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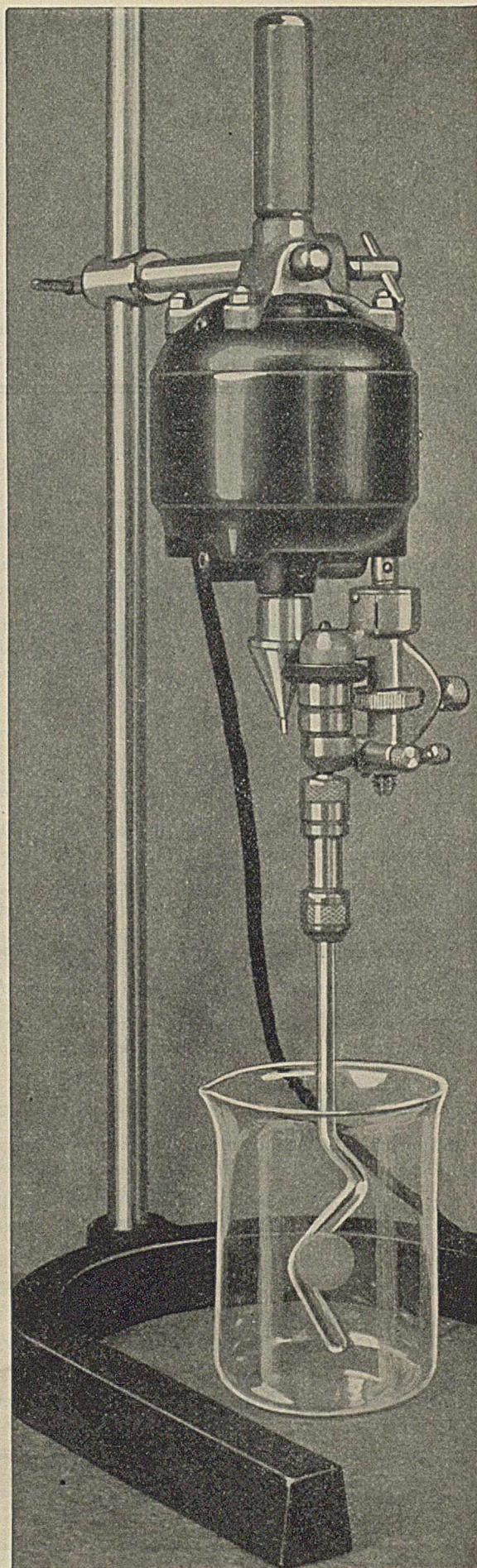
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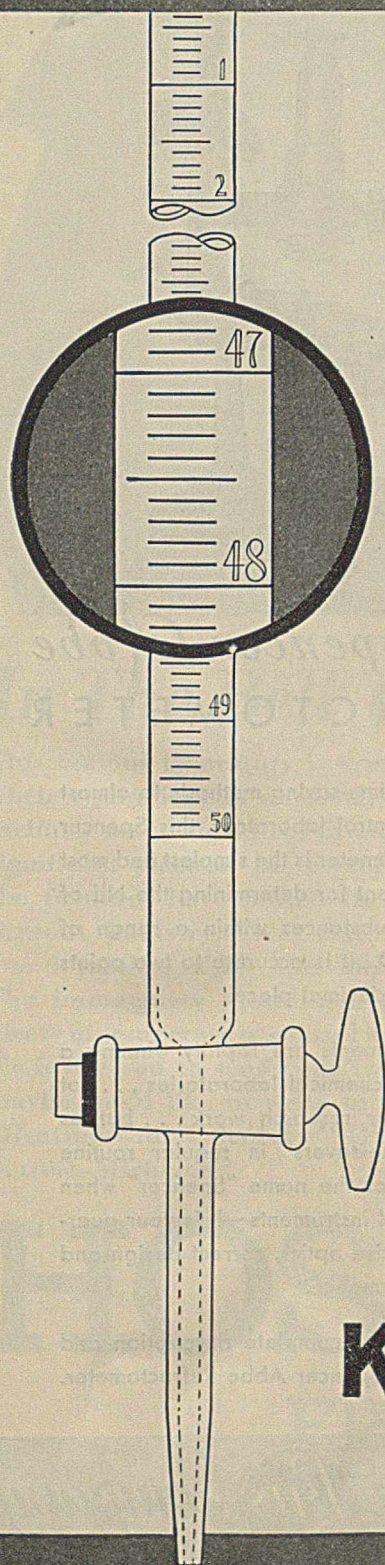
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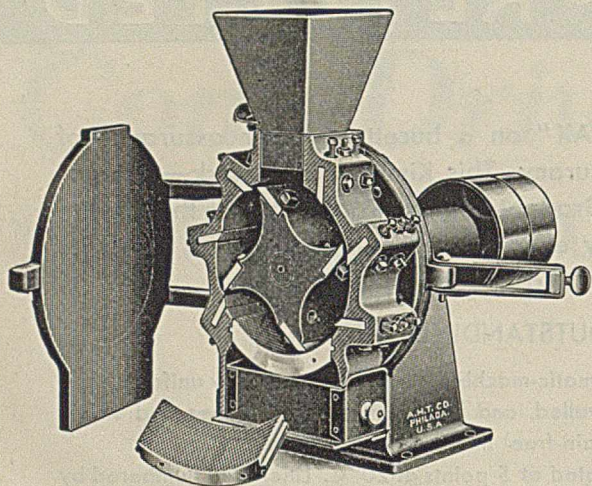
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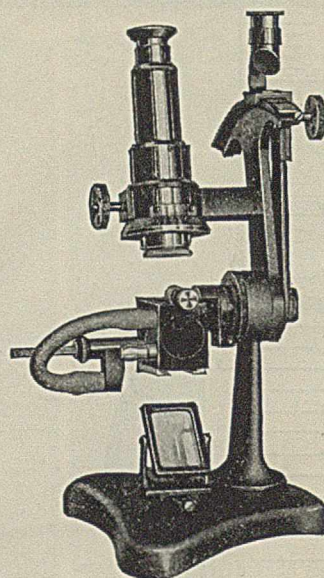
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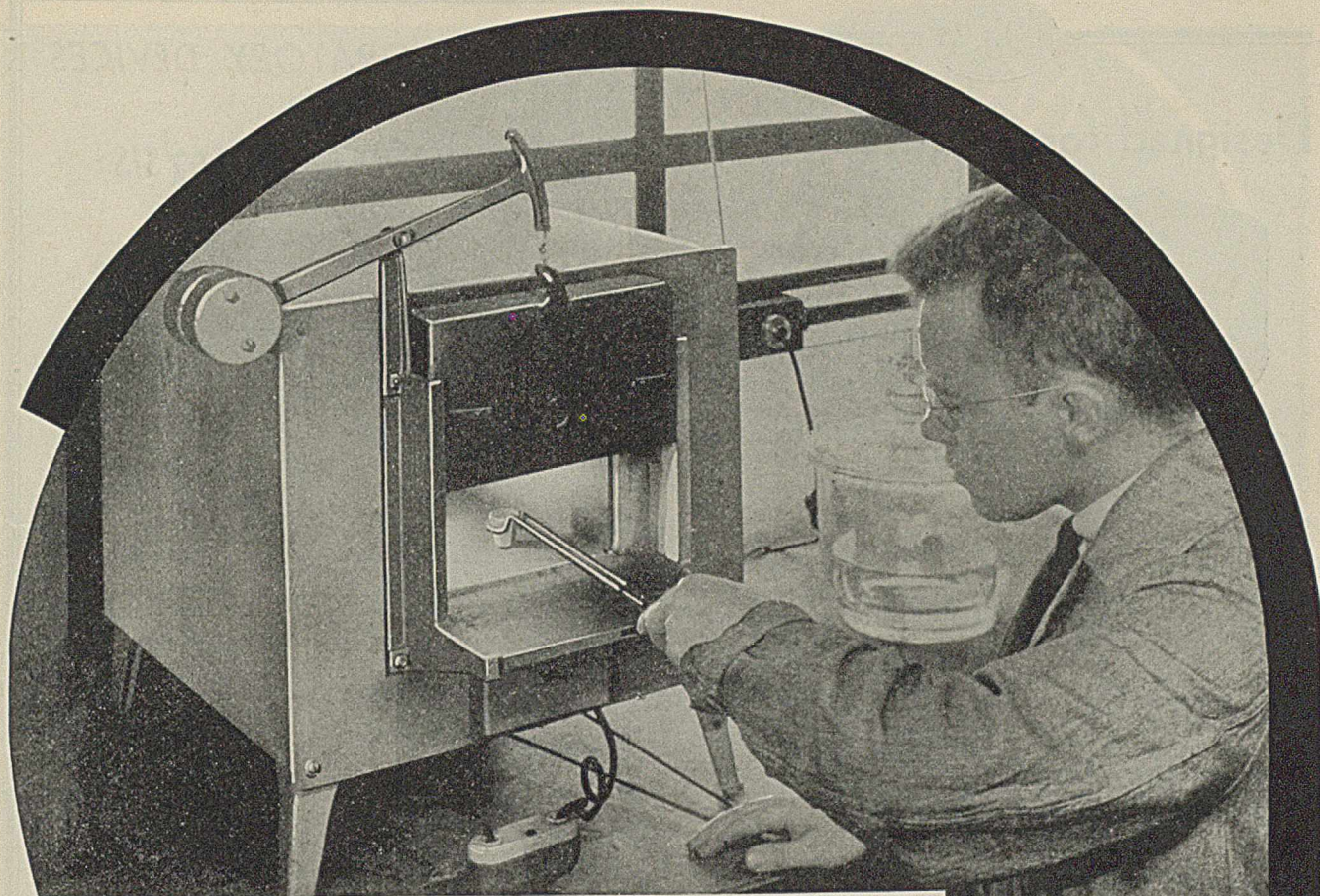
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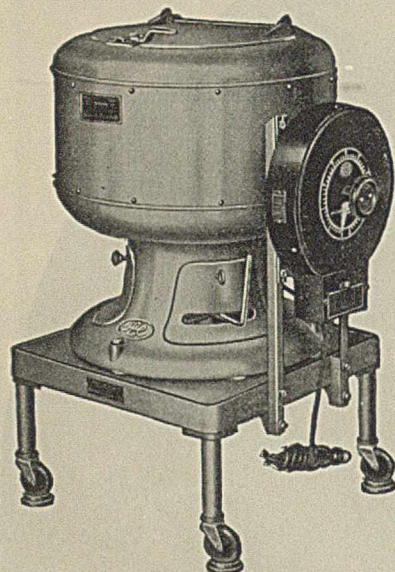
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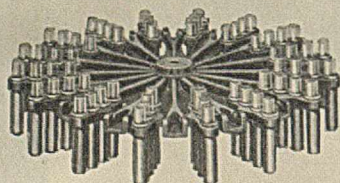
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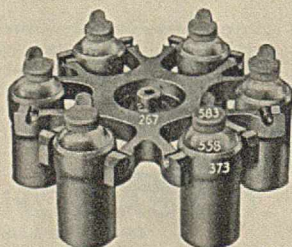
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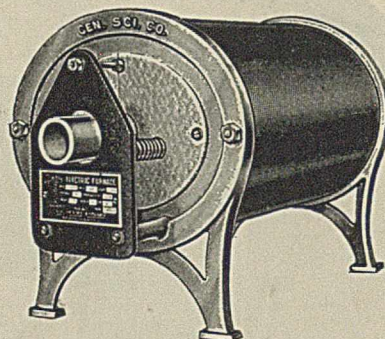


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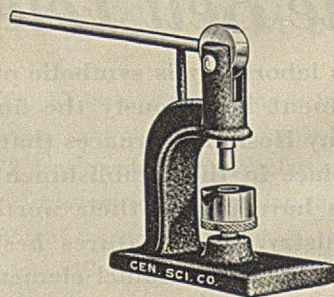
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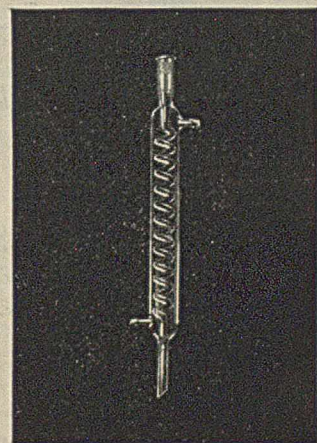


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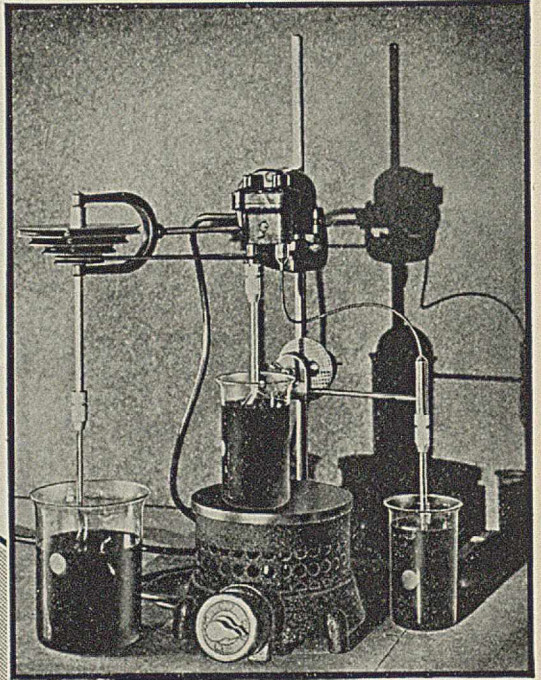
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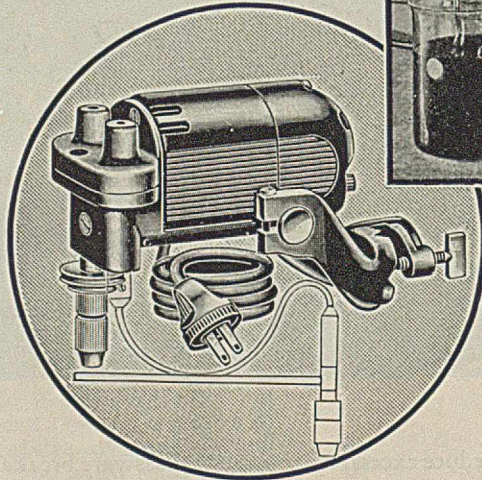


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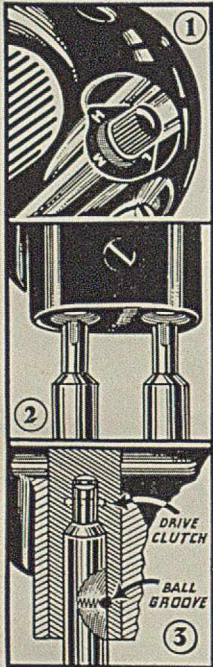
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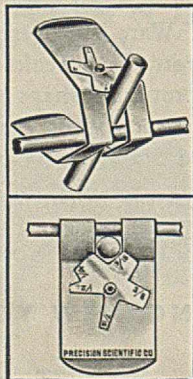
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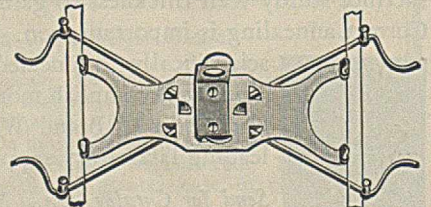
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Quantitative Spectroscopic Analysis of Solutions

WALLACE R. BRODE AND JAMES G. STEED, Department of Chemistry, The Ohio State University, Columbus, Ohio

THROUGH the use of the logarithmic sector method (1-4) data have been obtained on the quantitative estimation of columbium, beryllium, titanium, vanadium, tungsten, iron, molybdenum, chromium, lead, and cobalt. Data on a few of these elements (chromium, lead, and cobalt in particular, 5) have been prepared by other workers, but using different line pairs from those in the present analyses.

The method of analysis follows in general that described by Twyman and Hitchen (5) with certain modifications in the apparatus and manipulation. Two different quartz spectrographs were used in this study, a large Hilger (E-185) Littrow spectrograph (linear dispersion 7000 to 2000 Å. = 100 cm., Figure 1-A) and a medium Bausch and Lomb Spectrograph, No. 2820 (linear dispersion 7000 to 2000 Å. = 21 cm.,

Calibration curves have been determined for the quantitative spectrographic analysis of columbium, beryllium, titanium, vanadium, tungsten, iron, molybdenum, chromium, lead, and cobalt. These curves are given in both per cent of element and logarithm of the per cent of element present. The average deviation in the determination of samples of known composition was less than 5 per cent of the known concentration.

Figure 1-B). A logarithmic sector (2, 3) was used in front of the slits of each of these instruments, actuated by connection with the starter knob of a simple alternating current electric clock. In a modification of the Twyman and Hitchen solution spark apparatus 22-gage copper electrodes were used for both the upper and lower electrodes in place of the previously recommended carbon and gold electrodes. A Pyrex jet was found to be as satisfactory as a quartz jet. The copper lines produced in the spectra (Figure 1) were not objectionable and may reduce to some extent the slight error due to an excess of a foreign anion in the solution to be tested.

The spark was produced by a 20,000-volt 2-kilovolt-ampere transformer. The primary (110 volt) circuit had a resistance in it, to permit the passage of about 1 ampere.

TABLE I. QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF SOLUTIONS

COMPOUND USED	METHOD OF SOLUTION	CONCENTRATION RANGE (ELEMENT) %	INTERNAL STANDARD USED	CONCENTRATION OF STANDARD Grams/100 cc. water	AMOUNT OF STANDARD ADDED TO 100 CC. OF SOLUTION		LINE PAIR USED
					Cc.		
Columbic anhydride	K ₂ CO ₃ fusion plus water	0.005 to 1.0	KMnO ₄	2.8769 (1% Mn)	20		Cb 2927.82 Å. Mn 2933.06
Beryllium sulfate	Water plus 2% H ₂ SO ₄	0.0001 to 0.1	Bi(NO ₃) ₃ ·5H ₂ O	8.6580 grams Bi ₂ O ₃ ·1/2 H ₂ O dissolved in excess conc. HNO ₃ and diluted to 100 cc. (3.5% Bi)	50		Be 3131.32 } unresolved Be 3131.97 } Bi 3067.73
Beryllium sulfate	Water plus 2% H ₂ SO ₄	0.0005 to 1.0	KMnO ₄	2.8769 (1% Mn)	10		Be 2651 (6 unresolved lines) Mn 2939.31
Titanium dioxide	Sodium pyrosulfate fusion plus 5% H ₂ SO ₄	0.005 to 1.0	CrO ₃	10.0000 (5.2% Cr)	16.7		Ti 3383.765 Cr 3368.05
Vanadic anhydride	HCl (calculated amount plus 2%)	0.005 to 1.0	CrO ₃	19.2308 (10% Cr)	20		V 3093.13 Cr 3118.65 V 3130.270 Cr 3132.053
Tungstic anhydride	NaOH (calculated amount plus 2%)	0.005 to 4.0	KMnO ₄	2.8769 (1% Mn)	5		W 2589.2 Mn 2593.733
Ferrous ammonium sulfate	Water plus 2% H ₂ SO ₄	0.005 to 1.0	CoCl ₂ ·6H ₂ O	16.1424 plus 2% HCl (4% Co)	20		Fe 2382.039 Co 2378.62
Molybdic anhydride	NH ₄ OH (calculated amount plus 2%)	0.005 to 4.0	K ₂ Cr ₂ O ₇	2.2630 (0.8% Cr)	50		Mo 2848.21 Cr 2849.83
Chromic anhydride	Water	0.005 to 4.0	NiSO ₄ ·7H ₂ O	19.1479 plus 2% H ₂ SO ₄ (4% Ni)	10		Cr 3578.687 Ni 3524.543
Lead nitrate	Water plus 2% HNO ₃	0.4 to 4.0	Ni(NO ₃) ₂ ·6H ₂ O	19.9903 plus 2% HNO ₃ (4% Ni)	10		Pb 3683.472 Ni 3619.393
Cobalt chloride	Water plus 2% HCl	0.05 to 4.0	MnCl ₂ ·4H ₂ O	7.2055 plus 2% HCl (2% Mn)	100		Co 3453.514 Mn 3441.997

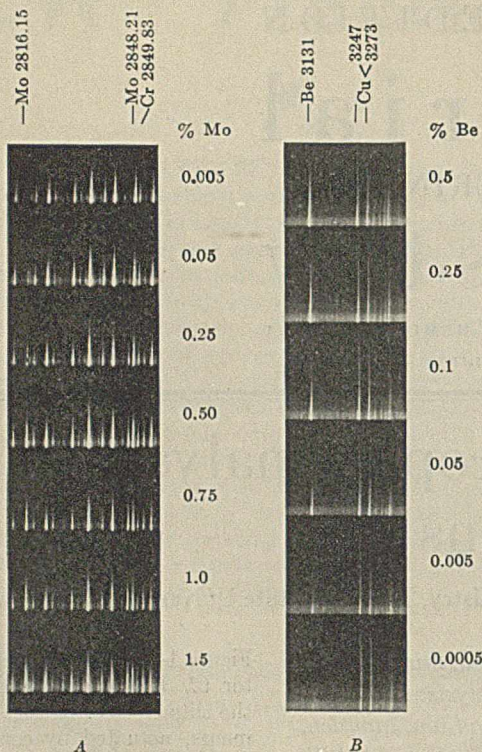


FIGURE 1. SPECTRUM PHOTOGRAPHS

A. Variation of concentration of molybdenum with chromium as internal standard.
 B. Variation of concentration of beryllium with manganese as internal standard.

A condenser (0.005 microfarad) was shunted across the secondary terminals of the transformer.

The solutions were prepared by weighing the quantity of pure material required to make a given volume of the most concentrated solutions used and diluting these with distilled water or other indicated solvent to yield the required concentrations. A known amount of the substance selected for the internal standard was then added to a definite volume of each solution and a photograph made of its spark spectrum. (The photographs were taken on Eastman 33 plates and developed with the Eastman formula D-76 developer with controlled conditions of temperature and time of development.) The lengths of the selected pair of lines were measured with a Bausch and Lomb plate magnifier containing a 20-mm. scale with which the length could be determined to within 0.02 mm. The lines selected for measurement conformed as nearly as possible to the requirements for homologous pairs as described by Gerlach and Schweitzer (1). The difference in length of two lines will represent the ratio of their intensities, since by the use of a logarithmic sector the line densities vary at a logarithmic rate. The difference between the length of the line of the standard and the length of the line of the element to be estimated was then plotted against the per cent of the element to be estimated (and also against the logarithm of the per cent

of the element to be estimated). These data are presented graphically in Figures 2, 3, and 4. Table I indicates the materials used for examination, the method of solution, the concentration range, and the line pairs measured.

The curves in Figures 2 to 4 may be used as standard or calibration curves in the analysis of unknowns. The procedure in such an analysis is to prepare a solution as indicated in Table I and, if the concentration of the element is approximately known, dilute the solutions to a concentration of approximately that of the center of the calibration curve and photograph its spark spectra. If the concentration is not approximately known, solutions should be prepared by tenfold dilution, so that each solution has one-tenth the concentration of each preceding solution. Three or four such solutions will in nearly all cases cover the desired concentration range. To each solution is then added the indicated amount of solution containing the internal standard and the spark spectrum is photographed. In obtaining these spectra the most dilute solutions should be photographed first and then the more concentrated in the order of their increasing concentration. This procedure reduces the possibility of contamination of dilute solutions with the stronger solutions. The minimum quantity of solution upon which the authors have made observations is about 2 cc. By the use of capillary tubing, however, it should be possible to use micromethods and obtain satisfactory analyses on 0.5 cc. or less. The amount of unknown element in the solution is determined by measuring the lengths of the standard and unknown lines and subtracting the standard from the unknown length; from the calibration curve it can be seen that this difference in length will represent a definite per cent of the element for which the analysis is made.

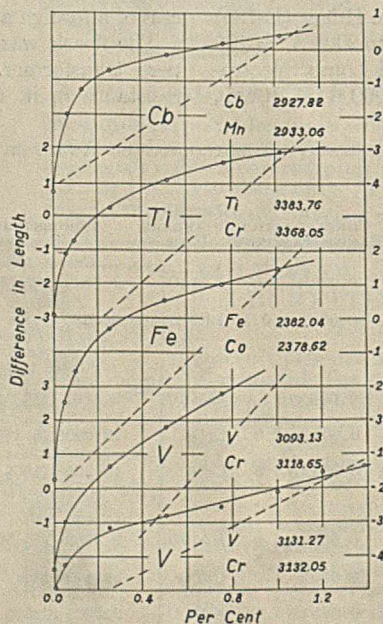


FIGURE 3. CALIBRATION CURVES FOR DETERMINATION OF PERCENTAGE OF UNKNOWN ELEMENT FROM DIFFERENCE IN LENGTH OF UNKNOWN AND STANDARD LINES

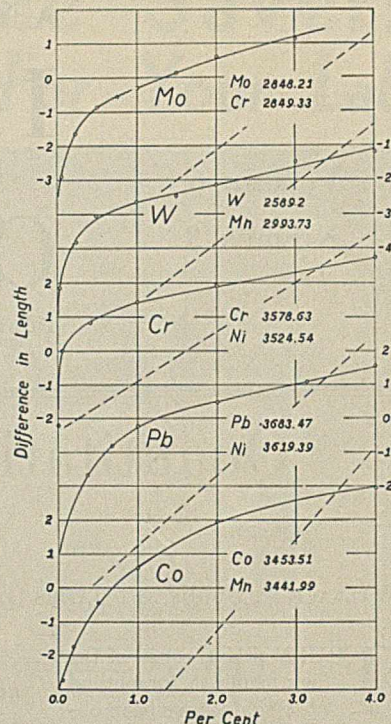


FIGURE 2. CALIBRATION CURVES FOR DETERMINATION OF PERCENTAGE OF UNKNOWN ELEMENT FROM DIFFERENCE IN LENGTH OF UNKNOWN AND STANDARD LINES

Dotted lines are logarithm of continuous curves. Slope of logarithm lines indicates concentration range over which the line pair selected may be used.

In Figure 2, the chromium, lead, and cobalt curves are shown together so as to indicate variations in the sensitivity range of the lines chosen for these ele-

ments.

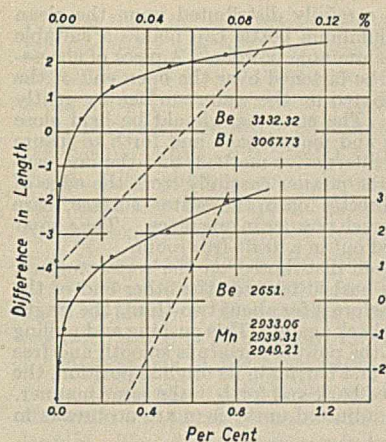


FIGURE 4. CALIBRATION CURVES FOR DETERMINATION OF PERCENTAGE OF BERYLLIUM

0.00 to 0.12 per cent in upper curve, 0.0 to 1.0 per cent in lower curve.

intrinsic intensity of the line and its ability to produce a reasonable photographic image, on the upper side by the point where the logarithm of the concentration plotted against the

ments. As will be noted, the logarithm curves have different slopes which correspond in general to the sensitivity range, chromium having a narrow range, lead a medium range, while cobalt has the widest concentration range over which this spectrographic method of analysis can be applied. This range of useful concentration for spectrographic analysis is limited on the low concentration side to the intrinsic

difference in line length ceases to follow the straight line obtained for the lower concentrations and begins to approach a constant value.

Within this working range of concentration the error of observation was less than 5 per cent of the observed value. While this is a rather large error where concentrations greater than 1 or 2 per cent are concerned, the value of the method increases for more dilute solutions where the error in determination of a solution containing 0.01 or 0.001 per cent of the element will still be less than 5 per cent of the observed value.

LITERATURE CITED

- (1) Gerlach and Schweitzer, "Chemische Emissionsspektralanalyse," Leopold Voss, Leipzig, 1931.
- (2) Hamburger and Holst, *Z. wiss. Phot.*, 17, 265 (1918).
- (3) Scheibe, "Spektroskopische Analyse," Akademische Verlagsgesellschaft, Leipzig, 1933.
- (4) Twyman et al., *Trans. Optical Soc. (London)*, 31, 169 (1930); 32, 1 (1931).
- (5) Twyman and Hitchen, *Proc. Roy. Soc. (London)*, A133, 72 (1931).

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Covering Capacity (on Water) of Aluminum Bronze Powder

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THE metallic flakes of aluminum bronze powder are characteristically different from the granular particles of nonmetallic pigments. They differ so much in shape, structure, and composition that the methods of examination and testing, well developed and standardized for other pigments, are in many cases inapplicable to the study of aluminum bronze powder. Aside from their flake-like shape and metallic base, the flakes differ from most granular pigments in having a film of polishing agent on their surface. This thin film, usually containing stearic acid as the major ingredient, modifies the appearance of the flakes and their general behavior when dispersed in a paint vehicle. The interfacial relations between powder and vehicle, as well as the size and shape of the flakes, play a part in the important phenomenon, known as "leafing."

For commercial purposes, it is customary to grade powders according to the approximate mesh size of the largest flakes. A standard varnish powder, for example, has all been through a 140-mesh screen or its equivalent. While a screen analysis may give some idea as to the major dimensions of the flakes, it tells little or nothing about their thickness (or thinness). Obviously, the thinner the flakes, the more flakes of any particular size per pound of powder. Furthermore, the thickness of flake will affect the leafing characteristics of the powder. During an investigation of the properties of aluminum bronze powder, the authors developed a method for measuring the average thickness of bronze powder flakes, which has been found very useful over a period of years. An outline of this method was first described in 1927 (1). Since then the method has been standardized in detail and technic of operation.

The method depends on the assumption that if all the flakes in a given weight of powder could be spread out in a film one

flake thick and packed close so as to eliminate interstices between the flakes as far as possible, the thickness could be calculated from the area of the film, its weight, and the density of the powder. A film which approximates these conditions can be obtained by proper manipulation of the bronze powder on a clean surface of water. A shallow rectangular pan with a flat rim is used as the container for the water and two flat, rigid strips of glass or metal which act as barriers are laid across the width of the pan to define the ends of the film of powder whose area is to be measured. When a weighed amount of powder is carefully dusted onto the water surface which completely fills the pan, it tends to spread out in a thin leafed film. The flat barriers, resting on the rim of the pan near each end, perform a very important function in "coaxing" the powder into a film one flake thick. The results of the measurement are expressed in terms of the area in square centimeters covered by a gram of powder and this value is termed the covering capacity. It should not be confused with the so-called covering power (square feet per gallon) of a paint.

Langmuir (2) and others have shown how stearic acid alone can be spread out on water in a film one molecule thick, and the dimensions of the molecule estimated in this way. In this experiment the polar molecules of stearic acid are uniformly oriented with the carboxyl group directed towards the water interface. In the case of the polished aluminum flakes, the film of stearic acid, many molecules thick, appears to be oriented and fixed upon the flakes. The powder flakes in the present method are only partly wet by the water and float upon the surface. By moving the metal strips back and forth upon the side rims of the pan, the floating film of powder between them can be stretched and compressed much like a fabric until all the flakes have been brought into the water interface. The powder is then compressed by moving

one of the strips until the flakes are all touching, as determined by the tendency of the film to wrinkle with the slightest additional compression. Its area is then measured.

DETAIL OF METHOD

It has been found most convenient to use a shallow rectangular aluminum pan about 14 cm. wide, 60 cm. long, and 1.3 cm. deep. The vertical walls are about 1.3 cm. thick and

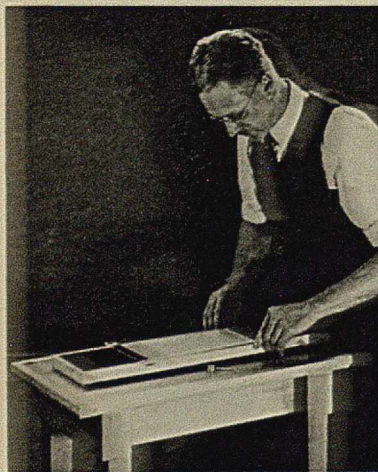


FIGURE 1. TEST EQUIPMENT, SHOWING METHOD OF MANIPULATION OF PLATE GLASS BARRIERS

are machined and finished smooth on the upper surface to insure good contact with the plate glass barriers. Two pieces of heavy plate glass about 2.5 cm. wide and several centimeters longer than the width of the pan are used to confine the surface film and to work the powder uniformly over the surface of the water. Before each determination the upper edges of the pan and the plate glass barriers should be rubbed with a piece of ordinary paraffin and the glass plates polished with a clean cloth. Water is poured into the pan until the surface is appreciably above the upper edges of the pan. The paraffined edges of the pan prevent the water from overflowing. Reasonable care should be taken to make sure that the height of the water surface above the edges of the pan is always the same. The use of distilled water is preferred and the temperature should remain constant at about 25° C.

The surface of the water in the pan is swept from end to end with one of the glass plates to remove the major portion of surface impurities, such as dust or grease. One of the glass plates is then laid across the pan near one end. Any surface impurities remaining are blown away from the water surface near the first glass barrier and the second glass plate is laid across the pan near the first, taking care that no surface impurities get between the two plates. The second barrier is then pushed nearly to the other end of the pan, sweeping all impurities before it. It is best to remove these impurities from the surface between the barrier and the edge of the pan by sweeping them over the edge of the pan with a piece of filter paper. The reason for doing this is that some of these impurities might creep under the barrier as it is moved back and forth and cause breaks in the powder film which is to be distributed on the clean water surface between the two barriers.

The two glass barriers are left near the ends of the pan with the clean water surface between them. An accurately weighed

sample of powder is then carefully distributed upon the clean water surface. A small aluminum bottle cap makes a suitable container for weighing the aluminum powder. A piece of cheesecloth or bolting cloth may be fastened over the open end of the cap and the powder distributed on the water surface by gently tapping the inverted cap. The container should be held close to the clean water surface and moved back and forth to insure uniform distribution. An alternative method, and the one usually employed, is to pour the powder carefully from the edge of the weighing container directly onto the water surface, care being taken not to get too much powder in one place. The above operations should be carried out in a draft-free room.

After the powder has been distributed on the water surface, one of the glass barriers is pushed towards the other end of the pan, sweeping the powder before it for about two-thirds the length of the pan, and then pulled back again. This pushing and pulling operation is repeated until the powder surface is smooth and free from breaks. Leaving the first barrier in its original position, the second barrier is then moved back and forth in the same manner. The two barriers are then adjusted until there are no breaks in the metallic film and wrinkles start to form near each barrier because of too great pressure. One of the barriers is then moved back until all the wrinkles at both ends of the film are removed. This barrier is then adjusted by increasing the pressure enough to form a few wrinkles and then decreasing the pressure just enough to smooth out the wrinkles. The barrier at the other end is then adjusted slightly. The length of film between the parallel barriers is measured. The barriers are again worked back and forth three or four times, and after adjusting as before the length is measured for a second time. This procedure is repeated until the length of film remains constant for three consecutive measurements. Knowing the weight of sample and the length and width of the metallic film, the area which one gram of powder will cover can be calculated.

Figure 1 shows the test equipment and illustrates the method of manipulating one of the plate glass barriers. The film of powder is shown well worked out on the surface of the water between the barriers. The small cup used for weighing the powder and distributing it over the water appears on the table, just in front of the rectangular pan.

The weight of powder taken will depend on the size of the pan and the grade of powder used. For the pan described in this paper, a sample of standard varnish powder weighing about 0.1 gram is satisfactory. When lining powders are used, a sample weighing 0.05 gram or less will be sufficient. It is preferable that not more than about three-fourths of the cleaned water surface of the pan be covered with the powder film. Experience teaches the operator the size of sample necessary for the pan used. About 15 to 20 minutes are required for making each covering capacity measurement. A skilled operator can make duplicate measurements on the standard varnish grade of powder which will not differ in area by more than about 50 sq. cm. for 1 gram of powder. Since 1 gram of this grade of powder will cover about 4000 sq. cm. of surface, the method is reproducible to within about 1 to 2 per cent.

When pressure is applied to the uniformly distributed powder film by moving one of the glass barriers, it first wrinkles and then folds up as more and more pressure is applied. As the pressure is reduced the film unfolds to a uniform surface. This procedure can be repeated again and again without dis-

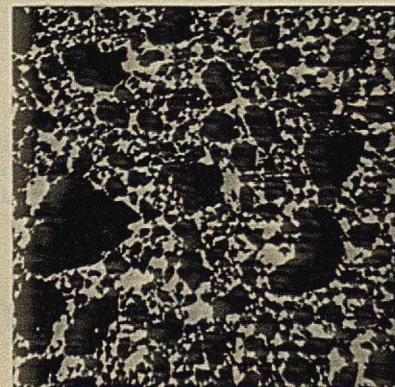


FIGURE 3. PHOTOMICROGRAPH (100 DIAMETERS) OF EXPANDED ALUMINUM BRONZE POWDER FILM AFTER TRANSFERENCE TO GLASS SLIDE

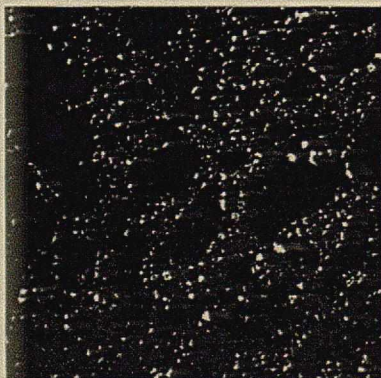


FIGURE 2. PHOTOMICROGRAPH (100 DIAMETERS) OF COMPRESSED FILM OF ALUMINUM BRONZE POWDER ONE FLAKE THICK ON WATER

rupting the film. It appears as if only the lower side of each powder flake was wet with the water. A microscopic examination of a well-worked powder film shows that it is, for all practical purposes, only one flake thick.

In Figure 2 is shown a photomicrograph of the aluminum powder film while on the water and compressed for measurement. The photomicrograph was taken with transmitted light and any voids appear as bright spots in the picture. An approximate estimate is that less than about 3 or 4 per cent of the area appears as voids uncovered by powder.

The well-worked aluminum powder film on a water surface gives an ideal way of obtaining a slide for examination under the microscope. The pressure on the metallic film is reduced by moving one of the glass barriers towards the end of the pan. One end of a cleaned microscope slide is dipped into the water and the slide immersed for about three-fourths of its length. The slide is then carefully raised under the powder film and withdrawn from the pan. A uniform film of powder adheres to the glass slide. This film is allowed to dry on the glass slide. The size distribution of the powder particles may then be determined with the aid of a microscope.

Figure 3 shows a photomicrograph, taken by transmitted light, of a film of powder spread on a glass slide. The film is not compressed and shows the individual flakes spread out and not touching.

The covering capacity of various grades of aluminum bronze powder will range from about 3000 to 12,000 sq. cm. per gram of powder, although both higher and lower values are obtained. The low range of values is obtained with the so-called "varnish" grades of powder and the higher values are obtained with some of the lining powders. Bronze powders are usually screened during manufacture in order to limit the maximum size of particle present in any grade. Even though a screen analysis may indicate that a series of powders are very close together in mesh size, the covering test may

demonstrate a considerable variation in average thickness of flake. In Table I are given data on a series of powders obtained from different commercial sources. They are graded about the same commercially, both on mesh size and appearance, but the maximum covering capacity exhibited is about 70 per cent greater than the minimum. While high covering capacity is, in general, a desirable characteristic, the conclusion does not necessarily follow that the highest covering power is always the best, as other characteristics must be considered in the evaluation of a powder for any particular use.

TABLE I. COMPARISON OF COVERING CAPACITY ON WATER AND MESH CHARACTERISTICS OF ALUMINUM BRONZE POWDERS

SAMPLE	COVERING CAPACITY Sq. cm./gram	SCREEN ANALYSIS			
		On 200- mesh screen	On 325- mesh screen	Through 325-mesh screen	Through 325-mesh screen
1	3040	18	30		54
2	3440	15	29		56
3	3720	12	32		56
4	4720	16	28		56
5	5280	17	28		55

While for most purposes, the covering capacity expressed in square centimeters per gram is sufficient, the calculated average thickness of flake is also of interest. The density of aluminum bronze powder is about 2.5 grams per cc. and covering capacities of 3000 to 12,000 sq. cm. per gram correspond with a flake thickness of about 0.0013 to 0.0003 mm. (0.000050 to 0.000012 inch).

LITERATURE CITED

- (1) Edwards, J. D., "Aluminum Bronze Powder and Aluminum Paint," p. 14, Chemical Catalog, 1927.
- (2) Langmuir, Irving, *J. Am. Chem. Soc.*, 39, 1848 (1917).

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Analysis of Mixtures of Oxalic and Citric Acids by Titration with Ceric Sulfate

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THE production of chemicals by the fermentative action of molds is becoming of increasing industrial importance. The present situation has been reviewed by May and Herrick (6). One of the most important developments is the production of citric acid, in which oxalic acid is likewise produced. In order to make adequate quantitative studies of this fermentation, a satisfactory analytical method of analysis for these acids needs to be developed, for, as stated by Currie (2), while the present methods "give fairly satisfactory results if used with discretion and patience, a really convenient and accurate method for estimating citric acid is still wanting." The present communication describes a method of analyzing citric acid in the presence of oxalic acid.

Oxalic acid is a very good reducing agent, and when present alone it may be titrated easily and accurately with any standard oxidizing agent such as permanganate. Citric acid, however, does not give a sharp end point with most oxidizing agents, and the final products of these reactions are not definitely known. Various methods for the analysis of citric acid have been suggested, some requiring rather elaborate manipulation. One of the most common methods, of which there are numerous modifications, is oxidation with

potassium permanganate, which has been studied in different phases by Perdrix (7), Deniges (8), Pratt (8), Kunz (5), Hartmann and Hillig (4). Williams, Mueller, and Niederl (10) used a photoelectric cell in a colorimetric method, and Currie (2) developed a fairly accurate iodometric method.

Willard and Young (9) described the use of ceric sulfate as a standard oxidizing agent and applied it to the oxidation of organic matter, including oxalic and other organic acids, as did Berry (1). This oxidizing agent seemed to offer possibilities for the determination of oxalic and citric acids in mixtures.

EXPERIMENTAL

The method used is essentially differential titration of the mixture of the two acids, determining first the total acidity of the mixture by titrating with standard base using phenolphthalein and then the total reducing power of the mixture by titrating with ceric sulfate solution. While oxalic acid is oxidized quantitatively to carbon dioxide and water by ceric sulfate, citric acid is not, and the fraction oxidized is dependent upon several factors, including temperature, concentration of both sulfuric acid and ceric sulfate, and the time of standing.

PREPARATION OF SOLUTIONS

CITRIC ACID. A solution of citric acid was prepared by weighing a sufficient amount of the recrystallized acid to make an approximately 0.02 *N* solution as an acid. This was dissolved in carbon dioxide-free water and sterilized in an autoclave under atmospheric pressure for 30 minutes. To this solution, after cooling, were added 2 drops of chloroform to prevent the growth of molds. After titration with standard base, this solution was diluted to make it exactly 0.02 *N*.

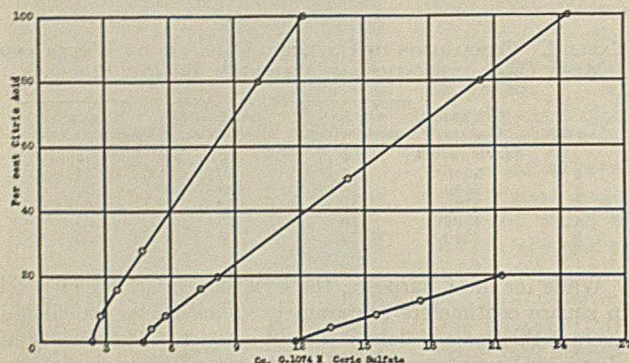


FIGURE 1. TITRATION OF 0.01 *N*, 0.02 *N*, AND 0.05 *N* ACID MIXTURES

OXALIC ACID. A solution of 0.02 *N* oxalic acid was prepared in a similar manner, except that the sterilization was omitted. Another oxalic acid solution to be used for back-titration was prepared and standardized against the ceric sulfate solution.

CERIC SULFATE. A ceric sulfate solution, prepared from pure ceric oxide according to the method of Willard and Young (9), did not give a sharp break when titrated electrometrically against sodium oxalate. When the technical oxide was used instead of the pure oxide, the break obtained was sharp. Formation of colloidal material in dissolving the oxide caused some difficulty, but this was overcome by changing the method of preparation. The method used is as follows:

Six hundred cubic centimeters of concentrated sulfuric acid in a 12-liter balloon flask were placed in a sand bath on an electric hot plate. A sturdy glass stirrer, run by a 0.125-horsepower motor, was introduced through a three-holed stopper. Through a second hole the ceric oxide was added, the third hole serving as a vent. Six hundred grams of ceric oxide were added, with constant stirring, while the solution was kept at 135° to 140° C. and the reaction allowed to continue for 4 hours, during which time the mixture became a paste. Sufficient water was added from time to time to maintain it as a paste. After 4 hours it was slowly diluted to 8 liters with water and heated at almost a boiling temperature for 8 hours. After settling, the clear reddish amber liquid was siphoned off and filtered while hot. The clear liquid was heated to about 90° C., and after adding 150 cc. of concentrated sulfuric acid was held at that temperature for from 24 to 30 hours. After filtering through a Gooch crucible, it was standardized against sodium oxalate. The solution should be between 0.1 *N* and 0.14 *N* if made in this manner. The ceric sulfate was standardized against pure sodium oxalate by dissolving 0.2 gram of the latter in 20 cc. of water and adding 2 cc. of 1 to 1 sulfuric acid. This was heated to 80° C. on an electric hot plate and titrated electrometrically with the ceric sulfate. An excess of 0.2 cc. of the latter will turn the solution a light yellow color and the potential change at the end point for 0.1 cc. of ceric sulfate is 0.2 volt. The end point is very sharp and definite.

ANALYSIS

For the oxidation of citric acid 25 cc. of the 0.02 *N* solution were treated with 75 cc. of the ceric sulfate solution to which 2 cc. of 1 to 1 sulfuric acid had been added. This mixture was heated in a water bath, the vessel containing the sample being immersed in the water at 90° to 95° C. for 1 hour.

The excess of the ceric sulfate was determined by titrating with standard oxalic acid electrometrically, heating the solution on a hot plate during the titration. The end point is obvious because of the decolorization of the ceric sulfate as it is reduced. Twenty-five cubic centimeters of the citric acid (0.02 *N* as an acid) required 22.91 cc. of the 0.1148 *N* ceric sulfate. Assuming that the citric acid is oxidized completely to carbon dioxide and water according to the equation



the tribasic acid is equivalent to 18 valence changes, as a reducing agent, and should therefore have a normality six times as great as a reducing agent than as an acid. The percentage oxidation in the above titration is given by the expression

$$\frac{(22.91)(0.1148)}{(25)(0.02)(6)} = 0.877 = 87.7 \text{ per cent}$$

Oxalic acid is oxidized quantitatively to carbon dioxide and water.

Three series of mixtures of oxalic and citric acids were prepared and oxidized in a similar manner. In Table I are given the cubic centimeters of 0.1074 *N* ceric sulfate required to oxidize 25 cc. of these acid mixtures, which were 0.02 *N*, 0.01 *N*, and 0.05 *N*, respectively, as an acid.

TABLE I. TITRATION OF ACID MIXTURES

0.01 <i>N</i> ACID			0.02 <i>N</i> ACID			0.05 <i>N</i> ACID		
Oxalic acid	Citric acid	0.1074 <i>N</i> ceric sulfate	Oxalic acid	Citric acid	0.1074 <i>N</i> ceric sulfate	Oxalic acid	Citric acid	0.1074 <i>N</i> ceric sulfate
%	%	Cc.	%	%	Cc.	%	%	Cc.
100	0	2.38	100	0	4.67	100	0	11.76
92	8	2.78	96	4	5.10	96	4	13.36
84	16	3.54	92	8	5.74	92	8	15.51
72	28	4.72	84	16	7.35	88	12	17.60
20	80	10.13	80	20	8.17	80	20	21.36
0	100	12.18	50	50	14.23
...	20	80	20.31
...	0	100	24.40

The data from Table I were plotted in Figure 1. With the exception of the points for the high percentages of oxalic acid the curves are straight lines. In the 0.05 *N* solutions, the higher concentrations of citric acid do not give a sharp

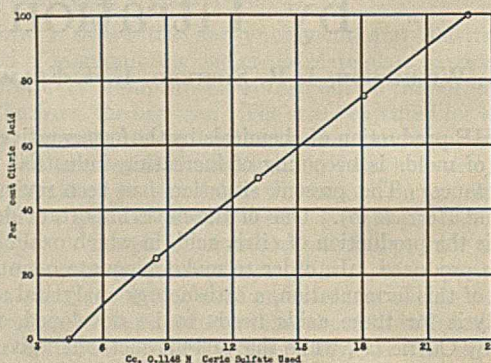


FIGURE 2. DETERMINATION OF ACIDS AFTER PRECIPITATION

end point. With the 0.01 *N* and 0.02 *N* solutions it is possible to use only 50 instead of 75 cc. of the ceric sulfate solutions and still get complete oxidation, but if this is done it is better to use but 1 cc. of the 1 to 1 sulfuric acid instead of 2.

A series of mixtures of the two acids was made by weighing out varying amounts of each, dissolving, and titrating the total acidity with standard sodium hydroxide. Portions of these which were equivalent to 25 cc. of 0.02 *N* acid were titrated with cerium sulfate solution. The data obtained are given in Table II, together with the percentages of the two acids as calculated from the titration curve.

TABLE II. PERCENTAGES OF ACIDS FROM 0.02 N CURVE

By WEIGHT		0.1074 N Ce(SO ₄) ₂ Used Cc.	By TITRATION	
Oxalic %	Citric %		Oxalic %	Citric %
91.64	8.36	5.77	91.9	8.1
78.58	21.42	8.24	79.8	20.2
67.00	33.00	10.30	69.5	30.5
61.41	38.59	11.65	62.8	37.2
39.01	60.99	16.38	39.6	60.4
22.07	77.93	19.96	22.2	77.8

Another series was made by weighing different amounts, titrating with standard base, diluting aliquot portions to both 0.02 N and 0.01 N, and then titrating 25 cc. of each with ceric sulfate. From the titration values the percentages of the two acids present were calculated, using the curves. The data are given in Table III.

TABLE III. PERCENTAGE OF OXALIC AND CITRIC ACIDS

By WEIGHT		0.1074 N CERIC SULFATE Cc.	FROM CURVE	
Oxalic %	Citric %		Oxalic %	Citric %
FROM 0.02 N CURVE				
85.77	14.23	7.03	85.8	14.2
69.08	30.92	10.42	69.0	31.0
53.34	46.66	13.60	53.5	46.5
38.28	61.72	16.71	38.1	61.9
21.48	78.52	19.98	21.8	78.2
FROM 0.01 N CURVE				
85.77	14.23	3.33	86.0	14.0
69.08	30.92	5.00	69.4	30.6
53.34	46.66	6.58	54.2	45.8
38.28	61.72	8.15	39.0	61.0
21.48	78.52	9.87	22.2	77.8

SEPARATION FROM OTHER ORGANIC ACIDS

Since in the process of fermentation these acids are produced along with other acids, it is necessary to separate them from the mixture before analyzing by the above method.

The first attempt to bring about this separation was by precipitating them as the barium salts, washing the precipitate until free from acid, and then adding an excess of sulfuric acid which precipitated the barium and changed the oxalic and citric acids back into the free acids. The excess of sulfuric acid was then removed by adding an excess of benzidine. This process should leave the free oxalic and citric acids with the excess of benzidine and it was hoped that they could be titrated in this mixture. Two difficulties were encountered—the benzidine was oxidized by the ceric sulfate and the precipitation of the excess of sulfuric acid in this solution by benzidine was not quantitative—and the method was therefore abandoned.

The second method was to precipitate the two acids as the lead salts, filter and wash free from acid, suspend the precipitate in water, and pass in hydrogen sulfide to precipitate the lead. The excess of hydrogen sulfide was removed from the solution by passing nitrogen gas through the solution until no test was given with lead acetate paper. This solution was then titrated with standard base, diluted to 0.02 N as an acid, and titrated with the ceric sulfate solution.

Three solutions of different normalities, all containing 42.6 per cent of oxalic acid and 57.4 per cent of citric acid, were prepared and treated as above. The separated acids were titrated with standard base, and amounts equivalent to 25 cc. of 0.02 N acid were titrated with the ceric sulfate solution. Seventy-five cubic centimeters of 0.1148 N ceric sulfate solution were added and the excess titrated with oxalic acid, 1 cc. of which was equal to 2.556 cc. of the ceric sulfate solution. The results are given in Table IV, in which the percentages of the two acids are obtained from Figure 2, which shows the relationship between the amounts of 0.1148 N ceric sulfate solution used in titrating 25 cc. of 0.02 N acid mixture and the percentages of the acids present. For accurate work this curve should be drawn on a large scale to enable one to read small amounts.

TABLE IV. DETERMINATION OF ACIDS AFTER PRECIPITATION

NORMALITY OF ACIDS	SAMPLE USED Cc.	OXALIC ACID USED Cc.	0.1148 N Ce(SO ₄) ₂ Used Cc.	OXALIC ACID %	CITRIC ACID %
0.02318	21.57	23.71	14.40	43.2	56.8
0.02571	19.45	23.70	14.42	43.0	57.0
0.02457	20.35	23.63	14.60	42.2	57.8

This shows that the percentages of the two acids present in a given mixture may be determined with an error of less than 1 per cent of the amounts present. Considering that the solutions used are but 0.02 N, the total acid present in 25 cc. would be but (0.02) (25) (0.045) gram of oxalic acid = 0.0225 and 1 per cent of this or 0.000225 gram is the error in weight due to the method.

CONCLUSIONS

A method has been developed for the analysis of mixtures of citric and oxalic acid by a differential titration, first as an acid and then by oxidation with ceric sulfate.

The accuracy is about 1 per cent of the total acid present. The two acids may be separated from mixtures of other organic acids obtained in fermentation processes by the insolubility of their lead salts. These salts are changed back to the free acids by treatment of the suspension of the lead salts with hydrogen sulfide, and after filtering the excess of hydrogen sulfide can be removed by passing nitrogen gas through the solution.

LITERATURE CITED

- (1) Berry, A. J., *Analyst*, 54, 461 (1929).
- (2) Currie, J. N., *J. Biol. Chem.*, 31, 15 (1917).
- (3) Denigès, G., *Compt. rend.*, 130, 32 (1900).
- (4) Hartmann, B. G., and Hillig, F., *J. Assoc. Official Agr. Chem.*, 10, 264 (1927).
- (5) Kunz, R., *Arch. Chem. Mikroskop.*, 8, 129 (1915).
- (6) May, O. E., and Herrick, H. T., U. S. Dept. Agr., *Circ.* 216 (1932).
- (7) Perdrix, M. L., *Bull. soc. chim.*, (3) 23, 645 (1900).
- (8) Pratt, D. S., U. S. Dept. Agr., *Circ.* 88 (1912).
- (9) Willard, H., and Young, P., *J. Am. Chem. Soc.*, 52, 129 (1930).
- (10) Williams, A. S., Mueller, R. H., and Niederl, J. B., *Mikrochemie (N. S.)*, 3, 269 (1931).

RECEIVED December 15, 1933.

ITALIAN SPONGE-PROCESSED LEMON OIL SITUATION. The February drop in quotations for Italian sponge-processed lemon oil to 4.50 lire per Sicilian pound, from the previous month's ruling quotation of 6.00 lire, was considered particularly serious, in view of the relatively high cost of the fruit. It is estimated locally that 1000 lemons yield 1.5 Sicilian pounds of oil and 3 kg. of citrate of lime, the total value of which at February quotations was not over 12.75 lire. The fruit itself cost about 8 lire per thousand. When other expenses were added, the prices mentioned above resulted in a definite loss. Producers are agitating vigorously for some action on the part of the government. Lack of demand and lack of ready cash resulted in sales at any prices

offered. In spite of the striking drop in prices, foreign demand was weak, whereas in preceding months, with much higher prices prevailing, there was much greater activity. Local well-informed sources rejected the supposition that foreign oil stocks were of sufficient size to account for the lull, and contended that, for some years past, no stocks of lemon oil had been created abroad. It is said that the price drop was probably due to a combination of factors, which included: the deliberate abstention from purchasing, by local exporters, with a view to further depressing the price level; the large stocks remaining from last year (which are said, inclusive of machine production, to have exceeded 1,600,000 Sicilian pounds), and the tightness of money.

Choice of Catalysts for the Hydrogen Electrode

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IN SPITE of the universal use of the hydrogen electrode, the metals available for the purpose have not been very systematically investigated. In a recent paper (2) there appeared a study of such catalysts which the writer wishes to supplement here, especially with the view of furnishing a practical guide to the laboratory technician.

CONSIDERATIONS GOVERNING CHOICE OF CATALYSTS

Hydrogen-electrode catalysts gradually lose their activity when exposed to hydrogen. This decay is produced by the hydrogen itself, although of course certain impurities when present may cause a so-called poisoning of the catalyst distinct from the above effect. In some cases the poisoning by impurities is more pronounced than the deactivation by hydrogen; in others the reverse is the case. Catalysts retain their activity when stored in oxygen or air.

Freshly electroplated platinum or iridium is always highly active, whether the deposit is smooth or black. The rate at which these deposits become deactivated when in use depends on their thickness and on the rate at which they are plated. Thick deposits, especially if plated very slowly, remain active for a longer time.

The decay of hydrogen-electrode catalysts is enormously accelerated by an increase in the temperature. Because of this a dry electrode may become entirely inactive when taken from the air into a hydrogen atmosphere, owing to the combination of the two gases at the surface, even if for only a fraction of a second. Previous wetting of the electrode is a necessary precaution when making a transfer of this kind.

Deviations from the equilibrium hydrogen potential are due to polarization of the hydrogen electrode by substances capable of oxidizing activated hydrogen or reducing hydrogen ion; and to leakage of H^+ (adsorbed during plating) from the electrode and consequent change in the H^+ concentration at the electrode surface. Polarizing impurities are found both in the solution (traces of dissolved oxygen) and in the electrode itself (base metals dissolved in the platinum). The effect of these impurities on the potential depends on their concentration and on the catalytic activity of the electrode, being less the greater the catalytic activity. Poisons do not directly cause deviations from the equilibrium potential but indirectly by affecting the catalytic activity. Because commercial gold (foil or wire) is usually much purer than commercial platinum, it makes a very desirable base for plating the catalysts.

The following recommendations are made as to the choice of catalysts:

For decidedly acid or basic solutions or for strongly buffered neutral solutions and also for maximum resistance to the action of poisons, platinum black.

For unbuffered neutral or slightly acid solutions, bright thin deposits of platinum or iridium. It may be desirable to plate these deposits from an alkaline bath in order to minimize the adsorption of H^+ by the metal (1).

For slightly basic, unbuffered solutions, bright thin iridium.

PREPARATION OF CATALYSTS

The quality of the deposits is impaired by evolution of hydrogen or by the uneven plating resulting when too great a portion of the current merely reduces the ions to a lower va-

lence without forming metal. For these reasons the concentration of the plating bath is specified and stirring is recommended in some cases, and not in others. The current densities should be as small as possible. The finished electrodes may be stored in distilled water with access to air. They should never be treated with chromic acid.

PLATINUM BLACK. This is plated with slow stirring from a 2 per cent solution of chloroplatinic acid containing a trace of lead acetate, which seems to promote adhesion of the deposit to the base. The current should be about 60 milliamperes per sq. cm. for 1 to 2 minutes. Nothing is gained by making the deposit very thick or by reversing the current at intervals. It is advisable to allow the electrode to stand a few hours in distilled water before using it.

BRIGHT PLATINUM. The plating solution is prepared by heating chloroplatinic acid on a sand bath to about 300° C. for an hour. The residue is dissolved in hydrochloric acid to give a 2 per cent solution of chloroplatinous acid in 1 *M* hydrochloric acid. The current density in this bath should be about 1 milliamperes per sq. cm. or less for 10 to 30 minutes without stirring.

