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CONTENTS

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Determination of Active Ingredients and Total Fatty Matter in Sulfonated and Sulfated Oils <i>Ralph Hart</i>	137	Detection and Volumetric Estimation of Alkali Metals <i>Robert S. Barnell</i>	183
A Standardized Test of Gasoline Color Stability <i>C. D. Lowry, Jr., M. A. Smith, and George B. Murphy</i>	140	Detection of Benzene in Alcohol <i>A. C. Lansing</i>	184
Determination of Alpha-Amylase <i>S. Jozsa and W. R. Johnston</i>	143	Destruction of Organic Matter in Plant Material by the Use of Nitric and Perchloric Acids <i>J. E. Giesecking, H. J. Snider, and C. A. Getz</i>	185
A Simple and Sensitive Test for <i>p</i> -Phenylenediamine <i>Oscar Heim</i>	146	Solutions for Colorimetric Standards. VI <i>M. G. Mellon and C. T. Kasline</i>	187
Photometric Investigation of the Ceruleomolybdate Determination of Phosphate in Waters <i>Rez J. Robinson and Henry E. Wirth</i>	147	Combination of Catalysts to Reduce Digestion Time in Determination of Nitrogen <i>Charles F. Poe and Margaret E. Nalder</i>	189
Analysis of Complex Gaseous Mixtures <i>Joseph W. Lang</i>	150	A Color Test for the Identification of Mono-, Di-, and Trinitro Compounds <i>R. W. Bost and Frank Nicholson</i>	190
Determination of Ammonia and of Amide Nitrogen in Plant Tissue <i>George W. Pucher, Hubert Bradford Vickery, and Charles S. Leavenworth</i>	152	An Improved Slow-Combustion Pipet for Gas Analysis <i>D. J. Porter and D. S. Cryder</i>	191
An Automatic Pipet for Rapid Delivery <i>W. T. Forsee, Jr., P. J. Thompson, and C. B. Pollard</i>	156	Copper Determination by Alpha-Benzoin Oxime in Copper-Molybdenum Alloy Steels <i>H. A. Kar</i>	193
Studies on Turbidity in Sugar Products. III <i>F. W. Zerban, Louis Sattler, and Irving Lorge</i>	157	Electrometric Titration <i>W. E. Shenk and F. Fenwick</i>	194
An Emergency Stopper for Nitric Acid Bottles <i>Darwin Harris</i>	162	Determination of Water and Hydrogen Sulfide in Gas Mixtures <i>Foster Fraas and Everett P. Partridge</i>	198
Determination of Arsenic in Coal <i>E. S. Hertzog</i>	163	Buret Assembly for Standard Reducing Solutions <i>G. J. Schollenberger</i>	199
Volumetric Determinations of Halides <i>Karl Bambach and T. H. Rider</i>	165	Note to Authors	200
Digesting Biological Materials for Calcium and Phosphorus Analysis <i>H. W. Gerritz</i>	167	Manometric Manostat <i>G. Bryant Bachman</i>	201
Impurities in White Sugars. VIII <i>J. A. Ambler and S. Byall</i>	168	Determination of Traces of Hydrogen Sulfide in Sewer Gases <i>W. J. Wiley</i>	202
Analysis of Combustibles in Flue Gas <i>R. N. Evans and J. E. Davenport</i>	174	A Direct-Reading pH Meter for Glass, Quinhydrone, and Hydrogen Electrodes <i>Allan Hemingway</i>	203
Volumetric Microdetermination of Chloride and Potassium Ions <i>Burlingame Bullock and Paul L. Kirk</i>	178	Determination of Sulfur in Plain and Alloy Steels <i>Louis Silberman</i>	205
Analysis of <i>n</i> -Butanol, Acetone, and Ethanol in Aqueous Solution <i>Leo M. Christensen and Ellis I. Fulmer</i>	180	Filtration of Hot Solutions <i>G. R. Yohe</i>	206
Estimation of Small Amounts of Lead in Copper <i>Bartholow Park and E. J. Lewis</i>	182	A Simple Laboratory Stirrer for Use on the Vacuum Line <i>George T. Austin</i>	206

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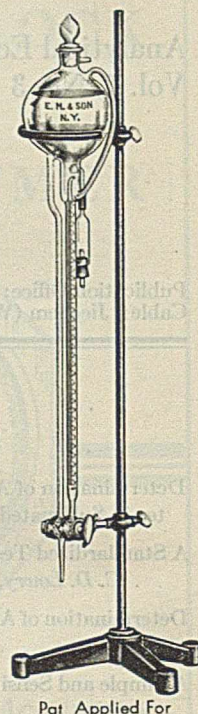
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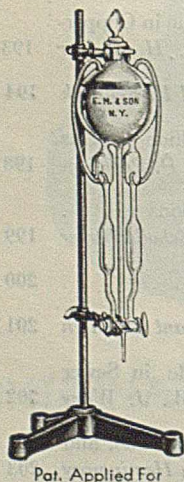
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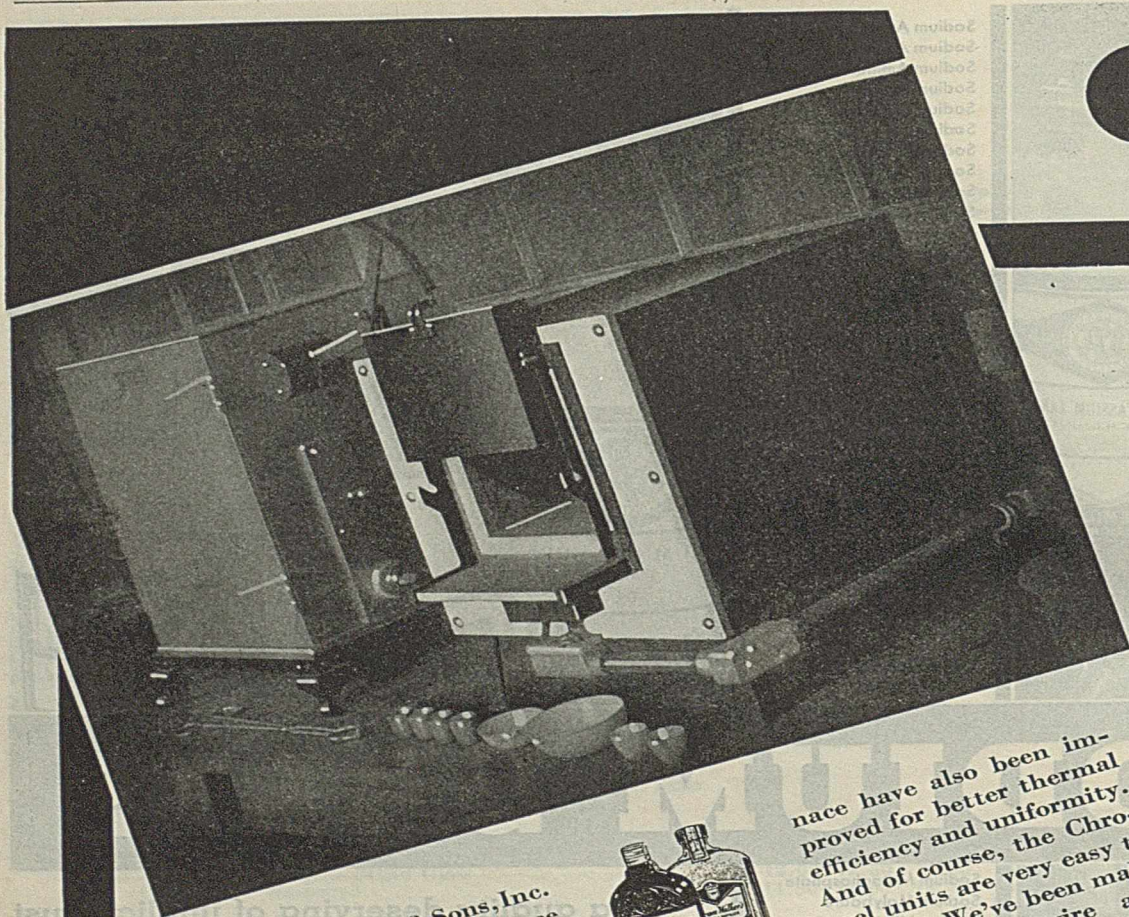
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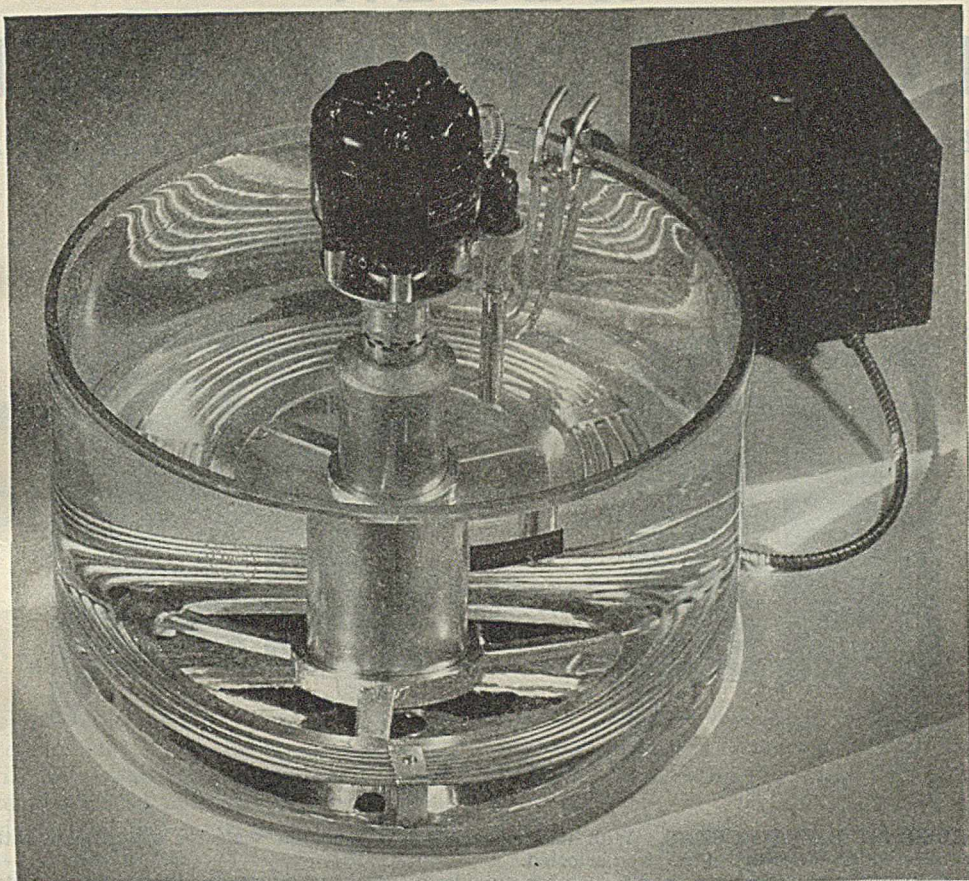
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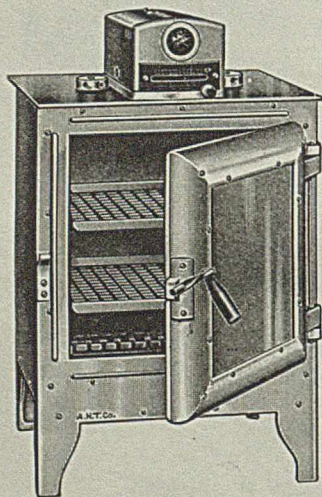
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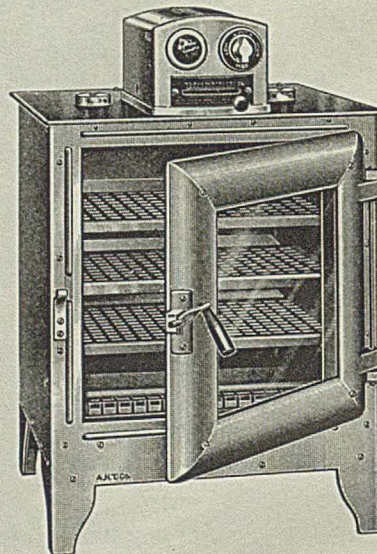
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INDUSTRIAL AND ENGINEERING CHEMISTRY

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HARRISON E. HOWE, EDITOR



Determination of Active Ingredients and Total Fatty Matter in Sulfonated and Sulfated Oils

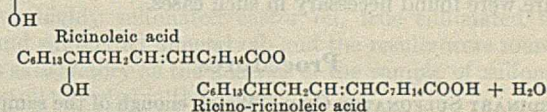
RALPH HART, The Hart Products Corporation, 1440 Broadway, New York, N. Y.

THE test for fatty matter is considered the most important determination in the analysis of sulfonated oils, primarily because the price of the oil is based upon it. This determination has consequently been the subject of considerable investigation for a good many years, with the result that a number of methods have been proposed, many of which are in use but unfortunately do not always yield concordant results. In response to a questionnaire addressed to mill and commercial laboratories and to manufacturers of sulfonated oils, Grimshaw (4) reports as many as 25 methods in use, giving results which in some cases differed by more than 10 per cent. Fahrion (3) analyzed a sample of sulfonated castor oil, containing about 80 per cent fatty matter, by three accepted methods and found that the results varied by as much as 4.7 per cent. Within the past few years attempts have been made by several technical and trade associations to standardize this test, among them the American Association of Textile Chemists and Colorists (A.A.T.C.C., 6). The sulfonated oil committee of this association has investigated several of the more reliable methods and has also proposed a new method, called the total active ingredients method. The proposed method not only yields the true fatty matter but is also applicable to true sulfonated fatty or mineral oils—that is, oils which are not decomposed by boiling with mineral acid—in which cases the other methods are useless. In this paper the results of an investigation of the Wizoeff, Herbig (Bureau of Standards), and total active ingredients methods are reported and compared.

Herbig and Wizoeff Methods

Upon sulfonating castor oil in the usual manner, some of the glycerides are hydrolyzed into free fatty acids, which subsequently are more or less polymerized. As far as the fatty matter itself is concerned, sulfonated castor oil may be considered to consist of glycerides, free fatty acids, and polymerized oil. According to Richardson and Walton (10), the glycerides in ordinary sulfonated castor oil consist mostly of diricin olein with some triricin olein. There is probably also present a sulfonated monoglyceride, which, however, is very unstable. The most important polymer is ricino-ricinoleic

acid, an ester formed from two molecules of the fatty acids with the elimination of water:



Higher polymers of the same type, having the general formula $\text{OH}(\text{C}_{17}\text{H}_{32}\text{COO})_n\text{C}_{17}\text{H}_{32}\text{COOH}$, have also been reported in the literature. Lactones, lactides, anhydrides, and similar polymers (8, 10) are generally assumed to be absent in the original oil or present in negligible quantities, but lactides may be formed upon boiling with mineral acids.

HERBIG METHOD. In the original Herbig method (8), which is the same as the Bureau of Standards method (1), the sample is boiled with strong hydrochloric acid (sp. gr. 1.19) for 15 minutes, the fat is then extracted, the solvent evaporated, and the residue dried at 105° to 110° C. Upon boiling with mineral acids, hydrolysis of the glycerides as well as polymerization of the fatty acids take place, giving low results for the fatty matter to the extent of the loss of glycerol in the first reaction and of water in the second. Hence any method based on acid decomposition alone is bound to give low results, which moreover may vary within certain limits, as will be shown below, with the method of decomposition.

In the author's work it was found that heating for 15 minutes was insufficient, since both the oil and water layers remained turbid, indicating incomplete decomposition. The heating was therefore continued for 1.5 hours, when both layers were entirely clear. In another series of tests with this method, the strong hydrochloric acid was replaced by 25 cc. excess of *N* sulfuric acid, above the amount required to neutralize the soap in the sample. The method with this modification is designated as the Herbig-A.A.T.C.C. method. The rest of the procedure was the same as the original Herbig method, with the further exception that the decomposition was carried out in an Erlenmeyer flask provided with a reflux condenser.

WIZOEFF METHOD. In the official method of the Wissenschaftliche Zentralstelle für Öl und Fettforschung (12) the

sample is boiled for over an hour with 50 cc. of strong hydrochloric acid, the fatty matter extracted and saponified with alcoholic potassium hydroxide, and finally the fatty acids are determined in the soap solution in the usual way. A number of investigations (9) have shown that sulfonated castor oil, as well as its acid-decomposed fatty matter, may be completely saponified, including the polymers. Saponification of the fatty matter must necessarily be accompanied by loss of glycerol from the glycerides and a gain of water due to the splitting of the polymers. Hence results by saponification methods may or may not correspond to the true weight of fatty matter in the original sample, depending upon whether or not the loss of glycerol is balanced by the gain of water absorbed by the polymers.

Total Active Ingredients Method

The total active ingredients method, suggested by the writer, was originally developed by the A.A.T.C.C. committee (5) on sulfonated oils in connection with the determination of organically combined sulfuric anhydride. It consists essentially of extracting the original sample with a solvent over concentrated salt solution, purifying the extract, and weighing the residue. The fatty matter, which is considered to be practically unchanged in composition and weight from that in the original sample and consequently may be designated as true fatty matter, is obtained from the residue by subtracting the organically combined sulfate group, which is nearly always determined in the analysis of a sulfonated oil. With some highly sulfonated oils, a middle layer is formed upon extracting with ether; hence some changes in the regular procedure were found necessary in such cases.

Procedures

ORDINARY SULFONATED OILS. Weigh enough of the sample to yield about 5 grams of anhydrous fat into a 250-cc. pear-shaped separatory funnel containing 50 cc. of a saturated solution of sodium chloride, some solid salt, 5 drops of a 0.1 per cent solution of methyl orange, and 50 cc. of ether. Decompose the soap with approximately *N* sulfuric acid until slightly acid (about 0.3 cc. excess). After settling for at least 5 minutes (all separations should be allowed to clear for that period), draw off the lower layer into a second separatory funnel and wash the ether layer with 25-cc. portions of the salt solution until practically neutral to methyl orange—i. e., until one drop of 0.5 *N* caustic turns the wash water strongly alkaline. Extract the combined water layers with two 25-cc. portions of ether and wash the latter with salt solution as in the first funnel. Combine the ether layers and shake for about 2 minutes with 10 cc. of 25 per cent solution of sodium sulfate, warmed to 55° C. Allow to settle for about 10 minutes and, to prevent crystallization of the salt, immerse the lower part of the funnel in a beaker of warm water. Draw off the lower layer as completely as possible, transfer the ether layer into a dry 250-cc. Erlenmeyer flask, rinse the funnel several times with ether, and evaporate to about 75 cc. Immerse the Erlenmeyer flask in ice water for 30 minutes, mixing frequently. Filter into a tared 150-cc. beaker, and wash the flask and filter paper with ether until free from fat (absence of oil stains on filter paper upon drying), catching the filtrate if necessary in a second beaker. Evaporate the filtrate to a total volume of about 20 cc., add exactly 2 cc. of 0.5 *N* alcoholic potassium hydroxide, mix by gently swirling the contents, and evaporate on the water bath until practically free of ether. Dry in a hot air oven at 108° to 112° C. for 1.5 hours, cool in a desiccator, and weigh. Repeat heating for 30-minute periods until constant weight is reached.

HIGHLY SULFONATED OILS. Extract the sample once with ether over salt solution and wash the ether layer as above, retaining the middle layer with the ether extract. The combined water layers are extracted twice with a mixture of 20 cc. of ether and 10 cc. of alcohol. The combined ether-alcohol layers are then washed with 25-cc. portions of salt solution until neutral to methyl orange. The extracts are finally combined in the first funnel and washed with 10 cc. of Glauber's salt solution as above. There should be no middle layer at this stage; if one is present, 5-cc. portions of alcohol are added until it disappears completely. The ether-alcohol layer is evaporated, chilled, and

filtered as in the regular procedure, except that the filter paper is washed with a mixture of 2 parts of ether to 1 part of alcohol. After evaporating the greater part of the solvent, exactly 1 cc. of 0.5 *N* alcoholic potassium hydroxide is added and the rest of the solvent evaporated on the water bath, evaporation being hastened by stirring with a glass rod, which is tared with the beaker. When practically free of solvent, 5 cc. more of the alkali are added and the residue is heated to constant weight.

Correction for alkali added, grams =

$$\frac{(K-H)}{1000} \times \text{normality of KOH} \times \text{cc. of KOH}$$

Corrected residue, per cent =

$$\frac{\text{weight of residue minus correction for alkali}}{\text{weight of sample}} \times 100$$

True fatty matter, per cent = per cent corrected residue minus per cent of organically combined NaSO_3^- .

The term NaSO_3^- represents the inorganic group in the total active ingredients in accordance with the formula $\text{RO} \left[\text{SO}_3^- \text{Na} \right]$ where R represents the fatty radical. The oxygen adjacent to the fatty radical is considered part of the fatty matter, since it is part of the hydroxyl group in ricinoleic acid and cannot readily be organically combined. The NaSO_3^- is calculated from the per cent of organically combined sulfur trioxide in the original sample as follows:

Per cent of organically combined NaSO_3^- =

$$\begin{aligned} & \text{per cent of organically combined } \text{SO}_3 \times \frac{\text{NaSO}_3^-}{\text{SO}_3} \\ & = 1.2875 \times \text{per cent of combined } \text{SO}_3 \end{aligned}$$

The combined salt solutions and the filter paper should show no fat upon acidification and boiling, or at most a trace. If deemed advisable, the salt on the filter paper may be dissolved in hot water, the filtrate added to the salt solutions, and the latter boiled with strong hydrochloric acid for about 1 hour. The fatty matter, if any, is then extracted once with about 30 cc. of ether, the extract washed free of mineral acid, and the residue after evaporating the solvent added to the active ingredients. The addition of alkali is necessary to prevent decomposition of the active ingredients during drying, indicated at first by the residue turning red (owing to methyl orange dissolved in the oil) and later by blackening and charring. In the case of highly sulfonated oil, considerably more alkali is required to render the oil stable to heating. The residue retains traces of alcohol or moisture very tenaciously and 2 to 3 hours' heating is required to obtain constant weight. However, with the quantity of alkali recommended the amount of decomposition is negligible, since 3 to 5 hours' additional heating after constant weight was reached showed no loss in weight and practically no change in the appearance of the oil. Further heating, however, finally caused both charring and loss of weight. It is advisable to evaporate the alcohol as much as possible before the alkali is added; otherwise the residue may jell and slow up volatilization of the solvents.

Results by Total Active Ingredients Method

A sample of sulfonated castor oil was analyzed by this method for true fatty matter by three different men and the results are given in Table I. All acidities in this paper were calculated on the original sample and then converted to milligrams of potassium hydroxide per gram of castor oil fatty acids as determined by the Wizeff method. The acidity of the original sample represents the free fatty acids plus the fatty acids as soap.

TABLE I. TRUE FATTY MATTER AND ACIDITIES BY TOTAL ACTIVE INGREDIENTS METHOD

Analyst	Total Active Ingredients %	SO_3 True Fatty Matter %	Acidities, Mg. KOH per Gram Fatty Acids	
			In true fatty matter	In original sample
1	71.32
2	71.43
3	71.29
Av.	71.35	64.65	117.6	119.2

The small drop from the original acidity indicates that the total active ingredients had probably undergone very little change during extraction and heating. Table II shows that the total is within 0.2 per cent of 100 per cent.

For further determination of the purity of the total active ingredients, the following additional tests were applied:

FATTY MATTER. The fatty matter in the total active ingredients was determined by the Herbig-A.A.T.C.C. method and was found to check with the fatty matter in the original sample obtained by the same decomposition method. This was to be expected from the fact that the wash waters and salts upon the filter paper upon decomposition with acid and boiling showed only a trace of fat.

COMBINED SULFURIC ANHYDRIDE. There was no decomposition of the sulfonated oil, since the combined sulfur trioxide in the total active ingredients determined by the A.A.T.C.C.-acid titration method (7) agreed with the value obtained on the original sample.

FOREIGN SALTS. The organically combined sulfur trioxide was determined also by the A.A.T.C.C.-gravimetric method (5, 7), which again checked with the original sample. Evidently the presence of foreign salt would have been indicated by a high result. The absence of foreign salt was also shown from the fact that upon chilling the residue after almost complete evaporation of the solvent before the addition of alkali, no separation occurred.

SOLVENT. The absence of solvent was proved by the fact that additional heating for over 4 hours at 110° C. had practically no effect on the constant weight.

TABLE II. COMPLETE ANALYSIS OF SAMPLE OF SULFONATED CASTOR OIL

Moisture	25.1
Inorganic salts	0.9
(Na-H) as soap	1.2
Free glycerol	1.2
Total active ingredients	71.4
Total	99.8

Results by Different Methods

The same sample was analyzed also by the Herbig-A.A.T.C.C., Wizeoff, and Herbig methods and the results, which are the averages of a number of tests, are listed in Table III.

It will be noticed that the total active ingredients method gave the highest result and the Herbig method the lowest—namely, 64.65 per cent compared with 62.63 per cent, or a difference of 3.3 per cent on the fat basis. The drop in acidity from 119.2 to 96.1 mg. in the Herbig method indicates that the low result in fatty matter is probably due to polymerization whereby water is eliminated. Undoubtedly there was also some loss of glycerol. Upon comparing the Herbig-A.A.T.C.C. method with the Herbig method, the fatty matter was 63.68 and 62.63 per cent, respectively, and the acidity 133.0 and 96.1 mg., respectively. It is thus evident that the results by decomposition methods alone may vary with the conditions of decomposition. In the Herbig-A.A.T.C.C. method, where dilute acid was used, there was evidently more hydrolysis of the glycerides than polymerization of the fatty acids, since the acidity is above the original sample; the reverse was true in the Herbig method. Both reactions must have occurred to a lesser extent in the Herbig-A.A.T.C.C. method, as the fatty matter by this method is more than 1 per cent greater than by the Herbig method.

The fatty matter by the Wizeoff method lies between the two Herbig methods. Since the Wizeoff result represents the pure fatty acids, the higher result by the Herbig-A.A.T.C.C. method definitely indicates the presence of glycerides, and the lower results by the Herbig method, polymers. The acidity of the fatty acids was made also before drying and was found to be 188.4 mg., compared with 184.2 mg. after drying for 2 hours at 100° to 105° C. The former is practically the theoretical neutralization value for castor oil fatty acids. Winokuti (11) found, upon heating castor oil fatty acids for 5 hours, that the acidity dropped only 0.3 mg. at 50° C. but 14.0 mg. at 105° to 110° C. The Wizeoff method yields a definite chemical compound—the pure fatty acids—and with

care concordant results are readily obtained. The main objection to this method is that the results may vary, as already stated, from the true amount of fatty matter present in the original oil. In the case of this sample, the fatty matter by this method was 2.3 per cent below the true fat as determined by the total active ingredients method. The difference may be even greater for a sample both high in glycerides and low in polymers, as, for example in a low sulfonated olive oil.

It will be observed that the highest result was obtained by the total active ingredients method. Unless splitting of the polymers occurs, which is considered not probable in acid solutions, the method yielding the highest result of fatty matter must necessarily be the nearest to the true content of fatty matter. Hence the fatty matter by the total active ingredients method is considered the most accurate of the methods tested. Similarly, the order of diminishing accuracy of the other methods is considered to be Herbig-A.A.T.C.C., Wizeoff, and Herbig.

If NaSO_4^- is subtracted from the total active ingredients instead of NaSO_3^- , the result for the sample analyzed checks closely with the Herbig-A.A.T.C.C. method. Whether or not this happens to be merely a coincidence was not determined. It was also noticed that higher results were obtained by the original Herbig method, in which boiling with strong hydrochloric acid is continued for only 15 minutes, than when boiled for 1.5 hours—undoubtedly because of less polymerization and hydrolysis. However, the turbidity of the contents after the short heating makes this procedure uncertain. The total active ingredients method was used to determine the fatty matter in samples of sulfonated olive oil, sulfonated tallow, highly sulfonated castor oil, true sulfonated fatty oil, and sulfonated mineral oil, and the results were found to be as satisfactory as the analysis of the sample of sulfonated castor oil reported in this paper.

TABLE III. COMPARISONS OF FATTY MATTER AND ACIDITIES DETERMINED BY DIFFERENT METHODS

Method	Fatty Matter %	Diff. %	Fatty Matter Based on T.A.I. Method %	Diff. %	Acidities, Mg. KOH per Gram Fatty Acids
Original sample	119.2
Total active ingredients (T.A.I.)	64.65	...	100.0	..	117.5
Herbig-A.A.T.C.C. (dilute acid)	63.68	0.97	98.5	1.5	133.0
Wizeoff	63.18	1.47	97.7	2.3	184.2
Herbig (strong acid)	62.63	2.02	96.7	3.3	96.1

Summary

The fatty acids or Wizeoff method for the determination of total fatty matter in sulfonated oils and the Herbig (Bureau of Standards) or acid-decomposition method were found to yield low results. Furthermore the Herbig method is subject to variations, depending upon the method of decomposition; stronger acid and continued boiling yield the lower results, probably due to increased hydrolysis and polymerization. A new method is proposed, called the total active ingredients method, which is considered to give the most accurate values. It consists essentially in separating and weighing the pure, undecomposed sulfonated oil. As a rule the results are higher than by the other methods. The weight of the fatty matter by this method corresponds to the true fatty matter in the original sample. The new method is also applicable to true sulfonated fatty and mineral oils, in which cases the other methods are useless as these oils are not decomposed by acids.

Acknowledgment

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Literature Cited

- (1) Bur. Standards, Commercial Standard CS43-32, January 26, 1933.
- (2) Fahrion, W., *Chem.-Ztg.*, **37**, 1372 (1913).
- (3) Fahrion, W., *Seifenfab.*, **35**, 365 (1915).
- (4) Grimshaw, A. H., *Am. Dyestuff Repr.*, **17**, 94 (1928).
- (5) Hart, R., *IND. ENG. CHEM., Anal. Ed.*, **5**, 413 (1933).
- (6) Hart, R., et al., *Am. Dyestuff Repr.*, **21**, 667 (1932).

- (7) Hart, R., *Ibid.*, **22**, 695 (1933).
- (8) Herbig, W., "Die Ole und Fette in der Textilindustrie," 2nd ed., p. 401, Stuttgart, Wissenschaftliche Verlagsgesellschaft m. b. H., 1929.
- (9) Juillard, P., *Bull. soc. chim.*, (3), **6**, 638 (1891).
- (10) Richardson, F. W., and Walton, W. K., *J. Soc. Chem. Ind.*, **31**, 105 (1912).
- (11) Winokuti, K., *Tech. Repts. Tohoku Imp. Univ.*, **10**, No. 3, 416 (1932).
- (12) Wizoeff, *Chem. Umschau Fette, Ole, Wachse Harze*, **38**, 34, 132 (1931).

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A Standardized Test of Gasoline Color Stability

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WHILE the bulk of the gasoline now sold is dyed, much is marketed water-white. Many gasolines which are colorless or nearly so when delivered to the filling station become discolored on exposure to strong light. This is particularly undesirable if the gasoline is to be dispensed in pumps with visible bowls, in which it may be exposed for considerable periods to daylight or even to direct sunlight. Before shipping, therefore, gasoline is often subjected to a test of its color stability, although this is not required by specifications, to determine whether it can be exposed to light without darkening.

The usual test of color stability is exposure of the gasoline to sunlight. There are, however, no generally accepted conditions for making the test. Sometimes the exposure is for a period of 2 hours, sometimes 8, or even longer. The container used may vary in size from a 113-cc. (4-ounce) bottle to a 37.85-liter (10-gallon) bowl. It is obvious, moreover, that "sunlight" is far from being a uniform illumination. The light from the sun varies in intensity and in spectral distribution of energy from hour to hour, from season to season, and from place to place.

A step toward precision in sunlight testing was made by Beard and Reiff (1) when they used an oxalic acid-uranyl acetate actinometer to measure the intensity of sunlight in order that each test sample might be subjected to the same amount of radiation. Hoeman (5) gaged sunlight exposure

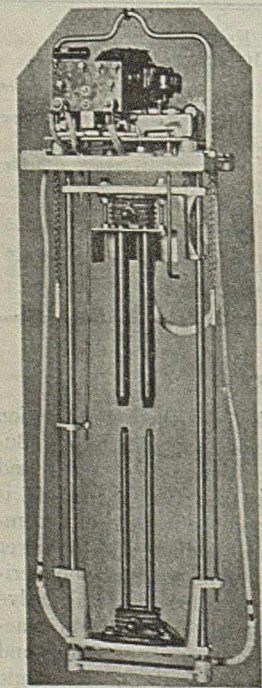


FIGURE 1. CARBON ARC LAMP

by the time of reduction of a ferric oxalate actinometer. He did not show, however, that the light which affected the actinometer was precisely that which caused the darkening of

gasoline. These methods of measurement, even if accurate, do not eliminate all the disadvantages of a sunlight test, as sun exposure can be made satisfactorily only in the middle of the day, not at all on cloudy days, and with difficulty in the weak sunlight of winter. Moreover, the length of time required when the sun is used as the light source, being a matter of hours, is inconvenient.

A satisfactory test of color stability should use a light of unvarying intensity and of sufficient strength to make possible a test of short duration.

Apparatus

These requirements are fulfilled, in the test to be described, by exposure to light from a carbon arc.

The light source used is a flame-type carbon arc, type C3A of National Carbon Company, pictured in Figure 1. It is a 60-ampere, 50-volt, vertical trim lamp, operating on alternating current, the carbons being fed automatically by an electric motor. The lamp, as manufactured, has two upper carbons 22 mm. in diameter and two lower 13-mm. carbons. The two pairs of carbons burn alternately, the arc shifting from one to the other every 20 to 30 minutes. The sizes are so proportioned that upper and lower carbons burn at the same rate, and the position of the arc does not change. Much of the work to be described was done with the lamp as purchased, and satisfactory results were obtained. However, the changing of the arc flame from one pair of carbons to the other during the period of exposure resulted in the illumination received by samples in different positions around the lamp being not quite the same. To increase the uniformity of illumination and the precision of the test, one pair of carbons was removed and the remaining pair placed in the exact center of the frame. The lamp was encased in a heavy sheet-metal housing, which is shown in plan in Figure 2. The samples were placed in slots in the housing, and these slots were water-jacketed to minimize rise in temperature. The center of each bottle was 30.5 cm. (12 inches) from the center of the arc, and no slots were placed where the shadow of the arc guide rods could fall upon them. The apparatus was connected to an efficient suction line, which served to create a draft, cooling the instrument and carrying off the gases produced.

Coblentz, Dorcas, and Hughes (2) have reported that the carbon arc "of all the artificial illuminants tested is the nearest approach to sunlight." A mercury arc lamp was used at the beginning of this study, but the carbon arc is preferred because of its uniformity and the closer resemblance of its illumination to sunlight. The arc was fitted with the "sun-

shine carbon," a cored carbon containing cerium, that gives a light similar to sunlight (3, 4) having a practically continuous spectrum from 2800 Å. through the longer wave lengths. In Figure 3 light from the arc is compared with average sunlight. The main difference between the two sources of illumination is the presence of a greater amount of short ultraviolet light in the arc spectrum than is present in that of the sun. Much of this light was filtered out by the glass in the tests made in glass bottles, but it was present when the testing was done in quartz containers.

Standardization of Test

As standard of reference for the arc test, the color drop of gasoline when exposed to the brightest summer sun was used. Samples of many gasolines were exposed to the sun on clear and cloudless days in July and early August. The rates of color change were measured and an exposure to the artificial light found which would give a color drop equal to that produced by the sun in a given period. The intensity of the sunlight was followed by measuring the rate of decomposition in an oxalic acid solution containing uranyl acetate (oxalic acid actinometer, θ) during the exposures, in order to make sure that there was no great variation in the sunlight on the different days on which the work was done. No results were discarded on the basis of actinometer measurements, so that the results represent average values for bright summer days.

In making a comparison of the effects of the sun and of the arc, a sample of gasoline in a 113-cc. (4-ounce) oil sample bottle was exposed to sunlight, beginning at noon, and its color on the Saybolt scale read every 10 minutes. At the same time samples of the same gasoline were exposed to the arc in bottles of ordinary glass, of Correx D glass (an ultraviolet transmitting glass of the Corning Glass Company), and of quartz, and the color was read every 5 minutes. To insure uniformity, the glass bottles used were all taken from a single shipment from the manufacturer. They had an average wall thickness of 0.16 cm., and measured in an ultraviolet spectroscope showed total extinction of light of wave length below 3200 to 3300 Å. The Correx D bottles were made up from tubing, had a wall thickness of 0.24 to 0.30 cm., and in the spectroscope showed partial extinction of light at 2800 to 2900 Å. and considerably lessened transmission at shorter wave lengths. The quartz bottles were 0.12 to 0.16 cm. in wall thickness and were transparent to ultraviolet as well as visible light.

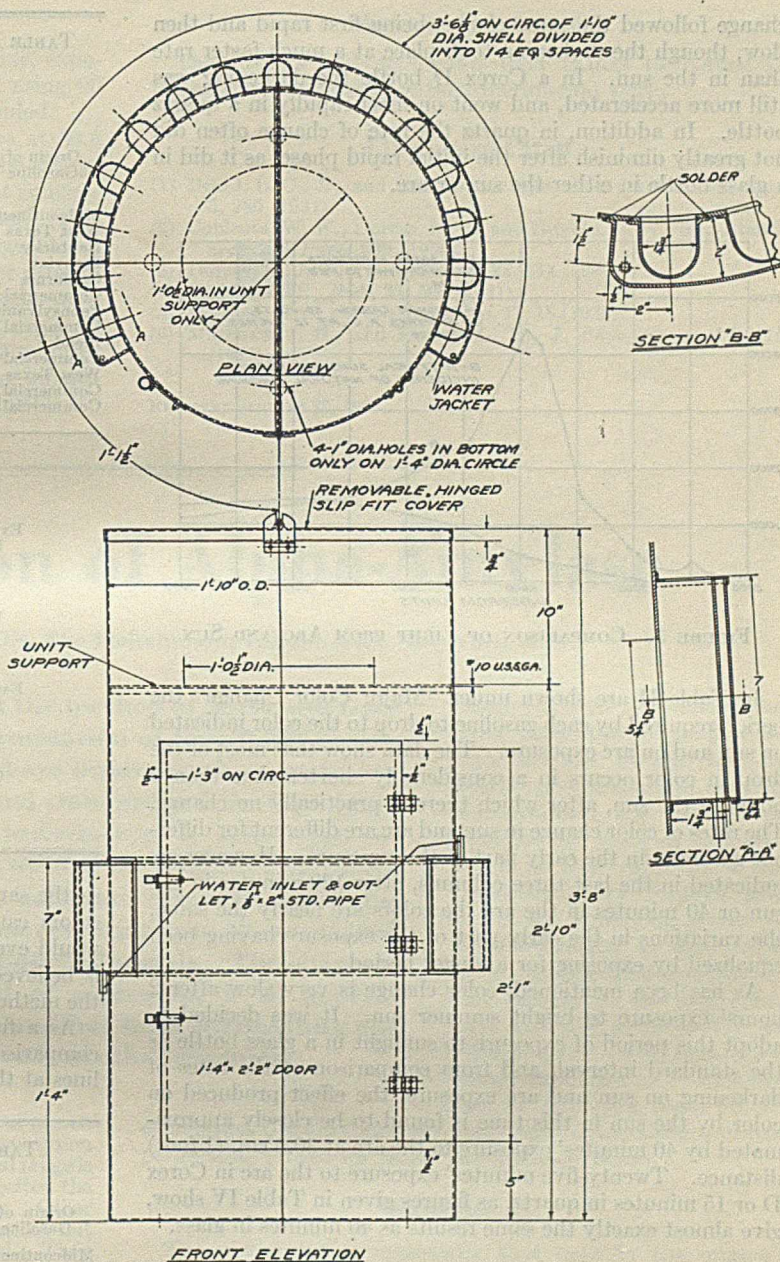


FIGURE 2. PLAN OF ARC HOUSING

Shell, cover, door, and water-jacketed sample holder made of No. 18 U. S. Standard GA galvanized sheet steel. Soldered construction throughout.

TABLE I. COLOR CHANGE IN GASOLINE EXPOSED TO SUN AND ARC

Time, min.	West Texas Gasoline			Commercial Gasoline B			
	Sun, glass	Arc, glass	Arc, quartz	Sun, glass	Arc, glass	Arc, quartz	Arc, Correx-D
0 (initial)	22	22	22	23	23	23	23
5	..	18	18	..	20	20	20
10	21	17	11	23	20	20	20
15	..	15	3	..	19	18	18
20	19	13	3	22	18	17	18
25	..	12	3	..	18	16	17
30	18	12	3	22	17	16	16
35	..	9	3	..	17	14	16
40	17	9	3	20	16	12	15
50	16	20
60	15	19
90	9
120	9	17
180	17
24 hours	17

Typical results of exposure to the sun and arc are given in Table I.

The first of these gasolines was unstable, the second fairly stable. Similar comparisons were made with 20 other gasolines. Some were commercial gasolines purchased at filling stations, probably blends of straight-run and cracked products, while others were cracked gasolines produced in experimental units from a variety of charging stocks. Nearly all the gasolines which were specially prepared for this study were refined with sulfuric acid.

As a rule it was found that when a gasoline contained in a glass bottle was exposed to the sun, there was at first a fairly rapid acquiring of color (which might be preceded by a short induction period) as measured by lowering of the reading on the Saybolt scale. After this initial stage, which usually lasted considerably less than 2 hours, the rate of drop in color was much less. After 2 hours, the change was very slow. On exposure to the arc in a glass bottle, the color

change followed the same course, being first rapid and then slow, though the darkening took place at a much faster rate than in the sun. In a Corex D bottle the darkening was still more accelerated, and went on most rapidly in a quartz bottle. In addition, in quartz the rate of change often did not greatly diminish after the initial rapid phase, as it did in a glass bottle in either the sun or arc.

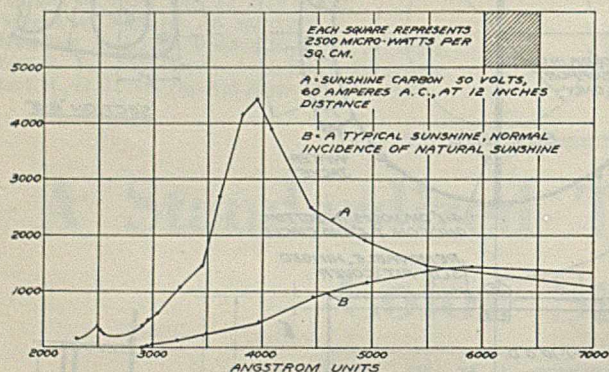


FIGURE 3. COMPARISON OF LIGHT FROM ARC AND SUN

In Table II are shown under "Major Color Change" the period required by each gasoline to drop to the color indicated on sun and on arc exposure. The data show that most of the drop in color occurs in a considerably shorter time than 2 hours in the sun, after which there is practically no change. The rates of color change in sun and arc are different for different gasolines in the early part of the exposure. However, as indicated in the last three columns, after 120 minutes in the sun or 40 minutes in the arc the colors are nearly the same, the variations in the early part of the exposure having been equalized by exposing for a longer period.

As has been mentioned, color change is very slow after 2 hours' exposure to bright summer sun. It was decided to adopt this period of exposure to sunlight in a glass bottle as the standard interval, and from comparison of the rates of darkening on sun and arc exposure, the effect produced on color by the sun in this time is found to be closely approximated by 40 minutes' exposure to the arc at 30.5 cm. (1 foot) distance. Twenty-five minutes' exposure to the arc in Corex D or 15 minutes in quartz, as figures given in Table IV show, give almost exactly the same results as 40 minutes in glass.

Effect of Temperature

Although reactions which are primarily photochemical are not significantly changed in rate by slight variations in temperature, it was considered desirable to maintain a uniform temperature in this test. The bottles containing the gasoline samples are cooled by a water jacket during exposure to the arc. The cooling minimizes temperature variation and checks loss of light ends.

To determine whether such temperature variations as might occur during routine use of this test would affect the results, comparative tests were made, in some of which the bottles were cooled as usual, and in others no water was circulated through the jacket, which allowed the gasoline to become warm.

The tests were of 40 minutes' duration in glass bottles and 15 minutes in quartz. The results are shown in Table III.

The slightly lower colors, when the samples were not cooled, are due to loss of light ends, which is appreciable when the bottles become warm. The sample of West Texas gasoline exposed without cooling, of 22 color, was made up to its original volume with 30 color gasoline and then was 24 color, the same

TABLE II. COMPARISON OF COLOR DROP IN EXPOSURE TO ARC AND SUNLIGHT

Origin of Gasoline	Original Color	Major Color Change		Color after 120 Min. Sun	Time to Same Color in Arc	Color after 40 Min. Arc	
		Color after exposure	Time in arc Min.				
Midcontinent	30	27	40	20	26	30	26
West Texas	30	25	90	30	24	35	23
Kentucky	29	26	40	15	25	40	25
Peruvian	29	27	40	10	26	15	25
California	28	19	40	30	17	45	18
Commercial A	27	21	80	25	18	Over 40	20
Pennsylvania	26	24	40	25	23	35	23
Commercial E	25	19	40	15	18	25	16
Blend F	24	7	80	25	0	Over 40	3
Commercial B	23	18	80	20	17	30	16
West Texas	22	15	60	15	9	35	9
Commercial C	22	2	80	30	-5	Over 40	0
Commercial D	21	13	50	30	12	30	12

TABLE III. EFFECT OF TEMPERATURE

Exposure, 40 minutes in glass Pennsylvania blended gasoline	With Cooling	Without Cooling
	Original color	27
Color after exposure	17	16
Final temperature, ° C.	48	84
West Texas cracked gasoline		
Original color	30	30
Color after exposure	24	22
Final temperature, ° C.	45	56
Exposure, 15 minutes in quartz		
Midcontinent		
Original color	30	30
Color after exposure	17	18
Final temperature, ° C.	44	57
California		
Original color	27	27
Color after exposure	26	25
Final temperature, ° C.	44	57

as the samples exposed with cooling. The variation in final colors caused by much greater temperature variation than would ever occur in the normal use of this test is slight. It is believed that errors caused by temperature differences, if the method is used as described, will be negligible.

As a final check on the accuracy of the accelerated test, comparisons are given in Table IV of the colors of 24 gasolines at the end of the test periods proposed.

TABLE IV. COLOR OF GASOLINES AFTER EXPOSURE

Origin of Gasoline	Initial Color	Color, Saybolt after Exposure to:			
		Sun in glass 120 Min.	Arc in glass 40 Min.	Arc in Corex-D 25 Min.	Arc in quartz 15 Min.
Midcontinent	30	26	26
West Texas	30	25	25
Blend A	29	25	25
Peruvian	29	26	25	..	25
Kentucky	29	25	25	..	22
California	29	21	23
Texas	28	23	..	22	23
California	27	25	..	23	25
Commercial A	27	18	20	19	20
Pennsylvania	26	23	23
Blend B	26	..	22	24	24
Blend C	25	17	16	17	18
Blend D	25	..	17	21	18
Blend E	24	..	21	21	22
Blend F	24	0	3	12	16
Commercial B	23	17	16	17	18
Commercial C	22	-5	0	-3	1+
West Texas	22	9	9	..	3
Commercial D	21	12	12	..	12
Blend H	21	..	19	20	19
Blend I	20	..	18	19	20
Blend J	19	..	17	17	18
Montana	19	13	..	13	15
California	17	14	..	13	14

On most samples there is little variation in the final results between the testing in bright sunlight, or by exposure to the arc in glass, quartz, or Corex D bottles.

Conclusions

As a reproducible test of color stability of gasoline, exposure to a carbon arc burning "sunshine" carbons using 60 amperes at 50 volts alternating current is recommended.

In the latitude of Chicago, 40 minutes' exposure at 30.5 cm. (1 foot) distance from this arc is equivalent, in the change in color produced, to a 2-hour exposure to brightest summer sun, the samples in both cases being in glass bottles. This is a sufficiently long exposure to differentiate between stable and unstable gasolines, and after this period further drop in color is usually slow. For routine work, further acceleration and nearly as accurate results may be obtained by using an exposure of 15 minutes in a quartz container or of 25 minutes in one of Corex D. This test has been used in these laboratories for 3 years and has proved rapid and reproducible.

Acknowledgment

The authors wish to express their thanks to Wayne L. Benedict for assistance in the experimental work.

Literature Cited

- (1) Beard, L. C., Jr., and Reiff, O. M., *IND. ENG. CHEM., Anal. Ed.* 3, 280 (1931).
- (2) Coblenz, W. W., Dorcas, M. J., and Hughes, C. W., *Bur. Standards, Sci. Paper* 539 (1926).
- (3) Dorcas, M. J., *IND. ENG. CHEM.*, 22, 244 (1930).
- (4) Greider, C. E., *Ibid.*, 23, 508 (1931).
- (5) Hoeman, E. C., *Oil Gas J.*, 32, No. 17, 18 (1933).
- (6) Mathews, J. H., and Dewey, L. H., *J. Phys. Chem.*, 17, 216 (1913).

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Determination of Alpha-Amylase

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DURING the last few years several investigators have studied the liquefying action of alpha-amylase on gelatinized starch.

Jozsa and Gore (6) have published a method for the determination of the liquefying power of malt diastase, based on viscosity measurements of a remarkably uniform starch paste, which enables rather accurate measurement of the amount of starch liquefied when alpha-amylase acts on the starch paste. However, they applied their experimental results rather inaccurately when they assumed that the liquefying power of a given malt was proportional to the amount of starch liquefied under the experimental conditions. This assumption leads to erroneous activity values unless the experimental range is narrowly limited. Fletcher and Westwood (1) have suggested the use of a restricted range, but this is not all satisfactory. Other workers (7) have proposed a rather complete modification, but their method of calculating activity values is not sound. They report values for the liquefying power of a pancreatin preparation which deviate from one another as much as 10 per cent. These deviations may be due to their method of calculation, which apparently involves an empirical determination of certain constants for a given preparation and then the extension of these constants to any alpha-amylase preparation. This extension is certainly not accurate because of wide deviations in the rate curves of various preparations, particularly when the substrate is largely converted. Their expression of liquefying power is also inaccurate, since it represents only an average value for the rate of conversion of substrate and is not proportional to the actual enzyme content—that is, a doubling of enzyme content would not double the liquefying power of the preparation as measured by them.

In view of the above, a fundamental revision of the method is certainly necessary. The authors believe that the revision herein proposed enables one to measure accurately the activity of an alpha-amylase preparation.

In order to calculate the concentration of alpha-amylase in a given enzyme preparation from the amount of starch liquefied under the specified conditions, the authors have introduced a new enzyme unit, the "liquefon," defined as that amount of starch-liquefying enzyme which will convert the standard starch paste at the rate of 25 mg. of dry starch per

In revising the method of Jozsa and Gore for the determination of liquefying power, the authors have improved the experimental technic and standardized the liquefying curve. By introducing a new type of enzyme unit termed the liquefon, they have been able to calculate accurate values for alpha-amylase activities from the measured amounts of liquefied starch. The enzyme-unit method of expression is of general applicability and has been successfully applied to the study of other enzymes.

minute at zero time under the given experimental conditions. Since the rate at zero time is directly proportional to enzyme concentration, the number of liquefons per gram of preparation is an exact measure of the alpha-amylase content and also of the liquefying power of the preparation at zero time under the specified conditions. The nature of the liquefon unit and its applicability to alpha-amylase have been previously discussed (4). In addition to the new method of

calculation the authors have made significant changes in experimental procedure which are outlined below.

Equipment

The equipment is essentially that used in the original method (6), but with the following changes: It is very important to select precipitating jars of uniform dimensions, since the stirring efficiency depends on the size of the jar. A pipet should be chosen which has a time of drainage from mark to mark of 165 to 190 seconds at 21° C. for the specified glycerol solution. A constant-temperature bath should be used and the water pumped through the jacket of the pipet.

The equipment could be easily modified, but it is always necessary to use reproducible technic.

Preparation of Standard Starch Paste

In making up the starch paste it is important to add the starch as soon as the water boils, in order to avoid any considerable loss of water. The first stirring should be for about 1.5 minutes and the second for 2 minutes. In cooling the paste one should use a water bath at about 20° C. Too rapid cooling produces an unstable paste. In the modified method sodium chloride is used to stabilize the enzyme infusions. Accordingly, a satisfactory paste, when mixed with 10 per cent of its weight of water containing 250 mg. of sodium chloride per 100 ml. and stirred for 1 minute, should

give the same outflow time at 21° C., within 10 to 15 seconds, as the glycerol solution specified (6).

The time of stirring will vary according to the efficiency of the stirrer, and each operator must adjust his conditions to obtain a standard paste. After stirring with salt solution, a satisfactory paste has an outflow time within 10 to 15

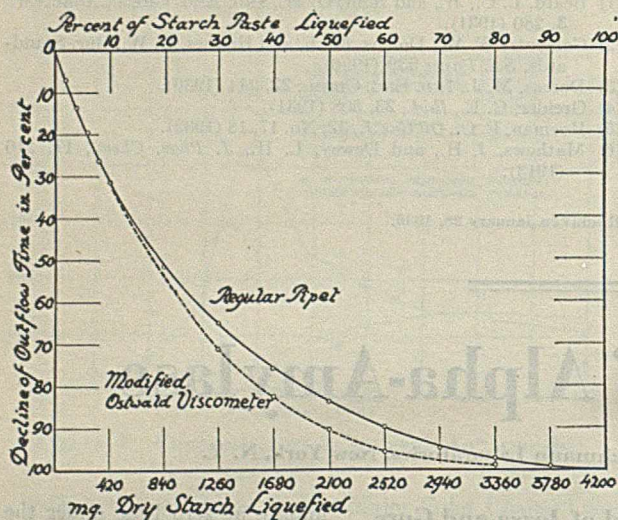


FIGURE 1. STANDARD LIQUEFYING CURVE

seconds of that of the glycerol solution, but for accurate measurements, the initial viscosity of the paste—that is, the viscosity of the paste after stirring with water or enzyme solution—should check the outflow time of the glycerol solution as closely as possible. Accordingly, a paste after stirring with 10 per cent of its weight of water containing 250 mg. of sodium chloride per 100 ml. has a correct initial viscosity if its outflow time checks that of the glycerol solution within 2 seconds. The starch paste before stirring with water is rarely constant enough in viscosity to enable the operator to get the correct initial viscosity at the first stirring, but the correct viscosity is easily attained. If the paste is too viscous after stirring for 1 minute with 10 per cent of dilute sodium chloride solution, it is only necessary to extend the stirring of a second blank a few seconds until a correct initial viscosity is obtained. Similar considerations apply in the case of a paste of low viscosity. The enzyme tests should be stirred for the same length of time that is determined for the blank.

Liquefying Curve

The "liquefying curve" as described in the original publication (6) represents the fundamental relation between viscosity and degree of liquefaction of the starch paste. Strictly, each pipet has its characteristic curve, but the authors have found that pipets of widely different outflow times gave essentially the same liquefying curve within 4 to 5 per cent deviation from an average curve. All the liquefying curves determined were smooth from beginning to end, which is not in agreement with the results of Fletcher and Westwood (1), who found the liquefying curve to be characterized by a rapid change in slope at about 5 per cent liquefaction. Their results are possibly due to insufficient mixing. The liquefied starch must be gently but thoroughly mixed into the starch paste, particularly when the percentage of liquefied starch is small—below 10 per cent liquefaction. In addition, the pipet must be carefully cleaned and dried before each measurement if the greatest accuracy is to be realized. The authors also checked the liquefying curve by using a modified Ostwald viscometer and found that it was perfectly smooth

throughout. Viscometers of the Stormer type were tried, but are unsuitable for this work because of the pronounced disintegrating action of the rotating cup.

Figure 1 shows the relationship between the percentage of starch liquefied and the percentage decline in outflow time for a pipet conforming to the specifications and for the modified Ostwald viscometer. Each point on the standard curve represents the average of sixteen measurements with various pipets and each point on the curve for the modified Ostwald viscometer the average of three measurements. This curve was plotted on large-size cross-section paper and the values of the variables were read from the graph. The data obtained are given in Table I.

