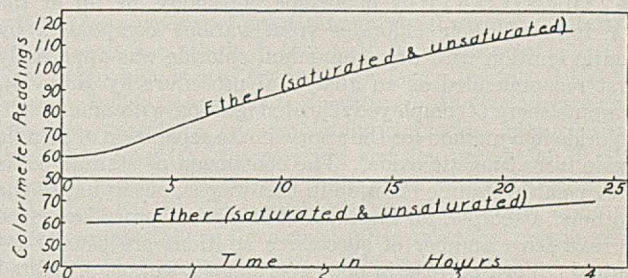


FIGURE 7

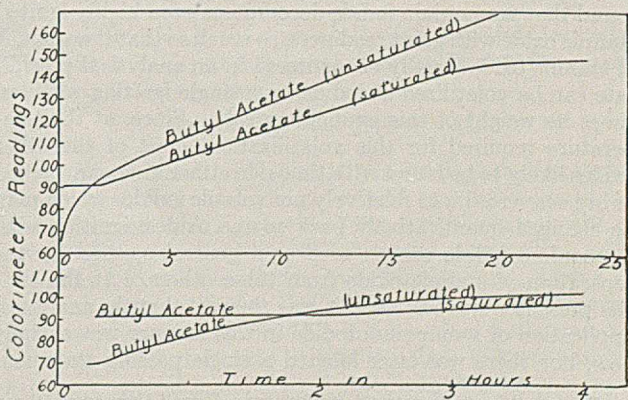


FIGURE 6

were allowed, and the extractor was added in three successive portions of 20, 15, and 15 ml. Extracts were then combined and placed in the colorimeter. The entire operation usually required about 12 minutes. Saturated extractors were prepared by shaking the extraction liquid in a separatory funnel just previous to use, with a hydrochloric acid, stannous chloride, and potassium thiocyanate solution of the same type as used in the actual analysis. Figure 6 illustrates the change in color of solution of 150 γ of rhenium (as the thiocyanate extract) in butyl acetate which had been shaken with the reagents and in untreated butyl acetate. It is apparent that the saturated extractor is preferable but that in neither case may it be assumed that such solutions constitute satisfactory semi-permanent standards.

Figure 7 is interesting in that it apparently makes little or no difference whether ether be saturated or unsaturated with respect to the reagents. However, erratic results are more often obtained in actual practice if the ether is not treated prior to extraction. This is in harmony with the findings of Geilmann and co-workers (2). Figure 8 is characteristic of cyclohexanol. The use of cyclohexanol eliminates to a large extent the peculiar results often obtained when ether is used as an extractor but has the decided disadvantage of separating slowly from the aqueous solution.

As a result of the study of the development of color in the Geilmann reaction it is recommended that when applied quantitatively to amounts of rhenium under 500 γ , the concentration of hydrochloric acid be held at 2.0 per cent, potassium thiocyanate at 0.4 per cent, and stannous chloride at 0.2 per cent. Seven minutes should in general elapse before extraction, and the solution should be shaken no more than is necessary to produce uniformity. Behavior of non-aqueous extractors has been studied and data are presented which indicate that such solutions do not constitute satisfactory permanent standards.

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RECEIVED August 10, 1935. Based upon the senior thesis of Bernard J. Babler, University of Wisconsin, 1935.

Separation of Stannic Oxide from Various Oxides by Ignition with Ammonium Iodide

Application to Analytical Purification of Ignited Stannic Oxide

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VOLATILIZATION of arsenic, antimony, or tin in the form of their chlorides from various compounds by gentle ignition with dry ammonium chloride was apparently first recommended as an analytical procedure by Rose (5). Rammelsberg (4) employed repeated ignition with ammonium chloride in a method for the approximate separation of stannic oxide from tungstic oxide. The conversion of stannic oxide into volatile stannic chloride in this way is, according to the authors' attempts, an impractical analytical procedure since an excessive number of successive ignitions are usually required. For example, in one experiment a sample of ignited stannic oxide weighing 0.5635 gram left a residue of 0.0127 gram of oxide after five successive ignitions with excess quantities of ammonium chloride. On the other hand it was found that ammonium iodide decomposes even highly ignited stannic oxide with great readiness, so much so that the amount of stannic oxide usually encountered in an analytical precipitate can be volatilized as iodide by a single ignition with ten times its weight of this ammonium salt. Since, at the temperature required for this volatilization, most of the other oxides likely to be found with tin oxide either are not attacked or are converted into relatively nonvolatile iodides which may be changed quantitatively back to the oxides, ignition with ammonium iodide can be used as a general method for the separation of stannic oxide from these others. At the time the present work was done it was thought that the analytical application of ammonium iodide in this manner was entirely new, but there was later located a single passing statement

by Moser (3) to the effect that metastannic acid could be separated from silicic acid by ignition with ammonium iodide. This present paper contains the results of experiments on the action of dry ammonium iodide at various temperatures on stannic oxide, ferric oxide, cupric oxide, lead oxide, nickel oxide, zinc oxide, antimony trioxide, tungstic oxide, and silicon dioxide, special attention being paid to the conditions for quantitative separations. As an example of the practical value of this general method there is given a rapid, convenient procedure for the determination of the exact stannic oxide content of ignited impure tin oxide precipitates, such as those obtained from the nitric acid treatment of common non-ferrous alloys.

Materials and Apparatus

J. T. Baker's reagent ammonium iodide was found to be sufficiently pure, particularly in regard to a low content of nonvolatile matter, to be used without further purification. One lot was found to leave no residue on ignition, while another contained an average of only 0.02 per cent nonvolatile matter. Though it is desirable for such analytical work to have a reagent that leaves no weighable residue on ignition, it was found that satisfactory results could be obtained even with ammonium iodide of lower purity by allowing for a blank correction according to the purity of the chemical and the amount taken for an ignition. The various oxides were all prepared from pure chemicals by conventional methods.

Ordinary porcelain crucibles were used in the ignition experiments, and, while in a few cases a gas burner was used as

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the source of heat, the great majority of the trials were made in a small electric crucible furnace especially constructed for the purpose. By means of a suitable resistance this could be held constant within 5° throughout the working range, a nitrogen-filled thermometer with bulb placed next to the crucible being used to determine the temperature.

General Procedure

In the experiments on the oxides the dried weighed samples were first thoroughly mixed with ten or more times their weight of powdered dry ammonium iodide in weighed crucibles. Except where a gas burner was used, ignition was then performed at a controlled temperature by placing a charged crucible in the electric furnace previously brought to the desired degree of heat. After ignition was complete as shown by the cessation of fumes, usually requiring from 10 to 15 minutes, the crucible was removed. In some cases crucibles were then ignited in the open air in order to convert any residual iodide completely to oxide. In others, where slightly volatile iodides were present, the residues were first treated with small volumes of concentrated nitric acid, followed by evaporation to dryness on the hot plate in order to decompose the iodides completely before the final ignitions were made. Finally the crucibles were reweighed in order to determine the weights of residual oxide or oxides. Qualitative observations of the products of the reactions were also made.

Reaction with Stannic Oxide

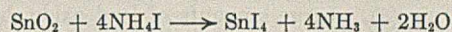
While there is evidence of action at slightly lower temperatures, the reaction between ammonium iodide and stannic oxide does not proceed with sufficient velocity and completeness for practical analytical purposes until about 400° C. is reached. At this point there is rapid evolution of brown vapors of stannic iodide from the mixture, accompanied by white fumes of subliming ammonium iodide and the purple vapors of gaseous iodide. If the reaction is carried out at a sufficiently high temperature, the characteristic orange-red thermoluminescence of iodine can also be seen. It seems probable that the transformation of the oxide into iodide in this way is caused by the action of the hydrogen iodide that

When mixed with a suitable excess of powdered ammonium iodide and heated at temperatures between 400° and 500° C., stannic oxide is quantitatively transformed into stannic iodide and can thus be completely volatilized. This behavior can be used as the basis of analytical procedures for the separation of stannic oxide from most other metallic oxides likely to be associated with it, since these either are not affected by such treatment or are converted more or less completely into nonvolatile iodides which can be transformed back to oxides. For example, impure ignited tin oxide, such as that resulting from the nitric acid treatment of common non-ferrous alloys, may be corrected for impurities in this way. The experiments show that this method of separation is simple, rapid, and accurate.

results from the thermal dissociation of the ammonium salt. If this is the case the essential reaction can be represented by the equation



It is to be observed in support of this explanation that the order of the ease with which ammonium iodide and ammonium chloride react with stannic oxide is the same as that of hydriodic acid and hydrochloric acid, the latter having practically no action. That the reaction with these ammonium salts proceeds more readily in both cases than with the corresponding aqueous acids is in agreement with other reactions in which halogen halides at high temperatures react even more readily than their aqueous solutions with given substances, especially when water is one of the products of the gaseous reactions. The iodine appearing as one of the products of the reaction between ammonium iodide and stannic oxide apparently results largely from the thermal decomposition of the hydrogen iodide, although it is possible that a small proportion may come from its oxidation on contact with air. A possible alternative mechanism for the reaction is that it involves a direct action between the two substances as shown by the stoichiometric equation

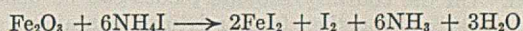


Against this may be cited experiments on heating mixtures of finely ground potassium iodide and stannic oxide in which no evidence of any transposition reaction could be detected, though from the somewhat analogous nature of the two iodides one might expect at least some reaction in the case of potassium iodide if ammonium iodide reacts by a double decomposition reaction. Audrieth (1) cites evidence, however, that tends to show that fused ammonium salts can themselves behave like acids, and while no actual fusion takes place in the case discussed here, it is possible, in part at least, that the reaction between ammonium iodide and stannic oxide results from such a direct interaction.

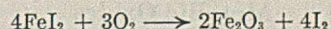
Reactions of Various Metallic Oxides

Since for purposes of practical analytical separation stannic oxide reacts too slowly below 400° C., little attention was paid to the behavior of the other oxides on ignition with ammonium iodide below this temperature. At 400° C. or above these are partially or completely converted into iodides, depending upon the temperature and the proportion of ammonium iodide. In general these other reactions appear to take place by the same mechanism as the stannic oxide reaction, except that in the case of ferric oxide and cupric oxide there are, in addition, oxidation-reduction changes.

The reaction with ferric oxide can be represented by the equation



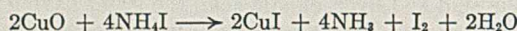
By gentle ignition in the open air the ferrous iodide formed in this manner can be oxidized quantitatively back to ferric oxide according to the equation



From the analytical viewpoint it was found that, if the treatment with ammonium iodide is carried out over a gas burner without much care as regards temperature control, the recovery of the ferric oxide is by no means quantitative, owing apparently to volatilization of some ferrous iodide during the ignition. By performing the ignition in an electric furnace at temperatures under 500° C. this loss does not occur, and recovery of all the oxide originally taken is then possible. From a practical manipulative standpoint the conversion of ferrous iodide to the oxide by simple air oxidation is not en-

tirely satisfactory, since there is danger of mechanical loss due to the formation of a certain proportion of very light, fluffy ferric oxide. For this reason it is better to treat the iodide with 2 to 3 ml. of nitric acid first, evaporate, then ignite the resulting nitrate to oxide.

The reaction of ammonium iodide with cupric oxide is analogous to that with ferric oxide as indicated by the equation



In this case, however, it is not so convenient to convert the iodide back to oxide by air oxidation, since this takes a longer time and more care than with ferrous iodide. Apparently no loss from volatilization of cuprous iodide occurs if ignitions are made at any temperature in the range 400° to 500° C.

The action of ammonium iodide on lead oxide can be represented by the equation

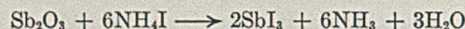


In this case also the ignition must be made with temperature control to prevent loss by volatilization. Conversion to oxide through nitric acid treatment is necessary for quantitative results since lead iodide is converted into oxyiodides by ignition in air (5). Large amounts of lead oxide, however, cannot be handled conveniently by this method, since then the conversion of the iodide back to oxide was found to require an excessive number of repeated treatments with the acid. With as much as 0.01 to 0.02 gram, far in excess of amounts likely to be found in impure tin oxide precipitates, the recovery is fairly satisfactory.

In the case of nickel oxide the equation representing the reaction is analogous to the one for lead oxide. From a manipulative viewpoint the behavior of nickel oxide is similar to that of ferric oxide, for not only is the conversion of the iodide back to oxide by direct ignition in air possible, but there is also likelihood of the formation of a fluffy form of this oxide which can lead to mechanical loss unless due care is taken.

With zinc oxide the reaction follows a course analogous to that of the last two oxides, but owing to the relatively low boiling point of zinc iodide considerable loss by volatilization occurs when the ignitions are conducted within the temperature range used for the preceding oxides. From the standpoint of the application of this method to the correction of impure tin oxide for impurities, it is fortunate that zinc is such a minor contaminant of such precipitates.

Antimony trioxide on ignition with ammonium iodide behaved in a manner very similar to that of stannic oxide. The equation for the volatilization can be written



Separation of these oxides is therefore not possible by this method. On the contrary the two oxides can be quantitatively volatilized together from mixtures containing other oxides, and this procedure can be applied with advantage in certain cases.

Separation of Stannic Oxide from Other Metallic Oxides

The separation of ferric oxide from stannic oxide is important practically because ferric oxide is often the chief contaminant of impure tin oxide. A number of experiments were, therefore, made on synthetic mixtures in which the weights of the oxides were so taken as to give samples that simulated badly contaminated tin oxide precipitates. In each trial a sample was weighed into a weighed crucible and intimately mixed with 1.5 grams of ammonium iodide. Ignition was performed at various temperatures, and the crucibles with their residues were then gently ignited to constant weight in air to obtain the amounts of residual oxide. Typical

results are shown in Table I. With an ignition temperature below 400° C. high results were obtained by reason of the nonvolatilization of some of the stannic oxide, whereas at 500° C. the results were low because of volatilization of some ferrous iodide during ignition. At the intermediate temperatures, however, the separation is, in general, good. Some experiments were also made on mixtures which had larger proportions of ferric oxide but, the results on these not being as satisfactory, the method is not to be recommended for such separations.

TABLE I. SEPARATION OF STANNIC OXIDE FROM FERRIC OXIDE BY IGNITION WITH AMMONIUM IODIDE

Temperature ° C.	SnO ₂ Taken Gram	Fe ₂ O ₃ Taken Gram	Fe ₂ O ₃ Residue Gram	Difference Error Gram
345	0.0993	0.0115	0.0220	+0.0105
395	0.1151	0.0094	0.0122	+0.0028
420	0.0932	0.0109	0.0106	-0.0003
420	0.0978	0.0112	0.0111	-0.0001
430	0.1027	0.0174	0.0177	+0.0003
430	0.1017	0.0119	0.0116	-0.0003
450	0.0943	0.0125	0.0122	-0.0003
450	0.0958	0.0111	0.0112	+0.0001
450	0.1066	0.0100	0.0101	+0.0001
450	0.0986	0.0100	0.0098	-0.0002
460	0.0983	0.0101	0.0097	-0.0004
460	0.0956	0.0116	0.0115	-0.0001
500	0.0984	0.0125	0.0116	-0.0009
500	0.0965	0.0140	0.0127	-0.0013

In addition to ferric oxide, cupric oxide is a leading contaminant of ignited stannic oxide precipitates. For this reason a number of experiments were made on synthetic mixtures that contained both these oxides in addition to a large relative excess of stannic oxide. These trials were carried out in the same way as the preceding except that the ignitions in air, because of the presence of cuprous iodide in the residues, were controlled as to temperature, the start being made at about 270° C. with a gradual rise to dull red heat. The results appear in Table II.

TABLE II. SEPARATION OF STANNIC OXIDE FROM FERRIC OXIDE AND CUPRIC OXIDE

Temperature ° C.	SnO ₂ Taken Gram	Fe ₂ O ₃ Taken Gram	CuO Taken Gram	Total Foreign Oxides		Error Gram
				Taken Gram	Found Gram	
400	0.1081	0.0090	0.0092	0.0182	0.0183	+0.0001
400	0.0988	0.0077	0.0123	0.0200	0.0202	+0.0002
425	0.0954	0.0104	0.0100	0.0204	0.0202	-0.0002
425	0.1036	0.0105	0.0095	0.0200	0.0199	-0.0001
425	0.0993	0.0022	0.0006	0.0028	0.0029	+0.0001
425	0.0992	0.0020	0.0008	0.0028	0.0028	±0.0000
450	0.1021	0.0085	0.0127	0.0212	0.0211	-0.0001
475	0.0918	0.0065	0.0094	0.0159	0.0159	±0.0000
500	0.1074	0.0079	0.0116	0.0195	0.0194	-0.0001
525	0.1074	0.0067	0.0083	0.0150	0.0146	-0.0004
525	0.0934	0.0097	0.0122	0.0219	0.0214	-0.0005

The totals agree satisfactorily except in the case of the runs made at 525° C. where some volatilization of the iodides probably occurred. A similar set of experiments was carried out in which, instead of air ignition, the nitric acid technic was used for the conversion of iodides to oxides. The results of these were in general also satisfactory.

Samples containing ferric oxide, cupric oxide, and lead oxide that were synthetic approximations to ignited tin oxide precipitates likely to be obtained in the analysis of common non-ferrous alloys were also analyzed in this way. In most of these the proportion of total "impurities" was purposely exaggerated in order to test the value of the method for handling grossly contaminated tin oxide. Because of the presence of lead oxide the reconversion back to oxides was made by the nitric acid method in all these trials. The data in Table III show that the recovery of the total added "foreign" oxides from the synthetic mixtures was satisfactory, especially in view of the possibility of the occurrence of cumulative weighing errors in the preparation of complex mixtures of this sort. As could be expected from the results

of the preceding experiments, the least satisfactory results were obtained on samples that were ignited at the lowest and the highest points in the temperature range.

TABLE III. SEPARATION OF STANNIC OXIDE FROM FERRIC OXIDE, CUPRIC OXIDE, AND LEAD OXIDE

Temperature ° C.	SnO ₂ Taken Gram	Fe ₂ O ₃ Taken Gram	CuO Taken Gram	PbO Taken Gram	Total Foreign Taken Gram	Found Gram	Error Gram
400	0.1682	0.0078	0.0096	0.0037	0.0211	0.0214	+0.0003
400	0.1376	0.0011	0.0016	0.0006	0.0033	0.0037	+0.0004
425	0.1101	0.0037	0.0055	0.0028	0.0120	0.0119	-0.0001
450	0.1453	0.0013	0.0008	0.0016	0.0037	0.0040	+0.0003
450	0.1130	0.0049	0.0053	0.0083	0.0185	0.0184	-0.0001
450	0.0959	0.0020	0.0014	0.0011	0.0045	0.0049	+0.0004
450	0.0981	0.0033	0.0076	0.0029	0.0138	0.0136	-0.0002
475	0.0990	0.0046	0.0054	0.0048	0.0148	0.0146	-0.0002
475	0.0978	0.0038	0.0030	0.0041	0.0109	0.0108	-0.0001
500	0.0819	0.0017	0.0011	0.0006	0.0034	0.0034	±0.0000
500	0.0642	0.0056	0.0032	0.0042	0.0130	0.0131	+0.0001
525	0.0875	0.0024	0.0017	0.0024	0.0065	0.0060	-0.0005

Behavior of Difficultly Soluble Oxides

The two oxides of this type considered here differ from the other oxides likely to be contaminants of stannic oxide in their behavior on ignition with ammonium iodide, for no conversion to iodides takes place. In the case of tungstic oxide some slight reduction to a lower oxide apparently occurs if the temperature of ignition is too high, but with silica there is no reaction.

Experiments on mixtures of tungstic oxide and stannic oxide showed that this general method is practicable for the separation of the two. Some results are shown in Table IV.

TABLE IV. SEPARATION OF STANNIC OXIDE FROM TUNGSTIC OXIDE

Temperature ° C.	SnO ₂ Taken Gram	WO ₃ Taken Gram	WO ₃ Residue Gram	Difference Error Gram
375	0.1280	0.1129	0.1147	+0.0018
400	0.0118	0.1126	0.1127	+0.0001
400	0.0770	0.0686	0.0685	-0.0001
425	0.0114	0.1634	0.1635	+0.0001
425	0.1164	0.0976	0.0972	-0.0004
450	0.0104	0.1504	0.1502	-0.0002
450	0.0906	0.1085	0.1086	+0.0001
475	0.1510	0.1419	0.1413	-0.0006

In these trials each sample was mixed with about 1.5 grams of ammonium iodide and ignited in the electric furnace at the given temperatures. The residual oxide was then simply weighed after volatilization of all excess iodide. The usual high results that come from incomplete removal of stannic oxide on using too low an ignition temperature are illustrated by the first value. In the remaining trials, with the exception of the last, the residual oxide had a normal appearance, and the separation was satisfactory. In ignitions made above 450° C. the oxide had a slight greenish color apparently due to superficial reduction, and low results were obtained. However, if concentrated nitric acid was added to such a residue and then removed by evaporation, the oxide regained its normal appearance and proper weight. In the separation of stannic oxide from tungstic oxide, therefore, it is best to ignite with ammonium iodide at a temperature between 400° and 450° C., but if too high a temperature happens to be used the residue can be oxidized back with nitric acid.

TABLE V. SEPARATION OF STANNIC OXIDE FROM SILICA

SnO ₂ Taken Gram	SiO ₂ Taken Gram	SiO ₂ Recovered Gram	Difference Error Gram
0.0923	0.0020	0.0021	+0.0001
0.1197	0.0016	0.0018	+0.0002
0.1930	0.0009	0.0012	+0.0003
0.1230	0.0021	0.0019	-0.0002
0.0992	0.0022	0.0019	-0.0003
0.1196	0.0007	0.0007	±0.0000

In Table V are shown the results of experiments on the separation of stannic oxide from silica.

In order to give a material similar to that likely to be met with in tin oxide precipitates contaminated with silica, that used in these trials was dehydrated silicic acid prepared by ignition, rather than crystalline silica. The samples were mixed with about ten times their weight of ammonium iodide, and the ignitions were conducted over a Bunsen burner at low red heat, no attempt at exact temperature control being made. The separation was satisfactory. For the purpose of correcting the weight of an impure stannic oxide precipitate contaminated with silica it is believed that this ammonium iodide volatilization method is probably more accurate, as well as more convenient, than the usual treatment with hydrofluoric and sulfuric acids, since the new method is conducted in the porcelain crucible used for igniting the oxide, whereas the other method necessitates transference to a platinum vessel. In addition, the process described here is somewhat more rapid.

Application to Determination of Tin in Alloys

It is commonly recognized that the ignited stannic oxide resulting from the nitric acid treatment of such alloys as brasses and bronzes is so contaminated with various impurities that, when exact results are desired, it must be subjected to some purification process. Practically the only method heretofore available for the treatment of such impure tin oxide has been the sodium carbonate and sulfur fusion process of Rose. This method is laborious and time-consuming, especially when a second treatment is required, which is often the case. Furthermore, several sources of error are inherent in it, such as that resulting from the introduction of silica by the action of the fusion mixture on the crucible. Treatment with ammonium iodide volatilizes stannic oxide quantitatively from synthetic mixtures of oxides that resemble in composition the impure tin oxide obtained from ordinary brasses or bronzes, for, if alloys containing arsenic, antimony, or phosphorus are excepted, the usual contaminants of the tin precipitate are ferric oxide, cupric oxide, lead oxide, zinc oxide, and nickel oxide. Actually, according to quantitative data furnished by Hillebrand and Lundell (2), and more extensively by Tilk and Holtje (6), ferric oxide and cupric oxide are the chief impurities, the others being normally present in almost negligible amounts. When applied to the purification of actual precipitates the ammonium iodide volatilization method was found to be very satisfactory. In simplicity and time required it is decidedly superior to the fusion method, and appears to yield more consistent and accurate results. The procedure used in these test analyses and recommended for general use is as follows.

Procedure

Ignite the separated metastannic acid to constant weight in a porcelain crucible. Then add to the impure tin oxide about fifteen times its weight of powdered ammonium iodide, and mix the two in the crucible intimately by means of a small spatula. Place the charged crucible in an electric crucible or muffle furnace maintained between 425° and 475° C. Allow it to remain there until all fumes have ceased to come from the crucible, about 15 minutes. Then remove the crucible and, after having allowed it to cool sufficiently, add 2 to 3 ml. of concentrated nitric acid. Evaporate to dryness on the hot plate and cautiously decompose the residual nitrates over a low burner flame. Follow this by ignition at low red heat to constant weight. The difference between this weight and the original weight gives the amount of pure stannic oxide present. A suitable correction should be applied if there is a weighable amount of nonvolatile matter in the ammonium iodide. To continue the analysis, dissolve the oxide residue out of the crucible by digestion with a few milliliters of hot concentrated hydrochloric acid. Dilute the resulting solution and filter it to remove small amounts of silica that may come from the filter paper ash. Finally add the solution and washings

to the filtrate being evaporated down for the determination of lead as sulfate. The remainder of the analysis is conducted in the usual way.

Results of Test Analyses

Twelve consecutive determinations of the tin content of Bureau of Standards brass sample No. 37b using 5.000-gram samples and several variations in the method of separating the metastannic acid with 1 to 1 nitric acid yielded the following percentage values based upon the weights of the impure tin oxide: 1.09, 1.06, 1.11, 1.08, 1.09, 1.08, 1.07, 1.04, 1.05, 1.06, 1.06, and 1.06. After purification of the precipitates by the above method the corresponding values were 1.00, 0.99, 1.00, 0.98, 0.99, 0.99, 1.00, 0.99, 0.99, 0.97, 0.98, and 0.98, the average being 0.99. Though the percentages of tin based upon the weight of impure oxide show a range of 0.07 per cent, due in part to deliberate variations in the method of treatment in order to introduce varying amounts of impurities, the values after purification show a range of only 0.03 per cent between the extreme results. The value established at the Bureau of Standards on this sample was 1.00 per cent using a volumetric method, while the co-operating analysts obtained by various gravimetric and volumetric procedures the percentages 0.99, 0.98, 0.91, 0.99, 1.01, 0.97, 0.99, 1.02, 0.98, and 1.03, the over-all average of 0.99 per cent being identical with the average of the present determinations.

The above procedure can also be applied to certain alloys that contain a higher percentage of tin, such as ordinary bronzes. It is even applicable to bronzes that contain a small proportion of antimony if the latter is known or determined and allowance is made for the corresponding amount of antimony oxide that is volatilized along with the stannic oxide during the ignition with ammonium iodide. While this method involves the use of a double correction, it apparently yields satisfactory results, as shown by test determinations made on Bureau of Standards cast bronze sample

No. 52. For these 1.0000-gram samples were taken, and for the antimony content the stated average value, 0.16 per cent, was used. Six consecutive determinations gave the following final values for the tin content: 7.85, 7.86, 7.87, 7.85, 7.87, and 7.88, the average being 7.86 per cent. The value established at the Bureau of Standards was 7.88 per cent, while the co-operating analysts obtained percentages ranging from 7.80 to 7.99, the over-all average being 7.90 per cent. In the case of this sample also the results were not only accurate but very consistent, the range between the extreme values of the single determinations being but 0.03 per cent.

Discussion

It is believed that this general method for the separation of stannic oxide represents a distinct advance over methods previously proposed, not only from the standpoint of accuracy, but also in respect to simplicity of manipulation and the rapidity with which results can be obtained. The ammonium iodide volatilization method can be applied to separations and materials other than those considered in this present paper.

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The Ignition of Silicic Acid

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SEVERAL years ago, one of us was disturbed upon being presented with a platinum crucible containing a jet-black substance which was stated to be the product obtained on igniting a sample of silica separated in the course of an ordinary analysis of a silicate. On interrogating the student, it was learned that the moist silicic acid, on a wet filter paper, had been placed in a well-covered crucible and the vessel and contents had been immediately subjected to the highest temperature attainable with a large Meker burner. In the belief that the color was due to carbon, the uncovered crucible and contents were heated for several hours without effecting a detectable change in appearance or in weight. By means of a suitable porcelain cover and inlet tube, oxygen was supplied to the crucible and the contents were heated for a 6-hour period in that atmosphere. The contents were unaltered in appearance and lost but 1.5 mg. in weight. A second and third heating for 6-hour periods produced a total loss of 3 mg. in weight. The color changed from black to dark gray.

These observations suggested to the writers that some compound of silicon might be responsible for the observed resistance to oxidation, although no reference to compound formation under these conditions could be found in the literature. To test this supposition, silica was precipitated from solutions of sodium silicate by the addition of hydrochloric acid, washed repeatedly by stirring and decantation to remove sodium

chloride, and collected on quantitative filter paper (Whatman No. 42, 7 cm.). Samples, while wet, were put in covered crucibles of platinum and of sillimanite, and immediately placed over Meker burners. Provided the silica and filter paper were wet and the crucibles covered, the ignition product was invariably dark in color. On treating the product with hydrofluoric acid and evaporating to dryness, a black powder was obtained which always left a small, black residue when ignited in the air. On examination under the polarizing microscope, this residue was found to be silicon carbide, SiC. A few imperfect, greenish blue crystals were found in one sample, which gave evidence of the characteristic pleochroism. The index of refraction of this substance was found to be higher than that of methylene iodide ($N = 1.74$), thus definitely excluding the possibility that the substance was merely silica mechanically darkened by carbon.

It is presumed that the carbide is produced by the action of the carbon, hydrocarbons or carbon monoxide, and hydrogen resulting from the ignition of the wet filter paper, although the temperature attained in a 20-cc. platinum crucible, when heated under the conditions of the experiments, was never higher than 930° to 950° C., as determined by means of a platinum-platinum rhodium thermocouple.

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Determining Copper in the Presence of Interfering Elements

A Modified Iodometric Method

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THE usual iodometric method of determining copper consists essentially of adding a soluble iodide to a solution of a cupric salt and titrating the liberated iodine with standard thiosulfate. In a recent article (1) the writers have shown that, if a soluble thiocyanate is added to the solution just before the end point is reached, some additional iodine is liberated and the reaction runs to completion in stoichiometric proportions. The end point is extremely sharp, partly because of the greater insolubility of cuprous thiocyanate and partly because the precipitate is white and retains no adsorbed iodine.

The present article gives the results obtained by using this modified method to determine copper in the presence of pentavalent arsenic and antimony, and ferric iron. These are the only elements commonly associated with copper which liberate iodine from iodides and thus make the titration unreliable. All these elements, in their lower valences, can reduce iodine and in that way also lead to incorrect results. It is, however, a simple matter to insure the presence of the higher valence only, so that this latter type of interference need not occur. The possible interference of selenium and manganese has also been considered.