If an alkaline plating bath is to be used, a 0.5 per cent solution of sodium chloroplatinate plus sodium hydroxide is prepared. The current density in this case will have to be high (10 milliamperes per sq. cm. or more) and no stirring used. The plating is continued until the thickness is 2 to 6 times that necessary just to cover the base. Beyond this thickness, increase in the objectionable features of the deposit (loss of smoothness) offsets any gain in the desirable ones (increased resistance to decay).

BRIGHT IRIIDIUM. The material for the plating bath is obtainable on the market in a form usually labeled iridium tetrachloride. A dilute solution of this (about 0.1 to 0.5 per cent) is used as a bath. The best results are obtained by using between 0.1 and 1.0 milliamperes per sq. cm. and allowing enough time to give a total thickness of from 2 to 6 times that which will just cover the gold base. This may require 3 or 4 hours. The bath should not be stirred.

TABLE I. CATALYTIC ACTIVITY AND DECAY OF ELECTRODES

TIME OF EXPOSURE TO HYDROGEN	(In 0.1 <i>N</i> hydrochloric acid)		
	BRIGHT PALLADIUM	BRIGHT PLATINUM	BRIGHT IRIDIUM
Hours	Amperes/ volt/sq. cm.	Amperes/ volt/sq. cm.	Amperes/ volt/sq. cm.
5	0.000035	0.019	0.020
23	0.0000041	0.017	0.019
48	0.0000035	0.013	0.018

PALLADIUM ELECTRODES

Many investigators have used palladium electrodes in the belief that a high capacity for hydrogen absorption necessarily implies good hydrogen-electrode properties. There is, however, very little connection between the absorption capacity and the catalytic activity of the surface for hydrogen activation, which latter is the quality desired in a hydrogen electrode. Palladium is not very active in this respect when compared to platinum or iridium and, even though palladium black may be sufficiently active to serve (because of sheer extent of area), still it is so far short of platinum black that there can be no advantage in its use. A comparison of the catalytic activity of bright palladium with that of bright platinum and bright iridium brings out the tremendous difference very clearly. A typical test is shown in Table I. The measure of catalytic activity is the slope of the polarization curve at the equilibrium potential (2).

CHECKING VALIDITY OF HYDROGEN-ELECTRODE POTENTIALS

It is common practice, when determining hydrogen-ion activity, to use two or more electrodes together. It is considered that the agreement of several electrodes is a satisfactory indication that they have reached the desired potential. With identical preparation of the catalysts we may expect them to have similar properties and that the effect of polarizing impurities on all electrodes may be the same—that the potentials will show close agreement even though they be far from the equilibrium value. The only certainty that we are reading the true equilibrium potential is by the agreement of electrodes of widely different catalytic activities. The prepa-

ration of electrodes of low activity is best accomplished by allowing bright electrodes to age in hydrogen a few days. They should not, however, be allowed to become too inactive, as an activity less than 0.001 makes the catalyst impractical for the purpose. For most ordinary work such refinement is not necessary.

LITERATURE CITED

- (1) Beans and Hammett, *J. Am. Chem. Soc.*, 47, 1215 (1925).
- (2) Hammett and Lorch, *Ibid.*, 55, 70 (1933).

RECEIVED December 30, 1933. In part based upon a dissertation submitted by Arthur E. Lorch to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the degree of doctor of philosophy, May 16, 1932.

A Method for Measuring the Dew Point of Natural Gases¹

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A GREAT quantity of natural gas escapes from the wells in oil fields. The greater part of this gas is methane, and the remainder is mostly a mixture of saturated hydrocarbons up to hexane, of which the higher-boiling constituents are valuable for addition to the low-boiling fractions of the natural oil. The separation of the higher homologs in the gas is usually carried out by compressing to about 20 atmospheres at most, and cooling to about -10° C. The object of the work described here was a study of the

change in slope, until it becomes zero at the critical point of the mixture. It follows that the dew pressure can be determined by measuring the isotherm.

THE APPARATUS

The use of an ordinary Cailletet piezometer, in which the gas is compressed into a narrow glass capillary tube, would obviously be unsatisfactory, because, as soon as liquid is formed, small drops might stick to the wall of the capillary tube and be enclosed by the mercury when this rises.

A diagrammatic sketch of the apparatus used by the authors is given in Figure 1.

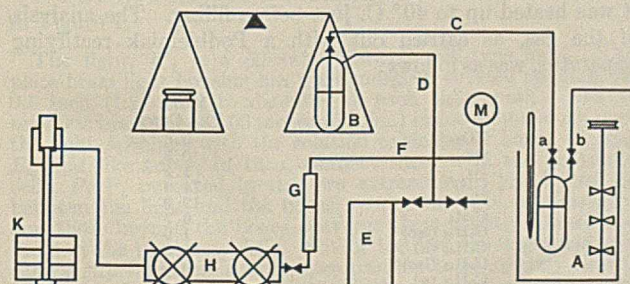


FIGURE 1. DIAGRAM OF APPARATUS

dew point of a gas mixture with a view to establishing the most efficient conditions for the extraction of the higher homologs.

THE METHOD

When an ideal gas (Boyle gas) is compressed at constant temperature, the product, pv , is independent of the pressure. In the case of a real gas, however, the value of pv changes with pressure, so that if pv is plotted against p , a curve is obtained which runs smoothly up to the pressure at which condensation of the gas starts. At this point there is a break and the curve becomes a straight line perpendicular to the p axis, as it is impossible to increase the pressure at constant temperature until all the gas has been liquefied. With a mixture of gases there is also a break in the curve at the condensation point, but the value of p does not remain constant during condensation and therefore the pv - p curve does not become perpendicular to the p axis. The difference in the slope of the two parts of the curve on each side of the break depends on the composition of the gas and also on the temperature. The higher the temperature the smaller the

change in slope, until it becomes zero at the critical point of the mixture. It follows that the dew pressure can be determined by measuring the isotherm.

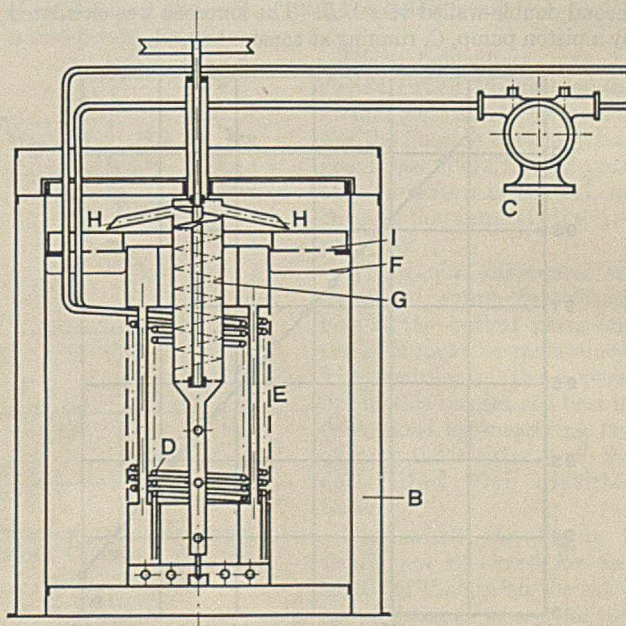


FIGURE 2. DIAGRAM OF THERMOSTAT

¹ Thirty-fourth publication of the v. d. Waals fund, Amsterdam, Holland.

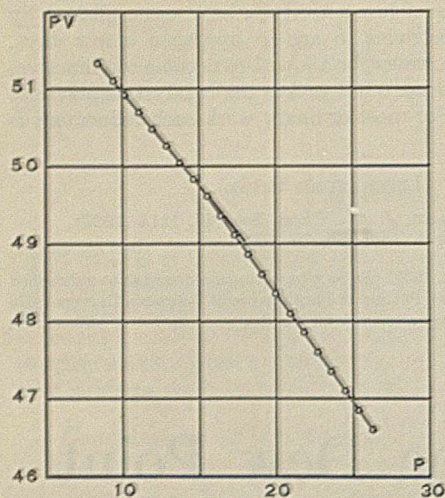


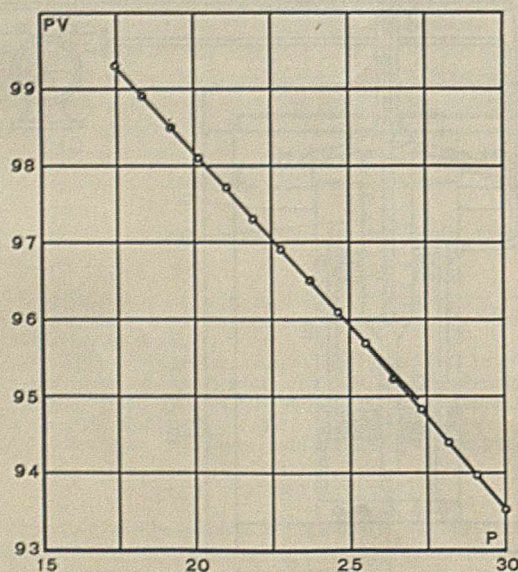
FIGURE 3. ISOTHERM AT 0° C.

cylinder *B* stands on one scale pan of a balance. The steel capillaries *D* and *C* (1.2 mm. outer, 0.8 mm. inner diameter) are flexible enough to give a balance sensitivity of 4 scale divisions per gram. To compress the gas under investigation the tap leading from cylinder *E* is opened, and the pressure of nitrogen in cylinder *B* increases, forcing the mercury through capillary *C* into bomb *A*. The decrease in volume of the gas in *A* is

equal to the volume of the mercury displaced from *B*, which can be calculated from the loss in weight of *B*. For accurate measurements of the pressure a pressure balance was used. Tube *F* leads to a leveling gage, *G*, which is coupled to the press, *H*, and from here to the pressure balance, *K*. When pressure equilibrium is reached, the pressure of the gas in *A* can be calculated from the load on the pressure balance, corrections being applied for the hydrostatic pressures of oil between *K* and the oil level in *G*, of nitrogen between *G* and the mercury level in *B*, and of the mercury between the levels in *A* and *B*.

TEMPERATURE CONTROL

The bomb which contains the gas to be examined is placed in a well-insulated thermostat. Above room temperature heating control as described by one of the authors (*I*) is used. Between room temperature and 0° the thermostat is cooled with the help of a cooling coil and the temperature is regulated in the same way. As it is essential for good regulation of temperature that the amount of heat removed from the thermostat by the cooling coil shall not fluctuate too rapidly, an arrangement was made whereby cooling liquid of constant temperature was introduced at constant rate into the cooling coil (Figure 2). Kerosene was used as the cooling liquid, being precooled in another copper coil, *D*, placed in a second double-walled vessel, *B*. The kerosene was circulated by a piston pump, *C*, running at constant speed.



A Photronic Colorimeter and Its Application to the Determination of Fluoride

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IN CONNECTION with the study of natural waters, a need was felt for a photoelectric colorimeter, and after some preliminary experimental work the apparatus here described was assembled. It uses as its light-measuring elements two Weston photronic cells, which are photoelectric cells of the type that transforms light energy directly into electrical energy without the use of an external e. m. f. In the present assembly the cells are electrically opposed and the current developed by them is balanced by means of a variable resistance. A sensitive galvanometer is used as the indicating instrument. The intensity of the light transmitted through a colored solution is measured in terms of the resistance that must be interposed to balance the photronic cells.

The apparatus has been satisfactorily used for the determination of fluoride in natural waters by a modification of the acetylacetone method described by Armstrong (1). In earlier tests the thiocyanate reagent and method, essentially as described by Foster (3), were used, but it has been found that the acetylacetone reagent is somewhat less susceptible to the effect of sulfate and chloride than the thiocyanate reagent.

DESCRIPTION OF APPARATUS

A schematic diagram of the apparatus and circuit is shown in Figure 1.

The light, *W*, is a 50-watt, 110-volt mill-type bulb. The plate-brass light housing has a ground-glass covered opening, *D*, 0.5 inch (1.27 cm.) in diameter in each light path. Heavy, seamless brass tubes 2.06 inches (5.2 cm.) inside diameter connect the light openings with the solution cabinets, or boxes, *B*₁ and *B*₂, and like tubes, in turn, connect these with the photronic cells, *P*, *P*, mounted in the two extremities. The lenses, *L*, between the light and the boxes, render the light rays parallel and those beyond the boxes converge them slightly toward the faces of the photronic cells. Slit *S*₁ has two moving parts and can be adjusted from a fully open position to completely closed. Slit *S*₂ has a single moving part which, when closed, will cover about one-third of the light path.

The Model 594 Weston photronic cells are of photovoltaic type and in operation resemble ordinary voltaic cells. The positive poles are connected directly and the negative poles are connected through the resistances. The variable resistance is a decade box of 11,110 ohms in steps of 1 ohm. The fixed resistance has a value of 1000 ohms. The galvanometer has a sensitivity of 0.025 microamperes per scale division. The resistance of the coil of the galvanometer is 1000 ohms. The 110-volt alternating current circuit, not shown, includes a switch and a double outlet for the lamps of the colorimeter and the galvanometer.

It was originally planned to compare the reference and unknown solutions. For this purpose two boxes, *B*₁ and *B*₂ of Figure 1, were provided in the set. To make such a measurement, the set is balanced, as in-

dicated below, with a cell filled with the reference solution in each box. The reference solution in the cell in box *B*₂ is replaced by the unknown solution and the set is balanced by adjusting the variable resistance, *VR*. The change in this resistance from the original setting of 1000 ohms to some new value measures the difference in light transmission of the two solutions. For the present purpose this offers no advantage, but there may be applications where it would be desirable. Likewise, the use of all-glass cells arranged in a horizontal position or Nessler cylinders in a vertical position might be indicated. Such modifications could be made without changing the electrical circuit.

The general arrangement of the set is shown in Figure 2. In the foreground are two glass cells of the type used. They are of metal, lacquered inside, with plain glass sides. To the left of the cells is an amber-colored glass, the resistance reading of which is frequently noted as a measure of the reproducibility of the instrument. The resistance required to compensate for this glass is 390 ohms, with variation from day to day not exceeding ± 3 ohms.

OPERATION OF PHOTRONIC COLORIMETER

Fifteen minutes before use, the lamps of the set and the galvanometer are turned on. The variable resistance, *VR*, of Figure 1, is set at 1000 ohms and the switch, *Sw*, is left open. Ten minutes later, the switch is closed and the slit, *S*₁, is adjusted until the galvanometer shows no deflection. The set is then kept in balance by adjusting the slit until it remains in equilibrium. This requires only a few minutes, after which the set is ready for use. The switch is opened and into the box, *B*₂, a reference solution in a glass cell is introduced. The switch is closed and the set brought back to balance by means of the variable resistance. (The adjustment of the slits should not be disturbed during the measurements.) The resistance is recorded.

The process is repeated with the unknown solution substituted for the reference solution, using the same glass cell.

The ratio of the resistance reading of the unknown solution to that of the reference solution bears a definite relationship to the concentration of the unknown solution. The method of establishing and interpreting this relationship will be discussed below.

Glass light-filters may be substituted in place of the ground-glass disks, *D*, Figure 1. For the fluoride determination green glass filters, having a low transmission in the red, increased the sensitivity appreciably.

Where small differences are significant, scrupulous cleanliness of the optical parts and the cells must be maintained. The condition of the apparatus in this respect can best be determined by measuring frequently the resistance of the cell filled with distilled water.

The switch, *Sw*, Figure 1, should not be closed for any length of time when the set is far off balance as a condition ensues which, in effect, resem-

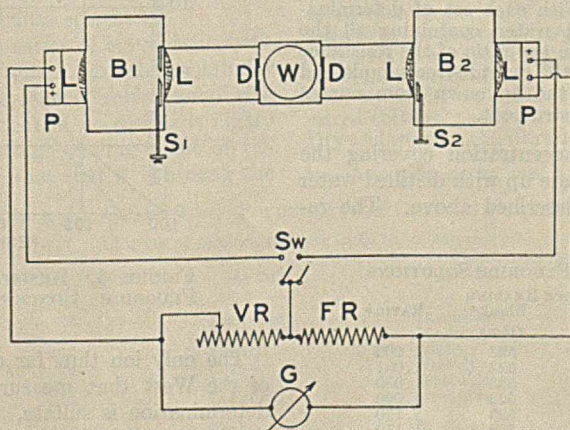


FIGURE 1. DIAGRAM OF PHOTRONIC COLORIMETER, SHOWING ELECTRICAL CIRCUIT

VR. Variable resistance
FR. Fixed resistance
G. Galvanometer
Sw. Double-pole single-throw switch
*S*₁, *S*₂. Variable slits
P. Photronic cells
L. Lenses
*B*₁, *B*₂. Boxes
D. Ground glass over openings
W. Light

bles polarization and from which the photronic cells recover rather slowly.

The electrical circuit here presented offers several advantages: a balanced circuit, which largely eliminates effects resembling polarization; a "null" measurement, indicated by a sensitive galvanometer; recorded values in terms of ohms resistance rather than scale divisions; quickly established equilibrium; and a negligible drift.

DETERMINATION OF FLUORIDE IN NATURAL WATERS

The procedure described by Armstrong (1) has been adapted for use with the photronic colorimeter. Only minor changes were found necessary.

REAGENTS. Ferric nitrate solution, 1 cc. = 0.2 mg. of iron in 0.02 *N* nitric acid; acetylacetone solution, 0.35 per cent aqueous solution; standard fluoride solution, 1 cc. = 0.1 mg. of fluoride; salt solution, 29.2 grams of sodium chloride and 30.1 grams of magnesium sulfate in 1000 cc. of water; 0.1 *N* nitric acid; *p*-nitrophenol indicator solution, 1 gram in 100 cc. of 70 per cent ethyl alcohol; approximately 1.0 *N* nitric acid; sodium hydroxide, carbon dioxide-free, approximately 0.5 *N*.

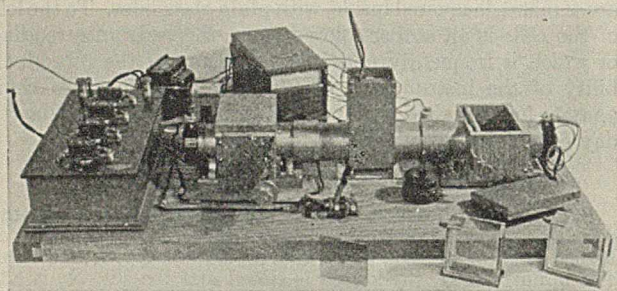


FIGURE 2. PHOTOGRAPH OF PHOTRONIC COLORIMETER

PROCEDURE. Transfer an aliquot of 100 cc. of the water or an aliquot containing not more than 0.5 mg. of fluoride to a 250-cc. beaker. Add one drop of *p*-nitrophenol indicator and 1.0 *N* nitric acid until colorless and 0.5 cc. excess. Bring to a boil and allow to boil 2 minutes, stirring vigorously to expel carbon dioxide. Remove from the flame and cool to room temperature.

While the samples are cooling, prepare the ferric-acetylacetone reagent, 10 cc. for each determination, as follows: 3 parts of acetylacetone solution, 2 parts of salt solution, 5 parts of ferric nitrate solution. Mix and allow to stand until ready for use.

When the samples are cool, add carbon dioxide-free 0.5 *N* sodium hydroxide until a faint yellow color of *p*-nitrophenol develops. Adjust to colorless with 0.1 *N* nitric acid, adding one drop in excess.

Make up to 110 cc. Add 10 cc. of the ferric-acetylacetone reagent and mix. After 10 minutes, compare in the photronic colorimeter as described above. With each set of determinations, include a sample of distilled water containing all the reagents but no fluoride. Calculate the ratio of the resistance reading of the unknown to that of the fluoride-free sample and read the fluoride concentration of the unknown from curves worked out in the calibration of the instrument.

Solutions of known fluoride concentration covering the range from 0 to 5 p. p. m. were made up with distilled water and analyzed by the procedure described above. The results are shown in Table I.

TABLE I. ANALYSIS OF PURE FLUORIDE SOLUTIONS

FLUORIDE P. p. m.	VARIABLE RESISTANCE READING		RATIO ^b
	Fluoride solution	Blank ^a	
0	523	523	1.000
0.5	534	523	1.021
1.0	549	523	1.050
2.0	570	523	1.090
3.0	591	523	1.130
4.0	612	523	1.170
5.0	633	523	1.210

^a Resistance required to balance a solution of the reagents in distilled water, in this case, the 0 p. p. m. fluoride solution.

^b Obtained by dividing the figures of column 2 by the corresponding figures in column 3.

It will be seen from these figures that for a change of 5 p. p. m. of fluoride the resistance changed 110 ohms or an

average of 22 ohms per p. p. m. Thus the indicated sensitivity for a change of one ohm is 0.05 p. p. m. of fluoride. The accuracy of the method is discussed below.

TABLE II. EFFECT OF SULFATE AND CHLORIDE ON DETERMINATION OF FLUORIDE

ANION	CONCENTRATION M.E./liter ^a	RATIOS OF RESISTANCE IN SALT SOLUTIONS TO RESISTANCE IN DISTILLED WATER	
		Fluoride, 0 p. p. m.	Fluoride, 5 p. p. m.
Sulfate	0	1.000	1.210
Sulfate	10	1.019	1.210
Sulfate	20	1.025	1.216
Chloride	0	1.000	1.210
Chloride	20	1.000	1.207

^a Milligram equivalents per liter.

The effect of chloride has been investigated over a greater range than is reported in Table II, and it is believed that the effect of this ion may be neglected in concentrations not exceeding 25 milligram equivalents per liter. Silica, borate, and phosphate, in amounts normally present in natural waters, likewise appear to be without measurable effect. Hydrogen ion is controlled sufficiently accurately by the procedure indicated above but it should be emphasized, in this connection, that carbonates must be expelled.

Sulfate appears to be the only ion commonly found in natural waters for which a correction must be made in the colorimeter readings.

The reagents here differ somewhat from those suggested by Armstrong. The salt solution is an addition to the list. In its absence, the bleaching effect of chloride and sulfate is much greater. Ferric nitrate in nitric acid is much more stable than ferric chloride. Such solutions have been in use for several months and appear to be unchanged.

CALIBRATION

Solutions of known fluoride concentration covering the range from 0 to 5 p. p. m. are made up with distilled water and analyzed by following the procedure described above. On one axis the fluoride concentration in parts per million is plotted and of the other the ratio of the resistances of the fluoride solutions to that of the fluoride-free solution. Such a curve is shown in Figure 3.

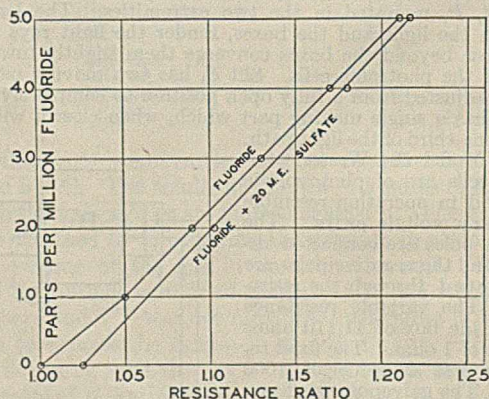


FIGURE 3. RESISTANCE RATIOS AT VARIOUS FLUORIDE CONCENTRATIONS IN PRESENCE OF SULFATE

The only ion thus far encountered in the natural waters of the West that measurably interferes with the fluoride determination is sulfate. It appears to be very difficult, if not impossible, to remove this constituent without a loss of fluoride, but, in view of the fact that the effect is approximately linear and additive, the correction for it is comparatively simple.

Prepare a set of pure fluoride solutions, as directed above, to which add 20 milligram equivalents of sulfate per liter, assuming

a 100-cc. sample. Complete the determinations and plot the curve. It will be found to be below but nearly parallel to the first, as reference to Figure 3 will show. In like manner complete additional curves to cover the range of sulfate likely to be encountered. Then, knowing the sulfate concentration of the sample, the fluoride concentration can be determined by interpolation. For example, suppose the determined resistance ratio is 1.150. If sulfate is absent, the indicated fluoride concentration is 3.5 p. p. m. If there are 10 milligram equivalents of sulfate, the corresponding fluoride is 3.4 p. p. m., and for 20 milligram equivalents the fluoride is 3.25 p. p. m.

ANALYTICAL RESULTS

Fluoride determinations on a series of natural waters are reported in Table III. In each case the fluoride was determined in duplicate.

TABLE III. FLUORIDE IN NATURAL WATERS

LAB. NO.	SULFATE M.E./l.	BLANK ^a Ohms	DUPLICATE DETERMINATIONS				P. p. m. fluoride	
			Resist- ance	Ratio	P. p. m. fluoride	Resist- ance		Ratio
7887	10.8	523	539	1.031	0.40	540	1.033	0.45
7909	12.3	522	537	1.029	0.40	537	1.029	0.40
8031	3.2	522	548	1.050	0.95	548	1.050	0.95
8078	3.0	522	549	1.052	1.0	549	1.052	1.0
8080	2.5	522	526	1.008	0.10	526	1.008	0.10
8090	0.5	522	544	1.042	0.85	543	1.040	0.80
8146	2.0	522	563	1.079	1.7	564	1.080	1.7
8164	2.5	521	549	1.054	1.05	549	1.054	1.05

^a Resistance, at balance, of a solution of reagents in distilled water.

To test the accuracy of the method, two experiments were undertaken. In the first, the fluoride concentrations of a series of natural waters were determined, then to each of separate aliquots 2 p. p. m. of fluoride were added and

the determinations were repeated. The determined values were within ± 0.1 p. p. m. of fluoride of the expected value. In the second experiment, a large sample of a natural water was collected. The sample contained 11.6 milligram equivalents per liter of sulfate. Triplicate determinations by the method here described showed 0.40, 0.40, and 0.45 p. p. m. of fluoride. Duplicate aliquots were concentrated and distilled by the hydrofluosilicic acid procedure described by Boruff and Abbott (2). The fluoride in these distillates was determined colorimetrically by the procedure here suggested and found to be 0.40 and 0.40 p. p. m. Other aliquots were distilled as above and the fluoride in the distillate titrated with standard thorium nitrate solution following Boruff's procedure (2). The result in this case was 0.45 p. p. m. of fluoride. It is concluded, therefore, that the accuracy of the procedure is within ± 0.1 p. p. m. of fluoride.

ACKNOWLEDGMENT

The author wishes to express his appreciation to F. N. Cowperthwait, of the Weston Electrical Instrument Corporation, for helpful suggestions, and to Geo. B. Collins, formerly of this laboratory, for assistance in assembling the colorimeter.

LITERATURE CITED

- (1) Armstrong, W. D., *IND. ENG. CHEM., Anal. Ed.*, 5, 300-2 (1933).
- (2) Boruff, C. S., and Abbott, G. B., *Ibid.*, 5, 236-8 (1933).
- (3) Foster, M. D., *Ibid.*, 5, 234-6 (1933).

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Use of Trichlorobenzene in Analysis of Graphite Greases

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COMMERCIAL greases frequently contain chemically inert materials, particularly graphite, from which it is troublesome to separate such ether-insoluble materials as calcium stearate. To carry out the separation for gravimetric determination of graphite, a number of solvents have been compared, some of them differing from the usual types. As a result of this a method for extraction of calcium stearate from graphite by trichlorobenzene has been developed. The method is also applicable to other heavy metal soaps such as aluminum stearate, magnesium stearate, etc., which are even more readily soluble than calcium stearate.

There are given in Table I the series of solvents investigated, their boiling points, and other desirable solubility data. These data show that a number of solvents will dissolve this heavy metal soap, but that in no case is it highly soluble in the cold solvent. The high boiling point of trichlorobenzene, combined with the fact that it is among the

better solvents, make it a very satisfactory reagent for such extraction. The following procedure for determination of graphite in greases containing calcium soap is illustrative of its use.

PROCEDURE

Heat 5 grams of the grease with 75 cc. of trichlorobenzene to about 165° C. Centrifugalize while still hot. Decant off the bulk of the trichlorobenzene. Heat the residue with a further quantity of solvent and repeat the operation. Shake the residue with a hot 50 to 50 alcohol-benzene mixture, filter through a tared filter paper, and wash with the same mixture. Dry the residue in the oven and weigh.

If very great accuracy is required, after trichlorobenzene extraction, shake with hot 50 to 50 alcohol-benzene mixture acidified with hydrochloric acid. Filter, and wash well, first with the mixed solvent, then with alcohol, and finally with hot water. Dry and weigh. All filtrations are rapid.

RECEIVED February 24, 1934.

TABLE I. QUALITATIVE SOLUBILITY OF CALCIUM STEARATE

(0.5 gram of calcium stearate in 10 cc. of solvent)

SOLVENT	BOILING POINT ° C.	SOLUBILITY ^a		
		At 20°	At 60°	At boiling point
Acetone	56	Insoluble	Insoluble	Insoluble
Benzene	80	Moderately	Moderately	Moderately
Butyl alcohol	117	Slightly	Slightly	Soluble but cloudy
Carbon tetrachloride	76	Slightly	Slightly	
Ethylene glycol monoethyl ether	135	Insoluble	Insoluble	Soluble but cloudy
Diethylene glycol	245	Insoluble	Insoluble	Calcium stearate melts clear
<i>o</i> -Dichlorobenzene	179	Slightly	Moderately	Moderately soluble
Isopropyl alcohol	83	Slightly	Slightly	Soluble but cloudy
Propylene dichloride	97	Insoluble	Insoluble	Separates rapidly on cooling
Trichlorobenzene	218	Slightly	Slightly	Slightly
Trichloroethylene	87	Slightly	Slightly	Completely soluble and clear at 165°
Toluene	111	Moderately	Moderately	Slightly
Turpentine	156	Slightly	Moderately	Moderately
Xylene	140	Slightly	Moderately	Soluble but cloudy

^a Slightly soluble, some had dissolved. Moderately soluble, roughly 50 per cent had dissolved.

Determination of Peroxidase Activity

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THE preservation of fruits and vegetables by freezing and subfreezing temperature storage often requires the inhibition or control of enzyme action. The degree of success with which these measures are applied determines to some extent how well the color, flavor, odor, and other characteristics of the fresh product are retained during storage. A study of these problems has required the adaptation or development of exact methods of determining enzymes applicable to the particular products.

Because of the rather general distribution of peroxidase and the need for control of its activity, a quantitative method of investigation was required. As the Guthrie (1) method seemed simple and required no expensive apparatus, it was studied. A preliminary study showed that this method did not give the maximum peroxidase activity of many products—for example, strawberries gave little or no peroxidase activity. This difficulty was corrected in part by thoroughly extracting the enzyme from all the tissue sample and making the determination at the optimum hydrogen-ion concentration for strawberry peroxidase.

The method as now worked out has the advantage of estimating, on a dry-weight basis, the total peroxidase activity of the entire sample in the presence or absence of catalase and at the optimum hydrogen-ion concentration for the peroxidase of the particular product examined.

EXPERIMENTAL WORK

The Guthrie method was changed in the following respects:

(1) An extract of the entire tissue sample replaced the pressed juice sample; (2) McIlvaine's dibasic sodium phosphate and citric acid buffer was used instead of sodium hydroxide and citric acid buffer; (3) the reaction of the medium was adjusted to the peroxidase optimum for the particular tissue examined; (4) the amount of all reagents and extracts was reduced 50 per cent, except for toluene which was added as required for complete solution of the indophenol; (5) an enzyme sample in which the peroxidase had been inactivated was added with each reagent blank; and (6) the results were expressed as milligrams of indophenol per decigram of dry substance in the enzyme sample.

In order to obtain maximum peroxidase activity, the samples were ground thoroughly with water or buffer solution and fine sand in a mortar, made up to volume with water or buffer solution, and aliquot samples used for representative determinations. This method gave a more complete extraction of the enzyme than is possible by using only the pressed juice. The point was illustrated by the analyses of two samples of similar tissue and equal weight taken from an individual pear. The peroxidase in samples A was extracted by grinding, while that in samples B was extracted by freezing, thawing, and 5500 pounds pressure per square inch (387 kg. per sq. cm.). The amount of peroxidase in each sample was represented by the milligrams of indophenol produced per decigram of dry weight of samples A and B.

The results are given in Table I for determinations made at both 6.0 and 6.4 pH.

TABLE I. PEROXIDASE ACTIVITY OF PEAR TISSUE

SAMPLE	REACTION OF MIXTURE, pH	INDOPHENOL PRODUCED ^a Mg./dg.
A	6.0	2.76
B	6.0	0.485
A	6.4	3.52
B	6.4	0.604

^a About 83 per cent of the peroxidase was not in the juice.

While it was noted that the α -naphthol-*p*-phenylenediamine mixture was more sensitive near the neutral point, this sensitivity varied with the kind of buffer used and finally with the

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compounds used to make up each buffer. Seven different kinds of buffer mixtures were examined. McIlvaine (2) and Sorensen (3) buffers were found to be less sensitive to the substrate than the other buffers at pH values near the optimum for peroxidase. The magnitude of the complete blanks varied from 20 to 50 per cent of the total indophenol formed, depending upon the kind of enzyme extraction as well as the proximity of the solution to neutrality.

The use of the McIlvaine or the Sorensen citrate-sodium hydroxide buffer mixture made it possible to determine the peroxidase activity at a higher pH value. This modification adds to the usefulness of the method, since it is no longer limited to a reaction of pH 4.5. Table II gives the amount of indophenol produced at the higher and lower pH values by aliquot samples from extracts of various products.

TABLE II. EFFECT OF HYDROGEN-ION CONCENTRATION UPON PEROXIDASE ACTIVITY

PRODUCT	SAMPLE	REACTION AT OPTIMUM pH		REACTION AT OR NEAR pH 4.5		CATALASE ACTIVITY OF PEROXIDASE SAMPLE IN OXYGEN Cc.
		pH	Indo-phenol ^a Mg./dg.	pH	Indo-phenol Mg./dg.	
Strawberry	1	6.8	1.98	4.5	0.03 ^b	0.02
Strawberry	2	6.8	2.33	4.5	0.02 ^b	0.02
Pear	3	6.2	4.95	4.5	0.42 ^b	0.00
Pear	4	6.2	5.01	4.5	0.45 ^b	0.00
Asparagus	5	6.4	113.0	4.4	20.0 ^a	1.98
Asparagus	6	6.4	112.2	4.4	21.0 ^a	1.98
Potato	7	7.0	60.7	4.4	7.2 ^a	0.20

^a McIlvaine buffer used.

^b Citric acid and sodium hydroxide buffer used.

These results show that one may substitute the McIlvaine buffer and increase the pH value with an increase of the peroxidase activity. The blanks with the McIlvaine buffers were lower than those with the citric acid and sodium hydroxide buffers.

As the peroxidase of many fruits and vegetables is wholly or partly inactive if determined at pH 4.5, determinations should be made at the optimum pH for the peroxidase being examined. This optimum for strawberries, pears, cauliflower, asparagus, and potatoes was found to be between 6 and 7 pH. One may compare the peroxidase activity of these tissues at the optimum pH values with the activity of the same extracts buffered to a lower pH value (Tables II and III). These results show a notable increase of peroxidase activity at or near the optimum pH value. Peroxidase determinations made by the Willstätter and Stoll method also showed that pear peroxidase was more active at 6.2 than at 4.5 pH.

The catalase in the peroxidase sample may be inactivated at a suitable low temperature with only a slight loss of peroxidase activity. This temperature varies with the product; thus, 60° C. was used for asparagus, while 50° C. was sufficient for pear extracts.

The following experiment was performed to show that pear peroxidase was more active at 6.2 than at 4.5 pH in the absence of catalase:

A 1 per cent chloroform-water extract of pear tissue, having a pH value of 4.56, was heated for 12 minutes at 50° C. to inactivate the catalase. To determine the absence of catalase, samples five times as large as the peroxidase samples were buffered to 6.2 pH and the chloroform was removed from each sample by shaking just previous to the catalase determination. Aliquot samples of this extract, which gave no catalase activity, were used for determination of its peroxidase activity at 6.2 and at 4.5 pH. The McIlvaine buffer was used for the 6.2 pH and the citric acid with sodium hydroxide buffer for the 4.5 pH determinations.

The results given in Table III show that pear peroxidase was also more active at the optimum pH value of 6.2 after the catalase had been destroyed.

TABLE III. PEROXIDASE ACTIVITY OF PEAR TISSUE AFTER CATALASE HAD BEEN INACTIVATED BY HEAT

SAMPLE	pH VALUE OF REACTION	PEROXIDASE ACTIVITY
		(INDOPHENOL PRODUCED) Mg.
1	6.2	3.62
2	6.2	3.62
3	6.2	3.69
4	6.2	3.75
5	4.5	0.46
6	4.5	0.44
7	4.5	0.37
8	4.5	0.47

The optimum pH of 6.2 for pear peroxidase was determined experimentally by making peroxidase determinations under controlled conditions and pH values ranging from 4.4 to 8.4. Aside from this, no constant relation has been noted between peroxidase and catalase activity, and it is doubtful if the presence of catalase interferes directly with the peroxidase determination. If this is true, the catalase in peroxidase samples need not be inactivated.

The reagents were used in the same relative proportion as outlined by Guthrie but halved in amount. To insure complete and rapid solution of the indophenol, it seemed best to vary the amount of toluene with amount of indophenol to be dissolved. The indophenol production is linear with the enzyme concentration in dilute solutions. It is best to adjust the enzyme sample so as to not exceed 3 mg. of indophenol per sample.

In order to make the determination of peroxidase comparable, a blank consisting of all reagents and peroxidase-inactivated extract was carried along with each test. The peroxidase in these blanks was inactivated by boiling for 20 minutes just previous to the determination.

The only change in the order of procedure was the addition of the substrate to the enzyme extract and finally the addition of the buffer with the hydrogen peroxide. To avoid part of the sensitivity effect of the reagents, the solutions should be held at a temperature of 25° C. before mixing.

The results were expressed as milligrams of indophenol produced by the peroxidase per decigram of dry substance in the enzyme sample. The dry-weight base was used because the water content of fresh, frozen, and stored frozen products varies considerably.

PROCEDURE RECOMMENDED

The suggested procedure for the determination of peroxidase activity is as follows:

Care should be exercised to obtain comparable samples of the product for both dry-weight and peroxidase determinations. The weighed peroxidase sample should be ground thoroughly with fine sand and afterwards made up to a definite volume with water or buffer solution. A measured volume of this enzyme solution is boiled for 20 minutes to destroy the peroxidase and then made up to the measured volume for peroxidase-free samples and indicated as the blank solution. A required volumetric sample of the enzyme solution is placed in a 100-cc. flask and to this are added 6.25 cc. of the substrate solution containing 0.02975 gram of *p*-phenylenediamine hydrochloride in water with 0.595 cc. of 4 per cent α -naphthol in 50 per cent alcohol. (Solutions are made up in these proportions for several samples at one time, brought together, and filtered just before using.) The reaction is started by the addition of 8.75 cc. of a solution containing 6.25 cc. of the optimum pH buffer and 2.5 cc. of 0.05 *N* hydrogen peroxide. The reaction progresses at 25° C. for 10 minutes and is stopped by the addition of 2.5 cc. of a 0.1 per cent aqueous solution of potassium cyanide. A blank determination, made up from all the reagents and the required volume of the blank solution, is carried along with each peroxidase sample. The indophenol produced is dissolved in toluene and separated from the aqueous solution by centrifugalizing for 1 minute. The amount of indophenol in the sample is determined by colorimetric comparison with a standard containing 50 mg. of indophenol per liter of toluene. The amount of indophenol produced by the sample, less that produced by its blank, gives the initial peroxidase activity. From the dry-weight determination, the peroxidase activity is reported as milligrams of indophenol per decigram of dry substance in the peroxidase sample.

LITERATURE CITED

- (1) Guthrie, J. D., *J. Am. Chem. Soc.*, 63, 242-4 (1931).
- (2) Mellvaine, T. C., *J. Biol. Chem.*, 49, 183-6 (1921).
- (3) Sorensen, S. P. L., *Ergebnisse Physiol.*, 12, 393 (1912).

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A Stirrer for Solvent Extraction

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IN THE extraction by means of immiscible solvents, such as ether-water or carbon tetrachloride-water, the need for intimate contact between the liquid layers is apparent.

Figure 1 shows two modifications of a stirrer designed in this laboratory. When the stirrer is rotated as indicated by the arrows, liquid is drawn from one layer and sprayed in fine droplets through the second phase. In this way intimate contact, with a large interfacial surface, is obtained. This stirrer is particularly advantageous for continuous extractions, since the body of the liquid which is being sprayed is practically undisturbed and may be drawn off continuously during the extraction.

On the left are shown the details of the stirrer used to lift a heavier liquid and spray it through the lighter liquid layer. When the stirrer is rapidly rotated counterclockwise, the movement of the jets, *B-B*, through the liquid cause a decrease in pressure in the hollow shaft of the stirrer. The heavier liquid, into which the open end of the shaft dips, is drawn up into the jets and sprayed through

the upper layer. This type of stirrer was designed and successfully used for the treatment of organic liquids with sulfuric acid, where the ratio of acid to organic liquid was very low and uniform treatment was essential.

On the right is shown the modification for downward flow. The principle of operation is the same. In this case the jets, *B-B*, rotate in the heavier liquid, and the lighter solvent is drawn through four small openings, *A-A*, in the upper part of the hollow shaft. This stirrer has been used with entire satisfaction for continuous ether extractions of aqueous solutions. The ether is added continuously below the water surface, the excess ether being drawn off through an overflow.

The stirrers used in this laboratory are made from 5-mm. inside diameter glass tubing. The jets are 1 cm. from the center and have about 0.5-mm. openings, turned at right angles to the cross arms (parallel to the direction of rotation). In the down-flow type the openings *A-A* are approximately 1 mm. in diameter.

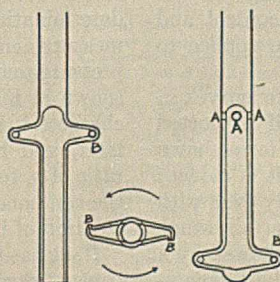


FIGURE 1

RECEIVED February 3, 1934.

Microanalysis of Gaseous Mixtures by Pressure-Temperature Curves

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IN CONNECTION with studies of certain gaseous reactions in this laboratory need was felt for a method for the accurate analysis of small amounts of hydrocarbon gases. Most of the existing methods (3, 5, 6, 12, 13, 15, 16, 17, 19, 20) are based on fractional distillation and hence require much larger samples than are available from laboratory experiments. Certain of the existing micromethods (1, 2, 4, 8, 11, 14) have not hitherto been applied to the analysis of hydrocarbon mixtures.

A method has been developed which requires a very small sample, less than 1 ml. at normal temperature and pressure, and has been applied satisfactorily to the analysis of synthetic and commercial samples of hydrocarbon gases, as well as to gaseous products obtained in this laboratory from the thermal decomposition of coal. The sample is not destroyed in the procedure and may be reanalyzed, the time required for an analysis is relatively short, and the only reagent required is liquid nitrogen of which a few liters suffice. A limitation of the method at the present time lies in the fact that it has not been found possible to determine saturated and unsaturated hydrocarbons of the same number of carbon atoms in the presence of each other.

The method is a physical one based upon the procedure proposed by Campbell (4) and depends upon the characteristic form of vapor pressure-temperature curves. Since the determination of only low-boiling hydrocarbons was desired here, the measurements were made over the range 78° to 298° K. By the use of suitable temperature-control and pressure-measuring devices, the method could be applied to higher boiling substances.

It is usual to plot vapor pressure-temperature curves in linear form, $\log p = 1/T$. If, however, p itself is plotted against the absolute temperature, a graph of the form shown in Figure 1, curve 1, results. From this curve it is evident that, for small values of p , p increases only slightly even with considerable change in T (a to b); then over a certain range there is a rapid change in slope (b to c); this is followed by a sharply rising, nearly linear portion (c to d). The temperature range of rapid change in slope (b to c) was designated by

A micromethod for analysis of gases by pressure-temperature curves, based upon the procedure of N. R. Campbell, has been developed. Less than 1 ml. of sample (N. T. P.) is sufficient for an analysis. The sample is not destroyed and may be reanalyzed. The time required for an analysis is 3 to 5 hours. The only reagent required is liquid nitrogen of which 1 to 2 liters suffice.

The method has been applied successfully to the analysis of synthetic mixtures of pure hydrocarbons, commercial gas samples, and gaseous products obtained in the thermal decomposition of coal in this laboratory.

In those cases where two components form a heterogeneous condensed phase, the determination is simple; if they form a homogeneous condensed phase and have normal boiling points lying close to each other, the determination is more difficult but still possible.

A limitation of the method as developed at the present time lies in the impossibility of determining saturated and unsaturated hydrocarbon gases of the same number of carbon atoms in a mixture. Methods of obviating this difficulty are given.

The method depends on a temperature difference between the evaporation bulb and the balance of the system, and hence can be applied to higher boiling mixtures if suitable pressure-measuring and temperature-control devices are used.

Campbell as "characteristic condensation temperature," but it is, of course, not a single definite temperature. The expression "initial vaporization temperature" (I. V. T.) will be used in this paper to designate this region. Curve 1 (Figure 1) portrays the relations in a closed system of one component when a vapor phase is in equilibrium with its liquid or solid phase. If the system is sufficiently large so that ultimately, owing to increasing temperature, the condensed phase disappears entirely, the curve takes the form shown in Figure 1, curve 2. The first portions of these curves are identical. If T_2 is the temperature at which the condensed phase disappears, the curve from e to f represents merely the expansion of the vapor ($p \propto T$), and, because of the comparatively small rate of change of p with T under such conditions, the change in direction of curve 2 results. If only a relatively small portion of the system undergoes the temperature change—i. e., if the vapor is allowed to expand into a "reservoir" of relatively large volume, maintained at some constant, higher temperature—the portion of the curve from e to f will approach the horizontal. Sharp corners, such as is shown at e , were not experimentally realized,

probably owing to adsorption on the walls of the condensing bulb at the relatively low pressures.

If two substances form separate phases in the condensed state, and if their I. V. T.'s are sufficiently far apart so that the more volatile will be relatively completely evaporated from the condensed phase before the vapor pressure of the second becomes appreciable, it is evident that a quantitative determination of the amount of each present can be made by measurements of p and T , and plotting p against T . The pressure-temperature relations in such a system will be as shown in Figure 1, curve 3. The I. V. T.'s, T_3 and T_4 , are characteristic of the components, with the exceptions noted later, and hence indicate the qualitative composition; the ratio of p_1 to p_2 gives the fraction by volume of the more volatile component present in the mixture and hence permits calculation of its quantitative composition.

If, as has been found to be the case in the hydrocarbon mixtures worked with in this laboratory, the two substances form one phase in the condensed state, a determination is still pos-

sible in many cases. Now, however, curve *ae* takes the form *ae*₁, since it is no longer the vapor pressure curve of the more volatile component but is a partial pressure curve of that component, the form of which, in accord with Raoult's law, will be a function not only of the vapor pressure of the more volatile component in the pure state, but also of the concentration of that component in the condensed phase. As a conse-

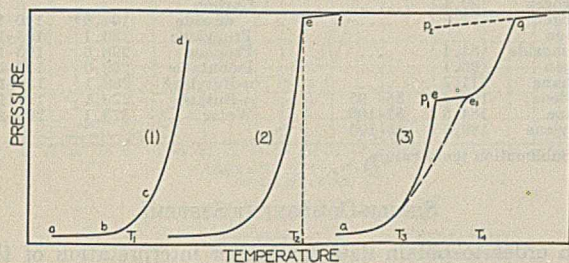


FIGURE 1. IDEALIZED PRESSURE-TEMPERATURE CURVES

quence, the values of *p* for any given temperature will be much lower. It is evident that in such a system, the flat portion of the curve, the period during which there is merely expansion of the vapor of the more volatile component, must be less clearly defined, and may indeed appear merely as a short region of change of slope. It follows that the definiteness of this relatively flat part of the curve, in a system where the substances form a single condensed phase, will be a function of the relative concentration of the components. If the more volatile component is present in great amounts, the flat portion may entirely disappear; if it constitutes only a small fraction of the total, the flat portion becomes more distinct. In some cases a reduction in total pressure was found to be of advantage. This was probably due to the fact that the more volatile component was eliminated from the condensed phase at a lower temperature and hence there was a longer temperature interval for the appearance of the definitive flat portion of the curve, before the I. V. T. of the less volatile component was reached.

In general, I. V. T.'s will be in the same order as the normal boiling points of the substances present. Their value can be approximately determined by plotting *p-T* curves from published empirical equations, where these cover the necessary low range, but the best method found in this laboratory of fixing these temperatures consists in plotting *p-T* curves of the pure components from experimentally determined values.

APPARATUS AND METHOD OF OPERATION

The apparatus shown diagrammatically in Figure 2 was constructed of Pyrex glass with no stopcocks or rubber connections in the main system in order to avoid absorption of hydrocarbons by rubber or grease.

The condensation and vaporization of the hydrocarbon gases took place in bulb *C* enclosed in thermostat *A* which was filled with liquid nitrogen to freeze out the condensable gases. Excess liquid nitrogen was drained through the vacuum-jacketed tube connection at the bottom of *A*. It was found that uniformity of temperature in bulb *C* was of the greatest importance in obtaining satisfactory results. To assure this necessary uniformity of temperature, a layer of copper about 1/3 mm. (0.013 inch) thick was deposited electrolytically on the outer surface of *C*, a copper shield was placed around it, and the intervening space, as well as the entire Dewar flask, *A*, was filled with copper turnings. The thermocouple,

B, was copper-constantan and was in direct contact with the copper coating of bulb *C*. The thermocouple was calibrated at the freezing point of mercury, carbon dioxide sublimation temperature, and boiling point of nitrogen. Good agreement was obtained with accepted values (18).

The lower Dewar flask, *D*, was filled with liquid nitrogen and provided with an electric heating coil, *E*, connected in series with a rheostat and an ammeter, which controlled the rate of evaporation of liquid nitrogen and thereby the rate of rise of temperature in thermostat *A*. If, however, the temperature did not increase sufficiently rapidly, a very slow stream of air was blown through the vacuum-jacketed tube connection into *A*. A temperature rise of 0.4° to 0.6° K. per minute was found to be satisfactory.

During an analysis the mercury was raised to a mark on the cut-off, *J*, the apparatus to the right serving only for evacuation of the system and for introduction of the sample. It is essential that the volume of *C*, *F*, and connecting tubing to the mark on *J* be maintained constant, but it is not necessary that either the total volume or the volume of *C* be determined for an analysis. Since almost 95 per cent of the total gas space is not thermostated, it is important that the room temperature be maintained constant within 1° K. to avoid significant errors in the pressure readings.

For accurate analyses of mixtures it is important that the pressure be determined for each 2° to 3° K. rise in temperature of bulb *C*, and that the time between corresponding pressure and temperature readings be a minimum. The pressure was determined by means of the McLeod gage *F*. The range was 3×10^{-1} to 1×10^{-6} mm. of mercury. In the first work the McLeod gage was supplied with the usual form of reservoir. It was later found that the special type, as shown at *G*, contributed greatly to the speed and precision of the pressure readings, since by one turn of the control valve, *X*, communication between *F* and *G* was closed, with the result that constant readings of the levels of the mercury columns were obtained at once.

To prepare the apparatus for an analysis, the entire system was first evacuated at room temperature to at least 10^{-5} mm.

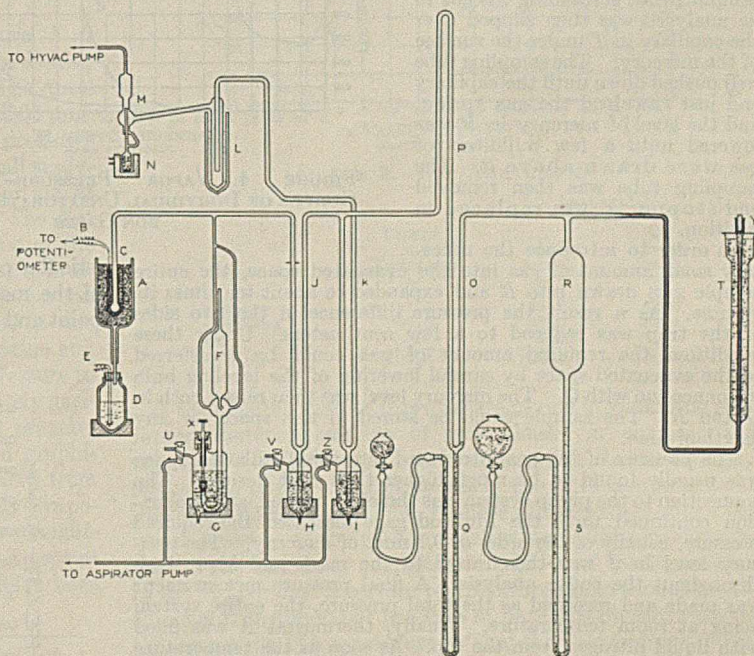


FIGURE 2. APPARATUS FOR MICROANALYSIS OF GASEOUS MIXTURES BY PRESSURE-TEMPERATURE CURVES

- A. Dewar flask with vacuum-jacketed tube connection
- B. Copper-constantan thermocouple in direct contact with freezing bulb
- C. Copper-jacketed freezing tube placed in a 2-mm. (0.079-inch) thick copper shield
- D. Lower Dewar flask containing liquid nitrogen
- E. Electric heating coil in series with rheostat and ammeter
- F. McLeod gage
- G, H, I. Mercury reservoirs
- J, K, O. Mercury cut-off tubes with mark provided on J
- L. Liquid nitrogen trap
- M. Mercury-vapor pump backed by a Cenco Hyvac oil pump
- N. Electric heater
- P. Connecting U-tube for introduction of sample
- Q, S. Mercury-filled U-tubes in connection with leveling bottles
- R. Expansion bulb
- T. Sampling reservoir
- U, V, Z. Two-way stopcocks for connection with atmosphere or suction
- X. Screw attachment connected with stopper for closing communication between reservoir *G* and McLeod gage
- Y. Ground-glass stopper provided with cup for holding weights

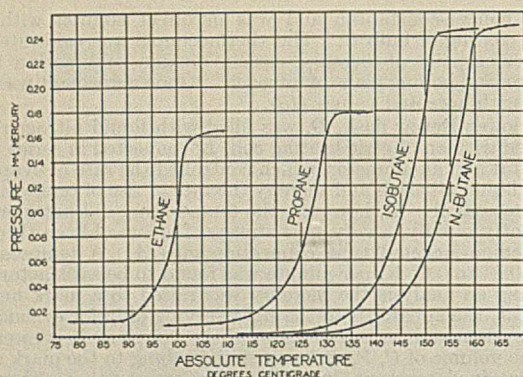


FIGURE 3. VAPOR PRESSURE-TEMPERATURE CURVES OF INDIVIDUAL SATURATED HYDROCARBON GASES

mercury, while the capillary connecting the sampling reservoir, *T*, with expansion bulb *R* and cut-off *O* were completely filled with mercury, and the level of mercury in the right-hand side of *P* was raised nearly to the top by means of the leveling bottle. A ground-glass stopper, *Y*, was provided to prevent the mercury from being drawn into the system from *T* during evacuation. As soon as the level of mercury in *P* was approximately 760 mm. above the surface in sampling reservoir *T*, the ground-glass stopper could be removed from the capillary. Before the introduction of the sample the apparatus was shut off from the pump system by partially filling cut-off *K* with mercury. The sampling tube containing the gas to be analyzed was then slipped over the capillary in *T* under the surface of the mercury. The sampling tube was pushed down until the capillary end just reached the gas space, and the level of mercury in *P* was lowered until a few milliliters of gas were drawn above *R*. The sampling tube was then removed and stopper *Y* was replaced in position.

In order to introduce the necessary small amount of gas into the evacuated space, the entire sample was drawn into *R* and expanded to about ten times its volume. As a result the pressure difference in the two sides of the trap was reduced to a few centimeters. Under these conditions the required amount of gas could be transferred to the evacuated space by careful lowering of the leveling bulb in connection with *Q*. The mercury level was then raised both in *O* and *R*. The sample could be stored in this space for any length of time.

The pressure of the gas introduced into the distillation space was usually found to be much higher than that desired. The connection to the pump system was therefore opened, and evacuation continued until the McLeod gage indicated the required pressure, usually of the order of 0.1 mm. of mercury. The mercury level in *J* was then raised to the mark and kept there throughout the entire analysis. A final pressure measurement was made and recorded as the total pressure, the entire system being at room temperature. Finally, thermostat *A* was filled with liquid nitrogen from the top. As soon as the temperature of tube *C* reached that of the liquid nitrogen (78° K.), the pressure of the system was again determined. The residual pressure was a measure of the noncondensable gases. The liquid nitrogen was then drained from the upper thermostat and the temperature was allowed to increase slowly at the desired rate. At intervals of 2° to 3° K. the temperature was recorded and the corresponding pressure measured. In most of the analyses, data were not obtained above 213° K.

If the results of the first analysis do not suffice to indicate definitely the pressures at which a given component has evaporated completely from the condensed phase, the analysis is repeated using slower rates of heating with more frequent pressure readings. Duplicate analyses, under such conditions, were usually found to establish definitely the pressures

at which complete evaporation of the various components had taken place.

TABLE I. INITIAL VAPORIZATION TEMPERATURES OF VARIOUS GASES

	BOILING POINT ° K.	I. V. T. ° K.		BOILING POINT ° K.	I. V. T. ° K.
Hydrogen	20.4	Carbon dioxide	194.6 ^a	110-120
Nitrogen	77.3	Propylene	226.1	105-125
Carbon monoxide	81.1	Propane	228.6	105-120
Oxygen	90.1	Isobutane	262.9	120-133
Methane	111.7	n-Butylene	268.1	130-145
Ethylene	169.3	85-95	n-Butane	279.1	125-140
Ethane	184.8	85-100	Water	373.1	200-220
Acetylene	189.5	85-100			

^a Sublimation temperature.

SINGLE-COMPONENT SYSTEMS

In order to obtain data for proper interpretation of the pressure-temperature curves of the various mixtures, pressure-temperature curves for individual hydrocarbon gases, of the highest purity obtainable commercially, were made. Figures 3 and 4 show the curves pertaining to the saturated and unsaturated hydrocarbons, respectively. It is evident that such data do not support the assumption of Campbell (4) of the existence for each gas of a "characteristic condensation temperature." It is also clear, however, that for all the gases studied there is a range of temperature over which the rate of change of pressure with temperature is relatively rapid. The exact definition of these temperatures is of no practical significance from the standpoint of the method, since, if two components have I. V. T.'s so close as to render their identity uncertain, no separation will be obtained; i. e., the character-

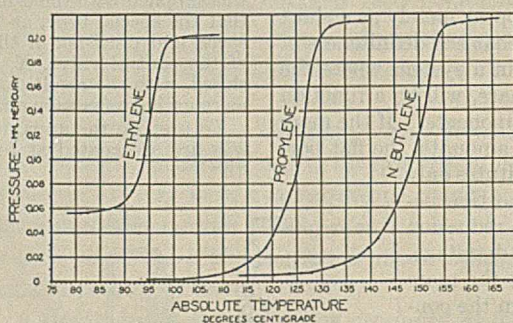


FIGURE 4. VAPOR PRESSURE-TEMPERATURE CURVES OF INDIVIDUAL UNSATURATED HYDROCARBON GASES

istic flat portion of the curve indicating complete evaporation of the more volatile component will never appear. Boiling point and I. V. T. for a number of gases are shown in Table I.

