

INDUSTRIAL AND ENGINEERING CHEMISTRY

ANALYTICAL EDITION



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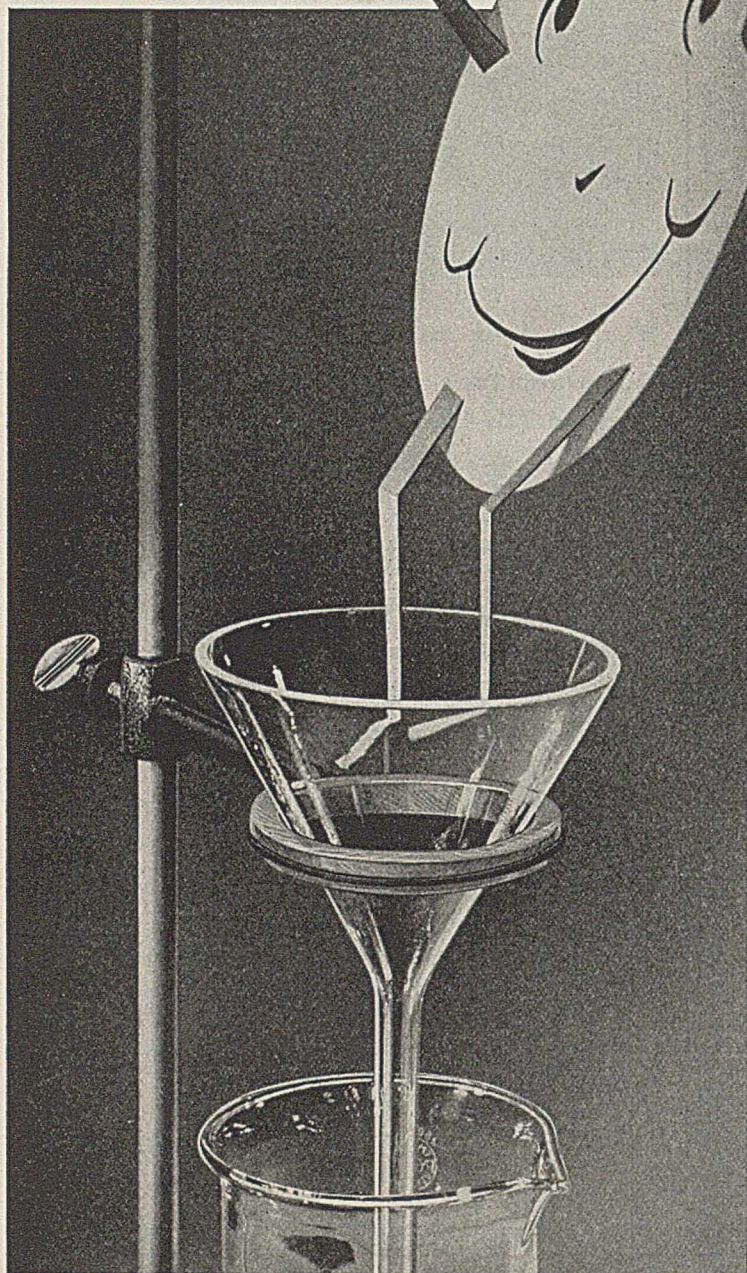
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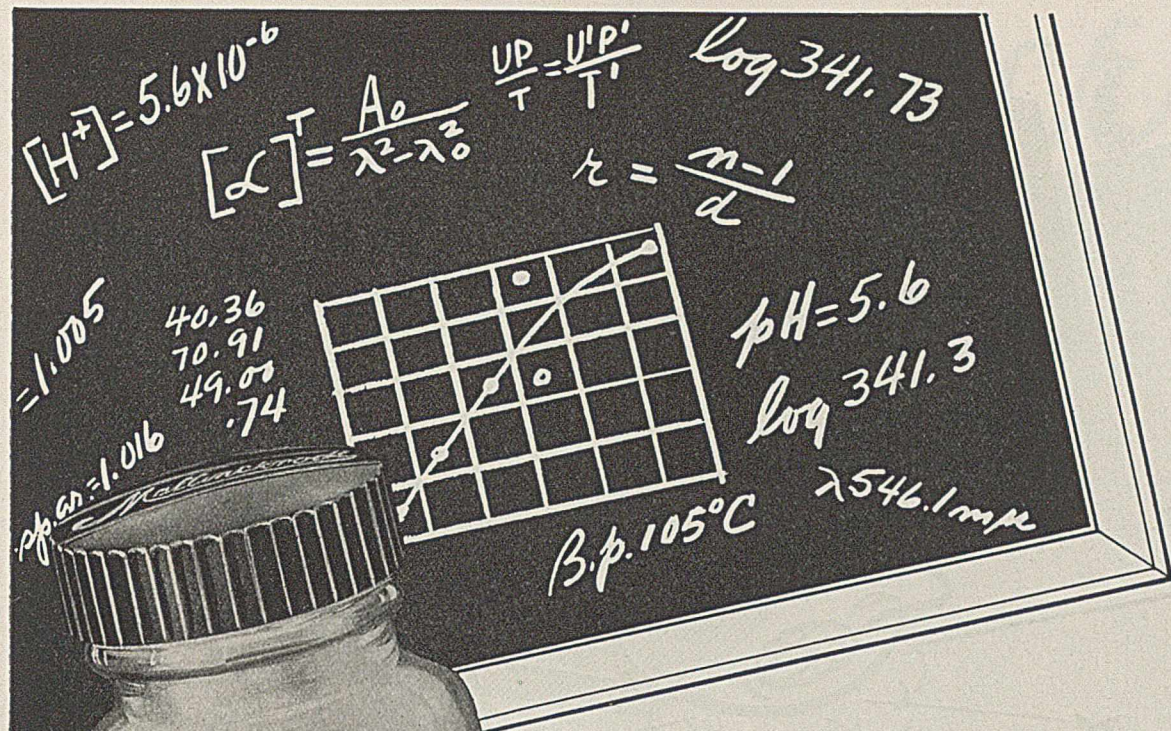
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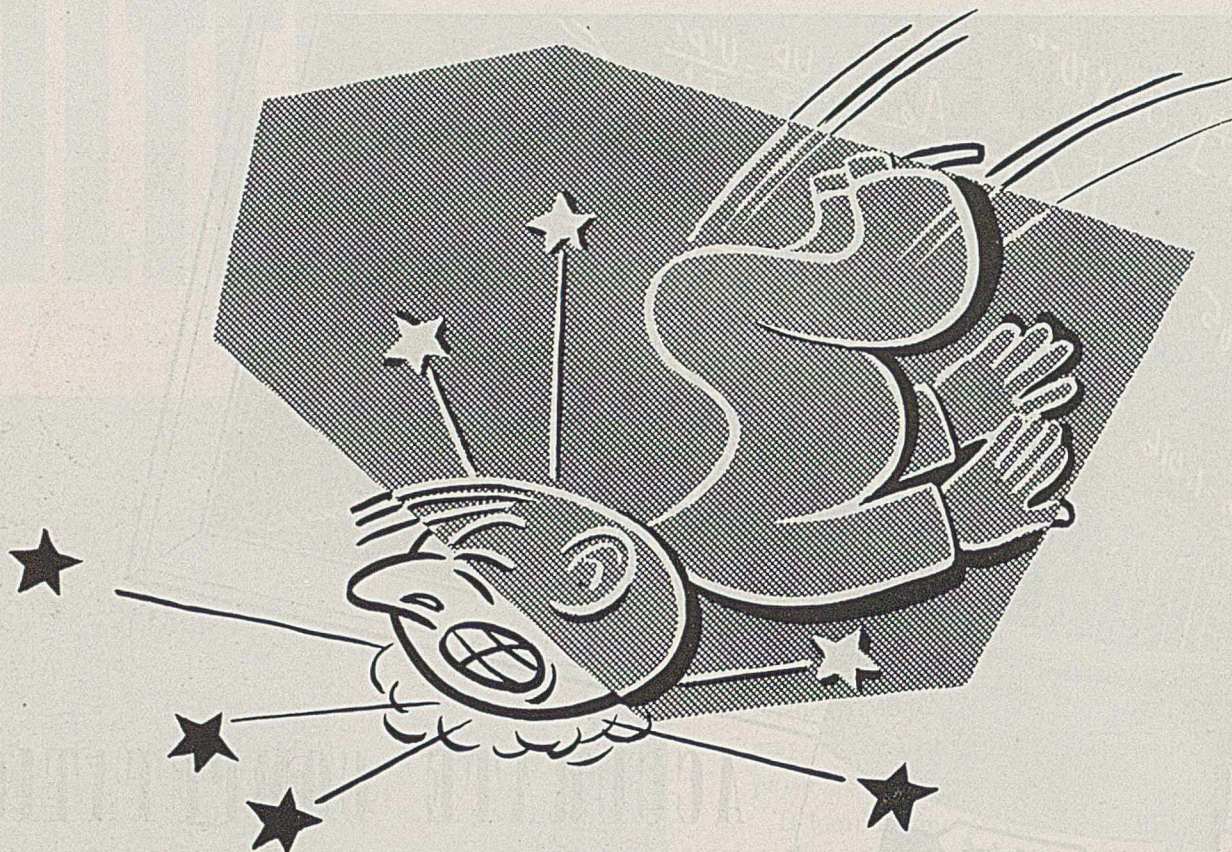
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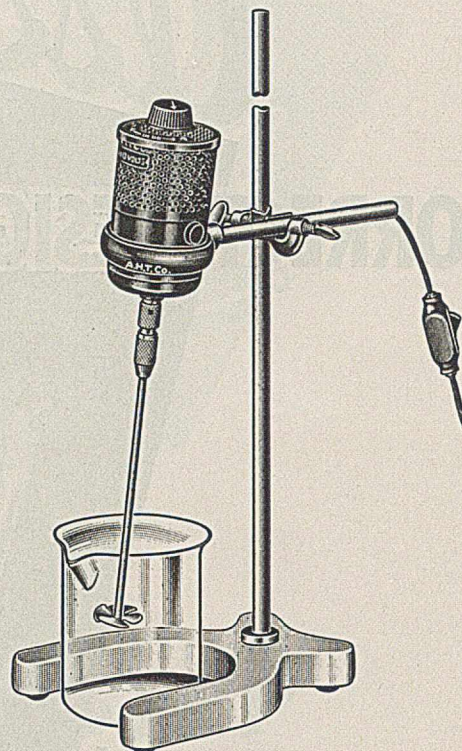
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Analysis of Commercial Fats and Oils

Report of American Chemical Society Committee

THE Committee on Analysis of Commercial Fats and Oils is ready to report the results of its investigation of six methods and recommends their adoption. These are the titer, the modified Gardner break test, the detection of tristearin in lard, the Villavecchia test for sesame oil, calculations of the hydroxyl value, and the smoke, flash, and fire points. Many data have been collected in the study of these methods, which has extended over a period of two to three years.

TITER. The committee has approved vertical stirring. The advantages over horizontal stirring are that it gives a sharper end point, is more convenient, and can easily be made mechanical by adapting a suitable motor and coupling arrangement to the stirrer.

The specifications for the titer thermometer have been revised. The new thermometer is more easily read, covers a greater range, and has been made partial immersion.

The committee has found that a differential temperature of 10° C. between the titer point and the bath is insufficient for low titers, and therefore recommends that this be increased.

The committee wishes to emphasize the fact that no changes have been made in the titer determination which will give results different from those that might be obtained with the horizontal stirring method, providing the latter is correctly performed. The committee believes that the proposed modification will make it easier for different chemists to obtain uniform and consistent results.

DETECTION OF TRISTEARIN IN LARD (BOEMER No.). The committee has found that the F. A. C. capillary tube method for melting points yields consistent and satisfactory results with both the glycerides and the fatty acids. Since this method is already official with the American Oil Chemists' Society and the AMERICAN CHEMICAL SOCIETY, and also because it is more convenient than the use of a sulfuric acid bath, the committee recommends its adoption for this determination.

Further work on the crystallization from acetone at 30° C. indicates that if care is taken, sufficient crystals of a definite composition can be obtained. The method has been rewritten for the purpose of clarifying some of the details.

SMOKE POINT. Several years ago the A. S. T. M. Cleveland open cup apparatus was adopted for use in the smoke, flash, and fire point methods. The committee now suggests that these methods be rewritten in accord with the latest revision of the American Society for Testing Materials.

VILLAVECCHIA TEST. The Villavecchia test for the qualitative detection of sesame oil was investigated and approved. This method is already official with the Association of Official Agricultural Chemists.

MODIFIED GARDNER BREAK. The modified Gardner break method for soybean oil was studied at the request of the Uniform Methods and Planning Committee of the American Oil Chemists' Society. This method is of old standing and has been previously studied by others. Only two minor changes are recommended. A tall-form beaker helps to prevent loss from foaming. The thermometer recommended will ensure better control of the temperature.

HYDROXYL VALUE. The committee recommends that the method for calculation of the hydroxyl value be included with the acetyl value determination. Details of this calculation may be found in the literature (1-5).

COLOR READING. The committee has approved the use of the 2.5-cm. (1-inch) column in the Lovibond system of color reading for oil and fat samples which cannot be read in a 13.335-cm. (5.25-inch) column. This item has been referred to the Color Committee for further handling.

INTERNATIONAL FAT COMMISSION PROGRAM. Unfortunately, the disturbances in Europe have held up the program of cooperation in the study of fat and oil analysis with the International Fat Commission. It is hoped that this may be resumed in the future.

GENERAL. Because of the large amount of work ahead, this committee has been enlarged during the past year. Its schedule for future work is as follows: (1) study of a method for the quantitative determination of peanut oil; (2) study of a method for the determination of insoluble bromides; (3) study of the various moisture methods for fats and oils; (4) study of methods for the determination of unsaponifiable matter; (5) study of methods for the determination of cholesterol and phytosterol; (6) further study of the F. A. C. color standards; and (7) some study of iodine number determinations.

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Modified Villavecchia Test (A. O. A. C.)

Qualitative Detection of Sesame Oil

REAGENTS. C. P. hydrochloric acid (sp. gr. 1.19). Villavecchia reagent, 2 ml. of c. p. furfural added to 100 ml. of 95 per cent ethyl alcohol.

PROCEDURE. Mix 10 ml. of the sample with an equal volume of the hydrochloric acid.

Add to this mixture 0.1 ml. of the Villavecchia reagent and shake well for 15 seconds.

Note the color of the lower layer as soon as possible after the emulsion has broken. If no pink to crimson color appears, the test may be reported negative at that point. If any color is observed in the lower layer, add 10 ml. of distilled water, shake again, and observe the color as soon as separation has taken place. If the color persists, report the test as positive. If the color disappears, sesame oil is not present.

Notes. Furfural gives a violet color with hydrochloric acid; therefore, it is necessary to use the dilute solution specified. It is advisable to read the color as soon as possible, so that the pink color, if present, may be observed before it is masked by the development of other noncharacteristic colors.

It is advisable, with the Villavecchia test as with others of a similar nature, to run control samples using as standards oils of known composition.

The test is applicable to hydrogenated as well as unhydrogenated sesame oil although not with the same degree of sensitivity. The committee has found that as little as 0.25 per cent of sesame oil can be detected, but is of the opinion that this limit should be accepted with reservations. It is the considered judgment of the committee that there is every assurance that at least 0.5 per cent of sesame oil is detectable and that the lower limit with respect to the fully hydrogenated oil is 1 per cent.

The sensitivity of the Villavecchia test to small quantities of sesame oil may be improved by increasing the amount of Villavecchia reagent up to 1 ml. However, doing this hastens the rate of development as well as the amount of noncharacteristic colors that are formed. Therefore, if greater amounts of the reagent are used, relatively greater care must be taken in the observation of the final color.

Detection of Foreign Fats Containing Tristearin in Unhydrogenated Pork Fats (Modified A. O. A. C.)

Applicable to Detection of Beef Fat in Lard and Sometimes Referred to as Boemer Number

REAGENTS. C. P. acetone. Alcoholic potassium hydroxide, 0.5 N. Hydrochloric acid (1 + 1).

APPARATUS. Centrifuge tube, 100-ml., or glass-stoppered cylinder of the same capacity.

Melting point tubes. Capillary glass tubing, inside diameter 1 mm., thin wall, convenient length 5 to 8 cm.

Thermometer. Any convenient thermometer of suitable range but with 0.1° or 0.2° C. subdivisions.

PROCEDURE. *Crystallization of Glycerides.*

1. Weigh 20 grams of the filtered sample into the centrifuge tube or cylinder. Adjust the temperature of the acetone to 30° C. and use at this temperature throughout. Add the acetone to the sample to the 100-ml. mark. Shake until a thorough mixture results and allow to stand for about 18 hours at a temperature of 30° ± 2° C.

2. Place the tube in a suitable centrifuge, whirl for 5 minutes, and pour off the supernatant liquid. If a centrifuge is not available a 100-ml. cylinder is used, in which case the supernatant liquid must be siphoned off.

3. Add another 20-ml. portion of the acetone to the crystals, shake, centrifuge, and decant or siphon as above.

4. Repeat operation 3, this time mixing well and pouring through a qualitative filter paper. Complete the transfer of the crystals and wash the contents of the filter paper with 5 small portions of acetone.

5. Apply a vacuum to remove as much of the acetone from the crystals as possible. Remove the paper from the funnel, place on a dry smooth surface, and break up any lumps with a spatula. Allow to dry thoroughly. The temperature of the glycerides must not be elevated to the melting point in drying

because this will materially influence the final results. After drying, comminute the mass and determine the melting point as directed below.

Preparation of Fatty Acids.

1. Remove a sufficient amount of the glycerides for the melting point determination and transfer the remainder into a 500-ml. Erlenmeyer flask. Add 100 ml. of the alcoholic potassium hydroxide. Place a small funnel in the neck of the flask to prevent loss on boiling and saponify by boiling for 1 hour.

2. Add 100 ml. of water to the soap solution and evaporate on the steam bath to remove as much of the alcohol as possible. Transfer to a 500-ml. separatory funnel. Add a sufficient amount of water to bring the total quantity used to about 250 ml. Neutralize with the hydrochloric acid (1 + 1) to separate the fatty acids, using a slight excess. Add 75 ml. of ethyl ether and shake.

3. Draw off the aqueous layer and wash the ether layer at least three times with water or until the washings are neutral to methyl orange. Withdraw the ethyl ether extract, filter, evaporate the ether on the steam bath, and dry the fatty acids at 100° C. for a few minutes. Protect the fatty acids at all times from ammonia fumes.

Determination of Melting Point.

1. Seal the glyceride melting point tubes at one end before introducing the crystals. Insert the crystals through the open end and force down into the closed end with a small glass rod or wire.

2. Prepare the fatty acid melting point tubes by dipping the open tubes into the melted acids so that the sample stands about 1 cm. high in the tube. Seal this end of the tube in a gas flame.

3. Allow the tubes containing the fatty acids to stand for 0.5 hour in ice water or hold in a refrigerator overnight (4° to 10° C.).

4. Fasten the melting point tubes containing the fatty acids and the glyceride crystals to the thermometer by a rubber band or any other convenient means. Adjust them so that the sections of the tubes containing the samples are adjacent to the bulb of the thermometer. Suspend the thermometer in a beaker of water (suitably agitated), so that the bottom of the bulb of the thermometer is about 3 cm. below the level of the water. The temperature of the water at this time must be at least 10° C. below the melting point of the sample. Heat the water at such a rate that the temperature will increase at about 0.5° C. per minute. The melting point is that point at which the samples become clear and liquid. Determine the melting points of the glycerides and fatty acids at the same time.

Calculations. If the melting point of the glycerides, plus twice the difference between the melting point of the glycerides and the melting point of the fatty acids, is less than 73° C. the lard is regarded as adulterated.

$$\begin{aligned} B. N. &= \text{Boemer number} \\ A &= \text{melting point of glycerides} \\ B &= \text{melting point of fatty acids} \\ B. N. &= A + 2(A - B) \end{aligned}$$

Notes. If the quantity of crystals obtained from 20 grams is insufficient, this amount may be increased, providing the acetone is increased proportionally.

The committee's investigation has indicated that 10 per cent beef fat can be detected with certainty and many times amounts smaller than this, even down to 5 per cent, can be found.

Tolman and Robinson have pointed out that this method is not applicable to hydrogenated pork fats.

The results on cooperative samples have indicated that if the melting point of the glycerides alone is used as a criterion, some pure samples of lard may be reported as adulterated. Therefore, use of this value alone is not recommended.

Smoke, Flash, and Fire Points

Applicable to Animal and Vegetable Oils and Fats

SMOKE. *Apparatus.*

1. Cleveland Flash Cup, A. S. T. M. Designation D92-33.

The Cleveland open cup is made of brass and conforms to the dimensional requirements prescribed in Table I. The beveled edge of the cup shall be at an angle of approximately 45°. There may be a fillet approximately 0.397 cm. in radius inside the bottom of the cup.

2. Heating Plate. A metal plate, 0.635 cm. in thickness and 15.24 cm. in width for supporting the flash cup. The plate

shall be of brass, cast iron, wrought iron, or steel. In the center of the plate there shall be a plane depression 0.079 cm. in depth, and of just sufficient diameter to fit the cup. There shall be a circular opening 5.50 cm. in diameter, cut through the plate, centering with the center of the above-mentioned depression. The plate shall be covered with a sheet of hard asbestos board 0.635 cm. (0.25 inch) in thickness, and of the same shape as the metal plate. In the center of the asbestos board is cut a circular hole just fitting the cup.

Heat may be supplied from any convenient source. The use of a gas burner, electric heater, or alcohol lamp is permitted, but under no circumstances are products of combustion or free flame allowed to come up around the cup. The source of heat shall be centered under the opening in the plate and shall be of a type that will not produce local superheating. If a flame heater is used, it may be protected from drafts or excessive radiation by any suitable type of shield, that does not project above the level of the upper surface of the asbestos board.

3. Thermometer, A. S. T. M. Open Flash.

	E1 (11C-39)	E1 (11F-39)
Liquid	Mercury	Mercury
Filling above liquid	Nitrogen gas	Nitrogen gas
Temperature range	-6° to +400° C.	+20° to +760° F.
Subdivisions	2° C.	5° F.
Total length	303 to 307 mm.	
Stem diameter	6.0 to 7.0 mm.	
Bulb diameter	Not greater than stem	
Bulb length	Not over 13 mm.	
Bottom of bulb to graduation line at	-6° C.	+20° F.
Distance	40 to 50 mm.	
Top of thermometer to graduation line at	+400° C.	+760° F.
Distance	30 to 45 mm.	
Top finish	Red glass ring	Red glass ring
Longer graduation lines at each	10° C.	10° F.
Graduations numbered at each multiple of	10° C.	20° F.
Immersion	25 mm.	1 inch
Special marking on thermometer	A. S. T. M. Open Flash	A. S. T. M. Open Flash
Scale error at any point up to	372° C.	700° F.
When standardized shall not exceed	1° C.	2.5° F.
Test for permanency of range	Subject to 360° to 370° C. for 24 hours	Subject to 680° to 700° F. for 24 hours
Marking on case	A. S. T. M. Open Flash	A. S. T. M. Open Flash
Standardization	-6° to +400° C.	+20° to +760° F.
	Standardize thermometer at ice point and at intervals of approximately 50° C. or 100° F. for 25-mm. or 1-inch immersion and for following temperatures of emergent mercury column:	

Thermometer Reading ° C.	Average Temperature of Emergent Mercury Column ° C.	Thermometer Reading ° F.	Average Temperature of Emergent Mercury Column ° F.
100	44	200	110
150	54	300	129
200	64	400	150
250	77	500	175
300	91	600	205
350	108	700	240

4. Cabinet. This shall be constructed of the materials and in accordance with the dimensions indicated in Figure 1.

Procedure. Fill the cup with the sample so that the top of the meniscus is exactly at the filling line of the cup. Adjust the position of the apparatus so that the beam of light is directed across the center of the cup. Suspend the thermometer in the center of the dish with the bottom of the bulb approximately 0.635 cm. (0.25 inch) from the bottom of the cup.

Heat the sample rapidly to within approximately 75° F. of the smoke point. Thereafter regulate the flame so that the temperature of the sample increases at a rate of not less than 9° or more than 11° F. per minute. The smoke point is taken as the temperature at which the sample gives off a thin bluish smoke continuously.

Notes. In some cases a slight puff of smoke appears before the sample begins to smoke continuously. This is to be disregarded.

It is essential to keep the cup entirely clean and free from any substances which might cause smoke to appear ahead of the true smoke point.

FLASH AND FIRE. Apparatus. The apparatus including the thermometer is identical with that used for the smoke point except that the cabinet is not used.

TABLE I. DIMENSIONAL REQUIREMENTS FOR CLEVELAND OPEN FLASH CUP

	Minimum Inches	Normal Inches	Maximum Inches	Minimum Cm.	Normal Cm.	Maximum Cm.
Inside diameter immediately below filling mark	2 ¹⁵ / ₃₂	2 ¹ / ₂	2 ¹⁷ / ₃₂	6.27	6.35	6.43
Outside diameter below flange	2 ²¹ / ₃₂	2 ¹¹ / ₁₆	2 ²³ / ₃₂	6.75	6.83	6.91
Inside height from center of bottom to rim	1 ⁹ / ₃₂	1 ⁵ / ₁₆	1 ¹¹ / ₃₂	3.25	3.33	3.41
Thickness of bottom	7/ ₆₄	1/ ₈	9/ ₆₄	0.28	0.32	0.36
Distance from rim to filling mark	2 ³ / ₆₄	3/ ₈	2 ⁵ / ₆₄	0.91	0.95	0.99
Distance from lower surface flange to bottom of cup	1 ⁷ / ₃₂	1 ¹ / ₄	1 ⁹ / ₃₂	3.10	3.18	3.26
Vertical distance from upper surface flange to rim	7/ ₆₄	1/ ₈	9/ ₆₄	0.28	0.32	0.36
Thickness of rim	5/ ₆₄	3/ ₃₂	7/ ₆₄	0.20	0.24	0.28
Width of lower surface of flange	9/ ₁₆	1 ⁹ / ₃₂	5/ ₈	1.43	1.51	1.59

Procedure.

1. Suspend the thermometer or hold in a vertical position by any suitable device, so that the bottom of the bulb is approximately 0.635 cm. (0.25 inch) from the bottom of the cup, and above a point half way between the center and back of the cup.

2. Fill the cup with the sample to be tested in such a manner that the top of the meniscus is exactly at the filling line at room temperature.

3. The test flame should be approximately 0.397 cm. (0.125 inch) in diameter. Apply the test flame as the temperature read on the thermometer reaches each successive 5° F. mark, so that the flame passes in a straight line (or on the circumference of a circle having a radius of at least 15 cm.) across the center of the cup and at right angles to the diameter passing through the thermometer. The test flame shall, while passing across the surface of the sample, be in the plane of the upper edge of the cup. The time for the passage of the test flame across the cup shall be approximately 1 second.

4. Heat the sample at a rate not exceeding 30° F. rise per minute until a point is reached approximately 100° F. below the probable flash point of the sample. Thereafter decrease the rate of heating; for at least the last 50° F. before the flash point is reached, the rate shall be not less than 9° F. nor more than 11° F. rise per minute.

5. Flash Point. Take as the flash point the temperature read on the thermometer when a flash appears at any point on

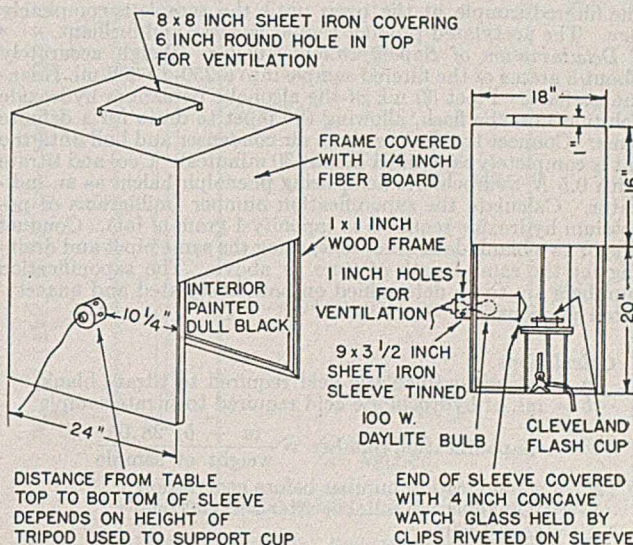


FIGURE 1. APPARATUS FOR DETERMINING SMOKE POINT

the surface of the sample. The true flash must not be confused with a bluish halo that sometimes surrounds the test flame.

6. Fire Point. After determining the flash point, continue the heating at the specified rate of 9° to 11° F. per minute, and apply the test flame at the specified intervals until the oil ignites and continues to burn for at least 5 seconds. The method of application of the flame shall be the same as for the flash point. The temperature read at the time of the flame application which causes burning for a period of 5 seconds or more is recorded as the fire point.

Notes. The flash point and fire point tests should be made in a room or compartment free from air drafts. The operator should avoid breathing over the surface of the sample. The room or compartment should be darkened sufficiently so that the flash may be readily discernible.

Acetyl and Hydroxyl Values

The acetyl value is defined as the number of milligrams of potassium hydroxide required for the neutralization of the acetic acid obtained on saponifying 1 gram of an acetylated fat or wax, and is a measure of the hydroxyl content of the sample. However, in using the André-Cook formula it must be remembered that the calculations are based on the weight of acetylated fat. The hydroxyl value may be defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of the sample. The hydroxyl value is based on the weight of the unacetylated fat (1, 2, 4).

REAGENTS. C. P. freshly distilled acetic anhydride (99 to 100 per cent). 0.5 *N* hydrochloric acid.

Alcoholic Potassium Hydroxide. Dissolve 40 grams of pure potassium hydroxide in 1 liter of 95 per cent redistilled ethyl alcohol. The alcohol should be redistilled from potassium hydroxide over which it has been standing for some time, or with which it has been boiled for some time, using a reflux condenser. The solution must be clear and the potassium hydroxide free from carbonates.

PROCEDURE. Acetylation (A. O. A. C. Method). Boil 50 ml. of the sample with 50 ml. of acetic anhydride under a reflux condenser for 2 hours. Pour the mixture into 500 ml. of distilled water in a beaker and boil for 15 minutes while bubbling a stream of carbon dioxide through the solution to prevent bumping. Siphon off the water, add 500 ml. more water, and boil again for 15 minutes. Repeat the siphonation and boil for 15 minutes with a third 500-ml. portion of water. Allow the mixture to cool and separate the aqueous layer, which should be neutral to litmus. Transfer the acetylated sample to a separatory funnel and wash with two 200-ml. portions of warm water. Separate as much of the water as possible, add 5 grams of anhydrous sodium sulfate to the acetylated sample, and let stand for 1 hour, agitating occasionally to assist in drying. Filter through a dry folded filter, preferably in an oven heated to 100° to 110° C., and keep the filtered sample in the oven until the sample is completely dry. The acetylated product should be clear and brilliant.

Determination of Saponification Number. Weigh accurately about 5 grams of the filtered sample into a 250- to 300-ml. Erlenmeyer flask. Pipet 50 ml. of the alcoholic potassium hydroxide solution into the flask, allowing the pipet to drain for a definite time. Connect the flask with an air condenser and boil until the fat is completely saponified (about 30 minutes). Cool and titrate with 0.5 *N* hydrochloric acid, using phenolphthalein as an indicator. Calculate the saponification number (milligrams of potassium hydroxide required to saponify 1 gram of fat). Conduct one or two blank determinations, using the same pipet and draining for the same length of time as above. The saponification numbers are to be determined on both acetylated and unacetylated portions.

Calculations.

a = ml. of hydrochloric acid required to titrate blank
b = ml. of hydrochloric acid required to titrate sample

$$\text{Saponification number} = \frac{(a - b) 28.05}{\text{weight of sample}}$$

S = saponification number before acetylation

S' = saponification number after acetylation

A = acetyl value

$$A = \frac{S' - S}{1 - 0.00075S}$$

H = hydroxyl value (3, 5)

$$H = \frac{S' - S}{1 - 0.00075S'}$$

To calculate the acetyl value from the hydroxyl value

$$A = \frac{H}{1 + 0.00075H}$$

Notes. Determination of acetyl value by the filtration method or distillation method is extremely difficult and unreliable. The André-Cook saponification method (1) yields accurate and concordant results on fats and oils containing stable hydroxyl groups such as castor oil, and is by far the simplest and easiest to manipulate. For blown oils and others having unstable hydroxyl groups none of the methods commonly used yields concordant results.

Modified Gardner Break Test

Applicable to Crude Soybean Oil

REAGENTS. C. P. hydrochloric acid (sp. gr. 1.19), and c. p. carbon tetrachloride.

APPARATUS.

1. Beaker, Electrolytic Type, Capacity 180 Ml.
2. Thermometer, A. S. T. M. Open Flash.

	E1 (11C-39)	E1 (11F-39)
Liquid	Mercury	Mercury
Filling above liquid	Nitrogen gas	Nitrogen gas
Temperature range	-6° to +400° C.	+20° to +760° F.
Subdivisions	2° C.	5° F.
Total length	303 to 307 mm.	
Stem diameter	6.0 to 7.0 mm.	
Bulb diameter	Not greater than stem	
Bulb length	Not over 13 mm.	
Bottom of bulb to graduation line at		
Distance	-6° C.	+20° F.
Top of thermometer to graduation line at	40 to 50 mm.	
Distance	+400° C.	+760° F.
Top finish	30 to 45 mm.	
Longer graduation lines at each	Red glass ring	Red glass ring
Graduations numbered at each	10° C.	10° F.
multiple of		
Immersion	10° C.	10° F.
Special marking on thermometer	25 mm.	1 inch
	25-mm. imm.	1-inch imm.
	A. S. T. M.	A. S. T. M.
	Open Flash	Open Flash
	372° C.	700° F.
Scale error at any point up to		
When standardized shall not exceed	1° C.	2.5° F.
Test for permanency of range	Subject to 360° to 370° C. for 24 hours	Subject to 680° to 700° F. for 24 hours
Marking on case	A. S. T. M.	A. S. T. M.
	Open Flash	Open Flash
	-6° to +400° C.	+20° to +760° F.
Standardization	Standardize thermometer at ice point and at intervals of approximately 50° C. or 100° F. for 25-mm. or 1-inch immersion and for following temperatures of emergent mercury column:	

Thermometer Reading ° C.	Average Temperature of Emergent Mercury Column ° C.	Thermometer Reading ° F.	Average Temperature of Emergent Mercury Column ° F.
100	44	200	110
150	54	300	129
200	64	400	150
250	77	500	175
300	91	600	205
350	108	700	240

3. Porcelain Crucible, Bitumen Type, A. S. T. M. Test D4-27, 1938.

Diameter at top	4.4 cm.
Diameter at bottom	3.6 cm.
Depth	2.5 cm.

PROCEDURE.

1. Heat a sufficient amount of the well-mixed sample to 75° C. (167° F.) and maintain at this temperature for about 5 minutes, so as to melt all fat-soluble particles which may be present.
2. Weigh 25 grams into the designated beaker, add 3 drops of the hydrochloric acid, and stir in thoroughly. Suspend the thermometer in the center of the oil-acid mixture, so that the bulb is completely immersed but not touching the bottom of the beaker. Apply heat so that the temperature rise will be 74° to 79.5° C. (165° to 175° F.) per minute. (Caution. Do not stir or otherwise disturb the sample after heating has begun.) Heat

to 289° C. (550° F.) and withdraw the flame. Cool to about 25° C. (77° F.) in a water bath or in air.

3. After cooling add, while stirring, 50 ml. of the carbon tetrachloride to dissolve the oil. Allow to stand for 1 hour, stirring at 15-minute intervals to remove any oil which may be occluded to the surface of or within the separated material.

4. The crucible should be prepared with medium fiber asbestos, and the pad must be thick enough to prevent breaking through. Wash the mat with water and alcohol and dry to constant weight before using.

5. Filter the sample with the aid of a vacuum, using a policeman to remove any traces of break from the beaker. Wash the break on the crucible well, using not less than five 20-ml. portions of carbon tetrachloride. Drain the crucible dry after each addition and break the vacuum when each new portion is added, to ensure removal of all traces of oil. Dry the crucible at 105° C. to constant weight and determine the weight of the residue on the crucible.

CALCULATION.

$$\% \text{ break} = \text{weight of residue} \times 4$$

Titer

Solidification Point of Fatty Acids

REAGENTS. Glycerol Caustic. Dissolve with the aid of heat, 250 grams of solid potassium hydroxide in 1250 grams of glycerol (dynamite or c. p. grade). To avoid foaming, do not heat above 135° to 145° C.

Sulfuric acid, 30 per cent by weight, may be readily prepared by adding 16 ml. of sulfuric acid (sp. gr. 1.84) to 70 ml. of water.

APPARATUS.

1. Two-liter Griffin low-form beaker.
2. Wide-mouthed bottle, capacity 450 ml., height 190 mm., inside diameter of neck 38 mm.
3. Test tubes, length 100 mm., diameter 25 mm., with or without rim. These tubes may have an etched mark extending around the tube at a distance of 57 mm. from the bottom to show the height to which the tube is to be filled.
4. Saponification vessel may be a flask, beaker, or casserole of a convenient capacity. The form is not important, so long as it is satisfactory for the saponification.
5. Laboratory thermometer, 0° to 150° C.
6. Stirrer, 2 to 3 mm. in outside diameter, one end bent in the form of a loop 19 mm. in diameter. Glass, Nichrome, stainless steel, or Monel wire may be used. The upper end can be formed to accommodate hand stirring or attached to a mechanical stirrer.
7. Titer Thermometer. Type, etched stem glass. Liquid, mercury. Range and subdivision, -2 to +68° C. in 0.2° graduations. Total length, 375 to 385 mm. Stem constructed of suitable thermometer tubing with a diameter of 6 to 7 mm. May be plain front or of the magnifying lens type. Red reading mercury is preferable but not obligatory.

Bulb, Corning normal or equally suitable thermometric glass. Diameter not less than 5.5 mm. but not greater than that of the stem. Length, 15 to 25 mm. Distance to -2° mark from bottom of bulb, 50 to 60 mm. Length of graduated scale, 300 mm. minimum. Length of unchanged capillary between lowest graduation mark and bulb, 13 mm. minimum.

Expansion chamber, to permit heating the thermometer to at least 85° C. Length of unchanged capillary between uppermost graduation mark and expansion chamber, 10 mm. minimum. Top finish, glass ring. Tubing above mercury evacuated or filled with nitrogen or other suitable inert gas.

Graduation. All lines, figures, and letters clear-cut and distinct; each degree mark longer than the remaining lines; graduations numbered at each multiple of 2°.

Immersion, 45 mm.

Marking. "F. A. C. Titer Test", serial number, and manufacturer's name or trade-mark etched upon the stem. The words "45-mm. immersion" also etched upon the stem, and a line etched around the stem 45 mm. above the bottom of the bulb.

Standardization. The thermometer may be standardized at optional intervals and for an average temperature of the emergent mercury column of 25° C.

Scale error at any point, when the thermometer is standardized at 45-mm. immersion, shall not exceed 0.2° C.

Case. The thermometer shall be supplied in a suitable case on which appears the marking: "F. A. C. Titer Test", -2° to +68° in 0.2° graduations.

Note. For the purpose of interpreting these specifications, the following definitions apply: The total length is the over-all length of the finished instrument. The diameter is that measured

with a ring gage or micrometer. The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing. The top of the thermometer is the top of the finished instrument.

PREPARATION OF FATTY ACIDS.

1. Weigh 110 grams of glycerol caustic into the saponification vessel, stir while heating to 150° C., add 50 ml. of melted fat, and reheat. In some cases a little additional caustic may be necessary to ensure complete saponification.

2. Continue stirring, being careful not to heat above 150° C., until completely saponified (see notes below).

3. Cool slightly, add 200 to 300 ml. of water, and after the solution of the soap add 50 ml. of the sulfuric acid, stirring during the addition. After separation of the fatty acids, add more water if desired and continue boiling until the fatty acids are completely melted and clear. If a gas burner is used for heating, the water level should be high enough to prevent scorching on the sides of the dish.

4. The aqueous layer containing the sulfuric acid may be removed from under the fatty acid layer by an appropriate siphon. Again add water and boil 2 or 3 minutes, making sure that all the fatty acids are melted and clear. Fats of high melting point are sometimes slow to melt and clear. The fatty acid layer should be carefully inspected while it is quiet, to be sure all has melted.

5. Siphon off water again and repeat, if necessary, with water as under operation 4 until wash water is neutral to methyl orange.

6. Carefully remove fatty acids so as not to include any water. Filter these while entirely melted through any rapid filtering paper. Heat the filtered acids on a hot plate to 130° C. to re-

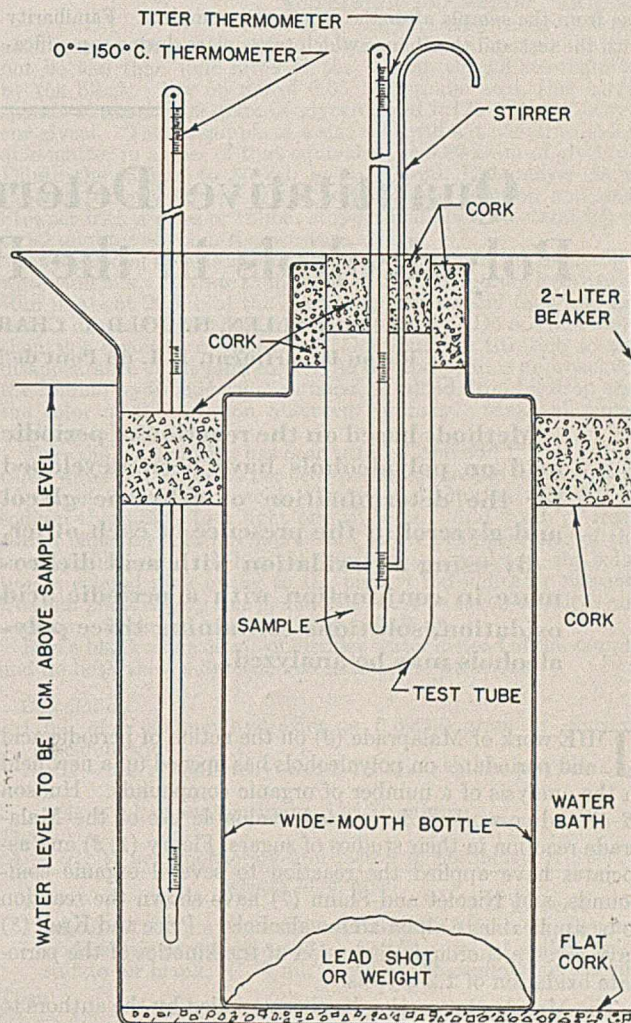


FIGURE 2. ASSEMBLY FOR STIRRING TITERS

Three corks located at equal distances apart between bottle and beaker hold the form rigid. Scale, approximately half actual size.

move traces of moisture and pour into the test tube, filling it to a height of 57 mm. from the bottom. The sample should not be held at 130° C. nor should it be reheated to this temperature more than once. If excessive moisture is present, decant the acids after standing for a few minutes, refilter and reheat. The acids must be thoroughly dry.

SOLIDIFICATION OF FATTY ACIDS.

1. Fill the water bath and adjust the temperature. The temperature of the water should be 20° C. for all samples having titers of 35° C. or higher, and 15° to 20° C. below the titer point for all samples with titers below 35° C. The water level should be 1 cm. above the sample level.

2. Place the test tube containing the fatty acids in the assembly as shown in Figure 2. Insert the titer thermometer to the immersion mark and equidistant from the sides of the tube.

3. Stir with the stirring rod in a vertical manner at the rate of 100 complete up and down motions per minute. The stirrer should move through a vertical distance of about 3.8 cm. The stirring may be performed by mechanical means by attaching a small motor with suitable reducing gears to the stirring rod. Start the agitation while the temperature is at least 10° C. above the titer point.

4. Stir at the directed rate until the temperature remains constant for 30 seconds, or begins to rise in less than a 30-second interval. Discontinue stirring immediately and observe the increase in temperature. Report as the titer the highest point reached by the thermometer. Duplicate determinations are normally expected to agree within 0.2° C.

Notes. Saponification is usually indicated by a change in the appearance of the mass, which finally becomes homogeneous. Frequently saponification is indicated by a thickening or increase in the viscosity of the mass, which again thins out after the reaction is complete. Also, soap bubbles begin to form and rise from the sample after the reaction is complete. Familiarity with the test and the change which takes place during saponifica-

tion usually enables one to determine the proper end point. Under some abnormal conditions, the above-mentioned indications may not be reliable, so that considerable care should be exercised to ensure complete saponification. The committee has investigated a number of proposed tests for complete saponification, but up to the present time none has been found which is reliable under all circumstances.

Sodium hydroxide cannot be substituted for potassium hydroxide in the glycerol method. This method is quick and satisfactory. If an alternate method of preparing the fatty acids is desired, the following may be used:

Saponify 50 grams of fat with 60 ml. of a solution of 2 parts of methanol to 1 part of 50 per cent sodium hydroxide. Dry, pulverize, and dissolve the soap in 1000 ml. of water in a porcelain dish and then decompose with 25 ml. of 75 per cent sulfuric acid. Boil the fatty acids until clear oil is formed, collect and settle in a 150-ml. beaker, and filter into a 50-ml. beaker. Heat to 130° C. as rapidly as possible with stirring, and transfer, after cooling somewhat, to the usual 1 × 4 inch (2.5 × 10 cm.) titer tube. The method of taking the titer, including handling the thermometer, is the same as that described in the standard method.

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APPROVED by the Supervisory Committee on Standard Methods of Analysis and by the Council at the 99th Meeting of the American Chemical Society, Cincinnati, Ohio, as official for the American Chemical Society.

Quantitative Determination of Certain Polyalcohols in the Presence of Each Other

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Methods based on the reaction of periodic acid on polyalcohols have been developed for the determination of ethylene glycol and glycerol in the presence of each other.

By using an oxidation with acid dichromate in conjunction with a periodic acid oxidation, solutions containing three polyalcohols may be analyzed.

THE work of Malaprade (6) on the action of periodic acid and periodates on polyalcohols has opened up a new field in the analysis of a number of organic compounds. Hudson (3-5) and co-workers have made valuable use of the Malaprade reaction in their studies of sugars, Fleury (1, 2) and associates have applied the reaction to several organic compounds, and Nicolet and Shinn (7) have shown the reaction to be applicable to alpha-amino alcohols. Price and Kroll (8) have given a thorough discussion of the kinetics of the periodate oxidation of 1,2-glycols.

The Malaprade reaction has been applied by the authors to the quantitative determination of certain polyalcohols in the

A qualitative test for distinguishing between glycerol and ethylene glycol is given, and a method for investigating unknown solutions containing polyalcohols is outlined. The methods give good results on synthetic solutions of known composition and have been in practical use for several years.

presence of each other, particularly glycerol and ethylene glycol. The reaction has also been used to distinguish qualitatively between solutions of ethylene glycol and glycerol. By using an acid dichromate oxidation in conjunction with the Malaprade reaction, a solution containing three glycols may be analyzed for each of the three components. This procedure is useful in the investigation of unknown solutions suspected of containing mixed glycols.

Glycerol and ethylene glycol may be determined in the presence of each other by either an acidimetric-iodometric procedure or a single acidimetric titration using a glass electrode in a potentiometric method.

The reactions of glycerol and ethylene glycol with periodic acid are given in the equations:

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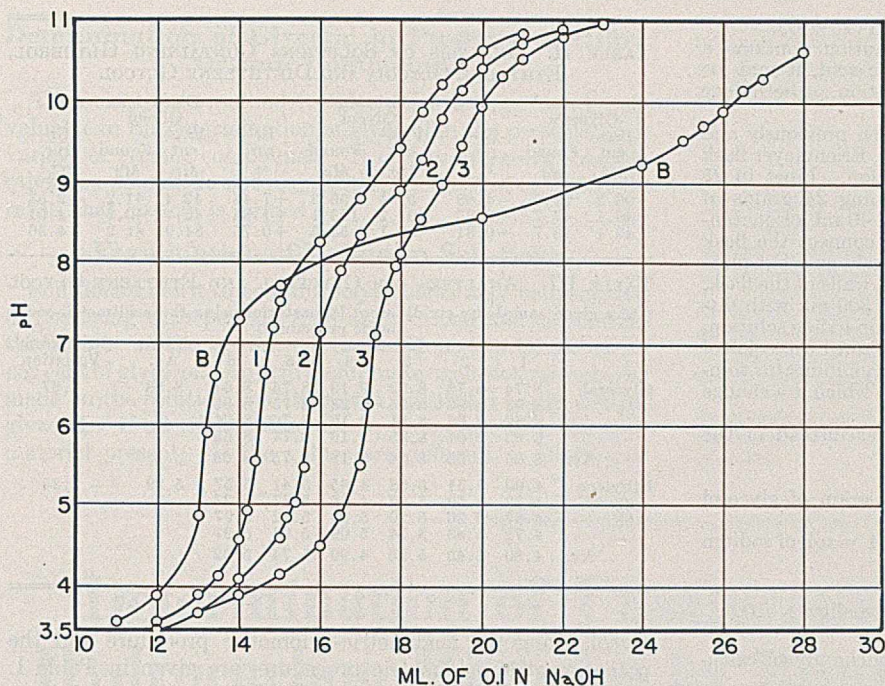
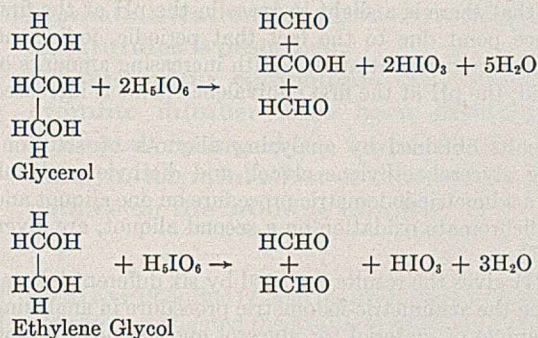


FIGURE 1. POTENTIOMETRIC TITRATION OF SOLUTION OF PERIODIC ACID AND OF GLYCEROL-ETHYLENE GLYCOL SAMPLES



Periodic acid may be considered as a monobasic acid or a dibasic acid according to the pH to which it is titrated. This is shown in curve B of Figure 1, which gives the potentiometric titration of a solution of periodic acid. It is seen that the first hydrogen is neutralized at a pH of about 5.5, and the second hydrogen at a pH of about 10.0. The inflection in pH at the second equivalence point is not very sharp.