The interference of pentavalent arsenic (arsenic acid) and ferric iron in the usual iodometric method for copper has been investigated recently by Park (2) who found that arsenic acid offered the chief difficulty. On account of its oxidizing character in the presence of mineral acids, he found it necessary to reduce the hydrogen-ion concentration by means of buffer solutions, but encountered the difficulty, which was not new, that the liberation of iodine by the cupric salt was excessively slow at the low acidity. He abandoned the use of acetates for this reason and used a buffered phthalic acid solution. To what extent the reaction runs in stoichiometric proportions under these conditions is not clear, as he standardized his thiosulfate with copper. Park found, in accordance with Mott (3) and others, that a soluble fluoride eliminated all difficulty with the iron. The latter is converted to a complex fluoride insufficiently dissociated to liberate iodine from potassium iodide.

Experimental

Metallic copper was from the sample used in the previous investigation (1), and contained 99.955 per cent of copper. Arsenic was used in the form of H_2KAsO_4 , and antimony as a potassium antimonate containing 46.5 per cent of the metal. A standardized solution of ferric nitrate furnished the iron. Thiosulfate solutions were standardized by means of resublimed iodine and the copper equivalent was calculated. While equally good or better results could be obtained by standardizing with copper, the authors considered it essential to use iodine as a standard in order to determine to what extent the reaction $2CuI_2 \rightleftharpoons 2CuI + I_2$ runs to completion during the titration. The thiosulfate solutions changed slightly in strength during the work and were frequently restandardized.

In preliminary experiments the authors determined empirical proportions of sulfuric and acetic acids and ammonia which would yield a buffer solution of sufficiently high pH to

prevent the oxidation of an iodide to free iodine by arsenic acid. The buffer solution adopted contained the equivalent of 9.3 cc. of 6 *N* sulfuric acid, 22.8 cc. of 6 *N* acetic acid, and 12.6 cc. of 6 *N* ammonia. This mixture in a total volume of 60 cc. has a pH value approximating 3.7 as determined by the hydrogen electrode. These proportions were used in all determinations given below. An acetate solution of this pH practically cannot be used in the usual iodometric determination of copper. In the presence of a thiocyanate, however, the reaction is rapid and the end point exceedingly sharp.

In all determinations given below the following procedure was used:

Known weights of copper were dissolved in nitric acid and 9.3 cc. of 6 *N* sulfuric acid, together with the interfering elements, added to the solution. The solution was then evaporated until all nitric acid was removed. After evaporation the residues were dissolved in 20 cc. of water and the acetic acid and ammonia added in the volumes noted above; the acetic acid was added first so that the solution was always acid. When iron was present the solution was deeply colored at this point. A basic precipitate containing iron may form, particularly if arsenic is present. One to two grams of sodium fluoride were next added, if iron were present, which immediately removed all color of iron and dissolved any precipitate. Usually a slight, apparently crystalline precipitate appeared at this point (Na_3FeF_6 ?) which, however, in no way interfered with the titration. After adding potassium iodide, the titration was carried out until most of the iodine was removed, then starch solution was added and, when the end point was nearly reached, 2 to 3 grams of ammonium thiocyanate, and the titration was completed.

Certain details of the above procedure require mention.

1. The complete removal of nitric acid was found to be necessary, not because nitric acid itself interferes in the titration, but because it appears to break down as the last of it is removed by evaporation from the strong sulfuric acid and the resulting nitrogen oxides liberate iodine later in the analysis. Blank tests in the absence of copper showed this conclusively and determinations of copper, in which the nitric acid was purposely not removed entirely, gave high results. The nitric acid can be removed conveniently either by evaporating until the sulfuric acid fumes strongly, or by carrying out the first evaporation until salts begin to crystallize and evaporating a second time after adding a small volume of hydrochloric acid. Both methods were used indiscriminately. Where there is difficulty with spattering, the second method is more convenient.

2. All evaporations were made by boiling the solutions, usually in 300-cc. flasks, over a free flame, holding the flasks nearly horizontal. To show that losses from this treatment were negligible, two solutions containing known amounts of copper were evaporated repeatedly in the manner described, adding 20 cc. of liquid to the residue after each evaporation. The loss in copper after ten such evaporations was less than could be detected by analysis.

3. The amount of sulfuric acid used can be varied, but there should be a corresponding variation in the amount of ammonia. The authors chose to use 10 rather than 5 cc. (used in the previous work) because evaporation and subsequent solution in water are a little easier, particularly in the presence of rather large amounts of salts.

TABLE I. DETERMINATION OF COPPER IN ABSENCE OF INTERFERING ELEMENTS

No.	(1 to 7, volume buret used; 8 to 17, weight buret used)		Error Mg.
	Pure Cu Taken Gram	Cu Found Gram	
1	0.1641	0.1641	0
2	0.1971	0.1970	-0.1
3	0.3208	0.3211	+0.3
4	0.1592	0.1591	-0.1
5	0.2198	0.2197	-0.1
6	0.1784	0.1785	+0.1
7	0.3034	0.3034	0
8	0.1529	0.1532	+0.3
9	0.2028	0.2031	+0.3
10	0.2585	0.2586	+0.1
11	0.3028	0.3033	+0.5
12	0.3543	0.3547	+0.4
13	0.1559	0.1558	-0.1
14	0.2008	0.2011	+0.3
15	0.2509	0.2511	+0.2
16	0.3027	0.3030	+0.3
17	0.3570	0.3575	+0.5

TABLE II. DETERMINATION OF COPPER IN PRESENCE OF TRIVALENT IRON

No.	(1 to 8, volume buret; 9 to 18, weight buret)			Error Mg.
	Fe Gram	Pure Cu Taken Gram	Cu Found Gram	
1	0.069	0.1536	0.1536	0
2	0.069	0.1785	0.1787	+0.2
3	0.069	0.2149	0.2149	0
4	0.069	0.3031	0.3033	+0.2
5	0.138	0.1595	0.1597	+0.2
6	0.138	0.1918	0.1918	0
7	0.069	0.2294	0.2293	+0.1
8	0.069	0.3076	0.3078	+0.2
9	0.069	0.1546	0.1546	0
10	0.069	0.2015	0.2017	+0.2
11	0.069	0.2548	0.2548	0
12	0.069	0.3027	0.3029	+0.2
13	0.069	0.3542	0.3545	+0.3
14	0.138	0.1525	0.1527	+0.2
15	0.207	0.2032	0.2031	-0.1
16	0.104	0.2744	0.2747	+0.3
17	0.138	0.3354	0.3359	+0.5
18	0.138	0.4021	0.4028	+0.7

TABLE III. DETERMINATION OF COPPER IN PRESENCE OF PENTAVALENT ARSENIC

No.	(1 to 8, volume buret; 9 to 17, weight buret)			Error Mg.
	As Gram	Pure Cu Taken Gram	Cu Found Gram	
1	0.125	0.1637	0.1639	+0.2
2	0.08	0.2138	0.2138	0
3	0.08	0.2100	0.2103	+0.3
4	0.17	0.3090	0.3092	+0.2
5	0.04	0.1788	0.1789	+0.1
6	0.08	0.2098	0.2100	+0.2
7	0.125	0.2385	0.2387	+0.2
8	0.17	0.3040	0.3042	+0.2
9	0.04	0.1033	0.1034	+0.1
10	0.08	0.1501	0.1504	+0.3
11	0.126	0.2041	0.2047	+0.6
12	0.21	0.3024	0.3023	-0.1
13	0.25	0.3502	0.3504	+0.2
14	0.29	0.4019	0.4023	+0.4
15	0.33	0.4412	0.4422	+1.0
16	0.125	0.1547	0.1549	+0.2
17	0.33	0.3004	0.3004	0

4. In adding acetic acid and ammonia it was found best to add them in the order mentioned, so that the solution never became basic. If the reverse order is used, the precipitate produced by ammonia is somewhat difficult to dissolve. Further, in the presence of manganese, it is essential to add the acetic acid first, as will be shown later.

5. The addition of sodium fluoride is, of course, necessary only when iron is present. It not only prevents the ferric iron from liberating iodine when potassium iodide is added, but it also completely prevents the ferric thiocyanate color when a thiocyanate is added near the end point. One gram of sodium fluoride is sufficient for somewhat more than 0.1 gram of iron.

6. Roughly, half the determinations were made with a calibrated volume buret and the others with a weight buret. With the latter, somewhat larger amounts of copper could be determined, but the percentage error by the two methods was nearly the same.

Determination of Copper Alone and in the Presence of Iron and Arsenic

The results obtained on copper alone are given in Table I. This series of determinations was carried out in order to show definitely that the method was reliable at the rather high pH necessary to prevent the oxidation of iodides by arsenic acid. The highest pH of the solutions in the authors' previous work was approximately 2.0, and iodides are oxidized freely by arsenic acid at that hydrogen-ion concentration. Tables II, III, and IV give the results on copper in the presence of iron, of arsenic, and of both iron and arsenic, respectively.

Tables II, III, and IV show that neither iron nor arsenic when present alone interferes with the copper determination under the conditions used even though either may be present in fairly large amounts; further, when iron and arsenic are present together, they do not interfere when present in moderate amounts. Although the amounts of iron and arsenic shown in Table IV are in excess of the amounts likely to be encountered in copper ores, it seemed of interest to find the quantities of these two elements which would limit the applicability of the method when they were both present. Table V gives these results.

The results are low, owing to the formation of a precipitate, presumably an iron arsenate, which contains some copper. No entirely definite line can be drawn between amounts which do and which do not vitiate the method, but a rather close idea can be obtained from the values in Tables IV and V. The use of a larger volume of solution did not solve the difficulty. If, in practice, such excessive amounts of iron and arsenic were found, it might well be possible to avoid the difficulty by using a smaller sample of material.

Determination of Copper in the Presence of Antimony

Pentavalent antimony in solution behaves very similarly to pentavalent arsenic as an oxidizing agent. At the pH used in all the authors' determinations it liberates iodine only in traces with extreme slowness and offers no difficulty on this account. Antimonic acid, however, is rather insoluble under

TABLE IV. DETERMINATION OF COPPER IN PRESENCE OF TRIVALENT IRON AND PENTAVALENT ARSENIC

No.	(1 to 7, volume buret; 8 to 9, weight buret)				Error Mg.
	Fe Gram	As Gram	Pure Cu Taken Gram	Cu Found Gram	
1	0.069	0.04	0.2072	0.2071	-0.1
2	0.069	0.08	0.1623	0.1619	-0.4
3	0.035	0.17	0.3006	0.3007	+0.1
4	0.069	0.17	0.1571	0.1571	0
5	0.069	0.125	0.2316	0.2314	-0.2
6	0.035	0.08	0.1887	0.1892	+0.5
7	0.139	0.04	0.3029	0.3032	+0.3
8	0.069	0.04	0.3016	0.3016	0
9	0.069	0.04	0.3036	0.3038	+0.2

TABLE V. DETERMINATION OF COPPER IN PRESENCE OF LARGER AMOUNTS OF BOTH TRIVALENT IRON AND PENTAVALENT ARSENIC

No.	(Weight buret used)				Error Mg.
	Fe Gram	As Gram	Pure Cu Taken Gram	Cu Found Gram	
1	0.035	0.21	0.3020	0.3015	-0.5
2	0.207	0.21	0.3005	0.2999	-0.6
3	0.138	0.29	0.1512	0.1509	-0.3
4	0.069	0.21	0.1496	0.1492	-0.4
5	0.069	0.21	0.4522	0.4515	-0.7
6	0.069	0.42	0.3010	0.3000	-1.0
7	0.069	0.29	0.3002	0.2989	-1.3
8	0.069	0.42	0.3017	0.3004	-1.3
9	0.069	0.42	0.3035	0.3023	-1.2
10	0.069	0.42	0.3028	0.3012	-1.6
11	0.207	0.29	0.3026	0.3009	-1.7
12	0.138	0.29	0.4541	0.4510	-3.1

the conditions necessary for the titration and when it precipitates it always adsorbs small amounts of copper. This behavior is very similar to that of metastannic acid. Whenever antimony is present in considerable amounts, therefore, the results are low. Table VI gives these results. Roughly, the limit of solubility of antimonious acid in the solution used corresponds to 0.020 gram of antimony and this value thus gives the limiting amount of antimony which will cause no difficulty in the titration.

TABLE VI. DETERMINATION OF COPPER IN PRESENCE OF PENTAVALENT ANTIMONY

No.	(1 to 3 and 6, volume buret; 4, 5, and 7, weight buret)			Error Mg.
	Sb Gram	Pure Cu Taken Gram	Cu Found Gram	
1	0.005	0.1569	0.1564	-0.5
2	0.005	0.2111	0.2112	+0.1
3	0.005	0.1792	0.1792	0
4	0.009	0.2039	0.2039	0
5	0.019	0.2044	0.2045	+0.1
6	0.024	0.3042	0.3029	-1.3
7	0.038	0.2037	0.2020	-1.7

Determination of Copper in the Presence of Selenium

Selenic acid is a strong oxidizing agent, and would, if present, liberate iodine. Under the conditions of the analysis, however, the element appears to be oxidized only to selenious acid and does not interfere. The results obtained are given in Table VII.

TABLE VII. DETERMINATION OF COPPER IN PRESENCE OF SELENIUM

Se Gram	(Weight buret used)		Error Mg.
	Pure Cu Taken Gram	Cu Found Gram	
0.005	0.2013	0.2013	0
0.0505	0.2020	0.2018	-0.2

Determination of Copper in the Presence of Iron and Manganese

The need to determine copper in the presence of appreciable amounts of iron and manganese is rare and the authors would not have considered the matter except that Park (3) states that in the presence of both these metals the results on copper are high, and gives data to show this effect. Disregarding his explanation, it seemed probable that the difficulty was due to the fact that in preparing his buffer solutions, Park made them ammoniacal before acidifying with phthalic acid, and manganous hydroxide, as is well known, forms a higher oxide rather rapidly when exposed to air. This, of course, would liberate iodine later in the analysis. The authors therefore carried out a number of determinations in the presence of manganese alone and in the presence of manganese and iron. The results are given in Table VIII.

TABLE VIII. POSSIBLE EFFECT OF MANGANESE ON DETERMINATION OF COPPER

(All the determinations were carried through as usual except that in Nos. 1 and 2 the ammonia was added before the acetic acid and the ammoniacal solutions allowed to stand 5 minutes before acidifying.)

No.	Pure Cu Gram	MnSO ₄ Gram	Fe Gram	Cu Equivalent
				of Iodine Liberated
1	None	0.55	None	0.0029
2	None	0.55	0.138	0.0075
3	None	0.55	None	None
4	None	0.55	0.138	None
5	0.2111	0.55	0.138	0.2106
6	0.1838	0.28	0.069	0.1837

Nos. 1 and 2 in Table VIII show the considerable effect due to manganese alone or in the presence of iron, when the solutions were allowed to become alkaline. Both effects are

greater than those obtained by Park, probably because the solutions were purposely allowed to stand, while ammoniacal, for some time in order to intensify the effect. Apparently the presence of iron hydroxide catalyzes the oxidation of the manganese, which accounts for the fact that Park found the effect of manganese appreciable only in the presence of iron. Nos. 3 to 6 show that manganese and iron do not affect the results if the solution is not allowed to become ammoniacal.

Summary

By using a modified iodometric method described recently, and controlling the hydrogen-ion concentration, copper may be determined accurately in the presence of pentavalent antimony and arsenic. The addition of a soluble fluoride (as first suggested by Mott) prevents the interference of iron and does not interfere with the accuracy of the determination. These are the only elements commonly associated with copper which interfere in the usual iodometric determination. Selenium does not interfere under the conditions used. An explanation of the reported interference of a mixture of manganese and iron has been found. Under suitable conditions, these elements do not interfere.

The method is reliable in the presence of rather excessive amounts of arsenic and iron. In the presence of antimony in amounts greater than about 20 mg. antimonious acid precipitates together with adsorbed copper and the results are correspondingly low.

The liberation of iodine from a soluble iodide by cupric copper takes place in stoichiometric proportions under the conditions used.

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RECEIVED October 2, 1935.

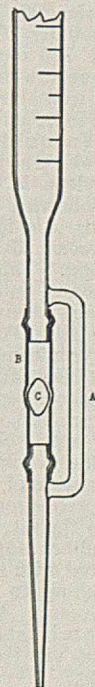
A New Buret for Alkali Titrations

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ALTHOUGH the ordinary rubber-tipped buret has long been recognized as not being strictly accurate for alkaline titration, it still finds wide use in many laboratories. One of the main objections to rubber-tipped burets is their lack of rigidity. The modification presented herewith provides a means whereby this difficulty is overcome and at the same time improves its usefulness. The new type of buret has been tried out by several individuals and all endorse it heartily.

The construction may be seen from the figure. A is a glass rod or sealed-off tube which fastens the tip rigidly in line with the main body of the buret. B is a short piece of a good grade of laboratory rubber tubing connecting the buret to the tip. C as shown in the diagram is a glass bead, but obviously it could be replaced by any of the various devices used in conjunction with rubber stopcocks.



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Semi-Micromethod of Analysis for Nitrogen

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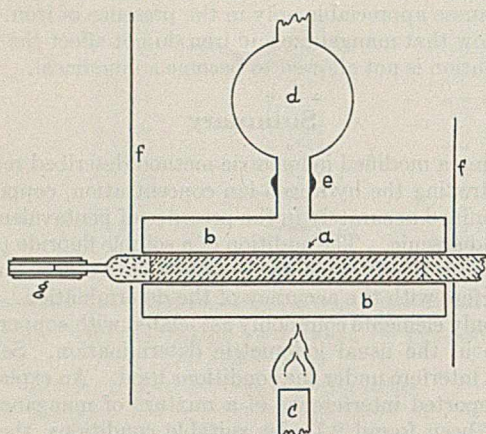


FIGURE 1. DIAGRAM OF APPARATUS

THE Dumas method for nitrogen (3) suffers from two important drawbacks: (1) the copper spiral placed at the end of the combustion tube catalytically reduces the carbon dioxide to carbon monoxide, and (2) this and the intermediate products of combustion are often incompletely oxidized unless the burning produces not more than two bubbles per 3 seconds.

The semi-micromethod described here avoids both difficulties by placing at the end of the tube a heated section containing iodine pentoxide, made by heating iodic acid in an oil bath for an hour at 170° C. At this temperature a minute amount of iodine pentoxide is decomposed, so small, however, that it may be neglected.

A section of the crushed oxide 13 cm. long, *a*, is placed in a combustion tube 56 cm. long and 1 cm. in diameter (Figure 1). The section is kept dehydrated by enclosing it in a copper jacket, *b*, containing boiling xylene (b. p. about 120° C. at Boulder, Colo., about 130° C. at 760 mm.). Since this temperature even in high altitudes is well above the melting point of iodic acid (110° C.), the iodine pentoxide is kept sufficiently dehydrated and active. The xylene is heated by burner *c*. Following this are a section of cupric oxide 5 cm. long and a section of reduced copper 5 cm. long. This is followed by a section of cupric oxide 15 cm. long, kept permanently in place by a small roll of copper gauze. The Pyrex condenser, *d*, should have at least four bulbs, each of about 150-cc. capacity to avoid danger from fire, and is sealed to the copper jacket with cementite, *e*. The asbestos screens, *f*, prevent heating of the nitrometer. The combustion tube is connected to the nitrometer by means of a rubber stopper, *g*, which is covered with a short piece of glass tubing to prevent diffusion of air into the apparatus. The combustion stand and set-up are similar to that of Pregl (3).

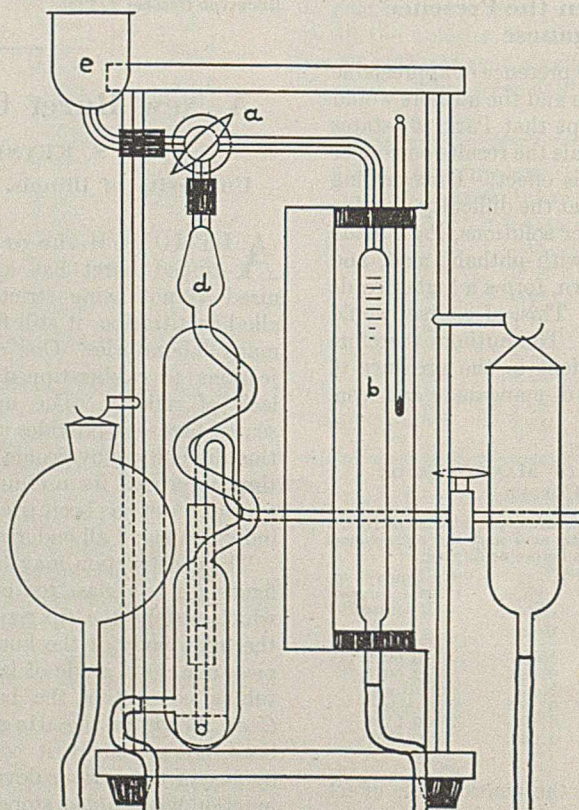


FIGURE 2. MODIFIED NITROMETER

The sample, 12 to 20 mg., weighed to 0.01 mg. on an analytical balance (5 to 10 minutes), should yield about 1.0 to 2 cc. of nitrogen, and is prepared for analysis as described by Pregl. After the combustion tube is connected to the nitrometer and carbon dioxide generator, the stopcocks are opened and the tube is scrubbed free of air. While the air is being removed, the burner, *c*, is lighted and the xylene brought to boiling as soon as possible. The flame is then lowered so that only gentle boiling occurs during the entire analysis. When the tube is free from air, the nitrometer is filled with potassium hydroxide and the combustion performed in the usual manner. The rate of burning may be such that as many as three to four bubbles of gas per second rise in the nitrometer, but a much faster rate for a few seconds does not endanger the result. The time required for burning the sample is usually about 30 to 45 minutes. The complete determination from the time of weighing of the sample until the results are obtained usually requires an hour.

With a freshly filled tube high results are obtained for the first 7 or 8 analyses, because traces of oxygen are generated by the iodine pentoxide. This may be removed from the gas by washing with a little pyrogallol-potassium hydroxide solution through funnel *e* (Figure 2). The only other difficulty encountered in a series of over two hundred analyses was the rare case where methane, a difficultly combustible gas, was generated as one of the products of decomposition of the burn-

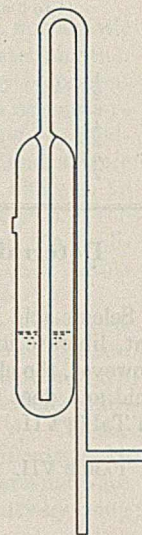


FIGURE 3. MERCURY VALVE

ing compound and was not completely burned (1). In this case there was no decrease in volume after washing the gas first with pyrogallol-potassium hydroxide solution, and then with ammoniacal cuprous chloride solution.

With careful work analyses do not vary more than ± 0.05 per cent.

A modified nitrometer devised for use with this apparatus (Figure 2) consists of an absorption tube connected by means of a three-way stopcock to a gas buret surrounded by a water jacket. The stopcock, *a*, is a capillary three-way stopcock of bore not exceeding 1.5 mm. The gas buret, *b*, is graduated in 0.05 cc. and can be read accurately to 0.01 cc.

When the combustion is finished the gas collected in the absorption buret, *d*, is transferred into the buret, *b*, and the volume read in the usual manner.

The mercuric iodide which forms in the nitrometer inlet

should be removed after about 40 combustions. It is advisable to treat all rubber tubing by Pregl's method to prevent diffusion of gases. Figure 3 shows a diagram of a mercury valve which replaces the one used by Hein in his Kipp generator (2). It is simpler and the materials for making it are more easily available.

Summary

The advantages of the semi-micromethod for nitrogen are: an ordinary analytical balance is used; the sample may usually be burned in the same length of time as that required for the microsample; using the modified nitrometer, the volume of nitrogen may be read in 2 minutes; a sudden increase

in the evolution of gas above the normal rate for a few seconds has no effect on the result; and special training is not necessary for accurate work.

A simple and easily made valve for the Kipp generator is illustrated.

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Studying the Hardness of Butter Fat

Apparatus and Routine Procedure

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IN A STUDY of factors which influence the physical properties of butter fat there was need for an inexpensive piece of apparatus which would measure accurately the relative hardness of different samples of butter fat. Available pieces of apparatus designed to measure the hardness of materials of similar consistency were not found applicable for various reasons, chief among which were lack of precision and inconvenience of operation within a small constant-temperature chamber. Perkins (2) in discussing several types of apparatus used in studies of fat hardness points out the inadequacies of each and describes a device which determines hardness by the depth of penetration into the fat of standard-size needles falling through a given distance. Apparatus based on this principle require relatively large samples of fat and the application of different weights, depending on the hardness of the fat and the diameter of the needle employed. Coulter and Hill (1) studied butter hardness with a modified apparatus designed to measure the body of cheese.

It was desired to determine the hardness of butter fat at ordinary temperatures with an apparatus which would operate within a constant-temperature water bath and give dependable results over a wide range of values. After building and testing several pieces of apparatus to determine hardness by the depth of penetration of needles of different sizes, by the weight required to crush or force plungers through a given amount of fat, and by a determination of the time required for plungers to sink a given distance into fat, the device here described was found most satisfactory. With this device, hardness is expressed as grams of mercury required to force a plunger 5 mm. in diameter through a disk of butter fat 6 mm. in thickness at 20° C.

The fat disks are made in a two-piece mold which is thoroughly chilled by placing it on the metal divisions of a tray of ice cubes. The base of the mold is a brass plate commonly used in histological technic for paraffin imbedding. A lead ring 4 cm. in diameter and exactly 6 mm. high forms the side of the mold. The melted fat, after thorough mixing at 50° C., is slowly poured into the mold and allowed to cool. A small label bearing the number of the sample is inserted at the edge of the mold. When thoroughly hardened, the top of the sample is leveled off even with the top edge of the mold with a straight-edged knife. The whole thing is then placed in ice water and after removing the base of the mold the fat disk is forced out of the ring with very slight pressure. A thin sheet of paper moistened and pressed firmly against the base of the mold to remove air bubbles may be used to prevent the sample of fat from sticking to the base as it hardens. Usually 2 or 3

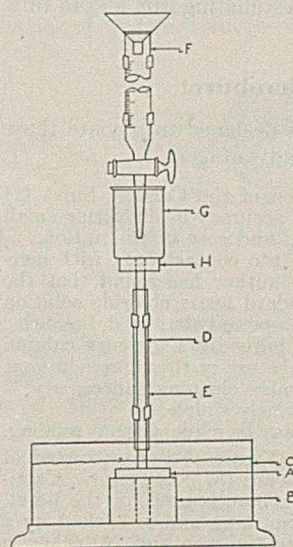
disks are prepared from each sample of fat and kept in ice water overnight or longer. Before the disks are ready for hardness determinations they must be kept for an arbitrarily chosen length of time at the temperature at which the determination is to be made.

Preliminary investigations revealed that the disks soften rapidly during the first 3 or 4 hours when taken from the ice-water bath and placed in the 20° C. bath. After 6 hours very little change in hardness takes place. Since 20° C. has been chosen as the optimal temperature for making these determinations, the disks are kept in a constant-temperature bath held at 20° ± 0.2° C. for 8 hours previous to performing the test. Above 20° C., soft samples of butter fat are difficult to handle; at lower temperatures hard samples tend to crack during the determinations.

The hardness determinations are made with the apparatus sketched herewith.

The fat disk, *A*, 6 mm. thick, is placed over the 9-mm. hole of the cork, *B*, which is cemented to the bottom of the water bath, *C*. The glass rod, *D*, 5 mm. in diameter working in the glass sleeve, *E*, is brought to rest on the disk. The plunger is 19 mm. in length and together with the mercury receptacle, *G*, and its support, *H*, weighs 50.0 grams. Mercury from the 25-cc. buret, *F*, is now run into the 50-cc. beaker, *G*, at a constant rate of 10 cc. per minute. The tip of the buret is approximately 1 cm. above the bottom of the beaker. The flow of mercury is stopped when its weight becomes sufficient to force the plunger through the disk of fat. When this occurs the rubber support, *H*, comes to rest with a sudden thump on the top of the sleeve, *E*. The volume of mercury is determined from the buret readings and its weight calculated.

The entire apparatus can be made of ordinary laboratory equipment. There are no mechanical parts to require special attention or repair. Constant temperatures are easily maintained with two water baths, one at the temperature of a mixture of ice and water and the other close



to room temperature. Hardness is determined at the most desirable temperature from the consumer's standpoint. Only small samples of butter are required for a determination and the number of determinations which can be made with one disk is limited only by the size of the disk. The disks may be remelted and used several times if necessary. Four determinations are usually made with a 4-cm. disk.

TABLE I. HARDNESS OF BUTTER FAT AT TEMPERATURES BETWEEN 18° AND 23° C.

(Hardness is expressed as grams of mercury required to force a plunger measuring 5 mm. in diameter and weighing 50.0 grams through a disk of butter fat 6 mm. in thickness at the temperatures indicated.)

Sample	18.0°	18.6°	19.2°	20.0°	20.6°	21.4°	22.0°	23.0°
	Herd Butter Fat							
1	343	267	206	136	95	51
2	261	216	171	111	70	30
3	270	216	175	127	91	47
4	247	193	148	99	67	34
	Cottonseed-Meal Butter Fat							
1	387	309	248	180	139	90
2	412	320	263	193	148	100
3	383	304	242	173	131	80
4	370	289	229	158	112	63

The following buret readings are typical for a series of determinations made on a sample of butter fat at 20° C.: 9.7, 9.2, 10.1, 10, 9.2, 9.0.

The results of hardness determinations performed at temperatures between 18° and 23° C., on four samples of butter fat produced by cows on standard herd rations and four samples produced by cows on heavy cottonseed-meal rations are given in Table I, and emphasize the importance of accurate temperature control. Furthermore they reveal marked differences in the two types of butter fat; differences which are less apparent in the usual fat-constants. The melting points of the herd butter-fat samples were only 3° or 4° lower than those of the cottonseed-meal butter fat, and differences in the iodine numbers were of the same magnitude.

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RECEIVED October 14, 1935.

