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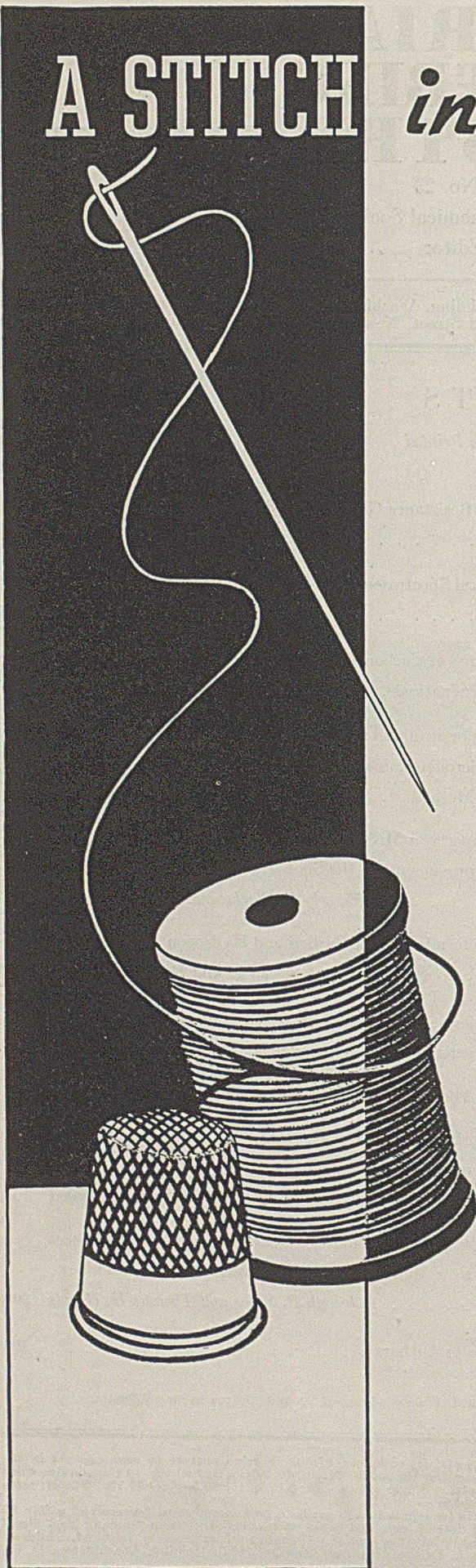
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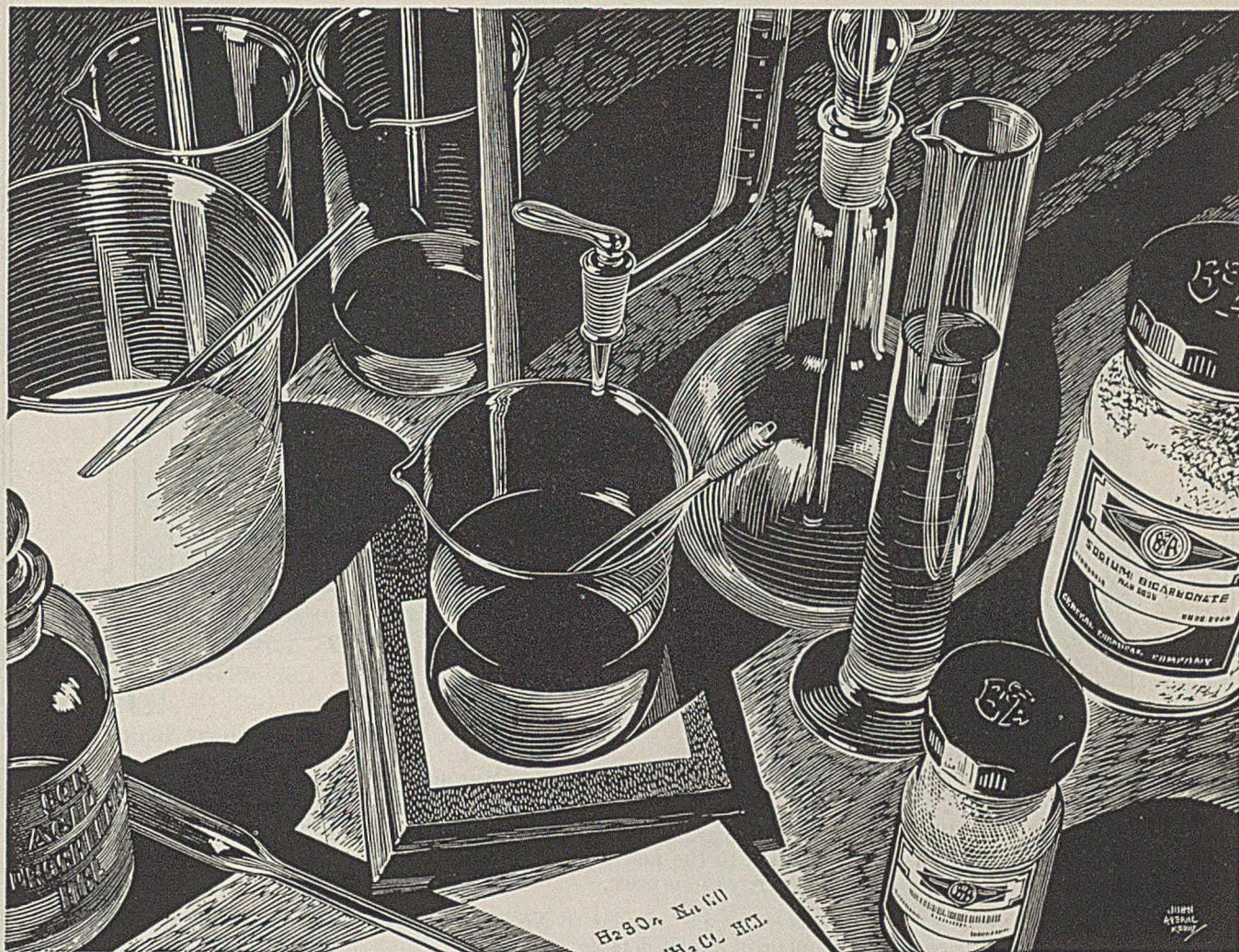
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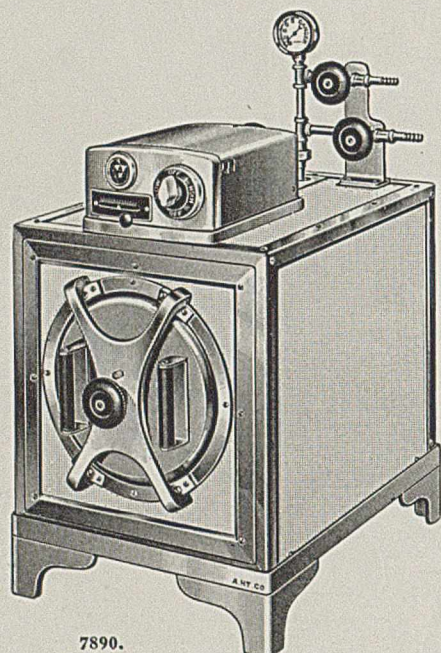
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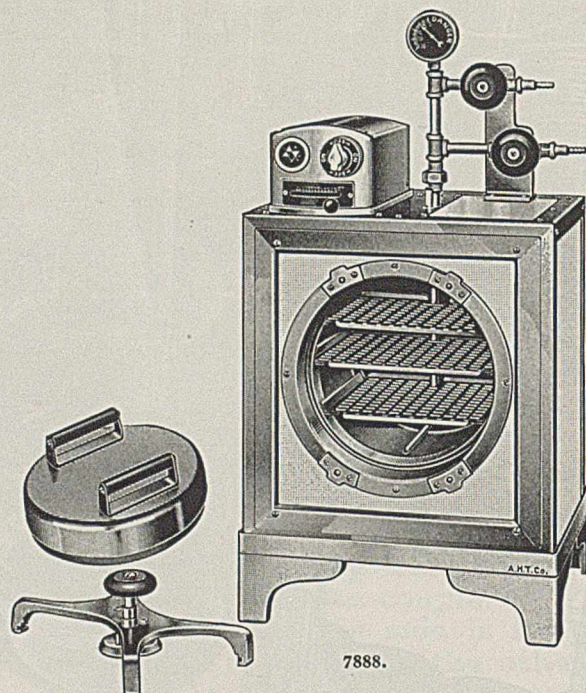
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INDUSTRIAL and ENGINEERING CHEMISTRY

Harrison E. Howe, Editor

The Phosphotungstate Method for Vanadium Spectrophotometric Study

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A spectrophotometric study of the phosphotungstate method for vanadium was made for the purpose of ascertaining optimum concentration of reagents, effect of acid and diverse ion concentrations, and stability.

Typical transmittancy curves are given covering the most useful range of concentration. Procedures are proposed for application of the method to the determination of vanadium in alloy steels.

LITTLE attention has been paid in the literature to the colorimetric determination of vanadium as a complex phosphotungstate, a method which, as pointed out recently by Sandell (4), possesses very definite advantages over the more common peroxide method. The present spectrophotometric study was therefore undertaken to establish the colorimetric behavior of the method under various conditions.