TABLE I. PERCENTAGE DECLINE IN VISCOSITY AS A FUNCTION OF THE AMOUNT OF STARCH LIQUEFIED

Viscosity Decline		Starch Liquefied		Viscosity Decline		Starch Liquefied	
%	Mg.	%	Mg.	%	Mg.	%	Mg.
1	0.3	13	51	19.4	819		
2	0.6	25	52	20.0	848		
3	0.9	38	53	20.6	873		
4	1.2	51	54	21.3	899		
5	1.5	63	55	22.0	929		
6	1.8	76	56	22.7	958		
7	2.1	89	57	23.4	988		
8	2.4	101	58	24.1	1017		
9	2.7	114	59	24.8	1047		
10	3.0	127	60	25.5	1076		
11	3.3	139	61	26.3	1110		
12	3.6	152	62	27.1	1144		
13	3.9	165	63	27.9	1178		
14	4.2	177	64	28.7	1211		
15	4.5	190	65	29.6	1249		
16	4.8	203	66	30.5	1287		
17	5.1	215	67	31.4	1325		
18	5.4	228	68	32.2	1363		
19	5.7	241	69	33.2	1401		
20	6.0	253	70	34.1	1439		
21	6.3	266	71	35.1	1482		
22	6.6	279	72	36.1	1524		
23	6.9	291	73	37.1	1566		
24	7.2	304	74	38.2	1612		
25	7.5	317	75	39.2	1655		
26	7.8	329	76	40.3	1701		
27	8.1	342	77	41.5	1752		
28	8.5	359	78	42.7	1802		
29	8.9	376	79	43.8	1849		
30	9.3	393	80	45.1	1904		
31	9.7	409	81	46.4	1959		
32	10.1	426	82	47.7	2013		
33	10.5	443	83	49.1	2073		
34	10.9	460	84	50.5	2132		
35	11.3	477	85	52.0	2195		
36	11.7	494	86	53.5	2258		
37	12.1	511	87	55.1	2326		
38	12.5	528	88	56.8	2397		
39	13.0	549	89	58.5	2469		
40	13.5	570	90	60.3	2545		
41	14.0	591	91	62.2	2626		
42	14.5	612	92	64.2	2710		
43	15.0	633	93	66.3	2799		
44	15.5	654	94	68.5	2897		
45	16.0	675	95	71.1	3001		
46	16.5	697	96	74.4	3140		
47	17.0	718	97	78.3	3305		
48	17.6	743	98	83.2	3512		
49	18.2	768	99	89.5	3778		
50	18.8	794	100	100	4220		

The values of Table I should be applicable to any pipet satisfying the prescribed conditions, with an accuracy of approximately 5 per cent. If greater accuracy is desired it is necessary to determine the characteristic curve of the given pipet. In using the standardized data it is only necessary to determine the final outflow time of the pipet. A fully liquefied starch is prepared according to the directions of the original method and its outflow time is recorded as the final outflow time of the particular pipet used. From the final and the initial outflow times the total range is obtained for a given pipet and the per cent decline in outflow time is calculated for a given measurement. The milligrams of starch liquefied are then read from the table. In order to have available a more complete evaluation of the standard curve, the authors derived the following equation which fits the curve with an accuracy of 1 to 2 per cent over the range from 0.0 to 90.0 per cent decline in outflow time:

TABLE II. STARCH LIQUEFIED

Decline %	Liquefons per 10 cc.	Starch Mg.	Decline %	Liquefons per 10 cc.	Starch Mg.	Decline %	Liquefons per 10 cc.	Starch Mg.	Decline %	Liquefons per 10 cc.	Starch Mg.
50.0	0.691	794	60.0	0.997	1076	70.0	1.601	1439	80.0	2.929	1904
50.2	0.696	799	60.2	1.006	1083	70.2	1.618	1448	80.2	2.971	1915
50.4	0.700	804	60.4	1.015	1090	70.4	1.637	1456	80.4	3.014	1926
50.6	0.705	809	60.6	1.024	1096	70.6	1.656	1465	80.6	3.057	1937
50.8	0.709	814	60.8	1.033	1103	70.8	1.674	1473	80.8	3.102	1948
51.0	0.714	819	61.0	1.043	1110	71.0	1.690	1482	81.0	3.146	1959
51.2	0.719	825	61.2	1.052	1117	71.2	1.709	1490	81.2	3.191	1970
51.4	0.725	831	61.4	1.061	1124	71.4	1.728	1499	81.4	3.236	1981
51.6	0.730	836	61.6	1.071	1130	71.6	1.747	1507	81.6	3.282	1991
51.8	0.735	842	61.8	1.080	1137	71.8	1.766	1516	81.8	3.329	2002
52.0	0.742	848	62.0	1.090	1144	72.0	1.785	1524	82.0	3.375	2013
52.2	0.746	853	62.2	1.100	1151	72.2	1.806	1532	82.2	3.429	2025
52.4	0.751	858	62.4	1.109	1158	72.4	1.826	1541	82.4	3.482	2037
52.6	0.756	863	62.6	1.119	1164	72.6	1.846	1549	82.6	3.537	2049
52.8	0.761	868	62.8	1.129	1171	72.8	1.866	1558	82.8	3.593	2061
53.0	0.766	873	63.0	1.139	1178	73.0	1.887	1566	83.0	3.650	2073
53.2	0.771	878	63.2	1.149	1185	73.2	1.906	1575	83.2	3.705	2085
53.4	0.777	883	63.4	1.159	1191	73.4	1.933	1584	83.4	3.763	2097
53.6	0.782	889	63.6	1.169	1198	73.6	1.956	1594	83.6	3.822	2108
53.8	0.787	894	63.8	1.179	1204	73.8	1.979	1603	83.8	3.880	2120
54.0	0.792	899	64.0	1.189	1211	74.0	2.003	1612	84.0	3.940	2132
54.2	0.799	905	64.2	1.201	1219	74.2	2.026	1621	84.2	4.005	2145
54.4	0.805	911	64.4	1.213	1226	74.4	2.049	1629	84.4	4.071	2157
54.6	0.811	917	64.6	1.225	1234	74.6	2.072	1638	84.6	4.139	2170
54.8	0.817	923	64.8	1.237	1241	74.8	2.095	1646	84.8	4.208	2182
55.0	0.824	929	65.0	1.249	1249	75.0	2.117	1655	85.0	4.277	2195
55.2	0.830	935	65.2	1.261	1257	75.2	2.143	1664	85.2	4.347	2208
55.4	0.836	941	65.4	1.274	1264	75.4	2.169	1673	85.4	4.419	2220
55.6	0.843	946	65.6	1.287	1272	75.6	2.195	1683	85.6	4.493	2233
55.8	0.849	952	65.8	1.300	1279	75.8	2.222	1692	85.8	4.567	2245
56.0	0.856	958	66.0	1.313	1287	76.0	2.248	1701	86.0	4.642	2258
56.2	0.862	964	66.2	1.327	1295	76.2	2.279	1711	86.2	4.725	2272
56.4	0.869	970	66.4	1.339	1302	76.4	2.310	1721	86.4	4.810	2285
56.6	0.876	976	66.6	1.352	1310	76.6	2.341	1732	86.6	4.896	2299
56.8	0.883	982	66.8	1.360	1317	76.8	2.372	1742	86.8	4.982	2312
57.0	0.889	988	67.0	1.379	1325	77.0	2.404	1752	87.0	5.072	2326
57.2	0.896	994	67.2	1.393	1333	77.2	2.435	1762	87.2	5.166	2340
57.4	0.903	1000	67.4	1.407	1340	77.4	2.467	1772	87.4	5.263	2354
57.6	0.910	1005	67.6	1.420	1348	77.6	2.499	1782	87.6	5.361	2369
57.8	0.917	1011	67.8	1.434	1355	77.8	2.532	1792	87.8	5.460	2383
58.0	0.924	1017	68.0	1.446	1363	78.0	2.565	1802	88.0	5.562	2397
58.2	0.931	1023	68.2	1.463	1371	78.2	2.597	1811	88.2	5.668	2411
58.4	0.938	1029	68.4	1.478	1378	78.4	2.630	1821	88.4	5.775	2426
58.6	0.946	1035	68.6	1.493	1386	78.6	2.662	1830	88.6	5.883	2440
58.8	0.953	1041	68.8	1.507	1393	78.8	2.694	1840	88.8	5.996	2455
59.0	0.961	1047	69.0	1.522	1401	79.0	2.727	1849	89.0	6.108	2469
59.2	0.968	1053	69.2	1.538	1409	79.2	2.766	1860	89.2	6.231	2484
59.4	0.975	1059	69.4	1.553	1416	79.4	2.806	1871	89.4	6.355	2499
59.6	0.983	1064	69.6	1.568	1424	79.6	2.847	1882	89.6	6.482	2515
59.8	0.990	1070	69.8	1.584	1431	79.8	2.888	1893	89.8	6.612	2530
									90.0	6.744	2545

$$S = 12.9P - 0.065P^2 + 0.0025P^3$$

where S = milligrams of starch liquefied
 P = percentage decline in outflow time

The standardization of the liquefying curve simplifies the method considerably and makes it more available to technological workers. The variable products of reaction produced by different amylase systems have no effect on the general applicability of the liquefying curve. This is shown by the fact that, for a given pipet, solutions having equivalent concentrations of liquefied starch, dextrans, and maltose have outflow times which deviate from one another by not more than 0.5 second. Evidence of this nature has also been submitted by Fletcher and Westwood (1).

Use of Sodium Chloride

Jozsa and Gore (2, 3, 5) have shown that sodium chloride is effective as a desorption or activating agent and that it tends to stabilize enzyme infusions. Accordingly, the authors have used sufficient sodium chloride in preparing their infusions to make a concentration of 25 mg. per 10 ml. of infusion. In addition to its effect on the enzyme, sodium chloride decreases the viscosity of the starch paste. This effect makes necessary the use of sodium chloride in the blank determination.

Procedure

The actual determination should be carried out as follows:

The 150-gram sample of starch paste is cooled to about 19.5° C., so that after stirring in the enzyme infusion or the sodium chloride solution, the temperature of the stirred paste is 21° ± 0.2° C.

The degree of precooling will vary with the stirrer and surroundings, but in any case the paste after stirring should be at 21° C. The correct time of stirring for the proper initial outflow time is determined by running one or more blanks. Using this correct time, 15 ml. of enzyme infusion are stirred into 150 grams of paste and the mixture is placed in the bath at 21° C. After 59 minutes the mixture is sucked into the pipet and its outflow time determined. The measurement of the outflow time of the mixture is begun just before the end of the hour reaction period in order to correct for the liquefaction occurring during the measurement. In order to check the stability of the paste, another blank should be run on 150 grams of paste which has stood for 1 or 2 hours at 21° C. The outflow time of this check blank should not deviate more than 3 or 4 per cent from the first blank. In pipetting the 15-ml. portions it is necessary to avoid the introduction of traces of saliva. A small cotton plug effectively prevents contamination.

Calculations

From the outflow time of a given mixture the percentage decline is calculated, and from this the amount of starch liquefied is obtained by reference to the table or equation. The enzyme content or activity of the infusion is derived from the amount of liquefied starch by means of the empirical equation:

$$\text{Log}_{10} L = (S - 1078) (0.000565)$$

where L = liquefons per 10 ml. of infusion
and S = milligrams of starch liquefied in 1 hour

From the concentration of the infusion the number of liquefons per gram of preparation is calculated. The number of liquefons per gram of preparation is an exact measure of the alpha-amylase content and also of the liquefying power at zero time.

An example of the calculation is given below:

	Outflow Time Sec.
Paste stirred with water for 60 seconds	181.5
Additional stirring 10 seconds (trial)	164.5
New sample stirred with water for 65 seconds (Outflow time with glycerol solution for this pipet is 170 seconds)	171.2
Initial outflow time	171.2
Final outflow time	56.5
Range	114.7
Outflow time with sample (10 mg. per 10 ml.) after 1 hour at 21° C.	91.8
Decline in outflow time: 171.2 - 91.8 = 79.4 seconds	
Per cent decline: $\frac{79.4}{114.7} = 69.2$	
Mg. of starch liquefied (Table II): 1409	
$\text{Log}_{10} L = (S - 1078) \times (0.000565)$ where S = mg. of starch liquefied L = liquefons per 10 ml.	
$\text{Log}_{10} L = 331 \times 0.000565 = 0.1870$ $L = 1.538$	

Since 10 mg. of the sample were used and this figure must be related to 1 gram of the sample, the result should be multiplied by 100. The alpha-amylase concentration of the sample is measured by the liquefon content, which is 154 liquefons per gram. Its liquefying power at zero time is 3850 mg. of dry starch per minute. Table II gives a convenient tabulation of data obtained from the liquefon-starch equation for the experimental range of 50 to 90 per cent decline in viscosity.

Preparation of Enzyme Solution

Using barley malt (diastatic or pale), 5 grams of malt are weighed into a 1000-ml. flask, 25 grams of sodium chloride are added, and the flask is filled up to the mark. After standing for 1 hour at room temperature with occasional shaking, it is filtered, rejecting the first 100 ml. of filtrate, 100 ml. of the filtrate are transferred into a 1000-ml. flask (or 50 ml. into a 500-ml. flask), and the flask is filled up to the mark.

In case of diastatic malt sirup 2, 5, 10, or 15 grams should be weighed (according to strength) and 25 grams of sodium chloride added, in the same manner as in the above sample.

Various amounts of different enzyme preparations must be used in order to obtain a liquefaction within 50 to 90 per cent decline in viscosity after 1 hour at 21° C. This range has been chosen as most suitable for accurate measurements. Table III gives the concentration of enzymic materials of various strengths in milligrams per 10 ml. necessary for proper application of the method.

TABLE III. ENZYMIC MATERIAL REQUIRED FOR ANALYSIS OF DIFFERENT PREPARATIONS

Liquefons per Gram	Enzymic Material per 10 Ml. Infusion Mg.
1-3	1000
2-6	500
5-15	200
10-30	100
20-60	50
50-150	20
100-300	10
200-600	5
500-1500	2
1000-3000	1

Acknowledgment

The authors wish to express their thanks to C. N. Frey, H. C. Gore, and Q. Landis for their valuable suggestions and keen interest in this work.

Literature Cited

- (1) Fletcher, L., and Westwood, J. B., *J. Inst. Brewing*, **36**, 550 (1930).
- (2) Gore, H. C., and Jozsa, S., *IND. ENG. CHEM.*, **24**, 102 (1932).
- (3) *Ibid.*, **24**, 99 (1932).
- (4) Johnston, W. R., and Jozsa, S., *J. Am. Chem. Soc.*, **57**, 701 (1935).
- (5) Jozsa, S., and Gore, H. C., *IND. ENG. CHEM.*, **24**, 95 (1932).
- (6) *Ibid.*, *Anal. Ed.*, **2**, 26 (1930).
- (7) Willaman, J. J., Clark, E. W., and Hager, O. B., *Biochem. Z.*, **253**, 94 (1933).

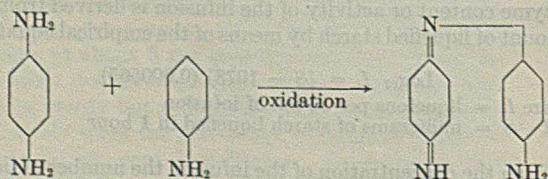
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A Simple and Sensitive Test for *p*-Phenylenediamine

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ACCORDING to Erdmann (5), the most sensitive test for *p*-phenylenediamine is the white precipitate of quinone dichlorodiimide produced with sodium hypochlorite, and he recommends diazotation and coupling with β -naphthol disulfonic acid (2) for its detection in fur. There are a number of other tests (1, 4), but all have been found unsuitable for detecting the small residual quantities of *p*-phenylenediamine occasionally present in black dyed fur.

The basis of the present test, originally intended to discover small amounts of *p*-phenylenediamine in fur which could not be found by tests commonly found and recommended for this purpose, is the formation of indamine when a mixture of *p*-phenylenediamine and aniline is oxidized.



Treat the test specimen with a small amount of a 3 per cent solution of acetic acid—for example, 6.452 sq. cm. (1 square inch) of fur with 1 to 2 cc. of acid—warm to about 45° C., squeeze the liquid out into a porcelain crucible, add 1 drop of an aniline solu-

tion (1 drop of aniline in 50 cc. of water), mix, and add a few crystals of potassium persulfate. The appearance of a blue-green color within about 5 seconds indicates the presence of *p*-phenylenediamine or its derivatives in which the (toxic) *p*-diamine structure has been preserved—for example, *p*-toluenediamine sulfate, which can be considered the salt of a methyl-substituted *p*-phenylenediamine, or dimethyl-*p*-phenylenediamine.

The test is a sensitive one: 0.05 cc. of a 0.00001 per cent aqueous solution (equivalent to 0.0005 mg. or 0.5 gamma of *p*-phenylenediamine) will give a distinct coloration. Interfering substances do not present difficulties. Other amido compounds—so-called oxidation dyes which are employed in pelt dyeing, such as amido phenols, *m*-amido anisol, *o*- and *m*-phenylenediamine—do not respond to the test, but if a trace of *p*-phenylenediamine is present with these substances it will be detected.

Literature Cited

- (1) Allen, A. H., "Commercial Organic Analysis," 5th ed., Philadelphia, P. Blakiston's Son & Co., 1925.
- (2) Erdmann, *Z. angew. Chem.*, **18**, 1377 (1905).
- (3) *Ibid.*, **19**, 1053 (1906).
- (4) Rosenthaler, L., "Der Nachweis organischer Verbindungen," 2nd ed., Stuttgart, Verlag von Ferdinand Enke, 1923.

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Photometric Investigation of the Ceruleomolybdate Determination of Phosphate in Waters

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WIDESPREAD interest in the occurrence and determination of small quantities of phosphate in water has resulted since Atkins (1) first applied the Florentin (6) modification of the Denigés ceruleomolybdate method (4) to oceanographic work. Although Atkins acknowledged using reagents prepared according to Florentin, he actually used a molybdate reagent with a sulfuric acid concentration greater than recommended in Florentin's original paper. This was probably due to his following the directions given in an abstract of Florentin's paper which specified that sulfuric acid 50 per cent by volume be used in the preparation of the reagent instead of 50 per cent by weight as given by Florentin.

It is well known (8, 10) that a certain acidity is necessary to prevent reduction of the molybdate reagent itself by the reducing agent and that the sensitivity of the reagent is dependent upon its acidity and molybdate ratio. After a critical study of the Denigés method, Truog and Meyer (10) suggested a molybdate reagent with a reduced acidity and a greater molybdate-sulfuric acid ratio than used by Atkins which in their opinion possessed the optimum sensitivity. Shortly thereafter the Denigés method as used by Atkins was studied spectrophotometrically by Buch (3), and by Grippen-berg (8) who suggested the possibility of using a reagent with a greater molybdate-sulfuric acid ratio to increase the sensitivity of the method. However, the Atkins reagent is the only one that has been used in oceanographic work.

Recently Urbach (11) estimated phosphates photometrically in natural waters, using the Bell-Doisy procedure. Unfortunately Urbach's investigations were for a range of phosphate concentrations much greater than normally occur in either the marine or fresh water of this region. Moreover, the original Bell-Doisy method cannot be applied directly to marine work because of the interference of the calcium ions. However, the Briggs modification of the Bell-Doisy method (2) does not have this criticism. Another method, first proposed by Fiske and Subbarow (5), also gave promise of a possible adaptation to marine work. Recently Giani (7) used this latter method photometrically but for approximately the same range of concentrations that Urbach employed. Because of their promise these four procedures were selected for investigation to determine their suitability for the photometric estimation of soluble phosphates, either in the saline or fresh waters of this locality.

Experimental

The phosphate concentrations were estimated by means of the Zeiss Pulfrich gradation photometer. One- and 5-cm. absorption cells were used for the larger phosphate concentrations and a 30-cm. tube for the lesser concentrations. The approximate absorption spectrum of a solution containing 0.005 milligram atom¹ of phosphorus as phosphate per liter was determined for each reagent. The maximum absorption

¹ Milligram atom, mg. at., is defined as the number of milligrams of the element divided by its atomic weight. This term is used in reporting oceanographic data.

is in the red portion of the spectrum, so the S-72 filter provided with the instrument was used for the remaining measurements. This filter has an effective range of 200 to 250 μ . The S-75 filter is less suitable, as the intensity of the transmitted light is insufficient to permit accurate matching of the fields.

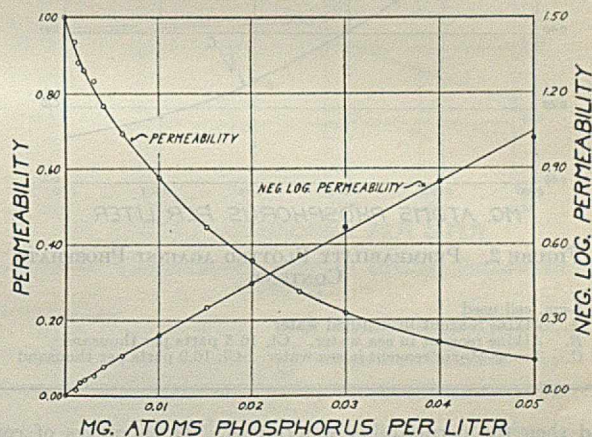


FIGURE 1. PERMEABILITY AND NEGATIVE LOGARITHM OF PERMEABILITY PLOTTED AGAINST PHOSPHATE CONTENT

Atkins reagent in distilled water using a 1-cm. cell. Specific absorption coefficient, 20

The time for the full development of the blue reduction color was determined for each reagent in distilled water and also in sea water. The Bell-Doisy-Briggs and Fiske-Subbarow reagents react very slowly. With these a constant intensity was attained only at the end of 1 and 3 hours, respectively. Using either the Atkins or Truog-Meyer reagents, the maximum intensity occurred 7 minutes after adding the reagents and there was no further change for an hour, after which fading became apparent. Visually fading begins within 10 minutes in marine waters and apparently is due to the formation of a greenish yellow color rather than the diminution of the blue reduction color.

The permeabilities—that is, the fraction of the light transmitted—of the various solutions in the 30-cm. cells were compared with distilled water in a similar cell. With the shorter cells air was used as the reference standard.

Reagents and Procedures

The reagents were prepared from high quality c. p. chemicals according to the following directions.

ATKINS MOLYBDATE REAGENT AND PROCEDURE. To prepare the sulfuric acid-molybdate reagent, 25 grams of ammonium molybdate are dissolved in 250 ml. of distilled water and then added to 750 ml. of sulfuric acid containing 375 ml. of 36 *N* arsenic-free sulfuric acid. The stannous chloride solution is prepared according to the specifications mentioned under the Truog-Meyer procedure.

One milliliter of the molybdate reagent was mixed with each 50 ml. of the sample, followed by one drop of stannous chloride solution. Time for maximum color development was allowed

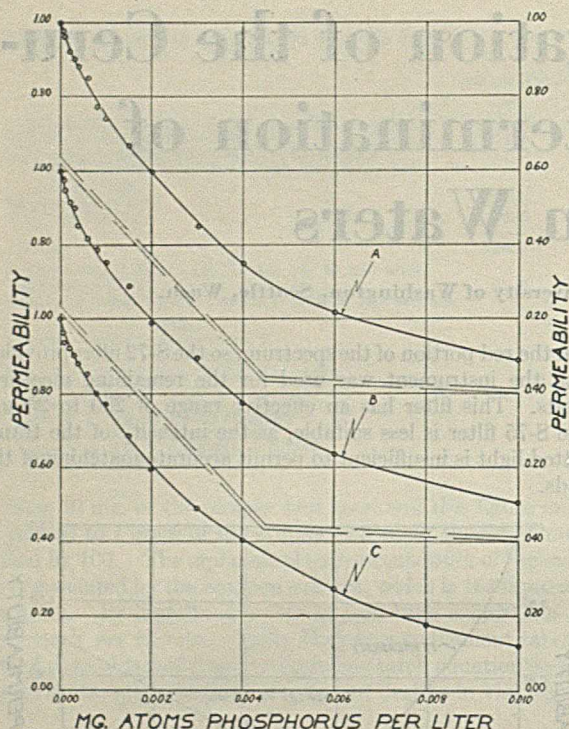


FIGURE 2. PERMEABILITY PLOTTED AGAINST PHOSPHATE CONTENT

5-cm. cell used

- A. Atkins reagent in distilled water
 B. Atkins reagent in sea water. Cl. 16.5 parts per thousand
 C. Truog-Meyer reagent in sea water. Cl. 16.9 parts per thousand

and then the permeability determined. Three ranges of concentrations were studied: 0.000 to 0.050 mg. at. of phosphorus per liter in distilled water using the 1-cm. cell (Figure 1); 0.000 to 0.010 mg. at. of phosphorus per liter in distilled water (Figure 2, A, and Figure 3, A) and 0.000 to 0.010 mg. at. in sea water of chlorinity 16.5 parts per thousand in the 5-cm. cell (Figure 2, B, and Figure 3, B); and 0.000 to 0.001 mg. at. in distilled water and in sea water of chlorinity 17.1 parts per thousand using the 30-cm. cell (Figure 4, E).

TRUOG-MEYER REAGENTS AND PROCEDURE. The sulfuric acid-molybdate reagent is made to contain 25 grams of ammonium molybdate and 280 ml. of 36 N arsenic-free sulfuric acid per liter. To prepare the stannous chloride solution, 25 grams of stannous chloride dihydrate are dissolved in 100 ml. of 12 N hydrochloric acid and then diluted to 1 liter. This solution is stored under a layer of oil for preservation as recommended by Truog and Meyer.

Two milliliters of the ammonium molybdate reagent and one drop of stannous chloride were added per 50 ml. of water sample. Two ranges of concentrations were considered: 0.000 to 0.010 mg. at. of phosphorus per liter composed one series (Figure 2, C) and 0.000 to 0.001 mg. at. the other (Figure 4, F). These concentrations were investigated in both distilled water and sea water, under the same conditions as with the Atkins reagent. The curves for this reagent in distilled water are not included, as they were almost identical with the corresponding curves for the Atkins reagent.

MODIFIED BELL-DOISY-BRIGGS METHOD. In the sulfuric acid-molybdate reagent, 50 grams of ammonium molybdate and 300 ml. of 36 N arsenic-free sulfuric acid are present per liter of reagent. One-half gram of hydroquinone is dissolved in 100 ml. of distilled water containing one drop of concentrated sulfuric acid to retard oxidation. A 20 per cent sodium sulfite solution is prepared each day.

To a 50-ml. sample of water were added 2.5 ml. of the acid molybdate reagent, 0.5 ml. of sulfite solution, and 0.5 ml. of hydroquinone in the order named. Since the sensitivity of this reagent was found to be materially less than that of the Atkins or Truog-Meyer reagents, only one range of concentrations was studied. This series extended from 0.000 to 0.010 mg. at. of phosphorus per liter in distilled water and sea water. The photometric comparisons were made in the 30-cm. tubes with

distilled water as the reference standard. The curves have not been included because of the unsatisfactory results.

MODIFIED FISKE-SUBBAROW METHOD. To prepare the sulfuric acid-molybdate reagent, 25 grams of ammonium molybdate are dissolved in a liter of dilute sulfuric acid containing 56 ml. of 36 N acid. To prepare the aminonaphtholsulfonic acid reagent, 0.5 gram of the dry powder is dissolved in 195 ml. of 15 per cent sodium bisulfite solution, 5 ml. of 20 per cent sodium sulfite are added, stoppered, and shaken until dissolved.

Five milliliters of the molybdate reagent and 2 ml. of the reducing agent were added separately to each 50 ml. of the water sample. Observations were made on series of concentrations ranging from 0.000 to 0.008 mg. at. of phosphorus per liter in distilled water and 0.000 to 0.010 mg. at. of phosphorus in ocean water of chlorinity 16.9 parts per thousand. The 30-cm. absorption cells were used. The curves have not been presented because of the unsatisfactory results.

Discussion of Results

The original Truog-Meyer and Atkins procedures were modified only in the amount of stannous chloride added. At first 3 drops of this solution were used for each 50 ml. of sample. However, this quantity is about thirty-five times the theoretical amount required in sea water and results in the formation of a yellow coloration in addition to the desired blue reduction product. The resulting greenish color makes accurate comparison with the standard solutions impossible by the usual Nessler tube or colorimeter methods of estimation. Reducing the volume of stannous chloride to one drop gives practically no yellow coloration within 10 minutes after adding the reagents and so is advisable in the visual estimation, even though the intensity of the blue color is reduced by 10 per cent as a result. Photometrically the formation of the greenish color does not interfere with the estimation, but the lesser quantity of reducing reagent was used because of the comparison afforded with the visual method.

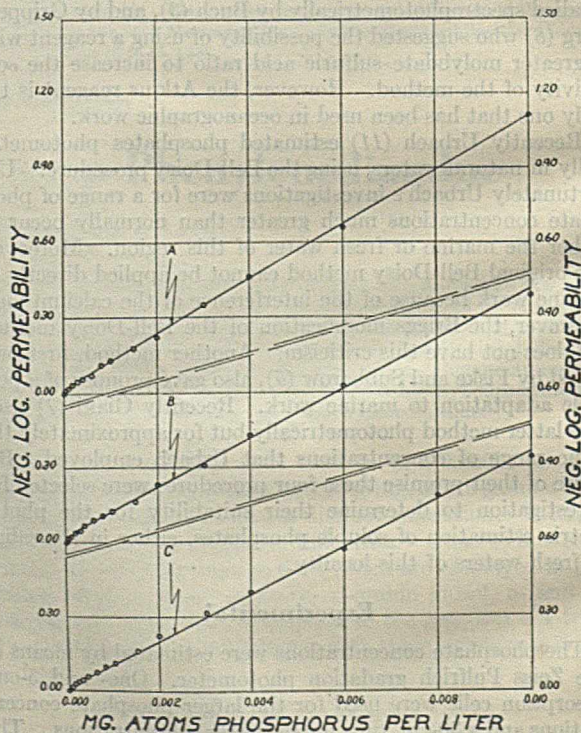


FIGURE 3. NEGATIVE LOGARITHM OF PERMEABILITY PLOTTED AGAINST PHOSPHATE CONCENTRATION

5-cm. cell used

- A. Atkins reagent in distilled water. Specific absorption coefficient, 22
 B. Atkins reagent in sea water. Specific absorption coefficient, 20
 C. Truog-Meyer reagent in sea water. Specific absorption coefficient, 20

When the molybdate reagents as recommended by Bell-Doisy-Briggs and Fiske-Subbarow were tried in sea water, a blue reduction color developed even with no phosphate present. Apparently this was due to reduction of the molybdate reagent itself in a solution whose hydrogen-ion concentration had been materially reduced by the buffer action of the sea water. Doubling the acid concentration of the reagents, as specified above, obviated this difficulty in sea water, yet permitted color development with phosphate in distilled water. Even with the increased acidity an appreciable blank was obtained. Neither the distilled water nor the reagents of Atkins or Truog-Meyer contained phosphate, as the permeability of the blank sample—that is, reagents in distilled water with no phosphate present—was identical with that of only distilled water and molybdate reagent. The sea water, supposedly phosphate-free, was similarly tested and found to contain 0.00005 mg. at. of phosphorus per liter. No correction was necessary for this small amount of phosphate.

Using the various reagents in both sea water and distilled water, standardization curves were constructed by plotting permeability readings, I , against concentration of phosphate. Neither these curves nor the many permeability readings in tabular form have been included in this report, as the authors feel that the standardization curves vary somewhat with conditions and so should be prepared by each experimenter.

The blank determinations, using only the reagents and no phosphate, naturally gave typical photometer readings, I_0 , thus making direct comparison of the various standardization curves difficult. To facilitate comparison, the photometer scale readings, I , were divided by the scale reading of the blank determination, I_0 , and these values plotted against the phosphate concentrations. This in reality means that the blank solution is now the reference standard and is arbitrarily assigned a permeability of one. It is the curves plotted from these values, I/I_0 , that are presented in this article.

In Figure 3 the negative logarithms of the recalculated permeabilities, I/I_0 , have been plotted against phosphate concentrations. These curves should be linear if Beer's law is applicable. Examination of Figure 3 shows that at low phosphate concentrations Beer's law does not hold exactly, as the color intensity is proportionally greater than at the higher concentrations. This is true for all four reagents. Grippenbergs found not only that a greater degree of reduction occurs in the lower concentrations of phosphate but that the reduction occurs in definite stages as the concentration of stannous chloride is increased. Undoubtedly this observation applies to other reductants, though it was not noted by Urbach, probably because of the higher concentrations of phosphate he was utilizing.

When using the same absorption cell, the slope of the curve, in which the negative logarithm of I/I_0 is plotted against phosphate concentration, is a measure of the sensitivity of the reagent. Moreover the sensitivity is proportional to the specific absorption coefficient. The specific absorption coefficient for the Fiske-Subbarow reagent was 4.4 and for the Bell-Doisy-Briggs reagent 3.3, compared with values of 19 to 23 for the Atkins or Truog-Meyer reagents. From this it may be seen that the two latter reagents are far more sensitive and preferable for the estimation of small quantities of phosphate, such as are found in water. For this reason the methods of Bell-Doisy-Briggs or Fiske-Subbarow are not to be recommended for water analysis except when the phosphate concentration is exceptionally large.

The sensitivity with the Atkins reagent was the greatest in the least concentrated solutions of phosphate, as was indicated by a specific absorption coefficient of 23 (Figure 4, *D*), compared with 20 (Figure 1) for the higher range of concentrations. This too shows numerically that Beer's law is not applicable. The specific absorption coefficients with the

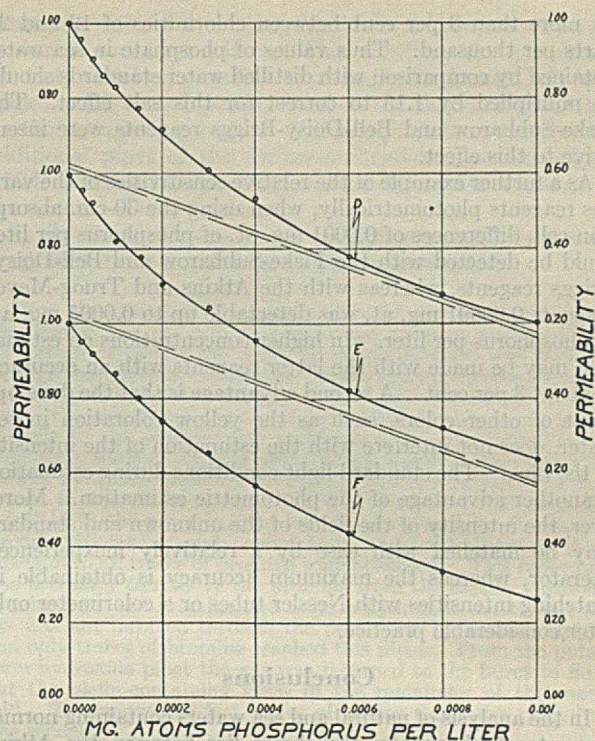


FIGURE 4. PERMEABILITY PLOTTED AGAINST PHOSPHATE CONTENT

30-cm. cell used

D. Atkins reagent in distilled water. Specific absorption coefficient, 23

E. Atkins reagent in sea water. Cl, 17.1 parts per thousand. Specific absorption coefficient, 20

F. Truog-Meyer reagent in sea water. Cl, 16.9 parts per thousand. Specific absorption coefficient, 20

Truog-Meyer reagent in sea water and in distilled water were essentially the same as with the Atkins reagent. This indicates that the sensitivities of the two reagents are approximately the same over this range of phosphate concentrations.

Truog (9) has noted that ordinary concentrated sulfuric acid is usually nearer 35 *N* than 36 *N*. This fact is not generally appreciated in the preparation of molybdate reagents, so that an Atkins reagent which was thought to be 13.55 *N* in reality was nearer 13.28 *N* when prepared and a Truog-Meyer reagent with a specified normality of 10.0 was found to be 9.7. Calibration curves were determined for reagents with these acidities and were found to be identical within the limits of experimental error. This leads to the conclusion that these variations in acidities make no appreciable change in the sensitivities of the reagents.

Grippenbergs work also showed that a reagent having the approximate composition of that of Truog-Meyer possessed an absorption coefficient the same or slightly less than that of Atkins. In general her results showed that increasing molybdate-sulfuric acid ratios, for a given acidity, increases the sensitivity of the reagent, though this was true for only certain portions of the range. She also found that, as a usual thing, an increase in the acidity for a given molybdate content decreases the sensitivity of the reagent. However, for certain acidities and molybdate contents increasing acidity makes little or no difference. That was found to be the case for that range including the Atkins and Truog-Meyer reagents.

The Atkins and Truog-Meyer reagents were found to be slightly less sensitive in sea water than in distilled water. This effect may be expressed numerically by the ratio of the specific absorption coefficients in distilled water and sea water. The average ratio of K_d , for distilled water, to K_s , for sea water, for these two reagents is 1.15 and does not vary

by more than 3 per cent between chlorinities of 12 and 20 parts per thousand. Thus values of phosphate in sea water obtained by comparison with distilled water standards should be multiplied by 1.15 to correct for this salt effect. The Fiske-Subbarow and Bell-Doisy-Briggs reagents were insensitive to this effect.

As a further example of the relative sensitivities of the various reagents photometrically, when using the 30-cm. absorption cell, differences of 0.0001 mg. at. of phosphorus per liter could be detected with the Fiske-Subbarow and Bell-Doisy-Briggs reagents, whereas with the Atkins and Truog-Meyer reagents 0.00001 mg. at. was detectable up to 0.0005 mg. at. of phosphorus per liter. In higher concentrations an estimation may be made with the latter reagents with an accuracy of about 3 per cent. A second advantage is that the development of other colors, such as the yellow coloration in sea water, does not interfere with the estimation of the intensity of the blue. The standard light conditions during estimation is another advantage of the photometric estimation. Moreover, the intensity of the fields of the unknown and standard may be matched with ease by a relatively inexperienced operator, whereas the maximum accuracy is obtainable in matching intensities with Nessler tubes or a colorimeter only after considerable practice.

Conclusions

In the analysis of natural and sea waters containing normal amounts of phosphate, the choice lies between the Atkins and Truog-Meyer procedures. The Bell-Doisy-Briggs and Fiske-Subbarow methods are usable only when extremely large quantities of phosphate are present.

The Truog-Meyer reagent possesses practically the same

sensitivity as the Atkins reagent for concentrations of phosphate found in water.

The correction for salt effect for the several reagents has been noted. This effect with either the Fiske-Subbarow and Bell-Doisy-Briggs reagent is negligible. With the Atkins and Truog-Meyer reagents 1.15 times as much color is obtained in a distilled water medium as in sea water.

The yellow color which develops in sea water and which interferes so much with the usual methods of comparison (either using Nessler tubes or a colorimeter) does not influence the photometric estimation.

Using the photometer, a high accuracy is obtainable. With a 30-cm. photometer tube, a difference of 0.00001 mg. at. of phosphorus per liter is readily detectable up to 0.0005 mg. at. In higher ranges of concentrations the estimation may be made with an accuracy of approximately 3 per cent.

Literature Cited

- (1) Atkins, W. R. G., *J. Marine Biol. Assoc. United Kingdom*, **13** (1), 119-150 (1923).
- (2) Briggs, A. P., *J. Biol. Chem.*, **53**, 13-16 (1922).
- (3) Buch, K., Con. perm. intern. pour l'exploration de la mer, *Rapports et procès verbaux*, **53**, 36 (1929).
- (4) Denigés, G., *Compt. rend.*, **171**, 802 (1920).
- (5) Fiske, C. H., and Subbarow, Y., *J. Biol. Chem.*, **66**, 375-400 (1925).
- (6) Florentin, D., *Ann. chem. anal. chim. appl.*, **3**, 295-6 (1921).
- (7) Gianì, M., *Giorn. chim. ind. applicata*, **15**, 432-5 (1933).
- (8) Grippenberg, S., Report of 18th Scandinavian Naturalist Congress (Copenhagen), August, 1929.
- (9) Truog, E., private communication.
- (10) Truog, E., and Meyer A. H., *IND. ENG. CHEM., Anal. Ed.*, **1**, 136 (1929).
- (11) Urbach, C., *Mikrochemie*, **13**, 31-54 (1933).

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Analysis of Complex Gaseous Mixtures

Using a Combination of the Podbielniak Distillation Column and the Shepherd Apparatus

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IN THE course of some work on the pyrolysis of propane, it was necessary to make quantitative determinations of nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, ethane, propylene, and propane in a mixture which might contain any or all of these components. Since this necessitated modifications of standard procedures, the methods used to overcome some of the difficulties involved may be of interest to others working with these gases.

Preliminary experiments showed that the determination of olefins with sulfuric acid of different strengths (1) or with hydriodic acid (2, 4) would not give accurate results. Further, the solubility of most of the other constituents in liquid propane precludes any possibility of the use of fractional condensation as an analytical procedure.

The sample was therefore separated into convenient fractions by distillation in a standard precision low-temperature Podbielniak column fitted with a 2.6-mm. microdistillation tube (5). The recommended procedure for introducing the sample was followed. Any components in the sample which were not conden-

sable at the temperature of liquid air and atmospheric pressure were bled off into a 100-cc. gas buret, but the larger part of the low-boiling gases in the sample were held in solution in the liquid propane at this temperature.

For receiving the fractions from the distillation, a special 100-cc. gas buret was used. This buret instead of being fitted with a compensator tube was connected at the bottom through a side tube to an auxiliary leveling tube of the same bore as the buret itself and located parallel to the buret in a water jacket. At the top the auxiliary leveling tube extended considerably above the gas buret and was open to the atmosphere, serving as a manometer to indicate the pressure of the gas in the buret with respect to the atmosphere. At the bottom the gas buret was also connected through a stopcock to a leveling bottle. During the distillation the three-way cock at the top of the gas buret connected this buret to the distillation column so that the auxiliary leveling tube in connection with the buret then served as a manometer to show the distillation pressure. During this time the rate of distillation could be controlled by the opening in the stopcock at the lower end of the gas buret, and by regulating the reflux in the column the mercury in the gas buret and in the auxiliary leveling tube could be kept at the same level.

When it was desired to separate a fraction, or when the buret was full, the three-way stopcock at the top of the buret was closed, the distillation interrupted by cooling, and the volume read. The three-way cock was then opened to a mercury-filled gas sampling tube and the distillate transferred. The capillary connections were filled with mercury both before and after each

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transfer, to insure the removal of all of the distillate and avoid any loss of hydrogen which might occur if a portion of the distillate were allowed to remain in the capillary tube which was connected by rubber tubing.

The first fraction was taken to include some of the ethylene—that is, the cut was made on the ethylene plateau of the distillation curve—and might contain hydrogen, carbon monoxide, nitrogen, methane, and ethylene. It was analyzed by absorption and combustion in the Shepherd apparatus. The next cut was sometimes made between the ethane and propylene plateaus, giving a second fraction which might contain ethylene and ethane. There is a difference in boiling points between ethane and propylene of about 40° C., which should be large enough to give a sharp break on the distillation curve. However, the column holdup is sufficient to introduce considerable error in the estimation of ethane, especially when only small quantities of this component are present. In samples where the ethane content was low, a measured volume of ethane was added to the sample in the column. This gave an ethane plateau upon which a cut could be made for an ethylene-ethane fraction and an ethane-propylene fraction. In the latter case, if sufficient time was allowed for refluxing, some of the propylene could be separated from the propane; and, if the distillation was interrupted after only a few cubic centimeters of the propylene had distilled, the ethane holdup could be minimized without undue contamination of the ethane-propylene fraction with propane. The last fraction contained the remainder of the propylene, the propane, and any higher homologs.

In samples where sufficient ethane was known to be present, no ethane was added. The first fraction was taken as described, the second was made on the break between the ethane and propylene, and the third was made to include about 50 cc. of propane. This third cut was further analyzed by absorption of the propylene and combustion of the ethane and propane remaining. Propylene and propane boil so closely together that a satisfactory separation could not be made by distillation alone; hence these gases were distilled off together as one fraction and their relative amounts determined by absorption of the propylene. The quantity of gas used for a distillation varied between 800 and 1000 cc.

Analysis of Fractions

The fractions obtained from the distillation were analyzed with a Shepherd gas-analysis apparatus according to the principles outlined by Shepherd (6). On account of the accuracy of measurement of gas volumes with this apparatus it was desirable to use it for the olefin absorptions as well as for the combustion analysis. Preliminary experiments showed that the solubility of paraffin gases in oleum did not permit the use of this reagent in the accurate determination of olefin gases. In the use of bromine water for the determination of olefins there are several difficulties:

1. If the gas contains a high percentage of unsaturates, it is difficult on account of the slow diffusion of bromine vapors to get these sufficiently mixed with the gas to react completely with the olefins present.

2. When mercury is used as the confining liquid in the gas buret it is necessary to avoid contact of bromine fumes with the mercury.

3. When the percentage of paraffins in the sample is high, the solubility of these gases in bromine water is sufficiently great to introduce serious errors in the determination of small amounts of olefins.

4. When excess bromine vapors are removed after reaction with olefins by absorption in sodium or potassium hydroxide, the evolution of oxygen by decomposition of the hypobromite formed must be avoided.

These difficulties were overcome as follows: Instead of the bromine water ordinarily used in gas analysis, a solution

saturated with both sodium chloride and bromine was used as the absorbing medium. This solution, it was shown by test, dissolves paraffins to a negligible extent. It was placed in the extra pipet provided on the Shepherd apparatus for the storage of nitrogen. Following this bromine pipet an additional pipet of the surface-absorption type was added which contained 25 per cent sodium hydroxide solution for the removal of bromine fumes.

As the result of considerable preliminary work, the following procedure for the olefin absorption was adopted:

After absorption of the carbon dioxide and measurement of the residue, the gas was passed to the bromine pipet. If the percentage of olefins was high, all of the mixture was bubbled through the solution. If low, part of the gas was bubbled through the solution and the remainder passed into the excess bromine fumes, the object being to expose as small a quantity of the gas as possible to the solution and at the same time to insure excess bromine in the gas. The brominated gas was next drawn into the sodium hydroxide pipet by suction applied to a rubber tube connected to the reservoir side. It was then forced through the manifold to the potassium hydroxide pipet used for the carbon dioxide absorption, and passed back and forth between these pipets until all traces of bromine were absorbed. This procedure was necessary to remove the bromine from the capillary connection between the bromine and sodium hydroxide pipets, but the gas was not bubbled through the potassium hydroxide solution and only traces of bromine reached this pipet. From the potassium hydroxide pipet the gas was returned to the buret to flush out the olefin-containing gases in the remainder of the manifold. To remove the last traces of olefins the entire procedure was repeated.

Any error caused by the evolution of oxygen in the sodium hydroxide pipet was minimized by frequent renewal of this reagent.

Those gases which were not absorbed were burned according to the combustion procedure recommended by Shepherd, using analyzed oxygen and a calibrated manifold.

There has been some criticism (3) of the so-called "simple arithmetic" calculations necessary for correcting for the capillary dead space in the Shepherd apparatus. However, if these corrections are arranged as a factor by which the volumes of the combustibles found may be multiplied to place them on the same basis as the constituents removed before combustion, much confusion can be eliminated. Furthermore, by proper arrangement of the terms this factor can be determined with a slide rule to an accuracy far greater than necessary.

This factor may be determined as follows:

Let F = correction factor
 S = original sample of gas
 S_1 = reading previous to combustion
 a = total volume of nitrogen added to sample from the gas space other than the buret
 b = volume of gas not subjected to combustion
 Then

$$F = \frac{S_1}{S_1 - \left(b - b \frac{a}{S_1 + a} \right)}$$

$b \frac{a}{S_1 + a}$ = volume of nitrogen left in the gas space outside of the buret

$b - b \frac{a}{S_1 + a}$ = volume of combustible gas not burned

The denominator, then, is the volume of the original gas which was subjected to combustion.

The use of this equation may be illustrated by an example:

S_1 = 78.20 cc.	H_2 uncorrected = 25.27 cc.
a = 3.60 cc.	CH_4 uncorrected = 35.50 cc.
b = 1.32 cc.	Residue uncorrected = 17.55 cc.
ab = 4.75 cc.	

$$F = \frac{78.20}{78.20 - \left(1.32 - \frac{4.75}{3.60 + 78.20} \right)}$$

$$F = \frac{78.20}{76.94} = 1 + \frac{1.26}{76.94} = 1.0164$$

$$\text{Corrected H}_2 = (25.27) (1.0164)$$

$$= (25.27) (1) + (25.27) (0.0164) = 25.68 \text{ cc.}$$

$$\text{Corrected CH}_4 = (35.50) (1) + (35.50) (0.0164) = 36.08 \text{ cc.}$$

The correct volume of nitrogen, it follows, is the final residue minus the volumes added to the combustibles found:

$$\text{Corrected N}_2 = \text{residue} - (25.27 + 35.50) (0.0164) \\ = 17.55 - 0.99 = 16.56 \text{ cc.}$$

If this calculation still seems too complicated, a chart or a table may be arranged for a particular apparatus, giving the correction factor for each precombustion reading.

Literature Cited

- (1) Brooks, *Chem. Met. Eng.*, **22**, 629 (1920).
- (2) Butlerow, *Ann.*, **145**, 275 (1868).
- (3) Matuszak, *IND. ENG. CHEM., Anal. Ed.*, **6**, 72 (1934).
- (4) Michael, *J. prakt. Chem.*, **60**, 445 (1877).
- (5) Podbielniak, *IND. ENG. CHEM., Anal. Ed.*, **5**, 172 (1933).
- (6) Shepherd, *Bur. Standards J. Research*, **6**, 121 (1931).

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Determination of Ammonia and of Amide Nitrogen in Plant Tissue

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THE determination of ammonia is the fundamental analytical operation upon which information regarding the amide content of plant tissues is based. Amides are invariably estimated by determining the increase in ammonia nitrogen after hydrolysis under suitable conditions, and, consequently, the accuracy of the information obtained is entirely dependent upon the accuracy with which the quantity of ammonia already present as ammonium ions is ascertained.

The problem presented by the analysis of plant tissues has much in common with the determination of ammonia in urine. Although urea is seldom present as a constituent of higher plants, several substances which are easily decomposed with the production of ammonia are frequently found in them, notably the amide glutamine; allantoin is not uncommon, and even asparagine, which is almost universally distributed, is not so stable that the possibility of its partial decomposition during the determination of ammonia can be safely overlooked.

No review of the extensive literature on the subject of ammonia and amide nitrogen determinations in plant tissues can be attempted here. The foundations of most of the present-day methods were laid by the distinguished French agricultural chemist Boussingault in 1850 (2); he first suggested distillation with magnesium oxide to determine ammonia in the absence of urea, he first employed a current of air through the apparatus to promote a rapid transfer of the ammonia, and he first suggested vacuum distillation if urea

The ammonia present in plant tissues as ammonium ions—that is, the so-called free or preformed ammonia—has been determined since the time of Boussingault by distillation with magnesium oxide, preferably *in vacuo*. A study of the possibilities of interference from a number of commonly found plant constituents, and of the conditions under which this determination is frequently conducted, has led to the suggestion of a technic that depends upon distillation *in vacuo* with a borax-sodium hydroxide mixture used in conjunction with a phosphate buffer solution. The ammonia is then nesslerized and determined in a Pulfrich spectrophotometer. Under these conditions, interference from other substances is minimal. The new reagent is particularly designed for determinations of ammonia in solutions to which phosphate buffers have been added, as the use of magnesium oxide is then inadmissible; its convenience, however, suggests that it may be generally applied with advantage.

were present. Furthermore he experimented, although unsuccessfully, with the idea of aeration of the ammonia, a procedure that has been highly developed by Folin (7). Only two fundamentally different ideas have been introduced into the field since that time; of these one—gaseous diffusion of the ammonia from cold alkaline solution to standard acid in an enclosed space—was suggested by Schlössing (17) in 1851, was almost immediately applied to the difficult problem of urine analysis by Neubauer (15), and has recently been placed on a modern footing by Conway and Byrne (6). The other new idea is the use of Permutit to absorb ammonia from faintly acid solution, first suggested by Folin and Bell (8) in 1917.

Although the work of Bosshard (1), Longi (14), Wurster (24), Folin (7), Castoro (3), Folin and Denis (9), Vickery and Pucher (20), Klein and Tauböck (11), and Schlenker (16), to mention only a few of the investigators who have dealt directly or indirectly with the problem, has furnished a mass of information regarding methods, and the precautions that must be observed in determining ammonia in plant tissues and in urine, only Bosshard and Castoro have specifically considered the possibility of serious interference from glutamine and suggested means for avoiding it. Bosshard precipitated the ammonia with phosphotungstic acid previous to distillation with magnesium oxide—an inconvenient procedure quite unsuited for microscale work; Castoro distilled *in vacuo* with magnesium oxide, but provided inadequate data in support of this method.

alkaline than pH 6.0. The evaporation to half its volume in the oven at 85° C. of a very dilute ammonium sulfate solution buffered at pH 6.95 involved the loss of 14 per cent of the ammonia present. A similar solution at pH 6.03 lost no ammonia under the same conditions.

For the present, then, it is necessary to specify that tissue should be dried at a temperature not exceeding 70° C., and as rapidly as possible. If the natural reaction of the tissue exceeds pH 6, drying without loss of ammonia is probably impossible. In any case, the most careful controls must be instituted in order to obtain information on the probable accuracy of the results. Ammonia determinations on tissue that has been dried at an uncontrolled temperature may have value for the calculation of the residual amide nitrogen, but probably have little physiological significance.

It is sometimes desirable for certain purposes to use water extracts prepared from the previously dried tissue. A method that has proved satisfactory is to transfer 5 grams to a 100-cc. volumetric flask with cold water, dilute to the mark, and shake by machine for several hours. The mixture is then centrifuged, filtered on dry paper if necessary, and 10-cc. aliquots are analyzed. Data that show the accuracy of this method are given below.

A hot-water extract of the dry tissue can also be prepared without undue risk if the glutamine content is not high. To this end, 5 grams of tissue and about 80 cc. of water are rapidly brought to a boil with careful stirring in a beaker, boiled for 3 minutes, cooled, transferred to a 100-cc. flask, made to volume, and centrifuged as before.

Distillation of Ammonia

If dry and finely ground tissue is employed, a sample of from 0.1 to 0.5 gram is thoroughly mixed with 10 cc. of phosphate-borate buffer, and is transferred with the aid of about 20 cc. of water to the distillation flask. If an extract is to be analyzed, a suitable aliquot (usually 25 cc. of fresh tissue extracts prepared as described) together with 10 cc. of buffer, is placed in the flask. The receiver is charged with 3 cc. of 0.1 *N* hydrochloric acid, the joints are lubricated with a little vaseline, and the apparatus is assembled, 3 cc. of sodium hydroxide-borate mixture being added just before inserting the air inlet tube. The apparatus is evacuated, and the air inlet is adjusted to provide a flow of 2 to 3 bubbles per second. The water bath, previously heated to 40° to 42° C., is raised so as to immerse the entire flask, and distillation is allowed to proceed for 15 minutes, the bath being maintained at the same temperature. The bath is lowered, air is admitted through the air inlet, the rubber connection on the vapor tube is opened, and the vacuum pump is disconnected. The vapor tube is rinsed inside and out into the receiver with a few cubic centimeters of water, and the distillate is transferred to a 25 × 200 mm. test tube graduated at 50 cc., or to a 50-cc. flask. Water to make about 35 cc. is added, 5 cc. of Nessler reagent are introduced, and the solution is made to volume and mixed.

Determination of the Ammonia

The light transmission of the nesslerized solution is read in a Zeiss Pulfrich spectrophotometer with light filter S-43. The control solution for the other side of the instrument is prepared by diluting 5 cc. of Nessler reagent to 50 cc. The extinction coefficient is calculated, and the equivalent in milligrams of ammonia nitrogen is obtained from the calibration curve. The final value is corrected for the apparatus blank as described below.

The use of the Pulfrich spectrophotometer to determine ammonia is one of the most valuable applications of this versatile instrument. The details have been worked out by Urbach (18, 19). The authors have confirmed the observation of Wirth and Robinson (23) that Nessler reagents prepared by different formulas yield different color values, but find that each type of solution gives highly reproducible results. The same calibration curve has been in use in this laboratory for more than a year with many different samples

of Nessler reagent prepared as described. It is necessary for each laboratory to establish the curve for its own reagent and instrument. Known quantities of ammonia nitrogen within the range 0.05 to 2.0 mg. are nesslerized, and read at 50-cc. volume against the control solution. The curve of extinction coefficient plotted against milligrams of ammonia nitrogen should be accurately a straight line between these limits. The curve used in this laboratory is such that extinction coefficient multiplied by 0.286 gives milligrams of ammonia nitrogen.

Accuracy in spectrophotometric work requires great care and considerable experience in reading the instrument. At least five settings should be made that agree within ± 1 scale division. Duplicate determinations that disagree by more than ± 0.005 mg. of nitrogen should be repeated. Cells should be selected that give readings in the range of 15 to 70 per cent transmission. The upper limit of convenient work is 0.4 mg. of nitrogen in the 50-cc. volume. Higher concentrations necessitate very short cells, and it is usually better to repeat the determination and take aliquots of the distillate.

All determinations are corrected for a small apparatus blank which is redetermined at frequent intervals. The apparatus is charged with 30 to 40 cc. of water, and the distillation is conducted as usual. The nesslerized distillate is read in a 3-cm. cell against the control solution with the control drum set at 50 instead of 100 per cent. The blank is, in the authors' experience, very constant within the limits 0.006 to 0.009 mg. of nitrogen, and can be duplicated within 0.002 mg. A higher blank as a rule indicates that something is wrong, and the source of trouble must be eliminated. The first distillation of the day usually runs high, and it is standard practice to run a blank distillation, after the apparatus has stood unused for some time, and to discard the distillate. The blank for the day is then determined; experience with the method will soon show how frequently a new blank should be run.

When a series of determinations is to be undertaken, the second flask and receiver are prepared during the distillation period, and little time is lost in substituting them.

Table I shows a series of recoveries of 0.5 and 2.5 mg. of ammonia nitrogen. Aliquots of the distillates of the larger quantities were taken before nesslerization, and the data serve to demonstrate that 2.5 mg. of ammonia nitrogen can be quantitatively distilled within the time limit recommended.

TABLE I. RECOVERY OF AMMONIA NITROGEN FROM AMMONIUM SULFATE

Taken Mg.	Found Mg.	Recovery %
0.500	0.500	100.0
0.500	0.514	102.8
0.500	0.504	100.8
0.500	0.495	99.0
2.50	2.48	99.2
2.50	2.47	98.7
		Av. 100.1

The average recovery is 100.1 per cent, with an uncertainty in individual cases of slightly less than ± 3 per cent. This is the precision to be expected of readings of the Pulfrich spectrophotometer. The method has been applied satisfactorily to the determination of quantities of ammonia ranging from 0.01 to 4.0 mg. The most convenient range is from 0.10 to 0.5 mg.

The application to plant tissues of the present method to determine ammonia involves a consideration of the possibilities of interference from other plant constituents. The most probable interfering substances are glutamine, allantoin, and urea; the stability of asparagine and adenine is also such as to require tests to demonstrate that their presence does not affect the result.

Table II shows in summary form a considerable volume

of data touching on these points. Data to illustrate the necessity for the presence of the buffer solution are included, together with data to show the effect of distillation with magnesium oxide in the absence of buffer solution. It is clear that, if buffer solution is used along with the borax-sodium hydroxide reagent, glutamine interferes to a very slight extent. Urea is rarely found in higher plants, and then only in small proportion; interference from this source is therefore usually negligible. Allantoin, which is more commonly found, is somewhat more stable, and adenine and asparagine show little if any instability under the conditions of the distillation.

Table III shows a series of determinations of the ammonia nitrogen of plant tissues which illustrates the reproducibility of the results, and also serves to show the applicability of the cold-water extraction method as applied to previously dried tissue. The tomato stem tissue is of particular interest, inasmuch as this sample contained 0.565 per cent of glutamine amide nitrogen, or the equivalent of 5.8 per cent of glutamine in the dry material. This sample when distilled *in vacuo* with magnesium oxide, yielded 0.147 per cent of ammonia nitrogen.