The first equivalence point comes at about the mid-point of methyl red indicator and it is possible to use this indicator for the titration. The change in pH at the second equivalence point is not sharp enough to permit the use of an indicator and a potentiometric method must be used. If we consider the reactions given above and regard periodic acid as a monobasic acid, with glycerol two equivalents of acid go to form three equivalents and with ethylene glycol one equivalent goes to form one equivalent. If periodic acid is considered as a dibasic acid, in the case of glycerol four equivalents go to form three equivalents, and in the case of ethylene glycol two equivalents go to form one equivalent.

It is possible, therefore, in an aqueous solution containing glycerol and ethylene glycol, to determine glycerol acidimetrically using methyl red as an indicator and to determine ethylene glycol by titrating potentiometrically to a pH of about 10.0. Alternatively, and more accurately, the ethylene glycol may be determined by an iodometric method.

Reagents and Apparatus

Standard sodium thiosulfate solution, 0.2 N. Potassium dichromate solution, 24 grams per liter. Potassium iodide solution, 20 per cent by weight.

Periodic acid solution, approximately 0.05 N, as a monobasic acid. Dissolve 11 grams of periodic acid (The G. Frederick Smith Chemical Company, Columbus, Ohio) in distilled water, dilute with distilled water to 1000 ml., and filter through a sintered-glass filter. Store the solution in a dark-glass bottle and keep closed with a glass stopper. This solution decreases slowly in oxidizing power with time. A blank on the solution must be run each day that analyses are made.

Standard sodium hydroxide solution, 0.1 N.

Erlenmeyer flasks, capacity 1000 ml. Glass-stoppered flasks are preferred, but rubber stoppers may be used if care is taken that no solution comes in contact with the rubber. Erlenmeyer flasks, with ground-glass joints, capacity 500 ml.

Glass electrode pH meter. Any suitable apparatus is satisfactory.

Procedure

ACIDIMETRIC-IODOMETRIC. In order to ensure the necessary excess periodic acid, the sodium thiosulfate required for a sample should not be less than four fifths of the sodium thiosulfate required by the blank. For 50 ml. of 0.05 N periodic acid, this corresponds to about 0.09 gram of glycerol and 0.125 gram of ethylene glycol. Take a sample of a size that will not contain oxidizable matter in excess of that equivalent to 0.09 gram of glycerol. Dilute the sample to 50 ml. in a 1000-ml. Erlenmeyer flask. Pipet in exactly 50 ml. of the periodic acid solution and mix. Stopper with a glass or rubber stopper and allow to stand for 40 to 80 minutes at room temperature.

At the end of the oxidation period, add about 100 ml. of distilled water and mix. Titrate in the flask with 0.1 N sodium hydroxide. Run in about 20 ml. of the sodium hydroxide and then add exactly 2 drops of methyl red indicator solution. Do not add more than this quantity of indicator. Continue the titration to the disappearance of the pink color. As the end point is approached, the sodium hydroxide solution must be added drop by drop and the color of the solution observed carefully. Make all buret readings to 0.01 ml.

Take the solution that has been titrated, and add 150 ml. of distilled water, 30 ml. of 20 per cent potassium iodide solution, and 25 ml. of 6 N sulfuric acid. Titrate the solution with 0.2 N sodium thiosulfate to a light orange color. Add 2 ml. of fresh starch indicator solution and titrate to the disappearance of the starch-iodine color. When the titration is completed, the solution is colored pink owing to the methyl red indicator present. The end point is very sharp, and care must be taken that it is not overrun. Make all buret readings to 0.01 ml.

Run a blank using 50 ml. of distilled water instead of the sample and do both the acidimetric and iodometric titrations.

Calculation.

1 ml. of N sodium hydroxide = 0.09206 gram of glycerol (acidimetric)

Let B = ml. of sodium hydroxide for blank on the periodic acid solution

A = ml. of sodium hydroxide for sample

$$\text{Then } \frac{(A - B) \times \text{acidimetric glycerol factor} \times \text{normality} \times 100}{\text{weight of sample}} = \% \text{ of glycerol} = G$$

1 ml. of N sodium thiosulfate = 0.023015 gram of glycerol (iodometric by periodic acid). Let B' = ml. of sodium thiosulfate for blank, A' = ml. of sodium thiosulfate for sample

$$\text{Then } \frac{(B' - A') \times \text{iodometric glycerol factor} \times \text{normality} \times 100}{\text{weight of sample}} = T$$

where T = glycerol and ethylene glycol calculated as % of glycerol

If $E = \%$ of ethylene glycol, then $E = 1.348(T - G)$.

DICHROMATE OXIDATION. In case the solution contains a third glycol, which is not oxidized by periodic acid, it may be determined by a separate dichromate oxidation. Diethylene glycol is an example of such a compound.

Take a sample one half the size of that taken previously and dilute to 25 ml. with distilled water in a 500-ml. Erlenmeyer flask with an interchangeable ground-glass connection. Pipet in 25 ml. of potassium dichromate solution containing 24 grams of potassium dichromate per liter and measure in 40 ml. of concentrated sulfuric acid. Add a few glass beads, connect the flask with a water-cooled condenser, and boil vigorously on a hot plate for 20 minutes. Rinse down the condenser and walls of the flask, cool to room temperature, and dilute to about 300 ml. with distilled water. Add 10 ml. of 20 per cent potassium iodide solution, mix, and titrate with 0.2 *N* sodium thiosulfate until the color of the solution becomes lighter. Add 1 ml. of starch indicator solution and continue the titration to the end point, which is a change from a dark opaque to a clear green color.

Run a blank using 25 ml. of distilled water instead of the sample.

Calculation.

1 ml. of *N* sodium thiosulfate = 0.006576 gram of glycerol (dichromate oxidation)

Let $B =$ ml. of sodium thiosulfate for blank, $A =$ ml. of sodium thiosulfate for sample

Then

$$\frac{(B - A) \times \text{dichromate glycerol factor} \times \text{normality} \times 100}{\text{weight of sample}} =$$

$X =$ glycerol, ethylene glycol, and diethylene glycol calculated as % of glycerol

$(X - T) \times 0.807 = \%$ of diethylene glycol.

POTENTIOMETRIC. Titrate a solution of 50 ml. of the periodic acid solution in 150 ml. of distilled water with 0.1 *N* sodium hydroxide, using a glass electrode pH meter to follow the change in pH. Determine the first equivalence point by noting the maximum change in pH with addition of sodium hydroxide. This equivalence point will be found to occur at a pH of about 5.5. Add more 0.1 *N* sodium hydroxide, equal to the volume required to reach the first equivalence point, and measure the pH of the solution. This will be about 10.0.

Oxidize a solution of the sample with periodic acid as described above. Dilute with 100 ml. of distilled water and titrate with 0.1 *N* sodium hydroxide to the first equivalence point, using the glass electrode pH meter to locate the point as in the blank. Record the volume of 0.1 *N* sodium hydroxide used, A . Continue the titration with 0.1 *N* sodium hydroxide to the pH found for the second equivalence point of the blank. Record the volume of sodium hydroxide as X .

Calculation.

1 ml. of *N* sodium hydroxide = 0.09206 gram of glycerol = 0.06205 gram of ethylene glycol

Let $B =$ ml. of sodium hydroxide for blank at first equivalence point

$A =$ ml. of sodium hydroxide for sample at first point

$X =$ ml. of sodium hydroxide for sample at second point

Then

$$\frac{(A - B) \times \text{glycerol factor} \times \text{normality} \times 100}{\text{weight of sample}} = \%$$
 of glycerol

$$\frac{(3B - X - A) \times \text{ethylene glycol factor} \times \text{normality} \times 100}{\text{weight of sample}} =$$

% of ethylene glycol

Analytical Results

The results obtained by analyzing aliquots of synthetic solutions containing known amounts of glycerol and ethylene

TABLE II. ANALYSIS OF SOLUTIONS CONTAINING GLYCEROL, ETHYLENE GLYCOL, AND DIETHYLENE GLYCOL

Glycerol			Ethylene Glycol			Diethylene Glycol		
Present	Found	Error	Present	Found	Error	Present	Found	Error
Mg.	Mg.	%	Mg.	Mg.	%	Mg.	Mg.	%
98.2	93.6	-4.68	52.4	56.3	+7.44	42.4	41.2	-2.83
49.1	47.7	-2.85	101.2	103.1	+1.88	42.4	40.7	-4.01
49.1	48.7	-0.81	53.1	53.5	+0.75	84.9	81.2	-4.36

TABLE III. ANALYSES FOR GLYCEROL AND ETHYLENE GLYCOL (On a given sample by six different laboratories using the acidimetric-iodometric procedure)

	Laboratory						Grand Av.	Maximum Variation
	1	2	3	4	5	6		
Glycerol, %	8.74	8.78	8.82	9.13	8.75	8.61	8.88	0.67
	8.92	8.93	8.95	9.28	8.75	8.85		
	8.82	9.06	8.81	9.16	8.76	8.64		
	8.92	9.01	8.85	9.16	8.74	8.63		
Av.	8.85	8.95	8.86	9.18	8.75	8.68		
Ethylene glycol, %	4.90	5.51	5.08	4.95	5.41	5.57	5.29	1.25
	4.72	5.59	5.46	4.88	5.77	5.27		
	4.87	5.26	5.20	5.02	5.82	5.97		
	4.72	5.33	5.24	5.09	5.94	5.27		
Av.	4.80	5.42	5.25	4.99	5.74	5.52		

glycol, using the acidimetric-iodometric procedure and the potentiometric acidimetric procedure, are given in Table I. The synthetic solutions were prepared from separate solutions which were standardized by oxidation with acid dichromate.

The potentiometric titrations of a blank and of three samples containing varying percentages of glycerol and ethylene glycol are shown by the curves given in Figure 1. It is to be noted that there is a slight increase in the pH at the first equivalence point due to the fact that periodic, iodic, and formic acids are being titrated. With increasing amounts of formic acid, the pH at the first equivalence point is increased slightly.

The results obtained by analyzing aliquots of solutions containing glycerol, ethylene glycol, and diethylene glycol, using the acidimetric-iodometric procedure on one aliquot and the acid dichromate oxidation on a second aliquot, are given in Table II.

Table III gives the results reported by six different laboratories using the acidimetric-iodometric procedure in analyzing a given sample of material for glycerol and ethylene glycol. The material was extracted with water and aliquots of the extract were analyzed. The individual results are given for each laboratory to show the variations encountered by a given analyst. The error in the determination of ethylene glycol is always higher than the error for glycerol, since the ethylene glycol is not determined directly.

Qualitative Test to Distinguish between Glycerol and Ethylene Glycol Solutions

Since glycerol reacts with periodic acid to produce formic acid, whereas ethylene glycol does not, a simple test may be devised to distinguish between the two when present alone.

Take about 2 ml. of the solution to be tested, add a drop of methyl red indicator solution, and cautiously neutralize with dilute sodium hydroxide or dilute acid, leaving the solution just on the alkaline side of methyl red. Take about 2 ml. of a solution of periodic acid, add a drop of methyl red, and adjust to the neutral point of the indicator, leaving the solution just on the alkaline side. An adjusted solution of sodium paraperiodate or potassium metaperiodate may be used. Mix the sample with the periodate solution and observe. If glycerol is present, the solution will turn pink immediately.

TABLE I. ANALYSIS OF GLYCEROL-ETHYLENE GLYCOL SOLUTIONS

Glycerol Present	Glycerol Found, A.-I. ^a		Glycerol Found, Pot. ^b		Glycol Present	Glycerol Found, A.-I. ^a		Glycerol Found, Pot. ^b	
	Mg.	Error %	Mg.	Error %		Mg.	Mg.	Error %	Error %
48.8	47.7	-2.25	53.2	+9.02	153.0	160.8	+ 5.10	155.9	+1.90
...	48.3	-1.02	49.6	+1.64	...	154.9	+ 1.24
49.1	49.7	+1.22	49.6	+1.02	149.4	149.0	- 0.27	153.9	+3.01
97.5	96.7	-0.82	101.0	+3.59	102.0	105.3	+ 3.24	103.7	+1.67
...	97.3	-0.21	103.9	+1.86
98.2	98.0	-0.20	98.4	+0.20	99.6	102.3	+ 2.71	106.1	+6.53
146.3	143.7	-1.78	150.5	+2.87	51.0	57.6	+12.94	50.5	-0.98
...	145.4	-0.62	145.0	-0.89	...	54.7	+ 7.25	53.9	+5.69
147.2	146.7	-0.34	149.1	+1.29	49.8	50.7	+ 1.81	52.7	+5.82

^a A.-I. = acidimetric-iodometric procedure.

^b Pot. = potentiometric acidimetric procedure.

Determination of Glycerol in Presence of Other Organic Compounds

The acidimetric method for glycerol has been found very valuable in the determination of glycerol in the presence of a variety of organic compounds. It is only necessary that the other compounds do not react with periodic acid or if they do react, that no acid is formed.

Examination of Unknown Solutions

Solutions known to contain polyalcohols may be examined by oxidizing with periodic acid as described and calculating the results of the acidimetric and iodometric titrations to per cent of glycerol. An acid dichromate oxidation may also be made on the solution and the result calculated to per cent of glycerol. If all three values check, then glycerol is the only material present. If the values are different, a mixture of

polyalcohols is indicated and a comparison of the figures obtained will permit some conclusions to be drawn as to the nature of the alcohols.

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Determination of Unsaturation in Aliphatic Hydrocarbon Mixtures by Bromine Absorption

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A modified and time-saving bromide-bromate titration for the determination of unsaturates is described.

Some sulfur compounds that affect the bromine number have been investigated and catalysts have been found which minimize the harmful effect of these sulfur compounds on the bromine number.

DURING 1929 Buc (1) and his co-workers of these laboratories investigated the available methods for the determination of the unsaturated content of petroleum fractions. In order to establish a reference method, they devised a catalytic hydrogenation process by which they were able to evaluate the methods being studied. The method of Francis (2) was selected as partially meeting the requirements of these workers, inasmuch as it proved excellent for the determination of straight-chain olefins, diisobutylene, and other branched-chain olefins of low molecular weight. They found, however, that a modification of the method was necessary on account of high results obtained, if applied to the determination of highly branched-chain unsaturates and to polymers.

Compounds That Affect Results

Buc and co-workers observed that with polymer mixtures the method gave results inordinately high for any purpose. They, therefore, modified the Francis method in the following manner:

Introduce into a g. s. flask from 5 to 10 grams of solid potassium bromide, and add the required volume of 0.5 N potassium bromide-bromate as determined by a trial titration, and 20 ml. of 10 per cent (by volume) sulfuric acid saturated with potassium bromide. Allow 3 minutes for liberation of bromine, and then cool the flask and contents in an ice-salt mixture for 10 minutes. Next add the previously cooled sample diluted with chloroform and shake vigorously for exactly 2 minutes. Finally add saturated potassium iodide solution and titrate with standard sodium thiosulfate.

The Francis and Buc methods were compared with polybutenes having an average molecular weight of 253.

Theoretical determination (from molecular weight)	Bromine No.	% of Theory
	67.4	100
Francis method		
1 ml. excess KBr-KBrO ₃	99.0	147
2 ml. excess KBr-KBrO ₃	112.7	167
Buc modification		
1 ml. excess KBr-KBrO ₃	57.0	85
2 ml. excess KBr-KBrO ₃	65.5	97

The Buc modification evidently gives values which more nearly agree with the theoretical value.

Mulliken and Wakeman (3) conducted research on the limits of applicability of the Francis bromide-bromate titration and modified it so that it could be used with a fair degree of accuracy for the titration of most alkenes. They also found that it could be used to determine the number of double bonds present in cycloalkenes and in alkadienes, although less accurately for their quantitative estimation. These workers found the method of doubtful value when applied under ordinary conditions, in the presence of atmospheric oxygen, to alkynes and to cycloalkadienes. Thomas, Block, and Hoekstra (4) again modified the method of Francis and of Mulliken and Wakeman and confirmed some of the latter-named authors' work. A conspicuous feature of the modification by Thomas *et al.* is the precaution of cooling in many steps of their procedure, which is a carefully regulated slow titration. They warn that the presence of diolefins in some cracked gasoline will cause an error by the bromide-bromate titration, although this is not large.

The authors found that a control chemist could determine the bromine number of nearly twice as many samples of gasoline per day if the trial titration were eliminated. Consequently, they modified the Buc bromide-bromate method to the following extent:

Introduce into a g. s. flask 20 ml. of 10 per cent (by volume) sulfuric acid saturated with potassium bromide and 15 ml. of *n*-heptane or other suitable solvent. Next add from 0.7 to 1.0 gram of the sample from a Lunge weighing pipet and stopper the flask immediately. Titrate directly with 0.5 N potassium bromide-bromate to a faint yellow color, swirling the flask during

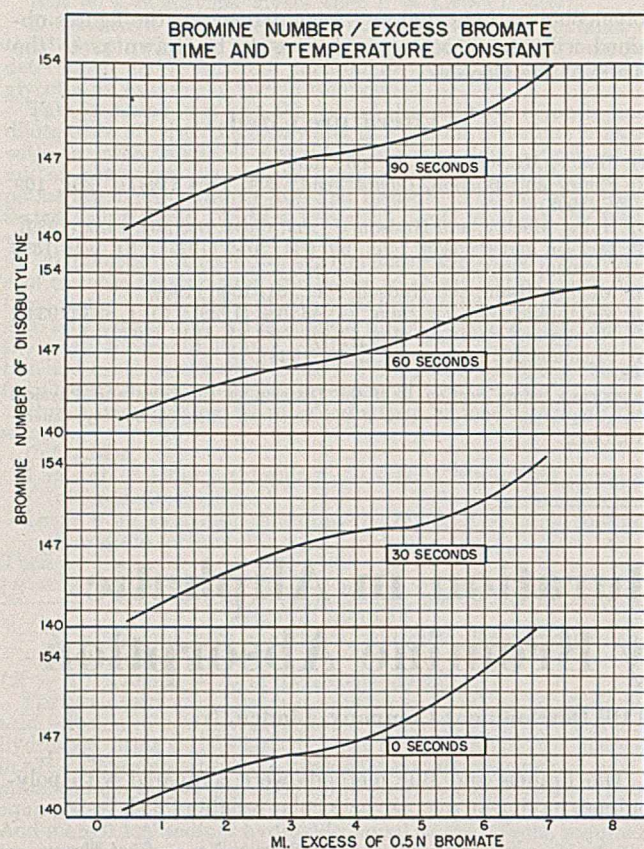
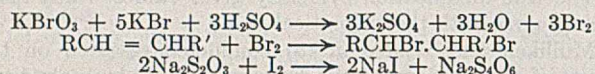


FIGURE 1

the titration, add 1 ml. of the potassium bromide-bromate solution in excess, and shake for 2 minutes. Finally add 5 ml. of saturated solution of potassium iodide and titrate the liberated iodine with 0.1 *N* sodium thiosulfate, using potato starch as an indicator.



$$\frac{0.0799 \times \text{normality of KBrO}_3 \times \text{net ml. of KBrO}_3 \times 100}{\text{weight of sample}} =$$

bromine number

This method, which has superseded the above-mentioned bromination methods in these laboratories, retains the limitations of the Buc modification. It differs, however, from all these methods in that a trial titration is unnecessary. The excess of potassium bromide-bromate, as shown in Figure 1, must be kept to a definite minimum.

It has not been found necessary to use a cooling medium with the authors' method for determining the bromine number of any of the compounds incorporated in the data of this paper.

Table I shows results on several pure compounds, synthetic blends made from mixtures of A. S. T. M. naphtha, *n*-heptane, diisobutylene, and heptene-1, and also on a number of saturated compounds. This table shows that the bromine numbers of the pure compounds determined at 0° C. and at room temperature are in close agreement with the theoretical calculations.

The values obtained on tri- and tetraisobutylene show irregularities that have been confirmed by some of the aforementioned workers. The bromine numbers of synthetic blends shown in Table I give further proof that prior cooling is unnecessary. The saturated compounds were run to show that they do not substitute during the determination.

Effect of Sulfur Compounds on Bromine Number

Qualitative experiments showed that certain sulfur compounds lowered the bromine number of unsaturates. The reaction of bromine with short-chain unsaturates is normally rapid, but the addition of varying amounts of sulfur compounds retards the reaction to such an extent that an apparent excess of halogen appears long before the calculated amount of potassium bromide-bromate necessary for complete bromination has been added. The reaction proceeds rapidly until the sulfur compounds are apparently oxidized. Subsequent additions of bromine, however, react very slowly, requiring vigorous shaking of the flask for 20 to 25 seconds after each addition. This is an indefinite and lengthy procedure. In order to obtain data that will have any significance, the titration must be stopped at some exact point. This is taken to be the first definite excess of bromine that does not disappear after a few (5) seconds' shaking. Experimental work, therefore, was carried out on this basis.

Solutions of diphenyl disulfide, isoamyl disulfide, benzyl mercaptan, and amyl and isoamyl mercaptan in diisobutylene were prepared in low concentrations in order to represent the varying amounts of sulfur compounds frequently found in gasoline. Diisobutylene was selected because it was available in large quantities and obtainable in a high state of purity.

At concentrations ranging from 0.02 to 2.0 per cent of the sulfur compound, diphenyl disulfide, isoamyl disulfide, benzyl mercaptan, and amyl mercaptan had no effect on the bromine number. Between 2.0 and 3.0 per cent of amyl mercaptan lowered the bromine number to a slight extent (about 10.0 per cent). Isoamyl mercaptan, however, lowered the apparent unsaturation to about 60 per cent of its proper value.

Table II shows that the first lowering of the bromine number takes place at a concentration of 0.2 per cent. The failure of diphenyl disulfide, isoamyl disulfide, and benzyl mercaptan to lower the bromine number of diisobutylene may have been due to their low concentrations. Since amyl mercaptan showed only a slight effect at a concentration between 2.0 and 3.0 per cent, mixtures containing 10 to 100 per cent of benzyl mercaptan, amyl mercaptan, and isoamyl disulfide in diisobutylene were prepared and the bromine numbers determined. The values in Table III show that at these higher concentrations, benzyl mercaptan, amyl

TABLE I. DETERMINATION OF BROMINE NUMBER

Sample	At 0° C.	At Room Temperature	Calculated Values
Diisobutylene	142.9	142.5	142.4
Heptene-1	162.6	162.8	163.0
Trimethylethylene	225.2	223.0	228.5
Triisobutylene	...	108.0	95.0
	...	105.0	95.0
	...	91.0	95.0
	...	67.0	95.0
Tetraisobutylene	...	47.0	71.0
	...	51.0	71.0
Synthetic Mixtures			
1	...	82.0	80.0
2	...	83.0	82.0
3	...	83.0	82.0
4	...	79.0	76.0
A. S. T. M. naphtha	...	4.0	...
<i>n</i> -Hexane	...	0	0
<i>n</i> -Heptane	...	0	0
Isooctane	...	0	0
Methylcyclohexane	...	0	0
Tertiary butyl chloride	...	0	0
<i>n</i> -Amyl chloride	...	0	0

TABLE II. EFFECT OF ISOAMYL MERCAPTAN ON BROMINE NUMBER OF DIISOBUTYLENE

Weight %	Bromine No. at Room Temperature	Weight %	Bromine No. at Room Temperature
2	86.2	0.4	104.8
1.6	103.4	0.2	139.7
1.2	81.1	0.1	144.0
0.8	89.4	0.02	144.0

TABLE III. EFFECT OF SULFUR COMPOUND DILUTIONS IN DIISOBUTYLENE
(Bromine number of diisobutylene, 143)

Concentration, Volume % Sulfur compound	Diisobutylene	Isoamyl Disulfide ^a			Benzyl Mercaptan ^a			Amyl Mercaptan ^a		
		Weight %	Room temp.	Calcd.	Weight %	Room temp.	Calcd.	Weight %	Room temp.	Calcd.
10	90	12.47	2.7	126.6	14.11	6.7	132.3	11.74	11.0	131.9
20	80	24.28	2.6	111.2	26.98	15.3	122.5	23.04	12.9	124.2
40	60	46.09	6.2	82.6	49.64	24.6	105.4	44.39	29.6	109.4
80	20	83.69	5.7	33.3	85.53	56.5	78.1	82.73	50.1	83.1
100	0	100.00	12.0	...	100.00	67.1	...	100.00	71.2	...

^a Eastman Kodak Co., Rochester, N. Y.

TABLE IV. EFFECT OF CATALYSTS

(On 10% by volume solutions of benzyl mercaptan in diisobutylene. 14.11% by weight benzyl mercaptan. Bromine number of diisobutylene, 143)

Catalyst	Bromine No. at Room Temperature
No catalyst	6.7
Ammonium molybdate	86.5
Sodium tungstate	106.4
Copper sulfate	110.3
Cobalt chloride	53.2
Sodium arsenate	101.1
Ferric chloride	119.7
Silver nitrate	121.0
Silver bromide (solid)	129.0
Uranium acetate (saturated solution)	129.0
Mercuric chloride	130.2
Platinic chloride (end point uncertain)	122.4
Zinc sulfate	129.0

mercaptan, and isoamyl disulfide prevent bromination of diisobutylene and that the bromine numbers found are apparently due to the sulfur compounds themselves.

Further investigation was made on a synthetic gasoline (Bromine No. 79.8) containing saturates, unsaturates, and aromatics to which 20 per cent benzyl mercaptan by volume (27.4 per cent by weight) had been added. The bromine number dropped from 89.4 (calculated) to 41.1.

A sample of current gasoline (Bromine No. 23.4) mixed with 10 per cent benzyl mercaptan by volume (14.06 per cent by weight) showed a change in the bromine number from the calculated value of 29.7 to 15.5. With 20 per cent mercaptan by volume (28.1 per cent by weight) the same gasoline was lowered from a calculated value of 35.4 to 26.5.

A possible explanation for the change in the bromine number of diisobutylene may be taken from the data, which show that isoamyl disulfide definitely affects this value. Mercaptans, also, influence the determination and it may be assumed that since they are easily oxidized to disulfides, the change is due to the presence of these latter compounds. Furthermore, no method depending upon bromine addition is reliable when the afore-mentioned types of sulfur compounds are present in appreciable amounts.

Since this paper represents preliminary work, no attempt has been made to determine the actual concentration at which each compound noticeably affects the bromine number.

Effect of Inorganic Catalysts

The obvious need of an agent to counteract the inhibitive effect of certain sulfur compounds led to a search for a suitable catalyst. The determination of the bromine number of a 10 per cent benzyl mercaptan solution in diisobutylene was, therefore, repeated using a number of catalysts as shown in Table IV. One milliliter of a 10 per cent aqueous solution of the catalyst was used with the exception of silver bromide, in which case 0.1 gram of the solid salt was employed.

The calculated bromine number of the benzyl mercaptan-diisobutylene mixture is:

Bromine number of diisobutylene = 143
Bromine number of benzyl mercaptan = 67.1
10% by volume benzyl mercaptan is equivalent to 14.11% by weight

$$\begin{aligned} \text{Then } 67.1 \times 14.11\% &= 9.46 \\ 143 \times 85.89\% &= 122.84 \\ \text{Calculated value} &= 132.30 \end{aligned}$$

The apparent bromine numbers of the other mixtures

were calculated in the same manner.

From Table IV it can be seen that silver bromide, uranium acetate, mercuric chloride, and zinc sulfate are the most efficient catalysts.

Inasmuch as results approaching the calculated value were obtained on a 10 per cent dilution of benzyl mercaptan with the aid of catalysts, it was decided to continue work on this compound along with isoamyl disulfide and amyl mercaptan in concentrations ranging from 10 to 100 per cent.

Bromine numbers were determined on five series of mixtures of amyl mercaptan, benzyl mercaptan, and isoamyl disulfide in diisobutylene, using (1) no catalyst, (2) uranium acetate, (3) mercuric chloride, (4) zinc sulfate, and (5) silver bromide. These values are shown in Table V. The data in this table show that the calculated bromine numbers of mixtures of benzyl mercaptan-diisobutylene, isoamyl disulfide-diisobutylene, and amyl mercaptan-diisobutylene can be nearly attained by the use of the salts of silver, uranium, mercury, and zinc as catalysts.

It is possible that these catalysts will be helpful in overcoming the inhibitive tendencies of similarly acting compounds which might be found in untreated gasoline. Pure aromatic hydrocarbons had no effect on the bromine number of diisobutylene, either with or without catalysts.

Conclusions

The modified procedure eliminates a trial titration and the necessity for cooling the sample prior to titration.

The method as described is applicable to straight-chain olefins, diisobutylene, and other branched-chain olefins of low molecular weight. With highly branched polymers, the method gives erratic results.

Certain sulfur compounds definitely affect the bromine number. At low concentrations isoamyl mercaptan and at higher concentrations benzyl mercaptan, amyl mercaptan,

TABLE V. EFFECT OF CATALYSTS ON BROMINE NUMBER OF DIISOBUTYLENE

Sulfur Compound Concentration	Volume %	Weight %	Bromine Number at Room Temperature					Calcd.
			No catalyst	Uranium acetate	Mercuric chloride	Zinc sulfate	Silver bromide	
Benzyl Mercaptan								
10	14.11		6.7	128.8	130.1	124.8	128.8	132.3
20	26.98		15.3	112.0	115.8	115.8	114.5	122.5
40	49.64		24.6	101.6	100.5	101.6	99.4	105.4
80	85.53		56.5	88.8	88.8	78.1
100	100.00		67.1	68.1	68.1	...
Isoamyl Disulfide								
10	12.47	2.7		111.1	113.8	123.3	123.3	126.6
20	24.28	2.6		108.2	106.9	106.9	109.5	111.2
40	46.09	6.2		70.0	70.0	76.2	82.5	82.6
80	83.69	5.7		30.7	20.4	13.6	13.6	33.3
100	100.00	12.0		15.3	...
Amyl Mercaptan^a								
10	11.74	11.0		132.8	132.8	131.9
20	23.04	12.9		124.7	123.5	124.2
40	44.39	29.6		104.5	104.5	109.4
80	82.73	50.1		75.9	68.7	83.1
100	100.00	71.2		71.2	71.2

^a Bromine number of diisobutylene (new lot), 140.0.

and isoamyl disulfide lower the bromine number of diisobutylene.

Silver, mercury, zinc, and uranium salts are efficient catalysts for overcoming the deleterious effect of these sulfur compounds.

Bromide-bromate methods for unsaturation are unreliable when certain types of sulfur compounds are present.

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Determination of Moisture in Native and Processed Cellulose

Titrimetric Determination Using Karl Fischer Reagent

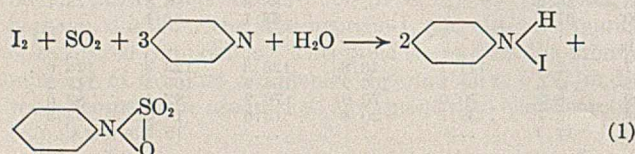
JOHN MITCHELL, JR.

Ammonia Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

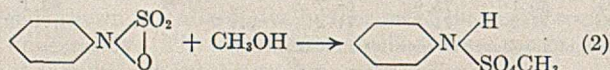
Moisture in various forms of cellulose is determined by cold extraction with methanol followed by direct titration for water with Karl Fischer reagent. The method is simple and precise. Recovery is more nearly complete than by the oven-drying techniques.

THE present standard procedures for the determination of moisture in such cellulose products as wood, paper, cotton, and regenerated cellulose are usually based on weight loss at carefully controlled temperatures. As quantitative methods, however, these analyses are limited to materials containing no other volatile substances. The tentative A. S. T. M. procedure for moisture in untreated paper, for example, specifies heating to constant weight at 100° to 105° C. a 6.5-sq. cm. sample of the paper (1). Several modifications of heating technique have been published recently. Göhde (4) described an electrically heated rotary dryer complete with built-in analytical balance and automatic temperature control. Evans and co-workers (2) outlined a micro-procedure involving water evolution followed by absorption in Dehydrite. None of these procedures can be considered general, however, because volatile materials other than water either render the methods inaccurate or necessitate empirical corrections.

In the present paper, a simple and efficient cold extraction technique is used in conjunction with a specific titrimetric method for water involving the use of Karl Fischer reagent (3). The reagent consists of a mixture of iodine, pyridine, and sulfur dioxide in methanol solution, and recent work in this laboratory (6) has shown that the following reactions are involved:



and



Reagents

Complete instructions for the preparation and standardization of Karl Fischer reagent have been published (6). [There are a few substances which interfere with the titration for water with Karl Fischer reagent. Reactive aldehydes and ketones react with the methanol to form acetals or ketals and formic acid is dehydrated (6). Boric acid is esterified quantitatively (5).] Dry methanol (<0.1 per cent water) was obtained from fresh drums of du Pont synthetic methanol.

Experimental Procedure

FOR REGENERATED CELLULOSE AND PAPER. Four or five pieces, each cut approximately 2.5 cm. (1 inch) square, are weighed into a 500-ml. glass-stoppered iodine flask containing 100 ml. of dry methanol. Since 0.5 mg. is the minimum amount of water readily detected by Karl Fischer reagent, the total sample should contain from 50 to 250 mg. of water. After standing 1 hour (shaking unnecessary) the mixture is titrated directly with Karl Fischer reagent to a permanent end point. After correction for water in the methanol, obtained by titration of 100 ml., the net water found represents the total available water in the sample.

FOR WOOD. A single sample, cut 2.5 × 1.9 × 0.3 cm. (1 × 0.75 × 0.125 inch) is weighed into 100 ml. of dry methanol as above. After 2 hours at room temperature the methanol is decanted into another 500-ml. glass-stoppered iodine flask and the wood washed with two 10-ml. portions of methanol. An additional 100 ml. of methanol is poured over the wood. This mixture is allowed to stand 18 hours. The net water found in the two successive methanol extracts is equivalent to the total water removed from the sample. It is desirable to titrate the first extract immediately after decantation. The second extract need not be decanted, as the wood is inert toward the reagent.

The most outstanding feature of these analytical procedures is the extraction step in which the low viscosity and favorable solvent properties of methanol combine to effect an equilibrium distribution of moisture between solvent and sample in a relatively short time. Methanol, also, is probably the best solvent for use with Fischer reagent. (Dioxane, for example, was tried and found to be slow and incomplete in its extraction properties.) Moisture in natural wood sections, wood pulp, paper, cotton linters, and regenerated cellulose is separated in from one to two extractions and may then be determined by titration with the above reagent. Regenerated cellulose, cotton linters, and paper require a single extraction. Average results from quadruplicate analyses of several samples are recorded in Table I together with comparative weight loss figures. Zimmerman (8) also reports having used Karl Fischer reagent for the determination of water in cotton, but his exact technique is not stated.

The approximate moisture content of cellulose was obtained from the oven-drying weight loss figures. Complete

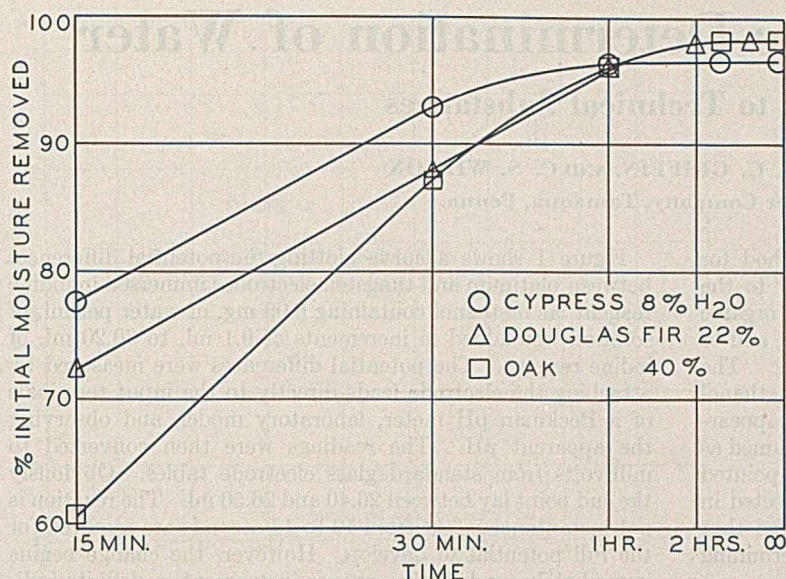


FIGURE 1. REMOVAL OF INITIAL MOISTURE ON FIRST EXTRACTION WITH METHANOL

water removal by the new procedure was accomplished by repeated extraction of individual samples guided by titration of the extracts. Rayon-type hardwood pulp and 95 per cent α -cellulose showed no moisture in the second extract.

TABLE I. DETERMINATION OF MOISTURE IN CELLULOSE

Substance	Water, %	Loss (102° C.), %
α -Cellulose, 98%	5.84 \pm 0.07	5.80
α -Cellulose, 95%	4.39 \pm 0.06	4.40
Cardboard	4.73 \pm 0.08	4.67
Cotton linters	6.09 \pm 0.04	5.96
Newspaper	5.18 \pm 0.06	5.17
Wood pulp, cellophane quality	4.20 \pm 0.08	4.18
Wood pulp, rayon type	4.47 \pm 0.06	4.44

Native woods require two extractions with methanol. Results obtained on 3-mm. (0.125-inch) thicknesses of kiln-dried cypress, air-dried Douglas fir, and partly-dried oak are summarized in Table II. The method may be used for either cross-cut or flat-grain wood.

TABLE II. DETERMINATION OF MOISTURE IN NATIVE WOOD

Wood	Weight % of Water by Extraction				Loss (102° C.) %
	1st ext.	2nd ext.	3rd ext.	Total	
Cypress ^a	7.68	0.28	0.00	7.96	7.69
Cypress ^b	7.63	0.31	0.00	7.94	7.68
Douglas fir ^b	6.83	0.32	0.00	7.15	6.55
	7.09	0.33	0.00	7.42	6.98
	25.22	0.55	0.00	25.77	24.49
	24.60	0.70	0.00	25.30	24.01
	25.05	0.52	0.00	25.57	24.98
	21.64	0.48	0.00	22.12	22.38
	21.66	0.45	0.00	22.11	21.98
	22.07	0.52	0.00	22.59	
Oak ^a	39.00	0.72	0.00	39.72	39.88
Oak ^b	39.60	0.66	0.00	40.26	40.69
	40.64	0.82	0.00	41.46	41.41
	39.17	0.75	0.00	39.92	40.86

^a Cut perpendicular to grain (cross cut).
^b Cut parallel to grain (flat grain).

Moisture recovery from the cell walls of the wood is evidently more nearly complete by the extraction procedure than by the oven-drying method: Duplicate samples of each cut of wood were dried to constant weight at 104° C. and then subjected to methanol extraction; based on the total water present, an increase in recovery of 4 per cent relative was found in cypress (flat grain), 5 per cent in cypress (cross cut), 2 per cent in Douglas fir (cross cut), and 1 per cent in oak (both cuts). It appears that regardless of the amount of water initially present the absolute amount remaining in the wood after drying is surprisingly constant, even though the

type or previous treatment of the wood is different (0.3 to 0.4 per cent for cypress; 0.4 to 0.5, Douglas fir; and 0.3, oak).

Discussion

Extraction of moisture from wood involves the removal of surface or loosely held water and that in the inner cell walls (?). The lower water recoveries by oven-drying (Table II) are in harmony with this assumption. The following experiments probably support this mechanism also. Initial experiments were conducted on air-dried Douglas fir. Individual samples, approximately 2.5 \times 1.9 \times 0.6 cm. (1 \times 0.75 \times 0.25 inch), were cut parallel to the grain and covered with dry methanol. Some were allowed to stand at room temperature (27° \pm 3° C.); others were refluxed. After definite time intervals the methanol was decanted and the wood washed with small portions of methanol. This procedure was repeated until extracts gave negative tests for water.

Approximately 97.5 per cent of the total water was obtained in the first extraction for periods ranging from 6 to 80 hours at room temperature and 2 to 4 hours' refluxing. An additional 2 per cent was obtained from a second extraction requiring a minimum of 16 hours at room temperature, while the remaining 0.5 per cent required a third treatment of 16 hours. The longer time required for the second and third extractions may be evidence of more strongly held water.

In order to decrease the over-all time, samples of kiln-dried cypress, air-dried Douglas fir, and partly-dried oak, half as thick (3 mm., 0.125 inch), cut perpendicular to the grain, were extracted at room temperature by the above procedure. In every case the third extraction showed no increase in water over that originally present in the methanol.

The per cent of water removed in the first extraction was calculated from the total of the several extractions of a given sample. In Figure 1 moisture removed in the first extraction of the three types of wood is plotted against reciprocal time, as the latter scale is advantageous in showing comparative water removal in the shorter periods of time. In 1 hour about 96 per cent of the total moisture is recovered, while in 3 hours the maximum of 98.5 per cent is attained. While these figures are approximately correct for a considerable range of initial moistures, there is some dependence on initial water content. This conclusion is brought out in Figure 1, and is supported by other experiments—for example, Douglas fir and oak, which had been partially dried to contain 5 to 10 per cent moisture, approached the recovery figures of cypress with 8 per cent initial moisture. The remaining 1.5 to 3.5 per cent moisture required about 18 hours for complete extraction.

Acknowledgments

The author is grateful to W. M. D. Bryant and Donald Milton Smith for their advice and interest in this investigation and to C. D. Bell for his preparation of wood samples.

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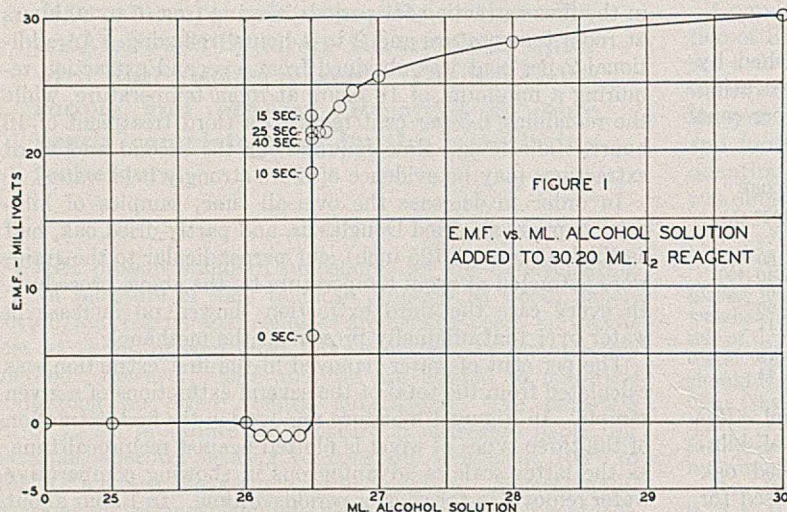
Fischer Volumetric Determination of Water

Application to Technical Substances

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IN 1935 Fischer (1) proposed a volumetric method for determining water which he applied successfully to the analysis of liquid sulfur dioxide, to a number of organic liquids including hydrocarbons, alcohols, and acetone, and to solids such as bleaching earth and hydrated salts. The method consisted of titrating the unknown with a methanol solution of iodine, sulfur dioxide, and pyridine to the appearance of the brown color of free iodine. Iodine is consumed as long as any water is present in the solution. Fischer pointed out that the colorimetric end point could not be detected in the presence of dark-colored substances and suggested that an electrometric method might be developed for determining the completion of the titration.



Kaufman and Funk (2) and Richter (3) have applied the method to the analysis of oils, fats, and such foodstuffs as flour, margarine, cocoa powder, marmalade, and malt extract. Kaufman and Funk also commented on the difficulty of determining the end point, especially in colored solutions.

In order to apply this titrimetric method for water to dark-colored solutions, the development of a potentiometric detection of the end point was undertaken. It was found, in the course of the work, that such a method gave a more sharply defined end point than the color change described by Fischer and the potentiometric detection has been used in routine analyses of a number of compositions of industrial importance.

It was easily demonstrable that there was a small but definite change in potential difference across a platinum-tungsten electrode pair immersed in Fischer's iodine reagent solution when it was decolorized by the addition of water dissolved in methanol, the tungsten becoming more positive with regard to the platinum. Preliminary experimental titrations showed that this change occurred more sharply and reproducibly with dropwise addition of solution if the titration was carried in the direction of adding water (dissolved in methanol) to the iodine reagent rather than in the direction described by the original authors—namely, the addition of iodine reagent to the moist sample.

Figure 1 shows a curve plotting the potential differences between platinum and tungsten electrodes immersed in iodine reagent, as methanol containing 6.09 mg. of water per ml. of solution was added in increments of 0.1 ml. to 30.20 ml. of iodine reagent. The potential differences were measured by attaching the electrode leads directly to the input terminals of a Beckman pH meter, laboratory model, and observing the apparent pH. The readings were then converted to millivolts from standard glass electrode tables. Obviously the end point lay between 26.40 and 26.50 ml. The reaction is not instantaneous but from 10 to 15 seconds are required for the full potential to develop. However, the change begins immediately, and, with a proper instrument, a definite indication that it is occurring manifests itself within the first second, during which time fully half the change in potential difference will have developed.

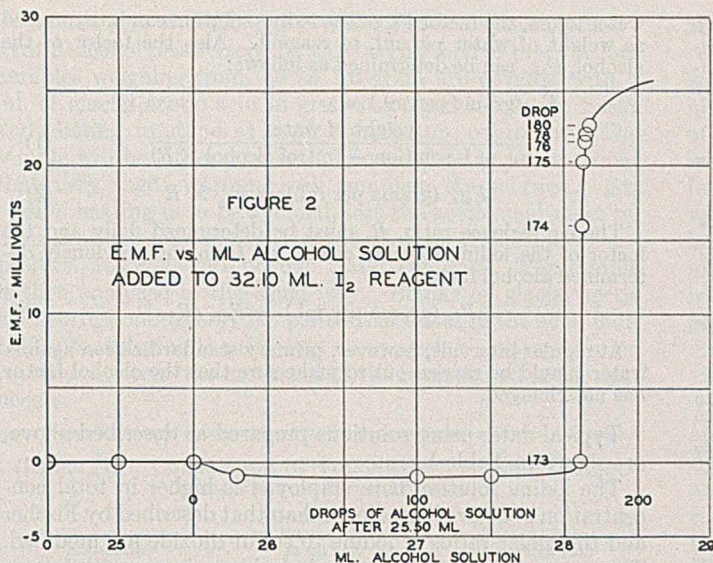
A second titration, using the same solution, was carried out in which the end point was approached by dropwise addition (1 drop per second) of the standard alcohol containing 6.09 mg. of water per ml. of solution to 32.10 ml. of iodine reagent. The break point is thus defined to within 0.05 ml. (Figure 2) and the equivalence factor of this iodine solution may be calculated as 5.34 ± 0.05 mg. of water per ml. of solution. If drops are added very rapidly (more than 5 per second) the end point will be overrun by as much as 0.1 ml. because of the slight time lag noted above. At 1 drop per second the overrun will not be greater than 1 drop, which is not over 0.015 ml. from an average buret tip. This may be neglected in routine work where quantities of water in excess of 100 mg. are being titrated.

Having established that a measurable change in potential difference of an electrode pair in the titrating solution occurs at approximately the maximum color change point, the problem resolved itself into choice of a suitable device for detecting this change and the development of proper conditions of reaction as regards solution strength, preparation of sample, exclusion of atmospheric moisture, etc.

Detection of End Point

The results presented above indicate that the instrument used to detect the potentiometric end point of the water titration must be very sensitive and give a positive reaction for a change of only a few millivolts, since the entire change is only 20 mv. and the time lag makes it imperative that the first part of this change be picked up by the detector. It was further demonstrated that current must not be drawn from the electrodes lest they polarize badly. A vacuum-tube millivoltmeter is thus strongly indicated. It need not record extents of voltage changes so long as it records the incidence of such changes. A number of suitable instruments are available commercially, only one of which will be mentioned here.

The laboratory model Beckman pH meter, used as an indicating instrument, has been found to meet the above requirements. It is used by attaching the electrode leads directly to the input ter-



minals and adjusting the meter so that the needle is at the mid-point of its scale when the electrodes are in the iodine solution before titration is started. Agitation is set up in the flask and alcohol containing a small amount of water is run in rapidly until the color changes from brown to orange. The key to the meter is then fastened down and the addition of alcohol is continued drop by drop.

When within about 1 ml. of the end point the needle will show a very slight deflection to one side, then it will swing deliberately across the mid-point and off the scale. The titrating solution is cut off when this second deflection has just started and if the end point is true the needle will continue across the scale. If the deflection is due to a temporary local concentration of the titrating alcohol at the electrodes, it will return to its original deflection and more drops of solution must be added from the titrating buret. This method of detecting the end point has been used satisfactorily for many determinations over a period of 2 years.

Doubtless other forms of vacuum-tube millivoltmeters are available commercially, which will serve equally well with the pH meter just described. The necessity of high sensitivity and circuit stability must, however, be vigorously emphasized. The sensitivity should be at least half scale deflection for an applied 20 mv., without drawing measurable current from the cell and under these conditions there must be no fluctuations as from variable power input, etc.

Titration Assembly

The titration assembly is schematically illustrated in Figure 3.

A is a Bakelite rod turned to the shape and size of a No. 6 rubber stopper with a cylindrical extension for a clamp.

The electrodes, *Pt* and *W*, pass through 0.3-cm. (0.125-inch) holes, and the glass stirrer, *S*, through a hole which is only slightly larger than the rod. The buret tip, *T*, passes through a slotted hole, permitting a bend in the tube to place the buret proper at one side of the set up. The buret tip must be long enough to pass completely through the stopper and dispense solution without wetting the Bakelite. Rubber and cork were both found to be unsuited for the stopper of this assembly because they absorbed vapors of the iodine reagent and became hygroscopic.

The buret of the assembly has a three-way stopcock for connection to a reservoir of standard solution of water in methanol. The reservoir in turn is protected with a tube of anhydrous calcium sulfate.

The stirrer is driven by a suitable variable-speed motor.

Copper leads to the pH meter (or other indicating vacuum-tube meter) are soldered to the electrodes, the joint with tungsten being made by immersing the wire in a cup of molten solder.

The assembly is completed by a platform at the proper height to bring the titrating flask, *F*, into position with its neck around the clamped Bakelite stopper. For convenience this platform is so mounted that it can be swung to one side.

After assembly of the electrode system, the tungsten wire must be cleaned and sensitized by dipping the ends of the electrode for 5 to 10 seconds in fused sodium nitrite in a porcelain crucible (5). The treatment must be carried out slightly above the melting point of the salt, lest the reaction with the tungsten be so vigorous that the wire is heated to incandescence and dissolves rapidly. The bath should be hot enough to cause a stream of minute bubbles to rise from the surface of the tungsten. The adhering sodium nitrite is removed by washing with a fine stream of water from a wash bottle, and the wire is dried by rinsing with acetone or methanol. Whenever the wire becomes tarnished, the process may be repeated.