The reaction upon which the method is based is carried out by adding sodium tungstate and phosphoric acid to an acid solution containing quinquevalent vanadium. An immediate reaction thereupon occurs in which a yellow or brownish yellow solution is formed, varying in hue and intensity with the vanadium concentration. The exact chemical nature of the yellow phosphotungstovanadate is somewhat obscure. That it is a coördinated compound of the so-called heteropoly type, in which V_2O_5 groups replace part of the W_2O_7 groups of phosphotungstic acid, seems likely.

HISTORICAL. Although Gibbs (1) first appears to have studied the phosphotungstovanadates in 1883, their use in colorimetric analysis did not begin until 1928 when Willard and Young (2, 8) utilized the yellow compound to determine small amounts of vanadium in tungstic acid residues. Vinogradov (5, 6) applied the method to the determination of vanadium in plant ash, while Sandell (4) recently adapted it to rock analysis after a preliminary extraction separation.

Experimental

REAGENTS. A standard vanadium solution was made up as shown in the following paragraphs.

¹ Present address, Dow Chemical Co., Midland, Mich.

c. p. vanadium pentoxide was dissolved in a slight excess of sodium hydroxide, the solution was filtered, and ammonium vanadate was precipitated by addition of ammonium chloride. The ammonium vanadate was filtered off, dried, and ignited to vanadium pentoxide in a muffle furnace at about 500° C. A standard vanadium solution (0.020 M in $NaVO_3$) was made by dissolving a weighed portion (1.819 grams) in sodium hydroxide solution, adding a slight excess of sulfuric acid, cooling, and diluting to 1000 ml. This solution was then standardized with potassium permanganate solution in the ordinary way.

All other reagents were of analytical reagent quality, no further attempt at purification being made.

APPARATUS. The Purdue spectrophotometer, described by Mellon and Kasline (3), was used for the determination of all spectrophotometric curves. The instrument has been modified somewhat, so that it is now of an automatic recording type, nearly all curves being recorded directly.

PROCEDURE. In general, solutions were made up in the following manner: By means of a pipet the required volume of standard vanadium solution containing 1 mg. of vanadium per ml. was measured into a 250-ml. beaker. Acid, distilled water, solution containing diverse ion, phosphoric acid, and sodium tungstate were then added in order, and the solution was brought to boiling, cooled, and diluted to 100 ml. Unless the effect of some other acid was of interest, nitric acid was always employed. Solutions containing diverse ions were added only during the experiments on the effect of diverse ions. The spectrophotometric curves were then determined, either being recorded directly by the instrument or the numerical data being taken at each 10 $m\mu$ interval at a 5 or 10 $m\mu$ band width. In most of this work the solution in question was compared with a standard solution whose curve was determined at the same time under the same conditions; consequently use of the more rapid direct-recording method was considered preferable.

Discussion of Results

Since in this study a large number of spectrophotometric curves of significance were determined, it was considered impractical to attempt to report the data in graphical form. Typical curves for 1-cm. cells are presented in Figure I covering the most useful concentrations for the phosphotungstovanadate complex. Because relative transmittancy values are of as much worth as absolute, the average and maximum differences between the curve in question and a standard curve are reported. The average of these transmittancy differences covers the range 400 to 540 $m\mu$, the significant portion of the curve, and is made without regard to sign. If the maximum difference is about 5 per cent or less and the average difference is 2 per cent or less, the solutions in general appear identical to the eye.

RATIO OF SODIUM TUNGSTATE TO PHOSPHORIC ACID. As is evident from Table I, the concentrations of sodium tung-

TABLE I. RATIO OF SODIUM TUNGSTATE TO PHOSPHORIC ACID^a

No.	0.5 M Na ₂ WO ₄ Ml.	90% H ₃ PO ₄ Ml.	Moles H ₃ PO ₄ : Moles Na ₂ WO ₄	Transmittancy Differences, Unknown and Standard	
				Max. %	Av. %
1	0.5	0.01	6.6:1	+40	20
2	0.5	0.05	33:1	+40	20
3	0.5	0.1	66:1	+40	20
4	0.5	0.5	330:1	+42.5	22
5	1.0	0.3	9.9:1	+15.5	7.4
6	2.0	0.2	3.3:1	-8.0	3.3
7	2.0	0.5	8.3:1	-6.5	2.7
8	2.0	1.0	16:1	-8.0	3.2
9	2.0	3.0	48:1	-4.0	1.9
10	2.0	5.0	83:1	+6.5	3.1
11	4.0	1.2	9.9:1	± 1.5	0.7
12	5.0	0.2	1.3:1	-1.5	0.4
13	5.0	0.5	3.4:1	-1.5	0.4
14	5.0	1.0	6.6:1	0	0
15	5.0	3.0	19:1	0	0
16	5.0	5.0	33:1	+5.0	1.2
17	8.0	2.4	9.9:1	± 1.5	0.8
18	10.0	1.0	3.3:1	+2.0	0.5
19	10.0	3.0	9.9:1	+2.0	0.5
20	10.0	5.0	16:1	+5.0	1.4
21	10.0	10.0	33:1	+6.0	1.9
22	10.0	15.0	48:1	+6.0	1.9
23	15.0	5.0	11:1	+4.0	1.0
24	15.0	10.0	22:1	+7.5	2.5
25	15.0	15.0	33:1	+7.5	2.5
26	10 ml. 10% phospho- tungstic acid	10.0	...	+24.5	9.3

^a No. 15 taken as standard; all solutions contain 5.0 mg. of vanadium in 1.00-cm. cells.

state and phosphoric acid may vary over a rather wide range without effecting a sensible change in the color characteristics of the solution. In general the molecular ratio of phosphoric acid to sodium tungstate may vary from 3 to 20 without causing any change visible to the eye. The solution must be at least 0.01 M in sodium tungstate for development of maximum color, and preferably not be more concentrated than 0.1 M. In lower concentrations of sodium tungstate, the solutions have a more brownish hue. A solution is recommended which is 0.025 M in sodium tungstate and 0.5 M in phosphoric acid, or which contains 5 ml. of 0.5 M sodium tungstate solution and 3 ml. of 90 per cent phosphoric acid per 100 ml.

Vinogradov (6) recommends the use of 10 per cent phosphotungstic acid. Experiments with this reagent, however, gave solutions whose intensity was much less than was obtained by the use of phosphoric acid and sodium tungstate alone. The effect of concentrations of reagents as recommended by Vinogradov is shown in Table I, No. 26.

EFFECT OF ACID. Table II shows the effect of various acids in concentrations up to 2.4 N. Up to this concentration, the solutions display a maximum variation in transmittancy of about 3 per cent at any wave length, while the total variation in hue and intensity is considerably less than can be detected visually. It was found, however, that the effect of acid was much greater in the cold, a distinctly brownish color being formed which was roughly proportional to the amount of acid and which faded slowly after several hours to the true yellow of phosphotungstovanadate. It was found necessary, therefore, to heat the solutions to boiling, such treatment apparently hastening the attainment of equilibrium.

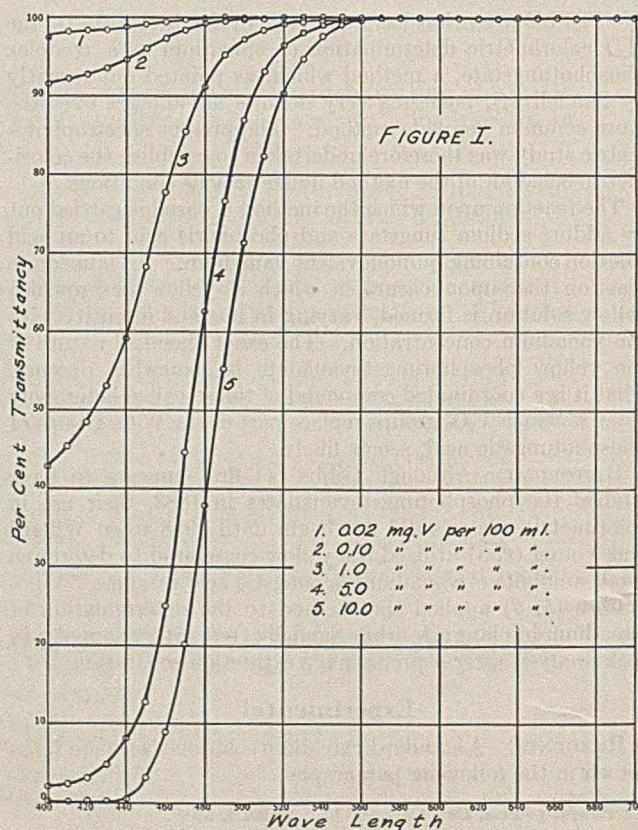
In more dilute solutions, containing 0.25 mg. of vanadium, the maximum color is not developed immediately in the cold, although the difference is not great enough to be of importance in visual work. The cold solution, on standing 2 or 3 hours, finally reaches the same point of equilibrium as the boiled solution. If the solution, therefore, contains less than 1 mg. of vanadium per 100 ml. or if matching is done by a duplication method, boiling is unnecessary, provided that ferric chloride is absent.