TABLE II. EFFECT OF DISTILLATION ON SUBSTANCES LIKELY TO BE ENCOUNTERED IN PLANT TISSUE

Substance	Ammonia N as Per Cent of Total N	
	Borax-NaOH	MgO
Glutamine with buffer	0.2 to 0.5	7.8
Glutamine without buffer	0.05 to 0.10	0.7 to 1.2
Allantoin with and without buffer	0.40	0.15 to 0.25
Urea with and without buffer	0.01 to 0.03	0.40
Adenine with and without buffer	0.00	0.03
Asparagine with buffer	0.75	0.00
Asparagine without buffer		0.3 to 0.6

TABLE IV. RECOVERY OF TOTAL AMIDE NITROGEN OF A MIXTURE OF GLUTAMINE AND ASPARAGINE

(Figures are milligrams of amide nitrogen)		
Asparagine Taken Mg.	Glutamine Taken Mg.	Amide N Recovered Mg.
0.40	0.10	0.488
0.40	0.10	0.508
0.40	0.10	0.506
0.40	0.25	0.644
0.40	0.25	0.642

TABLE V. TOTAL AMIDE NITROGEN CONTENT OF SEVERAL SAMPLES OF DRY PLANT TISSUE*

	%
Tobacco leaf B	0.052
Tobacco leaf C	0.053
Tobacco leaf I	0.043
Tobacco leaf J	0.043
Tobacco stem D	0.098
Tobacco stem E	0.099
Tobacco stem F	0.098
Tobacco stem G	0.070
Tobacco stem H	0.072
Tobacco stem I	0.070
Tobacco stem J	0.072
Tobacco stem K	0.050
Tobacco stem L	0.049
Tomato leaf, ammonia culture	0.448
Tomato leaf, nitrate culture	0.436
Tomato stem, ammonia culture	0.087
Tomato stem, nitrate culture	0.091
Beet roots, ammonia culture	0.885
Beet roots, nitrate culture	0.858
Beet roots, ammonia culture	0.098
Beet roots, nitrate culture	0.100
Beet roots, ammonia culture	0.460
Beet roots, nitrate culture	0.454

* The authors are indebted to H. E. Clark for the illustrative data on tomato and beet tissue.

with the 5 cc. of 12.5 per cent magnesium oxide suspension ordinarily employed, but it seemed better for many reasons to avoid magnesium entirely if possible. The borax-sodium hydroxide mixture used together with phosphate buffer solution was found to give the correct conditions for the distillation, and possessed the advantages of being a soluble reagent, and of giving no difficulty with the nesslerization if a little were carried over during the distillation. Magnesium, on the other hand, if carried over, yields a turbid solution useless for quantitative measurements and, should this accident occur, it is necessary to clean the entire apparatus with cleaning acid before it can be used again.

Nevertheless, for many purposes magnesium oxide is equally as good as the borax mixture suggested, and it is frequently employed in this laboratory. The authors avoid its use for tissues that contain notable amounts of glutamine, and it cannot safely be used if phosphate buffers have been employed in connection with glutamine determinations.

Discussion

The most important novel feature of the present procedure is the use of a borax-sodium hydroxide mixture in conjunction with a phosphate buffer as the alkaline reagent employed to displace the ammonia. The necessity of replacing the time-honored magnesium oxide with a different reagent was revealed in the course of attempts to determine the amide nitrogen of glutamine according to the procedure of Chibnall and Westall (5). A detailed study of the conditions under which this determination may be made showed that the amide group is completely hydrolyzed when glutamine is heated at 100° C. for 3 hours in a solution buffered in the range pH 6 to 7 (22), but that the distillation of the ammonia produced is frequently far from complete if phosphate buffers are employed. The difficulty was traced to the combined presence of phosphate and magnesium, and can probably be accounted for in terms of the partial precipitation of the ammonia as magnesium ammonium phosphate (13). It could usually be avoided if 2 cc. of *N* sodium hydroxide were added along

Determination of Amide Nitrogen

Recent studies of the stability of asparagine and of glutamine (22) have shown that the conditions for the complete hydrolysis of asparagine advocated by Vickery and Pucher (21) are unnecessarily severe. Inasmuch as asparagine is the most stable amide at present known to occur in plants, the total amide nitrogen may be determined under the conditions that have been shown to be adequate for the complete hydrolysis of this substance. These are as follows:

A 5-cc. aliquot of a water extract from the dried tissue prepared as described is mixed with 1 cc. of 6 *N* sulfuric acid in a 25 × 200 mm. test tube which is closed with a stopper that carries a short length of 1-mm. capillary tubing. The tube is heated for 3 hours in a constant-level boiling water bath, the contents are then transferred to the distillation apparatus with 20 cc. of water, 5 cc. of 1 *N* sodium hydroxide are added to neutralize most of the hydrolyzing acid, and 5 cc. of the borax-sodium hydroxide mixture are introduced. The ammonia is determined, and the quan-

tity found is corrected for the apparatus blank, and for the "preformed" ammonia determined directly upon a sample of the dried tissue, not upon the extract. Results that are probably somewhat more trustworthy from the chemical point of view are to be obtained from analyses of extracts from the fresh tissue prepared by the ether cytology method. In this case, however, the magnitude of the sampling error may become significant unless the greatest care is exercised.

Table IV shows that the recovery of total amide nitrogen from a mixture of glutamine and asparagine is essentially quantitative under the conditions described, and Table V illustrates the reproducibility of the results on several plant tissues.

Literature Cited

- (1) Bosshard, E., *Z. anal. Chem.*, **22**, 329 (1883).
- (2) Boussingault, J. B., *Ann. chim. phys.*, (3) **29**, 472 (1850); reprinted in "Mémoires de chimie agricole et de physiologie," p. 285, Paris, 1854; and in "Agronomie, chimie agricole et physiologique," 3, p. 233, Paris, 1864.
- (3) Castoro, N., *Z. physiol. Chem.*, **50**, 525 (1907).
- (4) Chibnall, A. C., *J. Biol. Chem.*, **55**, 333 (1923).
- (5) Chibnall, A. C., and Westall, R. G., *Biochem. J.*, **26**, 122 (1932).
- (6) Conway, E. J., and Byrne, A., *Ibid.*, **27**, 419 (1933).

- (7) Folin, O., *Z. physiol. Chem.*, **37**, 161 (1902).
- (8) Folin, O., and Bell, R. D., *J. Biol. Chem.*, **29**, 329 (1917).
- (9) Folin, O., and Denis, W., *Ibid.*, **11**, 527 (1912).
- (10) Grover, C. E., and Chibnall, A. C., *Biochem. J.*, **21**, 857 (1927).
- (11) Klein, G., and Tauböck, K., *Biochem. Z.*, **241**, 413 (1931).
- (12) Koch, F. C., and McMeekin, T. L., *J. Am. Chem. Soc.*, **46**, 2066 (1924).
- (13) Kostychev, S., "Chemical Plant Physiology," tr. by C. J. Lyon, p. 315, Philadelphia, P. Blakiston's Son & Co., 1931.
- (14) Longi, A., *Versuchs-Stat.*, **32**, 15 (1886).
- (15) Neubauer, C., "Anleitung zur qualitativen und quantitativen Analyse des Harns," p. 113, Wiesbaden, Kreidel, and Niedner, 1854.
- (16) Schlenker, F. S., *Plant Physiol.*, **7**, 685 (1932).
- (17) Schlössing, T., *Ann. chim. phys.*, (3) **35**, 153 (1851).
- (18) Urbach, C., *Biochem. Z.*, **259**, 351 (1933).
- (19) Urbach, C., *Mikrochemie*, **11**, 37 (1932).
- (20) Vickery, H. B., and Pucher, G. W., *J. Biol. Chem.*, **83**, 1 (1929).
- (21) Vickery, H. B., and Pucher, G. W., *Ibid.*, **90**, 179 (1931).
- (22) Vickery, H. B., Pucher, G. W., Clark, H. E., Chibnall, A. C., and Westall, R. G., in press.
- (23) Wirth, H. E., and Robinson, R. J., *IND. ENG. CHEM., Anal. Ed.*, **5**, 293 (1933).
- (24) Wurster, C., *Ber.*, **22**, 1901 (1889).

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An Automatic Pipet for Rapid Delivery

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IN PERFORMING quantitative experiments it is often advantageous to measure a volume of solution quickly and also to keep it free from some undesirable atmospheric gas. A pipet which does this quickly and efficiently, shown diagrammatically in Figure 1, has been used by the authors to deliver 0.5 *N* sodium hydroxide free from atmospheric carbon dioxide.

The simplicity of this apparatus is manifest by the fact that one stopcock, *A*, controls all operations except emptying the pipet. This stopcock plug is a regulation 2-mm. T-bore having special additional drilling. A diagonal hole is drilled from the point just opposite the vertical arm of the T, meeting an axial drilling from the end as shown in 4. The jet, *V*, is not necessary but is very convenient in case the pipet should overflow. The intake, *I*, is attached to a compressed air line, which must be equipped with a Bunsen valve and a scrubber which will remove moisture and carbon dioxide. The pipet may be attached to the solution bottle, *S*, by means of either a rubber stopper or a ground-glass joint. *R* is a reinforcing rod. *B* is an enlarged place in the line to lessen the chances of overflow. The jet, *J*, controls the level of the meniscus line, *M*.

Unless the pipet is small, some additional support is necessary. The authors used a clamp such as that shown by the Fisher Scientific Company, No. 5-778. One end was attached to the neck of the bottle and the other end to the body of the pipet. The use of a bottle as a container for the solution is proposed because it allows the entire set-up to be moved at any time. The specially drilled stopcock is the original and most unique part of the apparatus and any other part of the set-up could easily be changed so as to be more adaptable to the needs of the user.

To start operating the pipet set stopcock *A* as shown in position 1. This admits compressed air through *I* and *D* into the bottle, thus exerting a pressure on *S* and forcing the solution through *E* and *J* into *P*. At the same time, the pressure built up in *P* is released through *B* and *C* and out through *V*. After the level of the liquid in *P* has risen above *M*, the stopcock is turned through a one-fourth turn to position 2. This equalizes the pressure above the liquids in *P* and in the bottle, thus allowing the excess solution to siphon back from *P* into *S* until the liquid level corresponds to *M*. *A* is then turned to position 3 and *F* is opened. The air pressure is thus used to force the solution out quickly. If quick delivery is not required, *A* may be left at position 2 and the pipet will drain freely. When the pipet is not in use, *E* should be closed and *A* set at position 2. This excludes outside air from any part of the apparatus.

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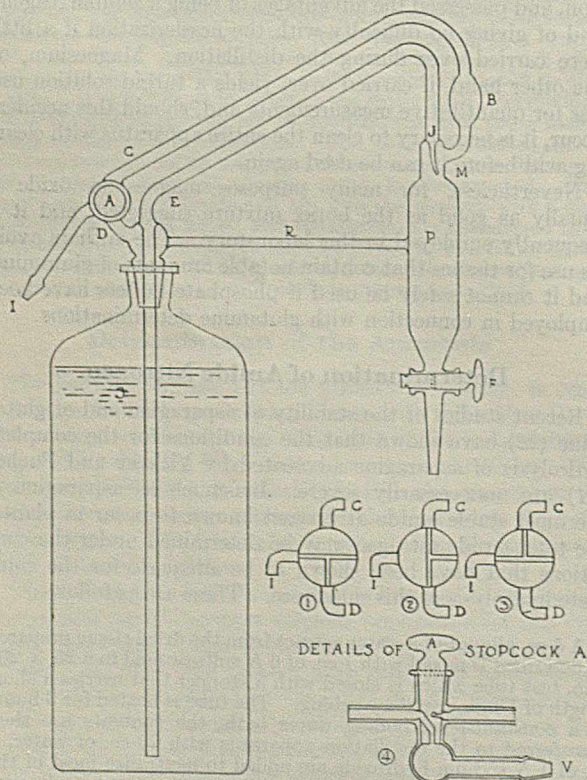


FIGURE 1. DIAGRAM OF PIPET AND STOPCOCK

Studies on Turbidity in Sugar Products

III. Transmittancy and Tyndall Beam Intensity of Solutions of Raw Cane Sugars

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IN THE preceding article of this series (5), reference was made to a statement by Sauer that the Tyndall beam intensity of colored turbid media can be corrected for absorption by applying a factor based on the optical density of the solution, but, in commenting on this, the writers pointed out that Sauer's procedure could not be used in the case of highly turbid cane-sugar products. Since then an article by Landt and Witte (2) on the same subject has appeared. These authors found that with solutions of beet-sugar products filtered through filter paper the results of turbidity determinations, made with the Pulfrich photometer and corrected by means of Sauer's factors, give a reliable measure of the turbidity, and further that there is a close proportionality between the absolute turbidity and the extinction coefficient of the solution.

In view of these findings of Landt and Witte, the writers have reexamined the experimental results obtained in series C of the previous paper, where mixtures of an unfiltered raw sugar solution, a filtered raw sugar solution, and a filtered white sugar solution, all of 60 Brix density, were investigated, and have calculated the absolute turbidities according to the procedure of Landt and Witte.

The absolute turbidity, t , of the standard block, No. 323, employed by the writers, was reported by Zeiss to equal 0.00282 of the intensity of the incident light, for the green screen L II. The intensity, H , of the four milk-glass disks 1 to 4 was found to be 146.2, 79.0, 24.3, and 18.1, respectively. The cells used were 2.46 mm. in thickness, so that the ratio, D , of the thickness of the standard block to that of the absorption cell was as 16.3 to 2.46 or 6.626. In order to interpolate between the values of the correction factor $f(k)$, given in Table 2 of Landt and Witte, a large graph was prepared based on the relationship: $K = a \log f(k)$.

The results of the calculations, for the three constituent sirups mentioned above, are shown in Table I, which is arranged in the same way as the corresponding Table 4 of Landt and Witte.

TABLE I. CALCULATION OF ABSOLUTE TURBIDITIES ACCORDING TO LANDT AND WITTE

	Unfiltered Raw Sugar Solution 5 U, 0 F, 0 W	Filtered Raw Sugar Solution 0 U, 5 F, 0 W	Filtered White Sugar Solution 0 U, 0 F, 5 W
Cell thickness, mm.	2.46	2.46	2.46
Filter used	L II	L II	L II
Milk-glass disk, No.	3	2	1
Reading, left drum	45.06	100	100
Reading, right drum	100	40.48	31.50
Relative turbidity	221.9	40.48	31.50
Same, corrected for turbidity of water	216.9	35.5	26.5
A, corrected turbidity/ H	8.926	0.449	0.181
Extinction coefficient (for 1.00 cm.)	3.8337	1.8423	0.000
Correction factor, $f(k)$	13.62	3.564	1.000
$A \times f(k)$	121.57	1.600	0.181
Absolute turbidity, $A \times f(k)$ $\times D \times t$	2.2715	0.0299	0.0034
Same, for 1 unit each	0.45430	0.00598	0.00068

It is noted that the absolute turbidity of the unfiltered raw sugar solution comes out much above 1, which is theoretically impossible, as pointed out by Landt and Witte. This would indicate that the correction factor, $f(k)$, taken from Table 2 of these authors, is very much too high for this type of product, probably because of multiple reflection.

The conclusion that the procedure used by Landt and Witte is not applicable to such products is further strengthened by the figures presented in Table II, which gives the absolute turbidities, based on direct calculations, for all the mixtures used in series C and listed in Table V of the preceding article (5). For comparison, it shows in the last column the absolute turbidities of the same mixtures, calculated by summing up the component effects of the constituents of each, as determined from the absolute turbidity for one unit of each sirup (last line in Table I).

TABLE II. FOUND AND CALCULATED ABSOLUTE TURBIDITIES OF SIRUP MIXTURES

Mixtures	Absolute Turbidity	
	According to Landt and Witte	Calcd. by adding absolute turbidities of constituents
5 U, 0 F, 0 W	2.2715	2.2715
4 U, 1 F, 0 W	1.5814	1.8232
3 U, 2 F, 0 W	0.7718	1.3749
2 U, 3 F, 0 W	0.4212	0.9266
1 U, 4 F, 0 W	0.1764	0.4783
0 U, 5 F, 0 W	0.0299	0.0299
4 U, 0 F, 1 W	1.3983	1.8179
3 U, 1 F, 1 W	0.7231	1.3696
2 U, 2 F, 1 W	0.4132	0.9211
1 U, 3 F, 1 W	0.1775	0.4729
0 U, 4 F, 1 W	0.0289	0.0245
3 U, 0 F, 2 W	0.8451	1.3643
2 U, 1 F, 2 W	0.4088	0.9160
1 U, 2 F, 2 W	0.1759	0.4676
0 U, 3 F, 2 W	0.0282	0.0193
2 U, 0 F, 3 W	0.4498	0.9106
1 U, 1 F, 3 W	0.1737	0.4623
0 U, 2 F, 3 W	0.0154	0.0139
1 U, 0 F, 4 W	0.1512	0.4571
0 U, 1 F, 4 W	0.0117	0.0088
0 U, 0 F, 5 W	0.0034	0.0034

For all mixtures containing unfiltered raw sugar solution, the calculated figures are much higher than the absolute turbidities found, whereas the calculated figures for the mixtures containing only filtered raw sugar and filtered white sugar solution are slightly lower than those found. Furthermore, if the absolute turbidity of one unit of unfiltered raw sugar solution is calculated from the mixtures containing in addition only white filtered sirup, the following figures are found:

Mixture	Value of 1 U
4 U, 0 F, 1 W	$(1.3983 - 0.0007)/4 = 0.3494$
3 U, 0 F, 2 W	$(0.8451 - 0.0014)/3 = 0.2812$
2 U, 0 F, 3 W	$(0.4498 - 0.0020)/2 = 0.2239$
1 U, 0 F, 4 W	$(0.1512 - 0.0027)/1 = 0.1485$

The values for one unit of unfiltered raw sugar solution calculated according to Landt and Witte vary enormously with the concentration, from 0.1485 to 0.4543. Similar discrepant results were obtained also for the absolute turbidities of the Filter-Cel-caramel mixtures discussed in the preceding paper.

The problem of the determination of turbidity in raw cane sugars has therefore been approached by the writers in a different manner, by using the empirical formulas which express the relationship between transmittancy and Tyndall beam intensity on the one hand, and the concentration of coloring matter and turbidity on the other, for the raw sugar employed in the previous investigation. These formulas are:

$$-\log T = C + N$$

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

where T = transmittancy of a 60 Brix solution of the sugar in a 2.5-mm. cell at a given wave length

R = Tyndall beam intensity, measured under the same conditions as T , and expressed in per cent of that of the standard turbid glass block of the Pulfrich photometer

C = concentration of coloring matter, expressed as $-\log T$

N = concentration of turbidity, also expressed as $-\log T$

The specific absorptive indexes corresponding to the $-\log T$'s have not been calculated, but they are directly proportional to them:

$$-\log t = 5.182 \times (-\log T)$$

For the particular sugar investigated, the following values of the constants $\log a$ and $\log k$ were found:

	Blue, 449 m μ	Green, 529 m μ	Red, 621 m μ
$\log a$	3.13056	3.77551	4.40555
$\log k$	1.42545	1.23280	1.16568

The writers did not have at their disposal a color filter with an effective wave length of 560 m μ , and for this reason the concentration of coloring matter as defined by Peters and Phelps (3) ($-\log t$ of the filtered solution at 560) could not be determined. The $-\log t$'s for the three wave lengths available represent therefore merely concentrations of coloring matter based on these wave lengths, but this does not in any way affect the conclusions reached.

In the continuation of this investigation, the transmittancy and Tyndall beam intensity of 60 Brix solutions of 62 other cane raw sugars from many sources have been measured, under the same conditions as specified above. The solutions were prepared by dissolving the sugar in the requisite quantity of water, straining through a 250-mesh bronze sieve to remove coarse particles, and adjusting the density to 60 Brix by refractometer. This solution will be referred to as the unfiltered solution, designated by subscript u . A portion of this solution was filtered through purified Filter-Cel, according to Balch's technic (1), and the resulting material is termed the filtered solution, marked by subscript f .

The values of C and N in both unfiltered and filtered solutions were found from the respective figures for T and R , as described in the previous article, by using greatly enlarged graphs similar to the one shown there. The results of the measurements and calculations are shown in Table III, for each of the three color screens.

Coloring Matter

According to Balch, the negative log of the transmittancy of the filtered solution (column headed $-\log T_f$) is a measure of the coloring matter present. All the solutions filtered through Filter-Cel still showed a residual Tyndall beam intensity, R_f , and hence contained measurable turbidity.

This brings up the question of the definition of "coloring matter," or of the dividing line between "turbidity" and "coloring matter" in a medium which, like a raw sugar solution, contains particles of varying sizes, from fairly coarse ones down to those of molecular dimensions. Peters and Phelps have specified that the solutions to be measured for color should show a minimum haze when placed, in a dark room, in the path of a strong beam of light and examined from an angle, and state that no physical constant which quantitatively measures the degree of transparency has so far been utilized. It appears that color determinations cannot be placed on a strictly comparative basis until the degree of transparency is defined. Entirely aside from the subject of selective adsorption of coloring matter by various filtering agents, such as Filter-Cel, asbestos, filter paper, etc., a line should be drawn between what Peters and Phelps term "suitable transparency" and the "lack of it." In the present investigation it is postulated that coloring matter be considered that portion of the dispersed material which gives a Tyndall beam of zero intensity under the experimental conditions used.

Since the Filter-Cel filtrates still showed measurable turbidity, the actual coloring matter contained in them must be smaller in quantity than indicated by the $-\log T$ of the

filtrates. In agreement with this, the values for the coloring matter C_f , calculated from $-\log T$ and R of the filtered solution, are smaller than $-\log T_f$. But the question whether the figures for C_f represent the correct concentration of coloring matter as defined above requires a detailed analysis of the data.

Balch concluded from his investigations that specially purified Filter-Cel does not cause selective adsorption of coloring matter, and this was found to be true also for the Filter-Cel used by the writers. This being the case, the quantity of coloring matter actually present in the unfiltered and the filtered solutions of the same raw sugar is necessarily the same—that is, C_u should equal C_f . The tables show that in many cases C_u is the same as C_f , within the limits of error, but in others there are wide divergencies. The explanation for this must be sought in the nature of the turbidity.

Turbidity

As a corollary to the relation between C_u and C_f , the turbidity calculated by subtracting $-\log T_f$ from $-\log T_u$ according to Balch, should be equal to the turbidity difference, $N_u - N_f$, provided, however, that the properties of the dispersed particles, such as average size, distribution of sizes, shape, light transmission, absorption, etc., are the same in different sugars. Conversely, if $-\log T_u - (-\log T_u)$ differs from $N_u - N_f$, the ratio between the two numerically expresses the integrated difference in the properties of the particles. Teorell (4) has shown that the $-\log T$ of equal concentrations of an aqueous sol varies with the average size of the particles and the same would apply in the case of a sol in a colored sugar solution. The difference between N_u and N_f , on the other hand, expresses the turbidity in terms of an arbitrary dispersion with fixed particle properties—viz., that existing in the sugar from which the writers' formulas were derived. The ratio between $N_u - N_f$ and $-\log T_u - (-\log T_f)$ is thus characteristic for each individual sugar, and serves as a "quality index" of the particles. Further investigations will have to show what these qualities are, and which of those mentioned above are the more important.

Since $N_u - N_f$ is a measure, in terms of a standard dispersion, of the turbidity filtered out by the Filter-Cel, N_u itself represents the total turbidity in the sugar, in the same terms.

Relation between C_u , C_f , and C

From what has been said, it is now evident why the coloring matter calculated from the transmittancy and Tyndall beam intensity of the unfiltered solution checks with that obtained for the filtered solution only in those cases where the total effect of the properties of the particles causing turbidity is the same as in the standard sugar. It may be inferred that in these same cases $C_u = C_f$, represents the actual coloring matter, corrected for the residual turbidity in the filtered solution. There are 19 samples among the total of 62 where, under the green screen, C_u equals C_f within ± 3 per cent. For the same 19 samples the C_f values, considered to be equal to C itself within the same limits, are from 0.011 to 0.027 lower than $-\log T_f$. It is interesting to note that for 38 of the other 43 samples the difference between $-\log T_f$ and C_f is within the same range as for the first 19, and that even for the remaining samples it does not exceed 0.031, although in all the 43 the differences between C_u and C_f vary widely. Nevertheless, the conclusion would not be justified that in these 43 cases the actual coloring matter also equals C_f within the experimental error. All that can be said with certainty is that C must be smaller than $-\log T_f$, but the actual difference cannot be derived from the existing data, because the properties of the residual turbidity in

TABLE III. TRANSMITTANCY, TYNDALL BEAM INTENSITY, TURBIDITY, AND COLOR OF RAW SUGARS

No.	Unfiltered Solution				Filtered Solution				$N_u - N_f$	-log T_u Minus -log T_f	Quality Index
	-log T_u	log R_u	N_u	C_u	-log T_f	log R_f	N_f	C_f			
A. Blue Filter											
1	1.216	1.842	0.515	0.701	0.774	0.818	0.052	0.722	0.463	0.442	1.048
2	0.373	2.011	0.155	0.218	0.159	1.301	0.023	0.136	0.132	0.214	0.617
3	0.935	1.939	0.388	0.547	0.603	0.867	0.035	0.568	0.353	0.332	1.063
4	1.004	1.884	0.406	0.598	0.694	0.807	0.040	0.654	0.366	0.311	1.177
5	0.611	2.123	0.287	0.324	0.490	1.200	0.050	0.440	0.237	0.122	1.943
6	0.567	2.085	0.253	0.308	0.394	1.269	0.044	0.350	0.209	0.173	1.208
7	0.779	1.962	0.314	0.465	0.546	1.070	0.045	0.501	0.269	0.233	1.155
8	0.742	1.888	0.257	0.485	0.534	0.875	0.029	0.505	0.228	0.209	1.091
9	0.784	2.302	0.448	0.336	0.354	1.103	0.027	0.326	0.421	0.431	0.977
10	0.427	2.093	0.196	0.231	0.238	1.175	0.024	0.214	0.172	0.189	0.910
11	0.608	2.178	0.303	0.305	0.355	1.087	0.027	0.328	0.277	0.253	1.095
12	0.888	2.013	0.390	0.498	0.530	1.077	0.044	0.486	0.346	0.358	0.966
13	1.098	1.779	0.418	0.680	0.766	0.780	0.047	0.719	0.371	0.332	1.117
14	0.462	2.212	0.247	0.215	0.259	1.434	0.041	0.218	0.206	0.203	1.015
15	0.509	2.237	0.276	0.233	0.206	1.448	0.036	0.170	0.240	0.303	0.792
16	0.754	2.119	0.358	0.396	0.455	1.060	0.034	0.421	0.324	0.299	1.084
17	0.580	2.299	0.332	0.248	0.283	1.126	0.023	0.260	0.309	0.297	1.040
18	0.727	1.964	0.283	0.444	0.462	1.019	0.032	0.431	0.251	0.264	0.951
19	0.889	1.951	0.367	0.522	0.593	1.032	0.048	0.546	0.319	0.296	1.078
20	1.218	1.844	0.518	0.700	0.785	0.759	0.050	0.735	0.468	0.433	1.081
21	0.771	1.914	0.292	0.479	0.482	1.144	0.043	0.439	0.249	0.290	0.859
22	1.706	1.745	0.798	0.908	0.970	0.674	0.088	0.902	0.731	0.736	0.993
23	1.520	1.659	0.629	0.891	0.891	0.732	0.061	0.830	0.568	0.629	0.903
24	0.360	2.140	0.182	0.178	0.184	1.459	0.035	0.149	0.147	0.175	0.840
25	0.338	2.292	0.224	0.114	0.108	1.618	0.039	0.070	0.185	0.229	0.808
26	0.356	2.014	0.149	0.207	0.189	1.221	0.022	0.168	0.128	0.166	0.771
27	0.663	2.122	0.312	0.351	0.411	1.115	0.033	0.378	0.279	0.251	1.112
28	0.562	2.372	0.350	0.212	0.268	1.116	0.022	0.248	0.328	0.295	1.112
29	0.660	2.040	0.286	0.374	0.448	1.145	0.040	0.408	0.247	0.212	1.165
30	0.442	2.067	0.209	0.233	0.283	1.115	0.023	0.260	0.186	0.159	1.170
31	1.269	1.805	0.531	0.738	0.806	0.784	0.053	0.753	0.478	0.463	1.032
32	0.736	2.123	0.349	0.387	0.424	0.948	0.024	0.400	0.325	0.312	1.042
33	0.536	2.165	0.265	0.271	0.242	1.047	0.017	0.225	0.248	0.294	0.844
34	1.434	1.731	0.606	0.828	0.900	0.533	0.043	0.857	0.563	0.535	1.062
35	0.351	2.087	0.167	0.184	0.214	1.216	0.023	0.191	0.144	0.138	1.043
36	0.546	1.970	0.209	0.337	0.407	0.992	0.025	0.382	0.184	0.139	1.324
37	0.514	2.134	0.244	0.270	0.283	1.338	0.036	0.247	0.208	0.230	0.904
38	1.132	1.673	0.393	0.739	0.849	0.642	0.045	0.804	0.348	0.283	1.229
39	0.440	2.313	0.269	0.172	0.291	1.447	0.046	0.245	0.223	0.149	1.497
40	0.523	1.879	0.175	0.348	0.404	1.080	0.030	0.374	0.145	0.118	1.229
41	0.706	2.196	0.361	0.345	0.418	1.085	0.032	0.386	0.329	0.289	1.138
42	1.048	1.846	0.415	0.633	0.735	0.899	0.054	0.680	0.361	0.314	1.150
43	1.331	1.938	0.633	0.698	0.744	0.843	0.050	0.694	0.583	0.586	0.995
44	0.566	2.190	0.288	0.278	0.335	1.129	0.027	0.307	0.261	0.232	1.125
45	0.584	2.288	0.330	0.254	0.291	1.301	0.035	0.257	0.296	0.293	1.010
46	0.553	1.857	0.180	0.373	0.405	1.121	0.033	0.372	0.147	0.147	1.000
47	0.500	2.132	0.238	0.262	0.284	1.123	0.023	0.261	0.215	0.215	1.000
48	0.659	2.393	0.412	0.247	0.332	1.247	0.035	0.297	0.377	0.327	1.153
49	0.694	2.018	0.291	0.403	0.463	1.080	0.036	0.427	0.255	0.230	1.109
50	0.429	2.003	0.172	0.257	0.315	1.191	0.029	0.286	0.143	0.114	1.254
51	1.009	1.730	0.350	0.659	0.719	0.819	0.044	0.675	0.306	0.290	1.055
52	0.734	2.401	0.459	0.275	0.288	1.330	0.036	0.251	0.423	0.446	0.948
53	0.568	2.148	0.274	0.294	0.252	1.233	0.027	0.225	0.247	0.316	0.782
54	0.621	2.290	0.351	0.270	0.324	1.386	0.045	0.279	0.306	0.298	1.027
55	0.783	2.226	0.416	0.367	0.381	1.179	0.035	0.346	0.381	0.401	0.950
56	0.387	2.295	0.238	0.149	0.193	1.193	0.020	0.173	0.218	0.194	1.124
57	2.614	0.684	0.921	1.693	1.841	1.778	0.124	1.717	0.797	0.774	1.030
58	0.984	2.004	0.443	0.541	0.630	0.860	0.040	0.590	0.403	0.354	1.138
59	0.694	2.266	0.382	0.312	0.371	1.261	0.040	0.331	0.342	0.323	1.059
60	0.471	2.096	0.215	0.256	0.273	1.197	0.026	0.247	0.189	0.198	0.955
61	0.670	2.205	0.347	0.323	0.408	1.075	0.030	0.377	0.317	0.263	1.205
62	0.821	2.294	0.467	0.354	0.393	0.908	0.020	0.373	0.447	0.427	1.047
B. Green Filter											
1	0.707	2.811	0.322	0.385	0.347	1.709	0.023	0.324	0.299	0.360	0.831
2	0.251	2.582	0.098	0.153	0.068	1.922	0.017	0.051	0.081	0.183	0.443
3	0.525	2.901	0.273	0.252	0.279	1.679	0.016	0.263	0.257	0.246	1.045
4	0.550	2.785	0.243	0.307	0.322	1.650	0.020	0.302	0.223	0.228	0.978
5	0.331	3.014	0.230	0.101	0.223	1.992	0.030	0.193	0.200	0.108	1.852
6	0.308	2.899	0.186	0.122	0.170	2.004	0.025	0.145	0.161	0.138	1.167
7	0.440	2.794	0.204	0.236	0.244	1.841	0.022	0.221	0.182	0.196	0.929
8	0.379	2.719	0.162	0.218	0.235	1.673	0.015	0.221	0.147	0.144	1.021
9	0.498	3.070	0.323	0.174	0.185	1.726	0.015	0.170	0.308	0.313	0.984
10	0.251	2.719	0.124	0.128	0.095	1.757	0.012	0.082	0.112	0.156	0.718
11	0.355	2.979	0.229	0.126	0.154	1.765	0.015	0.139	0.214	0.201	1.065
12	0.520	2.943	0.287	0.234	0.249	1.828	0.022	0.228	0.265	0.271	0.978
13	0.589	2.858	0.287	0.303	0.343	1.664	0.019	0.324	0.267	0.246	1.085
14	0.280	2.914	0.181	0.099	0.125	2.073	0.027	0.098	0.154	0.155	0.994
15	0.348	2.819	0.178	0.171	0.092	2.049	0.022	0.070	0.156	0.256	0.609
16	0.403	3.003	0.256	0.147	0.193	1.752	0.016	0.177	0.240	0.210	1.143
17	0.361	3.038	0.251	0.110	0.139	2.060	0.026	0.113	0.225	0.222	1.014
18	0.396	2.872	0.212	0.185	0.203	1.802	0.018	0.185	0.194	0.193	1.005
19	0.493	2.869	0.248	0.245	0.274	1.817	0.025	0.249	0.223	0.219	1.018
20	0.692	2.921	0.361	0.330	0.348	1.666	0.020	0.329	0.341	0.343	0.994
21	0.426	2.692	0.170	0.256	0.235	1.927	0.026	0.209	0.144	0.191	0.754
22	0.971	2.974	0.537	0.432	0.445	1.708	0.028	0.417	0.509	0.526	0.968
23	0.841	2.755	0.271	0.570	0.414	1.739	0.027	0.386	0.244	0.427	0.571
24	0.249	2.726	0.126	0.122	0.088	2.096	0.025	0.063	0.101	0.161	0.627
25	0.244	2.839	0.149	0.095	0.069	2.070	0.022	0.046	0.127	0.176	0.726
26	0.216	2.631	0.104	0.112	0.092	1.754	0.012	0.080	0.092	0.124	0.724
27	0.366	2.952	0.225	0.141	0.182	1.821	0.018	0.164	0.207	0.184	1.125
28	0.355	3.083	0.263	0.092	0.127	1.754	0.013	0.114	0.250	0.223	1.096
29	0.355	2.911	0.208	0.147	0.201	1.872	0.021	0.181	0.187	0.154	1.214
30	0.263	2.740	0.133	0.130	0.143	1.791	0.015	0.128	0.118	0.121	0.975
31	0.732	2.881	0.362	0.370	0.378	1.724	0.024	0.353	0.338	0.354	0.955
32	0.427	2.983	0.260	0.167	0.203	1.675	0.014	0.189	0.246	0.224	1.098
33	0.344	2.903	0.202	0.142	0.125	1.680	0.011	0.113	0.191	0.220	0.868
34	0.791	2.939	0.419	0.372	0.402	1.510	0.016	0.386	0.403	0.389	1.036
35	0.181	2.730	0.110	0.071	0.084	1.793	0.013	0.071	0.097	0.097	1.000
36	0.298	2.687	0.142	0.156	0.201	1.732	0.015	0.186	0.127		

TABLE III (Continued)

No.	Unfiltered Solution				Filtered Solution				$N_u - N_f$	$-\log T_u$ Minus $-\log T_f$	Quality Index
	$-\log T_u$	$\log R_u$	N_u	C_u	$-\log T_f$	$\log R_f$	N_f	C_f			
B. Green Filter (Continued)											
41	0.449	2.970	0.287	0.182	0.197	1.749	0.016	0.181	0.251	0.252	0.996
42	0.545	2.785	0.241	0.304	0.325	1.858	0.027	0.298	0.214	0.220	0.973
43	0.783	2.981	0.434	0.349	0.355	1.780	0.026	0.329	0.408	0.428	0.953
44	0.360	2.938	0.219	0.141	0.187	1.775	0.016	0.171	0.203	0.173	1.173
45	0.368	3.013	0.245	0.123	0.167	2.018	0.026	0.141	0.219	0.201	1.090
46	0.312	2.602	0.117	0.195	0.198	1.817	0.018	0.179	0.099	0.115	0.861
47	0.298	2.772	0.151	0.147	0.147	1.737	0.014	0.134	0.137	0.151	0.907
48	0.419	3.119	0.305	0.114	0.159	1.954	0.022	0.136	0.283	0.260	1.088
49	0.391	2.884	0.213	0.178	0.227	1.826	0.020	0.206	0.193	0.164	1.177
50	0.247	2.672	0.114	0.133	0.174	1.823	0.018	0.156	0.096	0.074	1.297
51	0.560	2.702	0.222	0.338	0.347	1.695	0.020	0.326	0.202	0.214	0.944
52	0.473	3.163	0.349	0.124	0.154	1.961	0.022	0.132	0.327	0.319	1.025
53	0.390	2.885	0.212	0.178	0.141	1.795	0.015	0.126	0.197	0.249	0.791
54	0.393	3.016	0.256	0.137	0.181	2.038	0.028	0.153	0.228	0.212	1.075
55	0.503	3.024	0.309	0.193	0.195	1.814	0.018	0.176	0.291	0.308	0.945
56	0.243	2.887	0.162	0.081	0.095	1.788	0.013	0.082	0.149	0.148	1.007
57	1.444	2.216	0.437	1.007	0.841	1.221	0.028	0.813	0.409	0.603	0.678
58	0.605	2.950	0.329	0.276	0.336	1.693	0.020	0.315	0.309	0.270	1.144
59	0.396	3.058	0.273	0.123	0.174	1.959	0.024	0.150	0.249	0.223	1.117
60	0.272	2.756	0.139	0.133	0.139	1.843	0.017	0.123	0.122	0.133	0.917
61	0.401	2.959	0.240	0.161	0.177	1.764	0.016	0.162	0.224	0.224	1.000
62	0.518	3.068	0.333	0.185	0.194	1.589	0.011	0.183	0.322	0.324	0.994
C. Red Filter											
1	0.401	3.628	0.250	0.151	0.129	2.353	0.012	0.117	0.238	0.272	0.875
2	0.177	3.109	0.068	0.109	0.031	2.315	0.009	0.022	0.059	0.146	0.404
3	0.293	3.565	0.191	0.102	0.108	2.245	0.009	0.099	0.182	0.185	0.984
4	0.307	3.557	0.193	0.114	0.130	2.266	0.010	0.120	0.183	0.177	1.034
5	0.176	3.578	0.157	0.019	0.098	2.497	0.016	0.083	0.142	0.078	1.821
6	0.182	3.469	0.127	0.035	0.065	2.428	0.012	0.053	0.115	0.097	1.186
7	0.250	3.503	0.160	0.090	0.116	2.438	0.014	0.102	0.146	0.134	1.090
8	0.203	3.397	0.122	0.081	0.094	2.532	0.017	0.078	0.105	0.109	0.963
9	0.351	3.651	0.239	0.112	0.108	2.259	0.010	0.099	0.230	0.243	0.947
10	0.162	3.313	0.097	0.066	0.041	2.229	0.008	0.034	0.089	0.121	0.736
11	0.216	3.564	0.166	0.050	0.060	2.262	0.009	0.052	0.158	0.156	1.013
12	0.319	3.586	0.206	0.113	0.105	2.390	0.012	0.092	0.194	0.214	0.907
13	0.310	3.572	0.198	0.112	0.120	2.325	0.011	0.109	0.187	0.190	0.984
14	0.156	3.457	0.123	0.033	0.046	2.546	0.014	0.032	0.109	0.111	0.982
15	0.249	3.388	0.131	0.118	0.040	2.468	0.012	0.028	0.119	0.209	0.569
16	0.227	3.618	0.184	0.043	0.070	2.292	0.009	0.061	0.175	0.156	1.122
17	0.236	3.585	0.177	0.059	0.052	2.556	0.016	0.037	0.161	0.183	0.880
18	0.213	3.470	0.140	0.073	0.059	2.312	0.010	0.050	0.131	0.154	0.851
19	0.289	3.524	0.178	0.111	0.125	2.410	0.014	0.112	0.164	0.163	1.006
20	0.382	3.641	0.264	0.118	0.127	2.326	0.011	0.116	0.253	0.255	0.992
21	0.255	3.335	0.122	0.133	0.112	2.515	0.017	0.095	0.105	0.143	0.734
22	0.553	3.790	0.383	0.170	0.177	2.372	0.014	0.163	0.369	0.375	0.984
23	0.477	3.646	0.289	0.188	0.158	2.397	0.014	0.144	0.275	0.319	0.862
24	0.172	3.272	0.092	0.081	0.045	2.547	0.015	0.030	0.077	0.127	0.606
25	0.179	3.403	0.118	0.061	0.042	2.583	0.011	0.031	0.107	0.136	0.787
26	0.139	3.195	0.073	0.065	0.038	2.236	0.007	0.031	0.066	0.101	0.654
27	0.215	3.540	0.149	0.066	0.077	2.331	0.012	0.065	0.137	0.138	0.993
28	0.233	3.626	0.188	0.045	0.057	2.231	0.011	0.047	0.178	0.176	1.011
29	0.206	3.498	0.146	0.060	0.076	2.430	0.013	0.063	0.134	0.130	1.031
30	0.167	3.318	0.099	0.068	0.069	2.278	0.009	0.060	0.090	0.098	0.918
31	0.405	3.626	0.251	0.154	0.153	2.346	0.013	0.140	0.238	0.252	0.944
32	0.251	3.586	0.197	0.054	0.097	2.231	0.009	0.088	0.188	0.154	1.221
33	0.246	3.444	0.143	0.103	0.081	2.182	0.007	0.073	0.136	0.165	0.824
34	0.450	3.724	0.307	0.143	0.146	2.188	0.009	0.137	0.298	0.304	0.980
35	0.108	3.273	0.080	0.028	0.041	2.289	0.009	0.033	0.072	0.067	1.075
36	0.170	3.294	0.095	0.075	0.098	2.261	0.009	0.088	0.086	0.073	1.178
37	0.206	3.323	0.108	0.098	0.091	2.388	0.012	0.079	0.096	0.115	0.835
38	0.325	3.516	0.187	0.138	0.179	2.237	0.011	0.168	0.176	0.146	1.205
39	0.157	3.498	0.133	0.024	0.072	2.581	0.017	0.054	0.116	0.085	1.365
40	0.153	3.216	0.079	0.074	0.086	2.326	0.010	0.076	0.069	0.067	1.030
41	0.310	3.542	0.190	0.120	0.111	2.265	0.010	0.101	0.180	0.199	0.905
42	0.269	3.552	0.180	0.089	0.136	2.454	0.015	0.120	0.165	0.134	1.231
43	0.464	3.676	0.295	0.169	0.149	2.435	0.015	0.133	0.280	0.316	0.886
44	0.250	3.490	0.157	0.093	0.111	2.299	0.010	0.101	0.147	0.139	1.058
45	0.231	3.554	0.168	0.063	0.093	2.442	0.014	0.080	0.155	0.138	1.123
46	0.189	3.211	0.085	0.104	0.106	2.329	0.011	0.095	0.074	0.083	0.892
47	0.211	3.370	0.119	0.092	0.087	2.220	0.008	0.079	0.111	0.124	0.895
48	0.311	3.665	0.228	0.083	0.089	2.391	0.012	0.078	0.216	0.222	0.973
49	0.226	3.481	0.147	0.079	0.115	2.381	0.013	0.102	0.135	0.111	1.216
50	0.152	3.250	0.084	0.068	0.088	2.320	0.010	0.078	0.074	0.069	1.073
51	0.305	3.460	0.166	0.139	0.165	2.328	0.013	0.152	0.153	0.141	1.085
52	0.337	3.720	0.256	0.081	0.095	2.405	0.012	0.083	0.244	0.241	1.012
53	0.285	3.444	0.155	0.130	0.092	2.328	0.010	0.082	0.145	0.193	0.751
54	0.254	3.582	0.182	0.072	0.096	2.483	0.015	0.081	0.167	0.158	1.057
55	0.346	3.606	0.221	0.125	0.112	2.353	0.012	0.101	0.209	0.233	0.897
56	0.159	3.413	0.115	0.044	0.060	2.292	0.009	0.051	0.106	0.099	1.071
57	0.739	3.527	0.362	0.377	0.310	2.195	0.014	0.296	0.348	0.429	0.811
58	0.375	3.631	0.241	0.134	0.160	2.262	0.011	0.149	0.230	0.216	1.065
59	0.246	3.639	0.196	0.050	0.085	2.457	0.014	0.071	0.182	0.162	1.123
60	0.169	3.329	0.101	0.068	0.064	2.368	0.011	0.053	0.090	0.105	0.857
61	0.245	3.543	0.169	0.076	0.108	2.294	0.010	0.098	0.159	0.137	1.161
62	0.339	3.651	0.234	0.105	0.090	2.124	0.007	0.083	0.227	0.249	0.912

the filtered solutions are not known. To solve this question it would be necessary either to devise a filtration method which removes the turbidity completely, or else to ascertain the exact effect of the properties of the residual turbidity in the filtered solution upon its transmittancy and Tyndall beam intensity.

Dispersion Quotient

Teorell also found that for equal concentrations of an aqueous white sol the "dispersion quotient"—i. e., the ratio between $-\log t$ at one wave length and that at another some distance apart from the first—varies with the particle size

of the sol, and that conversely, when the relation between particle size and dispersion quotient has once been determined for a particular substance, the particle size can be arrived at by measuring the dispersion quotient. The question naturally arose whether the dispersion quotient can be made use of to characterize the turbidity in raw sugars.

The dispersion quotient of the filtered solution of a raw sugar is identical with the absorption ratio of Peters and Phelps, designated as Q-ratio when it is based on $-\log t$ at $560 \mu\mu$ as the reference point, or as $R\lambda$ -ratio when it is based on that at another specified wave length, λ . The dispersion quotient of the unfiltered solution, on the other hand, is a function not only of the particle size of the turbid material, but also of the dispersion quotient for both coloring matter and turbidity. In the previous investigation it was further found that even when all the properties of coloring matter and turbidity are exactly the same, the dispersion quotient of the unfiltered solution varies with the ratio between the concentrations of coloring matter and turbidity. It is obvious therefore that the dispersion quotient of the unfiltered solution is a complex function of several variables and cannot be used as a measure of the particle size of the turbid matter.

This leaves for further consideration what may be termed the dispersion quotient for the filterable turbidity—that is, the quotient of $N_u - N_f$ at one wave length, for instance 449 (blue) or $621 \mu\mu$ (red), divided by that at another, for instance $529 \mu\mu$ (green). These dispersion quotients are shown in Table IV.

TABLE IV. DISPERSION QUOTIENTS FOR FILTERABLE TURBIDITY

No.	429 $\mu\mu$	529 $\mu\mu$	621 $\mu\mu$	No.	429 $\mu\mu$	529 $\mu\mu$	621 $\mu\mu$
1	1.549	1	0.796	32	1.321	1	0.764
2	1.630	1	0.728	33	1.298	1	0.712
3	1.406	1	0.708	34	1.397	1	0.739
4	1.641	1	0.821	35	1.485	1	0.742
5	1.185	1	0.710	36	1.449	1	0.677
6	1.298	1	0.714	37	1.677	1	0.774
7	1.522	1	0.802	38	1.554	1	0.786
8	1.551	1	0.714	39	1.351	1	0.703
9	1.367	1	0.747	40	1.629	1	0.775
10	1.536	1	0.795	41	1.311	1	0.717
11	1.294	1	0.738	42	1.687	1	0.771
12	1.306	1	0.732	43	1.429	1	0.686
13	1.390	1	0.700	44	1.286	1	0.724
14	1.338	1	0.708	45	1.352	1	0.708
15	1.538	1	0.763	46	1.485	1	0.747
16	1.350	1	0.729	47	1.569	1	0.810
17	1.373	1	0.716	48	1.332	1	0.763
18	1.294	1	0.675	49	1.321	1	0.699
19	1.430	1	0.735	50	1.490	1	0.771
20	1.372	1	0.742	51	1.515	1	0.757
21	1.729	1	0.729	52	1.294	1	0.746
22	1.436	1	0.725	53	1.254	1	0.736
23	1.436	1	1.127	54	1.342	1	0.732
24	1.455	1	0.762	55	1.309	1	0.718
25	1.457	1	0.843	56	1.463	1	0.711
26	1.391	1	0.717	57	1.949	1	0.851
27	1.348	1	0.662	58	1.304	1	0.744
28	1.312	1	0.712	59	1.373	1	0.731
29	1.321	1	0.717	60	1.549	1	0.738
30	1.576	1	0.763	61	1.415	1	0.710
31	1.414	1	0.704	62	1.388	1	0.705

It is evident that the dispersion quotients shown in Table IV can be a measure of particle size only if the particles do not show selective absorption. Paine and others have found that the colloids removed from sugar products by ultrafiltration are colored, and it is reasonable to suppose that the turbidity absorbs radiation selectively, just as the coloring matter does. An inspection of Table III shows that sugars 18, 35, 56, and 61 have quality indexes of 1.005, 1.000, 1.007, and 1.000, respectively, in the green, and the total effect of the particle properties is therefore the same in all of them, and the same as in the standard sugar. Nevertheless the dispersion quotients of the filterable turbidity vary markedly, being 1.294:1:0.675, 1.485:1:0.742, 1.463:1:0.711, and 1.415:1:0.710, respectively. If the dispersion quotients were the same in these four cases, any deviations from them in other sugars would indicate variations in par-

tle size, but since they are different it must be concluded that the dispersion quotient is affected at least partly by selective absorption by the particles. With the available data it is impossible to decide to what extent either particle size or selective absorption influences the dispersion quotient, but the latter is nevertheless useful further to characterize the nature of the turbidity.

Simplified Procedures

It would be very desirable in routine work to reduce the necessary manipulations, and especially to avoid filtration altogether, if possible. Although the results presented above indicated that the chances for such simplification must be small, this question was further investigated in order to evaluate the limitations of procedures in which the color or the turbidity concentration are derived from the data obtained with the unfiltered solution alone. In this connection many relationships between C_f or $-\log T_f$ under one color screen and values based on the transmittancy and Tyndall beam intensity of the unfiltered solution, under the same and one or both of the other color filters, have been studied. Such correlations do exist, but they are not sufficiently quantitative to be of practical value. It was found, for instance, that the ratio between C_f and C_u in the green, and also that between N_u and $-\log T_u - (-\log T_f)$ in the green decrease with the quotient of C_u in the blue divided by C_u in the green. The formulas giving these relationships are:

$$\frac{C_f}{C_u} = 0.65921 \frac{C_u(\text{blue})}{C_u(\text{green})} - 0.35896 \quad (1)$$

$$\frac{N_u}{[-\log T_u - (-\log T_f)]} = 0.47851 \frac{C_u(\text{blue})}{C_u(\text{green})} + 0.07571 \quad (2)$$

These formulas make it possible to calculate either C_f or T_f in the green from T_u and R_u in the blue and green, but the precision is low, as shown by the following figures:

	I	II
Mean error, per cent	± 11.3	± 11.8
Maximum error, per cent	$+73.6$	$+62.2$
	-28.1	-25.3
No. of cases within $\pm 5\%$	19	13
10%	36	31
15%	45	45
20%	53	57
25%	56	58
30%	58	59
35%	61	60
40%	61	61
65%	61	62
75%	62	..

Similar results were found for the relation between the ratio of C_f to C_u in the green, and the dispersion quotient for $-\log T_u$ in the red and green.

Statistical analyses of all the data were also prepared, but the results were no better. In these analyses the value of $-\log T_u - (-\log T_f)$ was used as the criterion. Formulas 3, 4, 5, and 6, in which (b), (g), and (r) denote the blue, green, and red screens, respectively, are given as examples of the best correlations found:

$$[-\log T_u - (-\log T_f)](g) = 0.50821 (-\log T_u)(g) + 0.000249 (-\log T_u)(b) - 0.030625 (-\log T_u)(r) - 0.17152 \log R(g) + 0.04199 \log R(b) + 0.09818 \log R(r) + 0.0709 \quad (3)$$

$$[-\log T_u - (-\log T_f)](r) = 1.1958 (-\log T_u)(r) - 0.2955 (-\log T_u)(g) - 0.0637 R(r) - 0.0181 \quad (4)$$

$$[-\log T_u - (-\log T_f)](r) = 0.7797 (-\log R_u)(r) + 0.4738 \frac{\log R(g)}{\log R(r)} + 0.0619 \frac{\log R(b)}{\log R(r)} - 0.4640 \quad (5)$$

$$[-\log T_u - (-\log T_f)](r) = 0.9937 (-\log T_u)(r) + 1.0024 \frac{\log R(g)}{\log R(r)} + 0.02132 \frac{\log R(b)}{\log R(r)} - 0.1448 \log R(r) - 0.4245 \quad (6)$$

The precision attainable by the use of these four formulas is as follows:

	III	IV	V	VI
Mean error, per cent	±19.0	±11.3	±10.5	±11.6
Maximum error, per cent	+85.9 -29.5	+38.4 -23.1	+40.1 -33.4	+48.1 -22.8
No. of cases within ± 5%	10	17	25	19
10%	19	35	37	32
15%	32	43	44	43
20%	38	51	50	54
25%	49	58	55	58
30%	54	57	60	59
35%	55	60	61	60
40%	56	62	61	61
45%	57	..	62	61
50%	59	62
70%	60
90%	62

It is interesting to note that the precision of the turbidity for the red is somewhat better than that for the green. This is probably due to the fact that the slope of the spectral curves is much smaller at the red than at the blue end.

Summary and Conclusions

The formulas developed in the previous paper (5), for calculating the concentration of coloring matter and turbidity in a certain raw sugar from the transmittancy and Tyndall beam intensity of its solution, have been applied to 62 other raw sugars. It has been found that the results obtained by this method check with those of Balch's method only in those cases where the properties of the particles causing the turbidity are the same as in the standard sugar. Conversely, the discrepancy between the results of the two methods serves to characterize the particle properties. Determinations of the transmittancy and Tyndall beam intensity of unfiltered

and filtered solutions of raw sugars make it possible (1) to express the concentration of the filterable turbidity, $N_u - N_f$, and also of the total turbidity, N_u , in terms of an arbitrary standard turbidity particle, whereas the difference between the absorptive indexes of the unfiltered and filtered solutions represents merely an optical measure; (2) to estimate the deviation from standard particle properties by the "quality index"—i. e., the ratio between $N_u - N_f$ and the turbidity according to Balch—at one wave length, preferably in the green; and (3) to characterize the absorption quality of the particles by the ratio between $N_u - N_f$ at one wave length and that at another wave length. Value 1 above is analogous to Peters and Phelps' characterization of color concentration by the $-\log t$ at a specified wave length; values 2 and 3 correspond to the characterization of the quality of the coloring matter by the Q or R ratios. It is of course fully realized that neither the color nor the turbidity problem in sugar products can be completely solved without further fundamental knowledge of the chemical and physical properties of the constituent dispersoids present as turbidity or coloring matter, and the procedure outlined in this paper is presented merely as a step in that direction.

Literature Cited

- (1) Balch, *IND. ENG. CHEM., Anal. Ed.*, 3, 124 (1931).
- (2) Landt and Witte, *Z. Ver. deut. Zuckerind.*, 84, 450 (1934).
- (3) Peters and Phelps, *Bur. Standards Tech. Paper* 338 (1927).
- (4) Teorell, *Kolloid-Z.*, 53, 322 (1930); 54, 58, 150 (1931).
- (5) Zerban, Sattler, and Lorge, *IND. ENG. CHEM., Anal. Ed.*, 6, 178 (1934).

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An Emergency Stopper for Nitric Acid Bottles

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REQUIRING a stopper for a bottle containing 98 per cent nitric acid, the author at a venture tried using a cork covered with four thicknesses of ordinary aluminum foil, thinking it would serve for a short time at least until the acid could be transferred. After a few days, it was found that the device was in perfect condition, there being practically no corrosion of the aluminum, and the cork was thoroughly sound. Moreover, it was superior to a glass stopper, since it was air-tight, allowing no leakage of fumes which sometimes occurs with glass-stoppered bottles containing fuming nitric acid.

In order to determine the efficacy of this method in the case of weaker acid as well, a bottle holding 80 per cent acid was closed with a stopper made in the same way as the original one, four thicknesses of foil over cork, and set away with the first bottle. After six months' storage at temperatures ranging from 60° to 80° F., both stoppers were in satisfactory condition. The aluminum in the bottle containing the 98 per cent acid was bright and completely intact, although it was removed several times to withdraw acid. There was some corrosion around the upper part of the stopper, where it did not extend into the bottle, due probably to the action of diluted acid. The foil in the other bottle, containing 80 per cent acid, was dulled somewhat on its inner surface, and was corroded around the circumference, where it was in contact with the glass and remained wetted with the acid. No acid had penetrated to the cork in either case.

This suggests that ordinary bottles with aluminum-covered corks may satisfactorily replace the more expensive glass-stoppered bottles for storing commercial fuming nitric acid. The foil from certain types of candy is easily available and is satisfactory, although a foil having a somewhat greater thickness is preferable. At least four thicknesses of the thinner material should be used. At intervals, the foil may be replaced if it shows corrosion.

The corrosion of aluminum by nitric acid is less the stronger the acid. Dilute acid attacks aluminum rather easily, so it is advised that the stopper be not used for acid weaker than 80 per cent, although it will serve for a short time. Eighty per cent acid in direct contact with aluminum penetrates the metal at the rate of about 0.006 inch per year, while 95 per cent acid penetrates about 0.0025 inch per year (1). The slight corrosion of aluminum in contact with the vapor of nitric acid from mixtures containing up to 20 per cent or more water is probably due to a relatively low water concentration in the vapor. Mixed nitrating acid could be stored in bottles stoppered with aluminum without trouble, since the vapors from such acid consist of nearly anhydrous nitric acid, even if the water concentration in the mixture is as high as 25 per cent.

Literature Cited

- (1) Frary, *IND. ENG. CHEM.*, 26, 1231 (1934).

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Determination of Arsenic in Coal

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THE arsenic content of coal has received very little attention in the United States, and few of the procedures for the determination of arsenic in various materials are suited to the analysis of coal. The Bureau of Mines therefore undertook to develop a specific method for the determination of arsenic in coal.

It seemed desirable to titrate the arsenic with some standard solution whose arsenic equivalent could be determined easily, rather than to depend on stains or mirrors that require considerable preliminary standardization before determinations on unknown samples can be made. As the arsenic content of coal is small, the usual titration methods applied to ores containing large amounts of arsenic would not be applicable without considerable modification. However, the method of Archbutt and Jackson (1) for the determination of arsenic in coke appeared to be well suited to the analysis of coal.

Method of Archbutt and Jackson

Fifty grams of coke are digested with 100 cc. of hot concentrated nitric acid for at least 2 hours to extract the arsenic. Coal reacts so violently with nitric acid that the acid must be added in small portions and heated cautiously. The mixture is diluted and filtered and the residue discarded. The filtrate is evaporated to dryness, taken up with water and sulfuric acid, and evaporated to sulfuric acid fumes to drive off the nitric acid. The residue is then taken up with water and repeatedly evaporated to sulfuric acid fumes to remove the last traces of nitric acid.