Apparatus and Materials

Besides the titration assembly and end-point detector, the required apparatus includes a reservoir and buret dispensing system for the iodine reagent, titrating flasks, and a weighing pipet. The reservoir and buret system for storing and dispensing the iodine reagent must be of all-glass construction and protected from the atmosphere by a tube of Drierite or other good desiccant. The Schilling automatic buret marketed by the Ace Glass Co. (Catalog No. 3325) with Style C reservoir has been found very satisfactory. For many titrations ordinary 150-ml. extraction flasks are suitable. If in the preparation of the sample for analysis it must stand in the titrating flask for some time, special 150-ml. extraction flasks fitted with 29/42 ground-glass stoppers are convenient and fit the titration assembly stopper. The weighing pipet, used in primary standardization of the solutions, may be of either the Lunge or the Smith type.

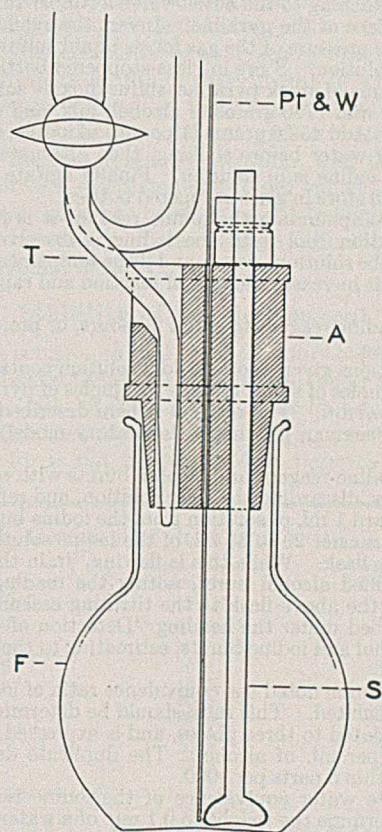


FIGURE 3. TITRATION ASSEMBLY

The materials necessary for the preparation of the solutions are listed below. Indicated sources have been found to be satisfactory. Unless specifically stated to the contrary, it is not to be inferred that other suppliers do not furnish materials of equal quality. Those listed were used without further purification.

Iodine, c. p., resublimed, Baker's analyzed or Eimer and Amend T. P.

Sulfur dioxide, liquid anhydrous, Matheson and Co.

Methanol, synthetic, E. I. du Pont de Nemours & Co., Inc.

Pyridine, No. 2-A refined, Barrett Company. c. p. pyridine supplied by two chemical supply houses and Barrett's 10-A pyridine were found definitely inferior to the 2-A pyridine recommended. The inferiority was manifested by a decreased stability of the reagent.

TABLE I. TYPICAL STANDARDIZATION DATA

Water Taken Gram	Iodine Reagent Ml.	Alcohol Solution Ml.	Water Equivalence Factors	
			Ml. I ₂ Ml. Alcohol R	Alcohol soln. Gram/ml.
..	27.70	32.42	0.854	..
..	24.10	28.32	0.851	..
..	24.47	28.82	0.849	..
..	24.45	28.80	0.849	..
			Av. 0.850	
0.2017	40.29	2.47	..	0.00529
0.2247	43.60	1.30	..	0.00529

Preparation and Standardization of Solution

ALCOHOL TITRATING SOLUTION. Mix approximately 10 grams of water with 2 liters of anhydrous methanol. Transfer to the reservoir supplying the buret of the titrating assembly and protect with a tube of Drierite or other desiccant. Its exact factor, which should be approximately 5 mg. of water per ml. of solution, will be determined as described below.

IODINE REAGENT. Prepare a stock solution of sulfur dioxide in pyridine as follows: Weigh into a flask 3.785 liters (1 gallon) of 2-A pyridine and add 203 grams of liquid sulfur dioxide for each kilogram of pyridine. Add the sulfur dioxide directly from the cylinder by attaching to the outlet valve a rubber tube extending under the surface of the pyridine. Invert the cylinder and open the valve; the pressure of the gas forces liquid sulfur dioxide into the pyridine solution. Store in glass-stoppered bottles.

To 1359 grams of stock pyridine-sulfur dioxide solution in a 5-liter container add 1786 grams of alcohol, mix, and cool to room temperature. Add 453.6 grams (1 pound) of iodine, stopper, cool under running water before shaking, then alternately swirl and cool until the iodine is in solution. Finally agitate the solution thoroughly and store in glass-stoppered bottles.

Note. In compounding the iodine reagent it is important to keep the solution cool until the iodine is dissolved. Heat is generated by the solution process and if the temperature is allowed to start rising it increases the rate of reaction and rapidly gets out of control.

Allow the iodine reagent to stand 24 hours, or preferably 2 or 3 days, before use.

The proportions given above yield a solution containing 1 mole of iodine to 2 moles of sulfur dioxide to 8 moles of pyridine.

STANDARDIZATION. The method is here described in terms of the use of a Beckman pH meter (laboratory model) as the end-point detector.

Rinse the iodine reagent and alcohol burets with solution from their reservoirs, discarding the rinse solution, and refill the iodine burets. Discard 1 ml. of solution from the iodine buret, note the reading, and transfer 20 to 35 ml. of the iodine solution to a 150-ml. extraction flask. While this is flowing, drain the tip of the previously refilled alcohol buret, noting the reading. Immediately transfer the above flask to the titrating assembly and proceed as described under the heading "Detection of End Point". Read the alcohol and iodine burets, estimating to the nearest 0.01 ml.

From the volume noted the equivalence ratio of iodine to alcohol can be calculated. This ratio should be determined in duplicate and calculated to three places, and is expressed as *R*. *R* = ml. of iodine per ml. of alcohol. The duplicate determination must agree within 5 parts per 1000.

The absolute water equivalence of the iodine is obtained as follows: Determine the weight to 0.1 mg. of a water-filled Smith weighing pipet. While iodine reagent is flowing into a titrating flask transfer 2 or 3 drops of water from the pipet to the flask. Restopper the pipet for later weighing. Take care that the ground-glass connections of the weighing pipet are dry; otherwise loss will occur due to evaporation. Swirl the flask and continue the addition of the iodine solution until an excess has been introduced, as indicated by a change from yellow to a dark brown color. Transfer the flask to the titrating assembly, depress the meter button with a weight, and back-titrate with aqueous alcohol as before.

From the previously calculated equivalence ratio, *R*, it is possible to calculate the excess of iodine used. From the total volume of iodine solution, the excess volume, and the weight of

water taken, the factor F_{I_2} of the iodine solution can be expressed as weight of water per ml. of reagent. Also the factor of the alcohol, $F_{alc.}$ can be determined as follows:

$$F_{I_2} \text{ (grams per ml.)} = \frac{\text{weight of water}}{\text{ml. of I}_2 \text{ solution} - (\text{ml. of alcohol} \times R)} \quad (1)$$

$$F_{alc.} \text{ (grams per ml.)} = F_{I_2} \times R \quad (2)$$

The equivalence ratio, *R*, must be determined daily and the factor of the iodine solution calculated from the previously determined alcohol factor

$$F_{I_2} \text{ (grams per ml.)} = F_{alc.}/R$$

At regular intervals, however, primary standardization against water should be carried out to make sure that the alcohol factor has not changed.

Typical data, using solutions prepared as described above, are shown in Table I.

The iodine solution here employed is higher in total concentration of active ingredients than that described by Fischer and the molar ratios of iodine to sulfur dioxide are modified. The greater concentration was desirable to increase the water equivalence of the solution and it was found unnecessary to have the great excesses of sulfur dioxide and pyridine shown in the original work.

Analysis of Samples

Transfer a sample prepared for analysis (see following section) to a titrating flask, choosing the sample size to contain between 0.05 and 0.2 gram of water. If the material is high in water content the sample should be transferred from a weighing pipet while the iodine solution is running into the flask. Add iodine reagent, with occasional swirling, until an excess has been added and back-titrate as described above under primary standardization with water. Calculation of the water content is made from the following equation:

$$\% \text{ of H}_2\text{O} = \frac{(\text{ml. of I}_2 - \text{ml. of alcohol} \times R) \times F_{I_2} \times 100}{\text{weight of sample}}$$

Data covering typical analyses (in duplicate) of solutions of high and low water content, which needed no preparation for analysis beyond transfer to the titrating flask, are shown in Table II. The titrating solutions are those whose standardization was described in the preceding section.

TABLE II. TYPICAL ANALYTICAL DATA ON WATER TITRATION

Sample Weight Gram	I ₂ Reagent Ml.	Alcohol Solution Ml.	R	F _{I₂}	H ₂ O %
0.2967	33.55	1.50	0.850	0.00529	57.6
0.2825	32.81	2.41	0.850	0.00529	57.6
0.5585	19.43	2.30	0.850	0.00529	16.5
0.6350	20.58	1.05	0.850	0.00529	16.4

Preparation of Sample

The titration method for water is applicable to a great many materials without special preparation of sample. The pyridine-methanol mixture of the iodine reagent is a good solvent for most organic liquids and many solids. Slight warming of sirupy materials in the reagent before titrating may hasten their dispersion, provided the material is inert to the ingredients of the mixture. Boiling of the solution should be avoided.

The moisture from insoluble powders may often be extracted by adding an excess of the iodine reagent, transferring to the titrating assembly, and agitating vigorously before back-titrating.

Other materials may be first dissolved or suspended in a measured volume of anhydrous solvent and titrated. Blanks on the solvent must, of course, be run. Of particular interest

is the analysis of flexible glue compositions containing polyhydric alcohol plasticizers, by this last method of preparation. Samples weighing from 0.5 to 1.0 gram are covered with 5 ml. of glacial acetic acid in glass-stoppered extraction flasks and allowed to stand at room temperature overnight. The sample will be either completely liquefied or so nearly liquid that very slight warming will complete the solution. Excessive heating is to be avoided, lest the acetic acid react by esterification with the polyhydric alcohol of the glue composition and give falsely high water contents. The sample is then analyzed in the usual way. Blanks on glacial acetic acid correspond to only 0.3 per cent of water in the acid, indicating that during the titration no appreciable water-forming reaction between the methanol of the reagent and acetic acid occurs.

that will combine with the acids formed in the titration reaction to yield salt and water interfere. In certain cases, when the inorganic hydroxide is known, a correction may be applied for its water of neutralization and the water content of the sample calculated. In theory, acids which may react with the methanol of the reagent to form water should interfere. However, glacial acetic acid appears to be titratable without giving high results. On the other hand, borates and boric acid give very high results, apparently through the formation of methyl borate and the splitting off of water which is titrated. The effect of other acids has not been investigated.

Accuracy of the Method

In Table III are shown typical duplicate and triplicate analyses of a number of sorbitol sirups and process solutions. Agreement between the results by the volumetric method and vacuum oven-drying is essentially good and the precision, as measured by agreement between duplicate analyses, is higher by the volumetric method than by oven-drying.

Table IV shows the analysis of a number of glue compositions, whose water contents, calculated from the water contents of the components and the evaporation loss during cooking, are as indicated in the second column. The glue used in preparing these mixtures was analyzed by oven-drying at 110° C., the official method of the National Glue Manufacturers Association, and by titration, with the comparative results indicated. This table again shows a high degree of precision and good agreement between the water found by titration and that calculated or analyzed by other methods.

Table V presents results of experiments in which weighed amounts of water were added to analyzed lots of Arlex D and E (see Table III) and the total amounts of water calculated. These were then analyzed by titration, and the difference was noted between calculated and found values.

The greatest difference between calculated and found is 0.5 per cent of the value and the average difference for the six is only 0.2 per cent of the value.

Stability of Iodine Reagent

The iodine solution should stand 24 hours before use and be standardized daily thereafter because the factor of the freshly made solution falls off sharply during the first day, then more slowly but continuously for weeks. The cause of this decrease in factor is not known. Most rigorous exclusion of

TABLE III. COMPARISON OF VOLUMETRIC WATER ANALYSIS WITH VACUUM OVEN-DRYING

Substance	Water Content by Vacuum Oven at 65° C.	Water Content by Titration
	%	%
Arlex		
Lot A	16.6, 16.2, 16.1	16.0, 16.0
Lot B	16.4, 16.3, 16.8	16.0, 16.0, 15.9
Lot C	16.1, 16.5	16.2, 16.2, 16.3
Lot D	6.0, 5.8	5.7, 5.8
Lot E	15.4, 15.9	16.0, 16.0
Lot F	15.8, 16.2	16.3, 16.3, 16.3
Lot G	16.0, 15.5, 15.7	15.7, 15.8
Lot H	15.7, 15.9	15.6, 15.5
Sorbitol sirup		
Lot 36	19.8, 19.9	19.8, 19.8
Lot 46	21.3, 21.4	20.6, 20.7
Lot 59	20.7, 20.7, 19.9	19.7, 19.7, 19.5
Process solution		
A32-9	56.8, 57.2	57.3, 57.1
A32-10	55.0, 54.7	54.7, 54.9
1322	54.4, 54.2	54.6, 54.6
1323	59.4, 59.7	59.4, 59.5
1324	70.3, 70.3	70.3, 70.3
1325	55.9, 56.1	55.4, 55.2
1318	57.0, 57.3	58.0, 58.1
1319	54.6, 54.3	54.3, 54.4
1320-A	56.7, 56.9	56.9, 56.9

Applicability and Interfering Substances

The volumetric method described herein has been successfully applied to a great number of products with no interference due to other volatile ingredients, solvents miscible with water, dark-colored substances, turbidity, or even complete insolubility in the reagent. It has been used to analyze solutions containing monohydric and polyhydric alcohols of all degrees of volatility, ranging from methanol through the glycols and glycerol to sorbitol and mannitol. Determinations have been made successfully on mixtures ranging from thick sirups of only a few tenths per cent water content to water-thin process solutions containing 70 per cent of water. Flexible glue compositions containing polyhydric alcohol plasticizers, for which no satisfactory water determination was previously available, have been successfully analyzed. The determination of water in oils, fats, and waxes, by titration, has been previously described (2, 3), and the utility of the method for these substances confirmed in this laboratory.

The determination is rapid, requiring for substances easily dispersible in the reagent not over 5 minutes for completion. This fact permits the control of water content in process solutions by direct analysis with almost no time lag. Results of the analysis are available when wanted instead of 24 to 48 hours later as by the oven method.

Substances which react rapidly with free iodine, such as highly unsaturated compounds, cannot be analyzed by the volumetric method under discussion. If the reaction with iodine is slow, however, good approximation of their water content can be obtained by titrating rapidly. This fact has also been pointed out by Richter (3). Inorganic hydroxides

TABLE IV. ANALYSIS OF GLUE AND GLUE COMPOSITIONS

Designation	Water Content Calculated, %	Water Content by Titration, %
Air-dried glue	16.50, 16.60 ^a	16.50
Glue composition		
RW-40-b	39.8	39.8, 40.2
RW-40-a	43.3	42.6, 42.6
13-0	30.5	30.0, 30.0
13-1	30.5	30.2, 30.2
13-2	30.5	30.0, 30.1
13-4	30.5	30.2, 30.0
13-6	30.5	30.2, 30.4

^a By oven-drying at 110° C.

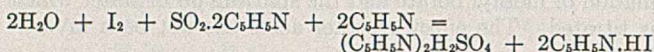
TABLE V. RECOVERY OF ADDED WATER

Weight of Sirup Grams	Water in Sirup Gram	Water Added Gram	Total Calcd. Water Gram	Water Found Gram	Difference Gram
Lot D Arlex (5.8% H ₂ O)					
1.6218	0.0941	0.0780	0.1721	0.1718	+0.0003
1.0670	0.0609	0.1589	0.2198	0.2210	-0.0012
1.7080	0.0990	0.2440	0.3430	0.3430	0.0000
Lot E Arlex (16.0% H ₂ O)					
0.538	0.0861	0.1073	0.1934	0.1940	-0.0006
0.568	0.0910	0.0784	0.1694	0.1694	0.0000
0.565	0.0905	0.2291	0.3196	0.3184	+0.0012

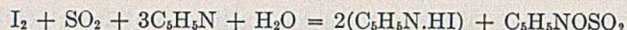
atmospheric moisture does not prevent it. Apparently, a very slow iodine-consuming reaction occurs within the solution. That it may be due, in part at least, to impurities in the pyridine is indicated by the fact that the rate of degradation varied with the source of the pyridine used.

Stoichiometry of Reaction

In the original paper describing this method Fischer (1) suggested the following equation to describe the reaction:



In the course of the present work it became obvious that this equation did not correctly express the titration because the water equivalence of the authors' reagent was never greater than 35 per cent of that called for by the above reaction. This failure to follow the stoichiometry of the postulated reaction did not interfere with its use, since the solution was easily standardized empirically. Since the completion of the experimental work described herein, Smith, Bryant, and Mitchell (4) have reported on a study of the fundamental reaction involved in titrations with the Fischer reagent. They find that the reaction is stepwise, that the only reaction involving water as a reactant is the following:



and that instead of pyridinium sulfate a methyl ester is formed according to the following reaction:



The theoretical consumption of iodine in the reagent is, accordingly, only 50 per cent of that proposed by Fischer. Smith and his co-workers found, moreover, that this factor was never reached in practice because of side reactions, and that freshly prepared reagent is usually equivalent to 70 per cent of the theoretical water, which would correspond to 35 per cent of theory on Fischer's proposed equation. This result is in harmony with that obtained in the present work.

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Effect of Ferric Sulfate in Shortening Kjeldahl Digestion

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IN 1868 Wanklyn (32) proposed the wet combustion of organic matter by the use of potassium permanganate as the oxidizing agent. Ten years later, Wanklyn and Cooper (33) attempted to extend this method to provide for the estimation of protein material by potassium permanganate in an alkaline solution. Kjeldahl (14) in 1883 introduced a method based on the decomposition of the nitrogenous materials without the production of volatile compounds by sulfuric acid, and completion of the oxidation by permanganate when the mixture was removed from the flame. This method, with two major modifications, is in common use today. The Gunning modification (10) provides for the addition of potassium sulfate or sodium sulfate to give a digestion mixture more favorable to the loss of water than of sulfur trioxide, and to raise the boiling point of the digestion mixture; the other modification uses mercury or copper as a catalyst.

Many attempts have been made to shorten the digestion time, and many substances have been used. These attempts have followed two main paths—(1) to raise the boiling point of the digestion mixture; and (2) to employ some substance more active than mercury as the metallic catalyst.

Harrel and Lanning (11) reviewed the use of varying amounts of sodium sulfate, with either mercury or copper as the catalyst, finding that between 14 and 20 grams of sulfate with mercury give a somewhat shorter digestion time and more accurate results than smaller amounts of sulfate and copper. Hydrogen peroxide methods have been used with varying success. Potassium dichromate has been tried, but Shewan (27) found that results are low, especially where two nitrogen groups are attached to a central carbon atom as in urea, caffeine, or creatine. Vanadium has been used. Parri (25) stated that vanadium pentoxide and cupric oxide give better results than either alone.

Perchloric acid has been suggested as a Kjeldahl reagent. Mears and Hussey (18) and Bimmerman and Frank (2) were

among the first to use it. Gauduchon-Truchot (7) published a review of perchloric acid methods and outlined a procedure that gives excellent results; it involves the dropwise addition of perchloric acid to the partially digested mixture until clearing takes place. Le Tourneur-Hugon and Chambionnat (17) presented a similar procedure. The usefulness of the method for general laboratory analyses is impaired by the extra step.

Much work has been done on the use of selenium and tellurium as catalysts, especially the former. The mechanism of the reactions involved was outlined by Illarionov and Soloveva (12) and by Sreenivasan and Sadasivan (29). The initial work of Lauro (15, 16) has been confirmed by Messman (19) and others (1, 4, 9, 20, 22, 23, 24, 26, 30, 34, 35). Experimenters do not agree on the correct proportion of selenium to use, and digestion methods and time (15 to 100 minutes) vary widely. In spite of the reported results, considerable doubt still exists in regard to the efficiency of selenium in reducing all the nitrogen present (except nitrates) to ammonia.

Davis and Wise (5) after a survey of the cereal laboratories of the country concluded that selenium is not universally adapted to general laboratory conditions. Nine of the ten collaborators obtained low results using selenium as the catalyst. Snider and Coleman (28) concurred and cited the disadvantages of bumping and frothing, unless special precautions are taken, the probability of low results, and the physical discomforts of the noxious fumes, suggestive of hydrogen selenide, which cause headache and a form of catarrh. Jany and Morvaj (13) stated that a shorter digestion period is permitted by use of copper and selenium together as the catalyst, but agreed that lower results are obtained than with mercury.

Gerritz and St. John (8) succeeded in shortening the digestion time by the use of dipotassium phosphate in various combinations with sodium sulfate and potassium persulfate. The present paper reports the results of a comparison of the four procedures proposed by Gerritz and St. John, together with further modifications studied by the authors, one of which is found to be suitable for routine laboratory procedure.

TABLE I. COMPARISON OF PROCEDURES OF GERRITZ AND ST. JOHN AND OFFICIAL METHOD

(25 ml. of H₂SO₄ and 0.6 gram of Hg in each determination)

Method	Catalysts				Time of Clearing Min.	Time of Digestion Min.	No. of Replicates	Total N in Sample P7192 %	Probable Error		Recovery Compared to Official %
	Na ₂ SO ₄ Grams	K ₂ HPO ₄ Grams	KOH + P ₂ O ₅ Grams	K ₂ S ₂ O ₈ Gram					Of single detrn. %	Of mean %	
Official Kjeldahl-Gunning-Arnold	10	0	0	0	40	150	12	2.62	0.004	0.001	100
Gerritz and St. John Method A	0	10	0	0	20	40	8	2.56	0.005	0.002	97.71
Method B	0	10	0	1	20	25	8	2.52	0.005	0.002	96.18
Method C	6	10	0	1	20	30	8	2.57	0.005	0.002	98.09
Method D	6	0	8 ^a	1	20	25	8	2.54	0.004	0.001	96.95

^a Four grams of each added separately.

TABLE II. COMPARISON OF EXPERIMENTAL PROCEDURES

(25 ml. of H₂SO₄ and 0.6 gram of Hg in each determination)

Method	Catalysts				Time of Clearing Min.	Time of Digestion Min.	No. of Replicates	Total N in Sample P7192 %	Probable Error		Recovery Compared to Official %
	Na ₂ SO ₄ Grams	K ₂ HPO ₄ Grams	Fe ₂ (SO ₄) ₃ Grams	MgSO ₄ Grams					Of single detrn. %	Of mean %	
Official Kjeldahl-Gunning-Arnold	10	0	0	0	40	150	12	2.62	0.004	0.001	100.0
Method I	6	10	0	0	20	25	8	2.50	0.003	0.001	95.42
Method II	6	10	0	0	20	40	8	2.56	0.004	0.001	97.7
Method III	0	0	0	10	8
Method IV	0	10	0	5	20	40	8	2.58	0.004	0.001	98.47
Method V	0	6	10	0	18	40	8	2.59	0.006	0.002	98.85
Method VI	0	10	6	0	15	40	8	2.63	0.004	0.001	100.4
Method VII ^a	0	10	6	0	15	30	8	2.62	0.003	0.001	100.0

^a Adopted.

Experimental

The experimental work consisted (1) of a comparison of the four procedures proposed by Gerritz and St. John, and (2) of a comparative study of seven modifications of the present authors.

The equipment used was a gas digestion rack of ten-flask capacity. In each run, eight replicates and two blanks were included. Mercury was used as the metallic catalyst in all cases except those in which mercury and copper were compared. A standard ammonium chloride solution in which 20 ml. equaled 0.0400 gram of nitrogen was first analyzed. The average of sixteen closely agreeing determinations by the official Kjeldahl-Gunning-Arnold method on 20-ml. samples of this solution was 0.0400 gram recovered.

The detailed comparison of methods was carried out on a sample of alfalfa, Laboratory No. P7192. The mean of twelve determinations by the official method on 2-gram portions of this sample was 2.62 ± 0.001 per cent, the probable error being computed by Bessel's formula. Table I gives the authors' comparisons of Gerritz and St. John's procedures.

All short methods were given the full heat of the burners from the start of the digestion. Clearing, except in the official method, occurred in approximately 20 minutes. In Method B, the potassium persulfate was added on clearing of the solution, the solution was brought to a boil again, and the flasks were removed. In Method C, the solution was boiled for 5 minutes after the addition of potassium persulfate on clearing. When this initial reaction subsided, the flasks were placed on the rack. Upon clearing, potassium persulfate was added, and the solution was again brought to boiling before removal from the flame. The digestion times used were the ones recommended by Gerritz and St. John.

Considerable heat was liberated by the reaction of sulfuric acid and dipotassium phosphate, causing a slight predigestion before the flask was placed on the flame. In the digestion, froth filled approximately half the flask; there was some spattering, but none into the neck of the flask. The spattering was not objectionable, as the residue left on the flask walls was either washed down quickly by the condensing acid fumes, or could be removed by twirling. On cooling the flask after digestion, a cake formed quickly. In all cases where phosphate was used this cake was easily soluble, in marked contrast to that where no phosphate was present. The beneficial effect of phosphate in the subsequent distillation was evident also, bumping being eliminated entirely. For these reasons, the retention of phosphate in further research on shortening the digestion time was deemed advisable, although the results obtained by the Gerritz and St. John procedures unmodified were too low to warrant their adoption.

Table II presents the data on the experimental procedures formulated by the present writers, including the one adopted. Method I was included in order to establish the effect of potassium persulfate in the digestion, using a combination of dipotassium phosphate and sodium sulfate (Table I, Method C). The actual digestion time, 25 minutes, was the same as in Method C, since in the latter about 5 minutes are required for removing the flasks, adding the persulfate, and replacing on the digestion rack. As results were low, Method II (40 minutes) was run. Since in 30 minutes Method C gave a slightly higher recovery using potassium persulfate than did Method II in 40 minutes, it is believed that potassium persulfate has some value in the determination, but not sufficient to compensate for the time required for the extra step involved. The combination of dipotassium phosphate and sodium sulfate in a 40-minute digestion gives the same recovery as 10 grams of anhydrous phosphate alone in Method A, using the same digestion time.

The use of magnesium sulfate, Method III, was attempted, but the mixture caked on the flame. Method IV gave a vigorous digestion, with much spattering, none going into the flask neck. The results were higher than any obtained to that time, but still low. Because of inability to increase the quantity of either reagent without danger of caking on the flame, no further research was done on this combination of catalysts.

Gerritz and St. John report a rerun of Methods C and D in which a combination of mercuric oxide, cupric oxide, and ferric sulfate was used as the catalyst. Results for this method, in which a small amount of ferric sulfate was used, were essentially the same as without it, and its use was not recommended. The idea of using the ferric ion as a catalyst is not new. Folin and Wright (6) in 1919 used 2 ml. of a 10 per cent solution of ferric chloride in combination with mercury and copper in an attempt to speed up the digestion, with slightly low results. It is believed that the ferric ion in small amounts is useless as a catalyst, since ferric sulfate, insoluble in hot concentrated sulfuric acid, forms at once.

A study of the literature led to the conclusion that methods based solely on raising the boiling point of the mixture, or on the use of catalysts such as selenium to take an active part

TABLE III. TOTAL NITROGEN BY OFFICIAL KJELDAHL-GUNNING-ARNOLD AND DIPOTASSIUM PHOSPHATE-FERRIC SULFATE METHODS

(25 ml. of H₂SO₄ and 0.6 gram of Hg used in all determinations)

Substance	Official	10 grams K ₂ HPO ₄ , 6 grams Fe ₂ (SO ₄) ₃
	%	%
Dried milk	5.56	5.56
Sugar	0.04	0.04
Milk + 1 gram sugar	5.61	5.61
Corn	2.99	2.99
Brome grass	2.96	2.96
Wheat	2.69	2.69
Wheat	2.75	2.75
Tailings	3.53	3.54
Tailings	3.23	3.24
Soybeans	6.12	6.12
Soybeans	5.98	5.99
Oats	1.83	1.84
Oats	2.05	2.05
Oat straw	0.49	0.49
Soil S4515	0.135	0.135
Soil S6757	0.148	0.149
Soil 1-188	0.255	0.256
Soil 1-190	0.093	0.093
Corn P7194	1.42	1.43
Alfalfa P7192	2.62	2.62
Alfalfa P7193	2.58	2.58
Corn P4190	1.78	1.78
Corn P4191	1.38	1.39
Tyrosine	7.73	7.73
Tankage	9.55	9.54
Milorganite	6.14	6.14
Agrinite	8.59	8.60
Orchard grass	3.44	3.44
Soybean leaves	2.42	2.42
Soybean leaves	2.64	2.63
Soybean stems	0.65	0.66
Soybean roots	1.39	1.39

in the digestion, could not be expected to give maximum efficiency.

Electric Kjeldahl heaters, giving an intense heat over a wide surface of the flask, greatly shorten the digestion time using the official method. Since the boiling point of the mixture is constant regardless of the heat applied, the explanation lies in the greater number of bubbles formed, chiefly sulfur dioxide and sulfur trioxide (3, 10, 21, 31), and in the greater contact of the organic matter with the gas (Table IV).

A successful attempt was made to give the advantages of the electric heater to the regular Bunsen burner digestion. An amorphous substance, insoluble in hot, concentrated sulfuric acid—one that plays no part in the reactions and will not form a cake—is needed. Such a substance will provide particles around which a film of the decomposing sample may form, and thus expose a greater surface to the action of sulfur trioxide; and it will also provide nuclei to facilitate the formation of bubbles. Ferric sulfate meets these requirements and is inexpensive.

In the first use of ferric sulfate (Method V), dipotassium phosphate was retained because of merits mentioned above. The digestion was vigorous. After the first few minutes the mixture became a paste and the color gradually changed to a light yellow, the time required being 18 minutes. After 40 minutes' digestion, the nitrogen recovery was low. This result is in accord with the conclusion of Harrel and Lanning (11) that low results are often due to insufficient sodium or potassium ion. Since a thinner paste and additional dipotassium phosphate were needed, the proportions were reversed in Method VI. Lightening to a bright yellow paste occurred in 15 minutes, and the recovery of nitrogen agreed with that obtained by the official method. It was then found (Method VII) that a 30-minute digestion is sufficient.

Substitution of sodium sulfate for dipotassium phosphate gave low results. Disodium phosphate was substituted for the potassium salt with no sacrifice in accuracy, but with disodium phosphate the digestion mixture did not lighten as rapidly and the cake formed was less easily disintegrated on dilution.

Table III presents the results of comparative analyses of a wide variety of materials by the official Kjeldahl-Gunning-Arnold method and the dipotassium phosphate-ferric sulfate method. Analyses were made in duplicate. (In the preceding experiments, all catalysts were weighed to the nearest milligram. In the analyses reported in Tables III, IV, and V, approximate weights were used.)

Comparison of Gas and Electric Heaters

The results of a comparison of gas and electric heaters are given in Table IV. A 60-minute period with electric heaters in the official determination gave complete digestion of the samples; and with the proposed method, using either gas or electric heat, a 30-minute period was sufficient. With forced draft digesters, it was necessary to reduce the draft in order to permit condensation of acid fumes in the flask necks. (Electric heaters were made available through the courtesy of the Regional Soybean Laboratory, U. S. Department of Agriculture.)

Comparison of Mercury and Copper as Catalysts

It was desired to test the effectiveness of copper as compared to mercury in both the official and proposed methods. Table V gives the results of analyses, all in duplicate, of ten samples of varying nitrogen content and character.

In the official method, no significant differences are observed with samples containing less than 86 mg. of nitrogen, with the exception of milk. In the new method, copper gave consistently low results, the error increasing with increasing amounts of nitrogen in the sample, rather than with increasing percentages. It is evident that copper is merely a slower catalyst than mercury. In the long digestion period of the official method, the time is sufficient for the effective action of copper with all samples except those containing the largest amounts of nitrogen.

TABLE IV. COMPARISON OF GAS AND ELECTRIC HEATERS, MERCURY CATALYST

Substance	Sample Weight Grams	N by Official Method		N by Proposed Method	
		Electric, 60 min.	Gas, 150 min.	Electric, 30 min.	Gas, 30 min.
		%	%	%	%
Orchard grass	1	3.43	3.44	3.44	3.44
Soybeans	1	6.12	6.12	6.12	6.12
Tankage	1	9.54	9.55	9.54	9.54
Soil 1-188	10	0.256	0.255	0.256	0.256
Soil 1-190	10	0.093	0.093	0.094	0.093
Soil S4515	10	0.136	0.135	0.136	0.135

Discussion

In the proposed method, clearing does not take place, in the sense that a water-white, transparent liquid forms as in the official method. The ferric sulfate is insoluble, and must be insoluble to carry out the basic principle of the method. At the start, a black foam fills more than half of the flask; this declines to a bright yellow paste in about 15 minutes and remains a yellow paste until the end. The full heat of the Bunsen burners is used from the beginning. Any organic matter on the flask walls is removed by the washing action of the condensing acid vapors, or by twirling, as is customary in the official method, after digesting for about 10 minutes.

Ferric sulfate remaining on the sides of the flask does not impair accuracy. If not washed down by the water on dilution, it may be removed by twirling the flask shortly afterwards. The flasks may be allowed to stand until cool (10 to 15 minutes). Because of the pasty nature of the mixture, what appears to be a hard cake will form, but on dilution this cake disintegrates, the ferric sulfate going into suspension. If this does not occur at once, the flask may be set aside to

TABLE V. COMPARISON OF MERCURY AND COPPER CATALYSTS

Substance	Sample Weight Grams	N by Official Method, 150-Min. Digestion		N by Proposed Method, 30-Min. Digestion		Difference, Hg - Cu %	N in sample Mg.
		Hg %	Cu %	Hg %	Cu %		
Soybean stems	2	0.66	0.66	0.66	0.66	0.0	13.2
Soybean roots	2	1.41	1.41	1.41	1.39	0.02	28.2
Orchard grass	1	3.44	3.42	3.44	3.40	0.04	34.4
Tailings	1	3.53	3.53	3.54	3.51	0.03	35.4
Soybean leaves	2	2.42	2.41	2.42	2.35	0.07	48.4
Soybean leaves	2	2.64	2.62	2.64	2.51	0.13	52.8
Milk	1	5.56	5.49	5.56	5.35	0.21	55.6
Soybeans	1	6.12	6.12	6.12	5.96	0.16	61.2
Agrinite	1	8.59	8.42	8.60	8.44	0.16	86.0
Tankage	1	9.55	9.29	9.54	9.31	0.23	95.4

cool before the distillation. Then, on twirling, the cake will usually disappear, although a small portion may remain. Apparently it is not acid. On addition of alkali and twirling, ferric oxide forms, and any remaining cake disappears at once or upon first application of heat. The sulfate ion supplied by the ferric sulfate and the hydrogen ion in dipotassium phosphate should be included in calculating the amount of alkali to be added.

Monopotassium or monosodium phosphate is not satisfactory unless more than 10 grams of the anhydrous salt are used, apparently because of the low content of potassium or sodium.

Because of the possibility of loss of ammonia by rapid heating at the start of the distillation, whether by the official method or by the proposed method, the flame should be kept low for the first few minutes until the mixture is boiling quietly at which time it may be increased. The distillation following the proposed method is more satisfactory than in the official method, in that bumping is eliminated; the authors have allowed some flasks to go almost to dryness without encountering bumping. No less than 45 minutes, and preferably 60 minutes for any method, is recommended for the distillation of 150 to 200 ml. of distillate.

The catalysts of the new method do not increase the activity of copper, and the short digestion time is inadequate for copper with all but the lowest amounts of nitrogen. The use of mercury is, therefore, essential in this method.

Summary

A study of the literature as well as laboratory comparisons of various known methods failed to reveal any practical means of shortening the time required for the Kjeldahl digestion based on raising the boiling point, using oxidants, or using catalysts such as selenium.

A method is proposed which provides more surface for oxidizing activity and for the formation of gas bubbles, without producing noxious fumes and with no increase in the number of steps in the procedure. Results by this method, using 10 grams of anhydrous dipotassium phosphate or 12 grams of the hydrated salt, and 6 grams of ferric sulfate with mercury as the metallic catalyst, accurately check those obtained by the official Kjeldahl-Gunning-Arnold method, and the time of digestion with gas burners is reduced from 2.5 hours to 30 minutes.

Bumping during distillation is eliminated through the use of dipotassium phosphate in the digestion, giving a different crystalline form to the precipitate.

Mercury has been proved more rapid than copper as a catalyst, and is essential in the proposed method.

The reagent cost is slightly greater than that of sodium sulfate, but because of saving in time, which usually amounts to a saving in labor, the determination by the proposed method is more economical, particularly where gas heat is used for digestion. It is the authors' experience that the number of determinations run in a day can be almost doubled.

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Patent Blue V as a pH and Redox Indicator—Correction

IN THE paper by Yoe and Boyd [*IND. ENG. CHEM., Anal. Ed.*, 11, 492 (1939)] substitute the following sentence for the last one in the fifth paragraph (first column) on page 493: "But in titrations with ceric sulfate using Patent blue V as indicator, a satisfactory end point is not obtained when a phosphate 'preventive solution' is employed." This substitution is intended merely to clarify our statement, not to explain it.

In our paper, the use of Patent blue V as indicator in ceric sulfate titrations was implied. Certainly, we did not intend to say that the Zimmerman-Reinhardt method cannot be used in ceric sulfate titrations for ferrous iron. Every year we make this titration (using ferroin as indicator) many times as a matter of laboratory routine.

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Analysis of Cationic Surface-Active Agents of Trivalent Nitrogen Type

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In spite of the growing application of cationic surface-active agents in the textile and related industries as dye auxiliaries and for finishing, there seems to be a lack of published literature on methods of analysis of such compounds. In this article a procedure is outlined applicable to commercial products of the fatty acid amido-amine type. This procedure includes directions for the determination of the acid used to render the products soluble, nitrogen as alkalinity, total active ingredients or amido-amine, free fatty acids, total fatty acids, condensed amine, and uncondensed amine.

DURING the past several years there has been a growing application in the textile industry of cationic surface-active agents as dye auxiliaries and for finishing. The products on the market are either quaternary ammonium compounds or the salts of trivalent nitrogen amines. It is stated that the quaternary ammonium compounds such as octylpyridinium ammonium chloride, $C_8H_5N(C_8H_{17})Cl$, promote a fine dispersion of vat and sulfur dyes and are consequently used to attain more level dyeing with and for stripping of such dyestuffs. A rather unstable quaternary ammonium compound such as octadecyloxymethylpyridinium chloride, $C_8H_5N(CH_2OC_{18}H_{37})Cl$, which upon heating in contact with cellulosic fibers combines with it, has been recommended as a permanent waterproofing treatment (5). However, the trivalent nitrogen amine salts, particularly the salts of fatty acid amido-amines such as oleylamidoethylene-*N*-diethylamine, $C_{17}H_{33}CONHC_2H_4N(C_2H_5)_2$, have so far found the greater application. They represent the condensation products of fatty acids and di- or polyamines. Because of opposite electrical charges, these cationic agents are substantive to cotton and similar fibers and consequently are readily exhausted from the treating bath. As a finish these compounds impart to the goods desirable pliability and smoothness which are more or less permanent. By conferring a positive charge on the fabric, treated cotton goods acquire an affinity for wool dyestuffs, and by forming insoluble salts with dyes containing a sulfonic or carboxylic group, cotton goods so dyed are rendered more or less fast to washing and perspiration. These treating agents are also recommended to assist impregnation with latex and as detergents in neutral or acid baths.

The products on the market are mostly water solutions of the salts of the amines, in the form of either liquids or pastes. There seems to be little or no literature on methods of analysis of such compounds. In this paper a procedure is outlined for the chemical analysis of the trivalent nitrogen compounds of the fatty acid amido-amine type. These methods consist essentially of isolating the amido-amine, hydrolyzing it into its fatty acids and amine constituents, and determining the

last two. These methods with some modification may be applied to certain sulfonated detergents of the fatty acid-amide type and possibly also to nylon (1), the new synthetic yarn, which is a polymer of the condensation product of a dicarboxylic acid and a diamine.

Procedure

ACIDITY OF AMIDO-AMINE SALTS. Enough of the sample to yield about 3 grams of the amido-amine is dissolved in 100 ml. of neutral alcohol in a 250-ml. beaker and the acidity determined by titrating with 0.5 *N* sodium hydroxide solution until neutral to phenolphthalein. Part of the acidity may be due to free fatty acids, the acidity of which is determined later. If the sample does not dissolve entirely in hot alcohol, the insoluble matter may represent filler such as dextrin, which is often incorporated in commercial cationic agents. In such cases the insoluble material is filtered off, before titrating, on a tared filter paper and dried to constant weight.

AMIDO-AMINE. The titrated solution is transferred to a 500-ml. separatory funnel, containing 100 ml. of a saturated sodium chloride solution and 100 ml. of ether. Solid salt is added if necessary until there is a slight excess and the mixture is thoroughly shaken. The contents are allowed to separate well and the lower layer is withdrawn into another separatory funnel. The solvent layer may be contaminated with water-soluble simple amines and inorganic salts such as sodium acetate, more or less soluble in the solvent. It is therefore washed two or more times with 25-ml. portions of the salt solution or until neutral to methyl orange. The wash waters are combined and extracted with two 35-ml. portions of a mixture of equal parts of alcohol and ether. The solvent layers from the washes are combined and, after washing with 25-ml. portions of salt solution until neutral to methyl orange, are added to the first extract. The wash waters contain the acid component of the sample, the acidity of which has already been obtained. The acid may be further identified by a steam distillation of the combined washes in the presence of excess phosphoric acid and testing the distillate in the usual manner.

The well-settled solvent layer is evaporated and the residue heated to constant weight at 110° to 115° C. The residue may be contaminated by inorganic salts varying from a trace to about 2.0 per cent. It is therefore ignited and the ash is deducted from the residue. If the ash, which consists mostly if not entirely of sodium chloride, is definitely alkaline, it shows the presence of sodium carbonate due either to alkaline salts such as sodium acetate which have not been completely washed out from the solvent layer or to uncondensed fatty acids which would be present as soda soap in the residue. The correction of the ash, which may be readily calculated, is practically insignificant and may be disregarded. The ash is retained for the determination of free fatty acids in the sample, as outlined below.

In order to obtain a supply of the amido-amine for the subsequent tests, enough of the sample to yield approximately 10 grams of the amido-amine is dissolved in 500 ml. of equal parts of ether and alcohol, the contents are neutralized with dilute sodium hydroxide until neutral to phenolphthalein, the lower layer after settling is discarded, and the solvent layer is washed with salt solution until it is neutral to methyl orange. To remove most of the salt contaminant, the solvent layer is evaporated to dryness, and the residue is dissolved in hot alcohol, filtered, and diluted with alcohol to about 500 ml. The concentration of the amido-amine solution is then determined by evaporating exactly 100 ml., heating the residue to constant weight, and igniting.

The tests that follow are made on aliquot portions of this solution. Tests that may be made on the amido-amine besides total nitrogen are: specific gravity, solidification point, iodine number, acetyl value, molecular weight, etc.

FREE FATTY ACIDS. The ash from the amido-amine determination is dissolved in water and titrated hot with acid to methyl orange. From the alkalinity of the ash, the probable

acid number of the original fatty acids, and the weight of the corrected amido-amine, the approximate percentage of free fatty acids may be calculated. There is a possibility that in the presence of coconut oil fatty acids, some of the soap might be soluble in the concentrated salt solution. In that case the salt solution after extracting the amido-amine should be acidified and the fatty acids extracted with ether. However, this phase was not experimentally investigated.

NITROGEN AS ALKALINITY. To exactly 100 ml. of the alcoholic solution of the amido-amine in a separatory flask are added 100 ml. of ether, 100 ml. of saturated salt solution, methyl orange indicator, and a measured quantity of 0.5 *N* hydrochloric acid until the lower layer, after vigorous shaking and settling, is strongly pink (about 2-ml. excess). Some excess salt is added, the contents are allowed to settle for about 15 minutes, and the clear lower layer is drawn off. The solvent layer at this stage may sometimes turn turbid and even show a precipitate, which settles in the interface, owing to the limited solubility of the amido-amine hydrochloride in the solvent. The precipitate, if any, is retained in the solvent layer. The solvent layer is washed with 25-ml. portions of salt solution until the last wash requires 0.1 to 0.15 ml. of 0.5 *N* sodium hydroxide solution to discharge the pink color due to methyl orange. The combined wash waters are then titrated for excess hydrochloric acid. The alkalinity of the sample is given by the net amount of hydrochloric acid used. The solvent layer is retained for the determination of total nitrogen.

TOTAL NITROGEN. The solvent layer from the alkalinity test is transferred to a Kjeldahl flask, the solvent evaporated, and the nitrogen determined in the usual way.

TOTAL FATTY ACIDS. Exactly 250 ml. of the alcoholic solution of the amido-amine are introduced into a 500-ml. round-bottomed flask, the solvent is evaporated, 200 ml. of 6 *N* hydrochloric acid solution and some pumice stone are added, and the contents are boiled vigorously under a water-cooled condenser for about 20 hours, or until a clear oil layer separates on the surface. After cooling, the contents are transferred to a 500-ml. separatory funnel, the flask is rinsed with about 25 ml. of hot alcohol, and the fatty acids are extracted with 100 ml. of ether. The layers are allowed to separate well, and the water layer is transferred to another separatory funnel and extracted with two 35-ml. portions of ether, which are added to the first extract. The water layer is retained for the determination of the simple amine. The solvent in the combined ether layer is evaporated and the fatty acids are heated to constant weight at 105° to 110° C. The usual tests may be applied to the extracted fatty acids: specific gravity, melting point, iodine number, acidity, saponification value, acetyl value, etc.

CONDENSED AMINE. The amine may be determined from the amine hydrochloride, by evaporating the water layer from the decomposition test, heating the residue to constant weight, and determining the hydrochloric acid by titration. However, it is more conveniently estimated by calculation. The amine is given by the difference between 100 per cent and the per cent of fatty acids found in the amido-amine, correction being made for the water eliminated during the condensation, which may be calculated from the content of amido-nitrogen. The equation for calculating the amine is as follows:

$$\% \text{ of condensed amine} = 100 - \% \text{ of fatty acids} + \frac{18}{14} (\% \text{ of total nitrogen} - \% \text{ of nitrogen as alkalinity}) \quad (1)$$

where the last item— $18/14$ (% of total nitrogen — % of nitrogen as alkalinity)—represents the water of condensation. The percentages are based on the purified amido-amine and not on the original sample. Where the nature of the amine is known, it may also be calculated from the total nitrogen found in the amido-amine.

To isolate the amine for identification purposes, the water layer from the decomposition step is evaporated to dryness and the residue is boiled with small portions of 0.5 *N* alcoholic potassium hydroxide until the sample is completely dissolved and the solution is barely alkaline to phenolphthalein. Care should be taken not to overneutralize; otherwise the amine will be contaminated with free potassium hydroxide, which is difficult to remove. The solution is filtered, most of the alcohol is evaporated, the residue is redissolved in a small quantity of alcohol, and filtered again, and the filtrate is evaporated on a water bath until no odor of alcohol is discernible. If necessary, it may be further purified by vacuum distillation. The amine may be tested for specific gravity, nitrogen, alkalinity, boiling point, molecular weight, etc.

UNCONDENSED AMINE. The difference between the nitrogen content of the original sample and of the amido-amine is a measure of the free or uncondensed amine present.

MOISTURE. Moisture is determined in the usual manner by a xylene distillation (2). The specific gravity of the distillate should be made and its acidity to phenolphthalein determined, as some or all of the acid used in rendering the amido-amine soluble will be found in the distillate.

Experimental

Commercial samples of the condensation products of oleic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, and hydroxyethyl ethylenediamine, $\text{NH}_2\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{OH}$, sample A, and of stearic acid, $\text{C}_{17}\text{H}_{35}\text{COOH}$, and triethylenetetramine, $\text{NH}_2\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$, sample B, were purified by dissolving in a mixture of equal parts of alcohol and ether, washing with concentrated salt solution until the wash water was practically neutral to methyl orange, evaporating the solvent, and heating the residue to constant weight. Experimental work on the procedure was conducted on these two samples, corrected for the presence of salt.

ACIDITY OF AMIDO-AMINE SALTS. Approximately 2-gram portions of sample A or B were dissolved in 100 ml. of neutral alcohol, exactly 10 ml. of 0.5 *N* solutions of hydrochloric acid, acetic acid, and formic acid, respectively, were added, and the acidity was determined by titrating with 0.5 *N* sodium hydroxide to phenolphthalein. The results expressed as milligrams of potassium hydroxide are given in Table I. Highly satisfactory results were obtained in alcohol of high concentration. On the other hand, titration in water solutions gave very low results; thus, in titrating a sample containing 285 mg. of formic acid, expressed as milligrams of potassium hydroxide, only 191 mg. were recovered.

TABLE I. ACIDITY OF AMIDO-AMINE SALTS

	(Expressed as mg. of potassium hydroxide)					
	Hydrochloric Acid		Acetic Acid		Formic Acid	
	Added	Found	Added	Found	Added	Found
	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
Sample A	287.3	287.3	282.5	282.7	285.1	284.7
Sample B	287.3	287.2	282.5	282.9	285.1	285.0

AMIDO-AMINE. The total active ingredients or the amido-amine were determined according to the procedure. The results were in excellent agreement and the recovery was practically 100 per cent in each case. To determine whether or not the simple amine, with which the sample may be contaminated, would be completely removed during the washing, hydroxyethyl ethylenediamine was added to about double its weight of sample A and the active ingredients were then determined. The addition of the amine did not affect the final results.

FREE FATTY ACIDS. If the sample contains any fatty acids not combined as amide or ester, they will be found in the form of soap in the extracted amido-amine. Attempts to wash out the soap from the residue proved unsuccessful. To determine the alkalinity of the soap in the presence of the amido-amine is impossible, since the amido-amine also reacts with the acid. However, upon ashing, the amido-amine-containing soap is converted to sodium carbonate, from the alkalinity of which and the probable acid number of the fatty acids the approximate quantity of the uncombined fatty acids may be calculated.