EFFECT OF DIVERSE IONS. Table III shows the effect of a number of diverse ions or solutes. In the case of interfering ions, a maximum concentration is specified at which an error of about 2 per cent would occur in comparing the solution with a standard containing none of the ion in question.

In addition to the ions listed in Table III, the following substances were found to have no effect on the concentrations stated (total volume, 100 ml.): 3 grams of NaCl; 5 grams of NaNO₃; 500 mg. of Mg⁺⁺, Ca⁺⁺, Sr⁺⁺, Ba⁺⁺, Zn⁺⁺, Cd⁺⁺, Hg⁺⁺, Al⁺⁺⁺, Pb⁺⁺, As (as H₃AsO₄), C₂H₃O₂⁻, and Br⁻; 25 mg. of Be⁺⁺; 100 mg. of Ag⁺; 125 mg. of Li⁺; 10 mg. of Th⁺; 100 mg. of ClO₃⁻; 50 mg. of SiO₂ (as Na₂SiO₃); 100 mg. of C₂O₄²⁻; 20 mg. of CN⁻; 100 mg. of citrate ion; and 100 mg. of tartrate ion.

At least four types of reactions were found to take place between the diverse ion and the other constituents of the solution. The first is the precipitation of the phosphotungstic acid by ammonium or potassium ions. Ammonium ion must be nearly completely absent. The second is the precipitation of some basic compound or slightly soluble phosphate. Antimony, tin, titanium, and zirconium were found to interfere in this way and, if present in large amounts, must be removed. The third is the formation of a color with the phosphotungstic acid. Only one element, molybdenum, was found to interfere in this way, and then, as shown in Table III, only in relatively large concentrations. The fourth type of reaction is the reduction of the phosphotungstic acid by some reducing agent such as stannous, iodide, or thiocyanate ion. Ordinarily reducing agents are eliminated during the process in which the vanadium is oxidized to the quinquevalent state; consequently the effect of such reducing agents is of little importance.

Ferric chloride appears to have an effect in the cold out of all proportion to its concentration. Thus 10 mg. of ferric ion as ferric chloride in a solution containing 0.25 mg. of vanadium causes development of a brownish hue which makes



visual matching with a standard impossible and which disappears on heating the solution to boiling. The authors were not able to corroborate Sandell's observation (4) that aluminum ion also interferes.

There is also a large class of ions which interfere because of their own color. These ions, for which maximum limits of concentration are specified, are the most important source of interference in the determination of vanadium by this method. In the case of ferric ion, a fairly large concentration, 100 mg. of iron as ferric nitrate, may be present without interference, since a colorless complex is formed with the phosphoric acid. Above a concentration of 200 mg. the interference becomes very appreciable even though additional phosphoric acid is added.

Of the elements mentioned above, none is likely to occur in vanadiferous material in amounts which might cause interference except iron and chromium. Molybdenum might interfere in certain high-molybdenum steels although in other types of materials no interference is likely.

STABILITY. The data showing the effect of age on a series of standard solutions may be summarized in the statement that the color is entirely stable for 24 hours, but fades slowly thereafter until at the end of a 2-week period a diminution of about 10 per cent has taken place.

APPLICATIONS. Vanadium determinations are required most frequently in two kinds of materials: rocks or minerals, and ferrous alloys. Sandell (4) has applied the phosphotungstate method to the determination of vanadium in silicate rocks, but no mention is made in the literature of its application to ferrous alloys.

Vanadium occurs as an alloying agent in ferrous alloys up to about 2 per cent along with iron, chromium, tungsten, and other elements. As shown previously, ferric ion does not interfere up to 100 mg. per 100 ml., and chromate up to 1 mg. of chromium per 100 ml. Assuming that a sample containing 1 mg. of vanadium is to be taken, iron does not interfere if the vanadium content is 1 per cent or more, while chromium will interfere if present in more than 1 per cent, as is ordinarily the case. Three classes of vanadium alloys may therefore be designated: (a) high-vanadium alloys (V, Cr, W alloys), containing 0.7 to 2.0 per cent of vanadium, in which chromium interferes but iron does not; (b) medium-vanadium (V, Cr alloys), containing 0.1 to 0.7 per cent of vanadium, in which both iron and chromium interfere; and (c) low-vanadium alloys (plain carbon steel, cast iron, etc.), containing less than 0.1 per cent of vanadium, in which it may be necessary to separate vanadium from a number of elements.

It was not considered practical to attempt to compensate for other colored ions by adding to the standard an amount equal to that present in the unknown, since the amount of such ions was not always known and the sensitivity would have been thereby greatly decreased.

A method for the separation of vanadium from chromium which was proposed by Willard and Gibson (7) was found to be satisfactory and the following procedures are based upon its use. Vanadium and chromium are oxidized by boiling with perchloric acid, the solution is diluted, lead perchlorate solution is added, and the resultant precipitate of lead chromate is filtered off. No attempt is made to dissolve the tungsten, nor is any effort made to recover vanadium from the tungstic oxide residue, such losses being too small to cause appreciable error in a visual colorimetric procedure.

Procedure

CR, W, V STEELS, 0.7 TO 2.0 PER CENT VANADIUM. Weigh 150 mg. of sample to the nearest milligram and transfer to a 100-ml. beaker. Add 10 ml. of hydrochloric acid (1 to 1), cover, and warm until all action has ceased. Push aside the cover, add a drop of nitric acid (1 to 1), and boil, swirling the liquid to make

TABLE II. EFFECT OF ACID

No.	Acidity	Age Min.	Treatment	Transmittancy Differences, Unknown and Standard	
				Max. %	Av. %
1	None	15	Boiled	-3.5	1.1
2	2.4 N in HNO ₃	15	Boiled	+5.0	1.2
3	2.4 N in H ₂ SO ₄	15	Boiled	0	0
4	2.4 N in HCl	15	Boiled	+3.0	0.7
5	2.7 N in HClO ₄	15	Boiled	+7.5	2.3
6	None	15	Cold	+11.5	3.8
7	0.3 N in HNO ₃	15	Cold	-9.0	5.3
8	1.2 N in HNO ₃	15	Cold	-16.5	8.1
		Hours			
9	None	5	Cold	+3.5	1.0
10	0.3 N in HNO ₃	5	Cold	+3.5	1.0
11	1.2 N in HNO ₃	5	Cold	+3.5	1.0
		Min.			
12	0.6 N in HNO ₃	15	Cold	+5.0	1.5
13	0.6 N in HNO ₃	15	Boiled	0	0

* Solutions 1 to 11 contain 5.0 mg. of vanadium per 100 ml.; solutions 12 to 13, 0.25 mg. of vanadium per 100 ml.; solutions 1 to 11 in 1.00-cm. cells, 12 to 13 in 4.98-cm. cells; solutions 3 and 13 taken as standards.

TABLE III. EFFECT OF DIVERSE IONS*

Substance	Limiting Concentration Mg. per 100 ml.	Effect
1	NH ₄ Cl	10 NH ₄
2	KCl	75 K
3	SbCl ₃	10 Sb
4	Bi(NO ₃) ₃	15 Bi
5	SnCl ₄	25 Sn
6	TiOSO ₄	20 Ti
7	ZrOCl ₂	1 to 3 Zr
8	Cu(NO ₃) ₂	10 Cu
9	Co(NO ₃) ₂	10 Co
10	Ni(NO ₃) ₂	35 Ni
11	Fe(NO ₃) ₃	100 Fe
12	MnSO ₄	40 Mn
13	K ₂ Cr ₂ O ₇	1 Cr
14	UO ₂ (C ₂ H ₃ O ₂) ₂	100 U
15	KCNS	>25 CNS
16	KI	10 I
17	Na ₂ MoO ₄	50 Mo
18	Fe(NO ₃) ₃	100 Fe
19	FeCl ₃	20 Fe
20	FeCl ₂	<10 Fe
21	AlCl ₃	>100 Al
22	AlCl ₃	>100 Al

* All solutions 0.025 M in Na₂WO₄ and 0.5 M in H₃PO₄; all contain 5.0 mg. of vanadium, except Nos. 17 to 21 which contain 0.25 mg. of vanadium; all solutions boiled except Nos. 19 and 20 which were kept at room temperature; all in 1.00-cm. cells except Nos. 17 to 21 in 4.98-cm. cells; for effect of AlCl₃ and FeCl₂ in the cold see Nos. 19 and 20.

sure that no tungsten sticks to the bottom. Continue to add nitric acid drop by drop until the tungsten is oxidized and appears as a bright yellow residue with no black particles visible. Add from a graduated cylinder 7 ml. of perchloric acid (60 per cent) and evaporate to fuming. Boil gently until the solution assumes the characteristic orange-red color of dichromate and then 2 or 3 minutes longer. Cool, add 40 ml. of water, heat to boiling, and add 5 ml. of 0.5 M lead perchlorate solution. Cool to room temperature and filter through a Gooch crucible, washing with a little cold water. To the filtrate add 10 ml. of nitric acid (1 to 1), 3 ml. of phosphoric acid (90 per cent), and 5 ml. of 0.5 M sodium tungstate solution. Heat to boiling, cool, and dilute to 100 ml. Compare with a sample containing 1.5 mg. of vanadium made by adding to the proper number of milliliters of standard vanadium solution, 60 ml. of water, 10 ml. of nitric acid (1 to 1), 3 ml. of phosphoric acid (90 per cent), and 5 ml. of sodium tungstate solution (0.5 M), heating to boiling, cooling, and diluting to 100 ml. Or compare in Nessler tubes with a series of standards made in a similar manner.