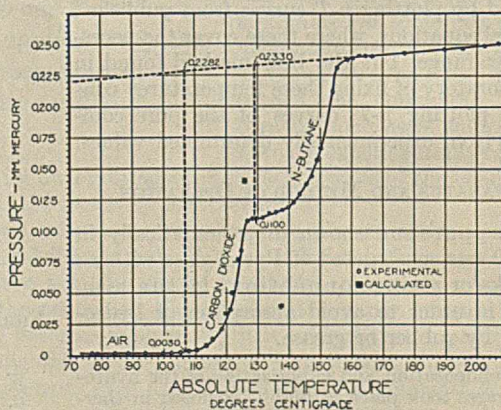


FIGURE 5. GAS MIXTURE 3

COMPONENT	ANALYTICAL RESULTS		
	AS PREPARED	As found	On air-free basis
Carbon dioxide	48.6	45.9	46.5
n-Butane	53.4	52.8	53.5
Air	..	1.3	..
Total	100.0	100.0	100.0

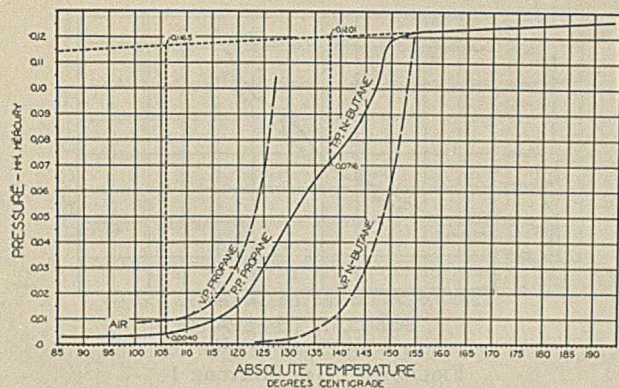


FIGURE 6. GAS MIXTURE 5

	COMP. AS PREPARED	ANALYTICAL RESULTS
	%	%
Propane	55.9	56.2
n-Butane	40.7	40.4
Air	3.4	3.4
Total	100.0	100.0

It is evident that with liquid nitrogen as a refrigerant no gas with a lower boiling point than ethylene can be condensed and analyzed by this method. All gases with lower boiling points will be found in the noncondensable fraction. In this paper all such noncondensable gases are designated as air, except where methane is known to be present.

TWO-COMPONENT SYSTEMS

HETEROGENEOUS CONDENSED PHASE. In Figure 5 is shown the analysis of a synthetic mixture of carbon dioxide (46.6 per cent) and n-butane (53.4 per cent). The total pressure in the system at room temperature was 0.2606 mm. and, after condensation, 0.0015 mm. These small pressures due to noncondensable gases appeared in practically all analyses. The curve shows a rapid change in slope starting at 108° K. and continuing for approximately 12°. The flat portion in the curve, indicating complete evaporation of the carbon dioxide from the condensed phase, appears at a pressure of 0.110 mm. This is the pressure exerted by carbon dioxide plus noncondensable gas, assumed to be air, at this temperature. The volume percentage of carbon dioxide and air in the mixture will be given by the ratio of this pressure to the total pressure of the sample if it could be completely gasified at this temperature. The value for the total pressure which would be exerted by the sample is obtained graphically by a straight-line extrapolation of the p-T curve from the temperature at which the sample has completely evaporated down to the temperature in question. Such a straight-line extrapolation is, of course, not exact; however, except at low temperatures the errors introduced by its use have been

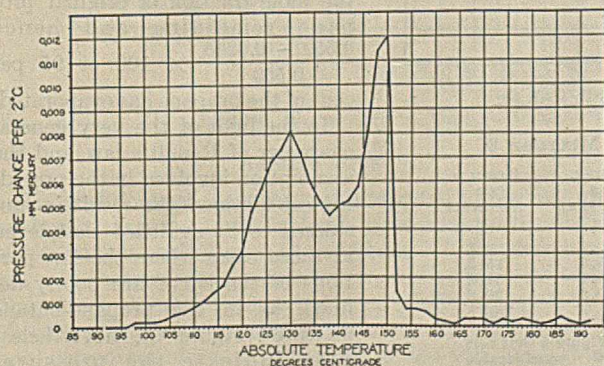


FIGURE 7. DIFFERENTIAL CURVE, GAS MIXTURE 5

shown to be negligible by a comparison of the results obtained by the use of this graphical extrapolation with those obtained when the extrapolation was made by the use of pT values for such gases as helium and nitrogen, which had been determined directly in the apparatus. The value for total p so obtained is 0.233 mm. Then $\frac{0.110}{0.233} \times 100$ or 47.2 per cent is carbon dioxide plus air. The butane must be $\frac{0.233 - 0.110}{0.233} \times 100$ or 52.8 per cent. The air is calculated in a similar way, $\frac{0.003}{0.228} \times 100$ and found to be 1.3 per cent.

The combined results are as follows: air 1.3 per cent, carbon dioxide 45.9, and butane 52.8, which are in satisfactory agreement with the composition as prepared. Calculated to an air-free basis, there is even better agreement: carbon dioxide 46.5 per cent, butane 53.5.

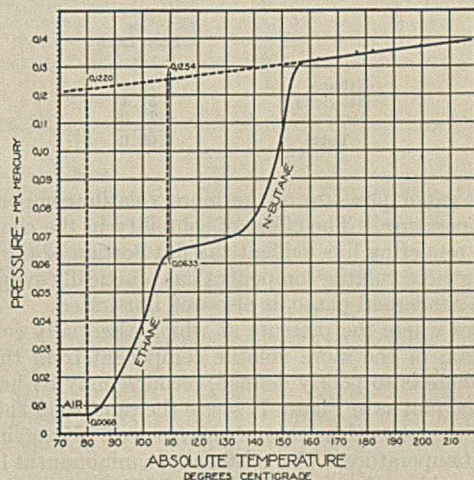


FIGURE 8. GAS MIXTURE 4

	COMP. AS PREPARED	ANALYTICAL RESULTS	
	%	As found %	On air-free basis %
Ethane	47.4	44.9	47.6
n-Butane	52.6	49.5	52.4
Air	..	5.6	..
Total	100.0	100.0	100.0

If the classification of this mixture as one in which the condensed material consists of two phases is correct, the value for total pressure at any temperature should be equal to the sum of the vapor pressures of the pure components at that temperature and, since, at those temperatures where the vapor pressure of the carbon dioxide is already considerable, that of the butane is negligible, the curve of total pressures in the system over a certain temperature range should nearly coincide with the vapor pressure of pure carbon dioxide over the same range of temperature. That this is the case is shown by the experimental and calculated values of Figure 5. The values for vapor pressure of carbon dioxide, shown as filled-in circles, were obtained (9) from the equation:

$$\log p = -\frac{0.05223 (26179)}{T} + 9.9082$$

HOMOGENEOUS CONDENSED PHASE. In Figure 6 is shown the p-T curve for a synthetic mixture consisting of 59.3 per cent propane and 40.7 per cent butane. The vapor pressure curves of the components from Figure 3 are also included. It is evident that the propane contained an appreciable amount of noncondensable gas. The effect of mutual solubility in the condensed phase is clearly shown. The total pressure in the system at any temperature is markedly lower

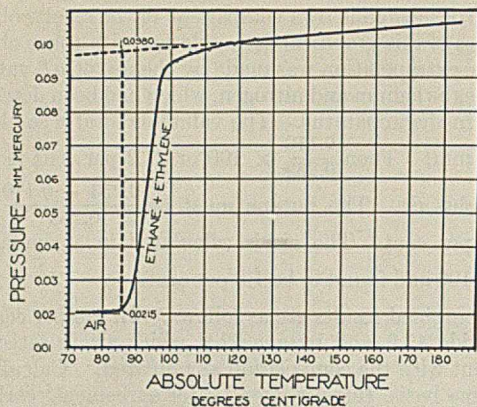


FIGURE 9. GAS MIXTURE 7

COMP. AS PREPARED	COMP. AS PREPARED
%	%
Ethane	26.7
Ethylene	51.4
Air	21.9
Total	100.0

than the vapor pressure of the more volatile component at that temperature. The effect of solubility in the condensed phase in rendering less evident the flat portion of the curve, where the more volatile component has practically evaporated from the condensed phase, is also well illustrated.

In cases where the pressure at which essentially complete evaporation of the more volatile component from the condensed phase is so poorly defined, recourse may be had to a differential plot as in Figure 7, where the same data shown in Figure 6 are plotted as rate of change per 2° K. against the absolute temperature. The existence of a minimum at 138° K. is clearly evident; hence the choice of 0.0716 mm. as the pressure marking complete evaporation of propane is confirmed. The total pressure in the system at 138° K. if both components were in the gaseous state would be 0.1201 mm. Of this, $0.0716 / 0.1201 \times 100$ or 59.6 per cent is propane plus air and 40.4 per cent butane. The agreement between butane as prepared and as found is satisfactory.

There was evidently $\frac{0.0040}{0.1165} \times 100 = 3.4$ per cent of a noncondensable impurity in the propane from which the sample was prepared. Orsat analysis proved this to be air.

In Figure 8 is shown the p - T curve for a synthetic mixture of ethane and butane. Although these two substances also form solid solutions, the flat portion is much more clearly defined because of the much greater difference between their boiling points and, consequently, their I. V. T.'s.

It has been assumed that the flat portions of the p - T curve are indications of the pressures at which the various components are eliminated from the condensed phase. By assuming Raoult's law one can calculate the mole fraction of the more volatile component present, in the condensed phase, at a given temperature. For example,

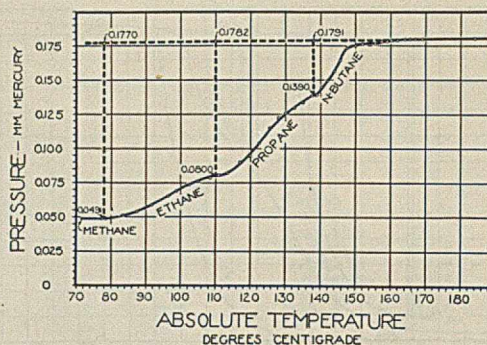


FIGURE 10. GAS MIXTURE 1

COMP. AS PREPARED	RESULTS OF ANALYSIS
%	%
Methane	28.0
Ethane	17.0
Propane	32.6
n-Butane	22.4
Total	100.0
	100.0

in Figure 6 the total pressure at 138° K. is 0.0716 mm. This is made up of the pressure of the air, 0.0056 mm., and of the partial pressures of the propane and butane, but these latter are given by the products of the vapor pressures of the pure gases at 138° K. and their respective mole fractions in the condensed phase. The vapor pressure of propane at 138° K. can be calculated (10) from the equation:

$$\log p = - \frac{0.05223 (19037)}{T} + 7.217$$

$$p = 1.03 \text{ mm. at } 138^\circ \text{ K.}$$

The vapor pressure of butane at the same temperature is found from Figure 3 to be 0.0057 mm. Hence,

$$0.0716 = 0.0056 + 1.03 M_p + 0.0057 M_b$$

where M_p , M_b = mole fractions of propane and butane, respectively

since $M_p + M_b = 1$
 $M_p = 0.058$

In the original mixture the mole fraction of propane was 0.559 and that of butane 0.407. If x equals the mole fraction of the original propane left in the condensed phase, and if we assume that none of the butane has evaporated (an approximation), then the following relation will hold:

$$\frac{x}{0.407 + x} = 0.058$$

Solving for x we find that 0.0245 is the mole fraction of original propane remaining and hence

$\frac{0.559}{0.559 - 0.0245} \times 100$ or 95 per cent of the propane has evaporated.

In the light of the very general character of Raoult's law and the assumption involved in the preceding calculations, the result is considered to be evidence that, even in those cases where the flat portions of the curve are poorly defined, as in the propane-butane mixture (Figure 6), nevertheless they indicate the pressures at which essentially complete

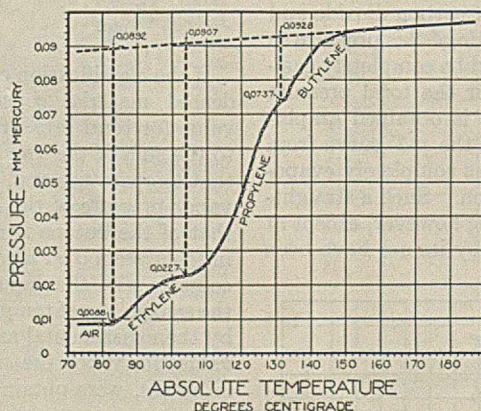


FIGURE 11. GAS MIXTURE 8

COMP. AS PREPARED	RESULTS OF ANALYSIS
%	%
Noncondensable	9.8
Ethylene*	24.5
Propylene	54.7
Butylene	20.8
Total	100.0
	100.0

* It is evident from Figure 4 that this component contained considerable amounts of noncondensable impurity, probably air.

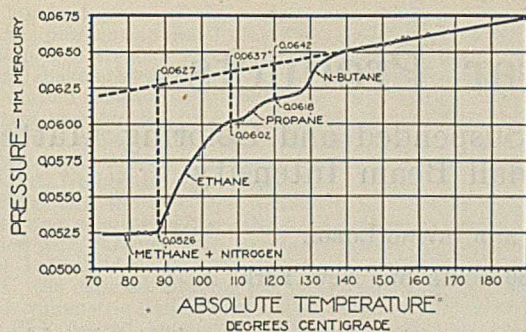


FIGURE 12. COAL DISTILLATION GAS 50

evaporation of a component from the condensed phase has taken place, and that consequently the agreement between the composition as prepared and that found by analysis is not due to compensating factors.

Where the I. V. T.'s overlap or lie close to each other, as in the case of two hydrocarbons such as ethane and ethylene, detection and determination are not possible. This is well illustrated by the curve showing the p - T relations in such a mixture (Figure 9). This interference constitutes a definite limitation of the present procedure. It is possible, however, to determine the total unsaturated hydrocarbons in an Orsat apparatus by absorption in bromine water or fuming sulfuric acid, and then to examine the residual saturated hydrocarbons by the method described. In case the composition of the unsaturated hydrocarbon portion is desired, it seems probable that it may be obtained by regeneration of the hydrocarbons from their alkyl bromides (?) followed by a separate analysis on the regenerated unsaturated gases.

SEVERAL-COMPONENT SYSTEMS

Finally, several synthetic gaseous mixtures of three or more components were prepared and analyzed. The method of calculation is essentially the same as that used for two-component systems. An example for four components is presented in Figure 10. The analysis of a mixture of unsaturated hydrocarbon gases is shown in Figure 11.

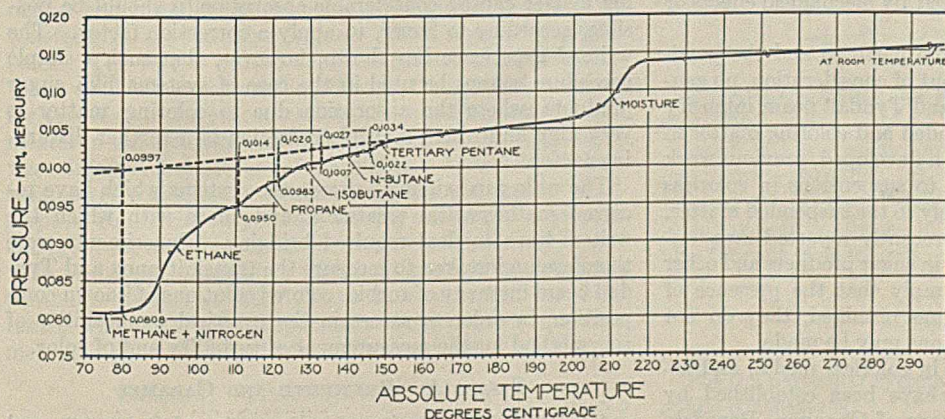


FIGURE 13. NATURAL GAS (CITY GAS OF PITTSBURGH)

APPLICATIONS

The usefulness of the method is illustrated by the following analyses: Figure 12 and Table II, gases from the distillation of bituminous coal; Figure 13 and Table III, Pittsburgh city gas. In these curves the breaks have been attributed to the compounds shown but have not been confirmed in all cases by comparison with synthetic mixtures. In every case the total percentage of hydrocarbons, saturated and unsaturated, was determined by Orsat analysis. In the first two of

these analyses the vapor pressure analysis was carried out on a residual sample from the Orsat, from which all constituents had been removed except the saturated hydrocarbons and nitrogen.

TABLE II. ANALYSIS OF GAS SAMPLE 50 OBTAINED FROM CARBONIZATION OF COAL

Av. of three detns.	%	By the conventional assumption that the satd. hydrocarbons consist of $CH_4 + C_2H_6$ only:
Carbon dioxide	1.82	Methane, %
Unsatt. hydrocarbons	0.88	Ethane, %
Oxygen	1.00	
Hydrogen	48.00	
Carbon monoxide	2.96	
Total satd. hydrocarbons	35.54	
Nitrogen	9.80	Av. weighted empirical formula of satd. hydrocarbons calcd. from the combustion data, $CH_{1.7}$
Total	100.00	

COMPOSITION OF SATURATED HYDROCARBONS

	I	II	III	Av.
	%	%	%	%
Methane	28.45	28.23	28.39	28.36
Ethane	4.36	4.81	4.75	4.64
Propane	1.68	0.80	0.87	1.12
n-Butane	1.05	1.70	1.52	1.42
Total	35.54	35.54	35.54	35.54

Av. weighted empirical formula calcd. for total satd. hydrocarbons, $CH_{1.7}$.

TABLE III. ANALYSIS OF SAMPLE OF PITTSBURGH CITY GAS

(January 24, 1933)

Av. of three detns.	%	By the conventional assumption that the satd. hydrocarbons consist of $CH_4 + C_2H_6$ only:
Carbon dioxide	Nil	Methane, %
Unsatt. hydrocarbons	0.88	Ethane, %
Oxygen	0.24	
Hydrogen	Nil	
Carbon monoxide	Nil	
Total satd. hydrocarbons	89.63	
Nitrogen	9.25	Av. weighted empirical formula of satd. hydrocarbons calcd. from combustion data, $CH_{1.7}$
Total	100.00	

COMPOSITION OF SATURATED HYDROCARBONS

	I	II	Av.
	%	%	%
Methane	71.06	70.87	70.97
Ethane	12.05	12.52	12.28
Propane	2.94	2.62	2.78
Isobutane	1.37	1.69	1.53
n-Butane	1.25	0.78	1.01
tert-Pentane	0.96	1.15	1.06
Total	89.63	89.63	89.63

Av. weighted empirical formula calcd. for total satd. hydrocarbons, $CH_{1.7}$.

LITERATURE CITED

- (1) Blacet and Leighton, *IND. ENG. CHEM., Anal. Ed.*, 3, 266 (1931).
- (2) Blacet, MacDonald, and Leighton, *Ibid.*, 5, 272 (1933).
- (3) Burrell, Seibert, and Robertson, *Bur. Mines, Tech. Paper* 104 (1915).
- (4) Campbell, *Proc. Phys. Soc. (London)*, 33, 287 (1921).
- (5) Davis and Daugherty, *IND. ENG. CHEM., Anal. Ed.*, 4, 193 (1932).
- (6) Dittrich, *Gas- u. Wasserfach*, 75, 849 (1932).
- (7) Gladstone and Tribe, *Ber.*, 7, 364 (1874).
- (8) Guye and Germann, *J. chim. phys.*, 14, 194 (1916).
- (9) International Critical Tables, Vol. III, p. 207, McGraw-Hill, 1926.
- (10) *Ibid.*, Vol. III, p. 208, 1926.
- (11) Langmuir, *J. Am. Chem. Soc.*, 34, 1310 (1912).
- (12) Podbielniak, *IND. ENG. CHEM., Anal. Ed.*, 3, 177 (1931); 5, 119 (1933).
- (13) Rosen and Robertson, *Ibid.*, 3, 284 (1931).
- (14) Ryder, *J. Am. Chem. Soc.*, 40, 1656 (1918).
- (15) Schaufelberger, *Petroleum World Oil Age*, 27, 73 (1930).
- (16) Shepherd, *Oil Gas J.*, 28, No. 6, 48 (1929).
- (17) Shepherd and Porter, *IND. ENG. CHEM.*, 15, 1143 (1923).
- (18) Southard and Andrews, *J. Franklin Inst.*, 207, 332 (1929).
- (19) Tropsch and Dittrich, *Brennstoff-Chem.*, 6, 169 (1925).
- (20) Van Dyck, *J. Inst. Petroleum Tech.*, 18, 145 (1932).

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Turbidity in Sugar Products

II. Effect of Independent Variation of Suspended and Coloring Matter on Transmittancy and Tyndall Beam Intensity

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THE first paper of this series (8) dealt with the transmittancy and Tyndall beam intensity of a raw sugar solution at varying depth of layer, and at varying concentration obtained by dilution with a clear, colorless sugar sirup. The proportion between suspended matter and molecularly dispersed coloring matter remained always the same. Under these circumstances the ratio between the Tyndall beam intensity and the transmittancy is, within a limited range, a power function of the depth or of the concentration of total light-absorbing material.

The various products of the sugar house present a much more complicated problem, because here coloring matter and suspended matter vary independently of each other. Furthermore, the size and shape of the suspended particles and their light-absorbing and reflecting properties may vary not only from one product to another, but also for one and the same product through coagulation or peptization produced by mechanical effects or by the mere time factor.

Even if the characteristics of the particles and the possibilities of change in them be left out of consideration, no general theory of the transmittancy and Tyndall beam intensity of systems containing both suspended and coloring matter in varying proportions has as yet been developed, previous work having been confined principally to suspensions in colorless media where absorption is due solely to the suspended matter. Cummins and Badollet (2) have recently reported measurements of Tyndall beam intensities in sugar products and other colored media; but while they imply that the presence of coloring matter affects the readings obtained, they do not specify how the necessary corrections may be made.

Formulas covering suspensions in colorless media, and assuming perfectly diffused light, have been established by Wells (7) on the basis of the theory of Channon, Renwick, and Storr. Wells shows that in such systems the optical density ($-\log T$) is not directly proportional to the depth or the concentration (Lambert-Beer law), but increases more slowly than either, because part of the incident light is lost by reflection or scattering. The rigorous equations are rather involved, but for limited ranges, and well within the limits of experimental error, the optical density increases linearly with a power function of the depth, the exponent being less than unity. The Tyndall beam intensity is an even more complex function of the depth or concentration of suspensions in colorless media. Wells gives a complete formula for that relation-

Equations have been derived and graphs constructed for two systems containing both coloring matter and turbidity, by means of which their concentration can be derived from measurements of transmittancy and Tyndall beam intensity.

In the two fairly closely related systems—Filler-Cel plus caramel solution, and unfiltered plus filtered sugar sirups—the relationships between color and turbidity concentration on the one hand and transmittancy and Tyndall beam intensity on the other have been found not to be identical. Consequently, a simplified mathematical treatment of the problem of determining turbidity and color in the presence of each other must be confined to the particular system which is being studied, and specific relationships which hold for one case cannot be applied indiscriminately to any other system. Photometric determinations are undoubtedly to be preferred to mere comparisons with empirical standards.

ship, but it contains eight constants and is too cumbersome to use in practice. Within limited ranges the simpler power formula, which applies to the optical density, affords in this case also close approximations to the experimental data.

Sauer (5) has derived certain formulas which are applicable to suspensions in colorless media, particularly for the Pulfrich photometer. According to him, if the absorption is so small as to be negligible, the Tyndall intensity is directly proportional to the thickness. If the absorption is considerable, it may be corrected for by applying a factor based on the optical density. Sauer states that the absorption due to coloring matter in true solution is usually slight in comparison to that caused by the suspended particles, and that if the cell thickness is properly chosen so that the absorption becomes negligible, the observed Tyndall beam intensity will vary directly with the total number of suspended particles. Even if the coloring matter caused considerable absorption, it should be possible, according to Sauer, to apply a correction factor. The writers' experience has shown, however, that such a simple procedure cannot be used in the case of systems like sugar products, where the absorption due to coloring matter is very high and where multiple reflection is a further disturbing factor.

The wide gap existing between the systems which have received mathematical treatment and those with which the writers have to deal required bridging. Experiments were therefore undertaken to measure the transmittancy and Tyndall beam intensity of turbid, colored solutions of known composition, in order to ascertain the practical applicability of this method for the measurement of turbidity and of color.

SERIES A. BENTONITE AND CARAMEL

In similar investigations Lindfors (4) and Balch (1) used bentonite to produce turbidity, and caramel as the coloring matter. The writers adopted these same materials in the first series of their experiments. Systems of this nature present great difficulties in technic, because of their instability. After considerable preliminary work a sufficiently stable turbid medium was prepared by suspending bentonite in a solution of gum acacia, which acted as a protective colloid.

The coloring matter was prepared according to Ehrlich's method (3) from Domino tablet sugar, by heating the powdered substance *in vacuo* in an oil bath at 200° C. and holding it at that temperature for one hour after all frothing had ceased.

One hundred grams of the caramel thus obtained were ground to a fine powder and dissolved in 200 cc. of distilled water. The solution was treated with 5 grams of x-ray grade of barium sulfate, shaken thoroughly with it, and filtered by suction through acid-washed asbestos on a Jena fritted glass funnel. The filtration was repeated ten times through the same pad, and the final filtrate was collected in a clean, dry filter flask. This caramel solution was found, on subsequent test, to be as free of suspended matter as freshly distilled water.

To prepare the mixtures containing specified quantities of turbid and coloring matter, the stock bottles of bentonite suspension and caramel were vigorously shaken and placed in a water bath held at 20° C. When the contents had reached 20° C. the caramel solution was placed dropwise in a series of 25-ml. volumetric flasks, from a 5-cc. microburet with a ground tip. The desired amount of bentonite suspension was then added from a graduated pipet, the stock bottle being well shaken before each removal. The mixture of bentonite suspension and caramel solution was diluted with distilled water nearly to the mark, and the volume finally adjusted at 20° C.

The photometer readings were taken after less than 2 hours. The flasks were slowly rotated for mixing. Even this gentle treatment seriously affects the Tyndall intensity readings, and for this reason the transmittancies were determined first, as these are only slightly affected. Thorough mixing is essential for the Tyndall measurements, but the suspensions must not be agitated vigorously. The cells were rinsed four times with the solution in order to insure complete removal of previously contained material. The cover of the cell was put in place, and the cell carefully washed with distilled water, dried, and polished. Special care must be taken to insure optically perfect cell walls.

Standardization of technic was found to be of paramount importance. Equal timing of similar operations, uniform rate of mixing, and the most scrupulous maintenance of comparable experimental conditions are mandatory if any significance is to be attached to any of the observed readings.

Thirty-five different mixtures of suspended and coloring matter were prepared, the bentonite concentration being varied in five steps and the caramel concentration for each of these suspensions in seven steps. The transmittancy and Tyndall beam intensity of all the mixtures were determined with the Pulfrich photometer (δ) in a 5.09-mm. cell, under the green and red filters—that is, at effective wave lengths of 529 and 621 $m\mu$, respectively.

On the basis of these measurements the mathematical relationships between the transmittancy and the Tyndall beam intensity on the one hand, and the concentration of coloring matter and turbidity on the other, were formulated, and the constants in the formulas evaluated for a number of typical cases. The results proved that the particular kind of bentonite used had an adsorptive effect on the caramel, and that for this reason the concentrations of suspended and coloring matter in the mixtures on which the observations were made, were different from those before mixing. Although the findings are of considerable interest from the standpoint of adsorption equilibria, they do not furnish a solution of the present problem, and the results are therefore omitted here.

It is evident that when Lindfors' method of preparing bentonite-caramel standards is used, it must first be ascertained whether or not the particular bentonite adsorbs caramel; if it does, the standards will be valueless.

SERIES B. FILTER-CEL AND Caramel

Experiments were next undertaken with Filter-Cel purified by acid washing and fractional sedimentation. The Filter-Cel suspension and caramel solution were prepared in the same manner as the corresponding materials in Series A. The transmittancies and Tyndall beam intensities of these mixtures were measured as described above, with the results shown in Tables I and II.

The relations between the transmittancy and Tyndall beam intensity on the one hand, and the concentration of turbidity and coloring matter on the other were now analyzed separately. The following symbols are used in this discussion:

N = cc. of bentonite suspension (concentration of turbidity)
 C = drops of caramel solution (concentration of coloring matter)
 T = per cent transmittancy
 D = optical density ($-\log T$)
 R = Tyndall beam intensity, in per cent of standard block¹

TABLE I. TRANSMITTANCIES OF FILTER-CEL-CARAMEL MIXTURES

DROPS OF CARAMEL	FILTER-CEL SUSPENSION						
	0 cc.	4 cc.	8 cc.	12 cc.	16 cc.	20 cc.	24 cc.
	RED FILTER, 5.09-MM. CELL						
0	100.00	98.42	82.18	80.58	76.39	72.70	65.14
4	99.02	88.28	81.78	76.80	68.18	65.72	63.36
8	90.90	84.62	77.96	71.96	67.14	64.58	59.75
12	89.58	79.20	75.02	67.39	63.99	61.07	57.95
16	81.82	74.56	70.64	64.26	60.91	57.11	54.79
20	76.68	73.28	66.76	58.73	58.06	54.18	50.75
	GREEN FILTER, 5.09-MM. CELL						
0	100.00	91.80	78.21	75.04	69.95	65.58	58.60
4	87.62	77.42	68.31	62.87	55.62	52.91	51.10
8	72.68	65.96	58.95	53.24	49.82	46.52	43.28
12	63.28	54.88	49.47	45.73	42.49	39.37	36.90
16	52.17	44.51	42.78	39.29	35.57	33.19	31.38
20	42.92	40.58	36.16	30.86	29.92	28.75	25.54

TABLE II. TYNDALL INTENSITIES OF FILTER-CEL-CARAMEL MIXTURES

DROPS OF CARAMEL	FILTER-CEL SUSPENSION						
	0 cc.	4 cc.	8 cc.	12 cc.	16 cc.	20 cc.	24 cc.
	RED FILTER, 5.09-MM. CELL						
0	50	1462	3254	4190	4979	5338	7118
4	114	1357	3098	4140	5267	6022	6379
8	103	1256	2842	3862	4807	5692	5972
12	136	1295	2427	3693	4639	5492	5933
16	200	1217	2341	3190	4489	4538	5476
20	122	959	2185	3069	4354	3923	5568
	GREEN FILTER, 5.09-MM. CELL						
0	18	465	1123	1513	1792	1947	2302
4	36	413	962	1284	1562	1701	1877
8	26	305	751	1030	1262	1437	1478
12	32	264	502	842	1131	1182	1284
16	36	188	438	530	913	950	1060
20	24	155	361	448	779	517	1065

TRANSMITTANCY. An examination of the transmittancy figures showed that when turbidity is constant and coloring matter varies, the optical density is directly proportional to the color concentration—i. e., that Beer's law holds for the coloring matter, irrespective of the turbidity present simultaneously. Expressed in a formula,

$$-\log T = cC, \text{ or } C = \frac{-\log T}{c} \quad (1)$$

Under the red filter $c = 0.00590$, and under the green filter 0.018075.

Balch had previously found that Beer's law does not apply for varying turbidity at constant color, and the writers pointed out (δ) that Balch's results satisfy a power formula. This has been confirmed in the present series of experiments. The formula is as follows:

$$N = kD^n, \text{ or } D = \left(\frac{N}{k}\right)^{\frac{1}{n}} \quad (2)$$

For the particular system investigated the numerical value of the constants is:

n	RED FILTER	GREEN FILTER
$\log k$	1.188	1.232
	2.24645	2.17266

¹ The absolute Tyndall beam intensity of standard block 323, used by the writers, is reported by Zeiss to equal 0.00282 of the intensity of the incident light, for the green screen, under the experimental conditions of the Pulfrich photometer. Corresponding figures for the blue and red screens have not been furnished. To calculate the absolute Tyndall beam intensity of a solution, 0.01 R is multiplied by the absolute intensity of the standard block for the same screen, and the product multiplied by a factor which varies with the vessel used as the container for the solution. For a 2.5-mm. plane parallel cell this factor is 6.5.

The absorptions due to the coloring matter and to the turbidity are additive, and the combined formula may therefore be written

$$-\log T = cC + \left(\frac{N}{k}\right)^n \quad (3)$$

When the values for C , N , c , k , and n are substituted in this formula, the transmittancies given in Table III are obtained.

TABLE III. CALCULATED VALUES OF T FOR STATED VALUES OF C AND N

VALUES OF C	VALUES OF N						
	0	4	8	12	16	20	24
	RED FILTER						
0	100.0	90.9	84.3	78.7	73.7	69.2	65.1
4	94.7	86.1	79.9	74.5	69.8	65.5	61.6
8	89.7	81.6	75.6	70.6	66.1	62.1	58.4
12	85.0	77.2	71.6	66.8	62.6	58.8	55.3
16	80.5	73.2	67.9	63.3	59.3	55.7	52.4
20	76.2	69.3	64.3	60.0	56.1	52.7	49.6
	GREEN FILTER						
0	100.0	88.5	80.7	74.2	68.6	63.7	59.2
4	84.7	74.9	68.3	62.8	58.1	53.9	50.2
8	71.7	63.4	57.8	53.2	49.2	45.6	42.5
12	60.7	53.7	49.0	45.0	41.6	38.6	36.0
16	51.4	45.5	41.5	38.1	35.3	32.7	30.4
20	43.5	38.5	35.1	32.3	29.8	27.7	25.8

Considering the experimental difficulties and possibilities of shifts in the colloid equilibrium during observations, the agreement between found and calculated values is good for the green filter. For the red filter the figures do not check so well, owing to the disturbing differences in tint in the two halves of the field.

The results show that no adsorption of caramel by the Filter-Cel took place, because in every case the ratio between the transmittancy of the turbid colored solution and that of the corresponding colored solution free from turbidity was the same as the ratio between the transmittancy of the turbid colorless solution and that of water. This is the rule which Balch (1) had previously found to hold when there is no adsorption.

TYNDALL BEAM INTENSITY. An examination of Table II shows that the Tyndall beam intensity increases with the turbidity at each color concentration.

With the turbidity constant and color varying, irregular figures are obtained at turbidity 0, due to small and unavoidable admixture of turbidity. At turbidities above 4, increasing color generally causes a decrease in the Tyndall intensity. As in the bentonite-caramel series, where the intensity first increased and then decreased, a few of the figures in Table II, between colors 0 and 4 under the red filter, show a tendency to rise, but above color 4 the maximum of the curve has evidently been passed.

Between the limits of turbidity from 4 up to 24 and of color from 4 up to 20, the Tyndall beam intensity is, at constant color concentration, an approximately linear function of the log of the turbidity concentration, according to the formula

$$R = a \log N - k \quad (4)$$

The values of the constants a and k were found to be

COLOR	GREEN FILTER		RED FILTER	
	a	k	a	k
4	1880	725	6189	2291
8	1488	573	5649	2101
12	1178	453	5156	1926
16	932	358	4706	1766
20	738	283	4295	1619

Both a and k are functions of the color concentration C :

$$\begin{aligned} a &= b d^{-c} \\ k &= c f^{-c}, \text{ or} \\ \log a &= \log b - (\log d) C \\ \log k &= \log e - (\log f) C \end{aligned}$$

The equation for R , as a function of C and N , may thus be written

$$R = b d^{-c} \log N - e f^{-c} \quad (5)$$

The numerical values for $\log b$, $\log d$, $\log e$, and $\log f$ in this particular system are

	GREEN FILTER	RED FILTER
$\log b$	3.37569	3.83130
$\log d$	0.025382	0.009915
$\log e$	2.96248	3.39673
$\log f$	0.025535	0.009175

The values of a and k cannot be extrapolated to zero color. With no coloring matter present, the values of $\log a$ and $\log k$ are

	GREEN FILTER	RED FILTER
$\log a$	3.33786	3.79302
$\log k$	2.92840	3.37566

If the values of a and k shown above are substituted in formula 4, the figures given in Table IV are obtained.

TABLE IV. CALCULATED VALUES OF R , FOR STATED VALUES OF C AND N

VALUES OF C	VALUES OF N					
	4	8	12	16	20	24
	GREEN FILTER					
0	463	1118	1501	1773	1980	2157
4	407	973	1314	1539	1721	1870
8	323	771	1033	1219	1363	1481
12	256	611	818	965	1079	1173
16	203	484	648	765	853	929
20	161	383	513	606	677	736
	RED FILTER					
0	1363	3232	4326	5101	5703	6195
4	1435	3298	4388	5161	5761	6251
8	1300	3001	3995	4701	5248	5696
12	1178	2730	3638	4280	4782	5190
16	1067	2484	3313	3900	4356	4729
20	967	2260	3016	3553	3969	4309

Under the green filter, the agreement between calculated and found values is satisfactory, except where the experimental values are obviously out of line as shown by a direct comparison of found values with those adjacent in different directions. Under the red filter, the agreement is not nearly as good as under the green, for the same reason as given in the discussion of the transmittancy figures. In both spectral regions the agreement is less good at high turbidity and high color. Here multiple reflection appears to become more pronounced, and this is probably one reason for the observed deviations.

By means of formulas 3 and 5 above, C and N in unknown mixtures of the caramel and Filter-Cel used in this series may be calculated after T and R have been determined, but the result may be ascertained more quickly and easily by means of a graph.

SERIES C. MIXTURES OF SUGAR SIRUPS

The next step in this investigation was to ascertain whether the relationships found for the Filter-Cel and caramel mixtures would also hold in the case of actual sugar products.

This problem was attacked by selecting a very dark raw sugar containing a large quantity of suspended matter, dissolving it to a sirup of 60° Brix, and removing coarse suspended matter by vacuum filtration through 250-mesh bronze gauze. Part of this sirup was carefully filtered through purified Filter-Cel and asbestos to free it as far as possible of suspended matter. A white sugar sirup was prepared from Domino sugar tablets, decolorized with Suchar, and filtered like the raw sugar sirup. All three sirups were finally adjusted again to 60° Brix by refractometer. Solutions containing varying proportions of coloring matter and turbidity were then made by weighing and mixing the three sirups in proportions of 0 to 5 parts of each.

If one part of unfiltered raw sugar sirup represents one unit of coloring matter (C) and one unit of turbidity (N), then

one part of filtered raw sugar sirup equals one unit of coloring matter plus a small amount of residual turbidity not removed by filtration, and one part of filtered white sirup represents zero color plus a small amount of residual turbidity.

The transmittancy and Tyndall beam intensity of all the mixtures were determined under three color screens, blue (449 m μ), green (529 m μ), and red (621 m μ), in a 2.5-mm. cell. The results of these measurements are shown in Table V, where U indicates one part of unfiltered raw sugar sirup, F one part of filtered raw sugar sirup, and W one part of filtered white sirup.

TABLE V. TRANSMITTANCIES AND TYNDALL BEAM INTENSITIES OF SIRUP MIXTURES

MIXTURES	TRANSMITTANCY			TYNDALL BEAM INTENSITY		
	Blue	Green	Red	Blue	Green	Red
5 C units						
5 U , 0 F , 0 W	2.15	11.40	29.25	59.34	913.3	5914
4 U , 1 F , 0 W	3.27	13.97	33.53	52.38	799.1	5117
3 U , 2 F , 0 W	4.23	17.17	40.50	35.95	492.9	3765
2 U , 3 F , 0 W	5.97	22.17	46.35	29.15	367.8	2376
1 U , 4 F , 0 W	7.87	26.87	54.25	19.04	194.5	1345
0 U , 5 F , 0 W	10.37	35.22	66.27	5.67	51.24	260.4
4 C units						
4 U , 0 F , 1 W	4.77	17.10	36.70	75.12	898.5	4925
3 U , 1 F , 1 W	5.93	21.40	42.92	59.12	600.8	3961
2 U , 2 F , 1 W	8.18	26.37	50.73	44.72	441.2	2816
1 U , 3 F , 1 W	11.93	33.08	60.47	30.03	274.4	1444
0 U , 4 F , 1 W	16.00	43.30	72.37	7.32	60.51	210.3
3 C units						
3 U , 0 F , 2 W	9.80	26.42	47.30	106.7	917.1	4187
2 U , 1 F , 2 W	13.33	33.92	55.30	81.2	592.9	3259
1 U , 2 F , 2 W	17.70	42.07	65.28	51.4	330.9	1708
0 U , 3 F , 2 W	24.45	53.17	77.85	12.9	90.3	333.8
2 C units						
2 U , 0 F , 3 W	21.07	42.33	60.62	128.9	863.8	3340
1 U , 1 F , 3 W	27.43	49.03	71.93	74.13	396.8	1641
0 U , 2 F , 3 W	40.23	64.87	83.05	10.91	55.08	208.5
1 C unit						
1 U , 0 F , 4 W	44.90	64.35	78.45	124.4	480.6	1737
0 U , 1 F , 4 W	62.03	80.50	90.62	14.03	54.15	160.7
0 C unit						
0 U , 0 F , 5 W	100.00	100.00	100.00	6.83	21.55	74.61

A preliminary examination of the transmittancy figures in Table V showed that at constant F each unit of U - W increases $-\log T$ by a constant amount, within the limits of error, and that the same is true for each unit of F - W at constant U . In other words, Beer's law appears to hold for both color and turbidity. The $-\log T$ increment for U - W is due to 1 C plus 1 N minus the residual turbidity in the filtered white sirup, while that for F - W represents 1 C plus the residual turbidity in the filtered raw sugar sirup minus the residual turbidity in the filtered white sirup.

In order to find the transmittancies for 1 C and 1 N , it is necessary to apply corrections for the residual turbidity in both filtered sirups. These corrections cannot be found from the transmittancy figures, because in the filtered raw sugar sirup the absorption effect of suspended and of coloring matter cannot be separately determined by this means, and because the white sugar sirup showed zero turbidity by the transmittancy method although the Tyndall beam method revealed measurable turbidity. Therefore the necessary corrections had to be derived from the Tyndall beam intensities.

TYNDALL BEAM INTENSITY. A glance at Table V shows that at constant color concentration there is an approximately linear relationship between parts of turbid sirup ($U = N$) and the Tyndall beam intensity under the green and red screens, but this relationship is obscured by the effect of the residual turbidity in the other two sirups, and more so under the blue screen.

In order to test this hypothesis of linear relationship between R and N , the values of R corresponding to one unit each of U , F , and W were calculated by the method of least squares from the experimental data given in Table V. In the series with 5 color units there are 6 equations, with two unknowns; in the series with 4, 3, and 2 color units there are 5, 4, and 3 equations, respectively, with three unknowns, but since the quantity of filtered white sirup was constant at each individual color con-

centration, a value for W , known to be small, had to be assumed as a first approximation. Two sets of equations were therefore set up, in one of which the turbidity in W was assumed to be zero, and in the other equivalent to one-third of that in F . The results of these two sets of equations showed that within these limits the value for W had little effect on the values of R corresponding to U and of F , which came out very nearly the same.

From these data formula 6 was derived, and this made it possible to calculate the values of R corresponding to 1 W at color concentrations 1, 2, 3, and 4, from that found experimentally at zero color concentration. With R for 1 W known, the R values of U and F at each color concentration could now be readjusted, and the final results of the calculations are shown in Table VI.

TABLE VI. VALUES OF R , FOR ONE UNIT OF U , F , AND W

	BLUE	GREEN	RED
5 C units			
U	11.94	183.2	1211
F	1.75	4.7	40.6
W	0	0	0
4 C units			
U	19.05	213.9	1265
F	2.60	13.64	70.4
W	0.14	1.68	10.7
3 C units			
U	36.57	298.0	1446
F	5.45	23.8	135
W	0.25	2.13	11.64
2 C units			
U	65.1	421.4	1672
F	6.15	17.0	81.7
W	0.43	2.69	12.64
1 C unit			
U	121.3	467.0	1682
F	10.95	40.5	105.7
W	0.77	3.41	13.74
0 C unit			
W	1.37	4.31	14.92

Simple addition of the R values for U , F , and W shown in Table VI results in the R figures given in Table VII, representing the adjusted values of the Tyndall beam intensities for the sirup mixtures. The corresponding values of N are also presented, calculated by dividing the R values for the mixtures by the corresponding R values for 1 U (equivalent to 1 N), as given in Table VI.

TABLE VII. ADJUSTED TYNDALL BEAM INTENSITY AND TURBIDITY CONCENTRATION VALUES OF MIXTURES LISTED IN TABLE V

MIXTURES	TYNDALL BEAM INTENSITY (R)			TURBIDITY CONCENTRATION (N)		
	Blue	Green	Red	Blue	Green	Red
5 C units						
5 U + 0 F + 0 W	59.7	916	6055	5.000	5.000	5.000
4 U + 1 F + 0 W	49.5	738	4885	4.147	4.026	4.034
3 U + 2 F + 0 W	39.3	559	3714	3.293	3.051	3.067
2 U + 3 F + 0 W	29.2	381	2544	2.440	2.077	2.101
1 U + 4 F + 0 W	18.9	202	1374	1.586	1.103	1.134
0 U + 5 F + 0 W	8.8	23.5	203	0.733	0.128	0.168
4 C units						
4 U + 0 F + 1 W	76.3	857	5071	4.007	4.008	4.009
3 U + 1 F + 1 W	59.9	657	3876	3.144	3.071	3.065
2 U + 2 F + 1 W	43.4	457	2692	2.280	2.133	2.120
1 U + 3 F + 1 W	27.0	257	1487	1.417	1.196	1.176
0 U + 4 F + 1 W	10.5	69.9	293	0.553	0.258	0.232
3 C units						
3 U + 0 F + 2 W	110.2	898	4350	3.013	3.013	3.016
2 U + 1 F + 2 W	79.1	624	3039	2.163	2.094	2.109
1 U + 2 F + 2 W	48.0	350	1728	1.312	1.174	1.203
0 U + 3 F + 2 W	16.9	75.7	417	0.461	0.254	0.296
2 C units						
2 U + 0 F + 3 W	131.5	851	3382	2.020	2.019	2.023
1 U + 1 F + 3 W	72.6	447	1692	1.114	1.060	1.072
0 U + 2 F + 3 W	13.6	42.1	201	0.209	0.100	0.120
1 C unit						
1 U + 0 F + 4 W	124.4	481	1737	1.026	1.029	1.033
0 U + 1 F + 4 W	14.1	54.1	161	0.128	0.116	0.096
0 C unit						
0 U + 0 F + 5 W	6.85	21.6	74.6	0.033	0.036	0.040

A comparison of the R values given in Table VII with those found experimentally (Table V) shows that the assumed linear relationship between N and R , at constant color concentration, actually holds. The deviations are partly due to experimental error, because it is very difficult to prepare

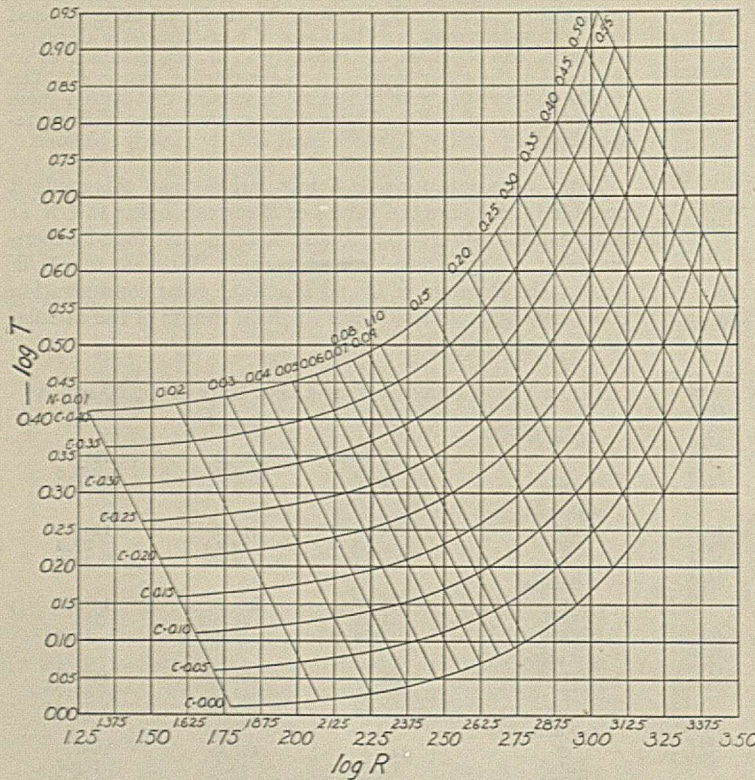


FIGURE 1. NEGATIVE LOG OF TRANSMITTANCY AND LOG OF TYNDALL BEAM INTENSITY, CORRESPONDING TO VARYING CONCENTRATIONS OF COLORING MATTER AND TURBIDITY EXPRESSED AS NEGATIVE LOGS OF TRANSMITTANCY

homogeneous mixtures of these heavy sirups. Another reason is that the suspended particles remaining after filtration are probably different in size from those filtered out. The error due to this cause is smaller the more efficient the filtration.

The relationship between R and N may be written

$$R = bN$$

where b is a constant.

The effect of the coloring matter on the Tyndall beam intensity may also be ascertained from Table VI. At constant turbidity the Tyndall beam intensity increases as the color decreases. When the logs of R for $U = 1, N = 1$ are plotted against C , a straight line is obtained. This relationship is expressed by

$$b = ak^{-c}$$

where k is a constant.

Combination of the two formulas above gives

$$R = aNk^{-c} \tag{6}$$

This formula is similar to the one found previously for the Filter-Cel-caramel series, but it is simpler because within the range investigated R is proportional to N itself, not to $\log N$. The values of the logs of the constants a and k in the above formula are

	BLUE	GREEN	RED
$\log a$	2.32117	2.79288	3.27835
$\log k$	0.25256	0.10687	0.03982

Upon substituting these constants and the known values of C and N in formula 6, the data presented in Table VIII are obtained. These show good agreement with the experimental values of Table VII in most cases.

TRANSMITTANCY. The corrections for the residual turbidity in the two filtered sirups, shown in Tables VI and VII, were now applied to the transmittancies also, and it was found that Beer's law holds for the range studied experimentally and well within the limits of error for both color and turbidity. The relationship may be expressed by the formula

$$-\log T = mN + nC \tag{7}$$

The values of the constants m and n are

	BLUE	GREEN	RED
m	0.15510	0.10408	0.07461
n	0.17718	0.08669	0.03416

Upon substituting these values and those for C and N in formula 7, the transmittancies shown in Table VIII are obtained. These agree satisfactorily with experimental values shown in Table V.

Since Beer's law holds for the transmittancies in respect to both C and N , these may be expressed directly in terms of $-\log T$, as previously proposed by Balch:

$$-\log T = C + N \tag{8}$$

In this case the constants in formula 6 assume the following values:

	BLUE	GREEN	RED
$\log a$	3.13056	3.77551	4.40555
$\log k$	1.42545	1.23280	1.16568

C and N may then be calculated from formulas 6 and 8:

$$\log R = \log a + \log N - (-\log T - N) \log k$$

whence
$$N + \frac{\log N}{\log k} = \frac{\log R}{\log k} - \frac{\log a}{\log k} + (-\log T)$$

The values of N corresponding to those of $N + \log N/\log k$ must be found from specially prepared tables or graphs, and C is then found from formula 8. Or the entire solution may be found from a graph, as shown in Figure 1.

TABLE VIII. CALCULATED TYNDALL BEAM INTENSITIES AND TRANSMITTANCIES OF MIXTURES LISTED IN TABLE VII

MIXTURES	TYNDALL BEAM INTENSITIES			TRANSMITTANCY		
	Blue	Green	Red	Blue	Green	Red
5 U, 0 P, 0 W	57.19	906.8	6001	2.18	11.12	28.59
4 U, 1 P, 0 W	47.44	730.1	4842	2.96	14.04	33.75
3 U, 2 P, 0 W	37.67	553.3	3681	4.01	17.74	39.85
2 U, 3 P, 0 W	27.91	376.7	2522	5.44	22.41	47.04
1 U, 4 P, 0 W	18.14	200.0	1361	7.38	28.30	55.54
0 U, 5 P, 0 W	8.38	23.21	201.6	10.01	35.75	65.56
4 C units						
4 U, 0 P, 1 W	81.99	929.7	5274	4.68	17.22	36.66
3 U, 1 P, 1 W	64.33	712.3	4020	6.36	21.56	43.19
2 U, 2 P, 1 W	46.65	495.4	2787	8.66	26.97	50.73
1 U, 3 P, 1 W	28.99	278.1	1546	11.89	33.76	59.66
0 U, 4 P, 1 W	11.32	59.84	305.2	16.05	42.31	70.15
3 C units						
3 U, 0 P, 2 W	110.3	893.9	4348	10.03	26.69	47.04
2 U, 1 P, 2 W	79.17	621.2	3041	13.58	33.27	54.99
1 U, 2 P, 2 W	48.02	348.3	1734	18.41	41.47	64.23
0 U, 3 P, 2 W	16.87	75.4	427	24.94	51.70	75.06
2 C units						
2 U, 0 P, 3 W	132.3	766.1	3197	21.50	41.35	60.36
1 U, 1 P, 3 W	72.94	402.2	1694	29.71	52.03	71.08
0 U, 2 P, 3 W	13.68	37.94	190	41.04	65.50	83.71
1 C unit						
1 U, 0 P, 4 W	117.4	499.4	1789	46.10	64.00	77.40
0 U, 1 P, 4 W	14.99	56.29	166.3	63.53	79.66	90.92
0 C unit						
0 U, 0 P, 5 W	6.91	22.34	75.93	98.83	99.14	99.32

The $-\log T$'s may finally be converted into $-\log t$'s by reducing them to the basis of 1 gram of dry substance in 1 cc. of solution and 1 cm. thickness.

Further research will have to show whether or not the relationships found for the particular raw sugar used in this investigation are applicable to color and turbidity determinations in other raw sugars. It is already known that the nature of the coloring matter varies from case to case, and this may be expected to be true for the turbidity also, especially as to particle size. Teorell (6) has found that the particle size of suspensions in colorless media may be determined by measuring either transmittancy or Tyndall beam intensity at several wave lengths, and it is possible that this observation may help to solve the present problem. Complete measurements with three color screens on about sixty different raw sugars have already been made, and turbidity has been determined in the same sugars by Balch's method. The data are being correlated in two different ways: First, the color and turbidity of each sugar are calculated by formu-

las 6 and 8, and correlation is attempted on the basis of Teorell's observations. The second method consists in a statistical analysis of the data, with the results by Balch's method as the criteria.

LITERATURE CITED

- (1) Balch, *IND. ENG. CHEM., Anal. Ed.*, **3**, 124 (1931).
- (2) Cummins and Badollet, *Ibid.*, **5**, 328 (1933).
- (3) Ehrlich, F., *Z. Ver. deut. Zuckerind.*, **59**, 746 (1909).
- (4) Lindfors, *IND. ENG. CHEM.*, **17**, 1155 (1925).
- (5) Sauer, private communication.
- (6) Teorell, *Kolloid-Z.*, **53**, 322 (1930); **54**, 58, 159 (1931).
- (7) Wells, *Chem. Rev.*, **3**, 331 (1927).
- (8) Zerban and Sattler, *IND. ENG. CHEM., Anal. Ed.*, **3**, 326 (1931).

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Determination of Viscosity of Dilute Solutions of Cassava Flour and Other Starches

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FROM the standpoint of laboratory testing the viscosity of starch is probably its most important variable characteristic. Certainly this is true among starches of the same kind. When starch solutions having the same concentration show the same viscosity, they will also with few exceptions have the same adhesive or sizing value. Furthermore, among starches of the same kind, uniformity with respect to viscosity frequently means uniformity with respect to other seemingly unrelated characteristics. Color, clarity, cleanness, resistance to fermentation, and fiber content can be suitably determined in the laboratory, but in general these characteristics have substantially less significance than viscosity. Broadly speaking, viscosity is the property which most largely distinguishes the various grades in any one kind of colloidal material. The direct determination of strength or sizing value on a laboratory scale is so complicated and difficult as frequently to give highly erroneous indications, even in the hands of experts.

Terms commonly used in the trade to describe the consistency of gelatinized starch solutions are viscosity, body, fluidity, plasticity, paste strength, and jelly strength. Viscosity, as it is commonly understood, has a meaning sufficiently correct and descriptive for all practical purposes when hot dilute solutions are referred to, and will be generally used in this article.

The testing of starch for viscosity has been considered a rather hopeless proposition. Although a number of enlightening articles (1, 2, 5, 6) have recently appeared, there is still much misunderstanding and lack of agreement on the subject. Each laboratory has had an individual and usually somewhat original method for testing, by which the results were reported in some arbitrary unit. This difficulty, however, has been well recognized and has caused little confusion. The real difficulties hindering the proper appreciation and common understanding of viscosity determinations have been far more obscure. Experienced laboratories have rarely been

After describing certain viscosity characteristics of some of the commonly known and widely used brands of cassava flour and other starches, various methods of testing are discussed and a new method and apparatus for preparing and testing dilute hot solutions are offered as standard for a large portion of the trade.

able to agree on the relative viscosities shown by a number of samples unless the differences were pronounced.

Substantial benefit should result to all if the general principles and difficulties involved in viscosity determination were more clearly understood.

In spite of general misapprehension regarding the starch viscosity test, it is becoming more generally realized that when all the conditions are known and properly controlled and the results properly interpreted, the values so obtained are as significant and as easy to duplicate as the average physical or chemical test used for industrial control.

VISCOSITY OF CASSAVA FLOUR

The two great uses of cassava flour by industry are for glue, which usually requires a cold concentrated alkaline solution, and for sizing, which usually requires a hot dilute neutral solution.

This paper is principally concerned with the testing of dilute solutions of untreated cassava flour. The testing of concentrated alkaline solutions requires different methods and conditions and should be considered as a separate field. Frequently a starch having a relatively high viscosity in concentrated solution will show a relatively low viscosity in dilute solution. Even among dilute solutions, concentrations cannot be changed substantially without the possibility of bringing about a drastic shift in their relative viscosities.

The results recorded in Tables I and II were all obtained in a like manner by using the methods and apparatus described below. The "Parts of Water" shown in these tables is the ratio of water to one part of starch or flour (containing 12 per cent moisture), which was present at the time the first test was made. The data presented show that the viscosity of colloidal solutions produced by gelatinizing starch in water is largely dependent upon the conditions surrounding the preparation of the solutions.

TABLE I. EFFECT OF COOKING ON VISCOSITY OF CASSAVA FLOURS

TEST	SAMPLE	KIND OF WATER	PARTS OF WATER	VISCOSITY IN CENTIPOISES AFTER COOKING								
				2 min.	7 min.	12 min.	15 min.	25 min.	35 min.	45 min.	55 min.	75 min.
1	A	Distilled	16.5 to 1	1980	1120	459	332	234	140	102	78	54
2	B	Distilled	16.5 to 1	166	140	127	102	78	54	54	27	27
3	C	Distilled	16.5 to 1	538	747	1220	1470	570	386	251	204	127
4	E	Distilled	16.5 to 1	870	676	580	465	371	262	224	166	78
5	F	Distilled	16.5 to 1	610	1020	1090	1160	665	...	305	...	166
6	F	Well	16.5 to 1	443	470	371	332	194	...	127	...	78
7	G	Distilled	16.5 to 1	550	482	472	305	166	...	78	...	27
8	G	Well	16.5 to 1	550	482	443	332	179	...	102	...	27
9	H	Distilled	16.5 to 1	1980	...	665	...	332
10	H	Distilled	18.5 to 1	1220	...	465	...	234
11	H	Distilled	22 to 1	371	...	270	...	127
12	H	Distilled	33 to 1	140	...	90	...	50
13	I	Distilled	16.5 to 1	1780	...	570	...	300
14	I	Distilled	33 to 1	194	...	140	...	54

TABLE II. EFFECT OF COOKING ON VISCOSITY OF COMMERCIAL STARCHES

TEST	KIND OF STARCH	PARTS OF WATER ^a	VISCOSITY IN CENTIPOISES AFTER COOKING								AFTER STANDING 24 HOURS IN COLD		
			3 min.	10 min.	15 min.	20 min.	25 min.	35 min.	45 min.	55 min.	75 min.	CONSISTENCY	CLARITY
15	Corn (Pearl)	12.5 to 1	708	747	890	635	482	340	214	Very firm jelly	Cloudy
16	Wheat	11.5 to 1	375	375	...	390	...	332	262	194	166	Firm jelly	Cloudy
17	Rice	11.5 to 1	498	260	...	243	...	204	179	140	78	Firm jelly	Cloudy
18	Potato (German)	21.5 to 1	2500	1660	1330	...	515	243	166	127	54	Liquid	Clear
19	Potato (Maine)	21.5 to 1	2400	1520	1200	...	580	247	140	127	54	Liquid	Clear
20	Sago	13.5 to 1	665	255	...	78	...	27	27	Soft jelly	Cloudy
21	Arrowroot	19.5 to 1	432	650	...	224	...	102	54	27	27	Liquid	Clear
22	Cassava	16.5 to 1	1800	810	277	194	140	54	27	Liquid	Clear

^a Distilled water used.