To test this method 0.1- to 1-gram portions of oleic acid were added to approximately 3-gram samples of sample A, which was extracted as in the procedure. The residue was then ashed and the alkalinity of the ash determined by titrating hot with 0.5 *N* hydrochloric acid until neutral to methyl orange. The results were somewhat higher than the calculated values—about 3 per cent. On the other hand, the ash of the original amido-amine of both samples contained only traces of alkalinity, showing them to be free of uncondensed fatty acids.

NITROGEN AS ALKALINITY AND TOTAL NITROGEN. In testing the amido-amine for alkalinity, the titration in water

solutions (by adding excess acid and titrating back) was found to be incomplete, and in alcohol titration the end point was not entirely satisfactory. The titration over salt solutions as outlined gives concordant results, which are believed to be accurate as shown under total fatty acids. The nitrogen as alkalinity and total nitrogen are given in Table II.

TABLE II. NITROGEN AS ALKALINITY AND TOTAL NITROGEN

	As Alkalinity			Total Nitrogen %
	I %	II %	Av. %	
Sample A	3.18	3.15	3.17	6.71
Sample B	2.57	2.59	2.58	6.85

HYDROLYSIS OF AMIDO-AMINE. Krieble and Holst (4) have made a study of the hydrolysis of formamide, acetamide, and propionamide under the influence of high concentration of hydrochloric acid and sulfuric acid. They found that each amide has a maximum velocity of hydrolysis at one particular acid concentration. The acid concentration is not the same for different amides. Krieble and Holst also note that sulfuric acid is the better catalyst before and hydrochloric acid after the maximum velocity is reached. The maximum velocity constant, *K*, for hydrochloric acid was somewhat better than for sulfuric acid. Thus, in the case of formamide, *K* for hydrochloric acid was 1.84 at 6 molal and 1.74 for sulfuric acid at 5.0 molal. They also state that for the same acid concentration the velocity constants were about the same, even though the amide concentration varied from 0.05 to 0.8 mole.

Hopper, MacGregor, and Wilson (3) have studied the hydrolysis of certain arylamides used as dye intermediates such as 2,4-dimethoxyanilide or 2-hydroxy-3-naphthoic acid. They hydrolyzed by boiling for about 6 hours with alkalis, using either 32 grams of potassium hydroxide dissolved in 200 ml. of alcohol or 50 grams of an organic base such as ethylenediamine or mono-, di-, and triethanolamine, per 15 to 20 grams of the sample. In the present experiments, while no extensive tests were made to determine the optimum condition for hydrolysis, the following qualitative results were obtained: Little or no decomposition seems to have taken place with ethylenediamine even after boiling for 10 hours, since no fatty matter could be extracted, after acidifying the solution. Sulfuric acid because of its high volatility would interfere with the subsequent steps in the procedure. The best results were obtained with 6 *N* hydrochloric acid—12 *N* produced excessive foaming and was not practical and 1.5 *N* and 3 *N* were much slower, when judged by the time it took for the fatty matter to separate in a clear oil layer. After about 20 hours of boiling with 6 *N* hydrochloric acid, the hydrolysis was practically complete, since the extracted fatty matter showed only traces of nitrogen.

TABLE III. TOTAL FATTY ACIDS

	I	II	Av.	Calculated
	%	%	%	
Sample A	79.8	80.0	79.7	79.62
Sample B	88.1	87.8	87.9	87.63

TOTAL FATTY ACIDS. In extracting the fatty acids, it was found impractical to wash the solvent layer free from hydrochloric acid because of the formation of troublesome emulsions, probably due to traces of the amido-amine. However, any hydrochloric acid remaining in the solvent layer is readily volatilized upon heating the residue to constant weight, as shown by the fact that when dissolved in alcohol, the residue was neutral to phenolphthalein, and when dissolved in water and acetic acid, the test for chlorides was negative. The yields of fatty acids compared with the calculated values are given in Table III. The fatty acids were calculated by

Equation 1. The condensed amine in the equation was calculated from the total nitrogen of the amido-amine and the formulas of the amines were used in the condensation. The differences between the experimental results and the calculated values are evidently within the experimental error.

Equation 1 may be used to check the accuracy of the nitrogen determination as alkalinity, since all the terms may be determined experimentally. Upon substituting in the formula the results obtained for the fatty acids, condensed amine, and total nitrogen, the nitrogen as alkalinity was calculated; the results were in good agreement with the determined values.

TABLE IV. CONDENSED AMINE

	From Equation 1	Based on Total Nitrogen
	%	%
Sample A	24.7	24.9
Sample B	17.6	17.9

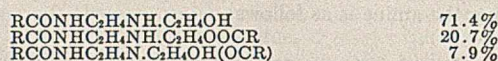
The fatty acids obtained from sample B gave the normal tests for stearic acid. The fatty acids from sample A, however, though liquid at room temperatures, gave low results—namely, iodine number of 63.5, acidity number of 177.8, and saponification value of 188.5, compared with 86, 194, and 198, respectively, for the oleic acid used in making the product. The low values may probably be attributed to the addition of hydrochloric acid to the double bond during the decomposition of the amido-amine. This phase of the problem, however, was not further investigated.

CONDENSED AMINE. Since the nature of the amines in these samples was known, it was possible to check the amines calculated from Equation 1 against the amine calculated from the total nitrogen. The results are in good agreement, as shown in Table IV.

TABLE V. PROBABLE COMPOSITION OF SAMPLES A AND B

	Sample A		Sample B, Mixture A	
	Found	Calcd.	Found	Calcd.
Fatty acids	79.9	80.2	87.9	87.7
Total nitrogen	6.71	6.73	6.85	6.86
Nitrogen as alkalinity	3.17	3.18	2.58	2.54

PROBABLE COMPOSITION OF SAMPLES A AND B. A simple calculation from the data obtained for sample A, in which, however, the possible presence of esterified diamide and the ester diamine was disregarded, indicates that the sample probably contains the following mixture:



where R represents the oleic acid residue. In the case of sample B, the data correspond to a mixture of 40 per cent of the diamide and 60 per cent of the triamide (mixture A), although several other mixtures are possible—for example, 50 per cent of the diamide, 30 per cent of the triamide, and 20 per cent of the tetraamide. In Table V are given the fatty acids and the nitrogen contents actually found and the values calculated for the probable mixtures.

Acknowledgment

The writer is greatly indebted to Virginia Raison of this laboratory for assistance with the analytical work.

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Estimation of *o*-Nitrophenol in *p*-Nitrophenol and *o*-Aminophenol in *p*-Aminophenol by Fluorescence Analysis

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A method is reported for the estimation of 1 per cent or less of *o*-nitrophenol in *p*-nitrophenol, or of *o*-aminophenol in *p*-aminophenol. The nitrophenol is reduced to aminophenol and the latter is made to react with benzoic acid. A fluorescence is produced as a by-product of the formation of phenylbenzoxazole from *o*-aminophenol, which is not produced by *m*- or *p*-aminophenol. By matching the fluorescence against standards, as little as 0.05 per cent of the ortho compounds can be detected.

A METHOD was needed for the estimation of low concentrations of *o*-nitrophenol (less than 1 per cent) in *p*-nitrophenol, and of *o*-aminophenol in *p*-aminophenol. The literature contains a few references to properties whereby *o*-nitrophenol may be separated or distinguished from *p*-nitrophenol.

Karrer and Nielsen reported the chromatographic separation of *o*- from *m*- and *p*-nitrophenol (7, 8). Bischoff and von Hedenström reported that *m*- and *p*-nitrophenol each react with diphenylxalate to form the dinitrophenyl ester of oxalic acid, but *o*-nitrophenol does not (1). Shikata and Hozaki (11) and Shikata and Watanabe (12) made a polarographic study of *o*, *m*-, and *p*-nitrophenol. Lecomte studied the infrared absorption spectra of these compounds (9).

A well-known method for separating *o*-nitrophenol from *p*-nitrophenol in the products of nitration of phenol is to steam-distill the mixture. *o*-Nitrophenol distills over without any considerable contamination of *p*-nitrophenol. For low concentrations of *o*-nitrophenol in the presence of considerable *p*-nitrophenol, however, sufficient of the para derivative does distill over so that a mere determination of the total nitrophenol in the distillate will lead to high values for *o*-nitrophenol. Hoeflake reported a method for the determination of *o*-nitrophenol in *p*-nitrophenol which involves a preliminary steam distillation to separate the ortho from the para isomer (4). Although this method is reported as satisfactory for concentrations of *o*-nitrophenol of the order of 8 to 10 per cent, it probably would not be satisfactory for concentrations of less than 1 per cent with which the method described here deals.

No method seems to have been reported for the estimation of low concentrations of *o*-aminophenol in *p*-aminophenol. Horn has reported that Fehling's solution will precipitate very difficultly soluble copper complexes from aqueous solutions of *o*-aminophenol and its aliphatic *N*-alkyl derivatives, but not from solutions of *m*- and *p*-aminophenol and their derivatives (5). He does not, however, give any data concerning a possible quantitative application of this test. Pestemer and Flaschka have studied the ultraviolet absorption of *o*-, *m*-, and *p*-aminophenol (10).

An attempt was made to devise a method based upon the fact that *o*-aminophenols react with carboxylic acids or their anhydrides to form benzoxazole derivatives, whereas *m*- and *p*-aminophenols do not. By reducing the nitrophenol to aminophenol and reacting the latter with a carboxylic acid, it was hoped that the benzoxazole which was formed could be determined gravimetrically as a measure of the *o*-nitrophenol.

This did not prove to be feasible. It was found, however, that, with either acetic or benzoic acid, a fluorescence is produced in the course of the reaction which can be seen after removing obscuring colors. This could be obtained in solution in benzene. *p*-Nitrophenol does not produce any fluorescence. *m*-Nitrophenol also should produce no fluorescence (as indicated by the failure of *m*-aminophenol to produce any). The intensity of the fluorescence can be used as a measure of the concentration of *o*-nitrophenol or *o*-aminophenol by matching against standards prepared from known mixtures of *o*- and *p*-nitrophenol, or *o*- and *p*-aminophenol. These standards maintain their fluorescence without obvious change for a period of weeks.

The fluorescence is not a property of the benzoxazole, but rather of accompanying by-products. Phenylbenzoxazole, prepared from benzoyl chloride and *o*-aminophenol, lost all its fluorescence when it was recrystallized sufficiently.

This work was confined to concentrations of from 0.0 to 1 per cent of *o*-nitrophenol or *o*-aminophenol. Starting with nitrophenol, it was possible to distinguish 0.05 per cent of *o*-nitrophenol from pure *p*-nitrophenol and from 0.1 per cent of *o*-nitrophenol; 0.25 per cent from 0.1 per cent and from 0.5 per cent; and 0.5 per cent from 1.0 per cent. Closer estimations were not tried. Starting with aminophenol, it was possible to distinguish each of the members of the series 0.0, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 per cent from the preceding and the following member. No attempt was made to make the method more precise or to distinguish concentrations between 0.0 and 0.05 per cent.

Method for Nitrophenol

The nitrophenol sample is boiled with zinc and hydrochloric acid to reduce it to aminophenol. The solution is extracted with ether, after adjusting it to a pH of about 5.1, so as to extract as much of the *o*-aminophenol and as little of the *p*-aminophenol as possible. The residue, after evaporating the ether, is fused with benzoic acid, which is then taken up in aqueous ammonia, from which the fluorescent material is removed by means of benzene. The fluorescent benzene solution is matched against standards which are prepared by treating synthetic mixtures containing known concentrations of *o*-nitrophenol in *p*-nitrophenol. (The latter is added in order to be sure that the fluorescence in the standards will be accompanied by such colored by-products as will be present in the sample.)

REAGENTS. *p*-Nitrophenol used for making up standards with *o*-nitrophenol was a recrystallized product which sintered at 112.5° C. (corrected) and melted at 113.5–114° C. (corrected). The freezing point was 113.37° C. (corrected).

Since the melting range of the *p*-nitrophenol did not preclude the possibility that a trace of *o*-nitrophenol might be present and so falsify the conclusions concerning the sensitivity of the method, a small quantity of *p*-nitrophenol which would be free of *o*-nitrophenol was synthesized by condensing nitromalonic dialdehyde with acetone (3). The nitromalonic dialdehyde was prepared through the bromomuconic acid (2), which in turn was prepared by the action of bromine upon furfural (13).

o-Nitrophenol was a recrystallized product which melted constantly at 44.8–45.3° C. (corrected) and had a freezing point of 44.88° C. (corrected).

PROCEDURE FOR DEVELOPMENT OF FLUORESCENCE. Boil 1.3 grams of nitrophenol under a reflux condenser for 15 minutes with 125 ml. of water, 30 ml. of concentrated hydrochloric acid, and 5 grams of zinc dust. Cool the mixture and filter off the unreacted

zinc. Wash with three 10-ml. portions of water. Treat the solution first with about 15 ml. of concentrated ammonium hydroxide and finally dropwise with about 2 per cent ammonium hydroxide until the pH is about 5.1. This adjustment is not very critical, so that it is sufficient to make the solution alkaline to Congo red paper and only faintly alkaline to red litmus paper. At this stage, no precipitation of zinc hydroxide will occur unless too much ammonia (but insufficient to redissolve the precipitated zinc hydroxide) has been added. If necessary, readjust the alkalinity to the proper point by means of dilute hydrochloric acid. Cool the solution to room temperature and extract with three 25-ml. portions of ether. This procedure causes the extraction of all or most of the *o*-aminophenol with little of the *p*-aminophenol. Wash the ether extracts twice with 5-ml. portions of water and evaporate just to dryness in a 100-ml. beaker. The evaporation should be carried out as rapidly as possible on a steam bath in order to prevent the formation of an adherent skin which cannot be mixed properly with the benzoic acid in the next step of the procedure. Continue the analysis without delay in order to avoid oxidation.

Scrape the residue as completely as possible from the bottom and sides of the beaker with a spatula and mix it thoroughly in the beaker with 5 grams of sublimed benzoic acid. Immerse the covered beaker in an oil bath heated to 155–160° C. After the contents have melted, continue to heat for 15 minutes. (Uncontrolled heating may lead to the formation of carbonaceous matter which is accompanied by the production of undesirable color.) Remove the beaker and allow its contents to cool to room temperature. Rub the melt with alternate portions of concentrated ammonium hydroxide and water by means of a flattened glass rod until all, or practically all, has dissolved to form a blue solution. Extract twice with 25-ml. portions of benzene. Treat the combined benzene extracts repeatedly with 10-ml. portions of 1 per cent sodium hydroxide solution until the alkali removes practically no more blue color from the benzene, and then with water until the washings are neutral to litmus paper. Place the washed benzene extract in a test tube (150 × 25 mm.) and compare the fluorescence (as described below) with that of a series of standards which have been prepared from synthetic mixtures of *o*-nitrophenol and *p*-nitrophenol, with the former present in concentrations ranging from 0 to 0.5 per cent.

MATCHING FLUORESCENCE AGAINST STANDARDS. A fairly good comparison may be made by the use of an ordinary desk lamp, shielding the eyes from the direct light of the lamp and allowing it to shine against the sides of the test tubes. The tubes are held vertically, with the bottom of the tubes on a dark background, and looked into from above.

A more sensitive method of comparison involves the use of some more intense source of ultraviolet rays such as an argon bulb, the light from which is passed through an appropriate filter in order to remove most of the visible rays. The comparison is carried out in a dark room by holding the tubes in a rack at arm's length and slightly above the eyes, and placing the lamp beneath the tubes. This procedure gives better results, particularly because the presence of some red color in the solutions from commercial samples of *p*-nitrophenol does not obscure the fluorescence as it tends to when ordinary lighting is used. With this technique two observers independently arranged in proper order the series of standards: 0.0, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 per cent *o*-aminophenol. With an ordinary electric bulb one observer reversed the 0.1 and 0.2 per cent standards.

VARIATIONS OF PROCEDURE. The first attempt in this work was prompted by the thought that it should be possible to convert *o*-nitrophenol to phenylbenzoxazole by melting it with benzoic acid in the presence of zinc dust, thus carrying out the reduction to aminophenol and the condensation to benzoxazole in one step, and to isolate and weigh the benzoxazole. With pure *o*-nitrophenol, the molten reaction mixture, after treatment with ammonia, yielded an ether extract which, upon evaporation, gave approximately the theoretical weight of crystals which melted at 98–101° C., with previous sintering at about 86° C. [phenylbenzoxazole which was prepared in this laboratory melted at 100.1–100.8° C. (corrected)]. The ether solution exhibited a greenish-yellow fluorescence. *p*-Nitrophenol similarly treated, however,

yielded a considerable noncrystalline residue, so that a gravimetric method could not be used to estimate the ortho isomer.

The use of a considerably larger sample of nitrophenol than that described in the procedure, in an attempt to increase the intensity of fluorescence, resulted in the production of considerable reddish impurities which tended to obscure the fluorescence.

Reduction of *o*-nitrophenol by means of zinc in the presence of glacial acetic acid, in place of benzoic acid, also resulted in the formation of a greenish-yellow fluorescence which could be extracted with ether after rendering the zinc soluble with a considerable excess of sodium hydroxide. This procedure did not give as intense a fluorescence, however, as the procedure with benzoic acid.

Although ether and benzene both bring out the fluorescence, benzene probably better than ether, alcohol diminishes it.

SENSITIVITY OF METHOD. The lowest concentration of *o*-nitrophenol which was tried was 0.05 per cent in admixture with *p*-nitrophenol. This gave a definite fluorescence which could be distinguished with no difficulty from the nonfluorescent solution obtained with the *p*-nitrophenol itself. It was not certain, however, that the *p*-nitrophenol was entirely free from traces of *o*-nitrophenol. In order to establish definitely that the method would detect 0.05 per cent of *o*-nitrophenol, analyses were made with the synthetic *p*-nitrophenol known to be free of the ortho isomer, and with the same *p*-nitrophenol to which 0.05 per cent of *o*-nitrophenol had been added. No fluorescence was obtained with the former, whereas the latter caused a definite fluorescence.

EFFECT OF *m*-NITROPHENOL. No mixtures containing *m*-nitrophenol and *o*-nitrophenol were tried. However, *m*-aminophenol gives no fluorescence.

Modifications in Nitrophenol Method Applied to Aminophenol

When the fluorescence method for nitrophenol was applied to aminophenol with, however, the omission of the reduction, no difficulty was encountered when purified aminophenols were used, as was necessary for the preparation of the standards. But when this procedure was applied to some commercial samples of *p*-aminophenol, such an intense red coloration was present in the benzene solution in which the fluorescence was to be observed, that it was impossible to make any comparison with the standard solutions. Several methods were tried in order to prevent the formation of the interfering color, or to remove it after it was formed, without, at the same time, materially diminishing the intensity of the fluorescence. This result could be reached by adding some new steps to the technique.

Dissolve 1 gram of the aminophenol in 100 ml. of water with 3 ml. of concentrated hydrochloric acid. Filter the solution, in order to get rid of some insoluble impurities which might tend to produce colorations, before adjusting the alkalinity and extracting with ether. Then proceed as with the nitrophenol samples through the extraction with benzene. Shake the final benzene extract with three 10-ml. portions of hydrochloric acid (1 part by volume of concentrated acid to 2 parts of water) or until no more color is extracted. Finally, if shaking with hydrochloric acid produces a dark coloration in the benzene extract, remove this by washing once or twice with ammonium hydroxide (1 part by volume of concentrated ammonium hydroxide to 1 part of water), followed by subsequent washing with the dilute hydrochloric acid. Before matching with the standards, filter through dry paper to remove any turbidity caused by moisture. This treatment removed only a negligible proportion of the fluorescence—for example, a 0.1 per cent standard after treatment could be distinguished from an untreated 0.05 per cent standard. But, if desired, the same treatment could be applied to the standards, thus preventing the treatment from affecting the *o*-aminophenol values.

Several other methods for removing the interfering coloring matter were tried, but none was successful. Boiling the ben-

zene extract with bone black removed the color, but also, at the same time, the fluorescence. Boiling the aqueous aminophenol solution with zinc and hydrochloric acid to simulate the conditions of the nitrophenol analysis did not help; nor did treatment with sodium bisulfite. Treatment of the hot hydrochloric acid solution of the aminophenol with bone black caused loss of fluorescence. Treatment in the cold did not remove the color.

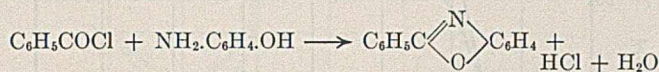
REAGENTS. *o*-Aminophenol was a recrystallized product which melted at 174.3–176.0° C. (corrected) with some darkening, and at 175.4–176.2° C. (corrected) when the melting point was taken from a bath which had been heated to within a few degrees of the melting point before the capillary containing the sample was immersed in the bath.

p-Aminophenol was recrystallized twice from a 1 per cent aqueous sodium bisulfite solution. When the melting points of the samples from each recrystallization were taken simultaneously in a bath which had been heated to about 180° C., before the capillaries were immersed, and with fairly rapid heating (to minimize decomposition), the products from both recrystallizations melted at 188–189° C. (corrected), with decomposition.

m-Aminophenol was recrystallized twice from toluene to a melting point of 124.4–125.2° C. (corrected), which did not change upon an additional recrystallization from alcohol.

Origin of Fluorescence

Phenylbenzoxazole was prepared by reacting *o*-aminophenol with benzoyl chloride according to the method of Hübner (6):



The crude product had a reddish-brown fluorescence in benzene. When the substance was recrystallized once from

alcohol and twice from acetone to a constant melting point of 100.1–100.8° C. (corrected), the fluorescence (now green instead of reddish brown) became progressively fainter and was barely perceptible in the final constant-melting material. An additional recrystallization from a petroleum hexane cut (boiling point 60° to 70° C.) did not change the melting point but did remove the last very faint traces of fluorescence. After standing for 16 months, the sample still exhibited no fluorescence in benzene.

It is evident that the fluorescence is caused by a by-product of the benzoxazole condensation and is not a property of the benzoxazole itself.

Acknowledgment

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Colorimetric Determination of Cobalt with Beta-Nitroso-Alpha-Naphthol

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ILINSKI (5) reported in 1884 that α -nitroso- β -naphthol and β -nitroso- α -naphthol give reddish-brown slightly soluble precipitates with cobalt salts. In the same year Hoffmann (4) was issued a German patent in which he described work done in 1883 on the reaction between cobalt and the nitrosonaphthols. A little later, Ilinski and von Knorre (6) reported the use of α -nitroso- β -naphthol for the separation of cobalt from nickel. This method of separation has been widely employed. Either the α,β or the β,α compound may be used; but until recently these reagents have been employed merely as precipitants, since the cobalt compounds precipitated in acetic acid solutions do not have the theoretical composition. In 1932, Mayr and Feigl (8) converted cobalt to the trivalent state before precipitating, and obtained a pure cobalt (III)-nitrosonaphtholate which could be dried and weighed directly.

The sodium salt of the α,β compound has been used for the colorimetric determination of cobalt by Atack (1) and Jones (7). Apparently the β,α compound has received very little attention, although Sarver (9) has recently used its 4-sulfonic acid derivative for the detection of cobalt, copper, and ferrous iron. Bellucci (3) reported that 1 mg. of cobalt in about 17 liters of solution can be detected colorimetrically

by means of the β,α compound as compared to 1 mg. in 1 to 2 liters with the α,β compound. The present study was made to determine the value of β -nitroso- α -naphthol as a colorimetric reagent for cobalt, the optimum conditions for its use, and the influence of ions most likely to interfere.

Apparatus and Reagents

All transmission measurements were made with the photoelectric spectrophotometer described by Barton and Yoe (2). The absorption cells have an internal thickness of 10 mm. The transmission values reported are on the basis that the transmission of the absorption cells filled with water is 100.0 per cent.

The β -nitroso- α -naphthol was obtained from the Eastman Kodak Company. The solid darkened at 156° and melted at 161–163° C. An aqueous solution of the sodium salt of the compound was prepared according to the directions of Atack (1) for the preparation of the sodium salt of the α,β compound. One-tenth gram of the reagent was mixed with 20 ml. of water, 1 ml. of molar sodium hydroxide was added, and the solution was heated until the compound completely dissolved and then diluted to 200 ml. The resulting 0.05 per cent solution is red, but when diluted to the concentration ordinarily employed—i. e., 0.0015 per cent—it is yellow with a slight reddish tinge. The reagent prepared in this way is stable for several weeks.

A standard stock solution of cobalt was made by dissolving 4.938 grams of cobalt nitrate hexahydrate in enough water to make 500 ml. This solution, containing 2.000 grams of Co^{++} per liter, was diluted to 10 p. p. m. and the dilution employed in the preparation of more dilute solutions as required.

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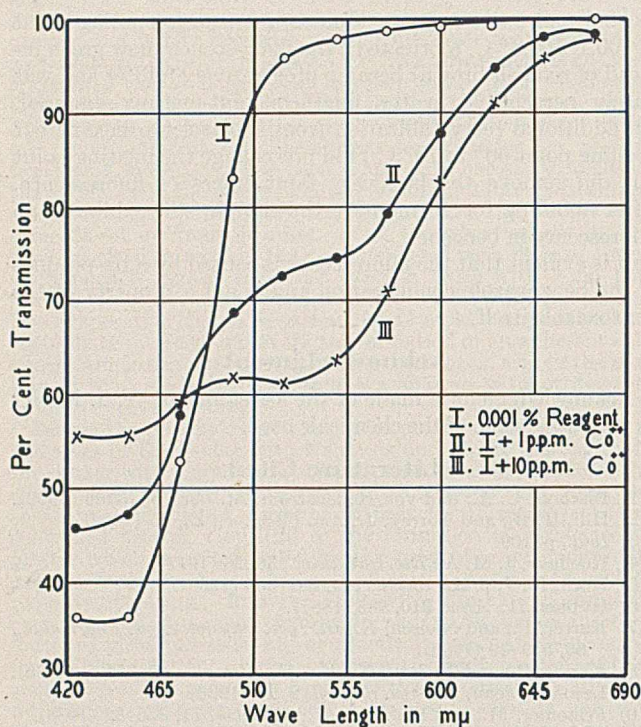


FIGURE 1. TRANSMISSION-WAVE LENGTH CURVE FOR REAGENT AND COBALT-REAGENT SOLUTIONS

Ammonium citrate solutions were prepared according to Snell and Snell (10) and contained approximately 0.6 gram of the salt per ml.

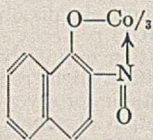
All other salts used were either reagent grade or c. p.

An approximately 3 M ammonia solution was made by diluting 100 ml. of concentrated ammonium hydroxide to 500 ml.

Optimum Conditions for Measurements

WAVE LENGTH. Transmission measurements were made at different wave lengths on reagent solutions and on cobalt-nitrosophthalate solutions in order to determine the wave length at which a maximum of sensitivity and a minimum of interference from the reagent are obtained. Figure 1 shows the transmission curves for a 0.001 per cent reagent solution (I), for a 0.001 per cent reagent solution containing 1.0 p. p. m. of Co⁺⁺ (II), and the same concentration of reagent with a large excess of Co⁺⁺ (III). All three solutions contained 5.0 ml. of ammonium citrate and 5.0 ml. of 3 M ammonia in 100 ml. of solution. It is apparent that the maximum difference between transmission of reagent solution and cobalt-nitrosophthalate solutions occurs at 525 and 550 mμ, respectively. Since the absorption of the reagent solution is considerably less at 550 mμ than at 525 mμ, the former wave length was chosen for transmission measurements involving transmission changes at only one wave length.

CONCENTRATION OF REAGENTS. Two milliliters of 0.05 per cent solution were used for 100 ml. of 1 p. p. m. Co⁺⁺ solution in the preliminary tests. This amount is slightly in excess of the 3 to 1 ratio required for the inner complex cobalt (III) salt



It was found, however, that there is a steady decrease in the transmission of the solutions at 550 mμ for about 25

minutes after mixing the reagents. The transmission is then fairly constant for several hours, until precipitation starts. When the concentration of reagent was increased to 3.0 ml. of 0.05 per cent solution in 100 ml. of 1 p. p. m. Co⁺⁺ solution, the transmission at 550 mμ became constant to within 0.1 or 0.2 per cent in 10 minutes or less after mixing the reagents.

Early in the investigation it became apparent that one of the principal disadvantages of the method is the pronounced influence of the ammonia concentration. The absorption of the cobalt-nitrosophthalate solutions at 550 mμ decreases markedly with increase in the concentration of ammonia.

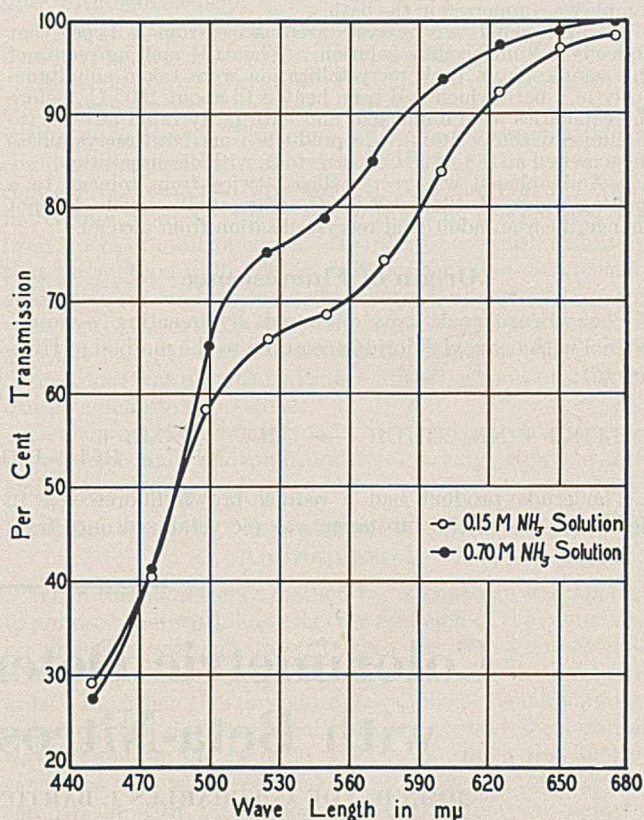


FIGURE 2. EFFECT OF AMMONIA CONCENTRATION ON TRANSMISSION OF 1 P. P. M. OF COBALT-REAGENT SOLUTIONS

Figure 2 shows the effect of a large increase in ammonia concentration on the transmission of a 1 p. p. m. cobalt solution containing 3.0 ml. of reagent solution and 5.0 ml. of ammonium citrate solution in 100 ml. The ammonia concentration chosen for work with 1 p. p. m. cobalt solutions—i. e., 5 ml. of 3 M ammonia in 100 ml. of solution—represents a compromise between two factors: sensitivity and stability. If the concentration of ammonia is increased, the sensitivity is reduced; if the concentration is decreased, precipitation of cobalt-nitrosophthalate starts more quickly. Solutions containing the above-mentioned amount of ammonia and 1 p. p. m. or less of cobalt are stable for several hours. An increase in the absorption at 550 mμ results when the complex cobalt salt begins to precipitate. In view of the instability of the cobalt-nitrosophthalate solutions at low ammonia concentrations, it seems advisable to make up fresh standards daily, if determinations are made by the standard series method. For accurate spectrometric and colorimetric work, frequent checks should be made on freshly prepared standard solutions.

Wide variations in the concentration of ammonium citrate have very little influence on the transmission of the cobalt

complex solutions at 550 $m\mu$. The change from 0.6 to 4.8 grams of ammonium citrate per 100 ml. of 1 p. p. m. cobalt in the cobalt-nitrosophthalate solution changed the transmission only 0.5 per cent. Ammonium tartrate gave similar results.

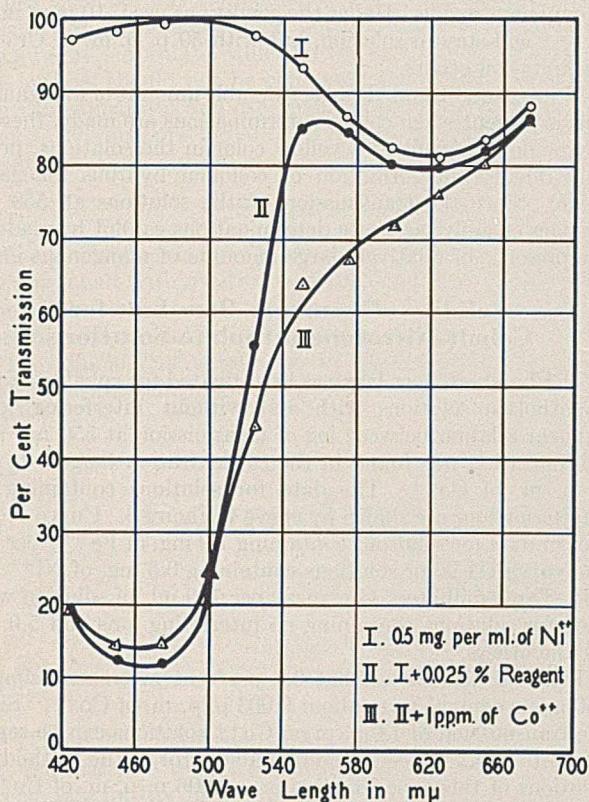


FIGURE 3. TRANSMISSION-WAVE LENGTH CURVES FOR NICKELOUS SOLUTIONS

The ammonium citrate serves to prevent the precipitation of small amounts of iron and certain other metals from the alkaline solutions. It also buffers the cobalt-nitrosophthalate solutions containing ammonia, permitting comparatively large amounts of sodium hydroxide, sodium salts, or ammonium salts to be added without causing a large change in the transmission of the solutions. The transmission at 550 $m\mu$ of a 1 p. p. m. Co^{++} solution containing 0.1 mole of sodium hydroxide per liter was 3.2 per cent higher than that of a similar solution without the sodium hydroxide. But in the presence of an equal amount of sodium chloride, the 0.1 molar sodium hydroxide produced only 0.6 per cent increase in the transmission.

ORDER OF MIXING REAGENTS. The usual procedure followed in preparing a cobalt-nitrosophthalate solution containing 1 p. p. m. of cobalt is to mix 10 ml. of 10 p. p. m. Co^{++} solution with 5.0 ml. of the ammonium citrate solution in a 100-ml. volumetric flask and add 5.0 ml. of 3 *M* ammonia solution. The solution is then diluted to 85 or 90 ml. with distilled water, 3.0 ml. of the 0.05 per cent reagent solution are added with shaking, and the solution is diluted to the mark and thoroughly mixed. If the ammonia and cobalt solutions are mixed before adding the ammonium citrate, the absorption is much less than when the usual procedure is followed.

REPRODUCIBILITY. To test the reproducibility of the reaction, five solutions of the cobalt complex salt were prepared by the above procedure and the transmission was measured at 550 $m\mu$. The average deviation from the mean transmission was 0.1 per cent.

Interference of Cations

It is frequently desirable to determine colorimetrically the concentration of one ion in the presence of another. The possibility of determining cobalt in the presence of several of the common metallic ions was studied.

NICKELOUS IONS. The interference of nickelous ions is readily apparent from Figure 3. Curve I represents a solution containing 50 mg. of Ni^{++} , 5.0 ml. of ammonium citrate solution, and 5.0 ml. of 3 *M* ammonia solution in 100 ml. The solution for curve II is the same as for I except that it also contained 5.0 ml. of reagent. The solution for III is the same as II except that it contained 1.0 p. p. m. of Co^{++} in addition to the other substances. The difference in transmission between solutions II and III at 550 $m\mu$ is 21.5 per cent, as compared to 28.8 per cent in the absence of interfering ions. The curves indicate that there is a reaction between the nickelous ions and the reagent.

Measurements of the transmission at 550 $m\mu$ of nickel-reagent solutions at intervals after mixing the reagents showed a change in transmission. The extent of the change and the length of time required for the transmission to become constant depend on the concentration of nickelous ions and on the concentration of reagent present. Increasing the concentration of reagent decreases the time required for the transmission to become constant.

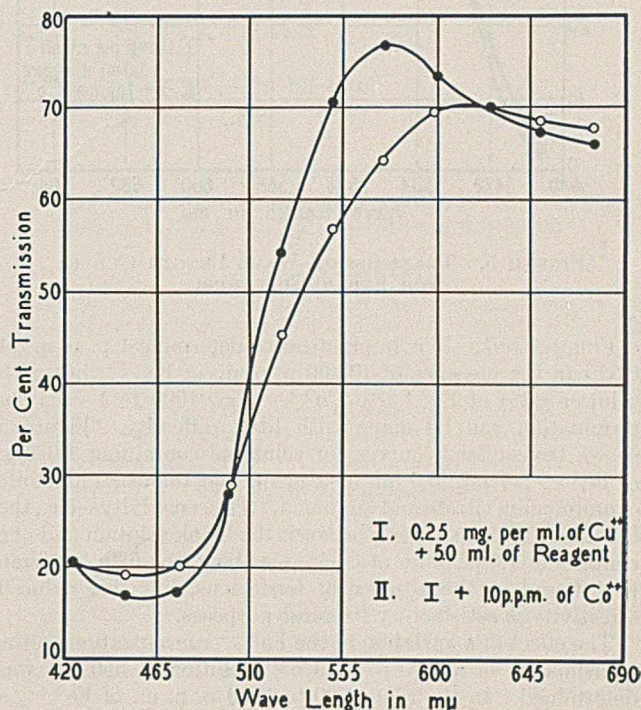


FIGURE 4. TRANSMISSION-WAVE LENGTH CURVES FOR CUPRIC SOLUTIONS (•, I; ○, II)

Variations in the nickel content of nickel-reagent solutions change the transmission at 550 $m\mu$ markedly, especially at the lower nickel concentrations. However, the same variations in nickel content of solutions containing 1.0 p. p. m. of Co^{++} caused little or no change in the transmission at 550 $m\mu$. This shows that for spectrophotometric determinations of cobalt it is not necessary to know accurately the nickel content of the sample.

CUPRIC IONS. Figure 4 shows transmission curves for two solutions containing 0.25 mg. per ml. of cupric ions. Solution II also contained 1.0 p. p. m. of Co^{++} . Five milliliters of reagent were used in 100 ml. of each solution. The curves

show that copper ions interfere to a greater extent than nickel ions, since the transmission difference at 550 $m\mu$ is 14.4 per cent, as compared to 23.2 per cent for similar solutions containing 0.2 mg. per ml. of nickelous ions.

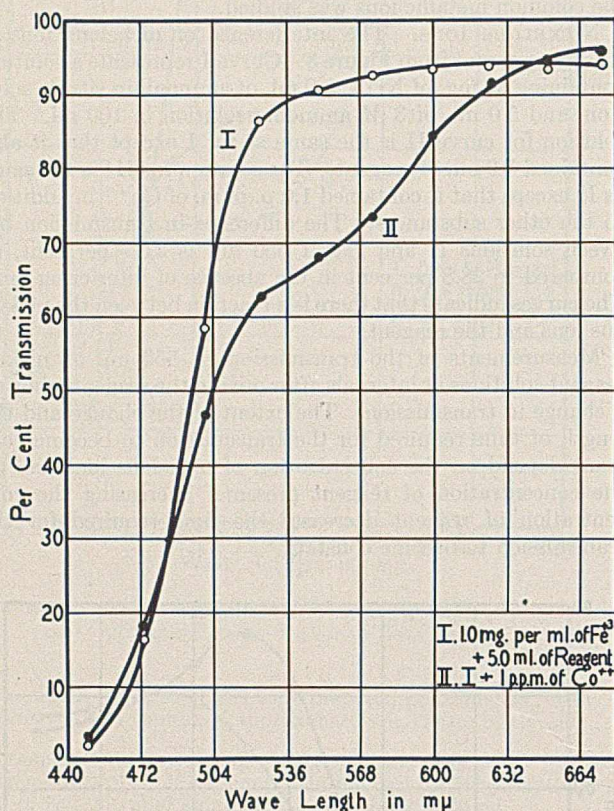


FIGURE 5. TRANSMISSION-WAVE LENGTH CURVES FOR FERRIC SOLUTIONS

FERRIC IONS. It is impractical to determine 1 p. p. m. of Co^{++} in the presence of 10,000 p. p. m. of Fe^{+++} , but with a lower ratio of Fe^{+++} to Co^{++} —e. g., 1000 to 1—the determination can be made with little difficulty. Figure 5 shows transmission curves for solutions containing 1.0 mg. of Fe^{+++} per ml., 5.0 ml. of reagent, and the usual amounts of ammonium citrate and ammonia. The sensitivity—i. e., the difference in transmission between the blank solution and one containing 1.0 p. p. m. of Co^{++} —is about one fifth less than that found in the absence of ferric ions, but this reduced sensitivity is satisfactory for most purposes.

The effect of a variation in the Fe^{+++} concentration on the transmission of a 1 p. p. m. Co^{++} solution at 550 $m\mu$ was determined. In the range 800 to 1200 p. p. m. of Fe^{+++} , a difference of about 20 p. p. m. of Fe^{+++} changed the transmission 0.1 per cent; hence, the iron content of the sample solution must be known fairly accurately, if error from this source is to be avoided.

The transmission at 550 $m\mu$ of a reagent solution containing 1000 p. p. m. of Fe^{+++} changed only slightly over a period of 2 hours after mixing the reagents, and the transmission of a similar solution containing 1 p. p. m. of Co^{++} did not change at all in this period. Visual observations, however, revealed a marked change in color within a few minutes after mixing the reagents. The solutions become yellower on standing. The change is probably due to the slow formation of colloidal hydrous ferric oxide. Increasing the concentration of ammonium citrate and decreasing the concentration of ammonia resulted in a decrease in the rate of change in color but did not entirely eliminate it. If the standard series

method is used, the effect of this change in color may be minimized by making up the sample solution and standard series at the same time.

CHROMIC IONS. Chromic ions do not interfere with the determination of cobalt to any appreciable extent, unless the concentration is high enough to cause precipitation of chromic hydroxide. Under the conditions used, 10 p. p. m. of Cr^{+++} will stay in solution, but with 50 p. p. m. of Cr^{+++} , precipitation occurs.

MANGANOUS IONS. If a considerable amount of manganous ions is present when cobalt determinations are made, there is a slow development of a yellow color in the solutions, probably due to the formation of colloidal hydrous manganic oxide. Since the transmission of the solutions at 550 $m\mu$ changes steadily, accurate determinations cannot be made in the presence of relatively large amounts of manganous ions.

Validity of Lambert-Beer Law for Cobalt-Nitrosophthalate Solutions

The Lambert-Beer law was investigated for cobalt-nitrosophthalate solutions with and without interfering ions. A linear relation between log of transmission at 550 $m\mu$ and concentration was found in the concentration range 0 to 1.0 p. p. m. of Co^{++} . The data for solutions containing no interfering ions are shown by curve I, Figure 6. Curve II is a plot of data for solutions containing 1.0 mg. of Fe^{+++} per ml. and curve III is for solutions containing 0.5 mg. of Ni^{++} per ml. Three milliliters of reagent per 100 ml. of solution were used for solutions containing no interfering ions and 5.0 ml. for the others.

Figure 6 also shows that 0.1 per cent in transmission at 550 $m\mu$ is equivalent to about 0.003 p. p. m. of Co^{++} . Since the transmission of 1.0 p. p. m. Co^{++} solutions can be reproduced to ± 0.2 per cent, the probable error of the method for solutions of this concentration is ± 0.006 p. p. m. of Co^{++} .

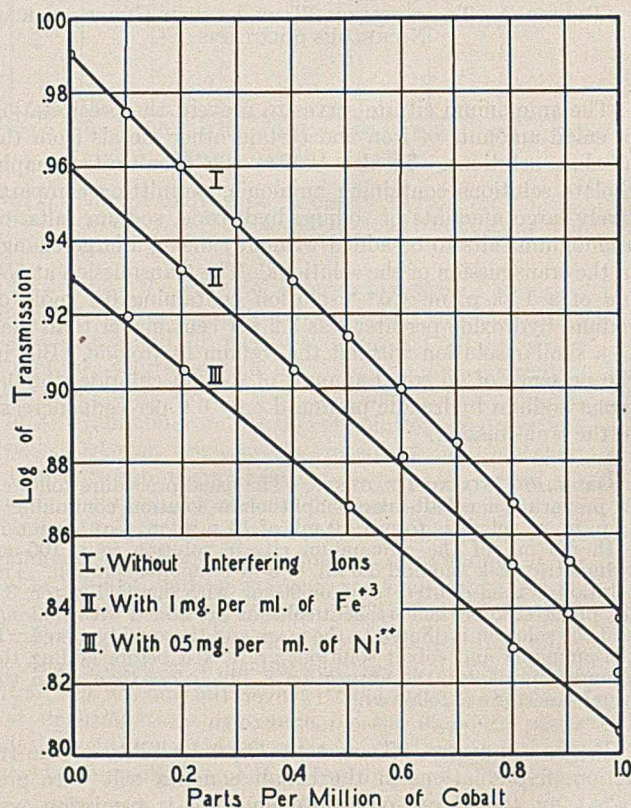


FIGURE 6. LOG TRANSMISSION-CONCENTRATION DATA FOR COBALT SOLUTIONS

Measurements with α -Nitroso- β -Naphthol

A few visual and spectrophotometric measurements showed that α -nitroso- β -naphthol has approximately the same sensitivity, 0.005 p. p. m., for cobalt ions as the β , α compound and that it is subject to the same limitations. Bellucci (3) claims that the β , α compound is ten or fifteen times more sensitive than the α , β isomer, but this was not confirmed by the authors. Absolute values for the sensitivities obtained by the authors should not be compared with those of Bellucci, since the apparatus and experimental conditions were not the same. The authors' visual observations were made in 50-ml. Nessler tubes (tall form) and in a roulette comparator (11).

Summary

In a spectrophotometric study of the colorimetric determination of cobalt with β -nitroso- α -naphthol the optimum conditions for measurements, the effect of salts, and the interference of certain metallic ions were determined.

The principal advantages of the method are its high sensitivity and reproducibility. The chief disadvantages are the

great influence of the ammonia concentration and the low solubility of cobalt-nitrosonephtholate.

Acknowledgment

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Correcting Ignited Silica Precipitates for Nonvolatile Material

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IT HAS long been standard practice in precise silica determinations to correct the weight of the ignited silica precipitate for the impurities present by volatilizing the silica as silicon tetrafluoride and then igniting and weighing the so-called "nonvolatile residue". This residue may amount to as much as 2 to 3 per cent of the weight of the silica and may contain a large number of constituents (2, 3, 8). Aurousseau (1) found over 30 per cent of the original titanium in this residue in the analysis of a certain silicate rock, and Bloor (2) found substantial amounts of both calcium and magnesium in the residues from certain clays.

Various methods have been used in correcting for this nonvolatile residue, all of which involve the assumption that the final residual material has the same effective weight as it had in the impure silica precipitate. Treatment of the silica precipitate with hydrofluoric acid alone is permissible if the residual material is not volatile on being evaporated to dryness with hydrofluoric acid and is converted to oxides by this evaporation or the subsequent ignition. However, Noyes and Bray (6) have shown that titanium is volatilized under similar conditions, and they minimize this loss by the addition of perchloric acid. In addition, after a treatment with hydrofluoric acid alone, alkaline earth elements would tend to remain as fluorides. Because of these undesirable effects a mixture of sulfuric and hydrofluoric acids is most commonly used, but this leaves the alkaline earths as the relatively stable sulfates, and, especially in the analysis of clays, the residue may contain a considerable proportion of calcium (2).

Kuzirian (4) proposed that the silica be treated with sulfuric acid prior to ignition; however, the sulfates thus formed are at least partially decomposed to silicates during the subsequent ignition. Pertusi and Di Nola (7) evaporated a hydrofluoric acid mixture to dryness, and then added oxalic acid to convert the fluorides to oxalates; in contradiction to the experiments of Noyes and Bray (6) they imply that the loss of titanium is not serious. Because of the apparent

limitations in these methods and of incomplete evidence as to their effectiveness, a study of processes for carrying out the correction of the silica precipitate has been made.

Experimental

In the experiments reported below the precipitates and residues were heated to constant weight in platinum crucibles over mantle burners producing a temperature of 1000° to 1200° C. The crucibles were cooled for a constant length of time and weighed within a closed, tared weighing bottle; weights were in general constant to 0.1 mg. The hydrofluoric acid and other reagents used were tested for nonvolatile materials and, where necessary, corrections for these were applied.

Methods Investigated

OXALIC ACID-HYDROFLUORIC ACID METHOD. The experiments of Noyes and Bray indicate that if titanium is to be provided for in the nonvolatile residue, an acid must be used which not only will be sufficiently nonvolatile to displace the fluorides but which will, by complex formation or otherwise, prevent the volatilization of titanium fluoride. Pertusi and Di Nola evaporated the silica precipitate twice to dryness with hydrofluoric acid, then treated with an excess of a saturated oxalic acid solution, evaporated to dryness, and ignited the residue. Using an artificial mixture containing 0.0917 gram of titanium dioxide, 0.0800 gram of ferric oxide, and 0.2023 gram of aluminum oxide they obtained a residue weighing 0.3700 gram. However, the experiments which are summarized in Table I indicate that there may be an appreciable loss of both titanium and aluminum by this process and that the percentage lost is apparently affected not only by the amount of these elements present but by the presence of other elements.

The titanium or aluminum oxide was ignited for 20 minutes at 1000° C., weighed, twice evaporated just to dryness with 10 ml. of 48 per cent hydrofluoric acid, treated with 10 ml. of a warm (40° to 50° C.) saturated oxalic acid solution, evaporated to dryness, again ignited, and weighed.

TABLE I. BEHAVIOR OF ALUMINUM AND TITANIUM OXIDES WITH HYDROFLUORIC AND OXALIC ACIDS

Experiment No.	Oxide Taken	(Method of Pertusi and Di Nola)	
		Original Weight	Loss of Weight
1	TiO ₂	15.15	6.15
2	TiO ₂	105.5	18.8
3	Al ₂ O ₃	152.8	12.4
4	Al ₂ O ₃	180.0	11.5
5	{ Al ₂ O ₃ TiO ₂	{ 165.5 152.0	{ 9.8

TABLE II. BEHAVIOR OF TITANIUM AND ALUMINUM OXIDES WITH A MIXTURE OF HYDROFLUORIC AND SULFURIC ACIDS

Experiment No.	Oxide Taken	Final Weight	
		Mg.	Mg.
1	TiO ₂	13.15	13.10
2	TiO ₂	187.0	186.8
3	Al ₂ O ₃	34.5	34.3

LOSS OF TITANIUM AND ALUMINUM WITH SULFURIC AND HYDROFLUORIC ACIDS. The experiments presented in Table II show that the loss of titanium and aluminum is negligible when sulfuric acid is used. In these experiments the ignited oxide was treated with a mixture of the two acids, evaporated to dryness, and ignited.