Determination of Iron by Titanium Titration and by α,α' -Bipyridine Colorimetry

Improved Analytical Procedure

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SINCE Knecht and Hibbert (4) published their monograph on titanous chloride, an increasing number of biochemists have employed this reagent in various reduction processes. It has been used particularly for the estimation of ferric and ferrous iron in biological materials. This involves a microtechnic using very dilute titanium solutions (5). It therefore becomes increasingly difficult to maintain the reducing agent at constant strength for a reasonable period. In general the reagent has been stored under hydrogen and the titration carried out with apparatus of the type designed by Knecht and Hibbert. Satisfactory results are obtained only when the greatest care is taken in purifying the hydrogen and in sealing the apparatus. The necessity for such extreme precautions has deterred the more general application of this valuable reducing agent and has caused many workers to avoid this method for estimating iron and to turn to colorimetric procedures.

Horizontal Microburet

The buret described below was designed to obviate these difficulties and has the following advantages:

1. It is essentially a modification of the Conway buret (2) and retains its excellent features of accuracy in delivering small volumes, simplicity of construction, and ease of calibration.
2. The titrating reagent comes into contact only with mercury. Under these conditions the author has found that the titer of the reagent against a standard ferric chloride solution remains practically unchanged over a period of at least 4 months.
3. Expelling the fluid from the buret by a mercury column gets rid of a common difficulty in the use of titanium solutions, that of sticking in the buret, and makes cleaning unnecessary.
4. Recharging the buret is extremely simple.
5. A large number of titrations may be made without refilling.

CONSTRUCTION. The apparatus (Figure 1) is constructed of soft glass and mounted on a 3-ply board (87 × 48 cm.). Capillary tubing of approximately 1-mm. bore is used for the buret, *f*, *e*. The buret proper, *f*, is 67 cm. long and is backed by a strip of graph paper, ten squares to the inch and 25 inches in

length. At the left end it is connected by pressure tubing to a small (2 × 5 cm.) mercury reservoir, *d*, and at the right end it is connected by a ground-glass joint to a three-way stopcock, *e*. The mercury reservoir, *d*, is adjustable to a height of 3 cm. above and below the level of tube *f* by means of the rack and pinion, *g*. The buret is connected by a second ground-glass joint to the reagent storage vessel, *a*, which has a capacity of 200 cc. and which in turn is connected by pressure tubing to a leveling bulb, *b*, of approximately the same capacity. The storage flask is painted with two coats of black enamel and set into the board by cutting out a strip. The delivery tube, supported by a bracket (13 × 13 cm.), is drawn out to a fine capillary, the tip of which has a clearance of 16 cm. from the base board (28 × 87 cm.).

The two ground-glass connecting pieces are used to facilitate assembling the apparatus. These unfortunately had hollow bulbs which the author anticipated would be difficult to fill with liquid and which might cause the liquid column to break. A continuous capillary joint was obtained by filling the bulbs (*a*, Figure 2) with sealing wax as follows:

A piece of copper wire of slightly larger diameter than the capillary bore was well smeared with vaseline and inserted through *c* to plug the capillary at *b*. The copper wire was then packed around, and bulb *a* completely filled with finely powdered sealing wax. By gentle heating the sealing wax was melted. The coating of vaseline made possible the withdrawal of the copper wire after the wax had solidified. The surface of the wax was ground with a small carpenter's bit so that the connecting piece, *d*, fit snugly.

CALIBRATION. This was carried out with titanous chloride solution and checked with mercury, weighing in each case the total of five deliveries of the graduated section. The entire graduated portion (250 divisions) had a volume of 0.718 cc.

PREPARATION OF TITANOUS CHLORIDE SOLUTION. Preliminary tests indicated that the most satisfactory thiocyanate end point could be obtained when the strength of the reducing agent was such that approximately 0.25 cc. (87 buret divisions) of the titanous chloride solution just effected the com-

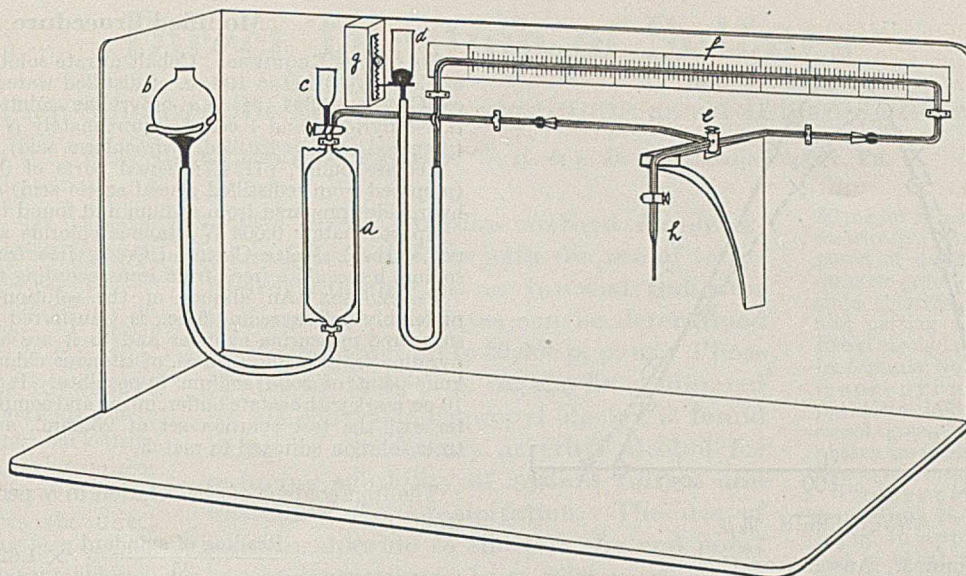


FIGURE 1. DIAGRAM OF APPARATUS

plete reduction of 0.05 mg. of Fe^{+++} in a total volume of 20 cc. An approximately 0.004 *N* titanous chloride solution was prepared as follows:

To 200 cc. of boiling *N* hydrochloric acid a 20 per cent titanous chloride solution was added, so that 0.25 cc. of the mixture just discharges the red color of 10 cc. of a ferric thiocyanate solution containing 0.05 mg. of Fe^{+++} . About 0.3 cc. of the 20 per cent titanous chloride solution is required.

CHARGING THE APPARATUS. The entire apparatus is first filled with mercury. The titanous chloride solution is quickly cooled and transferred to the storage vessel, *a*, through inlet *c* with the mercury level, *b*, lowered. Inlet *c* is sealed with a few drops of mercury. The mercury reservoir, *b*, is returned to its support which is high enough to give a slight positive pressure to the buret side of the apparatus. The stopcock of the storage vessel is turned to join *a* and *c* and by manipulating the three-way stopcock, *e*, with the mercury reservoir, *d*, lowered, the titrating point, *h*, and the buret to the zero point are filled with the reagent. The reagent is obviously discharged from the buret by raising the mercury level in *d*, adjusting stopcock *e* to join *f* and *h*, and using the stopcock on *h* to control the titration.

ACCURACY. The buret described above was constructed of glass tubing of slightly larger bore than that described by Conway. A delivery of 0.1 cc. represented 128 mm. on the graduated tube of his buret, while the same distance on the author's scale represents a volume of 0.145 cc. The error of delivery of the author's buret is, presumably, of similar magnitude to that given by Conway, but it may actually have been considerably lessened by using mercury to expel the fluid. The author has investigated the accuracy of the buret only for the particular purpose for which he wished to use it—namely, for titrating ferric thiocyanate.

A series of ten titrations of a standardized ferric chloride solution was made, employing a titrating vessel of the type already described (5) and carrying out the titration at 50° ($\pm 2^\circ$) with a slow stream of carbon dioxide bubbling through the solution. The volume of the solution was 20 cc. and comprised 10 cc. of the ferric chloride solution containing 0.05 mg. of Fe^{+++} , 5 cc. of 5 *N* hydrochloric acid, 4 cc. of water, and 1 cc. of 40 per cent potassium thiocyanate solution. The thiocyanate solution should not be added until just before commencing the titration. The height of the titration vessel was adjusted so that the tip of the buret was just below the surface of the liquid. The maximum variation in these titrations was equivalent to two buret divisions (0.0057 cc.) and represents an error of 2.2 per cent.

A further series of ten titrations was carried out with vary-

ing amounts of the ferric chloride solution from 1 to 10 cc. and under the conditions just described. The results showed that the same degree of accuracy can be maintained with a dilution of 15 γ of Fe^{+++} in a total volume of 20 cc. In the author's experience greater accuracy is not obtainable by using a more dilute titanous chloride solution or a smaller buret, since the sensitivity of the eye to the thiocyanate end point becomes the limiting factor.

Cobalt Nitrate Solution as a Color Standard

In the study of iron metabolism there is occasional need for an analytical procedure which can be relied upon to estimate amounts of iron of the order of 0.5 γ . Obviously volumetric methods are not applicable. Of the many colorimetric methods devised for this purpose, that recommended by Hill (3) has much to commend it. The many advantages of α, α' -bipyridine as a reagent for the microestimation of iron have been detailed by Hill.

The method has been in use in this laboratory for several years. While the author has confirmed, in every detail, the claims made for the reagent, he has not been entirely satisfied with the method of estimating the intensity of the pink color. Hill's procedure is analogous to that used for the colorimetric determination of pH and consists in preparing a series of standard tubes of varying dilutions of ferrous bi-

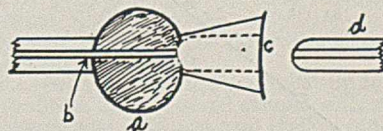


FIGURE 2. CONTINUOUS CAPILLARY JOINT

pyridine which are sealed after passing a small amount of sulfur dioxide through the solution. In the author's experience these color standards are liable to fade, particularly at high dilutions. Their preparation is also a laborious procedure which is not likely to commend itself to those desirous of making a very limited number of iron determinations in the shortest possible time.

When compared in a colorimeter, the color of a cobaltous nitrate solution matches excellently the color of ferrous bi-

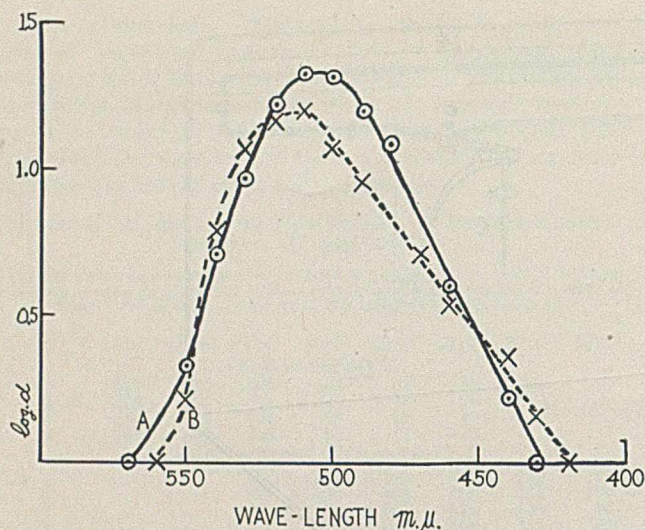


FIGURE 3. ABSORPTION CURVES

A, 2.5 per cent solution of cobalt nitrate
B, ferrous bipyridine solution containing 4.77 γ of iron per cc.

The two solutions were of the same color intensity. The data were obtained with a Bellingham and Stanley direct-reading spectrometer, using 5-cm. tubes and making the density readings with an Ilford wedge.

pyridine. Both solutions show selective absorption in essentially the same region of the visible spectrum (Figure 3). Within a range of iron concentrations from 0.25 to 3.0 γ per cc. the intensity of the pink color of ferrous bipyridine is directly proportional to the amount of iron present (Figure 4) and can be estimated with an accuracy of at least 10 per cent by reading against a cobalt nitrate solution containing 2.5 mg. of Co^{++} per cc. Observed through a thickness of 25 mm., a solution of cobalt nitrate containing 2.5 mg. of Co^{++} per cc. has a color intensity equivalent to that of a ferrous bipyridine solution containing 1.62 γ of Fe per cc.

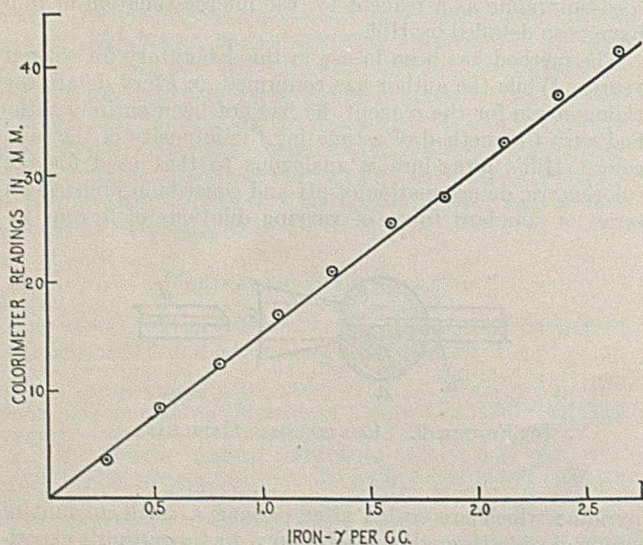


FIGURE 4. PROPORTIONALITY BETWEEN AMOUNT OF IRON PRESENT AND INTENSITY OF COLOR DEVELOPED WITH BIPYRIDINE

Values plotted represent the colorimeter readings in mm. of a cobalt nitrate solution containing 2.5 mg. of Co^{++} per cc. when the test solutions were set at 25 mm. The diagonal line represents the theoretical proportionality between iron present and color produced.

Composition of test solutions: 0.5 to 6.0 cc. of standard FeCl_2 solution containing 5.3 γ of Fe per cc.; 0.25 cc. of approximately 0.004 N TiCl_3 solution; 1.0 cc. of 0.004 M , α, α' -bipyridine. Diluted in each case to 10 cc. with acetate buffer, pH 4.7.

Modified Procedure

SOLUTIONS REQUIRED. Cobalt nitrate solution: 1.235 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100 cc. of distilled water (1 cc. = 2.5 mg. of Co^{++}). 0.004 M α, α' -bipyridine solution: 63.2 mg. of α, α' -bipyridine and 1 cc. of approximately N hydrochloric acid (prepared from redistilled hydrochloric acid) in 100 cc.

Acetate buffer, pH 4.7: equal parts of 0.2 N acetic acid (prepared from redistilled glacial acetic acid) and 0.2 N sodium hydroxide (prepared from sodium and found to contain no iron).

Approximately 0.004 N titanous chloride solution (the product of the LaMotte Chemical Co. is free from iron) or solid sodium hyposulfite freed from iron according to Hill.

PROCEDURE. An aliquot of the solution to be analyzed, preferably not exceeding 5 cc., is transferred to a 10-cc. glass-stoppered measuring cylinder and to it are added 1 cc. of bipyridine solution and 0.25 cc. of titanous chloride solution or a knife-point of solid sodium hyposulfite. It is diluted to the 10-cc. mark with acetate buffer, mixed and compared in a colorimeter with the test solution set at 25 mm., and the cobalt nitrate solution adjusted to match.

The iron content of the solution in γ per cc. is calculated from

$$\frac{\text{Reading of standard}}{25} \times 1.62$$

The colorimetry is most satisfactory within the range of 0.25 to 3.0 γ of iron per cc. If it is found that the color given by the test solution exceeds this limit, the solution should be diluted with acetate buffer and the measurement repeated.

Ferrous bipyridine develops its maximum color in a few minutes only in solutions more alkaline than pH 3.5. If the solution under examination is known to be pH 3.5 or above, the use of the acetate buffer is, of course, unnecessary. Specially pure cobalt nitrate or a particularly high degree of accuracy in preparing the standard solution is unnecessary, as cobalt nitrate solutions do not conform to Beer's law in that a relatively large increase in concentration is necessary to effect much change in the color of the solution.

These modifications greatly simplify a method which, as pointed out by Hill, has many important advantages over other methods proposed for the estimation of iron. The preparation and standardization of an iron solution are now unnecessary. Special purification of the reducing agent may be avoided by substituting titanous chloride for sodium hyposulfite. Furthermore, in the author's experience (5), the colorimetry with ferrous bipyridine with the amounts of iron under consideration is a decided improvement over that with ferric thiocyanate.

Unfortunately, the reagent α, α' -bipyridine is not procurable on the market, but it may be readily prepared from α -picoline according to Blau (1). J. M. Tracy in this laboratory has found that better yields are obtained by precipitating the copper picolinate with a saturated solution of copper sulfate instead of a 1 per cent solution and that more rapid steam-distillation, resulting in better crystallization of the product, is obtained by saturating the crude bipyridine solution with sodium chloride.

Acknowledgment

The author is indebted to George Hunter for many helpful suggestions.

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Direct Titration of Sulfates

Further Studies with Tetrahydroxyquinone as an Internal Indicator

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SCHROEDER (1) recently suggested a direct titration method for sulfates with the use of tetrahydroxyquinone as an internal indicator. A direct titration method of this type offers considerable advantage over other rapid methods where outside indicators, back-titrations, or filtrations are required. The method as described by Schroeder allows the direct titration of sulfate in a sample with a standard barium chloride solution, the end point being indicated by the appearance of the red barium salt of tetrahydroxyquinone. An extensive bibliography on sulfate determinations was given in Schroeder's paper and further reference is not required at this time.

Schroeder suggested the dispersion of the tetrahydroxyquinone with a large amount of potassium chloride to give a dilution that could be readily handled by using a few tenths of a gram of the dry mixture for each determination, this dry dispersion being necessary because the solutions of tetrahydroxyquinone are not sufficiently stable to be added to the sample in this form. This method of adding the tetrahydroxyquinone to the sample was followed in the present investigation. (The prepared tetrahydroxyquinone-potassium chloride mixture has been named by this laboratory THQ and will be referred to as such throughout this paper.)

The method suggested by Schroeder limited the range of sulfate in a 25-cc. sample between 80 and 800 p. p. m. and further suggested the use of equal quantities of ethyl alcohol or alcohol denatured by formula No. 30 or 3-A to reduce the solubility of the barium sulfate and hasten the precipitation, titrating with 0.025 *N* barium chloride in a solution neutralized to the acid side of the phenolphthalein end point. Phosphate was found to be an interfering ion.

It was the aim of this investigation to extend the sulfate range, which was found possible, and to find a diluent that could be used in place of ethyl or denatured alcohol, because of the difficulty of obtaining either the ethyl or the denatured alcohol in many plants, owing to certain government restrictions. Isopropyl alcohol was found to answer this purpose. Elimination of the phosphate ion is desirable and it was found that this ion could be eliminated up to 60 p. p. m. by changing the pH value of the titrating solution to about 4.0.

Experimental

The indicator used throughout this study was manufactured in the Betz laboratory and considerable quantities of this material have been supplied to the field.

Detailed directions are given below for a determination of sulfate by direct titration using THQ as the indicator.

MATERIALS AND REAGENTS. Standard barium chloride solution, the strength varying from 1 cc. = 1 mg. of SO₄ to 1 cc. =

The direct titration method for determination of sulfates with the use of tetrahydroxyquinone as an internal indicator is described. Sulfates can be determined by this method up to 30,000 p. p. m. Phosphates up to 60 p. p. m. can be eliminated by pH control. Isopropyl alcohol is found to be as satisfactory as ethyl alcohol for reducing solubility of barium sulfate and hastening the precipitation. The use of sodium chloride to sharpen the end point in concentrations above 2000 p. p. m. of sulfate is described. Results obtained by this method check gravimetric analyses within an average of 3 per cent. Comparison of results with the Betz-Hellige method is given.

50 mg. of SO₄, standardized gravimetrically. An indicator composed of disodium tetrahydroxyquinone ground with dried potassium chloride in a 1 to 300 ratio, and passing a 100-mesh screen. Ethyl alcohol or alcohol denatured by formula No. 30 or No. 3-A, or isopropyl alcohol. Phenolphthalein indicator and bromocresol green indicator (if phosphates are present). Sodium chloride crystals, c. p.

PROCEDURE A. Carefully neutralize a 25-cc. sample containing up to approximately 2000 p. p. m. of SO₄ with approximately 0.02 *N* hydrochloric acid until just acid to phenolphthalein. The temperature of the sample should be below 35° C. and it is advisable to work between 20° and 25° C. Add either 25 cc. of ethyl alcohol or alcohol denatured by formula No. 30 or No. 3-A or isopropyl alcohol. Introduce the THQ, the amount to be determined from Table I. It is best to use a small

cup to measure the mixture. Swirl the flask to dissolve the THQ; the solution will be colored a deep yellow. Titrate with standard barium chloride solution, the strength to be employed depending on the approximate sulfate content of the sample, in accordance with Table I. Add the standard barium chloride at a steady dropping rate with a constant swirling of the flask until the yellow color changes to a rose. The rose color should appear throughout the body of the solution and not as spots of color. This point is taken as the end point.

TABLE I. THQ REQUIRED FOR VARIOUS SULFATE CONCENTRATIONS

Sulfate Concentrations	Quantity of THQ Indicator	Dippers of THQ Indicator	Strength ^a of BaCl ₂ Solution	Sodium Chloride Crystals Required
P. p. m.	Gram			Grams
Up to 100 ^b	0.1	0.5	1	...
100 to 1000 ^b	0.2	1	1	...
1000 to 2000	0.2	1	4	...
2000 to 4000	0.4	2	10	2
4000 to 10000	0.4	2	10	4
10000 to 20000	0.6	3	50	8
20000 to 30000	0.8	4	50	8

^a 1 cc. = mg. of SO₄.

^b Subtract 0.1 cc. as a blank in titration.

PROCEDURE B (sulfate range from 2000 to 30,000 p. p. m.). Add solid sodium chloride to the sample in an approximate amount as given in Table I. The procedure is the same as in A for neutralization and titration.

PROCEDURE C (with phosphate ion present up to 60 p. p. m.). Carefully neutralize a 25-cc. filtered sample with approximately 0.02 *N* hydrochloric acid until just acid (yellow range) to bromocresol green (approximate pH 4). Follow procedure as in A or B; no correction will be required for the phosphate ion present.

The titration procedure employed was identical with that proposed by Schroeder. The end point is taken as the appearance of rose throughout the body of the solution, and is somewhat similar to a methyl orange end point in alkalimetry. To facilitate observation of the end point, a strong side illumination with a lamp was employed. It was found that because of the quantities of barium sulfate resulting, in higher concentrations of sulfates, either an adsorption of the indicator occurred or the end point was masked. To overcome this difficulty, additional quantities of the indicator

TABLE II. TITRATION OF SODIUM SULFATE

(All titrations were carried out at pH 8.3. 25 cc. of ethyl alcohol, denatured with No. 3-A or 30, were used.)

SO ₄ Present P. p. m.	SO ₄ Found P. p. m.	Error %	THQ Gram	BaCl ₂ Used Cc.
				1 cc. = 1.04 mg. of SO ₄ ^a
20	19.9	-0.5	0.1	0.48
40	37.5	-6.3	0.1	0.90
77.6	74.9	-3.5	0.1	1.80
101	98	-3.0	0.2	2.35
202	204	+1.0	0.2	4.90
404	399	-1.1	0.2	9.60
485 ^b	466	-4.0	0.2	11.20
504	516	+2.4	0.2	12.30
				1 cc. = 4.07 mg. of SO ₄
620	602	-2.9	0.2	3.65
907	904	-0.3	0.2	5.55
1550 ^b	1547	-0.2	0.2	9.50
1605	1612	+0.4	0.2	9.90
2132	2096	-1.7	0.2	12.85
3019	3030	+0.3	0.4	18.00
				1 cc. = 10.49 mg. of SO ₄
2403	2308	-3.9	0.4	5.50
3876	4016	+3.7	0.4	9.57
5426	5509	+1.7	0.4	13.13
5426 ^b	5287	-2.5	0.4	12.60
7558	7343	-2.8	0.4	17.50
9690 ^b	9441	-2.5	0.4	22.50
				1 cc. = 52.45 mg. of SO ₄
10856	11015	+1.4	0.6	5.25
15508	15106	-2.6	0.6	7.20
15508 ^b	15735	+1.4	0.6	7.50
21711 ^b	20980	-3.4	0.8	9.95
34117	32729	-4.0	1.0	15.60

^a 0.1 cc. blank was subtracted from values obtained when 1 cc. of BaCl₂ = 1.04 mg. of SO₄.

^b 25 cc. of isopropyl alcohol.

were added to allow the proper observation of the end point. The character of the color of the end point changed somewhat, owing to the presence of the precipitated barium sulfate, becoming more intense in higher concentrations. The results obtained are presented in Table II.

Isopropyl alcohol was used on some samples as indicated with equally successful results. Standard dippers were employed to measure the THQ indicator, each dipper holding 0.2 gram of the indicator. The results presented in Table II show that the method is applicable for the determination of sulfates up to approximately 30,000 p. p. m. of sulfate or approximately a 3 per cent solution of sulfate. All titrations in the tables are averages of two or more values, none of the volumes of barium chloride used deviating from each other by more than 3 per cent. An arithmetical average of forty-two determinations gave a 2.4 per cent error; twelve results of the forty-two were high, showing that in general results had a tendency to be slightly low. It has been found advantageous to use varying amounts of the THQ depending on the sulfate range in which the determination is being made (Table I).

Several other diluents besides isopropyl alcohol were tried and found unsatisfactory, including diacetone, furfural, formaldehyde, normal butyl and isobutyl alcohol, and acetone. Acetone at first gave some promise but the end point was not as clear as with either alcohol or isopropyl alcohol and results were not as accurate and further work on this diluent was abandoned. Schroeder investigated the effects of ions and mixtures of ions in synthetic solutions and stated that at least 320 p. p. m. of CO₃⁻, 200 p. p. m. of Al⁺⁺⁺, 1020 of SiO₃⁻, 400 of Mg⁺⁺, 200 of Ca⁺⁺, and 200 of OH⁻ could be tolerated without interference with the method. He also stated that PO₄⁻⁻⁻ required excess barium chloride, owing to the insolubility of some barium salt of PO₄⁻⁻⁻, and could be corrected by subtracting a blank from the total titration, the value of the blank depending on the quantity of PO₄⁻⁻⁻ present.

Serious drawbacks to the correction method for phosphate advanced by Schroeder are: (1) the phosphate content must be known and (2) corrections must be made for each strength of barium chloride titrating solution. Schroeder was working with only one strength of barium chloride but this investigation, covering a larger range of sulfate, required several strengths and would therefore require several correction factors for phosphate.

The complete removal of the PO₄⁻⁻⁻ by the aid of metals whose phosphates were insoluble and whose sulfates were soluble was attempted. It was found that other complications, such as the insolubility of oxides and hydrates of the metal and destruction or coloring of the THQ by these other metals and the precise control of the quantity or concentration of the metals required, were insurmountable obstacles for practical application.

Knowing that different barium salts of *o*-phosphoric acid form at different pH values, it was decided to attempt to form a more soluble salt at a lower pH. The following procedure was employed, using bromocresol green as indicator: The sample was neutralized just to the yellow range of the indicator, 25 cc. of alcohol were added and then the THQ. The THQ was stable in such a solution for at least 20 minutes, which is considerably in excess of time to complete the titration in a satisfactory fashion. Solutions with various sulfate and phosphate contents were titrated and it was found that by this procedure up to 60 p. p. m. of PO₄⁻⁻⁻ could be tolerated without interference, and above this value excess barium chloride solution was required to obtain the end point. Table III shows the results obtained by this procedure for elimination of interference by phosphates.

In using this lower pH value, care must be exercised to prevent excess acid being added to the solution, as such will destroy the THQ. Naturally, in titrating, the pH value of the solutions will gradually rise as the standard barium chloride employed has an approximate pH value of 7.0. The color of the titrating medium will therefore change slightly on account of the bromocresol green present, taking on a greenish tinge with a rise in pH value. This can be discharged by a drop or two of the 0.02 N hydrochloric acid. The intensity of the green color was held at a minimum by use of 0.1 cc. of 0.04 per cent bromocresol green, which was found sufficient to observe the neutralization. Where work is conducted continuously at this lower pH value, it might prove advantageous to buffer the barium chloride standard solution at a lower pH.

TABLE III. PHOSPHATE ELIMINATION BY pH CONTROL

(pH 4. 1 cc. of BaCl₂ = 1.04 mg. of SO₄. 0.1 cc. blank subtracted from values when 1 cc. of BaCl₂ = 1.04 mg. of SO₄.)

SO ₄ Present P. p. m.	SO ₄ Found P. p. m.	Error %	PO ₄ Present P. p. m.	BaCl ₂ Used Cc.
98.8	99.8	+1.0	17.6	2.40
98.8	99.8	+1.0	35.2	2.40
98.8	100.8	+2.0	62	2.42
97	108	+11.3	79	2.60
97	114	+17.5	92	2.75
415 ^a	415	0.0	62	3.90

^a 1 cc. of BaCl₂ = 4.07 mg. of SO₄.

Schroeder found that in each titration 0.1 cc. blank should be subtracted. This was necessary only when using the standard barium chloride where 1 cc. of barium chloride equals 1 mg. of SO₄. The only ions giving interference were Fe⁺⁺⁺, Fe⁺⁺, Al⁺⁺⁺, and PO₄⁻⁻⁻ in excess of 60 p. p. m. Iron in both the ferrous and ferric state must be maintained lower than approximately 5 p. p. m. This is not considered a serious drawback to the method, as in boiler waters soluble iron will seldom be found to this extent with higher pH values, most iron being present in the insoluble form. Where iron is present in a sample, it should be removed prior to titra-

TABLE IV. EFFECT OF SINGLE IONS AND OTHER MATERIALS

(pH 4. 25 cc. of isopropyl alcohol used. 0.1 cc. of blank subtracted from values when 1 cc. of BaCl₂ = 1.04 mg. of SO₄. Cl as listed was in excess of Cl as derived from KCl in the THQ prepared indicator.)