CR, V STEELS, 0.1 TO 0.7 PER CENT VANADIUM. Weigh a 0.5-gram sample to the nearest milligram. Transfer to a 250-ml. beaker, add 20 ml. of hydrochloric acid (1 to 1), cover, and heat until the steel is decomposed. Add 0.5 ml. of concentrated nitric acid drop by drop to oxidize the iron, evaporate to about 10 ml., add 5 ml. of concentrated hydrochloric acid, and transfer to a separatory funnel with not more than 5 ml. of water. Cool, add 30 ml. of ether, and extract most of the iron. Warm the aqueous layer on a hot plate to remove the ether, add 7 ml. of perchloric acid (60 per cent), evaporate to fuming, and continue as in the procedure above.

Tables IV and V show typical results which were obtained with these methods. The data in Table IV were obtained by

TABLE IV. ANALYSIS OF FERROUS ALLOYS^a

Type	V %	Cr %	W %	Sample Weight Gram	Transmission Differences, Unknown and Standard			
					420 m μ %	460 m μ %	500 m μ %	520 m μ %
Bureau of Standards No. 50a	0.97	3.52	18.25	0.105	0.1	0.5	-0.2	-0.6
Chromovan	0.79	12	...	0.129	-2.2	0.2	-0.7	-0.5
Bureau of Standards No. 30a	0.21	1.02	...	0.486	-1.2	0.3	-0.1	-0.5
Bureau of Standards No. 30c	0.235	0.977	...	0.434	0.1	0.7	-0.3	-0.3

^a Wave length in millimicrons.

TABLE V. ANALYSIS OF FERROUS ALLOYS

No.	V %	Cr %	W %	V Found %
1 ^a	1.0	3.5	18.2	0.97
2 ^a	1.01	4.5	17.5	0.96
3 ^b	0.21	1.02	..	0.21
4 ^b	0.235	0.977	..	0.21

^a Commercial alloys.^b Bureau of Standards alloys, Nos. 30a and 30c, respectively.

weighing out enough sample to give 1.02 mg. of vanadium, and after application of the above procedures the transmission data were determined in the spectrophotometer both for the unknown solution and for a standard containing 1.02 mg. of vanadium. The transmission differences at four wave lengths between the standard and unknown solutions are shown in Table IV. These differences are for the most part less than 2 per cent, showing that any error in the procedure is less than that inherent in a visual colorimetric method.

In Table V are shown the results which were obtained with the above procedures by comparing in 50-ml. Nessler tubes a sample containing from 1 to 1.5 mg. of vanadium per 100 ml.

with a series of standard solutions. The per cent of vanadium found is the average of observations made by several persons, individual results varying from 5 to 10 per cent from the average.

Summary

1. For determining vanadium by the phosphotungstate method a solution is recommended which is 0.025 *M* in sodium tungstate, 0.5 *M* in phosphoric acid, and 0.6 *N* in nitric, sulfuric, hydrochloric, or perchloric acids. Considerable leeway is possible in the choice of these conditions.

2. Heating the solution to boiling after addition of the reagents is necessary if more than 1 mg. of vanadium is present per 100 ml. or if the solution contains more than traces of ferric chloride.

3. Maximum concentration of diverse ions is specified.

4. The solutions are stable under recommended conditions for at least 2 days and fade only slowly thereafter.

5. Procedures are proposed for the application of the method to the determination of vanadium in alloy steels.

Literature Cited

- (1) Gibbs, O. W., *Am. Chem. J.*, 5, 395 (1883).
- (2) Hillebrand and Lundell, "Applied Inorganic Analysis," p. 354, New York, John Wiley & Sons, 1929.
- (3) Mellon, M. G., and Kasline, C. T., *IND. ENG. CHEM., Anal. Ed.*, 7, 187 (1935).
- (4) Sandell, E. B., *Ibid.*, 8, 336 (1936).
- (5) Snell, F. D., and Snell, C. T., "Colorimetric Methods of Analysis," p. 373, New York, D. Van Nostrand Co., 1936.
- (6) Vinogradov, A. P., *Compt. rend. acad. sci. U. R. S. S.*, 1931A, 249-52.
- (7) Willard, H. H., and Gibson, R. C., *IND. ENG. CHEM., Anal. Ed.*, 3, 88 (1931).
- (8) Willard, H. H., and Young, P., *IND. ENG. CHEM.*, 20, 764-8 (1928).

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Quantitative Electrodeposition of Zinc from Acid Citrate Solutions

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THE quantitative electrodeposition of metals permits of clean, rapid, and accurate analyses; but the methods described for the determination of zinc have not been considered as satisfactory as other gravimetric or volumetric procedures. A comprehensive study of important electrolytic procedures was made by Spear, Wells, and Dyer (5), who found that the alkaline zincate method was to be preferred, but that determinations would be, on the average, 1 per cent high. Investigations by Nickolls and Gaskin (1) have substantiated this observation.

The quantitative electrodeposition of zinc from acid citrate solutions was suggested by Parodi and Mascazzini (2) and recommended by Smith (4). Sand and Smalley (3) also recorded a method using citric acid, but their results do not show the accuracy requisite to an approved quantitative method. Wolman (8) observed that the presence of citric acid interfered with deposition. The available information on such important factors as current density, pH, and interfering ions is relatively incomplete and the purpose of this investigation is to establish the optimum conditions with respect to

citrate concentration, pH, deposition time, current density, and temperature, as well as to determine the effect of the presence of a number of foreign anions and cations.

Experimental

All reagents were of Mallinckrodt Chemical Works' analytical reagent quality. The metallic zinc was reported to have a maximum limit of 0.017 per cent impurity as iron, oxidized by potassium permanganate, and of 0.06 per cent impurity insoluble in sulfuric acid. A 5-gram sample so tested left no weighable residue. The zinc was melted in a porcelain crucible and drawn up into Pyrex tubing of 2-mm. inside diameter. The glass was removed and the zinc rod cut into lengths weighing approximately 0.2 gram each, which were weighed at once to eliminate any error due to subsequent corrosion. A 2.0580-gram sample was dissolved in sulfuric acid and the solution diluted to 500 ml. Three 25-ml. portions, each containing 0.1029 gram of zinc, were analyzed by precipitating the zinc as sulfide in formic acid solution and converting the sulfide to sulfate by the method of Sullivan and Taylor (6). In each determination results 0.0001 gram high were obtained. As this was well within the range of experimental error, it was assumed that the zinc was satisfactory. A further check was obtained by determining the zinc as zinc ammonium phosphate.

Preliminary experiments indicated that the pH was the most important factor involved in the determination and a systematic series of experiments was carried out for the purpose of establishing the permissible limits of pH and citrate concentration. In this series the pH varied from 2.9 to 7.4 with an accuracy of 0.02 unit in solutions whose citrate concentrations had the following values, expressed in moles per liter: 0.0250, 0.0312, 0.0375, 0.0437, 0.0500, 0.0625, and 0.0750.

The samples were prepared by dissolving weighed metallic zinc in 10 ml. of 3 M sulfuric acid and adding the required amount of citric acid. The solutions were diluted to approximately 175 ml. and the pH, as measured by a glass electrode, was adjusted by adding 40 per cent sodium hydroxide. The zinc was deposited on copper or copper-plated gauze cathodes having an approximate area of 1 sq. dm. The solutions were stirred by a rotating platinum anode. A current density of 1 ampere per sq. dm. was employed for a time interval of 2 hours. The plates were washed by the siphon method, dipped in acetone, and dried for 5 minutes at 85° C.

TABLE I. EFFECT OF pH AND CITRATE CONCENTRATION^a

pH	Error		
	0.0312 M citrate Gram	0.0375 M citrate Gram	0.0437 M citrate Gram
3.8	±0.0000	+0.0001 +0.0002	-0.0009
4.1	+0.0002	+0.0001 -0.0001	+0.0001
4.4	-0.0002	+0.0001
4.6	+0.0002 -0.0002
4.7	-0.0001	+0.0002
4.9	-0.0001 -0.0001
5.0	+0.0001	+0.0001
5.2	-0.0002
5.3	+0.0003	-0.0001	+0.0004
5.4	+0.0002
5.5	+0.0002

^a In each experiment approximately 0.2 gram of zinc, accurately weighed, was used.

It is indicated in Table I that pH values of 4.0 to 5.0 and that citrate concentrations of 0.0312 to 0.0437 M may be employed to give good results. The data do not represent average or selected values; every determination is recorded. In a total of fourteen determinations made the maximum error was 0.0002 gram, representing in the 0.2-gram sample a maximum error of 0.1 per cent and an average error of 0.0021 per cent. There was no tendency toward either positive or negative errors. The investigation was extended to either side of the limits of pH and citrate concentrations shown, but in the extended range of each of these variables the results were unreliable, although they were frequently accurate.