PERCHLORIC AND OXALIC ACIDS. The use of perchloric acid for dissolving fluorides (5) and the increasing use of this acid for the partial dehydration and precipitation of silicic acid suggested its use instead of sulfuric acid for displacing the fluoride from the residue. However, perchloric acid alone cannot be used, as the perchlorates of the alkali and alkaline earth elements decompose on ignition to give a residue containing chloride; furthermore, the oxidizing action accompanying this decomposition causes the platinum crucible to be appreciably attacked.

In an experiment demonstrating this effect 8.7 mg. of calcium oxide gave a residue weighing 12.1 mg. when evaporated with hydrofluoric acid and ignited for 5 minutes (theoretical for calcium fluoride, 12.0); upon treating this with 2 ml. of 9 N perchloric acid evaporating to dryness, and igniting for 1 minute the weight was 15.4 mg., which dropped to 11.2 after being ignited for 15 minutes. Upon being cleaned after ignitions of perchloric residues the platinum crucible lost as much as 2.5 mg. as compared with losses which usually were less than 0.1 to 0.2 mg. even after long ignitions.

In attempts to overcome these effects an excess of ammonium oxalate was added after evaporating the perchloric-hydrofluoric acid mixture almost or just to dryness. This was found to be effective in preventing attack on the crucible, but the solid had such a tendency to decrepitate and spatter that losses were likely to occur in the course of the operation. It was then found that the same effect could be obtained with solid oxalic acid and that the spattering was largely eliminated, the excess of oxalic acid subliming smoothly. The results of a series of experiments using this perchloric acid-oxalic acid treatment with various oxides are shown in Table III.

In these experiments the oxide was heated to about 1000° C. for 10 minutes, weighed, 1 ml. of 48 per cent hydrofluoric acid and 1 ml. of 60 per cent perchloric acid were added, the mixture was evaporated almost to dryness, and 50 to 75 mg. of solid oxalic acid were added. The mixture was heated until the excess of oxalic acid was sublimed, and the residue was ignited for 10 minutes and weighed, then again ignited for 20 minutes and weighed.

It is seen that the loss of titanium and aluminum has been reduced to an amount permissible with any except the most precise work; the fact that this loss is greater than with sul-

furic acid indicates that the latter acid has some specific property, possibly the ability to form complex compounds, which prevents the volatilization of the fluorides of these elements. The perchloric and oxalic acids have effectively decomposed calcium fluoride. Four determinations of the "nonvolatile residue" were made by this method in 0.5- to 1-gram samples of an ignited silica and gave an average value of 0.41 per cent; an average value of 0.45 per cent was obtained by the hydrofluoric-sulfuric acid method, the residue being shown by qualitative tests to be largely titanium.

TABLE III. BEHAVIOR OF VARIOUS OXIDES UPON BEING TREATED WITH HYDROFLUORIC, PERCHLORIC, AND OXALIC ACIDS

Experiment No.	Oxide Taken	Weight after Ignition for:	
		10 min.	30 min.
		Mg.	Mg.
1	CaO	10.3	10.5 ^a
2	CaO	7.7	7.75
3	TiO ₂	8.8	8.4
4	TiO ₂	9.1	8.7
5	TiO ₂	16.7	16.3
6	TiO ₂	12.0	11.6
7	Al ₂ O ₃	6.7	6.2
8	Al ₂ O ₃	33.4	33.2
9	Fe ₂ O ₃	10.3	10.0
10	MgO	5.9	5.7

^a Ignited for only 1 minute.

TABLE IV. BEHAVIOR OF OXIDES WITH HYDROFLUORIC AND OXALIC ACIDS

Experiment No.	Oxide Taken	Final Weight	
		Mg.	Mg.
1	CaO	27.0	29.0
2	CaO	26.2	28.6
3	CaO	57.6	63.9 ^a
4	Fe ₂ O ₃	13.9 ₅	14.10
5	TiO ₂	15.2	15.2
6	TiO ₂	13.6	13.5
7	Al ₂ O ₃	199.9	193.2
8	Al ₂ O ₃	77.0	72.4

^a This precipitate gradually lost 4.4 mg. upon being heated 135 min.

In none of the very large number of experiments in which perchloric acid has been heated with various organic compounds under the conditions of the above procedure has there been any indication of an explosion. This is undoubtedly due to the fact that the organic material is added in relatively large excess to a very small amount of perchloric acid. Care

TABLE V. BEHAVIOR OF OXIDES UPON TREATMENT WITH HYDROFLUORIC ACID AND WITH SUCCINIC AND OXALIC ACIDS

Expt. No.	Oxide Taken	Found	Acids Used			Remarks	
			HF	45% H ₂ C ₄ O ₄	H ₂ C ₂ O ₄		
1	CaO	50.5	66.3	10	1	No H ₂ C ₂ O ₄	
2	CaO	19.9	22.6	3	0.5	0.5	Three acids added together
3	CaO	14.5	14.4	10	1	0.6	H ₂ C ₄ O ₄ added with 3 ml. water, heated, HF added, evaporated, H ₂ C ₂ O ₄ added
4	CaO	22.4	22.4	5	0.5	0.6	HF added, then H ₂ C ₄ O ₄
5	CaO	22.6	22.6	3	0.5	0.6	As in Expt. 4
6	CaO	16.3	16.3	2	1	0.5	HF and H ₂ C ₄ O ₄ added, mixture heated to fusion of H ₂ C ₄ O ₄ , H ₂ C ₂ O ₄ then added
7	CaO	20.2	20.2	2	1	0.5	As in Expt. 6
8	CaO	17.3	20.5	2	1	0.5	As in Expt. 2
9	Al ₂ O ₃	20.2	20.2	10	1	0.6	As in Expt. 6
10	Al ₂ O ₃	19.0	18.8	10	1	0.6	As in Expt. 3
11	Al ₂ O ₃	25.7	24.8	1	1	0.5	As in Expt. 3
12	Al ₂ O ₃	8.4	7.9	2	1	0.5	As in Expt. 3
13	Al ₂ O ₃	37.0	35.6	2	1	0.5	As in Expt. 3
13a	Al ₂ O ₃	62.0	60.9	2	1	0.5	As in Expt. 3
14	TiO ₂	27.6	27.1	10	1	0.6	As in Expt. 3
16	TiO ₂	19.4	18.6	2	1	0.5	As in Expt. 6
17	TiO ₂	50.9	49.3	2	1	0.5	As in Expt. 3
17a	TiO ₂	29.0	27.7	2	1	0.5	As in Expt. 3
18	Fe ₂ O ₃	22.1	22.0	10	1	0.6	As in Expt. 3
19	SiO ₂	610	2.85	10	1	0.6	^a

^a This silica had been found by previous treatment with sulfuric and hydrofluoric acids to contain 0.45% of nonvolatile material, which agrees closely with residue obtained here; analysis of nonvolatile residue showed it to be largely titanium oxide.

should always be taken that only a small amount of perchloric acid is left in the crucible.

OXALIC AND SUCCINIC ACIDS SEPARATELY AND IN COMBINATION. Because of the known tendency of titanium and aluminum to form complex compounds with dicarboxylic acids, it seemed possible that the loss of these elements might be minimized by adding oxalic or some other high boiling dicarboxylic acid with the hydrofluoric acid; Pertusi and Di Nola evaporated to dryness with hydrofluoric acid and then used oxalic acid to displace any remaining fluoride. The results obtained with oxalic acid and hydrofluoric acid in such a procedure are shown in Table IV.

In these experiments the oxide was heated to about 1000° C. for 10 minutes and weighed, and 3 to 10 ml. of 48 per cent hydrofluoric acid were added together with from 0.5 to 2 grams of crystallized oxalic acid. The mixture was evaporated to dryness and ignited to constant weight.

Although the results are satisfactory with titanium, an appreciable amount of aluminum is lost and the oxalic acid alone has not decomposed the calcium fluoride. Other dicarboxylic acids were tried, including maleic, malonic, citric, and tartaric, but were unsatisfactory because of decrepitation or charring. Succinic acid seemed most promising, as it formed the anhydride which sublimed quietly. A series of experiments showed that this acid alone did not decompose calcium fluoride, but that decomposition was obtained if it was followed by oxalic acid. If the oxalic acid and succinic acids were added

simultaneously the conversion of fluoride to oxide was incomplete, probably because of rapid decomposition of the oxalic acid before the excess of fluoride was removed.

The results of experiments with these acids and various oxides (Table V) show that very satisfactory results can be obtained by the use of the two acids with calcium oxide but that there is still some loss with both titanium and aluminum.

Summary

An experimental study has been made of various methods for determining the "nonvolatile residue" in ignited silica precipitates by volatilizing the silica with hydrofluoric acid. For all except the most accurate work a treatment with perchloric and oxalic acids may be substituted to advantage for the sulfuric acid commonly used. Experiments with organic acids of high boiling point have not shown them to possess any marked advantages.

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Base-Exchange Capacity Determination of Soils and Other Materials Using Colorimetric Manganese Method

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CHEMISTS frequently have occasion to determine the base-exchange capacity of soils, clay minerals, artificial zeolites, and other substances. For this purpose a considerable variety of methods has been proposed. One of the commonly used methods involves saturation of the material in question with calcium by leaching with calcium chloride solution, after which the absorbed calcium is displaced by leaching with ammonium acetate solution and then determined after precipitation as the oxalate by titration with permanganate. Other methods based on the same principle but involving saturation with barium, ammonium, and other bases are in use, and methods involving electro dialysis are also employed. In an effort to provide a more rapid method, and particularly a colorimetric method adapted to micro work, it occurred to the writers that a procedure involving saturation with divalent manganese and oxidation of the manganese after displacement to permanganic acid offered possibilities. Tests of a procedure based on these principles gave very satisfactory results. The details of the procedure as finally developed follow.

Analytical Procedure

Place a 1-gram sample of the soil (air-dried and 20-meshed, or suitable quantity of other material in a 100-cc. centrifuge tube. Add 50 cc. of a 1 N manganous chloride solution, stopper the tube, and shake vigorously for 5 minutes. Remove and wash off the stopper and the sides of the tube with neutral 95 per cent alcohol. Clear the suspension by centrifuging for 5 minutes at about 1500 r. p. m. and pour off the supernatant liquid. Repeat this treatment five times with portions of 1 N manganous chlo-

ride. Five washings are sufficient for saturation with manganese. Remove the excess of manganous chloride by successive washings with 50-cc. portions of neutral 95 per cent ethyl or methyl alcohol, using the shaking and centrifuging procedure. Wash until washings no longer give a test for chlorides. Four washings usually suffice.

Displace the exchangeable manganese by washing with five successive 50-cc. portions of 1 N ammonium acetate, using the same shaking and centrifuging procedure as during saturation. Make up the washings to a volume of 500 cc. Place an aliquot of this solution containing 0.25 to 0.75 mg. of manganese, in a 150-cc. beaker and evaporate to dryness. To destroy carbonaceous material, wash down the sides of the beaker with 2 to 3 cc. of concentrated nitric acid, and again evaporate to dryness. If necessary, repeat this treatment until all carbonaceous material is destroyed. Two treatments usually suffice. Add 5 cc. of concentrated sulfuric acid, dilute cautiously with about 15 cc. of water, and then add 0.2 gram of para-sodium periodate. Boil gently until the color of permanganic acid appears. This oxidation is greatly promoted by having a small volume. Now dilute with water to a volume of about 90 cc., cover with a watch glass, and set on a hot plate at 85° to 90° C. for about 30 minutes to ensure complete oxidation. Distilled water often contains traces of reducing substances, and when nearly all the diluting water is added prior to heating, these reducing substances are quickly and completely destroyed by the excess of periodate. Cool and dilute to a volume of 100 cc. Compare with a standard permanganate solution by means of Nessler tubes or use a photoelectric colorimeter equipped with a 5200 Å. wave-length color filter.

For saturation and displacement, the leaching method may, of course, be used. The centrifuge method, however, expedites the process because of the disintegration of granules, vigorous agitation, and hence nondependence on slow diffusion. The

use of the special centrifuge tube and shaking machine described by Truog *et al.* (2) greatly facilitates the operation of the centrifuge method.

In microdeterminations a pointed centrifuge tube should be used. The special tube described by Pearson and Truog (1) is very convenient. The volume of liquid used in each treatment for saturation, washing, and displacement may be reduced to 25 cc. and the centrifuge tube should be stoppered while centrifuging to prevent dust contamination from the air. In micro work, all the displacing solution is used for the determination.

TABLE I. BASE-EXCHANGE CAPACITIES OF SOILS AND OTHER MATERIALS

Soil Type or Material	Calcium Saturation Method	Manganese Saturation Method	Ammonium Saturation Method
	Milliequivalents per 100 grams		
Miami silt loam (A horizon)	11.1	11.2	9.7
Carrington silt loam (A horizon)	16.9	17.2	16.5
Barnes silty clay loam (A horizon)	34.2	34.1	32.1
Laterite from Hawaii	11.0	10.8	10.2
Brown peat	90.5	91.0	89.3
Sarpy silt loam (A horizon)	9.3	9.5	8.4
Barnes silty clay loam (calcareous C horizon)	...	18.2	16.9
Bentonite	124.0	124.5	117.0
Artificial zeolite	293.1	293.0	294.2
Clay separate from Chico silty clay loam	48.5	48.0 ^a	...
Clay separate from Hagerstown silt loam	21.0	20.5 ^a	...
Bentonite	124.0	125.0 ^a	...

^a Determination made by microprocedure using sample weight of only 10 mg.

Preparation of Reagents

STANDARD PERMANGANATE SOLUTIONS. Prepare a solution of potassium permanganate which is 0.04 *N* with respect to Mn^{++} (0.1 *N* with respect to oxidation-reduction) by titration against sodium oxalate. Dilute 50 cc. of this solution to 1 liter. The resulting solution is 0.002 *N* with respect to Mn^{++} . Place exactly 50 cc. of this second solution in a 1-liter beaker, and add 850 cc. of water, 2.0 grams of para-sodium periodate, and 50 cc. of concentrated sulfuric acid. Heat to boiling, then cool to room temperature, transfer to a 1-liter volumetric flask, and dilute to the mark. This solution is 0.0001 *N* with respect to Mn^{++} , and is stable on long standing owing to the presence of the periodate.

APPROXIMATELY 1 *N* MANGANOUS CHLORIDE SOLUTION. Dissolve 98.9 grams of manganous chloride tetrahydrate in 1000 cc. of water. Filter through a fine-textured filter paper. The pH of this solution should be in the range of 6.5 to 7.0. Ordinary c. p. or pure manganous chloride tetrahydrate is satisfactory.

APPROXIMATELY 1 *N* AMMONIUM ACETATE. Dilute 67 cc. of c. p. concentrated ammonium hydroxide to about 800 cc., and add 57 cc. of c. p. concentrated acetic acid. Adjust to pH 6.8 with ammonia or acetic acid as the case requires and dilute to 1 liter.

Results

In order to check the accuracy of this method involving saturation with manganese, the base-exchange capacities of a wide variety of soils and other materials were determined by means of this method and two other methods involving saturation with calcium and ammonium, respectively.

In determining base-exchange capacity by means of the calcium ion the samples were first treated with neutral 1 *N* barium acetate solution to displace any exchangeable hydrogen. After saturation with calcium by treatment with neutral 1 *N* calcium chloride solution, the excess calcium chloride was removed by washing with 95 per cent methyl alcohol, and the exchangeable calcium, representing the base-exchange capacity, was displaced with 1 *N* ammonium acetate solution. The displaced calcium was determined by precipitation as the oxalate and titration with standard permanganate solution. In the method involving saturation with ammonium, the samples were saturated with ammonium by treatment with neutral 1 *N* ammonium acetate solution. After washing out the excess ammonium acetate, the exchangeable ammonium, representing the base-exchange capacity, was displaced with 1 *N* potassium chloride solution and determined by titration after the addition of a base and distillation.

The base-exchange capacities of a number of soils and other materials as found by means of the three methods are given in Table I.

The results obtained involving saturation with manganese and calcium are in good agreement, while those obtained involving saturation with ammonium are somewhat lower in those materials where the base-exchange capacity is due largely to clay minerals. In order to determine whether the base-exchange capacity of clay minerals is appreciably variable, depending upon the base used for saturation, further base-exchange capacity determinations of bentonite involving saturation with other bases were made. Samples of the ammonium-saturated bentonite were saturated with the various bases by treatment with an appropriate neutral salt solution. After the excess salt was removed by alcohol washings, the exchangeable base, representing the base-exchange capacity, was displaced with 1 *N* ammonium acetate solution and determined. Table II gives the salt solution used for saturation, the respective base-exchange capacities found, and the analytical procedure used in each case.

The results for base-exchange capacity of the bentonite when determined by means of the monovalent bases sodium, potassium, and ammonium are in good agreement. Considerable variation, however, occurs when the base-exchange capacity is determined by means of various divalent bases, and in all cases the capacities are higher than when determined by means of the monovalent bases. When the values for the divalent alkaline earth bases are compared, it is noted that they become increasingly greater as the strength of the base becomes less. Beryllium, which is the weakest base of this group, gives a value just double that obtained with the monovalent bases.

Preliminary investigations indicate that the clay acids, like other weak acids, form basic salts with certain divalent bases, and the weaker the base, the greater is this tendency to form basic salts. This would explain the variations in base-exchange capacity found with different divalent bases. Since it is impossible for monovalent bases to form basic salts, the use of these bases in the determination of base-exchange capacity gives results which are in good agreement, but usually lower than the results obtained with the divalent bases. These differences are hardly noticeable with materials of comparatively low base-exchange capacity, like some soils. With materials of high base-exchange capacity, however, the differences may become large.

Since calcium is normally by far the most abundant exchangeable base naturally found in soils, a method involving

TABLE II. BASE-EXCHANGE CAPACITY OF BENTONITE WITH DIFFERENT BASES

Base Involved	Solution Used for Saturation	Base-Exchange Capacity Found	Analytical Procedure Followed
		Milliequivalents per 100 grams	
NH ₄	1 <i>N</i> NH ₄ C ₂ H ₃ O ₂	117.0	Distilled and titrated with acid
Na	1 <i>N</i> NaCl	116.5	Precipitated and weighed as sodium zinc uranylacetate
K	1 <i>N</i> KCl	117.5	Volumetrically as cobaltinitrite
Ba	1 <i>N</i> BaCl ₂	118.2	Gravimetrically as barium sulfate
Sr	0.2 <i>N</i> SrCl ₂	119.5	Precipitated as strontium oxalate and weighed as strontium carbonate
Ca	1 <i>N</i> CaCl ₂	124.0	Volumetrically as oxalate
Mg	1 <i>N</i> MgCl ₂	130.8	Gravimetrically as magnesium pyrophosphate
Be	0.1 <i>N</i> Be(NO ₃) ₂ ^a	234.0	Gravimetrically as beryllium oxide
Mn	1 <i>N</i> MnCl ₂	124.5	Colorimetrically as permanganic acid

^a Solution had a pH of 4.0 due to hydrolysis.

saturation with a base which gives approximately the same value as saturation with calcium should be satisfactory for practical purposes. On this basis, the proposed colorimetric method involving saturation with manganese is satisfactory.

Summary

A rapid and accurate colorimetric method for the determination of the base-exchange capacity of soils and other materials has been developed involving saturation with divalent manganese by treatment with manganous chloride solution. After displacement, the manganese is oxidized to permanganic acid and determined colorimetrically. Color comparisons are conveniently made by means of either Nessler tubes or a photoelectric colorimeter. Comparative results obtained involving

saturation with calcium and manganese are in good agreement. Complete saturation with manganese is easily effected, since hydrogen and other common cations are readily displaced by manganese. Moreover, the method is sensitive and well adapted for micro work.

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Extraction of Alkalies in Rocks

Modification of the J. Lawrence Smith Extraction, Using Barium Chloride as a Flux

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THE J. Lawrence Smith method of extracting alkalies from rocks (7, 8) has largely replaced the older Berzelius procedure (1) in which the rock is decomposed with hydrofluoric and sulfuric acids. Smith's first studies on this subject dealt with the decomposition of silicates by sintering them with lime in the presence of fluxes of calcium fluoride or calcium chloride, either added directly or formed by the double decomposition of lime and ammonium chloride.

Twenty years later Smith devised the process used so extensively today.

In this process the sample, ground to an impalpable powder, is intimately ground with an equal weight of ammonium chloride and eight times its weight of calcium carbonate. This mixture is placed in a long crucible (known as a J. Lawrence Smith crucible) and first heated slowly until no odor of ammonia can be detected and the chloride ion has been fixed as calcium chloride, after which the charge is ignited strongly for 40 to 60 minutes. From the sintered cake thus obtained the alkalies are extracted as water-soluble chlorides essentially free from all impurities save sulfates and borates.

A few modifications of the J. Lawrence Smith procedure have appeared in the literature.

Somewhat similar is the method of Mäkinen (5) in which the finely ground sample is fused with calcium chloride alone. Büttner (3) proposes the use of barium carbonate instead of calcium carbonate, in this way obtaining more precise although apparently low results. Scholes and Wessels (6) sinter the sample with calcium carbonate and calcium chloride, made by treating calcium carbonate with a deficiency of hydrochloric acid and heating at 800° to 900° C. Breeman and Scholes (2) obtained best results in the J. Lawrence Smith method by heating at 800° C. for 45 minutes.

The method here described, involving simply the substitution of 1 gram of hydrated barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) for 0.5 gram of ammonium chloride, eliminates most of the deficiencies of the J. Lawrence Smith procedure. The preliminary slow heating of the charge to remove ammonia, a step which usually takes the writer 0.75 hour, is unnecessary and the charge is brought to redness by heating only sufficiently slowly to prevent expulsion of the powder. Another defect of the J. Lawrence Smith procedure is contamination of the alkali chlorides by sulfates, and the barium chloride procedure yields alkali chlorides essentially free of sulfates. Samples high in sulfates, such as alunite, in the J. Lawrence

Smith method do not yield sintered cakes but fused masses, difficult to remove from the crucible and to leach. Alunite, as well as all other samples tested, gives with the barium chloride method sintered cakes which shrink from the sides of the crucible and loosen when tapped lightly with the hand. The cakes also disintegrate readily in water.

Reagents

Barium chloride dihydrate. The analytical reagent grade is recrystallized to free it from alkalies.

Calcium carbonate, analytical reagent grade. If a blank test shows it to contain appreciable alkalies, it is purified by dissolving in hydrochloric acid and precipitating with ammonium carbonate.

Ammonium carbonate solution, a saturated solution in 1 to 1 ammonium hydroxide.

Procedure

Place 0.5 gram of the sample, accurately weighed, in a large agate mortar and grind to an impalpable powder, being careful to avoid loss of flying particles. Add about 1 gram of barium chloride and grind intimately with the sample. Add in small portions 4 grams of calcium carbonate, a little of which is first put in the J. Lawrence Smith crucible to cover the bottom, and grind to apparent uniformity. Transfer the mixture to the J. Lawrence Smith crucible and use a little of the calcium carbonate for rinsing the mortar.

Place the crucible with its contents in an inclined position in a firebrick chimney, the covered top extending out far enough to serve as a condenser. Heat to redness just slowly enough to prevent expulsion of the powder by the hot gases. Heat the crucible and contents to bright redness for half an hour and allow to cool.

Shake or tap the crucible lightly to loosen the sintered cake, or loosen with a platinum rod, and empty the cake into a platinum or fused silica dish. Cover with hot water and leave on the steam bath half an hour. Add hot water to the emptied crucible and digest in a hot-water bath. The sintered cake disintegrates into a fine powder in the hot water. Filter the contents of the crucible and dish into a capacious platinum dish, transfer the powder to the filter, and wash with about 500 ml. of hot water in small portions until essentially free of chlorides.

Evaporate the filtrate to a small volume, or even to dryness, take up in about 100 ml. of water, and precipitate the calcium by adding sufficient redistilled ammonia and an excess of ammonium carbonate at boiling temperature. Filter, and wash the precipitated calcium carbonate five times with hot water. Return the precipitate to the dish with a stream of water, dissolve in a slight excess of hydrochloric acid, neutralize with ammonia, and reprecipitate the calcium at boiling temperature with ammonium carbonate. Filter, and wash the precipitate six times with hot water.

Evaporate the combined filtrates in a platinum dish to dryness and carefully volatilize the ammonium salts by ignition short of redness. Cool, add 25 ml. of water to the covered dish, add a few crystals of ammonium oxalate and a drop of ammonium hydroxide, and place on the side of the steam bath for 15 minutes. Remove, allow to cool, add a few drops of ammonium carbonate solution (to precipitate barium not previously removed as carbonate), and after a few minutes filter and wash the precipitate with a weak solution of ammonium oxalate (0.1 per cent) containing a few drops of the ammonium carbonate solution. Evaporate the filtrate in a platinum dish to dryness and again volatilize ammonium salts at a temperature short of redness.

Cool, add a slight excess of hydrochloric acid to convert the alkali carbonates to chlorides, evaporate in a small platinum dish to dryness, then ignite at a barely perceptible red heat to constant weight. Dissolve the alkali chlorides in hot water, filter through a small ashless filter paper, wash thoroughly with hot water, place the filter paper in the dish, ignite, and weigh. Subtract the weight of the dish plus residue from that of the dish plus residue plus alkali chlorides to obtain the weight of alkali chlorides. In the filtrate, containing the chlorides of the alkalies, separate potassium (rubidium and cesium) from sodium (and lithium) by the chloroplatinate method as given by Hillebrand and Lundell (4), and obtain the weight of sodium chloride by difference.

A more accurate figure for sodium is probably obtained by weighing it as sulfate, after separating the potassium as chloroplatinate and removing the excess platinum with formic acid. Evaporate the sodium fraction from the precipitation of potassium chloroplatinate to dryness, take up in 20 ml. of water, add a few drops of formic acid, and again evaporate to dryness. Add a few milliliters of water and filter off the precipitated platinum, washing with hot dilute hydrochloric acid (1 to 99). To the filtrate in a small platinum dish add a slight excess of sulfuric acid, evaporate, dry, and ignite carefully to remove excess sulfuric acid. To remove the last trace of sulfuric acid dissolve the sodium sulfate in water, add a few drops of ammonia, again evaporate to dryness, and ignite to constant weight. Obtain the weight of sodium sulfate by difference after weighing the dish and insoluble residue.

Analytical Studies

CONTAMINATION OF ALKALIES BY MAGNESIUM. Incomplete removal of magnesium is believed by some analysts to be a defect of the J. Lawrence Smith method. Hillebrand and Lundell (4) suggest a treatment with saturated lime solution to ensure its removal. But during the ignition calcium oxide is formed and when the cake is put in water the resulting calcium hydroxide probably prevents solution of most of the magnesium. Furthermore, in the final ignition of the alkali chlorides a partial conversion of hydrated magnesium chloride to oxide would result and part of any magnesium remaining would be made insoluble.

Tests were made to determine how much magnesium from minerals rich in that element contaminated the alkali chlorides when the J. Lawrence Smith procedure and the barium chloride procedure, here given, were followed. Alkali chlorides obtained from a biotite (16.15 per cent magnesium oxide) from Ridgway, Va., by both procedures, gave no definite test for magnesium in a volume of 50 ml. by the ammonium phosphate test even after standing 3 days. Similar results were obtained on a sample of talc (31.7 per cent magnesium oxide) when treated by each method.

CONTAMINATION OF ALKALIES BY SULFATES. Alunite containing 20.93 per cent of sulfur trioxide was treated by both methods to test the removal of sulfates. After removal of most of the calcium as carbonate the solution from the ammonium chloride procedure contained 0.0268 gram of sulfate, probably all of which would be found in the alkalies finally weighed unless removed by special treatment with barium chloride. An experiment with the barium chloride procedure gave but 0.0006 gram of sulfate at the same stage in the process. As the solution at this point was found to contain a much larger quantity of barium, the sulfate probably escaped elimination owing to solubility, formation of colloidal barium sulfate, or inversion because of the alkaline nature of the solution.

TABLE I. COMPARISON OF RESULTS BY J. LAWRENCE SMITH AND BARIUM CHLORIDE METHODS

Procedure A: J. Lawrence Smith; Na weighed as NaCl; K weighed as K_2PtCl_6 .
 Procedure B: Barium chloride method; Na weighed as NaCl; K weighed as K_2PtCl_6 .
 Procedure C: Barium chloride method; Na weighed as Na_2SO_4 ; K weighed as K_2PtCl_6 .

Pro- ce- dure	Material and Location						
	Alunite, Marys- vale Utah %	Micro- cline, Bedford, Va. %	Monzonite porphyry, Henry Mts., Utah %	Biotite, San Diego, Calif. %	Albite, Pala, Calif. %	Beryl, Buckfield, Maine %	
Li_2O	A	1.17	...	0.56	
	B	0.01	...	1.20	
	C	1.17	...	0.47	
Na_2O	A	0.69	2.01	9.18	0.19	11.58 ^a	0.96
	B	0.53	2.05	9.16	0.42	11.80	...
	C	...	2.07	9.09	0.28	11.46	0.96
K_2O	A	5.34	13.66	0.94	8.90 ^b	0.30	0.43 ^b
	B	5.32	13.73	0.97	8.83 ^b	0.40	...
	C	...	13.64	1.01	9.02 ^b	0.42	0.42 ^b

^a Theory 11.49, taking K_2O as 0.40%, finding 0.08% CaO, and subtracting for orthoclase and anorthite.

^b (K, Rb, Cs): $PtCl_6$ reported as K_2O .

Another experiment showed that this small quantity of sulfate is subsequently removed, as the purified alkali chlorides failed to give a definite test for sulfate.

VOLATILIZATION OF ALKALIES DURING SINTERING PROCESS. Barium chloride melts at a temperature of about 962° C. and apparently the barium chloride method would require a higher temperature than the usual method for the reaction to begin, possibly resulting in volatilization of alkalies. It is believed, however, that with respect to loss of alkalies the barium chloride method has advantages, because the volatile gases (carbon dioxide and water) would be removed at a lower temperature, before the reaction begins, and would not serve to sweep out volatilized alkalies and prevent their condensation on the cooler part of the crucible.

COMPARISON OF THE TWO METHODS. Samples were available which had previously been analyzed for alkalies by the J. Lawrence Smith method and these results together with those by the new method are given in Table I. The monzonite porphyry listed contained 2.93 per cent of sulfur trioxide and special treatment was needed to remove it when the usual J. Lawrence Smith procedure was used.

The results for sodium may be slightly high where it is weighed as chloride because of incomplete drying and failure to remove the barium completely. On the other hand, the results for sodium may be slightly low because of too intense heating prior to weighing and volatilization of sodium chloride. For these reasons weighing the sodium as sulfate, as was done in procedure C of Table I, seems preferable.

Lithium was determined by the Palkin method as described by Wells and Stevens (9).

The results by the two methods are closely comparable and neither has the advantage as to completeness of extraction of alkalies. However, the barium chloride method offers a saving in time and the automatic elimination of sulfate.

Conclusions

A modification of the J. Lawrence Smith method for the extraction of alkalies from rocks and silicate minerals is described, in which barium chloride is substituted for the ammonium chloride customarily used in the sintering mixture. The two methods are of equal value in completeness of alkali extraction, but the modification allows a saving of time and automatically removes any sulfate the sample contains. The barium chloride method is advantageously used in analyzing alunites because a molten mass does not result and the cake is easily removed from the crucible and disintegrated in

water. Neither method seems to be affected by a large magnesium content in the sample.

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Stable 2,6-Dichlorobenzeneindophenol Solutions

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STANDARDIZED aqueous solutions of the oxidation-reduction indicator, sodium 2,6-dichlorobenzeneindophenol (sodium 2,6-dichlorophenolindophenol) have, for some time, had widespread use in the determination of vitamin C in biological materials (1, 2, 9, 10). Solutions of this dyestuff have also been used by this laboratory in studies on the state of oxidation of malt beverages (4, 5, 6).

The aqueous solutions of this dyestuff are relatively unstable, as shown in Table I, and require frequent fresh preparation and standardization and storage in the cold. This instability is a serious disadvantage in connection with the use of the indicator solution in brewing as well as for vitamin C tests, especially where means for frequent standardization and refrigeration are not available.

TABLE I. STABILITY OF AQUEOUS SOLUTIONS OF SODIUM 2,6-DICHLOROBENZENEINDOPHENOL

Temperature of Storage ° C.	Assay ^a			
	Initial	2 days	4 days	8 days
	Mg. per 100 ml.			
2	153	149	147	143
20	153	138	129	112
30	153	133	105	ca. 90
37	153	123	ca. 80	..

^a All assays in this paper are reported as mg. of sodium 2,6-dichlorobenzeneindophenol per 100 ml. of solution.

Attempts to improve stability by ether extraction of the dry dyestuff prior to dissolving in water, as suggested by Knight, Dutcher, and Guerrant (?), produced no marked improvement with the author's dyestuff. The use of nonaqueous organic solvents was then tried.

It was found that when the sodium 2,6-dichlorobenzeneindophenol was dissolved in dioxane acidified with glacial acetic acid, stable solutions were obtained. Results of assays of 0.005 M solutions of the dyestuff in dioxane which were stored at room temperature in the laboratory are tabulated in Table II. These results reflect the great improvement in stability obtained over the aqueous solutions and indicate a loss of strength of only about 2 mg. per month.

TABLE II. STABILITY OF DIOXANE SOLUTIONS OF 2,6-DICHLOROBENZENEINDOPHENOL AT ROOM TEMPERATURE

Sam- ple	Stand- ing	Assay	Sam- ple	Stand- ing	Assay	Sam- ple	Stand- ing	Assay
		Mg. per 100 ml.			Mg. per 100 ml.			Mg. per 100 ml.
	Months			Months			Months	
A	Initial	146	B	Initial	147	C	Initial	146
	1	144		2.5	144		2	141
	3.5	139						

The rate of evaporation of dioxane is not appreciably greater than of water (vapor pressure at 20° C.: dioxane, 26 mm. of mercury; water, 18 mm.) and no trouble should be encountered from this source. However, during the vitamin C titrations the volume of the dioxane solution added should not exceed more than about 10 per cent of the total volume, as the presence of excessive amounts of dioxane may interfere with the sharpness of the end points.

Commercial dioxane, especially if it has been standing for some time, contains small amounts of peroxides, but these can be eliminated almost completely by distillation. Traces of peroxides in the dioxane have no effect on the vitamin C titrations, but they do interfere in the standardization if the iodide-sulfuric acid method (3, 8) is used. Standardization of the dioxane solutions against one of the ascorbic acids avoids this interference.

Method of Preparation

Distill 500 ml. of dioxane, discarding the first 50 ml. and the last 50 ml. Weigh out sufficient sodium 2,6-dichlorobenzeneindophenol to give a final solution slightly stronger than needed (usually about 0.2 gram per 100 ml. for 0.005 M, but the assay of different batches of the dry indicator varies). This permits dilutions to exact strength if desired.

Stir the indicator into the dioxane and add 1 ml. of glacial acetic acid for every 100 ml. of solution. Stir thoroughly for about 15 minutes, breaking up any lumps with a stirring rod. Filter through a dry No. 42 Whatman filter paper and standardize the clear red filtrate.

Standardize against pure ascorbic acid in the usual manner, keeping the volume of added dioxane below about 10 per cent of the total volume.

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Removal of Sulfur from Laboratory Glassware

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TO REMOVE sulfur from laboratory glassware, all that is needed is tap water or hot water. Water should be allowed to remain in the glassware for a day or longer, and the removal may be accomplished by using a knife, file shank, or stirring rod as a reamer to aid loosening caused by the solvent power of the water. In more stubborn cases the sulfur is heated and run down the sides of the vessel, allowed to cool, and then given the water treatment. On standing, the sulfur cracks from the sides of the glassware and falls to the bottom.

Determination of Sodium in the Presence of Other Metals

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THIS paper concerns experimental work undertaken to ascertain whether sodium could be quantitatively determined by the magnesium uranyl acetate method in the presence of the following metals: beryllium, cerium, columbium, lanthanum, neodymium, tantalum, thallium, thorium, vanadium, and zirconium. Because of the necessity of removing silica from the samples to be analyzed, fluorine and sulfuric acid were also investigated.

The effect of many other metals has been reported by Barber and Kolthoff (1, 2), Kolthoff (7), Bridges and Lee (3), and others. Some of the work was done with the zinc uranyl acetate reagent. Their work was checked by this laboratory using the magnesium uranyl acetate reagent in place of the zinc uranyl acetate reagent in the presence of aluminum, calcium, chromium, iron, and titanium; the former gave as accurate sodium determinations in the presence of these metals as the latter.

All the sodium determinations were made with a slight modification of the method of Caley and Faulk (5) revised by Caley and Sickman (6). The reagent (in two solutions) is prepared as follows:

Solution A		Solution B	
Uranyl acetate	90 grams	Magnesium acetate	600 grams
Acetic acid	60 grams	Acetic acid	60 grams
Water to make	1000 ml.	Water to make	1000 ml.

Heat separately to 70° C. to obtain clear solutions. Mix and cool to between 20° and 30° C., and allow to stand overnight before using. Because of traces of sodium in the reagents, the solution will be saturated with the sodium magnesium uranyl acetate and the excess will be precipitated. Filter the reagent immediately before using at a temperature not to exceed 30° C. and carry out all subsequent work with the reagent at this temperature. Caley and Faulk recommend 20° C. for all work, but consistent results were obtained anywhere between 20° and 30° C., providing the precipitation and filtration were carried out at the same temperature at which the fresh reagent was filtered.

Reduce the volume of the neutral or slightly acid solution containing the sodium as the chloride or sulfate to 3 to 5 ml., rapidly

add 100 ml. of freshly filtered reagent, and mix the two solutions. Stir the solutions for 30 minutes and filter in a Gooch crucible, using gentle suction. Wash the precipitate with 10 ml. of the reagent and then with 20 to 30 ml. of alcohol previously saturated with the precipitate. Dry the crucible in an oven at 105° C. for 30 minutes and weigh as $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3(\text{UO}_2) \cdot (\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 6\frac{1}{2}\text{H}_2\text{O}$. The weight of precipitate times 0.0153 equals the weight of the sodium. In no case should more than 10 mg. of sodium be determined unless 10 ml. more of reagent are used for each additional milligram of sodium.

In these experiments volumes of standard sodium chloride solution equivalent to 1, 5, or 10 mg. of sodium were added to known amounts of the salts to be tested.

TABLE II. DETERMINATION OF SODIUM IN PRESENCE OF ANTIMONY

Antimony Mg.	Treatment	Sodium Determined Mg.
63	Antimony not removed	1.3
63	Antimony removed with H ₂ S	1.4
250	Antimony not removed	Heavy gelatinous precipitate formed upon addition of reagent

TABLE III. INTERFERENCE OF FLUORIDE

Compound	Na		Error Mg.	%
	Added Mg.	Found Mg.		
AlF ₃	280	None	2.22	..
AlF ₃	280	None	0.61	..
AlF ₃	140	10.0	11.25	+1.25
NaF	18.3	10.0 ^a	10.4	+0.4
Al ₂ (SO ₄) ₃	500	None	None	..
Al ₂ (SO ₄) ₃	500	10.0	10.22	+0.22
H ₂ SO ₄	1840	10.0	10.49	+0.49
AlF ₃ ^b	200	None	0.03	..
AlF ₃ ^b	200	None	0.04	..
NaF	18.3	10.0 ^a	9.60	-0.4
NaF	9.15	5.0 ^a	5.05	+0.05
NaF	1.83	1.0 ^a	1.05	+0.05

^a Sodium present as NaF.

^b Fluorine removed with H₂SO₄ before sodium determination.

TABLE I. DETERMINATION OF SODIUM

Metal	Form	Metal Mg.	Na Found—			Error	
			Na Added Mg.	Na Found Mg.	Na in Blank Mg.	Mg.	%
Be	BeSO ₄	19.2	None	None
			1.0	1.02	1.02	+0.02	+2.0
			5.0	4.82	4.82	-0.18	-3.6
Ce	CeO ₂ ^a + HCl	244	None	2.99
			1.0	4.02	1.03	+0.03	+3.0
			5.0	8.19	5.20	+0.20	+4.0
La	La ₂ (SO ₄) ₃	139	None	None
			1.0	0.97	0.97	-0.03	-3.0
			5.0	5.02	5.02	+0.02	+0.4
Nd	Nd ₂ O ₃ + HCl	90	None	None
			1.0	0.98	0.98	-0.02	-2.0
			5.0	5.03	5.03	+0.03	+0.6
Tl	TlCl	170	None	None
			1.0	1.00	1.00	0.00	0.0
			5.0	4.81	4.81	-0.19	-3.8
Th	Th(NO ₃) ₄	121	None	0.03
			1.0	1.02	0.99	-0.01	-1.0
			5.0	4.95	4.92	-0.08	-1.6
V	V ₂ O ₅ SO ₄	35	None	0.18
			1.0	1.17	0.99	-0.01	-1.0
			5.0	5.14	4.96	-0.04	-0.8
Zr	ZrSO ₄	142	None	0.01
			1.0	1.02	1.01	+0.01	+1.0
			5.0	5.10	5.09	+0.09	+1.8

^a Technical grade.

Table I shows the results of experimental work on elements which did not interfere with the sodium precipitation. As some of the salts used contained small amounts of sodium, blank experiments were made and a corresponding correction was made in the determined weight of each precipitate. This procedure seemed justified by the consistency of the values obtained.

Caley (4) reports that not less than 0.20 mg. of sodium can be determined, and this figure was taken by this laboratory as the maximum allowable error. The results of the experiments in Table I are all within this limit of error.

Interfering Elements

An attempt was made to determine sodium in the presence of columbium and tantalum. These metals formed heavy gelatinous precipitates upon addition of the acid reagent. For satisfactory sodium determinations these elements should be removed before determining sodium.

Several authors have reported that antimony precipitates with the reagent and such was the experience in this laboratory with large amounts (250 mg.) of antimony. On a sample containing smaller amounts of antimony (63 mg.) consistent results were obtained with and without removal of antimony with hydrogen sulfide (Table II).

Some of the samples for analysis of traces of sodium con-

tained 70 to 90 per cent of silica, 1 to 20 per cent of aluminum and other metallic oxides, and the remainder moisture.

Removal of the silica was attempted by adding hydrofluoric acid to the sample and volatilizing fluosilicic acid and the excess hydrofluoric acid on a hot plate. The residue was dissolved in hydrochloric acid and the sodium determined without removal of the metals. The results obtained were very erratic; some duplicate results differed as much as 100 per cent.

Experiments with pure aluminum fluoride, aluminum sulfate, sulfuric acid, and sodium fluoride (Table III) led to the conclusion that a readily soluble fluoride such as sodium fluoride will not interfere with the sodium determinations but varying amounts of aluminum fluoride will be precipitated in the concentrated reagent. This difficulty was overcome by adding 1 ml. of concentrated sulfuric acid with the hydrofluoric acid and evaporating to dryness. This procedure removed all the silica and fluoride and eliminated the former erratic results.

Summary

The magnesium uranyl acetate method for determining small amounts of sodium can be successfully used in the presence of beryllium, cerium, lanthanum, neodymium, thallium, thorium, vanadium, and zirconium. Silica, if present, can be removed with hydrofluoric acid and sulfuric acid. Columbium and tantalum will precipitate in the acid reagent, but no difficulty is encountered if these elements are removed previous to the sodium determination.

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Weighing Flask for Precision Standardization of Strong Alkalies in the Absence of Carbon Dioxide

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DURING a recent investigation involving the testing and use of several alkalimetric and acidimetric primary standards, it became necessary to carry out a large number of highly precise acid-base titrations in the absence of carbon dioxide. None of the weighing flasks described in the literature (1) was suitable for the purpose. This note describes a rapid and highly reproducible method for the standardization of strong alkalies under such conditions.

A 125-ml. Pyrex Erlenmeyer flask is fitted with a standard interchangeable two-in-one glass stopper, A, A', and inflow, B, and outflow, B', tubes carrying small ungreased stopcocks. The gas inlet tube is somewhat constricted at the tip to permit a fine stream of bubbles to present a maximum of surface and stirring effect. The complete assembly should not weigh over 60 grams.

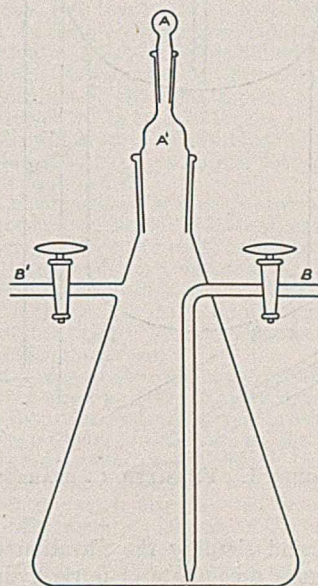
METHOD OF PERFORMING TITRATION. Suppose that it be required to standardize a stock solution of strong alkali, using either constant-boiling hydrochloric acid or an appropriately diluted solution of it. The flask, previously dried with a stream of dustless air and tared with a glass vessel of approximately equal surface, is weighed empty to the nearest hundredth gram (or milligram if desired). A roughly determined amount of the standard acid is introduced and the flask weighed again. Two or three drops of an indicator solution are added and weighed (if an aqueous indicator solution is used it may be weighed with the empty flask, but with an alcoholic indicator solution the above procedure is recommended to prevent loss by evaporation).

TABLE I. WEIGHT NORMALITY OF BARIUM HYDROXIDE SOLUTION

I	II	III
0.17875	0.17881	0.17888
0.17877	0.17881	0.17883
0.17876	0.17880	0.17887
0.17877	0.17881	0.17886

The flask is then connected directly to the stock buret, which is provided with a long tip carrying a small rubber stopper to fit stopper A'. A stream of nitrogen or carbon dioxide-free air is bubbled through the acid for several minutes, the alkali is added with one drop in excess, and the vessel is weighed with stopper A in place. Stoppers A and A' are then removed, the sides are washed down with freshly boiled distilled water, and the back-titration is performed with dilute acid from an ordinary buret. With practice, using two weighing flasks, four such determinations can be made per hour with high precision.

A set of consecutive results selected from the data for the standardization of nearly saturated solution of barium hydroxide is given in Table I. The conditions under which these titrations were carried out were extremely unfavorable, the humidity being close to the saturation point and the laboratory temperature about 30° C.



If a solid primary standard, such as benzoic acid or sulfamic acid, is employed, the procedure is similar, except that the standard is weighed into the flask from a weighing bottle and dissolved in an appropriate amount of water. No danger of overloading the analytical balance exists, since the maximum total weight of the flask and solution never exceeds 150 grams.

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A Filtering Apparatus

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IN SOME radioactive research in this laboratory, thorium-X is used. It is separated from the supply of radiothorium by adding gaseous ammonia to a hot hydrochloric acid solution of radiothorium containing iron. The radiothorium precipitates with the ferric hydroxide, leaving the thorium-X in the supernatant solution. The gaseous ammonia must be added to a hot solution of radiothorium to prevent the precipitation by the carbon dioxide from the air of a basic carbonate of thorium-X along with the ferric hydroxide.

from hot solutions, and also in adding reagents dropwise from a beaker.

A represents a rubber-covered clamp which can be adjusted by a screw, *G*, to take a number of different sized beakers.

B represents thumbscrews which can be used to regulate the positions of the stirring rod, the beaker, and the filter funnel. *D* is a 40-1 worm screw which allows the beaker to be tilted by the thumbscrew, *C*, so slowly that a liquid can be poured from the beaker at rates down to 1 drop in 3 seconds.

E is a coiled spring which holds the stirring rod against the lip of the beaker and moves the funnel support as the beaker is being tilted through an arc.

The special advantages of filtering with this apparatus over the usual hand methods are: (1) The beaker and rod are held so firmly that none of the precipitate is stirred up during the filtration. (2) The beaker can be kept hot with a small burner during the filtration. (3) The rate of filtration can be easily controlled by a slight turn of the thumbscrew, *C*, without stirring up the precipitate. (4) The supernatant solution can be decanted off to the last drop without carrying

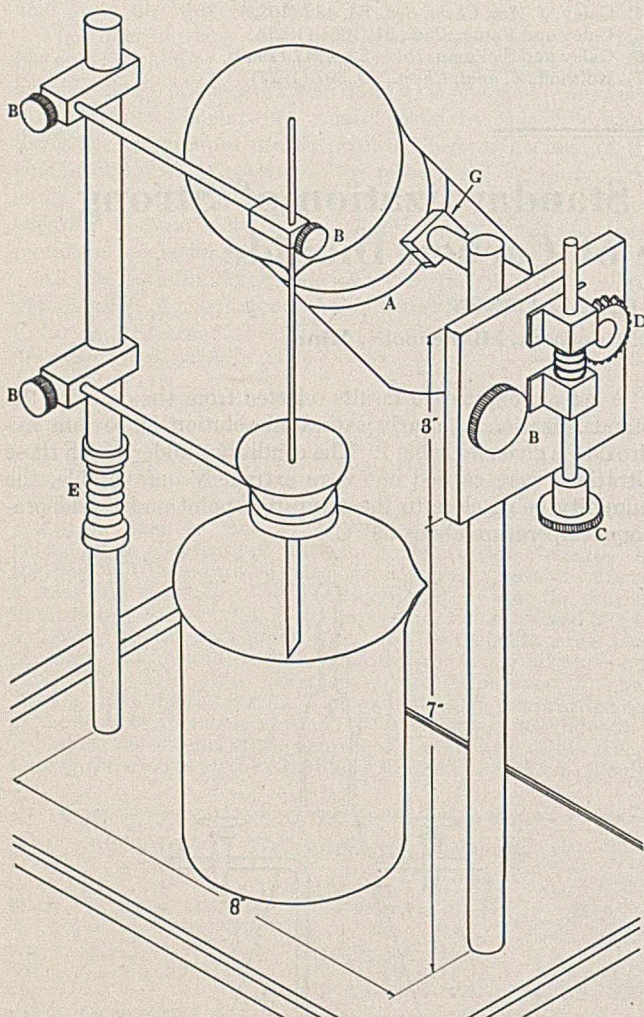


FIGURE 1. FILTRATION APPARATUS

To speed up and simplify the filtration of the solution from the gelatinous precipitate of ferric hydroxide, a filtration apparatus, illustrated in Figure 1, was designed. The hot beaker is held by a clamp on a solid support, so that the gelatinous precipitate settles to the bottom of the beaker. During the filtration, the precipitate is not stirred up, as is the case when the beaker is jiggled by holding in the hand. The supernatant solution can be decanted off to the last drop without carrying over into the filter the gelatinous ferric hydroxide, which so readily plugs up the pores of the filter paper and slows down the filtration.