The solution is placed in a distilling flask with ferrous sulfate and sodium chloride and the arsenic distilled off as arsenous chloride. The arsenous chloride and hydrogen chloride are caught in a small volume of water to which zinc sulfide is added to precipitate the arsenic as arsenous sulfide. The bright-yellow precipitate is a good qualitative test for the presence of arsenic. It is seen more easily if hydrogen sulfide is used instead of zinc sulfide, but the zinc sulfide takes less time to precipitate the arsenic completely. This precipitate is filtered off and dissolved by boiling in water. The resulting solution is concentrated, cooled, and titrated with 0.01 *N* iodine.

The Archbutt and Jackson method is accurate to within 0.0005 per cent of arsenous oxide. This is satisfactory for high-arsenic coals, but virtually all the American coals investigated contained less than 0.002 per cent of arsenous oxide, for which a more sensitive method was necessary.

Method Based on Gutzeit Test

The most accurate methods for estimating extremely small amounts of arsenic are the Gutzeit and the Marsh tests, both depending on the liberation of the arsenic as arsine. Of these the Gutzeit seems to be more practicable for use in the average chemical laboratory. It can easily detect 0.000001 gram of arsenous oxide, as this amount will produce a stain 0.3 cm. (0.125 inch) long.

The methods of decomposing and preparing samples for the Gutzeit test are numerous, and several of those recommended for coal have been tested. One is similar to that used by Archbutt and Jackson—the sample of finely powdered coal is digested with concentrated nitric acid and the nitric acid expelled by fuming with sulfuric acid.

In other methods the coal is digested with both nitric and sulfuric acids, but in all of them the nitric acid is eliminated by fuming with sulfuric acid. It is assumed that virtually no arsenic is lost during this fuming process; however, the results of a number of the bureau's experiments indicate that

this assumption is incorrect. The amount lost would be of little consequence were it not for the fact that the arsenic content of coal is usually a few ten-thousandths of 1 per cent. It seemed desirable, therefore, to eliminate the use of nitric acid and avoid fuming.

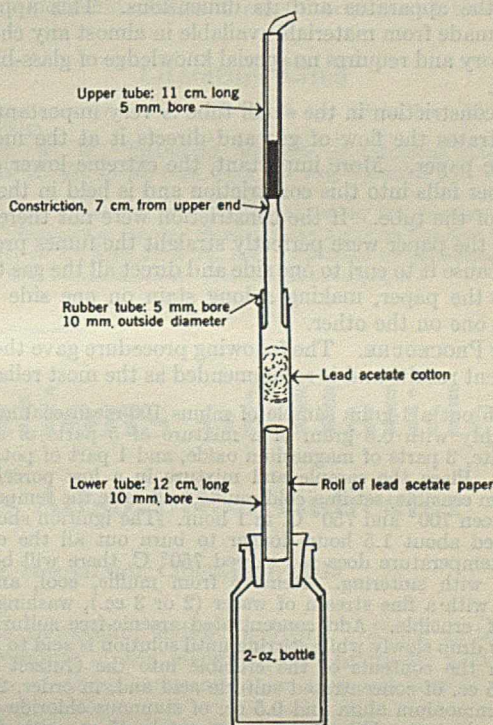


FIGURE 1. APPARATUS FOR GUTZEIT TEST

Nitric acid is also objectionable because of its noxious fumes and copious foaming, which make treatment of the mixture difficult in any vessel of reasonable size. Even after the coal is filtered off, the filtrate is likely to foam and cause trouble throughout the test. Foaming is especially undesirable in a Gutzeit bottle.

A procedure in which the carbonaceous matter is burned off and foaming thereby eliminated is more practicable. Some investigators have ignited coal with lime, sodium carbonate, or similar substances, relying on these reagents to retain the arsenic during ignition. The ash is then extracted with nitric acid and the nitric acid eliminated by fuming with sulfuric acid. In the method finally adopted in this investigation the residue after ignition was treated direct with sulfuric acid, so that there was no nitric acid to remove.

Method Developed

The procedure developed, although similar to many given in the literature, is an attempt to bring together the best features of all.

APPARATUS. The apparatus used is almost the same as that described by Scott (2) but is a little easier to make. To bore a straight hole through a very small rubber stopper is rather difficult, so the two tubes are joined with a small piece of rubber tubing. The constriction in the lower tube is not absolutely necessary and so has been eliminated. Figure 1

TABLE I. RECOVERY OF ARSENIC

Run	1	2	3	4
Coal used, gram	1	1	1	1
As ₂ O ₃ added, per cent	None	None	0.0005	0.0005
As ₂ O ₃ found, per cent	0.0004	0.0004	0.0009	0.0009

TABLE II. RECOVERY OF ARSENIC

Run	1	2	3	4
Coal used, gram	1	1	1	1
As ₂ O ₃ added, per cent	None	None	0.0005	0.0005
As ₂ O ₃ found, per cent	0.0005	0.0005	0.0010	0.0009

shows the apparatus and its dimensions. This apparatus can be made from materials available in almost any chemical laboratory and requires no special knowledge of glass-blowing technic.

The constriction in the small tube is very important, as it concentrates the flow of gas and directs it at the mercuric bromide paper. More important, the extreme lower end of the paper falls into this constriction and is held in the exact center of the tube. If the constriction were not there, even though the paper were perfectly straight the fumes probably would cause it to curl to one side and direct all the gas to that side of the paper, making a long stain on one side and a shorter one on the other.

TEST PROCEDURE. The following procedure gave the most consistent results and is recommended as the most reliable:

Weigh out a 1-gram sample of minus 100-mesh coal and mix thoroughly with 0.8 gram of a mixture of 5 parts of sodium carbonate, 3 parts of magnesium oxide, and 1 part of potassium nitrate. Place the sample and mixture in a low porcelain or platinum crucible, set in a cold muffle, and raise the temperature to between 700° and 750° C. in 1 hour. The ignition should be continued about 1.5 hours longer to burn out all the carbon. If the temperature does not exceed 750° C. there will be little trouble with sintering. Remove from muffle, cool, and wet residue with a fine stream of water (2 or 3 cc.), washing down sides of crucible. Add concentrated arsenic-free sulfuric acid drop by drop slowly while stirring until solution is acid to litmus.

Wash the contents of the crucible into the Gutzeit bottle. Add 3.5 cc. of concentrated sulfuric acid and, in order, 2 cc. of ferric ammonium alum and 0.5 cc. of stannous chloride from a graduated pipet. Dilute to approximately 45 cc. with distilled water, stir until thoroughly mixed, and place bottle in pan of water at approximately 25° C. Load the lower tube with a roll of lead acetate paper and lead acetate cotton, connect apparatus, and place mercuric bromide paper in the upper tube. Place two pieces of stick zinc in the bottle and cork immediately with the upper part of the apparatus. After 50 to 60 minutes remove the test paper, dip in melted paraffin, and compare with standards.

STANDARD STAINS. In preparing the standard stains add the arsenic solution, dilute with a little water, add 3 cc. of concentrated sulfuric acid, instead of 3.5 cc. as for the samples, and then add the other reagents as described. Standard stains should be made for 0.000, 0.002, 0.004, 0.006, 0.008, 0.010, 0.013, and 0.017 mg. of arsenic trioxides. The stains should be dipped in melted paraffin, not too hot, for a second and then cooled. They may be mounted on a piece of cardboard and kept in a calcium chloride desiccator in a dark place when not in use. The standard will fade gradually with time, but may be photographed to exact size and the print used in place of the stains. With a little practice the reading can be made as accurately as with standard stains, and the print will last indefinitely. Curves plotted through the tops of the stains can be used in place of a set of standards. The effect of ammonium hydroxide and hydrochloric acid in developing the stain was tested but was not thought to have any practical value.

Discussion of Results

Duplicate determinations by this method checked very well, but failed to prove that no arsenic was lost by volatilization.

It seemed reasonable to suppose that any method capable of retaining arsenous oxide added in the form of a standard solution would be likely to hold arsenic in any other form in the coal. A sample of Black Creek coal analyzing 1.56 per cent ash, 0.64 per cent sulfur, and 0.25 per cent iron was selected for the test. As the coal was of high purity, the effect of a large amount of inorganic matter was eliminated. Duplicate determinations were made with and without addition of arsenic. The results are given in Table I, and show that all the arsenic added was obtained and recovered.

The same experiment was repeated with a Montana coal analyzing 11.72 per cent ash, 1.22 per cent sulfur, and 1.02 per cent iron, to see if the results were equally satisfactory where the inorganic matter was relatively high. The results shown in Table II indicate that all the arsenic is retained and that all of it can be recovered by the Gutzeit test.

Table III gives the results of duplicate determinations on a number of coals for fixed and total arsenic by the Gutzeit method and shows how closely the results may be expected to check. Fixed arsenic is the arsenic found in the coal after it has been ashed without anything added to retain the arsenic. Duplicate runs by the method of Archbutt and Jackson are also shown and check the Gutzeit method very well within the limits of their error, which is certainly not greater than 0.0005 per cent.

TABLE III. COMPARISON OF DUPLICATE ANALYSES OBTAINED BY GUTZEIT AND ARCHBUTT-JACKSON METHODS

Sample	Bed	State	Method of Analysis		
			Modified Gutzeit Fixed As ₂ O ₃	Gutzeit Total As ₂ O ₃	Archbutt and Jackson Total As ₂ O ₃
			%	%	%
1	Jefferson	Ala.	0.0130	0.0140	0.0143
			0.0120	0.0140	0.0139
2	Black Creek	Ala.	0.0004	0.0004	0.0002
			0.0004	0.0004	0.0002
3	Corona	Ala.	0.0007	0.0007	0.0005
			0.0007	0.0007	0.0005
4	Mary Lee	Ala.	0.0015	0.0015	0.0011
			0.0015	0.0015	0.0011
5	Pittsburgh	Pa.	0.0007	0.0014	0.0009
			0.0010	0.0012	0.0013
6	Alma	W. Va.	0.0005	0.0008	0.0006
			0.0006	0.0007	0.0003
7	No. 6	Ill.	0.0007	0.0013	0.0010
			0.0007	0.0013	0.0011
8	Weir-Pittsburgh	Kans.	0.0007	0.0014	0.0010
			0.0007	0.0014	0.0005
9	Bear Creek	Mont.	0.0004	0.0009	0.0005
			0.0004	0.0009	0.0003
10	No. 3	Iowa	0.0008	0.0020	0.0026
			0.0012	0.0022	0.0023
11	Wadge	Colo.	Trace	0.0001	0.0002
			Trace	0.0001	0.0002
12	No. 9	Ky. (western)	0.0008	0.0015	0.0012
			0.0008	0.0015	0.0012
13	Pittsburgh	W. Va.	0.0006	0.0011	0.0003
			0.0007	0.0009	0.0004
14	Lexington	Mo.	0.0014	0.0016	0.0021
			0.0006	0.0018	0.0020

TABLE IV. SUMMARY OF ANALYSES IN ORDER OF INCREASING ARSENIC CONTENT^a

Sample	Bed	State	Fixed	Total	Iron	Sulfur	Ash
			As ₂ O ₃	As ₂ O ₃			
			%	%	%	%	%
11	Wadge	Colo.	Trace	0.0001	0.19	0.45	7.29
2	Black Creek	Ala.	0.0004	0.0004	0.25	0.64	1.56
3	Corona	Ala.	0.0007	0.0007	0.91	1.98	8.54
6	Alma	W. Va.	0.0006	0.0008	0.86	1.70	5.62
9	Bear Creek	Mont.	0.0004	0.0009	1.02	1.22	11.72
13	Pittsburgh	W. Va.	0.0007	0.0010	1.23	2.76	7.35
5	Pittsburgh	Pa.	0.0009	0.0013	0.82	1.55	6.37
7	No. 6	Ill.	0.0007	0.0013	2.64	4.47	10.48
8	Weir-Pittsburgh	Kans.	0.0007	0.0014	2.10	3.29	7.28
4	Mary Lee	Ala.	0.0015	0.0015	1.23	1.36	15.12
12	No. 9	Ky. (western)	0.0008	0.0015	2.82	4.44	14.50
14	Lexington	Mo.	0.0010	0.0017	2.95	4.76	19.46
10	No. 3	Iowa	0.0010	0.0021	5.02	7.17	19.12
1	Jefferson	Ala.	0.0130	0.0140	2.37	3.35	6.79

^a Arsenic determinations by modified Gutzeit method.

Table IV summarizes the analyses of all the samples tested in the order of increasing total arsenic. The arsenic does not increase in direct proportion to iron, sulfur, or ash, although there seems to be a general trend in that direction. However, as shown in Table V, in general the arsenic content increases as the other inorganic constituents increase.

TABLE V. AVERAGE ANALYSES OF GROUPS TAKEN FROM TABLE IV

Number of Samples Averaged	Total As ₂ O ₃ %	Iron %	Sulfur %	Ash %
2	0.0003	0.22	0.55	4.43
4	0.0009	1.01	1.92	8.31
4	0.0014	1.70	2.67	9.81
4	0.0048	3.29	4.93	14.97

Good checks in arsenic analyses were obtained with 1-gram samples of minus 100-mesh coal. For the high-arsenic Jefferson coal 0.1-gram samples were used satisfactorily. One cube of arsenopyrite which would just pass the opening in a 100-mesh screen would add 0.001 per cent of arsenous oxide to a 1-gram sample.

However, most of the analyses check within 0.0003 per cent, indicating that the arsenic is probably diffused in extremely fine particles throughout the coaly substance and is not concentrated in particles of arsenopyrite of any appreciable size.

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Literature Cited

- (1) Archbutt, L., and Jackson, P. B., *J. Soc. Chem. Ind.*, 20, 448-50 (1901).
- (2) Scott, W. W., "Standard Methods of Chemical Analysis," 4th ed., pp. 46-52, New York, D. Van Nostrand Co., 1925.

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Volumetric Determinations of Halides

Use of Dichlorofluorescein as an Adsorption Indicator

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ADSORPTION indicators for the argentometric determination of halides were suggested by Fajans and his collaborators (3, 4); and Kolthoff, Lauer, and Sunde (5) chose dichlorofluorescein as the most suitable substance for the purpose. They gave the results obtained with dichlorofluorescein in the argentometric titration of chlorides, and indicated that equally satisfactory results could be expected in the titration of bromides and iodides. Their work is mentioned in a recent textbook (7) on quantitative analysis, which stresses the value of their method only in the determination of chloride. Osterberg (8) used dichlorofluorescein as an adsorption indicator for the estimation of chlorides in the blood, carrying out the titrations in an acetone-water solution. During the past two years dichlorofluorescein has been used in these laboratories in many routine titrations with complete satisfaction. This paper will describe the use of the indicator for the analysis of organic hydrochlorides in alcohol solutions, and will give analytical data concerning the argentometric titration of bromides and iodides.

The chlorine analysis of Diothane (piperidinopropanediol diphenylurethan hydrochloride, 1, 9), a new local anesthetic, is an important control test. It is desirable to carry out such analytical work on Diothane with the sample in alcohol solution, and it was found that dichlorofluorescein is as satisfactory an indicator in 75 per cent alcohol solutions as in aqueous solutions. Other organic hydrochlorides prepared in the Merrell research laboratories and some anesthetics on the market have also been analyzed in this way.

Halogen determinations on many inorganic compounds have been carried out with dichlorofluorescein as the indicator; among them may be mentioned ammonium chloride, ammonium bromide, ammonium iodide, sodium chloride, sodium bromide, sodium iodide, calcium bromide, potassium

bromide, potassium iodide, mercuric chloride (after previous removal of the mercury), and hydriodic acid. The analyses of these inorganic salts were all carried out in aqueous solution.

Titration of Organic Hydrochlorides

The 0.05 *N* silver nitrate solution used was standardized against dried pure sodium chloride (Mallinckrodt analytical reagent) with the following procedure:

Approximately 0.12 gram of the sodium chloride was weighed and dissolved in 80 cc. of 75 per cent alcohol, 8 drops of dichlorofluorescein solution (0.1 per cent Eastman indicator, catalog No. 373, in 70 per cent alcohol) were added, and the solution was titrated with the silver nitrate until the coagulated silver chloride precipitate acquired a distinct pink color. This pink color on the silver chloride was taken as the end point; the addition of a few more drops of the 0.05 *N* silver nitrate caused a pink color through the entire solution.

TABLE I. TYPICAL TITRATIONS

NaCl Grams	AgNO ₃ Solution Cc.	Normality of AgNO ₃ Solution
0.1171	40.40	0.04959
0.1195	41.22	0.04958
0.1187	40.95	0.04959
0.1184	40.93	0.04950

In Diothane analyses a sample of about 0.85 gram was dissolved in 80 cc. of 75 per cent alcohol and the titration was carried out with the 0.05 *N* silver nitrate solution in the manner described above. Some results are: 8.17 per cent chlorine, 4 batches (Nos. 67751, 67977, 68131, 68593); 8.18 per cent chlorine, 2 batches (Nos. 67369, 68362); 8.16 per cent chlorine, 1 batch (No. 67934); theoretical, 8.17 per cent chlorine.

Other organic hydrochlorides analyzed are:

α -Methylpiperidinopropanediol diphenylurethan hydrochloride, 8.01 per cent chlorine; theoretical, 7.92 per cent chlorine.

α -Piperidino-*n*-propylphenylcarbamate hydrochloride, 11.82 per cent chlorine; theoretical, 11.87 per cent chlorine.

Procaine hydrochloride, 13.07 per cent chlorine; theoretical, 13.05 per cent chlorine.

Titration of Bromides and Iodides

Samples of ammonium bromide, sodium bromide, and potassium iodide were analyzed for halogen with silver nitrate solution and dichlorofluorescein and the results compared with those obtained on the same samples with the standard Volhard method. The 0.05 *N* silver nitrate solution was gravimetrically standardized, and the 0.03 *N* potassium thiocyanate solution used in the Volhard titrations was standardized against the 0.05 *N* silver nitrate solution, with ferric alum as the indicator. The procedure used in the Volhard titrations was essentially that described in the United States Pharmacopoeia (10), except for the weights of sample and strengths of the standard solutions employed. The procedure used in the dichlorofluorescein titrations was the same as that described for the determination of chlorine in Diothane, except that the titrations were carried out in aqueous solution and that samples of about 0.2 gram of the bromides and 0.3 gram of the potassium iodide were used. These titrations were carried out in neutral or almost neutral solutions; strong light was avoided, as darkening of the silver halide precipitates made the end point more difficult to detect.

TABLE II. TITRATION OF BROMIDE AND IODIDES

	Bromine		Iodine in Potassium iodide
	Sodium bromide	Ammonium bromide	
	%	%	%
Dichlorofluorescein method	77.96	82.13	76.74
Volhard method	77.93	82.11	76.73
Theoretical	77.66	81.59	76.45

These salts were all of U. S. P. quality; their deviations from theoretical halide content were due to the fact that they were not of reagent purity.

Discussion

Dichlorofluorescein is a satisfactory adsorption indicator for the argentometric titration of halides. Results of bromide and iodide titrations using this indicator compare favorably with those obtained with the standard Volhard method, but are usually slightly higher than those of the corresponding Volhard determinations; this can be expected from a consideration of the principles involved in the two methods. In one case, a slight excess of silver nitrate solution causes the dichlorofluorescein to be adsorbed on the silver halide particles and form its silver salt, which furnishes the end point; in the Volhard procedure, a slight excess of the thiocyanate solution produces the end point; since this excess of thiocyanate is subtracted from the quantity of silver nitrate solution added, the results should be slightly lower than in the titration in which dichlorofluorescein was used. Since only one standard solution need be used and no filtration is

necessary, a determination employing dichlorofluorescein as the indicator can be carried out in less time than one in which the Volhard method is followed. Possible errors due to selective adsorption of the excess silver nitrate on the silver chloride precipitate and the filter paper in the Volhard procedure are eliminated, and chances of manipulative error are lessened.

The speed, accuracy, and broadness of application of this procedure indicate that it may prove of value in determinations of un-ionized halogen in which the treatment of the sample during the analysis forms the corresponding sodium halide. Such an application may be seen in the modification of the Stepanow method proposed by Cook and Cook (2), in which the sample is digested with absolute alcohol and metallic sodium, resulting in the formation of sodium halide in the reaction mixture. The titration liquid would then contain the sodium halide, among other things, in an alcohol-water solution; and, as has been shown in this paper, dichlorofluorescein is a suitable indicator for such titrations. Other applications may lie in the sodium peroxide fusion method for organic halogen (6) or in the liquid ammonia-sodium process (11), in which the sample is dissolved in liquid ammonia, treated with sodium, and the sodium halide determined. In the latter method Vaughn and Nieuwland used both the Fajans procedure, with eosin as an indicator, and the Volhard method for their titrations.

Since the completion of this manuscript a new paper (5a) by Kolthoff has discussed the theory of adsorption indicators in some detail.

Summary

Dichlorofluorescein has been used as an adsorption indicator in the argentometric titration of organic hydrochlorides dissolved in alcohol, and inorganic halides in alcohol or aqueous solutions. The analytical results have been within experimental error of the theoretical values on pure chemicals or of values obtained by the standard Volhard procedure on chemicals of ordinary commercial purity. Possible further applications of the method have been suggested.

Literature Cited

- (1) Am. Med. Assoc., *J. Am. Med. Assoc.*, 103, 1777-8 (1934).
- (2) Cook, W. A., and Cook, Kathryn, *IND. ENG. CHEM., Anal. Ed.*, 5, 186 (1933).
- (3) Fajans and Hassel, *Z. Elektrochem.*, 29, 495 (1923).
- (4) Fajans and Wolf, *Z. anorg. allgem. Chem.*, 137, 221 (1924).
- (5) Kolthoff, I. M., Lauer, W. M., and Sunde, C. J., *J. Am. Chem. Soc.*, 51, 3273 (1929).
- (5a) Kolthoff, I. M., *Chem. Rev.*, 16, 87 (1935).
- (6) Lemp, J. F., and Broderson, H. J., *Ibid.*, 39, 2069 (1917).
- (7) Mitchell and Ward, "Modern Methods in Quantitative Chemical Analysis," pp. 9, 57, New York, Longmans, Green and Co., 1932.
- (8) Osterberg, A. E., *Proc. Staff Meetings Mayo Clinic*, 5, 300 (1930).
- (9) Rider, T. H., *J. Am. Chem. Soc.*, 52, 2115 (1930).
- (10) U. S. Pharmacopoeia X, p. 439.
- (11) Vaughn, T. H., and Nieuwland, J. A., *IND. ENG. CHEM., Anal. Ed.*, 3, 274 (1931).

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GOLD-COBALT ALLOYS NOT ENTIRELY SUITABLE FOR HIGH-GRADE RESISTANCE STANDARDS. Tests recently made at the National Bureau of Standards on alloys of gold and cobalt to determine their suitability for use in the construction of resistance standards show that, while some of these alloys are reasonably stable in resistance and have very small temperature coefficients of electrical resistance, their thermoelectric power against copper is very large. For this reason the bureau believes that they are inferior to gold-chromium alloys of about the same proportions.

This conclusion is important since the unit of electrical resistance is maintained in the national standardizing laboratories by means of wire-wound standards. The national laboratories are interested in improving the quality of these standards, either by improved methods of construction or by the development of better resistance alloys.

Besides stability, resistance alloys should have a low-temperature coefficient of resistance and a low thermo-electric power against copper.

Digesting Biological Materials for Calcium and Phosphorus Analysis

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IT IS OFTEN necessary to make both calcium and phosphorus determinations on biological materials, particularly in vitamin D studies where the calcium and phosphorus ratio is of importance. In most cases it has been customary to prepare samples separately for the determination of the two elements, especially where the percentage of phosphorus in a material is high.

A rapid method of removing organic matter which will permit the determination of both calcium and phosphorus in the digest permits a saving of time on the part of the analyst and a saving of equipment and reagents to the laboratory. The following procedure is adapted to plant and animal material and has been found to give excellent results on such materials as feed concentrates, feces, and grasses. It should also be possible to determine mineral elements such as iron, magnesium, and others not forming insoluble perchlorate salts on this digest.

Procedure

Weighed samples of suitable size are placed in 500-ml. Kjeldahl flasks. Twenty to 30 ml. of concentrated nitric acid are added and the flasks are placed on asbestos gauzes over medium flames. The contents are boiled gently with frequent mixing until the samples pass into a semi-colloidal solution. The particles of material become swollen and gel-like, then disintegrate, producing a finer suspension or a solution. Experience will indicate at what time this occurs, and the speed of the digestion may be accelerated materially by determining the length of time required for the material being analyzed to reach this stage. For the materials reported in this paper the flames were so adjusted that the treatment took 30 to 45 minutes. Heating to dryness must be avoided.

Ten milliliters of 70 per cent perchloric acid are now added to each and the flasks are placed over free flames. Very low flames are necessary during the perchloric acid oxidation; best results are obtained when just sufficient heat is applied to keep the solution boiling. Only a fine point of the flame should impinge on the flask. Higher temperatures tend to drive off the perchloric acid without materially accelerating oxidation.

When fuming begins, the flame is so adjusted that only a trace of the perchloric acid fumes reaches the upper region of the Kjeldahl neck. The heating is continued until the solution is practically colorless or only a faint yellow color remains. The solution is allowed to cool slightly and 50 ml. of distilled water are added. Vigorous boiling occurs which drives out the remaining nitrogen dioxide fumes, leaving a clear solution.

The solution is filtered into a volumetric flask, and the Kjeldahl is thoroughly washed with distilled water. When the solution has cooled it is made to volume and aliquots are taken for analysis. Calcium and phosphorus determinations may be completed by the usual procedures.

Results

Data reported have been obtained by official methods (1). In the comparisons reported duplicate samples were digested by the proposed method and at the same time duplicate samples were prepared according to official methods. The comparisons are given in Tables I and II. A plus sign indicates that results by the proposed method are higher, while a minus sign indicates that they are lower than the results by official methods of preparing the sample. A and B indicate duplicate digestions. Results by the two methods agree closely and the differences are essentially the same as differences between duplicates by the same digestion method.

TABLE I. CALCIUM DETERMINATIONS

Digested with Nitric and Perchloric Acids				Ashed				Diff. between Acid Digestion and Ashing %
A %	B %	Diff. %	Av. %	A %	B %	Diff. %	Av. %	
In Pasture Grass Volumetric Method								
0.94	0.93	0.01	0.94	0.93	0.93	0.00	0.93	+0.01
1.03	1.00	0.03	1.02	1.03	1.04	0.01	1.04	-0.02
0.98	0.98	0.00	0.98	0.97	0.99	0.02	0.98	0.00
1.07	1.08	0.01	1.08	1.06	1.08	0.02	1.07	+0.01
0.85	0.85	0.00	0.85	0.87	0.88	0.01	0.88	-0.03
0.87	0.89	0.02	0.88	0.88	0.84	0.04	0.86	+0.02
0.52	0.53	0.01	0.53	0.48	0.48	0.00	0.48	+0.05
0.57	0.59	0.02	0.58	0.57	0.56	0.01	0.57	+0.01
0.46	0.48	0.02	0.47	0.48	0.48	0.00	0.48	-0.01
0.34	0.33	0.01	0.34	0.34	0.34	0.00	0.34	0.00
In Poultry Feces, Volumetric Method								
0.67	0.72	0.05	0.70	0.73	0.69	0.04	0.71	-0.01
0.73	0.72	0.01	0.73	0.67	0.70	0.03	0.69	+0.04
3.87	3.89	0.02	3.88	3.89	3.82	0.07	3.86	+0.02
3.48	3.45	0.03	3.47	3.48	3.48	0.00	3.48	-0.01
3.56	3.56	0.00	3.56	3.51	3.53	0.02	3.52	+0.04
3.29	3.34	0.05	3.32	3.38	3.38	0.00	3.38	-0.06
3.56	3.57	0.01	3.57	3.61	3.57	0.04	3.59	-0.02
3.38	3.34	0.04	3.36	3.20	3.38	0.18	3.29	+0.07
3.24	3.23	0.01	3.24	3.20	3.25	0.05	3.23	+0.01
3.74	3.74	0.00	3.74	3.81	3.79	0.02	3.80	-0.06
3.29	3.27	0.02	3.28	3.25	3.25	0.00	3.25	+0.03
3.34	3.39	0.05	3.37	3.38	3.49	0.11	3.42	-0.05
In Poultry Feeds, Volumetric Method								
1.48	1.48	0.00	1.48	1.48	1.50	0.02	1.49	-0.01
2.27	2.30	0.03	2.29	2.28	2.24	0.04	2.26	+0.03
1.98	2.00	0.02	1.99	1.98	1.94	0.04	1.96	+0.08
1.90	1.94	0.04	1.92	2.00	1.99	0.01	2.00	0.00
1.70	1.73	0.03	1.72	1.86	1.88	0.02	1.87	-0.09
2.44	2.44	0.00	2.44	2.42	2.46	0.04	2.44	0.00
0.29	0.27	0.02	0.28	0.20	0.21	0.01	0.21	+0.06
0.20	0.26	0.05	0.24	0.22	0.26	0.04	0.24	0.00
0.20	0.25	0.05	0.23	0.24	0.28	0.04	0.26	-0.03
0.25	0.25	0.00	0.25	0.26	0.27	0.01	0.27	-0.02
3.23	3.24	0.01	3.24	3.17	3.19	0.02	3.18	+0.06

TABLE II. PHOSPHORUS DETERMINATIONS

Aliquots from Solutions Prepared for Calcium				Digested with Hydrochloric and Nitric Acids				Difference in Two Methods %
A %	B %	Diff. %	Av. %	A %	B %	Diff. %	Av. %	
In Pasture Grass, Volumetric Method								
0.50	0.50	0.00	0.50	0.59	0.59	0.00	0.59	-0.09
0.35	0.35	0.00	0.35	0.35	0.39	0.04	0.37	-0.02
0.44	0.44	0.00	0.44	0.47	0.47	0.00	0.47	-0.03
0.48	0.48	0.00	0.48	0.45	0.44	0.01	0.45	-0.03
0.46	0.47	0.01	0.47	0.45	0.44	0.01	0.45	+0.02
0.44	0.43	0.01	0.44	0.44	0.44	0.00	0.44	0.00
0.63	0.63	0.00	0.63	0.55	0.54	0.01	0.55	+0.08
0.67	0.67	0.00	0.67	0.64	0.64	0.00	0.64	+0.03
0.58	0.59	0.01	0.59	0.56	0.55	0.01	0.56	+0.03
0.51	0.52	0.01	0.52	0.53	0.53	0.00	0.53	-0.01
In Poultry Feces, Gravimetric Method								
0.98	0.98	0.00	0.98	0.96	0.94	0.02	0.95	+0.03
1.08	1.10	0.02	1.09	1.06	1.11	0.05	1.09	0.00
1.53	1.54	0.01	1.54	1.51	1.51	0.00	1.51	+0.03
1.50	1.50	0.00	1.50	1.49	1.55	0.05	1.52	-0.02
1.48	1.51	0.03	1.50	1.49	1.46	0.03	1.48	+0.02
1.49	1.48	0.01	1.49	1.52	1.54	0.02	1.53	-0.04
1.59	1.59	0.00	1.59	1.49	1.63	0.14	1.56	+0.03
1.52	1.52	0.00	1.52	1.57	1.60	0.03	1.58	-0.06
1.51	1.49	0.02	1.50	1.60	1.54	0.06	1.57	-0.07
1.62	1.57	0.05	1.60	1.55	1.59	0.04	1.57	+0.03
1.68	1.66	0.02	1.67	1.60	1.66	0.06	1.63	+0.04
1.61	1.61	0.00	1.61	1.52	1.53	0.01	1.63	+0.08
In Poultry Feeds, Gravimetric Method								
Digested with Nitric and Sulfuric Acids and Sodium Nitrate								
0.52	0.51	0.01	0.52	0.52	0.58	0.06	0.56	-0.04
0.99	1.01	0.02	1.00	0.96	0.84	0.12	0.90	+0.10
0.97	0.98	0.01	0.98	0.92	0.91	0.01	0.92	+0.06
1.00	1.00	0.00	1.00	0.97	0.95	0.02	0.96	+0.04
1.00	0.99	0.01	1.00	0.92	0.87	0.05	0.90	+0.10
1.11	1.08	0.03	1.10	1.06	1.11	0.05	1.09	+0.01
1.18	1.17	0.01	1.18	1.12	1.14	0.02	1.13	+0.05
0.57	0.56	0.01	0.56	0.61	0.61	0.00	0.61	-0.05
0.51	0.51	0.00	0.51	0.53	0.59	0.06	0.56	-0.05
0.55	0.51	0.04	0.53	0.61	0.51	0.10	0.56	-0.03
0.55	0.55	0.00	0.55	0.52	0.50	0.02	0.51	+0.04
2.30	2.29	0.01	2.30	2.25	2.16	0.09	2.21	+0.09

Discussion

Four-gram samples of pasture grass were digested in order to get sufficient calcium and phosphorus for the determinations. The time for digestion was about 1.5 hours. Two-gram samples of feed and feces were digested in 1.25 hours. When large amounts of potassium were present in the sample, more perchloric acid was required because of precipitation of potassium perchlorate.

The digestion is not difficult to conduct, but care must be taken that the sample is not boiled to dryness. Maximum speed of digestion will be obtained by noting carefully the time required for the nitric acid to emulsify the material. Insufficient heat tends to make the digestion lengthy, while excess heat boils off the nitric acid before its maximum effect is obtained. It is not advisable, therefore, to boil the nitric acid over a free flame. Best results, together with rapid digestion, were obtained by placing the flask on an asbestos

gauze over a gas flame in a Kjeldahl digestion rack and turning on a full flame.

The digestion produces a clear solution in a short time, thus effecting a saving of time and apparatus when both calcium and phosphorus are to be determined on the same material. It is much more rapid than ashing and may therefore prove more efficient even when calcium or other elements alone are to be determined. Iron, magnesium, and other elements not forming insoluble perchlorate salts might also be determined on the digest.

Literature Cited

- (1) Assoc. Official Agr. Chem., *Official and Tentative Methods*, 3rd ed., 1930.

RECEIVED March 22, 1935. This work was begun by the author while with the Division of Dairy Husbandry. Scientific Paper No. 310, College of Agriculture and Experiment Station, State College of Washington.

Impurities in White Sugars

VIII. Effects of Some Impurities on Decomposition of Sucrose during the Barley Candy Test

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Results obtained in the barley candy test for quality of sugar, a detailed description of which is given, are subject to variation due to slight differences in the routine of different operators, to differences in rate and duration of heating, and to different thermal properties of different pieces of apparatus. However, the results of a series of tests made by an experienced operator using the same utensils are comparable among themselves.

The effects of various salts and organic substances which may be present in white sugars were studied by making the candy test on a very pure standard sugar to which the nonsugar was added in known proportions. From the analyses of these candies it is seen that the nonsugars fall into three major groups: those of Group I increase the inversion of sucrose but inhibit caramelization or are without effect on either; those of Group II tend to inhibit inversion but increase the amount of caramelization;

and those of Group III increase both the inversion and degree of caramelization. The auto-inversion of sucrose and the different effects of the nonsugars on the decomposition of sucrose during the candy test are explained by evidence showing that sucrose acquires an enhanced acidic nature at high temperatures and, together with its decomposition products, reacts with the nonsugars present in the sirup, causing greater inversion and less caramelization when the resultant hot sirups are acidic in reaction and less inversion and greater caramelization when they are alkaline in reaction. The increase in both inversion and caramelization in the presence of the nonsugars of Group III, which are acidic in reaction, is due to secondary reactions of the particular nonsugar with the invert sugar and other degradation products formed from the sucrose during the test. Salts of volatile or unstable acids react as alkaline salts.

IT HAS long been a matter of general experience, especially among manufacturers of food products, that some commercial white sugars, when subjected to the elevated temperatures required in many processes, withstand the heating with less discoloration or with the formation of less invert sugar than others. Therefore there arose the practice of testing samples of new or prospective purchases of sugar (25) by quick, practical tests, the conditions of which approximate those to which the sugar would be subjected

during the making of the finished food product. The cause of such variations in stability of different lots of sugar is ascribed to the effects of the impurities, or nonsugars, contained in small amounts in the white sugar, and hence it becomes of interest to know the effects of the commonly occurring nonsugars on the heat-resisting qualities of sucrose.

The practical tests developed for this purpose are of two types, the caramelization test, in which the dry sugar is heated, and the so-called "barley candy" test, in which a

small batch of hard candy is made from the sugar and water. The former is extensively used in Europe, where various modifications have been advanced from time to time. These were comprehensively studied by Pucherna (33), who proposed a standardized technic which he claims will yield reproducible results and which he used to study the effects of various nonsugars on a standard sugar. In this country, however, the barley candy test originally devised by Samuel C. Hooker of the American Sugar Refining Company (28) is generally used, because it more nearly approximates the actual conditions under which the sugar is to be used. To obtain reproducible results in either type of test, rigorously uniform conditions of rate and duration of heating and careful control of all factors in any way influencing these conditions must be maintained.

In the barley candy test, the personal variations of manipulation by different individuals in the timing and sequence of the motions necessary for carrying out the test have so great an influence on the candy produced that absolute reproduction of results by two different persons is very difficult of attainment, even though each follows the details of the test with the utmost precision. However, when one has become so familiar with the technic involved that his personal time reactions and rates have become automatic and standardized, he will be able to compare the candies made from different sugars, provided he not only has maintained uniform conditions of heating but also has used the same utensils throughout the entire series of tests, which is essential in order to eliminate variations of heating caused by the differing thermal properties and surface areas of different pieces of apparatus (36).

In order to arrive at a just evaluation of the quality of sugars by this test, no substance other than water should be used with the sugar. If some other substance is added in the test, as for example, glucose sirup, the interpretation of the results obtained is complicated by the fact that the material added and the impurities contained in it may have affected the heat-resisting qualities of the sugar. Even the mineral and organic compounds in the water used with the sugar may increase the discoloration or inversion of the sucrose (23), and therefore, if possible, the test should always be conducted with distilled water. Conversely, if a sugar is known to behave satisfactorily in the barley candy test, it may be adopted as a standard and other substances may be added to it or dissolved in the distilled water in order to ascertain the effect of the added material on the stability of the sugar toward heat.

All commercial white sugars, whether derived from sugar cane or sugar beets, contain nonsugar substances in amounts varying in the different grades from a few thousandths of 1 per cent in the purest sugars to about 0.5 per cent in the sugars of lower purity (25). Chemically these impurities are substances of many types, both organic and inorganic. Although at present it is impossible to detect most of them as individual substances, many of the inorganic elements and radicals and some of those classes of organic compounds, the individual members of which have common reactions due to like atomic groupings in their molecular structures, may be detected and even determined quantitatively. The total nonvolatile inorganic components are determined as the ash, which, of course, is susceptible of complete quantitative analysis. But, in interpreting such analyses, it must be borne in mind that they do not indicate the combinations originally present in the sugar because of pyrolytic changes which have taken place during the ashing process. Thus, sulfates and chlorides in the sugar may be partly lost (15), the former by reduction to sulfites or sulfides, the latter by reduction to chlorine or by displacement by less volatile acidic radicals. Carbonates, which are generally present

in the ash, are formed, in part at least, by the interaction of basic oxides with the carbon dioxide produced by the burning of the sugar and its organic impurities. Nitrates and nitrites will be altered or entirely lost, and ammonium salts will be volatilized. Phosphorus, sulfur, and nitrogen in organic combinations may be lost or converted into inorganic compounds, depending on the amount and character of the basic oxides present and on the technic used in the incineration. The solution of the ash may be alkaline in reaction, whereas the solution of the sugar is nearly neutral or even slightly acid.

Methods have been described whereby it is possible to determine in white sugars small quantities of silica and organic and inorganic phosphates (17), of sulfates and organic and inorganic sulfites (6), of labile organic sulfur (1), of chlorides (4), and of total, protein, "amino acid," ammonium, nitrate, and nitrite nitrogen (3, 38). Iron has been determined directly in the sugar (21), or may be determined in the ash. Aluminum, calcium, magnesium, sodium, and potassium must be determined in the ash. There are no methods of determining in white sugars such organic nonsugars as the saponins (34), individual proteins (38), gums (25, 29), waxes (12), fats and oils (29), and polyphenolic compounds (6), all of which have been shown to be present and no doubt exert some influence on the decomposition and discoloration of sucrose during heating.

All barley candy tests made in the Carbohydrate Division are carried out in a copper casserole beaten from 0.16-cm. (0.0625-inch) stock, 11.6 cm. (4.56 inches) and 5.7 cm. (2.25 inches) in diameter at top and bottom, respectively, and 6.5 cm. (2.56 inches) deep, with a hollow handle 5 cm. (2 inches) long, made of the same stock, riveted to the side, into which is fitted a handle of oak about 17.5 cm. (7 inches) long.

Two hundred and twenty-seven grams (0.5 pound) of sugar and 90 cc. of distilled water are placed in the casserole, thoroughly mixed, and heated on a Chaddock burner in a place shielded from draughts with constant stirring, until all the sugar has dissolved, after which the sirup is left undisturbed until it commences to boil. The pressure and velocity of the gas admitted to the burner are so regulated that they are constant and bring the sirup to boiling in 5 to 5.5 minutes from the time heating was started. The casserole is then immediately covered with a 15-cm. (6-inch) watch glass, and the sirup is allowed to boil undisturbed. (If the sirup foams so badly on boiling that there is danger of its overflowing, the casserole is lifted momentarily from the burner to allow the foam to subside and the watch glass is placed in position as soon as the foam breaks and danger of overflowing has passed. When such foaming occurs it is noted as a characteristic of the sugar.)

Exactly 15 minutes after the heating was started the watch glass is removed and heating is continued, with constant stirring with a standard thermometer, until the temperature of the boiling sirup reaches 176° C. During the entire test the pressure and velocity of the gas are kept constant. The total time of heating is some interval between 21 and 25 minutes, and, if the gas is properly regulated, does not vary more than ± 0.5 minute in the different tests of any series. As soon as the sirup has reached the temperature of 176° C. it is quickly poured out on a cold, clean, dry cooling plate of polished copper, 35 \times 35 \times 0.6 cm. (14 \times 14 \times 0.25 inches) in dimensions. When the candy plaque so formed has cooled and hardened, it is broken up, bottled, and used as soon as possible for analytical determinations.

Barley candies made from a high purity, low-ash sugar and distilled water were adopted as standard and compared with candies made from the same lot of sugar with distilled water in which there was dissolved or suspended the particular nonsugar whose effect on the sugar during heating was to be studied. In order to accentuate the effect of the nonsugar so that differences in the quantitative analyses of the candies might clearly be attributed to the effect of the added substance and not to the unavoidable experimental errors of technic and analysis, quantities of the nonsugars were used which in general greatly exceed those now to be found in white sugars. This also provided a means of over-

TABLE I. ANALYSES OF BARLEY CANDIES MADE WITH VARIOUS NONSUGARS

Nonsugar Added	Wt. Added Gram	pH	Color	A	B	C	A-B Hydrolyzable Anhydrides	100 - (A + C) Nonhydro- lyzable Products
				Sucrose by Acid Inversion on Dry Solids %	Sucrose by Invertase on Dry Solids %	Reducing Substances as Invert Sugar on Dry Solids %		
None; average of 2 tests	0.0	4.7	29	96.67	96.36	1.95	0.31	1.38
Group I								
NaCl	0.1	4.7	26	95.64	94.33	2.86	1.31	1.50
NaCl	0.2	4.5	26	94.83	92.73	3.89	2.10	1.23
KCl	0.1	4.5	26	95.77	94.60	3.25	1.17	0.98
KCl	0.2	4.6	22	96.20	94.72	3.25	1.48	0.55
BaCl ₂ ·2H ₂ O	0.2	4.8	15	88.16	80.25	11.99	7.91	-0.15
CaCl ₂	0.2	3.9	56 ^a	38.54	17.31	59.68	21.23	1.78
KNO ₃	0.1	5.4	15	94.06	91.35	4.94	2.71	1.00
Na ₂ SO ₄	0.2	4.3	25	96.10	95.71	2.55	0.39	1.35
K ₂ SO ₄	0.2	4.5	23	96.91	95.45	2.38	1.46	0.71
MgSO ₄	0.1	4.7	13	93.01	88.29	7.72	4.72	-0.73
KH ₂ PO ₄	0.2	4.5	32	93.06	90.03	5.73	3.03	1.21
CaCO ₃	0.2	6.5	29	96.52	95.99	1.99	0.53	1.49
CaSO ₄	0.1	4.1	19	96.76	96.28	2.58	0.48	0.66
Potassium acid tartrate	0.1	3.9	21	88.37	83.28	12.36	5.09	-0.73
Group II								
NaHCO ₃	0.1	4.7	140	96.76	97.13	0.85	-0.37	2.39
NaHCO ₃	0.2	4.5	192	97.34	98.03	0.79	-0.69	1.87
Na ₂ CO ₃ ; average of 2 tests	0.1	4.6	166	97.83	97.66	1.14	0.17	1.03
K ₂ CO ₃	0.1	5.1	126	96.62	96.69	1.14	-0.07	2.24
NaNO ₂	0.2	5.2	108	97.68	97.75	1.11	-0.07	1.21
Na ₂ SO ₄	0.2	4.7	73	96.92	96.54	1.11	0.38	1.97
NaC ₂ H ₃ O ₂ ·3H ₂ O	0.2	4.6	73	96.69	95.99	0.97	0.70	2.34
Na ₂ HPO ₄ ·2H ₂ O	0.2	4.5	100	97.37	97.15	1.09	0.22	1.54
Sodium glycerophosphate	0.2	4.7	62	97.01	96.50	1.29	0.51	1.30
Calcium gluconate	0.2	4.2	38	97.20	96.66	0.84	0.54	1.96
Sodium citrate	0.2	4.7	71	98.07	98.00	1.01	0.07	0.92
Group III								
NH ₄ Cl	0.2	b	b	b	b	b	b	b
(NH ₄) ₂ SO ₄	0.05	3.7	81	25.50	7.68	60.47	17.82	14.03
NH ₄ H ₂ PO ₄	0.1	3.1	90	27.66	9.37	69.33	18.29	3.01
Asparagin	0.1	4.7	45	95.93	94.00	3.73	1.93	0.34
Glutamic acid	0.05	4.1	57	59.59	43.59	41.23	16.00	-0.82
Glycine	0.05	4.7	59	97.11	96.26	2.39	0.85	0.50
Fe(SO ₄) ₂ ·XH ₂ O	0.02	4.1	c	52.07	34.21	45.57	17.86	2.36
FeSO ₄ ·7H ₂ O	0.1	3.8	d	47.28	25.42	53.68	21.86	-0.96

^a The color developed during the pouring and the early stages of cooling over the copper plate.

^b Test could not be completed. Caramelization set in at 152° C., with very slow increase in temperature. After 22.5 minutes of heating, the temperature

was only 155° and the sirup was black, smoking, and starting to froth over.

^c Color was red-brown, not comparable with caramel.

^d Color was greenish gray, not comparable with caramel.

coming any buffering effect of the small quantity of ash in the standard sugar. The data obtained from the analyses of these candies are tabulated in Table I.

The colors of the candies were determined by comparison with a standard caramel solution (5), and the values given in the table are percentages of the standard color as measured colorimetrically under illumination from a standard daylight lamp. Sucrose was determined by double polarimetric methods before and after hydrolysis with invertase (7) and with hydrochloric acid (8). Reducing substances were determined as invert sugar by the Munsen-Walker method (9). To eliminate errors due to the absorption of moisture from the air by the candies, the percentages of sucrose and reducing substances were calculated on the basis of total solids as determined by drying solutions of the candies on sand in a vacuum at 70° C. (10). The pH was determined colorimetrically in a solution of 15 grams of the candy in cold, neutral water.

The results indicate that the nonsugars fall into three major groups. Group I is composed of those which inhibit color formation while increasing the amount of reducing substances, or are without material effect on either. The nonsugars of this group are salts whose aqueous solutions are neutral or acidic in reaction. Group II includes those nonsugars which increase the color formation but decrease the amount of reducing substances. These nonsugars are salts which have an alkaline reaction in water solution and also salts of strong bases with easily volatile acids or with unstable acids derived from very volatile anhydrides. Group III is made up of those nonsugars which increase both the formation of color and of reducing substances. These are ammonium salts, amino acids and amides, and iron salts.

Discussion

NONSUGARS AND THE INVERSION OF SUCROSE. An explanation of the action of the various nonsugars may be found by considering the properties of sucrose, invert sugar, and their decomposition products in conjunction with those of water and of the nonsugars themselves. Prinsen-Geerligs (32), Dedek and Terechov (19), Stearn (37), Urban et al. (40), Pucherna (33), and others have demonstrated that sucrose itself has weakly acidic properties (cf. Percival, 30). The quantity of hydrogen ions liberated from sucrose is apparently enhanced by elevation of temperature, and this causes the so-called "auto-inversion" of pure sucrose by heat (36). The ionization of water is also increased at higher temperatures (13, 39) and is, therefore, a contributing factor in the inversion of sucrose, but, from the evidence presented in the following paragraphs, it seems to be of minor significance in comparison with the increased ionization of sucrose.

The auto-inversion of sucrose is strikingly shown by the following experiments, which were made with dry sugars according to Pucherna's technic (33) for the caramelization test. Because of the fact that he used as standard a sugar having an ash content of 0.013 per cent, which, as will be shown, is just above a critical value, Pucherna missed some interesting observations in regard to the instability of pure sucrose toward heat. After having been dried for 2 hours at 100° C., 6.5-gram samples of the sugars were heated for 15 minutes in test tubes in an oil bath preheated to and maintained constant at 170° C. The samples were removed, allowed to cool in the air, and analyzed. A few typical results are given in Table II.

From this table it is evident that sugars having an ash content of about 0.010 per cent or less may undergo much greater inversion by heat than sugars of higher ash content, and that as little as 0.010 per cent of ash may reduce very efficiently the degree of auto-inversion of the sucrose. The different degrees of inversion shown by the sugars having an ash content of approximately 0.010 per cent or less must be caused by the differing composition and proportion of the nonsugars present in the different lots of sugar from which the samples were taken. When this test is carried out with dry sugars at 170° C., the ash content of 0.010 per cent is thus seen to be an average critical value, in that, with sugars whose nonsugars are of usual composition, this quantity of ash is just sufficient to act as a buffer against the increased liberation of hydrogen ions from the sucrose under the conditions of the test. If a different temperature is used in the test, a different value for this critical ash content is to be expected. If the sugars contain unusual or abnormal impurities, the critical value will again be altered, due to the different buffering effects of the ash constituents and of the other nonsugars present. The organic and volatile impurities also play a part in the inversion of sucrose and, if present in abnormal quantities, may require greater quantities of ash for effective buffering.

In the experiments in which he added sodium acetate, Pucherna noted a distinct odor of acetic acid rising from the mixtures during the heating. He ascribed this to the expulsion of acetic acid from the sodium acetate by the sucrose, which was reacting with the sodium acetate in the manner of a nonvolatile acid at elevated temperature, expelling the more volatile acetic acid. Although there may be some doubt of the validity of this explanation, because his standard sugar, containing 0.013 per cent of ash, might have contained constituents capable of liberating small quantities of acetic acid by acid exchange at the high temperature, his idea is probably correct.

The following experiments show the acidic nature of sucrose in aqueous solution at the boiling point:

Two distilling flasks were connected to condensers whose ends dipped into duplicate solutions made by mixing 25 cc. of 1 per cent sulfanilic acid solution, 25 cc. of 0.5 per cent α -naphthylamine hydrochloride solution (11), and 50 cc. of distilled water. In each flask were placed 500 cc. of a 0.1 per cent solution of recrystallized sodium nitrite of neutral reaction, and, after 25 grams of sugar containing 0.002 per cent ash had been dissolved in one of them, both solutions were slowly and simultaneously distilled. Before the solutions began to boil, the reagent in the receiver connected with the solution containing the sugar began to turn pink, indicating the presence of nitrous acid, while the other reagent remained colorless until the nitrite solution began to boil. After 5 minutes of boiling, the reagent into which the sugar solution was being distilled was very much deeper in color than the other. Before 15 minutes had elapsed, so much nitrous acid had been displaced from the sugar solution that the red dye formed in the reagent began to flocculate. At the end of 25 minutes the reagent receiving the distillate from the simple nitrite solution was still a clear red with no trace of a precipitate. The greater production of dye in the receiver from the sugar solution shows that this solution contained more hydrogen ions than the other, resulting in the liberation of larger quantities of nitrous acid, which in turn decomposed into its gaseous anhydride, N_2O_3 . The source of this larger quantity of hydrogen ions can only be the sucrose, which must have ionized sufficiently to act as a nonvolatile acid and displace the unstable nitrous acid from its salt. Similar results were also obtained with more concentrated sugar solutions, which contained up to 255 grams of sugar in 100 cc. of nitrite solution.

Since sucrose in solution shows this tendency to furnish hydrogen ions at high temperatures, the inverting action of the salts in Table I becomes apparent from the following considerations. The ash in very pure sugar, such as was used for the standard, is not sufficient in quantity to buffer the solution against the ionization of sucrose, and the hydro-

gen ions liberated from the sugar cause the hydrolysis of un-ionized sugar molecules to an extent dependent on the hydrogen-ion concentration. This accounts for the auto-inversion of sucrose by heat, which is more pronounced in Pucherna's method (Table II) than in the barley candy test.

In the presence of the neutral salts of Group I (with the exception of calcium carbonate and sulfate) there are formed in the hot solution the ions of strong acids which do not easily volatilize from very dilute solutions until high temperatures and high concentrations of the acids and of hydrogen ions (39) have been reached. Therefore, here these acids are not removed until late in the cooking of the candy (if at all), and their strong inverting power results in the hydrolysis of larger quantities of sucrose. The results agree with this reasoning. The concentration of the constant boiling mixture of hydrochloric acid is lower than that of the constant boiling mixture of nitric acid and, as Table I shows, less invert sugar is formed in the presence of potassium chloride than in that of potassium nitrate. When the sulfates of the alkalis and of calcium are present, the fact that less invert sugar is formed, although sulfuric acid is not volatile at the temperatures of the candy test, is in agreement with the fact that sulfuric acid is a weaker, less powerfully inverting acid than hydrochloric or nitric acids and the

TABLE II. ANALYSES OF SUGARS OF VARIOUS ASH CONTENTS AFTER HAVING BEEN HEATED 15 MINUTES AT 170° C.

Sugar	Ash %	Reducing Substances as Invert Sugar		Color	
		%		Original	Alkalinized
1	0.001	8.75	19	600	
		9.34	18	584	
2	0.004	8.70	12	628	
		9.20	12	576	
3	0.007	34.68	9	552	
		30.64	10	520	
4	0.008	0.30	16	18	
5	0.009	0.47	26	30	
6	0.010	1.61	32	152	
7	0.010	0.46	22	28	
8	0.012	2.44	19	360	
9	0.015	0.61	34	50	
10	0.017	0.61	22	32	
11	0.022	0.63	32	35	
12	0.040	0.54	29	56	
13	0.095	0.68	41	71	
14	0.124	0.44	28	38	
15	0.254	0.54	49	64	

hydrogen ions first liberated from the sucrose would react with the sulfate ion to form the HSO_4^- ion, which has relatively little inverting power. In all cases, acidic decomposition products of either sucrose or invert sugar contribute to the formation of invert sugar in virtue both of their own acidity (14) and of the argument just presented.

The greater inversion in the presence of the chlorides of the alkaline earths is in line with the fact that these salts are more inclined to hydrolyze into free acid and basic salts than are the corresponding salts of the alkali metals. In this respect, calcium chloride is more unstable than barium chloride, and it is found that the former is more powerfully active as an inverting agent in the candy test than the latter. The fact that calcium carbonate is an excellent buffer is well known, and is shown in Table I by the facts that it causes no change in the quantity of invert sugar formed as compared with the standard candy, and that the pH of the candy has the exceptionally high value of 6.5.

Those nonsugars of Group II which have an alkaline reaction in aqueous solution act as buffering agents against the acidic properties of sucrose and, by suppressing the concentration of hydrogen ions, tend to inhibit the inversion of sucrose. Sodium nitrite acts in the same way because of the instability of nitrous acid and the volatility of its anhydride, as already discussed. The removal of the nitrite

ion leaves an alkaline solution, resulting in the suppression of the ionization of the sucrose and therefore in a decreased degree of inversion.

The nonsugars of Group III are acidic in water solution and therefore cause inversion of sucrose. The small quantity of glycine used and its weak acidic nature (18) are probably responsible for the very slight increase in reducing substances formed and for no appreciable loss of sucrose in comparison with the standard. It is placed in Group III rather than in Group II because the quantity of reducing substances formed indicates that it is lacking in the buffering effect characteristic of Group II.

NONSUGARS AND PRODUCTION OF COLOR DURING THE CANDY TEST. The decomposition of sucrose in acid solution results in the formation of invert sugar as the first product. In alkaline solutions, the decomposition seems to follow a different course which is still but little understood (22, 35). For the purposes of this discussion, however, it will suffice to assume that the reaction is a decomposition of sucrose with the formation, among other products, of reducing substances of true aldehydic or ketonic types and also that a slight degree of inversion takes place in consequence of localized momentary liberation of hydrogen ions. With this assumption, the discoloration or caramelization of sugars during the test results from the further decomposition by heat of invert sugar and the reducing substances containing the carbonyl group in solutions of differing concentrations of hydrogen ions.

When heated alone or with very dilute or weak acids, both the sugars comprising invert sugar pass, with little discoloration, into a series of anhydrides, ranging from simple anhydrides such as glucosan, levulosan, and ω -oxymethylfurfural, through reversion products of the oligosaccharide type to highly polymerized, more completely dehydrated products of colloidal nature. Evidence that such a series of dehydration products is formed in the candy test may be deduced from Table I. Many of the simpler anhydrides of dextrose and of levulose are not only dextro-rotatory—for example, α -*D*-glucosan, $[\alpha] = +69.4^\circ$; levulosan, $[\alpha] = +18.6^\circ$ —but are also hydrolyzed back to the original sugars by strong acid (41), such as is used in determining sucrose by acid inversion. Hence the value for sucrose as determined in the double polarimetric method using acid (column A, Table I) is generally in excess of that as determined in the method using invertase (column B, Table I) which acts only on the sucrose. The difference in the values obtained by the two methods (A - B) may, therefore, be taken as a rough approximation of the quantity of those anhydrides and reversion products formed during the test which are hydrolyzed by acids to invert sugar. It is to be noted that, in Group I, this difference is generally greater the larger the percentage of reducing substances. Likewise, 100 per cent minus the sum of the values for sucrose by acid inversion (column A) and of the reducing substances (column C), $[100 - (A + C)]$, furnishes a rough approximation of the quantity of nonreducing and nonhydrolyzable anhydrides and degradation products, including those which, by progressive and extensive dehydration and polymerization as the boiling sirup loses more and more water by evaporation during the later part of the test, have become colloidal. [The negative values in both columns, A - B and $100 - (A + C)$, arise from the accumulation of experimental errors and indicate that the values are only rough approximations.]