Table I shows the effects of cooking on the viscosity of a number of samples of cassava flour, representing brands imported from Java and more or less regularly appearing on the market in this country and which so far as is known had not been treated in any manner for the purpose of modifying their viscosities.

Table II shows the effect of cooking on the viscosity of samples of a variety of starches consumed in large quantities by many industries, and known to the trade as first-quality raw or thick-boiling. In these tests the parts of water have been varied substantially for the different starches in order to give viscosities somewhere near the same order for each starch during a portion of the cooking period; also to give bodies of sufficient thickness to be sensitive to the cooking operation. Each starch can be diluted so that the resulting viscosity is very little affected by heat and agitation; for example, if the sago starch had been cooked with 21.5 parts of water, as was done with the potato starch, the sago solution would have shown a very low viscosity which would hardly have been affected by the cooking operation, whereas at the higher concentration used a rapid change in viscosity was shown.

Figure 1 shows graphically the results of tests 1, 2, 3, and 4 of Table I. These flours were all cooked with the same amount of water and were selected to illustrate the wide differences in viscosity frequently found among raw or unmodified cassava flours; also to show the necessity of measuring the viscosity at more than one point in the cooking operation.

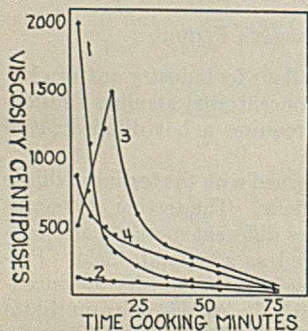


FIGURE 1. EFFECT OF COOKING ON VISCOSITY OF SELECTED SAMPLES OF CASSAVA FLOUR

1. Sample A, 16.5 to 1
2. Sample B, 16.5 to 1
3. Sample C, 16.5 to 1
4. Sample E, 16.5 to 1

14 show the relative position of the viscosity curves for H and I at 33 to 1; the positions of these flours is reversed with respect to viscosity, sample I showing the highest viscosity for this concentration.

Figure 3 presents graphically the results of the tests in Table II. Some care must be exercised in drawing conclusions from

a group of curves of this kind. The samples used for these tests are typical of the average for each starch, but it should not be assumed that all samples of any one kind of starch would conform to the type shown here. However, the curves clearly indicate that potato, cassava, sago, and arrowroot solutions are more drastically affected by heat and agitation than those of wheat, corn, and rice; also that potato solutions cover the greatest viscosity range, while wheat covers the least.

EFFECT OF HEAT AND AGITATION.

Viscosity is usually rapidly reduced by continued application of either heat or agitation, particularly when heat and agitation are combined. Cassava flour and several other starches have a large percentage of their viscosity which is easily destroyed, provided the solutions are sufficiently concentrated, this percentage varying greatly among different brands of the same kind of starch. In general, however, those starches which show the highest initial viscosity also have the largest percentage of easily destroyed viscosity, so that when starch solutions are subjected to a prolonged period of heat and agitation the solutions of initially high viscosity are liquefied more rapidly. Flours which give solutions of initially high viscosity may after a prolonged or severe cooking period show a viscosity which does not differ substantially from that shown by the so-called low-viscosity flours, when both are subjected to the same treatment.

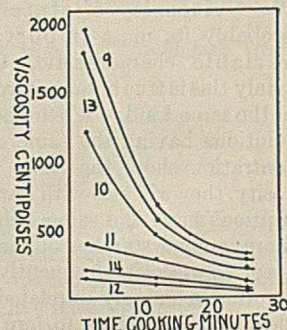


FIGURE 2. EFFECT OF CONCENTRATION ON VISCOSITY OF CASSAVA FLOUR

9. Sample H, 16.5 to 1
10. Sample H, 18.5 to 1
11. Sample H, 22 to 1
12. Sample H, 33 to 1
13. Sample I, 16.5 to 1
14. Sample I, 33 to 1

All kinds of cassava flour as well as other starches develop a maximum viscosity at some point in the cooking operation, but the amount of cooking required to develop this maximum viscosity varies greatly. Curve 3, sample C, in Figure 1 shows that in order to develop the maximum viscosity for this sample, about 10 minutes' more cooking is required than for the other samples of cassava flour. This delayed development of the maximum viscosity is not frequently shown by samples of cassava flour, although other starches—corn, arrowroot, and wheat (Figure 3)—usually show this characteristic.

Two flours may develop similar maximum viscosities at the same point in the cooking cycle, but one flour may show greater resistance to the thinning action of further heat and agitation and therefore at some later point in the cooking cycle be substantially thicker than the other. (Compare curves 1 and 4, Figure 1.)

EFFECT OF SMALL CHEMICAL CHANGES. It is becoming fairly well recognized that the viscosity of starch solutions can be greatly affected by very small concentration of electrolytes. Ripperton (5) has shown the effect of some chemical additions and also that equal additions to different samples of the same variety of starch do not always produce the same relative change. Wiegel (7) states that viscosity changes were different in Thuringer glass from those in Jena glass. Attention is called to tests 5, 6, 7, and 8 of Table I. Cassava flour F was used for tests 5 and 6 and a very large reduction in the viscosity was produced by substituting first-class well water in 6 for the distilled water of 5. Cassava flour G was used for tests 7 and 8. No practical change in viscosity was produced when the well water of 8 was substituted for the distilled water of 7. These tests clearly indicate the importance of small quantities of electrolytes and show that all flours do not react in the same manner; also that gross errors might result when an attempt is made to anticipate the viscosity of pure water solutions from data obtained from chemical solutions or vice versa.

EFFECT OF CONCENTRATION. Viscosity determinations and curves can be decidedly confusing unless the concentration is stated and the possible effect of varying the concentration is clearly understood. Significant viscosity studies and practical accurate testing have been hindered because water concentrations far below commercial requirements have been used, frequently between 30 and 100 to 1. Viscosity tests at these very low concentrations (Figure 2) are easier to make and to duplicate, but unfortunately the results so obtained lack significance. A number of samples of flour will usually show roughly similar relative viscosities at substantially different concentrations, but there are many exceptions. It is also obvious, on account of the very sensitive nature of the more viscous solutions, that the relative divergence in viscosities of flours increases with concentration.

GENERAL METHODS OF TESTING

In recent years many methods of preparing starch solutions for viscosity determinations have been suggested. Harvey (3) passed live steam through a water-starch suspension and regularly drew off portions to be tested until he obtained a relatively constant value. The viscosity curve so obtained was considered an index of the viscosity of the starch and he therefore became one of the first to suggest the curve or the necessity of more than a one-point test. His apparatus and methods, however, lacked standardization and the means for delicate control. Wolff (8) brought starch into solution on a water bath, then boiled and stirred the mixture for 2.5 minutes. His test was apparently a one-point method and the extremely important factors of heat and agitation must have been difficult to control accurately. Ripperton (5), recognizing the paramount importance of the methods used to prepare solutions of starch and especially the effect of heat and agitation, devised a refined method in which he carefully controlled heat and completely eliminated agitation. His method was apparently adapted for a one-point determination and because he eliminated agitation, which actively enters into all commercial uses of gelatinized starch, appears lacking in practical value.

Grimshaw (2) has presented a number of methods used by different starch manufacturers, differing widely in the manner in which the solutions are prepared. In general the methods used to provide heat and agitation are meagerly de-

scribed and do not offer adequate means for either control or standardization. It would seem difficult for laboratories employing any of them consistently to obtain a practical degree of agreement. Furthermore, the methods are not convenient for the determination of the viscosity curve. Caesar (1), with an excellent discussion of the principles involved in viscosity determinations of starch pastes, described a new apparatus and method for obtaining a complete picture of the changes which occur during the cooking and cooling periods. The method, however, does not appear suitable for

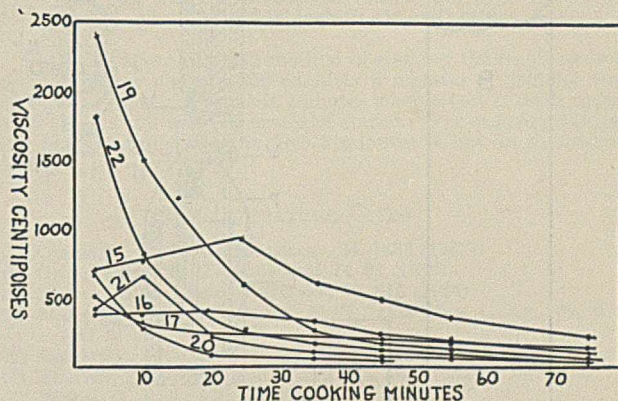


FIGURE 3. EFFECT OF COOKING ON VISCOSITY OF COMMERCIAL STARCHES

15. Corn, 12.5 to 1	20. Sago, 13.5 to 1
16. Wheat, 11.5 to 1	21. Arrowroot, 19.5 to 1
17. Rice, 11.5 to 1	22. Cassava, 16.5 to 1
19. Potato, 19.5 to 1	

ordinary control work because of its complicated nature, the length of time required to make the test, and the lack of sensitivity in the boiling range. Mangels and Bailey (4) in a study of the relative viscosities of wheat starches used cold solutions of chemicals as gelatinizing agents and found that different reagents showed different relationships between the starches. Obviously the values obtained by using chemical gelatinizing agents cannot be used with certainty to predict values when water and heat are used as the gelatinizing agents.

The writer has observed a number of viscosity methods used by the laboratories of the starch-consuming industries, rather than by starch manufacturers as described by Grimshaw (2), and has found laboratory methods also decidedly different in both principle and technic. The manner in which starch solutions were prepared for testing frequently has had no apparent relation to the manner in which the solutions were prepared for plant consumption. It has been suggested that the different requirements of the consuming industries would eliminate the possibility of adopting a standard method of viscosity determinations, but it appears that the great majority of plants using starch as a size prepare their starch by boiling it with from 10 to 20 parts of water and use it at a temperature at or near the boiling point.

The large number of methods for viscosity testing now used by the trade can be roughly divided into four general classes:

1. The starch is gelatinized in water by heat supplied from a hot water bath. The temperature employed, the time of cooking, and the agitation vary enormously. When the cooking period is comparatively short, no indication is given as to how much cooking is required to develop the maximum viscosity or what resistance the starch may have to longer cooking and agitation. When the cooking period is comparatively long, all starch solutions tend to be reduced to the same viscosity level and all indications of the body developed by a limited amount of cooking, as well as the point where the starch develops its maximum viscosity, are obscured. Accurately controlled heat and agitation seem difficult to obtain and duplicate, especially

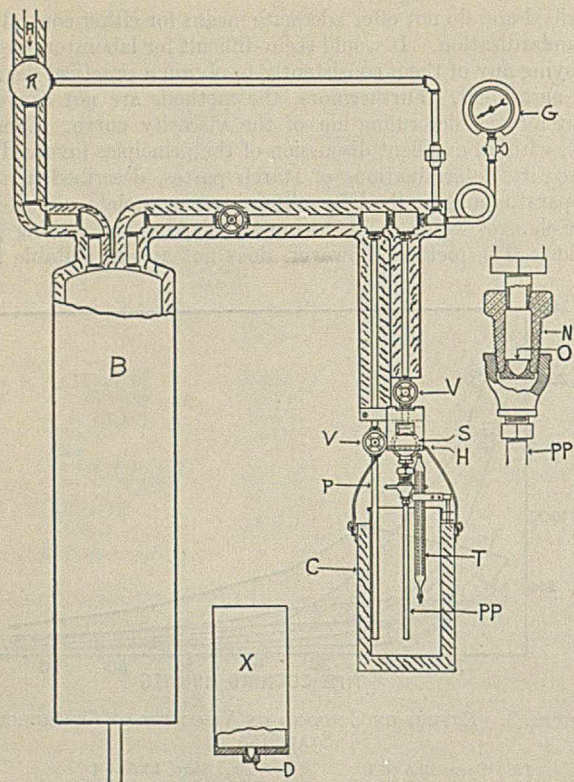


FIGURE 4. DIAGRAM OF VISCOSITY-TESTING APPARATUS

- A. Steam entry
 B. Water separator
 C. Boiling can, copper-lined, well-insulated walls and bottom, 12 inches (30.5 cm.) deep, inside diameter 5.75 inches (14.6 cm.)
 D. Viscometer orifice. Standard brass spray tip (Monarch Manufacturing Works, Inc.) Type 631, size 0.25 inch (0.635 cm.). The 0.125-inch (0.317-cm.) diameter orifice tip, weighing 8.1 grams, and the 0.22-inch (0.556-cm.) diameter orifice tip, weighing 7.1 grams, were selected as most suitable.
 G. Pressure gage
 N. Brass reducing plug, tapped for 0.25-inch (0.635-cm.) steam orifice
 O. Steam orifice. Standard brass spray tip, Monarch type 631, 0.25 inch (0.635 cm.), with orifice hole 0.04 inch (0.102 cm.) diameter, made by No. 60 drill
 P. Unrestricted steam pipe, size 0.25 inch (0.635 cm.)
 PP. Orificed steam pipe, size 0.25 inch above orifice and 0.125 inch (0.317 cm.) below. Extending to depth of 1 inch (2.54 cm.) above center and bottom of boiling can
 R. Pressure regulator, to maintain constant steam pressure of 25 pounds
 S. Strainer, size 0.5 inch (1.27 cm.), made by Tryme Manufacturing Co., Westfield, Mass.
 T. Thermometer, detachable. Mercury bulb suspended 4 inches (10.2 cm.) from bottom and 2 inches (5.1 cm.) from side of boiling can.
 V. Globe valves, size, 0.25 inch (0.635 cm.)
 X. Viscometer cup. Brass, outside diameter 3 inches (7.6 cm.); outside height 5.875 inches (14.9 cm.). Walls made of No. 18 Stubs gage Star Brand seamless brass tubing, bottom thickness 0.187 inch (0.47 cm.), tapped in center of bottom for insertion of 0.25-inch (0.635-cm.) orifice; weight of cup without orifice, 530 grams.

in different laboratories, when heat is applied by means of a water bath and agitation is supplied by some other means.

2. Frequently the starch is cooked for a short or long period, then allowed to cool by standing several hours. The firmness of the jelly so formed is measured either by some jelly-strength apparatus or more frequently by comparing the feel of the jelly with that of a standard sample. Starches so tested are usually used by the factory operation in a hot liquid state. Since the consistency of a cold starch solution which has stood for several hours without agitation is only very poorly related to its consistency while hot and agitated, this method quite frequently gives erroneous results. Furthermore, the consistency of a cold starch jelly is very difficult to measure or estimate accurately.

3. Starch is often gelatinized in cold or hot water by means of caustic soda, and then tested. Since dilute solutions of starch are rarely gelatinized by caustic for practical application and since such a method of gelatinization will not reliably indicate the consistency of starch during or after cooking with water alone, this method seems to have limited practical value.

4. Starch is cooked by running live steam directly into the solution. The temperature rises to near the boiling point of water and remains steadily at that point during the operation, the agitation of the solution during the cooking being controlled by the amount of steam released. This method is employed by the great majority of large starch consumers in their plant operations and for that reason has especial significance when adapted to a laboratory method for indicating the practical value of a sample of starch. So far as is known, however, this method has not been generally used with success in the laboratory because its action is rapid and requires a very definite control. The new apparatus described below makes use of this method of cooking and discloses means for accurate control.

Many different kinds of instruments are used in measuring the consistency of starch. Most of them are satisfactory for practical purposes, but some are better adapted to the testing of hot dilute solutions than others. The stationary orifice type, including the Saybolt, the Engler, the Scott, and the ordinary glass funnel, are widely used. These instruments usually require some sort of temperature control to keep solutions from cooling too much during the test. The orifice is also subject to stoppage if clots or lumps of cooled starch solution collect, and the solution to be tested must be removed from the cooking container in order to pass it through the orifice. The frictional and torsional types, such as the Störmer and the MacMichael, also require removal of the solution from the cooking container as well as temperature control to prevent cooling of the solution in the viscometer. The readings, however, are not appreciably affected by small lumps or clots.

The Bingham-Greene plastometer, where the solution is extruded through a capillary under pressure, has also been used but is best adapted to thick pastes lacking the viscous nature of hot dilute starch solutions.

Nivling has developed an automatic continuous recording viscometer for large-scale industrial uses where the pressure required to deliver a given volume of liquid at a constant rate is used as a measure of viscosity.

PROPOSED VISCOSITY TEST

Having in mind the general lack of confidence and agreement in the results of viscosity testing and the great variety of methods used, a new method was developed which it is believed provides controlled conditions which can be easily duplicated. Boiling with live steam is the method of cooking employed, because it is widely used by the plant operations of large consumers. Heat and agitation are definitely controlled by a constant flow of dry steam through a standard orifice. It has previously been shown that a sample of starch frequently has a peculiarly individual as well as a rapidly changing viscosity, so that for many purposes a single-point determination during the cooking operation has little or no practical significance. This new method, because it easily permits a continuous testing of the solution during the cooking period, is suited for the determination of the viscosity curve.

An important feature of this method is the viscometer, which is a modification of the original Perkins viscometer described in U. S. Reissue Patent 13,436. The modified viscometer is a metal cup with an orifice screwed into its bottom. The cup is simply placed in the solution to be tested and the time required for its submergence is measured by a stop watch. This viscometer eliminates many of the objectionable features of the viscometers now in common use. The solution is not removed from the cooking can during the test. No special temperature control of the viscometer or solution is necessary during the measurement, since the viscometer passes through a large quantity of solution contained in the insulated cooking can rather than a comparatively small amount of solution passing through a rather large viscometer. This viscometer is easy to make, inexpensive, practically unbreakable, and

very easy to clean. Its accuracy as well as the ease and time required for its manipulation have been highly satisfactory. It has been developed to measure the degree of thickness or thinness of dilute solutions of starch in terms having practical utility and not to determine whether the consistency is truly viscous or whether a set of readings follows some mathematical equation. A good viscometer for practical purposes should indicate only differences which are apparent to the skilled practical man.

METHOD OF TESTING. Place 3000 cc. of distilled water at about 75° F. (23.89° C.) in the boiling can and stir in the proper amount of starch. Open valve pipes *P* and *PP* to drain condensation and heat them; then close the valves, attach the boiling can to hook *H*, and open wide the valves or pipes *P* and *PP*. After 20 seconds the mixture will gelatinize and the flow of steam through *P* must be reduced immediately, so that the force of the steam will not blow the paste out of the can. Continue to manipulate the valve for *P*, so that the temperature is brought steadily up to 190° F. (87.78° C.) in exactly 1.5 minutes. Thereupon, immediately close the valve for *P* but allow the constant flow of steam through *PP* and the constant agitation caused thereby to continue as long as desired. The temperature of the solution rises rapidly to the boiling point, where it remains. It has been the custom of this laboratory when testing cassava flour for ordinary control purposes to use 200 grams and to remove the can for testing 3 minutes after opening valve pipe *P*. At this point the viscometer cup with a 0.22-inch (0.556-cm.) orifice is placed in the solution; the time required for the cup to submerge is the viscosity measure. Exactly 2 minutes after the removal of the can it is replaced and boiling is continued until the total time elapsed has reached 17 minutes, whereupon the can is again removed and tested with a 0.125-inch (0.317-cm.) orifice in the viscometer. The first reading with the 0.22-inch (0.556-cm.) orifice can be converted into equivalent readings for

the 0.125-inch (0.317-cm.) orifice by means of a predetermined set of values, and these viscosity readings in seconds can be converted into centipoises after standardizing the 0.125-inch (0.317-cm.) orifice against solutions having a known viscosity in centipoises. For ordinary purposes readings in seconds are preferred.

STANDARDIZING APPARATUS. To standardize the cooking apparatus, open wide the valve for pipe *PP* and allow steam to flow until the pipe is hot; then put 4000 cc. of water at a temperature of about 70° F. (21.1° C.) into the cooking can and place it on the hook. The time required to raise the temperature from 75° to 100° F. (23.89° to 37.78° C.) should be approximately 3 minutes and 13 seconds.

The viscometer cup is standardized by measuring the time required for it to sink in water at approximately 75° F. (23.89° C.). The cup with an 0.125-inch (0.317-cm.) orifice sinks in 19.3 seconds and with the 0.22-inch (0.556-cm.) orifice the time is 7.1 seconds.

With this apparatus and method of cooking the condensation should be very close to 350 cc. after 3 minutes of cooking and 30 cc. for every additional 10 minutes when a test is made using 3000 cc. of water and 200 grams of starch. For ordinary testing the condensation after the first 3 minutes is not an important factor.

LITERATURE CITED

- (1) Caesar, G. V., *IND. ENG. CHEM.*, 24, 1432 (1932).
- (2) Grimshaw, A. H., *Textile World*, 74, 61 (1928).
- (3) Harvey, E. H., *Amer. J. Pharm.*, 96, 816 (1924).
- (4) Mangels, C. E., and Bailey, C. H., *IND. ENG. CHEM.*, 25, 456 (1933).
- (5) Ripperton, J. C., Hawaii Agr. Expt. Sta., *Bull.* 63 (1931).
- (6) Thurber, F. H., *IND. ENG. CHEM.*, 25, 565 (1933).
- (7) Wiegel, E., *Kolloid-Z.*, 62, 310 (1933).
- (8) Wolff, O., *Chem.-Ztg.*, 51, 1001 (1927).

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Determination of Dielectric Constants by Means of Radio

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IN CONNECTION with research work, a method of determining dielectric constants accurately with an inexpensive apparatus was desired. The heterodyne beat method was the most convenient one to use, but a source of constant radio frequency was needed to obtain good results. Broadcasting stations should serve for this purpose, as they are required by federal regulations to keep within twelve cycles of their assigned carrier frequency to guard against interference with stations operating in adjacent channels.

If the frequency of the carrier was varied by the audio frequency superimposed upon it, a composite of which is transmitted by the sending station, the radio could not be used as a source of constant oscillations. There is, however, no shift in carrier frequency but audio modulation adds what are called side bands on each side of the carrier wave and removed from it a number of cycles equal to the modulating frequency. Another oscillator coupled to a radio receiving the modulated carrier wave of the broadcasting station can be made to form an audible beat note which has a frequency equal to the difference in cycles between carrier and the oscillator. This beat note, together with a jumble of distorted music, is given out by the radio. By slowly tuning the variable oscillator the beat note can be made to become lower in frequency and the music less distorted until, at what is called zero beat, the music is undistorted and can be heard exactly as if the second oscillator were not in operation.

Having a method of setting a variable oscillator to constant frequency, the usual procedure of the heterodyne beat method

for determining dielectric constants was then followed. As is known, the dielectric constant may be taken as the ratio of the capacity of a given condenser filled with the medium to be measured, divided by the capacity of the same condenser evacuated or, for most practical purposes, filled with air. By connecting the measuring condenser in parallel with a condenser previously calibrated, the capacities are added, and if the standard condenser had been set for zero beat with the broadcast station it must be detuned an amount equal to the capacity of the measuring cell again to have zero beat. Repetition of the process with air and an unknown substance in the measuring cell makes it possible to calculate the dielectric constant.

APPARATUS

Figure 1 is a diagram of an ordinary variable oscillator. The measuring cell is similar to that used by Smyth and Morgan (8), except that the plates are insulated by beads of glass fused to stiff platinum wires which are welded to the cylindrical plates (5). The standard capacity is a General Radio Type 222-L condenser. The condenser system was constructed outside of the oscillator proper, and joined to it by means of the binding posts, *P*, *P'*.

A Stewart-Warner Model 102-A superheterodyne radio was used to obtain the radio frequency from the broadcasting station. The coupling between the radio set and the variable oscillator was adjusted until the error involved in detecting

zero beat was less than that in reading the scale on the standard condenser.

In order to correct for parasitic capacity, the cell was calibrated by filling it with pure, dried benzene, as is done in the ordinary procedure.

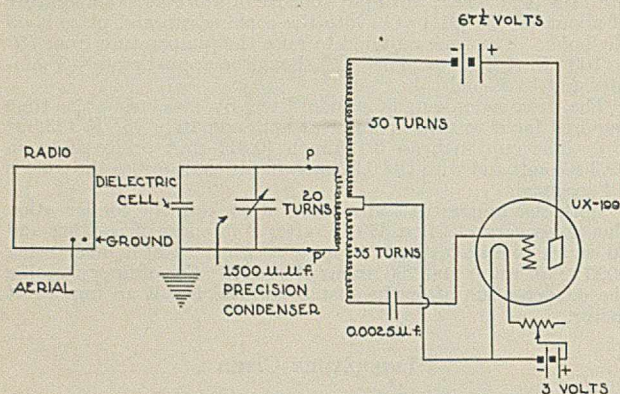


FIGURE 1. DIAGRAM OF VARIABLE OSCILLATOR

Station WGN, Chicago, operating on 720 kilocycles, was used as a source of constant frequency. Their schedule is continuous throughout the day, and the signal in this locality is of sufficient intensity for the work. Other stations may be used, and for purposes of comparison, WBBM, on 770 kilocycles, and WMAQ, on 670 kilocycles, were also used, with no variation in results. With wave lengths near the long wave limit of the broadcast band, the point of zero beat was not sharp, while with shorter wave lengths than that of WBBM, the condenser had too large capacity for the coil used.

MEASUREMENTS OF DIELECTRIC CONSTANTS

In order to test the accuracy of the method, dielectric constants of some known substances were determined. The results of these measurements together with those obtained by other workers are listed in Table I. The agreement is good.

TABLE I. DIELECTRIC CONSTANTS OF *m*-XYLENE, CARBON TETRACHLORIDE, AND ETHYL ACETATE IN BENZENE

<i>m</i> -XYLENE			
<i>t</i> , °C.	ε	ε	
	Otto and Wenzke	Pyle (7)	
36	2.349	2.353	
31	2.354	2.359	
28	2.360	2.365	
26	2.363	2.370	
20	2.369	2.374	

ETHYL ACETATE IN BENZENE AT 25° C.			
<i>c</i> ₂	ε	<i>c</i> ₂	ε
	Otto and Wenzke	Smyth and Walls (9)	
0.04020	2.435	0.0310	2.410
0.05656	2.505	0.0475	2.477
0.1188	2.754	0.0614	2.532
0.1420	2.849	0.1060	2.708
....	...	0.1575	2.912

CARBON TETRACHLORIDE			
<i>t</i> , °C.	ε	ε	
	Otto and Wenzke	Stranathan (10)	
20	2.219	2.221	
30	2.196	2.200	
40	2.182	2.180	
50	2.150	2.159	

Dielectric constant data on organic compounds are obtained primarily for the purpose of calculating their electric moments. As a further check on this method dipole moments of a number of compounds were determined. The data on this work are given in Table II.

TABLE II. DATA FOR DETERMINATION OF DIPOLE MOMENTS OF BROMOBENZENE, *p*-NITROTOLUENE, AND ETHYL BROMIDE IN BENZENE AT 25° C.

<i>c</i> ₂	<i>d</i>	ε	<i>P</i> ₁₂	<i>P</i> ₂
BROMOBENZENE ^a				
0.02104	0.8860	2.347	27.88	83.62
0.03134	0.8936	2.385	28.46	83.48
0.03668	0.8974	2.401	28.72	83.16
0.05633	0.9130	2.469	29.85	82.88
0.07708	0.9279	2.547	30.85	80.74
<i>p</i> -NITROTOLUENE ^b				
0.007925	0.8736	2.495	29.89	432.1
0.01086	0.8747	2.563	30.82	407.4
0.02064	0.8783	2.841	34.32	396.9
0.02094	0.8785	2.845	34.38	394.2
0.02769	0.8809	3.024	36.44	379.2
0.03984	0.8855	3.345	39.84	356.9
0.04877	0.8887	3.583	42.13	343.4
ETHYL BROMIDE ^c				
0.01084	0.8759	2.324	27.40	93.1
0.02984	0.8848	2.413	28.58	90.2
0.03604	0.8878	2.441	28.93	89.1
0.04497	0.8920	2.482	29.45	88.2
0.05804	0.8983	2.544	30.20	86.3

^a $P_{\infty} = 83.9$; $PE = 33.92$; $\mu = 1.55 \times 10^{-18}$.

^b $P_{\infty} = 448$; $PE = 37.9$; $\mu = 4.44 \times 10^{-18}$.

^c $P_{\infty} = 94.2$; $PE = 18.5$; $PA = 11$; $\mu = 1.77 \times 10^{-18}$.

The electronic polarization of bromobenzene was obtained from the refractive index for the sodium D line, and the density of the pure liquid. That of *p*-nitrotoluene was obtained from the same measurements on solutions in benzene, and for ethyl bromide the electronic polarization was taken from the literature. Atomic polarization was neglected in the case of bromobenzene and *p*-nitrotoluene, but the value for ethyl bromide was taken from Smyth and Morgan (8). The values obtained— 1.55×10^{-18} for bromobenzene, 4.44×10^{-18} for *p*-nitrotoluene, and 1.77×10^{-18} for ethyl bromide—compare favorably with the values in the literature, as listed in Table III.

TABLE III. ELECTRIC MOMENT VALUES

	MOMENT $\times 10^{18}$
BROMOBENZENE	
Bergmann (1)	1.49
Williams (12)	1.50
Müller and Sack (6)	1.52
Das (2)	1.53
K. Höjendahl (3)	1.56
Tiganik (11)	1.53
<i>p</i> -NITROTOLUENE	
Tiganik (11)	4.44
K. Höjendahl (3)	4.31
Williams (12)	4.50
ETHYL BROMIDE	
Smyth and Morgan (8)	1.86
Mahanti (4)	1.79

The fact that the values obtained by the use of the radio are within the experimental deviations of other investigators shows clearly that this method is useful and accurate for measuring dipole moments.

LITERATURE CITED

- (1) Bergmann, Engel, and Sandor, *Z. physik. Chem.*, B10, 106 (1930).
- (2) Das, *Indian J. Physics*, 5, 441 (1930).
- (3) Höjendahl, *Physik. Z.*, 30, 391 (1929).
- (4) Mahanti, *Ibid.*, 31, 546 (1930).
- (5) Morgan and Lowry, *J. Phys. Chem.*, 34, 2385 (1930).
- (6) Müller and Sack, *Physik. Z.*, 31, 815 (1930).
- (7) Pyle, *Phys. Rev.*, 38, 1065 (1931).
- (8) Smyth and Morgan, *J. Am. Chem. Soc.*, 50, 1547 (1928).
- (9) Smyth and Walls, *Ibid.*, 53, 527 (1931).
- (10) Stranathan, *Phys. Rev.*, 31, 653 (1928).
- (11) Tiganik, *Z. physik. Chem.*, B13, 425 (1931).
- (12) Williams and Schwingel, *J. Am. Chem. Soc.*, 50, 362 (1928).

RECEIVED November 16, 1933.

JAPANESE DYE PRODUCTION AND FOREIGN TRADE, 1933. It is conservatively estimated that the production of synthetic dyestuffs in Japan during 1933 increased by approximately 40 per cent in volume over the output during 1932. The increase in production of cotton textiles and rayon during 1933 probably increased the demand for dyestuffs by at least one-third.

Estimation of Small Amounts of Bismuth, Antimony, Tin, and Molybdenum in Copper

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A NUMBER of methods for separating small amounts of bismuth from large amounts of copper have been proposed. Those generally used depend upon separation of the bismuth as a basic salt, which may be nitrate, sulfate, chloride, or bromide in a slightly acid solution, or upon the formation of an insoluble carbonate or phosphate in ammoniacal solution. In the latter case iron is usually added to help collect the precipitated bismuth. Most of these methods work satisfactorily for comparatively large amounts of bismuth but are not sufficiently sensitive for extremely small amounts.

(about 30 minutes), allowed to stand until the precipitate settled out, and then filtered through a No. 4 Jena glass filter. The precipitate was washed with a little water, and the combined filtrate and washings were treated with potassium bromide and permanganate as before. After settling, the solution was filtered and the combined precipitates were dissolved with 50 cc. of hot concentrated hydrochloric acid. The pH of the filtrates varied between 2.0 and 2.6.

The hydrochloric acid solution was concentrated to about 30 cc., neutralized with ammonium hydroxide, acidified with 1 cc. of concentrated hydrochloric acid, diluted to 100 cc., heated to boiling, and treated with hydrogen sulfide until precipitation was complete. The sulfides were filtered out on a glass filter, washed with water, and dissolved with 25 cc. of hot concentrated nitric acid, followed by 10 cc. of hot concentrated hydrochloric acid. The solution of sulfides was evaporated to about 5 cc., 10 cc. of hydrochloric acid were added, and the solution was evaporated to 3 or 4 cc. It was diluted to exactly 5 cc., and portions of this concentrate were used to impregnate graphite electrodes which were dried in an oven at 100° C. and subsequently arced to give spectrograms. These spectrograms were compared with others made from solutions containing known amounts of bismuth, tin, antimony, and molybdenum, according to the procedure described by Nitchie (2).

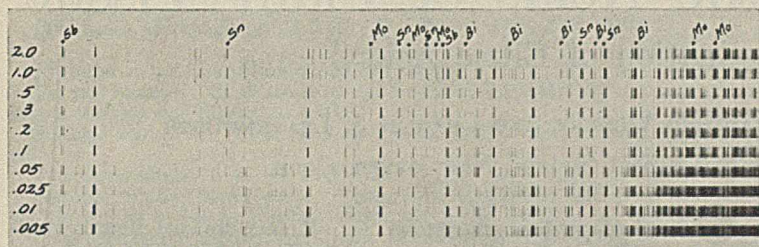


FIGURE 1. SPECTROGRAMS OF STANDARD SOLUTIONS

In a previous paper (3) it was shown that antimony may be separated from copper by precipitating manganese dioxide in the slightly acid solution. During this work it was noticed that some bismuth accompanied the antimony and manganese dioxide, but recent experiments have shown that its precipitation is not quantitative. Bismuth was found spectrographically in each of three consecutive manganese dioxide precipitates thrown out of 1 liter of copper nitrate solution to which had been added 2 mg. of bismuth.

Moser and Maxymowicz (1) have shown that the precipitation of bismuth oxybromide by means of potassium bromate-potassium bromide mixtures is capable of detecting about 0.3 mg. of bismuth in 100 cc. of solution. They also have succeeded in separating 13 mg. of bismuth from about 13 grams of copper, although their error was large (13 mg. added, 20 mg. found).

By combining the precipitation as oxybromide with a simultaneous precipitation of manganese dioxide it is possible to separate less than one part of bismuth from a million parts of copper.

One hundred grams of copper were boiled with concentrated hydrochloric acid, washed with distilled water, and dissolved in 400 cc. of concentrated nitric acid. The solution was evaporated to dryness on a steam bath, diluted with 1 liter of water, heated to boiling, and treated with 1 N sodium carbonate solution until a slight permanent precipitate formed. This was dissolved by the addition of 1 cc. of concentrated nitric acid. To the clear boiling solution were added 10 cc. of 20 per cent potassium bromide solution (a precipitate of silver bromide usually formed at this point), and 10 cc. of 3 per cent potassium permanganate solution. At this point manganese dioxide precipitated and bromine was liberated. The solution was boiled until free from bromine

Tin, antimony, and molybdenum are quantitatively precipitated along with the bismuth.

This was proved in the following manner:

Three consecutive precipitations of manganese dioxide were made in a solution of 100 grams of refined copper. Practically all the antimony, tin, and bismuth were found in the first precipitate. Traces of antimony, tin, and bismuth were found in the second precipitate, but the third precipitate was spectroscopically free from all three elements. To the filtrate from the third precipitation was added 0.1 mg. of each of the four impurities, and three more consecutive precipitations were then made. The first precipitate contained all four elements. The second contained a trace of tin but no trace of the other three. The third was spectroscopically free from all four.

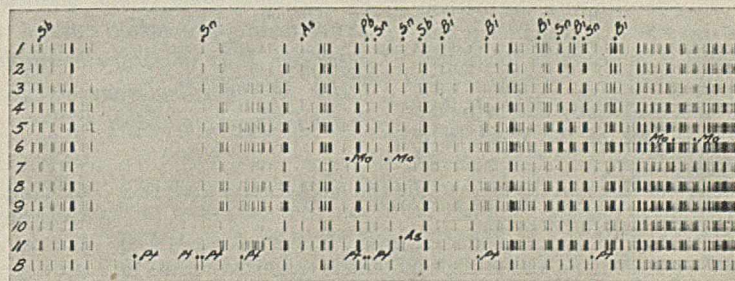


FIGURE 2. SPECTROGRAMS FROM SAMPLES AND BLANK

This procedure was repeated with the addition of 2 mg. of each impurity. The results were practically the same. All the impurities were found in the first and second precipitates, but none in the third.

Silver and arsenic precipitate along with the other elements, but no experiments were performed to ascertain whether or not the precipitation is complete. A little lead also was found in the final concentrate but experiments showed that precipitation was

not quantitative. Lead was found in each of three consecutive precipitations brought down in the manner described above.

A number of samples of refined copper from various sources were analyzed, with the results shown in Table I.

TABLE I. ANALYSIS OF REFINED COPPER

SAMPLE	ANTIMONY %	TIN %	BISMUTH %	MOLYBDENUM %
1	0.00013	0.00017	0.0045	None
2	0.002	0.0015	0.0005	None
3	0.0013	0.0012	0.00016	None
4	0.0004	0.00007	0.00015	None
5	0.0002	0.0003	0.00002	None
6 ^a	0.00018	0.00018	< 0.00001	0.00015
7 ^a	0.00017	0.00004	< 0.00001	0.0005
8	0.00005	0.00018	0.000025	None
9	None	0.00005	< 0.00001	None
10	0.00003	0.0001	< 0.00001	None
11	0.00005	0.00015	< 0.00001	None
Blank	None	0.00001	None	None

^a An unmelted cathode deposited from a leached solution.

Figure 1 shows a number of spectrograms of the standard solutions, using 0.1 cc. for each exposure. Concentrations are given in milligrams per 5 cc. Figure 2 shows spectro-

grams made from the samples tested and the blank obtained by electrolyzing the filtrate from sample 9, dissolving the deposit in nitric acid, and treating as a sample. Some platinum was dissolved from the electrode in the process, as may be seen.

The section of the spectrum shown in the figures extends from about 2590 Å. on the left to 3200 Å. on the right, and includes the most persistent lines of all of the elements sought.

ACKNOWLEDGMENT

The author wishes to thank for their coöperation the Copper and Brass Research Association and the many copper refiners who furnished the samples.

LITERATURE CITED

- (1) Moser and Maxymowicz, *Z. anal. Chem.*, **67**, 248 (1925-26).
- (2) Nitchie, *IND. ENG. CHEM., Anal. Ed.*, **1**, 1 (1929).
- (3) Park and Lewis, *Ibid.*, **5**, 182 (1933).

RECEIVED December 9, 1933.

Determination of the Acids of Plant Tissue

III. Determination of Citric Acid

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CITRIC acid, when treated with potassium permanganate and potassium bromide under the proper conditions, is converted into the insoluble substance pentabromoacetone. This reaction was originally employed by Stahre (6) for the qualitative recognition of citric acid, but was placed upon a quantitative basis by the work of Kunz (4), and of Hartmann and Hillig (1); it is now widely used for the determination of citric acid in plant tissues. In order to obtain trustworthy results with the method as described by Hartmann and Hillig, it is desirable to subject at least 50 mg. of citric acid to the oxidation; furthermore, the transfer of the precipitate to the filter, and the subsequent washing and drying, require the most careful attention to details of technic.

Although of great value for many types of analytical studies, Hartmann and Hillig's method is seriously limited in usefulness for the investigation of citric acid metabolism owing to the large amount of citric acid required for accurate results. Nevertheless the specificity of the oxidation reaction upon which it is founded makes it the method of choice for the determination of citric acid. The authors have therefore sought to improve the pentabromoacetone method so that the filtration, with its attendant and necessary solubility correction, may be avoided and trustworthy results may be secured on relatively small quantities of citric acid.

Citric acid is oxidized to pentabromoacetone by potassium permanganate in the presence of potassium bromide. The oxidation product is extracted by petroleum ether, dehalogenated by sodium sulfide, and the bromide ion produced is titrated with silver nitrate. Quantities of citric acid of the order of 1 to 20 mg. can be determined in this manner with an accuracy of ± 5 per cent. Malic acid alone of the common organic acids interferes in any way with the determination, and the error introduced by the presence of this substance is ordinarily so small as to be negligible. Inasmuch as the conversion of citric acid to pentabromoacetone is not quantitative, although in constant proportion under the conditions described, it is necessary to employ a correction factor in the calculation of the results. This factor is approximately 1.12.

It was obvious that a volumetric method to determine pentabromoacetone would be necessary. Accordingly, the authors have studied several procedures whereby this substance can be dehalogenated and the halogen determined. Kometiani (2) has described a method for the dehalogenation of pentabromoacetone by warm alcoholic sodium iodide in the presence of acetic acid. A careful investigation of this reaction showed that quantitative results could be obtained only under the most rigidly controlled conditions; in the authors' hands the conditions described by Kometiani invariably yielded results from 30 to 40 per cent too high. Furthermore it was observed that pentabromoacetone is

unstable in ethyl alcohol solution. The reaction was not investigated in detail, but within 3 hours at least 15 per cent of the pentabromoacetone in a 0.035 per cent solution of this substance in alcohol had been converted to a product that was no longer dehalogenated by sodium iodide; after 72 hours the conversion was greater than 75 per cent. Incidentally it was noted that pentabromoacetone is unstable in ether solution also, but it appears to be stable when dissolved in chloroform or in petroleum ether.

If a freshly prepared solution of pentabromoacetone in alcohol is treated with silver nitrate, a precipitate of silver bromide separates in a few minutes at room temperature. A study of this reaction showed that it was entirely unsuited

for quantitative work; dilute (0.02 *N*) alcoholic silver nitrate liberated bromine equivalent to only 32 per cent of the substance (2 atoms = 35.25 per cent) when the solution was boiled under a reflux condenser for 45 minutes, whereas more concentrated silver nitrate solutions liberated from 60 to 70 per cent (4 atoms = 70.63 per cent) under similar conditions.

The authors have therefore turned to a reaction described by Kretov, Panchenko, and Savich (3), according to whom aliphatic halogen compounds are completely dehalogenated on being heated for a short time with alcoholic sodium sulfide solution. It was found that pentabromoacetone reacts quantitatively even with aqueous sodium sulfide in the cold; after acidification with sulfuric acid and removal of the hydrogen sulfide by boiling, the bromide can be conveniently determined by titration with silver nitrate in the usual way. Advantage was therefore taken of this modification of the reaction described by the Russian authors for the development of an accurate volumetric method to determine citric acid in small quantities.

REAGENTS

Sulfuric acid, 50 per cent: a mixture of equal volumes of concentrated acid and water.

Potassium bromide, 1.0 *M*: 11.9 grams diluted to 100 cc.

Potassium permanganate, 1.5 *N*: 47.4 grams diluted to 1000 cc.

Bromine water: saturated aqueous solution.

Ferrous sulfate: 20 grams of crystalline salt, 1 cc. of concentrated sulfuric acid diluted to 100 cc.

Sulfuric acid, 2 *N*: 28 cc. of concentrated acid diluted to 500 cc.

Petroleum ether: b. p., 35° to 50° C.

Sodium sulfide, 4 per cent: 4 grams of crystalline sodium sulfide diluted to 100 cc., prepared fresh every 2 to 3 days.

Hydrogen peroxide (halogen-free): 4 grams of sodium peroxide dissolved in 50 cc. of water with careful cooling and faintly acidified to Congo red with 50 per cent sulfuric acid (7 to 8 cc. required); prepared fresh every week.

Silver nitrate, 0.05207 *N*: 8.8462 grams of pure silver nitrate diluted to 1000 cc. 1 cc. = 2.00 mg. of citric acid or 4.714 mg. of pentabromoacetone or 4.162 mg. of bromine.

Ammonium thiocyanate, 0.05207 *N*: 3.96 grams diluted to 1000 cc. and standardized against the silver nitrate.

Ferric ammonium sulfate (ferric alum): 100 grams dissolved by warming with 100 cc. of water. Warm slightly to dissolve crystals before using.

PREPARATION OF SOLUTION AND OXIDATION OF CITRIC ACID

The organic acids are extracted by ether from a 2-gram sample of dried and powdered tissue according to the technic described by Pucher, Vickery, and Wakeman (5). The procedure is designed for the determination of from 1 to 20 mg. of citric acid.

An aliquot part of the organic acid solution that will contain a suitable quantity (usually 10 cc.) is diluted with water to 25 cc., and 3 cc. of 50 per cent sulfuric acid are added. The mixture is boiled gently for a few minutes to expel traces of ether, is cooled, and 3 cc. of bromine water are added. After being allowed to stand 5 to 10 minutes, the solution is filtered with gentle suction through asbestos in a Gooch crucible into a 150-cc. beaker marked at 40 cc.; a suitable apparatus for this filtration is readily devised from a desiccator. The precipitate is washed with small quantities of water until the 40-cc. mark is reached and 2 cc. of potassium bromide are added, followed by 10 cc. of potassium permanganate. The oxidation is allowed to proceed at room temperature for 10 minutes, the solution is then chilled to 10° to 15° C. in an ice bath, and ferrous sulfate solution (20 to 30 cc. usually) is added until the manganese dioxide is dissolved.

EXTRACTION OF PENTABROMOACETONE

The oxidation mixture is transferred to a 125-cc. pear-shaped separatory funnel previously cleaned with chromic-sulfuric acid, and the beaker is carefully rinsed into the funnel with 25 cc. of petroleum ether, used in small portions. The funnel is shaken vigorously and the aqueous layer is drawn off. The ether is

transferred to a second funnel. The aqueous solution is shaken again with 20 cc. of petroleum ether and is then discarded. The two ether extracts are combined and washed four times with 3- to 4-cc. quantities of water to remove traces of inorganic halides. A 5-cc. quantity of 4 per cent sodium sulfide is added, and the mixture is thoroughly shaken; if pentabromoacetone is present the aqueous solution becomes red, the intensity of the color being very closely proportional to the amount of citric acid originally present. (This color reaction can be used to determine from 0.05 to 1.0 mg. of citric acid photometrically; the details of the method are at present being studied.) The aqueous layer is drawn off into a 125-cc. Erlenmeyer flask, and the petroleum ether is shaken with a second 5-cc. quantity of sodium sulfide, and then three times successively with 3 to 4 cc. of water, each extract being added to the flask; 20 cc. of water, 3 cc. of 2 *N* sulfuric acid, and a few small angular quartz pebbles are added, and the solution is boiled gently for 10 minutes to expel hydrogen sulfide. It is then cooled and 1.5 *N* potassium permanganate solution is added (1 to 3 cc. usually) until a red color permanent for 15 to 20 seconds is obtained. The color is discharged by the addition of an excess of halogen-free hydrogen peroxide; 5 cc. of concentrated nitric acid and 10 cc. of standard silver nitrate are added, the solution is cooled and stirred to coagulate the silver bromide (a few drops of ether assist at this point), 2 cc. of ferric alum are added, and the solution is titrated with standard thiocyanate to a faint salmon-pink color. The end point can be duplicated to 0.02 cc. with experience. Multiplication of the number of cubic centimeters of standard silver nitrate used by the factor 2×1.12 gives the quantity of citric acid in the aliquot of the organic acid solution taken.

DISCUSSION

The oxidation of citric acid to pentabromoacetone is as complete at room temperature as at 45° to 48° C., the temperature recommended by Hartmann and Hillig. A series of experiments in which the oxidation was conducted at 10°, 25°, and 45° to 48° C. gave recoveries of citric acid that varied less than 0.2 per cent. Oxidation at room temperature was therefore adopted as being more convenient.

No conditions for the oxidation could be devised in which the yield of pentabromoacetone, calculated as citric acid, was greater than 90 per cent. The reaction does, however, yield a constant proportion of pentabromoacetone under rather widely varied conditions. Hartmann and Hillig likewise noted that the yield was not quantitative and suggested that a correction factor of 1.05 be used, in addition to a weight correction for the solubility of pentabromoacetone.

The petroleum ether extraction technic described entirely eliminates this solubility correction; this is the more desirable inasmuch as the solubility of pentabromoacetone was found to be appreciably greater in solutions derived from plant extracts than in solutions obtained by oxidation of the pure acid. In eight determinations of the pentabromoacetone that remained in solution, after filtration of the crystalline product obtained essentially as described by Hartmann and Hillig, the quantity found varied from 1.1 to 2.1 mg. per 100 cc. with an average value of 1.56 mg. per 100 cc. This average is in close agreement with Hartmann and Hillig's figure of 1.7 mg. per 100 cc. Four solutions derived from the oxidation of extracts from tobacco leaf contained 2.3 to 3.3 mg. per 100 cc., the average being 2.53 mg. It must be emphasized, however, that these determinations were made on solutions obtained in the course of a routine procedure; there was no assurance that equilibrium had been attained, nor was the salt content of the solutions controlled; under these circumstances somewhat wide variations of the solubility might be expected.

The choice of solvent for the extraction of pentabromoacetone from the reaction mixture is of great importance. Ordinary ether gave fairly satisfactory results when pure citric acid was employed, and when the procedure was carried through promptly, although it was somewhat more difficult to wash this solvent free from inorganic halides. When ordinary ether was used for the extraction of oxidation mixtures obtained from tobacco leaf extracts, however, the

presence of an interfering halogen compound derived from the oxidation of malic acid was detected in the extract. Furthermore, ether solutions of pentabromoacetone are not stable on standing. The brominated oxidation product of malic acid is not extracted from the reaction mixture by petroleum ether, and pentabromoacetone is stable at room temperature in this solvent; its use is therefore essential to the success of the present method.

The removal of the pentabromoacetone from the petroleum ether by aqueous sodium sulfide and its simultaneous dehalogenation are quantitative. The average recovery of pentabromoacetone, calculated as citric acid, in eight experiments in which the equivalent of quantities of from 5 to 19 mg. of citric acid were taken was 99.2 per cent. The error in the determination of quantities as small as 1.3 mg. was not greater than ± 8 per cent; the variation with the larger amounts was ± 2 per cent.

The sodium sulfide extract must be acidified and freed from hydrogen sulfide before titration with silver nitrate. Nitric acid, if used for this purpose, may give rise to small losses of halogen, consequently sulfuric acid must be employed. The solution, after being boiled for 10 minutes, is usually yellow or brown in color, and silver nitrate is promptly reduced if added; the interfering impurities are, however, easily removed by oxidation with potassium permanganate. It is best to add the permanganate rapidly until a red-brown color persists after 10 to 15 seconds agitation, and then add the hydrogen peroxide until the solution becomes colorless. Some difficulty may be experienced at this point, as it is not easy to distinguish the color of the excess of permanganate. It is essential, however, that an excess be present, as otherwise the silver bromide subsequently precipitated will be contaminated with reduced silver. The solution is frequently slightly turbid owing to the presence of sulfur and, when large amounts of citric acid have been taken, may be faintly yellow.

The factor employed in the calculation of the results depends upon a series of analyses of known quantities of citric acid, both alone and in the presence of malic acid. The effect of the presence of from 25 to 30 mg. each of fumaric, maleic, succinic, pyruvic, oxalic, and tartaric acids on the recovery of from 1 to 16 mg. of citric acid was tested in separate experiments. No interference was detected. Malic acid, however, was found to exercise a small effect and was therefore given especial attention.

The quantities of pentabromoacetone found by titration after the oxidation of from 0.6 to 1.9 mg. of citric acid corresponded to 90.3 \pm 4.8 per cent in six experiments. When 6.4 mg. of citric acid were taken, the recovery was 87.5 \pm 1.5 per cent in eight experiments. When from 12.8 to 16 mg. were taken, the recovery was 89.0 \pm 0.6 per cent in seven experiments. The average recovery over the range 0.6 to 16.0 mg. was therefore 88.9 per cent or, if the smallest quantities are not taken into consideration, 88.3 per cent. This value leads to a factor of 1.133.

Analyses of mixtures of from 3 to 16 mg. of citric acid with 30 mg. of malic acid gave an average recovery of 90.8 per cent in seven experiments; analyses of mixtures of 16 mg. of citric acid with from 6 to 12 mg. of malic acid gave a recovery of 89.1 per cent in seven experiments. The average figure of 90.0 per cent recovery may therefore be taken as the most probable value of the recovery of quantities of citric acid in the range of 3 to 16 mg. in the presence of from 6 to 30 mg. of malic acid. This leads to a factor of 1.111.

It therefore seems justifiable to take the average of these factors—namely, 1.12—as an empirical factor to employ for the calculation of the citric acid from the titration value of the pentabromoacetone derived from the oxidation of mixtures which may or may not contain malic acid. The accuracy of the results so obtained is certainly well within ± 5 per cent.

Data are presented in Table I which illustrate the reproducibility of the results obtained by the present method when applied to an extract from tobacco leaf tissue. The solution analyzed represented a mixture of the organic acid fractions obtained by extraction with ether from a number of different samples, and was of such a concentration that a 10-cc. aliquot part represented 0.200 gram of the dried leaf. For purposes of comparison, analyses by the gravimetric method of Hartmann and Hillig are also shown. In column 6 are given the solubility corrections, determined by the present method in the filtrates, to be added to the weight of the pentabromoacetone found. In column 7 are the solubility corrections calculated from Hartmann and Hillig's correction factor. In the last two columns these two corrections are respectively applied to calculate the proportion of citric acid in the tissue.

TABLE I. CITRIC ACID DETERMINED IN TOBACCO LEAF TISSUE BY THE PENTABROMOACETONE METHOD

SODIUM SULFIDE METHOD			GRAVIMETRIC METHOD						
ALIQUOT	CITRIC ACID		ALIQUOT	CITRIC ACID	SOLUBILITY CORRECTION				
Cc.	Mg.	%	Cc.	Mg.	Found	Calculated			
25.0	13.96	2.79	25.0	10.93	3.0	1.9	2.79	2.57	
25.0	14.40	2.88	25.0	11.02	2.6	1.9	2.72	2.58	
20.0	11.97	2.99	25.0	11.91	2.6	1.9	2.90	2.76	
20.0	11.97	2.99	50.0	25.99	3.9	2.1	2.99	2.81	
20.0	11.74	2.94	50.0	26.20	2.7	2.1	2.89	2.83	
20.0	11.60	2.90							
10.0	5.68	2.84							
10.0	5.66	2.83							
10.0	5.76	2.88							
5.0	2.68	2.68							
5.0	2.70	2.70							
	Av.	2.84					Av.	2.86	2.71
		± 0.15						± 0.14	± 0.14

^a Determined by analysis of filtrate after filtration of the pentabromoacetone.

^b Calculated from Hartmann and Hillig's factor of 1.7 mg. per 100 cc. o reaction fluid.

^c From data in column 6.

^d From data in column 7.

The results in the table have not been corrected by the factor 1.12; when this is applied the average result by the sodium sulfide method is 3.18 per cent. When Hartmann and Hillig's factor of 1.05 is applied to the data obtained by the gravimetric method, the average result is 3.00 per cent from the data in column 8, or 2.84 per cent from the data in column 9. It would therefore appear that the sodium sulfide method gives slightly higher results than the gravimetric method. The difference, however, may be more apparent than real, inasmuch as it is largely a matter of the choice of factors.

LITERATURE CITED

- (1) Hartmann, B. G., and Hillig, F., *J. Assoc. Official Agr. Chem.*, 10, 264 (1927); 13, 99 (1930).
- (2) Kometiani, P. A., *Z. anal. Chem.*, 86, 359 (1931).
- (3) Kretov, A. E., Panchenko, A. N., and Savich, K. K., *J. Gen. Chem. (U. S. S. R.)*, 1, 419 (1931).
- (4) Kunz, R., *Arch. Chem. Mikroskop.*, 7, 285 (1914).
- (5) Pucher, G. W., Vickery, H. B., and Wakeman, A. J., *IND. ENG. CHEM., Anal. Ed.*, 6, 140 (1934).
- (6) Stahre, L., *Nord. Farmaceutik Tids.*, 2, 141 (1895).

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CORRECTION. In the paper, "Acidity Titration of Low-Grade Rosins," *IND. ENG. CHEM., Anal. Ed.*, 6, 122 (1934), references were not made to the work of Tingle, *J. Am. Chem. Soc.*, 40, 873 (1918), showing results obtained with the use of a pocket spectroscope in titrating sulfuric acid solutions colored by copper sulfate and by extracts of tea and stick licorice, or to the work of Macmillan and Tingle, *J. IND. ENG. CHEM.*, 12, 274 (1920), on determining the acidity of red wines and fruit juices. The omission of these references was inadvertent and the writer wishes to call attention to the work of these authors. W. C. SMITH

Double-Acid Method of Optical Analysis of Beet Products

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THE inadequacy of methods for the determination of sucrose and raffinose in beet products has been recognized for some time. The various modifications of the Clerget inversion are known to give questionable and inaccurate results, the errors being of unknown and varying magnitudes. Various procedures have been proposed to eliminate some of the sources of error, but the beet-sugar chemist has apparently found them wanting, as is evidenced by their failure to receive general acceptance.

The double-acid method described in this paper has been found both accurate and practical.

All beet-sugar products contain optically active substances of three classifications—sucrose, raffinose, and a group of polarizing nonsugars. In addition, small quantities of invert sugar, usually of negligible influence on the polarizations, are sometimes present. It is then self-evident that any single inversion method giving only two polarizations, the direct and inverted, and therefore only two equations, is inadequate. The beet chemist almost universally ignores the polarizing value of these nonsugars and therefore seldom, if ever, obtains accurate results. It will be shown that the magnitude of these errors is such that they cannot be rightfully ignored.

Another fault in the generally accepted methods is the use of various clarifiers or decolorizing agents in the inverted polarization. Even the best of these introduce no small discrepancies in the final results.

Appreciating the importance of the errors involved in the current single-acid inversion methods, Paine and Balch developed the double-enzyme method (1, 9, 10) which permits the evaluation of the three unknowns. This is admittedly the most basic and accurate method yet devised. Though this enzyme method filled a long recognized need in beet-sugar chemistry, it has not been accepted for general use because, if properly conducted, the enzyme inversions require more time than is usually available and the cost is prohibitive. The cost of the purchased enzymes used in the work reported in this paper was about \$1 per determination and it is doubtful that enzymes of as satisfactory quality can be prepared more cheaply. Anyone who has worked with enzymes is also familiar with the difficulty occasionally experienced of securing satisfactory enzyme preparations and of being sure of the completeness of the melibiase inversions.

A method previously proposed has been further developed for the determination of sucrose and raffinose in beet products which cannot be analyzed accurately by any single-acid inversion method. Advantage is taken of the fact that the optically active nonsugars become inactive in strongly acid solutions, as in a Clerget inversion, by making two acid inversions and polarizing one in its neutralized solution. The polarizing effects of this ammoniacal neutralization have been established, as well as the effects of leading and deleading upon the inversion constants. Analyses of molasses from widely separated districts, comparing the results by the established single-acid inversion methods, the double-enzyme method, and the newly proposed method, show the double-acid method to be comparable to the double-enzyme inversion method, whereas the single-acid inversion methods in general use give results that are seriously in error. Analyses of synthetic sirups by the double-acid method account satisfactorily for known amounts of sucrose added to beet molasses. The effect of molasses impurities upon inversion constants is considered in a preliminary manner.

The method has been developed and used at the Johnstown molasses refinery during the past 6 years, and is now offered as a substitute for the admittedly basic but impractical double-enzyme method.

What the beet-sugar chemist needs is a method that will give the actual sucrose and raffinose in a product at no great expenditure of time or money. The method offered here was developed with these thoughts in mind.