This filtering apparatus has been found useful in a number of laboratory procedures in separating precipitates, especially

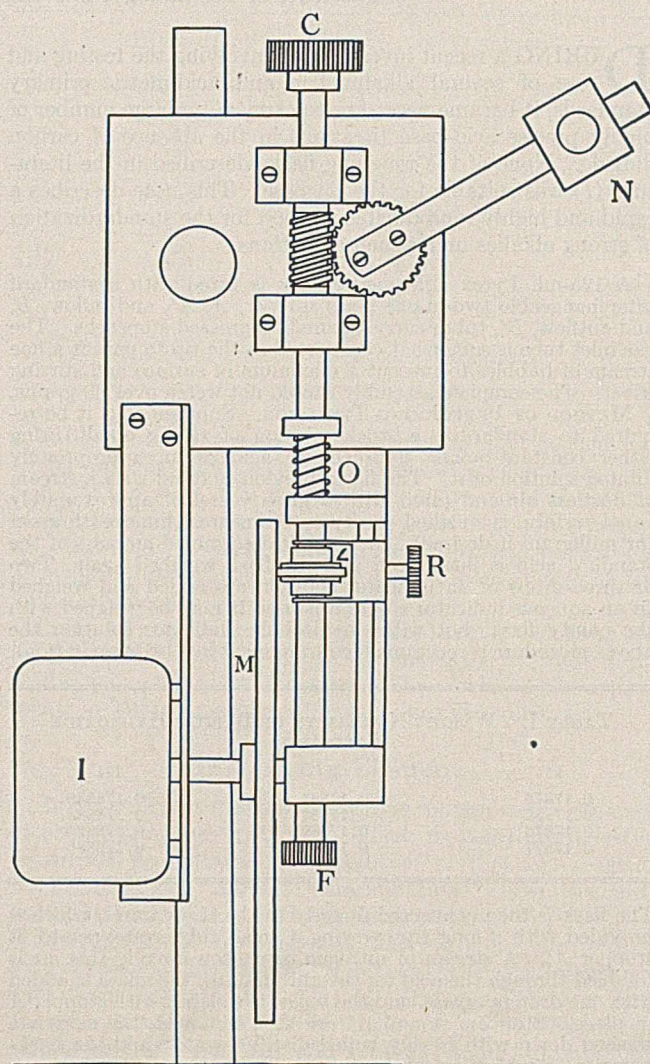


FIGURE 2. MOTOR ATTACHMENT

the precipitate over into the filter. (5) The precipitate can be thoroughly washed by decantation and still remain in the beaker.

In Figure 2 is shown a motor attachment that eliminates all handwork in a filtration.

The thumbscrew, *C*, is moved from its position in Figure 1 to the one shown in Figure 2. *I* is a constant-speed synchronous motor (sold by Herbach and Rademan, Philadelphia), to which is attached a 4.5-inch Dowmetal disk, *M*, which revolves at a rate of one revolution per hour. *L* is a 0.625-inch drive wheel of rubber or neoprene controlled by the setscrew, *R*, which is used to

regulate the speed at which the beaker is tilted. *F* controls a slip coupling, held in position by the spring, *O*, by means of which the beaker is set for the start of the filtering. This coupling can be disconnected and the filtering done by turning the thumbscrew, *C*. *N* is an adjustable counterweight to balance the weight of the beaker with its solution.

The filtering apparatus has been in constant use for several months and has given complete satisfaction. The equipment is being developed for the market by the E. H. Sargent Company, Chicago, Ill.

Machine for Testing Dentifrice Abrasion

RALPH W. SMITH, Ste. Genevieve Lime Company, Ste. Genevieve, Mo.

This paper describes the design and operation of a machine for running production control tests on the abrasiveness of precipitated calcium carbonates. The machine is also used for testing dentifrices to determine if their abrasiveness is sufficiently low to class them as safe. Numerous test series indicate that the machine is sensitive, dependable, and accurate within the limits necessary for its purpose. Its special advantages are described and other uses are suggested.

THE machine described here was designed primarily for plant production control tests on the comparative abrasiveness of precipitated calcium carbonates, U. S. P., and for such uses it must be accurate, sensitive, rapid, and easily operated. A study of numerous existing machines (and papers relating wholly or partially to the subject) indicated that it was difficult to build a machine on which duplicate abrasion results could be obtained. Other experimenters (11, 12) state:

The development of a test suitable for finer powders, which requires an inert abraded surface giving loss large enough to be weighed or estimated chemically while the feed of an abrasive material is maintained steady and the bearing area is controlled, is more difficult . . . The method of feeding the plate with a suitably thin film of the suspension under the test is the most essential part of the present apparatus . . . Reproducible results could be obtained only if a certain somewhat critical film thickness is fed to the plate . . . If too much suspension passes it causes abrasion only of the far edge, whilst with too thin a film the plate runs unsteadily and again a small loss is obtained.

Although disks (silver and glass) were run in groups of three on each table, the losses were not uniform for the individual runs. Repeat tests did not give the same relative amounts of loss.

In the machine just referred to (11) a much larger antimony or metal surface was used (5×3.75 cm., 2×1.5 inches) than the one described in this paper (4.5×12 mm.) and at times the larger antimony block became convex or concave.

The writer believes the considerable difference in speed of rubbing and total rubbing distance between the inner and outer edges of the antimony specimen with the larger surface caused the concave or convex abrasion. Comparing the speed of rubbing contact and total travel distance during the test, the extreme variation between the inner and outer edges on the large specimen was 21 per cent, whereas the variation with the much smaller specimen was only 3 per cent. Later

modifications in this apparatus have apparently overcome some of these difficulties and have also improved the ease of working (10).

The machine here described (using the small specimen) is not easily affected by film thickness, nor is there a lack of abrasion uniformity on the edges of the metal specimens. A series of about 500 tests indicates that this machine is not easily affected by operation or manipulation conditions except variations in the abrasive characteristics of the materials tested.

Abrasion Machine

METHOD OF DRIVE. A constant-speed, governor-controlled, vibrationless dictaphone motor (2, Figure 1) is used for driving the machine. Copying the design of other similar machines, a worm-and-gear direct drive from the motor to the first counter shaft was used at first, but this produced vibration which not only multiplied abrasion loss on the metal specimen blocks from three to five times, but also made it impossible to check closely on repeat tests. In the present arrangement the motor is fastened in vertical position to a plate which is bolted to a heavy wooden block, 17, mounted on rubber feet. For additional weight and consequent absorption of vibration, a piece of steel shaft (5 cm., 2 inches, in diameter by 25 cm., 10 inches, long) is inserted in a hole drilled in the wood block. Thus minor vibration is absorbed by inertia of the heavy block on rubber feet and the method of drive to the first countershaft.

The abrasion machine itself is entirely separate from the motor drive and is placed about 20 cm. (8 inches) away from the motor shaft. The machine is also mounted on rubber (typewriter feet, 16), and the only connection between the motor and the abrasion machine is the belt drive, which is a light rubber band, 14, cut from a large inner tube. The elasticity and vibration-absorption quality of this rubber belt are a final guarantee that no vibration will reach the abrasion machine.

From the top pulley of the first countershaft on the abrasion machine, a sewing-machine belt, 12, drives the second countershaft, vertically mounted, on top of which is fitted the aluminum-alloy test pan. All four shaft bearings on the abrasion machine proper are high-grade, ground ball bearings, 15, which also eliminate vibration and reduce friction to a minimum. In designing this machine, consideration was given to the desirability of including a two-direction motion because of the related problems of surface flow on metal specimens and the tendency of particles to rest in similar positions. Two-direction motion, however, was not added because of the mechanical difficulty of producing it without also introducing lost motion and the consequent bump and pile-driver effect of the specimen holder at the end of each stroke.

TEST PAN. The aluminum test pan (Castalloy, 4) is integral with the countershaft on which it is mounted, so that it will run true. In the pan is a recess into which wax, 5, is poured for the abrasion contact surface. Five brass machine screws permit the pan to be taken off after every test to wash the plate.

CUTTING TOOL. The lathe-type cutting tool, 11, is used to cut the wax to a true flat surface. Before starting a test, the wax surface is planed true and then scraped lightly with a safety-razor blade. After the wax surface has been prepared in this manner, the specimen holders show no up-and-down movement with the machine in operation on an abrasion test.

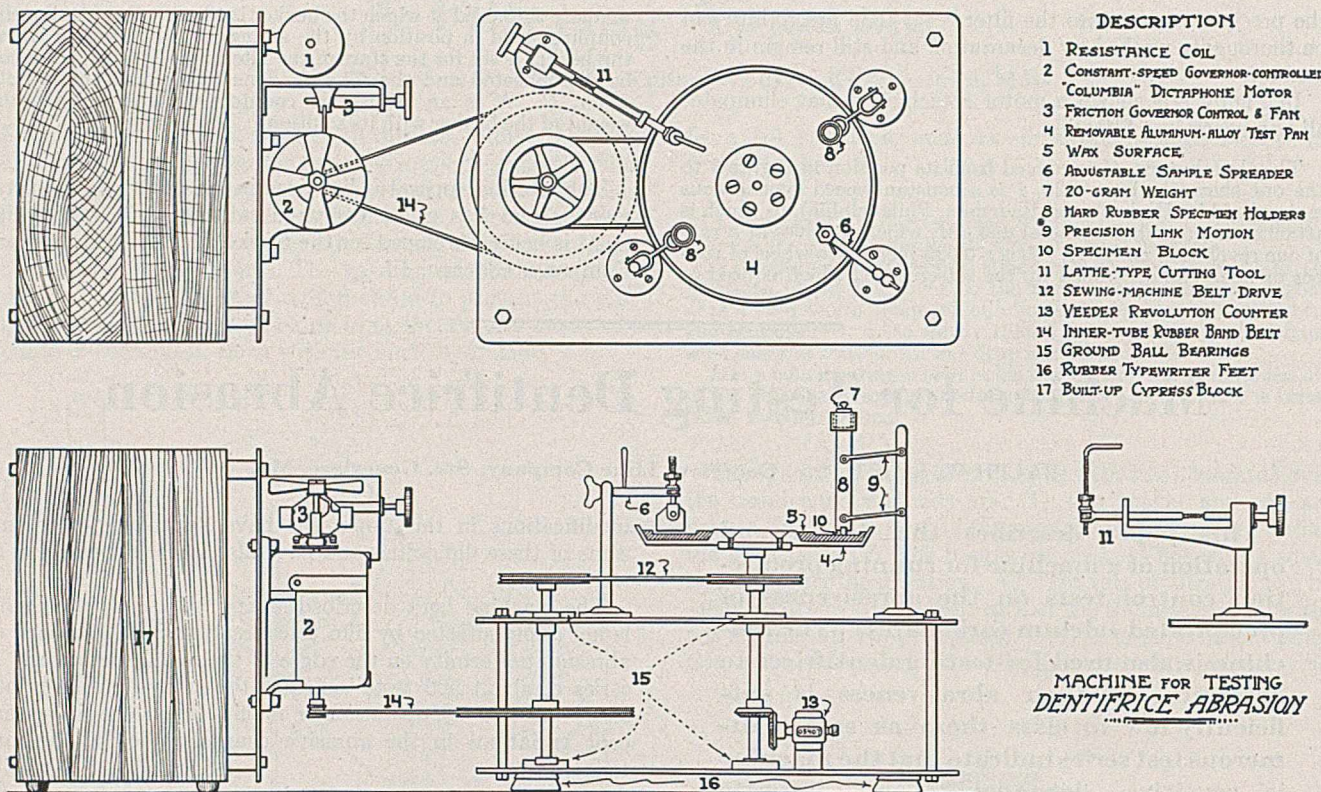


FIGURE 1. MACHINE FOR TESTING DENTIFRICE ABRASION

SPECIMEN HOLDERS. The machine has two duplicate specimen holders, 8, opposite each other, so that two specimens can be used as a check. Precision manufacture is necessary in the entire machine, but especially in the link motion, 9, on the specimen holders, to eliminate lost motion. The vertical circular rod is of hard rubber; the weight holder and link-motion arms are brass. The distance between the upper and lower arm link should be at least 5 cm. (2 inches), so as to prevent the rod from tilting when the machine is in operation.

Considerable experimentation was necessary with various methods of holding the specimen, 10, so that it would rub uniformly on the slurry. Satisfactory results were obtained by not fastening the block to the rod. The groove in the bottom of the rod (into which the specimen fits) is about 0.3 mm. wider than the specimen; it is not cut entirely across the end of the rod, but ends with a shoulder against which the end of the metal specimen abuts. Thus the rod and its 20-gram brass weight, 7, with a total downward thrust of 63 grams, ride on the metal specimen without actually being fastened to it.

Many tests were run in order to determine the exact dimensions of the groove in the rod and location of the shoulder, so as to abrade the specimens properly. The specimen blocks are 4.5 mm. wide by 12 mm. long; the vertical measurement on a new specimen is 5 to 6 mm., and this is gradually reduced to about 4 mm. after the specimen has been used. For uniform abrasion 5 mm. of the 12-mm. specimen should project in front of the rod; otherwise wear on the specimen surface is not uniform. Using the above proportions, the specimens, even in the very early stages of an abrasion test (20 or 30 revolutions), show uniform wear over the entire surface, indicating uniform pressure, lack of vibration, and initial uniform abrasion.

Uniformity of abrasion rate was checked in a series of tests in which the specimens were removed at the end of every 2000 revolutions, weighed, and put back in the machine, up to 16,000 revolutions (standard test ends at 6000 revolutions). The loss for each 2000 revolutions checked closely (Table I).

SPREADER. An adjustable sample spreader, 6, turns the slurry over, mixes it, and presents new material continuously to the specimens during the testing cycle. The slurry is made sufficiently thin so that the track will close up in the space between the two specimen holders where there is no spreader. The

spreader is adjustable up and down; it can also be turned up out of the way to allow easy removal of the aluminum plate. When a test is completed, small rubber bands are hooked from the top of the specimen holders to the supporting rod to hold the specimen holders vertically upright, close to the supporting rod, and out of the way.

REVOLUTION COUNTER. The revolution counter, 13, is driven directly by the pair of brass miter gears shown in Figure 1. The counter has a reset device, so it can be quickly turned back to zero for a new test.

MATERIALS. The abrasion machine proper is made from materials which will not rust nor corrode: brass, aluminum, hard rubber, and Allegheny metal. This is important because the machine will be used for production control tests over a period of years, and it must remain in close adjustment, so that this year's results may be checked against those to be obtained in future years.

Metal Specimens

The rubbing area measurement of 4.5 by 12 mm. was selected in order to check results obtained on a similar machine in a commercial laboratory. A small specimen with the long measurement tangent to the transcribed circle also seemed desirable, because difference in total distance of abrasive rubbing travel between the outer and inner edge of the narrow specimen is so little in relation to the diameter of the transcribed circle. Tests were run with antimony and silver blocks in pairs. In all the tests made with these metal speci-

TABLE I. UNIFORMITY OF ABRASION

Revolutions	Carbonate Specimen 1		Carbonate Specimen 2	
	Sb Mg.	Ag Mg.	Sb Mg.	Ag Mg.
2,000	1.4	1.6	0.7	0.9
4,000	2.8	3.3	1.5	1.7
6,000	4.3	4.9	2.3	2.6
8,000	5.8	6.5	3.0	3.5
10,000	7.2	8.2	3.8	4.5
12,000	8.5	9.8	4.5	5.5
14,000	9.8	11.4	5.3	6.4
16,000	11.1	13.0	6.1	7.2

mens, there was no observable discoloration on the metal which would indicate oxidation and resultant possible alteration of abrasive action or change in final weight of specimen.

All specimens were carefully filed to exact dimensions, then polished on a fine-grained razor hone. All surfaces were tested carefully to see that they were square; otherwise the specimens might be tilted slightly during the test, and this would result in uneven pressure and unreliable test results. Specimens were weighed accurately on a Voland precision balance, accurate to 0.1 mg. (0.0001 gram), before starting each test. Both the silver and antimony blocks were tested for microcharacter hardness by C. H. Bierbaum (Lumen Bearing Company), who developed the Bierbaum hardness tests (2, 3). The Bierbaum average hardness figure was 231 for antimony and 200 for the silver specimens, showing the silver to be somewhat softer than antimony. This was checked by the abrasion results, in which all abrasives tested showed a somewhat higher abrasion loss with silver than with antimony. The specimens were accurately weighed after each test was completed, and repolished on the razor hone before a new test was run. A specimen can be used for about 100 tests.

The decision to use metal specimens was based on a study of available pamphlets (1, 8, 11, 13) relating to this type of work, and personal discussions with experimenters, dentists, and teachers in dental schools. While the abrasion of metal specimens in a machine of this type probably does not exactly parallel the wear of tooth structure in the oral cavity, yet the use of metal specimens standardizes test conditions much more than would be possible with tooth specimens, especially for production control tests. A series of tests using human teeth and horse teeth was seriously considered but abandoned after a discussion of the problem with dentists and others. Brady (4) indicated "that it was impossible to prepare tooth specimens of a standard moisture content. The variation was so much at different times, even after keeping the specimens at a constant temperature for 12 hours, that it was impossible accurately to weigh loss caused by abrasion in a machine".

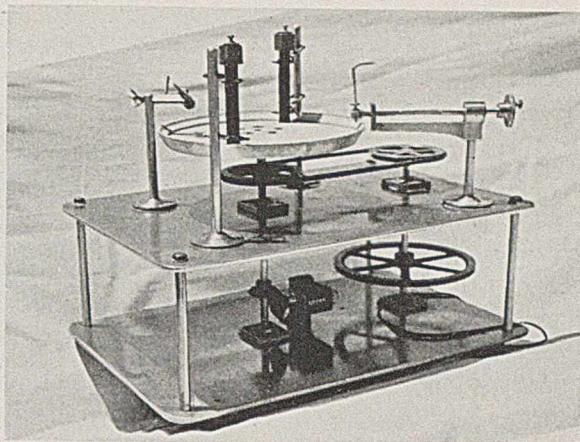


ABRASION MACHINE ONLY, SEEN FROM ABOVE
Clear view of specimen holders and removable wax plate

Micrometer measurement of loss seemed too delicate for satisfactory commercial work (not on a pure research basis). Furthermore, there is the difficulty of preparing and maintaining satisfactory tooth specimens; pure surface areas are difficult to prepare, and tooth substances vary in hardness (5, 6, 7).

Wax Surface

In the early tests biological embedding paraffin (melting point 56° to 58° C.) was used in the aluminum plate. This material was fairly satisfactory, but it developed cracks after a week or so, and on warm days showed a tendency to flow or groove slightly. It was found that 50 per cent of carnauba



ABRASION MACHINE ONLY, SEEN FROM ABOVE
Cutting tool and spreader show clearly

wax (melting point 85° C.) and 50 per cent of paraffin produced a surface much harder than paraffin, but it was somewhat brittle and cracked worse and more easily than paraffin. The proportion was gradually reduced to 20 per cent of carnauba wax and 80 per cent of paraffin, and this made a completely satisfactory plate. One application of this mixture has been used for one month of continuous abrasion testing without showing a single flaw, crack, or groove. The higher melting point of carnauba wax in a 20 per cent mix apparently toughens the paraffin by just the proper amount. Blank tests, using water only and no abrasive, show about 0.3 mg. of abrasion loss with 6000 revolutions. This is not subtracted from test results when using an abrasive because the metal specimens are not in direct contact with the wax but rub on the abrasive slurry.

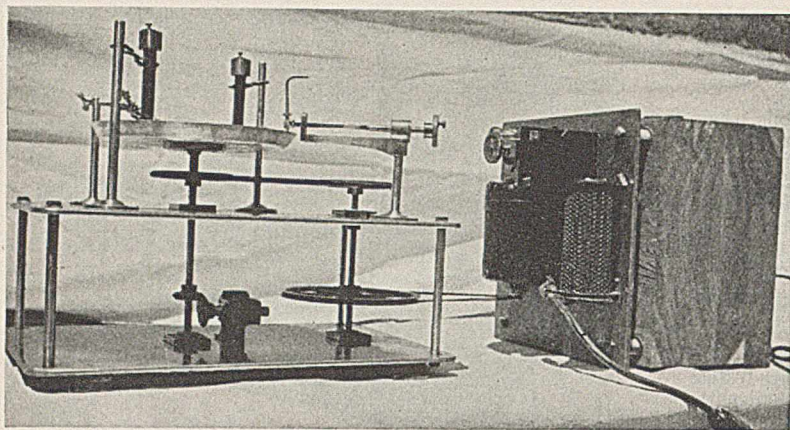
To help prevent cracking of the wax surface, the concave surface of the aluminum plate is drilled half-way through with about 300 holes, 3 mm. (0.125 inch) in diameter, scattered uniformly over the entire surface under the area covered by the wax. The wax plate should not be washed with cold water, as this sometimes causes shrinkage cracks in the wax. In applying new wax to the plate (after consecutive resurfacing operations have cut the wax too thin for further tests) the plate is heated and the old wax poured out. While the plate is still hot the new wax is poured in, and the entire plate is allowed to anneal over a period of several hours. This is done by setting the plate on a piece of corrugated cardboard (which acts as a heat insulator and will not rapidly withdraw heat from the plate) and then covering the plate with a corrugated box which retains the heated air above the plate and allows slow cooling. Too rapid cooling develops cracks and results in an unsatisfactory plate.

While with various types of surfaces it is possible to alter the results of an abrasion test (10), the comparative results on a wax plate show the relative differences in abrasion power. These relative differences are reliable for plant production control tests and for purposes of investigation that do not become deeply involved in pure research.

Slurry Consistency

Although this machine was designed primarily for testing precipitated calcium carbonate, it works equally satisfactorily with dental powders and creams. Since the absorption of different grades of carbonate varies considerably, it was necessary to establish a satisfactory standard procedure for making a slurry of the material to be tested. Some carbonates because of their high absorption require four times as much water to produce a slurry of the same consistency as a low absorption carbonate.

TEST FOR DETERMINING ABSORPTION. Weigh 15 grams of material, put it in a 100-cc. Nessler tube and gradually add water



MACHINE CONNECTED TO GOVERNOR-CONTROLLED DICTAPHONE MOTOR DRIVE
Weighted cypress block for vibration absorption at right

from a buret with occasional shaking until the mass becomes wet enough to rattle in the tube. Now add the water, 0.5 cc. at a time with shaking after each addition, until 3 or 4 drops of slurry will drip from the tube when it is held downward at an angle of 30°.

On the basis of this test, and in order to determine the effect of thinning or thickening the slurry (of a single carbonate), tests were made on a group of carbonates with assorted absorptions (Table II). The amount of water was increased and decreased considerably above and below the quantity determined by the absorption test, and the tests covered the entire range between upper and lower slurry limit that would act satisfactorily in the machine.

These tests indicate that within these limits a change in the slurry consistency did not visibly alter the results. Thus when testing carbonates that quantity of water was added which was indicated by the absorption test, and when testing an unknown material an absorption test was first made. Long experience with this machine has indicated to the operators the proper consistency to which dental powders and creams should be thinned in order to flow properly on the plate.

In Table II it is of interest to note that the abrasion loss increases as the density changes from heavy to extra light. The probable explanation for this is that in the process of precipitation both calcite and aragonite are formed. Tests by W. T. Schaller of the U. S. Geological Survey, Washington, D. C., indicated that the percentage of calcite was greater in the heavy than in the extra light, although definite figures were not supplied. The lower hardness and density of the calcite should thus lower the abrasion loss in the heavy, and since test results are in accord with this postulate it may be evidence of the machine's sensitivity to minor changes in the abrasive character of materials.

TABLE II. EFFECT OF SLURRY CONSISTENCY

Carbonate Grade	Mix Based on Absorption Test		Upper and Lower Limit Tests			
			Thin		Thick	
	CaCO ₃ Grams	H ₂ O Cc.	H ₂ O Cc.	Loss Mg.	H ₂ O Cc.	Loss Mg.
Heavy	30	25	30	3.2	20	3.1
Medium heavy	30	40	50	3.4	32	3.5
Medium light	30	60	75	3.5	50	3.4
Extra light	30	100	120	3.7	85	3.8

Sensitivity

The work of Ray and Chaden (8), Souder and Schoonover (12), and Wright and Fenske (13) on scratch tests indicated that a satisfactory abrasion testing machine should be sensitive to minute quantities of strongly abrasive materials.

To determine sensitivity of this machine, two series of tests were made, in one of which pulverized silica was added, and in the other, pulverized emery, gradually reducing the amount of each hard abrasive until its effect was lost. A master sample of precipitated calcium carbonate (on which the abrasion figure had been established at 2.1 mg.) was used for making the slurry in which the various quantities of silica and emery were thoroughly mixed. These tests showed that the addition of 0.5 per cent of pulverized silica (95 per cent through 325-mesh) multiplied the abrasion loss four times, whereas 0.1 per cent of silica increased the abrasion figure 33 per cent. In the case of emery dust (80 per cent through 325-mesh, 99.9 per cent through 200-mesh) the addition of 0.2 per cent multiplied the loss five times, whereas 0.05 per cent increased the abrasion loss about 40 per cent. Table III gives these results in detail.

Thus the emery and silica tests show that the machine is sensitive to hard abrasives, and that it also responds to the much higher hardness of the emery.

Downward Pressure

In order to determine the relation of downward pressure (on a specimen) to abrasion loss, a series of tests was made on several master carbonate samples (of different densities) starting with 43 grams' pressure (empty specimen holder with no weight in the weight holder) and increasing the weight by increments of 20 grams up to 143 grams. These tests showed a mild increase in abrasion loss with an 83-gram pressure, and a decrease below the average with 143 grams (Figure 2). It seems probable that when the pressure is increased enough (143 grams) it reduces the amount of slurry that can penetrate between the specimen and plate, thereby reducing abrasion loss. It was therefore decided to use 63 grams because it resulted in an average loss about halfway between the maximum and minimum.

TABLE III. ABRASION LOSS

Silica Content %	Abrasion Loss Mg.	Emery Content %	Abrasion Loss Mg.
10.0	13.8	0.20	10.0
2.0	10.4	0.10	5.5
0.5	8.8	0.05	3.0
0.2	4.0
0.1	2.8
None	2.1	None	2.1

Other Uses for Machine

During the summer of 1938, Will Coghill, supervising engineer of the U. S. Bureau of Mines Southern Experiment Station saw this machine in operation at Ste. Genevieve and thought it might have application in the investigation of abrasion caused by grinding industrial materials, such as coal, silica, hematite, clay, etc. A preliminary survey (with the assistance of the station's staff at Tuscaloosa, Ala.) was confined principally to pulverized coal, with a few tests on pyrite, silica, and coal waste, using carefully sized fractions: >28- <35-mesh, >35- <48-mesh, >48- <65-mesh, >65- <100-mesh, >100- <150-mesh, >150- <200-mesh, and >200-mesh. At first a few tests were run using a water slurry, but this was soon abandoned and tests were run on dry powder, because these materials are pulverized commercially in the dry state. Somewhat to the author's surprise, the mechanical action of the machine with dry tests was satisfactory. According to recent information, this station of the U. S. Bureau

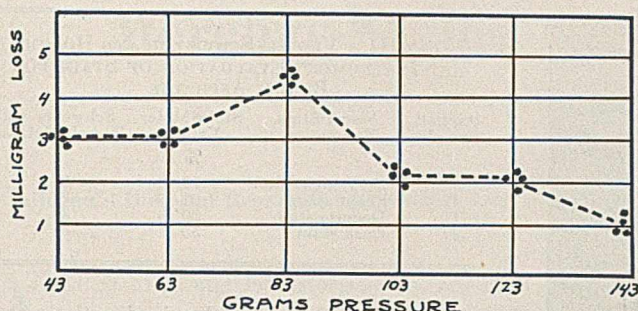


FIGURE 2. EFFECT OF PRESSURE ON ABRASION LOSS

of Mines built a similar machine in order to continue the investigation. Describing this work, Sheppard and Dasher wrote (9):

After some use, two other possibilities of the machine were realized: (1) the specimen holder's radius arms could be pivoted so that the tangential reaction force between the specimen and sample could be measured; and (2) a roller could be substituted for the sled and the grindability of coal measured.

The combination of the two possibilities resulted in the development of that which, to our knowledge, is the only machine capable of direct measurement of the net power required to grind coal or other material. Abrasiveness testing was discontinued and development of the new grindability method begun.

Conclusions

After numerous changes in design, the present machine under standard test conditions is apparently not easily affected by any operation or manipulation conditions except variations in the abrasive characteristic of the material being tested.

An essential part of the design is the elimination of vibration by separating the drive motor from the machine and using a light rubber belt drive. Other essentials are: removable test pan, cutting tool for producing a true wax surface, accurately precisioned specimen holders, method of holding specimens, proportions of specimen holders, dimensions and

preparation of specimens, method of preparing wax surface, sample spreader, revolution counter, and all-rustless material.

Antimony and silver test specimens were decided upon for dentifrice testing. The sample slurry consistency is determined by a simple absorption test, and the machine's test results are not affected by thinner or thicker slurry.

Although the machine was developed primarily for simple research and control tests on precipitated calcium carbonate, it also works satisfactorily on dental powders and creams. It is sensitive to minute quantities of very hard pulverized abrasives (silica and emery) when mixed in a standard low-abrasive carbonate sample.

Variations in downward pressure on specimens cause only mild changes in test results, maximum loss occurring with 83 grams' pressure. This machine suggested an idea which was developed by the U. S. Bureau of Mines into a grindability machine for coal and other materials.

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An Asphalt Gloss- and Stain Meter

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A photoelectric device is described that permits a quantitative determination of the gloss of asphaltic bitumen. A procedure for determining quantitatively the degree to which asphalts stain absorbent materials is outlined.

THE gloss of an asphalt and its tendency to stain surrounding absorbent material are two properties which have hitherto been evaluated by visual observation and consequently have been subject to the interpretation of the individual observer. A dull surface may be an indication of the presence of excessive wax, which often results in lowered ductility, decreased weathering stability, and poor adhesive properties. The tendency of asphalt, particularly roofing asphalt, to stain surrounding material is detrimental to the appearance of the finished roof.

Apparatus

An instrument of the type designed for use on hard surfaces, such as paints and varnishes, has been modified for use with plastic asphaltic bitumen. A general view of the instrument

with auxiliary equipment is shown in Figure 1, and a schematic cross section in Figure 2. The unmodified instrument was purchased from the Research and Development Company, New York, N. Y.

Gloss Measurement

The structure, size, and rate of formation of wax crystals in an asphalt, which influence the degree of light reflection, are controlled as far as possible by the treatment of the sample previous to gloss measurement. The asphalt is heated to at least 60° C. (140° F.) and poured into shallow trays which are placed in an air thermostat at 25° C. (77° F.). A sealed container immersed in a water bath is also convenient for this purpose. After 24 hours, the tray is laid upon a flat surface under the glossmeter and the legs are adjusted for height until the deflection of the microammeter is at the maximum. In the case of the asphalt whose gloss is chosen as the standard (a 40-50 penetration Mexican asphalt), the deflection is adjusted to correspond to 100 scale divisions. Hence, the greatest deflection produced by the sample under test will indicate the percentage gloss.

An example of an application of the glossmeter is given in Table I, in which are listed the properties of a number of fractionated cuts from a residue. When the gloss evaluations by visual inspection are compared with those obtained with the glossmeter, the glossmeter values may vary from 107 to

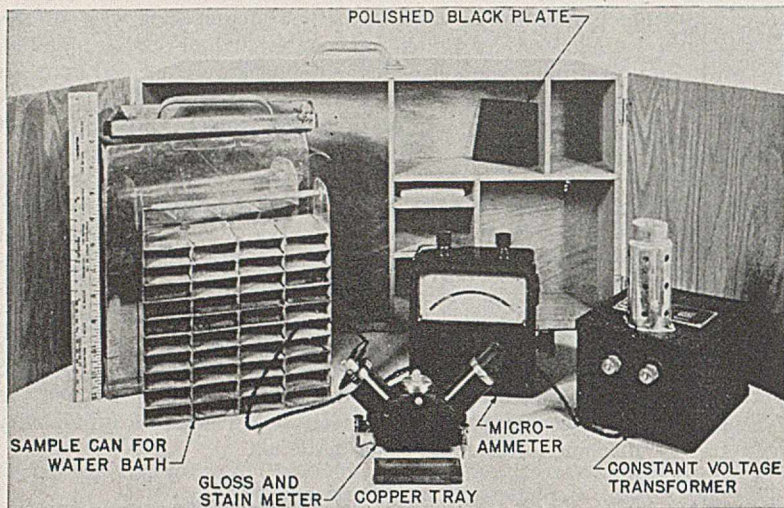


FIGURE 1. GENERAL VIEW OF METER WITH ACCESSORIES

TABLE I. COMPARISON OF GLOSSMETER MEASUREMENTS WITH VISUAL CLASSIFICATION AND WAX CONTENT ON FRACTIONS FROM RESIDUE A

Cut No.	Penetration at 25° C. (77° F.)	Softening Point (Ring and Ball)		Saybolt Furoil Viscosity at 98.9° C. (210° F.)	Holde Wax (1) Wt. %	Gloss Measurements %	Visual Appearance
		° C.	° F.				
1	2	80.6	177	...	1.16	107	Bright
2	20	56.1	133	...	1.61	95	Bright
3	230	36.7	98	378	2.24	90	Bright
4	>300	151	2.69	89	Bright
5	>300	82	3.00	85	Slightly dull
6	>300	54	4.85	84	Dull
7	>300	39	4.93	81	Dull

TABLE II. SURFACE GLOSS AS AN INDICATION OF EFFECTIVENESS OF PROCESSING

Cut No.	Untreated Stock		First Processing		Second Processing	
	Gloss measurement %	Visual appearance	Gloss measurement %	Visual appearance	Gloss measurement %	Visual appearance
1	91	Hazy	103	Bright	111	Bright
2	84	Hazy	101	Bright	111	Bright
3	79	Dull	90	Hazy	101	Bright
4	77	Dull	84	Hazy	88	Hazy
5	67	Dull	80	Dull	85	Hazy
6	66	Dull	74	Dull	78	Dull
7	62	Dull	72	Dull	77	Dull
8	57	Dull	67	Dull		

89 per cent, yet the asphalts appear "bright" to the eye. In the range from 85 to 81 per cent the gloss is rapidly lost; below 84 per cent the only subjective term available is "dull".

The use of the glossmeter in gaging the effectiveness of a particular type of processing to remove wax is indicated in Table II. The effect of the treatment is clearly shown in the improvement in gloss.

Stain Measurement

In one test used by the roofing industry to determine the tendency of an asphalt to stain absorbent materials the asphalt is placed in the lid of an 0.089-liter (3-ounce) seamless can and covered with a Whatman No. 5 filter paper, cut to fit the lid, and weighted with a 5-gram iron washer. Heretofore the extent to which the asphalt stains the filter paper after contact with it for 32 hours at 79.4° C. (175° F.) has been estimated by visual observation. By placing

TABLE III. VISUAL, SCHWEYER AND HOWELL, AND INSTRUMENT EVALUATION OF STAIN FOR BLOWN ASPHALTS

Asphalt Sample	Visual Stain Estimation	Stain-Meter Values	Schweyer and Howell Method
		%	
A	Very slight stain	73	1
B	Slight stain	61	2
C	Definite stain	50	3
D	Dark stain	35	5

the instrument described herein directly on the paper with the photoelectric cell in the top position, one can read the degree of staining in terms of the amount of light diffused from the sample, the standard (no stain, 100 per cent reading) being obtained by adjusting the instrument so that a deflection of 100 scale divisions results when an unused Whatman No. 5 filter paper is placed on a glossy black surface.

A comparison of visual and instrument evaluation of the staining characteristics of several blown asphalts from various sources is given in Table III. The visual method is, of course, subjective, and liable to personal errors of estimation which are eliminated in the quantitative instrument method.

The staining characteristics of asphalt may also be evaluated by the method of Schweyer and Howell (2) which depends upon the number of sheets of cigaret paper discolored when in contact with the asphalt sample. The results of this method and the instrument evaluation method on the same asphalts are also compared in Table III. The values obtained by the Schweyer and Howell method are to some extent quantitative but do not give the range of values, and consequently the degree of accuracy, given by the proposed stain meter method. Moreover, variations in the quality of the cigaret paper affect the reproducibility of the test.

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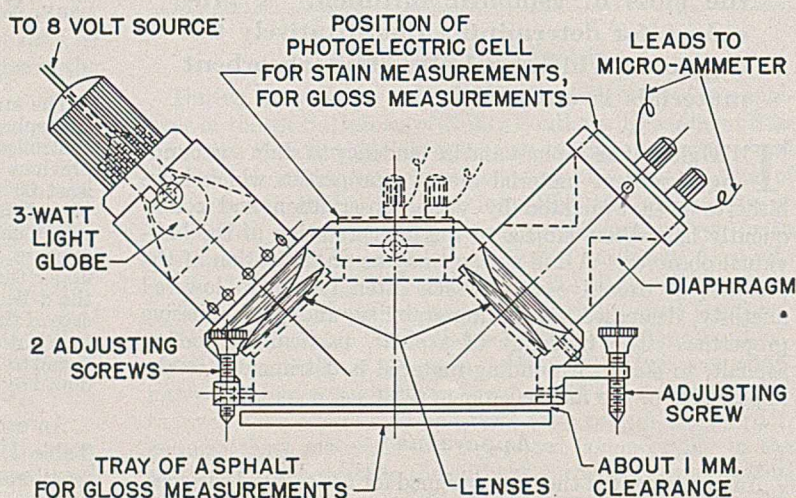


FIGURE 2. DIAGRAM OF METER

Mercury-Sealed Vessels for the Storage of Solutions

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VAN SLYKE and his associates (8, 10) have made extensive use of mercury-sealed vessels to protect the contents stored in them against loss and against contamination by constituents of the laboratory air. Such vessels have been used to preserve gas-free reagent solutions, solutions that react with carbon dioxide or oxygen, samples (such as blood) that would otherwise take up or lose gases, gaseous reagents, and samples of gases.

Recently a number of storage vessels (5) have been designed and used by Hanke (2, 3, 7), Guest and Holmes (1), Holmes (6), Sendroy (9), and Hastings (4). In these later forms various advantages were realized: elimination of contact between the stored solution and the glass stopcock which often results in sticking or leakage (1-4, 6, 7, 9); transfer of control of flow to a cock in the mercury stream (1-4, 7, 9); compactness and mechanical strength (1, 4, 6, 9); elimination of separate supports (4, 6, 9; also, 1, when made with a flat base); accurate measurement of the volume of stored solution delivered, with graduated mercury reservoir (3); automatic sealing of the delivery tube with mercury (6); and ease of construction from standard parts (9). At least one advantage of earlier apparatus (10, extraction of gases in the storage vessel itself) was sacrificed. Undoubtedly other unpublished modifications are in use in different laboratories.

Many modifications and combinations of various features are possible and at least a dozen different forms have been used with satisfactory results in this laboratory. A few of these are described in this communication.

Although one or more of these vessels is almost indispensable in many of the methods of gasometric analysis using the apparatus of Van Slyke and Neill (10), they are by no means limited to use with this apparatus. Several of those mentioned above are adaptable without modification to other purposes in the laboratory. From any one of the five described below, solutions can be delivered into an open beaker or flask. In four of these the amount delivered is measured. If even momentary exposure to air is to be avoided, the solution may be delivered under oil with the tip of the delivery tube immersed in the oil; or the tip of the delivery tube may be immersed in a pool of mercury in the bottom of the beaker during delivery of the solution, and then a drop of mercury may be drawn into the delivery tube before it is removed, to protect the stored solution against contamination as it passes through the contents of the beaker.

Vessels with Attached Burets

The form shown in Figure 1 may be used for general purposes. Because it is compact and freely movable it is particularly suitable for use with other apparatus (such as Van Slyke's) to which it may be taken and at which it may be held in place in one hand while the other hand is free for other manipulations. It has a large chamber for the storage of solution and a large reservoir for mercury. It requires no accessory support.

The operation of this vessel is simple, the flow of solution being controlled by the stopcock while the volume is observed in the graduated tube. When this buret has been emptied to the zero mark, it is refilled by tipping the vessel (to the right in the drawing) with the cock closed, until solution flows into it and the mercury flows back into the storage chamber, *S*.

Before the initial filling with solution, the vessel is filled as far

as possible with mercury by pouring it through *C* while the vessel is held in the horizontal position. The last portion of air is expelled by filling the buret in the upright position with mercury admitted through the stopcock from *C*; transferring the trapped air to the buret in the horizontal position, and expelling air again in the vertical position. Solution is then forced in through the delivery tube under moderate pressure, or drawn in by applying suction at the top of *C*. For subsequent fillings, since the solution has then already been replaced by mercury, it is necessary only to draw in fresh solution.

Since adequate protection against air is afforded by merely immersing the tip in a cup containing mercury, this is sufficient precaution during a series of determinations. To avoid extrusion of a few drops of solution due to expansion with rise of room temperature during longer intervals, it is advisable to draw mercury into the delivery tube by application of suction at the top of *C*. It is often convenient to do this by means of a rubber tube attached to *C* and held in the mouth while both hands are free for other operations.

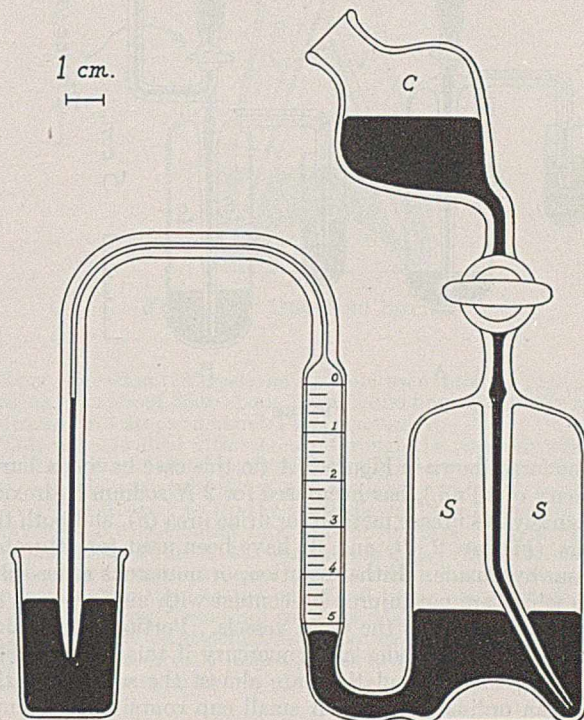


FIGURE 1. GENERAL-PURPOSE VESSEL

Within reasonable limits, there is nothing critical about the measurement of the parts of this vessel. One has been used which had a storage chamber with a capacity of 15 ml. and a buret (of 6-mm. tubing) graduated at intervals of 0.05 ml. to a total capacity of 0.35 ml. Another had a capacity of 100 ml. with a buret (of 12-mm. tubing) graduated at intervals of 0.2 ml. to a total of 5.0 ml. The tubing between the buret and the reservoir must, of course, be large enough for the solution and mercury to flow freely past each other in refilling the buret.

The compactness of vessels such as the one just described limits the maximum capacity of the buret to about 5 ml. Larger burets are available in the forms illustrated in Figures 2 and 3, which are suitable for use wherever the circumstances permit their being held in fixed supports. The simple

graduated mercury reservoir used by Hanke (3) has been adapted to this purpose in the vessel shown in Figure 2, A. The burets in Figure 2 may have capacities up to about 40 ml., and the one in Figure 3 may be made to hold at least 20 ml.

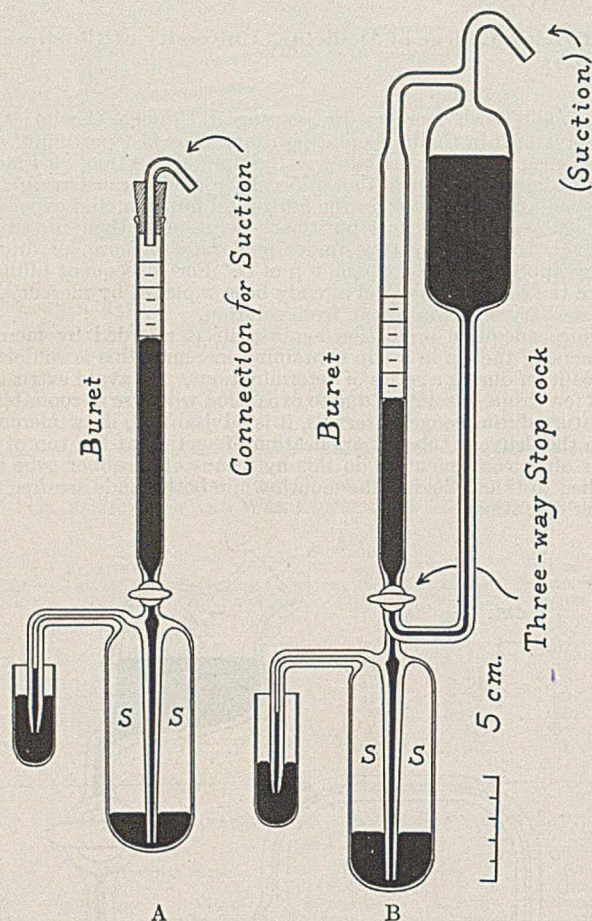


FIGURE 2

The form shown in Figure 2, A (in this case having a buret capacity of 10 ml.), has been used for 2 *N* sodium hydroxide in Van Slyke's urease method for urine urea (8), and both the others (Figures 2, B, and 3) have been used for saturated sodium hydroxide. Either solution, or numerous other solutions which are not injured by contact with mercury, can be stored in any one of the three vessels. Portions of solution may be delivered under oil or mercury if this is preferable; otherwise, the manipulations are almost the same as in the use of an ordinary buret. A small cup containing mercury which seals the outlets of the vessels is shown in each drawing. These are supported on blocks or in clamps so that they may be easily dropped out of the way.

For the first filling of the vessel shown in Figure 2, A, mercury is poured in through the buret until it runs out from the delivery tube. The top of the buret is connected with a water suction pump by a rubber tube in which a trap is placed to catch the mercury, and the solution is drawn into the solution storage bulb through the delivery tube. For subsequent fillings, since the solution has then already been replaced by mercury, it is only necessary to draw in fresh solution. When, during use, the mercury has reached the lower end of the graduations, the buret may be refilled either by pouring mercury in at the top or by attaching the suction tube at the top and drawing the mercury in through the delivery tube.

The vessel of Figure 2, B, differs from that of A in the addition of a large mercury reservoir from which the buret may be conveniently refilled. The construction and operation of the buret, reservoir, and three-way cock are practically the same as those

of an ordinary buret equipped with reservoir and three-way cock. One method of filling the vessel is as follows: Mercury is drawn in through the delivery tube by suction at the top of the apparatus until it flows over the top of the buret into the reservoir and fills the reservoir, and then the buret is alternately filled and discharged into the solution chamber, *S*, until all air has been expelled from *S*. By again applying suction, solution is drawn into the chamber through the delivery tube and mercury is drawn over the top of the buret into the reservoir.

In this vessel, as shown, a slight advantage in ease of filling was sacrificed for a permanent connection for suction. A straight piece of 12-mm. tubing may be substituted for the vertical part above the reservoir, and the connection to suction may be made as in Figure 2, A.

After drawing mercury into the delivery tube in both vessels of Figure 2, it is desirable to place a clamp on the suction tube and leave it in place to maintain the reduced pressure in the space above the mercury and thus relieve the pressure of mercury on the cock.

The apparatus shown in Figure 3 is superior to those of Figure 2 in accuracy as well as in some other respects. The mercury meniscus in the other two is often irregular, owing to contact with walls that have been intermittently exposed to air. In this form in which the mercury in the buret is always in contact with a uniform solution, and with clean walls wet by this solution, the meniscus remains regular and constant in all positions and at all times. When an unmeasured amount of solution greater than the total volume

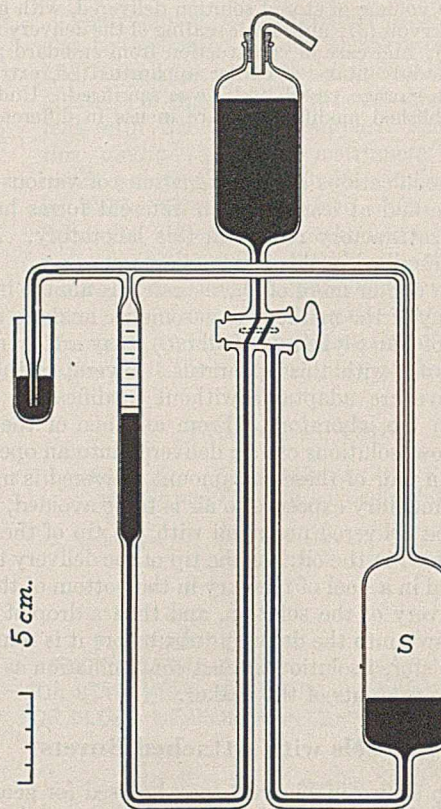


FIGURE 3

of the buret is to be withdrawn, it can be delivered directly from the storage chamber without repeated filling of the buret. There is less danger of disturbing any precipitate which may have settled out. These characteristics, which are also advantageous with other solutions, make the apparatus especially suitable for storage and measurement of saturated sodium hydroxide.

The entire apparatus is first filled by gravity with mercury from the reservoir. The solution is then drawn into the storage chamber through the delivery tube by the application of suction

at the top of the reservoir. The positions of the three-way cock for filling or delivering from the storage bulb or for delivering from the buret are evident from the drawing. To refill the buret, a groove on the face of the plug of the stopcock is turned to connect the tubes below the cock, allowing mercury to flow from the buret to the bulb and forcing solution over into the buret.

To avoid loosening of the plug due to excessive pressure of mercury, the stopcock is placed near the top of the apparatus.

The stopcock might be improved by substituting a V-shaped bore for the groove and arranging the bores so that the three positions of flow would be equally spaced through one complete turn of the cock, or a 120° Y-shaped cock could be used. The one shown is easily made from the more generally available three-way cock. The groove (indicated by dotted lines, on the side away from the observer) is cut by means of a small narrow grindstone.