The importance of having the pH closely regulated is shown by Figure 1. When the pH was less than 3.2, the deposits were usually localized and grossly crystalline and were accompanied by large negative errors. When the pH was greater than 6.5, the deposits were dark and accompanied by large positive errors. Between these values the plates were smooth and bright and exhibited no tendency toward oxidation when exposed to air for several hours.

A study of the time interval necessary for complete deposition has shown that with samples weighing 0.2 gram, 80 to 90 minutes are sufficient and the deposition may be lengthened to 2 hours. Complete removal of the zinc may be determined by either of two methods: The addition of 0.5 ml. of saturated hydrogen sulfide water to 1 ml. of the electrolyte should produce only a very faint opalescence. The addition of 0.1 ml. of 0.5 M potassium ferrocyanide to 1 ml. of the electrolyte should cause only a faint opalescence after a time interval of 1 minute. The sulfide test is recommended, although either

may be used. The deposition and precipitation experiments are shown in Table II.

TABLE II. TIME FOR COMPLETE DEPOSITION

Time Min.	Error Gram	Potassium Ferrocyanide	Hydrogen Sulfide
15	-0.0524	Heavy ppt.	Heavy ppt.
30	-0.0150	Heavy ppt.	Heavy ppt.
45	-0.0085	Heavy ppt.	Heavy ppt.
60	-0.0012	Heavy ppt.	Light ppt.
75	+0.0003	Very light ppt.	Marked opalescence
90	+0.0003	Faint opalescence	Faint opalescence
105	+0.0001	No opalescence in 1 minute	No opalescence after 8 hours
120	+0.0002	No opalescence in 6 minutes	No opalescence after 8 hours

Current densities of 0.75, 1.00, and 1.25 amperes per sq. dm. gave quantitative results, but with 1.50 there was heavy needling and the deposits had dark areas. An initial temperature of 25° C. gave accurate determinations. There was an increase of 10° to 15° C. during the electrolysis. Other temperatures were not used. In practice methyl red-methylene blue may be used to fix the pH of the solution at its proper value. The pH should be the same as or slightly lower than the pH at which the indicator is colorless.

That care is required in removing the cathode from the bath is emphasized by a determination of the solubility of the deposited zinc in its electrolyte. The zinc in four solutions, each containing approximately 0.2 gram and at the optimum pH and citrate concentration, was deposited and the cathodes were carefully removed. The errors for the determinations were +0.0001, +0.0003, +0.0001, and +0.0002 gram, respectively. The zinc deposits were again immersed in the electrolyte for the indicated time intervals and Table III shows the loss in weight caused by solution of the deposited zinc. If convenient, the plates should be washed by the siphon method; but the wash-bottle method may be used if the cathodes are carefully and thoroughly washed as the beakers are lowered while the electrical circuit is still closed.

The development of a quantitative method for the determination of zinc must include a study of the interference to be expected when ions other than zinc are present. The ammonium-ion concentration was varied from 0.0001 to 2.0 M without affecting the quantitative character of the deposition.

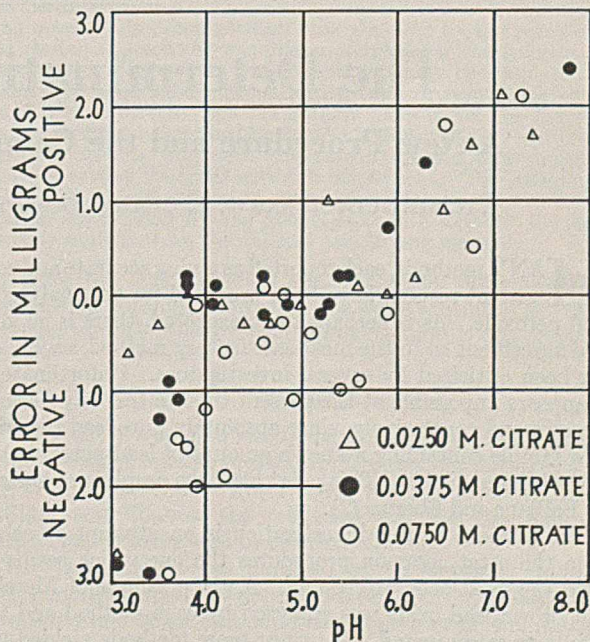


FIGURE 1. THE EFFECT OF pH

TABLE III. SOLUBILITY OF ZINC IN ELECTROLYTE

Zinc Taken Gram	Zinc Found Gram	Zinc Loss Gram	Immersion Time Sec.
0.1994	0.1956	0.0038	30
0.2001	0.1946	0.0055	60
0.2036	0.1937	0.0099	90
0.2037	0.1901	0.0136	120

TABLE IV. EFFECT OF NITRATE IONS

NO ₃ ⁻ Moles/l.	Zinc Taken Gram	Zinc Found Gram	Error Gram	Appearance
0.10	0.2035	0.0088	-0.1947	Localized
0.01	0.2038	0.2021	-0.0017	Good
0.001	0.1993	0.1994	+0.0001	Good
0.0001	0.2010	0.2008	-0.0002	Good

Table IV shows that the nitrate-ion concentration may be as large as 0.001 *M* without interfering with the determination. For the complete deposition of copper from nitrate solutions, the addition of urea has been suggested (7). When urea is added to the zinc electrolyte it not only fails to improve the deposition but actually results in an even larger negative error; therefore urea must not be present in the electrolyte. The determination of zinc in alloys frequently involves the previous determination of nickel as nickel dimethylglyoxime. It has been learned that this reagent must not be present, since a concentration as low as 0.002 *M* causes a large negative error, which could not be prevented by heating with concentrated sulfuric acid to sulfur trioxide fumes. Of the more common metals aluminum, chromium, magnesium, and tin do not interfere with the deposition. Antimony and arsenic prevent complete deposition, while bismuth, cadmium, cobalt, copper, iron, lead, manganese, mercury, nickel, and silver are deposited with the zinc. In each experiment 0.050 gram of foreign metal was added to a 0.2-gram sample of zinc.

Recommended Procedure

Prepare a zinc sulfate solution free from heavy metals except aluminum, chromium, magnesium, and tin. To this solution, contained in a volume of about 175 ml., add 1.5 grams of citric acid and sufficient 40 per cent sodium hydroxide to make the solution neutral or very slightly acid to methyl red-methylene blue. Dilute the solution to 200 ml. and electrolyze for 1.5 to 2.0 hours or until the addition of 0.5 ml. of saturated hydrogen sulfide water to 1 ml. of the electrolyte produces not more than a faint opalescence. Use a copper or copper-plated gauze cathode and a rotating platinum anode. The current density should be 1 ampere per sq. dm. To prevent mechanical loss of the solution, the beaker should be covered with a split watch glass. Wash the deposit carefully as it is being removed from the electrolyte, dip into acetone, dry at 85° C., and weigh.

The method has been successfully used by college sophomores for the determination of zinc in brass.

Summary

Zinc may be determined quantitatively by electrodeposition from an acid sulfate solution containing 0.0375 mole per liter of citric acid if the pH is between 4 and 5. With a current density of 1 ampere per sq. dm. deposition is complete in 1.5 hours. Nitrate ions, dimethylglyoxime, urea, and the following foreign metals interfere with the deposition: antimony, arsenic, bismuth, cadmium, cobalt, copper, iron, lead, manganese, mercury, nickel, and silver. No interference is caused by ammonium ions, aluminum, chromium, or tin.

Literature Cited

- (1) Nickolls, L. C., and Gaskin, J. G. N., *Analyst*, 59, 391 (1934).
- (2) Parodi, G., and Mascazzini, A., *Gazz. chim. ital.*, 7, 169 (1877).
- (3) Sand, H. J. S., and Smalley, William, *Chem. News*, 103, 14 (1911).
- (4) Smith, Edgar F., "Electroanalysis," 4th ed., p. 109, Philadelphia, P. Blakiston's Son & Co., 1907.
- (5) Spear, E. B., Wells, E. E., and Dyer, B., *J. Am. Chem. Soc.*, 32, 530 (1910).
- (6) Sullivan, E. C., and Taylor, W. C., *J. IND. ENG. CHEM.*, 1, 476 (1909).
- (7) Willard, H. H., and Furman, N. H., "Elementary Quantitative Analysis," 2nd ed., p. 382, New York, D. Van Nostrand Co., 1935.
- (8) Wolman, L., *Z. Elektrochem.*, 3, 537 (1897); *J. Chem. Soc.*, 74Aii, 50 (1898).

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The Determination of Lead Peroxide

A New Procedure and the Comparison of Formerly Used Procedures

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MANY methods, each reported as giving accurate and consistent results, have been proposed for the analysis of lead peroxide. As is perhaps to be expected, there is no general agreement as to the most satisfactory method, each having been criticized by several investigators. Unfortunately, it appears impossible at the present time to test any method directly and conclusively, since absolutely pure lead peroxide or a sample containing a known amount of lead peroxide has never been available. This point has been amply emphasized by LeBlanc and Eberius (7).