In alkaline solution, however, both dextrose and levulose undergo deep-seated and complex isomerizations and degradations accompanied by caramelization and oxidation (2, 16, 21, 42). Furthermore, the reducing substances formed by the degradation of the sugars in alkaline solutions, especially those containing an aldehydic carbonyl group,

of which methyl glyoxal is one (21), show the property, characteristic of aldehydes, of undergoing condensations and polymerizations in alkaline media, with formation of highly colored colloidal matter. Thus the invert sugar formed by localized hydrolysis of sucrose and the aldehydes formed by degradation of sucrose and invert sugar are quickly converted into organic nonsugars which do not hydrolyze in acid solution to regenerate the original reducing substances. The differences between the sucrose values (A - B) are, therefore, smaller in the presence of the alkaline or potentially alkaline nonsugars of Group II than in that of the acidic or potentially acidic substances of Group I. Also a greater formation of nonhydrolyzable condensation products is indicated by the fact that 100 per cent minus the sum of the sucrose by acid inversion and the reducing substances $[100 - (A + C)]$ is generally greater in Group II than in Group I.

Similar considerations applied to the substances in Group III indicate in general the formation of large amounts of anhydrides capable of being hydrolyzed back to invert sugar by acid (A - B) and also, in some instances, the production of large amounts of products of the nonhydrolyzable type $[100 - (A + C)]$, some of which arise from reaction of invert sugar and its degradation products with the particular nonsugar added in the test (27).

Lundén (26) emphasizes the fact that some of the colored substances in sugar have properties resembling those of acid-alkali indicators, since they are colorless or pale yellow in acid solution and brown in alkaline solution. The transition point is not sharp because the coloring matter is not homogeneous. He therefore recommends that all sugar solutions be adjusted to a definite pH before measuring the color as a means of determining the quality of a sugar. However, since the candy test is for the purpose of testing the color produced under conditions approaching those of actual use, this adjustment of pH does not seem necessary for practical testing.

Pucherna (33) makes two color determinations, one on the 0.5 *N* solution of the heated sugar and a second after heating the 0.5 *N* solution for 10 minutes on the steam bath with 0.5 cc. of 2 *N* sodium hydroxide (the "original" and "alkalinized" colors, respectively, of Table II). He interprets the increase in color as a measure of the quantity of the invert sugar formed during the test, since invert sugar in alkaline solution decomposes with the formation of intensely colored products. Table II shows that this procedure gives a rough approximation of the invert sugar formed only in the cases of those sugars which have an ash content greater than 0.01 per cent. Since these sugars also show greater color formation without the treatment with alkali, the second determination, that of the alkalinized color, seems unnecessary for practical purposes.

Although the coloring matters produced have the properties of indicators, there is apparently no relationship between the colors and the pH of the solutions of the candies in cold neutral water as recorded in Table I. A brief consideration of the effects of temperature on the ionization of water and of the nature of the candy will show that such a relationship is not necessarily to be expected. While the ionization constants and the pH of the neutral point in highly concentrated sugar solutions at high temperatures are unknown, it has been demonstrated that the ionization of pure water is progressively increased by elevation of the temperature and therefore that the pH of the neutral point of water decreases as the temperature increases (13). It is reasonable to suppose that the same phenomenon takes place in sugar solutions but to a different degree.

The boiling sirup in the candy test is a supersaturated sugar solution which, when suddenly cooled by pouring on the cold copper plate, becomes an amorphous glass of super-

cooled molten sugar of great viscosity and low water content. This sudden change in temperature presumably fixes the colored substances as they existed in the hot sirup, and changes them into strongly dehydrated colloids with loss of their sensitivity as indicators until they are redispersed by the action of relatively high concentrations of hydrogen or hydroxyl ions. Thus the colors of the candies seem to indicate conditions of ionization, pH and buffering during the candy test differing from those obtaining at ordinary temperatures, and may be considered as indicators showing roughly the conditions of acidity or alkalinity in the sirup at 176° C. On long standing, after the candy has come to more stable conditions by the crystallization of the sucrose, whereby the colored material and other nonsugars accumulate in the film of less viscous sirup in the interstices between the crystals (24), the color, as determined by comparison of a fresh solution of the candy with standard caramel solution (5), gradually increases. This would indicate either a slow oxidation of the coloring matter to more intensely colored products, or, in Group I, an adjustment of the color to the pH of the candy at ordinary temperatures made possible by the increased mobility of ions in the less viscous film of sirup.

The dark color of the candy containing calcium chloride is definitely due to decomposition reactions subsequent to the heating. The boiling sirup at 176° C. is practically colorless, but darkens as it is poured out and the darkening continues while the plaque is cooling. There is also an evolution of a small amount of smoke. This discoloration may be due either to oxidation or to further dehydration of some of the practically colorless decomposition products of invert sugar.

The slight increase in color in the presence of potassium dihydrogen phosphate is probably due to cumulative experimental errors and, in any case, is so slight as to be negligible.

The nitrogenous nonsugars of Group III (Table I) cause the production of highly colored candies in spite of the acidity indicated by the high percentage of reducing substances, because they react so readily with invert sugar to form the intensely colored melanoidins of Maillard (27). The complete caramelization of the sugar in the presence of ammonium chloride is in harmony with the frequent use of small quantities of ammonium salts in the commercial production of caramel.

The colors of the candies containing iron salts are not comparable with those of caramel solutions because of the well-known fact that iron enters into reaction with polyhydric alcohols to form intensely colored complex compounds and because of charring of the sugars by the free acid liberated by hydrolysis of the iron salts. An experiment with 0.2 gram of ferric chloride resulted in complete caramelization and frothing at about 150° C., as in the case of ammonium chloride. This is in agreement with the generally recognized fact that iron is an extremely objectionable impurity (31) and is to be eliminated from sugars and sugar products as far as possible.

Acknowledgment

The authors are indebted to G. L. Keenan, of the Micro-analytical Division, Food and Drug Administration, U. S. Department of Agriculture, for a crystallographic examination of a freshly prepared barley candy. He found that the "product was glassy in character and singly refractive when examined with crossed nicols."

Literature Cited

- (1) Ambler, *IND. ENG. CHEM., Anal. Ed.*, 3, 341 (1931).
- (2) Ambler, *IND. ENG. CHEM.*, 22, 357 (1930).
- (3) Ambler, *Intern. Sugar J.*, 29, 282, 437, 498 (1927); Ambler and Byall, *IND. ENG. CHEM., Anal. Ed.*, 4, 34 (1932); Ambler and Snider, *Ibid.*, 4, 37 (1932).
- (4) Ambler and Byall, *Ibid.*, 4, 341 (1932).
- (5) *Ibid.*, 3, 135 (1931); Balch, *IND. ENG. CHEM.*, 22, 255 (1930).
- (6) Ambler, Snider, and Byall, *Ibid.*, *Anal. Ed.*, 3, 339 (1931).
- (7) Assoc. Official Agr. Chem., "Official and Tentative Methods of Analysis," 3rd ed., Sect. XXXIV, paragraphs 21, 22, pp. 370-2, 1930.
- (8) *Ibid.*, Sect. XXXIV, paragraph 23, pp. 372-3.
- (9) *Ibid.*, Sect. XXXIV, paragraphs 37, 38, p. 379.
- (10) *Ibid.*, Sect. XXXIV, paragraph 4, p. 364.
- (11) *Ibid.*, Sect. XXXVII, paragraph 14, p. 405.
- (12) Bardorf, *Can. Chem. Met.*, 11, 231 (1927); *IND. ENG. CHEM.*, 22, 907 (1930).
- (13) Bjerrum, *Intern. Critical Tables*, Vol. VI, p. 152, New York, McGraw-Hill Book Co., 1929.
- (14) Browne, C. A., "Handbook of Sugar Analysis," pp. 656-7, New York, John Wiley & Sons, 1912.
- (15) Browne and Gamble, *Facts About Sugar*, 17, 552 (1923).
- (16) Bruyn, de, and van Ekenstein, *Rec. trav. chim.*, 14, 156, 203 (1895); 16, 257, 262, 274, 282 (1897); *Nef, Ann.*, 367, 214 (1907); 376, 1 (1910); 403, 204 (1914).
- (17) Byall and Ambler, *IND. ENG. CHEM., Anal. Ed.*, 4, 325 (1932).
- (18) Clark, W. Mansfield, "Determination of Hydrogen Ions," 3rd ed., Baltimore, Williams and Wilkins Co., 3rd ed., p. 41, 1928.
- (19) Dedek and Terechov, *Z. Zuckerind. čechoslovak. Rep.*, 50, 349 (1925-6).
- (20) Eastick, Ogilvie, and Lindfield, *Intern. Sugar J.*, 14, 428 (1912).
- (21) Evans, W. L., et al., *J. Am. Chem. Soc.*, 47, 3085 (1925); 48, 2665 (1926); 50, 1496 (1928); *Chem. Rev.*, 6, 281 (1929); Dekker, *Proc. Congr. Intern. Soc. Sugar-Cane Tech.*, 3rd Congr., Surabaya, 1929, p. 580.
- (22) Herlesova, *Z. Zuckerind. čechoslovak. Rep.*, 53, 744 (1929-30); *Listy Cukrovar.*, 47, 467 (1929); Spengler, Landt, and Ost, *Z. Ver. deut. Zuckerind.*, 80, 751 (1930); 81, 487 (1931); 82, 885 (1932); Fischler, Hauss, and Täufel, *Biochem. Z.*, 265, 181 (1933).
- (23) Jordan, *Food Ind.*, 4, 89 (1932).
- (24) Keane, Ambler, and Byall, *IND. ENG. CHEM.*, 27, 30 (1935).
- (25) Lebeson, *Mfg. Confectioner*, 7, No. 5, 19 (1927).
- (26) Lundén, *Centr. Zuckerind.*, 33, 1013 (1925).
- (27) Maillard, *Ann. chim.*, 5, 258 (1916); Ripp, *Z. Ver. deut. Zuckerind.*, 76, 627 (1926); Ambler, *IND. ENG. CHEM.*, 21, 47 (1929).
- (28) Murphy, *Candy Manufacturer*, Sept., 1921, p. 37; Paine, Badollet, and Keane, *IND. ENG. CHEM.*, 16, 1252 (1924); Spencer, G. L., and Meade, G. P., "Hand Book for Cane Sugar Manufacturers and Their Chemists," p. 189, New York, John Wiley and Sons, 1929; Ambler, *Mfg. Confectioner*, 7, No. 1, 17 (1927); Windt, *Ibid.*, 12, No. 8, 20 (1932); 13, No. 10, 24 (1933); Kennedy, *Ibid.*, 13, No. 5, 18 (1933).
- (29) Paine and Balch, *Facts About Sugar*, 21, 566 (1926); *Intern. Sugar J.*, 28, 472 (1926).
- (30) Percival, *J. Chem. Soc.*, 1934, 1160.
- (31) Prinsen-Geerligs, H. C., "Cane-Sugar and Its Manufacture," 2nd ed., pp. 269-71, London, Norman Rodger, 1924; Spengler and Tödt, *Z. Ver. deut. Zuckerind.*, 81, 550 (1931); Stanek and Pavlas, *Z. Zuckerind. čechoslovak. Rep.*, 57, 81 (1932-33).
- (32) Prinsen-Geerligs, H. C., *Z. Ver. deut. Zuckerind.*, 45, 320 (1895).
- (33) Pucherna, *Z. Zuckerind. čechoslovak. Rep.*, 55, 144, 663 (1930-31).
- (34) Rehorst, *Z. Ver. deut. Zuckerind.*, 79, 155 (1929); van Scherpenberg, *Centr. Zuckerind.*, 37, 129 (1929).
- (35) Reis, *Z. Zuckerind. čechoslovak. Rep.*, 57, 89 (1932-33); 58, 116 (1933-34).
- (36) Rice, *Mfg. Confectioner*, 14, No. 8, 34 (1934).
- (37) Stearn, *J. Phys. Chem.*, 35, 2227 (1931).
- (38) Steuart, *Food*, 3, No. 26, 79 (1933).
- (39) Tödt, *Z. Ver. deut. Zuckerind.*, 82, 817 (1932).
- (40) Urban and Shaffer, *J. Biol. Chem.*, 94, 697 (1932); Urban and Williams, *Ibid.*, 100, 237 (1933).
- (41) Vogel and Georg, "Tabellen der Zucker und ihrer Derivate," pp. 60-5, Berlin, Julius Springer, 1931.
- (42) Waterman, *Chem. Weekblad*, 14, 119 (1917).

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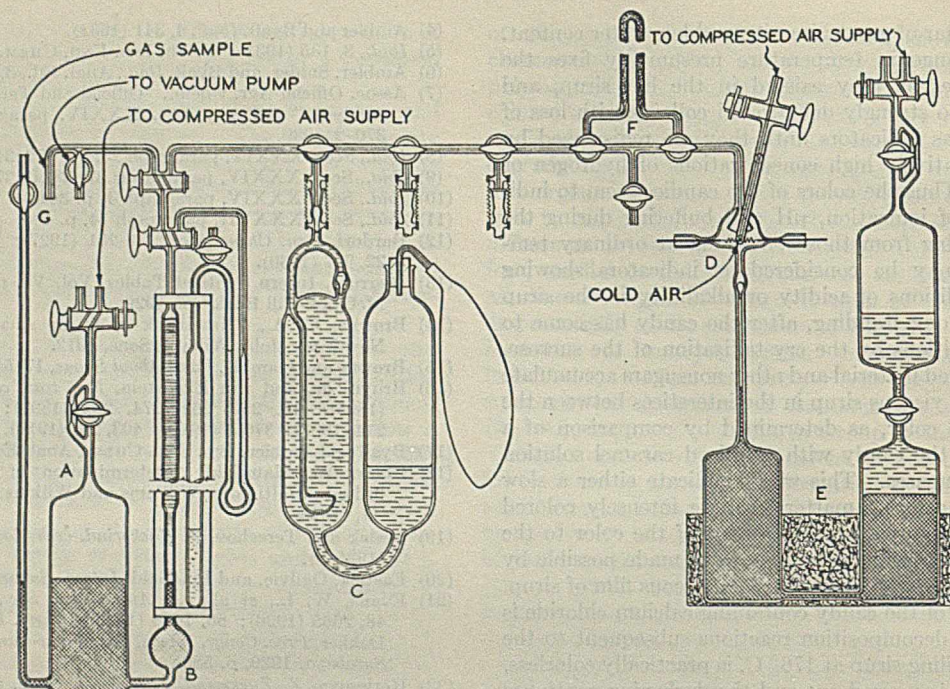


FIGURE 1. APPARATUS FOR MODIFIED FLUE-GAS ANALYSIS

- A. Assembly, including capillary by-pass for raising and lowering mercury in buret by compressed air
- B. Buret. Volume, 80 ml. Graduations, 0.1 ml. and 0.02 ml.
- C. Gas-absorption chamber, including check valve and glass device for breaking up gas into fine bubbles
- D. Total combustion chamber. Spiral platinum wire, No. 30, 11 cm. long. Tungsten lead-in wires
- E. Assembly, including check valve and mercury reservoir for combustion chamber
- F. Slow-combustion copper oxide tube
- G. Excess-pressure safety valve

Analysis of Combustibles in Flue Gas

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IN AN ATTEMPT to reduce the unaccounted-for loss in steam-generator efficiency tests, a study has been made of methods for estimating the combustible gas stack loss. The standard method of gas analysis (2, 3) calls for separate determinations of carbon dioxide (acidic oxides), oxygen, unsaturates, carbon monoxide, hydrogen, and hydrocarbon (assumed to be methane and ethane), each of which may be reasonably expected to be present in flue gas in varying amounts. Although a high degree of precision may be obtained with care when using the apparatus described by the Bureau of Mines (2), it was considered advisable to modify the standard procedure somewhat for flue-gas analysis in appreciation of the various factors connected with steam-generator efficiency tests—uninterruption of sampling during the test, the presence of small amounts of combustibles, the ultimate use of the data in heat calculations, and the accuracy of the determination of the other test data.

An apparatus for the direct determination (catalytic combustion) of the combustibles in flue gas has also been developed. Through the use of a synthetic flue gas, the laboratory stage of development has been completed, and valuable information can be obtained at a power station by means of this apparatus.

A laboratory procedure for flue-gas analysis, designed to estimate the loss due to incomplete combustion, is described, including a comparison of the results of field and laboratory procedures of flue-gas analysis from a recent efficiency test on a modern steam-generating unit. A laboratory apparatus which, employing a synthetic flue gas, is capable of measuring this loss directly is also described.

Modified Flue-Gas Analysis

Watson and Ceaglske (12) describe a modified procedure of gaseous fuel analysis in which a triple combustion method is employed for gas samples of a high calorific content. In the authors' work, carbon monoxide was determined independently and the standard procedure shortened, thus reducing the opportunity for error because

fewer manipulations are necessary and at the same time yielding results of value for steam-generator efficiency tests. The determination of acidic oxides followed by total combustion over a heated platinum spiral completes the analysis.

The constructional details of the method of obtaining representative laboratory samples are described elsewhere (5). A 2-liter gas sample was taken continuously over a period of 4 hours, during which time the gas from the stack slowly displaced mercury in a Pyrex sampling bottle. The use of mercury both in obtaining the laboratory sample and as the confining liquid in the buret avoided the uncertainty of the solvent action of other liquids. Samples were taken at 15-minute intervals for analysis in the standard Orsat apparatus in the field.

The procedure employed in the laboratory consisted of (a) measurement of sample of such volume that the reading oc-

curred on the constricted portion of the buret; (b) absorption of acidic oxides and (c) of oxygen in the usual manner; (d) addition of oxygen previously purified and stored in a third absorption pipet, in an amount such that the volume could be read in the constricted section of the buret; and (e) total combustion of all combustibles over a heated platinum spiral followed by the observation of the total shrinkage and of the total carbon dioxide formed. It followed that variations of 0.01 cc. in the original volume of the sample, the shrinkage, and the carbon dioxide formed on total combustion could be detected, since the constricted section of the buret was graduated to 0.02 cc. Furthermore, it is obvious that step *c* may be omitted unless a check on the field determination of oxygen is desired.

The novel features of the apparatus (Figure 1) include the transfer of gas by means of a mercury piston and compressed air, a constriction in the buret to obtain small volume changes, pressure stop-cocks (4), glass-seated valves in the absorption pipets (1), and a combustion pipet of small volume protected by a glass-seated check valve. The volume (5 cc.) of the combustion chamber must be included in the manifold error but may be made small if filled with nitrogen. Ordinarily, if the hydrocarbon content in the flue gas was low (0.1 per cent) the carbon dioxide remaining in the manifold was neglected, but when greater amounts were present the gas, after removal of the carbon dioxide, was passed into the combustion assembly, followed by a repetition of the procedure for removing carbon dioxide. The combustion of the residual gas remaining after analyses did not show a change in volume greater than 0.01 cc.

TABLE I. ANALYTICAL DATA ON POSSIBLE HYDROCARBONS IN FLUE GAS

Hydrocarbon	Volumetric Ratio upon Combustion ^a	Heat of Combustion, Kg.-cal./g.	Carbon Dioxide Formed per Gram of Hydrocarbon Grams
Methane	2	13.1	2.7
Ethane	1.25	12.2	2.9
Propane	1	12.0	3.0
Butane	0.875	11.7	3.0
Ethylene	1	11.9	3.1
Propylene	0.835	11.7	3.1
Butylene	0.75	11.5	3.1
Amylene	0.7	11.5	3.1
Acetylene	0.75	12.0	3.4
Propine	0.67	11.8	3.3
Butine	0.625	..	3.3
Pentine	0.6	..	3.2
Benzene	0.42	10.1	3.4
Weighted average	1	12	3.0

^a Ratio between shrinkage and carbon dioxide formed.

The heat equivalent of the carbon dioxide formed on combustion was calculated from the approximate heat data in Table I. Thus a gram of the mixture of the listed hydrocarbons would yield 3 grams of carbon dioxide and liberate 12 kg.-calories upon combustion. This statement is true to roughly 10 per cent, but a result of this accuracy is satisfactory in reducing the unaccounted-for loss in steam-generator efficiency tests. The following equations illustrate the method in which the gas analysis data were used:

Let *A* = per cent of carbon monoxide (determined independently)
B = per cent of carbon dioxide found on total combustion
C = per cent of shrinkage observed

$$B - A = \text{per cent of hydrocarbon} \quad (1)$$

$$C - \frac{1}{2} A = \text{per cent of shrinkage due to hydrocarbon and hydrogen} \quad (2)$$

$$C - \frac{1}{2} A - (B - A) = \text{per cent of shrinkage due to hydrogen} \quad (3)$$

$$\frac{2}{3} [C - \frac{1}{2} A - (B - A)] = \text{per cent of hydrogen} \quad (4)$$

The assumption made in Equation 3 follows from an analysis of the relation between the shrinkage data and the carbon dioxide formed on combustion found also in Table I. The formation of the hydrocarbons by thermal decomposition and other secondary reactions in the flue gas renders it prac-

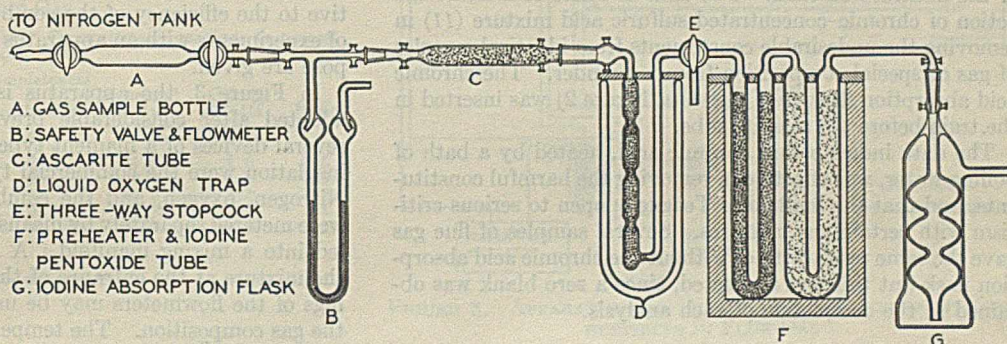


FIGURE 2. APPARATUS FOR DETERMINATION OF CARBON MONOXIDE

tically impossible to predict their chemical nature but, in order to utilize the experimental data, the choice of a ratio of 2 enables one to say that there is definitely present the percentage of hydrogen thus calculated, and a ratio of 1 appears more likely in view of a large amount of test data on flue-gas analysis. Thus, in a group of fifty analyses, only ten showed the presence of hydrogen using a ratio of 1 and but five samples contained hydrogen assuming a ratio of 2. The authors are aware of certain absurdities under special cases in which particular mixtures of hydrocarbons and hydrogen may be assumed (3, p. 128) but these inconsistencies are not so glaring on a heat of combustion basis. The application of the analytical results in equation form to steam-generator efficiency tests is given in formulas for estimating combustible stack loss in steam-generator efficiency tests, where quantities refer to wet flue gas.

$$\frac{V_{HC} \times w_{CO_2} \times W \times 4000}{D} = \text{loss in calories per gram of coal due to presence of hydrocarbons in flue gas}$$

$$\frac{V_{H_2} \times W \times 2.784}{D} = \text{loss in calories per gram of coal due to presence of hydrogen in flue gas}$$

$$\frac{V_{CO} \times W \times 2.765}{D} = \text{loss in calories per gram of coal due to presence of carbon monoxide in flue gas}$$

V_{HC} = volume in cc. of carbon dioxide resulting from combustion of hydrocarbon in 1 cc. of flue gas

V_{H_2}, V_{CO} = volumes in cc. of hydrogen and carbon monoxide, respectively, in 1 cc. of flue gas

w_{CO_2} = weight in grams of 1 cc. of carbon dioxide at 25° C. and 1 atmosphere pressure

W = weight in grams of flue gas per gram of coal

D = density of flue gas at 25° C. and 1 atmosphere pressure

4000 = calories per gram of carbon dioxide resulting from combustion of hydrocarbons (Table I)

The apparatus for the independent determination of carbon monoxide is shown in Figure 2 in which interchangeable ground joints were used throughout. The type of apparatus was originally described by Teague (9). More recently, Vandaveer and Gregg (11) have pointed out the chemical nature of certain interfering substances when iodine pentoxide was used in the determination of carbon monoxide. The

vapor pressure of these substances (aldehydes and ethylenic unsaturates) has not been determined for the individual members of the two classes of compounds, but in a paper by Leighton and Blacet (6) attention is called to the fact that propionaldehyde was not entirely removed by a liquid air trap. A special composition of illuminating gas (approximately 1 per cent combustible) also gave evidence in this laboratory of a substance which was slowly carried through the liquid oxygen trap by the carrier gas, nitrogen, and which was oxidized by the iodine pentoxide. Qualitative tests indicated that aldehydes were absent and that the interfering substance was of the unsaturated class. The data in Table II indicate the action of chromic-concentrated sulfuric acid mixture (11) in removing the undesirable constituents from identical samples of gas of special composition from a cylinder. The chromic acid absorption flask (not shown in Figure 2) was inserted in the train before the ascarite tube.

The data indicate that chromic acid, heated by a bath of boiling water, was effective in removing the harmful constituents, and that the method of Teague is open to serious criticism with certain gas mixtures. Several samples of flue gas gave the same result with or without the chromic acid absorption flask but this was suspected, since a zero blank was obtained at the completion of each analysis.

TABLE II. REMOVAL OF INTERFERING SUBSTANCES IN THE DETERMINATION OF CARBON MONOXIDE

Sample Volume	Time Increments	Liberated Iodine as Carbon Monoxide		Remarks
		Increments	%	
40 Cc.	60	0.11		No chromic acid
	45	0.12		
	45	0.00		
40	60	0.10		Chromic acid at room temperature
	45	0.08		
	45	0.00		
40	60	0.09		Chromic acid heated by a bath of boiling water
	45	0.00		

TABLE III. COMPARISON OF FIELD AND LABORATORY FLUE-GAS ANALYSES

Run	Per Cent by Volume, Wet									
	1	2	3	4	5	6	7	8	9	10
Laboratory:										
Hydrogen	0.03	0.03	0.04	0.03	0	0	0.05	0.04	0.04	0.06
Hydrocarbon	0.09	0.21	0.04	0.03	0.07	0.06	0.07	0.07	0.07	0.02
Carbon monoxide	0.05	0.20	0.13	0.09	0.05	0.03	0.05	0.08	0.12	0.26
Oxygen	4.7	4.1	4.4	4.9	4.6	4.5	4.6	4.5	4.9	4.1
Carbon dioxide	14.6	14.8	14.6	14.3	14.4	14.5	14.1	14.4	14.3	14.6
Field:										
Carbon monoxide	0.05	0.08	0.04	0.03	0.03	0.02	0.04	0.07	0.04	0.06
Oxygen	3.7	3.4	3.6	4.0	3.7	4.0	4.1	4.0	3.8	3.4
Carbon dioxide	14.8	15.0	14.9	14.5	14.8	14.5	14.4	14.5	14.6	15.1
	Combustible Energy Loss, Per Cent									
Hydrogen	0.1	0.1	0.2	0.1	0	0	0.2	0.2	0.1	0.2
Hydrocarbon	1.1	2.4	0.5	0.4	0.8	0.7	0.9	0.9	0.8	0.2
Carbon monoxide (lab.)	0.2	0.7	0.5	0.3	0.2	0.1	0.2	0.3	0.4	0.9

In Table III, the analytical results (5) from the laboratory and field procedures (Orsat) are compared. Each laboratory percentage represents an average of 6 analyses while, over the same period of time (24 hours), each field percentage represents an average of 96 analyses. The field carbon monoxide determinations (ammoniacal cuprous chloride) gave lower results than the laboratory method and the divergence apparently increased with larger percentages of carbon monoxide. Oxygen in the field (alkaline pyrogallate) was unexpectedly much lower than in the laboratory (sodium hyposulfite). The absorption of thermal radiation from the steam generator by

the dark-colored alkaline pyrogallate, thus raising the temperature of the solution, was possibly responsible for this difference. The carbon dioxide determinations in the field and laboratory are in quite good agreement. The equivalent percentage of the combustibles (5) on the thermal efficiency basis is also included in Table III.

Catalytic Combustion Method

The value of the direct determination of the calorific content of flue gas lies in the fact that in one measurement the most significant property of the gas sample is obtained relative to the efficiency of the combustion of fuel. The results of experiments with an apparatus designed for the above purpose are given.

In Figure 3, the apparatus is shown which was finally adopted after considerable previous experimentation with several devices of a filament type. The external heater and insulation were the commercial type of combustion furnace. Nitrogen, oxygen, and the combustible gas from cylinders were metered separately by means of flowmeters (14) and then led into a mixing manifold. A fourth flowmeter measured the mixture at the entrance of the combustion tube. Readings of the flowmeters may be used as an approximation to the gas composition. The temperature indicator was a Leeds & Northrup thermocouple potentiometer with an external galvanometer. The wattmeter was a Weston Model 310, scale 75-150 watts. The thermocouple metals were No. 36 platinum and platinum-10 per cent rhodium wire. The cold junction was immersed in an ice-water mixture contained in a Dewar flask.

Experiments on the type of catalyst were confined to platinum, quartz, and hopcalite. Hopcalite was found to be unsatisfactory. Quartz at 850° C. was found to be as effective as platinum in converting the hydrocarbons to carbon dioxide and water, but the rise in temperature attending the combustion with the former catalyst was only one-twentieth that of the latter. It was therefore felt that the thermal conductivity as well as the chemical stability were the more important properties of the catalyst. The oxide catalysts at 350° C. described by Yant and Hawk (13) were not used in the authors' work when it was found that platinum gave satisfactory results. Experiments on the variation of weight and length of platinum catalyst indicated that a tightly fitting platinum cylinder 4 cm. in length and filled with platinum scrap (total weight 4.25 grams) served to give adequate sensitivity to the temperature indicator. Thus a gas mixture containing 0.4 per cent methane, 4 per cent oxygen, and the balance nitrogen, produced a rise in temperature of 37° C. at a gas flow of 20 cc. per second. The temperature of the catalyst was 850° C. Since hydrogen and carbon monoxide burn more readily than the gaseous hydrocarbons, it was important that the gas mixture reach the metallic catalyst with no previous combustion. The catalytic mass must therefore be placed at the end of the furnace at which the gas mixture enters.

It is clear that secondary reactions must be avoided. The removal of sulfur dioxide and carbon dioxide would eliminate many possibilities. Extrapolation of the data of Nernst (7) indicated that a negligible amount of nitric oxide would be formed at 850° C. when air was passed over platinum. When the acidic oxides were removed, the composition of the synthetic flue gas striven for in the laboratory was 4 per cent oxygen, 0.3 to 1 per cent combustible, and the balance nitrogen. Inasmuch as the commercial gases containing hydrocarbons were not purified, the total carbon dioxide formed by combustion as previously described is reported as per cent methane and this amount when compared with the amount of carbon dioxide formed by contact with the catalyst gives the completeness of combustion. The illuminating gas had the

following percentage composition obtained by analysis: carbon dioxide, 2.15; unsaturates, 5.7; oxygen, 1.6; hydrogen, 39.0; carbon monoxide, 22.2; paraffins, 17.5. The heat of combustion (I_2) of the illuminating gas (450,000 joules) was estimated utilizing the following data: carbon monoxide determined by the iodine pentoxide method, carbon dioxide and shrinkage formed on combustion after removal of unsaturates, and carbon dioxide and shrinkage formed on total combustion.

TABLE IV. RELATION BETWEEN RATE OF GAS FLOW AND COMPLETENESS OF COMBUSTION OF METHANE IN SYNTHETIC FLUE GAS

(Platinum catalyst; temperature 850° C.; wattmeter readings to nearest 0.25 watt)

Rate Cc./sec.	Composition of Gas ^a		Completeness of Combustion	Measured Watts	Calcd. ^b Watts	Ratio
	O ₂ %	CH ₄ %	%			
20	4.2	0.25	90	4.0	1.6	2.5
26.5	5.4	0.5	90	8.0	4.3	1.9
32.5	4.6	0.55	95	10.0	6.2	1.6
43	3.3	1.05	95	17.75	15.7	1.1
46.5	4.7	0.5	70	8.0	5.9	1.3

^a Balance nitrogen.

^b Calculated, based on per cent combustion.

Sample calculation:

$$\frac{0.0025 \times 20 \times 890,160}{22,400 \times \frac{298}{273}} \times 0.9 = 1.6$$

$$\text{Ratio} \frac{4.0}{1.6} = 2.5$$

The experimental procedure found to work satisfactorily was to hold constant the wattage of the furnace and adjust the wattage of the auxiliary heater so that zero deflection in the thermocouple circuit was obtained when no combustible was present in the flowing gas and when the hot junction was at 850° C. When determining the heat value of a gas mixture (10), the change in the wattage of the auxiliary heater necessary to maintain zero deflection of the galvanometer in the thermocouple circuit was noted. The wattage of the auxiliary heater was maintained at a higher value than the anticipated watt-equivalent of the gas. The temperature at the external heater was approximately 1000° C., owing largely to radiation and the end effect.

In Table IV the rate of flow of the gas is compared with the completeness of the combustion. It is doubtful whether one can distinguish between 90 and 95 per cent. The column headed Ratio was obtained by comparing the measured change in watts in the auxiliary heater to the value obtained from the composition of the gas. This ratio should remain constant at a definite gas flow and be independent of the individual combustible compounds in the gas. The increased rate of flow of gas with its larger calorific content must be judiciously balanced with the completeness of combustion, in order that the maximum effect be obtained on the measuring instruments. Variations of 1 per cent in velocity (flowmeter reading) were shown to cause a 10 per cent error in the heat equivalent of the gas, when the rate of gas flow was approximately 20 cc. per second.

In Table V are compared the three different types of combustibles used in the experiments in order to illustrate the reproducibility of the apparatus. Some of the variations in the individual determinations are large and may be attributed, in part, to the fact that separate gas analyses were not made on each individual determination. Instead the readings of the flowmeter served to estimate the gas composition. A period of 3 to 4 minutes was required to obtain the maximum effect resulting from combustion. A comparison of the heat values of three types of combustible gas shows a good agreement when the uncertainty in the estimated heat of combustion of illuminating gas is considered. When the catalytic

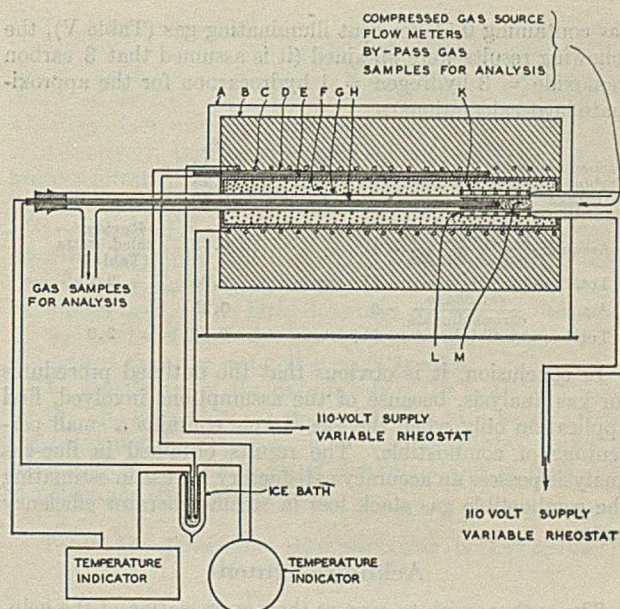


FIGURE 3. APPARATUS FOR DIRECT DETERMINATION OF COMBUSTIBLES IN FLUE GAS

- A. Aluminum box
- B. External heater insulation
- C. External heater
- D. Quartz sheath for thermocouple, 2 mm. outside diameter
- E. Quartz tube, 3-mm. wall, 22 mm. outside diameter
- F. Asbestos fiber insulation
- G. Quartz tube, 1.5-mm. wall, 8 mm. outside diameter
- H. Quartz sheath, for platinum-platinum-rhodium thermocouple, 2 mm. outside diameter
- K. Quartz tube, support for auxiliary heater
- L. Auxiliary heater. No. 30 nichrome wire
- M. Platinum cylinder and platinum chips (catalyst)

TABLE V. CALORIFIC CONTENT OF SYNTHETIC FLUE GAS

(Temperature of platinum catalyst, 850° C. Rate of gas flow, 20 cc. per second. Complete combustion except for the first two methane (0.35 per cent) runs, which were 95 per cent complete. Wattmeter readings to nearest 0.25 watt. Gas composition 3.8 per cent oxygen, tabulated per cent combustibles, and balance nitrogen.)

Measured Watts	Calcd. ^a Watts	Ratio	Comparison of Calorific Content of Synthetic Flue Gases ^b	
			Experimental	Calculated
0.35 Per Cent Methane				
5.75				
5.5				
4.75				
6.0				
5.0				
5.5				
5.5				
Av. 5.4	2.55	2.1		
0.7 Per Cent Hydrogen				
4.25				
4.25				
3.25				
3.25				
3.0				
Av. 3.6	1.6	2.2		
0.27 Per Cent Illuminating Gas				
2.25				
2.25				
2.25				
2.25				
Av. 2.25	1.0	2.2		
0.54 Per Cent Illuminating Gas				
4.25				
4.25				
4.25				
4.0				
Av. 4.2	2.0	2.1		

^a The molal heats of combustion (8) in joules used in the calculations were methane, 890,160; hydrogen, 284,850; carbon monoxide, 282,890.

^b Contained methane, hydrogen, or illuminating gas.

combustion method was compared with the procedure of flue-gas analysis described earlier in the paper on a sample of

gas containing 0.54 per cent illuminating gas (Table V), the following results were obtained (it is assumed that 3 carbon monoxide = 3 hydrogen = 1 hydrocarbon for the approximate heat calculations):

Carbon monoxide	%	
Carbon dioxide (total)	0.12	
Shrinkage	0.28	
Hydrogen estimation	0.75	
Assume: $\frac{\text{shrinkage}}{\text{carbon dioxide}} = 1$	0.35	Revised calcd. watts (Table V)
Total combustible in terms of hydrogen	0.95	2.2
Assume: $\frac{\text{shrinkage}}{\text{carbon dioxide}} = 2$	0.25	
Total combustible in terms of hydrogen	0.85	2.0

In conclusion, it is obvious that the outlined procedures for gas analysis, because of the assumptions involved, find application only when the gas sample contains a small percentage of combustible. The results obtained in flue-gas analysis possess an accuracy satisfactory for use in estimating the combustible gas stack loss in steam-generator efficiency tests.

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Literature Cited

- (1) Burrell, gas-analysis apparatus designed by Gas Chemists' Committee of Subsidiary Companies of U. S. Steel Corp.
- (2) Burrell, G. A., and Seibert, F. M., U. S. Bur. Mines, *Bull.* 197 (1926).
- (3) Dennis, L. M., and Nichols, M. L., "Gas Analysis," rev. ed., New York, Macmillan Co., 1929.
- (4) Evans, R. N., *IND. ENG. CHEM.*, 24, 856 (1932).
- (5) Hardie, P. H., and Cooper, W. S., *Trans. Am. Soc. Mech. Engrs.*, 56 (paper FSP-56-15, November, 1934).
- (6) Leighton, P. A., and Blacet, F. E., *J. Am. Chem. Soc.*, 54, 3165 (1932).
- (7) Lewis, G. N., and Randall, M., "Thermodynamics and the Free Energy of Chemical Substances," 1st ed., p. 559, New York, McGraw-Hill Book Co., Inc., 1923.
- (8) Rossini, F. D., *Bur. Standards J. Research*, 6, 1-35 (1931).
- (9) Teague, M. C., *J. IND. ENG. CHEM.*, 12, 964 (1920).
- (10) Triggs, W. W., Brit. Patent 352,817 (July, 1931).
- (11) Vandaveer, F. E., and Gregg, R. C., *IND. ENG. CHEM., Anal. Ed.*, 1, 129 (1929).
- (12) Watson, K. M., and Ceaglske, N. H., *Ibid.*, 4, 72 (1932).
- (13) Yant, W. P., and Hawk, C. O., *J. Am. Chem. Soc.*, 49, 1454 (1927).
- (14) Yuster, S., *IND. ENG. CHEM., Anal. Ed.*, 4, 224 (1932).

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Volumetric Microdetermination of Chloride and Potassium Ions

Application of the Potassium Method to Sea Water

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A NUMBER of years ago it became desirable to develop a simple titrimetric halide method for use in routine class work. The easy and sensitive adsorption indicator method of Fajans and co-workers (2, 3) seemed to offer every possibility of easy adaptation to the microscale. The best indicator for this purpose seemed to be dichlorofluorescein, originally introduced by Kolthoff, Lauer, and Sunde (9). One of the authors (P.L.K.) accordingly made a study of the use of this indicator in titrations of small amounts of halide ion (0.2 to 0.5 mg. in samples of about 1 ml.). By introducing a few improvements into the macromethod as originally given (9), an entirely satisfactory micromethod was evolved. It seemed possible to adapt this method to the determination of potassium through titration of the chloride in the precipitate of potassium chloroplatinate. Since the standard chloroplatinate method, which is one of the most dependable methods for determination of potassium, is gravimetric, a considerable simplification would be introduced.

The alternatives to the chloroplatinate method for potassium are not free of objection. The perchlorate method is also gravimetric and is subject to difficulty on account of the rather high solubility of the potassium perchlorate. The cobaltinitrite method with its various modifications (4, 10, 12, 15) is always subject to the use of an unstable reagent and the difficulty of obtaining a precipitate of constant known composition.

An easy and entirely satisfactory method for the determination of potassium in any medium to which the standard chloroplatinate method is applicable was accordingly de-

veloped. It depended on the reduction of the platinum in the precipitate to the metallic state by use of metallic magnesium in neutral solution, and the titration of the chloride released with silver nitrate, using dichlorofluorescein as indicator. In addition to the obvious advantage of being volumetric, there is a threefold factor relating the chloride to the potassium in the precipitate.

Experimental

CHLORIDE DETERMINATION: For test purposes, pure potassium chloride solution was used for analysis. The samples were of the order of 1 ml. of 0.01 *N* solution, titrated directly with 0.005 *N* silver nitrate solution, using a 10-ml. buret calibrated in 0.02-ml. divisions. The sample was conveniently contained in the cut-off end of a test tube. The conditions under which a visible end point with dichlorofluorescein was obtained were: The solution had to be approximately neutral; the amount of indicator could not exceed 2 drops of 0.01 per cent solution of dichlorofluorescein; acetone had to be added in amounts approximating the original volume of the sample; and illumination had to be from the side or rear of the observer, instead of being in the rear of the sample as is customary.

The reaction of the sample could be assured by observation of the indicator itself. At the correct reaction the indicator was greenish and fluorescent and, if this was not the case, acid or base was added. Too much indicator definitely obscured the end point, too small a fraction being adsorbed on the precipitate. The titration was best performed in a partially darkened room by the light of a daylight lamp placed at the side of the observer. A black background was preferable to a white one. The addition of acetone to the solution was found to be absolutely necessary with the samples used. Alcohol was an aid, but was definitely inferior to acetone. The effect was in all probability on the dis-

persion of the precipitate, a point which may be critical in view of the small amount of total precipitate and the fact that the color change occurs on this, rather than in the solution. When the titration was carried out in this manner, the end point was sufficiently visible and extremely sharp and reproducible. Table I gives the results of the study of this titration.

TABLE I. RESULTS OF TITRATION

0.0100 N Potassium Chloride Sample ML.	Acetone ML.	0.00503 N Silver Nitrate Titer ML.	Nitrate Calculated ML.
1.00	0	Indistinct end point	1.99
1.00	0	2.1 (approx.)	1.99
1.00	1	2.00	1.99
1.00	2	1.99	1.99
1.00	2	2.00	1.99
1.00	2	1.99	1.99
1.00	3	1.99	1.99
0.50	1	1.02	0.995
0.50	2	1.005	0.995
0.50	2	1.00	0.995
2.00	3	3.97	3.98
2.00	3	3.98	3.98

Table I indicates that the amount of acetone is not critical, but that its presence is necessary if the end point is to be distinct. This method has been in use in routine class work on simple solutions and certain biological materials for a period of some years and has amply demonstrated its reliability and ease. Interference by other ions is rare, except in the case of considerable amounts of phosphate, which definitely obscures the end point. Experience has shown it to be dependable in the determination of chloride, bromide, and iodide ions in combination with cations of all valences and types. The reproducibility and accuracy of this titration on the microscale is far superior to that obtained with the micro-Volhard or Mohr titrations, and the method is considerably more rapid than the Volhard titration.

POTASSIUM DETERMINATION: For preliminary testing of the method, samples of about 1 or 2 ml. of 0.01 or 0.005 N potassium chloride solution were used. Later, sea-water samples of 1 or 2 ml. were used to test the applicability of the method to solutions of high and varied salt content. The general method which gave satisfactory results with the sea-water samples is given below.

The sample was pipetted into a small porcelain crucible having a capacity of about 10 ml. Excess chloroplatinic acid solution (1 ml. of a solution containing 0.5 per cent platinum) was added and the solution evaporated to dryness on a steam bath. The general method of washing, which was applicable both to simple solutions and to sea water, was as follows:

Two successive 1-ml. portions of 80 per cent alcohol saturated with potassium chloroplatinate were used, followed by two or three similar portions of 20 per cent ammonium chloride, which had been shaken with potassium chloroplatinate, followed by three or four similar washings with the 80 per cent alcohol used previously. The final washing with alcohol was primarily for removal of the ammonium chloride, and the completeness of this removal was checked by observing whether a crust of ammonium chloride formed on the filter when the alcohol evaporated. With simple potassium solutions less careful washing could be used without affecting the results.

The precipitate, along with any asbestos which was used on the filter, was washed back into the crucible with 1 or 2 ml. of hot water. A small amount of powdered metallic magnesium was added to the neutral solution, and the mixture again evaporated to dryness on the water bath. When dry, a known amount of water, usually 3 ml., was added to dissolve the chlorides and the mixture filtered through a small dry filter paper. The chloride in an aliquot of the filtrate, usually 1 ml., was titrated with 0.005 N silver nitrate from a 10-ml. buret as described above, using dichlorofluorescein as indicator.

The filtration of the potassium chloroplatinate was the only point of technic that called for special consideration. While any small asbestos or sintered-glass filter could be adapted to this purpose, it was found that a filter stick of sintered glass was by far the most convenient. Such a filter has been described by Kirk (6), with a method of manufacture by

Kirk, Craig, and Rosenfels (7). It has been found far simpler and almost equally satisfactory to prepare a somewhat coarser grade of sintered-glass filter stick by the method described by Kirk (5). These filter sticks were mounted in a battery of six, which could be raised and lowered individually or collectively, thus making possible any number of simultaneous filtrations up to the number of filter sticks so mounted. Asbestos was used over the ends by simply sucking a layer of it on the filter from a flask of suspended shreds in water, as described by Miller and Kirk (11). The type of filter stick described by Emich (1) was not tried, but could probably have been used. The filter described by Kirk and Schmidt (8) was used satisfactorily, but was somewhat slower and less convenient than the sintered glass filter stick.

The calculation of the data involves the factor to correct for the aliquot and an atomic ratio of 1 to 3 which relates the potassium to the chloride in the precipitate. Table II gives the results of a series of determinations of potassium in potassium chloride solutions.

TABLE II. POTASSIUM DETERMINATION IN POTASSIUM CHLORIDE SOLUTIONS

Sample ML.	Normality	Titer 0.00496 N Silver Nitrate ML.	Calculated Potassium Found		Error Mg
			Mg.	Mg.	
Aliquot, 0.983 ML. from 2.906 ML.					
0.983	0.0100	2.00	0.384	0.383	-0.001
0.983	0.0100	2.01	0.384	0.384	0
0.983	0.0100	1.99	0.384	0.381	-0.003
0.983	0.0100	1.98	0.384	0.378	-0.006
0.983	0.0100	1.98	0.384	0.378	-0.006
0.983	0.0100	1.99	0.384	0.381	-0.003
0.983	0.0100	2.01	0.384	0.384	0
Aliquot, 0.983 ML. from 5.812 ML.					
1.966	0.0100	2.00	0.768	0.765	-0.003
1.966	0.0100	2.00	0.768	0.765	-0.003
1.966	0.0100	1.99	0.768	0.764	-0.004
Aliquot, 1.999 ML. from 2.906 ML.					
0.983	0.0051	2.10	0.196	0.198	+0.002
0.983	0.0051	2.07	0.196	0.195	-0.001
0.983	0.0051	2.12	0.196	0.199	+0.003

Sea water was chosen as a material on which to check the applicability of this method to mixed salt solutions, since the content of potassium is low, while that of other salts, particularly those of sodium, is high. The results of this study are shown in Table III.

TABLE III. POTASSIUM DETERMINATION IN SEA WATER

Ml. of Sea Water	Sample	Potassium in Original Sea Water Sample Mg./Ml.	Deviation from Mean Mg.
0.983		0.342	-0.002
0.983		0.344	0
0.983		0.344	0
0.983		0.346	+0.002
0.983		0.344	0
1.97		0.342	-0.002
1.97		0.342	-0.002
1.97		0.344	0
1.97		0.346	+0.002
1.97		0.344	0
0.983	+ 0.397 mg. added potassium	0.343	-0.001
0.983	+ 0.397 mg. added potassium	0.346	+0.002
0.983	+ 0.397 mg. added potassium	0.341	-0.003
0.983	+ 0.397 mg. added potassium	0.341	-0.003
0.983	+ 0.397 mg. added potassium	0.346	+0.002
Mean 0.344			

The reduction of potassium chloroplatinate to chloride and platinum with metallic magnesium in neutral solution had several advantages: The excess magnesium could be filtered off after reduction, thus avoiding later complications due to reduction of silver ion used in titration; magnesium effectively reduced the chloroplatinate in a neutral solution, thus avoiding any neutralization before titration; and the magnesium ion formed during the process had no effect upon the chloride titration. The use of formaldehyde for reduction was attempted, but it was found that a condensation

product resulted which could be removed only by the use of considerable amounts of hydrogen peroxide and boiling.

Whereas the use of alcohol saturated with potassium chloroplatinate is rather general, this is a particularly necessary precaution with small amounts of precipitate. When alcohol of any strength was used without this preliminary saturation, low results invariably resulted. Eighty per cent alcohol, saturated with potassium chloroplatinate, was used because of the greater solubility of sodium salts in this strength than in stronger alcohol solutions (14). It should also be noted that any aldehyde or acetic acid, which are common contaminants of alcohol, may produce some reduction of the chloroplatinate, giving low results (13).

It is apparent that this procedure will be satisfactory in any case in which the gravimetric chloroplatinate method may be used. This volumetric modification is rapid, simple in operation, and appears to yield on small samples an accuracy which is superior to that which would be obtained gravimetrically, since the deviations are not greater than would be expected from ordinary weighing deviations on the microbalance.

Further work is in progress on the application of these methods to biological fluids.

Literature Cited

- (1) Emich, F., and Schneider, F., "Microchemical Laboratory Manual," p. 69, New York, John Wiley & Sons, 1932.
- (2) Fajans, K., and Hassel, O., *Z. Elektrochem.*, **29**, 495 (1923).
- (3) Fajans, K., and Wolff, H., *Z. anorg. allgem. Chem.*, **137**, 221 (1924).
- (4) Hubbard, R. S., *J. Biol. Chem.*, **100**, 557 (1933).
- (5) Kirk, P. L., *IND. ENG. CHEM., Anal. Ed.*, **7**, 195 (1935).
- (6) Kirk, P. L., *Mikrochem.*, **14**, 1 (1933).
- (7) Kirk, P. L., Craig, R., and Rosenfels, R. S., *IND. ENG. CHEM., Anal. Ed.*, **6**, 154 (1934).
- (8) Kirk, P. L., and Schmidt, C. L. A., *J. Biol. Chem.*, **83**, 311 (1929).
- (9) Kolthoff, I. M., Lauer, W. M., and Sunde, C. J., *J. Am. Chem. Soc.*, **51**, 3273 (1930).
- (10) Maw, C. B., and Miller, K. R., *Proc. Utah Acad. Sci.*, **8**, 61 (1931).
- (11) Miller, R. P., and Kirk, P. L., *Mikrochem.*, **14**, 15 (1933).
- (12) Schueler, J. E., and Thomas, R. P., *IND. ENG. CHEM., Anal. Ed.*, **5**, 163 (1933).
- (13) Strebinger, H., and Holzer, H., *Z. anal. Chem.*, **90**, 81 (1932); Makris, C. G., *J. Pharm. Chim.*, **13**, 569, 570 (1931).
- (14) Treadwell, F. P., and Hall, W. R., "Analytical Chemistry," 6th ed. p. 59, New York, John Wiley & Sons, 1924.
- (15) Van Rysselberge, P. J., *IND. ENG. CHEM., Anal. Ed.*, **3**, 3 (1931).

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Analysis of *n*-Butanol, Acetone, and Ethanol in Aqueous Solution

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IN THE butyl-acetonic fermentation of corn mash and other suitable substrates, *n*-butanol, acetone, and ethanol are produced in the ratio of about 6 to 3 to 1. Hydrogen, carbon dioxide, acetic acid, butyric acid, and acetylmethylcarbinol are also formed, but the yield and proportion of the three solvents are of particular interest. It becomes necessary, therefore, in laboratory research on this process, to have available a rapid routine method for measuring these products. The method should also be applicable when only small amounts of the materials are available.

Reilly and Ralph (6) have reported the densities of the aqueous solutions of the three solvents. Bogin (1) developed a quantitative method based upon the determination of the total concentration of the three in the aqueous distillate, the measurement of the acetone by the usual iodometric method, and the determination of the *n*-butanol-ethanol ratio by titration of the anhydrous alcohols with water.

Werkman and Osburn (7) developed a procedure for the analysis of solutions of *n*-butanol and ethanol, based upon their oxidation with potassium dichromate and phosphoric acid, the acetone having been previously removed with 2,4-dinitrophenylhydrazine. The butanol yielded 90.7 per cent butyric acid and 9.3 per cent acetic acid, while the ethanol yielded only acetic acid. The acid ratio was determined by partitioning with isopropyl ether. Johnson (5) used a similar method, except that he measured the acid ratio by a modified Duclaux procedure. Fang (2) developed a method based upon measurement of the refractive index, determination of acetone by the usual iodometric method, and a second measurement of refractive index after partition with carbon tetrachloride, which removed *n*-butanol to a considerably greater extent than it did the acetone or ethanol.

Several methods have been used in these laboratories for the analysis of the two alcohols and, as a result, procedures

have been developed for their determination which have met all requirements for speed, simplicity, and accuracy. They have been thoroughly checked by a number of individuals and found to be well suited for routine use.

The fermentation mixture, representing a known weight of substrate, is neutralized to pH 7.0 to 7.5, and about one-third is carefully distilled into a receiver submerged in cold water. Usually 100 cc. of distillate are thus collected. All calculations are then based upon this volume of distillate. If it is of interest to estimate only the total solvent yield, the specific gravity, 25°/25°, is measured and the solvent concentration calculated by means of Equation 1. This equation holds for a 6 to 3 to 1 ratio, but is inaccurate when the ratio varies appreciably from the above proportion. The total concentration should not exceed about 10 grams per 100 cc. and is usually kept below 5 grams per 100 cc.

$$\text{Total solvents, grams/100 cc.} = (1.0000 - \text{sp. gr. } 25^\circ/25^\circ) 698 \quad (1)$$

The dipping refractometer may also be used to measure the total solvent concentration. The reading, 25°/25°, is expressed by Equation 2, in which *R* is the dipping refractometer reading and *B*, *A*, and *E* are the concentration of *n*-butanol, acetone, and ethanol, respectively, in grams per 100 cc. With a ratio of 6 to 3 to 1, the total solvent concentration is given by Equation 3.

$$R = 13.25 + 2.646B + 1.800A + 1.610E \quad (2)$$

$$\text{Total solvents, grams/100 cc.} = 0.437 (R - 13.25) \quad (3)$$

When it is desired to separate and identify the products, sufficient distillate to yield about 200 cc. of anhydrous solvents is saturated with sodium chloride, about one-fourth distilled into a cold receiver, and saturated with anhydrous potassium carbonate. The solvents separating are further

dried with anhydrous potassium carbonate and carefully fractionated. The usual derivatives can then be prepared. If no other compounds than *n*-butanol, acetone, and ethanol are present, and this is ordinarily the case, the procedures described below may be applied.

The data presented were obtained by the use of aqueous systems of the highly purified solvents.

The acetone is determined by the Goodwin (4) modification of the Messenger method. The interference from ethanol is negligible, unless it be present in much larger amounts than is the acetone. One gram of acetone consumes as much iodine as 100 grams of ethanol under the conditions employed in the analysis.

Determination of Ethanol and *n*-Butanol

When a mixture of *n*-butanol, acetone, and ethanol is oxidized with potassium dichromate and sulfuric acid, the reducing value of the solution depends upon the concentration of sulfuric acid, time, and temperature, as shown by Fauser (3). He found that 10 minutes' exposure of a 30- to 40-cc. mixture in a 2.5 × 25 cm. test tube in a boiling water bath gave easily duplicated results if the sulfuric acid concentration was carefully adjusted. Two flat portions were observed in the curve when reducing value was plotted against acid concentration, one when 10 volumes of acid per 30 cc. of mixture were used, and the second when 40 cc. of mixture contained 25 cc. of concentrated sulfuric acid. The difference between the reducing values obtained under these different conditions was found to be due entirely to the *n*-butanol and acetone. The procedure for the determination of the alcohols is as follows:

Ten cubic centimeters of original distillate containing not more than 5 grams of alcohols are diluted to 100 cc. and 10 cc. of this dilution are added to a cold mixture of 10 cc. of 0.4 *N* potassium dichromate and 10 cc. of concentrated sulfuric acid in a 2.5 by 25 cm. test tube. Two glass rods are dropped into the tube and the contents thoroughly mixed. A stopper carrying a 1-mm. capillary tube, the lower end of which is bent at right angles, is inserted and the tube placed in a vigorously boiling water bath. After 10 minutes' exposure, it is cooled and diluted to 400 cc. in a 1-liter Erlenmeyer flask. Fifteen cubic centimeters of a 20 per cent potassium iodide solution are then added, the flask is stoppered and allowed to stand 2 minutes, and the iodine released is titrated with 0.1 *N* sodium thiosulfate. A blank is run in the same way. The difference is designated as M_1 and has a value shown by Equation 4, in which M_1 is in cubic centimeters of 0.1000 *N* dichromate consumed, B is equal to the weight, in grams, of butanol in the original distillate, A , the acetone, and E , the ethanol, on the same basis.

$$M_1 = 6.92 B + 0.891 A + 8.78 E \quad (4)$$

A second titration is made to obtain another equation, and one of two procedures may be used. In one, a second oxidation, exactly like the above, is applied to a sample of distillate extracted with carbon tetrachloride. Twenty cubic centimeters

The extraction of butanol is not a linear function of concentration, and the correction represents the deviation from the linear relation assumed in applying the constant, 2.75. The terms have the dimensions used above.