THEORY OF DOUBLE-ACID METHOD

It has often been noted that the polarizing effect of the optically active nonsugars becomes zero in a strongly acid solution, such as the 0.634 N hydrochloric acid of a Clerget inversion. This has been observed in the Research Laboratory of the Great Western Sugar Company, and has also been confirmed by Paine and Balch (9) and by Zerban (15). This does not necessarily hold true for raw beet juice, but has frequently been demonstrated to hold in all beet-factory products following carbonation, and it is with such products that the beet-sugar chemist is generally concerned when determining true sugar or raffinose. For the present the chemist should confine himself to the double-enzyme method with cossettes or diffusion juice, but further work as to the adaptability of this new method to these materials is anticipated. As offered here, the

new method is developed primarily for the accurate analysis of molasses, raw massecuite, and all other products following carbonation.

If it is tentatively accepted that the optical activity of the nonsugars becomes zero in a strongly acid solution and is restored upon neutralizing, it is possible to determine the polarizing effect of these substances. This can be done by making two acid inversions, polarizing the one in the acid and the other in its neutralized solution. The nonsugar effect is zero in the acid polarization, but has its full normal value in the neutralized solution. The difference between these two invert polarizations will then be the polarization of the nonsugars, after correcting for the effect involved in the neutralization itself. Hereafter the polarizing effect of these nonsugars, designated in a previous paper (16) as Z , will be termed the N value. The direct polarization may then be corrected for this contained N value, leaving only two unknowns, sucrose and raffinose, which can be calculated from the two equations. This is the basic principle of the double-acid method.

This method requires very little more time or expense than the single-acid inversion methods now in general use, and the results obtained are comparable to those by the double-

TABLE I. ANALYSES OF MOLLASSES, COMPARING DOUBLE-ACID AND DOUBLE-ENZYME METHODS

No.	SOURCE	STEFFEN OR NON-STEFFEN	CAMPAIGN	SUCROSE		RAFFINOSE		N VALUE	
				Double acid %	Double enzyme %	Double acid %	Double enzyme %	Double acid	Double enzyme
1	Gering, Nebr.	S	1932-33	45.54	45.82	3.68	3.61	-1.78	-1.84
2	Gering, Nebr.	S	1932-33	48.68	48.70	3.93	4.02	-1.96	-2.15
3	Scottsbluff, Nebr.	S	1932-33	49.12	49.32	3.03	3.06	-1.61	-1.87
4	Lyman, Nebr.	NS	1932-33	50.96	50.98	1.25	1.42	-1.54	-1.89
5	Bayard, Nebr.	NS	1932-33	49.63	49.56	1.38	1.47	-1.74	-1.83
6	Minatare, Nebr.	S	1932-33	47.44	47.31	2.65	2.87	-1.46	-1.72
7	Gering, Nebr.	S	1932-33	48.95	49.02	3.49	3.43	-2.07	-2.04
8	Mitchell, Nebr.	NS	1932-33	48.49	48.52	1.30	1.29	-1.69	-1.72
9	Gering, Nebr.	S	1932-33	48.10	48.38	4.18	4.09	-1.99	-2.10
10	Lyman, Nebr.	NS	1932-33	51.30	51.48	1.20	1.25	-1.56	-1.84
11	Greeley, Colo.	NS	1932-33	52.64	52.61	1.17	1.31	-1.61	-1.84
12	Windsor, Colo.	NS	1932-33	48.80	48.59	0.81	0.90	-1.62	-1.58
13	Windsor, Colo.	S	1932-33	48.52	48.46	2.71	3.03	-1.52	-2.05
14	Longmont, Colo.	S	1932-33	48.41	48.43	2.76	2.89	-1.59	-1.86
15	Sterling, Colo.	S	1932-33	47.00	46.82	3.11	3.22	-1.10	-1.12
	Johnstown, Colo.	S	1932-33	47.00	46.82	3.11	3.22	-1.10	-1.12
16	Grand Jet., Colo.	S	48.31	48.30	3.20	3.26	-1.12	-1.32
17	Windsor, Colo.	NS	1929-30	47.02	46.91	1.52	1.70	-1.42	-1.61
18	Fort Collins, Colo.	S	1929-30	48.90	49.07	3.57	3.43	-1.65	-1.57
19	Windsor, Colo.	NS	1929-30	47.92	47.71	1.54	1.55	-1.69	-1.50
20	Fort Collins, Colo.	S	1929-30	47.40	47.34	3.56	3.35	-1.96	-1.50
21	Billings, Mont.	S	1932-33	48.74	48.81	3.49	3.43	-1.18	-1.13
22	Lovell, Wyo.	NS	1932-33	49.48	49.38	1.57	1.75	-1.17	-1.41
23	Worland, Wyo.	S	1932-33	49.38	49.43	3.59	3.57	-1.23	-1.26
24	Paul, Idaho	S	1932-33	49.14	49.04	3.45	3.44	-1.49	-1.40
25	Idaho Falls, Idaho	S	1931-32	50.00	50.02	3.27	3.24	-1.28	-1.25
26	Garland, Utah	S	1931-32	49.74	49.52	2.94	3.10	-1.25	-1.42
27	Mt. Pleasant, Mich.	NS	1932-33	50.71	50.75	1.21	1.30	-2.95	-3.14
28	Caro, Mich.	S	1932-33	47.67	47.38	2.72	2.87	-2.00	-1.98
	Averages			48.86	48.85	2.58	2.64	-1.62	-1.71
	Differences				0.01		0.03		0.09

enzyme method, in almost all instances. As Lundell (7) has recently suggested, it is well to mention at this time the cases where the proposed method will not work.

If a molasses contains a large percentage of invert sugar or its decomposition products, dependable analyses cannot be obtained by the double-acid method. Examples of this will be shown later where California beet molasses were analyzed. However, the failure of the proposed procedure on such materials holds true also with any acid inversion method. The chemist must in this case resort to the double-enzyme inversions if definitely accurate results are desired, but the double-acid method will give more accurate results on such materials than will any of the single-acid methods in present use.

When first presented (16), the double-acid method was in more or less of an empirical stage, but during the past year considerable work has been done on the factors and constants involved, and the method has been applied to the analysis of a large variety of molasses and synthetic products with satisfactory results.

In the analyses reported herein, carefully standardized apparatus was used. The polariscope used was a Bausch and Lomb, double-field, single quartz wedge compensating, Bates and Jackson scale type. The polarizations reported are the averages of no less than ten observations after being corrected to Bureau of Standards tested quartz plates of the same or nearly the same optical value.

EXPERIMENTAL APPLICATIONS

The logical procedure for testing the accuracy of this double-acid method in a practical way was to apply it to the analysis of a variety of actual samples of known composition. The most severe test of any such method is with molasses in which the impurities, raffinose and optically active nonsugars, are concentrated to the highest degree. A large number of beet-molasses samples from widely separated districts covering the entire sugar-producing area of the United States were gathered for this purpose. Samples were obtained from many of the beet-sugar companies representing both Steffen and non-Steffen process houses, mostly from the 1932-33 campaign, but a few of earlier production. Such a variety should be representative of different beet-growing conditions and areas, as well as operating conditions.

All these samples were analyzed by the double-enzyme and double-acid methods. In the enzyme method the official A. O. A. C. procedure (1) was followed, with a few modifica-

tions. The enzyme inversions were made at room temperature and were allowed to stand for 24 hours to insure complete inversion. They were then made to volume, were covered with a few drops of toluene, and were left another 24 hours to eliminate mutarotation.

In both methods the original solution was made up at 1.0 *N* concentration (26 grams of molasses per 100 ml.), and the invert readings were made at 0.5 *N* concentration in a 400-mm. jacketed tube. Before completing the lead solution to volume, it was well deaerated under vacuum; experience has shown that the neglect of this precaution may in extreme cases cause an error of as much as 0.2° in the direct polarization of a molasses containing much entrained air. From the final values of both methods a deduction of 1.0 per cent was made to allow for the volume of the lead precipitates. This deduction, whether made or not, obviously affects both methods alike.

The acid inversions were made by the Walker procedure (14), slightly modified. The Browne and Gamble (4) inversion constants of -33.00 and 0.514 for sucrose and raffinose, respectively, were used in the calculation of the double-acid analyses. The negative constituent of the divisor was corrected in each case by the formula: $-(32.1 + 0.07g)$ where *g* is the grams of sucrose taken for the inversion. Some claim that the negative constituent varies with the total sugar or dry substance concentration in accordance with Vosburgh's rule (13) rather than with the sucrose concentration. However, since the official double-enzyme method (1), as used here, corrects the divisor on a sucrose basis, the divisors in the acid analyses were also based on sucrose to permit true comparisons. The neutralization correction in the double-acid analyses was obtained as later described.

The results by enzyme analysis were taken as the basic or true compositions of the various samples. The percentages of sucrose, raffinose, and the *N* values found by the two methods are shown in Table I.

In comparison with the enzyme values, the results in Table I leave little to be desired as to the dependability of the double-acid procedure. If Lundell's apt and logical suggestions (7) were followed, all such results would be recorded to only one decimal and the differences on individual samples would appear even smaller. However, even considering the unreasonable second decimal, the two methods check very closely, certainly well within analytical error limits.

The average raffinose by the two methods agrees within

less than 0.1. Previously (16) it was found necessary to apply a correction factor of 1.18 to the raffinose percentage found by double-acid inversion. The explanation of this discrepancy is uncertain but it is possible that in the former work proper consideration was not given mutarotation in either the acid or enzyme analyses. Slight changes and improvements have also been made in the general procedure of the new method. At any rate the double-acid method is now shown to give accurate raffinose values without the application of any arbitrary correction factor.

That the basic premise of this double-acid method is sound, is shown by the agreement between the *N* values determined by the double-acid and double-enzyme methods in Table I, the average difference again being less than one-tenth. The range of *N* values by both methods is about -1.0° to -2.0° (in one case, sample 27, -3.0°). In this connection it is interesting to compare the values of Kindt (6), who found, after complete fermentation of the sugars in molasses, residual *N* values of a range of -1.6° to -2.7° .

The double-acid, as well as any single-acid inversion, is not dependable when applied to a product containing an unusually high percentage of invert sugar or its decomposition products. This probably explains the fact that the double-acid and double-enzyme analyses of six California molasses do not check each other, as shown in Table II. It has not been definitely proved, however, whether the discrepancies are entirely due to this cause or whether the behavior of the optically active nonsugars in these molasses is partly responsible. These samples contained considerable invert sugar and were of such low pH that the presence of appreciable quantities of decomposition products was apparent. Even though the double-acid results on such materials are not very comparable to those by enzymes, they are more so than are the single-acid inversions. Any acid inversion method will not even approximate the true raffinose percentage in such materials if the enzyme figures are accepted as correct. Evidently, the chemist working with such products has a problem peculiarly his own and must resort to enzyme inversions if the true compositions of his materials are required.

Too much attention must not be given the *N* values in Table II because, as determined by enzymes, they are too high. Invert sugar, and probably its decomposition prod-

ucts, cause the *N* value as calculated from enzyme inversions to be falsely large.

In Table III are shown the sucrose percentages in fifteen molasses samples as determined by three modifications of the commonly used single-acid methods compared to the double-acid and the basic double-enzyme results. The beet-sugar chemist has generally been reporting the sucrose in molasses from 1 to 3 per cent too low, as the result of the inadequacy of the methods used. In fact, when these results are expressed in terms of true purity, his results have been as much as 4.3 points too low and seldom within 1 point of the true value. Such discrepancies are too great to be continually ignored, either by the chemist or by the industry as a whole.

Unfortunately the methods now in common use do not give results that are low by any consistent amount. As shown in Table III, a result may be within 0.1 of the truth with one molasses, yet on another low by over 3.0 points. To make the case against the methods now in general use even more serious, they are not low by any consistent value at a given factory during one campaign. It has been found that the true purity of molasses was reported from 0.77 to 2.62 low at one factory during the past campaign and from 0.98 to 3.10 low at another. As a result of these errors it is difficult, if possible at all, to compare operating results from one time to another. This very likely explains why extraction does not always coincide with reported changes in molasses purities.

Though the predominating cause of the errors in the single-acid inversion methods lies in ignoring the *N* value, the reagents used for decolorizing the inversions cause appreciable and variable errors. The double-acid method inverts the same leaded and delead solution that is used for the direct polarization, as is the case with the enzyme inversion. However, even if the single-acid inversions were also commonly made on the leaded and delead solution, the results would be low by very inconsistent amounts, due to the variations in the *N* values. As shown in Table I, the *N* value varies in molasses from different districts from -1.12 to -3.14 and even greater variations have been found. Again, this *N* value is not consistent for a given factory or district. During one campaign at one factory the polarizing effect of these nonsugars varied from -1.17 to -2.67 and at another from -0.87 to -2.37° S.

TABLE II. ANALYSES OF CALIFORNIA MOLASSES
(Double-acid, double-enzyme, and single-acid inversion)

No.	SOURCE	STEFFEN OR NON-STEFFEN	CAMPAIGN	SUCROSE			RAFFINOSE			-N VALUE-		pH	INVERT SUGAR ON DRY SUBSTANCE
				Double acid %	Double enzyme %	Single acid %	Double acid %	Double enzyme %	Single acid %	Double acid	Double enzyme		
29	Santa Ana	S	1932	47.62	46.48	47.16	-0.37	0.61	-0.51	-1.55	-2.24	6.0	2.93
30	Alvarado	NS	1932	50.19	49.49	47.54	-0.51	0.30	-0.29	-2.09	-2.85	6.9	0.61
31	Oxnard	S	1932	48.53	48.39	45.72	0.39	1.10	1.36	-1.96	-3.15	6.9	1.20
32	Santa Ana	S	1933	53.77	51.49	48.24	-0.55	0.84	1.14	-2.13	-2.46	7.1	1.88
33	Alvarado	NS	1933	51.94	51.12	49.90	-0.08	0.56	-0.08	-2.04	-2.44	7.6	0.68
34	Tracy	S	1933	52.42	52.18	...	0.50	0.84	-1.62	-1.98	7.0	0.64

TABLE III. PER CENT SUCROSE IN MOLASSES
(Double-acid, single-acid, and double-enzyme methods)

SAMPLE	DOUBLE ACID		DARCO CARBON ^b		SINGLE ACID HYDROSULFITE ^b		Sucrose	ZINC ^b		DOUBLE ENZYME SUCROSE
	Sucrose	Difference ^a	Sucrose	Difference ^a	Sucrose	Difference ^a		Sucrose	Difference ^a	
2	48.68	-0.02	45.26	-3.44	48.70	
3	49.12	-0.20	46.40	-2.92	49.32	
4	50.96	-0.02	49.67	-1.31	50.63	-0.35	50.80	-0.18	50.98	
5	49.63	0.07	47.84	-1.72	48.85	-0.71	48.91	-0.65	49.56	
6	47.44	0.13	45.10	-2.21	45.81	-1.50	45.86	-1.45	47.31	
7	48.95	-0.01	45.76	-3.20	46.99	-1.97	47.12	-1.84	48.96	
8	48.49	-0.03	46.95	-1.57	47.92	-0.60	48.52	
9	48.10	-0.28	45.02	-3.36	46.30	-2.03	48.38	
10	51.30	-0.18	50.50	-0.98	51.46	-0.02	51.48	
11	52.64	0.03	51.20	-1.41	51.88	-0.73	52.29	-0.32	52.61	
12	48.80	0.21	46.89	-1.70	47.60	-0.99	47.82	-0.77	48.59	
13	48.52	0.06	46.06	-2.40	47.26	-1.20	47.14	-1.32	48.46	
14	48.41	-0.02	45.90	-2.53	46.63	-1.80	46.80	-1.63	48.43	
21	48.74	-0.07	46.46	-2.35	47.47	-1.34	47.64	-1.17	48.81	
22	49.48	0.10	46.85	-2.53	47.94	-1.44	49.38	

^a Difference from the enzyme results.

^b Decolorizers used on the inversions. Sample numbers agree with those in Table I.

The results in Table III strongly indicate the need of a change in methods by the beet-sugar chemist, and the same results, along with those of Table I, show the superiority of the double-acid method over those in common use.

ANALYSIS OF SYNTHETIC MIXTURES

One of the prime requisites of a method is that it will truthfully tell how much sugar has been crystallized out and removed when a sirup of a given high purity has been reduced to a molasses of definite purity. The simplest way to test a method for this purpose is to reverse this condition by adding a known amount of sucrose to a given amount of molasses and then to analyze the molasses and the resulting synthetic sirup of enriched purity. This was done with three different molasses and the sucrose was determined by the double-acid method. As a matter of interest the enzyme analyses were also determined on two of these samples. The percentages of sucrose, raffinose, and *N* values found by analysis as compared to the actual compositions, calculated from the original molasses and sugar added, are given in Table IV.

TABLE IV. SUGAR ADDITION TESTS

METHOD	EXPERIMENT					
	EXPERIMENT 1		EXPERIMENT 2		EXPERIMENT 3	
	Double acid	Double enzyme	Double acid	Double enzyme	Double acid	Double enzyme
Original molasses, per cent sucrose	48.76	48.84	49.82	49.84	47.58	
Original molasses, per cent raffinose	1.29	1.26	1.10	1.26	3.00	
Original molasses, <i>N</i> value	-1.66	-1.74	-1.40	-1.70	-1.32	
Mixture, grams molasses	30.000	30.000	30.000	30.000	30.000	
Mixture, grams sucrose	100.048	100.048	100.075	100.075	99.990	
Per cent sucrose found	88.14	88.17	88.44	88.44	87.83	
Per cent sucrose calculated	88.18	88.20	88.43	88.43	87.90	
Difference	-0.04	-0.03	-0.01	-0.01	-0.07	
Per cent raffinose found	0.39	0.30	0.37	0.32	0.77	
Per cent raffinose calculated	0.30	0.29	0.25	0.29	0.69	
Difference	0.09	0.01	0.12	0.03	0.08	
<i>N</i> value found	-0.42	-0.18	-0.34	-0.24	-0.35	
<i>N</i> value calculated	-0.38	-0.40	-0.32	-0.39	-0.30	
Difference	-0.04	0.22	-0.02	0.15	-0.05	

At first it was planned to purify the sucrose used in these sugar addition tests, but a highly refined AA sugar from a west coast refinery was obtained of such quality that it was deemed unnecessary. This sugar gave an ash of only 0.003 per cent by incineration and had a specific conductance of 0.26 which corresponds to about 0.001 per cent soluble ash. The invert sugar content was found to be less than 0.003 per cent as determined by Schoorl's method using Luff's solution (11, 12). The sugar polarized 100.0 when tested against a Bureau of Standards quartz plate of 100.75° S. This sugar was therefore used as sucrose in this and all following work, after making the proper corrections for the small amount of contained moisture.

The results in Table IV show the double acid to be thoroughly dependable from one purity to another because the quantity of sugar added to, or removed from, a sirup can be accurately determined by its use. The original molasses used in these tests were of about 60 purity and the enriched molasses, or synthetic sirups, were of about 93 purity, a range in purities which covers those usually encountered in actual practice.

The double-acid method also permits the accurate determination of raffinose and *N* value as well as sucrose, upon diluting these substances with a large amount of sugar. Table IV indicates that under such a test the double-acid method is as reliable a procedure as the double-enzyme inversion.

AGREEMENT OF DIFFERENT ANALYSTS

Experience has shown that different analysts, working independently, can check their own and one another's results within satisfactory limits by the double-acid method. Table

V indicates just as satisfactory an agreement by the double-acid as by the double-enzyme method.

TABLE V. CHECK ANALYSES BY TWO ANALYSTS, PER CENT SUCROSE IN MOLASSES

SAMPLE	DOUBLE ACID			DOUBLE ENZYME		
	Jones	Kingsley	Difference	Jones	Kingsley	Difference
1	45.54	45.53	0.01	45.84	45.79	0.05
2	48.70	48.67	0.03	48.73	48.66	0.07
3	49.13	49.10	0.03	49.26	49.37	0.11
4	51.04	50.89	0.15	50.94	51.01	0.07
9	48.06	48.14	0.08	48.36	48.40	0.04
10	51.28	51.32	0.04	51.58	51.37	0.21
11	52.66	52.63	0.03	52.56	52.66	0.10
15	47.00	46.99	0.01	46.81	46.82	0.01
16	48.14	48.47	0.33	48.15	48.44	0.29
21	48.73	48.75	0.02	48.74	48.88	0.14
23	48.41	49.34	0.07	49.49	49.37	0.12
24	49.35	48.94	0.41	49.20	48.87	0.33
25	50.04	49.95	0.09	49.98	50.05	0.07
26	49.76	49.72	0.04	49.58	49.46	0.12
27	50.76	50.65	0.11	50.79	50.71	0.08
28	47.65	47.64	0.01	47.20	47.56	0.36

For further information two molasses samples were sent to each of nineteen laboratories and were analyzed by the double-acid procedure. Although few of the chemists had had any experience with the new method, the results showed a very satisfactory agreement.

NEUTRALIZATION CORRECTION

The double-acid method requires the neutralization of one of the acid inversions before polarization, and the effect of the neutralization on the rotation of invert sugar has to be established and taken into consideration. Jackson and Gillis (5) have shown the advantages of neutralizing the hydrochloric acid with ammonia rather than sodium hydroxide. They also determined the effect of neutralizing an acid inverted solution, containing 10 ml. of 6.34 *N* hydrochloric acid, with 10 ml. of 6.34 *N* ammonium hydroxide.

While Jackson and Gillis employed a constant sucrose concentration, Brown (2) afterwards pointed out that the effect of salts on polarization could be expressed in a general formula in which the effect is made proportional to both sucrose and salt concentration. On this basis the Jackson and Gillis values indicate that in the neutralized inversion the presence of the ammonium chloride and the absence of the hydrochloric acid should increase the numerical value of the acid polarization by 0.0066 *S*, where *S* is the percentage sucrose concentration. When first offered, this method used a neutralization correction of 0.33 for molasses of 50 per cent average sucrose concentration.

Jackson and Gillis did their work on pure aqueous solutions of sucrose, but in the double-acid method the inversions and neutralizations are made upon solutions that have been previously leached with basic lead acetate and delead with ammonium dihydrogen phosphate. It seemed reasonable that the presence of the resulting ammonium acetate and acetic acid would have some effect upon this neutralization correction.

To establish the neutralization effect at various sucrose concentrations, with different amounts of basic lead acetate (55° Brix) followed by deleading with ammonium phosphate, three curves were determined as shown in Figure 1.

A represents the neutralization effect, as sugar degrees, at different sucrose concentration when 20 ml. of lead acetate were added to each 100 ml. of a solution, 50 ml. of which were used for inversion after deleading. This is the amount of lead reagent ordinarily used in the analysis of molasses. The resulting straight-line curve gives the neutralization correction as 0.0081 *S*.

B is plotted from the results found at various sucrose concentrations when no lead acetate was used. The correction under these conditions is 0.0047 *S*. Although this does not coincide with the value of 0.0066 *S* calculated from Jackson and Gillis' data, it represents the necessary correction as found by the authors when the neutralization is made under the specified conditions.

It is evident from Figure 1 that the ammonium acetate and acetic acid resulting from leading and deleading increase the polarizing value of the neutralization correction. At 100 sucrose concentration, 20 ml. of lead increase the correction by 0.34° S, or the difference between 0.47 and 0.81. This difference decreases as the sucrose concentration approaches zero, at which point the correction becomes zero regardless of the amount of lead used.

C was determined and plotted with the use of 4.6 ml. of lead acetate per 100 ml., to prove the neutralization correction to be proportional to the lead acetate used at any given concentration of sucrose. This rather odd amount of lead was used because it was that used in the enriched molasses sirups of about 88 per cent sugar given in Table IV.

In all the experiments plotted in Figure 1, the neutralizations were made by slowly adding 6.34 N ammonium hydroxide to the cooled acid invert with methyl red as the internal indicator. The solution was whirled while adding the ammonia, to avoid destruction of invert sugar by localized concentration of the ammonia. In all tests exactly 1 ml. of excess ammonia was added. This is specified to assure polarization of the neutralized invert in alkaline solution in which the nonsugars have their full optical value. This excess has been found not to change the polarization by any determinable amount.

Figure 1 shows this neutralization correction to be proportional to the two variables, sucrose concentration and milliliters of lead acetate used. From A and B the correction for 5 per cent sucrose concentration intervals and 2 ml. lead acetate intervals were calculated, as given in Table VI. C, determined experimentally, coincides with such a line calculated from the differences between A and B.

Raffinose concentration apparently has little, if any, effect upon this neutralization correction. A solution containing 17 per cent raffinose gave a neutralization effect of only 0.08° S when 20 ml. of lead acetate were used and a 32 per cent solution gave a correction of only 0.12° S. Mixtures of sucrose with as much as 20 per cent raffinose were found to give neutralization corrections within less than 0.10° S of that for the sucrose alone. Therefore in the practical applications of this method it is necessary to consider only the sucrose concentration when using Table VI.

It is somewhat inconvenient to estimate the sucrose concentration for the factors from which sucrose is to be calculated. For all general purposes no appreciable error will be introduced into the calculation if the direct polarization *P* is used instead of *S*, when taking the neutralization correction from Table VI. *P* is generally greater than *S* on account of the raffinose present, but unless the raffinose percentage is

much greater than is generally encountered, the difference is negligible when applying the neutralization correction.

While the neutralization correction has been worked out in considerable detail to cover all conditions, it may be simplified for practical purposes by using a constant value for any particular product. Thus, for molasses clarified with 20 ml. of lead subacetate per 26 grams, the value of 0.40 may be

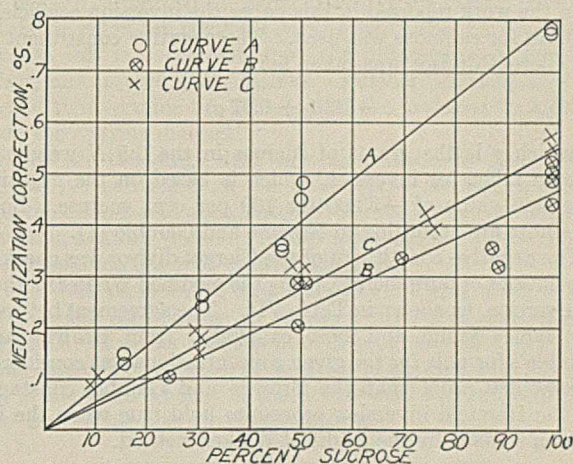


FIGURE 1. NEUTRALIZATION CORRECTION

used, which corresponds to 49 per cent sucrose and will not vary essentially within the ordinary range of sucrose percentage in molasses.

INVERSION CONSTANTS

The method of inversion used in all this work was that suggested by Walker (14), slightly modified. Walker proposed heating the solution to 65° C., then adding the hydrochloric acid, and allowing to cool spontaneously for at least 15 minutes. However, in the latter part of his paper he suggests heating to 67° C. With low-grade products, such as beet molasses, a little difficulty has been found in obtaining complete inversion when the solution is heated to only 65° C., and for this reason the solutions in this method are heated to 68° to 69° C. Upon adding the 10 ml. of hydrochloric acid (d₄²⁰ 1.029) the temperature at the start of inversion was found to be 64° C., dropping at the rate of about 1° per minute to 53° C. at the end of 15 minutes. This temperature is therefore somewhat comparable to that suggested by Jackson and Gillis (5). This modification of Walker's procedure was used in preference to that of Jackson and Gillis, because

TABLE VI. NEUTRALIZATION CORRECTION

CONCENTRATION ^a PER CENT SUCROSE	LEAD SUBACETATE (55° BRIX)											
	ML./100 ml.											
	0	2	4	6	8	10	12	14	16	18	20	
5	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.04	0.04	
10	0.05	0.05	0.05	0.06	0.06	0.06	0.07	0.07	0.08	0.08	0.08	
15	0.07	0.08	0.08	0.09	0.09	0.09	0.10	0.11	0.11	0.12	0.12	
20	0.09	0.10	0.11	0.11	0.12	0.13	0.13	0.14	0.15	0.16	0.16	
25	0.12	0.13	0.13	0.14	0.15	0.16	0.17	0.18	0.19	0.19	0.20	
30	0.14	0.15	0.16	0.17	0.18	0.19	0.20	0.21	0.22	0.23	0.24	
35	0.16	0.18	0.19	0.20	0.21	0.22	0.24	0.25	0.26	0.27	0.28	
40	0.19	0.20	0.22	0.23	0.24	0.26	0.27	0.28	0.30	0.31	0.32	
45	0.21	0.23	0.24	0.26	0.27	0.29	0.30	0.32	0.33	0.35	0.36	
50	0.24	0.25	0.27	0.29	0.30	0.32	0.34	0.35	0.37	0.39	0.41	
55	0.26	0.28	0.30	0.31	0.33	0.35	0.37	0.39	0.41	0.43	0.45	
60	0.28	0.30	0.32	0.34	0.36	0.38	0.40	0.42	0.45	0.47	0.49	
65	0.31	0.33	0.35	0.37	0.39	0.42	0.44	0.46	0.48	0.50	0.53	
70	0.33	0.35	0.38	0.40	0.42	0.45	0.47	0.50	0.52	0.54	0.57	
75	0.35	0.38	0.40	0.43	0.45	0.48	0.51	0.53	0.56	0.58	0.61	
80	0.38	0.40	0.43	0.46	0.48	0.51	0.54	0.57	0.59	0.62	0.65	
85	0.40	0.43	0.46	0.49	0.52	0.54	0.57	0.60	0.63	0.66	0.69	
90	0.42	0.45	0.48	0.51	0.55	0.58	0.61	0.64	0.67	0.70	0.73	
95	0.45	0.48	0.51	0.54	0.58	0.61	0.64	0.67	0.70	0.74	0.77	
100	0.47	0.50	0.54	0.57	0.61	0.64	0.67	0.71	0.74	0.78	0.81	

^a Direct polarization *P* may be used instead of per cent sucrose.

it is more convenient for a large number of determinations at one time and the manipulation is somewhat more fool-proof.

The inversions were all allowed to stand 2 hours before cooling and making to volume. Two hours were taken to assure complete inversion and allow as much time for the destruction of mutarotation as would generally be permissible in actual practice.

In the work reported in this paper the inversion coefficient of 0.514 for raffinose was used. The negative constituent of the Clerget divisor was taken as:

$$-(32.1 + 0.07 g)$$

in which g is the grams of sucrose in the 0.5 N weight of sample taken for inversion, which is based on the negative inversion value of -33.00 for 100 per cent sucrose. Both constants are according to Browne and Gamble (4).

The negative constituent of the Clerget divisor was checked on solutions of pure sucrose, using the modified Walker method of inversion, as shown in Table VII. The agreement between the values found and those calculated from Browne and Gamble's formula for the given concentrations was considered satisfactory proof that the Browne and Gamble constants for the Herzfeld inversion procedure hold true when the inversion is made by the modified Walker method.

TABLE VII. INVERSION CONSTANT OF SUCROSE (MODIFIED WALKER METHOD)

(No lead acetate added)				
SUCROSE %	SUCROSE USED IN INVERSION Grams	OBSERVED IN 400-MM. TUBE	CALCULATED TO 100 SUCROSE	BROWNE AND GAMBLE
50.000	6.500	-16.27	-32.54	-32.56
88.089	11.451	-28.81	-32.71	-32.90
24.872	3.233	- 8.10	-32.57	-32.33
69.492	9.034	-23.75	-32.74	-32.73
50.098	6.513	-16.28	-32.50	-32.56
50.098	6.513	-16.24	-32.42	-32.56
88.493	11.504	-29.21	-33.01	-32.91
88.742	11.536	-29.20	-32.90	-32.91
		Av.	-32.67	-32.68

This basic negative constituent of -33.00 was determined by Browne and Gamble on pure sugar solutions, but the inversions in the double-acid method are made in the presence of the ammonium acetate and acetic acid resulting from the leading and deleading of the sample before inversion. This salt and acid were found to have a slight effect upon the inversion constant.

Sugar solutions of various concentrations were leaded and delead with the amounts of lead corresponding to the purity of a beet product of such sugar contents. For 50 per cent sugar, 20 ml. of lead acetate were used as in a molasses, proportionally less at higher sugar concentrations. The invert polarizations found are given in Table VII. The differences between the values found and those of Browne and Gamble for the given concentrations are also shown.

It would appear that the inversion constant, when made on leaded and delead solutions, is about 0.21 numerically less than when determined with pure aqueous solutions. The higher differences found with the 96 per cent solutions indicate that the inversion value becomes less as the sucrose concentration approaches 100.

If the results given in Table VII are accepted, the basic negative constituent becomes -32.79 instead of -33.00 . Such a change in the Clerget divisor would lower a determined sucrose percentage by about 0.10. Since the adoption or rejection of this change in the inversion constant involves such a small difference in the analytical results, Browne and Gamble's -33.00 is used in the double-acid method. However, it is hoped that other data as to the effect of leading and deleading upon the inversion constants will be presented, for

such data would be of general value and would probably apply to the enzyme as well as the acid formulas.

The raffinose inversion coefficient for the modified Walker inversion method was determined with the use of a very pure raffinose prepared by Hungerford and Nees. The results showed some variation and the average was a little lower than the Browne and Gamble value of 0.514. Fortunately, however, the structure of the Creydt formula is such that small variations in the raffinose coefficient have little effect upon the calculated sucrose or raffinose percentages. The value of 0.514 has been accepted and used in this work.

In the double-acid method the Clerget divisor is taken as proportional to the concentration of sucrose rather than dry substance. Several investigators have confirmed Vosburgh's rule (13) that the divisor is proportional to total sugar concentration and some prefer to make it proportional to dry substance in the analysis of an impure product. The authors have not been able to find any definite evidence in the literature that this divisor varies with the total dry substance of such materials as molasses. As the amount of raffinose in beet products is relatively small, it makes little difference whether it is considered in evaluating the divisor.

As is the case with the neutralization correction, for all general purposes the Clerget divisor may be taken as being proportional to the direct polarization P rather than S . However, dry substance may be used by those who prefer this basis.

The acid inversions from some molasses are so dark that it is difficult to read them with any reasonable degree of accuracy in the ordinary polariscope. Several methods of overcoming this are open to the analyst, such as using shorter polariscope tubes, more dilute solutions, or some decolorizer. The last mentioned has been chosen as introducing the least chance of error.

To insure inverted solutions of light enough color to permit accurate polarizations, 0.1 gram of sodium hydrosulfite is added when necessary to the invert solution just before adding the Clerget acid. This small amount of hydrosulfite has been found sufficient to decolorize the delead solution of even the darkest molasses without introducing any determinable error. Browne (3) mentions the objection to the use of this salt as a decolorizer, but he is speaking of greater amounts than the 0.1 gram used in this method. It has been found in a great many tests that this small amount of sodium hydrosulfite does not affect the invert polarization to any amount readable in the polariscope. In Table VIII some of the inversions were made with and some without this hydrosulfite, yet no different invert values were found.

TABLE VIII. INVERSION CONSTANT OF SUCROSE (MODIFIED WALKER METHOD) AFTER LEADING AND DELEADING

SUCROSE %	SUCROSE USED FOR INVERSION Grams	OBSERVED IN 400-MM. TUBE	NEGATIVE POLARIZATION Calculated to 100 sucrose	Browne and Gamble	DIFFERENCE
50.383	6.549	-16.30	-32.34	-32.56	-0.23
49.634	6.452	-16.05	-32.34	-32.55	-0.21
49.634	6.452	-16.05	-32.34	-32.55	-0.21
88.660	11.526	-28.99	-32.70	-32.91	-0.21
88.677	11.528	-28.98	-32.68	-32.56	-0.23
49.995	6.499	-16.22	-32.44	-32.56	-0.16
49.995	6.499	-16.20	-32.40	-32.56	-0.16
96.139	12.498	-31.53	-32.79	-32.97	-0.18
96.139	12.498	-31.38	-32.63	-32.97	-0.34
96.256	12.513	-31.38	-32.60	-32.98	-0.38
96.256	12.513	-31.43	-32.65	-32.98	-0.33
96.256	12.513	-31.43	-32.63	-32.55	-0.22
49.950	6.494	-16.15	-32.33	-32.55	-0.22
49.950 ^a	6.494	-16.16	-32.35	-32.55	-0.20
49.950	6.494	-16.15	-32.33	-32.55	-0.22
49.950 ^b	6.494	-16.18	-32.39	-32.55	-0.16
49.992	6.499	-16.18	-32.37	-32.55	-0.18
49.992 ^a	6.499	-16.20	-32.40	-32.55	-0.15
49.992	6.499	-16.21	-32.42	-32.55	-0.13
49.992 ^b	6.499	-16.18	-32.37	-32.55	-0.18

Av. -0.21

With 0.1 gram of sodium hydrosulfite in the inversion:

LEAD PRECIPITATE VOLUME

As in any accurate analysis of an impure product, the double-acid method requires a correction for the volume of the lead precipitate. With most beet-sugar products, especially molasses, the error caused by this precipitate volume cannot be avoided by the use of dry lead acetate, as is the case with comparatively high-grade raw sugars which require a very small lead addition. With beet molasses it is customary to add 20 ml. of lead subacetate per normal weight of sample. The addition of an equivalent amount of dry lead would cause appreciable volume changes of which it would be impossible to take account.

Brown has found in numerous determinations by his centrifugalization method (8) an average value of 1 ml. for the precipitate volume of a normal weight of molasses clarified with 20 ml. of lead subacetate (55° Brix) and made to 100 ml. There is some variation in different molasses, but this is relatively small. Therefore in the analysis of molasses, 1 per cent of the sucrose and raffinose is deducted from the calculated percentages to correct for the concentration error resulting from this precipitate volume. Similar corrections should be made for other products according to the purity and amount of lead subacetate added. Corrections of the same kind should also apply in the double-enzyme method.

IMPURITY EFFECTS

The impurities, other than the optically active nonsugars represented by the N value, may be termed the molasses impurities. Although presumably themselves optically inactive, they do affect the polarizations, both direct and inverted. This is what is sometimes called the salt or concentration effect. The literature presents very little information on this subject, yet it is fundamental. In the analysis of beet products by the double-enzyme method, Brown (2) has pointed out the desirability of attempting to eliminate the salt effect by always making the direct polarization at twice the concentration at which the invert polarization is made, because the Jackson and Gillis data (5) show that the effect of inorganic salts on the polarization of invert sugar is about twice that on the polarization of sucrose.

To obtain data on the magnitude of these effects, a Steffenized molasses was leached and de-leached in the usual manner with basic lead acetate and ammonium phosphate, and all the raffinose and sucrose were then fermented off by repeated inoculations with bottom yeast, the alcohol being distilled off at reduced temperatures between fermentations. After four fermentations, the absence of sucrose and raffinose was confirmed by both invertase and melibiase inversions.

From this impurity solution and pure sucrose, a synthetic sirup of 60 purity containing approximately 50 per cent sucrose was prepared and analyzed. The results were surprising.

The analysis of the synthetic mixture gave the following results as compared with the calculated values for the sucrose alone. The acid invert value was arithmetically decreased by 0.95° S. The observed direct polarization was lowered 0.83° S. When corrected for the determined N value, the direct polarization was increased 1.09° S.

The impurities evidently move both the invert and corrected direct polarizations to the right by approximately equivalent amounts. However, when the raffinose formula is applied, the calculated percentage of sucrose is decreased by about 0.46. The net effect therefore tends to give sucrose results that are falsely low.

Paine and Balch (9) found the direct polarization to be decreased by the addition of nonsugar molasses impurities to a smaller extent than the invert is increased. This appears to be in contradiction to the writers' observations, but is not necessarily so. Paine and Balch were considering the total effect of the impurities, including the depressing influence of the optically active nonsugars or N value, which was doubt-

less a negative value. The authors also found the total effect to decrease the direct polarization, but after correcting for the determined N value the net effect was to increase the polarization. It is probable that the same actually held true with the impurities used by Paine and Balch. The effects upon the inversions cannot very well be compared, because Paine and Balch used enzymes while the authors' results were on acid inversions. If the enzyme inversion values are shifted to the right to the same extent as the direct, no error is introduced in the resulting sucrose by the enzyme formula, because this is dependent upon the difference between the direct and invert polarizations. Further investigation is needed to determine the net effect of the molasses impurities upon the enzyme method.

Since all the single-acid inversion methods give lower sucrose percentages than the double-acid method, the fact that the double-acid apparently gives results that are slightly low on low-purity products makes the case against the methods in common use even more pronounced.

This work on molasses impurities has not progressed to the point where any change in the acid inversion constants is suggested. Further work is now in progress. For the time being this salt or concentration effect of the molasses impurities is therefore ignored in the double-acid method, which is also true of all acid inversion methods.

DETAILS OF DOUBLE-ACID METHOD

The double-acid method gives three determined polarizations, the direct (P), the invert read in the acid solution (I), and the neutralized invert (I'). After applying the proper neutralization correction to I' , the algebraic difference between I and the corrected I' is the polarizing effect of the nonsugars, or N . This is generally a negative value and when subtracted algebraically from P gives what the direct polarization would have been if it had not been affected by the N value. This corrected direct polarization, designated P' , is then the polarization of the sucrose plus raffinose and may be used in the usual Clerget formula in conjunction with I to calculate the sucrose and raffinose percentages.

Several different formulas may be set up on this basis to calculate a double-acid analysis. As presented here, the Clerget divisor is taken to vary with the sucrose concentration, or with the direct polarization as approximately representative of the total sugars present. If desired, it may be taken as proportional to dry substance. The same may be said of the neutralization correction K in the formulas as taken from Table VI.

The double-acid method in detail may be given as:

Transfer 130 grams of the sample, or its equivalent, to a 500-ml. Kohlrausch flask, add the necessary basic lead acetate, and make to 400 to 450 ml. with water. Deaerate under vacuum until all visible gas bubbles are removed, using a few drops of ether or amyl alcohol to break the foam if necessary. Make to 500 ml. at 20° C., mix, and filter. Deleach the filtrate with the minimum of powdered ammonium dihydrogen phosphate, and filter, using a little filter aid if desired. Polarize in a 200-mm. tube to obtain the direct polarization P .

Pipet 50 ml. of the de-leached filtrate into each of two 100-ml. Kohlrausch flasks. Add 15 ml. of water and heat to 68° to 69° C. in a 70° C. water bath. Remove from bath and immediately add 10 ml. of hydrochloric acid (d_4^{20} 1.029). Allow to cool spontaneously for 2 hours and then cool to 20° C. Make the one invert to 100 ml. at 20° C., mix, filter if necessary, and polarize at 20° C. in a 400-mm. tube, the reading being the invert polarization I . To the second invert add 1 or 2 drops of 0.2 per cent methyl red indicator solution and neutralize with 6.34 N ammonium hydroxide, adding the ammonia very slowly from a buret while constantly whirling the flask. Then add exactly 1 ml. in excess. Make to 100 ml. at 20° C., filter if necessary, and polarize in a 400-mm. tube, to obtain the neutralized invert polarization I' .

The N value, sucrose, and raffinose are then calculated by the formulas:

$$\frac{N}{P'} = \frac{I' - I + K}{P - N}$$

$$S = \frac{0.514 P' - I}{0.514 + (0.321 + 0.00009 S)} = \frac{0.514 P' - I}{0.835 + 0.00009 S}$$

$$\text{or } \frac{0.514 P' - I}{0.514 + (0.321 + 0.00009 P)} = \frac{0.514 P' - I}{0.835 + 0.00009 P}$$

$$R = 0.54 (P' - S)$$

where N = polarizing effect of the optically active nonsugars
 P' = true direct polarization of the raffinose and sucrose
 S = per cent sucrose
 R = per cent raffinose
 K = neutralization correction, to be obtained from Table VI as proportional to either S or P and milliliters of lead used per 100 ml. of leaded solution

The following notes on the technic of the method may be of value:

1. If amyl alcohol is used to break the foam while deairing, do not use more than 3 or 4 drops, because this alcohol is optically active and is not volatile at room temperatures.

2. Make all filtrations under wetted bell jars resting on wetted rubber mats, or with the filters covered with large cover glasses. Discard the first 10 to 15 ml. of each filtrate.

3. The amount of ammonium phosphate necessary to delead may be determined by adding small incremental amounts and testing for complete precipitation by testing a drop with a solution of potassium iodide or with a further crystal of ammonium phosphate. An undue excess of phosphate must be avoided, for each 1 gram excess per 100 ml. depresses the direct polarization $0.35^\circ S$.

4. As much as 0.1 gram of sodium hydrosulfite may be added with the inverting acid if the solution is dark.

5. The calculated percentages of sucrose and raffinose should be corrected for the volume of the lead precipitate. In molasses this may be done by deducting 1 per cent of the calculated percentage from itself. This correction will be proportionately less on higher purity products, varying with the decrease in impurities and amount of lead acetate used.

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LITERATURE CITED

- (1) Assoc. Official Agr. Chem., Official and Tentative Methods, p. 373 (1930).
- (2) Brown, *IND. ENG. CHEM.*, 17, 39 (1925).
- (3) Browne, "Handbook of Sugar Analysis," p. 221, Wiley, 1912.
- (4) Browne and Gamble, *J. IND. ENG. CHEM.*, 13, 793 (1921).
- (5) Jackson and Gillis, *Bur. Standards, Sci. Paper* 375, 169-71 (1920).
- (6) Kindt, *Ind. saccar. ital.*, 26, 50 (1933).
- (7) Lundell, *IND. ENG. CHEM., Anal. Ed.*, 5, 221 (1933).
- (8) Osborn and Brown, *Facts About Sugar*, 27, 434 (1932).
- (9) Paine and Balch, *IND. ENG. CHEM.*, 17, 240 (1925).
- (10) Paine and Balch, *J. Am. Chem. Soc.*, 49, 1019 (1927).
- (11) Schoorl, *Arch. Suikerind.*, 33, 273 (1925).
- (12) Schoorl, *Z. Untersuch. Lebensm.*, 57, 566 (1929).
- (13) Vosburgh, *J. Am. Chem. Soc.*, 43, 219 (1921).
- (14) Walker, *J. IND. ENG. CHEM.*, 9, 490 (1917).
- (15) Zerban, *J. Assoc. Official Agr. Chem.*, 12, 158 (1929).
- (16) Zisch, *Facts About Sugar*, 27, 211 (1932).

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Determination of Minute Quantities of Sulfide Sulfur

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THE method developed in the western branch laboratory of the National Canners Association for the determination of small quantities of volatile sulfide sulfur is a modification of that described by Drushel and Elston (3). The principal differences are in the method of evolution and the type of apparatus used in collecting the stain on the lead acetate paper. The sulfide gas upon evolution from an acid solution is continuously carried along and through a lead acetate-impregnated paper diaphragm by a stream of an inert gas such as nitrogen. The nitrogen, by intimately diluting the sulfide gas, permits a uniform coating of lead sulfide and sweeps the reaction flask free from residual sulfide gas. A uniform deposition of the stain is further aided by means of a 1- to 2-inch (2.5- to 5-cm.) bed of small glass beads or standard Ottawa sand. The impregnated paper disk is closely fitted between two ground-glass joints of thick-walled glass tubing which are held together by a band of Gooch rubber tubing so that all gas leaving the reaction flask must pass through the paper.

Under the conditions of the experiment sulfur dioxide does not interfere and only the sulfide which is evolved by acid is determined. The diameter of the chamber tube employed is governed by the amount of sulfide present. For amounts of volatile sulfide sulfur between 0.008 and 0.080 mg. a 32-mm. tube was found to be satisfactory, and under these conditions an accuracy of ± 0.002 mg. of sulfur is possible. The delicacy of the test is increased by using chamber tubes of smaller diameter.

STANDARDS

The paper found to give good results was Schleicher and Schull No. 589 black ribbon filter paper. It is sensitized by soaking for one hour in a saturated neutral lead acetate solution and air-dried by vigorous waving, followed by an air blast. The paper may then be cut in disks to fit the appropriate chamber tube. Indications are that impregnated paper will retain its sensitivity for several months if kept protected in a closed container.

Standard stains are prepared by evolving the sulfur from weighed samples of Bureau of Standards steels such as No. 14b basic open hearth steel containing 0.031 per cent of volatile sulfur. This method of standardization was found preferable to the usual practice of diluting strong standard sodium sulfide solutions, as the dilution necessary to obtain small amounts of the standard resulted in immediate oxidation of some of the sulfur.

After deposition of the lead sulfide stain the disks are thoroughly washed in distilled water and dried between sheets of white blotting paper. They are preserved by keeping them in the dark while not in use, as oxidation to colorless lead sulfite occurs when exposed to sunlight, particularly in the case of very faint stains.

METHOD

The sample is placed in a 1000-cc. Erlenmeyer flask with about 100 cc. of distilled water and the system swept with nitrogen to remove excess air, after which 50 cc. of 1 to 1 hydrochloric acid

(special arsenic-free hydrochloric acid gives a perfect blank for this work) are added by means of a dropping funnel. Some operators may prefer to use 100 cc. of 1 to 1 phosphoric or sulfuric acid to eliminate the necessity for a moist cotton plug for absorbing any escaping hydrochloric acid fumes. The contents of the flask are heated to boiling and a stream of nitrogen (about 5 mm. of pressure) is continually passed through the system until all sulfide has been evolved. The residual gas is washed out of the flask by increasing the nitrogen stream (to about 30 mm. pres-

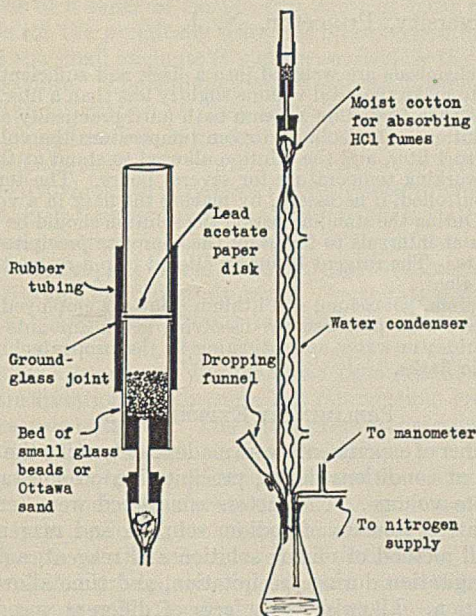


FIGURE 1. DIAGRAM OF APPARATUS

sure) during the last 2 minutes of the determination. The disk is then removed, washed in distilled water, dried, and compared with the standards. For small quantities direct comparisons of color can be made, but with the heavier deposits it is necessary to compare with standards by holding them in front of a source of light.

APPLICATIONS OF METHOD

This method has been found useful in this laboratory in the analysis of foodstuffs, including raw and canned products, and for the determination of very small quantities of sulfide sulfur in water. In the case of water it is capable of estimating minute amounts by acidifying a large volume of the sample and passing the evolved gas through a chamber tube of small diameter. When samples cannot be examined at the source,

the method cited by Collins (2), using crystalline cadmium chloride to preserve the sulfur from oxidation, can be used. The resulting precipitate may thus be examined for sulfide content at the convenience of the analyst by acidifying the precipitate in the reaction flask and proceeding as in the preparation of standards.

During a recent investigational study this laboratory had occasion to determine the amount of sulfide stain imparted to the inside of tinned containers by different food products. As the tin itself contains an appreciable amount of sulfide sulfur, a stripping solution was developed that would remove only the stain and not extract sulfur from either the tin or the base plate. The sample was immersed for 2 minutes in 25 cc. of a boiling solution consisting of 20 cc. of 1 per cent sodium hydroxide solution and 5 cc. of 40° Be. sodium silicate, followed by washing with distilled water. The alkaline solution of sulfide was then transferred to the 1000-cc. flask, swept with nitrogen, acidified, and the sulfur determined as in standards.

The sulfur content of tin coatings can be determined by the disk method to a fair degree of accuracy by the use of large disk chambers. The stream of nitrogen should be greatly increased to insure intimate dilution of the hydrogen sulfide generated. The depth of the filter (Ottawa sand or small glass beads) should also be increased to about 3 inches (7.5 cm.) in order to insure an even deposition of stain on the larger disk. Instead of using the lead plumbite method of stripping tin from tin plate, a method developed by Bohart (1) is used in this laboratory. In this method a tin-plate disk (area 4 sq. in., 25.8 sq. cm.) is placed in a beaker containing about 25 cc. of 1 per cent sodium hydroxide solution, the surface of the disk being sprinkled with pieces of cupric oxide wire. Solution of the tin, excluding that in the alloy layer, is effected in about 2 hours at room temperature, whereas a hot solution accomplishes this reaction within a few minutes. The action may be accelerated at both temperatures if desired, by increasing the concentration of sodium hydroxide. After thoroughly rinsing the disk, the solution is filtered and transferred to the generating flask, where the sulfide is evolved and estimated.

LITERATURE CITED

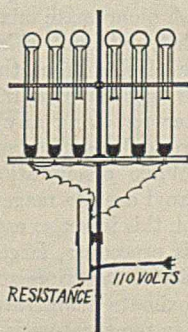
- (1) Bohart, G. S., unpublished work.
- (2) Collins, W. D., U. S. Geol. Survey, *Water Supply Paper* 596-H, p. 237 (Feb. 21, 1928).
- (3) Drushel and Elston, *Am. J. Sci.*, 42, 155 (1916).

RECEIVED December 28, 1933.

A Micro Hot-Plate for Protein Hydrolysis

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SMALL samples (0.1 gram) are hydrolyzed in 6×0.75 inch (15.2×1.9 cm.) test tubes. A micro hot-plate supplies heat to each test tube. The reflux condensers are 3×0.375 inch (7.6×0.95 cm.) test tubes, a bulb blown on the end of each, resting inverted in the large test tubes. The method results in efficient condensation in an all-glass system, uniform heating, and fool-proof simplicity. With it tryptophane was determined in sixty samples with a probable error of 0.05 per cent.



SET-UP OF APPARATUS

Each test tube rests upon a flat spiral of 6 inches (15.2 cm.) of 30-gage Chromel wire. The spirals are bolted to an asbestos board, in series with a rheostat or suitable resistance.

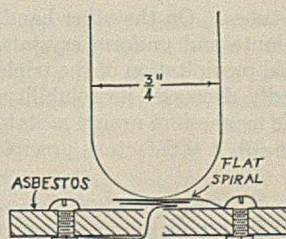


DIAGRAM OF HOT-PLATE

The test tubes are held upright by the cross-piece from a test tube rack, the six holes being directly over the six hot spirals. The cross piece, the asbestos board, and the resistance are supported on a ring stand by three buret clamps.

RECEIVED March 2, 1934.

Rapid Centrifugal Estimation of Small Amounts of Sodium

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SEVERAL workers have shown that small amounts of sodium can be determined with fair rapidity through precipitation as a triple uranyl acetate, either by weighing the precipitate or by dissolving it and applying suitable volumetric or colorimetric procedures. However, where a large number of samples must be examined in a short period, as in biochemical investigations, a very rapid method for estimating small amounts of sodium would seem desirable, even though it involved some loss in accuracy. It has been found that measuring the amount of a precipitate by collecting it in a capillary tube under centrifugal force and reading the volume leads to a satisfactory solution of the problem, since triple acetate precipitates are not only voluminous but, under proper conditions, can be obtained in minute uniform particles that pack in capillary tubes in a readily reproducible manner.

APPARATUS

The centrifuge made by the International Equipment Co., designated as Size 1, Type C, was used throughout the experiments. It was provided with a standard head having places for two carriers designed to hold Goetz phosphorus tubes. A special tube was also used, provided with a capillary of similar length but of smaller internal diameter for experiments with precipitates too small in amount to permit accurate reading of their volumes in the 0.20-cc. capillaries of the Goetz tubes. This special tube was made by removing the capillary from a Goetz tube and attaching one with a uniform internal diameter of approximately 1.5 mm. and a length of 35 mm. The lower end of this capillary was sealed off squarely to avoid reading errors that might originate from a rounded or tapering bottom, for instead of graduating and calibrating the tube in the usual manner it was found simpler, and just as satisfactory, to measure the lengths of the columns of collected precipitate by means of a millimeter scale. The Goetz tubes, however, were calibrated for each etched 0.01-cc. interval with mercury. A simple and convenient tool for removing packed precipitates from the capillaries was made by giving a screw-shaped twist to the flattened end of a short length of stiff wire. Thin pipets made by drawing out glass tubing were also found convenient in cleaning the capillary tubes. The more usual apparatus used in the experiments requires no special description.

REAGENT AND SOLUTIONS

An aqueous reagent was not found practical for these determinations, since comparatively large crystals varying somewhat in size are formed by precipitation in an aqueous system, and these fail to pack in a sufficiently consistent and reproducible manner in capillary tubes. On the other hand, an alcoholic reagent produces minute and uniform crystals, probably because of the more rapid precipitation of the triple acetate in a medium that markedly decreases its solubility. By slightly modifying an alcoholic magnesium uranyl acetate reagent recommended by Kahane (3), a satisfactory precipitant was produced.

For the preparation of a liter the following quantities are required: uranyl acetate ($2\text{H}_2\text{O}$), 30 grams; magnesium acetate ($4\text{H}_2\text{O}$), 150 grams; acetic acid (99 per cent), 20 cc.; and ethyl alcohol (95 per cent), 500 cc.

These chemicals are weighed into a flask and sufficient water is added to make the total volume slightly less than a liter. The mixture is then heated on a steam bath until practically all salts are in solution. On cooling to room temperature the volume is adjusted to 1 liter, and the solution allowed to stand at the subsequent working temperature for several hours. The temperature is controlled, if necessary, by placing the flask in a vessel of water. During the standing period the solution should be stirred or shaken at intervals to facilitate the complete precipitation of excess salts. The reagent is finally filtered into a reagent bottle of brown glass.

The sodium, potassium, and lithium solutions employed in the experiments were prepared by dissolving given amounts of the pure chlorides in water and adjusting to the proper volumes in volumetric flasks.

PRELIMINARY EXPERIMENTS

A number of experiments were made to determine the effects of different conditions during precipitation on constancy of precipitate volume. The factors considered were temperature, relative volumes of sodium solution and reagent, the order and method of mixing solution and reagent, agitation and nonagitation during precipitation, and time allowed for precipitation. Likewise the effects of different speeds and times of centrifugalizing on the final volumes occupied by precipitates were studied, together with the rates at which these volumes were attained.

PROCEDURE

Mount a clean dry centrifuge tube of suitable type in an upright position under a motor stirrer fitted with a thin stirring rod, and if necessary provide for approximate temperature control by partly immersing the tube in a beaker of water maintained at the desired temperature. Place 10.0 cc. of reagent in the tube by means of a pipet, followed by 2.00 cc. of the unknown solution, containing not more than about 2 mg. of sodium, likewise added with a pipet. Immediately mix the two solutions and stir for 10 minutes at such a rate that little or no precipitate settles out. Without rinsing off the stirring rod, remove the tube, stopper it, and place it in a previously counterbalanced centrifuge tube carrier. Centrifugalize immediately at some definite speed between 1600 and 2000 r. p. m. for 10 minutes, and then for a few successive 3-minute periods until a constant precipitate volume is reached. Standardize the tube with known amounts of sodium in the form of a standard sodium chloride solution, using the same procedure.

Unless the centrifuge vessel is thoroughly cleaned before use the precipitate adhering to the upper walls of the tube may cause difficulty. The precipitate will be completely thrown into the capillary, however, if the vessel is cleaned with dichromate mixture, washed with water, rinsed with alcohol, and finally dried in an oven at 100° to 110° C. to remove the alcohol from the capillary. In cleaning the capillary the successive liquids are best introduced by thin pipets, after removing any previous precipitate by means of the wire tool described above.

While precipitations made with an aqueous magnesium uranyl acetate reagent require rather close temperature control, this is not so essential with a reagent of the type used in this procedure, largely because of the much decreased solubility of the triple acetate in strong alcoholic solutions. Approximate temperature control is required only when the room temperature is more than 4° to 5° C. from the temperature at which the reagent was prepared, for only in this

case is there danger of erratic results from increased or decreased precipitation.

It is essential that the reagent be added to the centrifuge vessel first, for a reversal of this order may lead to erroneous results due to trapping of sodium solution in the capillary where it can escape precipitation during stirring. The recommended volumes of reagent and solution were chosen on the basis of a series of experiments as being most generally suitable for the practically complete precipitation in a short time of the small amounts of sodium covered by the range of the procedure. The sodium solution is to be added ordinarily as an aliquot portion of some known volume prepared in a small volumetric flask or graduated tube.