The purpose of this investigation is an attempt to select from the most common procedures the one which seems to yield the most accurate results. A given sample of Merck's c. p. brown lead oxide was analyzed by each method and the results were compared. If two or more methods yielded the same values and if the procedures seemingly satisfied the re-

quirements of a satisfactory quantitative analysis, it was assumed that the validity of these methods had been established.

Examination of Existing Methods

All the proposed determinations of lead peroxide are dependent upon the oxidizing power of tetravalent lead. The sample is placed in solution by reduction to a soluble divalent lead compound, the corresponding oxidation being suitably measured, usually by volumetric methods. The most common procedures are the Bunsen, the Diehl-Topf, the Schaeffer, and the Lux.

BUNSEN METHOD. The Bunsen (19) method depends upon the liberation of chlorine when lead peroxide is dissolved in an excess of hot hydrochloric acid, the chlorine being absorbed in excess potassium iodide and the liberated iodine titrated with

standard sodium thiosulfate. Pamfilov and Ivanceva (14) feel that the method is basically unreliable because of a side reaction between chlorine and water vapor. The LeBlanc and Eberius modification (7) is designed primarily to increase the ease of manipulation and does not circumvent this side reaction.

Using the LeBlanc-Eberius modified Bunsen procedure on the sample of Merck's c. p. lead peroxide, the authors have found lead peroxide contents of 92.2, 91.7, 91.3, 92.0, and 92.2 per cent (average, 91.9 per cent). These analyses were made strictly according to the specific directions given by LeBlanc and Eberius. As will be shown, there is reason to believe that these results are low. The addition of a multiple-bulb potassium iodide absorption tube in series with the five-bulb tube recommended by LeBlanc and Eberius resulted in a more nearly quantitative absorption of chlorine with a subsequent increase of the average 91.9 per cent of lead peroxide to an average value of 96.3 per cent. The method is cumbersome and slow and not to be recommended except for the analysis of lead peroxide samples extremely resistant to solution.

TABLE I. DETERMINATION OF LEAD PEROXIDE

Sample	Weight Gram	0.03036 <i>N</i> Oxalate Solution ML.	0.0827 <i>N</i> Ceric Sulfate ML.	Purity %
Blank		10.00	36.71	
PbO ₂	0.3631	10.00	1.28	96.5
PbO ₂	0.2951	10.00	7.90	96.6
PbO ₂	0.3198	10.00	5.54	96.4
Blank ^a		10.00	36.70	
PbO ₂	0.3276	10.00	4.71	96.6
PbO ₂	0.3271	10.00	5.39	96.3
PbO ₂	0.2718	10.00	10.17	96.6
Blank		10.00	36.71	
Pb ₂ O ₄	0.7843	10.00	11.60	90.8
Pb ₂ O ₄	0.5929	10.00	17.75	90.7
Blank		10.00	36.71	

^a This blank is one of several which were run with approximately 0.3 gram of PbO carried through the PbO₂ procedure to show that the presence of lead produces no measurable catalytic decomposition of the oxalate.

DIEHL METHOD. The Diehl method as modified by Topf (18) depends upon a measurement with thiosulfate of the iodine liberated when lead peroxide dissolves in an excess of potassium iodide acidified with acetic acid buffered with sodium acetate. The method has been adopted by the Bureau of Standards (1) and very specific directions have been fixed for the analysis. A comprehensive discussion of the method is given by Milbauer and Pivnicka (11). The difficulties with the method are said to involve an incomplete solution of the sample and the possibilities of side reactions associated with the iodine (7).

The authors have found that this method yields rather consistent results: 97.1, 96.9, 96.8, 96.9, 96.8, and 97.0 per cent (average value, 96.9 per cent) of lead peroxide on the same Merck's sample referred to above under the Bunsen method. The time required for complete solution of the sample approximated 30 minutes. The authors could observe (by blank determinations) no atmospheric oxidation of the potassium iodide, no volatilization of iodine, and no precipitate of lead iodide. In view of these facts they feel that the method yields accurate results, although these are about five per cent higher than those observed with the LeBlanc-Eberius modification of the Bunsen method and about 0.6 per cent higher than those obtained with a more nearly complete absorption of the chlorine.

SCHAEFFER METHOD. The Schaeffer method (16) involves the use of excess hydrogen peroxide acidified with nitric acid for the solution of the sample. The excess is back-titrated with permanganate. Furman and Wallace (9), using a potentiometric ceric sulfate end point in place of the permanganate, report satisfactory analyses of red lead by this method and, moreover, agreement with the Bunsen values. Kraeff (5) finds this method inferior to the Diehl-Topf; Kreshkov and Iljuchin (6) have attempted to measure the volume of oxygen liberated and have been criticized by LeBlanc and Eberius (8) because they neglected to consider the catalytic decomposition of hydrogen peroxide in contact with lead dioxide; Mellon, Reed, and Wilkins (10), Pamfilov and Ivanceva (12), and Busvold (2) recommend it.

The authors have attempted to use the method, following explicitly the directions given by Furman and Wallace (9). Evidently the procedure, although applicable to red lead or freshly precipitated lead peroxide, is of no great value in the analysis of the Merck sample referred to above. The solution time approximated 3 hours and no question can exist but that some sort of a side reaction vitiated the results observed. On the Merck sample the authors obtained lead peroxide contents of 87, 84, and 91 per cent.

LUX METHOD. The Lux method (9) depends upon the solution of the lead peroxide in an excess of oxalic acid acidified with nitric acid, a back-titration with standard permanganate determining the amount of oxalic acid consumed during solution. This method, including its modifications by Sacher (15) and Ipiens (4), has been severely criticized by Pamfilov and Ivanceva (13) and LeBlanc and Eberius (7).

The authors have found that the chief and, in their opinion, the only error of this method lies in a decomposition of the oxalate by the nitric acid. As an illustration, 10.00 ml. of sodium oxalate which were known to require 36.71 ml. of 0.0827 *N* ceric sulfate for oxidation required only 36.60 ml. of the ceric sulfate when the oxalate was diluted with 200 ml. of water, acidified with nitric acid, and titrated at 80° C. If, as is recommended in the Lux method, the oxalate and nitric acid mixture is heated on a steam cone (94° to 96° C.) for 15 minutes (in order to dissolve the lead peroxide), 10.00 ml. of the oxalate required but 36.22 ml. of ceric sulfate. Obviously, the Lux method as originally described must be modified if it is to yield accurate data.

Modification of the Lux Method

The largest source of error in the Lux method may be eliminated by use of the following procedure:

To approximately 0.33 gram of lead peroxide (0.7 gram of red lead) 10.00 ml. of standard (0.3 *N*) oxalate are added, acidified with 25 ml. of 70 to 73 per cent perchloric acid, covered with a watch glass, heated on a steam cone at 94° to 96° C. until solution is complete (the most resistant lead peroxide samples required about 40 minutes), diluted with 200 ml. of distilled water, heated to 80° C., and titrated with standard (0.08 to 0.1 *N*) ceric sulfate.

The ceric sulfate was standardized against Bureau of Standards sodium oxalate using the procedure recommended by Willard and Young (20) and identical normality factors were obtained using the above lead peroxide procedure without, of course, the lead peroxide sample. This correspondence indicates that there is no measurable decomposition of oxalic acid by the perchloric acid during the heating conditions adopted for the solution of the sample. The sodium oxalate solution may be standardized against the ceric sulfate potentiometrically or from a corrected visual end point (20), but the authors have found the electron beam spectrometer described by Smith and Sullivan (17) extremely sensitive, reliable, and most convenient. A platinum-tungsten electrode system was used with this instrument. The volumetric ratio of the ceric sulfate to the oxalate was 3.671 ± 0.002, whether determined by the above procedure without the lead peroxide sample or by the Willard and Young method.

During the lead peroxide analyses blank determinations were carried through identically the same routine. The data obtained on the Merck's lead peroxide sample are given in Table I.

Summary

By the use of a common sample attempts have been made to select the most reliable method for the analysis of active oxygen in lead peroxide. The Bunsen method as modified by LeBlanc and Eberius, the Schaeffer, and the Lux methods were all tested and found to be unsatisfactory.

The Lux method was modified by replacement of nitric with perchloric acid and permanganate with ceric sulfate and by observation of the end point electrometrically with the use of an electron beam spectrometer. The method gives very consistent results entirely free from side reactions:

Acknowledgment

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Literature Cited

- (1) Bur. Standards, *Circ.* 90 (May 23, 1922).
- (2) Busvold, *Chem.-Ztg.*, 56, 106 (1932).
- (3) Furman and Wallace, *J. Am. Chem. Soc.*, 51, 1449 (1929).
- (4) Ipiens, *Z. anal. Chem.*, 53, 261 (1914).
- (5) Kraeff, *Verf. kroniek*, 6, 294 (1933).
- (6) Kreshkov and Iljuchin, *Z. anal. Chem.*, 93, 180 (1933).
- (7) LeBlanc and Eberius, *Ibid.*, 89, 81 (1932).