Instead of extracting with carbon tetrachloride, a second equation may be obtained by carrying out the oxidation under different conditions. Ten cubic centimeters of original distillate, containing not more than 2 grams of alcohols per 100 cc., are diluted to 100 cc., and 5 cc. of this dilution are added to a cold mixture of 25 cc. of concentrated sulfuric acid and 10 cc. of 0.4 *N* potassium dichromate in a 2.5 by 25 cm. test tube and the procedure for M_1 is followed. A blank is run in the same way. The difference in titration is multiplied by two to give the value, N , shown in Equation 6, in which the dimensions are as above.

$$N = 24.62 B + 17.68 A + 8.84 E \quad (6)$$

From these values, ethanol and *n*-butanol may be calculated by means of Equations 7, 8, and 9.

$$B = 0.25 (M_1 - M_2) - 0.01 M_2 - 0.07 A + \text{correction} \quad (7)$$

(see Table II)

$$B = 0.057 (N - M_1) - 0.96 A \quad (8)$$

$$E = 0.114 M_1 - 0.788 B - 0.0787 A \quad (9)$$

In Table I are given data showing the application of the above equations to various mixtures of the pure solvents. The use of these relations is not confined to mixtures, for they are equally applicable to the solvents alone.

TABLE I. ESTIMATION OF BUTYL AND ETHYL ALCOHOL IN MIXTURES WITH ACETONE

Solvents in Original Distillate, G./100 Cc.			M_1		M_2		BuOH Found, G./100 Cc.		EtOH Found, G./100 Cc.	
BuOH	Me ₂ CO	EtOH	Calc.	Error	Calc.	Error	Calc.	Error	Calc.	Error
By Oxidation-Extraction Method										
3.81	0.87	0.88	34.0	18.0	3.81	±0.00	0.81	-0.07		
3.52	0.87	1.07	34.3	19.8	3.50	-0.02	1.06	-0.01		
3.52	1.72	0.29	26.7	12.1	3.53	+0.01	0.22	-0.07		
4.32	1.08	0.29	32.4	14.0	4.27	-0.05	0.22	-0.07		
0.59	0.21	0.10	4.9	2.7	0.59	±0.00	0.08	-0.02		
1.17	0.43	0.19	9.9	5.4	1.18	+0.01	0.18	-0.01		
1.76	0.64	0.29	15.0	8.1	1.71	-0.05	0.27	-0.02		
2.35	0.86	0.39	19.7	10.6	2.33	-0.02	0.32	-0.07		
2.93	1.07	0.48	25.0	13.2	2.96	+0.03	0.46	-0.02		
3.09	1.29	1.07	31.7	18.9	3.11	+0.02	1.07	±0.00		
4.32	1.29	0.00	30.1	11.6	4.29	-0.03	-0.06	-0.06		
0.00	1.72	1.17	11.2	10.2	-0.02	-0.02	1.15	-0.02		
By Double-Oxidation Method										
1.50	0.75	0.30	13.4	52.2	1.49	-0.01	0.29	-0.01		
0.80	1.00	0.40	9.5	40.6	0.81	+0.01	0.37	-0.03		
0.40	1.00	0.40	6.7	30.9	0.42	+0.02	0.37	-0.03		
1.50	0.90	0.30	13.5	54.7	1.48	-0.02	0.29	-0.01		
1.50	0.60	0.30	13.4	49.6	1.48	-0.02	0.30	±0.00		
1.00	0.50	1.00	13.2	39.0	0.99	-0.01	0.99	-0.01		
1.00	0.50	0.50	11.6	37.6	1.00	±0.00	0.49	-0.01		
1.00	0.50	0.40	10.7	37.0	1.02	+0.02	0.39	-0.01		
1.00	1.00	1.00	16.2	50.7	1.00	±0.00	0.97	-0.03		
0.24	0.11	0.04	2.1	7.8	0.22	-0.02	0.04	±0.00		
0.41	0.15	0.00	10.2	37.6	1.42	+0.01	0.05	+0.05		
1.25	0.00	0.30	11.6	33.9	1.27	+0.02	0.33	+0.03		

Summary

Methods suitable for the rapid routine analysis of aqueous solutions of *n*-butanol, acetone, and ethanol are described. Acetone is measured by an iodometric method and the al-

TABLE II. STANDARD CORRECTIONS FOR EQUATION 4

BuOH Uncorrected G./100 Cc.	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0	+0.02	+0.04	+0.06	+0.08	+0.10	+0.12	+0.14	+0.16	+0.18
1	+0.19	+0.21	+0.22	+0.24	+0.25	+0.26	+0.27	+0.28	+0.29	+0.30
2	+0.31	+0.32	+0.32	+0.33	+0.33	+0.33	+0.33	+0.33	+0.32	+0.31
3	+0.31	+0.30	+0.28	+0.27	+0.25	+0.23	+0.21	+0.19	+0.17	+0.14
4	+0.12	+0.10	+0.07	+0.05	+0.02	±0.00	-0.03	-0.06	-0.09	-0.11
5	-0.14	-0.18	-0.18	-0.21	-0.23	-0.28	-0.28	-0.31	-0.33	-0.36
6	-0.39	-0.42	-0.44	-0.46	-0.49	-0.52	-0.54	-0.57	-0.59	-0.61

of the distillate are placed in a test tube with 40 cc. of carbon tetrachloride, shaken, and allowed to stand 2 hours at 25° C. It is essential that the temperature be closely controlled. Ten cubic centimeters of the aqueous solution are removed, diluted to 100 cc. and 10 cc. of this dilution oxidized as above, to obtain a value, M_2 , which is represented by Equation 5.

$$M_2 = 2.75 B + 0.386 A + 8.22 E \text{ plus correction} \quad (5)$$

cohols are measured by oxidation with dichromate and extraction with carbon tetrachloride, or by oxidation at two different concentrations of sulfuric acid in the oxidizing mixture. The methods are equally accurate and rapid. For purposes of checking, a combination of the methods may be employed. As a means of proving the identity of the prod-

ucts, both the oxidation and the oxidation-extraction methods, taken in conjunction with measurement of specific gravity and the dipping refractometer reading, will prove of value.

Acknowledgment

Many individuals contributed to the development of these methods. In particular, thanks are due Donald Starr, Gerrish Severson, Ernest Fauser, L. C. Bryner, and A. R. Kendall.

Literature Cited

- (1) Bogin, C. D., *IND. ENG. CHEM.*, **16**, 380 (1924).
- (2) Fang, H. C., *Iowa State Coll. J. Sci.*, **6**, 423 (1932).
- (3) Fauser, E. E., thesis for M.Sc. Degree, Iowa State College, 1934.
- (4) Goodwin, L. F., *J. Am. Chem. Soc.*, **42**, 39 (1920).
- (5) Johnson, M. J., *IND. ENG. CHEM., Anal. Ed.*, **4**, 20 (1932).
- (6) Reilly, J., and Ralph, E. W., *Sci. Proc. Royal Dublin Soc.*, **15**, 597 (1919).
- (7) Werkman, C. H., and Osburn, O. L., *IND. ENG. CHEM., Anal. Ed.*, **3**, 387 (1931).

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Estimation of Small Amounts of Lead in Copper

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LEAD occurs in most refined copper in about the same amount as other metallic impurities, from a few to several hundred parts per million. Several methods have been proposed for its separation and estimation. Heath (1) and Jones (2) separate lead as dioxide by electrolyzing a nitric acid solution of the copper. Keffer (3) separates the lead by co-precipitation with calcium carbonate from an ammoniacal solution before electrolysis. Electrolytic methods for lead are open to criticism because some of the lead is apt to deposit with the copper; other elements, such as bismuth and manganese, may deposit with the lead; the composition of the deposited lead peroxide varies; and prevention of mechanical loss while handling the deposit is difficult.

In order to find a better method for the separation of lead from copper the authors have tried a number of schemes, all based on the formation of an insoluble lead salt and its collection by some occluding agent. The method adopted proved capable of separating and estimating, with an error of about 50 per cent, as little as one part of lead in one million parts of copper.

Purification of Reagents

Nitric, hydrochloric, and acetic acids and ammonium hydroxide were tested for lead by distilling 500 cc. of each from a silica still, dissolving the residue in distilled nitric acid, concentrating to 5 cc., and then testing the concentrate spectrographically. These reagents were lead-free.

Solutions of manganese sulfate (25 per cent), ferrous ammonium sulfate (20 per cent), calcium chloride (20 per cent), and disodium hydrogen phosphate (50 per cent) were rendered lead-free by adding a few cubic centimeters of a saturated solution of lead-free copper sulfate, saturating with hydrogen sulfide, filtering off the precipitated sulfides, and repeating until a precipitate was obtained which showed no spectrographic trace of lead. Usually the third precipitate was lead-free.

Ten per cent potassium dichromate solution was treated with a little of the lead-free ferrous ammonium sulfate solution, ammonium hydroxide was added, and the mixed precipitate of iron and chromium hydroxides was filtered out and tested. This procedure was repeated until the precipitate gave no test for lead.

Five per cent potassium permanganate solution was treated with a little of the lead-free dichromate solution and then repeatedly with ferrous ammonium sulfate and ammonium hydroxide until a lead-free precipitate was obtained.

The authors were unable to remove the rather large amount of lead present in the c. p. reagent brand of ammonium carbonate. Lead-free ammonium carbonate solution was prepared by passing carbon dioxide into a solution of two parts of water to one part of strong ammonium hydroxide until a precipitate formed.

taining about 0.5 mg. of lead were washed in hydrochloric acid to remove surface impurities and dissolved in 200 cc. of nitric acid. From this point the procedure varied.

Procedure

1. The sample was taken to fumes with sulfuric acid, diluted to 500 cc., and heated to boiling and then 2 cc. of manganese sulfate solution were added. Ten cubic centimeters of permanganate solution were added with constant stirring and the solution was allowed to stand overnight. The precipitate was dissolved and reprecipitated as PbS, which was then dissolved in nitric acid and tested spectroscopically for lead.

2. Ammonium hydroxide was added to neutralize the excess nitric acid, the solution was diluted to 500 cc., and 15 cc. of acetic acid were added. The pH of the solution at this point, determined by means of a quinhydrone electrode, was 2.0. Ten cubic centimeters of the dichromate solution were added and then the manganese dioxide precipitation was carried out as described under (1). Each of three consecutive precipitates showed a small amount of lead.

3. The excess nitric acid was boiled off, 15 grams of borax were added, and the solution was diluted to 500 cc. The pH was 2.8. Three manganese dioxide precipitates, after the addition of dichromate solution, failed to remove all of the lead.

4. The solution was prepared as in (3), but 25 cc. of ferrous ammonium sulfate were added instead of the manganese sulfate and permanganate. Three consecutive precipitations all showed lead.

5. Four grams of Norite were added to a solution prepared as in (3) and the mixture was stirred mechanically overnight. The Norite was filtered out and extracted with hot nitric acid. This procedure failed to remove any lead from the solution.

6. The nitric acid solution was diluted to 500 cc., and then 10 cc. of dichromate solution, 25 cc. of ferrous ammonium sulfate solution, and enough ammonium hydroxide to bring down a small amount of copper hydroxide were added. Next 200 cc. of concentrated ammonium hydroxide were added and the solution was heated to 80° C. and filtered hot. Three consecutive precipitates all showed a small amount of lead.

7. This procedure was the same as (6), except that 3 cc. of manganese sulfate and 10 cc. of permanganate solutions were substituted for the iron. A complete separation was not obtained.

8. To the hot ammoniacal solution containing dichromate 4 grams of Norite were added. After a few hours of stirring the Norite was filtered out and extracted with nitric acid. No lead was removed by this method.

9. To the cold ammoniacal solution were added 50 cc. of ammonium carbonate solution, followed by 5 cc. of calcium chloride solution. It was found that if the calcium chloride was added before the ammonium carbonate (method of Keffer, 3) a much less efficient separation was made. The mixture was stirred well and allowed to stand overnight, and the precipitate filtered out and tested in the usual way. Although this procedure gave a better separation than any of those previously mentioned, it was unsatisfactory. Three consecutive precipitates all showed lead.

Table I gives a summary of the various schemes of separation which were tried. In each case 50 grams of copper con-

TABLE I. SEPARATION OF SMALL AMOUNTS OF LEAD FROM COPPER

Nature of Solution	Insoluble Lead Salt	Collector	Result
1 H ₂ SO ₄	PbSO ₄	MnO ₂	Unsatisfactory
2 HNO ₃ + HOAc (pH 2.0)	PbCrO ₄	MnO ₂	Unsatisfactory
3 HNO ₃ + Na ₂ B ₄ O ₇ (pH 2.8)	PbCrO ₄	MnO ₂	Unsatisfactory
4 HNO ₃ + Na ₂ B ₄ O ₇ (pH 2.8)	PbCrO ₄	Fe(OH) ₃	Unsatisfactory
5 HNO ₃ + Na ₂ B ₄ O ₇ (pH 2.8)	PbCrO ₄	Norite	Unsatisfactory
6 NH ₄ OH	PbCrO ₄	Fe(OH) ₃	Unsatisfactory
7 NH ₄ OH	PbCrO ₄	MnO(OH) ₂	Unsatisfactory
8 NH ₄ OH	PbCrO ₄	Norite	Unsatisfactory
9 NH ₄ OH	PbCO ₃	CaCO ₃	Unsatisfactory
10 NH ₄ OH	Pb ₃ (PO ₄) ₂	Ca ₃ (PO ₄) ₂ + CaCO ₃	Satisfactory

TABLE II. SEPARATION OF LEAD IN COPPER

Sample	% Lead	Sample	% Lead
1	0.0010	8	0.0010
2	0.0008	9	0.0008
3	0.0007	10	0.0020
4	0.0060	11	0.0005
5	0.0011	12	0.0007
6	0.0008	13	0.0010
7	0.0010	14	0.0008

10. This method was used in all subsequent work, and will therefore be described in detail. A 50-gram sample of copper was washed with hot concentrated hydrochloric acid, followed by distilled water, and dissolved in 200 cc. of concentrated nitric acid. The brown fumes were boiled off, and 1200 cc. of water and 350 cc. of concentrated ammonium hydroxide were added. Then 2 cc. of disodium phosphate and 50 cc. of ammonium carbonate solutions were added, the solution was mixed well, and 25 cc. of calcium chloride solution added all at once with stirring. After standing overnight it was filtered through a No. 4 Jena glass crucible. The precipitate was dissolved in 25 cc. of hydrochloric acid, neutralized with ammonium hydroxide, then acidified with a few drops of acid and saturated with hydrogen sulfide before filtering. The sulfides were dissolved in nitric acid and concentrated to 5 cc. All the lead is separated by this method. A

second precipitation showed no trace. Two milligrams of lead were added to this lead-free copper solution and a third precipitation was made. This contained the 2 mg. A fourth precipitate again showed no lead.

A number of samples of refined copper from various sources were subjected to this method. The results obtained by comparison of their spectrograms with those of standards taken on the same plate, according to the method of Nitchie (4), are given in Table II.

Preparation of Standards

SOLUTION A. Three grams of lead-free copper were dissolved in 300 cc. of nitric acid.

SOLUTION B. One gram of test lead was dissolved in a little nitric acid and diluted to one liter.

Four cubic centimeters of B and 6 cc. of A were mixed. Then 5 cc. of the mixture were mixed with 5 cc. of A to give the second standard, and 5 cc. of the second standard were mixed with 5 cc. of A to give the third standard. In this way nine standards were prepared with the following concentrations: 2, 1, 0.5, 0.25, 0.125, 0.0625, 0.0312, 0.0156, and 0.0078 mg. per 5 cc.

When 0.1 cc. of each of the standards was dried on a graphite electrode and arced, the lead line at 2833 Å. graded nicely in intensity and was visible in the first seven. The smallest amount of lead detectable by this method and by the particular Gartner Littrow-type spectrograph used in this work was therefore 6×10^{-7} gram.

Literature Cited

- (1) Heath, "Analysis of Copper," p. 221, New York, McGraw-Hill Book Co., 1916.
- (2) Jones, *Analyst*, 58, 11 (1933).
- (3) Keffer, "Methods in Non-Ferrous Metallurgical Analysis," p. 118, New York, McGraw-Hill Book Co., 1928.
- (4) Nitchie, *IND. ENG. CHEM., Anal. Ed.*, 1, 1 (1929).

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Detection and Volumetric Estimation of Alkali Metals

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IT IS SOMETIMES not easy to decide by means of common reagents whether or not the alkalinity of an ash is due to alkali metal. For example, an ash from a mixed base grease containing calcium and sodium presents somewhat the same flaky appearance as an ash from a calcium soap grease. The usual flame test is uncertain in this case.

Soap Formation as a Test

The qualitative test here outlined makes use of the insolubility of alkaline-earth oleates and the solubility of alkali oleate in water.

A portion of the hot, aqueous, filtered extract of the alkaline ash is added with shaking to a hot alcoholic solution of oleic acid until the mixture is alkaline to phenolphthalein. The alcoholic strength must be kept above 50 per cent at all times to prevent hydrolysis of the soap formed. The solution is evaporated on the steam bath with a current of air blowing into the flask until the odor of alcohol is very faint. Five volumes of distilled water are added to the aqueous residue, the solution is warmed and shaken, and any alkaline-earth soaps are filtered off. The filtrate is examined for ability to froth on shaking, and tested for alkali soap by the addition of barium chloride solution. A white, curdy precipitate confirms alkalinity due to alkali metal in the ash. A faintly opalescent filtrate that does not froth, nor increase in cloudiness upon the addition of barium chloride, is

sometimes encountered when alkaline earth compounds alone are present. It should not be confused with the soapy frothy filtrate, yielding a precipitate with barium chloride, due to alkali soaps.

This test has the advantage of preferentially detecting alkalinity due to sodium or potassium, not showing sodium or potassium that may be also present in neutral combination as chlorides or sulfates. Other sodium or potassium reagents give information only as to the total content of these metals. This test is particularly adapted to distinguish sodium and potassium from calcium in the ash of lubricating greases.

Quantitative Volumetric Determination

The quantitative estimation was designed primarily as a fairly rapid method for alkali metals in the ash obtained by the ignition of petroleum products and compounds. It has been extended to the determination of these metals in their sulfates, to which form many other of their salts can be easily converted.

It is applied in the cases cited by treating the ash or salt with concentrated sulfuric acid, and decomposing the excess sulfuric acid and heavy metal sulfates by heating carefully until no more sulfur trioxide fumes are given off.

TABLE I. RESULTS ON KNOWN MIXTURES

Mixture	Weight of Sample Grams	Sodium Carbonate		Sodium Found	
		In mixture %	Found %	In mixture %	Found %
Ammonium sulfate, calcium hydroxide, and sodium carbonate	0.176	35.2	35.2	15.3	15.3
Fused sodium chloride	0.240	37.1	37.2	16.1	16.2
	0.366	39.4	39.1
	0.146	40.0
				Potassium	
Potassium nitrate	0.406	38.6	38.6
	0.230	38.5

The sulfated residue is dissolved as far as possible in water. Solid barium hydroxide is added in excess to precipitate sulfates as barium sulfate, and to convert sodium and/or potassium sulfate to the hydroxide.



The precipitate, which may include other undissolved alkaline-earth sulfates, is filtered off and washed well with hot water, and ammonium carbonate is added to the boiling combined filtrate and washings to precipitate soluble alkaline-earth compounds as carbonates. The carbonates are filtered off, washed well with hot water, and the filtrate is boiled down to one-fifth of its volume to decompose and get rid of excess ammonium carbonate. (There should be no odor of ammonia at this point.) After cooling, any slight precipitate of alkaline-earth carbonates is filtered off, washed with water at room temperature, and the combined filtrate and washings are titrated to a methyl orange end point with 0.1 *N* acid in the usual manner. The acid consumed is calculated to per cent sodium or potassium, as the case may be.

If they are both present, this titration would represent the total alkalinity due to alkali metals.

Since the estimation is based on getting the alkali metals in the form of soluble compounds, it is not necessary to burn off all carbon or ignite the ash to constant weight. This reduces the loss by volatility of alkali metal compounds, which is a troublesome factor in the usual gravimetric determinations of the alkali metals. It is hoped that this method may be useful in estimating alkali metals in other fields of analytical procedure.

Results on Unknown Mixtures

Neutrally bound alkali metals in the ash may be calculated from the difference between the result obtained by the method as outlined and the result obtained by determining the alkalinity of the ash to methyl orange. Results of tests on ash from soda-base grease, containing 0.93 per cent of total sulfur, showed the following:

Alkalinity of ash as sodium, uncorrected	30.8	30.9
Total sodium by this method, per cent	34.6	34.8
Neutrally bound sodium, per cent	3.8	3.8

Acknowledgment

The author wishes to thank Harry Levin and Karl Uhrig for helpful criticisms and suggestions.

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Detection of Benzene in Alcohol

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BENZENE may occur in alcohol in small amounts, and is undesirable in alcohol used for some purposes. The presence of benzene may be due to faulty process, or to accidental contamination. When the benzene content is too small for any of the turbidity tests with water, indications of its presence are usually obtained through taste and odor. Unfortunately, taste and odor tests do not give uniformly positive selective indications of the presence of benzene in low concentration. A direct and sensitive chemical test for small amounts of benzene in alcohol is therefore of value in the examination of alcohol.

A reliable method was desired for detecting benzene in concentrations of the order of 1 part by volume in 10,000, in alcohol of good quality otherwise. After unsatisfactory results by other methods a procedure involving concentration of the benzene by extraction, nitration of the extract, and color reaction of the nitration product was devised and applied with satisfactory results.

Reagents Required

Carbon tetrachloride, reagent grade.

Acetone, reagent grade.

Amyl alcohol (redistilled crude fusel oil) refluxed with strong caustic soda solution, and distilled from the alkali, collecting for use the dry fraction boiling at 128° to 132° C.

Nitrating acid: 70 grams of reagent 20 per cent oleum, 45 grams of reagent sulfuric acid of specific gravity 1.84, and 43 grams of reagent nitric acid of specific gravity 1.42.

Sodium sulfate solution, containing 10 grams of the anhydrous salt in 100 cc. of solution.

Caustic soda solution, 140 grams of reagent (sticks) made up to 250 cc. at room temperature.

Procedure

If the alcohol contains much above 0.01 per cent benzene by volume, as indicated by test on the undiluted sample, it is diluted

to approximately that value with alcohol free from benzene. A 40-cc. portion is placed in a 100-cc. glass-stoppered cylinder with 6 cc. of carbon tetrachloride. Distilled water is added to the 90 cc. mark, followed by 10 cc. of sodium sulfate solution. The cylinder is stoppered, shaken thoroughly, and allowed to stand until the layers separate sharply. Five cubic centimeters of the bottom layer are transferred by pipet to a test tube. Three cubic centimeters of nitrating acid are measured in a small cylinder and added to the test tube, which is shaken carefully but thoroughly. During 10 minutes the tube is shaken twice more, and at the end of that time, 20 cc. of distilled water are added, preferably rapidly from a cylinder. After mixing by pouring into another test tube and back again, the bulk of the water layer is decanted and discarded. The lower layer with a small amount of water layer is placed in an evaporating dish on an electric hot plate. When the carbon tetrachloride is gone, the dish is emptied into the same test tube just used, and is rinsed into this tube with 1 cc. of amyl alcohol. The dish is then rinsed into the tube using 4 cc. of caustic soda solution. The tube is mixed by swirling and then 1 cc. of acetone is added, the tube is swirled again, and placed in a rack for observation of color produced in the top layer.

Indications

Pure benzene at the concentration 1 in 10,000 by volume in a rectified alcohol of ordinary purity gives by this test a red color with a purple quality in the top layer. This color holds for some hours, and finally fades to a dull orange-red. As the benzene content rises above 0.01 per cent, the color produced soon becomes too dark for identification, and dilution with alcohol free from benzene is necessary. Pure toluene gives a slightly brownish yellow and reagent xylene (chiefly *m*-xylene) produces a definite though not intense green, which fades in 30 minutes, giving way to a dull orange. Blank runs should always be run in duplicate with a test series; they give a light clear lemon yellow. Thorough cleaning of the apparatus between tests is necessary to maintain blank indications. Among other hydrocarbons tested, denaturing gasolines gave yellow colors of somewhat orange cast and a cer-

tain kerosene gave a reddish color, readily distinguished from the benzene color.

Precautions

If suitable concentration methods and adequate precautions are used, concentrations of benzene well below 1 in 10,000 should be detected. Exclusion of chlorides from the extraction is necessary, as the subsequent nitration seems sensitive to their presence. A lower salt concentration than that used gave erratic results and a high salt concentration precipitated solids into the bottom layer. Exclusion of water from the nitration mixture is imperative. The pres-

ence of oxidizable material, such as excessive amounts of alcohol from the extraction or stopcock lubricant, interfere probably by their effect in the nitration. Care in preventing this effect is fully as important as efficient extraction of the benzene in the carbon tetrachloride.

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Destruction of Organic Matter in Plant Material by the Use of Nitric and Perchloric Acids

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THE destruction of organic matter by some form of ashing generally precedes the determination of the mineral constituents in plant material. Two undesirable features of the ashing process suggest the need of a wet oxidation method similar to the Kjeldahl digestion: (1) The method of ashing commonly used for calcium and magnesium determinations is not applicable for potassium and phosphorus determinations on account of the loss of the more volatile compounds of potassium and phosphorus while ashing; and (2) the residues after ashing may be in a slowly soluble form.

Perchloric acid either alone or in mixtures with other acids has been widely used in the oxidation of organic materials of animal origin previous to the determination of the mineral constituents. Kahane and associates (4) have made the most comprehensive study of these methods and have developed a method for determining silica in plant materials (5). Winter and Bird (11) have used perchloric acid similarly for determining aluminum in plants.

The properties of perchloric acid, as well as those of the perchlorate ion, make it a very desirable oxidizing agent for the analysis of organic substances. No water-insoluble perchlorates of the metals have been reported. Furthermore, cold perchloric acid, either dilute or concentrated, is not affected by ordinary reducing agents. The dehydrating action of perchloric acid on silica, shown by Willard and Cake (10), aids in the quantitative separation of silica.

Since hot concentrated perchloric acid may react violently with organic substances, the reaction intensity must be controlled. It has been found advisable to pretreat samples of plant material with nitric acid before adding perchloric acid. With substances very high in fat it may be necessary to pretreat the sample several times with nitric acid before it can be oxidized with perchloric acid without a loss of a portion of the sample. The perchloric acid should be diluted with water and nitric acid.

Experimental Procedure

The following method of wet oxidation was applied to a wide variety of plant materials, including sweet clover (roots and tops), alfalfa hay, red clover hay, alsike clover hay,

timothy hay, redtop hay, wheat straw, cornstalks, corncobs, corn (grain), and soy beans:

Place a 4-gram sample of the material to be oxidized in a 400-ml. beaker and add 10 ml. of nitric acid (sp. gr. 1.42). Cover the beaker with a watch glass and heat gently until any rapid initial reactions have subsided. Then heat to boiling and boil until the contents of the beaker are almost dry. Remove the beaker from the hot plate and add 10 ml. of dilute nitric acid (1 to 1) and 10 ml. of perchloric acid (70 to 72 per cent). Replace the cover glass and heat very gently to a low boiling temperature (avoid superheating). Maintain this temperature until all organic material has been removed from the sides of the beaker and from the solution, which will be indicated by a colorless or slightly colored solution. Remove the cover glass, allow the beaker to cool a few minutes, and wash any adhering salts into the beaker. (If the cover glass is washed with perchloric acid, the contents of the beaker need not be cooled.)

Evaporate to dryness at a temperature just below the boiling point in a clean hood. If potassium is to be determined on the residue, the ammonium salts should be removed at this point. After the removal of ammonium salts, add 5 ml. of hydrochloric acid (1 to 1) and 10 ml. of water. Heat until all salts are dissolved. Filter into a suitable volumetric flask. Wash the silica residue thoroughly with hot water and make the filtrate up to volume. Aliquot portions of the filtrate may be taken for subsequent analyses.

The above method was applied to the plant materials studied and calcium, magnesium, potassium, and phosphorus were determined. Known amounts of calcium from a standard solution of calcium acetate, magnesium from a standard solution of magnesium sulfate, and potassium and phosphorus from a standard solution of potassium dihydrogen phosphate were then added to a duplicate sample of the material and the determinations repeated, using the same procedure. The acids and salts used were taken from the usual laboratory stock of c. p. reagents. Calcium was precipitated as the oxalate and titrated with permanganate as directed by Wiley (9). Magnesium was determined by the method of Handy (2) as modified by Truog and Chucka (8). The method of Schueler and Thomas (6) was used for potassium. Phosphorus was precipitated as the phosphomolybdate and titrated with sodium hydroxide according to the method given by Treadwell and Hall (7). Table I shows the amounts of calcium, magnesium, potassium, and phosphorus recovered.

TABLE I. RECOVERY OF PHOSPHORUS, POTASSIUM, CALCIUM, AND MAGNESIUM ADDED TO PLANT MATERIAL AND OXIDIZED WITH PERCHLORIC ACID

	Added, Mg.	Total, Mg.	Recovered, Mg.	Added, Mg.	Total, Mg.	Recovered, Mg.
Phosphorus						
Wheat straw	0	2.50	0	0	3.29	0
	2.00	4.50	2.00	0.60	3.91	0.62
	2.00	4.48	1.98	0.60	3.94	0.65
Sweet clover	0	2.00	0	0	1.92	0
	2.00	4.00	2.00	0.60	2.46	0.54
	2.00	3.95	1.95	0.60	2.49	0.57
Calcium						
Wheat straw	0	8.2	0	0	3.01	0
	14.5	22.6	14.4	7.10	9.90	6.89
	14.5	22.6	14.4	7.10	9.99	6.98
Sweet clover	0	31.4	0	0	10.76	0
	14.5	45.9	14.4	7.10	17.91	7.15
	14.5	45.5	14.1	7.10	17.82	7.06
Potassium						
Magnesium						

TABLE II. TOTAL CALCIUM AND TOTAL MAGNESIUM FOUND IN PLANT MATERIAL

(When oxidized with nitric-perchloric acid and when ashed without treatment according to A. O. A. C. method)

Sample Number	Calcium		Magnesium		
	By HClO ₄ , %	By ashing, %	By HClO ₄ , %	By ashing, %	
Wheat straw	902	0.38	0.30	0.14	0.11
	907	0.22	0.18	0.10	0.08
Sweet clover tops	W407	1.58	1.53	0.55	0.50
Sweet clover roots	N309	0.36	0.29	0.38	0.23
Sweet clover tops	C	0.74	0.76	0.61	0.67
Sweet clover roots	C	0.18	0.17	0.31	0.25
Redtop hay	WS	0.26	0.18	0.27	0.16
Timothy hay	R408E	0.30	0.19	0.17	0.16
Alfalfa hay	R409E	2.24	2.29	0.51	0.51

TABLE III. TOTAL PHOSPHORUS AND TOTAL POTASSIUM FOUND IN PLANT MATERIAL

(When ashed with H₂SO₄ (method given by Wiley) and oxidized with nitric-perchloric acid)

Sample Number	Phosphorus		Potassium		
	By HClO ₄ , %	By ashing, %	By HClO ₄ , %	By ashing, %	
Alfalfa hay	401	0.15	0.14	0.96	0.83
	403	0.20	0.22	0.73	0.69
	404	0.20	0.23	0.93	0.83
Red clover hay	408	0.20	0.20	0.80	0.67
	409	0.20	0.21	0.96	0.93
Alsike clover hay	401	0.15	0.15	1.16	0.99
	402	0.29	0.25	1.12	1.01
Wheat straw	902	0.25	0.22	1.69	1.50
	907	0.25	0.22	2.33	2.13

In order to test the accuracy of the nitric-perchloric acid method of destroying organic matter a corresponding set of samples was ashed, and calcium, magnesium, potassium, and phosphorus were determined as before. The method of the Association of Official Agricultural Chemists (1) was used for ashing the samples previous to the determination of calcium and magnesium, and the sulfuric acid method of Wiley (9) was used for potassium and phosphorus. As a further comparison, the method of Howk and DeTurk (3) was used for phosphorus. Samples of wheat straw, redtop hay, sweet clover tops, and sweet clover roots were found to contain 0.26, 0.15, 0.18, and 0.32 per cent of phosphorus, respectively, by the Howk and DeTurk method, as compared to 0.27, 0.16, 0.19, and 0.32 per cent by the nitric-perchloric acid method. The results of the other comparisons are given in Tables II and III.

Discussion of Results

The amounts of calcium, magnesium, potassium, and phosphorus added were very satisfactorily recovered with the use of the nitric-perchloric acid procedure (Table I).

Tables II and III show that there is not always good agreement between the nitric-perchloric acid and the ashing methods. It will be noted from Table II that in cases of disagree-

ment calcium and magnesium are always lower when the samples are ashed. With the nitric-perchloric acid method one obtains a white residue of dehydrated silica, but when the sample is ashed for calcium and magnesium determinations, the residue is usually gray, indicating the incomplete oxidation of carbon. Furthermore, the calcium and magnesium in the ash are not readily soluble in the dilute acid used in extraction. Low results under such conditions suggest the incomplete removal of calcium and magnesium from the residue obtained upon ashing. Likewise, the ashing method for potassium tends to give lower results than the nitric-perchloric acid method. Since potassium compounds are volatile at high temperatures, a loss of potassium might be expected in using the ashing procedure.

The results of the three methods used for the phosphorus determinations agree very closely.

In view of these results and the plausible explanations thereof, it would seem that the proposed method of wet oxidation of this class of materials is from the standpoint of both accuracy and convenience superior to the ashing methods.

Summary

A method involving the wet oxidation of the organic matter in plant materials previous to the determinations of calcium, magnesium, potassium, and phosphorus has been devised. This method has been found to be rapid in that only one sample is required for the four determinations. The calcium, magnesium, potassium, and phosphorus are left in a condition in which they are readily soluble in dilute acids and no loss through volatilization of phosphorus or potassium was encountered.

The method used for preventing violent reactions between the perchloric acid and the organic substances was found to be effective in all cases.

Literature Cited

- (1) Assoc. Official Agr. Chem., "Official and Tentative Methods," 3rd ed., p. 102 (1930).
- (2) Handy, J. O., *J. Am. Chem. Soc.*, **22**, 31 (1900).
- (3) Howk, B. W., and DeTurk, E. E., *IND. ENG. CHEM., Anal. Ed.*, **4**, 111 (1932).
- (4) Kahane, E., "L'Action de l'Acide Perchlorique sur les Matières Organiques. I. Généralités. II. Applications," Paris, France, Hermann et Cie, 1934.
- (5) Lematter, L., Boinot, G., Kahane, E., and Kahane, M., *Compt. rend.*, **192**, 1459 (1931).
- (6) Schueler, J. E., and Thomas, R. P., *IND. ENG. CHEM., Anal. Ed.*, **5**, 163 (1933).
- (7) Treadwell, F. P., and Hall, W. T., "Analytical Chemistry," 6th ed., Vol. II, p. 503, New York, John Wiley & Sons, 1924.
- (8) Truog, E., and Chueka, J. A., unpublished data, University of Wisconsin, 1934.
- (9) Wiley, H. W., "Principles and Practices of Agricultural Analysis," p. 554, Easton, Pa., Chemical Publishing Co., 1914.
- (10) Willard, H. H., and Cake, W. E., *J. Am. Chem. Soc.*, **42**, 2208 (1920).
- (11) Winter, O. B., and Bird, O. D., *Ibid.*, **51**, 2964 (1929).

RECEIVED March 20, 1935.

"Cold Light" Filter Developed

A filter for obtaining "cold light" has been developed by K. S. Gibson, chief, colorimetry section, National Bureau of Standards. This filter transmits a very narrow band in the green, and the luminous efficiency of this transmitted energy is extremely high—about 99 per cent of the maximum possible. The result is "cold light" or light practically without heat.

The transmitted band of light has a wave length of 560 millimicrons, a spectral region which is of particular importance in the colorimetry of sugar solutions, in optical pyrometry, in abridged spectrophotometry, and in photometry. Four components are used in the construction of the filter, two being made of Corning and two of Jena glass.

Solutions for Colorimetric Standards

VI. Ferric Chloride

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FOR the preparation of certain colorimetric standards various individuals (1) have proposed aqueous solutions of ferric chloride acidified with hydrochloric acid. Apparently recognizing some correlation between the hue of the solution and the amount of acid used, Army made the acid concentration 1 per cent.

In preparing and using such a standard it is desirable both to recognize the factors affecting its color and to specify a set of conditions, following which will yield a reproducible system. The object of the present study, therefore, was to determine the significant facts concerning the colorimetric characteristics of the solution, including quantitative measurements, by means of a new spectrophotometer, of the effect of different amounts of acid.

A number of observations related to this problem have been previously reported as facts. The pale yellow hue of a freshly prepared, dilute aqueous solution becomes brownish on standing at room temperature, because of the formation of a sol of hydrous ferric oxide (6). This hydrolysis may be reversed by a small quantity of hydrochloric acid (20), but the resulting brilliance is not quite that of the original (18). The more dilute the unacidified solution, the less is the proportion of total iron present in true solution (10, 19). Acid stabilizes the solution (15). Adding concentrated hydrochloric acid turns a dilute, aqueous solution a deep, yellowish brown (19). This reaction, together with several of a similar nature between such a solution and various other reagents, indicates the formation of complex ions (6, 15, 19, 21). Over considerable ranges of concentration, Beer's law does not hold for solutions containing some acid (11, 12). The character and intensity of absorption of light by the solution depends upon the concentration, hydrolysis, and acidity (8).

Experimental Work

MATERIALS. Using ferric chloride, prepared by chlorinating iron wire (2), and concentrated hydrochloric acid, two stock solutions were prepared, one 4.10 M in ferric chloride and 0.1 M in acid, and one 10.9 M in acid only. Mixtures of these with water provided the different concentrations desired. Colloidal dispersions of hydrous ferric oxide were made by adding definite amounts of the stock solution of ferric chloride to boiling water and diluting to 100 ml. when cool.

PROCEDURE. The transmission measurements were made with a new photoelectric spectrophotometer built by the General Electric Company according to the design of A. C. Hardy. As the literature thus far contains only an abstract (9) concerning the principle of the instrument and a paragraph (16) on its construction, brief reference is made here to significant items regarding its use.

The assembly consists essentially of two units, a manually adjusted double monochromator and an automatic balancing photoelectric polarizing photometer. The photoelectric cell serves merely as a null device for detecting differences in intensity in the two light beams entering an integrating sphere. In operation a Rochon prism is rotated automatically until the two light beams match in intensity. At this point the percentage transmission may be read directly on a counter connected in the automatic mechanism.

The operation of this instrument was relatively simple, measurements being made by setting the wave-length scale, adjusting

the three slits to give the desired width of spectral band at the given wave length, and reading the transmission on the photometer scale. The general practice was to make readings at intervals of 10 m μ from 400 to 700 m μ and then to check the readings back to the starting point. All data were obtained by dividing the transmission for the solution by that for the solvent. Measured cells were used and the data calculated to a thickness of 10.0 mm. by means of a special Keuffel and Esser slide rule based upon the application of Lambert's law.

To test the accuracy of the instrument the wave-length scale was calibrated in terms of lines from a mercury arc lamp and a helium tube (7), and the photometer scale was checked before each series of measurements by means of Bureau of Standards glasses (blue, amber, and red). Two solutions recommended by the Bureau of Standards (5) served to supplement the glasses. It is believed the calibration rendered the wave-length values accurate to 1 m μ . Since the instrument checked the values for the standard glasses within 0.5 per cent, the error in the transmittancies may be expected to be of this order of magnitude. The readings going up and down any curve were generally reproducible within ± 0.2 per cent, indicating satisfactory precision. The average was taken for the values obtained going in the two directions. For relatively flat parts of a curve the slits were set for a 10 m μ band and then reduced for the steep parts to 5 or 3 m μ . These narrower bands somewhat decreased the sensitivity and precision.

It seems appropriate to mention certain advantages of the instrument in comparison with the visual one used for previous papers in this series. Of outstanding interest was the elimination of the personal equation in matching intensities, with its attendant optical fatigue. The time required for operation

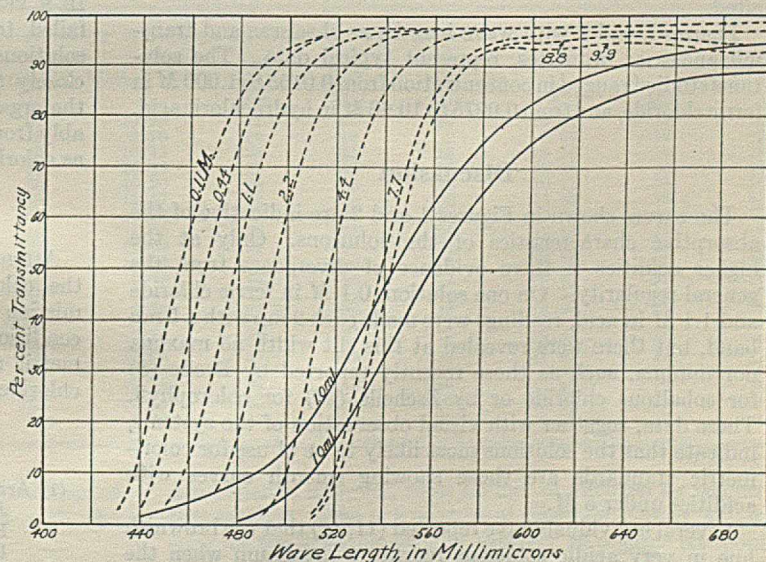


FIGURE 1. SPECTRAL TRANSMISSION CURVES

Broken lines, solutions 0.1 M in ferric chloride and varying molarities in hydrochloric acid. Solid lines, colloidal dispersions prepared from 1 and 10 ml. of a solution 4.1 M in ferric chloride and 0.1 M in hydrochloric acid.

was much less. With the sample and light source nearly 3 meters apart and with most of the optical system between them, heating of the sample was practically eliminated and only monochromatic light passed through it. Illumination of the dark room did not affect the measurements. The accuracy and precision in the blue and red regions was undoubtedly much superior to that obtained in the previous

papers. Preliminary checking of a few solutions has indicated considerable uncertainty in values there reported for wave lengths below 450 and above 650 μ . At that time, however, the data were the best that could be obtained with the facilities available.

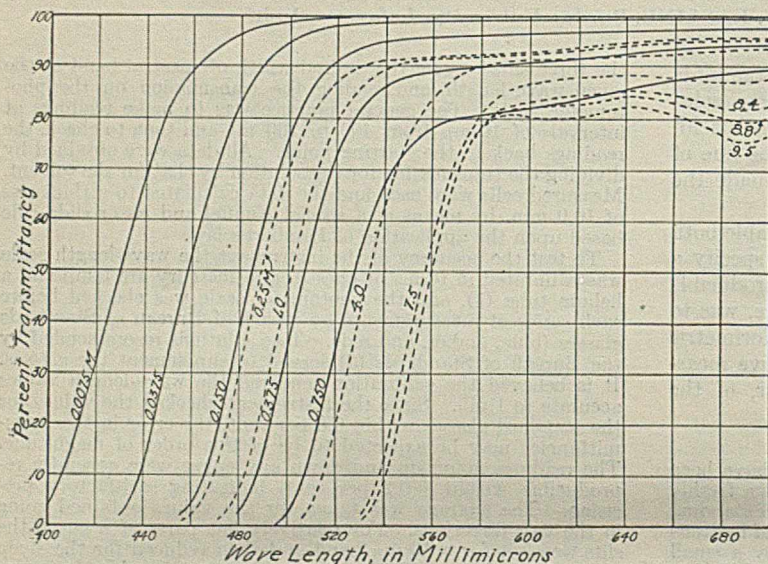


FIGURE 2. SPECTRAL TRANSMISSION CURVES

Broken lines, solutions 0.3 M in ferric chloride and varying molarities in hydrochloric acid. Solid lines, solutions 1.0 M in hydrochloric acid and varying molarities in ferric chloride.

In addition to the determination of the transmission data qualitative experiments were made which resulted, in general, in a confirmation of the observations recorded in the literature cited.

Figures 1 and 2 with wave lengths as abscissas and transmittancies as ordinates, represent typical data. The solutions studied ranged in concentration from 0.0155 to 1.000 M in ferric chloride, and from 0.0275 to 10.66 M in hydrochloric acid.

Discussion

The curves shown in Figures 1 and 2 are indicative of the absorptive characteristics of the solutions. Only at the higher acidities is there evidence of divergence from the general regularity. On one solution, 0.1 M in ferric chloride and 1.1 M in acid, readings were made each 2 μ with a 5 μ band, but there were revealed at this slit width no maxima nor minima, such as those recently reported by Brode (3) for cobaltous chloride or by Zscheile (22) for chlorophyll. These data, together with visual observation of the systems, indicate that the solutions most likely to be of use for colorimetric standards are those showing smooth curves with acidities under 5 M .

Several individuals have reported (11, 12) that the brownish hue in very acidic solutions reaches a maximum when the concentration of acid is approximately 9 M , the exact point depending upon the concentration of iron. For this phenomenon Figure 1 does not show the expected reversal of curves. Solutions of such acidities are probably of no value for colorimetric work.

In Figure 1 the curves for the interesting colloidal dispersion of hydrous ferric oxide should be considered as merely illustrative of the form characteristic of such systems. While a carefully prepared dispersion seems relatively stable, its reproducibility is very questionable unless under very closely controlled conditions. Apparently it is a problem of obtaining particles of the same size.

Calculation of monochromatic data (13) for solutions 0.5 M in ferric chloride and 0.275 to 8.8 M in acid showed that the colorimetric purity is high in all cases (97 to 99 per cent). The relative brilliance decreases with increasing acidity at least up to 8.8 M while the dominant wave length shows the reverse change.

Solutions 0.3 M in ferric chloride and 0.25, 1.0, and 7.5 M in acid were diluted to five times their original volume, keeping the acidity constant, and measured in 5-cm. cells. The curve for the data thus obtained for the 0.25 and 1.0 M solutions came 6 to 10 μ to the left of those in Figure 2 for the same solution measured before dilution in 1-cm. cells. For these two concentrations this represents distinct divergence from conformity to Beer's law, but the data obtained in the same way for the 7.5 M solution were practically identical.

Little or no dichromatism was indicated for a solution 0.25 M in ferric chloride and 0.44 M in acid when the luminosities were calculated according to Clark's method (4) and plotted against wave lengths.

The curves for three solutions, 0.1666 M in ferric chloride and 0.27 M in acid, one 5 years old, one 18 months old, and one freshly prepared, each made by a different individual, checked each other within the experimental error, confirming Arny's observations (1) on stability and reproducibility. However, solutions 0.02 M in acid were not sufficiently acidic to prevent hydrolysis, with resultant fading

and formation of a precipitate.

Sidgwick has discussed (17) certain striking properties of ferric chloride which he attributes to its electronic structure. In a variety of organic solvents carbon tetrachloride alone failed to dissolve it in substantial amounts. Curves for solutions in chloroform and in glacial acetic acid resembled closely those shown here for the lower acidities. Many of the organic solutions fade more or less rapidly (14), presumably from the reduction of the iron, rendering them worthless as colorimetric standards.

Summary

Attention has been directed to various factors affecting the color of solutions of ferric chloride. Spectral transmission curves show the type of absorption under different conditions. The best range of concentrations for colorimetric standards is probably from 0.5 to 0.02 M in ferric chloride and from 5.0 to 0.05 M in hydrochloric acid.

Literature Cited

- (1) Arny, H. V., *8th Intern. Congr. Appl. Chem.*, 26, 319 (1912); *J. Am. Pharm. Assoc.*, 12, 839 (1923); Arny, H. V., and Pickhardt, E. G., *Druggists' Circ.*, 57, 131 (1914); Arny, H. V., and Ring, C. H., *J. Franklin Inst.*, 180, 198 (1915); *J. IND. ENG. CHEM.*, 8, 309 (1916); Crookes, W., Odling, W., and Tidy, C. M., *Chem. News*, 43, 174 (1881); Kolthoff, I. M., *Pharm. Weekblad*, 59, 104 (1922); Ritchie, K. S., *IND. ENG. CHEM.*, 19, 1289 (1927); Taub, A., *J. Am. Pharm. Assoc.*, 16, 116 (1927).
- (2) Biltz, H., and Biltz, W., "Laboratory Methods of Inorganic Chemistry," p. 69, New York, John Wiley & Sons, 1909.
- (3) Brode, W. R., *J. Am. Chem. Soc.*, 53, 2457 (1931).
- (4) Clark, W. M., "Determination of Hydrogen Ions," p. 160, Baltimore, Williams and Wilkins, 1928.
- (5) Davis, R., and Gibson, K. S., *Bur. Standards Miscellaneous Pub.* 114, 41 (1931).
- (6) Donnan, F. G., and Basset, H., *J. Chem. Soc.*, 81, 939, 955 (1902); Pickering, S. U., *Ibid.*, 105, 483 (1914).
- (7) Gibson, K. S., et al., *J. Optical Soc. Am.*, 10, 169 (1925).

- (8) Gmelin, L., "Handbuch der anorganischen Chemie," No. 59, part B, p. 257, Leipzig, Verlag Chemie. G. m. b. H., 1929.
 (9) Hardy, A. C., *J. Optical Soc. Am.*, 24, 162 (1934).
 (10) Heymann, E., *Z. anorg. Chem.*, 171, 26 (1928).
 (11) Hostetter, J. C., *J. Am. Chem. Soc.*, 41, 1535 (1919); Jones, H. C., and Anderson, J. A., *Am. Chem. J.*, 41, 202 (1909).
 (12) Lemoine, G., *Ann. chim. phys.*, [6], 30, 376 (1893); Moore, B. E., *Phys. Rev.*, 12, 166 (1901).
 (13) Mellon, M. G., *J. Phys. Chem.*, 33, 1931 (1930).
 (14) Mellon, M. G., and Foster, Violet, *Ibid.*, 33, 963 (1930).
 (15) Müller, E., *J. prakt. Chem.*, 90, 129 (1914).
 (16) Nutting, R. D., *J. Optical Soc. Am.*, 24, 135 (1934).
 (17) Sidgwick, N. V., "The Electronic Theory of Valency," p. 93, Oxford University Press, 1929.
 (18) Smith, T. B., "Analytical Processes," p. 69, Arnold and Co., 1929.
 (19) Smith, T. B., *Ibid.*, p. 329.
 (20) Spring, W., *Rec. trav. chim.*, 18, 238 (1899).
 (21) Weinland, R., "Einführung in die Chemie der Komplex-Verbindung," p. 100, F. Enke, 1924.
 (22) Zscheile, F. P., *J. Phys. Chem.*, 38, 1 (1934).

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Combination of Catalysts to Reduce Digestion Time in Determination of Nitrogen

I. In Organic Compounds

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CONFIRMING the work of other investigators, it has been found in this laboratory (3) that 30 per cent hydrogen peroxide hastens the digestion in the determination of nitrogen in organic compounds by the Gunning process. Various combinations of catalysts, with and without strong hydrogen peroxide, have also been used in this laboratory in the determination of nitrogen in dairy products (6). In this communication, there is reported the quantitative reduction in time when nitrogen is determined in organic compounds with the aid of strong hydrogen peroxide and a mixture of copper, mercury, and selenium as catalysts.

In every case, the samples containing catalysts cleared much more rapidly than the controls. The use of the combination of copper, selenium, and mercury effects the greatest saving of time. In some cases the use of strong hydrogen peroxide with these three catalysts somewhat reduces the digestion time over that obtained when these catalysts were used without the hydrogen peroxide, but not enough time was saved to warrant the additional expense and trouble. The use of selenium alone or in combination with other catalysts has been claimed by several investigators (2, 4, 5, 7) to cause some loss of nitrogen. The results of the present

TABLE I. DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS

Compound	Theoretical %	Gunning Method		1 g. CuSO ₄		0.5 g. HgO		CuSO ₄ + HgO + Se		CuSO ₄ + HgO + Se + H ₂ O ₂	
		Min.	%	Min.	Min.	Min.	%	Min.	%		
Acetanilide	10.37	90	10.26	21	20	10	10.41	10	10.33		
Acetphenetidin	7.70	119	7.70	16	16	9	7.68	10	7.68		
<i>o</i> -Aminobenzoic acid	10.21	60	10.15	28	31	18	10.16	18	10.10		
<i>m</i> -Aminobenzoic acid	10.21	61	10.18	29	42	13	10.16	12	10.17		
<i>p</i> -Aminobenzoic acid	10.21	60	10.20	25	33	13	10.13	15	10.11		
<i>dl-d</i> -Amino- <i>n</i> -butyric acid	13.58	128	13.57	38	42	22	13.69	16	13.61		
Aminocaproic acid	10.68	254	10.74	26	27	21	10.63	18	10.67		
Aminocaprylic acid	8.79	250	8.63	28	32	22	8.84	18	8.73		
Amino-isobutyric acid	13.58	131	13.59	36	41	21	13.48	16	13.45		
Benzidine	15.21	300	15.36	26	25	9	15.16	8	15.20		
<i>p</i> -Bromoacetanilide	6.54	140	6.45	29	33	21	6.42	17	6.58		
3-Bromo-4-acetylamino toluene	6.14	210	5.94	29	33	21	6.12	17	6.22		
<i>p</i> -Bromoaniline	8.14	120	8.05	22	29	18	8.09	18	8.20		
<i>o</i> -Chloroacetanilide	8.26	212	8.26	30	34	11	8.17	12	8.24		
<i>p</i> -Chloroaniline	10.99	230	10.85	29	34	18	10.88	18	10.85		
1,4-Diaminobutane-hydrochloride	17.39	165	17.38	27	25	17	17.45	17	17.32		
<i>p</i> -Dimethylaminobenzaldehyde	9.39	214	9.26	33	39	22	9.26	22	9.24		
<i>o</i> -Tolylurea	18.65	210	18.44	29	27	19	18.62	17	18.79		
<i>p</i> -Tolylurea	18.65	215	18.48	30	27	20	18.59	17	18.77		
2,4,6-Tribromoaniline	4.25	60	4.30	28	31	23	4.30	17	4.28		

The method employed was the Gunning modification of the original Kjeldahl method, which is official with the Association of Official Agricultural Chemists (1).

In each of a number of digestion flasks, 0.25 gram of the organic compound was placed with 10 grams of nitrogen-free potassium sulfate and 20 cc. of concentrated sulfuric acid. To four of the flasks were added the following catalysts: (1) HgO, 0.5 gram; (2) CuSO₄·5H₂O, 1 gram; (3) HgO, 0.3 gram; CuSO₄·5H₂O, 0.5 gram; and Se, 0.1 gram; (4) the same ingredients as (3) with the addition of 1 cc. of strong hydrogen peroxide every 5 minutes until the solution cleared. The fifth flask contained no added catalyst. The contents of each flask were digested over electrically heated plates, all units of which were of the same construction and gave the same amount of heat. Each sample was heated until the liquid cleared.

Table I gives the comparisons of the times necessary for the clearing to take place and some quantitative results.

experiments, however, show no loss of nitrogen by the use of this catalyst. Use of a mixture of selenium, copper, and mercury for the determination of nitrogen in organic compounds does not seem to have been tried by other investigators.

Literature Cited

- (1) Assoc. Official Agr. Chem., "Official and Tentative Methods of Analysis," 3rd ed., 1930.
- (2) Davis, C. F., and Wise, M., *J. Cereal Chem.*, 10, 488 (1933).
- (3) Dewey, B. T., thesis, University of Colorado.
- (4) Osborn, R. A., and Krasnitz, A., *J. Assoc. Official Agr. Chem.*, 17, 339 (1934).
- (5) Sandstedt, R. M., *J. Cereal Chem.*, 9, 156 (1932).
- (6) Schafer, R. R., thesis, University of Colorado.
- (7) Snider, S. R., and Coleman, D. A., *J. Cereal Chem.*, 11, 414 (1934).

RECEIVED April 15, 1935.

A Color Test for the Identification of Mono-, Di-, and Trinitro Compounds

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IN SPITE of the fact that most color reactions are viewed with suspicion in qualitative organic analysis, there are certain instances where they may conserve time and lead to many short cuts in the identification of a given compound. In other cases color tests serve to detect traces of impurities in a compound, the presence of which it might otherwise be difficult to show. In view of these facts the work reported herein was undertaken.

Janovsky and Erb (3) showed that violet or reddish brown colors were obtained when nitroazo compounds were treated with acetone and potassium hydroxide. In 1891 Janovsky (2) studied the reaction between acetone and the dinitro substitution products of benzene, toluene, and naphthalene in the presence of potassium hydroxide. A year later von Bitto (1) reported the action of aldehydes and ketones on *m*-dinitrobenzene, dinitrotoluene, and α -dinitronaphthalene with potassium hydroxide, as well as of certain trinitro compounds. The mechanism of the reaction between acetone and 2,4-dinitrochlorobenzene in the presence of sodium hydroxide has been explained by Reitzenstein and Stamm (4).

Taylor and Rinckenbach (6) and Rudolph (5) have reported the colors produced by a few mono-, di-, and trinitro bodies under the aforementioned conditions. Taylor and Rinckenbach point out that the color produced by trinitro compounds will obscure those produced by dinitro bodies when the two

types are present in mixtures. The authors have confirmed this observation.

It seemed desirable to extend the work of previous investigators in this field and to determine, if possible, the limitations of the color test in detecting nitro compounds. In this paper are given data on many mono-, di-, and trinitro compounds of benzene, showing the effect of the presence of various substituted groups, such as aldehyde, alkyl, amino, ester, carboxyl, halogen, hydroxyl, and methoxy, as well as the position of the nitro groups in the molecule, on the color produced.