All three vessels are limited vertically by the height to which mercury can be drawn by suction. At 730 mm. the flow is inconveniently slow; approximately 650 mm. is a more practical limit. The cost and weight of mercury impose an indefinite restriction on the size of the storage bulb and mercury reservoir. A more definite limit is imposed by the tendency of these, and similar vessels having stopcocks on the mercury side, to extrude solution during a rise in room temperature. This can be avoided, if the volume of the delivery tube is not too small a fraction of that of the storage bulb, by drawing sufficient mercury into the delivery tube to allow for expansion of the solution. This limit has not been established, but the author's largest satisfactory vessel has a capacity of about 200 ml.

Mercury-Sealed Dropping Bottle

For some purposes the mercury-sealed dropping bottle shown in Figure 4 is convenient. In it, the main part of the stored solution is well protected by the two columns of mercury. The fraction of a drop of solution at the tip of the delivery tube becomes contaminated if it is not removed, but this is often not important. For example, when the vessel is used to hold 5 *N* sodium hydroxide for absorption of carbon dioxide in some of Van Slyke's gasometric methods, it is necessary only that the capacity of the solution to absorb more carbon dioxide be not impaired after prolonged standing. In such cases the simplest procedure is adequate. If, in other cases, it is important to eliminate all contamination, the exposed droplet of solution in the tip may be flushed out easily.

In the upright position, the mercury column in the delivery tube, *A*, is balanced against that in *B* and *C*. When the vessel is tipped toward the left (in the sketch) to the horizontal position, the mercury columns in both *A* and *B* exert pressure toward the outlet. At the same time the mercury in the storage chamber, *S*, flows to the side of this chamber, exposing the lower end of *A* in the solution. The mercury in *A* flows out, and solution follows. After the vessel is returned to the vertical position, mercury flows into *A* until it again balances the column in *B* and *C*. (One additional drop of solution is forced out ahead of the mercury.) In ordinary use the vessel is then set aside until again needed.

To meet more exacting requirements of purity of the solution, the last fraction of a drop, which becomes contaminated on standing, may be forced out of the outer end of *A* by tilting the vessel enough so that mercury flows to the tip but not enough to lift the lower end of *A* out of the mercury in *S*. The contamination may be still further reduced by washing the outer end of the capillary with plain water or carbon dioxide-free acidulated water held in a small cup, cut from the closed end of a 15-mm. test tube or from the bottom of a small vial. The tip of the delivery tube is immersed in the washing solution, and the vessel is rocked gently back and forth until the capillary has been thoroughly flushed. Contact with air may be completely avoided by delivering the reagent through oil above the contents of the vessel into which it is received.

The construction of the dropping bottle is evident from Figure 4. When the vessel is standing upright, the highest part of the delivery tube, *A*, must be at a level slightly higher than that to which reservoir, *C*, is to be filled. The extreme tip of this tube is bent downward to prevent the solution from running back along the outside and to facilitate washing with a few drops of water. The shape of the storage chamber of the vessel shown is preferred

to a cylindrical one because the broad base makes it more stable and the placing of the tubes gives a higher head of mercury and a more dependable flow of solution.

The specifications of this vessel are not critical except in the following respects. The tube *A* should be of tubing having an inside diameter of 0.3 mm. if the solution is to be delivered dropwise, possibly slightly smaller for solutions less viscous than 5 *N* sodium hydroxide. If larger amounts are to be delivered with less control of the volume, larger capillaries may be used. However, a small size is desirable for the purpose of reducing the volume of solution and the area of capillary wall exposed to air between deliveries to the least amounts compatible with satis-

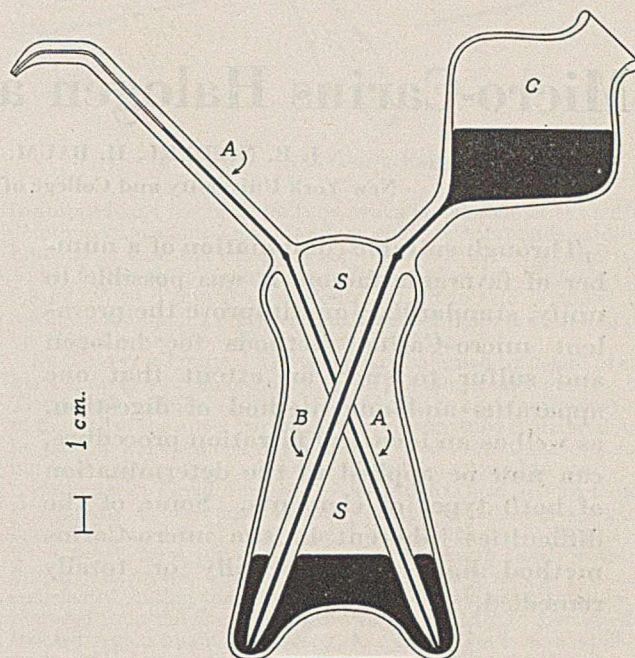


FIGURE 4. DROPPING BOTTLE

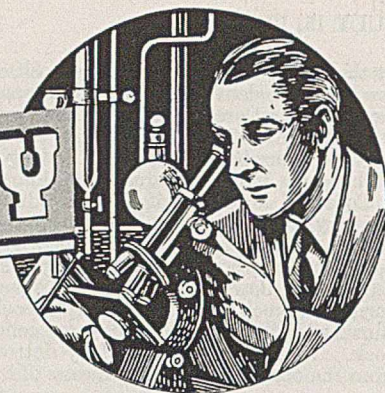
factory operation. Vessels have been used having capacities ranging from about 25 to about 100 ml., and having delivery rates of from 1 or 2 drops to about 1 ml. per second.

This vessel is filled with mercury through the reservoir while it is held in the horizontal position with the reservoir up, the outer end of the delivery tube down, and the inner end of this tube up. It may be necessary to tip the vessel beyond the horizontal and apply suction to the outlet tube to remove the last bubble of air. It is filled with solution in the upright position. The solution may be placed in the mercury reservoir and drawn into the vessel by application of suction to the outlet, oil being placed above the solution if the brief exposure to air is deleterious; or a slender rubber tube may be attached to the outlet tube and the solution may be drawn in directly from the flask in which it is prepared by application of suction to *C*.

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- (10) Van Slyke, D. D., and Neill, J. M., *J. Biol. Chem.*, 61, 523 *et seq.* (1924); especially p. 536 and Fig. 6 (p. 535), apparatus for extraction and storage.

MICROCHEMISTRY



Micro-Carius Halogen and Sulfur Determination

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Through suitable combination of a number of favorable factors it was possible to unify, standardize, and improve the prevalent micro-Carius methods for halogen and sulfur to such an extent that one apparatus and one method of digestion, as well as an identical filtration procedure, can now be applied to the determination of both types of elements. Some of the difficulties inherent in the micro-Carius method have been partially or totally remedied.

THE micro-Carius determination of halogen and sulfur possesses numerous advantages, not only as a method to be taught to students, but also as a generally useful analytical procedure. Despite its simplicity, it is most reliable and can be applied to liquids and volatile substances as well as to solids. Furthermore, it offers a high degree of precision because it has no blank and because it involves simple stoichiometric reactions.

Prevailing objections to the Carius determination are: the danger of explosions, the long heating period, and the possibility of contaminating the reaction product with glass splinters.

An investigation is here described which was undertaken to minimize the above-mentioned difficulties and to unify as well as standardize the apparatus and the procedures. It was found that a combination of the early micro-Carius method of Emich (1) with the conventional micro-Carius method of Pregl (7) aids in overcoming the first two objections while application of the method of differential weighing of the silver halide precipitate in the case of halogen determination, and application of the benzidine method of Guillemet (3) and Weygand and Hennig (9) in the case of the sulfur determination, serve to eliminate the last objection.

The apparatus and procedure employed in this work were those described by Niederl and Niederl (6), except where modifications are specifically mentioned.

Apparatus

BOMB FURNACE (6, p. 122). Any metal block or cylinder with suitable borings for the pressure tubes can be used. The heating may be done by gas or electrically (4).

PRESSURE TUBES (6, p. 122). The pressure tubes are of straight-walled Pyrex glass without a constricted end. They are 20 cm. long, 9 to 10 mm. in inside diameter, and should have a

minimum wall thickness of 1 mm. and a round (semicircular) bottom. Tubes which possess a visible seam are unsatisfactory.

FILTER TUBES (6, p. 128). The original Pregl filter tube (7) with its capillary constriction and asbestos mat, as well as filter tubes having a sealed-in fritted-glass plate with or without an additional asbestos mat, can be used. The latter type is preferred, as it is easier to

clean and the weight seems to show a greater constancy. A filter plate of No. 3 porosity will retain the silver halide or the benzidine sulfate. However, these filters do not have a uniform porosity and filters of the same number usually show a wide variation in filter speed. Each filter tube should therefore be tested for its speed of filtration as follows: When the filter tube is placed on the filtration apparatus and attached to a good water pump, operating at maximum pressure, it should filter water at a rate of 70 ml. per minute.

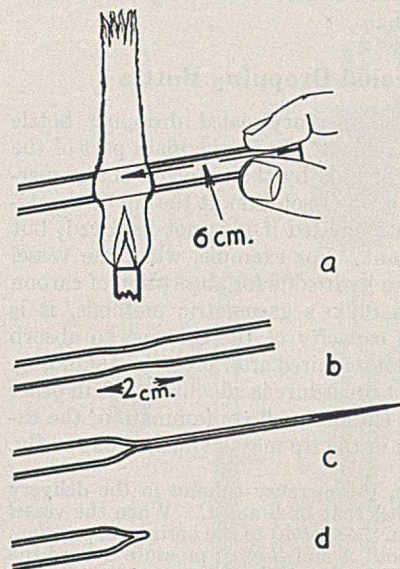


FIGURE 1. SEALING PRESSURE TUBE WITH TIRRIFF BURNER

The retentivity of a filter tube is checked by its performance with a standard precipitate of silver bromide which is prepared by precipitating 5 mg. of potassium bromide, dissolved in 5 ml. of halogen-free distilled water, with 2 ml. of 3 per cent silver nitrate solution in the presence of 1 ml. of concentrated nitric acid. The silver bromide is coagulated by heating and is then filtered, dried, and weighed as usual. Satisfactory filter tubes should retain the calculated amount of silver bromide to within 3 to 5 parts per thousand.

Table I illustrates the behavior of three sample filter tubes when retentivity of silver bromide was investigated. The experimental error in each case was positive.

A new filter, as well as a used one in which the pores have become clogged, is cleaned by boiling it for 30 minutes in nitric acid (1 to 1), then boiling in distilled water, and rinsing three times with halogen-free distilled water. This treatment is important for the achievement of constancy of weight with the filter. Difficulty has been experienced in weighing to constant weight filter tubes which have been previously cleaned with sulfuric acid-bichromate cleaning mixture in the conventional manner. The same filter tubes upon subsequent treatment with nitric acid readily became constant in weight.

DRYING BLOCK (6, p. 25). Any metal block (copper, brass, aluminum, etc.) with suitable borings for the filter tube and the thermometer is suitable. The heating may be done by gas or electrically.

Reagents

FOR HALOGEN DETERMINATION (6, p. 119). All initial and precipitation reagents must be halogen-free.

Distilled water; concentrated nitric acid (specific gravity 1.4); silver nitrate crystals; 30 per cent aqueous potassium iodide solution (2), prepared by dissolving 30 grams of potassium iodide in enough distilled water to bring the total volume of the solution to 100 ml. The solution must be repeatedly filtered to ensure complete freedom from any suspended foreign matter such as dust particles, filter paper fibers, etc. The solution is kept in a dark-glass bottle. Ethyl alcohol, 95 per cent.

FOR SULFUR DETERMINATION (6, p. 143). All reagents employed must be free of sulfate ion.

Distilled water; concentrated nitric acid (specific gravity 1.4); sodium chloride; sodium bromide; 2 per cent aqueous solution of benzidine hydrochloride, prepared by dissolving 5 grams of benzidine hydrochloride in 40 ml. of 1 N hydrochloric acid and adding enough 50 per cent alcohol to make 250 ml. of solution. The solution is brought to boiling, cooled, and filtered. The solution, which must be filtered from time to time, is kept in a glass-stoppered bottle. Ethyl alcohol, 95 per cent.

TABLE I. RETENTIVITY OF FILTER TUBES

Filter	Observed Weight of KBr Mg.	Weight of Silver Bromide		Deviation Parts/1000
		Found Mg.	Theory Mg.	
1	5.120	8.103	8.079	+3
2 ^a	6.071	9.602	9.579	+2
3	6.438	10.188	10.160	+3

^a Precipitate was dissolved in 5% thiosulfate solution and filter tube was weighed second time empty.

Procedure

PREPARATION AND WEIGHING OF SAMPLE. A 5-mg. sample is usually taken for the chlorine or sulfur determination, 7-mg. for the bromine, and 10-mg. for the iodine determination. Using an analytical balance of proper sensitivity and precision instead of a microchemical balance (5), it was found that a 12-mg. sample was sufficient for the determination of chlorine or of sulfur but that at least 20 mg. are required for substances containing bromine or iodine. The amount of silver halide formed often weighs less than the original substance, so that the special case applies where the sample weight is greater than the weight of the reaction product ($s > r$).

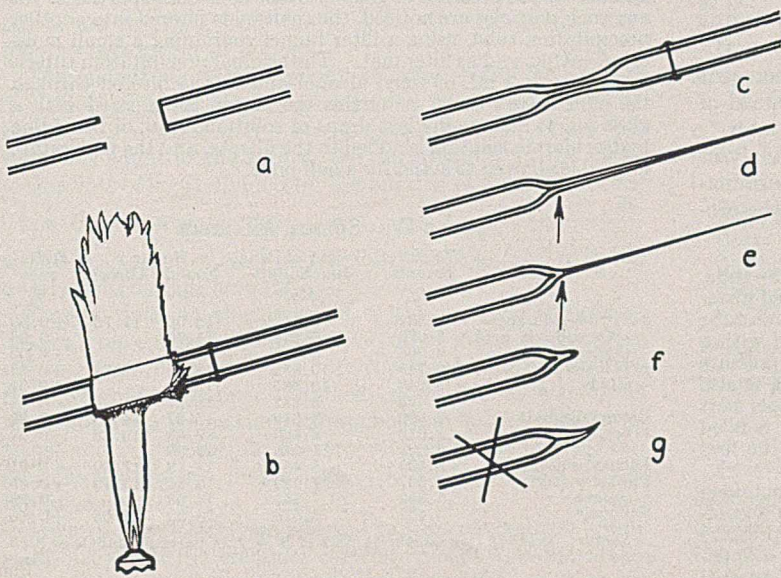


FIGURE 2. SEALING PRESSURE TUBE WITH BLAST LAMP

The sample is introduced into the pressure tube in the usual manner—i. e., dry solid samples by means of the long-stem weighing tube (6, p. 33), low boiling liquids (up to 200° C.) by means of a capillary pipet (6, p. 178), high boiling liquids (above 200° C.), and semisolids by means of capillaries open at both ends (6, p. 35). Then, in the case of the halogen determination, a crystal of silver nitrate [not more than a 10 per cent excess over the required amount (10 mg. for chlorine and 15 mg. for bromine and iodine)]

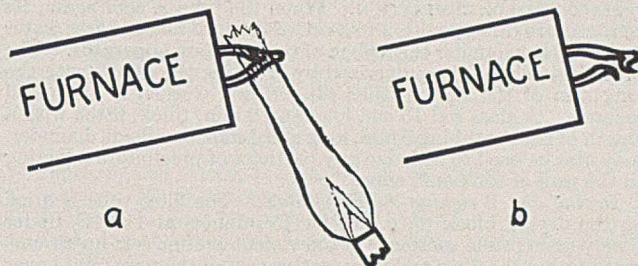


FIGURE 3. RELEASING PRESSURE

is dropped into the pressure tube, while in the case of the sulfur determination about 5 mg. of sodium chloride or bromide (sodium bromide in case the sample has proved difficult to oxidize) are added to the sample contained in the pressure tube. After this 0.3 ml. (5 to 6 drops) of concentrated nitric acid is added by means of a dropping pipet without a rubber bulb, in such a manner that it rinses the wall of the pressure tube.

SEALING THE TUBES. The tubes may be sealed by means of the blast lamp or with an ordinary Tirrill gas burner as suggested by Tiedcke (8). Before the tube is sealed off, the nitric acid adhering to the wall of the upper portion of the pressure tube is driven down by passing the open end of the tube several times through a soft but nonluminous flame until dry. It is then allowed to cool.

Sealing with Tirrill Burner (8). The tube is held in both hands in a slightly inclined position and is heated by means of a hissing flame (15-cm., 6-inch, outer cone, 5-cm., 2-inch, inner cone) at a point 6 cm. from the open end, the tube being slowly rotated during this process (Figure 1, a). When the glass has softened sufficiently, so that the tube shows signs of collapsing, the tube is removed from the flame and is drawn out slightly to form a constricted region about 2 cm. long, b. The flame is now applied again at the base of the constriction to cause the tube to collapse, taking care that the original wall thickness is maintained as the tube narrows down. After the tube has completely collapsed, it is withdrawn from the flame and pulled out to a long capillary, c. This capillary is sealed at its base in the flame to a pointed seal, d, and the whole end is then well annealed under a good coating of soot. The tube is kept in a vertical position until it is cold.

Sealing with Blast Lamp. In sealing the pressure tube over a blast lamp it has been found best first to seal on another piece of the same tubing to serve as a handle (Figure 2, a). The tubing is then heated throughout a distance of 3 cm. at a point about 6 cm. from the junction, being held steady in the flame without pulling, until the walls thicken (b, et seq.). A wide central capillary should still remain, however, c. The tubing is then pulled as nearly vertically as possible and the extended capillary is heated at its base with a small, sharp flame, d. This is pulled out again and after cutting off with the flame, e, the end is fire-polished, f. A heavy, solid glass sheath, g, should be avoided.

DIGESTION. The tube is wiped clean with a cloth and placed in the furnace. Heating for only half an hour (instead of the usual 5 hours) at 300° C. is usually sufficient for most organic halogen and sulfur compounds. At the end of this time the tubes are allowed to cool to room temperature in the furnace and are then pushed out with a glass rod, so that the sealed tip projects about 1 cm. from the end of the furnace. The tip is cautiously heated by lightly passing the luminous flame of a Bunsen burner over it until any liquid caught in the tip is driven down into the cool portion of the tube. The tip is then heated directly at one point with the burner flame normal to the glass surface (Figure 3, a). The internal pressure causes the softened glass of the capillary tip to pop, b.

OPENING THE TUBE. The tube with its pressure released is best opened by means of a small Griffen glass-cutting wheel having V-shaped jaws in which the tube is supported and rotated. A continuous scratch is made around the tube just

below the point of taper in the halogen determination, while in the sulfur determination the scratch is made in the center of the tube. The molten tip of a thin glass rod is applied just above the mark with the tube held vertically, and this is repeated if necessary, until a crack encircles the tube. The tubing is then pulled apart and the edge is fire-polished.

Filtration

HALOGEN DETERMINATION. When the tube is cool again, its contents are diluted with 2 to 3 ml. of distilled halogen-free water and it is placed under the siphon of the filtration apparatus. The precipitate should be pulverized by crushing the lumps with the long arm of the siphon, then filtered and washed in the usual manner. A glass rod 15 cm. long and 2 mm. thick, fitted with a length of rubber tubing 7 mm. long and 4 mm. in outside diameter, may also be used to dislodge any particles of precipitate adhering to the wall of the bomb tube.

Drying and Weighing the Precipitate. The filter tube is dried on the drying block (6, p. 26) for 15 minutes at 110° C. under barely perceptible suction. A too violent suction sets up air currents within the filter and may scatter part of the precipitate over the dust filter.

Dissolving the Silver Halide. In the conventional halogen determinations the filter tube is weighed first without and then with the halide, the difference in weight being that of the halide. This method, however, precludes the presence of glass splinters.

It has been found best to weigh the filter tube and precipitate first and to dissolve the silver halide afterwards with the potassium iodide solution (2). The filter tube is filled with the potassium iodide solution by means of a medicine dropper and the solution is allowed to drip slowly under the pressure of its own head or under gentle suction. This is repeated a second time with another portion of the same solution. Each washing should take 5 minutes. If the precipitate has not dissolved by this time, the treatment is repeated. Particles of glass should not be mistaken for undissolved halide. Finally, the filter is washed twice again, but more rapidly, with potassium iodide solution, five times with distilled water, and three times with alcohol. It is then dried, wiped, and weighed, as before. In case different halogens (Cl-Br, Cl-I, Br-I, or Cl-Br-I) are present, each and every halogen is dissolved separately with the appropriate solvent for the silver halide in question, the washing, drying, and weighing procedure is applied to the remaining precipitate, and finally the potassium iodide procedure is used.

TABLE II. TYPICAL HALOGEN ANALYSES

(Precipitate dissolved in 5% sodium thiosulfate solution)					
Substance	Weight of Sample Mg.	Weight of Silver Halide Mg.	Halogen Found %	Halogen Theory %	Difference %
<i>o</i> -Chlorobenzoic acid	5.243	4.855	22.91	22.64	+0.27
	4.249	3.832	22.31		-0.33
	5.711	5.201	22.53		-0.11
<i>p</i> -Nitrobromobenzene	6.704	6.290	39.92	39.56	+0.36
	7.708	7.209	39.80		+0.24
Dibromoresorcinol-diethylketone compound	6.856	3.510	21.79	21.71	+0.08
	7.131	3.584	21.39		-0.32
<i>p</i> -Chlorothymol	5.725	4.384	18.94	19.20	-0.26
	5.572	4.288	19.04		-0.16

Typical results are given in Table II, where 5 per cent sodium thiosulfate solution was used as a solvent instead of the more efficient potassium iodide solution adopted later.

Table III is a selection of undergraduate student analyses made by students previously unfamiliar with the determination. Potassium iodide solution was used to dissolve the precipitate.

SULFUR DETERMINATION. The lower part of the pressure tube, which contains the oxidation mixture, is filled with distilled water and the resulting solution is transferred to the precipitation tube (Figure 4, *a*), which is 15 cm. in length and is provided with a No. 7 standard ground-glass joint. The same part of the pressure tube is again filled with distilled water and this washing is also transferred to the precipitation test tube. Then the upper part of the pressure tube, the tip of which has been resealed, is filled once with distilled water and this washing is added to the first two portions.

Apparatus for Evaporation. The sulfate solution as obtained above has to be evaporated to dryness. This may be accomplished in several ways, but evaporation under diminished pressure in a closed system has been found most convenient. The apparatus for the evaporation under diminished pressure (Figure 4) consists of the precipitation tube, *a*, the water bath, *b*, and the

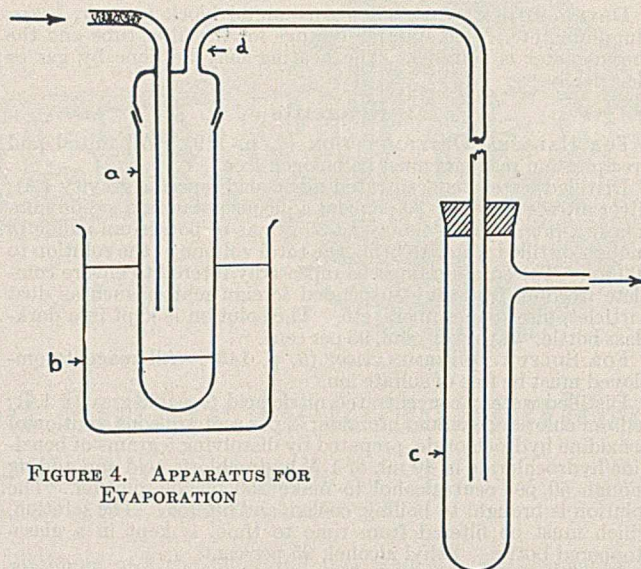


FIGURE 4. APPARATUS FOR EVAPORATION

side-arm suction tube, *c*. *a* is fitted with a standard glass stopper of a gas wash bottle, *d*, possessing also a No. 7 ground-glass joint. Into the upper portion of the gas inlet tube is inserted a wad of cotton which serves as a dust filter. The tube also carries a pinch-cock to regulate the flow of air. The air inlet tube should extend into the precipitation tube to about 5 mm. above the surface of the liquid. By means of a suitably bent glass tube, the outlet tube of the stopper, *d*, is connected to the side-arm suction tube, *c*, which serves as both a suction flask and a trap.

TABLE III. UNDERGRADUATE STUDENT ANALYSES

(Precipitate dissolved in 30% potassium iodide solution)					
Student Unknown	Weight of Sample Mg.	Weight of Silver Halide Mg.	Halogen Found %	Halogen Theory %	Difference %
<i>o</i> -Chlorobenzoic acid	7.567	7.001	22.89	22.64	+0.25
<i>p</i> -Chlorothymol	3.063	2.387	19.28	19.20	+0.08
	4.050	3.198	19.53		+0.33
	7.632	5.809	18.83		-0.37
	0.952	0.727	18.90		-0.30
	0.978	0.753	19.05		-0.15
3,5-Dibromopyridine	3.616	5.795	68.20	67.47	+0.73
	5.148	8.143	67.31		-0.16
<i>p</i> -Dichlorobenzene	2.999	5.913	48.78	48.24	+0.54
<i>p</i> -Bromoacetanilide	6.637	5.902	37.84	37.33	+0.51
Monobromocamphor	7.834	6.218	33.78	34.58	-0.80
	3.301	2.629	33.89		-0.69

Precipitation. As soon as the liquid has evaporated, 3 ml. of distilled water are added to the residue and the solution is examined for the presence of glass or other nonsoluble particles. If any such particles are noticed, the solution is filtered into another precipitation tube, using a filter funnel containing a small moistened cotton wad as filter mat. The original precipitation tube is washed with 2 ml. of ethyl alcohol and this is filtered through the same cotton wad. After this the cotton is squeezed with a glass rod to remove the last drops of solution, 1 ml. of benzidine hydrochloride solution is added to the filtrate, and the precipitate formed is allowed to stand for a half hour.

TABLE IV. SULFUR ANALYSES

Substance	Weight of Sample Mg.	Weight of Benzidine Sulfate Mg.	Sulfur Found %	Sulfur Theory %	Difference %
3-Nitro-6-chlorobenzenesulfonic acid (hydrate)	5.587	5.947	12.06	11.76	+0.30
	5.079	5.229	11.70		-0.06
	6.095	6.278	11.74		-0.02
<i>p</i> -Toluene-sulfonamide	6.740	10.939	18.54	18.71	-0.17
	6.243	10.285	18.72		+0.01
	5.495	8.882	18.37		-0.34
Benzyl disulfide	6.600	8.849	15.27	14.98	+0.29
<i>o</i> -Tolyl thiourea	5.012	8.420	19.09	19.18	-0.09
	6.593	11.046	19.08		-0.10
Dibutyl sulfone	3.409	5.454	18.18	17.99	+0.21
Phenyl- <i>p</i> -tolyl sulfone	6.507	7.930	13.84	13.79	+0.05
	5.850	7.251	14.08		-0.29
Sulfonal ^a	3.452	8.578	28.23	28.08	+0.15

Factor: 0.11362 (log 05543) (1 part of S = 7.28 parts of BaSO₄ or 8.80 parts of C₁₂H₁₂N₂H₂SO₄)

^a This compound required 5 mg. of NaBr, 0.5 ml. of HNO₃, and 3 hours for digestion.

Filtration. The filtration is carried out in the same way as the halogen determination. The precipitation tube is washed out with a total of 5 ml. of 95 per cent alcohol in small portions. These washings are transferred to the filter in the same way as the precipitate. If any particles still adhere to the walls of the precipitation tube, a glass rod may be used to remove them.

The solubility of benzidine sulfate in water has been determined; 1 ml. of a saturated aqueous solution contains 0.2 mg. of benzidine sulfate. Under the above filtration conditions 1 ml. of wash water was found to contain 0.086 mg. of benzidine sulfate, a fact which led to the adoption of 95 per cent ethyl alcohol, in which the reagent is not precipitated, as wash liquid. In drying the precipitate a strong current of air may be used, since the precipitate forms a hard mat which is not easily disrupted by air currents.

Cleaning the Filter. The filter is filled with concentrated sulfuric acid, which is drawn off after a few minutes by means of suction. It is then washed with about 100 ml. of boiling distilled water and tested for the presence of sulfate ions by filtering a few milliliters of water through the filter and adding 1 ml. of benzidine hydrochloride solution to the filtrate.

Typical results are given in Table IV.

Summary

Some micro-Carius procedures for halogen and sulfur were unified and then standardized. Inherent difficulties of the otherwise universally applicable and reliable Carius method were wholly or partially remedied. The danger of explosion was practically eliminated by reducing the amount of concentrated nitric acid used from 0.8 ml. to 5 to 6 drops and by shortening the period of digestion from 5 hours to 0.5 hour.

The danger of contamination of the reaction product with glass splinters was eliminated in the case of the halogen determination by applying the method of differential weighing, involving the treatment of the silver halide with a concentrated aqueous solution of potassium iodide, and in the case of the sulfur determination by filtering the sodium sulfate solution before precipitation with benzidine hydrochloride.

One and the same filtration method and apparatus are used for both halogen and sulfur determination. Specifications for filter tubes suitable for these determinations are given.

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Precision of the Microelectrolytic Determination of Copper

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IT IS the purpose of this paper to estimate the magnitude of the precision of the steps in the microelectrolytic determination of 1 to 2 mg. of copper, using apparatus in common use in microchemical work. The scope is limited to solutions containing no other metal but copper. The results will also be used in subsequent work as a basis for estimating the errors resulting from the presence of other metals during the separation of copper.

The magnitude of the precision is expressed as the average deviation of a series of measurements from the arithmetic mean. By definition (6) the "average deviation from the mean" is equal to the sum of the deviations from the mean (regardless of sign) divided by the number of determinations.

Thus D_a , the average deviation, equals $\frac{d_1 + d_2 + \dots + d_n}{n}$,

where d_1 , d_2 , and d_n are individual deviations and n is the number of determinations.

Specific data on the precision of the microelectrolysis of copper from solutions containing no other metal than copper are rare. In most cases the only comparable figures are the final weights of copper obtained, experimental conditions have not been maintained throughout a series of observations, and few details on the precision of the individual operations are given. Table I gives a brief summary of the literature.

Most of the electrolyses referred to were carried out in hot solutions and with voltages varying from 2.0 to 3.1 volts. The solutions were usually stirred either by heating or by bubbling air through them.

The earlier authors (3, 11) used the Nernst torsion balance, which under best circumstances is sensitive to ≈ 0.0005 mg. Following the work of Pregl (10), other authors have used the more nearly standard types of microbalance. It is not to be expected that the precision with the two types of balances is strictly comparable; indeed, none of the later work compares with that of Riesenfeld and Moller in high precision.

TABLE I. SUMMARY OF LITERATURE

Observer	Weight of Copper Determined Mg.	Deviation Mg.
Benedetti-Pichler (2)	15-20	0.09
Brill and Evans (3)	0.3-1.1	0.015
Clarke and Hermance (4)	0.1-1	0.005
Emich and Donau (5)	7-41	0.15
Hernler and Pfenigberger (7)	0.1-1	0.019
Okacs (8)	0.3-3.6	0.03
Phillippi and Hernler (9)	0.1-2	0.005-0.029
Riesenfeld and Moller (11)	0.1883	0.0005 ^a

^a A Nernst balance sensitive to 0.0005 mg. was employed.

Experimental

In the following work, a Sartorius, air-damped microbalance with a sensitivity of 0.00135 mg. per division, with protected beam was used (0.00135 mg. is required to shift the rest point one tenth the distance between successive lines on the pointer scale). It was located in a special balance case in a quiet part of the building. Temperature

variations of more than 2°, air drafts, and rapid changes in humidity were avoided.

The cathode was handled with clean white cotton gloves, except that bone-tipped forceps were used when putting it on or taking it off the balance.

PRECISION OF REST POINT OF BALANCE. Twelve series of observations of the rest point of the empty balance were obtained during the course of the present investigation. Each series represents a succession of from four to seven rest points with intermediate raising (and lowering) the beam. A typical group of successive rest points is: -10, -8, -3, -6.5, -4. The average deviation, D_a , from the mean of these readings is 2.2 divisions, which is equivalent to ± 0.003 mg. [While Pregl states that the Kuhlmann balance is accurate to 0.001 mg., Benedetti-Pichler (1) points out that this accuracy can be attained only as the average of several determinations. A single weighing is likely to be in error by as much as ± 0.005 mg.] For the twelve series of observations, the average value of D_a is ± 0.0031 mg.

PRECISION OF SETTING RIDER. The precision with which the rider could be reset in the same position was determined next. This operation involves successive determinations of the rest point with intermediate raising and lowering of the beam and the rider. Five series of observations gave an average value of D_a equal to 0.0042 mg.

This value is slightly larger than the corresponding value of 0.0031 mg. when the rider was not involved. It is concluded therefore that the added operation of resetting the rider between successive rest points decreases only slightly the precision in using the balance.

HANDLING CATHODE AND WEIGHTS. After determining the rest point with cathode and weights on the balance, both were removed, the rider and beam were raised, all were once more placed on the balance, and the rest point was re-determined. Six series of observations of 4 to 7 determinations each gave an average value for D_a of 0.0043 mg. It may be concluded that no error is contributed by the operation of handling the cathode and weights.

EFFECT OF CLEANING AND DRYING BARE CATHODE. Four series of observations, in each of which the cathode was several times cleaned in 1 to 1 nitric acid, washed with water and alcohol, dried at 110° C. for 5 minutes, and weighed, gave an average value for D_a of 0.0038 mg. That this value is of the same order of magnitude as in the previous operation indicates that no additional error occurs in this step.

DRYING CATHODE WITH DEPOSIT. Two methods of drying were investigated: (1) After washing with water and alcohol, the latter was set on fire and the cathode gently waved until the alcohol was completely burned; and (2) after washing with alcohol the cathode was placed in an oven at 110° C. for 5 minutes. When the first method was repeated three times on the same cathode and copper deposit, successive weights were 5.452, 5.481, and 5.492 mg. The deposit was clearly tarnished after the second drying. When cathode and deposit were heated by the second method for 5, 10, 125, and 380 minutes, successive weights were 5.870, 5.872, 5.872, and 5.881 mg. Only after the longest period of heating was a tarnish observed. It is obvious that oven-drying at 110° is superior to drying by the heat of the burning alcohol, since the latter leads to oxidation of the deposit. The error involved in heating at 110° for 5 to 10 minutes is also insignificant.

PRECISION OF SAMPLING. The delivery of a 5-ml. volumetric pipet (delivery time, 20 seconds) was observed by weighing to the nearest milligram the weight of water delivered. After cleaning the pipet with cleaning solution and washing, it was filled above the mark with water, the excess wiped off with a towel, the meniscus lowered to the mark, the tip touched against glass, and the water allowed to run

TABLE II. PRECISION OF STEPS IN ELECTROLYTIC OPERATION

Operation	Average Deviation	
	Cumulative Mg.	Individual Mg.
1. Determining rest point		± 0.003
2. Setting rider	± 0.004 (includes 1)	± 0.001
3. Handling cathode and weights	± 0.004 (includes 2)	0.000
4. Cleaning cathode	± 0.004 (includes 3)	0.000
5. Drying deposit and cathode	0.000
6. Sampling by aliquots	± 0.002

TABLE III. WEIGHTS OF COPPER OBTAINED FROM ALIQUOT SAMPLES

Solution	Apparatus	No. of Determinations	Theoretical	Mean	Av.
			Weight Mg.	Weight Mg.	Deviation Mg.
1	Pregl	12	1.398	1.391	± 0.014
1	Pregl	8	1.398	1.387	± 0.020
2	Pregl	4	1.502	1.495	± 0.015
2	Pregl	4	1.502	1.492	± 0.018
2	Clarke	10	1.502	1.504	± 0.012
2	Clarke	10	1.502	1.508	± 0.010

out. When delivery stopped, the adhering drop was touched against the receiver wall after counting five. In sampling, the same procedure was always followed. Eleven determinations of the volume of the pipet gave extremes from +0.009 to -0.007 ml. with an average deviation of ± 0.0035 ml. This corresponds to about ± 0.0011 mg. of copper in each aliquot containing 1.5 mg. of copper. The precision in filling a 250-ml. volumetric flask used in this work is of the order of ± 0.1 ml., which corresponds to less than 0.001 mg. of copper in a total of 1.5 mg. The precision in sampling will therefore amount to ± 0.002 mg. when both sources of error are included.

The results up to this point are summarized in Table II. The second column gives the cumulative value of the precision for each step. The third column gives the amount contributed by the individual operation. It is apparent that the predominating error is in the weighing operation and particularly in the reproducibility of the rest point. When all the operations are performed which, with the exception of the special operation of electrolyzing the copper, make up the complete determination, the precision value may be as great as the sum of the values for operations 3, 5, and 6. Since the first three operations are performed twice in any complete electrolytic determination, the precision magnitude of operation 3 is counted twice. The resulting value for the sum of all operations (except electrolysis) is therefore ± 0.010 mg. This value represents a maximum rather than a statistical value for the precision, since the precisions for the integral parts are not necessarily additive.

PRECISION OF ELECTROLYTIC DEPOSITION. Having estimated the precision of all other operations save electrolysis, this operation was now added to the series already performed. Both Pregl (10) and Clarke (4) types of apparatus were used.

Procedure with Pregl Apparatus. The solution (7 to 8 ml.) was brought slowly to a boil and electrolysis started at 2.8 volts. After 3 to 4 minutes the burner was turned off and the solution permitted to cool for the remainder of the electrolysis. Electrolysis was continued 25 minutes. Urea (30 to 40 mg.) was added, the condenser and cell were washed down with 1 to 2 ml. of water, and the electrolysis was continued for 5 minutes. The voltage was raised to 3.0 to 3.3 volts for the last several minutes. The solution was then cooled (if not already cold), and the cathode was lifted out, washed, rinsed in alcohol, and dried at 110° C. for 5 minutes.

Procedure with Clarke Apparatus. The solution (7 to 8 ml.) was heated to 50° to 60° C. and electrolysis started at 2.6 to 2.7 volts. The solution was stirred by bubbling air through at a rate of 3 to 4 bubbles per second. Electrolysis was continued 25 minutes, 30 to 40 mg. of urea were added, the cell was washed down, the air tube was withdrawn and flushed, and electrolysis was continued another 5 minutes at 3.0 to 3.5 volts. At the end of this time the cell was drained slowly and flushed with 50 to 60

ml. of water. The current was then discontinued, and the cathode was withdrawn, rinsed in alcohol, and dried 5 minutes at 110° C.

Two copper solutions were prepared by dissolving weighed amounts of Kahlbaum's reagent copper in nitric acid followed by evaporation with sulfuric acid to fumes, diluting, and making up to 250 ml. Five-milliliter aliquot samples were taken for analysis.

It was early determined that 5 or 10 minutes at 2.5 volts seemed sufficient to deposit all the copper. However, occasional erratic results led to increasing this time to 20 or 30 minutes. Voltages higher than 2.8 volts led to high results and oxidized deposits. Best results were obtained when the voltage was held at about 2.5 volts during most of the electrolysis and then raised to 3 to 3.5 volts for the remaining 5 minutes. A drop of alcohol as suggested by Benedetti-Pichler prevented spraying by the emerging gas bubbles.

Table III gives the results of the determinations of copper in the aliquot solutions using the Pregl and Clarke electrodes and apparatus.

Discussion

It is apparent that the precision with the Clarke apparatus is somewhat better than with the Pregl type. For the Clarke apparatus it is about equal to the precision of the sum of all the other operations except deposition of the metal. This leads to the conclusion that copper can be deposited with a precision better than that of the rest of the electrolytic operation—i. e., that the error in depositing copper is insignificant in comparison with the sum of all the other errors in the complete determination.

The mean weight of copper obtained in the second set of results with the Pregl apparatus is considerably lower than the mean of the results with the Clarke apparatus. This supports the general experience in this laboratory when using the Pregl apparatus. It is difficult to avoid touching the cathode when withdrawing it from the cell. This would doubtless scrape off some of the plate and give low results. Further, breaking the circuit while the electrolyte is still in contact with the solution is likely to lead to some redissolving of the copper deposit and thus account for the low results obtained with the Pregl apparatus.

Summary

The magnitudes of the precision of the various operations of a complete microelectrolysis have been estimated in terms of the average deviations of series of observations.

Errors in using the microbalance predominate over the errors of handling cathode and weights, of cleaning and drying the cathode, and of sampling by aliquots.

The precision with which copper can be deposited is somewhat better with the Clarke apparatus than with the Pregl type. For the Clarke apparatus 1 to 2 mg. of copper can be determined with a precision of ± 0.010 to ± 0.012 mg. for a series of determinations.

The precision for the complete determination using the Clarke apparatus (± 0.010 mg.) is of the same order of magnitude as for the sum of all the integral operations (± 0.010 mg.) except the deposition of the metal. This leads to the conclusion that the errors in depositing copper are insignificant by comparison with the sum of all the other errors.

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Detection of Aromatics in Air

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THE processing of aromatic materials in industry involves a potential hazard to the health of the personnel—exposure to aromatic vapors in the atmosphere. It has been reported (1) that 100 p. p. m. of aromatics is the maximum aromatic concentration in which a man may work safely. In the past, the lack of a method for the determination of aromatics in the atmosphere in the presence of other hydrocarbons made it impractical to define the areas where the concentration of aromatics necessitates protective devices for the workers, in industrial processes such as the sulfur dioxide extraction of petroleum distillates. An analytical procedure that possesses simplicity and a sufficient degree of accuracy has been devised for indicating whether the aromatic concentration presents such a health hazard.

The Bureau of Mines (2) lists most of the methods, based on the measurement of physical properties, reported in the literature—namely, fractional distillation, specific gravity, sorption on solid sorbents, and the use of the interferometer and the spectrograph. Because of the very small quantities of aromatics present, distillation, specific gravity measurements, and gain in weight of a sorbent are inapplicable. The use of the interferometer or the spectrograph requires a skilled operator and expensive equipment.

In addition to the nitration method described by the Bureau of Mines (2), several other methods were investigated. The chemical methods, utilizing the color change brought about by sulfonation or nitration, were found to be unsuited to refinery practice, probably because of organic dust particles in the atmosphere. Attempts to utilize the differences in solubility of picric acid in aromatics and paraffins by titration with caustic or by color differences failed because only traces of aromatics were present in the atmosphere, and the results were inaccurate. Utilization of the difference in index of refraction by absorption in a low-boiling paraffin (*n*-heptane) was unsatisfactory because at the low temperature necessary to prevent "weathering", ice from moisture in the atmosphere rapidly plugged the equipment. On the other hand, the use of a high-boiling paraffin resulted in failure because its index of refraction was too close to that of the aromatics.

Description of Apparatus

The sample of air to be tested is obtained in a 5-liter Pyrex glass short-necked flask, fitted with a tight-fitting rubber stopper through which are inserted two 3- to 4-mm. straight-bore glass stopcocks and a low-temperature thermometer (Figure 1). A long, fine capillary tube is used to withdraw the condensed sample from the flask. Indices of refraction are determined with an

TABLE I. DATA ON AROMATIC CONTAMINANT

10% off on Engler distillation, ° F.	243		
50% off on Engler distillation, ° F.	262		
90% off on Engler distillation, ° F.	298		
Mean average boiling point, $\frac{243 + 262 + 298}{3}$, ° F.	268		
Temperature of air in pump room, ° F.	110		
Absolute pressure of air in pump room, mm.	750		
Aromatic content of pump liquid, fraction by volume	0.85		
Density of pump liquid at 60° F.	0.8493		
Before extraction with 4 volumes of 99.5 per cent sulfuric acid	0.7500		
After extraction with 4 volumes of 99.5 per cent sulfuric acid	0.7500		
Condensation and absorption of unknown sample from pump room	1.3315		
Refractive index of condensate at 68° F.	1.3315		
Condensation and absorption of air containing known concentrations of pump liquid			
Pump liquid, cc. per 5 liters of air	0.0005	0.0025	0.0125
Aromatics in air, p. p. m.	19	93	464
Refractive indices of condensed liquid at 68° F.			
	1.3305	1.3318	1.3360
	1.3308	1.3319	1.3360
	1.3305	1.3320	1.3316
	1.3306	1.3319	1.3360

Abbe refractometer at some constant, convenient temperature (either 20° C., 68° F., or tap-water temperature).

Procedure

For clarity, the procedure and model calculations are presented in detail.

Several 5-liter flasks are evacuated to about 2 mm. of mercury absolute pressure, and the air sample is obtained by opening one of the stopcocks in the atmosphere suspected of contamination; two or three air samples should be taken for the purpose of checking. A sample of the liquid causing the contamination is also obtained and the temperature of the air at the point of sampling is read and recorded.

A portion of the liquid sample is tested for Engler distillation, aromatic content, and density before and after extraction with 4 volumes of 99.5 per cent sulfuric acid.

Exactly 0.5 cc. of methyl alcohol is measured into the flask containing the air sample through one of the stopcocks and the alcohol is permitted to evaporate completely in the closed flask by warming up to about 37.78° C. (100° F.). The flask and contents are then cooled to -56.67° C. (-70° F.). A portion of the condensed liquid is removed from the bottom of the flask with the capillary tube and its index of refraction is read at the chosen temperature.

Next, 100-cc. blends, containing 0.1, 0.05, 1.25, and 2.5 cc. of liquid contaminant in methyl alcohol, are made up to obtain the data for a curve of "refractive index of the condensed liquid vs. liquid volume in cc.", which is drawn to compare the known concentrations of the hydrocarbon with that present in the unknown air sample.

Exactly 0.5 cc. of each of these blends is measured in turn into partially evacuated 5-liter flasks and the vacuum is broken by admitting hydrocarbon-free air. The flask is then closed, the liquid is allowed to evaporate and then chilled down according to the procedure outlined in the foregoing paragraph, and the refractive index of the condensed liquid is determined at the chosen temperature.

Indices of refraction are plotted against the known volumes of contaminant contained in each 0.5 cc. of the blends to produce a curve from which the cubic centimeters of liquid contained in the unknown air sample may be determined.

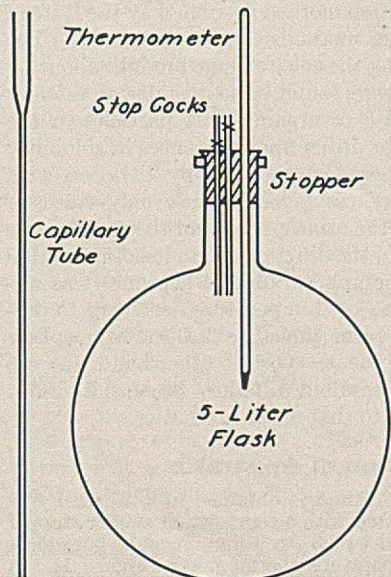


FIGURE 1. APPARATUS

Calculations

In order to calculate the parts of aromatic vapors per 1,000,000 parts of air from the cubic centimeters of hydrocarbons present in 5 liters of the air sample, the following equations are used:

$$\frac{d - (1 - x_a)d_p}{x_a} = d_a = \text{density of aromatics at } 15.56^\circ \text{ C. (60}^\circ \text{ F.) present in liquid sample taken from source of contamination (1)}$$

where x_a represents the aromatic content of the liquid sample in fraction by volume, and d and d_p represent, respectively, the density at 60° F. of the liquid sample before and after extraction with 4 volumes of 99.5 per cent sulfuric acid.

$$9120 \times \frac{cc \times x_a d_a}{m} \times (460 + t) \times \frac{760}{p} = \text{volumes of aromatics vapor per million volumes of air (2)}$$

where cc represents the amount of total hydrocarbons expressed as volume of liquid (in cc.) present in the air sample (as read from the calibration curve of refractive index of condensate vs. cc. of liquid hydrocarbon introduced into the flask), m the molecular weight of the aromatics, and t and p the temperature in ° F. and the absolute pressure in millimeters of mercury, respectively, of the contaminated air.

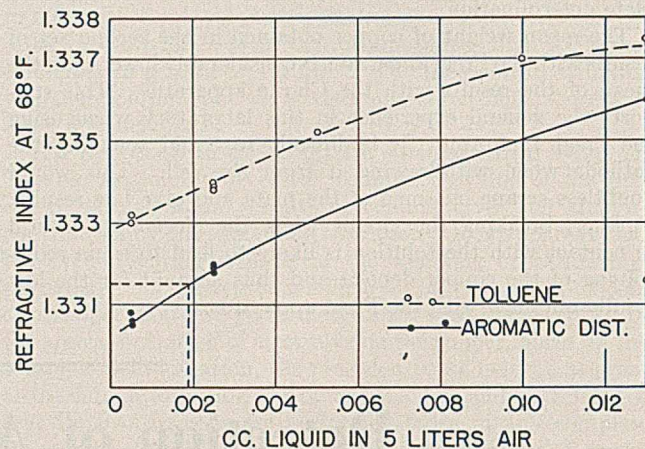


FIGURE 2. REFRACTIVE INDEX OF CONDENSATE VS. CONCENTRATION IN AIR

Table I shows the data obtained on a sample of aromatic distillate which was contaminating the atmosphere.

The curve in Figure 2 has been drawn to fit the data obtained on the 5-liter samples of air containing various known amounts of pump liquid. As shown by the dotted lines, the volume of pump liquid (0.0019 cc.) present in 5 liters of the unknown air sample was determined from the refractive index (1.3315) of the condensate produced.

According to the dotted lines of Figure 3, the average molecular weight (112) of the pump liquid is estimated from the mean average boiling point (131.11° C., 268° F.).

Substituting in Equation 1, $\frac{0.8493 - (0.15) \times 0.7500}{0.85} = 0.867$, the specific gravity of the aromatics present in the liquid sample taken from the source of contamination.

Substituting in Equation 2, $9120 \times \frac{0.0019 \times 0.85 \times 0.867}{112} \times (460 + 110) \times \frac{760}{750} = 65$ parts per million (by volume) of aromatics present in the unknown air sample.

Development and Accuracy of Method

In the development of a procedure for determining aromatics in the atmosphere, consideration was given to the fact

TABLE II. DETERMINATION OF TOLUENE

Liquid toluene, cc. per 5 liters of air	0.0005	0.0025	0.005	0.010	0.0125
P. p. m. in air	23	116	232	465	580
Refractive indices of condensed liquid at 68° F.	1.3332	1.3339	1.3352	1.3370	1.3375
	1.3330	1.3340	1.3370
	1.3330	1.3340	1.3375
	1.3330	1.3338

that, if all the hydrocarbons present in the air sample were absorbed in a given volume of a liquid absorbent, it would be possible to calculate the amount of hydrocarbons present in the air from refractive indices of the alcohol-hydrocarbon mixture, the alcohol, and the hydrocarbons, provided a liquid sample of the hydrocarbons present in the air were available.