- (8) *Ibid.*, 93, 447 (1933).
- (9) Lux, *Ibid.*, 19, 153 (1880).
- (10) Mellon, Reed, and Wilkins, *Proc. Indiana Acad. Sci.*, 37, 255 (1937).
- (11) Milbauer and Pivnicka, *Z. anal. Chem.*, 53, 345 (1914).
- (12) Pamfilov and Ivanceva, *J. Gen. Chem., U. S. S. R.*, 3, 262 (1933).
- (13) Pamfilov and Ivanceva, *Z. anal. Chem.*, 79, 186 (1929).
- (14) *Ibid.*, 88, 23 (1932).
- (15) Sacher, *Chem.-Ztg.*, 35, 731 (1911).
- (16) Schaeffer, *J. IND. ENG. CHEM.*, 8, 237 (1916).
- (17) Smith and Sullivan, *J. Soc. Chem. Ind.*, 56, 104T (1937).
- (18) Topf, *Z. anal. Chem.*, 26, 296 (1887).
- (19) Treadwell and Hall, "Analytical Chemistry," 7th ed., Vol. 2, p. 563, London, John Wiley & Sons, 1930.
- (20) Willard and Young, *J. Am. Chem. Soc.*, 50, 1322 (1928).

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Photoelectric Grading of White Sugars and Their Solutions by Reflectance and Transmittancy Measurements

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THE examination of granulated sugars for the purpose of quality control includes a classification of the finished sugars for general appearance and an evaluation of the color and turbidity of the sugar solutions.

Granulated sugars are graded on appearance by visual comparison with arbitrarily selected sugars, usually under artificial daylight illumination. Both whiteness and grain size are taken into consideration by the observer, and a sugar may be graded low because of slight yellowness, grayness, or large or uneven grain size. Not only does grain size affect the coarseness of the surface structure of a sugar sample, but it also affects all attributes of the color because of varying penetration of light into the assembly of crystals. Disagreement among observers in grading sugar is due largely to the individual judgment involved in balancing yellowness against coarseness. While this method of grading is simple and rapid, it has the disadvantages of subjectivity and lack of a permanent numerical evaluation of appearance.

The need for a rapid objective method for evaluating the general appearance of granulated sugars was pointed out by Buse (7). After some experimentation, he concluded that reflectance measurements on sugars were not suited for this purpose. Visual measurements, using a Zeiss Pulfrich photometer and a white-lined sphere to provide diffuse illumination, were found unsatisfactory because sufficiently small distinctions in reflectance values could not be made. Substitution of a photoelectric cell, using the same type of illumination, gave higher precision but the method as used was judged to be impractical for grading purposes.

An attempt by the authors to evaluate the appearance of granulated sugars by reflectance measurements, using a single photoelectric cell and directional illumination, has already been reported (18). Further work, using an improved photoelectric apparatus, has shown that good correlation exists between the appearance of a sample of granulated sugar and its reflectance relative to magnesium oxide. Photoelectric reflectance measurements are there-

fore proposed as an objective method for evaluating the appearance of granulated sugars for industrial purposes.

A specially designed optical system in the photoelectric apparatus to be described permits measurement of the transmittancy of sugar solutions as well as measurement of reflectance of the sugar in granulated form. With this arrangement it is possible to obtain in a single instrument (1) an index for the appearance of a crystalline sugar in terms of reflectance, (2) an index for apparent color of the unfiltered sugar solution in terms of its transmittancy for green and red light, and (3) an index of turbidity of the solution in terms of its transmittancy for red light.

The solutions of all commercial granulated sugars contain coloring matter and suspended particles, the latter ranging in size from colloidal to coarse. The presence of coloring matter and turbidity in these solutions adversely affects the quality. The spectral composition of light passing through such a solution is influenced not only by selective absorption but also by selective scattering, and for this reason difficulties are encountered when one attempts to determine coloring matter and turbidity separately. This difficulty with sugar products in general has been discussed by several writers (2, 20, 22, 27). The first step advocated by a number of investigators in the determination of coloring matter in sugar solutions is removal of the turbidity as completely as possible by careful filtration, with specially prepared asbestos (22), specially purified kieselguhr (2), or silica gel (28). However, some investigators believe that such filtration may not remove the turbidity completely enough and in fact may remove some of the coloring matter. The coloring matter in these filtered sugar solutions, as well as in the more highly colored intermediate sugar liquors, is usually determined by means of a color comparator such as the Stammer, Duboscq, Campbell-Hurley (1), or similar instrument (14), or by measuring the specific absorptive index— $\log t$, usually for light of wave length 560 millimicrons, with a spectrophotometer (4, 8, 22, 24, 27, 28) or an abridged spectrophotometer (3, 4, 15, 19, 20, 23, 25).

Methods for determining turbidity in sugar solutions have been discussed by Zerban, Sattler, and Lorge (27, 28). The method used for a number of years in the Bureau of Chemistry and Soils, U. S. Department of Agriculture, has been that of Balch (2), in which the difference between the specific absorptive index of the solution with and without filtration is used to express turbidity.

Most of the color and turbidity determinations in sugar solutions have been made on instruments employing visual measurements. In recent years the use of photoelectric cells has made possible greater speed, precision, and objectivity of measurements. The limitations and advantages of photoelectric instruments for such purposes have been discussed by Gibson (10). Photoelectric instruments have been used for determining coloring matter in sugar solutions by Sandera (23), Holven and Gillett (15), Jackuschoff (16), Herke and Rempel (13), and Bruckner and Becker (6), and for turbidity indication by Gillett and Holven (11).

It is believed that the photoelectric apparatus and method proposed by the authors for determining the apparent color and turbidity in sugar solutions without recourse to filtration fulfills a need for a simple, rapid evaluation of quality for purposes of industrial control. The determination of apparent color in the unfiltered solutions is based on the fact that with increasing amounts of yellowish coloring matter the ratio of green to red transmittancy, T_g/T_r , should decrease. If the suspended matter in the solution were to scatter light nonselectively, this ratio would be independent of turbidity. The use of this ratio in this connection was suggested by its previous use as an index of chromaticity of rosin samples containing suspended dirt particles (5, 12). However, in the case of sugar solutions, for which a varying proportion of the scattered light is selective, this ratio is not entirely independent of the suspended matter. For sugar solutions, then, the ratio T_g/T_r may be considered to indicate only the apparent color and not the true color of the solution. The results so far obtained, together with the simplification gained by elimination of filtering of solutions, appear to justify its use in evaluating the color quality factor for practical purposes. The form adopted for the apparent color index is $I_c = 100(1 - T_g/T_r)$, since in this form $I_c = 0$ for a hypothetical sugar solution free from coloring matter and turbidity, and increases with increasing amount of coloring matter. The apparent color could, of course, be expressed simply by the difference between the specific absorptive indexes for green and red light, but since the instrument scale indicates transmittancy and since only a practical quality index for solutions of constant depth and concentration is desired, it is believed that no advantage would be gained by using the more usual logarithmic form of expression.

The turbidity index proposed is $I_t = 100(1 - T_r)$, which is simply the per cent absorbency (22) of the unfiltered sugar solution for red light. This index is practically independent of the coloring matter in solutions of white sugars because there is virtually no light absorption in the red part of the spectrum by the small amount of coloring matter present. In this form, the turbidity index would be zero for a sugar solution free from suspended matter and having only a relatively small quantity of coloring matter present, and would increase with increasing turbidity. Reduced to the form of specific absorptive index (22) $(-\log T_r)/bc$, where b is the depth of the solution in centimeters and c is

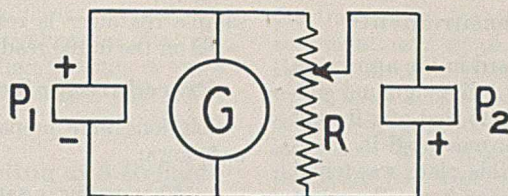


FIGURE 1. COMPENSATING PHOTOELECTRIC CIRCUIT

P_1 , measuring photocell; P_2 , compensating photocell; G , galvanometer; R , potentiometer-rheostat

its concentration in grams per cubic centimeter of solution, the result should approximately agree numerically with Balch's turbidity figure (2).

Apparatus

A diagram of the compensating photoelectric circuit used in the apparatus is shown in Figure 1.

P_1 and P_2 are photronic cells in a parallel connection with a 22-ohm mirror galvanometer, G , of sensitivity $0.36\mu\text{A}$. per mm. and a 35-ohm precision-wound 12.5-cm. (5-inch) diameter Leeds & Northrup potentiometer-rheostat, R . The latter carries a uniform scale calibrated from 0 to 100. This photoelectric circuit and the conditions under which the scale indicates light transmission or reflectance by a prepared sample have been described in detail elsewhere by one of the authors (5). These conditions include choice of (1) suitable photocells, (2) a low resistance value for the potentiometer-rheostat, and (3) moderate illumination of the photocells.