SO ₄ Present P. p. m.	SO ₄ Found P. p. m.	Error %	BaCl ₂ Used Cc.	Ion Present P. p. m.
1 cc. of BaCl ₂ = 1.04 mg. of SO ₄ ; 0.2 gram of THQ				
97	98	+1.0	2.40	PO ₄ 62
97	100	+3.0	2.40	Fe ⁺⁺⁺ 6.4
98.8	100	+1.2	2.40	Fe ⁺⁺⁺ 4
98.8	100	+1.2	2.40	SiO ₂ 1500
98.8	98.8	0.0	2.35	Tannin 80
98.8	100	+1.2	2.40	Mg 120
98.8	98	-0.8	2.38	Ca 344
98.8	96	-2.8	2.30	Ca 688
98.8	98	-0.8	2.35	Cl 3920
98.8	133	+34.8	3.20	Cl 15680
1 cc. of BaCl ₂ = 4.07 mg. of SO ₄ ; 0.2 gram of THQ				
1646	1620	-1.6	9.95	PO ₄ 62
1646	1652	+0.4	10.15	Fe ⁺⁺⁺ 8.0
1646	1645	0.0	10.10	Fe ⁺⁺⁺ 5.8
1646	1610	-2.2	9.90	SiO ₂ 1500
1646 ^a	1628	-1.1	10.00	Tannin 80
1646	1669	+1.4	10.25	Mg 1440
1646	1628	-1.1	10.00	Ca 344
1646	1661	+0.9	10.20	Cl 7840
1646	1677	+2.0	10.30	Cl 47040
1 cc. of BaCl ₂ = 52.45 mg. of SO ₄ ; 0.6 gram of THQ				
13160 ^{b,c}	13108	-0.4	6.20	PO ₄ 62
13160	12798	-2.7	6.10	Fe ⁺⁺⁺ 8.0
13160	12798	-2.7	6.10	Fe ⁺⁺⁺ 5.8
13160	13467	+2.3	6.40	SiO ₂ 1500
13160 ^{a,c}	13217	+0.4	6.30	Tannin 80
13160 ^a	12798	-2.7	6.10	Tannin 80
13160 ^{b,c}	12798	-2.7	6.10	Al 6.0
13160	13647	+3.5	6.50	Mg 1440
13160 ^c	13008	-1.2	6.20	Ca 344
13160	13008	-1.2	6.20	Ca 344
14160	12798	-2.7	6.10	Cl 23520

^a 0.5 cc. of bromocresol green used in neutralization because of brown color from tannin.
^b 6 grams of NaCl used in titration.
^c 25 cc. of ethyl alcohol denatured by No. 3-A or 30.

tions, as otherwise the THQ is colored green and destroyed. The results with Al⁺⁺⁺ show that even 6 p. p. m. cannot be tolerated in lower sulfate concentrations. Here again, little difficulty is expected, as soluble Al⁺⁺⁺ is seldom found in appreciable concentrations in boiler waters. In higher sulfate concentrations (about 13,000 p. p. m.) 6 p. p. m. of Al⁺⁺⁺ can be tolerated. It is believed that the sulfate content is only indirectly responsible for this and probably the higher concentrations of the tetrahydroxyquinone required overcome the interference with the Al⁺⁺⁺. Tolerances of the various other ions studied were in general high and in water work at least will exert no influence on the method. SiO₃--- can be tolerated up to 1500 p. p. m., tannin up to 80, Mg⁺⁺ at least 1440, Ca⁺⁺ to at least 344, and higher depending on the sulfate content (one of these two variables determines the tolerance of the other, due to the solubility of calcium sulfate in the system), and Cl⁻ up to 15,000 and higher depending on the sulfate content. Above 2000 p. p. m. of sulfates, sodium chloride can be used advantageously to sharpen the end point (Table V).

The effect of temperature was studied and it was found that the temperature of the sample should be held below 35° C. Higher temperatures destroy the indicator.

It was realized that detection of the end point in this titration might prove difficult for inexperienced or nontechnical operators, and several agents were investigated that might tend to give a more readily discernible end point under all conditions. The use of xylene cyanole, a green dye, was investigated and found to be of no aid in this work. This dye was selected because of its possible application in clarifying the methyl orange end point in alkalimetry work.

In the higher sulfate concentrations, the end point might be termed as somewhat "sliding"—that is, the solution starts to change color before all the sulfate is stoichiometrically precipitated, probably because the increased amount of THQ required promotes the reaction between the indicator

and the barium ion. To eliminate this difficulty, the use of sodium chloride was found advantageous. It has been determined that any agent furnishing sodium ion and not interfering otherwise with the titration could be employed. A small amount of the solid sodium chloride added to the solution where the sulfate concentration was above 2000 p. p. m. not only caused a very rapid change of color at the end point, but considerably increased the accuracy of the determination in this range. However, with sulfate concentrations materially below 2000 p. p. m., high results were obtained, due to a delayed end point. The results in higher ranges with the use of this sodium chloride are presented in Table V.

TABLE V. EFFECT OF NaCl FOR SHARPENING THE END POINT

SO ₄ Present P. p. m.	SO ₄ Found P. p. m.	Error %	BaCl ₂ Used Cc.	NaCl Used Grams
1 cc. of BaCl ₂ = 1.04 mg. of SO ₄ ; 0.2 gram of THQ				
pH 8.3				
97	108	+11.0	2.60	0.5
97	106	+9.0	2.55	0.2
291	408	+4.0	9.80	1.0
1 cc. of BaCl ₂ = 10.49 mg. of SO ₄ ; 0.4 gram of THQ				
3292	3273	-0.6	7.80	2.0
6584	6630	+0.7	15.80	2.0
1 cc. of BaCl ₂ = 52.45 mg. of SO ₄ ; 0.6 gram of THQ				
13160	13113	-0.4	6.25	4.0
19740	19511	-1.2	9.30	4.0
26320	25805	-2.0	12.30	15.0
26320	26015	-1.1	12.40	5.0
32900	32519	-1.2	15.50	5.0
32900	32834	-0.2	15.65	10.0
pH 4				
13160	13113	-0.4	6.25	10.0

0.1 cc. blank subtracted when 1 cc. of BaCl₂ = 1.04 mg. of SO₄. 25 cc. of ethyl alcohol denatured with No. 3-A or 30.

TABLE VI. RESULTS OBTAINED ON ACTUAL BOILER- AND FEED-WATER SAMPLES

Sample	Sulfate Found			Percentage Error Based on Gravimetric	
	Gravimetric	THQ	Betz-Hellige	THQ	Betz-Hellige
1	9.1	9.4	8.7	+3.3	-4.4
2	206	204	205	-1.0	+0.5
3	22	27	21	+22.7	-4.4
4	722	712	700	-1.4	-3.0
5	1461	1458	1400	-0.2	-4.0
6	9833	9492	9700	-3.4	-1.3
7	2315	2277	2250	-1.7	-2.8
8	66	61	67	-7.6	+1.5
9	2193	2214	2150	+1.0	-2.0
10	23602	24337	22500	+3.1	-4.7
11	484	494	455	+2.1	-6.0

Only a few tests were made adding sodium chloride with sulfate concentrations below 2000 p. p. m., but these were sufficient to indicate that a delayed end point producing high results was obtained. The effect of the sodium chloride when a titration is carried at pH 4 and in the presence of various ions was found to give the same results as at pH 8.3.

The final test of the method was obtained by comparing results by titrations of a number of boiler-water samples to results obtained by gravimetric analysis and precipitation as barium sulfate. A comparison of results was also made by the Betz-Hellige method recently proposed (2), this being particularly applicable to accurate sulfate determinations in lower concentrations. As the sulfate content of boiler water samples will not usually run above 2000 to 3000 p. p. m., and it was desired to test above this range, some samples containing a fairly high sulfate content were taken and concentrated by evaporation.

Fairly good agreement was obtained throughout the range, the percentage error being greater in the lower concentrations. Below 100 p. p. m., greater accuracy will be obtained by the Betz-Hellige method, while in the higher concentrations, the

tetrahydroxyquinone gives the better result. Results can be expected to check with gravimetric with an average of about 3 per cent error.

TABLE VII. ANALYSIS OF SOLUTIONS USED

Sample	Total Hardness	Cl		HCO ₃		CO ₃		OH		Dis-solved Solids		Fe	SiO ₂	PO ₄	pH	
		P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.					
1	24	4	14	57	6.7	
2	40	72	56	40	700	10.9	
3	58	12	60	6.9	
4	12	224	..	216	72	2208	0.5	30	ii	11.1	
5	2	496	..	448	156	4432	11.5	
6	0	1408	..	2552	320	19330	1.5	4	0	0	11.9	
7	2	116	..	116	762	5700	0.5	6	0	0	11.9	
8	88	12	29	6.9	
9	0	254	..	152	540	5932	0.5	19	25	11.9	
10	Analysis about same as No. 9.										SO ₄ increased by Na ₂ SO ₄	
11	13	190	..	264	62	57	11.1	

During the past 3 months over 5000 water samples have been analyzed in the Betz laboratories employing the tetrahydroxyquinone method for the sulfate determination. Over ten operators are employed in this work and no difficulty has been experienced with this method.

Conclusions

The tetrahydroxyquinone method for sulfate determination has been shown to be accurate up to approximately 30,000 p. p. m. or a 3 per cent solution of SO₄. Isopropyl alcohol can be used with equally accurate results in place of ethyl alcohol for lowering the solubility of the barium sulfate and hastening the precipitation. The phosphate ion, up to 60

p. p. m., can be tolerated by adjusting the pH value of the sample before titration to approximately 4.0 with the aid of bromocresol green as an indicator. With the exception of iron and aluminum, other ions normally present in boiler feed waters give no difficulty. It was found that solid sodium chloride could be used to advantage to sharpen end points with sulfate concentrations above 2000 p. p. m. A comparison of gravimetric, tetrahydroxyquinone, and Betz-Hellige methods on boiler-water and boiler-feed samples shows that acceptable results in all concentrations were obtained. It is believed that this method of sulfate determination will have possible application in determination of sulfates in fuel, cement, rubber, and numerous other fields.

Acknowledgment

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Determination of Sulfate

An Attempt to Determine Sulfate by Titration with Lead Nitrate, Using Eosin as Indicator

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THIS is a report of an attempt to titrate sodium or potassium sulfate directly with standard lead nitrate solution, using eosin as indicator. The work arose from a problem of analysis in the phase-rule study of certain systems involving sulfates, in which it was desired to find a rapid method for the direct determination of the sulfate.

A titration with lead nitrate in the presence of some potassium iodide as internal indicator, using the appearance of the yellow lead iodide as the end point, was attempted first; after considerable work on this method, it was given up as impracticable. The writer then learned that the method had been suggested as far back as 1853 by Levol (8), and subsequently by several other chemists since that date (5, 10, 12), and that the same conclusion had been reached as to its inadequacy by other investigators who examined the method (7, 9, 11). (Levol was also the first to announce, in 1853, this type of titration even for chloride, using the appearance of yellow silver phosphate as the end point, instead of silver chromate, in an otherwise typical "Mohr" titration.) The use of potassium iodide paper as an external indicator for this titration is known as Pappenheim's method (11), and although it was criticized as impracticable by Mohr (11), Vinogradov (18) as recently as 1935 found it the best of the volumetric methods for the determination of sulfate by means of lead salts. The only other applications of lead salts in the volumetric determination seem to be in certain electrometric methods (14, 20), and in indirect methods, in which the sul-

fate is precipitated with an excess of lead nitrate (13) or lead acetate (4), and the excess of lead salt is titrated by chromate or molybdate, respectively. Roy (15), suggesting the titration of lead by means of sulfate with fluorescein as external indicator, mentions the possibility of using such a titration for the indirect estimation of sulfate. Apparently, however, no method has yet been suggested for the direct titration of sulfate with lead salts by means of an adsorption indicator. The reader is referred elsewhere for reviews of the volumetric methods for sulfate, most of which involve the use of barium chloride as standard solution (1, 16).

Suggested Method

The present method makes use of eosin as an internal indicator for the direct titration of sodium or potassium sulfate with standard lead nitrate solution. The end point is indicated by the appearance of the red lead salt of eosin, C₂₀H₇Br₄O₅Pb (2), bringing about a change from the yellowish flesh color of the mixture of precipitate and solution to a light but distinct pink-red. The following solutions were used:

The sodium and potassium sulfate solutions were prepared from c. p. anhydrous salts, and standardized by evaporation to dryness at 250° C. and direct weighing of the residue. Strengths used were from 0.1 M to 0.32 M.

The lead nitrate solutions, also prepared from c. p. reagent material, were standardized by treating a measured volume with a known weight of pure potassium iodate, filtering off the pre-

precipitate of lead iodate and determining the excess potassium iodate by adding excess of potassium iodide and sulfuric acid to the filtrate and titrating the liberated iodine with sodium thiosulfate solution previously standardized against the same pure potassium iodate. The values so obtained were checked by repeating the procedure, using pure potassium chromate instead of potassium iodate, and also by the gravimetric method of precipitating and weighing lead chromate. Another method used for standardizing the lead nitrate solution was evaporation to constant weight at 85° to 90° C.

The indicator solution was a 0.5 per cent solution of eosin Y, $C_{20}H_6Br_2O_5Na_2$, in water.

The results given in A, Table I, and in Table II are from a series of titrations of 0.1 *M* sodium sulfate with 0.1 *M* lead nitrate, using 12 drops of indicator, the procedure being as follows:

The sodium sulfate solution (from 6 to 20 cc.) is measured by buret into a 250-cc. Erlenmeyer flask, enough water being added, if necessary, to bring the total volume at the end point of the titration to 30 cc. After the addition of 12 drops of indicator, the lead nitrate solution is run into the flask drop by drop, with vigorous shaking. When a certain amount of lead sulfate has been precipitated, as by the addition of 2 to 3 cc. of the lead solution, the whole mixture is something between yellow and flesh color. Each drop of the lead solution causes a red coloration which disappears into the comparative yellow color of the mixture on shaking and mixing. The end point is the appearance and persistence of a distinct pink throughout the mixture. It is most important that the titration be finished very slowly and with vigorous shaking to insure the re-solution of the red lead-eosin salt formed by each drop added as the end point is approached.

The best results are obtained with the use of a reference color, with approximately the same amount of lead sulfate in it as will be present in the sample being titrated, prepared by mixing equivalent volumes of the lead nitrate and sodium

sulfate solutions, with the same amount of indicator and in the same total volume. With some practice, however, the end point is distinct enough even without a reference color. The results summarized in Table II were obtained some with and some without such a reference; out of 72 titrations, 7 gave bad results and were omitted in making up this table.

Effect of Variations

Owing, of course, to the relatively high solubility of lead sulfate and to the properties of both the eosin solution and the lead-eosin compound formed, the end point of such a titration will be markedly affected by changes in conditions, such as total volume, presence of foreign salts, etc. Some study was made of the effect of the variations of these factors with the following results:

TOTAL AMOUNT OF SULFATE THAT CAN BE TITRATED. The best range is from 0.1 to 0.15 gram of SO_4^{--} ; the maximum amount is about 0.2 gram, the equivalent of about 18 to 20 cc. of 0.1 *M* lead nitrate solution. Beyond this the titration is too doubtful. The quantity of precipitated lead sulfate becomes so great as to obscure the color change required for the end point.

TOTAL VOLUME AT END POINT. In the titrations reported in Table II, the total volume at the end point was 30 cc. in each case, except where the sum of the two solutions themselves amounted to more. If the final volume is much above 30 cc., the colors are diluted too much, so that it is again difficult to detect the end-point change. However, some variation is possible. Thus, with 40 cc. as the final volume, 10 titrations (with no omissions), using in each case about 15 cc. of the 0.1 *M* lead nitrate solution and with no foreign salts present, gave a relative error of 0.4 per cent as an absolute average and +0.11 per cent as the algebraic average, with extremes of -0.5 and +0.7 per cent. Some of these results are listed in Table I, B.

STRENGTH OF TITRATING SOLUTION. In the present work various concentrations of the lead nitrate were tried as titrating solutions, from 0.1 *M* to 0.5 *M*. The best results as a whole (most widely applicable and reproducible) were obtained with 0.1 *M* lead nitrate, the results for which are reported in Table II. If a stronger solution of lead nitrate is used in titrating, although the end point is sharper, the relative errors remain the same, since the total amount of sulfate that can be titrated also remains the same as with the 0.1 *M* solution—that is, a maximum of the equivalent of 8 to 9 cc. of 0.2 *M* solution. With 19 runs using 0.2 *M* solution, with a total volume at the end point of 30 cc. again, the average absolute error was 0.47 per cent, and the algebraic average error +0.23 per cent.

INDICATOR TO BE USED. The quantity of indicator recommended, 12 drops of 0.5 per cent eosin, was also determined by experiment, and is intended for the amounts of sulfate indicated in Table II. For smaller amounts of sulfate it is better to use proportionately less indicator, and a proportionately smaller final volume at the end point.

EFFECT OF ALCOHOL. It was hoped that alcohol, through its effect on the solubility of lead sulfate, might cause the end point to be sharper, an effect found by Nikaido (12) in the attempt to use potassium iodide as indicator in the titration of sulfate with lead nitrate. In the present method, however, because of its effect on the color of eosin solution and apparently also on the solubility or stability of the lead-eosin compound, alcohol in amounts greater than 3 to 4 per cent is found to interfere, delaying the end point so much that the titration becomes impossible. With smaller amounts of alcohol, while there is no appreciable interference there is at the same time no improvement in the titration.

EFFECT OF DEXTRIN. The addition of dextrin as a protective colloid was also tried, inasmuch as the color to be ob-

TABLE I. RESULTS OF TYPICAL TITRATIONS
(Using 0.1 *M* lead nitrate)

	Total Volume Cc.	Foreign Salts Grams	Na ₂ SO ₄ Present Gram	Na ₂ SO ₄ Found Gram	Error Gram	Per Cent Error
A	30	None	0.0878	0.0881	+0.0003	+0.3
	30	None	0.0910	0.0909	-0.0001	-0.1
	30	None	0.1341	0.1339	-0.0002	-0.2
	30	None	0.1594	0.1588	-0.0006	-0.4
	30	None	0.1610	0.1613	+0.0003	+0.2
	30	None	0.1751	0.1745	-0.0006	-0.3
	30	None	0.1778	0.1781	+0.0003	+0.2
	30	None	0.2104	0.2098	-0.0006	-0.3
	30	None	0.2661	0.2673	+0.0012	+0.5
	B	40	None	0.2185	0.2184	-0.0001
40		None	0.2186	0.2192	+0.0006	+0.3
40		None	0.2201	0.2214	+0.0013	+0.6
40		None	0.2185	0.2174	-0.0011	-0.5
C	30	NaClO ₃	0.1762	0.1768	+0.0006	+0.3
	30	1.0	0.1762	0.1767	+0.0005	+0.3
	30	1.5	0.1732	0.1723	-0.0009	-0.5
	30	2.0	0.1766	0.1769	+0.0003	+0.2
D	40	0.2	0.2185	0.2198	+0.0013	+0.6
	40	0.6	0.2202	0.2207	+0.0005	+0.2
	40	0.6	0.2214	0.2222	+0.0008	+0.4
E	30	NaNO ₃				
	30	0.1	0.1743	0.1744	+0.0001	+0.1
	30	0.5	0.1773	0.1777	+0.0004	+0.2
	30	1.0	0.1763	0.1767	+0.0004	+0.2
	30	0.05 NaCl	0.2215	0.2215	0.0000	0.0
	30	0.02 KI	0.2143	0.2140	-0.0003	-0.1

TABLE II. TITRATION OF 0.1 *M* Na₂SO₄ WITH 0.1 *M* Pb(NO₃)₂

(No foreign salts, total volume 30 cc.)	
No. of runs	65
Na ₂ SO ₄ titrated, grams	0.08 to 0.28
Pb(NO ₃) ₂ used, cc.	6 to 20
Errors, grams of Na ₂ SO ₄ :	
Extremes	-0.0012 to +0.0015
Absolute average	0.00055
Algebraic average	-0.00004
Errors, per cent of Na ₂ SO ₄ :	
Absolute average	0.33
Algebraic average	-0.03

served is always that of the mixture of precipitate and solution, but again with no improvement; small amounts do not interfere, while larger amounts cause the end point to appear too soon.

EFFECT OF ACIDITY. The solution must be neutral. The slightest quantity of free acid or base interferes with the normal operation of the indicator. Perhaps a neutralizing buffer could be found which would make the titration possible in such cases, but this was not attempted in this work.

EFFECT OF FOREIGN SALTS (Table I, C, D, E). The effect of certain added salts was also studied, and it was found that potassium and sodium chlorate would not interfere if not more than 1 to 2 grams were present. Thus, with from 0.1 to 2.0 grams of sodium chlorate present, in 27 titrations involving 11 to 16 cc. of 0.1 *M* lead nitrate, the relative error found was 0.35 per cent as absolute average, and +0.29 per cent as the algebraic average, with extremes of -0.2 to +0.8 per cent. Up to 1 gram of sodium or potassium nitrate did not interfere: Using 0.1 to 1.1 grams of sodium nitrate in 11 runs requiring from 12 to 15 cc. of the 0.1 *M* lead nitrate solution, the algebraic relative error was +0.32 per cent with extremes of -0.2 to +0.9 per cent. A few tests also showed that 0.05 gram of sodium chloride and 0.02 gram of potassium iodide likewise did not interfere: errors: 0.0, 0.1 per cent. Finally, in experiments with the stronger titrating solution (0.2 *M*) the effect of added salts was found to be about the same as with the 0.1 *M* solution.

In these titrations with foreign salts present, the reference color used in each case was that for a mixture containing approximately the same quantity of the foreign salt.

Conclusion

In comparison with certain other similar methods recently suggested for the direct titration of sulfate, the method is similar in principle to that of Schroeder (titration with barium chloride, with tetrahydroxyquinone as internal indicator, 16) and to that of Strebinger and Zombory (an indirect method using sodium rhodizonate as indicator, 17). Schroeder's method applies to quantities of 2 to 20 mg. of sulfate, while the eosin-lead nitrate titration works best for much larger quantities. (Ampt, 1, reports no success in attempts to repeat Schroeder's procedure.) Batchelder and Meloche (3) have reported experiments on the titration of sulfate with barium chloride, using methyl red as a hydrolytic adsorption indicator, with a relative error of 3 per cent in the titration. The method of Wellings (19), in which sulfate is precipitated with standard barium hydroxide in the presence of Mg^{++}

or Mn^{++} and with fluorescein as adsorption indicator, involves an average relative error, in the published results, of =0.45 per cent in 13 analyses. This is about the same as the error in the procedure here reported, and although Wellings' method appears to have a wider applicability, the end point, according to Iyer (6), is not sharp, and becomes "very indistinct" in the presence of potassium chloride and potassium nitrate.

Summary

From 0.10 to 0.25 gram of sodium sulfate may be determined by direct titration with 0.1 *M* lead nitrate solution in a total (final) volume of 30 to 40 cc., using 12 drops of 0.5 per cent eosin as indicator. The solution to be titrated must be neutral. The best results are obtained in the titration of about 0.15 to 0.20 gram of sodium sulfate and with the use of a reference color. The determination is then accurate to about 0.0005 gram of sodium sulfate. The presence of 1 gram of alkali nitrate or 2 grams of alkali chlorate does not interfere.

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Gravimetric Determination of Selenium in Alloy Steel Copper Chloride-Perchloric Acid Method

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SELENIUM, like sulfur (2), may be separated from alloy steels by solution of most of the iron, chromium, nickel, etc., in copper-potassium chloride reagent. The method of attack (1) has been by (1 to 1) hydrochloric-nitric acid. Perchloric acid is added, the solution is fumed, cooled and diluted, and the silica is filtered off. The filtrate is made 30 per cent acid by volume with hydrochloric acid, sulfurous acid is added in excess, and the selenium is thus separated and filtered off on a Gooch, dried at 105° C., and weighed.

Copper Chloride Method

Transfer 5 grams of the steel (up to 0.4 per cent of selenium) to a 600-cc. beaker, and add about 500 cc. of the copper chloride. Place the beaker on a steam bath and stir frequently. With electrical stirring the sample is dissolved in less than 45 minutes. Filter the precipitate on paper and wash with hot water, then return the paper to the beaker. The paper contains all the carbon, sulfur, and selenium, but only portions of the iron, chromium, and silica. Add 10 cc. of the zinc oxide-nitric acid solution, 50 cc. of water, and 15 cc. of perchloric acid and evaporate the solution to perchloric acid fumes. Formation of chromic

acid indicates sufficient heating. Cool the beaker, add 50 to 60 cc. of water with shaking, and boil out the chlorine. Filter off the silica and wash with hydrochloric acid (1 to 1) and water. The volume of the filtrate is 100 to 125 cc. Add 100 to 125 cc. of concentrated hydrochloric acid and 100 cc. of strong sulfurous acid. Heat the beaker on a steam bath for 3 hours, then cool. Filter the selenium on a Gooch, wash with hydrochloric acid (1 to 1), then water. Dry the crucible at 100° C., then weigh, ignite, and weigh again. The loss in weight is selenium.

SOLUTIONS. Zinc oxide-nitric acid reagent: 200 grams of zinc oxide sifted into 1 liter of concentrated nitric acid. Copper chloride reagent: 500 grams of $(KCl)_2 \cdot CuCl_2 \cdot 2H_2O$, 100 cc. of hydrochloric acid, and 2000 cc. of water.

The advantages of the copper chloride solution method are:

The bulk of the silica is removed in the first filtration, so that only a small amount of silica need be washed for selenium as compared to the large amounts of gelatinous silica in the acid attack method.

In the precipitation of the selenium, only about 1 gram of possible contaminants is likely to be present as compared to 5 grams in the acid attack method.

While an extra filtration is required, less attention is needed, and less time is required for fuming and for acid treatment.

TABLE I. SELENIUM DETERMINATIONS

Sample	Selenium Found	
	Acid solution %	Copper chloride %
1	0.25, 0.26 ^a	0.26, 0.26
2	0.38, 0.37 ^b	0.38
3	0.35, 0.36 ^b	0.38
4 ^c	0.26, 0.26, 0.26, 0.26, 0.25
5 ^c	0.32

^a Contractor, 0.24 per cent selenium.

^b R. C. Coburn, chief chemist, Navy Laboratory, Munhall, Pa.

^c Contractor, 0.31 per cent selenium.

Table I gives data on check determinations. Small size of samples prevented more extensive checks.

Summary

Both sulfur and selenium are successfully separated from alloy steels by the copper chloride solution method. The method has several advantages over the aqua regia solution attack.

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Detection of Rhenium in the Sodium Carbonate Bead

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THE blowpipe reactions of rhenium have been investigated by Geilmann and Wrigge (2), who conclude that 0.05 per cent of the metal can be detected by heating a 10-mg. concentrate in an open tube, reducing the sublimate with sulfur dioxide, and observing the color of the deposited film. They also describe the behavior of the element in beads of molten borax, in anhydrous sodium thiosulfate, and in a mixture of sulfur and sodium carbonate, in all of which the rhenium salts form black dispersions or films of either the metal or the sulfide. The fact that manganese compounds produce a characteristic green coloration with fused sodium carbonate suggested that salts of the homologous element, rhenium, might also produce a color reaction in the sodium carbonate bead that would be serviceable in the identification of the metal.

On fusing a minute fragment of potassium perrhenate with anhydrous sodium carbonate, the bead assumes a black color which persists for about 1 minute, measured from the time of the disappearance of the initial red glow. The color of the bead then changes to yellow, the intensity of which slowly diminishes and disappears entirely at the end of about 10 minutes. Reheating the colorless bead in the flame, the same set of color transformations is observed. The formation of the black bead was also observed by Geilmann and Wrigge, who employed a mixture of sulfur and sodium carbonate as the flux.

The color changes, black-yellow-white, are given by rhenium compounds when the bead is heated either in the Bunsen flame or in the oxidizing or reducing flames produced with the blowpipe. The intensity is not influenced by the addition of oxidizing agents like potassium nitrate or chlorate, as is the case with the green manganate compound formed under the same conditions.

The yellow color of the bead is not due to sodium rhenate,

Na_2ReO_4 , as might be expected from the similar reaction in the case of manganese, for that compound possesses a green color and is unstable at high temperatures (?). Since the color of the rhenium bead is the same in both the oxidizing and reducing flames, it would seem that the formation of the yellow compound is not attended with a change in valence. I. and W. Noddack have observed that when potassium perrhenate is fused with sodium hydroxide in the presence of excess air, a yellow-colored compound is formed in which the rhenium possesses the same valence as in the original perrhenate salt, and have demonstrated that the yellow salt thus formed is sodium mesoperrhenate, Na_2ReO_5 . As this compound is readily decomposed by water into sodium perrhenate and sodium hydroxide, so that on reheating the yellow mesoperrhenate can again be formed, it seems probable that the yellow bead formed in this test owes its color to the formation of sodium mesoperrhenate.

When present to a predominating extent, manganese hides the color reactions produced by rhenium in the bead. The presence of the element can be established in mixtures, provided the manganese content is less than 50 per cent of the sample, by heating the bead in the reducing flame of the Bunsen burner, or preferably that of the blowpipe flame. Under these conditions the green manganate compound is not formed, thereby permitting the observation of the yellow color due to the rhenium compound, which is formed in both the oxidizing and reducing flames.

Of the elements which form colored melts with sodium carbonate, only chromium is apt to be mistaken for rhenium. The yellow bead formed by sodium chromate can be differentiated from that formed by rhenium in that the color imparted by the latter is not permanent and fades shortly after its formation. The compounds of tungsten and molybdenum do not interfere with the color reactions of rhenium in the

sodium carbonate bead, as in the presence of this flux they form colorless melts. Molybdic acid imparts a transitory black color to the bead, which disappears as the bead melts and remains colorless on cooling. The yellow coloration due to rhenium can plainly be observed with samples of sodium tungstate and molybdate that contain 1 per cent or more of potassium perrhenate.

Sensitivity of the Reaction

The characteristic color changes are readily discernible when 1 mg. of potassium perrhenate is fused into a bead of sodium carbonate weighing 30 mg. With smaller quantities, the initial black coloration is not visible, but the yellow color of the bead can be observed, though the transformation to the colorless stage is much more rapid, as can be seen from Table I.

To establish the minimum quantity of rhenium that can be detected in the bead, calibrated platinum spirals were dipped into solutions of known rhenium content, and the solvent was carefully evaporated by holding the wire about 5 cm. (2 inches) above a microflame. This process deposited on the wire rhenium salts whose weight could be approximated from the concentration of the solution and the capacity of the spiral. When the evaporation was completed the coil was dipped into sifted anhydrous sodium carbonate and heated in a small Bunsen flame until the salt fused.

The spirals are conveniently made by winding several turns of No. 30 platinum wire on a glass rod or other circular form 1 to 2 mm. in diameter and mounting the coil in a glass rod. The spiral is calibrated by dipping the clean wire while hot in distilled water and measuring its increase in weight. The volume of water or solution picked up by the coil varies with the number of turns and will remain constant, even after many operations, provided the wire is kept clean and the sodium carbonate is removed by solution in dilute hydrochloric acid. Repeated tests on a spiral having a capacity of 0.0033 cc. did not show a greater variation in volume than 5 per cent. This method of securing minute weighed samples was first described by Truchot for use in the study of flame spectra (8).