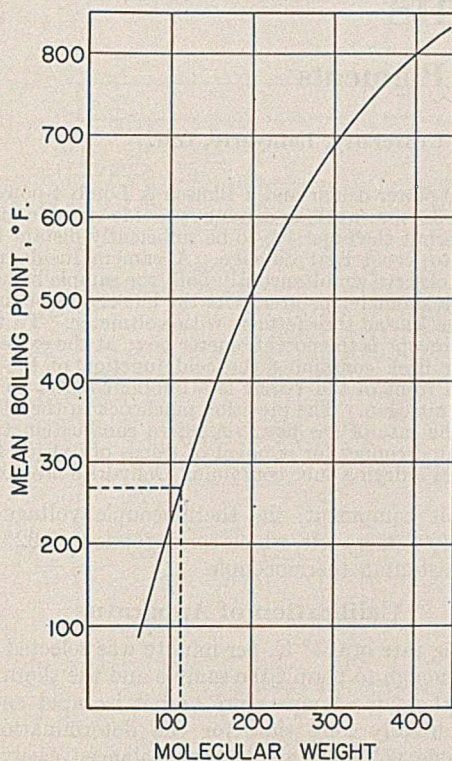


FIGURE 3.5. MOLECULAR WEIGHT OF HYDROCARBONS vs. MEAN BOILING POINT

Methyl alcohol was chosen as the absorbent because its refractive index is less than that of the aromatic hydrocarbons and is about the same as that of water. The former relationship makes possible the calculations required, and the latter relationship minimizes the error introduced by variations in humidity of the air sample.

In testing out the possibilities of applying the foregoing principles to determine the amount of aromatics present in the atmosphere, blends of 0.0005, 0.0025, 0.0050, 0.010, and 0.0125 cc. of liquid toluene with 0.5 cc. of methyl alcohol were measured into 5-liter flasks at 26.67° C. (80° F.) and an absolute pressure of 760 mm., evaporated in the closed flasks by warming the mixture to about 37.78° C. (100° F.), and then cooled to -56.67° C. (-70° F.). Table II shows refractive indices of the condensate obtained in each case.

These data, which are plotted in Figure 2, show that, since the refractive index of the condensate was not equal to that of a mixture of the methyl alcohol and hydrocarbons injected into the flask, only a partial condensation of both the methyl alcohol and the hydrocarbon vapors must have been obtained when the vapors were cooled from the temperature of com-

plete vaporization of the liquids to -56.67° C. (-70° F.). It would therefore be impossible to calculate the hydrocarbon vapor present in a sample of air from the quantity of methyl alcohol injected and refractive indices of the condensate obtained at -70° F. and the methyl alcohol employed. In order to estimate the concentration of hydrocarbon in the unknown air samples, every analysis must therefore be accompanied by cooling of air samples containing known concentrations of the hydrocarbon distillates in question and the same volume of methyl alcohol as that used in the unknown sample and then constructing a curve of "refractive index vs. the volume of hydrocarbon distillate used". The amount of hydrocarbon present in the unknown sample can then be read from this curve by means of the refractive index of the condensate obtained at -70° F. and the concentration of aromatics expressed in terms of parts per million can be calculated.

An inspection of the distribution of the points which determined the curves for both toluene and the aromatic distillate in Figure 2 shows that, for concentrations in the range of 100 p. p. m. (0.00215 cc. of toluene and 0.0027 cc. of aromatic distillate per 5 liters of air), the method is accurate to about 15 p. p. m. of aromatics. For concentrations in the range of 400 p. p. m. (0.0086 cc. of toluene and 0.0108 cc. of aromatic distillate per 5 liters of air), the method is accurate to only about 80 p. p. m.

Derivation of Equation for Determining Aromatic Vapors in Air

- Let *cc* = cubic centimeters of liquid hydrocarbons contained in 5 liters of the contaminated air
- d* = density at 60° F. of liquid hydrocarbons
- d_p* = density at 60° F. of liquid hydrocarbons after extraction with 4 volumes of 99.5 per cent sulfuric acid
- d_a* = density at 60° F. of liquid aromatics removed by extraction with 4 volumes of 99.5 per cent sulfuric acid
- x_a* = volumetric fraction of aromatics in hydrocarbon sample (determined by extraction with 4 volumes of 99.5 per cent sulfuric acid)
- m* = average molecular weight of liquid aromatics
- t* = temperature of contaminated air at time of sampling, ° F.
- p* = absolute pressure of contaminated air at time of sampling, millimeters of mercury

$$\frac{d - (1 - x_a)d_p}{x_a} = d_a = \text{specific gravity of liquid aromatics}$$

$$cc \times x_a d_a = \text{grams of aromatic vapor in 5 liters of air at } t^\circ \text{ F. and absolute pressure, } p \text{ mm. of Hg}$$

$$\frac{cc \times x_a d_a}{m} = \text{moles of aromatic vapor in 5 liters of air at } t^\circ \text{ F. and absolute pressure, } p \text{ mm. of Hg}$$

$$\frac{cc \times x_a d_a}{5m} = \text{moles of aromatic vapor in 1 liter of air at } t^\circ \text{ F. and absolute pressure, } p \text{ mm. of Hg}$$

$$\frac{cc \times x_a d_a}{5m} \times \frac{460 + t}{460 + 32} \times \frac{760}{p} = \text{moles of aromatic vapor in 1 liter of air under standard conditions of temperature and pressure}$$

$$\frac{cc \times x_a d_a}{5m} \times \frac{460 + t}{460 + 32} \times \frac{760}{p} \times 1,000,000 = \text{moles of aromatic vapor in 1,000,000 liters of air under standard conditions of temperature and pressure}$$

$$\frac{cc \times x_a d_a}{5m} \times \frac{460 + t}{492} \times \frac{760}{p} \times 1,000,000 \times 22.4 = \text{liters of aromatic vapor in 1,000,000 liters (parts per million) of air under standard conditions of temperature and pressure}$$

$$\text{Collecting constants except that for pressure, } \frac{22.4 \times 1,000,000}{5 \times 492} \times \frac{cc \times x_a d_a}{m} \times (460 + t) \times \frac{760}{p} =$$

$$9120 \times \frac{cc \times x_a d_a}{m} \times (460 + t) \times \frac{760}{p} = \text{p. p. m. of aromatics}$$

No attempt is made to correct for the relative volatilities of the components.

Summary

The analytical method devised for estimating the atmospheric aromatic contents consists of cooling a blend of the unknown air sample and the vapor of a fixed volume of methyl alcohol on one hand, and blends of air samples containing known concentrations of the aromatic distillates in question and the vapors of a fixed volume of methyl alcohol on the other, to -56.67°C . (-70°F .) and obtaining refractive indices of the condensates.

This method is reasonably simple and gives an accuracy

within 15 parts per million for critical concentrations of 100 parts per million.

Acknowledgment

The authors extend thanks to the Humble Oil and Refining Company for permission to publish their findings.

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Microscope Hot Stage for Determination of Melting Points

Application to Carotenoid Pigments

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THE usual method of determining melting points by means of a Berl block or a liquid bath surrounding a melting point tube does not give satisfactory results when applied to such compounds as the carotenoid pigments. The melting point of these compounds observed in this manner is really an indication of decomposition; it is not a sharply defined point and considerable material is required. Values for the melting point of alpha-carotene reported in the literature vary from 178.5°C . (11) to 188°C . (8), a range of 9.5°C . For beta-carotene the reported values vary from 177.8°C . (11) to 187.5°C . (10), a range of 9.7°C . The range of any one determination is usually 1°C . or more. The sintering point is usually observed slightly below the melting range.

A number of hot stages for melting point determination have been described (1, 3, 4, 5, 9), but the apparatus discussed here includes refinements which add greatly to the precision of measurement. To the authors' knowledge, this technique has not been applied previously to carotenoid pigments, to which it is very well adapted. Its use should add significance to the melting point as a physical constant in carotenoid chemistry.

Description of Apparatus

The hot stage is constructed as shown in Figure 1. The two copper plates are placed on the stage of a polarizing microscope, and the sample is placed on a circular cover glass in the upper recess of the lower plate. A spring clip holds the cover glass in place, so that the crystals are directly over the 0.156-cm. (0.0625-inch) hole passing through the axis of the copper plates. The sample is thus illuminated from below with polarized light and is observed through the analyzing Nicol prism of the microscope.

The stage is heated electrically by means of a coil of 60 cm. (2 feet) of No. 24 Nichrome wire having a resistance of 3.4 ohms. The core, machined from lava and baked to hardness, is recessed in the bottom of the lower block around the central hole. An annulus of lava is cemented under the heating element to enclose it within the block.

Control of the heating rate is effected by a Variac variable transformer, Type 200-C. Heating rates of from 0.1° to 6.5°C . per minute can be maintained at any temperature from that of the room to 250°C .

The temperature within the apparatus is measured by a Leeds & Northrup portable precision potentiometer and an iron-constantan thermocouple. The hot junction of the couple, about 1 mm. in diameter, is located within 1 or 2 mm. of the sample. The leads are brought diagonally through the lower plate in a porcelain tube, cemented in place. Two holes lead from the outside to the central chamber for the passage of nitrogen through the apparatus.

Figure 2 shows how the hot stage is insulated from the microscope stage by a Pyrex support on an asbestos plate. A Leitz

Periplan 20-power ocular and a Bausch & Lomb 4-power objective with a 38-mm. working distance provide suitable magnification and permit the objective to be sufficiently distant from the hot stage to avoid heat damage. A camera lucida makes it possible to observe simultaneously both the sample being melted and the galvanometer pointer. At the left center of the photograph is the Variac transformer, with voltmeter. To the right of the microscope is the potentiometer box; at the extreme right is a Dewar flask containing the cold junction of the thermocouple. In front of the Variac is a bubble counter to measure the flow of nitrogen. The precision pinchcock in the foreground regulates the rate of gas flow. A micro combustion tube containing heated copper for removal of traces of oxygen from the nitrogen and a drying tube containing Dehydrite are not shown.

With this equipment, the thermocouple voltage can be estimated to 1 microvolt, which corresponds to 0.02°C . with an iron-constantan thermocouple.

Calibration of Apparatus

A heating rate of 0.3°C . per minute was selected because it is slow enough to permit the sample and the thermocouple to attain the same temperature and it is rapid enough to avoid an unduly long time for the determination. The thermocouple voltage may be kept balanced easily at this heating rate. The voltage necessary to maintain a heating rate of 0.3°C . per minute at any desired temperature was determined by measurement of the block temperature increase with time for four voltages. Rates of heating were plotted against temperature for each voltage. The temperature at which a given voltage heated the apparatus at the desired rate (0.3°C . per minute) was then plotted against that voltage. The result was a straight line from which can be read the voltage necessary to heat the block at 0.3°C . per minute at any temperature from room temperature to 250°C .

When a melting point is to be determined, the sample, which may be a single crystal if necessary, is placed in position and the apparatus is heated at 22.5 volts, corresponding to a current of 6 amperes, the upper limit of the heating element. Within 1.5° to 2.0° of the anticipated melting point, the voltage is set at the point necessary to maintain a heating rate of 0.3° per minute. The response to voltage change is sufficiently rapid to allow maintaining solid and liquid phases as desired. Thus, if the sample does not decompose, several melting points may be determined with the same sample. Nitrogen should flow through the apparatus during the entire heating procedure. About 1.5 minutes before the expected melting point is reached, the flow of nitrogen is stopped to ensure temperature equilibrium. When anisotropic crystals are observed between crossed Nicol prisms, the melting point is observed as a sudden disappearance of

double refraction. The time necessary for the complete determination is about 30 minutes.

To test the reliability of the apparatus, melting points of purified samples of well-known compounds were determined covering the temperature range of 40° to 175° C. Results are reported in Table I.

These determinations have a maximum difference of 0.13° C. between successive crystallizations of the same material. The precision of successive determinations on fresh samples of these materials is $\pm 0.04^\circ$ C. or less. It is concluded that the melting points of these compounds, determined by this method, are not significantly different from those reported in the literature.

Two determinations on fresh samples of potassium thiocyanate, heated at different rates, 0.25° and 0.73° C. per minute in air, gave 175.31° and 175.29° C. Four months

TABLE I. COMPARISON OF MELTING POINTS

Substance	Reported Melting Point ° C.	Grade and Treatment	Observed ^a Melting Point ° C.
<i>p</i> -Tolyl amine	42-43 (6)	Eastman, after treatment with bone black and recrystallization from ethanol	42.95
	43.7 (7)		42.87
<i>p</i> -Nitroaniline	147.5 (6)	After second recrystallization from ethanol	42.89
	147.3 (2)	Eastman White Label	42.82
	148.0 (7)	After recrystallization from ethanol	147.20
Potassium thiocyanate	173.2 (6, 7)	Mallinckrodt's c. p. recrystallized from ethanol	175.38
		After second recrystallization from ethanol	175.31
			175.29

^a Each observed melting point is for a fresh sample in air. All samples were dried in a vacuum of 15 microns of mercury (measured by a Pirani gage) for 4 hours at room temperature.

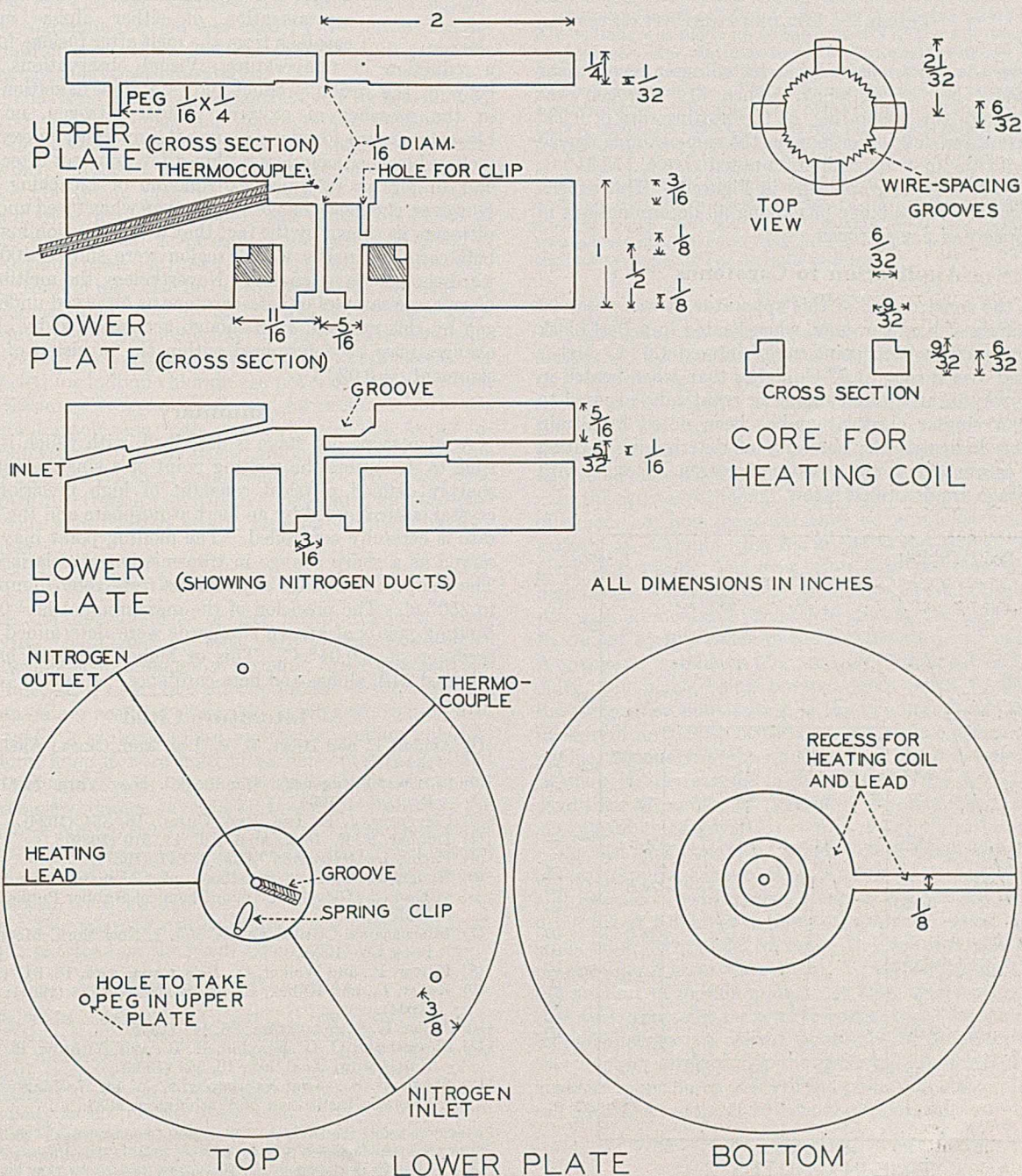


FIGURE 1. DIAGRAM OF MELTING POINT APPARATUS

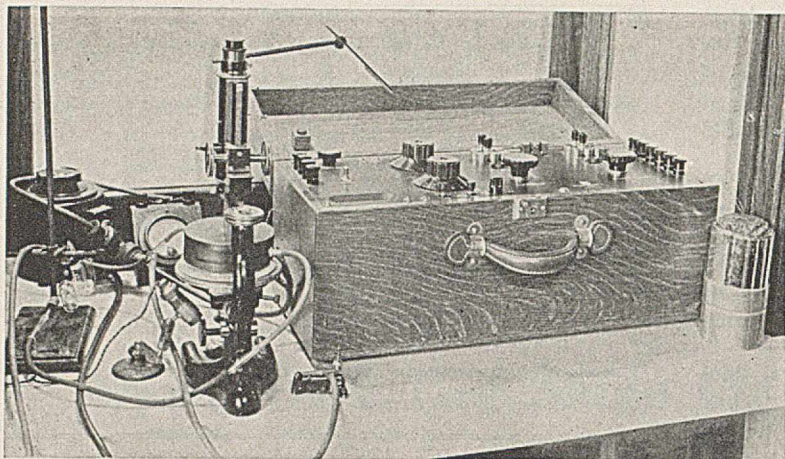


FIGURE 2. MELTING POINT APPARATUS

later, when the same material was tested again, concordant results could not be obtained. Then dry nitrogen was passed through the apparatus; at the heating rate of 0.33° per minute three determinations on the same sample agreed exactly with the first determination noted above, 175.31° C. The results are shown graphically in Figure 3. This experiment shows the advisability of making all determinations in an atmosphere of dry nitrogen.

Application to Carotenes

Before the construction of this apparatus, it was observed that a sample of beta-carotene, when heated in a Berl block in an evacuated melting point tube, sintered 1.6° C. higher and melted over a range 1.2° C. higher than when heated in the same way in an ordinary melting point tube exposed to the air. A similar observation has been noted by Strain (12). This indicated the necessity of determining melting points of carotenoids in the absence of oxygen. Results with the hot stage are described below.

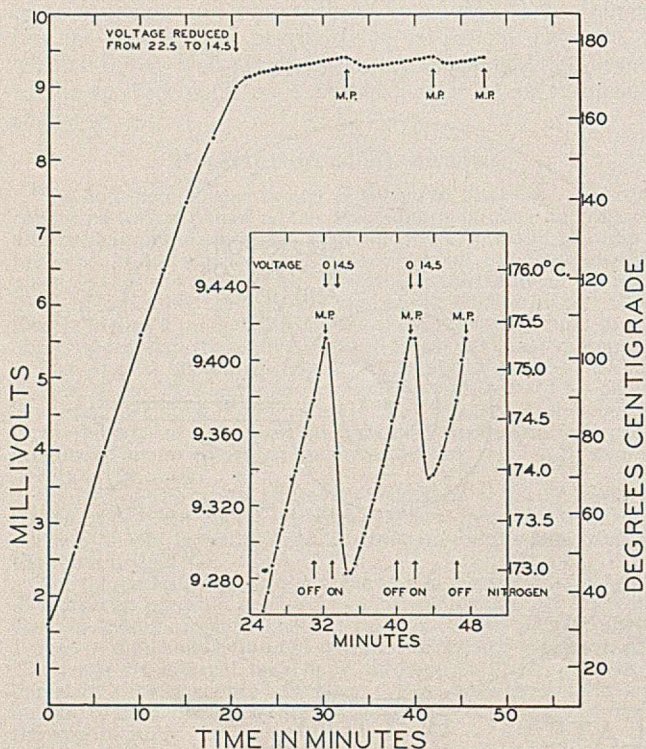


FIGURE 3. MELTING POINT OF POTASSIUM THIOCYANATE

A sample of beta-carotene was recrystallized four times from carbon disulfide-ethanol and dried 20 hours at 84° C. in vacuum. Three melting point determinations, made under nitrogen, were as follows: 179.78° , 179.81° , and 179.81° C. In air, this sample melted at 178.51° C., 1.3° C. lower than under nitrogen. When oxygen was passed through the apparatus during a melting point determination, this sample melted at 168.63° C., 11.2° C. lower than under nitrogen.

A sample of alpha-carotene, four times recrystallized from carbon disulfide-ethanol and dried at room temperature in a vacuum of 10 microns of mercury (measured by a Pirani gage), melted at 184.45° C. under nitrogen. After 3 weeks' storage at 0° C. in vacuum, it melted at 184.37° C. under the same conditions. In air, this sample melted at 180.73° C., or 3.7° lower than under nitrogen. Under oxygen, it melted at 172.78° C., or 11.6° C. lower than under nitrogen.

The authors have never observed a recrystallization of either alpha- or beta-carotene from the melt after fusion, following a reduction in temperature. Visual observations on the color of the fusion product indicate that oxidation occurs in the presence of oxygen. Under nitrogen, no visible bleaching occurs for many hours after melting; in oxygen the melt is bleached colorless within a few minutes after fusion; and in air an intermediate amount of bleaching occurs. However, chemical change occurs, even when fused under pure nitrogen, as shown by the fact that the absorption maxima of beta-carotene in the visible region were shifted 100 \AA. toward shorter wave lengths. Nevertheless, the melting point of separate samples of beta-carotene as observed under nitrogen by this method, even though accompanied by chemical change, may be determined within the precision of the instrument, $\pm 0.02^\circ$ C.

Summary

A microscope hot stage is described, with which it is possible to determine the melting point of a single crystal as a sharply defined physical constant of high precision. The crystal is surrounded by an inert atmosphere and the heating rate is carefully controlled. The melting point may be observed as a sharp change in transmission of polarized light. The temperature range available is from room temperature to 250° C. The precision of the measurement is $\pm 0.02^\circ$ C. Melting points of known standards were determined with a precision of $\pm 0.04^\circ$ C. This or higher precision has been attained with alpha- and beta-carotenes.

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PRESENTED before the Division of Biological Chemistry at the 98th Meeting of the American Chemical Society, Boston, Mass. Based on a section of a thesis submitted to the faculty of Purdue University by J. W. White, Jr., in partial fulfillment of the requirements for the degree of master of science, August, 1939.

Determination of Indium by Micromethods

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INDIUM occurs in nature in low percentages, usually less than 0.2 per cent of the major constituents with which it is associated. When macromethods are used for its determination, a very large sample must be taken and the necessary quantitative separations are difficult to handle. However, using an original sample no greater than that taken for the usual macroanalysis, the separations and concentrations may combine both macro- and microtechniques, while the final determination is on a micro scale.

Qualitatively, indium has been detected by chemical microscopic methods (4), by qualitative analytical tests (12), by the polarographic method (9), and by the spectrographic method (3, 13) which was also used in the discovery of indium. The spectrographic method was used by the author for detecting indium in residues and concentrates during the development of analytical procedures.

Indium has been determined quantitatively by gravimetric, volumetric, spectroscopic, and polarographic methods. It may be determined gravimetrically by weighing the oxide, In_2O_3 , which is formed on heating the hydrated oxide (11, 19, 20). This oxide may be precipitated by ammonium hydroxide, by sodium hydroxide (if the solution is boiled to coagulate the colloidal suspension which tends to form, 6, 21), by organic bases (15), and by a hydrolysis method (11, 13, 20). Indium may also be determined as the sulfide if the precipitate is dried in a stream of hydrogen sulfide (11). The use of 8-hydroxyquinoline has been proposed by Geilmann and Wrigge (8) for a semimicroprocedure. Volumetric methods reported for indium chloride use potentiometric titration with potassium ferrocyanide (2), and for indium acetate use potassium ferrocyanide with diphenyl benzidine as an internal indicator (10). The spectrographic and polarographic methods could be classified as micromethods. However, both offer difficulties from a quantitative viewpoint, and the purpose of this investigation was to develop more satisfactory procedures.

Proposed Electrolytic Method

Before the development of the microprocedure, many electrolytic macrodeterminations were made. Electrolytes such as formic acid, ammonium formate, hydroxylamine sulfate, sulfuric acid, hydrazine sulfate, sodium acetate, tartaric acid, ammonium acetate, citric acid, boric acid, sodium acid sulfite, oxalic acid, ammonium hydroxide, sodium chloride, and sodium fluoride were tried in various combinations and proportions, and it was found that oxalic acid made ammoniacal to methyl orange gave the best results. A study of the deposition of indium from this electrolyte by the methods of Sand (17) and Fischer and Schleicher (7) showed that a total cell voltage of 2.1 volts was necessary to start indium deposition; to obtain complete deposition, a potential of 3 volts was required. The microdeposition method was developed from the results obtained on the macroexperiments.

Apparatus and Reagents

The electrodeposition cells of Pregl (14) and Clarke and Hermance (5) were used for the microelectrodeposition. Pregl's cell has several disadvantages (5) and except for a few preliminary experiments, the cells of Clarke and Hermance were used.

The reagents used in all the investigations were of regular analytical quality except for the oxalic acid, which was Kahlbaum "for analysis" brand.

Indium metal, purchased as spectroscopically pure, was found by further spectroscopic examination to contain traces of cad-

mium and iron. To remove these, it was purified by two reprecipitations with ammonium hydroxide, removal of iron by cupferron, reprecipitation by ammonium hydroxide, electrodeposition from oxalic acid solution, resolution in sulfuric acid, and final reprecipitation with ammonium hydroxide. This hydrated indium oxide was then dissolved in a calculated amount of *N* sulfuric acid and made up to 1 liter. This solution was standardized by the accepted macrogravimetric indium oxide method. The average of three determinations showed that it contained 0.3992 ± 0.0004 mg. of indium per ml.

Microdeposition Procedure

The solution containing about 2 mg. of indium was put in the small Clarke and Hermance cell, 1 gram of solid oxalic acid and several drops of methyl orange indicator were added, and the solution was made alkaline by the use of concentrated ammonia. The volume was made up to the capacity of the cell, about 5 ml., with water. The platinum anode and properly weighed platinum cathode were placed in the cell, and the small air stirring tube was put into position. The air for the stirring was passed through a wash bottle containing concentrated ammonium hydroxide, so that it would be saturated and not reduce the ammonia concentration in the cell. The electrolysis was run for about 30 minutes at 3 volts and at a temperature of 70° to 80° C. The electrode was washed with water and alcohol while the current was still on and then the alcohol was allowed to run out of the cell, the current was turned off, and the electrodes were removed. The cathode was quickly air-dried and weighed. The increase in weight equals the indium deposited as metallic indium.

Discussion

It was found necessary to adjust the concentration of the ammonium hydroxide by the use of the methyl orange indicator. An average of six determinations made without any control on the quantity of ammonium hydroxide gave a variation of 17 parts per thousand, while four depositions made with ammonium hydroxide controlled by methyl orange gave an average deviation of only 6 parts per thousand.

In the early experimental work, high results were frequently obtained. A high concentration of ammonia causes the transfer of platinum from the anode to the cathode and thus gives high results, but even after this had been corrected, high results continued to be obtained. Blank determinations run with ammoniacal oxalic acid showed the high results to be caused by impurities in the Kahlbaum (c. p.) oxalic acid. A change to Kahlbaum "for analysis" brand solved this difficulty, the blank being lowered from 0.038 to 0.003 mg. Spectrographic examination of the two brands showed many lines from impurities in the c. p. brand, but practically none in the "for analysis" brand. A blank determination should be made on the reagents in the cell under the actual working conditions in order to determine whether they are pure enough for the analysis.

To test the possibility of removing small quantities of indium from large amounts of solution by the use of a Clarke and Hermance cell for large volumes, depositions were made using about 8 mg. of indium, 10 grams of oxalic acid, and ammonium hydroxide to make the solution alkaline. In practically all cases the amount deposited was greater than the amount of indium added. It was, therefore, concluded that this cell might be used to concentrate the indium from dilute solutions but that it would not be practical to weigh this deposit directly for the true indium content. It is, however, possible to dissolve the indium deposited from this cell and then redeposit it from the small cell.

Results

Using the proposed method, sixteen determinations gave a mean value of 2.007 mg. with a deviation of ± 10 parts per

¹ Present address, Calco Chemical Division, American Cyanamid Company, Bound Brook, N. J.

thousand. The expected value was 1.996 mg. Since the indium had been added from a 5-ml. pipet, an error in measurement of 1 drop would be equivalent to 0.02 mg. of indium, which would be about equal to the deviation obtained above. When a weight buret was used, the average of three determinations gave a mean value of 0.3984 mg. of indium per ml. with a deviation of 2 parts per thousand; the expected value was 0.3992 mg. per ml.

Alternate Microprecipitation Method

It was independently found that 8-hydroxyquinoline, afterwards proposed by Geilmann and Wrigge (8) for a semi-micromethod, could be used to precipitate indium (16). Using this reagent, the microchemical method of Benedetti-Pichler (1) for the determination of aluminum was modified as a quantitative micromethod.

The micro filter flask, as described by Schwartz-Bergkamp (18), was used throughout the determination. The flask was washed with hydrochloric acid and water and dried at 140° C. in a micro drying oven with suction for 5 minutes. On removal, it was wiped with a damp cloth and a chamois, and allowed to stand in the balance room for 20 minutes. The weight was taken and the process repeated until constant weight was obtained. The solution containing the indium was transferred to the flask, a drop of concentrated hydrochloric acid was added, 0.5 ml. of 8-hydroxyquinoline solution (prepared by dissolving 5 grams of reagent in 12 grams of acetic acid and 83 grams of water) was added, and the flask was placed on a steam bath. When warm, 2 N ammonium acetate was added, drop by drop, until the solution remained turbid. In about 1 minute the precipitate became crystalline and then 0.5 ml. more of the ammonium acetate solution was added. The flask was left on the steam bath 10 minutes longer, after which the precipitate was filtered off through the porous plate on the side of the flask. It was washed five times with hot water and the same procedure of drying and weighing was carried out. The formula for the precipitate is $\text{In}(\text{C}_8\text{H}_6\text{ON})_3$, and the factor for metallic indium is 0.2099.

Five analyses were made on samples containing approximately 1 mg. of indium. The average value obtained was 0.391 mg. of indium per ml. and the average deviation for a single determination was found to be ± 12 parts per thousand. The expected value was 0.399 mg. of indium per ml. These solutions were measured out in a microburet; the possible error in measurement would be approximately 0.02 ml. or 0.008 mg. of indium. The experimental results obtained were within the experimental error.

Application to a Synthetic Mixture

A synthetic mixture representing an artificial sphalerite (see Dana's "Minerology") was prepared, having the following percentage approximate composition:

ZnS	90
CdS	2
FeS	6
MnS	1.5
Tl	0.25
In	0.200
	99.95

Five milliliters of indium solution (1.996 mg. of indium) were added to 1 gram of a dry mixture of the other components.

The mixture was dissolved in concentrated hydrochloric acid and nearly neutralized with ammonium carbonate. One gram of ammonium chloride was added, and the volume made up to about 50 ml. Sulfur dioxide was passed into the solution to reduce the iron to the ferrous state. The solution was made slightly acid by adjustment with 6 N ammonium carbonate and hydrochloric acid. Then a solution containing freshly precipitated barium carbonate was added until an excess remained. This was allowed to stand, with occasional shaking, for several hours and filtered. This procedure separates the indium and aluminum from most of the zinc, manganese, and ferrous iron.

The precipitate was dissolved in 6 N hydrochloric acid, and bromine was added to oxidize any sulfite to sulfate. Then sulfuric acid was added until all the barium had been precipitated as barium sulfate. This precipitate was digested, filtered, and washed with hot water. One gram of ammonium chloride was added to the filtrate and the volume was made up to 50 ml. with

water. Ammonium hydroxide was added in excess and the solution was boiled for a short time. The precipitated hydroxides were removed and dissolved in 6 N sulfuric acid. (If a large amount of aluminum was present, it was removed at this point by separating the indium by electrodeposition in the larger Clarke and Hermance cell. The deposited metal was dissolved from the cathode with nitric acid and the solution concentrated to fumes after the addition of a little sulfuric acid.) The sulfuric acid solution was made up to a volume of 50 ml., so that it contained about 10 per cent of sulfuric acid. To remove any remaining iron, 25 ml. of 0.5 per cent cupferron reagent were added. After standing about an hour, the precipitate was filtered off and washed. The filtrate was concentrated by evaporation and indium was determined by electrodeposition in the small cell. In the development of this method, all discarded precipitates and filtrates were tested spectroscopically to show the absence of indium.

The results of two analyses made by this procedure were:

	Mg.
Found	2.064
	2.055
Av.	2.06 or 0.21%
Expected	1.996 or 0.20%

Analysis of a Natural Sphalerite

The same method was applied to a natural sphalerite from the Moyer mine at Leadville, Colo. Because of the small amount of the mineral available and the low percentage of indium, only a micromethod was practical. A qualitative spectrographic analysis showed indium, a trace of tin, and the other usual constituents of a sphalerite. The 0.28 per cent of indium found in this sample was in agreement with quantitative spectrographic estimations which have been made on other sphalerite samples.

Acknowledgment

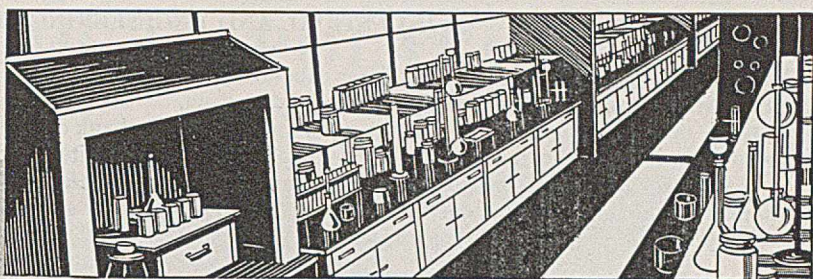
The writer wishes to express his appreciation to J. Papish of Cornell University, under whose supervision this research was conducted, for his criticisms and suggestions.

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PRESENTED before the Microchemical Section at the 92nd Meeting of the American Chemical Society, Pittsburgh, Penna. From a portion of the thesis presented to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of doctor of philosophy.

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JOSEPH W. HOWARD, Montana State University, Missoula, Mont.

THE new \$300,000 Chemistry-Pharmacy Building at Montana State University was completed during the autumn quarter of 1939. The building was financed with federal aid as a PWA project. The architects were Hugenin and DeKay of Helena, Mont. It is constructed of reinforced concrete with a brick surface and is earthquake-proof.

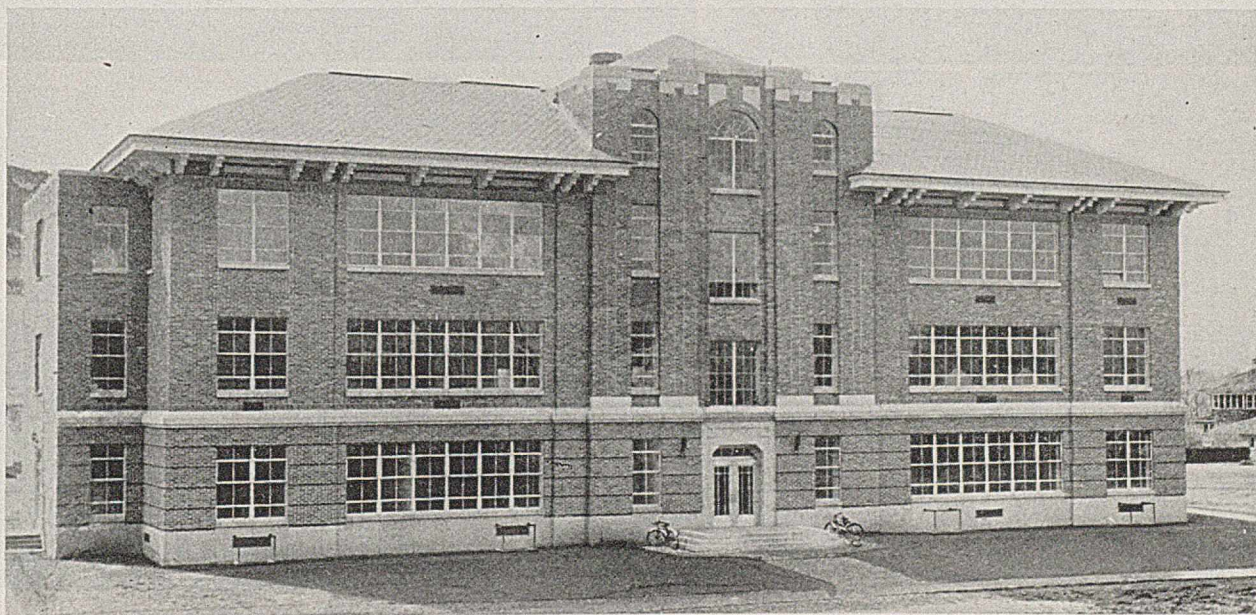
The full basement contains a large general storeroom which supplies all the science departments of the university. In addition, there are separate storerooms for the Department of Chemistry and School of Pharmacy, rest rooms, and a switchboard and storage battery room. Extending from the basement, with its ceiling outside of the building, is a special room for chemicals which are considered fire hazards.

The first floor contains a large lecture and preparation room, four classrooms of varying capacities, a combined chemistry-pharmacy library, a model drugstore, the office of

the dean of the School of Pharmacy, and a research laboratory, as well as a freight receiving room and office for the storeroom keeper.

The second floor is occupied by the School of Pharmacy with two offices, a storeroom, a balance room, and separate laboratories for galenical pharmacy, dispensing, drug analysis, advanced analysis, and research and pharmacognosy, and a special dispensary for the University Health Service.

The third floor contains the laboratories for physical chemistry, quantitative analysis, organic chemistry, physiological chemistry, a storeroom, three offices, two research laboratories, a combustion-Kjeldahl room, dark room, constant-temperature room, balance room, and two rest rooms. The desks in the organic and physiological laboratories are equipped with cold water, steam, compressed air, gas, and electricity, while those in quantitative analysis have hot water in place of steam. All these laboratories have adequate hoods and steam baths.

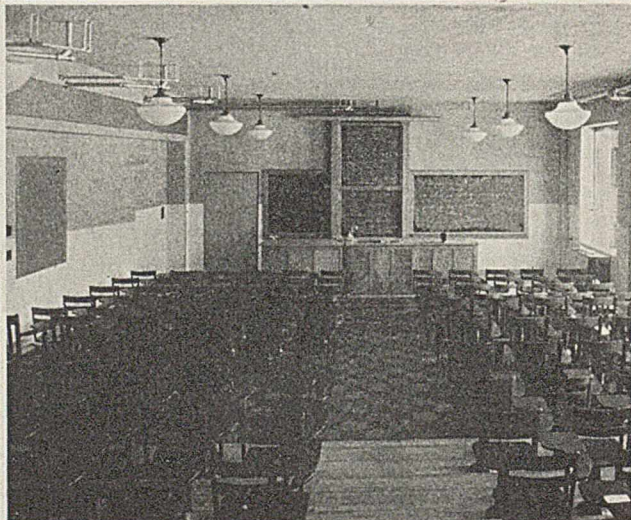
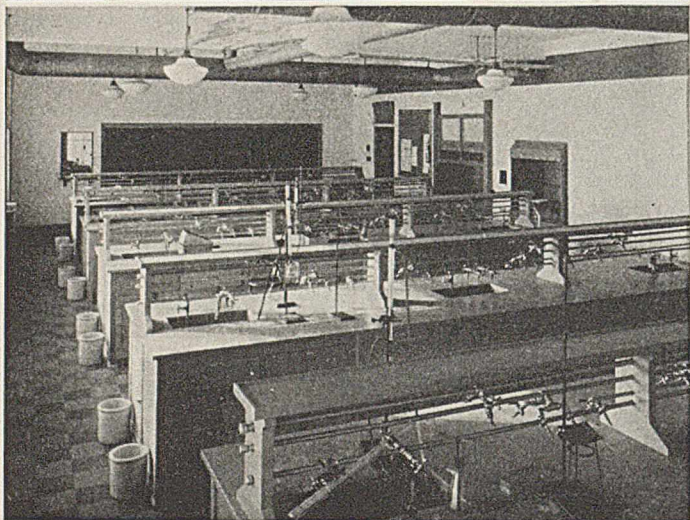
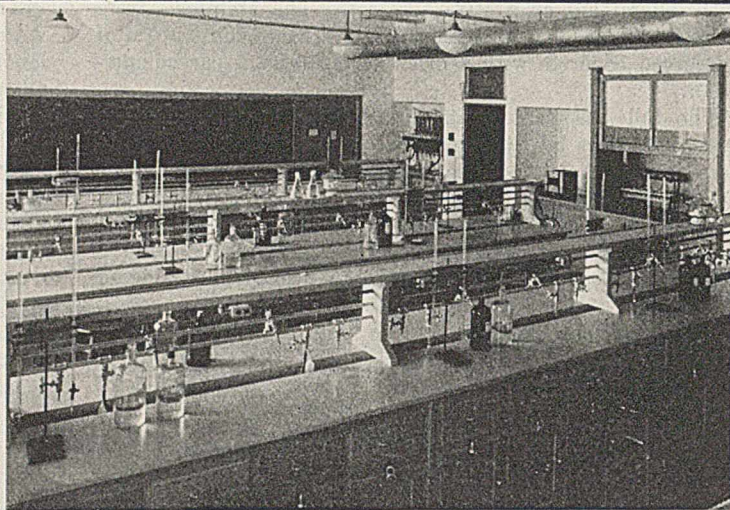
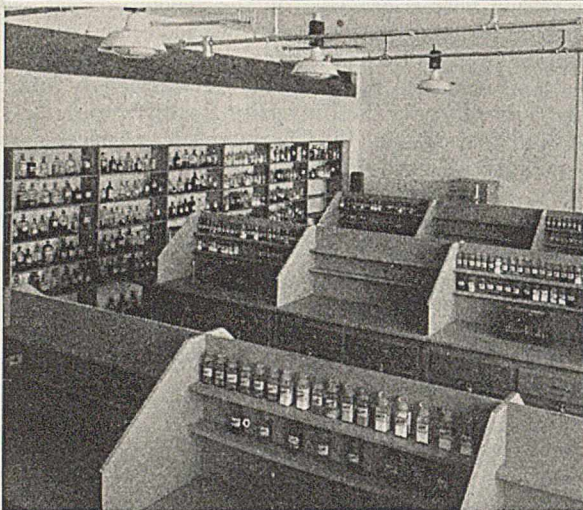
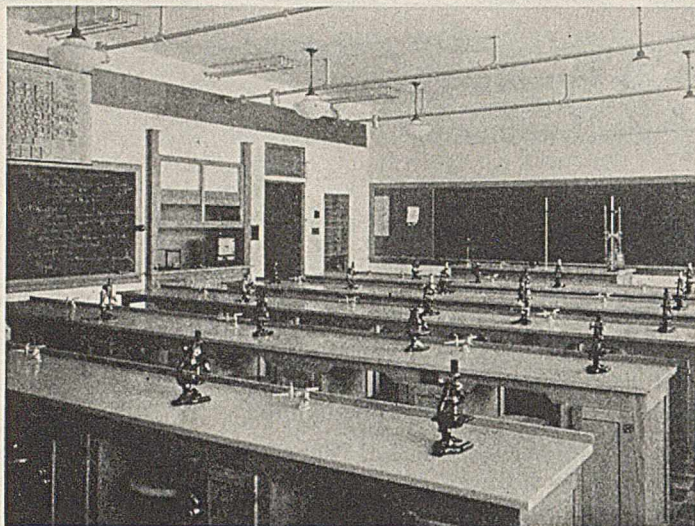


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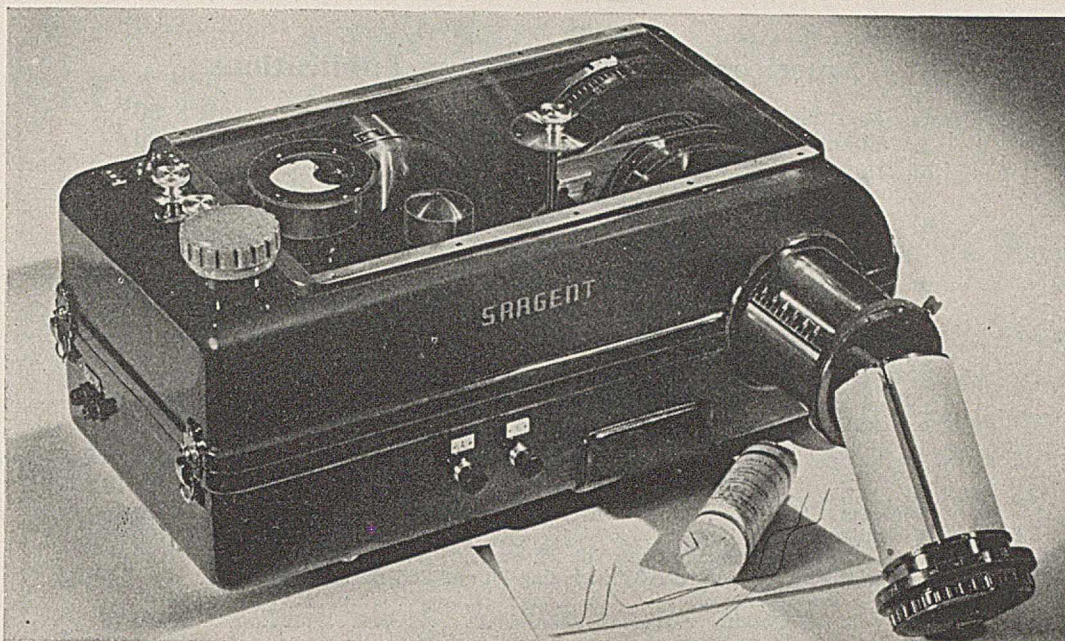
hoods. At each end of the laboratory there is a bank of fourteen individual hoods for use with hydrogen sulfide. Each bank of hoods is supplied from a tank of hydrogen sulfide and has its separate suction fan.

Other features of the building are adequate outlets for direct and alternating current, a freight elevator which connects all the storerooms, and air-conditioning throughout.



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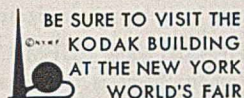
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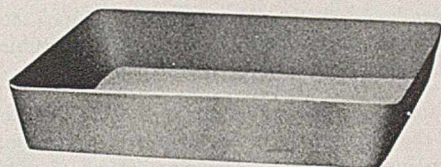
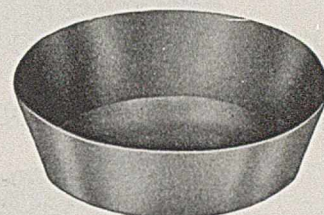
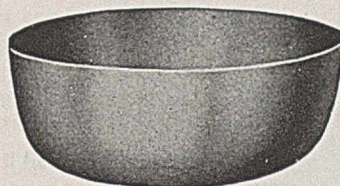
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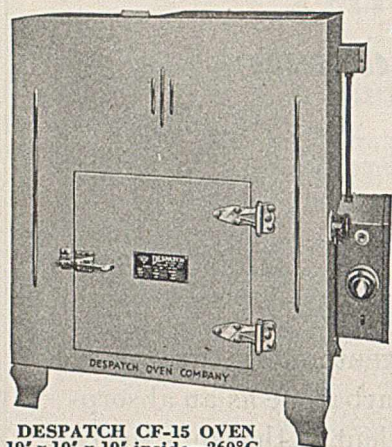
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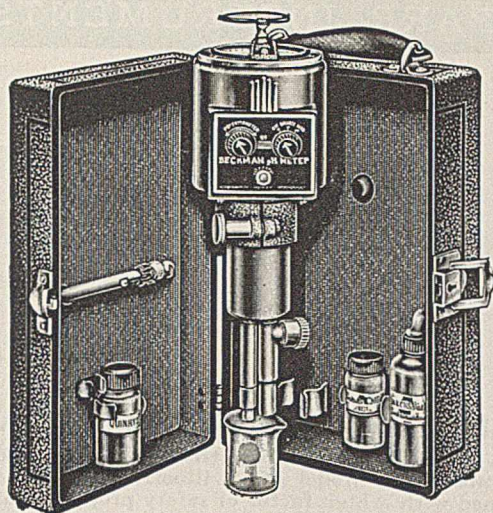
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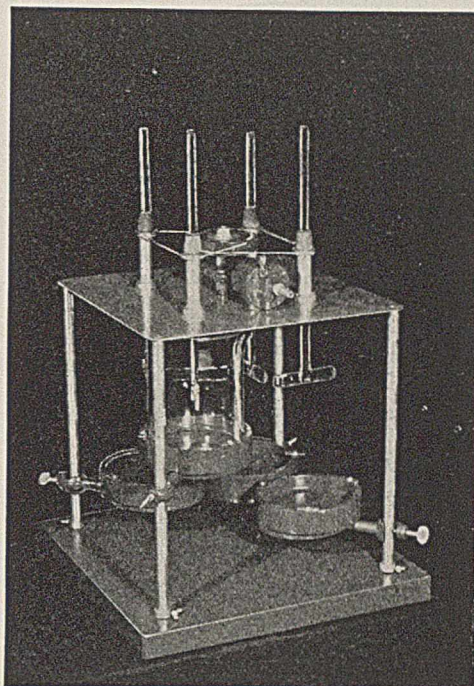
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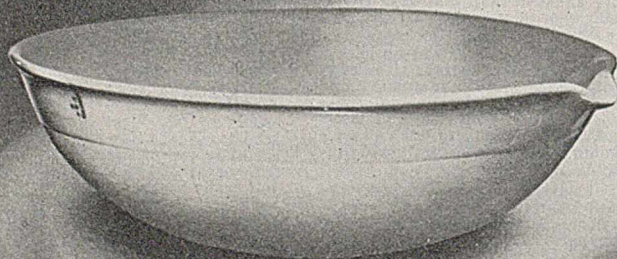
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