Immediate mixing of solution and reagent is necessary in order to avoid erratic variations in precipitate volumes which may be caused, under conditions of relatively low alcohol and salt concentrations, by the formation of larger particles than those formed rapidly in the thoroughly mixed solutions where concentrations are uniformly high. Precipitation by simply allowing the mixed solutions to stand, or combinations of standing and stirring, were found to lead to unsatisfactory results, both because of the increased time needed for complete precipitation and because less reproducible precipitate volumes were obtained. The latter effect was ascribed to the formation of larger, less uniform precipitate particles than those produced by immediate rapid stirring. The nonsettling of the precipitate during stirring serves as an index of a stirring rate sufficient to bring about practically complete precipitation in the stated time. Furthermore, less uniformly packed precipitates are obtained on centrifugalizing if more than a small fraction of the precipitate is allowed to settle in the capillary during stirring. By the use of a sufficiently thin stirring rod a negligible portion of the precipitate is left on it upon removal from solution; no time need be lost in cleaning off the stirrer, and errors that might be introduced by the use of wash liquids are avoided. A rod about 1.5 to 2.0 mm. in diameter provided with a short 45° bend at the tip, to be immersed below the surface during stirring, is satisfactory, and also provides efficient stirring without danger of loss from splashing.

It is important to employ the same centrifuge speed for all standardizations and determinations, in order to obtain the same degree of packing in all individual precipitates. With the type of centrifuge and head used in the experiments, speeds of 1600 r. p. m. or above are preferable, in that the triple acetate precipitates then pack to a constant volume in a very short time as compared with available lower speeds. With tubes and carriers of the usual type speeds above 2000 r. p. m. are not advisable by reason of the danger of breakage.

Frequently, the upper surface of a packed precipitate is not quite level after the first period of centrifugalizing. This source of difficulty in reading the volume may be remedied by stirring the high part of the surface layer of the precipitate with a stiff wire before recentrifugalizing.

With the usual two- or four-place centrifuge head and a corresponding number of calibrated tubes, it is possible to make a like number of determinations at the same time, provided enough motor stirrers are available to make precipitations simultaneously prior to centrifugalizing. This is necessary in order that the individual samples may be subjected to identical treatment, which is one of the chief requirements in this type of analysis.

RESULTS WITH SODIUM SOLUTIONS

Typical results obtained by the above procedure, using a Goetz tube and sodium chloride solutions of known value, are shown in Table I. The tube was standardized by using the average precipitate volume found in the case of the six 2.00-mg. samples. Expressed on a unit basis, a quantity of

triple acetate precipitate corresponding to 1.00 mg. of sodium thus occupies an average volume of 0.078 cc. This value was then used to convert the volume readings of all the individual trials into milligrams of sodium. The results are, in general, satisfactory from the viewpoint of the difference errors, especially if the averages are considered. The percentage errors are more than could be tolerated with larger amounts of sodium, but with the quantities involved here these deviations are not serious, inasmuch as the procedure is not intended for a micromethod; in fact, the results compare favorably with those obtainable gravimetrically on similar amounts. With the Goetz tube, about 2.5 mg. of sodium are the maximum that can be determined. Somewhat larger amounts could be estimated by means of a longer or wider capillary, but upward extension of the range would probably incur a corresponding loss of accuracy. Because of the rounded lower end of the capillary on the standard Goetz tube and its diameter, the estimation of amounts of sodium below 0.2 mg. involves considerable uncertainty due to reading errors.

TABLE I. ESTIMATIONS OF SODIUM WITH GOETZ TUBE

SODIUM TAKEN Mg.	FINAL VOLUME OF PRECIPITATE Cc.	SODIUM FOUND Mg.	DIFFERENCE ERROR Mg.
2.00	0.162	2.08	+0.08
2.00	0.160	2.05	+0.05
2.00	0.155	1.99	-0.01
2.00	0.161	2.06	+0.06
2.00	0.148	1.90	-0.10
2.00	0.150	1.92	-0.08
1.00	0.080	1.03	+0.03
1.00	0.079	1.01	+0.01
1.00	0.081	1.04	+0.04
1.00	0.080	1.03	+0.03
1.00	0.076	0.97	-0.03
1.00	0.078	1.00	±0.00
0.50	0.042	0.54	+0.04
0.50	0.042	0.54	+0.04
0.50	0.039	0.50	±0.00
0.50	0.042	0.54	+0.04
0.20	0.016	0.21	+0.01
0.20	0.013	0.17	-0.03
0.20	0.015	0.19	-0.01
0.20	0.013	0.17	-0.03

TABLE II. ESTIMATIONS OF SODIUM WITH SPECIAL CENTRIFUGE TUBE

SODIUM TAKEN Mg.	FINAL LENGTH OF PRECIPITATE COLUMN Mm.	SODIUM FOUND Mg.	DIFFERENCE ERROR Mg.
0.50	26.0	0.52	+0.02
0.50	24.0	0.48	-0.02
0.50	23.5	0.47	-0.03
0.50	26.5	0.53	+0.03
0.20	9.0	0.18	-0.02
0.20	9.0	0.18	-0.02
0.20	8.7	0.17	-0.03
0.20	10.0	0.20	±0.00
0.10	4.0	0.08	-0.02
0.10	3.5	0.07	-0.03
0.05	1.0	0.02	-0.03
0.05	1.3	0.03	-0.02
0.10 ^a	5.0	0.10	±0.00
0.10 ^a	5.3	0.11	+0.01
0.05 ^a	2.5	0.05	±0.00
0.05 ^a	2.0	0.04	-0.01

^a In these cases the sodium solutions were reduced to a volume of 1.0 cc.

In order to examine more closely the degree of accuracy obtainable by this centrifugal method when dealing with only a few tenths of a milligram of sodium, a number of determinations were also made by means of a special tube, the construction of which has been described above. These results are shown in Table II. In this series the average of the readings obtained with the 0.50-mg. quantities was used to standardize the tube, so that 1.0 mm. in length of precipitate column was considered as representing 0.02 mg. of sodium in all the individual trials. When the amount of sodium being estimated is about 0.1 mg. or less, incomplete

precipitation due to the solubility of the precipitate becomes appreciable. This can be remedied either by using a lesser volume of sodium solution, as shown in the last four determinations, or by standardizing the tube at intervals with like small amounts of sodium instead of on the basis of a single larger quantity. With the procedure given, 0.05 mg. of sodium appears to be about the smallest amount that can be precipitated successfully. In general, in the case of samples containing only a few tenths of a milligram of sodium the use of a centrifuge vessel with a somewhat narrower capillary than that of the Goetz tube leads to more satisfactory results.

INFLUENCE OF OTHER IONS

Owing to the lack of quantitative data in the literature concerning interference effects with a reagent of the type required in this method, experiments were also made to determine the permissible limits of elements like potassium and lithium that normally accompany sodium. Instead of determining these limits by the more usual methods the centrifugal method was considered more suitable for the immediate purpose, since by this means not only could the usual co-precipitation effects be studied, but also any possible influence of foreign ions on the volumes of precipitates due merely to changes in particle size. The above procedure was applied, therefore, to 2.00-cc. samples of chloride solutions containing varying amounts of foreign ion alone, or with added fixed amounts of sodium. The results are set forth in Tables III and IV. It is apparent that potassium and lithium interfere seriously when present in sufficiently high concentration, probably because of the formation of the corresponding double uranyl acetates, with resultant increase in precipitate volume over the normal value. Lower concentrations of potassium or lithium apparently do not change the particle size or volume of the sodium precipitate. Contamination of the sodium precipitate increases with rise in amount of sodium being precipitated, in accordance with the usual co-precipitation effect. Somewhat more than 5 mg. of potassium may be present if the amount of sodium being determined lies in the lower part of the range covered by the method, but not when higher amounts of sodium are being precipitated. In general the use of an alcoholic instead of an aqueous reagent for direct sodium determinations results in considerably increased interference from potassium (1, 2). This is not serious enough, however, to prevent the use of this centrifugal method for most samples of natural products, since the potassium-sodium ratio in such materials is not often high.

TABLE III. EFFECT OF PRESENCE OF POTASSIUM

POTASSIUM PRESENT	SODIUM TAKEN	AMOUNT OF PRECIPITATE	APPARENT AMOUNT OF SODIUM FOUND	DIFFERENCE ERROR
Mg.	Mg.	Mm.	Mg.	Mg.
5.0	0.00	0.0	0.00	±0.00
10.0	0.00	0.0	0.00	±0.00
15.0	0.00	0.5	0.02	+0.02
20.0	0.00	3.0	0.08	+0.08
5.0	0.10	3.7	0.09	-0.01
5.0	0.10	4.3	0.11	+0.01
7.5	0.10	4.5	0.11	+0.01
7.5	0.10	4.0	0.10	±0.00
10.0	0.10	6.0	0.15	+0.05
10.0	0.10	5.5	0.14	+0.04
Cc.				
3.0	1.00	0.078	1.00	±0.00
3.0	1.00	0.076	0.97	-0.03
5.0	1.00	0.085	1.09	+0.09
5.0	1.00	0.088	1.13	+0.13
10.0	1.00	0.097	1.24	+0.24
10.0	1.00	0.092	1.18	+0.18

Lithium interferes only slightly more than potassium. There is much less discrepancy between interference effects with the alcoholic and aqueous types of reagent in the case of lithium. With other ions the alcoholic reagent was

found to react in essentially the same manner as the aqueous type, but it may sometimes cause difficulty in the presence of substances readily precipitated by dilute alcohol. This source of interference may obviously be circumvented by treating the sample solutions with alcohol and filtering before further preparing them for the addition of the reagent, provided that sodium is not removed by such an operation.

TABLE IV. EFFECT OF PRESENCE OF LITHIUM

LITHIUM PRESENT	SODIUM TAKEN	AMOUNT OF PRECIPITATE	APPARENT AMOUNT OF SODIUM FOUND	DIFFERENCE ERROR
Mg.	Mg.	Mm.	Mg.	Mg.
5.0	0.00	0.0	0.00	±0.00
10.0	0.00	1.0	0.04	+0.04
15.0	0.00	4.5	0.11	+0.11
20.0	0.00	5.5	0.14	+0.14
5.0	0.10	4.0	0.10	±0.00
5.0	0.10	3.5	0.09	-0.01
7.5	0.10	5.0	0.13	+0.03
7.5	0.10	5.7	0.14	+0.04
10.0	0.10	6.0	0.15	+0.05
10.0	0.10	7.0	0.18	+0.08
Cc.				
3.0	1.00	0.078	1.00	±0.00
3.0	1.00	0.080	1.03	+0.03
5.0	1.00	0.088	1.13	+0.13
5.0	1.00	0.094	1.21	+0.21

TABLE V. TEST ANALYSES OF WATERS

SAMPLE	SODIUM CONTENT	DETERMINATION	TUBE READINGS	SODIUM FOUND	ERRORS
	P. p. m.		Mm.		
A	10.0	1	10.0	10.0	±0.0
		2	10.3	10.3	+0.3
		3	10.0	10.0	+0.0
		4	9.3	9.3	-0.7
		Av.	9.9	9.9	-0.1
B	18.8	1	22.3	17.8	-1.0
		2	24.0	19.2	+0.4
		3	23.5	18.8	±0.0
		4	23.0	18.4	-0.4
		Av.	23.2	18.6	-0.2

Sample A, synthetic water made from pure salts, contained the following ions in parts per million: Ca, 50; Mg, 20; Na, 10; K, 5; Li, 5; NH₄, 1; Fe, 1; Cl, 120; SO₄, 21.
Sample B, artesian well water from Princeton, N. J. The sodium content was determined gravimetrically by evaporation of a 250-cc. portion and application of the usual magnesium uranyl acetate method.

TEST ANALYSES

In order to test its practicality this centrifugal procedure was also applied to several complex samples of known sodium content. Among these were two waters, the one a synthetic mineral water with a purposely exaggerated potassium and lithium content, the other a natural water in which the sodium had been carefully determined gravimetrically. The results are shown in Table V. For the analysis of sample A, 500 cc. of the water, acidified with hydrochloric acid, were first evaporated to dryness in a platinum dish. The residue was then dissolved in distilled water and the resulting solution adjusted to a volume of 50.0 cc. in a volumetric flask. Aliquot portions of 2.00 cc. were withdrawn for each determination, which was performed with the special centrifuge tube. This method of reducing the volume was used in order that each millimeter of precipitate column might represent 1 p. p. m. of sodium in the original water on the basis of the previous calibration of this tube. The results are satisfactory, although there is a certain compensating error involved in this good agreement, since the volumes of the precipitates are slightly larger than they should be for the calculated 0.20 mg. of sodium present in each sample. Table II shows that this amount, when precipitated from pure sodium solutions, produced precipitate columns with an average length of 9.2 mm. The small average additional volume obtained in the case of the water samples was found to be due to a slight contamination of the sodium precipitate with calcium sulfate precipi-

tated by the alcoholic reagent. However, this source of error does not appear serious. In the analysis of sample B separate volumes of the water were concentrated in platinum for the individual determinations, and each 2.00-cc. sample used in the procedure represented 25.0 cc. of the original water. The results agree satisfactorily with the gravimetric value, which is itself probably close to the truth.

Trial determinations on samples of milk indicated that the method could also be applied with success to biological material after suitable preliminary treatment to remove organic matter and phosphates. Oxidation with hot concentrated nitric acid in a quartz vessel was used to eliminate organic matter, while the addition of a slight excess of uranyl acetate reagent to a dilute solution of the ash, previously made slightly acid with acetic acid, served to remove the phosphate. The filtrate from the uranyl phosphate was then adjusted to a

suitable volume and aliquot portions were used for the determinations.

CONCLUSIONS

The centrifugal method appears well adapted to the rapid estimation of small amounts of sodium in a variety of materials, especially for routine use on a long series of samples of a similar nature. Results can be rapidly obtained, especially when sets of tubes and carriers are used for two or more simultaneous determinations.

LITERATURE CITED

- (1) Caley, *J. Am. Chem. Soc.*, **54**, 432 (1932).
- (2) Caley and Foulk, *Ibid.*, **51**, 1664 (1929).
- (3) Kahane, *Bull. soc. chim.*, **47**, 382 (1930).

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Determination of Pentosans in Vegetable Materials Containing Tannins

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When the pentosan content of cottonseed hulls or burrs is estimated according to the usual Tollens method, low results are obtained. The decrease in pentosan yield ranges from 2.50 to 47.0 per cent, depending upon the amount of tannins contained in the material to be tested, as well as its condition. The influence of tannins on the determination of pentosans is particularly important in the case of hulls damaged in storage.

In addition to the effect of tannins on the furfural

yield during distillation according to Tollens, lignin probably also exerts an influence, but it failed to be proved by experiment.

To gain a correct idea of pentosans in cottonseed hulls, in addition to the determination of xylose from hulls by means of acid hydrolysis according to Tollens, determination of pentosans in the hull residue should be carried out. The total of both determinations gives a more accurate idea of the pentosan content in the original material.

THE pentosan content of vegetable materials is usually determined by the Tollens method. However, it is necessary to follow the standard procedure strictly, any deviation leading to erroneous results (2, 3).

The principal defects of the method are:

1. The impossibility of distinguishing among individual pentosans, all forming furfural with hydrochloric acid.
2. Furfural may also be formed from substances such as galactan and galacturonic or glucuronic acids, which are components of pectin substances.
3. Should the substance to be tested contain sugars other than pentosans, methylfurfural would be formed from methyl pentosans (fucose, rhamnose). ω -Oxymethylfurfural is obtained from a number of hexoses—glucose, mannose, galactose, fructose—hence also from starch, cellulose, and other polysaccharides from which these sugars are formed by hydrolysis. Because furfural derivatives—methylfurfural and ω -oxymethylfurfural—are also obtained, the determination is very difficult.

Other defects of the method are the variable composition of the condensation product of furfural with phloroglucinol, its solubility in acid solution, etc.

No data were found in the literature concerning the influence on the yield of furfural, and hence on the results of the determination of pentosans of components of plant tissue, which under no conditions form furfural by themselves. The aim of the present work is to ascertain the influence of such components, using cottonseed hulls and burrs.

SOURCES OF FURFURAL LOSS

Attention was first drawn to the fact that cottonseed hulls contain tannins. When tannins are boiled with furfural and hydrochloric acid, insoluble condensation products are obtained. This is the basis of the method used in the analysis of tannins, or the so-called Lauffmann's furfural precipitation numbers, whereby the highest figures are obtained for pyrocatechol tanning substances, which include the tannin of cottonseed hulls. In fact, when an aqueous extract of cottonseed hulls was heated with furfural under the conditions of Lauffmann's reaction, insoluble condensation products of furfural with tannin were readily formed. It is more than probable that such condensation takes place when furfural is obtained from materials containing tannins, which obviously leads to a considerable decrease in the yield of furfural.

The second source of losses in the yields of furfural may be another condensation reaction, occurring under conditions similar to those that take place when pentosans are determined according to Tollens—the condensation of furfural with lignin (4). Hulls contain 30 per cent of lignin. When furfural is boiled with lignin and hydrochloric acid, chemically inert resinous substances are formed. It is possible that tannins and lignin cause the decrease in yield of furfural when analytically determined. This suggestion agrees with the data obtained by Freudenberg and Harden (1), which show

that, when lignin is treated with hydrochloric acid, form-aldehyde is formed, is precipitated in the distillate by phloroglucinol, and forms the precipitate which by its relation to alcohol resembles methylfurfuralphloroglucide and oxymethylfurfuralphloroglucide; because of this the determination of pentosans in wood should give too high results.

Freudenberg and Harden, however, obtained only 0.6 to 0.8 per cent as phloroglucide, instead of 2 per cent of form-aldehyde. The remainder, in their opinion, is fixed by protocatechuic acid liberated during the reaction.

Under the authors' experimental conditions no increase in the phloroglucide yield was caused by the formation of formaldehyde. This may be accounted for by the presence of tannins and related insoluble phlobaphenes. On the other hand, the alcohol-soluble fraction was in no case present in the precipitate in appreciable amount. This leads to the conclusion that the influence of lignin on the determination lies mostly in the formation of insoluble condensation products with furfural. Freudenberg and Harden, however, worked with pure lignin, containing no pentosans.

EXPERIMENTAL

The first problem was to prove experimentally the existence of such an influence. For this purpose hulls from one oil mill (1929) stored in the laboratory were used. Table I shows the chemical analysis of these hulls.

TABLE I. CHEMICAL ANALYSIS OF HULLS

DETERMINATION	%	DETERMINATION	%
Pure cellulose	45.82	Alcohol extract	0.54
Pentosans in hulls	12.02	Water extract	8.54
Methyl pentosans	Traces	Tannins in water extract	3.94
Lignin	23.71	Nitrogen general	0.63
Ether extract	0.65	Ash	1.79

As will be noted, the determination according to Tollens showed that pentosans formed 12.02 per cent of the weight of hulls. In comparing these results with other data their correctness seemed doubtful, because it is known that 26 per cent of xylose can be obtained from cottonseed hulls which contain 29.9 per cent of pentosans. There are also indications that hulls may contain up to 37.9 per cent of pentosans.

It was decided first to check the contents of pentosans in the sample in an indirect way. It was necessary to remove the tannins from the hulls and see how the yield of furfural according to Tollens was changed, also to obtain xylose from the hulls by means of acid hydrolysis, determine the yield of xylose according to Tollens, and then determine the pentosans remaining in the hulls.

For the removal of tannins the hulls were heated with distilled water in an autoclave for 2 hours under 1.5 atmospheres' pressure. During the heating the hulls lost 8.9 per cent of their dry weight. An analysis of the water extract obtained and of water-extracted hulls was made (Tables II and III). Tannins were determined according to the official standard method with powdered leather, sugar according to Bertrand, pentosans or xylose according to Tollens, cellulose according to Cross and Bevan, and lignin according to König (with 72 per cent sulfuric acid).

TABLE II. ANALYSIS OF WATER EXTRACT

DETERMINATION	PER CENT OF WEIGHT OF INITIAL DRY HULLS
Loss in weight of hulls when first boiled in water	8.90
Solid residue of water extract	7.11
Tannins in water extract	6.92
Sugars according to Bertrand	0.24

The authors' assumption about the influence of tannins on the yield of furfural when determined according to Tollens is confirmed by the experiment. During the extraction with water nearly all the tannins are removed from the hulls. And 21.42 per cent of pentosans, when determined according

to Tollens, is found remaining in the extracted hulls. If computed to the weight of hulls before treatment with water, 19.51 per cent is found. In determining pentosans in the original hulls, the method of Tollens did not detect 7.49 per cent of pentosans (19.51 - 12.02), which is of course a defect of the method. After water extraction, the hulls were exposed to a second heating for 2 hours in an autoclave with 4 per cent sulfuric acid solution at 2 atmospheres' pressure. During that time hydrolysis of pentosans to xylose took place. The acid extract, as well as hulls obtained after the second heating with acid, were again analyzed (Tables IV and V). Table IV shows that the acid extract contains 22.47 per cent of pentosans compared to the weight of hulls used, or 20.47 per cent compared to the weight of hulls before heating in water and acids. Moreover, 1.81 per cent of the initial weight remains in the hulls after both extractions.

TABLE III. ANALYSIS OF HULLS AFTER WATER EXTRACTION

DETERMINATION	PER CENT OF BONE-DRY HULLS	
	Before water extraction	After water extraction
Pure cellulose (free from pentosans)	46.63	51.25
Pentosans according to Tollens	19.51	21.42
Methyl pentosans	Traces	Traces
Lignin	17.50	19.21
Ash	0.76	0.83

Thus the experiments for obtaining xylose directly from cottonseed hulls show their pentosan contents to be 20.47 + 1.81 = 22.28 per cent. This is considerably more than the 12.02 per cent as determined in the initial hulls (Table I), and also more than the 19.51 per cent found in hulls extracted with water. It is obvious that the lower results of the two latter determinations are due to the influence on furfural of hull components extraneous to pentosans—in the first case the influence of the tannins and in the second possibly also that of the lignin of hulls.

Estimating the pentosan content to be 22.28 per cent, this yield can by no means be considered as the highest possible, because the authors have not determined the pentosans that passed into the water extract with the tannins. Moreover, when the residue of hulls was analyzed after the second boiling with acid, the possibility of the influence of lignin on the yield of furfural when pentosans are determined is not excluded.

TABLE IV. ANALYSIS OF ACID EXTRACT

DETERMINATION	WEIGHT OF DRY HULLS	
	Before water extraction	Before acid extraction
	%	%
Loss in weight of hulls in second boiling	33.19	...
Loss in weight of hulls in first and second boilings	42.09	...
Sugars in boiling liquid, according to Bertrand	...	26.30
Pentosans in acid extract, according to Tollens	20.47	22.47

TABLE V. ANALYSIS OF HULLS AFTER EXTRACTION WITH 4 PER CENT SULFURIC ACID

DETERMINATION	DRY HULLS	
	Before water extraction	After acid extraction
	%	%
Pure cellulose (free from pentosans)	40.39	69.75
Pentosans according to Tollens	1.81	3.02
Methyl pentosans	Traces	Traces
Lignin	12.63	21.81
Ash	0.072	0.133

In further experiments it was decided to use samples of hulls obtained from mills at various ages and also samples of burrs, the so-called Chingalak, and to determine more accurately the influence of lignin on the yield of furfural when pentosans are determined according to Tollens. For this purpose samples were prepared of hulls and burrs from which tannins were partly removed and then, by further treatment, lignin was removed by chlorination. Chloro-lignin is removed from the hulls by treatment with a 3 per

TABLE VI. DETERMINATION OF PENTOSANS IN HULLS AND BURRS

EXPT.	MATERIAL FOR DETERMINING PENTOSAN CONTENT	YIELD OF FURFURAL			CHANGES OF FURFURAL YIELD TO SUBSTANCE BEFORE TREATMENT
		LOSS IN WEIGHT DURING PRELIMINARY TREATMENT	To bone-dry substance	To bone-dry substance before treatment	
		%	%	%	%
1	Mill hulls (fresh)	...	13.345
2	Same hulls after water extraction (100° C.)	7.05	15.485	14.392	+4.047
3	Same hulls after water extraction and chlorination	26.25	14.657	10.754	-2.591
4	Same hulls after water extraction and first and second chlorinations	38.99	13.159	7.937	-5.348
5	Ginnery burrs	...	7.726
6	Same burrs after water extraction	35.06	10.584	7.318	-0.408
7	Same burrs after water extraction and chlorination	52.29	11.734	5.876	-1.850

cent solution of sodium sulfite. It is probable that part of the pentosans are removed at the same time, which makes it exceedingly difficult to show experimentally the influence of lignin on the yield of furfural.

In Table VI results of the determination of pentosans in hulls and burrs after various treatments are shown, as well as losses in weight because of these treatments.

Experiment 2 shows that here, also, the removal of tannins from the hulls resulted in an increase of 1.047 per cent of furfural yield as compared to the yield from hulls before extraction. This increase is in accordance with the increase of 1.789 per cent of the weight of initial hulls in the determination of pentosan content. The error in determination is equal to

$$\frac{1.789 \times 100}{22.76} = 7.86\%$$

where the denominator 22.76 is the amount of pentosans corresponding to the furfural content in experiment 1 (13.345 per cent). This quantity of furfural was held by the tannins of the hulls during the distillation of furfural according to Tollens. Here the increase in furfural yield after treatment with water is not so large as it was for hulls in the first determination. This is no doubt due to the difference in the properties of the hulls (those stored for a long time and those which are fresh).

tains substances which supply furfural, when heated with acid, the influence of burr tannins on the furfural yield is also apparent. Substances forming furfural in burrs are different from those in cottonseed hulls, since in the case of burrs some components of pectin substances play a considerable part. The water extract prepared for chemical analysis contained 2.097 per cent of pentosans compared to the weight of burrs, which corresponds to the theoretical yield of 1.23 per cent of furfural. If we add 1.23 per cent of furfural from substances passed into the water extract to the yield of furfural calculated on the weight of initial burrs (experiment 6 in Table VI), or 7.318 per cent, we shall have $1.23 + 7.318 = 8.548$ per cent of furfural from burrs after water extraction. The difference $8.548 - 7.415 = 1.133$ per cent of furfural, or 1.93 per cent of pentosans when its yield is determined from untreated burrs—is obviously concealed during the determination on account of the influence of tannins. The error of the determination is

$$\frac{1.133 \times 100}{7.415} = 15.2\%$$

Table VII shows results of further experiments which were carried out on materials of different age before and after a slight treatment with water. These experiments were made to determine how the content of pentosans and other compounds capable of reducing furfural changed with variation

TABLE VII. EXPERIMENTS WITH MATERIALS OF DIFFERENT AGES

EXPT.	MATERIAL FOR DETERMINATION OF PENTOSANS	LOSS IN WEIGHT OF MATERIAL TREATED WITH WATER	YIELD OF FURFURAL TO DRY SUBSTANCE	BEFORE TREATMENT	
				calculated to weight of dry substance	Changes of furfural yield to substance
		%	%	%	%
10	Mill hulls (sample 3) fresh	...	14.442
11	Same hulls after treatment with water	6.325	16.170	15.147	+0.705
12	Mill hulls (sample 4) with moldy odor	...	14.408
13	Same hulls after treatment with water	6.255	15.758	14.769	+0.361
14	Hulls from seeds 35 days old	...	13.395
15	Same hulls after treatment with water	21.452	17.690	13.895	+0.500
16	Hulls from seed 60 days old	...	12.010
17	Same hulls after treatment with water	14.899	14.656	12.472	+0.462
18	Hulls from seed 80 days old	...	12.181
19	Same hulls after treatment with water	4.314	12.754	12.204	+0.023
20	Burrs from opened bolls	...	10.658
21	Same burrs after treatment with water	25.814	13.627	10.110	-0.548
22	Burrs from bolls 20 to 30 days old	...	9.991
23	Same burrs after treatment with water	28.530	12.430	8.883	-0.008

Experiments 3 and 4 (Table VI) show that pentosans are very firmly combined with the cellulose of the hulls and the greater part is not removed even by repeated chlorination. When yields are compared to the initial weight of hulls used for treatment, the increase in yield of furfural in hulls is not shown. Apparently a large part of the pentosans, not considered by the authors quantitatively, disappears from the hulls during chlorination and sulfite treatment. Thus the attempt to prove by experiment the influence of lignin on the yield of furfural remains unsuccessful.

From experiments 6 to 7 it is evident that treatment of burrs with water does not result in an increase of furfural yield. Inasmuch as the water extract of burrs always con-

in the age of the raw material, and to verify the influence of tannins on the process of determining pentosans.

As seen from experiments 11, 13, 15, 17, and 19, treatment of all the samples of hulls with water resulted in an increase of furfural yield. Using the calculation for initial substance (before treatment with water) we have an increase of furfural yield from 0.023 for collected hulls and 0.705 per cent for mill hulls (or 0.039 and 1.21 per cent pentosans).

For samples of hulls 35 days old this increase is larger than for hulls from ripe seeds. This is in full conformity with the known fact that, with increased age of seeds the tannin content is diminished and its character is changed. While the tannins of unripe seeds readily pass into a water extract,

forming a colorless solution, for the most part tannins from ripe seeds are converted into more complicated compounds (lignin), and the remaining tannins become colored substances with a phlobaphene character, passing with more difficulty into the water extract than the tannins of hulls from unripe seeds.

Burrs (experiments 21 and 23) did not show any increase in furfural yield over their weight before treatment with water, but taking into consideration that a considerable part of the substances apt to form furfural have passed into the water extract one has to admit the influence of tannins on the yield of furfural here.

Where tannins are present in a substance to be examined, it is necessary to consider the possibility of decrease in yield of furfural, and hence a decrease in pentosan content, determined according to Tollens. The influence of tannins is shown by experiments to determine furfural yield from a sample after removing tannin extract with water and comparing the furfural yield to the weight of substance before extraction. If there is an increase in furfural yield after removal of tannins their influence on the determination of pentosans according to Tollens becomes apparent. If the yield of furfural is lower after extraction with water, it is possible that substances forming furfural (as with burrs) belong to the group of substances readily soluble in water. In this case it would prove useful to determine the furfural yield from a water extract after precipitating the tannins.

The determination of pentosans according to Tollens is quite insufficient for accurate work with substances containing tannins (and perhaps also lignin) and must be supplemented by the extraction of tannins from the substance and by direct hydrolysis of pentosans to xylose. The pentosan content (furfural-forming substances in general) is to be determined as a total of three determinations—in water extract (after precipitation of tannins), in acid extract, and in the residue after hydrolysis with acid.

The influence of lignin on the determination of pentosans according to Tollens can as yet be only supposition, but at the first opportunity the authors plan to investigate by experiment the existence of such an influence. The importance of tannins in the determination of pentosan content is of greater influence than all the other known errors of the Tollens method; it leads to lowered results, whereas the other defects of the method give exaggerated results.

LITERATURE CITED

- (1) Freudenberg, K., and Harden, M., *Ber.*, 60B, 581-5 (1927).
- (2) Haar, A. W. van der, "Anleitung zum Nachweis, zur Trennung und Bestimmung der reinen und aus Glukosiden u. s. w. erhaltenen Monosaccharide und Aldehydsäuren," p. 63, Gebrüder Borntraeger, Berlin, 1920.
- (3) Hess, K., "Chemie der Zellulose und ihrer Begleiter," p. 123, Akademische Verlagsgesellschaft, Leipzig, 1928.
- (4) Phillips and Weihe, *IND. ENG. CHEM.*, 23, 286-7 (1931).

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Filtering Fruit Juices and Plant Extracts

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THE large-scale laboratory filtration of fruit juices and aqueous extracts of plant material is often a very troublesome operation when suction flasks and Büchner funnels only are to be used. Some years ago the authors in the Research Laboratory of the California Fruit Growers Exchange developed a method for orange juice that has since been successfully applied in many instances. In effect, the operation combines ordinary laboratory suction filtration with the principles of industrial filtration. The filter is prepared as follows:

A piece of filter cloth if available, or a fairly heavy piece of muslin, is cut to fit loosely into the bottom of a Büchner funnel of suitable size. A slurry of paper pulp of a type commercially available for filter mass is prepared in water. A thin layer of the pulp slurry is poured onto the filter and distributed evenly, and then suction is applied to drain the mass thoroughly, care being

There are two objects of the alternate layers of paper pulp and filter aid. Extremely fine particles are easily retained by the filter, so that brilliantly clear filtrates result. By using and removing successively the paper-pulp filter mats, a large quantity of liquid may be filtered with the minimum of dilution or loss in starting the filtering operation.

FILTRATION

The liquid to be filtered is agitated with an amount of filter aid appropriate to the material. About 250 cc. were found sufficient for a liter of orange juice. In pouring the mixture of liquid and filter aid onto the filter, care must be taken not to disturb the mat. It is advisable to place a small watch glass in the center and to pour upon it. Filtration is begun with only as much vacuum as is required to maintain a flow through the mat. Suction is increased gradually as the mat clogs.

A cake of diatomaceous earth will build up in the funnel. When this becomes too thick for convenience, the filter may be sucked fairly dry without raising the vacuum, and, with suction off, the built-up cake and the top layer of pulp may be removed from the next thin layer of filter aid. Filtration may be continued as before.

Operating in this manner, the authors were able to filter with an 8-inch (20-cm.) Büchner funnel as much as 20 liters of orange juice through one prepared filter mass at a rate of about 15 liters per hour. The method has since been applied to a variety of products, such as pectin solutions and tannin extracts, without difficulty.

Various grades of natural and calcined diatomaceous earth filter aids are available. The use of higher grades of material may be desirable in some cases.

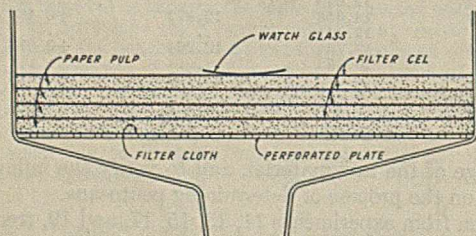


FIGURE 1. CROSS SECTION OF FILTER

taken, however, that the pulp does not become compressed too tightly. Now a dilute suspension of a commercial filter aid, such as Filter-Cel, is prepared and, without disturbing the pulp mat, a thin layer of the diatomaceous earth is allowed to spread out on the pulp. Moderate suction is then applied to pull this down on the pulp. These operations may be repeated several times, building up alternate layers of pulp and filter aid until the funnel is about half full, if a large quantity of liquid is to be filtered.

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Determination of Small Quantities of Sodium Carbonate

Warder's Method with Improved Technic

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FOR the determination of sodium carbonate in commercial caustic soda, there is no satisfactory direct volumetric method, and usually a determination of carbon dioxide is resorted to (5). Winkler's method yields higher results, owing to the precipitation of barium silicate (3, 4), and to the precipitation of basic barium carbonate (6), when carried out according to the usual procedure.

Theoretically Warder's (8) method is suitable for mixtures containing much hydroxide and little carbonate (2), like commercial caustic soda, but the usual procedure is far from precise. Slight errors in the two end points affect the result seriously. If 45 cc. of a standard acid are used for the complete titration and an error of 0.04 cc. is made at each end point, the result for carbonate would be affected by 0.36 per cent when the errors are cumulative in nature.

Han and Chao (1) have devised a procedure for precisely measuring the difference between the two end points and have used it for determining the carbonate content of volumetric sodium hydroxide solutions. The result checked within 0.02 per cent against the gravimetric evolution method. This procedure, however, is not suitable for caustic soda that contains an appreciable quantity of acid-consuming impurities.

Impurities that might occur in appreciable quantities in commercial caustic soda are sodium silicate, sodium aluminate, iron, lime, and magnesia. Sodium silicate behaves like sodium hydroxide during the titration and offers no interference in the carbonate determination. Sodium aluminate is decomposed with the separation of aluminum hydroxide at the first end point (7). Aluminum hydroxide as well as ferric hydroxide, lime, and magnesia consume part of the acid for the second end point and, when present in appreciable quantities, cause a positive error in the carbonate determination.

The author has recently further modified the procedure. The error due to acid-consuming impurities was prevented by filtering the solution after reaching the first end point, but before adding any acid for the second end point. From the data obtained not only the quantity of sodium carbonate can be accurately calculated, but also that of sodium hydroxide. Although carbon dioxide determination yields accurate results for sodium carbonate, yet the sodium hydroxide content of the sample when calculated from total alkali and carbonate is slightly high unless due correction is made for the acid-consuming impurities present. Certain details of Han and Chao's procedure have also been simplified so that it can be more conveniently used for commercial work.

PROCEDURE

The procedure differed from that of Han and Chao (1) in the following points:

1. No carbon dioxide-free air was used for sweeping the Erlenmeyer flask during all titrations.
2. The long nozzle of the buret for *N* hydrochloric acid was inserted into a two-holed rubber stopper, the other hole of which carried a soda-lime guard tube.
3. Instead of 0.01 *N* solutions, 0.02 *N* hydrochloric acid and 0.02 *N* sodium hydroxide were used for the precise measurement of the difference between the two end points. During the addition of 0.02 *N* solutions, the Erlenmeyer flask was not protected

from atmospheric carbon dioxide, but the titration was quickly performed.

4. The solution was filtered through a 9-cm. filter and washed with 35 cc. of ordinary distilled water if appreciably turbid at the first end point.

DISCUSSION

Table I gives typical results expressed in per cent of sodium carbonate calculated on the weight of the solid sample. The results were slightly higher than the gravimetric method, but close agreement was obtained by applying a correction of -0.03 . The procedure has been successfully used in summer as well as in winter, with room temperatures ranging from 10° to 31° C. With samples high in carbonate and iron content, the location of the first end point was somewhat difficult. In such an event, the titration was continued until the pinkish tint of the indicator was completely discharged.

TABLE I. COMPARISON OF GRAVIMETRIC AND VOLUMETRIC METHODS

SAMPLE WEIGHT IN 3450 CC. OF SOLUTION ^a	GRAVIMETRIC DETERMINATIONS		VOLUMETRIC DETERMINATIONS			
	CO ₂	Na ₂ CO ₃	NOT FILTERED		FILTERED	
			0.02066 <i>N</i> HCl ^b	Na ₂ CO ₃ ^c	0.02066 <i>N</i> HCl ^b	Na ₂ CO ₃ ^c
	Gram	%	Cc.	%	Cc.	%
Lime Process, A	0.0521	0.61	5.49	0.62	5.48	0.62
Bottom of drum	0.0520	0.61	5.55	0.63	5.54	0.62
142.18 grams	0.0520	0.61	5.38	0.61	5.48	0.62
		(0.61)		(0.62)		(0.62)
Lime Process, B	0.0698	0.80	7.64	0.85	7.21	0.80
Bottom of drum	0.0699	0.80	7.52	0.84	7.20	0.80
145.44 grams	0.0705	0.81	7.37	0.82	7.18	0.80
		(0.80)		(0.84)		(0.80)
Electrolytic	0.0852	1.02	8.56	1.00		
Av. sample	0.0845	1.01	8.69	1.02		
139.31 grams	0.0844	1.01	8.77	1.03		
		(1.01)		(1.02)		
Löwig Process	0.1269	1.43	12.63	1.41		
Top of drum	0.1267	1.43	12.87	1.43		
147.49 grams	0.1265	1.43	12.64	1.41		
		(1.43)		(1.42)		
Löwig Process	0.1132	1.32	11.45	1.32		
Middle of drum	0.1124	1.31	11.54	1.33		
142.58 grams	0.1130	1.32	11.61	1.34		
		(1.32)		(1.33)		
Löwig Process	0.1682	1.93	17.25	1.97	16.80	1.92
Bottom of drum	0.1678	1.93	17.83	2.04	17.10	1.95
144.62 grams	0.1673	1.92	17.32	1.98	17.05	1.95
		(1.93)		(2.00)		(1.94)

^a For gravimetric determination 500 cc. and for volumetric determination 45 cc. of solution were used.

^b Volume used for the second end point.

^c A correction of -0.03 has been applied.

With extremely impure caustic, the sample solution can be allowed to settle and a clear portion used for the titration. Any aluminum hydroxide formed at the first end point is removed by filtration. The boiling can be omitted if methyl orange or bromophenol blue is used as indicator for the second end point. The color change, however, is not sharp with 0.02 *N* acid.

LITERATURE CITED

- (1) Han and Chao, *IND. ENG. CHEM., Anal. Ed.*, 4, 229-32 (1932).
- (2) Kolthoff-Furman, "Volumetric Analysis," Vol. II, p. 118, Wiley, 1929.
- (3) Lindner, *Z. anal. Chem.*, 72, 135-54 (1927).
- (4) Lindner, *Ibid.*, 78, 188-98 (1929).
- (5) Solvay Process Co., "Solvay Bulletin," No. 2, sheet 2, 1925.
- (6) Sorensen and Andersen, *Z. anal. Chem.*, 47, 279-94 (1908).
- (7) Thomson, *Chem. News*, 52, 20 (1885).
- (8) Warder, *Am. Chem. J.*, 3, 55 (1881).

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Quantitative Determination of Coumarin in Plant Material

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COUMARIN is widespread in the plant kingdom. In certain species of forage plants it is present in sufficient quantity to impart a disagreeable taste, disliked by farm animals. An investigation of the coumarin content of various strains of sweet clover developed by the Department of Agronomy at the West Virginia Agricultural Experiment Station necessitated the quantitative determination of this substance. Methods for the determination of coumarin in vanilla extract are not well suited to the removal and determination of coumarin in plant tissues, and a search of the literature showed only the method of Obermayer (2) available for this purpose.

EXPERIMENTAL

In Obermayer's method, 10 grams of air-dry sweet clover meal are extracted with ether, the extract is transferred to a 500-cc. distilling flask, and the ether evaporated at room temperature. After removal of the ether, 300 cc. of a 25 per cent solution of calcium chloride are added and the coumarin is distilled from this solution. The temperature at the end of the distillation should be 179° to 180° C. An aliquot part of the distillate is then titrated with 0.1 *N* potassium permanganate in a special manner described by the author.

Since the method does not state how long the extraction with ether should be continued, the first problem was to determine the extraction period necessary for the complete removal of the coumarin. To accomplish this a battery of ten Soxhlet extractors was set up and duplicate determinations were run on five varying periods of extraction of the same material. Ten-gram samples of sweet clover were extracted for periods of 24, 30, 37, 49, and 72 hours, respectively.

The results showed that the titration value of the sample increased up to 30 hours of extraction, after which it decreased. Just why extracting 37 to 72 hours gave lower results than 30 hours was not clear. However, it was thought that the long-continued heating of the extract in the receiving flask might affect its titration value. Next a series of samples were extracted in quadruplicate for periods of 2, 4, 8, and 12 hours, the receiving flask being replaced by a new flask at the end of each period. This made a total of 26 hours' extraction.

Titration of 100-ml. aliquots of the distillates at the end of 2 hours and after an additional 4, 8, and 12 hours of extraction required 18.99, 8.34, 7.66, and 6.81 ml. of 0.1 *N* potassium permanganate, respectively, or a total of 41.80 ml. for the total 26 hours. These values are the mean of four distillations. Since the titration value for the final extraction period was so large (6.81 ml.), the extractions were continued for additional periods of 24, 40, and 20 hours. The mean titration values for 100-ml. aliquots of these extracts were 5.50, 4.78, and 4.00 ml. of 0.1 *N* potassium permanganate, respectively, or a grand total of 56.08 ml. for 110 hours.

These values are considerably higher than those secured from continuous extraction over similar periods without change of receiving flasks, indicating that long-continued heating of the ether extract in the receiving flask does reduce the titration value. The final 20-hour extract gave a relatively high titration and a positive Wichmann-Dean (1) test for coumarin, indicating that the coumarin is not completely removed even after 90 hours of extraction.

Three additional series, in which 5-gram samples of the same material were employed, were extracted in triplicate by varying periods for a total of 26 hours. The extracts were combined and the composite extract was distilled and titrated as before. The samples were then subjected to further extraction for periods of 70 and 24 hours.

In series 1 the flasks were replaced at intervals of 2, 5, 7, and 12 hours, and the 100-ml. aliquot required 20.87 ml. of 0.1 *N* potassium permanganate. Additional 70- and 24-hour periods of extraction gave permanganate requirements of 4.16 and 0.82 ml., respectively, or a total of 25.85 ml. for 120 hours.

In series 2 the flasks were replaced at intervals of 4, 9, and 13 hours, and the 100-ml. aliquot required 17.73 ml. of 0.1 *N* potassium permanganate. Additional 70- and 24-hour periods of extraction gave permanganate requirements of 3.95 and 0.94 ml., respectively, or a total of 22.62 ml. for 120 hours.

In series 3 the sample was extracted continuously for 26 hours without replacement of the receiving flask, and the 100-ml. aliquot required 14.25 ml. of 0.1 *N* potassium permanganate. Additional 70- and 24-hour periods of extraction gave permanganate requirements of 3.62 and 0.95 ml., respectively, or a total of 18.82 ml. for 120 hours.

Examination of the values for the 26-hour extraction periods in series 1, 2, and 3 shows beyond question that the longer the sample is extracted before the flask is replaced, the lower the titration secured. In addition to this disturbing factor of loss on continued extraction the difficulty of complete removal of coumarin is a serious problem. The final 24-hour extraction period in all three series gave a positive Wichmann-Dean (1) test for coumarin but required 1 ml. or less of the potassium permanganate solution for titration, indicating that 120 hours of extraction is sufficient, although impractical, for its complete removal. Results secured from more finely ground material, to pass a 0.5-mm. sieve, were almost identical with those previously given.

EXTRACTION BY STEAM DISTILLATION

Since the ether-extraction method for removing coumarin from the sweet clover samples was found both difficult and variable as to results, some other method for its removal was sought. Inasmuch as coumarin is known to be volatile with steam, the possibility of its removal from the samples by steam distillation under reduced pressure was considered.

The procedure described below was finally adopted, although various modifications were tried as successive steps in the development of the method seemed to warrant.

A 5-gram sample ground to pass a 1-mm. sieve is placed in a 1-liter, long-neck, round-bottom Pyrex flask, and 80 cc. of water are added and mixed with the sample. The flask is fitted with a 2-hole rubber stopper carrying a Kjeldahl distillation bulb and a steam inlet tube which extends to the bottom of the flask. The distilling flask is joined through the connecting bulb to a 25-inch (63-cm.) Allihn condenser and the flask immersed in a boiling water bath. A 4-liter Pyrex beaker serves as a transparent bath through which the steam distillation can be observed and controlled. A 1-liter suction flask is fitted to the condenser to collect the distillate. The entire system is then connected to a water suction pump by rubber tubing attached to the side tube of the receiving flask. A mercury manometer is inserted in the line for measuring the pressure.

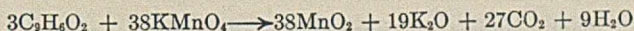
It is convenient to run the distillations in duplicate by attaching two sets of apparatus to the same steam jet and to the same suction pump. Screw clamps at suitable points in the line assist in controlling the rate at which the steam is admitted and distributed to the flasks and the pressure reduced. A stream of dry steam is passed into the flasks for 1 to 2 minutes until the contents reach a vigorous boil and the distillate begins to drip

from the condenser. At this time the pressure is reduced as rapidly as possible but at such a rate as to prevent boiling over, until the pressure in the system is 140 mm. of mercury. The distillation is continued at 140 mm. until the flasks are dry, after which they are disconnected and removed from the water baths. The connecting bulb, steam inlet tube, and inside of the distilling flask are rinsed down with an additional 80 cc. of water and the contents redistilled as before.

This procedure is repeated until six distillations have been made, after which the condenser is rinsed down into the receiving flask and the distillate transferred to a 1-liter volumetric flask. The flask is made up to volume, and 50-ml. aliquots of distillate are treated with 4-ml. of 0.25 *M* lead acetate, stirred, covered, and allowed to stand several hours or overnight. The excess lead is then precipitated by adding 0.17 *M* disodium phosphate in a quantity just equivalent to the 4-ml. of lead acetate used (this amount having been determined previously by titration) plus 0.5 ml. additional. The precipitate of lead phosphate is allowed to settle for 30 minutes and 25 ml. of zinc sulfate solution,¹ made by dissolving 200 grams of zinc sulfate in 1 liter of water, are added and mixed. The whole is permitted to stand at least 4 hours, after which the combined precipitates of lead tannate, lead phosphate, and zinc phosphate are removed by centrifuging in a 100-cc. centrifuge tube. The supernatant liquid is poured off into a 500-cc. Erlenmeyer flask, the precipitate washed twice with 25 cc. of water, and the washings are combined with the original decantation. This solution is then titrated indirectly with 0.1 *N* potassium permanganate according to the method of Obermayer (2) as follows:

A measured quantity of potassium permanganate solution is added in excess (usually 25 ml.), the total volume diluted to approximately 150 cc., and heated on an asbestos board for 10 minutes. The hot solution is filtered through an asbestos mat in a Gooch crucible, the mat washed, and the excess permanganate decomposed with a known amount of 0.1 *N* oxalic acid solution added in excess. The resulting solution is acidified immediately with 25 cc. of 2 *N* sulfuric acid and the excess oxalic acid titrated with 0.1 *N* potassium permanganate, during which the temperature is maintained at 70° to 80° C.

The permanganate titration accounts for only about 93 per cent of the total coumarin where pure coumarin is used, which necessitates the use of a titration factor. Blank titration values on reagents should be subtracted from the total titration values. The equation for the reaction as qualified may be written as follows:



PRELIMINARY TRIALS

Preliminary work indicated that steam distillation might be utilized for the removal of coumarin. It soon became apparent that several distillations were necessary to remove the coumarin completely from a given sample and that in this procedure a small but unknown quantity of noncoumarin reducing material was carried over into the distillate along with the coumarin. Since it was desired to determine the coumarin removed by titration with 0.1 *N* potassium permanganate, the presence of reducing substances other than coumarin presented a serious objection to the proposed method unless these substances could be either eliminated or evaluated in satisfactory manner and proper correction made.

In a typical preliminary trial, duplicate 5-gram samples were distilled four times, and each distillate was made up to 500 ml. A 30-minute period of distillation at atmospheric pressure was carried on before the pressure in the system was reduced and 60 cc. of water were added instead of 80 as in the final method. Fifty-milliliter aliquots from each of the four distillates required 10.50, 4.05, 1.75, and 0.51 ml. of 0.1 *N* potassium permanganate, respectively, or a total of 16.81 ml. for the four distillations. Wichmann-Dean tests for coumarin in the distillates indicated that most of the permanganate requirement was due to coumarin.

The next factor to receive consideration was the effect of using different degrees of reduced pressure, and consequently

¹ The number of milliliters of zinc sulfate solution used should be the same as that of the 0.1 *N* potassium permanganate added in the next step. If less than 25 ml. of potassium permanganate are added the zinc sulfate may be correspondingly reduced.

different temperatures, in the distillation flasks. Thermometers were placed in the distillation flasks and a mercury manometer was inserted in the line. Three different degrees of temperature and pressure were tried with 5-gram samples in duplicate and the distillation procedure last described. The temperatures and pressures used and the mean values secured are shown in Table I.

TABLE I. EFFECT OF DIFFERENT DEGREES OF TEMPERATURE AND PRESSURE ON THE STEAM DISTILLATION OF SWEET CLOVER

DISTILLATION NUMBER	0.1 <i>N</i> KMnO ₄ REQUIRED FOR 50 ML. OF DISTILLATE		
	150 mm. of mercury and 60° C.	270 mm. of mercury and 73° C.	390 mm. of mercury and 82° C.
	<i>Ml.</i>	<i>Ml.</i>	<i>Ml.</i>
1	12.23	13.05	14.30
2	2.80	3.46	2.83
3	1.05	1.31	1.13
4	0.53	0.60	0.60
Total	16.61	18.42	18.86

The results show a considerable effect of temperature and pressure on the total titration value. The fourth distillation was uniformly low in each case, which may be taken to indicate that most of the coumarin is removed by four distillations. Qualitative tests for coumarin on equal volumes of distillates from the lowest and highest temperatures tried showed that the distillates from the 60° distillation contained as much coumarin as those from the 82° distillation and indicated a greater removal of noncoumarin reducing material at the higher temperatures and pressures. This point was confirmed by direct test for tannin derivatives.

It seemed desirable also to secure additional data on the effect of time of distilling at atmospheric pressure, before reducing the pressure for distillation to dryness.

Consequently quadruplicate sets of four distillations each were carried out, the time of distillation at atmospheric pressure being varied from 5 to 30 minutes. The reduced pressure used was 140 mm. of mercury, which gave a distillation temperature of 59° C. Pressures lower than 140 mm. were tried but were found to be less satisfactory in manipulation. Five-gram samples were used, the distillates made up to 500 ml., and 50-ml. aliquots were titrated. Total titration values secured by adding the values for each set of four distillations are given. The 5-, 10-, 15-, 20-, and 30-minute distillation periods required 14.24, 14.63, 14.82, 15.05, and 15.28 ml. of 0.1 *N* potassium permanganate, respectively, these values being the mean of four determinations.

The results show somewhat higher values for the longer periods of heating; qualitative tests for noncoumarin reducing substances in the first distillates in each set also indicated a higher content of this material in the distillates from the longer periods of heating. Determinations of the vapor pressure curve for coumarin above and below its melting point in the range of the distillation temperatures being employed gave unexpected results, and the question arose as to whether the preliminary period of distillation at atmospheric pressure might not be dispensed with entirely. Several trial runs showed that this could be done to advantage, in that the quantity of noncoumarin reducing substances was diminished and the time required to complete a distillation was shortened without affecting the removal of coumarin. The effect of maintaining the water bath at 63° to 66° C. was also tried, but the lower temperature required a longer period for distillation, which again resulted in an increased quantity of noncoumarin material.

For these reasons the procedure was modified in that 80 cc. of water were added instead of the 60 cc. originally used, and as soon as the contents of the flask reached a rolling boil, usually requiring 1 to 2 minutes, the pressure was reduced. The time required to reduce the pressure in the distillation flask to 140 mm. of mercury was 3 to 4 minutes, and the total period of distillation about 8 minutes for each 80-cc. portion

of water added. It was found also that moderate variations in the amount of water added (75 to 100 cc.), in the reduced pressure utilized (135 to 145 mm.), and in the fineness of the sample (passing a 0.5 to 1 mm. sieve), were without appreciable effect upon the results secured.

NONCOUMARIN REDUCING SUBSTANCES

Prior to this time, efforts had been made to learn the general nature of the compounds other than coumarin affecting the permanganate titration. Behavior toward Fehling's solution and ferric chloride, qualitative tests for lignin, sapo-

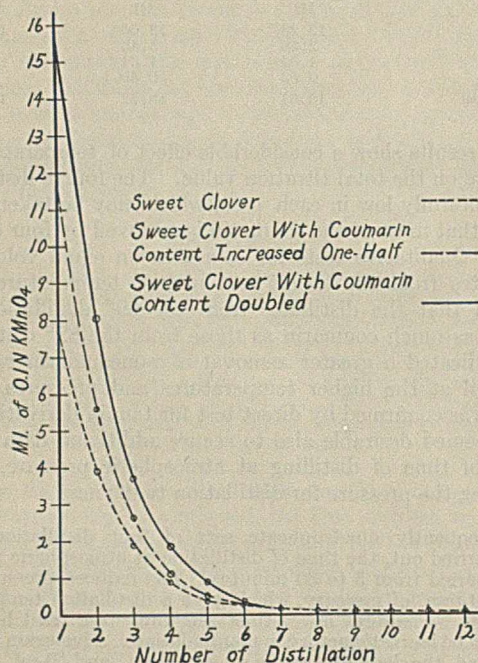


FIGURE 1. DISTILLATION CURVES FOR SWEET CLOVER ALONE AND REINFORCED WITH PURE COUMARIN

nins, formaldehyde, and tannins and their derivatives had been run on numerous distillates. Of the various tests made, only that for pyrogallol and related substances, resulting in a brownish precipitate with Nessler's reagent, was positive. Dilute solutions of pure pyrogallol and Nessler's reagent gave a test very similar to the test obtained with sweet clover distillates and Nessler's reagent.

In order to ascertain the effect of steam distillation on material of high tannin content, a 5-gram sample of tea was distilled four times and each distillate made up to 500 ml. Fifty-milliliter aliquots required 0.30, 0.20, 0.17, and 0.10 ml. of 0.1 *N* potassium permanganate, respectively. Even though tea is high in tannins, only relatively small amounts are removed by the steam-distillation method.

Further information was now desired relative to the behavior of samples of varying coumarin content under steam distillation. Accordingly, sweet clover samples having a high and a low coumarin content were distilled over and over until the distillates gave little or no permanganate titration. Along with these samples, similar samples were reinforced with varying amounts of a solution of pure coumarin, and distilled repeatedly. The amounts of coumarin added were of sufficient quantity to increase that naturally present by approximately 50 and 100 per cent, respectively. The titration values of a representative sample with and without added coumarin are shown graphically in Figure 1. The points on the curves are all means of four determinations.

Irrespective of their coumarin content, the samples behave similarly under steam distillation. They also show essentially equal titration values for the seventh distillation. It appears clear, therefore, that all the coumarin is removed from the sample in six distillations and that the titration values beyond the sixth are due to noncoumarin reducing substances. The test for tannin materials and also that for coumarin support this view. It was not possible to secure a Wichmann-Dean test for coumarin beyond the fifth distillate.

In an effort to eliminate the noncoumarin material distilled over during the removal of coumarin, samples of sweet clover were distilled repeatedly and the distillates treated with a solution of neutral lead acetate. The distillates always gave a distinct precipitate with lead acetate additions, and the delead solutions gave lower titration values than the untreated distillates. Further, solutions of pure coumarin when treated with lead acetate gave quantitative values for the coumarin added, showing it to be unaffected by the treatment. Somewhat contrary to expectation, trials with sweet clover distillates showed that it is immaterial whether the precipitates of lead tannate, lead phosphate, and zinc phosphate are removed separately, or all together, provided time for complete precipitation is allowed in each case. Filtration through asbestos mats on Gooch crucibles can be substituted for centrifuging with equally good results. The centrifuge method is preferred because it is more rapid and convenient.

In a typical example showing the effect of treatment with lead acetate, duplicate 5-gram samples were distilled eight times and the distillates made up to 500 ml. Fifty-milliliter aliquots were taken for direct titration and for titration after treatment with lead acetate. When titrated directly the eight aliquots required 6.60, 3.16, 1.54, 0.70, 0.44, 0.39, 0.16, and 0.12 ml. of 0.1 *N* potassium permanganate, respectively. After leading and de-leading the corresponding requirements were 6.46, 3.08, 1.37, 0.54, 0.31, 0.22, 0.02, and -0.01 ml., respectively. The two series differ by an almost constant amount and the potassium permanganate requirement of the treated distillates approximates zero for the seventh and eighth distillations.

Plant materials containing only small amounts of coumarin and considerable amounts of volatile reducing substances not precipitated by lead acetate could not be determined accurately by this method. However, it has been applied to soy-bean hay, cowpea hay, alfalfa hay, tonka beans, privet leaves, and other plant tissues in less extensive trials than with sweet clover but with satisfactory results.

APPROXIMATE METHOD FOR COMPARATIVE PURPOSES

Although six distillations are required to remove all the coumarin from a sample of sweet clover, nevertheless a close approximation to this value may be secured by discontinuing the distillations at the end of the fourth and omitting the lead acetate treatment of the distillates. About 95 per cent of the total coumarin present in the sample is removed in the first four distillations. On the other hand, when calculated as coumarin the noncoumarin reducing material in these same four distillations varies from 3 to 5 per cent. By this procedure the small amount of coumarin left in the sample is approximately equal to, and offset by, the noncoumarin titratable material which distills over.

This shorter method has been shown to be sufficiently accurate for sorting different strains of sweet clover of varying coumarin content and is being utilized for that purpose in this laboratory. It greatly reduces the amount of time and labor required where large numbers of samples are handled. Where greater accuracy is desired, the longer procedure, involving a larger number of distillations and treatment with lead acetate, is used.