The described method of bead formation was adopted, in preference to the standard procedure of placing the sample on a fused bead, because its use minimizes the loss of material during weighing and as a result of decrepitation in the flame. The method has the further advantage that by building the bead with successive additions of sodium carbonate, traces of a metal left on the wire by the evaporation of the solution impart a deep color to the initial minute bead, thereby rendering detection more certain. The sodium carbonate is sifted so as to avoid rubbing off any of the sample deposited on the wire.

Observations were made first on a solution of pure rhenium metals, standardized by dissolving a weighed quantity of the element in 8 M nitric acid and neutralizing the excess acid by the addition of sodium carbonate, and checked by a second solution containing potassium perrhenate. The results recorded in Table I show that a minimum of 0.015 mg. of rhenium can be detected in the absence of other heavy metals through the formation of a yellow bead and the slow disappearance of its color.

TABLE I. DETECTION OF RHENIUM IN SODIUM CARBONATE BEAD

Concn. of Standard Solution Mg./cc.	Volume Cc.	Rhenium Mg.	Color of 10-Mg. Na ₂ CO ₃ Bead	Per- sistence Sec.
50 Re	0.0033	0.165	Deep yellow	65
10 Re	0.0033	0.033	Yellow	15
5 Re	0.0031	0.016	Faint yellow	10
15.3 KReO ₄	0.0033	0.030	Yellow	15
7.6 KReO ₄	0.0033	0.015	Faint yellow	10
12 KReO ₄	0.0008	0.006	Faint yellow ^a	15

^a Color visible only in a 2-mg. Na₂CO₃ bead.

Similar observations were made with manganese salts in order to obtain data for a comparison of the relative sensitivity of the bead test for the two metals. Table II reveals that, in the absence of other metals, 0.0008 mg. of manganese can be detected in a bead of sodium carbonate weighing 10

mg. That the limit for rhenium, 0.015 mg., is not of the same order of magnitude can be attributed to two factors: (1) that the transformation to the mesoperrhenate in the sodium carbonate melt is not quantitative, and (2) that the eye is more sensitive to green light than to yellow.

TABLE II. DETECTION OF MANGANESE IN SODIUM CARBONATE BEAD

Concn. of Standard Solution Mg./cc.	Volume Cc.	Manganese Mg.	Color of 10-Mg. Na ₂ CO ₃ Bead
2.94 KMnO ₄	0.0034	0.0035	Emerald green
1.47 KMnO ₄	0.0033	0.0017	Green
0.74 KMnO ₄	0.0033	0.0008	Grayish green
0.37 KMnO ₄	0.0034	0.0004	Very faint green ^a
3.00 MnSO ₄	0.0054	0.0060	Deep green
0.30 MnSO ₄	0.0078	0.0009	Grayish green
0.30 MnSO ₄	0.0033	0.0004	Very faint green ^a

^a Color visible only in a 2-mg. Na₂CO₃ bead.

Tests were made on the detection of minute quantities of rhenium in the presence of the other elements with which it is commonly associated. It was found that in a mixture of 1 part of manganese and 3 parts of rhenium the manganese did not interfere with the detection of 0.05 to 0.1 mg. of rhenium provided the bead was heated in the reducing flame. Also, 0.025 mg. of rhenium can be detected in a 3-mg. sample of either sodium tungstate or molybdate. A single crystal of cesium perrhenate, as formed under the conditions of the microscopic test for rhenium (1), transferred to a platinum loop and fused with sodium carbonate, gave a yellow bead the color of which persisted for 0.5 minute.

The bead test for rhenium cannot be applied directly to mineral specimens, as even its richest ore, molybdenum glance, seldom contains more than 0.004 mg. of the element per gram (6). The reaction is serviceable in confirming the presence of the metal in the salts crystallized for the microscopic identification of the element, such as cesium and rubidium perrhenates (1) or cesium iodorhenate (5), and in testing concentrates obtained by analytical processes in which the rhenium is systematically separated from the other elements (4).

Summary

Rhenium can be distinguished from the other elements by the formation of a transitory yellow sodium carbonate bead. The reaction is observable with 0.015 mg. of the metal when the bead is heated in either the oxidizing or the reducing flame, and is not interfered with by the presence of tungstates or molybdates. The test can be applied in the presence of small quantities of manganese by heating the bead in the reducing flame.

Acknowledgment

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Rotenone Determination by Colorimetric Methods

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JONES and Smith (2), realizing the necessity for a sensitive colorimetric test for rotenone, modified the Durham qualitative reaction in an attempt to render the blue color more lasting. The modification, although a sensitive qualitative test, failed to make the color permanent enough for quantitative work. Gross and Smith (1) discovered a red color reaction which they developed into an accurate colorimetric test, but the test was limited to rotenone in acetone solution. Because of the restriction to acetone solution, difficulties were encountered in applying this test to liquid insecticides having refined kerosene bases. The Jones-Smith-Durham test was found useful for detecting rotenone in some liquid insecticides but it failed in several cases when rotenone was known to be present. One substance which interfered with this test was the oil of sassafras.

In the search for a more universal test, the authors found that rotenone in the presence of hydrochloric acid and certain phenols developed color reactions in certain organic solvents. These reactions varied from violet-red to deep blue in color, depending upon the solvent and phenol selected. The organic solvents used were chloroform, ethylene dichloride, carbon tetrachloride, ether, alcohol, and acetone. Phenol and some of the homologs of phenol, such as guaiacol and thymol, also reacted similarly in the solvents named. Small amounts of hydrogen peroxide, nitric acid, and light exerted a marked influence in accelerating the reaction. Isorotenone gave a blue color. Acetylrotenone gave no characteristic color within an hour, but upon standing for several hours a blue-violet color developed.

The advantages of the tests developed over the older methods are its increased sensitivity, making possible an accurate quantitative test satisfactory within the limits stated, and the fact that substances usually found in insecticides do not interfere with the reaction. Some samples of commercial rotenone gave results approximately 15 per cent higher than the known rotenone content. Gross and Smith (1) obtained similar results with their test, which they attributed to the presence of deguelin or some unidentified compounds. The difference in color observed in the detection of rotenone and certain rotenone derivatives may be used as a future basis for investigation in differentiating such substances, as well as serving as an identity test upon comparison with known standards.

A qualitative and two quantitative tests were developed which were not interfered with by substances usually found in proprietary liquid insecticides containing extracts of pyrethrum flowers, aliphatic thiocyanates (Lethane), or oil of sassafras.

The following qualitative test is sensitive to 0.01 mg. of rotenone per ml.:

Dilute 1 to 2 ml. of the insecticide or solution containing rotenone to 5 ml. with chloroform. Add 5 ml. of a chloroform solution of thymol (10 grams of thymol to 100 ml. of chloroform). Add 3 ml. of a nitric acid-hydrochloric acid mixture (0.2 ml. of

concentrated nitric acid to 100 ml. of concentrated hydrochloric acid). Agitate for about 30 seconds. A bluish green to blue color appears when rotenone is present. The color usually appears in from 30 seconds to 2 minutes and deepens on standing. In the presence of the yellow coloring matter of pyrethrum flowers and of derris extract, the color is green and turns upon standing to a bluish green and finally to blue.

Two quantitative tests were developed. No. 1 can be applied to almost colorless liquid insecticides, such as those which contain rotenone and aliphatic thiocyanates (Lethane). If the insecticide base is a refined kerosene, an amount of refined kerosene equal to the amount of liquid insecticides used in the test must be added to the standards.

TEST 1. To 10 ml. of a chloroform solution containing from about 0.05 to 2.5 mg. of rotenone per ml. in a glass-stoppered cylinder, add 10 ml. of a chloroform solution of thymol (10 grams of thymol to 100 ml. of chloroform) and 2 ml. of a reagent made by adding 2.5 ml. of 3 per cent hydrogen peroxide to 100 ml. of concentrated hydrochloric acid. Agitate for 1 minute, loosen the glass stopper, and expose the cylinder to the intense radiation of a quartz mercury vapor lamp having a minimum output of 1000 microwatts per square centimeter in the field of exposure. (The use of bright sunlight produced similar results in approximately 3 hours.) A greenish blue color begins to appear in the chloroform layer in about 15 minutes. At the end of 30 minutes, compare with standards containing known quantities of pure rotenone prepared at the same time in the same manner. When the rotenone sample is not in solution in a hydrocarbon base, concentrated hydrochloric acid may be used in place of the reagent described.

TEST 2. To 5 ml. of an acetone solution containing from 0.1 to 2.0 mg. of rotenone per ml. in a glass-stoppered cylinder, add 5 ml. of an acetone solution of thymol (10 grams of thymol to 100 ml. of acetone), 0.1 ml. of 3 per cent hydrogen peroxide, and 5 ml. of concentrated hydrochloric acid. A reddish violet color appears within 30 seconds. After 1 minute place the glass container in a water bath at about 20° C., and at the end of 20 minutes compare with rotenone standards, similarly prepared, at the same time.

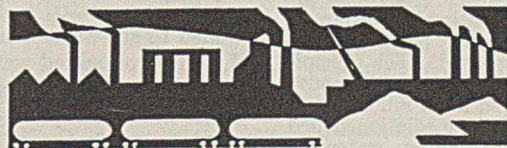
When the liquid insecticide contains pyrethrum and rotenone (not derris extract) in a refined kerosene base, proceed as follows:

Prepare an extract of pyrethrum with refined kerosene. (Add 1.8 kg., 4 pounds, of pyrethrum to 3.785 liters, 1 gallon, of refined kerosene and allow to stand at least 2 days.) Filter and preserve. Match the color of the insecticide, approximately, with the extract by diluting with refined kerosene. Prepare a chloroform solution of rotenone of suitable concentration. Use the diluted pyrethrum extract and rotenone solution in preparing the standards using the same amount of extract in the standards as insecticide used in the test. Proceed as in quantitative test No. 1.

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Determination of Iron in Sea Water

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CONSIDERABLE interest attaches to the heavy metals present in small amounts in sea water. Of these, iron is particularly important, for there is little doubt but that it may be a limiting factor in the growth of certain organisms. Thompson, Bremner, and Jamieson (3) reviewed the literature on this subject and proposed a method for the determination of total iron in the water.

Any study of the availability of iron must involve its separation into the several possible forms of combination. Thompson and Bremner later (1) modified their method and determined both "soluble" and "total" iron in a number of samples of water. The present paper describes an attempt to determine the concentration of "free dissolved ferrous and ferric ions," and since a somewhat different method of analysis is used the results are not strictly comparable with those of Thompson and Bremner, who evaporated filtered samples with sulfuric acid to eliminate interfering substances such as fluoride and organic matter, and then determined iron colorimetrically with thiocyanate, extracting the color with isoamyl alcohol.

The method here described depends primarily upon the precipitation of iron as sulfide. The results therefore include iron in all forms of combination yielding ferrous ions in the concentrations demanded by the solubility product of ferrous sulfide. Ferric ions are also included, owing to the reducing action of the sulfide ion in the concentrations used. Admittedly, organic matter interferes with the precipitation, but whether this actually occurs in sea water and, if so, how much of the iron is held in such organic combination, is outside the present discussion.

Much of the early work on heavy metals in sea water was based upon their precipitation by sulfide, but unless some method of concentration is used the removal is incomplete in such high dilutions. However, the fortunate presence of magnesium in relatively large amounts makes it possible to use a process of co-precipitation, the extremely small quantities of ferrous sulfide resulting from the addition of alkaline sulfide being carried down quantitatively by the larger amount of basic magnesium salts simultaneously formed. The iron is brought into solution again in small volume, oxidized, and finally estimated colorimetrically with thiocyanate.

A serious difficulty with this latter reaction has always been the instability of the colored compound in water solution. While trying various methods of extraction it was observed that ethylene glycol monobutyl ether, which is a moderately good extractive, will, when dissolved in the solution in small amounts, stabilize the color reaction and retard the fading long enough to permit colorimetric comparison in the water solution without extraction by any organic solvent.

Method Used

A 500-ml. sample of sea water is filtered through a Seitz filter and transferred to a 1-liter Erlenmeyer flask. Five milliliters of ammonium sulfide reagent are added and the solution is brought to boiling for a few moments. A fine magnesium precipitate should form, which settles quickly on standing. If the precipitate fails to appear, the solution is not sufficiently alkaline, and a small amount of ammonium hydroxide (ordinarily not more than 5 ml.) should be added and the boiling repeated. The precipitate is filtered on a small paper filter in a Gooch crucible, under gentle suction. After washing, it is dissolved in 20 ml. of dilute hydrochloric acid (approximately 2.5*N*) and the solution boiled to remove hydrogen sulfide. Then 2 ml. of bromine water are

added and the excess bromine is boiled off. When the solution has cooled, 5 ml. of concentrated hydrochloric acid are added, and the solution is made alkaline with concentrated ammonium hydroxide. In this way iron is precipitated, with only small traces of magnesium. The precipitate is filtered off on a small Whatman paper (No. 42) and dissolved by running 20 ml. of 2.5*N* hydrochloric acid through the filter. The filtrate is caught in a 100-ml. Nessler tube and made up to the mark. Then 2 ml. of ethylene glycol monobutyl ether and 10 ml. of a 10 per cent solution of potassium thiocyanate are added and the contents of the tube mixed by covering the ground end of the tube with a glass plate and inverting. The color is compared with a set of standards in similar tubes. These are prepared by adding 5 ml. of concentrated hydrochloric acid and the desired amount of standard iron solution (0.002, 0.005, 0.01, 0.015, 0.02 mg. of iron as ferric alum) to Nessler tubes and treating with potassium thiocyanate and the ether as before. The colors will remain permanent for an hour or more.

If preferred, the color comparison may be carried out in a long-tube colorimeter, which makes closer differentiation possible than with the use of Nessler tubes, but it is very doubtful whether in the long run the results are any more accurate.

Occasionally samples of c. p. hydrochloric acid and ammonium hydroxide are found which are practically iron-free. If not, the reagents may be made by redistilling the purified gases into pure water. The ammonium sulfide reagent is made by running hydrogen sulfide into iron-free ammonium hydroxide through a purification train consisting of a wash-bottle and a 120-cm. (4-ft.) tube packed with glass wool.

The bromine water was tested daily for the presence of iron taken from the glass. The greatest source of error was found in the filter paper. This was minimized by soaking all filter paper and pads in 1 to 1 hydrochloric acid and washing carefully.

BLANKS. In the early stages of the work, before reagents were adequately purified, blank values from 0.005 to 0.0065 mg. were found. Later this was consistently lowered to 0.002 to 0.004 mg. Each reagent was separately tested as a possible source of iron, with the following results, when reduced to the basis of a single determination:

	Mg.
Bromine	0.0008
(NH ₄) ₂ S	0.0010
HCl	0.0028
NH ₄ OH	0.0010
Total	0.0054

DUPLICATE DETERMINATIONS. The following pairs of results were obtained at various times from duplicate samples, independently precipitated and treated:

Mg. of Iron Found							
0.012	0.005	0.018	0.017	0.015	0.023	0.005	0.015
0.010	0.004	0.017	0.019	0.015	0.021	0.004	0.015
0.0044	0.0077	0.0052	(comparison made in colorimeter)				
0.0045	0.0073	0.0053					

Recovery of Added Iron

The test of the adequacy of the method is in the completeness with which added quantities of iron may be recovered. Known amounts of iron, in the order of magnitude which might be expected to be present in the original water, were added to sea-water samples with the results shown in Table I. The iron added was in the form of ferric ammonium sulfate. It is evident from the completeness of the recovery that ferric iron is completely reduced to ferrous by the sulfide ion, before precipitation of ferrous sulfide.

TABLE I. RECOVERY OF ADDED IRON

Before Adding Iron Mg.	Iron Added Mg.	Found after Adding Iron Mg.	Iron Recovered Mg.	
0.01	0.02	0.025	0.015	
0.01	0.03	0.04	0.03	
0.015	0.02	0.04	0.025	
0.015	0.02	0.035	0.02	
0.012	0.03	0.042	0.03	
0.01	0.02	0.035	0.015	
0.001	0.005	0.0082	0.0052	Comparison in colorimeter
0.002	0.005	0.0068	0.0048	
0.015	0.010	0.025	0.010	
0.017	0.010	0.025	0.008	High blank (0.007 mg.) Reagents and paper impure
0.010	0.010	0.023	0.013	
0.012	0.010	0.023	0.011	
0.010	0.010	0.021	0.011	
0.005	0.010	0.015	0.010	
0.004	0.010	0.015	0.011	
0.007	0.010	0.015	0.008	
0.005	0.010	0.017	0.012	
0.008	0.010	0.017	0.009	
0.008	0.010	0.018	0.010	
0.005	0.010	0.015	0.010	
0.004	0.010	0.015	0.011	

TABLE II. DUPLICATE SAMPLES FILTERED IN DIFFERENT WAYS

	(Mg. of iron found)				
No. 42 paper	0.0045	0.017	0.025	0.017	Comparison in colorimeter
Seitz filter	0.002	0.010	0.023	0.010	
No. 42 paper	0.004	0.003	0.0009	0.0004	
Seitz filter	0.0003	0.0003	0.0004	0.0000	

TABLE III. INFLUENCE OF FLUORIDE

Fe in Original Water Mg.	Fluoride Added to Sample Mg.	Iron Found Mg.
0.018	0.25	0.017
0.017	0.25	0.019
0.012	0.25	0.010
0.012	0.50	0.011
0.012	0.75	0.013
0.016	1.00	0.015
0.016	0.50	0.021
0.016	1.00	0.015

Filtration

Obviously, if the original water is not filtered to remove suspended matter results will be high, owing to iron contained in such material, even though the subsequent treatment is not vigorous enough to oxidize or decompose completely the organic iron compounds contained in diatoms, etc. This is borne out by the results shown from Station 1731, the samples from which were not filtered, and which are higher than any others. The results given in Table II, comparing duplicate samples, one of which had been filtered through No. 42 filter paper and the other through a Seitz filter, indicate that water treated in the latter way is more completely free from iron-bearing suspended matter. The samples in which Thompson and Bremner (1) determined "soluble iron" were filtered through No. 42 paper, which may account for their slightly higher results.

The varying results following different methods of filtration are evidently due not to iron dissolved from the filter

material, but rather to the varying efficiency of different filtration technics in the removal of very fine suspended matter, bacteria, or other microorganisms containing iron. The greater portion of the total iron of the water is in suspension.

Influence of Fluoride

Thompson, Bremner, and Jamieson mention the possible occurrence of iron in the form of a ferrifluoride complex, which inactivates the iron as far as the thiocyanate reaction is concerned. Although this may be true, the presence of fluoride has no influence on the determination and recovery of iron by the present method. The amount of fluoride in the water should be sufficient to form such complex ions with much more than the iron already present; nevertheless, added iron is recovered quantitatively. Furthermore, fluoride was added to water samples containing small amounts of iron, which were precipitated and determined both before and after the addition of fluoride. The results shown in Table III es-

TABLE IV. IRON IN SEA WATER

Location	Depth M.	Tem- perature ° C.	Sal- inity 0/00	Iron Mg./cu. m.	Location	Depth M.	Tem- perature ° C.	Sal- inity 0/00	Iron Mg./cu. m.
Station 1731 38° 06' N., 68° 54' W.	0	28.20	36.02	19 Not	Station 2220 42° 17' N., 69° 36' W. (Gulf of Maine)	0	13.96	31.73	6
	50	26.81	36.00	41 filtered		20	13.88	31.95	0
	100	23.42	36.40	30 Compare		40	4.09	32.64	0
	150	20.95	36.58	16 with fol-		60	3.66	32.79	0
	200	18.65	36.42	16 lowing		80	3.65	32.92	4
	860	4.71	34.96	15 stations		120	3.98	33.25	4
	1685	3.48	34.94	8 Filtered		175	6.07	33.96	18 (?)
						200	6.48	34.12	0
Station 1732 37° 21' N., 68° 31' W.	0	27.67	35.90	13	Station 2224 43° 12' N., 69° 18' W. (Gulf of Maine)	0	12.68	32.00	0
	1370	4.65	34.96	4		40	5.57	32.60	0
	2390	3.42	34.96	6		80	4.15	32.80	0
	2830	3.11	34.97	10		175	3.94	33.22	0
	3830	2.50	34.87	8	Station 2227 42° 15' N., 67° 16' W. (Gulf of Maine)	0	12.56	32.28	4
Station 1734 36° 27' N., 68° 38' W.	0	25.64	36.00	9		40	5.01	32.82	0
	50	21.03		2		80	4.78	33.12	0
	87	19.75	36.56	3		175	5.39	33.80	0
	175	18.55	36.51	5	Station 2228 41° 57' N., 67° 06' W. (Gulf of Maine)	0	9.63	32.52	0
	365	17.96	35.53	5		30	9.59	32.52	0
	550	17.00	36.35	6		50	9.61	32.52	0
	730	14.43	35.90	1					
	900	10.21	35.34	4					
	1330	4.82	34.96	8					
	1550	4.08	34.97	2					
	2440	3.45	34.96	2					
Station 2450 39° 37' N., 69° 57' W.	0	22.23	33.15	10	Surface Samples near Woods Hole				
	50	9.35	34.39	4	Woods Hole Harbor (8/6/34)				6
	500	5.08	34.96	6	(8/8/34)				8
	1000	3.88	34.96	14	(8/28/34)				7
	2200	3.29	34.96	8	(8/28/35)				3
Station 2458 35° 54' N., 67° 47' W.	0	27.8	36.26	6	Woods Hole Eel Pond				0
	100	22.84	36.47	6	Mouth of Great Pond				4
	200	18.93	36.56	6	Head of Waquoit Bay				10
	500	17.97	36.49	12	Tarpaulin Cove				6
	1000	10.2	35.25	14	Buzzards Bay, K-1				3
	2500	3.37	34.90	8	Buzzards Bay, K-2				0
					Vineyard Sound, L-1				0
					Vineyard Sound, L-2				0

establish the fact that fluoride in several times the normal concentration has no influence on the determination of iron by this method.

Iron in Sea Water

Sea-water samples from a number of places within cruising distance of Woods Hole were analyzed by the above procedure. The results in Table IV show that there is a small but significant amount of free inorganic iron—i. e., iron precipitable as sulfide—generally present in the water. The concentration is seldom more than 10 mg. per cubic meter, or ten parts per billion. This is about one-quarter to one-twentieth of the amount of total iron found in the waters of the Puget Sound area, by the authors mentioned.

The figures of Thompson and Bremner (2) for "soluble iron" are also somewhat higher than those shown here, except in the case of their one deep, off-shore station, where results were much the same as at Stations 1732 and 1734. Their discovery of a maximum iron concentration at 1000 to 1200 meters seems to have its counterpart here, too, at Stations 2450, 2458, and possibly 1734, although at the first of these, at least, it does not coincide with the depth of minimum

oxygen concentration, which the above authors think is related to it.

The water is occasionally free of this form of iron, especially on the surface near the shore, and sometimes at other depths, as at Stations 2220–28 in the Gulf of Maine. Whether this is entirely due to utilization of the metal biologically, or whether this same process is the cause of the vertical differences in concentration (as was shown to be the case with total iron, 3), cannot be decided conclusively from the present data. At any rate, the growth of diatoms would seem to depend principally upon other forms of iron than those responding to this method of analysis. Presumably these are in the nature of organic or nondissociable compounds.

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Determination of Reducing Sugars and Sucrose in Plant Materials

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Details are given for the clarification of extracted plant materials and for determining reducing sugars.

The reducing sugars are oxidized with alkaline potassium ferricyanide; the ferrocyanide formed in the reaction is titrated in acid solution with ceric sulfate, which oxidizes the ferrocyanide back to ferricyanide, giving a measure of the reducing sugars present. The indicator used for the titration is *o*-phenanthroline ferrous sulfate.

Using five different dry plant materials and squash sap, the results obtained were from 0 to about 5 per cent higher by this method than by the Munson-Walker method. The method is rapid and convenient, and covers a wide range of the sugar contents encountered in plants.

THE Munson-Walker method (5), most widely used for determination of reducing sugars in plants, gives satisfactory results when samples containing large amounts of sugars are used. Reliable results, however, cannot be obtained when the samples to be analyzed contain small amounts of sugar. The Committee on Methods of Chemical Analysis of the American Society of Plant Physiologists (1) referring to this method states, "As a general rule, reductions giving less than 20 mg. of copper should not be weighed directly, and even at this figure the percentage error is high."

The volumetric methods used at present for the determination of sugars in plants are not satisfactory. The writer, using two known reactions, developed a method which gives satisfactory results when reducing sugars are determined in plant tissues and saps. The reaction between the ferricyanide and reducing sugars was first suggested by Gentile (3). Furman and Evans (2) have shown that ferrocyanide can be oxidized quantitatively by ceric sulfate. Whitmoyer (6) was first to utilize these reactions and devised a microchemical method to determine pure glucose, fructose, and invert sugar for amounts between 0.5 and 2.0 mg.

In the present method, precise results can be obtained with samples containing between 1.0 and 10.0 mg. of reducing sugars. The method is short, the solutions are stable, and a sharp end point is obtained in the titration.

Materials and Solutions

INDICATOR. A 0.025 *M* solution of *o*-phenanthroline ferrous sulfate was used as an indicator. It was made by dissolving 0.695 gram of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water; 1.485 grams of *o*-phenanthroline monohydrate were added and stirred until all dissolved, giving a dark red solution, which was then made up to 100 cc. volume. Two drops of the indicator were used in each determination. Care should be taken to use exactly the same amount of indicator in each determination, because the ferrous sulfate in the indicator is oxidized by the ceric ion. A blank should therefore be run on the indicator used. The blank was found to be 0.30 cc. when a 0.0135 *M* ceric sulfate solution and 2 drops of the indicator were used. The end point was a sharp change from orange-brown to pale green. The indicator was obtained from the G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio.

CERIC SULFATE. The ceric sulfate was obtained from the same source as the indicator and standardized against 0.1 *N* ferrous sulfate as follows:

The ferrous sulfate was first standardized against 0.1 *N* potassium dichromate by dissolving 6.95 grams of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water to which 20 cc. of 1 to 1 sulfuric acid had been added and diluted to 250 cc. Twenty-five cubic centimeters of the approximately 0.1 *N* ferrous sulfate were transferred with a calibrated pipet into a 300-cc. Erlenmeyer flask to which 15 cc. of 1 to 1 sulfuric acid and 25 cc. of water were added. One drop of the *o*-phenanthroline ferrous sulfate was added and titrated against standard 0.1 *N* potassium dichromate until the pink solution turned bluish green. It took 27.5 cc. of the 0.1 *N* potassium dichromate to neutralize 25 cc. of the ferrous sulfate. The concentration of the ferrous sulfate was therefore 0.11 *N*.

To 8.3063 grams of ceric sulfate dissolved in water, 75 cc. of 1 to 1 sulfuric acid were added and the solution was diluted to 250 cc. (The molecular weight of ceric sulfate being 332.25, this should be a 0.1 *N* solution.) A 25-cc. aliquot of this ceric sulfate solution was transferred to a 300-cc. Erlenmeyer flask. Fifteen cubic centimeters of 1 to 1 sulfuric acid, 25 cc. of water, and one drop of the indicator were added, and the solution was titrated with the standard ferrous sulfate. The change from the colorless or slightly green to orange-pink was taken as the end point. To neutralize 25 cc. of ceric sulfate 12.75 cc. were required. The concentration of the ceric sulfate was 0.0539 *N*, which is 53.9 per cent purity of the ceric sulfate used.

The ceric sulfate obtained from the G. Frederick Smith Chemical Company is not completely anhydrous and contains other rare earth metals. However, as the ceric ion is the only quadrivalent ion effective in the oxidation, the other metals do not interfere.

A dilute ceric sulfate solution suitable for use in sugar analysis was made by placing 8.3 grams of the ceric sulfate in about 500 cc. of water to which 100 cc. of 1 to 1 sulfuric acid had been added and diluting to 1 liter at room temperature.

This dilute ceric sulfate solution was standardized against the standard 0.11 *N* ferrous sulfate solution in the following manner:

A 2-cc. aliquot of the ferrous sulfate solution was transferred to a 300-cc. Erlenmeyer flask and 15 cc. of 1 to 1 sulfuric acid, 25 cc. of water, and one drop of the indicator *o*-phenanthroline ferrous sulfate were added. The solution was then titrated with the dilute ceric sulfate solution until the pink color disappeared, changing to bluish green and then becoming colorless. Two cubic centimeters of the 0.11 *N* ferrous sulfate required 16.25 cc. of the ceric sulfate. The concentration of the ceric sulfate solution was therefore 0.0135 *N*. The solution was very stable; its concentration did not change after standing for 3 months.

The ceric sulfate solution could also be standardized by the method of Willard and Young (?).

ALKALINE POTASSIUM FERRICYANIDE. A mixture of 4 grams of potassium ferricyanide and 24 grams of sodium carbonate was used to make up 1 liter of solution. The container of this solution was painted black and when not in use was kept in the dark. Under these conditions the alkaline potassium ferricyanide solution remained stable during 6 weeks.

STANDARDIZATION OF CERIC SULFATE AGAINST GLUCOSE. An aliquot of 1, 2, 5, and 10 cc. of pure 1 per cent anhydrous glucose, $[\alpha]_D^{25}$ 52.5, was placed in each of four 100-cc. volumetric flasks and made up to volume. A 10-cc. aliquot from each of these flasks, containing 1, 2, 5, and 10 mg. of glucose, was placed in a 200-cc. Erlenmeyer flask, and 25 cc. of alkaline potassium ferricyanide were added to each flask. The flasks with their contents were placed on the steam bath, so that they were immersed about one-third. After exactly 10 minutes the flasks were removed and cooled to room temperature by immersing them in running water for a few minutes, 10 cc. of 5 *N* sulfuric acid were added, and the flasks were well shaken. Two drops of the indicator, *o*-phenanthroline ferrous sulfate, were added and the solution was titrated with the 0.0135 *N* ceric sulfate solution.

The amount of ceric sulfate used, after subtracting the blank due to the indicator, was directly proportional to the amount of glucose taken. One milligram of glucose was equivalent to 2.14 cc. of 0.0135 *N* ceric sulfate.

Description of Method

CLARIFICATION OF PLANT EXTRACT. The plant extract should be clarified so that it is devoid of any coloring matter

and must be water-clear. Any organic coloring matter present in the solution is, apparently, oxidized by the ceric ion and high results are obtained.