Phenomenal as it may seem, mononitro compounds give no color with the reagent, dinitro compounds give a purplish blue color, while trinitro compounds produce a blood red color, except where an amino, substituted amino, or hydroxyl group is present. Acylation of the amino or hydroxyl group does not alter the inhibiting effect of such groups on the color test. The substitution of an alkyl group for an amino hydrogen does not alter the inhibition of the amino group, whereas the substitution of a methyl group for enolic-hydrogen permits the compound to respond to the general color test. Noteworthy examples are 2,4-dinitroaniline, 2,4-dinitrophenol, 2,4-dinitroacetanilide, 2,4-dinitrophenylacetate, 2,4-dinitrodiethylaniline, and 2,4-dinitroanisole.

In cases where the benzene nucleus is richly substituted, as in 2,4-dinitromesitylene, 2,4,6-trinitromesitylene, and 2-

TABLE I. COLOR IN MONONITRO COMPOUNDS

Compound	Reagent	Diluted with H ₂ O	HCl Added	CH ₃ COOH Added	Acid Solution Treated with NaOH
<i>p</i> -Nitrochlorobenzene	None	None	None	None	None
<i>p</i> -Nitrobromobenzene	None	None	None	None	None
<i>m</i> -Nitroaniline	None	None	None	None	None
Nitrobenzene	None	None	None	None	None
<i>m</i> -Nitrobenzaldehyde	None	None	None	None	None
<i>m</i> -Nitrobenzoic acid	None	None	None	None	None
<i>p</i> -Nitrobenzoyl chloride	None	None	None	None	None
3-Nitro phthalic acid	None	None	None	None	None
<i>p</i> -Nitroanisole	None	None	None	None	None
<i>o</i> -Nitrotoluene	None	None	None	None	None
<i>m</i> -Nitrotoluene	None	None	None	None	None
<i>p</i> -Nitrotoluene	None	None	None	None	None
3-Nitro-4-aminotoluene	Orange	Yellow	No change	No change	No change
3-Nitro-4-aminotoluene benzoate	Reddish orange	Light yellow	Yellowish green	Yellowish green	Reddish orange

TABLE II. COLOR IN DINITRO COMPOUNDS

Compound	Reagent	Diluted with H ₂ O	HCl Added	CH ₃ COOH Added	Acid Solution On HCl soln.	Made Basic with NaOH On CH ₃ COOH soln.
<i>m</i> -Dinitrobenzene	Purplish blue	Light purple	Yellowish brown	Reddish purple	Red	Red
2,4-Dinitrochlorobenzene	Purplish blue	Light purple	Lemon yellow	Wine red	Wine red	Wine red
3,5-Dinitrobenzoic acid	Purplish blue	Light purple	Wine then pink	Dark blue	Purple	Purple
3,5-Dinitromethylbenzoate	Blue	Faint blue	Crimson then pink	Blue	Purplish blue	Blue
2,4-Dinitroanisole	Purplish blue	Faint violet	Greenish yellow	Purplish red	Wine red	Wine red
2,4-Dinitrothioanisole	Blue	Faint blue	Yellow	No change	Color restored	Color restored
2,4-Dinitrotoluene	Blue	Faint blue	Greenish yellow	Purple	Purplish blue	Purplish blue
2,6-Dinitro- <i>p</i> -cymene	Purplish blue	Faint violet	Light yellow	Faint reddish brown	Light yellowish brown	Faint pink
2,4-Dinitromesitylene	None	None	None	None	None	None
3,5-Dinitro salicylic acid	Yellow	Faint lemon yellow	Reddish orange	Pink	Yellow	Yellow
2,4-Dinitrophenylacetate	Reddish orange	Greenish yellow	None	Lemon yellow	Reddish orange	Yellowish orange
2,4-Dinitrophenol	Yellowish orange	Faint greenish yellow	Faint lemon yellow	Yellowish green	Yellowish orange	Yellowish orange
2,4-Dinitroresorcinol	Brownish green	Faint brownish green	Light brown	Greenish brown	Greenish brown	Greenish brown
2,4-Dinitroaniline	Red	Pink	Lemon yellow	Orange red	Red	Red
2,4-Dinitroacetanilide	Reddish orange	Greenish yellow	Color discharged	Color discharged	Original color restored	Original color restored
2,4-Dinitrodiethylaniline	Reddish orange	Pink green fluorescence	Color discharged	Color discharged	Reddish orange	Light reddish orange
<i>p</i> -Dinitrobenzene	Greenish yellow	Faint greenish yellow	Colorless	Colorless	Original color restored	Original color restored
<i>o</i> -Dinitrobenzene	None	None	None	None	None	None

TABLE III. COLOR IN TRINITRO COMPOUNDS

Compound	Reagent	Diluted	HCl Added	CH ₃ COOH Added	Acid Solution Made On HCl soln.	Basic with NaOH On CH ₃ COOH soln.
1,3,5-Trinitrobenzene	Red	Light red	Blood red	Wine red	Reddish brown	Blood red
2,4,6-Trinitrotoluene	Red	Faint pink	Red	Red	Red	Red
2,4,6-Trinitroanisole	Red	Faint pink	Orange red	No change	Orange yellow	Red
2,4,6-Trinitrobenzoic acid	Red	Pink	Red	Red	Pink	Pink
2,4,6-Trinitrobenzaldehyde	Brownish red	Faint brownish red	Brownish red	Brownish red	Brownish red	Brownish red
2,4,6-Trinitrophenylhydrazine	Brownish red	Faint brownish red	Brownish red	Brownish red	Dark brownish red	Dark brownish red
2,4,6-Trinitrophenol	Reddish orange	Light orange red	Orange	Reddish orange	Yellowish orange	Reddish orange
2,4,6-Trinitrophenylacetate	Reddish orange	Greenish yellow	No change	Reddish brown	No change	Reddish brown
2,4,6-Trinitro- <i>m</i> -cresyl acetate	Orange yellow	Yellowish green	No change	Slightly darker	No change	Color lightened
2,4,6-Trinitro- <i>m</i> -cresol	Orange	Light lemon yellow	Lemon yellow	Lemon yellow	Reddish orange	Reddish orange
2,4,6-Trinitroresorcinol	Greenish yellow	Light greenish yellow	Orange yellow	No change	Greenish yellow	No change
2,4,6-Trinitroresorcinylic acetate	Greenish yellow	Light greenish yellow	No change	No change	No change	No change
2,4,6-Trinitromesitylene	None	None	None	None	None	None
2,4,6-Trinitro-1,3-dimethyl-5- <i>ter</i> -butyl benzene	None	None	None	None	None	None

4,6-trinitro-1,3-dimethyl-5-*ter*-butyl benzene, no color is produced.

The steric effect of the nitro group in the isomeric dinitrobenzenes is noteworthy. *m*-Dinitrobenzene readily responds to the test, *p*-dinitrobenzene gives a reddish yellow which soon passes into a greenish yellow color, while *o*-dinitrobenzene gives no color at all.

The test is extremely delicate in most cases—for example, 2,4-dinitrobenzene is sensitive to one part in 1,500,000. Since mononitro compounds fail to respond to the test, it is possible to detect traces of di- or trinitro compounds in mononitro compounds as impurities by this method, but it is not possible to detect dinitro compounds in the presence of trinitro compounds.

Procedure

One-tenth gram of nitro compound is dissolved in 10 ml. of acetone and 3 ml. of 5 per cent sodium hydroxide are added with shaking. At this point a purplish blue color will appear for dinitro compounds, while a blood red color is produced by trinitro bodies. Mononitro compounds fail to give a color. Exceptions to these tests have been dis-

cussed above. These colors are true only for the benzene series. If it is desired to produce a less intense color, a smaller amount of alkali should be used in the test.

In Tables I, II, and III are given the results with various nitro compounds under different conditions.

Summary

Mononitro compounds of the benzene series produce no color with the reagent, dinitro compounds a purplish blue color, and trinitro compounds a blood red color.

The presence of the amino, substituted amino, or hydroxyl group in the nucleus interferes with the test. Acylation of these groups does not remove the interference.

The test is extremely sensitive.

Literature Cited

- (1) Bitto, B. von, *Ann.*, 269, 377 (1892).
- (2) Janovsky, *Ber.*, 24, 971 (1891).
- (3) Janovsky and Erb, *Ibid.*, 19, 2158 (1886).
- (4) Reitzenstein and Stamm, *J. prakt. Chem.*, 81, 168 (1910).
- (5) Rudolph, *Z. anal. Chem.*, 66, 239 (1921).
- (6) Taylor and Rinckenbach, U. S. Bur. Mines, *Bull.* 219, 122 (1923).

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An Improved Slow-Combustion Pipet for Gas Analysis

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SINCE 1876 when Coquillon (3) proposed the use of a platinum spiral for slow-combustion analysis of hydrocarbon gases, this method has come to be practically standard. In the usual method the combustion pipet is filled with oxygen or air and the combustible gas is slowly introduced at the top of the pipet where it comes in contact with the heated platinum spiral and combustion ensues (2, 4). Improvements upon the basic design of this pipet have been made by Weaver and Ledig (8) and Matuszak (7).

A deposit of carbon is often found on the pipet wall above the spiral after a series of combustions, and when burning some gases such as isobutane, combustion is incomplete to the extent that when the gases are passed the second time over the hot spiral an explosion often occurs.

In one pipet designed to secure more perfect combustion and decrease the danger from explosions, the gas to be burned is introduced through a capillary platinum jet located in the

side wall of the pipet and impinges directly upon the heated spiral (1). Convection in this case should aid in keeping the spiral surrounded by oxygen rather than hot products of combustion, yet it is possible that the combustible gas might be swept away before reaching the heated zone.

To secure safety in operation and accuracy in results, complete combustion must be secured, and the most logical method of securing complete combustion is to burn a pre-heated mixture of the combustible gas and an excess of oxygen. Any such mixture with a sufficiently high concentration of combustible to be useful in gas analysis is explosive, so the usual pipet cannot be used.

Drehschmidt (5) passed combustible mixtures through 100 mm. of platinum capillary tubing of 0.7 mm. internal and 2.5 mm. external diameter, which he heated by a Bunsen flame. His platinum tube deteriorated rapidly with use and had to be renewed because of leakage. Weaver and Ledig

(8) describe forms of glass or quartz capillary tubes containing fine heated spirals which are useful for determining small amounts of oxygen in a gas, or small traces of combustible in oxygen or air. Lutz (6) has found such apparatus not satisfactory for use in general slow-combustion analysis.

Design

In a preliminary design of a slow-combustion pipet in which the combustible gas could be mixed with oxygen and passed over an ignitor, the gas was led through 2.5 cm. of platinum tubing of 0.9 mm. internal and 1.0 mm. external diameter with an insert of 0.45-mm. platinum wire. The small annular space remaining for passage of gas prevented passage of flame or explosion wave for all combustible mixtures tried, including electrolytic gas at very low flow rates. One to two millimeters from the

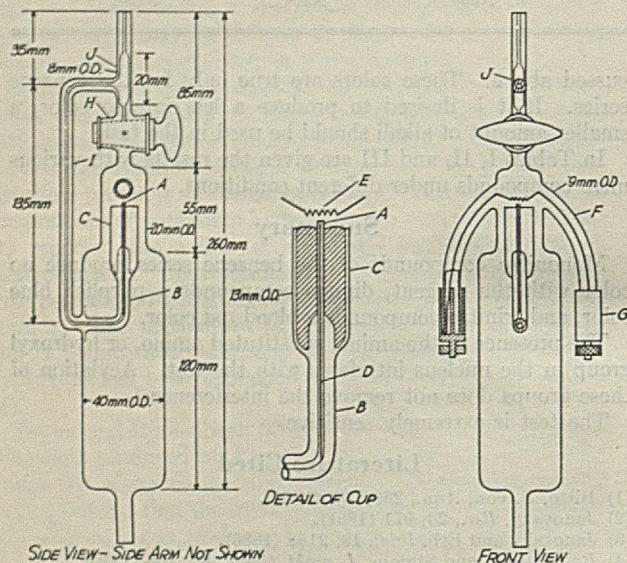


FIGURE 1. DIAGRAM OF PIPET

end of this inlet tube were placed the various ignitors. An unsupported platinum spiral, platinum spirals on quartz and refractory supports, and a refractory mixture containing thorium and aluminum oxides, alundum cement, and water-glass binder with internal spiral of platinum wire were tried as ignitors. It was found that, because of the radiating power of the refractories and the protection which they afforded the platinum wire, the gas could be burned more rapidly on them than on the bare platinum. However, this design was not satisfactory, as the tip of the platinum tube became hot enough to cause carbon deposition, even in the presence of 100 per cent excess oxygen. In a short time the tube became fouled, and the analyses were inaccurate. Unless the gas was passed into the pipet at a slow rate the platinum tube became overheated at a point dangerously near the inlet end. Consequently, some method of cooling the capillary was thought necessary, and the pipet illustrated was developed.

The pipet is constructed of Pyrex glass as shown in Figure 1. A platinum tube, A, 2.5 cm. long, 0.9 cm. internal diameter, is sealed into capillary B and projects 2 mm. above the level rim of cup C. A length of 0.45-mm. platinum wire, D, is inserted into the top of the platinum tube to the bend in B. A ten-turn helix, E, of 0.2-mm. platinum wire is supported 3 mm. above the tip of the tube by 0.45-mm. platinum leads which are brought into two side arms, F, to which steel terminals, G, are secured with sealing wax.

Operation

When the pipet is filled with mercury, the side arms and cup should be clean and dry. With stopcock H open, the mercury level is raised above the tip of the platinum tube. Stopcock H is then closed and mercury run into B until it rises in I above the level of H. By lowering the mercury level in I any air trapped in B is forced out by the rising mercury, and then with H open the remaining space in the pipet may be filled with mercury.

A sample of gas requiring from 40 to 60 cc. of oxygen for combustion is measured and stored in the potassium hydroxide pipet. After a thorough rinsing of the manifold and manometer with nitrogen, 100 cc. of oxygen are measured in the buret. With stopcock H open, oxygen is run into the pipet until the mercury level is 1 to 2 cm. below the rim of the cup. By closing H and raising the mercury level in the pipet, any mercury remaining in I or B is blown up into the enlarged section, J, above the stopcock. The mercury level is brought to just below the rim of C and the spiral heated to a bright red. With the combustion pipet shut off from the manifold, the remaining oxygen is thoroughly mixed with the combustible sample by passing back and forth from the potassium hydroxide pipet to the buret several times. With the pressures in the pipet and buret equalized and H always closed, the gas is allowed to flow slowly into the pipet. By decreasing the current through the spiral as the gas rate is increased, the sample may be burned as fast as 40 cc. per minute.

After all the gas has been passed into the pipet, 10 cc. are withdrawn and passed in again several times to burn the unexposed portions in the connection between buret and capillary tip, and then the entire volume is passed over the spiral a few times before determining the resulting volume and carbon dioxide. Any combustible gas in the potassium hydroxide or connections will yield an additional fraction of a cubic centimeter of contraction and carbon dioxide on a repeated series of passes over the spiral.

Performance

Typical combustion data on commercial hydrocarbon gases of unknown purity or composition were secured by the same operator to compare the performance of this new pipet with that of the standard Burrell pipet. Each column of Table I represents the average of three combustions.

On the basis of the values of n for saturated hydrocarbons (C_nH_{2n+2}), the percentage of ethane in the mixture is calculated to be 59.9 and 56.8 per cent by the new and Burrell pipets, respectively, compared with the measured value of 58.3 per cent.

TABLE I. TYPICAL COMBUSTION DATA

	Methane		Ethane		Methane, 41.74% Ethane, 58.26%	
	Burrell	New	Burrell	New	Burrell	New
Sample taken, cc.	23.65	22.70	16.98	18.82	19.75	20.38
Hydrocarbon in sample, cc.	23.33	22.38	17.36	19.32	19.31	20.10
Carbon atoms, calculated	1.215	1.189	1.914	1.865	1.612	1.594
Hydrocarbon found, per cent	98.65	98.60	102.29	102.65	97.77	98.62

It appears that the accuracy of results obtainable with this pipet is equal to the accuracy obtainable with the Burrell pipet. For the greatest accuracy, the platinum spiral should be located not less than 3 mm. above the tip of the platinum tube and the temperature of the platinum tube should be kept as low as possible.

This pipet offers the added advantage of complete safety in operation, as evidenced by the fact that over 125 combustions have been performed by both experienced and inexperienced analysts on a pipet of this type, using gases varying from methane-hydrogen mixtures to isobutane and n-pentane, with no flash-backs or explosions.

Literature Cited

- (1) Bayley, C. H., *Can. J. Research*, 7, 680 (1932).
- (2) Burrell, G. A., Seibert, F. M., and Jones, G. W., *Bur. Mines, Bull.* 197, 51, 83 (1926).
- (3) Coquillon, J., *Compt. rend.*, 83, 394 (1876); 84, 458, 1503 (1877).
- (4) Dennis, L. M., "Gas Analysis," p. 145-7, New York, Macmillan Co., 1929.
- (5) Drehschmidt, H., *Ber.*, 21, 3242 (1888).
- (6) Lutz, W. A., Master's Thesis, Pennsylvania State College, 1934.
- (7) Matuszak, M. P., *IND. ENG. CHEM., Anal. Ed.*, 6, 77 (1934).
- (8) Weaver, E. R., and Ledig, P. G., *J. IND. ENG. CHEM.*, 12, 368 (1920).

Copper Determination by Alpha-Benzoin Oxime in Copper-Molybdenum Alloy Steels

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THERE are two methods in common use for separating the copper from copper-molybdenum alloy steels or from molybdenum alloy steels containing copper as an impurity.

In the first method the steel is dissolved in dilute sulfuric acid and, if vanadium is present, oxidized with potassium chlorate. Both copper and molybdenum are precipitated by hydrogen sulfide gas or sodium thiosulfate. The precipitate is filtered and ignited to oxide. The oxides are fused with potassium bisulfate and the melt is dissolved with dilute hydrochloric acid. The copper is precipitated from the slightly acid (hydrochloric) solution by 5 per cent sodium hydroxide. The paper holding the copper hydroxide is fumed with sulfuric and nitric acids and the solution filtered. The filtrate is again saturated with hydrogen sulfide gas, filtered, and the residue ignited to oxide. This method is long and the work is very delicate in regard to finding a suitable condition to precipitate the copper with the exact amount of sodium hydroxide. Also, ignition of copper sulfide to oxide is not an easy task.

The second method is similar to the first one in regard to dissolving and precipitating the copper and molybdenum either by hydrogen-sulfide gas or sodium thiosulfate. The sulfides of both metals are ignited and the oxides are dissolved in dilute nitric acid. The solution is filtered and copper is separated by electrolysis. This method is also long, and complete deposition of copper by electrolysis is not sure, especially when the copper content of the steel is low.

The obstacles mentioned above are removed and the time is considerably shortened by using α -benzoin oxime for precipitating the copper.

Procedure

Transfer 2 to 5 grams of the sample, depending on the copper content of the steel, to a 600-cc. beaker. Add 50 to 100 cc. of 10 per cent sulfuric acid and heat until action is complete.

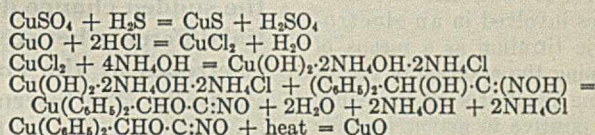
If vanadium is absent, dilute the solution to 250 cc. with hot distilled water and heat to boiling. Add 1 gram of sodium thiosulfate for each gram of steel, dissolved in 10 to 50 cc. of water. Boil the solution 10 to 15 minutes and allow precipitate to settle. If vanadium is present, add a few crystals of potassium chlorate to the sulfuric acid solution, and heat to dissolve the insoluble. Dilute to 400 cc. with hot water. Saturate with hydrogen sulfide gas for 15 minutes, and allow precipitate to settle.

Filter on a close paper, using slow suction, and wash the paper and the beaker a few times with hot 1 per cent sulfuric acid. Transfer the paper to a silica crucible and ignite at dull red heat. Cool the crucible, add 10 cc. of hydrochloric acid, and heat to dissolve the residue. Transfer the solution to a 400-cc. beaker, add 2 to 3 drops of nitric acid, and treat with excess of ammonia. Heat to boiling and filter into a 600-cc. beaker. Wash with hot ammoniacal water and discard the paper.

Dilute the filtrate to 250 cc. with water and heat to boiling. Add 10 to 15 cc. of a 2 per cent alcoholic solution of α -benzoin oxime slowly and while stirring constantly. Boil for 1 minute. Add some ashless pulp and filter on a rapid paper. Wash 5 or 6 times with hot 3 per cent ammonia water, and ignite the paper in

a silica crucible. Cool and weigh the precipitate. Multiply the weight by 80 and divide by the number of grams of the sample, to get the copper content of the steel.

Reactions involved in the procedure:



If steel is alloyed with tungsten, transfer 2 to 5 grams of the sample to a 600-cc. beaker, add 50 cc. of concentrated hydrochloric acid, and heat until action is complete. Add 5 cc. of nitric acid and evaporate to dryness. Cool. Add 25 cc. of hydrochloric acid and heat to dissolve the iron, chromium, etc. Add a few crystals of potassium chlorate, and continue heating until tungstic oxide is completely separated. Add 150 cc. of water, heat to boiling, and allow precipitate to settle. Filter and wash with cold 5 per cent hydrochloric acid about 10 times. Add 10 to 25 grams of citric acid and render the solution alkaline by ammonia. Acidify the solution with hydrochloric acid and add 2 cc. excess for each 100 cc. of solution.

Heat to boiling and saturate with hydrogen sulfide gas. Filter and proceed in the same way as described above.

Experiments proved that the most suitable medium for the precipitation of copper by α -benzoin oxime was ammoniacal solution. Molybdenum, which can be quantitatively precipitated in acid solution, yields no precipitate in ammoniacal solution.

This method functions on all grades of steel where molybdenum and copper are present, either as impurities or as alloying elements. The accuracy has been checked against a complete range of U. S. Bureau of Standards steel samples (Table I). By means of the method described above accurate copper analysis can be made in 1 hour, whereas the former methods required from 3 to 6 hours.

TABLE I. CHECK ANALYSES

Standard Samples	Average Cu Reported	Results by Method
	%	%
20c	0.255	0.263
30c	0.099	0.105
32b	0.117	0.13
33b	0.114	0.120
35a	0.267	0.27
72	0.064	0.07
73	0.033	0.04
101	0.055	0.062
106	0.142	0.16
111	0.122	0.135

Feigl (1) has reported on the use of α -benzoin oxime for copper determination in other materials.

Literature Cited

(1) Feigl, F., *Ber.*, 56, 2083 (1923).

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NEW LINES DISCOVERED IN COPPER SPECTRUM. Thirty new lines in the arc spectrum of copper have been discovered by C. C. Kiess of the National Bureau of Standards, using infra-red sensitive photographic plates. All of these lines, except one, are accounted for as combinations between terms derived from an analysis of the previously known spectrum.

One of the major duties of the bureau's spectroscopy laboratory, it is pointed out, is to furnish as complete descriptions of the

spectra of the chemical elements as modern observational methods will permit. These serve as reference standards for other workers in this field. For the element copper, radiometric observations made elsewhere several years ago failed to reveal any lines in its arc spectrum in the range from 8100 to 12,000 Å. The new types of photographic plates that are sensitive to infra-red light now show this region to contain many lines of great importance in working out the atomic structure, it was stated.

Electrometric Titration

Device for Automatically Stopping at a Predetermined End Point

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THIS device makes use of the potential difference between the two electrodes involved in an electrometric titration as a means of stopping the addition of the titrating agent at a set end point. It is positive in action, is made up largely of standard parts, and in operation requires little trained attention; the reproducibility of its end point equals, or closely approaches, that obtained with careful manual operation requiring continuous attention during the whole course of the titration. The only analogous automatic device of which the authors are aware is that described by Müller and Partridge (1), who used the color-change of an indicator as a means of actuating a photoelectric cell to shut off the flow of the titrating agent.

If the potential between the two electrodes is to be used to actuate the control, the circuit must be such that the current drawn from the titration cell is exceedingly small; otherwise there will be serious polarization of the electrodes which is likely to alter the electromotive force of the cell so much as to make uncertain the determination of the true end point. Moreover, there is the condition, applicable to any accurate electrometric titration, that the development of the electrode potential must very nearly keep pace with the addition of the titrating agent. This requires that the electrodes come rapidly into substantial equilibrium with the solution in immediate contact with them, and there must be stirring so thorough that the ion concentrations in the solution at the electrodes are at any instant substantially the same as in the solution as a whole. Unless these conditions are met, the electrodes will not actuate the cut-off until some excess of the titrating agent has left the buret; yet with proper calibration even this need not cause an appreciable error in the result.

An apparatus which meets the requirements, whose only source of power is the lighting circuit and a single No. 6 dry cell, was built about two years ago and proved to be satisfactory.

Description of Apparatus

The set-up, shown in Figure 1, consists essentially of two dissimilar electrodes, a vacuum-tube amplifier circuit, a solenoid-operated clamp which stops the flow of the titrating agent from an ordinary buret by pinching a short rubber tube attached to the tip of the buret, and a suitable stirrer. The potential between the electrodes is introduced into the grid circuit of the amplifying tube, and amplified so that a change of approximately 5 millivolts produces a change in the grid potential at the thyatron sufficient to cause a positive interruption of its plate current at the next alternation of its plate voltage. This interruption of the output of the thyatron deenergizes the solenoid and so closes the clamp which normally is held open by the current against a spring.

A device is described which automatically stops an electrometric titration by utilizing the sudden change developed in the potential difference between two dissimilar metal electrodes at the end point to actuate a shut-off. The instrument is made of easily obtainable parts and requires no source of power besides the lighting circuit and a single dry cell; it is practically independent of fluctuations in line voltage. Its usefulness is demonstrated by application to three titrations—the titration of Fe^{++} with potassium dichromate, of $\text{Cr}_2\text{O}_7^{--}$ with Fe^{++} , and of Zn^{++} with potassium ferrocyanide.

The amplifying circuit, shown schematically in Figure 2, is of the two-tube bridge circuit type (2) which has the advantage that the operating point at which the output voltage is zero is not affected by fluctuations in supply voltage. Since the thyatron used (*FG-57*) has a cut-off grid potential of -1 volt, and 1 volt corresponds to about 5 millivolts input, any change in the supply voltage changes the cut-off point of the circuit by much less than 5 millivolts on the electrode potential. In order to make even this error small, the voltage regulator tube maintains the somewhat critical control-

grid and screen-grid potential nearly constant for a change of ± 10 per cent in supply voltage.

Since some small current is drawn from the titration cell, it is advantageous to avoid the use of a constant half-cell such as the calomel or silver chloride electrode, and instead to use two dissimilar metal electrodes, both in direct contact with the titrated solution. The authors chose the electrode system, platinum-tungsten. In presence of a vanishing active ion concentration, the potential change of tungsten is usually much less than that of platinum, and so tungsten may replace the more cumbersome half-cell commonly used as a reference electrode in potentiometric titrations. The selected electrode system is readily obtained, convenient, and easy to keep in order; an occasional ignition of the platinum wire in the flame of a burner and a rubbing of the tungsten with fine emery suffices. Very little attention need be paid to the electrodes when in continuous service; but it is advisable to treat them as described if they have been in disuse for any length of time. For electrometric work generally ignition of the platinum electrode is so much the best pre-treatment to insure a sharp end point that it is wise always to employ a simple wire electrode which may easily be removed and ignited and to avoid more complex, difficult to ignite, electrodes of larger surface, such as foil sealed into glass.

The amplifying circuit is arranged to operate at any desired potential difference between the electrodes whether the difference is increasing or decreasing as the end point is passed. For a given titration this potential difference is greater on that side of the end point in which the reaction between the solution and the platinum electrode is less reversible. If the direction of the titration is toward decreased reversibility, the end point is marked by a sudden and very pronounced increase in the observed potential of the cell. This happens with many common oxidation reactions; but it does not follow that all oxidations are accompanied by a rise in potential or that the reverse is true of reductions; for, since the actual potential difference depends upon the relative reversibility of the electrode reactions on the two sides of the end point, it cannot be said that oxidation always makes for an increasing potential and reduction the reverse. In order that a reaction may serve as an analytical tool, it is necessary that the re-

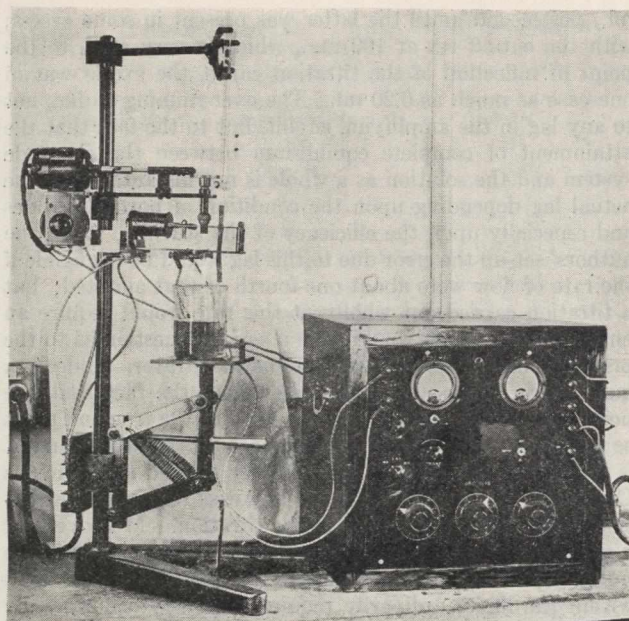


FIGURE 1. ASSEMBLY FOR AUTOMATIC CONTROL OF ELECTRO-METRIC TITRATIONS

versibility of the potential of an inert electrode in contact with the titrated solution change as the end point is passed; this holds for the electrode pair adopted, which may, therefore, be used for electrometric titrations involving oxidation, reduction, neutralization, and precipitation reactions.

The instrument is set to interrupt the current to the solenoid at a definite potential. This means that the potential at the proper end point must be known for the electrode system selected, but this is not such a drawback as it may appear. On the more reversible side of the end point the observed difference in potential between tungsten and platinum is usually quite small, but in the near vicinity of the end point it changes sharply with a small added amount of the titrating solution. The precise setting of the cut-off may, therefore, vary within a considerable range without affecting appreciably the corresponding volume of the titrating solution required. The best way to ascertain the proper cut-off point for a particular titration is to plot the titration curve as obtained with the identical electrodes and a good potentiometer. The inflection of this curve, about the mid-point of the abrupt change in potential, fixes the proper cut-off. Fortunately the position of the inflection is little affected by differences in concentration of ions other than those entering directly into the titration reaction. In many cases the automatic titrator may also be set by using a color indicator, determining the cut-off potential when the color change occurs, and setting the instrument accordingly for subsequent titrations; but this is a less desirable procedure.

The method of setting the apparatus to cut off at any desired potential is quite simple, and once the setting is made it need not be readjusted unless the apparatus is shut down or a different titration is to be performed. For any particular cut-off point, say 100 mv., the procedure for adjusting and using the apparatus is as follows (Figure 2):

1. Plug in the power supply and allow the filaments to heat for 5 to 10 minutes, being sure that switch S_3 is in the "off" position.
2. Throw switch S_1 to *STD* and switch S_2 to either *INCR* or *DECR*, depending upon whether the electrode potential is increasing or decreasing at the end point.
3. Adjust potentiometer P until the voltmeter V reads 100 mv.
4. Adjust rheostat R_1 (coarse adjustment) until the plate current, as indicated by ammeter A , is within the range in which the tube is most sensitive to a change in grid voltage. This range varies with the type of the tube, the plate load resistance (R_{P1}), and the plate supply voltage. For the circuit shown a current of about 0.4 ma. is proper.
5. Close switch S_3 and adjust R_x until the pilot light just turns on. If in the course of this adjustment the plate current goes much above 0.4 ma., R_1 should be readjusted to decrease it to 0.4 ma. and then R_x reset.
6. Turn R_2 (fine adjustment) until the pilot light just goes out. The cut-off of the apparatus is now set at 100 mv. The setting may be checked by turning potentiometer P in the opposite direction until the light just goes out; the reading on the voltmeter then indicates the cut-off point and should be 100 mv.
7. With the solution to be titrated in position start the stirrer, throw switch S_1 to *TITN*, buret the buret, then force open the solenoid-operated clamp to start the titration. The solenoid is purposely made too weak to open the clamp, but when the clamp is opened manually the solenoid is sufficiently powerful to hold it open as long as the solenoid is energized. The pilot lamp is illuminated whenever the solenoid is energized. The rate of flow from the buret may be controlled by the regular buret cock, but it is advisable to attach a rather fine glass tip to the lower end of the rubber tube leading from the buret. The authors found a rate of addition of the titrating solution of 1 drop (0.025 ml.) per second satisfactory. Much depends upon the efficiency of the stirring. The stirring device (shown in Figure 1), equipped with a glass stirrer with two sets of blades, was operated as rapidly as feasible within a beaker somewhat more than half full of liquid.

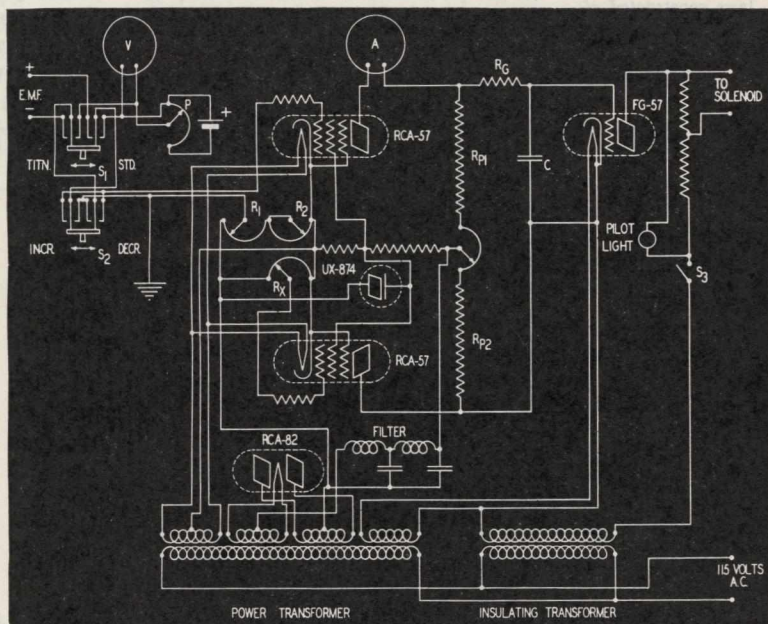


FIGURE 2. SCHEMATIC CIRCUIT DIAGRAM

- V . Weston model 301 switchboard direct current voltmeter, double scale, 0 to 200 mv., 0 to 1000 mv. No. 6 dry cell placed across terminals through voltage divider
 A . Weston model 301 switchboard milliammeter, 0 to 1 ma.
 $RCA-57$. Triple-grid amplifier tube, Radio Corporation of America
 $UX-874$. Voltage regulator tube, used here to help maintain constant the screen grid and control grid biases
 $FG-57$. Thyatron tube, General Electric Company
 $RCA-82$. Full-wave mercury vapor rectifier tube, Radio Corporation of America
 R_1 and R_2 . Rheostats of about 400 ohms; R_x rheostat of about 50 ohms
 R_g . 1-megohm fixed resistance
 C . Condenser, 0.02 mfd.
 Filter is composed of two 30 henry inductances and 4 mfd condensers
 RP_1 and RP_2 . 500,000-ohm fixed resistors; the potentiometer connected between them has 200,000 ohms total resistance
 Power transformer, American Transformer Company; 4 secondaries: 2.5, 2.5, 870, and 5 volts, rating 75 va.
 Insulating transformer, American Transformer Company; 1 to 1 ratio of sufficient size to supply current required by solenoid

8. When the pilot lamp goes out, the flow of reagent from the buret is cut off, and the buret is read. If the pilot lamp should happen to remain lighted though the clamp has closed, the power supply has probably been interrupted during the course of the titration, and it is necessary to open the clamp to allow more reagent to flow until the true end point is reached.

The amplifier as constructed uses 115 volts alternating current as power supply at any frequency from 25 to 60 cycles per second and, consequently, is slightly larger and heavier than would be necessary for 60-cycle operation alone. The only parts which are influenced by the frequency are the two transformers, which have to be designed for the lowest frequency that is to be used. A 25-cycle transformer will work satisfactorily at 60 cycles but a 60-cycle transformer will probably burn out at 25 cycles. The main items required are readily obtainable with the exception of the solenoid-operated clamp, which must be made. This is illustrated in some detail in Figure 3. The amplifier proper was built for about \$125, exclusive of case.

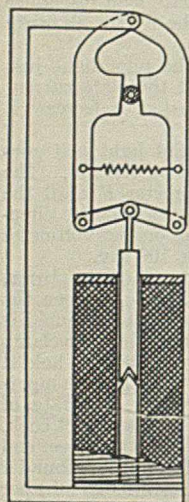


FIGURE 3. DETAIL OF CLAMP ACTUATED BY SOLENOID

Jaws constructed of 0.16-cm. (0.0625-inch) brass. Solenoid core about 0.925 cm. (0.375 inch) diameter.

Applications

These reactions were selected for the purpose of testing the automatic titrator—namely, the titration of Fe^{++} with potassium dichromate, of $\text{Cr}_2\text{O}_7^{--}$ with Fe^{++} , and of Zn^{++} with potassium ferrocyanide.

TITRATION OF Fe^{++} WITH POTASSIUM DICHROMATE. It is especially

desirable to control the dichromate titration of iron automatically because it is frequently necessary to determine the iron content of a large number of samples of ores and slags under conditions that make a reasonable degree of accuracy with a minimum of skilled attention essential.

A 25-ml. portion of a stock solution of ferrous sulfate was acidified with hydrochloric acid, and the usual reduction with stannous chloride was carried out, followed by addition of mercuric chloride; it was then titrated with a 0.1 *N* solution of potassium dichromate (which had been recrystallized three times and dried to constant weight at 200° C.), and proved to be 0.0667 *N*.

The full line in Figure 4a is the electrode potential curve of this titration, in the near vicinity of the end point, as followed with an appropriate potentiometer; this serves to standardize the iron solution as well as to fix the proper end-point potential between the platinum-tungsten electrodes. The broken line is the curve for a similar titration, except that phosphoric acid and the color indicator diphenylamine sulfonic acid had been added. The difference in potential at the two inflections, 120 and 100 mv., is not regarded as significant for it is at most equivalent to two drops of the titrating solution. The organic color indicator does, however, lower the observed oxidation potential in presence of excess of dichromate. The true electrometric and the color end points are very nearly coincident, the former occurring just before the latter.

Table I presents typical results of a number of subsequent titrations of the stock iron solution, carried out by the automatic titrator set at the cut-off potential stated. Addition of the color indicator showed that the titrator did not stop the flow of the dichromate solution, about one drop (0.025

ml.) per second, until the latter was present in some excess; with the cut-off set at 100 mv., which is very close to the point of inflection of the titration curve, the excess was in one case as much as 0.20 ml. The over-running is due, not to any lag in the amplifying circuit, but to the fact that the attainment of complete equilibrium between the electrode system and the solution as a whole is not instantaneous, the actual lag depending upon the condition of both electrodes and especially upon the efficiency of the stirring. With the authors' set-up the error due to this lag would be negligible if the rate of flow were about one-fourth of that adopted; but a titration carried out wholly at this rate would require an hour or more, which would raise a serious question as to the practical usefulness of the automatic titrator. Indeed a question as to its usefulness arises from the fact that the point at which it cuts off is not as close to the true end point as is the color-change of the indicator. On the other hand, it is unaffected by the presence of highly colored ions, such as Cr^{+++} , Ni^{++} , and Cu^{++} , and in any case requires no attention during the whole course of the titration. Moreover, for a given set-up and a given rate of flow of the solution from the buret, the error, being substantially constant, can be brought within the limits ordinarily required in analytical work by application of a small correction, about 0.10 ml. in this case. According to the data in Table I, the error was reduced somewhat by setting the cut-off at 75 mv., and became negative with the cut-off set at 50 mv.; it may therefore be partly taken care of by setting the circuit to actuate the cut-off somewhat in advance of the potential difference at the true end point as determined by preliminary titration with a good potentiometer. In a series of similar titrations, therefore, the use of the automatic titrator would yield results of sufficient accuracy with a great saving in time and attention required on the part of a skilled operator.

TITRATION OF $\text{Cr}_2\text{O}_7^{--}$ WITH Fe^{++} . The titration of $\text{Cr}_2\text{O}_7^{--}$ with Fe^{++} is the reverse of the titration just discussed.

The color indicators of the diphenylamine group cannot be added to the dichromate solution because they are destroyed by the strong oxidizing agent; so that it is necessary to add an excess of Fe^{++} , then the indicator, and to determine the excess Fe^{++} with a standard solution of potassium dichromate. This complication is avoided by the use of the automatic titrator. Figure 4b shows the end-point curve of two typical titrations of the standard dichromate solution; the solutions as titrated contained about 20 per cent by volume of reagent hydrochloric acid. The potential change in the near vicinity of the end point is much larger for a given increment of the titrating solution than is the case for the reverse titration. The mean of several titrations in close agreement showed the Fe^{++}

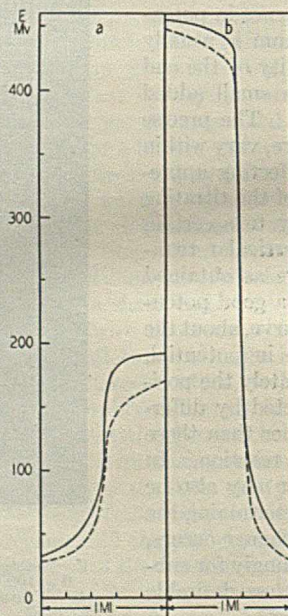


FIGURE 4. ELECTRODE POTENTIAL CURVE IN NEAR VICINITY OF END POINT FOR TITRATION OF:

(a) Fe^{++} solution with 0.1 *N* $\text{Cr}_2\text{O}_7^{--}$ solution; full line, color indicator absent; broken line, color indicator present; (b) $\text{Cr}_2\text{O}_7^{--}$ solution with 0.1 *N* Fe^{++} solution; two typical titrations

TABLE I. TITRATION OF Fe^{++} WITH 0.1 N POTASSIUM DICHROMATE
(True end point at 16.68 ml.)

Cut-off Setting	Volume Shut Off Automatically	Error
Mv.	ml.	ml.
100	16.66	-0.02
100	16.84	+0.16
100	16.86	+0.20
100	16.84	+0.16
75	16.76	+0.08
75	16.61	-0.07
75	16.81	+0.13
50	16.62	-0.06
50	16.61	-0.07

TABLE II. TITRATION OF $\text{Cr}_2\text{O}_7^{--}$ WITH Fe^{++}

Cut-off Setting	Volume 0.1 N $\text{K}_2\text{Cr}_2\text{O}_7$ Taken	Equivalent	Error
		Volume 0.1 N FeSO_4 Shut Off Automatically	
Mv.	ml.	ml.	ml.
350	20.00	20.04	+0.04
	20.00	20.05	+0.05
	20.00	20.09	+0.09
	25.00	25.10	+0.10
	25.00	25.14	+0.14
300	20.00	20.15	+0.15
	20.00	20.10	+0.10
	20.00	20.09	+0.09
	30.00	30.02	+0.02
250	20.00	20.04	+0.04
	20.00	20.10	+0.10
	20.00	20.16	+0.16
	20.00	20.15	+0.15
	20.00	20.16	+0.16
100	20.00	20.21	+0.21

solution (not the same solution referred to above) to be 0.0669 N, and the end-point inflection to lie close to 250 mv.

Table II presents the data obtained with the automatic titrator. A considerably greater range in the setting is permissible than with the reverse titration, as the curves indicate. A setting of 100 mv. is, however, clearly too low; the error with the higher settings is not serious but always positive.

DETERMINATION OF ZINC WITH POTASSIUM FERROCYANIDE. The volumetric determination of zinc with potassium ferrocyanide is particularly suited to the automatic titrator because the reaction is inherently slower than most of those utilized by the analyst. The rate of addition of the titrating agent may therefore be several times as fast as that ordinarily used, and the titrator will stop the flow 1 to 2 ml. before the true end point by virtue of a temporary accumulation of ferrocyanide. The pilot lamp relights a few seconds after the cut-off is made. By manipulating the buret cock the rate of flow of the titrating solution is reduced to less than 1 drop per second, the clamp is reopened, and the titration completed. Much time is saved by this procedure.

A standard solution of zinc was prepared by dissolving zinc metal distributed by the Bureau of Standards for use in thermometry (99.993 per cent Zn) in hydrochloric acid. The solution as prepared contained 0.01084

gram of zinc per ml. Samples of this solution were titrated electrometrically with a solution of potassium ferrocyanide at 65° C. To each sample 13 ml. of reagent ammonia and 3 ml. of excess hydrochloric acid, methyl orange serving as the indicator, were added before titrating. Figure 5 gives the end-point curve of two typical titrations; 400 mv. was adopted as the end-point potential. One milliliter of $\text{K}_4\text{Fe}(\text{CN})_6$ was found equivalent to 1.034 ml. of Zn^{++} from the titration curves.

The titrations made with the automatic titrator, which are listed in Table III, were also made at 65° C. The results for this ordinarily rather troublesome titration are regarded as favorable.

TABLE III. DETERMINATION OF Zn^{++} WITH POTASSIUM FERROCYANIDE

Cut-Off Setting	Volume Zn^{++} Solution Taken	Equivalent Volume	Error
		$\text{K}_4\text{Fe}(\text{CN})_6$ Shut Off Automatically	
Mv.	ml.	ml.	ml.
400	20.00	20.14	+0.14
	20.00	20.11	+0.11
	20.00	20.04	+0.04
50.00	50.00	50.22	+0.22
	50.00	50.17	+0.17
	50.00	50.18	+0.18

It may be pointed out that on all the titrations cited a correction of -0.10 ml. applied to the buret reading at the close of the titration brings the error involved within acceptable limits for most analytical work. This correction is largely a function of the authors' working conditions, particularly of the rate of addition of the titrating solution and the effectiveness of the stirring.

Literature Cited

- (1) Müller and Partridge, *IND. ENG. CHEM.*, 20, 423 (1928).
- (2) Nottingham, *J. Franklin Inst.*, 209, 287 (1930).

RECEIVED March 19, 1935.

Busy Year Planned by the Paper Section of National Bureau of Standards

With the assistance of funds from other government agencies and from outside organizations, the paper section of the National Bureau of Standards expects to expand its research activities during the ensuing year.

A new project recently initiated is a study of the possible effect on papers of fumigating gases used to rid written and printed materials of destructive insects. This was undertaken at the request of the National Archives and with their financial assistance.

A new venture, which will take the section into a new field, is a study of the stability of prints contained on motion picture films. This form of record material has assumed great importance, librarians, educators, and others interested in the spreading of knowledge and in preserving it being deeply interested in the possibilities of film records.

With the assistance of a fund granted for the purpose to the National Research Council by the Carnegie Foundation, it is planned to make a year's study of the resistance of the film records to various degrees of temperature, humidity, and light. It is hoped that this work can later be expanded into a comprehensive study of the many other problems concerning miniature records, and of problems related to sound recordings.

Direction of the participation in the standardizing activities of the T. A. P. I. Paper Testing Committee will be continued. The committee has developed 37 standard testing methods and has 14 more under development at the present time. Additional testing work consists of an attempt to develop a device for measuring in numerical terms the rate of failure of printed currency under conditions that produce appearance and loss of strength similar to those caused by actual service wear. This work is supported by the Treasury Department.

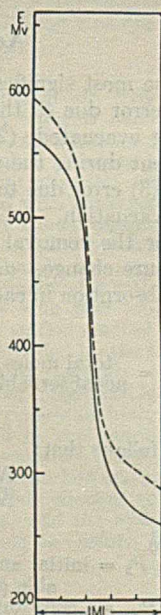


FIGURE 5. ELECTRODE POTENTIAL CURVES IN NEAR VICINITY OF END POINT

Two typical titrations of a zinc solution with potassium ferrocyanide

Determination of Water and Hydrogen Sulfide in Gas Mixtures

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IN TRANSFERRING gas mixtures at atmospheric pressure from their containers to an apparatus for analysis the use of a displacing liquid may cause the loss of a condensed constituent, while certain constituents may react with mercury and thereby prohibit the use of an evacuating pump containing this liquid. The problem in both cases can be solved by utilizing the evacuation method if proper absorbents are placed between the pump and the gas container to remove the interfering constituents and allow their quantitative determination. Absorption of this type at constantly diminishing pressure gradually decreases in efficiency as lower pressures are approached, owing to the fact that the partial pressure of each nonabsorbable constituent constantly diminishes while the partial pressure of each absorbable constituent over its absorbent remains substantially constant. In such a case the net absorption between a given set of pressure limits, rather than the specific absorption at any particular pressure, determines the accuracy of the analysis. This paper presents an apparatus and procedure for the analysis of gas mixtures containing water vapor

and hydrogen sulfide, which are typical examples of gases having the interfering properties of condensability and reactivity with mercury. The method, however, is general and may be applied to a variety of other gases.

Apparatus

The apparatus used with this method of analysis, as shown in Figure 1, consists of a Töpler pump connected to the sample bulb with the necessary absorption tubes intervening between the pump and sample bulb. The volume of the absorption tubes should be as small as consistent with the use of an adequate amount of absorbent.

Method of Operation

The procedure is essentially to evacuate the system up to stopcock *D*, to allow the sample bulb gas to fill the absorption system slowly up to stopcock *K*, and then to complete the evacuation, collecting the nonabsorbed gases in reservoir *M*. The volume of the dry nonabsorbed gases is determined in the buret of an Orsat apparatus. Absorption tubes *I* and *J* are filled with dry air through a drying tube containing magnesium perchlorate attached to stopcock *K* at *H*. They are then disconnected and weighed, after being carefully wiped free of mercury from the immersion seals. No difficulty will be encountered in removing this mercury if it is clean, preferably freshly distilled, and if a small camel's-hair brush with fairly stiff bristles is used. The motion of the brush should be short and jerky. The absorption tubes are always weighed with their rubber connections removed. Between absorptions and weighings the openings are closed by rubber connections into which are inserted small glass rods.

Accuracy of Analysis

The most significant sources of error may be classified as (1) error due to the imperfect absorption as the sample is being evacuated, (2) error due to desorption of the absorbent during the first evacuation of the absorption tubes, and (3) error due to the fraction of the sample not removed by evacuation.

For the removal of infinitesimal portions of gas with a pressure change, $-dP$, the amount of absorbable gas lost by nonabsorption in each portion is represented by the equality:

$$dN_A = \frac{\text{total moles}}{\text{nonabsorbable}} \times \frac{\text{fractional}}{\text{pressure change}} \times \frac{\text{pressure of absorbable gas}}{\text{pressure of nonabsorbable gas}}$$

It follows that:

$$\frac{N_A}{N_N} = 2.3 \frac{P_A}{P_1} \log \frac{P_1}{P_2} \quad (1)$$

where

P_1, P_2 = initial and final partial pressures of the nonabsorbable gas

P_A = constant partial pressure of the absorbable gas over the absorbent

N_A = moles of absorbable gas not absorbed after passing over the absorbent

N_N = moles of nonabsorbable gas in bulb at pressure P_1

Provided the absorbable component does not constitute the major portion of the gas and the volume of the absorp-

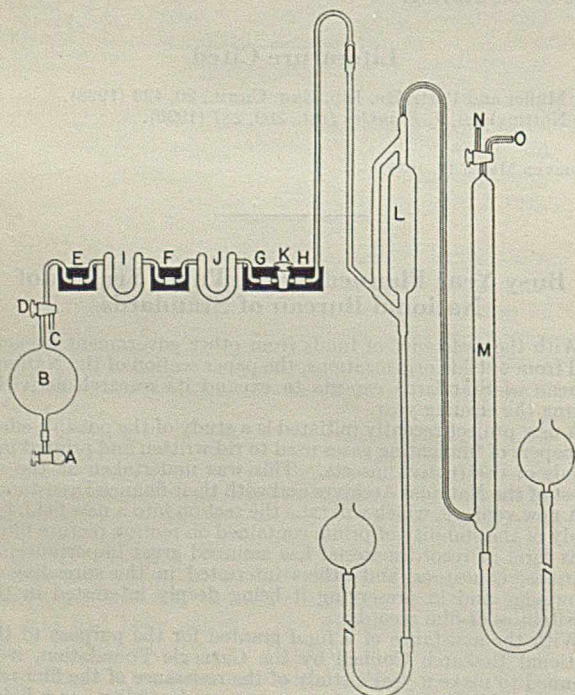


FIGURE 1. LAYOUT OF ABSORPTION SYSTEM

- A. Water sample bulb
- B. Air and hydrogen sulfide sample bulb, 200 cc. capacity
- C. Flushing aperture used in filling sample bulb
- D. Three-way cock
- E, F, G, H. Mercury-immersed rubber tube connections. Glass tubing meeting end to end inside thin rubber tubing
- I, J. Absorption bulbs for water and hydrogen sulfide, respectively
- K. Two-way cock
- L. Töpler pump, 200-cc. chamber
- M. Gas reservoir, 230 cc.
- N. Vent
- O. Connection to Orsat gas analysis apparatus

tion tubes is only a small fraction of the total volume, P_1 may be calculated from the volume of the sample bulb.

The error due to deabsorption of a reversible adsorbent during the first evacuation of the absorption tubes is small, as is shown by an application of Equation 1.

Corrections for the incomplete evacuation of the sample bulb can be made to the analyzed values of the proper constituents. When the ratio of the initial and final pressures is of sufficient magnitude, this correction is omitted.

TABLE I. ANALYSIS OF KNOWN GAS MIXTURES

Analysis	Actual			Analyzed			Final Pressure of Evacuation, Mm. Hg
	Air, S.T.P.	H ₂ S, S.T.P.	H ₂ O, Gram	Air, S.T.P.	H ₂ S, S.T.P.	H ₂ O, Gram	
	Cc.	Cc.	Gram	Cc.	Cc.	Gram	
1	197.5	0.0	0.0000	197.2	-0.3	0.0004	5 ^a
2	157.0	41.2	0.0000	156.9	40.8	0.0000	5 ^a
3	158.5	40.2	0.1035	159.0	40.1	0.1038	1
4	166.8	31.6	0.0980	166.0	31.3	0.0978	1

^a Values corrected for residual gas in sample bulb.

An absorbent for hydrogen sulfide which carries a very low partial pressure of the gas above it and which is very selective in the presence of many other gases is partly dehydrated copper sulfate pentahydrate. The use of this reagent as an absorbent for hydrogen sulfide was originated by Fresenius (1, 2), who recommended the dehydration for 4 hours at 150° to 160° C. of copper sulfate absorbed from solution by pea-sized pumice. For the present work it was found better to omit the pumice and to dehydrate 10- to 20-mesh particles of the pentahydrate for the same time at this temperature. Part of the reagent space on the exit side of the absorption tube should be filled with anhydrous calcium chloride to recover any water removed from the copper sulfate.

Since it was impossible to employ calcium chloride as a drying agent for gases containing hydrogen sulfide, magnesium perchlorate (anhydrous) was used in 1, the absorption tube for water vapor. An appreciable dehydration of the copper sulfate absorbent is the only objection to the use of magnesium perchlorate. Using these reagents, the method was checked with samples of gas of known composition.

Samples of gas containing known amounts of air, hydrogen sulfide, and water vapor were prepared in bulbs B and A of Figure 1. Bulb A provided with a stopcock contained the water for the sample, and when evacuated and weighed before and after the addition of water gave the known amount of water. It was attached to bulb B with rubber tubing sealed with Duco cement. Bulb B was then evacuated and filled with known amounts of air and hydrogen sulfide calculated from the known volume of the bulb and the pressure changes measured on a mercury manometer. A small-bore tube connected the manometer with bulb B; since the air was introduced into the bulb first and the hydrogen sulfide last, little or no hydrogen sulfide reacted with the mercury in the manometer. Outlet C provided by the three-way cock served for flushing purposes in filling the bulb.

The hydrogen sulfide was prepared from iron sulfide and hydrochloric acid and washed by bubbling through potassium hydroxide saturated with hydrogen sulfide. Prepared in this manner it did not contain hydrogen or hydrocarbon impurities, since the determined and actual values for air or nonabsorbed gas in the analysis of mixtures of air and hydrogen sulfide checked as well as in the analysis of air alone. Both the air and the hydrogen sulfide were dried over phosphorus pentoxide before being introduced into bulb B.

Analyses of the samples are shown in Table I. The residual air after absorption of the water and hydrogen sulfide was measured volumetrically with the customary corrections for temperature and pressure. The deviation of the determined values for water vapor from the actual varies from +0.0004 to -0.0002 gram. The partial pressure of water vapor over magnesium perchlorate is considerably less than 0.1

mm. (4), so that the variations that do occur are caused by the limitation of the gravimetric determination of the absorbed water rather than by the limitation of the absorption.

The calcium chloride at the exit end of the copper sulfate tube should maintain in the gases leaving this tube a partial pressure of water vapor around 0.3 mm. (3). Assuming that the gases entering the copper sulfate tube are absolutely dry, then the amount of water picked up by these gases and lost from the copper sulfate tube may be calculated by means of Equation 1 as a negative absorption of hydrogen sulfide. This calculation gives for all four analyses the value of -0.2 cc. The actual deviations are -0.3, -0.4, -0.1, and -0.3 cc., respectively. Although the determination of hydrogen sulfide is not as accurate as that of water vapor and air, the method is not condemned, since other absorbents may be chosen. The use of this particular reagent was decided upon because of its selectivity in the presence of a variety of gases, so that it was quite possible to analyze mixtures of gases containing in addition hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, and ethylene.

Literature Cited

- (1) Dennis, L. M., "Gas Analysis," p. 272, New York, Macmillan Co., 1925.
- (2) Fresenius, R., *Z. anal. Chem.*, **10**, 75 (1871).
- (3) McPherson, A. T., *J. Am. Chem. Soc.*, **39**, 1317-19 (1917).
- (4) Willard and Smith, *Ibid.*, **44**, 2255 (1922).