SUMMARY

The steam distillation method for removing coumarin from plant tissues has certain decided advantages over the ether extraction method. It gives excellent results with sweet clover and seems to apply successfully to other species also. For comparative purposes where a high degree of accuracy is unnecessary, the number of distillations may be reduced and the distillates titrated directly without further treatment.

For more accurate results the number of distillations is increased, and the noncoumarin reducing substances are removed by precipitation with lead acetate.

LITERATURE CITED

- (1) Dean, J. R., *J. IND. ENG. CHEM.*, 7, 519 (1915).
- (2) Obermayer, E., *Z. anal. Chem.*, 52, 172-91 (1913).

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Determination of Bromide in the Presence of Large Excess of Chloride

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DURING a study of the metabolism of brominated compounds, a number of the methods previously reported for the determination of bromides in the presence of large excess of chlorides proved unsatisfactory. Most of them depend upon the oxidation of the bromide to bromine under conditions so regulated as to avoid the simultaneous production of chlorine. When the concentration of bromide is small and that of chloride is high, this is impossible; to overcome this difficulty the bromine first obtained is frequently converted to bromide and is then reoxidized in a similar manner. In some processes even a third oxidation is used. Usually the bromine finally obtained is determined iodometrically. Each oxidation introduces the possibility of loss of bromine, and if any chlorine is carried over in the last oxidation it will be reported as bromine. The procedure of Behr, Palmer, and Clark (1) gave the most satisfactory results, but even with very careful manipulation it was accurate to only about 2 per cent. Since this was not sufficient for the authors' purposes, the following procedure was worked out: The bromine is liberated by means of moderate excess of chlorine water, collected in sodium sulfite solution, and titrated potentiometrically in sulfuric acid solution with potassium bromate. This procedure has been satisfactorily used by one of the authors in collaboration with R. C. Corley for the analysis of about fifty urine samples in a study of the excretion of bromides following the ingestion of brominated compounds.

MATERIALS AND APPARATUS

Potassium bromide for use in making known solutions had to be synthesized, since the best obtainable potassium bromide contained "not more than 0.75 per cent potassium chloride." Bromine was freed of chlorine by shaking with three successive portions of aqueous sodium sulfite and separating. The purified bromine was then reduced by sulfur dioxide and water, and the resulting hydrobromic acid solution was redistilled until free of sulfuric acid, and neutralized with c. p. potassium hydroxide. The potassium bromide obtained in this manner was recrystallized twice and dried at about 110° C.

Chlorine water was made by absorbing in water the chlorine obtained by electrolysis of hydrochloric acid. To remove any traces of bromine from the hydrochloric acid, it was diluted to about constant boiling strength, treated with chlorine, and boiled. The strength of the chlorine water was checked iodometrically from two to three times a week.

The potassium bromate was a c. p. product recrystallized and dried at about 110° C.

Sulfuric acid, potassium hydroxide, copper sulfate, and

sodium chloride of c. p. or reagent quality grade were used without further purification. The sodium chloride was found to contain 0.001 per cent of bromide. The chloride in the other chemicals was reported from 0.001 to 0.005 per cent, and undoubtedly the bromide was only a small fraction of this. With the exception of the chlorine water, all solutions were made by weighing the appropriate substance and making up to volume in calibrated volumetric flasks.

The apparatus for liberating the bromine from the solution of halides consisted of a 50-ml. flask with an inlet tube extending from top to bottom, and a delivery tube leading to an absorption train of two test tubes, illustrated in Figure 1. Suction is applied at *F*. *A*, *C*, and *D* are ungreased ground-glass joints. A rubber stopper was used at *E*, since the air passing it no longer contains bromine vapor. This apparatus was designed for samples not exceeding 25 ml. A larger flask would be desirable for larger samples, and if the bromine content is high, the absorption system should also be enlarged.

A Leeds & Northrup student potentiometer with a portable, enclosed lamp and scale galvanometer was used to measure the potentials.

PROCEDURE

The bromine in the sample to be analyzed should be present as bromide ion. For materials in which the bromine is in organic combination, or when organic material is mixed with the bromide, the ashing method of Behr, Palmer, and Clark (1) was found to be very satisfactory.

Sodium sulfite amounting to about 20 mg. plus three to five times the estimated weight of bromine in the sample is weighed out, dissolved in water, and put into the absorption tubes, with about 80 per cent of the sulfite in the first tube. The rapid oxidation of sulfite by air makes the large excess necessary. While a slow stream of air is sucked through the apparatus, the sample is introduced through the inlet tube, rinsed down, made acid with sulfuric acid, and chlorine water estimated to be in slight excess

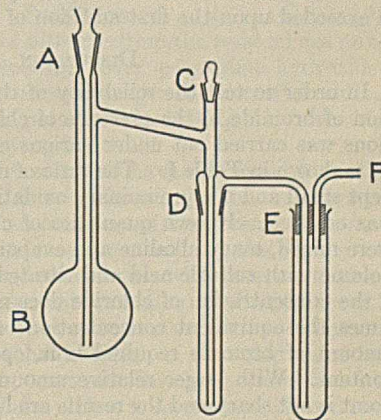


FIGURE 1. APPARATUS FOR LIBERATING BROMINE

of the bromine content is introduced. The flask is heated to about 100° C. for 10 to 15 minutes and cooled. Two or three further additions of chlorine water are made, heating the flask after each addition. Unless the bromine content is very small it is desirable to use a total of not more than three times the theoretical amount of chlorine water, and the later additions are made smaller than the first one unless the development of color on the second addition shows that the first was too small.

The air stream is then stopped, and the contents of the absorption tubes are rinsed into a small beaker suitable for the titration, made alkaline, and evaporated on a steam bath. A drop of 1 per cent copper sulfate is added before evaporation to catalyze the oxidation of the excess sulfite by air. After evaporation the sides of the beaker are rinsed down and the sample is again evaporated to insure the oxidation of all of the sulfite, made up to suitable volume with about 7.5 *N* sulfuric acid, and titrated potentiometrically with standard potassium bromate, using a platinum wire electrode as indicator, and a 0.1 *N* calomel electrode as reference. The solution is stirred by a small mechanically driven glass stirrer throughout the course of the titration. The titration vessel is surrounded by ice to minimize the loss of bromine.

Before addition of any bromate the potential is erratic and of no significance. The potential after the addition of a small quantity of potassium bromate (0.02 ml. was usually used) is a very useful indicator of sulfite; if sulfite is still present, the potential remains low, below 0.3 volt, but if it has been completely oxidized, the potential goes to 0.57 to 0.61 volt. The end point is taken as the point of maximum rate of change of potential with added potassium bromate. The authors have used Fenwick's (3) formula for calculating the end point. The end-point potential varies from case to case, from 0.78 to 0.83 volt, probably because of the variation in the concentration of dissolved bromine. When no bromide is initially present in the solution to be titrated, the end-point potential is exceeded upon the first addition of bromate.

DISCUSSION

In order to test the reliability of the potentiometric titration of bromide in the presence of chloride, a series of titrations was carried out under various conditions, with the results shown in Table I. The ratio of chloride to bromide was kept small and the preliminary oxidation with chlorine water was omitted. Known quantities of chloride and of bromide were mixed, made alkaline and evaporated, made to suitable volume with sulfuric acid and titrated. Series 1 shows that if the concentration of chloride does not exceed two to three times the equivalent concentration of bromide present, the amount of bromate required is independent of the chloride content. With larger relative amounts of chloride the end point is not sharp and the results are high. For this reason a controlled amount of chlorine water is employed in the first oxidation.

Series 4 and 5 show that an increase in final volume, with corresponding decrease in acid concentration, decreases the amount of bromate used toward the stoichiometric value. With appropriate adjustment of acid concentration and of volume at the end point, the stoichiometric ratio of bromate to bromide may be obtained, but when the concentration of bromide is very small, such adjustment makes the titration very tedious, for under these conditions the potentials are slow to reach steady values. For this reason it is recommended that in the determination of small quantities of bromides, the volume of solution at the end point be kept small, the final acid concentration be from 6 *N* to 7 *N*, and that known samples be run under the same conditions and the corresponding correction factor be applied. In effect the bromate is standardized by the known bromide solution.

Table II gives some results of the complete procedure. From 0.3 to 1.0 gram of sodium chloride was added to the samples containing more than 1 mg. of bromide, and approximately 30 mg. of sodium chloride to those containing less than 1 mg. Very great excesses of sodium chloride were

avoided to obviate large corrections for the bromide in the sodium chloride. There is no reason to believe that larger amounts of chloride would in any way interfere with the liberation of bromine. The "Bromine Present" of Table II is the sum of the bromine added as potassium bromide and that present as impurity in the sodium chloride. When the conditions of titration were such that a stoichiometric ratio was not expected, the appropriate factor obtained from Table I was applied. The calculations for experiment 7 of Table II are given for illustration.

Bromine added: as potassium bromide, 0.8035 mg.; as impurity in 117 mg. of sodium chloride, 0.0012 mg.; total, 0.8047 mg. Approximately 0.75 ml. of 0.04 *N* chlorine water was used to liberate the bromine, which was absorbed in about 25 mg. of sodium sulfite. Near the end point the potassium bromate was added in 0.04-ml. portions. Fenwick's (3) formula indicated the end point at 1.688 ml. of 0.0598 *N* potassium bromate, corresponding to 0.8068 mg. of bromine. However, an examination of series 6 of Table I shows that the titration under these conditions gives results which average 0.8 per cent too high; subtracting 0.8 per cent or 0.0064 mg., a final corrected value of 0.8004 mg. is obtained.

TABLE I. TITRATION OF BROMIDE IN THE PRESENCE OF MODERATE QUANTITIES OF CHLORIDE

SERIES	MOLE RATIO Cl to Br	VOLUME AT END POINT ml.	ACIDITY <i>N</i>	BROMINE PRESENT	BROMINE FOUND	RECOVERY
				Mg.	Mg.	%
1	0.0	121	6.2	199.3	200.5	100.6
	1.0	121	6.2	199.3	200.7	100.7
	2.0	121	6.2	199.3	200.8	100.7
	3.0	121	6.2	199.3	200.6	100.6
	4.0	121	6.2	199.3	200.5	100.6
2	2.0	166	6.3	199.3	199.7	100.2
	2.0	166	6.3	199.3	199.7	100.2
	2.0	166	6.3	199.3	199.8	100.2
3	0.5	24	6.3	39.94	39.91	99.9
	0.5	24	6.3	39.94	39.99	100.1
	1.0	24	6.3	39.94	39.99	100.1
	1.0	24	6.3	39.94	39.89	99.9
4	0.5	9	6.7	3.991	4.022	100.8
	1.0	9	6.7	3.991	4.009	100.5
	1.0	9	6.7	3.991	4.015	100.7
	2.0	9	6.7	3.991	4.015	100.7
5	1.0	14	5.4	3.991	3.991	100.0
	2.0	14	5.4	3.991	3.991	100.0
	2.0	14	5.4	3.991	3.994	100.1
	2.0	14	5.4	3.991	3.988	99.9
	2.0	14	5.4	3.991	3.996	100.1
6	1.0	4.7	6.4	0.8035	0.8079	100.6
	1.0	4.7	6.4	0.8035	0.8114	101.0
	1.0	4.7	6.4	0.8035	0.8066	100.5
	2.0	4.7	6.4	0.8035	0.8119	101.0
	2.0	4.7	6.4	0.8035	0.8119	101.0
7	1.0	3.3	6.8	0.4006	0.4031	100.6
	2.0	3.3	6.8	0.4006	0.4059	101.3
	2.0	3.3	6.8	0.4006	0.4035	100.7
	2.0	3.3	6.8	0.4006	0.4050	101.1

TABLE II. DETERMINATION OF BROMIDE IN LARGE EXCESS OF CHLORIDE

EXPT.	BROMINE PRESENT Mg.	BROMINE FOUND Mg.	RECOVERY %
1	39.94	39.96	100.1
2	39.94	39.88	99.8
3	3.994	3.985	99.8
4	3.994	3.997	100.1
5	3.994	3.995	100.0
6	0.8064	0.8088	100.3
7	0.8047	0.8004	99.5
8	0.8038	0.8018	99.8
9	0.4009	0.3998	99.7
10	0.4009	0.4026	100.4
11	0.4009	0.4017	100.2
12	0.4009	0.4012	100.1

EFFECTS OF IODIDES

When the iodide content is small relative to the bromide content, no care is necessary to insure its removal. Some experiments were performed in which iodide equivalent to the bromide present was added. By adding at least six equivalents of chlorine water for each equivalent of iodide present, the iodide was completely oxidized to iodic acid and retained in the flask. The subsequent titration showed no evidence of iodide, and gave normal results for the bromide.

Data upon the application of this method to the analysis of urine samples appear in Table III.

TABLE III. DETERMINATION OF BROMIDES IN NORMAL URINE (2)

SUBJECT	24-HOUR URINE Cc.	BROMINE FOUND Mg.	REMARKS
A	1300	13.18	Usual diet Table salt
A	1300	9.32	Usual diet C. P. salt
B	1313	5.50	Usual diet C. P. salt
B	1010	6.60	Usual diet C. P. salt
C	1800	14.70	Usual diet Table salt

SUMMARY

A method for the determination of bromides in the presence of large excess of chlorides has been developed. The bromide

is liberated by chlorine water in moderate excess, collected in sodium sulfite solution, and titrated potentiometrically after air oxidation of the excess sulfite. For 4 mg. or more of bromine present as bromide the maximum error is about 0.2 per cent, and for a bromine content of from 0.5 to 1 mg. the error is about 0.5 per cent. Moderate quantities of iodides do not interfere.

LITERATURE CITED

- (1) Behr, Palmer, and Clark, *J. Biol. Chem.*, **90**, 133 (1930).
- (2) Corley, R. C., and Newton, E. R., unpublished results.
- (3) Fenwick, F., *IND. ENG. CHEM., Anal. Ed.*, **4**, 144 (1932).

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Improved Apparatus for Quantitative Estimation of Helium in Gases

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THERE are two general methods in use for determining the rare gas content of natural gases. Cady and McFarland (3) determined only the helium content, whereas Moureu and Lepape (13) estimated the total rare gas content and then further separated it into helium and neon, argon with small amounts of krypton and xenon, and krypton and xenon with small amounts of argon. In both methods use is made of the ability of charcoal, discovered by Dewar (7), to adsorb all gases except helium, neon, and hydrogen when cooled in liquid air. It was the experience of Cady and McFarland that hydrogen was freely adsorbed under these conditions, neon much less than hydrogen, and helium very slightly. Their apparatus consisted of a preliminary tube for condensing methane and other hydrocarbons, two tubes filled with charcoal, and two U-dips to condense moisture and mercury vapor, all immersed in liquid air. In addition there were two Plücker tubes, an automatic Sprengel pump, and a tube in which the helium was collected and measured. The purity of the gas was tested by observing its spectrum, and if any nitrogen was found present, the gas was again passed through the charcoal. This is essentially the apparatus which has been used by the U. S. Bureau of Mines and described by Seibel (16). Other workers who have used essentially the method of Cady and McFarland are Czako (6), McLennan (12), Yamada (13), Yamaguti and Kano (19), Chlopin and Lukasuk (5), and Butescu and Atanasiu (2). Erdmann (8) mixed oxygen with the hydrocarbons and hydrogen and exploded the mixture. Moureu and Lepape burned hydrogen, carbon monoxide, and the hydrocarbons to carbon dioxide and water over heated copper oxide. Carbon dioxide was then absorbed by potassium hydroxide, water by phosphorus pentoxide, and the nitrogen and oxygen were combined with heated calcium or magnesium. When no further pressure drop could be noticed and only the noble gases were distinguishable spectroscopically, the volume of gas was measured. Argon, krypton, and xenon were adsorbed by charcoal cooled with liquid air and the volume of the remaining helium and neon was measured. Through partial vaporization, argon with slight amounts of krypton and xenon is sometimes estimated, or xenon and krypton with slight amounts of argon.

Many authors have used at least the principle of the method of Moureu and Lepape. Bamberger (1) as well as Ewers (9) removed the last traces of nitrogen from the residual gas mixture with oxygen by sparking over potassium hydroxide. Other workers removed the total nitrogen content, after adding oxygen, by sparking over potassium hydroxide and removing the excess oxygen with pyrogallol.

Paneth (14, 15) and his students have developed a micro-method by means of which they claim to be able to estimate 10^{-7} cc. of helium with an accuracy of 2 per cent. Sokolov (17) has constructed a balance for measuring the density of the unadsorbed helium and neon for use with gases containing at least a helium and neon concentration totaling 0.1 to 0.2 per cent. A method for the continuous separation of helium from a gas mixture by the adsorption of the other gases by charcoal at liquid air temperatures has been described by Cherepennikov (4). He also claims to have accomplished the removal of all gases except helium by circulating the gas through charcoal cooled with solid carbon dioxide, regenerating the charcoal after each cycle.

The volume of gas sample used by different workers varies widely. Cady and McFarland used 13 to 15 liters, McLennan about 6 liters, Moureu and Lepape 200 cc., and Paneth, Gehlen, and Peters only 10 cc. With the exception of Chlopin and Lukasuk, who used a modification of an apparatus described by Guye and Germann (10), all workers cited have used a complex apparatus. The essential part of the simplification introduced by the latter authors lay in the combination of a vacuum pump, McLeod gage, and storage reservoir. The apparatus described in the present communication is a further adaptation of the apparatus of Guye and Germann to the analysis of helium.

DESCRIPTION OF APPARATUS

A diagram of the apparatus is given in Figure 1.

The tube *C* containing 30 grams of charcoal serves, when cooled with liquid air, to adsorb all the gases contained in the sample except helium (and some neon). The combination mercury pump and modified McLeod gage *E* serve to create a high vacuum, to measure the volume and pressure of the original sample, to cir-

culate the residual gas over the charcoal, and to collect and measure the residual helium under various reduced pressures. The distance between 1 and the mercury level in *D* must be less than barometric height. Between 1 and the lower end of *E* it has a volume of 142.6 cc. The gage and pump also serve as one arm of a manometer to measure the gas pressure. A capillary tube *B* inserted in the main line and provided with platinum terminals serves as a Plücker tube, but does not have the usual disadvantage of increasing the volume of the apparatus. *A* and *H* are filled with fused calcium chloride to keep the air in the manometer tubes clean and dry.

By means of the three-way stopcock 1 the apparatus may be evacuated, the gas recirculated over the charcoal, or the system *B*, *C*, *E* evacuated, leaving gas stored in the tube between 1 and 2. By the use of stopcock 2, gas may be pumped from *C* and connecting tubes and stored in the calibrated tube between cocks 1 and 2 until succeeding strokes of the pump can no longer collect appreciable quantities. Then by leaving cock 1 closed and 2 open the volume and pressure may be determined. The upper part of this tube is calibrated in 0.01 cc. and the lower part in 0.10 cc. The side tube *S* of the same bore as the upper part of the gage tube may be inserted so as to correct for capillary depression when reading on the upper tube. The right side opening of cock 3 connects to the water pump, serving to make the mercury enter *D*. The left side is made of a small capillary tube so that if the cock is opened wide to the air, the air enters *D* slowly and the mercury is prevented from rushing into *E* too rapidly. At 4 there is a ground joint float having the mercury rise to a barometric height. It might equally well have been constructed of a porous diaphragm, but evacuation through a

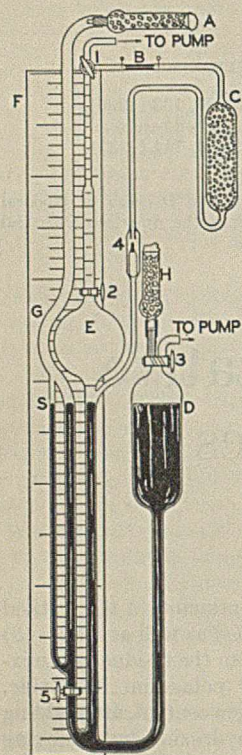


FIGURE 1. DIAGRAM OF APPARATUS

porous diaphragm is somewhat slower. Stopcock 5 serves to keep the mercury in *G* from falling when *D* is evacuated. An electric heater is conveniently fastened to the metal framework so that it can be placed over the charcoal during preliminary activation. The same support serves to hold the liquid air flask in position. The entire apparatus is mounted on a board surrounded by a molding so as to hold any spilled mercury, and is compact, portable, and easily adaptable to field work.

EXPERIMENTAL PROCEDURE

The apparatus is prepared for an experiment by turning stopcocks 1 and 3 so as to connect with the water aspirator. Stopcock 2 is left open, but 5 is closed. The electric heater is placed over *C* and is maintained at 360° C. for 1.5 hours. Under these conditions the mercury level is as indicated in the diagram, and the gases liberated in *C* have a free passage by way of 4, 2, and 1 to the aspirator. By reversing stopcock 3 air is admitted to *D* and the mercury rises in *E*. When the mercury reaches stopcock 1, it is closed and compartment *D* is again evacuated. The valve at 4 closes as the mercury rises, and falls again as soon as the mercury falls in *E*. The pressure in *C* is now greater than in *E*, so that gases pass from *C* to *E*. Stopcock 1 is kept closed until, after the next stroke of the pump, the mercury again has almost reached it, when it is opened and the entrapped gas discharged. This is continued after short intervals of time to permit the establishment of pressure equilibrium until no appreciable additional amounts of gas can be removed. The discharge through the Plücker tube *B* serves as a very convenient indication of the vacuum within. After evacuation with the mercury pump, the discharge is still visible but is usually very weak.

The heater is now removed and the charcoal tube allowed to cool to room temperature. If there is no leak in the apparatus, this cooling brings about sufficient adsorption of the residual gases to prevent any further discharge through the Plücker tube. If the apparatus stands thus overnight without sufficient gas entering to permit a discharge, it may be considered to be free of leaks.

The gas sample is now dried by passing it through concentrated sulfuric acid before it is admitted at stopcock 1. Prior to opening 1, air is allowed to enter at *D* and the mercury rises to 1. The sample is now admitted through 1, 3 being opened carefully in the direction of the aspirator, and stopcock 5 is opened. A simple calculation will now give the reduced volume of the sample at the particular temperature. Stopcock 5 is now closed and 1 is carefully turned to admit the sample through *B* to *C*, which has been previously immersed in liquid air. Stopcock 3 may be opened to the atmosphere, as all the gases except helium and neon are adsorbed in *C*. The mercury is now allowed to pass stopcock 1. As the gases enter *C* the liquid air begins to boil vigorously. The residual gases are allowed to remain in contact with the charcoal for 10 minutes to insure complete condensation of all adsorbable gases. If there is any helium present, it is now made evident by the discharge through the Plücker tube. It is convenient to have a tube filled with a sample known to contain helium as a comparison standard mounted close to the apparatus so that both may be viewed with the pocket spectroscope. Some mercury lines will usually be found, but in the authors' case, no neon was visible.

With stopcock 1 still closed, the mercury in *E* is lowered by evacuating *D*. As the mercury falls away valve 4 opens, and when the *Y* passage is cleared the helium residue expands into *E*. Using the apparatus now as a mercury pump, the gas in *E* is compressed into the tube between 1 and 2. Stopcock 2 is then closed and the operation repeated. With each stroke of the pump more helium is confined between 1 and 2. After six or eight strokes, there is again no discharge in *B*. This pumping to a low pressure is necessary to avoid adsorption, since it has been shown by Dewar and later by Homfray (11) that 2.5 cc. of helium are adsorbed by 1 gram of charcoal at liquid air temperatures, at atmospheric pressure. Stopcock 5 is opened and the gas volume is measured at various points between 1 and 2 at pressures indicated by the difference in mercury levels in tubes *G* and *E*. The actual pressure on the gas is found by subtracting this difference from the barometric pressure. If greater volumes of the gas sample are desired, it is only necessary to pass the helium into *C*, then pass additional volumes into *E*.

Experiments were run on gases containing from 0.23 to 0.52 volume per cent of helium. Analyses using all the way from one charge (142.6 cc.) to seven charges (1000 cc., approximately) were made, showing that no increase in accuracy was obtained by using larger samples than 142.6 cc. Results checked each other consistently to 0.01 volume per cent.

LITERATURE CITED

- (1) Bamberger, *Monatsh.*, 17, 604 (1896); 19, 114 (1898).
- (2) Butescu and Atanasiu, *Petroleum Z.*, 23, 391 (1928).
- (3) Cady and McFarland, *J. Am. Chem. Soc.*, 29, 1523 (1907).
- (4) Cherepennikov, Russian Patent 25,598, Mar. 31, 1932; *Prirodnaie Gazui*, 2, 83 (1931).
- (5) Chlopin and Lukasuk, *Ber.*, 58, 2392 (1925).
- (6) Czako, *Z. anorg. Chem.*, 82, 249 (1913).
- (7) Dewar, *Chem. News*, 90, 90 (1904); *Proc. Roy. Soc. (London)*, A74, 122 (1904).
- (8) Erdmann, *Ber.*, 43, 777 (1910).
- (9) Ewers, *Physik. Z.*, 7, 224 (1906).
- (10) Guye and Germann, *Compt. rend.*, 159, 154 (1914).
- (11) Homfray, *Z. phys. Chem.*, 74, 157 (1910).
- (12) McLennan, *J. Chem. Soc.*, 117, 923 (1920).
- (13) Moreau and Lepape, *J. chim. phys.*, 11, 63 (1913); *Compt. rend.*, 171, 942 (1920).

- (14) Paneth, Gehlen, and Peters, *Z. anorg. allgem. Chem.*, 175, 383 (1928).
 (15) Paneth and Peters, *Z. phys. Chem.*, 134, 353 (1928).
 (16) Seibel, U. S. Geol. Survey, *Professional Papers* (Rogers) 121, 41-2 (1921).
 (17) Sokolov, *Neftyanoe Khozyaistvo*, 19, 292 (1930).
 (18) Yamada, *Rept. Aeronaut. Research Inst., Tokyo Imp. Univ.*, 1, No. 6, 171 (1923).
 (19) Yamaguti and Kano, *Ibid.*, No. 13, 347 (1926).

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Continuous Determination of Carbonate-Caustic Ratio in a Carbon Dioxide Absorption System

Conductance Apparatus Used in the Bureau of Mines Helium Plant

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REMOVAL of carbon dioxide from helium-bearing natural gas by scrubbing with a solution of caustic soda is the initial operation at the Amarillo Helium Plant. The spent caustic solution is treated with lime in a recausticizing system and then recycled (γ). For optimum economy in operation it is essential that when the predetermined ratio of carbonate to caustic at which the solution is considered to be spent is reached, it will be accurately known by a method free from personal error and continuous in performance.

An apparatus, operating on the change in electrical conductivity accompanying the decrease in free hydroxide content of the caustic solution, has been developed for continuous determination of the composition of the solution. Satisfactory results are possible only when the total sodium-ion concentration of the caustic solution remains essentially the same for different batches. The apparatus may be calibrated to read in terms of free caustic, carbonate, or ratio of carbonate to caustic. The rate of conversion of the caustic is also indicated. The apparatus, as described below, has operated satisfactorily for several months and has proved of value.

THEORETICAL DEVELOPMENT

An early application of the method of analysis, which has been used for the apparatus, was made by Cain and Maxwell (2) to determine carbon in steel. Later, Hirsch (3) proposed to call such a method "conductance analysis." The method has general application, but special consideration must be given each problem.

When two electrolytic solutions are mixed, the conductivity of the resulting mixture cannot, in general, be calculated from the conductivities of the components by the law of simple mixtures, because each component affects the dissociation of the other and changes the total number of ions present. In mixtures containing weak electrolytes it is sufficiently exact, for most purposes, to assume that such electrolytes obey the law of mass action. If the mixture contains only one strong

An apparatus based on the variation in electrical conductivity accompanying a change in the hydroxide content of a caustic solution, has been installed at the Bureau of Mines Amarillo Helium Plant to give a continuous record of the sodium hydroxide content, or the ratio of sodium carbonate to sodium hydroxide, in a solution used for removing carbon dioxide from natural gas. The instrument indicates the rate at which the hydroxide is reacting with carbon dioxide to form the carbonate, and is adaptable to automatic control of the system for removal of carbon dioxide or to an alarm for indicating a spent solution. It has proved to be sufficiently accurate for plant purposes, to be reliable, and to require but a minimum of attention.

electrolyte its degree of dissociation may be assumed to be practically unchanged by the presence of a weak electrolyte. If there are two or more strong electrolytes present the ionization equilibrium of each component will be influenced by the presence of the ions of the other electrolytes, and calculation of the degree of dissociation is difficult. Arrhenius (9) was the first to investigate the relation that must exist between solutions of two electrolytes having a common ion, in order that they may not exert any mutual influence when mixed in any proportions. He demonstrated the isohydric principle showing that — when the concentration of the

common ion in each of two solutions is the same before mixing no alteration in the degree of ionization occurs after mixing.

Mixtures of hydroxide and carbonate resulting from partial neutralization become isohydric at equivalent ionic concentrations. White (10) states a principle, introduced by Arrhenius, which concerns intermediate mixtures: "In a mixture of two salts with a common ion each salt has a degree of ionization equal to that which it would have when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture." White points out that Bray and Hunt (1) have tested this principle and have found, in mixtures of sodium chloride and hydrochloric acid, that the measured values of the specific conductance agreed closely with the values calculated on the assumption that the degree of ionization, and therefore the equivalent conductance, of each compound depended on the total concentration.

In the present case, the total alkali concentration, $C_{NaOH} + C_{1/2Na_2CO_3}$, remains unchanged throughout the absorption cycle, except for a maximum dilution of 0.9 per cent per mole of sodium hydroxide converted, and the specific conductance k of any mixture may be calculated, for all practical purposes, from

$$k = \wedge C_{NaOH} + \wedge C_{1/2Na_2CO_3}$$

where

\wedge = equivalent conductance at total alkali concentration
 C = concentration in gram equivalents per cc.

The conductance range for use in designing the electrical circuit may be calculated by means of this equation.

The fresh caustic solutions contain approximately 70 grams per liter of sodium hydroxide and 9 grams per liter of sodium carbonate, which is equivalent to a solution containing 76.8 grams per liter of sodium hydroxide, or 1.92 *N*. The spent solution has an approximate concentration of 9 grams per liter of sodium hydroxide and 90 of sodium carbonate. Since the total alkali concentration remains the same, the equivalent conductance of each compound does not change from its value at 1.92 *N*. The specific conductance of the two solutions have been calculated by substituting the appropriate values (4) in the above equation.

Fresh solution:

$$k_{18^\circ} = 131.8 \times \frac{70}{40.0 \times 1000} + 35.0 \times \frac{9}{53.0 \times 1000} \\ = 0.237 \text{ ohm}^{-1}$$

Spent solution:

$$k_{18^\circ} = 131.8 \times \frac{9}{40.0 \times 1000} + 35.0 \times \frac{90}{53.0 \times 1000} \\ = 0.089 \text{ ohm}^{-1}$$

The change in specific conductance, corresponding to a change in the specific resistance of

$$\frac{1}{0.089} - \frac{1}{0.237} = 7.0 \text{ ohms}$$

is ample for accurate measurements with an instrument suitable for plant installation.

This method of analysis postulates a constant sodium-ion content. Owing to dilution from the reaction, the normality of the caustic solution with respect to sodium ions decreases as the conversion to carbonate proceeds. The error resulting from dilution may be practically eliminated by an empirical calibration since the effect remains essentially the same for different batches. It is desirable to evaluate the error introduced both by a change in sodium-ion content during the reaction and also by different initial concentrations to determine the applicability of an apparatus for continuous analysis.

The normality of the caustic solution with respect to sodium is changed from 1.92 to 1.89, through a theoretical dilution of 0.9 per cent per mole of sodium hydroxide converted. This corresponds to a change in specific resistance of from 7.0 to 6.9 ohms, which is equivalent to a 2.16 per cent change in the weight per cent ratio of sodium carbonate to sodium hydroxide. A change of normality of 1 per cent during conversion, therefore, causes an error of 1.3 per cent in the ratio. The effect of different initial concentrations may be calculated in the same manner by determining the change in ratio corresponding to an assumed change in concentration. It is calculated that a change in normality of 1 per cent from the value on which the calibration of an apparatus is based will cause an error of 0.9 per cent in the measured ratio.

GENERAL DESIGN OF APPARATUS

Electrical methods in analytical work are becoming more commonly used because of their rapidity, accuracy, and adaptation to control. The design of the apparatus follows the standard practice for industrial application, as exemplified in numerous commercial instruments using the Wheatstone-bridge method for measurement of resistance—for example, in instruments for measuring condenser leakage and boiler-water concentration.

Measurements of conductivity are subject to a positive error due to polarization of the electrodes. This error may be minimized and made practically negligible by a combined

use of properly prepared electrodes, large electrode area, a high-frequency current, and a high-resistance cell. Jones and Josephs (5) recommend the use of cells having high cell constants (length divided by cross section) so that the resistance to be measured will be large, thereby reducing polarization and heating effects in the cells. Convenient installation at the Amarillo Helium Plant requires the use of 60-cycle current, and the high conductivity of the solution makes it necessary to reduce the electrode area and increase the spacing to increase the cell constant. Constructional difficulties limit the size of the cell, so that while the cell constant is as large as practicable the resistance is yet small. The electrodes are platinized to reduce the polarization error.

By using a balanced Wheatstone bridge a detecting instrument of high sensitivity may be employed with the small current required. Readings are also practically independent of variation in line voltage, and the accuracy of measurement is not influenced by changes in the characteristics of the indicating instrument, since the latter indicates only the null point.

The caustic solution contains impurities such as calcium, silicon, magnesium, iron, and aluminum compounds in small amounts, but probably in sufficient quantity to affect the agreement between the calculated and the measured resistance of the solution. To exclude as many variables as possible it would be desirable, if practicable, to eliminate the effect of impurities by making relative measurements using two cells, one containing the fresh solution and the other containing the solution as it is cycled. It is not possible to do this in the installation described because measurements of the relative change in resistance would require the same ratio of sodium hydroxide to sodium carbonate in each batch of fresh solution to be cycled. It is impracticable to obtain this in plant operation. A fixed resistor having a resistance equivalent to the average of that of the fresh solutions is used in place of a second cell. The error introduced by using only one cell is small and decreases as the solution becomes spent. Although the initial content of sodium hydroxide may differ in the various batches, the total alkali content is approximately the same in each case, and the ratio of carbonate to caustic at which the solution is considered to be spent is fixed at a definite value. To protect the electrodes in the cell and prevent a change in surface area, a solution filter is placed before the cell.

The circulating caustic solution is at temperatures ranging from 65° to 35° C. Temperature compensation cannot be accomplished by the usual method of manual or automatic adjustment of a resistance in the bridge circuit because of the variable composition of the solution. For that reason the conductivity cell is thermostated. The solution, however, must be precooled before final adjustment of the temperature in the thermostat.

It has been proved experimentally (5) that under some conditions the use of water in the thermostat and the grounding of the thermostat may result in serious errors due to three causes: (1) Capacitance is introduced by the grounded conducting liquid in the thermostat, (2) the walls of the glass cell may act as a dielectric in a condenser, allowing alternating

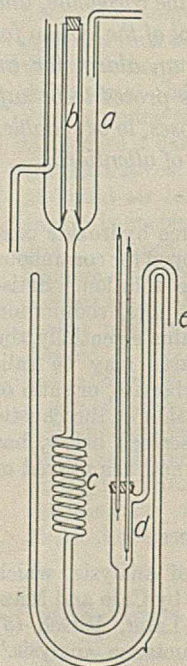


FIGURE 1. DIAGRAM OF APPARATUS

current to flow outside the cell and thus decrease the measured resistance of the cell, and (3) the alternating current in the cell may induce eddy currents in the water outside the cell, having the effect of increasing the apparent resistance. The errors from these causes are directly proportional to the cell resistance and to the frequency and may amount to 0.5 per cent in extreme cases.

Under conditions where errors resulting from use of water would be serious, oil may be used as the thermostat liquid.

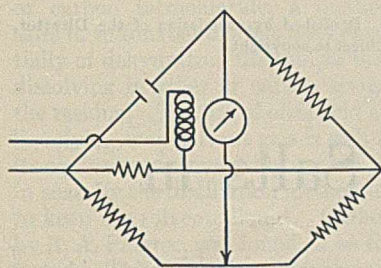


FIGURE 2. ELECTRICAL CIRCUIT

However, in the installation at the Amarillo Helium Plant the error introduced into the measurements by the use of water as the thermostat liquid is considered to be less than 0.1 per cent because of the relatively low resistance of the cell and the comparatively low frequency of the current. Consequently, advantage has been taken of some of the more desirable physical properties of water as a thermostat liquid in using it rather than oil without introducing an appreciable error.

CONSTRUCTION OF APPARATUS

Figure 1 indicates the arrangement of the conductivity apparatus as finally constructed.

A regulated flow of solution through the cell is obtained with the constant-head device *a*. The solution is filtered through the alundum tube *b*, and its temperature is equalized in the coil *c*, which is immersed in the thermostat with the cell *d*. The solution is discharged into the drain at *e*. The conductivity cell contains the two electrodes, which are platinum wires fused into soda-glass tubes. The electrode spacing is adjustable. Electrical connection is made through mercury which fills the tubes. The thermostat is a large Dewar tube filled with water, the temperature of which is controlled at 30° C. by a toluene-mercury thermoregulator operating an immersion heater. The water is stirred by a slow stream of air.

The electrical circuit is shown in Figure 2. Since no resistance-recording instrument was available, a Leeds & Northrup potentiometer recorder was adapted for use as a conductance-measuring instrument. This was done by replacing the galvanometer assembly with one designed for alternating current and by replacing the potentiometer circuit with a Wheatstone-bridge arrangement. The 110-volt source of alternating current was supplied to the galvanometer field coil and the bridge through a 1 to 1 insulating transformer because it was difficult to prevent current leakage from the immersion heater. To insure the currents through the galvanometer and through the bridge circuit being in phase the potential of 4 volts for the bridge was taken from the galvanometer-field coil circuit by means of a potential divider. (This arrangement of the recorder and electrical circuit follows standard practice in commercial conductivity recorders.)

CALIBRATION OF APPARATUS

Four solutions were made up from the spent and the fresh caustic for preliminary calibration, their compositions being determined by the method of Winkler (8). Data for calibration were also calculated for the solutions, but the agreement was not close, probably because the effect of the impurities in the solution had not been taken into account and because of inaccuracies in obtaining a cell constant (apparatus for precise conductivity measurements was not available). The preliminary results served only to establish the trend of the calibration curve. Since the apparatus was designed for use under plant conditions it was essential that its calibration should agree well with routine analytical results. Final cali-

bration was made while the instrument was in operation. Recorder readings were taken, at the times the periodic analyses of the solution were made, over a period of several weeks. The data obtained are plotted in Figure 3. The curves are drawn only for the range of the instrument, although their courses have been determined by calculation and extrapolation to zero sodium hydroxide and sodium carbonate contents.

OPERATION AND RELIABILITY OF APPARATUS

As installed in the Amarillo Helium Plant, the apparatus has required attention only in cleaning the filter daily and the electrodes occasionally. The alundum filter used must be porous enough to filter rapidly and yet must retain the extremely fine suspended material in the caustic solution which seems to collect first upon the electrodes. Alundum tubes made of mixture RA-68 (Norton Co.) have proved satisfactory for the filter. With the filter cleaned daily, the surfaces of the electrodes remain apparently unchanged for several weeks. As frequently as experience shows it to be necessary the electrodes should be cleaned, rinsed in distilled water, and plated with platinum black deposited from a 10 per cent platinum chloride solution containing 0.025 per cent of lead acetate. Current for the plating may be supplied from one or two dry cells, reversing the polarity of the electrodes every 30 seconds.

The lag in the apparatus is largely determined by the rate of overflow at the filter. In the installation described this may be as rapid as desired, since the overflow is returned to the system. The rate of flow through the cell should be slow enough to insure equalization of the temperature, and may be adjusted by changing the liquid head or by using a capillary in the line after the filter. The normal rate of flow through the cell is about 10 cc. per minute.

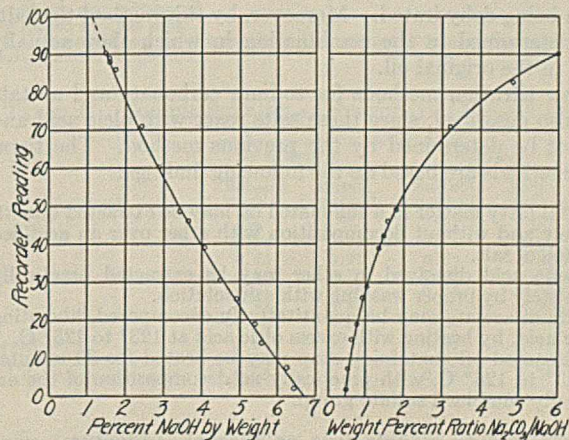


FIGURE 3. CALIBRATION CURVES

In estimating the accuracy of the apparatus, variations in frequency, impurities, dilution, and total alkali content must be considered, as well as the sensitivity of the recorder. With a frequency of about 1000 cycles, the error due to polarization, which is always present when current passes through an electrolyte and which causes a discrepancy between the true and apparent resistance, is small with platinized electrodes if the resistance is above a critical value. It has been empirically determined (6) that the error introduced by reducing the frequency below 1000 cycles varies, approximately, inversely as the square root of the frequency within the range 60 to 1000 cycles. If the error in measurement is 0.1 per cent at 1000 cycles, about 0.4 per cent error will be introduced at 60 cycles. If the cell is calibrated at 60 cycles this error may be considered negligible.

In the installation described calibration is made at 60 cycles, and discrepancies caused by variation in line frequency need not be considered in the relative measurements. The most serious source of error is expected to be that due to variations in total alkali content. Based on results obtained with the apparatus in use under plant conditions, the precision of the instrument may be given as ± 2 per cent of the ratio of carbonate to caustic.

LITERATURE CITED

- (1) Bray, W. C., and Hunt, F. L., *J. Am. Chem. Soc.*, 33, 781 (1911).
- (2) Cain, J. R., and Maxwell, L. C., *J. IND. ENG. CHEM.*, 11, 852 (1919).

- (3) Hirsch, Paul, *Z. anal. Chem.*, 68, 160 (1926).
- (4) International Critical Tables, Vol. VI, pp. 247, 248, and 254, McGraw-Hill, 1929.
- (5) Jones, Grinnell, and Josephs, R. C., *J. Am. Chem. Soc.*, 50, 1049 (1928).
- (6) Leeds & Northrup, *Catalog*, 48 (1930).
- (7) Seibel, C. W., *Chem. & Met. Eng.*, 37, 550 (1930).
- (8) Suchier, A., *Z. angew. Chem.*, 44, 534 (1931).
- (9) Taylor, H. S., "Treatise on Physical Chemistry," 2nd ed., Vol. I, p. 692, Van Nostrand, 1930.
- (10) White, E. C., *J. Am. Chem. Soc.*, 50, 2148 (1928).

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Determination of Inorganic Salts in Sulfonated Oils

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IN THE committee discussion prior to the adoption of Commercial Standard CS43-32 of the Bureau of Standards for the grading of sulfonated (sulfated) oils, a simple method was abandoned because of the lack of an adequate method for determining alkali sulfates and chlorides in such products. A new method is here outlined that determines these salts readily and accurately. It depends upon the fact that dehydrated sulfonated oils become miscible with carbon tetrachloride in the presence of oleic acid and the inorganic salts are insoluble in the mixed solvent. The addition of oleic acid directly to the oil also prevents the sample from jellying upon being dehydrated. Moreover, by this method the salts are determined in the combination in which they actually exist in the original oil.

New titration methods for sodium carbonate and acetate are also described, since these salts react with oleic acid and cannot be determined by the previous method. The titration methods are based on the following findings:

Total fatty matter in a sulfonated oil may be extracted quantitatively and without decomposition with ether over an acidified solution of salt.

Acetic acid dissolved in ether may be extracted practically completely by proper washing with salt solution.

Sodium acetate may be quantitatively decomposed, liberating acetic acid, by heating with excess oleic acid at 123° to 125° C.

Sulfonated oil containing soap may be heated for 30 minutes at 123° to 125° C. with practically no decomposition of the organically combined sulfate group.

Incidental to manufacture or through admixture, commercial sulfonated oils may contain various amounts of inorganic salts, such as alkali chlorides, sulfates, and less frequently acetates, carbonates, etc. The determination of inorganic sulfate in sulfonated oils is part of the regular procedure for finding organically combined sulfuric anhydride by the barium sulfate methods, but the other inorganic salts are practically always included with the "undetermined," largely because no satisfactory direct method of analysis for inorganic salts has been described. A satisfactory method would not only round out the analysis of a sulfonated oil but would also be of great assistance in grading or classifying such products. Thus, in connection with Commercial Standard CS43-32 of the Bureau of Standards (3), the committee was in favor of grading sulfonated oils by subtracting from 100 per cent the sum of the moisture and inorganic salts, but this method had to be abandoned because the methods for determining inorganic salts were unsatisfactory.

Herbig (8) determines inorganic sulfate by dissolving the sample in ether, washing with a saturated solution of sodium chloride, and precipitating the sulfate in the wash water with barium chloride. To overcome troublesome emulsions, which highly sulfonated oils tend to form, he replaces one third of the ether with benzene. If emulsions still persist, Herbig dissolves the oil in absolute alcohol, filters, dissolves the residue in hot water and determines the inorganic sulfate in the filtrate. Nishizawa (10) attributes these emulsions to the comparatively easy solubility of the normal or disodium salt of sulfonated oils in concentrated sodium chloride solution, and further states that the compound is salted out with considerable difficulty even in the presence of solid sodium chloride. On the other hand, the monosodium salt is practically insoluble in saturated sodium chloride solution. Accordingly he modifies the Herbig method by first converting the compound to the monosodium salt with hydrochloric acid, using methyl orange as the indicator.

In the official method of the Wissenschaftliche Zentralstelle für Öl- und Fettforschung (12) a mixture of 40 per cent ether and 60 per cent amyl alcohol is used as solvent for the oil; otherwise the procedure is the same as the Herbig benzene-ether method (8). Burton and Robertshaw (2) determine total inorganic salts by digesting the dehydrated sample with alcohol or alcohol-ether, filtering, dissolving the residue in hot water, and determining the solids in the filtrate by evaporation. The inorganic salts, they state, are not completely precipitated with alcohol in the case of many sulfated oils. Some tests made in this laboratory indicate that the Burton and Robertshaw method may yield good results with sodium sulfate but is not satisfactory with sodium chloride using 95 per cent alcohol as one of the solvents. The results on a sample, in which the inorganic salts contained about 90 per cent sodium chloride and the rest sodium sulfate, were as follows:

SOLVENT	INORGANIC SALTS	
	Added	Found
	%	%
2 parts ethyl ether and 1 part 95 per cent alcohol	7.84	6.32
2 parts ethyl ether and 1 part absolute alcohol	7.84	7.52

Difficulties may also be experienced with the alcohol-ether solvent in the case of dehydrated oils containing at the same time large amounts of fatty glycerides or mineral oils, and neutral soap. The former are sparsely soluble in alcohol and the latter in ether.

Another method for total inorganic salts is that of Hart (4, 5). According to this method, total nonvolatile inorganic salts are determined indirectly from the ash, fixed alkalinity, and organically combined sulfuric anhydride in the sample. This procedure is also the official method of the American Leather Chemists Association (1). It yields reliable and accurate results, except in the presence of ammonium salts and sodium acetate; the former is volatilized during the ignition and the latter changed to the carbonate. Moreover the formulas are calculated for sodium salts and in the presence of potassium it becomes necessary to determine the metallic elements.

McBain and McClutchie (9) state that soda soaps dissolve and form jellies in nonpolar solvents, such as benzene, xylene, etc.,

and also that sodium oleate and stearate exhibit no signs of gelation in acetone or chloroform.

The writer finds that sulfonated oils, particularly when neutralized and dehydrated, dissolve in ethyl ether or carbon tetrachloride with great difficulty, giving practically non-filterable solutions. However, the dehydrated oil becomes miscible with these solvents upon the addition of oleic acid. Taking advantage of this fact and also of the practically negligible solubility of sodium chloride and sulfate in ether or carbon tetrachloride, a method for determining these salts in sulfonated oils has been developed. It consists essentially of dehydrating the sample in the presence of oleic acid, dissolving in ether or carbon tetrachloride, and filtering off the residue. The use of oleic acid as a coupling agent and for liquefying soap-solvent gels is well known (7). Oleic acid or its equivalent is invariably used in the determination of water in soap by the distillation method (6) to prevent foaming and to keep the solvents liquid. Carbon tetrachloride, suggested by R. A. Pingree, was found to be the best of several solvents tested. This method was developed as a part of an investigation being carried out by a subcommittee on sulfonated oils, appointed by the American Association of Textile Chemists and Colorists.

PROCEDURE FOR ALKALI SULFATES AND CHLORIDES

Weigh 3 to 5 grams of the sample into a 250-cc. beaker, add an approximately equal amount of oleic acid and about 0.5 cc. of 1 *N* caustic soda, and heat in an oil bath to 105–110° C. until practically water-free. Then raise the temperature to 118–120° C., keeping it there for about 5 minutes. The dehydrated sample should remain liquid and homogeneous upon cooling, otherwise more oleic acid is required. Dissolve the dehydrated sample in 100 cc. of carbon tetrachloride (50° to 55° C.) and filter through a Gooch crucible or through a counterpoised filter paper. The last traces of the residue may readily be transferred by allowing the solvent to evaporate, when the salt is easily detached from the glass wall. Wash the residue with three 15-cc. portions of a 2 per cent solution of oleic acid in carbon tetrachloride, warmed to 50–55° C., and then with six 15-cc. portions of hot carbon tetrachloride and two 15-cc. portions of ether, or until free from oil, care being taken that the top of the filter is thoroughly washed. Dry at 125° to 130° C. for 45 minutes, and repeat drying until constant weight is obtained. The residue is finally ignited and again heated to constant weight. The last weight is taken as the final result. Any appreciable difference between the "dried" and "ignited" residues indicates either volatile salts or fatty matter. Obviously in the presence of ammonium or other volatile salts, the "dried" residue should be taken as the final result.

The ordinary sulfonated oil was found to be stable when heated as outlined as long as there was some soap present, even as little as 2.0 per cent on the weight of the sample. There was also no reaction between the salt and the free fatty acids upon heating. This was shown by the fact that the alkalinities of a sample containing salt were identical before and after heating. If a reaction did occur, soap would form and the alkalinity of the sample would be correspondingly increased. Evidently alkali added to stabilize the oil will not affect the result, provided it is all converted into soap. Oleic acid is added to the carbon tetrachloride in the first washings in order to prevent precipitation of soap on the residue. The determination of the dried as well as the ignited residue is suggested in order to detect the presence of insoluble fatty matter or ammonium salts, or incomplete washing. The residue, of course, may be analyzed for its constituents by the usual methods for inorganic analysis. It is to be noted that this method yields the alkali salts in the form actually present in the original oil, including chlorides which are not determined by the barium sulfate method.

In Table I are listed sulfonated products, containing sodium or ammonium sulfate or sodium chloride, that were analyzed for their salt content by the solvent method and, in a few

cases, also by the Herbig or barium sulfate method. The figures represent the averages of several analyses. The differences in the amount of sodium sulfate by the two methods for samples 1 and 2, given in the last column, were 0.04 and 0.08 per cent, respectively, and for sample 3 containing ammonium sulfate the difference was 0.21 per cent. Sample 4 showed 4.93 per cent of sodium chloride by the solvent method, compared with 4.91 per cent added. In all cases the residues upon ignition, with the exception of sample 8, showed a slight loss. Sample 8 is a special product, brought on the market within the past few years as a detergent, and is supposedly a condensation product of a fatty acid and a sulfonated amino compound. Ignition of the dried residues was accompanied by slight charring, apparently due to adsorbed fatty matter. In the remaining samples listed in Table I, the reliability of the solvent method is indicated by the small differences in weight between the "dried" and "ignited" residues. That soaps of saturated fatty acids do not interfere with the method is shown by sample 6, representing a neutralized sulfonated tallow, which upon ignition lost only 0.12 per cent.

TABLE I. INORGANIC SULFATES AND CHLORIDES IN SULFONATED OILS

SAMPLE	DESCRIPTION	NATURE OF SALT	INORGANIC SALT				
			SOLVENT METHOD	BA-RIUM SULFATE METHOD	DIF-FERENCE	DIF-FERENCE	
			Dried %	Ignited %	Difference %	Difference %	
1	Sulfonated castor oil	Na ₂ SO ₄	0.92	0.83	0.09	0.79	0.04
2	Sulfonated castor oil	Na ₂ SO ₄	6.72	6.64	0.08	6.56	0.08
3	Sulfonated castor oil	(NH ₄) ₂ SO ₄	8.52	8.73	0.21
4	Sulfonated castor oil	NaCl	5.00	4.93 ^b	0.07
5	Highly sulfonated oil ^a	Na ₂ SO ₄	2.92	2.84	0.08
6	Sulfonated tallow	Na ₂ SO ₄	6.41	6.29	0.12
7	Sulfonated mineral oil	Na ₂ SO ₄	0.25	0.22	0.03
8	Sulfonated detergent ^c	NaCl	18.52	17.75	0.77
		Na ₂ SO ₄					

^a 93 per cent sulfonated.

^b Added 4.91 per cent.

^c Commercial sample of a condensation product of a fatty acid and a sulfonated amino compound.

TABLE II. SODIUM SULFATE IN SULFONATED CASTOR OILS

ANALYST	SODIUM SULFATE			
	SAMPLE C		SAMPLE C-1	
	Solvent method %	Barium sulfate method %	Solvent method %	Barium sulfate method %
1	0.74	0.75	6.74	6.22
2	0.83	0.79	6.64	6.56
3	0.78	0.76	6.63	6.55
4	0.81	0.76	6.64	6.03
5	0.81	0.85	6.55	6.90
6	0.95	0.71	6.86	7.16
Grand av.	0.82	0.77	6.68	6.57
Greatest difference	0.21	0.14	0.31	1.13
Av. deviation from mean	0.05	0.03	0.08	0.31

To determine the possibility of agreement among different analysts using the solvent method, members of the American Association of Textile Chemists and Colorists subcommittee on sulfonated oils were asked to analyze by the new method two samples of sulfonated castor oil, samples C and C-1, containing various amounts of sodium sulfate. For purpose of comparison, the samples were also analyzed by the barium sulfate method. The results, which represent the averages of check analyses, are given in Table II. It will be observed that for sample C the average was 0.82 per cent by the solvent method and 0.77 per cent by the gravimetric method, or a difference of only 0.05 per cent; and for sample C-1 the results were 6.68 and 6.57 per cent, respectively, or a difference of 0.11 per cent. The agreement in results for sample C-1, as shown by the greatest difference and the average deviation from the mean, was considerably better for the solvent method than the gravimetric method—namely, 0.31 and 0.08 per cent compared with 1.13 and 0.31 per cent, respectively.

DETERMINATION OF SODIUM ACETATE AND SODIUM CARBONATE

The solvent method unfortunately cannot be used in the presence of sodium acetate or carbonate, since these salts react with the free fatty acids to form soap when the oil is dehydrated. It has also been found that solid sodium acetate, thrown out of the neutralized oil during dehydration, reacts quantitatively with the excess oleic acid added to the solvent to effect solution of the oil. This reaction takes place even at temperatures below the boiling point of the solvent. Trotman (11) made experiments to determine whether different proportions of oleic acid are able to decompose sodium acetate completely when distilled with steam. When only small quantities were used, decomposition was practically complete, the acetic acid in the distillate corresponding to the whole of oleic acid taken. When larger quantities of oleic acid were taken, only a portion was recovered as acetic acid.

A method available for acetate is to determine the acetic acid by steam distillation with phosphoric acid. However, the volatility of fatty acids (11) with steam and the presence of carbonate may interfere with the accuracy of this method. Alkali carbonates may be determined as in soap analysis, by taking advantage of their insolubility in alcohol. The dehydrated sample is digested in absolute alcohol or with a mixture of ether, and the residue after filtration is washed free of titratable salts, such as sodium acetate, etc. The residue is then dissolved in hot water and the carbonate determined in the filtrate by titration.

More rapid and convenient titration methods for both alkali carbonates and acetates have been developed in this laboratory and seem to be accurate within 0.2 per cent. Since sodium acetate cannot be accurately titrated with the usual indicators because of free acetic acid, it becomes necessary to remove the acid either by volatilization or by washing. The titration methods are based on the following findings: Total fatty matter in a sulfonated oil may be extracted quantitatively without decomposition with ether over an acidified solution of salt; acetic acid dissolved in ether may be extracted practically completely by proper washing with salt solution; sodium acetate may be quantitatively decomposed, liberating acetic acid, by heating with excess oleic acid at 123° to 125° C.; and a sulfonated oil containing soap may be heated for 30 minutes at 123° to 125° C. with practically no decomposition of the organically combined sulfate group. The titration method is varied somewhat, depending upon whether or not the sample contains carbonates, acetates, or both.

PROCEDURE IN PRESENCE OF CARBONATES ONLY

ALKALINITY AS SOAP (A_s). Dissolve 5 grams of the sample in 100 cc. of water contained in a separatory funnel and add 25 grams of sodium chloride, 5 drops of 0.1 per cent solution of methyl orange, and 60 cc. of ether. Titrate with 0.5 *N* sulfuric acid until distinctly acid (about 2 cc. excess), shake well, and allow the layers to separate. Wash the ether layer with two 25-cc. portions of saturated salt solution and the combined water layers with 30 cc. of ether. Retain the water layers for the following determination. Combine the ether layers, add 0.5 cc. of 0.5 *N* caustic soda, evaporate the bulk of the ether, add 100 cc. of neutral alcohol, and titrate with 0.5 *N* sodium hydroxide until neutral to phenolphthalein. The result (as well as all other alkalinities) is expressed in milligrams of potassium hydroxide per gram of sample and represents the alkalinity corresponding to the soap (A_s).

TOTAL ALKALINITY (A_t). This test is similar to the determination of total alkali in soaps. The combined water layers from the previous analysis are boiled to expel carbon dioxide and the titration is completed. The result equals the sum of the alkalinities corresponding to the soap (A_s) and carbonate (A_c), or

$$A_t = A_s + A_c$$

Hence,

$$\% \text{ sodium carbonate} = \frac{(1)}{(10)} \frac{\text{Na}_2\text{CO}_3}{2 \text{ KOH}} (A_t - A_s) = 0.09447 (A_t - A_s)$$

PROCEDURE IN PRESENCE OF ACETATES ONLY

ALKALINITY AS FREE FATTY ACIDS (A_f). Follow the usual procedure for free fatty acids—namely, dissolve 5 to 10 grams of the sample in 100 cc. of neutral alcohol, warm if necessary, and titrate with 0.5 *N* sodium hydroxide until neutral to phenolphthalein. Calculate the result as milligrams of potassium hydroxide per gram of sample.

COMBINED ALKALINITY AS SOAP (A_s) AND AS FREE FATTY ACIDS (A_f). Dissolve 5 grams of the sample in 100 cc. of water contained in a separatory funnel and add 25 grams of sodium chloride, 5 drops of 0.1 per cent methyl orange solution, and 60 cc. of ether. Add an excess of approximately 0.5 *N* sulfuric acid (about 2 cc. excess), shake well and allow to separate. Wash the ether layer with three 100-cc. portions of concentrated salt solution or until neutral to phenolphthalein. Discard the water layers. The ether layer is then treated and titrated as under "alkalinity as soap" above. The result in this case represents the combined alkalinities of the soap (A_s) and of the free fatty acids (A_f). The alkalinity of the soap is evidently the difference between this determination and the alkalinity of the free fatty acids.