A water-clear plant extract can be obtained if the clarification is carried out in a small volume and a small amount of charcoal (carboraffin) is added. The plant material, after extraction with 80 per cent alcohol and evaporation of the alcohol, is concentrated to not more than 10 cc. Five cubic centimeters of saturated neutral lead acetate are added and the excess of lead is removed with 10 cc. of saturated disodium phosphate. (The use of oxalate for deleading should be avoided because of its oxidation by the ceric sulfate.) Carboraffin (0.3 gram) is added and the mixture is allowed to stand with occasional shaking for half an hour. It is then filtered on a small Büchner funnel containing a thin layer of talc on a filter paper, prepared as follows:

Fifty grams of talc powder are shaken with 500 cc. of water until a uniform suspension results. About 25 cc. of the suspension are poured through a small Büchner funnel supplied with a wet 5.5-cm. filter paper and a 250-cc. suction flask, using little suction. The uniformly thin layer of talc is sucked free of liquid, washed with a little water, and sucked free of liquid again. The water in the suction flask is poured out and the flask rinsed with water. Full suction is then applied and the plant extract containing the clarifying agents is filtered through the dry talc filter. The precipitate on the filter is finally washed with water.

HYDROLYSIS OF SUCROSE IN PLANT EXTRACT. A 50-cc. portion of the clarified plant extract was taken and one or two drops of methyl red were added. The solution, which was slightly basic because of the excess of disodium phosphate used in the clarification, was neutralized with a few drops of 10 per cent acetic acid to bring to the acid color of methyl red. The pH of the solution was 4.9. Two to four drops of a 1 per cent solution of Wallerstein invertase scales were added. (The invertase was obtained from The Nulomine Co., 111 Wall St., New York, N. Y.) It is necessary to run a blank on this invertase, as it has a slight reducing power. The solution was allowed to stand for 2 hours at 28° or overnight at room temperature, made up to volume, and 10-cc. aliquots were used for the determination of reducing sugars. The acid hydrolysis of sucrose as used by Lehmann (4) was also found to be satisfactory. Fifty cubic centimeters of the clarified plant extract were transferred to a 200-cc. Erlenmeyer flask, heated to 70° for 10 minutes, then cooled rapidly in running water, and sufficient 15 per cent sodium hydroxide was added to neutralize to phenolphthalein. The actual amount of alkali needed was determined on a duplicate sample, so that no indicator was added to the solution to be analyzed. The neutralized solution was then made up to 100-cc. volume and 10-cc. aliquots were used for the determination of reducing sugars.

PROCEDURE. The following method was adopted for the determination of reducing sugars and sucrose:

One to two grams of dry material were weighed into glass thimbles provided with sintered glass porous bottoms and placed in Soxhlet extractors. One hundred and twenty-five cubic centimeters of 80 per cent alcohol were added to each of the 300-cc. Erlenmeyer flasks, connected with the extractors to the reflux condensers, and extracted for 6 hours. The flasks with the alcoholic extracts were placed on a steam bath, evaporated to about 10 cc., then cooled to room temperature, and cleared with 5 cc. of saturated neutral lead acetate. The excess lead was removed with 10 cc. of saturated disodium phosphate, 0.3 gram of charcoal was added, and the mixture was allowed to stand, with frequent shaking, for 30 minutes. The precipitate with the charcoal was then filtered on a small Büchner funnel supplied with a thin talc layer on a filter paper prepared as described above. The flasks were rinsed with cold water and the final washing of the precipitate on the Büchner was made with warm water. The clear solutions were diluted in volumetric flasks to 100 or 200 cc.

Aliquots of 10 cc. were transferred to 200-cc. Erlenmeyer flasks, 25 cc. of alkaline ferricyanide were added, and the flasks were heated on the steam bath, cooled, acidified, and titrated with 0.0135 *N* ceric sulfate as described above.

The 10-cc. aliquots should not contain more than 10 mg. of reducing sugar. If more than this amount is present, the

ferricyanide used is not sufficient to oxidize all of the reducing sugars. This can easily be detected by the disappearance of the yellow color of the ferricyanide, the solution becoming colorless after being heated on the steam bath. In that case the sugar solution should be diluted to a suitable volume.

A standard 25-cc. buret was used for the titration with the ceric sulfate. For blank determinations and for samples containing not more than 4 mg. of reducing sugar, a 10-cc. buret calibrated to 0.05 cc. was used.

When plant saps which did not contain much chlorophyll and other coloring matter were analyzed, 5-cc. samples were taken and clarified as in the case of the extracted plant material but were not filtered with suction on a Büchner funnel. Instead, they were filtered on an ordinary funnel and filter paper directly into 100-cc. volumetric flasks.

The sucrose was determined as follows: 50-cc. aliquots of the clarified plant extracts were placed in 100-cc. volumetric flasks and one or two drops of methyl red were added. The solution was then neutralized with a few drops of 10 per cent acetic acid to bring to the acid color of methyl red. Four drops of a 1 per cent solution of Wallerstein invertase scales were added and the flasks were placed at 28° for 2 hours or left overnight at room temperature. The flasks were then diluted to volume; 10-cc. aliquots were taken and determined as in the case of reducing sugars.

A blank was simultaneously run with water and the same dose of invertase using 2 drops of the *o*-phenanthroline indicator as in the sugar determinations.

CALCULATION OF RESULTS. If, for example, in determining reducing sugars, a 10-cc. aliquot of the clarified extract from 2 grams of dry material diluted to 200 cc. required 16.2 cc. of the standardized ceric sulfate, the blank being 0.30 cc., the calculation is made as follows:

$$\frac{(16.2 - 0.3) \times 20 \times 100}{2.14 \times 2000} = \text{per cent of reducing sugar}$$

Experimental Results

The titration was 0.30 cc. of 0.0135 *N* ceric sulfate, when 10 cc. of water and 2 drops of the indicator were used.

A blank, substituting water for the plant extract, required 0.30 cc. of 0.0135 *N* ceric sulfate. Since the amounts used in titrating the indicator and the indicator plus reagents were the same, apparently the buffering effect due to the acetate and phosphate has no noticeable effect on the reducing power of the solution.

A blank on the invertase showed a titration of 0.38 cc. of the 0.0135 *N* ceric sulfate.

In order to determine whether any sugar was adsorbed by the lead precipitate, charcoal, and talc, pure glucose was subjected to the same treatment as the plant samples. The results in Table I show a complete recovery of the glucose; hence no sugar was lost in the process of clarification.

TABLE I. EFFECT OF CLEARING ON PURE SUGAR SAMPLES

Glucose Dissolved in 100 Cc. Mg.	Glucose Recovered Mg.	Glucose Recovered %
50.00	50.06	100.1
50.00	50.00	100.0
50.00	49.92	99.8
100.00	99.84	99.8
100.00	100.10	100.1

Different plant materials were analyzed by the volumetric and Munson-Walker methods. The results are shown in Table II. The values for the ten samples determined by the volumetric method were higher by 1.17 to 4.27 per cent than by the Munson-Walker method.

TABLE II. COMPARISON OF VOLUMETRIC WITH MUNSON-WALKER METHOD

Plant Material	(Reducing sugars calculated as glucose)		Munson-Walker Method		Difference %
	Volumetric Method Glucose per gram of dry material	Glucose in dry material %	Glucose per gram of dry material	Glucose in dry material %	
Before Hydrolysis					
Swiss chard	30.4	3.04	29.4	2.94	3.40
Cauliflower leaves	34.2	3.42	32.8	3.28	4.27
Sugar cane	86.2	8.62	85.2	8.52	1.17
Sugar beets	57.4	5.74	55.7	5.57	3.05
Sunflower leaves	41.0	4.10	39.4	3.94	4.06
After Hydrolysis					
Swiss chard	57.2	5.72	55.6	5.56	2.88
Cauliflower leaves	83.0	8.30	79.8	7.98	4.01
Sugar cane	158.4	15.84	152.8	15.28	3.67
Sugar beets	115.0	11.50	111.5	11.15	3.14
Sunflower leaves	70.0	7.00	67.7	6.77	3.43

In another experiment 1-gram samples of the same plant material were mixed before extraction with 50 mg. of pure glucose with 80 per cent alcohol, and the reducing sugars were determined by the volumetric method as before. There was a good recovery of glucose added to the samples, as may be seen from Table III.

TABLE III. RECOVERY OF PURE GLUCOSE, USING THE VOLUMETRIC METHOD, WHEN MIXED WITH PLANT MATERIAL

Plant Material	(Reducing values calculated as glucose)			
	Glucose per Gram of Dry Material Mg.	Glucose per Gram of Dry Material after Adding 50.0 Mg. of Glucose Mg.	Glucose Recovered Mg.	Recovery %
Swiss chard	30.4	80.1	49.7	99.4
Cauliflower leaves	34.2	82.8	48.6	97.2
Sugar cane	86.2	137.5	51.3	102.6
Sugar beets	57.4	106.4	49.0	98.0
Sunflower leaves	41.0	91.5	50.5	101.0

Table IV shows the results obtained when expressed squash saps were determined by the volumetric and Munson-Walker methods. The results obtained by the volumetric method in 10 samples run higher from 0 to 4.83 per cent than the Munson-Walker method.

TABLE IV. COMPARISON OF VOLUMETRIC WITH MUNSON-WALKER METHOD WHEN PLANT SAP WAS USED

Volumetric Method		Munson-Walker Method		Difference between Methods %
Glucose in 5 cc. of sap Mg.	Glucose in 1 liter of sap Grams	Glucose in 5 cc. of sap Mg.	Glucose in 1 liter of sap Grams	
110.0	22.00	105.0	21.00	4.76
61.3	12.26	59.0	11.80	3.90
78.4	15.68	78.4	15.68	0
79.2	15.84	78.5	15.70	0.89
75.4	15.08	73.2	14.64	3.00
88.6	17.72	85.6	16.12	3.51
32.3	6.46	31.4	6.28	2.87
71.7	14.34	68.4	13.20	4.83
67.9	13.58	66.0	13.20	2.88
77.4	15.48	74.6	14.92	3.75

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The Assay of the Platinum Metals

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THE determination of the platinum metal content of the silver bead has always been recognized as exceptionally difficult, because of the similarity of properties of metals of the platinum group, the necessity of working with small quantities of the metals, and the absence of methods for separating and determining such metals as rhodium, iridium, osmium, and ruthenium.

The authors have been engaged in determining the platinum metal content of a certain Canadian mineralized property and consequently were faced with the necessity of devising a method for the complete extraction and determination of the platinum metal group. A search through the literature dating back to the discovery of the metals yielded no method for the analysis of the bead which could be considered at all satisfactory from the point of view of the complete individual separation of the platinum group and of effecting complete solution of such metals as rhodium and iridium when these are present together in the cupelled bead.

Much valuable work has been done on the determination of the individual platinum metals and on restricted separations, such as the separation and determination of platinum and palladium by Krauss and Deneke (9). Paal and Amberger (11) established the foundations for a new method of separation of the platinum metals in the use of the oxides of the metals precipitated in a medium of controlled acidity. Wichers, Gilchrist, and Swanger (12) extended very successfully these and other researches to the complete wet separation of the platinum metals and devised a macroprocedure for their determination, which the authors have found of exceptional value. Their work was not designed to apply to the assay bead containing members of the platinum group, gold, and silver. The authors have made use of this work in an attempt to devise a simple and accurate procedure for the fire assay of the platinum metals. The present report deals with some of the individual problems encountered during the development of the combination method of assay.

Distribution of Palladium

The procedures for parting the silver-platinum metal bead by means of sulfuric acid may be divided into two classes. In the modified parting method, advocated by Graham (8) for routine analysis, an attempt is made to remove the silver from the platinum metal residue. The parting is stopped at the last appearance of gas bubbles, and undoubtedly the amount of palladium dissolved will depend upon the interpretation of the end point. In the second, the bead is parted in boiling sulfuric acid. Fulton and Sharwood (4) state that when the bead is parted by this method palladium is dissolved, leaving the remaining metals in the residue, and that "whether this solution is complete or not has not been demonstrated." In a footnote they mention that "Lodge holds to the contrary."

Beads were made up containing the proportion of platinum metals found in ore concentrates from various localities chosen

A new procedure has been developed for the separation of palladium from silver in sulfuric acid solutions obtained as a result of parting the platinum-silver bead, and for the treatment of iridium and rhodium, which are dissolved by means of a short sodium peroxide fusion in a silver crucible. Palladium is tenaciously retained in the residue left after having parted the bead with sulfuric acid, and hence provision must be made for its extraction from the residue. The effect of dimethylglyoxime on rhodium, iridium, osmium, and ruthenium solutions is shown.

because of the variable ratio of palladium to the rest of the platinum metals. Those chosen contained the following approximate percentages of metals: Ontario concentrates, 78.0 silver, 8.3 platinum, 9.4 palladium, 0.6 rhodium, 0.6 iridium, and 3.0 gold; South African concentrate I, 61.4 platinum, 34.3 palladium, 1.0 iridium, and 2.6 rhodium; South African concentrate II, 83.5 platinum, 9.2 palladium, 0.9 iridium, and 0.8 rhodium. Each bead contained about 12 parts of silver to 1 part of platinum metals.

The bead was flattened and rolled into a cornet, 20 cc. of concentrated sulfuric acid were added, and the whole was boiled for 20 minutes. (The authors have since observed that there is a consistent loss of platinum metals during the flattening of the bead unless extreme precautions are taken. In a forthcoming paper this matter will be discussed more fully.) The sulfuric acid was removed, a second portion of 15 cc. of concentrated sulfuric acid added, and the mixture boiled for 15 minutes in some cases and for 30 minutes in others. The residue was washed thoroughly with hot water and dilute sulfuric acid until the washings showed no test for palladium with dimethylaminobenzilidene rhodanine, as described by Feigl (3). The residue was dissolved in the usual way with aqua regia and the nitric acid removed. When gold was present it was removed by reduction with oxalic acid which also precipitated small amounts of palladium.

The gold was filtered off and the filtrate containing platinum and palladium made up to 30 cc. with hot water. The acidity of this solution was adjusted to pH 4 by means of a filtered 10 per cent solution of sodium bicarbonate and bromophenol blue indicator. Two cubic centimeters of a filtered 10 per cent solution of sodium bromate were added and the solution was boiled for 15 minutes. The addition of the sodium bicarbonate solution was then continued to an acidity of pH 6, using bromocresol purple as indicator. The brown palladium dioxide was filtered through a small filter paper and washed with hot water freshly distilled. (Distilled water which has been exposed to fumes of ammonia or acids will vary considerably from its usual pH of about 6. Particularly in the case of rhodium, the dioxide is carried through the filtering medium as suspended material if the wash water is much more basic than pH 6. In this case the water can be adjusted by addition of dilute sulfuric acid.) The palladium dioxide was dissolved by pouring 4 cc. of a hot hydrochloric acid solution (1 to 1 by volume) through the filter paper and washed with about 30 cc. of hot water. The palladium was precipitated with dimethylglyoxime and filtered through a No. 00 Munktell's 7-cm. filter paper. The washed compound was ignited, reduced, cooled in an atmosphere of carbon dioxide and then air, and finally weighed as metal. When gold was absent the palladium was precipitated from the acid solution of palladium and platinum as the dioxide and then with dimethylglyoxime as described above. The results obtained are given in Table I.

TABLE I. DISTRIBUTION OF PALLADIUM IN BEAD ON PARTING WITH SULFURIC ACID

Sample No.	Type of Concentrate	Palladium Content Mg.	Time of Parting Min.	Residue Mg.
1	Ontario	24.18	20 and 15	1.56
2	Ontario	24.03	20 and 15	1.36
3	Ontario	24.51	20 and 30	0.92
4	Ontario	23.19	20 and 30	1.00
5	South Africa I	18.36	20 and 15	2.21
6	South Africa I	17.85	20 and 30	2.38
7	South Africa II	5.04	20 and 15	0.41
8	South Africa II	4.98	20 and 30	0.00
9	South Africa II	5.14	20 and 30	0.35

Distribution of Platinum, Rhodium, Osmium, and Ruthenium

Throughout these experiments it was observed that when the second parting was continued for 30 minutes, and particularly in those cases not recorded where the parting time was longer, while the amount of palladium present generally decreased, yet appreciable amounts of platinum and rhodium passed into the solution. These facts indicate that it is necessary, when the bead is parted by means of boiling sulfuric acid, to provide for the separation of palladium in the aqua regia extract of the residue and for the separation of platinum and rhodium from the sulfuric acid palladium solution.

Fulton and Sharwood (5) state that the sulfuric acid solution obtained from parting does not contain ruthenium or osmium. When ruthenium and osmium were present in the bead in appreciable proportions and the sulfuric acid solution was boiled, osmium was collected in sodium hydroxide solution and precipitated as the hydrated dioxide. When sodium bromate was then added to the sulfuric acid solution, ruthenium was distilled off and collected in sodium hydroxide solution and also precipitated as the hydrated dioxide. When the aqua regia extract was distilled, osmium was collected and precipitated as the dioxide. Fusion of the final residue with sodium peroxide and subsequent distillation of the fusion showed the presence of large quantities of both osmium and ruthenium.

Separation of Palladium from Large Amounts of Silver

Heretofore silver has usually been separated from palladium (and small amounts of other platinum metals) in the sulfuric acid solution resulting from the parting of the assay bead, by precipitating it as the chloride. The precipitate always occludes palladium. To overcome this difficulty silver is precipitated from a dilute solution, and the chloride is dissolved and reprecipitated. After concentrating the filtrates, a small amount of silver chloride may appear and have to be removed. Complete separation of the two metals by this method is tedious and time-consuming.

The precipitation of palladium dioxide at pH 6, used by Gilchrist (7) to separate palladium (together with rhodium and iridium) from platinum, can also be used to separate palladium from silver, and offers a direct method of removing palladium from the sulfuric acid solution, in the presence of relatively large amounts of silver. This was demonstrated as follows:

A palladium sulfate solution was prepared from palladium chloride by repeated precipitation of the dioxide according to the directions given by Gilchrist (7) and solution of the dioxide in sulfuric acid (1 to 1). To four 10-cc. portions of this acid solution 800-mg. portions of silver carbonate were added, followed by boiling to dissolve the silver sulfate. The resulting solutions were neutralized to pH 4 with sodium bicarbonate, using bromophenol blue as indicator. Each solution was then treated with 5 cc. of a 10 per cent solution of sodium bromate, boiled, and neutralized to pH 6, as indicated by bromocresol purple. After boiling the solution for 20 minutes, the precipitate of brown palladium dioxide was collected in a porcelain micro-Gooch crucible with asbestos mat (a small filter paper could be used) and washed with hot water of pH 6. The crucible was placed in a beaker and treated with 4 cc. of hot hydrochloric acid (1 to 1), in which the precipitate dissolved rapidly. The acid solution was diluted to about 30 cc., and filtered from the asbestos and a small amount of silver chloride. Palladium was precipitated from these solutions with dimethylglyoxime, ignited in air, reduced in hydrogen, cooled in carbon dioxide, and weighed. The results obtained were 0.0219, 0.0219, 0.0219, and 0.0218 gram. Direct determination of palladium in 10 cc. of the palladium sulfate solution yielded 0.0219 gram.

In applying this procedure to the sulfuric acid obtained in parting the assay bead, after diluting it and filtering off the

insoluble residue, the filtrate is evaporated to a volume of about 3 cc. The viscous residue is cooled only slightly, diluted with hot water, and the solution boiled if necessary to dissolve the silver sulfate. The separation of palladium is done as already described. Small amounts of rhodium, ruthenium, and platinum are likely to accompany palladium in the sulfuric acid parting. Rhodium and ruthenium will precipitate with palladium as dioxides but will not accompany it when it is finally precipitated with dimethylglyoxime. Traces of platinum which are carried down with the palladium dioxide, unless proper precautions are observed, will later contaminate the precipitate of palladium dimethylglyoxime if filtration of this precipitate is delayed longer than an hour.

The tendency of platinum to form a precipitate with dimethylglyoxime on standing was confirmed by adding an excess of the reagent to a solution of chloroplatinic acid prepared by dissolving platinum in aqua regia and eliminating the nitric acid. A blue precipitate, which has been described by Cooper (2), appeared within about 30 minutes. On the other hand, 0.1 per cent solutions of rhodium, iridium, ruthenium, and osmium, whether as sulfates or chlorides, failed to show any precipitate with dimethylglyoxime in 4 days. The observation that rhodium and iridium do not contaminate the palladium dimethylglyoxime precipitate has also been reported by Gilchrist (7).

Determination of Palladium and Platinum in Residue

The residue from the parting of the bead with sulfuric acid is digested with dilute aqua regia (1 to 5) to dissolve gold (if present), platinum, and residual palladium. If gold is absent, the solution is diluted with about 30 cc. of water for each 25 mg. of palladium, and the palladium separated from platinum by the dioxide precipitation, after which it is precipitated with dimethylglyoxime and added to the palladium obtained from the parting solution. Traces of rhodium and iridium which are dissolved by the dilute aqua regia will be precipitated with the palladium as dioxides, but will be eliminated by the precipitation with dimethylglyoxime. As previously noted, small amounts of platinum carried down by the dioxide precipitate may contaminate the dimethylglyoxime precipitate if filtration of the latter is delayed.

Reduction of platinum by means of sodium formate from a solution adjusted to pH 6 is recommended for the determination of platinum after the removal of palladium. Sodium bromate interferes with the reduction and must first be destroyed by evaporation with hydrochloric acid.

If gold is present, the hydrochloric acid solution of gold, platinum, and palladium is placed in a cup fashioned from 20 grams of sheet lead and evaporated carefully, silver is added and the whole is cupeled. The bead is parted with nitric acid in the usual manner and gold remains as a residue.

Treatment of Rhodium and Iridium

If rhodium and iridium are present in the assay bead, they remain as an insoluble residue after parting with sulfuric acid and treatment with dilute aqua regia. According to Fulton and Sharwood (4), treatment with strong aqua regia dissolves the iridium, leaving a residue which is considered to be rhodium, but the authors' experience does not confirm this. The literature records no satisfactory method for getting into solution the residue obtained at this stage of the assay procedures. Ignition with sodium chloride in a current of chlorine is extremely inconvenient. Sulfuric acid is used by Gilchrist (6) to dissolve freshly precipitated rhodium, and by Zhemchuzhnyi (13) in sealed tubes to dissolve rhodium sponge, but it scarcely attacks rhodium which has been previously cupeled with silver. Fusion with sodium peroxide or a mixture of sodium

peroxide and hydroxide in a silver or nickel crucible has been employed by many workers, including Claus (1), Noyes and Bray (10), and Wichers, Gilchrist, and Swanger (12), to convert refractory platinum metals and their alloys into soluble forms but not, in general, for quantitative purposes. A procedure based on this method of attack has been developed which results in complete solution of as much as 50 mg. of combined rhodium and iridium left after cupeling and parting the silver bead, and treating the residue with dilute aqua regia.

The aqua regia solution is filtered from the residue, and the paper containing the latter is dried and ashed in a silver crucible. About 1.5 grams of sodium peroxide are added, the crucible is covered, and the contents are heated to dull redness for 5 minutes. After cooling, the crucible is covered with water in a 250-cc. beaker. After the resulting reaction, the crucible is transferred to a small casserole and washed with dilute nitric acid. This solution and additional nitric acid to make 10 cc. of concentrated acid are added to the alkaline solution. Iridium forms a blue alkaline solution which turns yellow when acidified. Rhodium settles out as a brown substance which has not yet been identified but is presumably an oxide. After boiling for 15 minutes to dissolve silver, the solution is filtered from the brown rhodium compound.

The paper and contents are digested with 10 cc. of concentrated sulfuric acid in a small Erlenmeyer flask. Small quantities of fuming nitric acid are added from time to time, between intervals of boiling, to destroy organic matter, and digestion with the boiling sulfuric acid is continued until the solution becomes clear and yellow. The solution is then diluted somewhat, added to the nitric acid solution, and the whole evaporated to a volume of 3 cc. If sulfuric acid is added directly to the nitric acid solution, without filtering off the rhodium compound, the latter collects in rings on the walls of the beaker as evaporation progresses and is not easily gotten into solution. Separate treatment of the brown rhodium material, and filter paper, can be completed in not more than 20 minutes. Rhodium or iridium not attacked by the sodium peroxide fusion would appear as an insoluble residue after solution of the brown rhodium compound and destruction of the filter paper in sulfuric and nitric acids. In many trials of this procedure no trace of unattacked rhodium or iridium has been found.

The small volume of sirupy liquid obtained on evaporation of the combined solutions is cooled slightly (not enough to solidify) and diluted with hot water. After boiling to dissolve all salts, the rhodium and iridium are separated from the relatively large amount of silver by precipitating their dioxides at pH 6, exactly as was done to separate palladium from silver, except that 10 cc. of the 10 per cent solution of sodium bromate are used instead of 5 cc. The precipitate is filtered off, washed, and dissolved in hydrochloric acid in the same way as the palladium dioxide precipitate, except that warming on the steam bath is necessary to dissolve it. After removing and washing the crucible, the solution is first evaporated to a small volume, then diluted and filtered. The residue of asbestos and a small amount of silver chloride is thoroughly washed with hot water.

If a paper filter (7 cm., Whatman No. 42) is used instead of asbestos to collect the dioxides, most of the precipitate is dissolved from the unfolded paper into a 150-cc. beaker with hot hydrochloric acid. The paper is destroyed with 3 cc. of concentrated sulfuric acid and small quantities of nitric acid in a 50-cc. Erlenmeyer flask. After diluting and again evaporating to eliminate nitric acid, this solution is combined with the main solution of the dioxides and the whole diluted to precipitate silver chloride, which is then removed by filtering. If the silver chloride is colored, the paper and contents are again treated with sulfuric and nitric acids; then a few drops of hydrochloric acid are added, and the resulting solution is diluted and filtered into the hydrochloric acid solution. This treatment is repeated once more, if necessary.

In a number of experiments designed to test quantitative recovery of rhodium and iridium which had been dissolved by the foregoing procedure, pure rhodium and iridium sponges were used instead of a mixed residue previously cupeled with silver. This was done because it has not yet been established whether the residue left after treatment with dilute aqua regia is free from other metals, or whether losses of rhodium or iridium occur during cupelation. Rhodium was determined, in the solutions resulting from the procedure, by precipitation with hydrogen sulfide and ignition to metal, in the

manner described by Gilchrist (6). Similarly, Gilchrist's procedure was used for the determination of iridium. In both cases smaller volumes were used.

The results obtained in four trials of the procedure on rhodium and four on iridium are given in Table II.

TABLE II. SOLUTION OF IRIDIUM AND RHODIUM BY FUSION WITH SODIUM PEROXIDE IN A SILVER CRUCIBLE

Sample No.	Iridium		Rhodium	
	Used Mg.	Recovered Mg.	Used Mg.	Recovered Mg.
1	25.1	25.1
2	24.8	24.6
3	24.8	24.6
4	24.3	24.2
5	23.5	23.5
6	27.4	27.4
7	29.4	29.0
8	28.6	28.2

Low results, such as No. 7 and No. 8, indicate that the dioxides were not completely dissolved from the Gooch crucible. All the results given have been corrected for blanks amounting to 0.7 or 0.8 mg., which are caused mainly by impurities, such as iron and copper, in the silver crucible. The amount of the blank is reduced if a smaller amount of sodium peroxide is used. This is possible when treating the small amounts of iridium and rhodium usually encountered in the assay of platinum ores and concentrates.

In addition to its analytical use, the procedure for the solution of rhodium and iridium has proved an efficient and rapid method for the preparation of salts from the pure metal sponges.

The Silver Crucible

Some of the silver crucibles used were purchased from Johnson Matthey and Company. The amount of silver corrosion during the 5-minute fusion with 1.5 grams of sodium peroxide is about 500 mg. or more. This means that an ordinary crucible of spun silver lasts for about twelve fusions.

It was decided to prepare thick-walled silver crucibles; and these were made by means of pure silver placed in a nickel crucible which was heated in a furnace until the silver melted. The whole was cooled slowly and the molded silver cut down to the required size in a lathe. One such crucible prepared by the authors has already made fifty fusions and will last many more. The outside dimensions of a suitable crucible may be suggested as: height, 2 cm.; top diameter, 2.4 cm.; bottom diameter, 2.1 cm.; wall thickness, 0.4 cm. Crucibles made by fusing silver chloride and soda ash often contain appreciable chlorides.

Summary

When a bead with a silver-platinum ratio of 12 to 1 is parted with boiling sulfuric acid it is necessary to provide for the separation of palladium in the aqua regia extract.

Palladium can be removed completely from the sulfuric acid parting solution by means of the dioxide precipitation.

Osmium, ruthenium, rhodium, and platinum are partially dissolved from the bead by means of boiling sulfuric acid.

Platinum salts with dimethylglyoxime produce an indigo-blue or bronze compound. Osmium, ruthenium, iridium, and rhodium salts dissolved in dilute hydrochloric acid or dilute sulfuric acid do not produce a precipitate on standing in contact with alcoholic dimethylglyoxime solution for 4 days.

A suitable condition for the sodium formate reduction of platinum is from solutions the acidity of which has been adjusted to pH 6.

Rhodium and iridium can be dissolved by a short fusion with a small proportion of sodium peroxide in a silver crucible and removed from the resulting silver solution by hydrolytic precipitation.

Acknowledgment

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A Thermionic Titrimeter without Batteries

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SINCE the vacuum tubes in a Wheatstone bridge circuit used by Hiltner (3) and others (1, 4-7) are capable of simultaneously acting as rectifiers of alternating current and as statically controlled variable resistors for the bridge, it appeared possible to power a thermionic voltmeter with ordinary alternating current. Trial not only showed it to be possible but also showed that the mere substitution of alternating for the usual direct current power enabled the device to measure alternating as well as direct current applied voltages.

Many vacuum-tube voltmeters have been described for chemical purposes since their introduction by Goode (2). This multiplicity of offerings is not indicative of a generally unsatisfactory performance of vacuum-tube voltmeters but rather is the result of advances in electrical engineering which enable succeeding authors to offer operational improvements of real value. More recently Hiltner (3) introduced a novel method of reducing the grid current to an exceedingly low value, negligible so far as titrations are concerned. His method required no manual adjustments, as contrasted to previous methods of regulating the grid current. He attained alternating current operation by the conventional method of rectifying the alternating current before applying it to the tubes. In the interim between presentation of the titrimeter described in this paper at the 88th meeting of the AMERICAN CHEMICAL SOCIETY in September, 1934, and the present time, during which it was thoroughly tested and developed, a circuit very similar to Hiltner's has been offered by Garman and Droz (1). They used alternating current power through the usual means of first rectifying and filtering it. Their chief contribution is introducing into chemical literature and chemical vacuum-tube apparatus the principles of mu-balance in combination with a Wheatstone bridge circuit. This rather elegant method of eliminating the effects of line voltage variations is probably effective, but considerable use of the more simple circuit to be described has shown that it is stable enough for purposes of titration. This paper presents a much simpler modification of the Hiltner voltmeter, adapting the circuit to alternating current power without a special rectifying tube and using American vacuum tubes.