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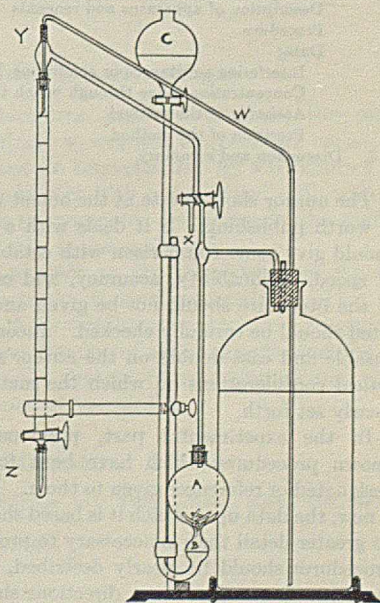
Buret Assembly for Standard Reducing Solutions

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STANDARD solutions of reducing agents—for example, titanous and ferrous salts—are required for certain volumetric determinations. They have the disadvantage of rapid deterioration unless the air remaining in the storage bottle is replaced by an inert gas. Various assemblies of apparatus for their preservation and delivery at full strength have been suggested, but the writer has seen none which seems to present all the advantages of the form sketched.

A standard buret is used, readily detached for cleaning. The automatic zero-point arrangement is easily adjusted and is reliable. The solution does not come in con-



tact with rubber. It is constantly under pressure of inert gas, but the necessary connections are of such nature that chance of loss of either solution or gas from leaks is remote. The assembly is portable and may be set in a cupboard when not required.

The gas generator, *ABC*, was made from the bulbs of two 250-ml. separatory funnels sealed to a length of heavy tubing in which a 100-ml. bulb had been blown, and bent as sketched. This bulb, *B*, is essential, as it takes care of changes in gas volume from variations in temperature and pressure as well as excess gas evolved from dilute hydrochloric acid adhering to the zinc sticks or marble fragments in *A*. *ABC* is attached to the rod of the retort stand on which the apparatus is assembled by wrappings of friction tape. The container for solution may be a 2.5-liter acid bottle, which is prevented from shifting on the rectangular iron base of the support by four rubber-protected bolts.

Part *Y* supplies inert gas to protect the solution while in the buret, and is slightly tapered below to expand a soft-rubber sleeve within the mouth of the buret, making a secure connection. The siphon tube for solution passes through *Y*, and is attached to it at the top only; the joint is made gas-tight with soft de Khotinsky or similar cement, permitting precise adjustment of the zero point by warming to soften the cement. The space within *Y* below is open, to allow gas to enter the buret freely. It is important that the vertical part of the siphon tube at the top be quite narrow and no longer than necessary, to insure satisfactory performance; the slight bend at the tip directs the stream against the wall of the buret, avoiding bubbles.

To fill the buret, stopcock *X* is turned to release gas, while at the same time gentle suction may be applied to a rubber tube

(not shown) attached at *X*; excess pressure in the bottle then forces the solution through the siphon. When the buret is filled to slightly over the zero point, stopcock *X* is reversed to readmit the inert gas; equalization of the pressure in buret and bottle then permits excess solution to siphon back into the bottle, leaving the buret filled just to the zero point, ready for the titration. The bottle may be refilled through the opening in the stopper shown plugged by a piece of rod, without disturbing any other connection. This opening also serves to vent the bottle when displacing air by gas after filling. The sleeve, *Z*, on the tip of the buret contains a little of the solution, and prevents stoppage by crystallization if in place while the buret is not in use.

Every set-up of this type is open to the criticism that evaporation from the surface of the solution in the bottle, with condensation on the walls above, results in a lack of uniformity in the solution. This apparatus is not so heavy that it cannot be shaken as a unit to remix the solution, but there is also danger that on long standing water vapor may diffuse into the gas generator and thus be permanently lost from the bottle. A layer of pure paraffin oil just sufficient to cover the solution is an effective remedy; the only objection is the fact that oil appears to contain dissolved oxygen, so that the titer will decrease for several days after the first filling, unless the oil has been given a thorough preliminary treatment with the same reagent.

RECEIVED March 22, 1935.

Note to Authors

IN THE preparation of manuscripts authors should address themselves to specialists in their particular fields, rather than to the general reader. If the article describes a new method, the author should endeavor to tell the complete story, so that the reader will not have to wait for succeeding contributions or duplicate the unpublished tests in order to find out whether he can apply the method in his own work.

The following is suggested as a general outline to be followed in preparing analytical methods for this edition:

1. Preliminary statement or introduction, in which the need for the method should be stated, brief reference to other methods or literature given, etc.
2. Experimental:
 - Outline of proposed method
 - Description of apparatus and reagents
 - Procedure
 - Data:
 - Interfering substances or conditions
 - Concentration range through which the method is applicable
 - Accuracy of the method
 - Precision of the method
3. Discussion and summary

The author should state at the outset why he thinks the paper is worth publishing. If it deals with a method of analysis, he should give some comparison with established methods in point of speed, applicability, accuracy, and cost. Extensive reviews of the literature should not be given and such references as are cited should be carefully checked. Incorrect references are inexcusable and cast doubts on the author's reliability. The theoretical considerations on which the method is based should be clearly set forth.

In the experimental part, previously published or well-known procedures which have been followed should only be designated or references given to them. If, however, the method is new, the data upon which it is based should be presented but in no greater detail than is necessary to prove its soundness. New procedures should be clearly described, that readers can easily duplicate the work. Loose directions should be avoided, unless

the author knows that no possible harm can result from the most liberal interpretation that can be made of such expressions as "to the faintly acid solution," "wash the precipitate," "ignite," etc. If new or uncommon reagents are needed, the author should state their probable cost, where they can be purchased if rare, or how they can be prepared, if not on the market.

The author should distinguish carefully between precision and accuracy. Briefly but somewhat roughly stated, accuracy is a measure of degree of correctness; precision is a measure of reproducibility. The precision of a result does not necessarily have anything to do with its accuracy; it serves merely as a measure of the duplicability of the procedure in the hands of a given operator. No claim for accuracy should be made unless the author believes that he has satisfactorily established the correct result.

The author should be frank and define the limitations of the method. Tests dealing with the effects of foreign compounds should be made on mixtures in which the ratios of the compounds sought to the foreign compounds are varied and simulate conditions that are likely to be encountered in practice. If the author has made no such tests, he should state that he has no knowledge of the effects of foreign substances. It is desirable that possible applications of methods should be stated.

A summary or prefatory abstract should acquaint the reader with the main points of the article. This should give concisely where possible the substances determined, nature of material to which determination is applicable, interfering substances, range of concentration to which method is applicable, whether or not a sensible constant error is involved—that is, the accuracy of the method—and its precision. Either the summary or the prefatory abstract is so often used by abstractors that the author may well spend considerable time in their preparation, in order to be certain that proper emphasis is given to the main features of the contribution.

Our "Suggestions to Authors" is available to those unfamiliar with the form of manuscript and illustrations preferred by INDUSTRIAL AND ENGINEERING CHEMISTRY.

Manometric Manostat

G. BRYANT BACHMAN, The Ohio State University, Columbus, Ohio

THE apparatus here described has been used successfully by the writer for controlling pressures between one and 850 mm. It is particularly convenient for maintaining a given pressure either below or slightly above atmospheric pressure during distillations.

The electrical circuit used is that of Hershberg and Huntress (1). The manometer, which is made of 8-mm. tubing, is provided with a 1-mm. stopcock at the bottom and an ordinary stopcock at the top of the open arm. There are also two platinum wire contacts, P_1 and P_2 , on the open arm. Contact P_1 is conveniently located about 12 cm. from the bottom bend in the manometer tubing and should be sharpened to a fine point. The meter stick is set in such a position that the 10-cm. mark is exactly level with the tip of contact P_1 , for convenience in making readings. Relay A (2000-ohm telephone relay) is fixed to a carriage which is moved by means of a screw, from leak L_1 to leak L_2 . The leaks consist of ordinary needle valves soldered at the open end to 2-cm. long brass rods through which fine holes 0.05 cm. (0.02 inch) have been drilled. Stopcock S_1 serves to admit or remove mercury from the manometer, stopcock S_2 to close off the leaks completely if desired, and stopcock S_3 to fix the volume of air in the otherwise open arm of the manometer.

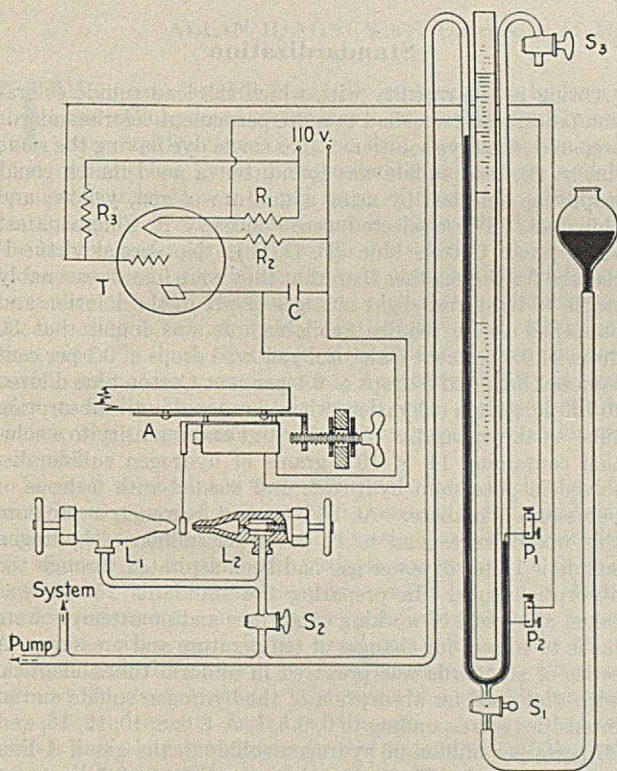


FIGURE 1. DIAGRAM OF APPARATUS

Resistance R_1 is a 40- to 60-watt lamp, R_2 a 25- to 40-watt lamp, and R_3 a 3- to 5-megohm resistance of 2-watt capacity. Condenser C is of 5 mfd. rating. T is a 71-A vacuum tube. All of the apparatus, exclusive of the manometer, may be easily mounted in a box 25 × 15 × 15 cm. (10 × 6 × 6 inches) with the controls placed conveniently on the outside.

The operation of the apparatus is simple. If it is desired to maintain a pressure below atmospheric pressure, S_2 is opened, the pump is started, and the amount of mercury in the manometer is adjusted by means of the leveling bulb so

that the difference in height between the two mercury levels subtracted from the barometric pressure gives the pressure desired. Introducing more mercury into the manometer increases the degree of vacuum attained. Removing mercury has the reverse effect. The relay is set so that its armature operates against L_2 . L_1 may then be used as an auxiliary leak. As soon as the desired pressure is attained, S_2 is closed to prevent changes in the atmospheric pressure from influencing the controlled pressure.

If it is desired to operate at pressures above atmospheric, the vacuum pump is replaced by an air-pressure pump and the relay is set to operate against L_1 . In this case L_2 may be used as an auxiliary leak. The height of P_1 above the lower end of the meter stick determines the amount of pressure above atmospheric that may be controlled. Ordinarily this will not need to be more than 30 or 40 mm. if the object in view is to maintain a pressure of 760 mm. However, at high altitudes or for other reasons it may be desirable to maintain an increased pressure of several hundred millimeters over the prevailing atmospheric pressure. In such cases P_1 must be fixed in the manometer tube at a correspondingly higher level or a third contact introduced. As soon as the desired pressure is attained S_2 is closed.

Advantages of Manometric Manostat

Except for the electrical control, which may be much simplified (2, 3), the apparatus is relatively inexpensive. The glass parts may be easily put together by an amateur glass blower.

All pressures from a few millimeters to 100 mm. or more above the prevailing atmospheric pressure may be controlled with an accuracy of ± 0.2 mm. or less. Changes in the controlled pressure due to changes in the atmospheric pressure are avoided.

The settings are rapidly and easily made.

A closed-arm manometer which will eventually become inaccurate with frequent operation is avoided.

The manometer is easily drained, cleaned, and refilled through S_1 .

Chief Disadvantages

Like all constant-volume pressure controls, the manometric manostat is subject to ambient temperature variations. These may be avoided or corrected for by surrounding the open arm of the manometer with a tube filled with water in which is immersed a thermometer according to the manner prescribed for burets used in gas analysis.

The apparatus is subject to the disadvantages inherent in all manostats using mercury as the contact liquid (1). In the writer's opinion these disadvantages are not as great as those which arise from the use of other liquids, such as sulfuric acid which rapidly absorbs organic vapors and water and hence must be renewed frequently.

Literature Cited

- (1) Hershberg and Huntress, *IND. ENG. CHEM., Anal. Ed.*, **5**, 144, 344 (1933).
- (2) Jacobs, *Ibid.*, **7**, 70 (1935).
- (3) McConnell, *Ibid.*, **7**, 4 (1935).

RECEIVED January 26, 1935.

Determination of Traces of Hydrogen Sulfide in Sewer Gases

A Convenient Field Method

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IN THE course of a recent investigation of a sewage system it became necessary to make a large number of determinations of the concentration of hydrogen sulfide in the sewer gases. As the sewer was about 20 meters (60 feet) below ground level and determinations at numerous different places were to be made on the same day, it was desirable that an apparatus be devised that would obviate the

necessity of the manipulator's descending the man-holes and would be strong and rapid in use. The concentrations of hydrogen sulfide to be measured varied from about 0.1 to 30 parts per million. A high degree of accuracy in the measurements was unnecessary. The apparatus and method described were found to cover all the requirements, and when used in the field gave results with an accuracy of at least 10 per cent of the quantity measured.

The principle of the method employed was the absorption of the hydrogen sulfide in potassium hydroxide and its colorimetric determination, using potassium plumbate and

from stout tubing circled the aspirator bottle and served the dual purpose of holding the absorption tube and acting as a cushion for the bottle in its case. This case was three-sided and stoutly constructed of wood, so as to be a neat fit for the bottle. The front was left open except for a small ledge to prevent the bottle sliding forward. The siphon tube ended with a length of rubber tubing which slipped through a hole in the base of the case. The height of the case was just sufficient to enable the aspirator to be lifted over the ledge for removal for refilling with water. Extensions to two sides of the case enabled it to be placed on the ground without interfering with the action of the siphon. Thirty-three meters (100 feet) of plaited cord were attached to the case so that it could be lowered down a manhole.

A case similar to that used for some types of portable pH colorimetric apparatus was used to hold the comparison tubes, a bottle of 5 per cent potassium hydroxide and one of potassium plumbate, and a stock of absorption tubes, as these were used for only one determination before being washed.

Standardization

Owing to the rapidity with which the lead sulfide coloration fades, resort was had to more permanent color standards prepared from dye solutions. No single dye having the same tint as the lead sulfide was found, but a good match could readily be obtained by using a mixture of red, yellow, and blue dyes. Those selected were Ponceau 3 R, Chlorazol fast yellow, and Cotton blue (B. D. H.). No special virtue is claimed for these, other than that they were found reasonably stable to light and slight changes of pH in the solution and happened to be readily available. It was found that 30 drops of 0.1 per cent Chlorazol yellow, 5 drops of 0.1 per cent Ponceau 3 R, and 8 drops of 0.1 per cent Cotton blue diluted to 100 cc. gave a coloration, when compared in the absorption tubes of the apparatus, of similar tint and intensity to a solution containing 14×10^{-6} grams of hydrogen sulfide dissolved in potassium hydroxide and treated with 5 drops of potassium plumbate. At 25° C. and barometric pressure this would correspond to 10 parts per million of hydrogen sulfide if 1 liter of sewer gas had been aspirated through the absorption tube. In preparing the standards 25° C. was taken as typical of working conditions and no attempts were made to correct for changes of temperature and pressure. A series of standards was prepared in uniform tubes identical with that used for absorption of the hydrogen sulfide and of intensities corresponding to 0, 0.5, 1, 2, 4, 6, 8, 10, 12, 16, and 20 parts per million of hydrogen sulfide in the gas if 1 liter were aspirated. The color corresponding to 0.5 part per million when the tube was examined longitudinally against a white base was quite definite. In preparing these standards comparison was made with sodium sulfide solutions carefully analyzed by titration with iodine and thiosulfate and added to 5 per cent potassium hydroxide, the color being developed with 5 drops of potassium plumbate in an identical manner to that used in an actual determination.

The color of a dye standard was measured with a Lovibond tintometer and it was found that after one month in the diffused light of the laboratory it had not changed. However, the standards used were exposed to light only when a comparison was being made.

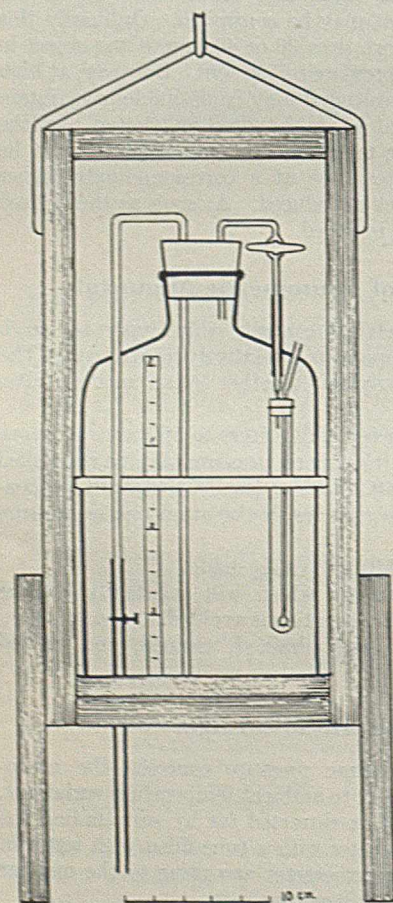


FIGURE 1

a series of comparison tubes containing dye solutions prepared so as to correspond to various concentrations of the gas.

Apparatus

The apparatus (Figure 1) consisted of a graduated 4-liter Winchester bottle which with a siphon acted as an aspirator. This drew the gases through an absorption tube consisting of a 15 x 1.3 cm. test tube with a mark etched at a height corresponding to 10 cc. This was filled to the mark with 5 per cent potassium hydroxide solution. The bubbling tube terminated in a bulb having three small orifices, so that the gas divided into three fine streams of bubbles. A glass tap regulated the rate of flow of gas through the absorption tube. A rubber band made

In order to be sure that the simple absorption tube used was effective, mixtures containing 5 and 15 parts per million of hydrogen sulfide in air were prepared in an apparatus similar to that described by Truesdale (1). These were aspirated at the rate of 1 liter in 10 minutes through the absorption tube. On adding potassium plumbate, the color developed was immediately matched with the previously prepared dye standards and found to correspond with a practically complete absorption of the hydrogen sulfide.

Determination

The determination on the field was simple and rapid. The siphon was started and the sampling apparatus immediately lowered down the manhole to within 30 cm. (1 foot) of the sewage. After 10 minutes, when 1 liter of the gas had been aspirated, it was brought to the surface, the absorption tube was removed, 5 drops of potassium plumbate were added to

its contents, and the color was immediately compared with the dye standards. The total time involved, including packing and unpacking, was generally less than 15 minutes at any particular place. When the concentration of hydrogen sulfide was lower or higher than corresponded to the standards, a larger or smaller quantity of the gas was aspirated through the apparatus.

Acknowledgment

The author's thanks are due to J. B. Henderson, Queensland Government Analyst, for permission to publish this description.

Literature Cited

(1) Truesdale, E. C., *IND. ENG. CHEM., Anal. Ed.*, 2, 299 (1930).

RECEIVED March 15, 1935.

A Direct-Reading pH Meter for Glass, Quinhydrone, and Hydrogen Electrodes

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THE glass electrode is rapidly replacing the hydrogen and quinhydrone electrodes. It reaches equilibrium very rapidly, there being no drift due to "poisoning." It is not affected by oxidizing-reducing substances, and is applicable through a wide pH range of 0 to 11.5. There is no removal of dissolved gases, such as carbon dioxide, due to the bubbling of hydrogen through the solution whose pH is to be measured. One difficulty with the glass electrode has been that the high resistant membrane makes balancing of the opposing e. m. f. from a potentiometer a difficult operation, since the high resistance of the glass reduces the balancing current to a small value. Another difficulty is that when a continuous current is drawn from a glass-electrode system the membrane polarizes, changing its equilibrium potential.

In order to eliminate these difficulties several schemes (1) have been suggested. One which possesses certain inherent advantages is the method, first suggested for glass electrodes by Morton (2), in which the variable known e. m. f. from a potentiometer, the glass-electrode assembly, and a high-grade condenser are in series, the potentiometer e. m. f. opposing the cell e. m. f. in the usual way. The condenser is charged to the difference of potential between the potentiometer and the glass electrode. By means of a suitable tapping key the condenser is discharged through a voltage amplifier with a ballistic galvanometer in the plate circuit of the last tube. When the voltage of the glass-electrode assembly is balanced by an equal e. m. f. from the potentiometer, the ballistic discharge is zero. A small residual e. m. f., due to grid current, can be made negligibly small by a suitable choice of tube, grid resistance, and grid condenser (3).

Improvements of this new circuit over one previously described (1) consist in the use of alternating current vacuum tubes whereby storage batteries are eliminated. Vacuum tubes of higher amplification are used, with the result that an inexpensive portable microammeter replaces the type R galvanometer. The temperature-correction device, whereby the potentiometer is converted into a pH meter for any temperature, and the accessory potentiometer as well as the con-

nections for quinhydrone and hydrogen have necessitated complete redesigning and revising of the circuit.

Construction of Meter

The ballistic principle has been utilized in a direct-reading pH meter designed for rapid and simplified measurements (Figure 1).

The upper circuit is a Leeds & Northrup potentiometer of the student type. The variable voltage is obtained from a variable decade of nine 40-ohm coils and a 40-ohm slide wire. When balanced as a simple potentiometer with the standard cell, there is a 100-millivolt potential drop across each 40 ohms. The wiring of the potentiometer was changed to the modified form as shown. The glass electrode assembly, represented diagrammatically, contains a calomel half-cell attached to the main potentiometer. A salt bridge connects to a vessel which contains the standard buffer or the solution whose pH is to be measured. The inside of the glass membrane contains a quinhydrone half-cell which makes contact with a highly insulated tapping key. An accessory potentiometer containing switch S_1 supplies a variable voltage by means of a coarse (1000-ohm) and a fine (100-ohm) adjustment. A microammeter (zero center) with a suitable shunt can be thrown to three different positions, Q , S , and G , by double pole triple-throw switch S_2 . The lower circuit is a voltage amplifier system using alternating current tubes for filament supply. It was found advisable to use a dry-cell B-battery supply for steadiest conditions. The resistors and condensers should be of good grade material (Shallcross resistors are used) and it is recommended that the 0.1-microfarad condenser in the grid circuit of the first tube be mica to eliminate absorbed charge.

The resistance values given are those for an older type of potentiometer. If another type of potentiometer is used, the shunt and series resistances can be calculated from the formulas

$$\text{Series resistance} = R(1 - K_T)$$

$$\text{Parallel resistance} = \frac{K_T}{1 - K_T} \cdot R$$

where R is the total resistance of coils and slide wire from which the variable voltage is obtained. K_T is the voltage per

unit pH and is a function of temperature. If a newer type of student potentiometer (Leeds & Northrup) is used, where $R = 2300$ ohms—that is, twenty-two 100-ohm coils plus 100-ohm slide wire—then the series and shunt resistances are as follows:

Temperature, ° C.	15	25	35	45
K_T , volts	0.5713	0.5912	0.6110	0.6309
Series resistance, ohms	986.9	940.4	895.6	848.8
Parallel resistance, ohms	3065	3325	3613	3931

The slide wire and coils of the potentiometer, from which the known balancing voltage is obtained, are shunted by a variable resistance so that the potentiometer dial reads not voltage but pH. The 100-millivolt potential drop across each coil and slide wire in the main potentiometer, after introducing the shunt, is reduced to 57 to 61 millivolts, the exact shunt resistance and voltage drop depending on temperature. A simple calculation and calibration give the proper shunt resistance for each temperature used. In order to maintain the total circuit resistance the same after introducing the shunt, a variable series resistance is placed in series with the slide wire and decade coils. The series resistances for various temperatures can be computed. A single-pole double-throw switch, S_2 , throws into the circuit the extra series and parallel variable resistors, thus changing the in-

clude the calomel half-cell voltage plus asymmetric potential of the glass membrane plus the quinhydrone voltage of the inner half-cell.

Operation of Meter

In an actual manipulation, switch S_1 is closed and the microammeter connected to S . Switch S_2 is thrown on "volts" and the preliminary standard cell balance is made by adjusting the main potentiometer circuit resistors and tapping key T_1 until a balance results. This is the usual procedure for any potentiometer. The filament heating circuit is closed (not shown on diagram), as well as the B-battery switch, S_5 , and the accessory potentiometer switch, S_6 . These are assembled as a single switch. The microammeter is thrown to position G . (It is advisable to shunt the microammeter with a low resistance while making this manipulation and it is important that the filament heating current be started before switching to G . The reason is that the microammeter in position G measures the difference between two opposing currents—namely, the plate current of the last tube and the balancing current from the last 22 volts of the B-batteries. If the filament is cold, there is a considerable unbalance due to the nonexistence of the plate current.) A buffer of known pH is placed in the container outside the glass membrane. The temperature is read and thereafter maintained constant.

The settings of the variable resistor in series and parallel with the main potentiometer slide wire and coils are made, the settings being obtained from the previous calibration. Switch S_2 is closed toward the side marked pH, and the main potentiometer dial is set on the pH of the standard buffer. Thus, if a standard acetate buffer pH = 4.63 is used, the main potentiometer scale is set on 0.400 (coil decade) + 0.063 (slide wire). The double pole switch, S_3 , usually remains fixed in position G for glass-electrode work. The accessory potentiometer (containing switch S_4) is now adjusted, using both fine and coarse adjustments, while key T_2 is tapped until there is no ballistic throw on the microammeter with maximum sensitivity (shunt infinity). The accessory potentiometer then remains fixed. To measure the pH of any unknown solution, the unknown replaces the standard buffer and key T_2 is tapped while the main potentiometer is varied, the accessory potentiometer remaining fixed. When a balance is obtained, the main potentiometer reads the pH of the unknown. Any number of determinations may be made after this single preliminary calibration with standard cell and standard buffer, provided the battery voltages of the two potentiometers do not change.

The pH measurement is simple, involving only a preliminary standard cell and standard buffer adjustment with appropriate dial settings and operation of the proper switches. This instrument has been in operation for 3 months and has given excellent results. It has been operated by students and technicians with no knowledge of vacuum-tube technic. A simple pH measurement can be made in about 10 minutes, including the time required for the constancy of the filament and batteries. Once in adjustment, repeated measurements can be made in one minute.

No temperature calculation is necessary. This is taken into consideration by the variable calibrated resistors in parallel and in series with the slide wire and coils.

It is not necessary to know the value of the voltage of the calomel half-cell, the quinhydrone half-cell, nor the asymmetric potential. This remains constant for a given temperature and is balanced out by the accessory potentiometer. The main potentiometer balances the membrane potential, which varies directly with the pH.

In order to use the instrument for measuring quinhydrone and hydrogen-electrode potentials, switches and binding posts are provided (Figure 1).

The accuracy of the instrument is about 0.02 pH. The instrument is easily portable, the ammeter is inexpensive and of rugged construction, and the vacuum tubes are of standard type and inexpensive. Such an instrument will have its greatest range of usefulness in biological and industrial laboratories where rapid measurements are desirable by technicians not especially expert in vacuum-tube operation. Although the operation is simple, it is recommended that those un-

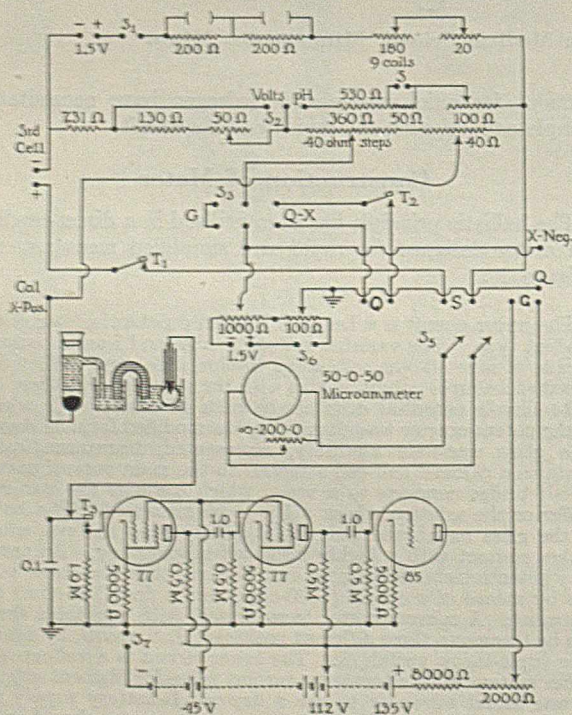


FIGURE 1. DIAGRAM OF METER

strument by means of a single switch from a voltage potentiometer to a potentiometer reading in pH units. The setting of these two variable resistors is determined by temperature and is read from a table obtained by a preliminary calibration which, once made for a given instrument, remains fixed.

An additional accessory potentiometer is placed in series with the glass-electrode system and the main potentiometer. It is interposed between the main potentiometer and the condenser to be charged. This potentiometer balances out the voltages, which for a given temperature are fixed and in-

familiar with vacuum-tube circuits consult a radio engineer for minor details of construction before an attempt is made to build such an assembly. The approximate costs of the various parts are: amplifier resistors, \$5; tubes, \$4; paper condensers, \$1; mica condenser, \$5; condenser discharge key, \$3; batteries, \$4; filament transformer, \$2; microammeter and shunt, \$15; accessory potentiometer, \$2; shunt and

series resistors for main potentiometer (with dials), \$4; student potentiometer, \$70.

Literature Cited

- (1) Hemingway, A., *IND. ENG. CHEM., Anal. Ed.*, 5, 278 (1933).
- (2) Morton, C., *J. Chem. Soc.*, 1930, 2, 1528.
- (3) Morton, C., *Ibid.*, 1931, 2977.

RECEIVED December 26, 1934.

Determination of Sulfur in Plain and Alloy Steels

A Perchloric Acid Modification of Meineke's Method

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THE time required for gravimetric determination of sulfur in steels by Meineke's method may be decreased by substituting perchloric acid evaporation for hydrochloric evaporation. The steel is dissolved in the potassium-copper chloride solution which leaves insoluble all the sulfur, carbon, some chromium, iron, molybdenum, etc. The residue may be taken up in acids, and fumed down with perchloric acid. The insoluble material is then separated from the soluble sulfates which are precipitated after reduction of chromates.

When running a batch of sulfurs the points which deserve consideration are: the substitution of paper for Gooch crucibles; a single evaporation with perchloric acid, instead of several with hydrochloric acid, to get rid of nitric acid; and a slight danger of spattering during evaporation of the acid.

The determination of sulfur after fuming a sample by perchloric acid has been applied for some time to sulfur in rubber, so that it is only a matter of application to steels. The steels under consideration were those containing molybdenum or selenium which give low results by the evolution method, and any high-sulfur steels which may tend to give low results by that method.

Procedure

Five grams of steel are transferred to a 600-cc. beaker or flask and covered with 500 cc. of the potassium-copper chloride solution. The solution is kept at about 90° C., as on a steam bath. Copper immediately comes out of the solution, and the reaction is complete when the bright red metal has redissolved. The solution is kept covered at all times, but agitated frequently to hasten solution if desired. With hand stirring, the time required is 2 or more hours.

The hot solution is filtered through a fast filter paper, and washed with hot water. The paper is removed from the funnel, placed in a beaker, covered with strong bromine water, and agitated with a glass rod. Now 10 cc. of zinc oxide-nitric acid, and 8 cc. of c. p. perchloric acid are added. The beaker is heated to destroy the paper and drive out the nitric acid and the excess perchloric acid. Upon completion of heating, as indicated by the formation of chromic acid (if chromium is present), or by the clarification of the fumes in the beaker, and condensation of perchloric acid on the sides of the beaker, the beaker is removed from the heat and cooled. As carbon does not interfere, heating need not be continued to oxidize it.

The residue, usually solid, is dissolved in water, diluted to about 100 to 150 cc., and boiled to remove chlorine. The silica (and carbon) is filtered off on paper and washed with water. To the filtrate are added 10 cc. of peroxide (to reduce chromic acid), the solution is diluted to 200 cc. and boiled, and sulfates are precipitated with barium chloride, as is customary. The weight of barium sulfate in grams divided by 5 and multiplied by 0.1373 gives the weight of sulfur found per gram.

This perchloric acid modification for the determination of sulfur checks Meineke's method.

To show that various reagents encountered in analysis of sulfur do not interfere, a series of four sets was run as follows:

1. 25 cc. of approximately 0.1 N sulfuric acid, run for sulfates.
 2. 25 cc. of approximately 0.1 N acid plus 10 cc. of zinc oxide-nitric acid reagent and 8 cc. of perchloric acid.
 3. 25 cc. of approximately 0.1 N acid plus 1 gram of potassium chlorate and 5 cc. each of nitric and hydrochloric acids and 8 cc. of perchloric acid.
 4. As in 2, and in addition 0.0586 gram of potassium chromate (0.0200 gram of chromium), and peroxide.
- Results (grams of sulfur): (1) 0.0403, 0.0402; (2) 0.0403, 0.0402; (3) 0.0403; (4) 0.0403, 0.0402.

TABLE I. TYPICAL ANALYSES

	C	Mn	P	S	Si	Ni	Cr	Mo
	%	%	%	%	%	%	%	%
Author's laboratory	3.00	0.62	0.169	0.082	2.37	1.80	0.37	0.60
Outside laboratory	3.00	0.70	0.11	0.06	2.31	1.91	0.37	0.70
	3.10	0.56	0.085	^a	2.35	1.82	0.35	0.60
	3.00	0.68	0.051	0.064	2.30	1.87	0.40	0.62
	...	0.43	0.021	^b	0.34	..	13.14	..
	0.086	0.40	0.022	0.221	0.27	0.22	13.3	..
	0.11	0.37	0.014	^c	0.30	..	13.1	0.55
	0.15	0.37	0.016	...	0.25	..	13.1	0.56

^a Evolution, 0.034; gravimetric, 0.067, 0.068 (author); 0.071, 0.072 (R. C. Coburn).

^b Evolution, 0.256; gravimetric, 0.348, 0.344.

^c Gravimetric, 0.09, 0.08 (author); 0.089, 0.089 (R. C. Coburn). Meineke, 0.077 (author); 0.08, 0.09 (R. C. Coburn).

Analysis of a selenium steel by the gravimetric method gave 0.246 and 0.245, and by the evolution method 0.132 per cent. Another gave 0.256 and 0.112 per cent, respectively.

Bureau of Standards steels analyzed for sulfur gave the following results: No. 10d, 0.030; author, 0.026, 0.026; No. 22b, 0.041; author, 0.034, 0.034.

Solutions Used

The following reagents were used: 500 grams of (KCl)₂-CuCl₂·2H₂O; 100 cc. of hydrochloric acid; and 2000 cc. of water. The zinc oxide-nitric acid reagent was prepared by sifting 200 grams of zinc oxide into 1 liter of concentrated nitric acid.

Conclusion

A modified method for the Meineke gravimetric sulfur determination, suggested because of greater speed in operation, has been applied successfully to molybdenum, selenium, and high-sulfur steels.

RECEIVED February 18, 1935.

Filtration of Hot Solutions

G. R. YOHE, Ohio Wesleyan University, Delaware, Ohio

THE problem of filtering hot concentrated solutions in recrystallization processes is sometimes perplexing, for the solution in the funnel and the main part of the solution must be kept hot to prevent premature crystallization. The use of a jacketed funnel is common, but not too satisfactory when large quantities of rather slow-filtering solutions are being handled (1).

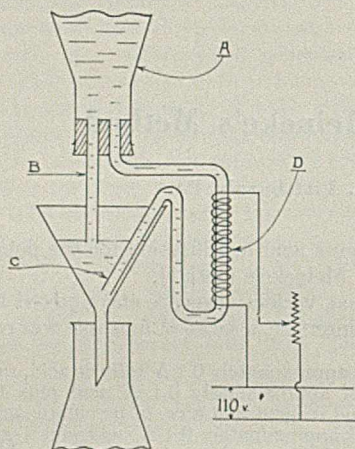


FIGURE 1. DIAGRAM OF APPARATUS

The device described here is of service in filtering large volumes and keeping the solution hot with a minimum of attention from the experimenter, and has been found satis-

factory with water and benzene solutions. In one test experiment an asbestos filter was used with a strongly acid, concentrated solution of sodium hydrogen sulfate; this solution filtered very slowly, yet no difficulty was experienced in keeping the temperature (measured in the funnel) at 70° to 75° C. for the several hours required for the filtration. The device has the advantages that it heats not the funnel but the solution being filtered, and that it automatically keeps the funnel filled and therefore requires attention only at the start and at the finish of the filtration.

The design of this apparatus may be varied. The section at D may be inclined, and a free flame used as the source of heat if nonflammable solvents are used. The writer has used a jacketed tube with steam heat for benzene solutions, but the electric heating unit seems most satisfactory for all purposes.

Constant level is maintained in the funnel because air is not admitted to inverted flask A until the level in the funnel goes below the end of tube B. Working on the thermo-siphon principle, the coolest of the solution in the funnel is withdrawn through tube C, heated at D, and returned to A. When the level in the funnel falls below the end of B, air enters here, and the flow of the liquid through the heating coil is temporarily reversed. This does no harm. Care must be taken to see that the stopper in flask A is securely in place.

In constructing the heating unit, D, the glass tube is covered with thin asbestos paper, then wound with No. 26 chromel wire (resistance of heating coil about 10 ohms), and covered with asbestos insulation. It has been found that a current of about 2 to 4 amperes results in satisfactory heating.

Literature Cited

- (1) Caldwell, J. R., *IND. ENG. CHEM., Anal Ed.*, 7, 76 (1935).

RECEIVED March 13, 1935.

A Simple Laboratory Stirrer for Use on the Vacuum Line

GEORGE T. AUSTIN, 311 East Armory Ave., Champaign, Ill.

IN LABORATORY work with small quantities of organic chemicals, it is frequently necessary to stir for extended periods of time. For laboratories not having pressure lines, the vacuum stirrer shown above will be found very convenient. It is extremely inexpensive, requires little time to make, and is powerful. If carefully made it will stir viscous liquids, and is especially applicable for use in the synthesis of the Grignard reagent. For schools, it is very handy for students in second-semester organic work, where it is inadvisable and expensive to place electric motors in their hands.

The housing is a small can, such as is used to contain chocolate. The tin blades for the vanes are made from any sheet metal, and may be soldered together and fastened to the shaft with de Khotinsky cement, or any other available wax. The fitting between the shaft and the bearing should be tight to prevent leakage of air, and should be lubricated with light oil. The use of a nozzle on the air inlet increases the power greatly. A second air inlet will increase the power. A little variation in the size of the opening will lead to better results. The connection of the shaft to a longer one is accomplished by means of a rubber policeman. For use in potentiometric titration, or where a mercury seal is not required, the shaft may be an unbroken rod with the propeller sealed upon the end as shown in Figure 1.

RECEIVED March 12, 1935.

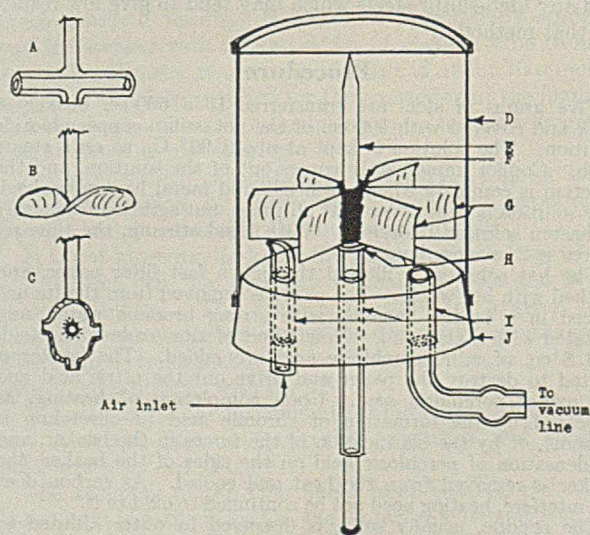
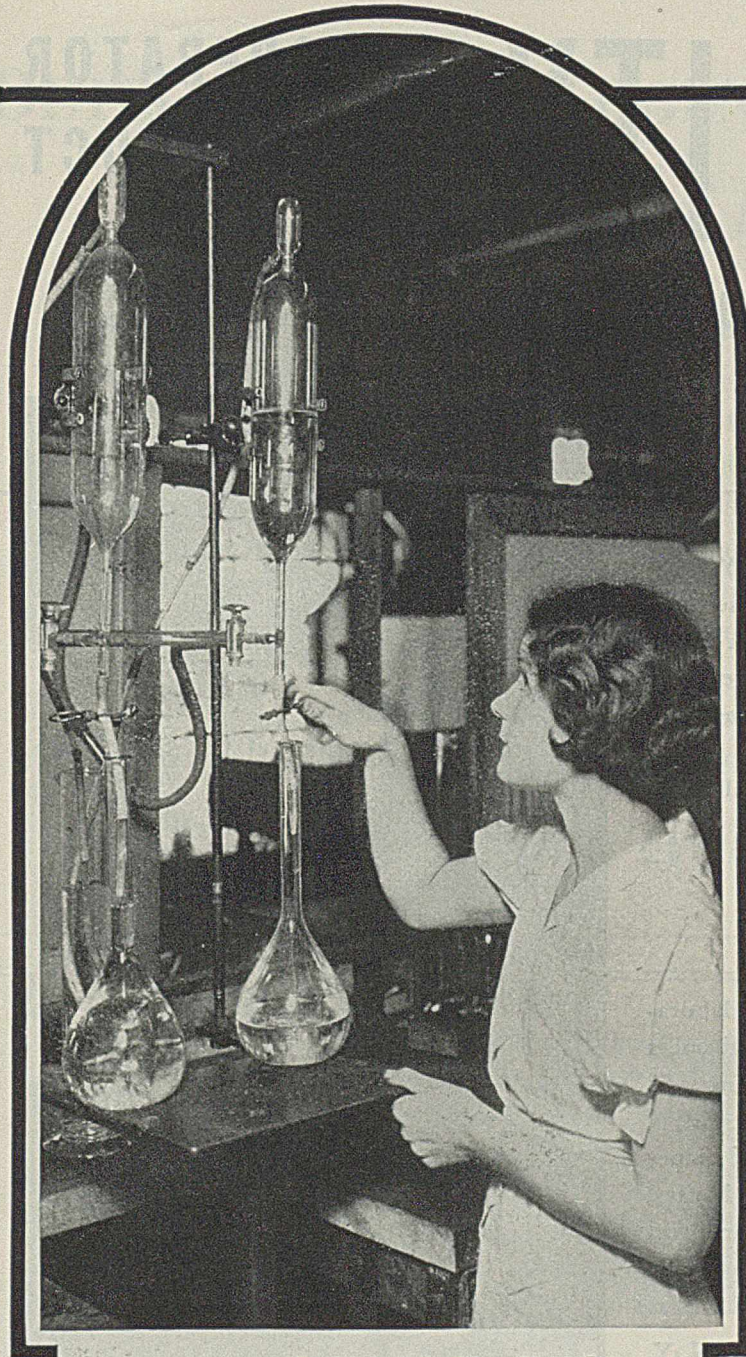
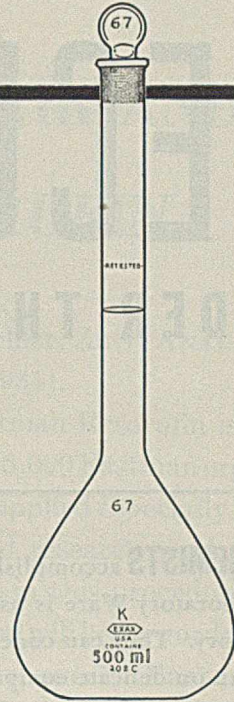


FIGURE 1. DIAGRAM OF STIRRER

- | | |
|--|--------------------------|
| A, B, C. Best types of agitators for use with this stirrer | G. Sheet-steel vanes |
| D. Small tin can | H. Two small washers |
| E. 3-mm. glass rod | I. 5-mm. tubing |
| F. de Khotinsky cement | J. No. 11 rubber stopper |



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50 ml.	0.10 ml.	0.20 ml.
100 ml.	0.16 ml.	0.30 ml.
200 ml.	0.20 ml.	0.40 ml.
250 ml.	0.24 ml.	0.50 ml.
500 ml.	0.30 ml.	0.60 ml.
1000 ml.	0.60 ml.	1.00 ml.
2000 ml.	1.00 ml.	2.00 ml.

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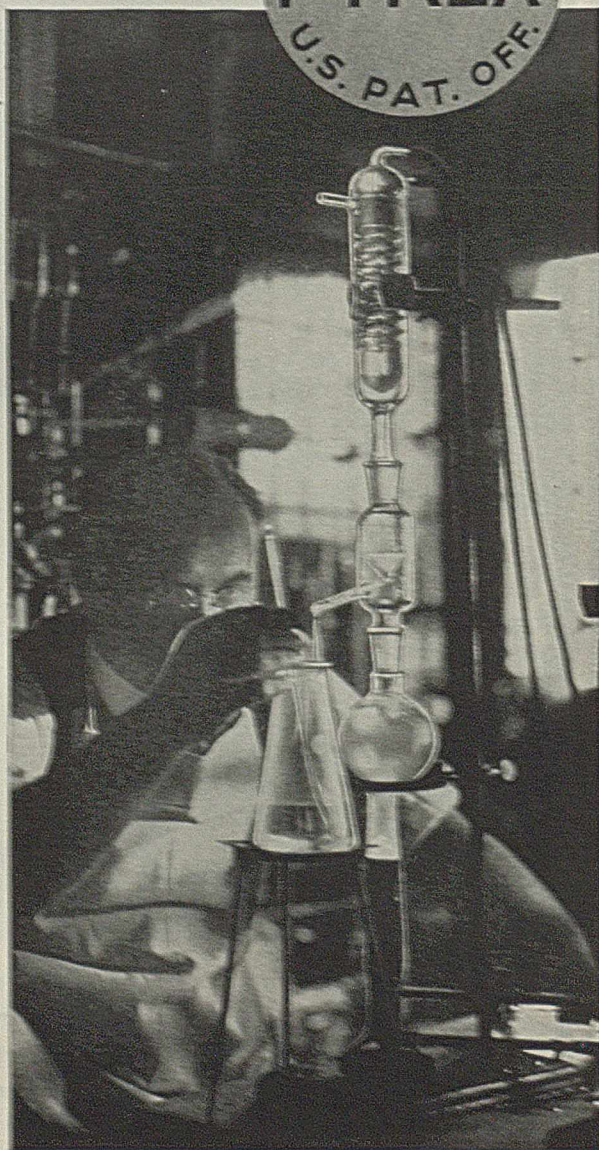
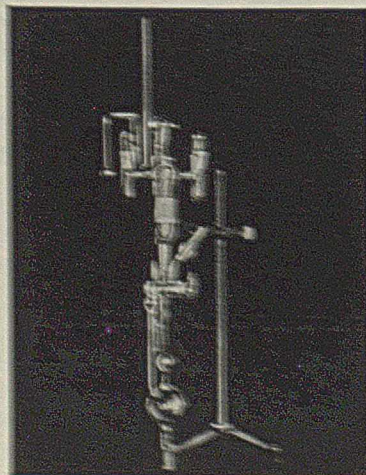
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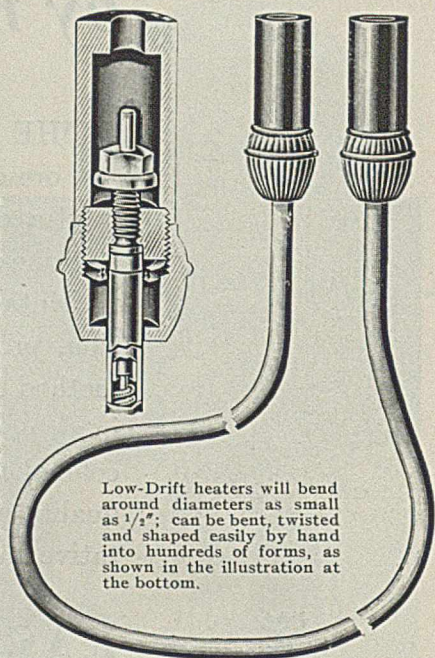
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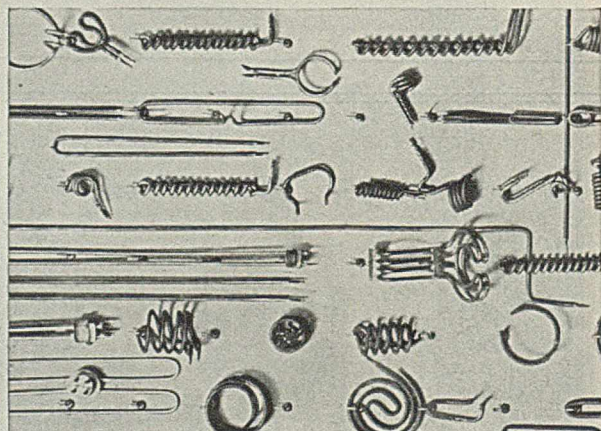
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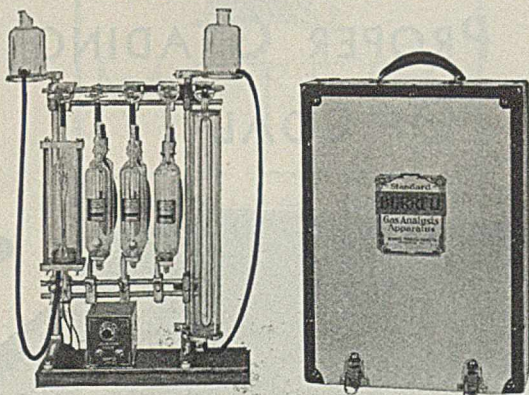
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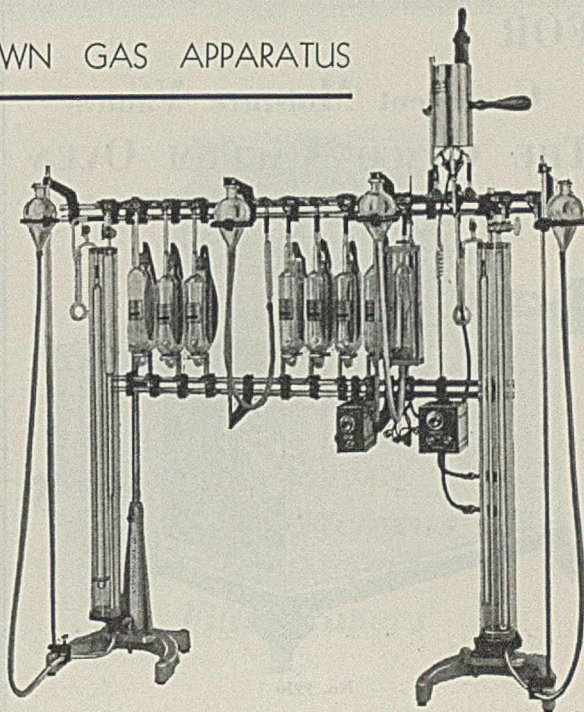
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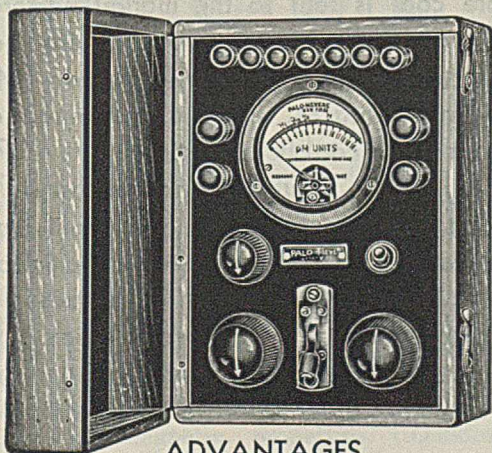
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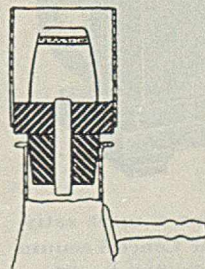


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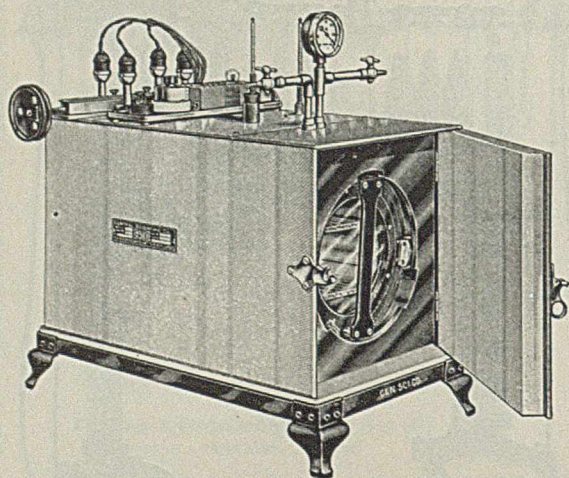
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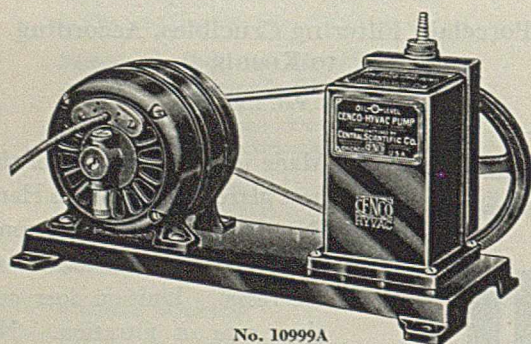
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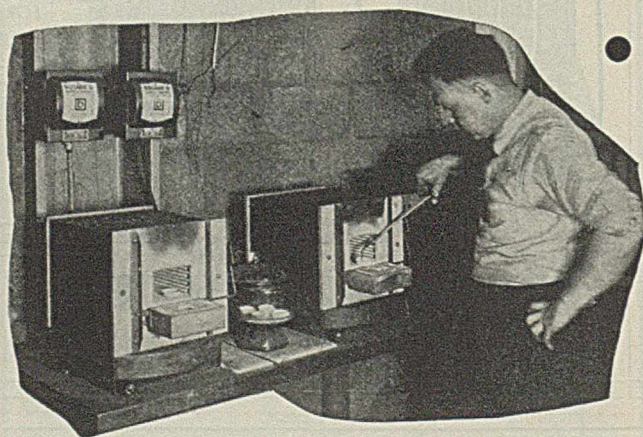
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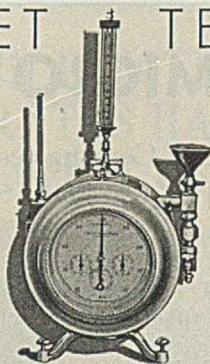
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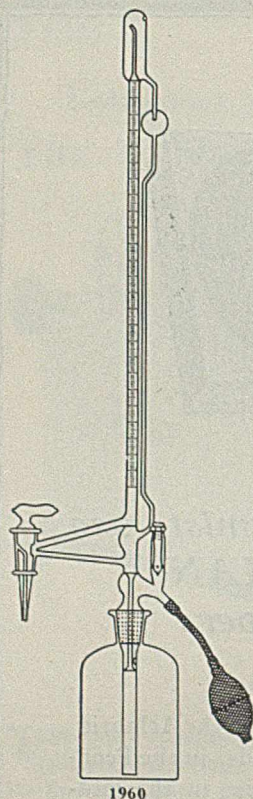
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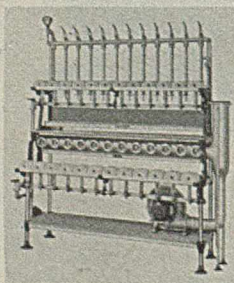
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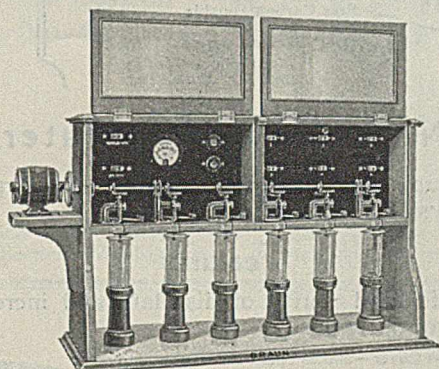
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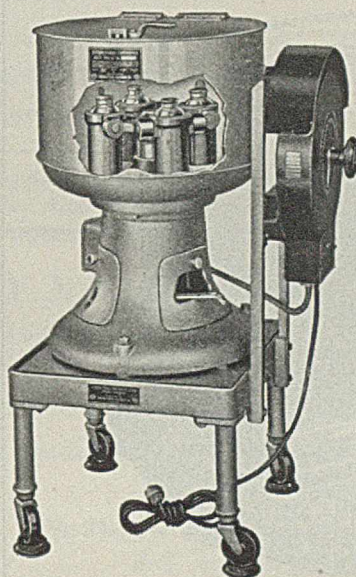
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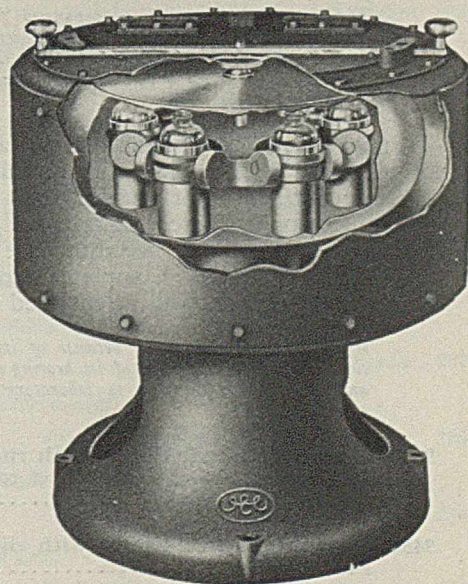
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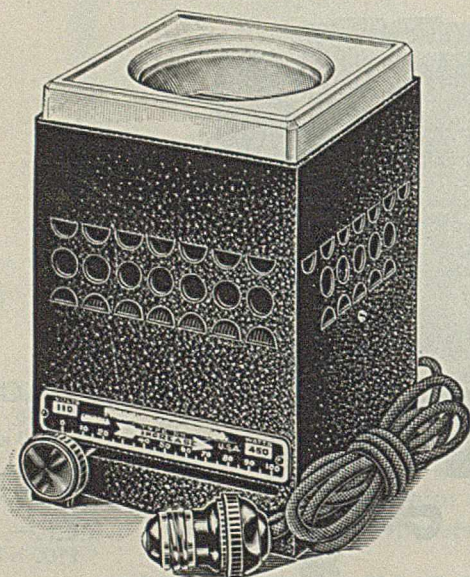
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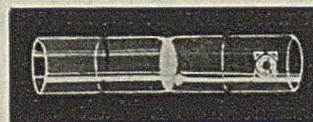
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