TOTAL ALKALINITY (A_t). Heat with constant stirring 5 grams of the sample with approximately twice its weight of oleic acid in a 250-cc. beaker, immersed in an oil bath, for 30 minutes at 123° to 125° C. Dissolve in 50 cc. of water, add 5 drops of methyl orange solution, and titrate with 0.5 *N* sulfuric acid until distinctly acid (about 2 cc. excess). Transfer to a separatory funnel, add sodium chloride to make a 25 per cent solution, and extract with four 75-cc. portions of ether or until the ether layer is practically neutral to phenolphthalein. Discard the ether layers, rinse the funnel with water, and complete the titration in the combined water layers. The titration represents the combined alkalinities of the soap and the acetate (A_h), or

$$A_t = A_s + A_h$$

Hence, sodium acetate may be calculated from the following formula:

$$\% \text{ sodium acetate} = \frac{(1)}{(10)} \frac{\text{NaAc}}{\text{KOH}} (A_t - A_s) = 0.1462 (A_t - A_s)$$

PROCEDURE IN PRESENCE OF SODIUM CARBONATE AND SODIUM ACETATE

ALKALINITY AS SOAP (A_s). The fat is extracted, washed, and titrated as in "combined alkalinity as soap and as free fatty acids" above. The wash waters, however, are retained for the following test. Evidently in the presence of carbonates there can be no free fatty acids present; hence, the result represents the alkalinity corresponding to total soap (A_s).

ALKALINITY AS SOAP (A_s) AND AS CARBONATE (A_c). The combined water layers from the previous determination are heated under an air condenser to expel carbon dioxide. The condenser is then washed down with water and the titration of the contents completed until neutral to phenolphthalein. The titration obviously represents the combined alkalinities of the soap and carbonate. Hence, the difference between the last two determinations represents the alkalinity of the carbonate (A_c), from which the per cent of sodium carbonate may be calculated as follows:

$$\% \text{ sodium carbonate} = \frac{(1)}{(10)} \frac{\text{Na}_2\text{CO}_3}{2 \text{ KOH}} A_c = 0.09447 A_c$$

TOTAL ALKALINITY (A_t). This is determined exactly as in the presence of acetates only. The result represents the combined alkalinities of soap, carbonate, and acetate, or

$$A_t = (A_s + A_c) + A_h$$

The alkalinity of the acetate may now be determined since all the other terms are known. The per cent of sodium acetate may then be calculated from the corresponding alkalinity by the following formula:

$$\% \text{ sodium acetate} = \frac{(1)}{(10)} \frac{\text{NaAc}}{\text{KOH}} (A_h) = 0.1462 (A_h)$$

Three samples of oil, containing known amounts of sodium carbonate, sodium acetate, and a mixture of the two, were analyzed according to the titration methods and the results

TABLE III. ALKALI CARBONATES AND ACETATES IN SULFONATED OILS BY NEW TITRATION METHODS

	SAMPLE A	SAMPLE B	SAMPLE C
	Mg. KOH/g.	Mg. KOH/g.	Mg. KOH/g.
Alkalinity as free fatty acids (A_f)			
Found	0.00	4.5	0.00
Calculated	0.00	4.4	0.00
Alkalinity as soap (A_s)			
Found	34.0	28.4	34.2
Calculated	33.4	29.0	33.4
Total alkalinity (A_t)			
Found	59.2	49.9	56.9
Calculated	59.8	49.6	56.9
Alkalinity as soap (A_s) and as carbonate (A_c)			
Found	45.9
Calculated	46.6
Sodium carbonate	%	%	%
Found	2.38	..	1.11
Calculated	2.49	..	1.25
Difference	0.11	..	0.14
Sodium acetate			
Found	..	3.14	1.61
Calculated	..	3.01	1.51
Difference	..	0.13	0.10

are given in Table III. Sample A was made by mixing a titrated solution of sodium carbonate with an equal amount of a neutralized sulfonated oil of known alkalinity. Sample B was a mixture of a titrated solution of acetic acid exactly neutralized with caustic soda, and an equal amount of a sulfonated oil with known alkalinity and acidity. Sample C was a mixture of 25 per cent each of the carbonate and acetate solutions, and 50 per cent of the neutralized sulfonated oil. The results in Table III are the averages of several determinations in each case. It will be noted that the amount of sodium carbonate found in sample A differed from the calculated value by 0.11 per cent, that the difference in sodium acetate for sample B was 0.13 per cent, and the differences in sodium carbonate and sodium acetate for sample C were 0.14

and 0.10 per cent, respectively. The accuracy of these results is well within the experimental error and is considered satisfactory for the analysis of sulfonated oils.

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LITERATURE CITED

- (1) Alsop, W. K., and Schultz, G. W., *J. Am. Leather Chem. Assoc.*, **16**, 525 (1921).
- (2) Burton, D., and Robertshaw, G. F., *J. Intern. Soc. Leather Trades Chem.*, **17**, 293 (1933).
- (3) Commercial Standard CS43-32, "Grading of Sulfonated (Sulfated) Oils, Saponifiable Type," Bur. Standards, January 26, 1933.
- (4) Hart, R., *J. Am. Leather Chem. Assoc.*, **15**, 404 (1920).
- (5) *Ibid.*, **16**, 159 (1921).
- (6) Hart, R., *J. IND. ENG. CHEM.*, **10**, 598 (1918).
- (7) Hart, R., *Ibid.*, **21**, 85 (1929).
- (8) Herbig, W., *Chem. Umschau Fette, Öle, Wachse Harze*, **34**, 330 (1927).
- (9) McBain, J. W., and McClutchie, W. L., Jr., *J. Phys. Chem.*, **36**, 2567 (1932).
- (10) Nishizawa, K., *Chem. Umschau Fette, Öle, Wachse Harze*, **38**, 1 (1931).
- (11) Trotman, S. R., and Gee, G. N., *J. Soc. Dyers Colourists*, **49**, 132 (1933).
- (12) Wizöff, *Chem. Umschau Fette, Öle, Wachse Harze*, **38**, 34, 132 (1931).

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Determination of Alpha-Cellulose

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THE test for alpha-cellulose has long been a matter of controversy. In 1911 Jentgen (1) suggested a test for resistant cellulose and advised its use in determining the suitability of fibers for viscose manufacture. Since that time so many other suggestions have been made, most of them mere variations of Jentgen's original test, that tests have been drawn up by a committee of the Division of Cellulose Chemistry of the AMERICAN CHEMICAL SOCIETY (2) and by the German Chemical Society (3). In both cases, however, the methods are purely empirical, the determination having been chosen which gives the most consistent results. This is admitted to be true and everyone recognizes the limitations in using the determination.

The concentration of the alkali used in the treatment of cellulose by these two methods is of importance. In the present research a sample of paper was treated with sodium hydroxide of strength varying from 1 to 17.5 per cent for 45 minutes and for 24 hours at room temperature following the procedure prescribed by the AMERICAN CHEMICAL SOCIETY's committee. The data are offered in Table I and are plotted in Figure 1.

TABLE I. EFFECT OF TIME AND CONCENTRATION OF ALKALI

SODIUM HYDROXIDE %	ALPHA-CELLULOSE	
	45 minutes	24 hours
	%	%
1	96.27	95.78
2	93.22	91.94
4	91.48	90.73
10	88.74	87.41
17.5	87.94	86.40

It will be seen that the effect of the concentration of the alkali is much greater than the effect of time, after some period less than 45 minutes. For this reason, runs were made with 17.5 per cent sodium hydroxide on a sample of pulp for 2, 5, 10, 30, and 45 minutes, and on a sample of absorbent cotton for 1, 2, 5, 10, and 50 minutes. The method proposed by the divisional committee of the AMERICAN CHEMICAL SOCIETY was followed as far as possible. The period after maceration was changed as required for runs down to 15 minutes' total mercerization. Runs of 10 minutes' duration were treated with the alkali in four parts, 2.5 minutes apart, and were macerated continuously. Runs of 5 minutes or less were treated with the total volume of alkali all at once and were macerated for the full time. The results of durations less than one minute were variable and showed that the solution failed to wet the sample completely or to have sufficient contact to act uniformly on the sample. The data are given in Table II and are plotted in Figure 2.

TABLE II. EFFECT OF TIME
(17.5 per cent sodium hydroxide used)

TIME Min.	ALPHA-CELLULOSE	
	Cotton %	Pulp %
1	98.9	..
2	98.8	88.2
5	98.7	87.5
10	98.7	86.5
30	..	86.4
45	..	86.1
50	98.5	..

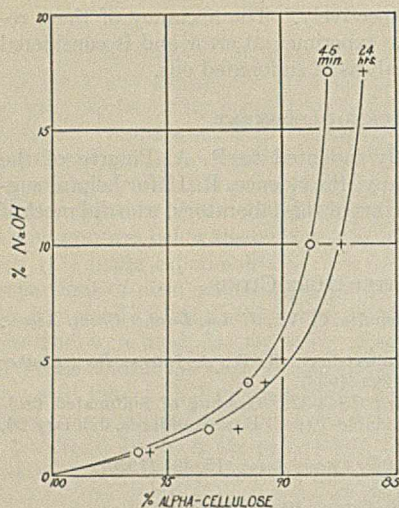


FIGURE 1. EFFECT OF TIME AND CONCENTRATION OF ALKALI

slowly than the non-alpha-cellulosic part of the material, we can easily explain the forms of these curves. The non-alpha-cellulosic part is peptized more rapidly until it is almost gone, the loss of alpha-cellulose during this interval being very small. This is represented by the horizontal portion of the curves. When this part is nearly all peptized, the rate of loss immediately falls off because the attack on the alpha-cellulose is very slow. The nearly vertical rise in the curves brings this out clearly. The position and form of the break in the curve will, of course, depend on the sample used. If it is almost pure alpha-cellulose, as in the case of cotton, the amount of impurities will be small and will be removed quickly. The break in the curve will be sharp. If there is much material in addition to the alpha-cellulose in the sample, it will take longer to remove it, and the change from the period when the main reaction is the taking out of impurities, to the period when there is only a slow attack on the alpha-cellulose, will be more gradual.

A second series of runs was made using 10 instead of 17.5 per cent sodium hydroxide. The pulp was the same as that used with the stronger alkali, in the preceding experiment. The results of this treatment are given in Table III and plotted in Figure 2.

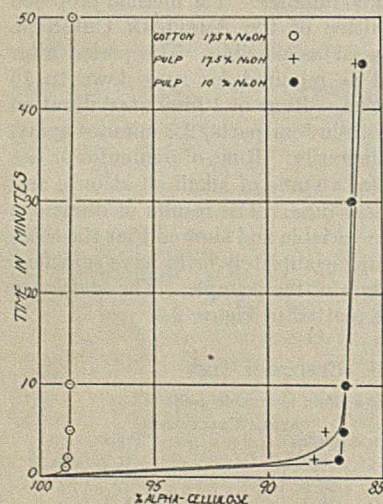


FIGURE 2. EFFECT OF TIME AND CONCENTRATION ON ALPHA-CELLULOSE FROM COTTON AND PULP

In both cases, there is a great loss suffered by the cellulose in the first few minutes of reaction, and this rate of loss suddenly decreases until the cellulose becomes nearly nonreactive. Apparently the time before this break occurs and the sharpness of the break depend upon the source of the cellulose used.

If the alpha-cellulose is attacked much more slowly than the non-alpha-cellulosic part of the material, we can easily explain the forms of these curves. The non-alpha-cellulosic part is peptized more rapidly until it is almost gone, the loss of alpha-cellulose during this interval being very small. This is represented by the horizontal portion of the curves. When this part is nearly all peptized, the rate of loss immediately falls off because the attack on the alpha-cellulose is very slow. The nearly vertical rise in the curves brings this out clearly. The position and form of the break in the curve will, of course, depend on the sample used. If it is almost pure alpha-cellulose, as in the case of cotton, the amount of impurities will be small and will be removed quickly. The break in the curve will be sharp. If there is much material in addition to the alpha-cellulose in the sample, it will take longer to remove it, and the change from the period when the main reaction is the taking out of impurities, to the period when there is only a slow attack on the alpha-cellulose, will be more gradual.

Although the 10 per cent alkali is more effective in the shorter times, both 10 and 17.5 per cent solutions give the same values after 45 minutes of reaction. From this one sample it would appear that the 10 per cent alkali changes the shape of the curve at the break somewhat.

From the data of Neale (2) we can calculate roughly the end concentration of the sodium hydroxide solutions. He gives the following figures obtained

by the change in titer method: initial concentration, 5.17 equivalents per liter; adsorption, 0.486 to 0.493 equivalents per mole of cellulose. By taking the adsorption of the cotton in the 17.5 per cent sodium hydroxide (5.25 equivalents per liter) to be 0.490, one is able to determine approximately the reduction of the concentration in the solutions during the treatment. With a 3-gram sample using 75 cc. of 17.5 per cent sodium hydroxide, the concentration will fall only 0.4 per cent, so that the end concentration will be 17.1 per cent. A 4-gram sample will reduce the concentration to 17.0 per cent and a 2-gram sample to 17.2 per cent. The size of the sample therefore need not always be exactly 3 grams.

At least one author (5) offers the suggestion that the losses in alpha-cellulose suffered during the aging of alkali pulps in the viscose process are due to oxidation by the air. However, the action must be very slow. Identical samples of absorbent cotton were treated with 17.5 per cent sodium hydroxide at room temperature for 50 hours. Both were in stoppered flasks. Through one, air was bubbled which had passed through 17.5 per cent sodium hydroxide previously. The residues recovered were: air-free, 98.7 per cent; air-saturated, 98.6 per cent. The effect of oxygen in the air, then, for any alkali treatment using cold 17.5 per cent sodium hydroxide can be neglected.

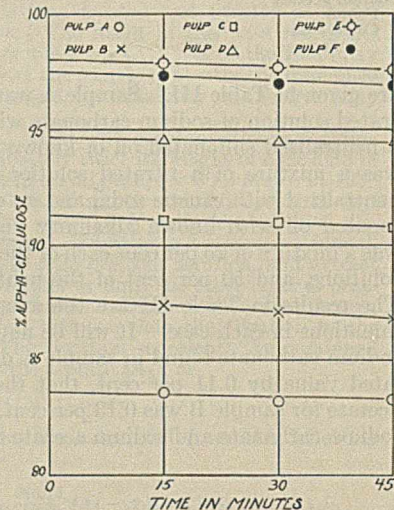


FIGURE 3. DETERMINATION OF ALPHA-CELLULOSE IN COMMERCIAL PULPS

TABLE III. EFFECT OF TIME

(10 per cent sodium hydroxide used)	
TIME	ALPHA-CELLULOSE
Min.	%
2	86.88
	86.90
5	86.78
	86.56
10	86.54
	86.65
30	86.34
	86.32
45	86.04
	85.72

PROPOSED METHOD

In view of these facts, the author proposes for the present a method for the determination of alpha-cellulose which is based on the stability of the cellulose to attack by sodium hydroxide. Samples are run according to the method proposed by the AMERICAN CHEMICAL SOCIETY'S committee for two or three different times, say, 15, 30, and 45 minutes. These times should be sufficient to cause the points to fall on the vertical flat of a curve similar to those in Figure 2. By extrapolation back to zero time, the alpha-cellulose content of the original sample should be given.

It is claimed as an advantage of this method over any other, that the time factor is eliminated. No standard time is necessary; in fact, as long as the points lie well beyond the break, the times may be chosen to suit the sample or convenience. Since the attack on the alpha-cellulose is slow,

extreme accuracy in measuring the time of reaction is not necessary. Slight error in time will result in practically no error in the ultimate alpha-cellulose result. The ratio of the sample to the reagent need not be exact, provided it is within certain limits (1 to 4 grams in 75 cc. of solution). The main precaution seems to be the use of carbonate-free alkali throughout the treatment.

The suggested method has been tested on six commercial paper pulps, the alpha-cellulose content of which had been determined previously by the manufacturer, and the results are shown in Table IV and in Figure 3.

TABLE IV. DETERMINATION OF ALPHA-CELLULOSE IN COMMERCIAL PULPS

PULP	MANUFACTURER'S VALUE	PER CENT RESIDUE AFTER:			VALUE BY:	
		15 min.	30 min.	45 min.	Calculation	Curve
A	84.02	83.03	82.95	83.57	83.60	83.75
		83.75	83.36	82.97		
		84.02	83.14	83.50		
B	87.63	87.44	87.08	86.88	87.69	87.50
		87.35	87.07			
C	91.26	91.01	91.10	90.75	91.21	91.25
		91.15	90.78	90.80		
		91.06	90.67	90.74		
D	94.90	94.54	94.44	94.46	94.56	94.60
E	98.54	97.87	97.70	97.63	97.89	97.97
F	98.42	97.33	96.97	96.94	97.23	97.10

It was found more convenient and perhaps a little more accurate to calculate the percentage of alpha-cellulose back to zero time than to plot the data and estimate the value from the extrapolated curve. This was done by determining the loss for the 15-minute periods, 15 to 30 minutes' reaction and 30 to 45 minutes' reaction. The average of these two is designated $\Delta\%/ \Delta T$. Using the 15-, 30-, and 45-minute values as bases, the alpha-cellulose at zero time can be calculated by adding to these values $\Delta\%/ \Delta T$, $2\Delta\%/ \Delta T$, and $3\Delta\%/ \Delta T$, respectively. For example, using the data from pulp F:

DIFFERENCE IN LOSS FROM:		%T	ALPHA-CELLULOSE CALCULATED FROM:			AVERAGE
15 to 30 min.	30 to 45 min.		15	30	45	
17	7	12	97.99	97.94	97.99	97.97

The average of these zero values is taken as the calculated result. The method of calculating gets rid of any errors in plotting and drawing the curve and in estimating the extrapolated value.

SUMMARY

A preliminary study of the effect of concentration of alkali on the tentative standard method proposed by the Division of Cellulose Chemistry of the AMERICAN CHEMICAL SOCIETY determination of alpha-cellulose was made.

In studying the effect of time on the treatment of cellulose with 17.5 per cent sodium hydroxide a characteristic curve was found which showed rapid losses in weight of cellulose at first and soon approached a nearly constant value. A curve of the same type giving the same nearly constant value was found for 10 per cent sodium hydroxide.

A method for the determination of alpha-cellulose has been proposed temporarily which eliminates exact specifications of time and sample-reagent ratio. The suggested method has been tested on six commercial pulps.

ACKNOWLEDGMENT

The six pulp samples used in testing the method suggested above were furnished, together with the manufacturer's data, through the kindness of G. A. Richter of the Brown Company. Other pulp stock was furnished by the Strathmore Paper Company.

The author is indebted to Professor Bancroft for suggestions and criticism in this work.

LITERATURE CITED

- (1) Jentgen, *Kunststoffe*, 1, 165 (1911).
- (2) Neale, *J. Textile Inst.*, 22, T320 (1931).
- (3) Ritter et al., *IND. ENG. CHEM., Anal. Ed.*, 1, 52 (1929).
- (4) Schwalbe, *Papier-Fab.*, 23, 477, 697 (1925) [*Chem. Abs.*, 20, 283, 502 (1926)].
- (5) Waentig: *Papier-Fab.*, 25, 112 (1921) [*Chem. Abs.*, 22, 4974 (1928)]; 26, 64 (1928) [*Brit. Chem. Abs.*, B47, 564 (1928)].

RECEIVED January 15, 1934. This work was done by the author in partial fulfillment of the requirements for the degree of doctor of philosophy at Cornell University.

Determination of Sulfur in Benzene or Gasoline Modification of A. S. T. M. Lamp

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IN A RECENT article, Gillis (2) describes a modification of the standard A. S. T. M. lamp which provides for better control of the flame. A similar lamp of somewhat simpler construction has been in use in the author's laboratory for about three years, and has been particularly successful with benzene and its blends, which ordinarily give more trouble than gasoline itself.

The modified lamp is sketched in Figure 1. The glass tube A, which carries the wick as in the standard A. S. T. M. lamp, is made somewhat longer than usual to accommodate the sleeve B, which is a glass tube of slightly larger diameter. Because of the variation in tubing diameters, it has been found advisable to make the sleeve of tubing sufficiently larger than A to require some sort of flexible packing which provides the necessary friction to hold the sleeve in place. If a glass-to-glass friction is used, sticking is likely to occur at a most inopportune moment, with disastrous results. Even a smooth-sliding sleeve as made up may bind in use, because of expansion of the inner tube when heated by the combustion of the material under test. A small piece of cotton wicking in the annular space serves as a satisfactory packing material.

In operation the sleeve is simply moved up and down on the tube carrying the wick. If the flame is too high, the sleeve is pushed up, and vice versa. Very close adjustment may be made by rotating the sleeve slightly as it is moved up or down.

The principle of flame control in this lamp is apparently the same as that employed in one of the lamps proposed by Edgar and Calingaert (1) who used a movable brass outer tube, but its construction is simpler, and the control, in the author's experience, more satisfactory.

LITERATURE CITED

- (1) Edgar and Calingaert, *IND. ENG. CHEM., Anal. Ed.*, 2, 104 (1930).
- (2) Gillis, *Ibid.*, 5, 421 (1933).

RECEIVED DECEMBER 9, 1933.

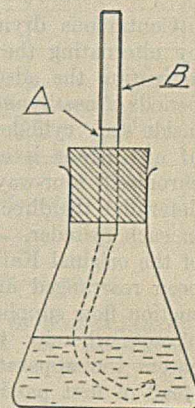


FIGURE 1

Improved Analyzer for Carbon Monoxide in Air

H. W. FREVERT AND E. H. FRANCIS, Holland Tunnel Offices, New York, N. Y.

A CONTINUOUS carbon monoxide recorder for small concentrations in air has been described by Fieldner, Katz, and Meiter (1), and by Katz and others (3). In this apparatus the oxidation of the carbon monoxide as it comes in contact with a granular catalyst results in a temperature rise in the air stream within the catalyst cell, which is transmitted to a recording potentiometer through a series of differential thermocouples. The cell potential is directly proportional to the carbon monoxide concentration in the absence of readily oxidizable or inhibiting impurities which affect the catalyst.

To remove moisture and other condensable constituents the air sample is passed through a train of concentrated sulfuric acid, soda-lime and charcoal, and calcium chloride, previous to passing through the hopcalite catalyst. Fourteen instruments of this type were installed at the Holland Tunnel (2) where they record carbon monoxide in the seven exhaust air ducts leading from each of the two tubes for vehicular traffic between New Jersey and Manhattan. In practice the use of sulfuric acid as an air drier is objectionable because of its corrosive nature and the difficulties of frequent renewal and disposal. This led to the development of a modified form of the analyzer, which is here described. The acid train whose chief function is the removal of moisture has been replaced by duplicate adsorbers using either silica gel or activated alumina. Alumina of 1.2 to 2.4 mm. size was used in tests on this apparatus and in the preliminary tests reported in this paper.

DESCRIPTION OF APPARATUS

Continuous drying is obtained by alternating the adsorbers and activating the adsorbent between periods of use by means of a heater inside each cylinder. Interchange of cylinders is effected by synchronized four-way cocks which determine the direction of air flow in each cylinder. The other parts of the original Katz analyzer have been rearranged and modified for suction flow supplied by a rotary blower, whereby the air sample enters the apparatus directly instead of first passing through the blower and then to the apparatus. This arrangement eliminates the possibility of contamination of the adsorbent or the catalyst by oil spray from the blower.

The adsorbers *A* and *B* in Figures 1 and 2 have an inner adsorbent cylinder of 8.9-cm. (3.5-inch) brass tubing, 40 cm. long, filled with 1.2-mm. to 2.4-mm. (8- to 14-mesh) alumina to within 10 cm. of the top. This tube is surrounded by a 2.5-cm. jacket through which cooling water flows during the cooling period

following activation of the adsorbent and throughout the succeeding 8-hour period in which the adsorbent is drying air. This is surrounded by a 2.5-cm. jacket of loose asbestos to improve the conservation and distribution of heat in the adsorbent during the activation, when the jacket is empty and contributing to the insulation of the adsorbent. The unit *a*, Figure 2, for supplying the activating heat to the passing air stream is a 200-watt element from a reflector heater suspended from a cover plate through which two spark plugs, *b*, are screwed for terminal connections. The heater circuits are connected to limit switches, *W*, shown in Figure 1, which control the sequence of heating through contact with fingers on the cooling water cocks, *c* and *d*.

The analyzer is connected to the 110-volt alternating current electrical supply through the 2-pole fused switch, *t*, Figure 1, to which the three-heat immersion heater inside boiler *C* is connected directly. The supply to the motor and activating heaters passes through an overload relay magnetic switch, *u*, which cuts off the supply to the heaters when the motor stops. A push button, *v*, starts and stops the motor and heaters independent of the boiler supply.

Below the adsorbers are water tube air coolers, *e*, Figure 2, surrounded by water in the cooling reservoir *D*, which cool the moisture-laden air from each adsorber when it is being activated by the downward passage of hot air. The coolers communicate with catch bulbs below and with the four-way cock, *f*. This cock turns simultaneously through a vertical connecting bar with the upper four-way cock, *g*, communicating with the top of the adsorbers.

The three-way cock, *h*, is connected to the inlet side of cock *g* and is the means of providing additional air while activating to insure a more even heat distribution in the adsorbent. Following activation this air, since it contains moisture, is not allowed to enter the cooling adsorbent but is diverted through by-pass *i* to the blower, *r*, by a turn of the cock. The quantity of air passing into this three-way cock is regulated by plug cocks *j* to give a temperature not greater than 340° C. at the top of the alumina and not less than 150° C. at the bottom.

Cooling water enters at both ends of reservoir *D* through valves *k*, and passes through the tubes of the coolers to the center. Three-way cocks *c* and *d* admit water from the reservoir to the cooling jackets of the adsorbers or empty them as required.

Precautions were taken to insure a proper operating sequence by the use of the blocking cross bars, *s*, Figure 1, attached to the vertical connecting bar, which synchronize the movement of water cocks *c* and *d* with the position of the four-way air cocks.

The water when flowing through the jackets passes through the outlet tubes, *l*, whose ends are water-sealed in adjoining overflow compartments in trap *m*, from which the water passes to the steam bath condenser of the cell assembly, *C*. The water trap compartments are joined by a small hole which allows water to pass from either side to seal both tubes against entrance of air when one adsorber jacket has been emptied. A jacket is drained previous to activating the adsorbent through the three-way cocks *c* or *d* by which process air enters to displace the water through the overflow compartment in the water trap, *m*.

A cylinder of 330 cc. of charcoal, *n*, removes quantities of hydrocarbon vapors from the air sample which

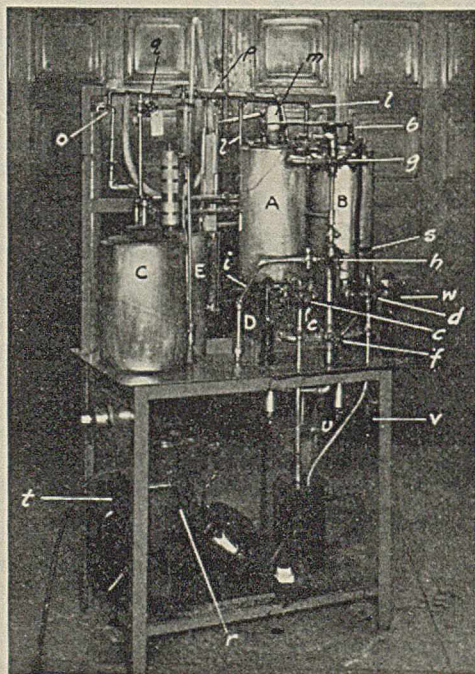


FIGURE 1. CONTINUOUS ANALYZER FOR CARBON MONOXIDE IN AIR

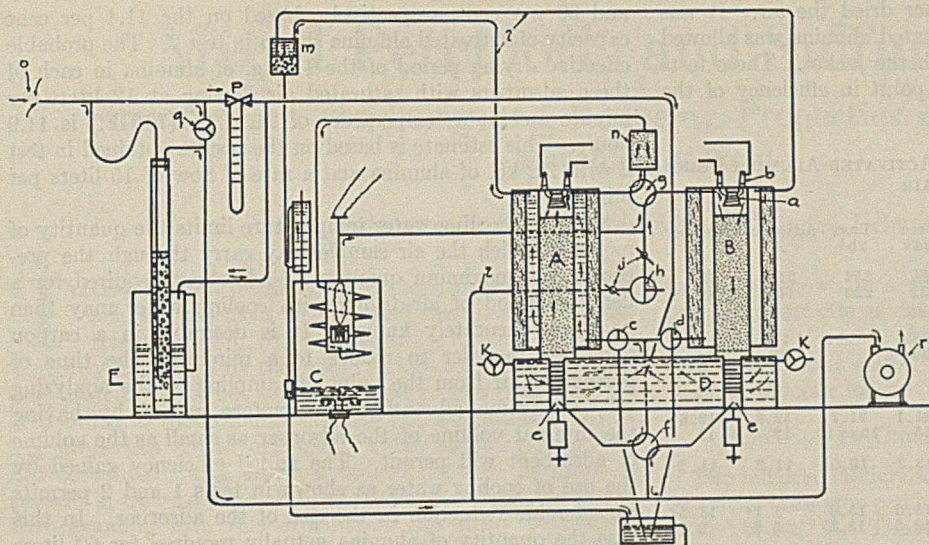


FIGURE 2. FLOW DIAGRAM OF CARBON MONOXIDE ANALYZER

might affect the accuracy of the analyzing cell. This has a screw cap at one end for periodical replacement of the activated charcoal.

OPERATION

The air sample is continuously drawn into the apparatus at *o*. That in excess of 12 liters per minute to the flowmeter, *p*, by-passes through the regulating valve, *q*, and through the flow compensator, *E*, directly to the blower, *r*.

At the point of sequence illustrated in Figure 2, the regulated flow from the flowmeter passes into cock *f* and upward through adsorber *A*, through charcoal cylinder *n*, and into the preheating coil inside the steam bath at *C*, from which it passes through the catalyst chamber also enclosed by the steam bath. The return air from the catalyst chamber reenters the four-way cock, *g*, together with additional air from the room for activating purposes through three-way cock *h*. The increased flow of about 30 liters per minute enters adsorber *B* and passes downward over the heater and through the adsorbent which at the end of 4 to 6 hours acquires a temperature of about 320° C. at the top and 180° C. at the bottom. The air leaves the adsorber through the after-cooler, *e*, from which it reenters the four-way cock, *f*, and joins the previously by-passed air to the blower, *r*.

At the end of the 4- to 6-hour activating period the water cock, *d*, is turned 90° to fill the water jacket of the activated adsorber, and the auxiliary air entering cock *h* is diverted to the blower by a 90° turn of the cock. A finger on the water cock has contacted a limit switch which shuts off the activating heater. Adsorber *A* continues to dry the air sample and adsorber *B* receives the dry return air from the cell until the end of the 8-hour period.

At the end of the 8-hour period the four-way cocks, the water cock below adsorber *A*, and the three-way air cock, *h*, are turned 90°, whereby the path of the air sample is transferred from *A* to *B*, water is drained from the cooling jacket of *A*, the limit switch is actuated to start the heater, and room air is diverted into *A* for activation of the adsorbent. The operations mentioned before are repeated in succeeding cycles, commencing with the turning of cocks *c* and *h* at the end of 4 to 6 hours to cool the activated adsorbent in *A*.

A drying period of 8 hours per adsorber was selected because it allows a convenient time for reactivating and cooling and because it coincides with the working hours of operators who would operate the analyzer when in service. The rate of flow of 12 liters per minute produced the best sensitivity

in the catalyst cell with a minimum of variation for small changes in air velocity.

AIR-DRYING TESTS

Preliminary tests at a flow rate of 15 liters per minute, using adsorbers roughly similar in form to those described, were used as a basis for determining the cylinder size required for the 8-hour period.

These adsorbers were constructed of 22-gage sheet iron, were 51 cm. long, and contained an inner adsorbent cylinder 10.2 cm. in diameter which was surrounded by a concentric 2.5-cm. air jacket. One of the cylinders was further jacketed with a 2.5-cm. layer of asbestos over the air jacket.

The 8- to 14-mesh alumina, obtained in 1931, was reactivated downward with heaters suspended above the adsorbent as in the analyzer described. Thermocouples placed in the top and bottom of the adsorbent beds indicated temperatures of activation and adsorption.

In tests made with these adsorbers and with the analyzer later constructed, air saturated by bubbling through a bottle of water at room temperature and precooling at 12.8° to 21.7° C. was passed through the activated alumina and the effluent air was tested at intervals for moisture with a weighed tube of phosphorus pentoxide. The air dryness determinations for these tests appear in Figure 3, which shows the relation between grams of moisture per cubic meter of air and the time from start of the run when the dryness tests were made.

Other data in connection with the tests are given in Table I. The quantity of moisture adsorbed is calculated from the moisture entering in the saturated air at the temperature stated, corrected for moisture which passed through the adsorbent.

The object of tests 1 and 2 was to determine the effective drying period of the activated alumina adsorbent with and without water-cooling. In test 1, 2.2 kg. of the alumina were activated and tested for adsorption in check runs 1a and 1b in the asbestos-insulated air-jacketed cylinder. In test 2 an equal quantity of alumina was similarly tested in a cylinder of the same size with water passing through the jacket during adsorption. The relative efficiencies of the adsorbent under these two conditions are indicated in Figure 3.

A laboratory test on adsorbers *A* and *B* of the assembled analyzer is reported in test 3 of Table I. The apparatus was run as for the continuous analysis of air, with one ad-

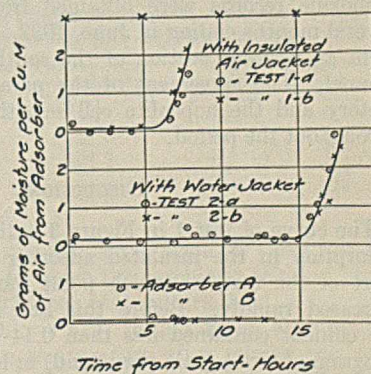


FIGURE 3. EFFECT OF WATER JACKET AROUND CYLINDER OF ACTIVATED ALUMINA ADSORBENT

sorber being activated as the other dried the air. It was shut down overnight and the activated alumina was allowed to cool with water flowing through the jacket. These tests were not continued to the break point in efficiency of the adsorbent.

TABLE I. ADSORPTION TESTS WITH ACTIVATED ALUMINA USING SATURATED AIR

	TEST 1a ^a	TEST 1b ^a	TEST 2a ^b	TEST 2b ^b	TEST 3 ^c	
					Adsorber A	Adsorber B
Activation temperatures, ° C.						
Near top of alumina	279	310	260	254	316	332
Near bottom of alumina	254	266	232	229	149	204
Adsorption temperatures, ° C. ^d						
Near top of alumina	66	67	38			
Near bottom of alumina		60	39		32	35
Entering air						
Saturation temperatures, ° C.						
Flow, liters per min.	18.1	19.4	21.1	21.7	12.8	12.8
Moisture, grams per cu. meter	15	15	15	15 to 16	12	12
	15.6	16.5	18.2	19.0	11.2	11.2
Period of complete drying, hours						
	6.0	6.0	15.0	15.0	8.1 ^e	13.5 ^e
Flow of air, cu. meters	5.4	5.4	13.5	13.5	5.8	9.7
Estimated moisture adsorbed						
Grams	84	89	245	255	65	108
Per cent of activated alumina	3.8	4.0	11.1	11.6	4.6	7.8
Cooling water						
Approximate flow, liters per hour			90	90	90	135
Temperature, ° C.			21.1	21.7	12.8	12.8

^a 22-gage sheet-iron adsorber; adsorbent cylinder, 10.2 × 51 cm., 0.08-cm. wall; air jacket and asbestos covering; 2.2 kg. of alumina.

^b 22-gage sheet-iron adsorber; adsorbent cylinder, 10.2 × 51 cm., 0.08-cm. wall; water jacket; 2.2 kg. of alumina.

^c 16-gage, 3.5-inch brass tube; adsorbent cylinder, 8.9 × 40 cm., 0.13-cm. wall; water jacket; 1.4 kg. of alumina.

^d As indicated when adsorption zone reached level of thermocouple junctions.

^e Test discontinued before break in adsorbent efficiency.

Following these tests the experimental analyzer was connected to an air-sampling line in parallel with the analyzer regularly in service on this line and continuous carbon monoxide records were obtained from both analyzers for several months ending in June, 1932. The air sampled came from an upgrade section of the south tube of the Holland Tunnel. The agreement of the parallel records was satisfactory and the hopcalite cell sensitivity remained normal throughout the period.

DISCUSSION

The curve of test 1 in Figure 3 indicates a break point in adsorption in the insulated adsorber at 6 hours from the start of the test, at which point moisture in the effluent increased rapidly. Before this break in drying efficiency the effluent contained less than 0.14 gram of moisture per kilogram of air (1 grain per pound) or less than 0.18 gram per cubic meter. Test 2 curve indicates a similar break point at 15 hours for the same quantity of alumina in the same size cylinder when water-cooled. Part of the moisture found in the effluent in test 2a apparently came from moisture adsorbed at the top of the bed before the test began and again at 7.5 hours from the start of the test when the run was stopped overnight. The adsorptive capacity of the alumina was multiplied three times by the 21° to 29° C. of cooling effected by the water. The dry alumina had adsorbed 3.9 per cent of its weight of moisture in test 1 and 11.4 per cent in test 2 when moisture broke through.

No gain of moisture in the effluent air from adsorbers A and B was found for the periods of test. The average moisture content of the air coming from adsorber A was 0.07 gram per cubic meter of air and from adsorber B, 0.04 gram.

The effective adsorptive capacities remaining in adsorbers A and B when the runs were stopped are estimated at 60

and 30 per cent, respectively, based on the 11.4 per cent capacity of activated alumina shown in test 2. The probable effective drying period of the 1.4 kg. of alumina in each of these adsorbers with saturated air flowing at 12 liters per minute and at a temperature of 21.1° C. (70° F.) is 11.9 hours. This estimate is based on the results obtained in test 2 with 2.2 kg. of alumina and a rate of flow of 15 liters per minute.

Since the cooling water temperature limits the quantity of moisture which the air sample may carry through the pre-cooler, the maximum quantity of adsorbent required for a definite period of air-drying with cooling water may then be fairly accurately known. It is desirable in a carbon monoxide recorder to reduce to a minimum the time of passage of air from the point of sampling to the analyzing cell, and some advantage is therefore gained by having the internal volume of the adsorber as small as the volume of adsorbent will permit. The added efficiency gained by the use of cooling water as shown in tests 1 and 2 permits considerable reduction in the size of the adsorber. In this case the quantity of alumina actually required for 60 liters of saturated air (1 liter per minute for 1 hour) with cooling water at 21.1° C. (70° F.) was 10 grams or 12 cc.

SUMMARY

The carbon monoxide recorder is an important control instrument in the ventilation of the Holland Vehicular Tunnel. Special maintenance and some hazard are involved in the use of sulfuric acid in the air-drying and purifying train of the original design. For this reason a substitute drier was developed which consists of duplicate cylinders containing granular adsorbent. This is reactivated in place as the analyzer continues to operate by a heater inside the cylinder, assisted in part by the recirculation of the dry return air from the analyzing unit of the recorder.

Since preliminary tests indicated the desirability of cooling the adsorbent during use to increase drying capacity, the adsorbers are jacketed for cooling with water. The water is drained from the jacket during the activating period, but the activating air stream passes through a cooler as it leaves the adsorbent.

The maintenance required for the operation of the analyzer consists of valve manipulation twice in every 8 hours or other drying period selected, and removal of water from the condensation trap below the adsorbers as required. Although the possibility of simplification of valve arrangement and other parts of the apparatus has become apparent its operation was satisfactorily carried on by the operators in charge of ventilating equipment in the building.

LITERATURE CITED

- (1) Fieldner, A. C., Katz, S. H., and Meiter, E. G., *Eng. News-Record*, 95, 423 (1925).
- (2) Katz and Frevert, *IND. ENG. CHEM.*, 20, 564 (1928).
- (3) Katz et al., U. S. Bur. Mines, *Tech. Paper* 355.

RECEIVED December 23, 1933.

CORRECTION. Our attention has been called to a minor inaccuracy in our article "Extraction of Triethanolamine Oleate from Aqueous Solution," appearing in *IND. ENG. CHEM., Anal. Ed.*, 6, 78 (1934). The statement was made, referring to extraction of fatty acid from triethanolamine soaps, "Normally, soaps other than those of abietic acid are not decomposed by extraction of an aqueous solution with ethyl ether." We should have added "by recognized methods," since small amounts of fatty acid are extracted from aqueous solutions of neutral soap by ethyl ether. This is adequately provided for in the usual methods.

This in no way invalidates our conclusions, since the extraction of oleic acid was high in experiments 2 and 5, in which 0.05 M triethanolamine, the alkali of the soap under discussion, was present in excess. FRANK M. BIFFEN AND FOSTER DEE SNELL

Mixed Perchloric and Sulfuric Acids

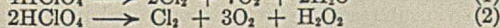
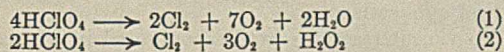
I. Simultaneous Oxidizing and Reducing Properties of Hot Concentrated Perchloric Acid

G. FREDERICK SMITH, University of Illinois, Urbana, Ill.

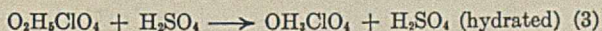
THE oxidation reactions of hot, concentrated perchloric acid are the basis of important reactions of quantitative analysis (3, 6). The intensity of these oxidations is greatly influenced by the extent to which the acid has been dehydrated. With hot acid of strength greater than that corresponding to the formula $O_2H_5ClO_4$ (4), simultaneous reducing properties are in evidence. These reducing properties are accounted for if either hydrogen peroxide or ozone is present in traces as a result of the decomposition. Reactions corresponding with this explanation can easily be demonstrated. The acid strength of 70 to 72 per cent perchloric acid is conveniently increased to 85 per cent or higher by the addition of sufficient 96 per cent sulfuric acid or fuming sulfuric acid. For many reactions of analytical importance, these principles require a close study of conditions. It is the purpose of this paper to describe the general aspects of this subject.

DECOMPOSITION IN PRESENCE AND ABSENCE OF MILD REDUCING AGENTS

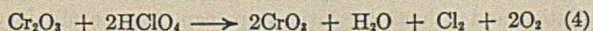
By concentrated perchloric acid, this paper refers to that strength between 70 and 85 per cent $HClO_4$ by weight (roughly, that concentration between dioxonium perchlorate and oxonium perchlorate, $O_2H_5ClO_4$ and OH_3ClO_4). Hot, concentrated perchloric acid decomposes mainly according to reaction 1. A secondary reaction, 2, is also possible to a slight extent.



Both reactions are intensified in proportion as the concentration increases. Reaction 3 indicates the formation of oxonium perchlorate using concentrated or fuming sulfuric acid.



An important example of a reaction using hot concentrated perchloric acid as an oxidizing agent is the oxidation of trivalent chromium to the hexavalent state in the process of Willard and Gibson (6) for the quantitative estimation of chromium in chromite, ferrochrome, and stainless steel. In a study of this method, Lundell, Hoffman, and Bright (2) state that the oxidation is never quite complete. The following reaction is shown to be quantitative only to the extent of 99.5 per cent completion:



If chlorine and oxygen are the only decomposition products, it is difficult to offer a reason for this. In the presence of a small amount of hydrogen peroxide the following reaction explains the fact:



Reactions 1 and 4 are much more intense than 2 and 5. The difference accounts for the 0.5 per cent reversal of reaction 4. Reactions 2 and 4 are intensified by increasing the strength of perchloric acid. By properly regulating conditions of time, temperature, and acidity, the Willard and Gibson method (6) can be made to give more accurate results,

as will be shown in a subsequent paper. The influence of hydrogen peroxide as described may easily be duplicated by the addition of a trace of it to a hot, dilute solution of chromic acid in perchloric acid. The chromium is instantly reduced to green chromic ion.

OXIDATION OF CHROMIC OXIDE TO CHROMIC ACID

Two hundred milligrams of chromic oxide were treated with 50 ml. of oxonium perchlorate (84.79 per cent $HClO_4$) and heated to 168° C. The reaction mixture was allowed to cool. Red crystals of chromic oxide, insoluble in concentrated perchloric acid, formed and the acid was colorless. Upon standing 12 hours at room temperature, the acid became colored owing to the presence of green chromic perchlorate. Repeating the heating of the acid and oxidation of chromium, the results are duplicated (reactions 4 and 5).

The oxidation of chromic oxide was tested with increasing strengths of perchloric acid produced from various proportions of 15 per cent fuming sulfuric acid and 72 per cent perchloric acid (Table I). Parallel experiments were made replacing chromic oxide by small amounts of manganese perchlorate, $Mn(ClO_4)_2 \cdot 6H_2O$. The manganese was momentarily oxidized to permanganate and the reaction rapidly reversed as shown by the immediate decolorization due to hydrogen peroxide formed simultaneously. The reaction is intensified in the presence of a little phosphoric acid.

TABLE I. OXIDATION OF CHROMIUM AND MANGANESE BY CONCENTRATED PERCHLORIC AND SULFURIC ACIDS

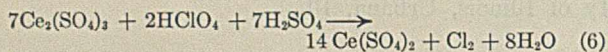
SULFURIC ACID 15 per cent fuming ml.	PERCHLORIC ACID 72 per cent ml.	TEMPERATURE AFTER MIXING FROM 25° C. TO ° C.	Cr ₂ O ₃ OXIDATION TO Cr ₂ O ₇ ²⁻ ° C.	Mn ⁺⁺ OXIDATION TO MnO ₄ ⁻ ° C.
10	10	82.0	136	150
12	8	84.4	128	137
13.3	6.6	86.5	120	128
15	5	88.4	119	125
10 (95 %)	10	40.0	168	...

The heat attained upon mixing the acids of Table I is an indication of the extent to which the perchloric acid has been dehydrated. By using 75 per cent sulfuric acid, a mixture with 72 per cent perchloric acid results in no appreciable evolution of heat. The temperature after mixing was observed in a 30-ml. Dewar test tube, evacuated but not silvered, and the temperature maximum found using a small Anschütz thermometer.

It will be seen that the dehydration of perchloric acid by the sulfuric acid in all cases was equivalent, at least, to the formation of oxonium perchlorate, since the temperature at which the chromium was oxidized is equal to or less than that required by the 84.79 per cent perchloric acid as previously described. The greater the dehydration of perchloric acid, the lower is the temperature of oxidation. In all cases in Table I the oxidation of chromium was clearly reversed to an obvious extent, as shown by the color change resulting upon allowing the solutions to cool and stand. In the case of the higher concentrations of perchloric acid, the reduction was complete in a few hours. This indicates the magnitude of hydrogen peroxide formation as governed by perchloric acid concentration.

OXIDATION OF TRIVALENT CERIUM TO TETRAVALENT STATE

Solutions of cerous perchlorate in hot, concentrated perchloric acid are not oxidized to ceric perchlorate at 168° to 200° C. Mixtures of equal parts of 96 per cent sulfuric acid and 72 per cent perchloric acid oxidize cerous sulfate readily to ceric sulfate at approximately 140° C. The reaction is as follows:



Ceric sulfate is insoluble in 75 to 95 per cent sulfuric acid and in the reaction mixture of acids outlined above. The substitution of 75 for 96 per cent sulfuric acid is found to result in more complete oxidation of cerium at 185° C. In accordance with the principles previously described, this is accounted for through the practical elimination of hydrogen peroxide as a minor decomposition product of hot, concentrated perchloric acid.

The principle of reaction 6 has been applied to the preparation of ceric sulfate, both in the form of the anhydrous salt and in its addition compounds with ammonium sulfate. The data are included in a subsequent paper. Ceric perchlorate has been prepared in solution by the electrolytic oxidation of cerous perchlorate in a perchloric acid solution by Fichter and Jenny (1). It is possible that a mixture of perchloric and sulfuric acids may be found desirable in the quantitative determination of cerium. A preliminary study has been made with favorable results.

USES FOR MIXED ACIDS IN ANALYTICAL STUDIES

The many advantages found in the determination of chromium following perchloric acid oxidation (6) make the method popular in routine plant control analyses. With technical grades of 68 to 70 per cent perchloric acid (free from chromium) the method is less costly. By employing mixtures of perchloric and sulfuric acids, the method can be cheapened further and at the same time other advantages besides economy in the cost of perchloric acid can be shown.

Mixed perchloric and sulfuric acids have been used satisfactorily in the oxidation of potassium ferrous and ferricyanides to liberate the ferric ion as a standard procedure in the evaluation of titanous solutions. Perchloric acid alone can be used in this case, but the method is cheaper using the mixed acids.

The addition of perchloric acid to 96 per cent sulfuric acid for the destruction of organic matter in the familiar Kjeldahl nitrogen determination has been proposed. Attempts to diminish the time of digestion following this process have proved highly successful. Unfortunately, the process in certain applications gives low results, presumably due to loss of nitrogen in the digestion period. If the concentration of sulfuric acid is lowered to 75 per cent and the 72 per cent perchloric acid is then added to the hot sulfuric acid, the oxidizing power is not materially diminished and there is little tendency toward the formation of hydrogen peroxide as a decomposition product. The change thus proposed may eliminate the disturbing reactions previously mentioned. The problem is being investigated in these laboratories.

The dehydration of silica by hot, concentrated perchloric acid in the method of Willard and Cake (5) has become an important analytical procedure. With a mixture of 96 per cent sulfuric acid and 72 per cent perchloric acid, the intensity of the dehydration may be sufficiently high without showing a tendency to convert the perchlorates present to sulfates.

Such an application would result in the obvious advantage of economy in cost of perchloric acid where it is applicable. The subject is being investigated.

If the dehydration of perchloric acid by sulfuric acid is objectionable, other methods are available. Anhydrous magnesium perchlorate in various proportions can be dissolved in 72 per cent perchloric acid. Phosphoric anhydride or acetic anhydride may be substituted for the anhydrous magnesium perchlorate.

SIGNIFICANCE OF HYDROGEN PEROXIDE DECOMPOSITION OF PERCHLORIC ACID

It is difficult to demonstrate experimentally the formation of hydrogen peroxide by the decomposition of hot, concentrated perchloric acid according to reaction 2, except by interpretation of the resulting effects as shown. Attempts to distill out hydrogen peroxide at a low temperature by passing air through a mixture of 96 per cent sulfuric acid and 72 per cent perchloric acid were not successful. Such an experiment using anhydrous perchloric acid might be more successful. If the decomposition products of hot, concentrated perchloric acid do not include hydrogen peroxide, the reactions obtained are exactly analogous to those that would be obtained if hydrogen peroxide or ozone were formed. The odor of ozone was never apparent. The simultaneous formation of hydrogen peroxide and chlorine as decomposition products would be expected to result in side reactions destroying the hydrogen peroxide.

If hydrogen peroxide can be shown to be formed in the reactions of hot, concentrated perchloric acid, or is conceded to have been shown by the studies of the present series of papers, then perchloric acid must be classified as a true peracid. Present interpretations of the molecular structure of anhydrous perchloric acid and its lower hydrates do not include the assumption of oxygen to oxygen linkages as would be the case if it had true per-acid properties. This question is of far less importance than is the knowledge of the practical influence of the formation of hydrogen peroxide upon the analytical applications.

No violent reactions were encountered in connection with this work.

SUMMARY

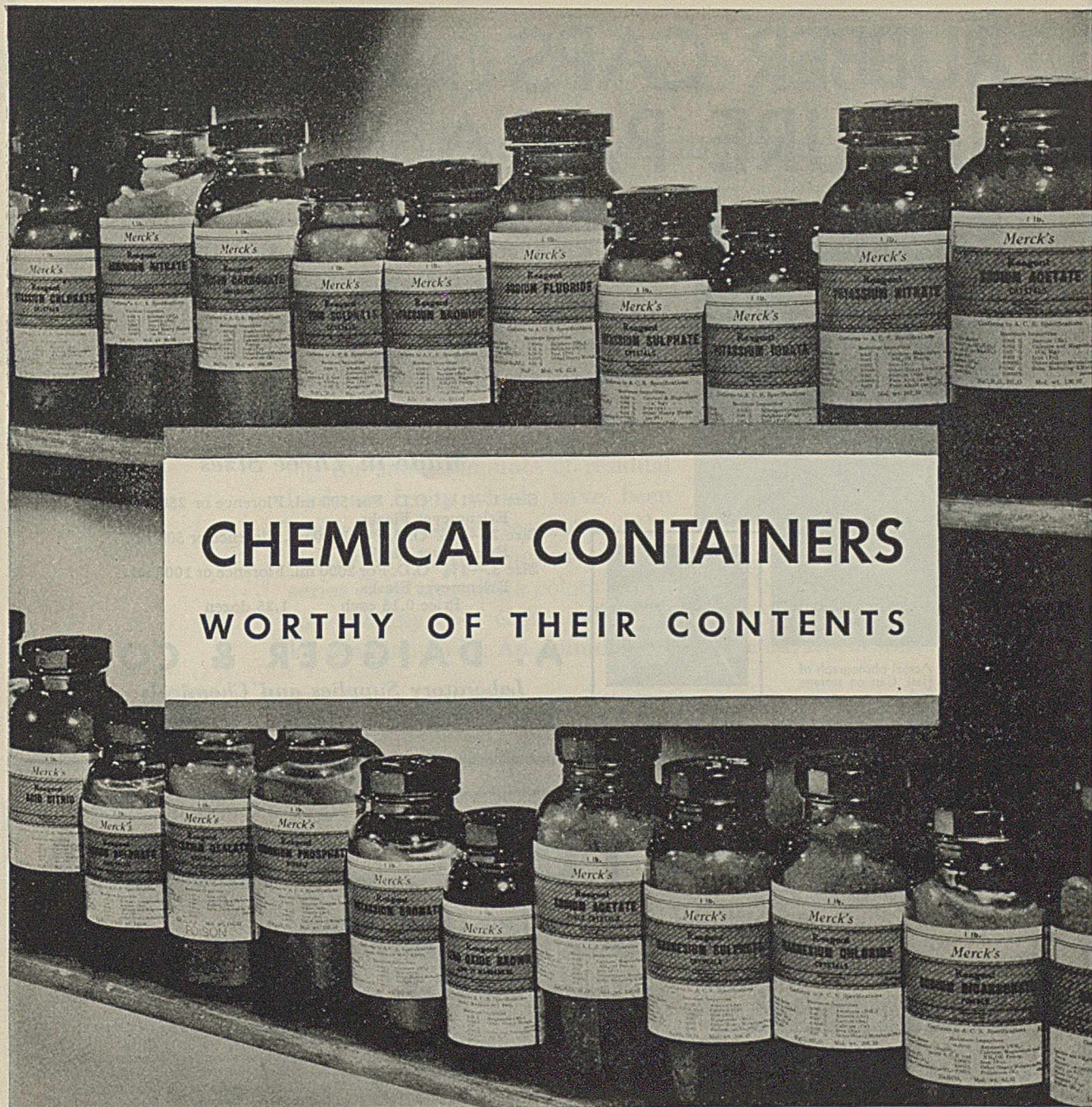
Hot, concentrated perchloric acid has been shown to have reducing as well as oxidizing properties. The oxidation reactions result from the decomposition to form chlorine and oxygen. The reducing properties are assumed to result from the simultaneous formation of hydrogen peroxide. An experimental demonstration of its reducing properties has been made.

The reducing reactions of hot, concentrated perchloric acid increase directly with the concentration and temperature. The conditions can be adjusted over a wide range by the use of mixtures of sulfuric acid and perchloric acid and by working at different temperatures. A proper balance between oxidation and reduction relationships can then be obtained.

LITERATURE CITED

- (1) Fichter and Jenny, *Helv. Chim. Acta*, 6, 328 (1923).
- (2) Lundell, Hoffman, and Bright, "Chemical Analysis of Iron and Steel," p. 299, Wiley, 1931.
- (3) Smith and Deem, *IND. ENG. CHEM., Anal. Ed.*, 4, 227 (1932).
- (4) Smith, Rees, and Hardy, *J. Am. Chem. Soc.*, 54, 3513 (1932).
- (5) Willard and Cake, *Ibid.*, 42, 2208 (1920).
- (6) Willard and Gibson, *IND. ENG. CHEM., Anal. Ed.*, 3, 88 (1931).

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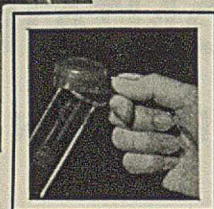
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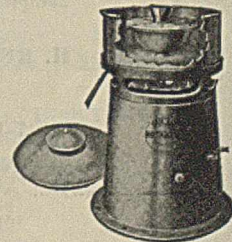
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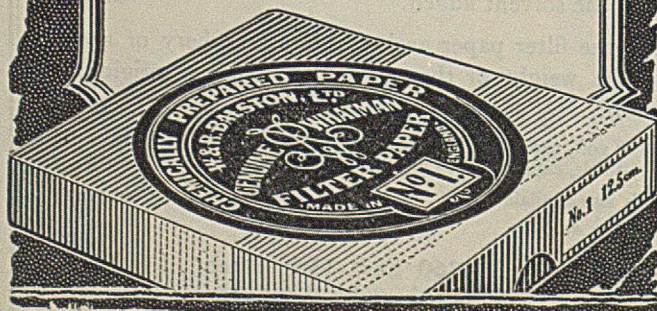
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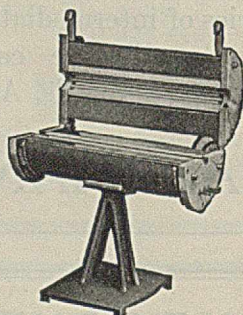
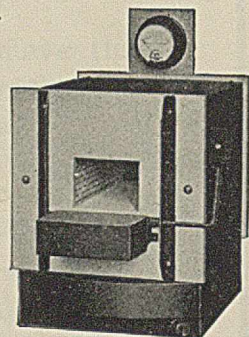
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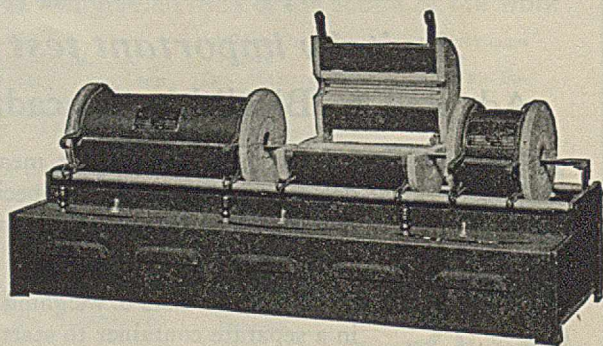
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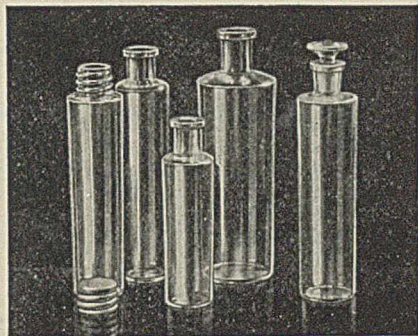
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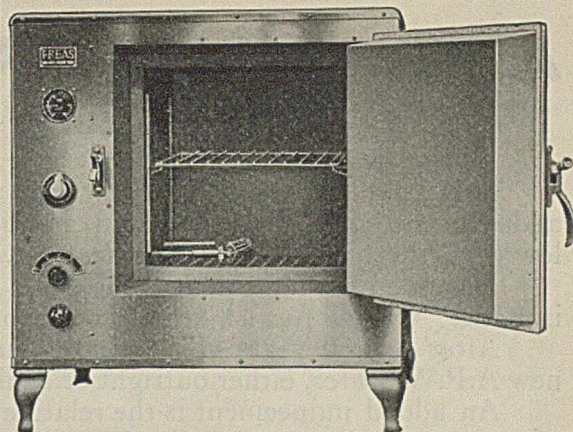
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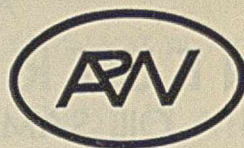
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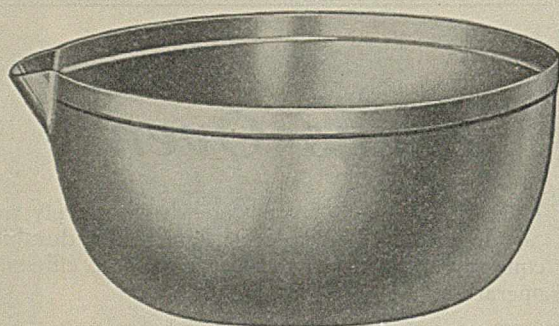


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