Because of the inherent stability of the Wheatstone

bridge at and near balance, the use of self-biasing, and the use of a twin-type tube to obtain the advantage of identical vacuum and thermal fluctuations for both triode systems, together with a heater-type cathode, the usual fluctuations in the voltage of commercial lines have so little influence on the device as to be entirely negligible for potentiometric titrations but great enough to prevent better than about 0.1 pH precision in pH measurements.

As the name implies, the titrimeter is more useful and reliable for making titrations than for measuring equilibrium voltages, as in pH measurements with hydrogen and quinhydrone electrodes. The titrimeter passes sufficient current (0.1 to 0.5 microampere) so that it will not read the zero current voltage of such cells, but it can be employed to determine pH by using standard buffers to determine the small correction due to this small current. It cannot be used with the glass electrode.

This titrimeter is distinguished from all others based on the principle of the Wheatstone bridge by the fact that the tubes in the arms of the bridge not only serve as variable resistors but also simultaneously rectify the alternating current used to power the device and thus do away with all batteries and the necessity of a rectifying tube and filter system. The result of this dual function of the tubes is a remarkably simple circuit that requires fewer parts and is therefore simpler and more economical to construct, more fool-proof, and more convenient to use. It does not easily get out of order. One of these instruments has been in frequent use for more than a year without giving any trouble. These advantages make it particularly suitable for chemists, who are usually not familiar with thermionic circuits.

Much experimental work has influenced the selection of the following circuit constants and materials as the best compromise with regard to sensitivity, stability, ease of operation, low grid current, convenient assembly, and general availability of parts.

Circuit Materials

TUBE. RCA-53. RCA-6A6 is identical in characteristics except that it has a 6.3-volt heater; otherwise it can be substituted for RCA-53 without change.

METER. Weston microammeter, type 440, scale 0-150, 75 divisions, 3.5-ohm coil.

TRANSFORMER. Since the power requirements are

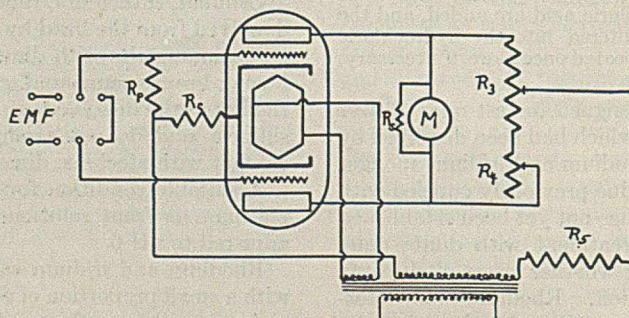


FIGURE 1. WIRING DIAGRAM

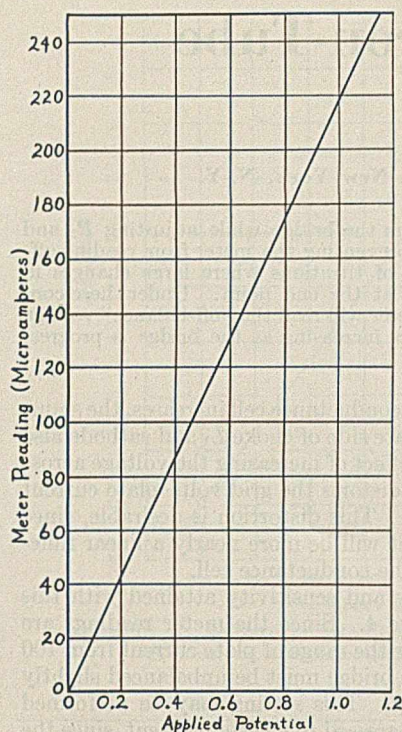


FIGURE 2. CALIBRATION CURVE

low, any good radio power transformer designed for midget sets and capable of delivering 10 ma. at 220 volts for the heater will be satisfactory. Should the high-voltage secondary of the transformer to be used be higher than 220 volts, the excess is dissipated by R_5 (Figure 1).

GRID SWITCH. Any type of double-pole double-throw switch can be used. A Federal anti-capacity switch can be recommended for its neat appearance, ease of assembly, and ease of operation.

FIXED RESISTORS. R_p determines the grid current; its value depends on the characteristics of the tube, and since these vary it is impossible to give any definite value. Four tubes re-

quired values between 50,000 and 200,000 ohms. The determination of this value is the only adjustment the builder of the titrimeter is required to make. This resistor is very conveniently handled when designed to be inserted in grid leak mountings, thus facilitating adjustment whenever a new tube is put into operation.

R_2 is a wire-wound resistor having 1000 ohms and capable of dissipating about 3 watts. Only a small fraction of this amount of power will actually be dissipated, but a wide margin is recommended as an aid in preventing a noticeable temperature rise which would change the resistance and cause drifts in the zero setting of the titrimeter.

R_3 is a wire-wound resistor whose value will depend on the value of the high-voltage winding of the transformer being used. It should be capable of dissipating three watts and have a resistance as given by the equation $R_3 = 480 (E_T - 220)$, where E_T = transformer voltage.

R_4 is a shunt resistor for the microammeter and has the value of 20 ohms.

VARIABLE RESISTOR. R_5 is a midget-type radio potentiometer whose resistance is 2000 ohms. It must be wire-wound.

R_1 is a midget radio potentiometer whose resistance is 50 ohms. It must also be wire-wound. If a radio rheostat is chosen for R_1 it should be the type with no "off" position. The settings of R_3 and R_4 have no bearing on the accuracy or sensitivity of the titrimeter, but the value of R_4 for measuring sensitivity depends on the effective resistance of the tubes and of the meter, and the value given is the proper one for the parts recommended.

To minimize grid current the following procedure is used:

A fairly sensitive galvanometer (a pointer type is satisfactory) is connected to the e. m. f. binding posts and the grid switch is thrown to include the galvanometer in the grid circuit. R_p is then varied between wide limits when attached to first one grid and then the other. When R_p is attached to one of the grids the galvanometer will show minimum current for some certain value of R_p . This minimum current must under no condition exceed 0.5 microampere, and if the proper value of R_p is used the minimum can be made 0.1 microampere and even less. In a later paper it will be shown that a grid current no greater than this has no effect on the titration cell.

It is important that the positive voltage being applied in measurements be connected to the same grid to which R_p is connected. A reversal of applied polarity immediately causes a grid current of several tenths of a microampere to

flow through the grid circuit. It is of course necessary to adjust the connection of the microammeter so that the negative binding post is connected to the plate corresponding to the grid to which R_p is connected.

The voltage to be measured is connected to the e. m. f. terminals, but the bridge circuit must first be balanced by throwing the grid switch to connect the two grids directly, and adjusting R_3 and R_4 until the meter shows zero current. Upon throwing the grid switch to include the e. m. f. between the grids, the bridge will be unbalanced by this potential to the extent shown by the reading of the meter.

If a meter other than that specified is used, its resistance must not be greater than 50 ohms unless one is willing to sacrifice sensitivity. The sensitivity to be expected with the above materials is 0.22 microampere per millivolt impressed on the e. m. f. terminals. Various factors combine to make repeated readings of the same impressed voltage show a maximum variation of about 0.75 microampere, so that one cannot read with certainty closer than about 4 millivolts of applied potential.

Higher sensitivities than that given can be obtained by decreasing the value of R_2 , the sensitivity being about double at zero ohms. However, there is a loss of stability as sensitivity is gained by this method and the difficulty of controlling the grid current is increased. Higher sensitivities may also be obtained with tubes of types 47, 2A5, and possibly 2A3, by using them in a two-tube circuit, but this is more than counterbalanced by the difficulty of maintaining calibration, by the necessity for using large resistors, by the greatly increased cost, and by other disadvantages.

As a direct-reading voltmeter it must be calibrated if the meter specified is used. Figure 2 shows a calibration curve. The calibration will not change until the tube emission becomes weak after very long use. The zero point should be checked before beginning a titration or making a voltage reading. The apparatus must be calibrated separately for measuring direct and alternating current voltages. The applied alternating current voltage to be measured must be phased properly. If the alternating current voltage being measured is of the same frequency as that applied to power the voltmeter and if it is also in phase or 180° out of phase with the voltage used for power, connecting the applied potential one way to the voltmeter causes no response, whereas the reverse connection results in meter readings proportional to the applied alternating current voltage.

Summary

A simple thermionic voltmeter without batteries has been described which operates from the alternating current lighting circuit, and is particularly convenient for potentiometric titrations. It is sensitive to 3 or 4 millivolts and the grid current, which is usually not over 0.1 microampere, has no effect on the titration cell.

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A Continuous-Reading Electron-Tube Conductance Meter

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SEVERAL investigators have discussed continuous-reading conductance meters. Thus Jander and Schorstein (3) use a galvanometer with a bridge, while Sand and Griffin (1) use a dry rectifier with a bridge network. Treadwell (4) and Callan and Horrobin (2) supply the voltage to the cell and read relative resistance with a vacuum-tube device. Many of these methods are not very sensitive or lack general portability and require the use of calibration curves.

A vacuum-tube instrument has been constructed which incorporates an oscillator supplying audio frequency voltage to a self-contained bridge, a detector, and direct current meter which indicates the resistance of a conductance cell. These functions are performed with a single 6A6 tube whose circuit elements are properly arranged so that meter readings are a linear function of the resistance of the conductance cell. The instrument derives all power from alternating or direct current mains.

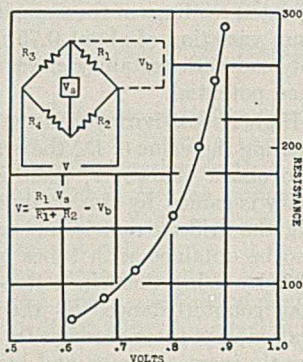


FIGURE 1. TYPICAL CURVE

Theory

The output voltage of a bridge is a parabolic function of the resistance of any one of its arms. A typical example is shown in Figure 1. The plate current-grid volts curve of a vacuum tube is not a linear function in the region of high negative values of grid voltage. A typical curve for a high mu triode is shown in Figure 2. (Direct current voltages were used in these calculations for simplicity and are permissible since the curves are used as illustrations only.) If these curves can be completely superimposed, an instrument may be constructed in which the plate current of an electron tube is a linear function of the resistance of one arm of a bridge. Complete superimposition is difficult to attain in practice, but may be approximated sufficiently to satisfy the requirements of conductance titrations.

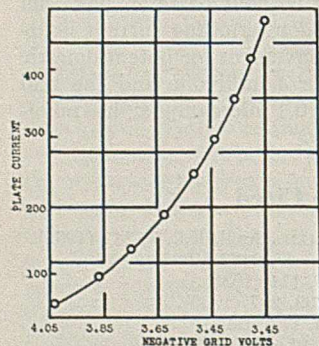


FIGURE 2. TYPICAL CURVE FOR HIGH MU TRIODE

Operation

The upper section of the triode 6A6 (Figure 3) is used as an oscillator and the alternating voltage developed across resistance R_6 is applied to the bridge through condensers C_2 and

C_4 . The voltage from the unbalanced bridge is applied to the primary of the step-up transformer T_2 . The stepped-up voltage is applied to the grid of the lower section of the triode which is negatively biased to zero plate current by adjustment of R_3 . A sensitivity control, R_2 , is used to attenuate the alter-

nating current voltage from the bridge while adjusting R_3 and to reduce the sensitivity, preventing the meter from reading off-scale in the performance of titrations where large changes in resistance are anticipated at the end point. Under these conditions of operation the meter will read the "off-balance" voltage of the bridge, the readings increasing as the bridge is progressively unbalanced.

As the resistance of the conductance cell increases, the shunt resistance between the plate side of choke L_1 and cathode also increases. This has the effect of increasing the voltage across the bridge terminals and distorts the grid volts-plate current curve shown in Figure 2. This distortion is desirable, since the resulting plate current will be more nearly a linear function of the resistance of the conductance cell.

The degree of linearity and sensitivity attained with this set-up is shown in Figure 4. Since the meter readings are linear with resistance over the range of plate current from 100 to 500 microamperes, the bridge must be unbalanced slightly before readings are taken. This setting may be performed after the titration has progressed to a certain extent, since the first readings are usually excluded in the final determination of the end point. This has a further advantage because almost full scale of the meter may be used in the region near the end point for greater accuracy.

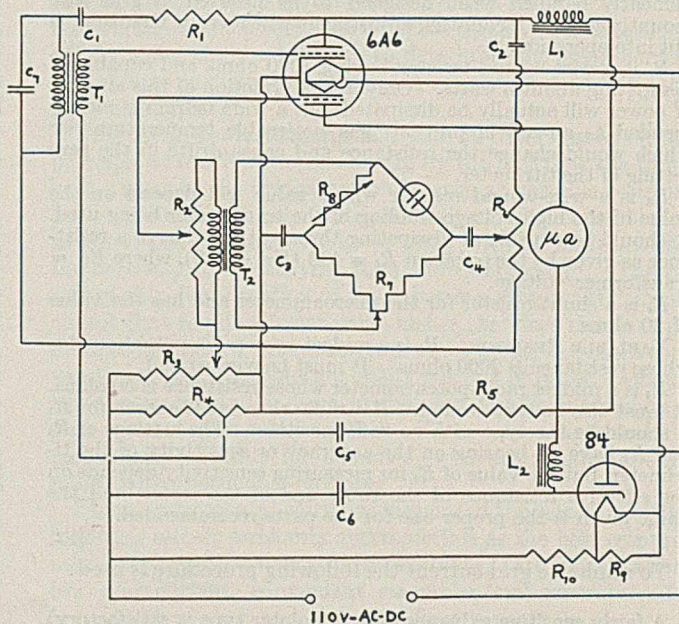


FIGURE 3. DIAGRAM

- R_1 . 5 to 7 megohms, 1 watt
- R_2 . 1-megohm volume control
- R_3 . 50,000-ohm volume control
- R_4 . Voltage divider, 1000 ohms, 25 watts
- R_5 . Voltage divider, 20,000 ohms, 25 watts
- R_6 . Volume control, 15,000 ohms
- R_7 . General radio potentiometer, 1000 ohms
- R_8 . General radio potentiometer, 100 ohms
- R_9 . 15 ohms, 100 watts
- R_{10} . 140 ohms, 100 watts
- C_1 . Condenser, 0.01 mfd., mica
- C_2, C_3, C_4 . Condensers, paper, 0.5 mfd., 200 volts
- C_5 . Electrolytic condenser, 8 mfd.
- C_6 . Electrolytic condenser, 4 mfd.
- T_1 . Low ratio audio transformer
- T_2 . Single-button carbon microphone transformer
- L_1 . Choke, 30 H. 200 ohms
- L_2 . Choke, 30 H. 200 ohms
- μa . 0-500 microammeter

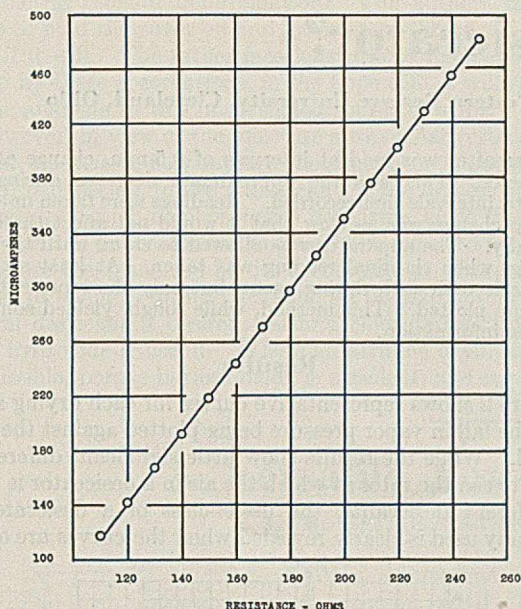


FIGURE 4. LINEARITY AND SENSITIVITY ATTAINED
Plate current—resistance of conductance cell

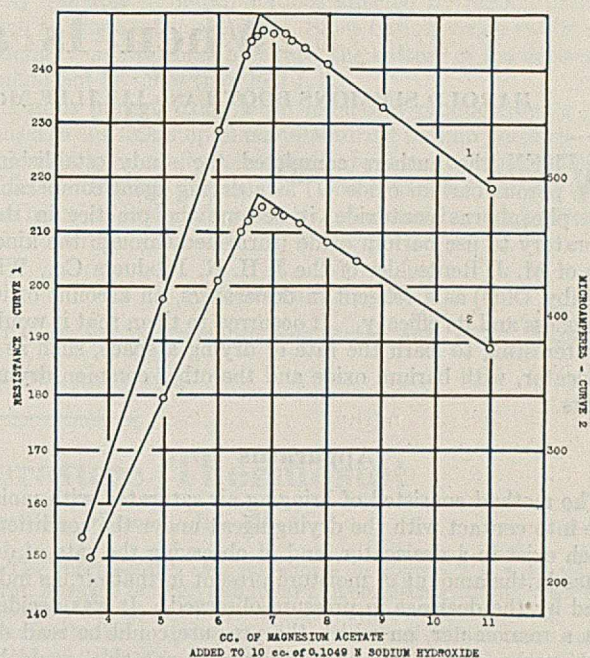


FIGURE 5. CONDUCTANCE TITRATION

Construction

The oscillating circuit was designed to offer a maximum in stability and yet lend itself to easy construction.

Transformer T_1 must be correctly poled to permit oscillations, and resistance R_1 should be as high as possible yet allowing sufficient energy feed-back to sustain oscillations. A high value of this resistance assures smooth operation and good wave form. The setting of R_4 is not critical and may be adjusted for maximum oscillator output (-2 to -3 volts are usually satisfactory). T_1 may be any low-ratio audio transformer, and since many of these units have a natural period of oscillation at approximately 1000 cycles per second, condenser C_7 may be omitted.

The bridge may be standard equipment or may consist of large-size wire-wound potentiometers since no calibration is required. Since the ratio of resistance in the bridge arms determines the curvature of the curve shown in Figure 1, the values must be as stated to attain the desired linearity. If, however, the apparatus is to be designed to measure higher resistance values of the conductance cell, the resistance of the bridge arms as well as the impedance of transformer T_2 should be increased proportionately. Meter readings are relative and the proper setting of resistors R_7 and R_8 may conveniently be determined for a particular range of resistance by substitution of a variable resistance box for the conductance cell. The settings of R_7 and R_8 are varied until equal increments of resistance produce equal increments of microamperes.

The inclusion of a rectifier and filter system permits satisfactory operation on both alternating and direct current mains.

Figure 5 illustrates a typical titration curve. In each case 10 cc. of 0.1049 N sodium hydroxide subsequently diluted to 200 cc. were titrated with magnesium acetate. The end point for curve 1, taken by the usual bridge methods, is 6.73 cc.; for curve 2 taken with the instrument it is 6.71 cc.

The error may be assumed to rest entirely with the inaccuracies encountered in the extrapolation.

The circuit described here does not represent the only one suitable for the purposes outlined. It represents rather a simple scheme which may be translated into a compact instrument and the cost of the parts, including the meter and cabinet, need not exceed twenty-five dollars. A more complicated circuit extending the principles described here could certainly be made in which the conditions of linearity are more closely approximated. It is the ardent hope of the author that such circuits will be devised to further the technique of conductance titrations.

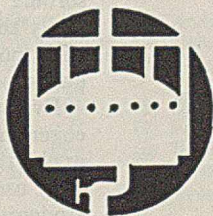
Summary

A vacuum-tube conductance meter deriving power from alternating or direct current mains combining an audio oscillator-bridge and a detector-meter system has been described. The application to conductometric titrations has been illustrated and it has been shown that meter readings are linear with resistance over four-fifths of the meter range.

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When Is a Desiccator?

HAROLD SIMMONS BOOTH AND LUCILLE MCINTYRE, Western Reserve University, Cleveland, Ohio

WHEN the authors completed the study establishing porous barium oxide (1) as a drying agent comparable with phosphorus pentoxide, it became the practice in this laboratory to use barium oxide (furnished through the kindness of M. J. Rentschler of the J. H. R. Products Co., Willoughby, Ohio) as a reagent in desiccators, on account of its cheapness and its efficacy. It occurred to them that it would be interesting to learn the rate of drying a space, such as a desiccator, with barium oxide and the other common drying agents.

Apparatus

The method consisted of bringing air saturated with moisture into contact with the drying agent under the conditions which exist in a desiccator, and of observing the rate of decrease in the amount of moisture present in that air, as indicated by the decrease in pressure observed. It was decided that a manometer, on which the pressure could be read directly owing to a Toricellian vacuum on one side, could be used to measure the drop in vapor pressure sufficiently accurately for this purpose.

In preparation for a run, moist air was drawn through the gas-washing bottles through stopcocks 4 and 5, while 3 (Figure 1) was closed, into the gas holder, *D*, by applying suction to the outlet at the bottom of *D*. Water was then run into *D* from vessel *C* through stopcock 6 until the pressure inside *D* equaled that of the outside atmosphere. All stopcocks were closed and the moist air was allowed to stand overnight in *D*.

One hundred grams of the fresh drying agent were put into a Petri dish which just fitted the bottom of the desiccator. The lid on the desiccator was greased with a stopcock grease of proved low vapor pressure, and the cross piece of the wooden frame holding the desiccator in place was fastened down. A rubber stopper of a size near that of the handle of the desiccator lid was fastened to the wooden cross piece so that when the latter was in place, the pressure upon the handle of the cover of the desiccator was relieved by the elasticity of the stopper. The desiccator was sealed to the apparatus near stopcock 1 by DeKhotinsky cement.

Stopcock 2 was opened, and the manometer, *B*, and the desiccator were evacuated. Stopcock 2 was then closed and the apparatus allowed to stand overnight to be sure that no slow leaks would develop. The next day stopcocks 3 and 5 were opened and the water-saturated air was forced into the desiccator by allowing water to run into bottle *D* from vessel *C* through stopcock 6 until the pressure in the desiccator was about 760 mm. As soon as the stream of air was shut off, the vapor pressure was read on the manometer and the time recorded. The pressure was read at intervals of 1 minute until the fall in pressure was slow

and thereafter was read at intervals of 0.5-mm. change on the manometer. This was the approximate decrease during the 1-minute intervals first recorded. Readings were taken until the pressure change was so slow that it would not affect the curve materially. The apparatus was allowed to stand until the next morning, when the final reading was taken. At least six runs were made with each drying agent, but only the representative ones were plotted. This method, while rough, yielded some interesting information.

Results

Figure 2 shows representative curves for each drying agent used, the fall in vapor pressure being plotted against the time elapsed. While the results show little significant differentiation between the rates at which the air in a desiccator is dried by different desiccants, the uselessness of a desiccator as commonly used is clearly revealed when the curves are exam-

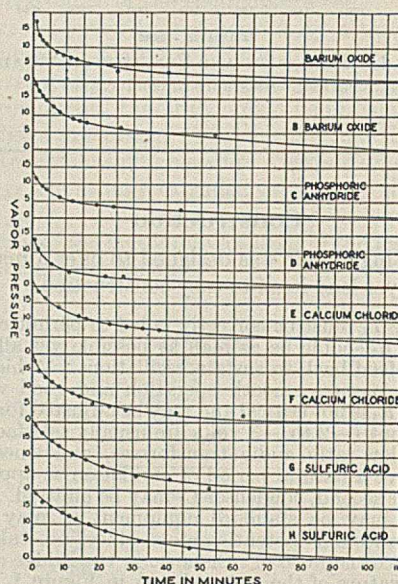


FIGURE 2. REPRESENTATIVE DRYING CURVES

ined. The average analyst has a holy respect for the power of a desiccator to keep his ignited crucibles dry during the cooling process, yet is careless about keeping the desiccator closed and about opening for only the briefest time. The writers have seen a student open a desiccator, go to the oven or electric crucible furnace, get his crucible, return, and put it in the desiccator to "cool in a nice dry atmosphere." Let us assume that half of the air in the desiccator has been displaced, and that the air let in is half saturated, or roughly that a partial pressure of 5 mm. of water vapor is now in the desiccator. The crucible will attain practically room temperature in 10 minutes, in which time the drying agent will have lowered the partial pressure of the water vapor in the air in the desiccator only 2 mm., while the crucible is simultaneously adsorbing the moisture from the air in the desiccator. Generally the air in the analytical laboratory is nearly saturated with moisture, so that the probable moisture content in the desiccator would be much higher.

Even some textbooks advise the student not to place the cover on the desiccator until the crucible has cooled somewhat or else the expansion of air will blow the cover off and break it! Why use a desiccator at all if that is the criterion? How can students following such advice ever get constant weight on a

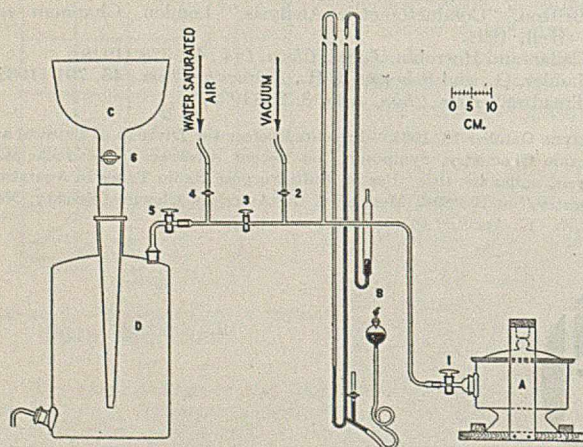


FIGURE 1. APPARATUS

gravimetric calcium determination? The authors tell students to hold the cover on and let some of the heated air escape if it will. The rather facetious title of this paper is inspired by these observations, in the hope that it will serve to arouse analysts to this unsuspected source of error.

However, in view of the moisture always inadvertently admitted, no matter how rapidly the desiccator is opened and closed, it is useless to use a desiccant of the highest absolute drying power such as phosphorus pentoxide, since the object cooling in the desiccator will ordinarily be removed for weighing before the space can be dried completely. Save for the danger of spilling, sulfuric acid should be satisfactory. If a neutral desiccant is desired, calcium chloride free from calcium hydroxide is useful. Where an alkaline drying agent is permissible, porous barium oxide is excellent, and is particu-

larly valuable in determinations affected by carbon dioxide, such as gravimetric calcium. Since barium oxide swells considerably on absorbing moisture, the bottom of the desiccator should not be more than half full.

Porous barium oxide is an industrial product, being produced in the first step in manufacturing barium peroxide, and is available more cheaply than anhydrous calcium chloride, which is difficult to prepare. The exhausted barium oxide can be used for the preparation of standard barium hydroxide solutions for alkalimetry.

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RECEIVED April 1, 1935.

A Versatile Low-Temperature Thermostat

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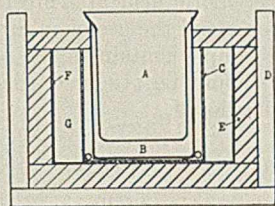


FIGURE 1

definite quantity of a vapor, and the determination of vapor pressure, temperature, composition diagrams, etc.

A number of investigators have described thermostats which may be operated at low temperatures (1, 2, 4-6). Some are rather elaborate pieces of apparatus, while others are relatively simple. The thermostat described here is easily made from materials found in any well-equipped laboratory, and has been used to maintain a constant temperature in the range $+25^{\circ}$ to -75° C. The fluid used in the bath may be acetone, alcohol, or kerosene, depending on the temperature to be maintained. Acetone freezes at -94.6° and retains its mobility at the temperature of solid carbon dioxide. Alcohol becomes viscous below -40° . Kerosene may be used for temperatures to about -40° C.

The container for the bath is a 3-liter Pyrex beaker, A, which is set in a 4-liter beaker, B. The air space between the two beakers serves to prevent the bath from cooling too rapidly. The formation of ice between the beakers may be prevented by sealing the crack with rubber cement used to fill cuts in the tread of automobile tires. The nested beakers are placed in a can, C, whose diameter is 5 cm. (2 inches) greater than that of the larger beaker, and centered by a ring made from rubber tubing of appropriate size. The can containing the beakers is placed in a wooden box, D, fitted with cork lining, E, built around the square tin can, F. If a constant temperature is wanted for several hours only, the space between the outer beaker and can C is filled with a slush of well-crushed dry ice and alcohol. If a constant temperature is wanted for a considerable time, the space, G, is also filled with crushed dry ice.

The bath is stirred with a turbine paddle attached to a Bakelite or metal rod, the other end of which is connected to the shaft of a small induction motor. An induction motor is desirable to avoid igniting the vapors from the bath.

Since the bath is constantly being cooled, it is necessary to supply heat to maintain a constant temperature. This is done by means of a heating coil made from 10 cm. of No. 24 resistance wire welded or clamped to leads made of No. 18 iron wire, which are connected to the secondary terminals of a 25-watt toy transformer. The current in the primary circuit of the transformer is made and broken by a relay as the temperature varies. The proper amount of heat necessary to offset the cooling is obtained by adjusting the voltage.

THE commercial production of solid carbon dioxide has made available an economical and convenient method of obtaining temperatures down to -78° C. A constant low temperature is desirable for many operations, such as the study of reaction rates, the saturation of a gas with a

The thermostatic element shown in Figure 2 is a bimetallic strip, A, made of brass and invar and consisting of four bows with the open end of the bows directed toward the long axis. The distance between the open ends of the bow will increase or decrease on warming, depending on whether the invar is on the inside or outside of the bow. A brass or preferably glass or Bakelite rod, B, rests on the lower end of the last bow. The upper end of the rod fits into a cup attached to a screw, E, threaded onto a piece of spring brass, C, one end of which has a fixed position. Screw E is adjusted so as to place a slight tension on the spring arm, C. The other end rises and falls with a change of temperature in the bath, making and breaking the grid current of a radio relay circuit (3). A thermionic relay control of some sort is required, since no sparking should occur between the contacts.

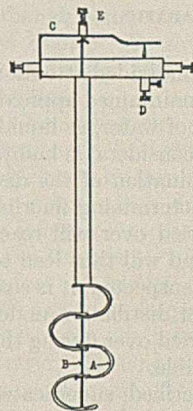


FIGURE 2

To start the thermostat, the bath is cooled to a temperature slightly below that wanted by pieces of dry ice in a small wire sieve, such as that used for straining tea or coffee, or a cup made of wire screen, immersed so that the liquid comes in contact with the cooling agent. The gas bubbles have only a short distance to go before reaching the surface of the liquid and the usual overflow is thus avoided. The stirring motor is started and screws E and D are adjusted so that heat is being supplied to the bath. When the proper temperature is reached the screws are adjusted so that the heat is discontinued.

To increase the temperature of the thermostat, it is only necessary to cause the heater to go on, and when the proper temperature is reached to adjust screw E, place a slight tension on rod B, and turn screw D so that the heater goes off.

The temperature of the bath is constant $\pm 0.01^{\circ}$ C. About 5.5 kg. (12 pounds) of dry ice were required to maintain a temperature of -38.1° C. for nearly 18 hours and 45 kg. (100 pounds) were used during a week.

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RECEIVED December 23, 1935.

Improved Apparatus for Isolation of Fluorine

Willard and Winter Method

W. K. GILKEY, H. L. ROHS, AND H. V. HANSEN

Calumet Chemical Company, Joliet, Ill.

IN THE determination of small amounts of fluorine according to the method of Willard and Winter (2), hydrofluosilicic acid is distilled from a sulfuric or perchloric acid solution of the sample, the temperature of the solution being held at about 135° C. by the addition of water at the proper rate to maintain this temperature.

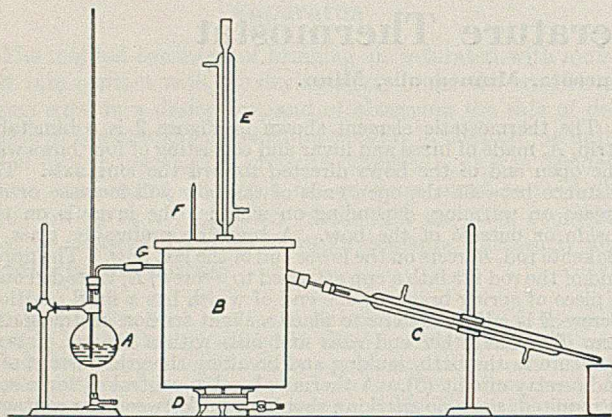


FIGURE 1. DIAGRAM OF APPARATUS

This method of distillation requires the undivided attention of the analyst if the temperature is to be maintained approximately constant. Moreover the addition of water, as liquid, to the hot contents of the flask results in considerable bumping with the attendant danger of contamination of the distillate. This is a source of error when determining fluorine in phosphates (1), as the phosphate carried over will react like fluorine in the subsequent titration and will thus lead to high results. Where such entrainment is suspected, it is customary to subject the distillate to another distillation under the same conditions. The phosphate carried over during the second distillation ordinarily will be negligible.

By the use of the apparatus herein described, superheated steam is substituted for water, thereby eliminating the danger of bumping; also the contents of the distilling flask are maintained at a constant temperature by being immersed in the vapors of a boiling liquid. The above-mentioned difficulties are thus avoided.

Apparatus

Referring to Figure 1, steam is generated in flask A which is provided with a safety tube, the purpose of which is to prevent the contents of the distilling flask from being sucked back in case the pressure in A falls below atmospheric. The steam passes from A into a copper tube which is wound around the inside of vessel B. (B was made of brass, but copper or steel would undoubtedly have been equally satisfactory.) This vessel, containing boiling tetrachloroethane, is heated by gas burner D and is provided with condenser E and thermometer F. In passing through the copper tube, the steam becomes superheated to the temperature maintained within the vessel. This superheated steam is then passed through a glass tube into the bottom of the distilling flask where it bubbles through the acidified sample and is subsequently condensed in C.

Figure 2 shows a detailed section of B and its contents. The heavy, removable lid has a machined groove in which a cork gasket is inserted. Since the organic vapor contained in B at-

tacks rubber, all stoppers are of cork and must be selected and drilled carefully if leaks are to be avoided. (Corks could be eliminated by using ground-glass joints. The cork through which the steam enters the flask can be eliminated by using a glass seal at this point. The obvious disadvantage is the increased danger of breaking the joint when assembling the apparatus for a determination.) In this laboratory the distilling flask used is of the Claisen type, but probably a simple distilling flask would be satisfactory. The tetrachloroethane used in B is the Eastman technical grade. It is nonflammable and boils at 145° C. A depth of about 2 cm. in the bottom of the vessel is sufficient.

According to Willard and Winter, there is danger of violent oxidation of organic matter by perchloric acid at temperatures exceeding 135° C.; they recommend the use of sulfuric rather than perchloric acid if the sample contains much organic matter. This substitution should be observed when tetrachloroethane is used as a heating liquid.

Procedure

The procedure in making a distillation is as follows:

Flask A is disconnected from the copper tube at the rubber connection, G (Figure 1). The distilling flask, which contains a few glass beads, the sample, and the perchloric or sulfuric acid, is placed in position, all joints (except G) are made tight, and the burner, D, is lighted. Since the sample is usually added as an aqueous solution or suspension, the dilution of the acid is ordinarily so great that the contents of the flask will begin boiling at a relatively low temperature, but the boiling point will gradually rise as the water distills off. When the rate of flow from condenser C becomes small, flask A, which has been made ready and is now delivering steam, is connected to the copper tube and the steam distillation allowed to continue until a sufficient quantity of distillate is collected.

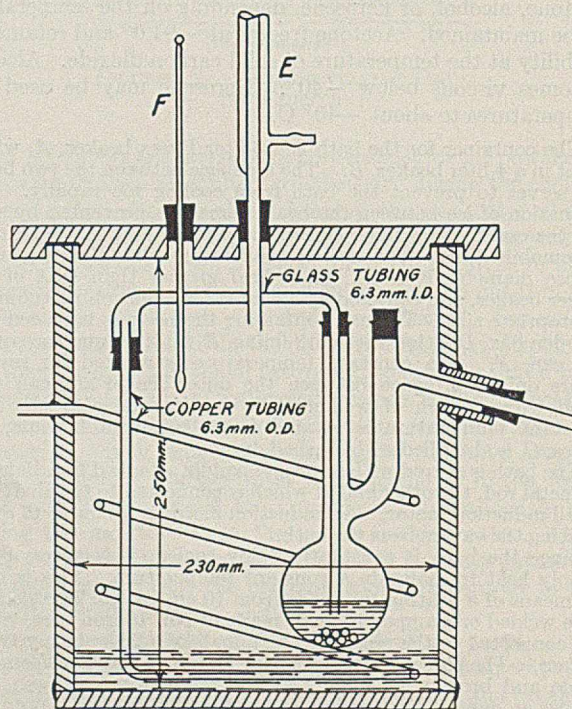


FIGURE 2. SECTION OF B AND ITS CONTENTS

A leaky cork will allow steam to pass into the organic vapor contained in vessel *B*. Even a small leak of this kind manifests itself as a noticeable drop in the temperature indicated by thermometer *F*.

Results

The apparatus has been in almost daily use in this laboratory for several months, and except for occasional leaks around corks has given no trouble whatever. Results ob-

tained with it, exercising only the precaution mentioned, have repeatedly checked those obtained with the original method of distillation using extreme care.

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RECEIVED November 7, 1935.

Improved Micromanometer

HARRY W. SMITH, JR., American Gas Association Testing Laboratories, Cleveland, Ohio

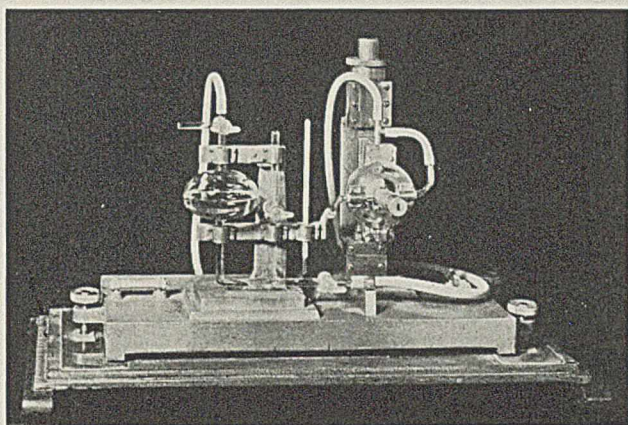


FIGURE 1

A SIMPLE, convenient, and rugged design of micromanometer, adaptable to routine measurements of minute pressures and pressure differentials, has been developed by engineers of the American Gas Association Testing Laboratories and successfully used by both the Cleveland and Los Angeles laboratories for several years.

The American Gas Association micromanometer consists, as shown in Figures 1 and 2, primarily of a heavy metal base, equipped with suitable leveling screws and indicating levels, and supporting reasonably massive columns carrying, respectively, the micromanometer screw assembly and the gage liquid reservoir. The reading meniscus lies in a short length of straight 0.25-inch glass tubing inclined at a slight angle from horizontal (generally in the neighborhood of 3°) and securely affixed to a thick-brass annular plate attached to the micrometer screw. This plate may be rotated and clamped to its carriage in order to permit adjustment of the slope of the meniscus tube. The other arm of the gage, comprised of a liquid reservoir bulb 3 to 4 inches in diameter, preferably with straight vertical sides, is clamped rigidly to the left brass column and connected to the movable meniscus tube by a length of thick-walled rubber tubing as short as possible and directed uniformly upward so that bubbles may not be trapped therein.

At its mid-point, the meniscus tube is supplied with a cross hair or engraved hairline. The meniscus is observed through a magnifying eyepiece of the variety commonly used for reading precise calibrated mercury thermometers. It is often necessary to locate a light disk, painted in flat white, behind the hairline and in line with the eyepiece, to facilitate reading in questionable light.

Forty threads per inch, corresponding to a linear pitch of 0.025 inch, should be cut on the micrometer screw, the diameter of which should not be less than 0.5 inch. At the Testing Laboratories the screw head is divided 25 divisions to the

circle, affording a division mark on the instrument for every 0.001 inch of pressure. By interpolating between the divisions in fifths, accurate readings may be made to 0.0002 inch.

Both openings of the glass gage system, the two pressure connections, are fitted with vent branches including glass stopcocks. All glass tubing clamps on the apparatus are fashioned of brass but lined with rubber to preclude breakage by shock or expansion.

The Testing Laboratories employ methyl alcohol as the gage liquid, since it does not affect the rubber tubing, possesses an accurately known specific gravity, and exhibits a low surface tension. Distilled water or any other liquid may, of course, be used with proper care so long as the specific gravity is known. If the instrument is constructed as indicated, precise readings may be made with it in 30 seconds. Additional speed of measurement may, of course, be attained if the slope of the meniscus tube is set at more than 3° from level, although some sensitivity is sacrificed thereby. A slope of less than 3° destroys the ease of adjustment necessary for routine usage and adds little or nothing to the accuracy of readings.

When using the micromanometer it is essential that the meniscus be brought to the point of adjustment on the cross hair always by turning the micrometer head in the same direction (that which draws the meniscus tube upward). This procedure overcomes errors due to play in the micrometer screw threads and failure of the movable assembly to drop against the friction of its ways.

Contrary to frequent belief, it is not mandatory that the sides of the liquid reservoir be absolutely vertical at the risk of error. So long as the volume of the liquid in the gage remains the same, the volume between the hair line (when the meniscus is adjusted upon it) and the surface of liquid in the reservoir must be the same, and therefore the level of the liquid in the reservoir bulb is, at the completion of any adjustment, identical with that obtained with atmospheric

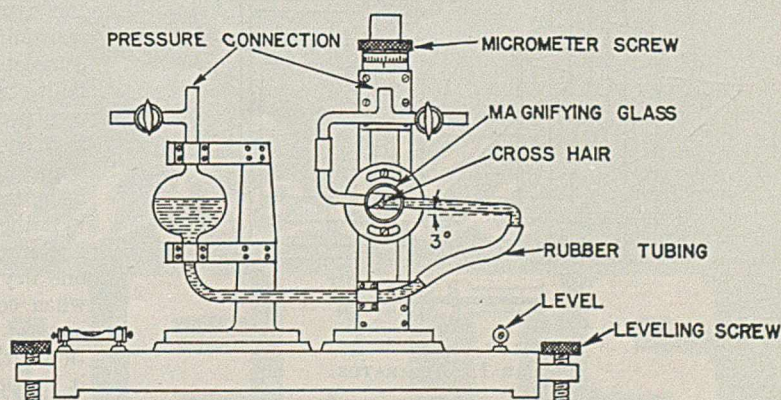


FIGURE 2

pressure at both points of pressure connection. The walls of the reservoir should be reasonably straight and its diameter reasonably large only to minimize the small errors due to evaporation, wetting of gage walls, and oscillation of the meniscus during adjustment.

In operation, the meniscus is simply adjusted to the hair-line with atmospheric pressure at both ends of the gage, a micrometer head reading taken, the pressure or pressure differential condition that is to be measured established by turning suitable cocks, the meniscus readjusted to the hair-line, and the micrometer head again read. The simple difference between the two readings, in marked divisions,

gives the pressure or the differential directly in 0.001 inch of gage fluid column. Since the instrument is so sensitive, it is often necessary to protect the pressure connections from drafts, to check on temperature variations, and to read the zero adjustment of the meniscus frequently whenever a long series of observations is being made.

Being at once elementary in theory, simple in operation, inexpensive in construction, rapid in adjustment, precise, direct-reading, and rugged, the American Gas Association Testing Laboratories' micromanometer should find wide use in many industrial fields.

RECEIVED January 7, 1936.

Device for Determining Rate of Siphoning in Metal Extraction Systems

R. S. ASBURY, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

IN THE course of investigations on the solvent extraction of bituminous coal in a steel Soxhlet apparatus at elevated temperatures and pressures, an indicating system has been developed for determining the frequency of siphoning. Extraction in such an apparatus requires intermittent siphoning and, since this could not be observed, an indicator within the extractor was necessary. The indicating system is simple and inexpensive and could be adapted to any apparatus in which knowledge of frequency of transfer of liquid from one part to another was required, and in which visual observation was impossible or inadvisable. The apparatus developed has been in satisfactory operation for over 8 months,

using as solvents aniline and tetralin at temperatures to 400° C., and at pressures to 25 atmospheres.

As shown in Figure 1, the system consists essentially of a metal siphon tube, *A*, from the siphon cup above (not shown); a bucket arrangement, *B*; insulators, *C*; an insulated lead to the exterior, *D*; and an indicating system, *E*. All metal parts of the indicator proper except the main steel frame are made of nickel. The siphon tube, *A*, extends down into a grounded metal frame, *F*, which holds the buckets, *B*, loosely between two pivot bearings, *G*. A second metal framework, *H*, insulated from the first and held rigidly by small radio-type stand-off electrical insulators, *C*, serves as contact between the buckets and the wire lead to the exterior. This frame, *H*, also limits the downward motion of the buckets, which are counterbalanced by an attached weight, *K*. The insulated lead to the exterior, *D*, consists of a glass-insulated copper wire, *M*, to which is soldered a copper washer, *O*, compressed between two Bakelite washers, *N*, within the steel body of the closure as shown. The high-pressure closure is approximately 17.5 cm. (7 inches) above the extractor, but only at the higher temperatures is it necessary to cool the portion containing the Bakelite disks to prevent their decomposition.

Liquid overflowing through the siphon tube causes one of the buckets to fill, descend, and spill its contents. This movement of the bucket past the siphon tube, *A*, prevents more liquid from entering and raises the other bucket of the unit to a position where it now receives the overflow and in turn fills and descends. The downward motions of the buckets are stopped by the frame, *H*. The buckets continue this oscillation as long as liquid flows from the siphon tube. Each time contact of one of the buckets with *H* is made within the extractor, the electrical circuit through the dry cell, resistance, milliammeter, and steel wall of the extractor is completed and the pointer of the meter moves to its upper limit; when this contact is broken the pointer returns to zero position. By counting the swings of the pointer the frequency of siphoning can be determined, and knowing the approximate volume of each bucket, the amount of liquid being transferred can be estimated.

In the system used in this laboratory the external resistance in the indicating circuit, *E*, is so adjusted that current from one dry cell causes the meter to register one milliamper when contact is made within the bomb. With this small amount of current flowing through the circuit, the deterioration of the nickel contacts used is negligible. In certain cases, it has proved desirable to use platinum contacts.

RECEIVED December 23, 1935.

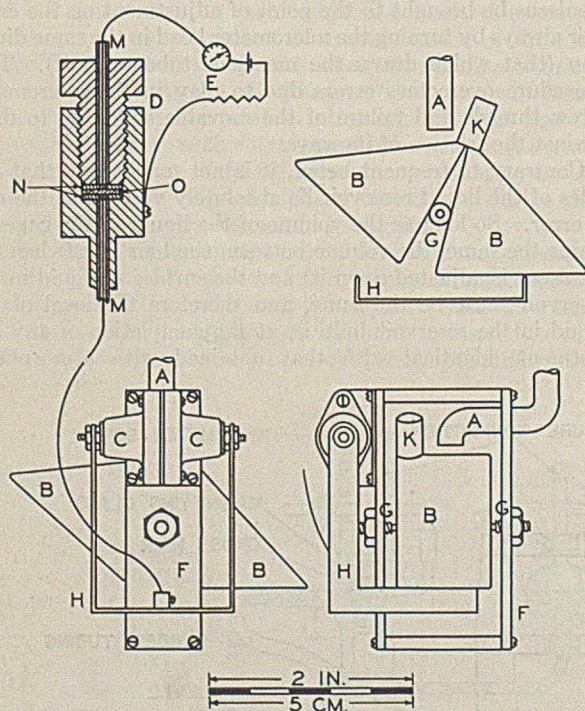


FIGURE 1. APPARATUS






Upper left, high-pressure closure
Upper right, essential parts

Lower left, front view
Lower right, side view

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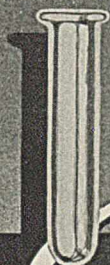


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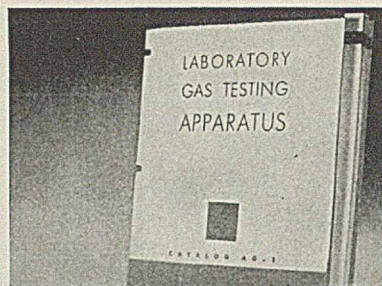
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Total Bacteria per cc.	none

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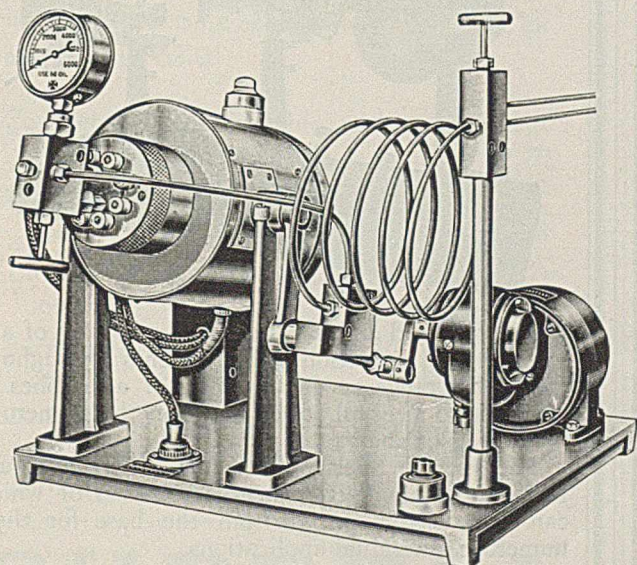
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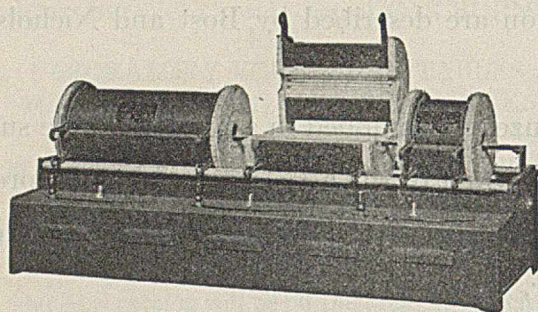
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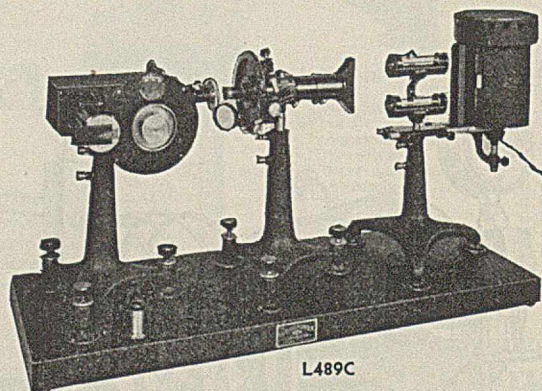
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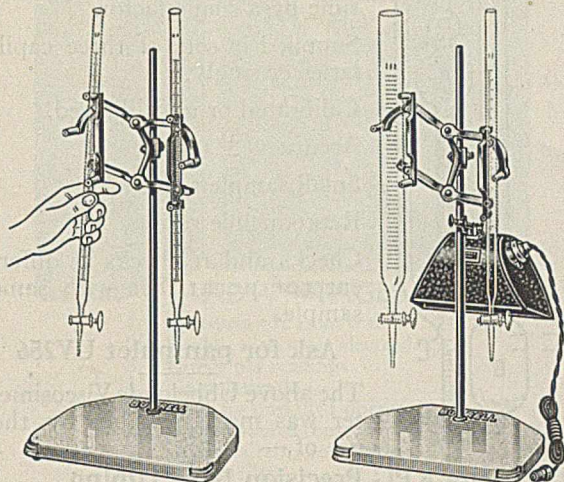
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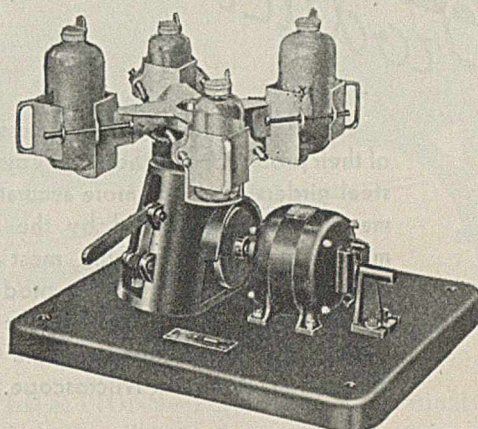
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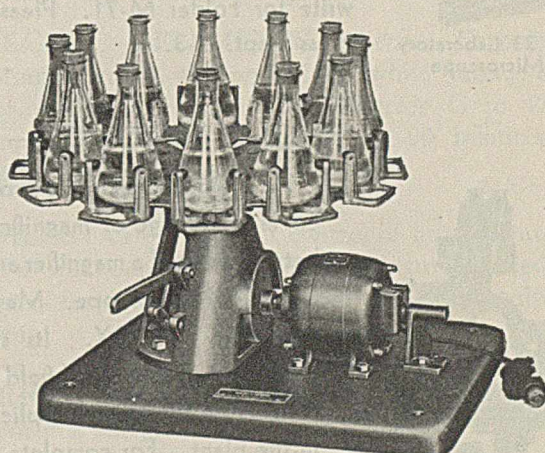
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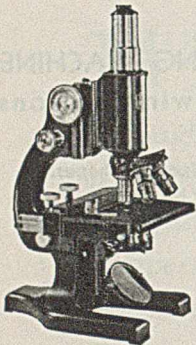
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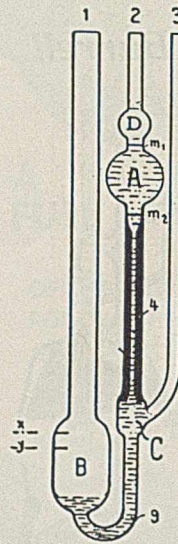


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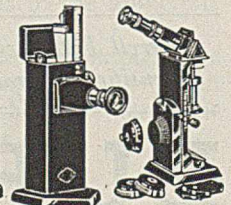
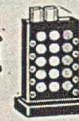
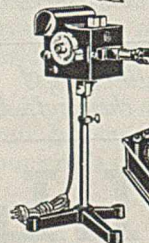
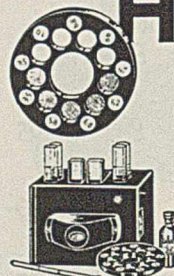
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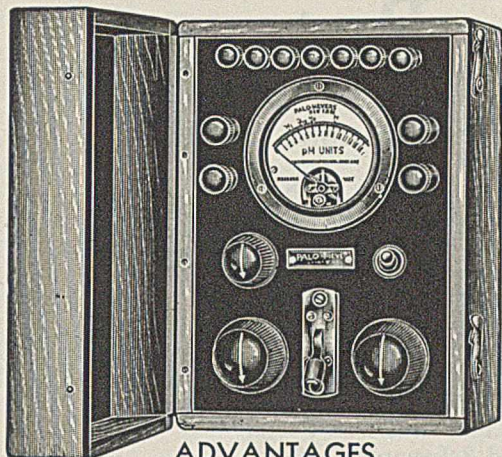
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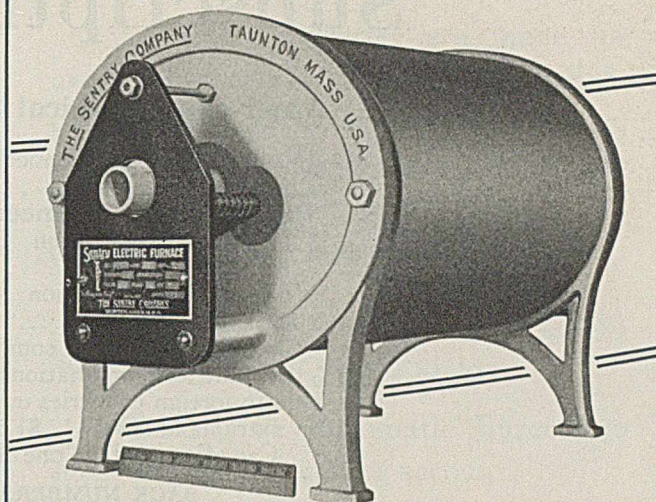
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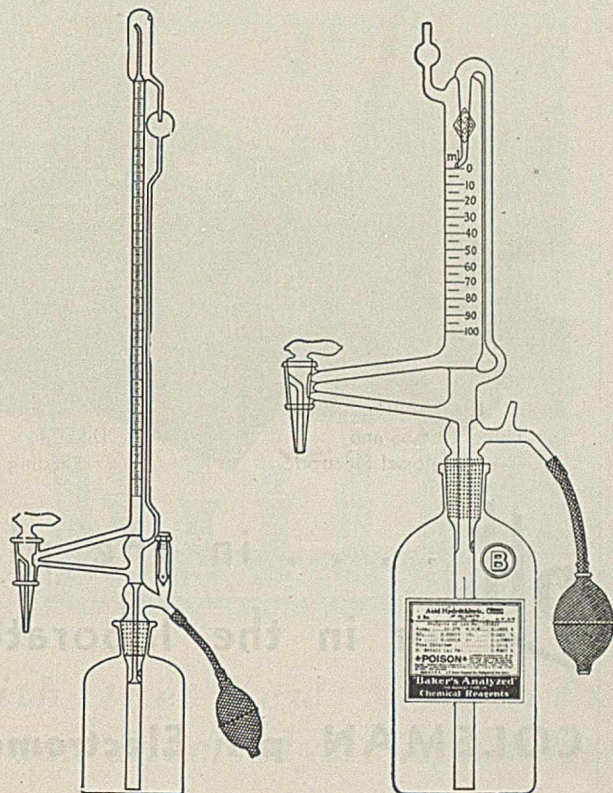
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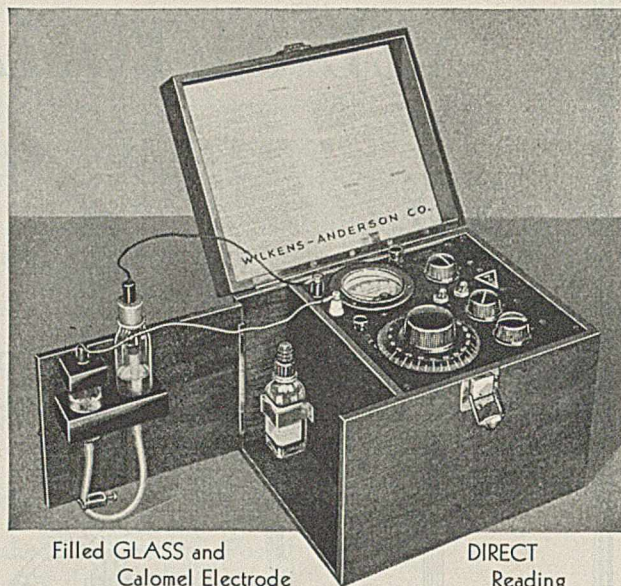
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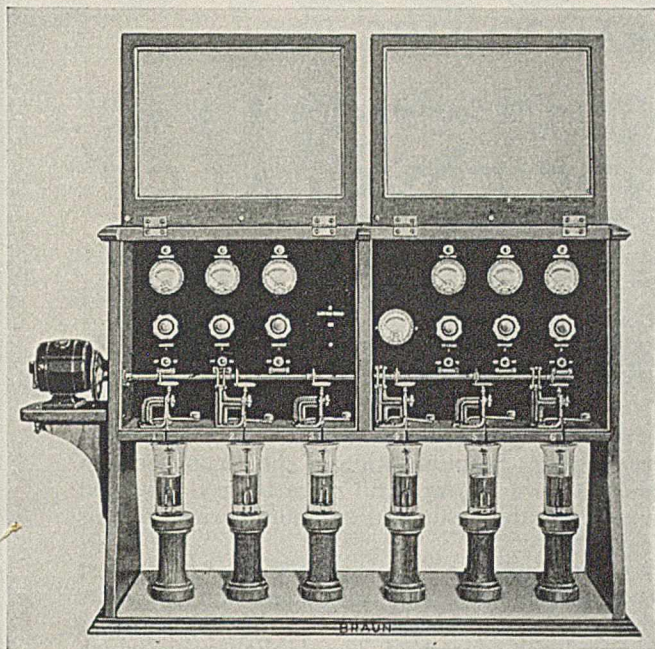
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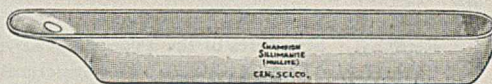
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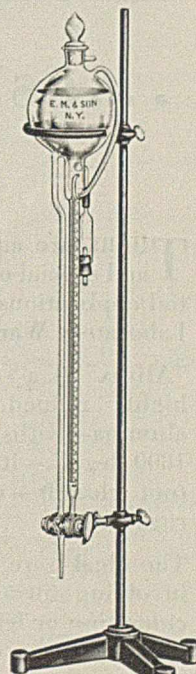
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