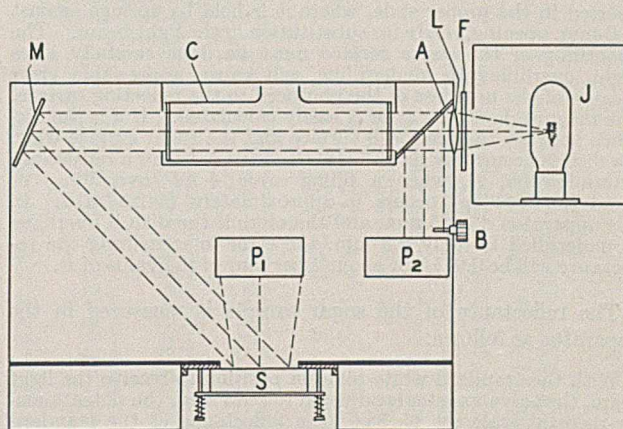


FIGURE 2. OPTICAL ARRANGEMENT OF PHOTOELECTRIC PHOTOMETER

The optical arrangement illustrated schematically in Figure 2 was designed for measuring both transmission and reflectance by a substitution method and is similar to that described by one of the writers (5).

A beam of light from a 50-watt projection lamp, J , passes through a color filter, F , is made parallel by a lens, L , and is divided by a clear glass plate, A , roughly 10 per cent of the light being reflected onto the "compensating" photocell, P_2 , while the main beam transmitted by the plate, A , passes through a compartment containing an absorption cell, C . After reflection by a mirror, M , the collimated beam strikes the standard white reflecting surface, S , at an angle of 45° , and a cone of diffusely reflected light is received by the "measuring" photocell, P_1 , placed directly above and with its sensitive surface parallel to the standard reflecting surface. A sliding shutter operated by a screw, B , provides a means of making small adjustments in the light intensity received by photocell P_2 . The filter, F , cell, C , and standard white plate, S , are mounted on slides and can be withdrawn from the light beam or replaced as required. For reflectance measurements cell C is removed and either the standard white plate or a sugar sample is brought into the beam at S by moving the appropriate slide. For transmission measurements, the standard white plate is kept fixed in the beam at S , and the cell C is moved in and out of the beam as required. The lamp may be run from 110-volt alternating current lighting mains. Line voltage fluctuations produced no perceptible galvanometer fluctuations with the particular pair of photocells used. This stability (5) would not necessarily exist if another pair of photocells were substituted; voltage regulation may be required for pairs of photocells in some cases.

Procedure for Reflectance Measurements

The working standard of reflectance used in the apparatus was an opaque white glass plate with a finely ground surface having a reflectance of 0.856 relative to that of a freshly prepared magnesium oxide (21) surface, measured in place in the instrument. The reflectance of this plate was found to remain constant over a period of about 3 months when frequently washed with soap and water. When set aside and not used for 3 months, its reflectance after washing was found to have decreased by 1.2 per cent, but after slight regrinding of the surface its original reflectance was restored. If properly cared for, it is believed that such a glass plate makes a satisfactory working standard, though its reflectance should be checked occasionally.

Care in the preparation of the sugar sample for a reflectance measurement is important.

The granulated sugar is poured into a metal dish 63 mm. in diameter and 16 mm. deep, and the top surface of the sugar layer is smoothed off with a Petri dish having a flat ground bottom, using only moderate pressure and a slightly circular motion until the sugar surface is accurately flush with the edge of the metal dish. After being thus filled, the dish of sugar is inserted in the proper slide, where it is held by springs against a 56-mm. opening, ready for substitution in the light beam. The smoothing of the sugar surface must be done carefully since slight overfilling or underfilling will cause appreciable error because of the nearness of the photocell to the reflecting surface. The magnitude of this error is easily calculated. If d is the distance between the photocell surface and the sugar surface when the dish is accurately flush-filled, the error made in a reflectance determination, R , when a filling error $+\Delta d$ (overfilling) or $-\Delta d$ (underfilling) occurs is approximately $(\pm 2\Delta d/d)R$. In this apparatus d is 55 mm. and therefore if the dish is overfilled or underfilled by only 0.3 mm. the error in measuring the reflectance will be $0.011R$ or about 1 per cent of the value of R .

The reflectance of the sugar sample is measured in the apparatus as follows:

With the standard white plate in position to receive the light beam, the galvanometer is adjusted to read zero, the potentiometer-rheostat scale set to 85.6 (the reflectance of the standard white plate), the lamp turned on, and the shutter, B , moved until the galvanometer again reads zero. The slide carrying the sample is then moved so that the sugar sample replaces the standard white plate. The galvanometer deflects and the balance of the circuit is restored by adjusting the potentiometer-rheostat. The scale reading then indicates the reflectance of the sample relative to magnesium oxide.

The reproducibility of measurements on this apparatus is very satisfactory, the average deviation for a number of readings on a given prepared sample being less than ± 0.1 on the 0 to 100 scale. All reflectance values reported here are the average of 6 determinations, 3 readings on the first preparation of the sample and 3 more on refilling the dish with the same sugar sample. The results are expressed to four significant figures for the purpose of this paper, but in practice for grading sugar one reading on one filling, or preferably one reading on each of two different fillings, is sufficient, in which case only 3 significant figures should be reported. The accuracy of the reflectance measurements is of course not as high as the precision (reproducibility) of the measurements, and depends on many factors, such as the degree of elimination of specularly reflected light from the photocell, the care with which the white plate is standardized against magnesium oxide, the constancy of the reflectance of the white plate, and the care used in filling the sample dish.

If proper precautions are taken it is believed that the reflectance errors should not be greater than 1 per cent. For the purpose of the present investigation, however, obtaining reproducible results is more important than obtaining true reflectance values and, even when refilling of the

sample container is resorted to, results are reproducible to ± 0.2 on the 0-100 reading scale.

Procedure for Transmittancy Measurements

Solutions were prepared for transmittancy measurements as follows:

A 150-gram sugar sample is dissolved in distilled water at room temperature and made up to 250 ml. of solution. This high concentration was selected because it is far enough below saturation to permit dissolving without use of heat and at the same time sufficiently concentrated to stabilize the suspension of particles. The minute bubbles of occluded air present in a freshly prepared solution may be removed by applying vacuum or allowing the solution to stand several hours. The solution is then transferred to a 150-mm. absorption cell having plane and parallel ends, and allowed to stand a minute to permit any newly formed air bubbles to rise to the top of the cell before placing it in the instrument. Another absorption cell, similar to but only half as long as the solution cell, is filled with distilled water from the same source as that used in making up the solutions, and serves as the reference cell for the transmittancy measurements.

A 150-mm. solution cell was chosen because of the small amount of coloring matter present in white sugar. A solvent cell approximately half this length was used for the following reasons: (1) the concentrated sugar solutions used contain only 51.2 per cent of water; (2) water of this depth appreciably absorbs red light beyond about 690μ , with a maximum absorption at 760μ (θ); (3) the filter used when measuring the transmittancy of the solution for red light freely transmits light absorbed by the water, and the photonic cell shows appreciable response to radiation in this part of the spectrum. Thus the use of a reference cell about 75 mm. long containing distilled water compensates for selective absorption of red light by the water in the solution as well as for reflection losses at the glass surfaces of the cell, and very nearly true solution transmittancy is obtained.

TABLE I. RANKING OF TEN GRANULATED SUGAR SAMPLES

Sample No.	By Visual Grading, 7 Observers (A-G)							By Reflectance Measurements R %	
	A	B	C	D	E	F	G		Av.
I	1	1	1	1	1	2	1	1	93.33
II	2	3	3	2	2	4	2	2	92.33
III	3	2	2	5	3	3	3	3	91.53
IV	9	7	7	4	8	7	4	7	91.18
V	6	4	4	7	5	8	5	5	91.15
VI	5	6	6	6	6	5	9	6	89.73
VII	4	5	5	3	4	1	6	4	89.68
VIII	10	9	10	10	10	10	7	10	88.50
IX	8	10	9	9	7	9	8	9	87.98
X	7	8	8	8	9	6	10	8	87.37
Correlation coefficient	0.70	0.87	0.85	0.81	0.79	0.51	0.88	0.84	...

In making transmittancy measurements, balancing of the photoelectric circuit is similar to that described for the reflectance measurements, except that one starts with the scale set to read 100 with both the standard white plate and the 75-mm. cell of water in position in the light beam. After the circuit is balanced, the water cell is replaced by the 150-mm. solution cell and when the circuit is rebalanced, the scale indicates the transmittancy of the solution.

The transmittancy of each unfiltered sugar solution was measured first with a blue-green filter (Corning light shade blue-green No. 428, 3.4 mm. thick) and then with a red filter (Corning traffic red No. 245). The spectral transmissions of these filters were measured and the approximate spectral centroids effective for the conditions used were calculated assuming (1) a color temperature of 2850°K . for the lamp, and (2) a spectral response curve for the photonic cell the same as given by the Weston Electrical Instrument Corporation (26). The calculated values were 535μ for the blue-green filter, 655μ for the red filter, and 590μ for the

lamp-photocell combination without a filter (as used for the reflectance measurements). These values are of course only approximate, but their inclusion here permits a more fundamental interpretation of the reflectances and transmittancies reported.

Correlation between Visual Grading and Reflectance Measurements on Granulated Sugars

Ten samples of granulated sugar were selected at random, placed in numbered sample boxes, and given to seven observers, who were requested to arrange the samples in descending order of good appearance, each according to his individual judgment. The reflectances of these samples were then measured on the photoelectric apparatus. In Table I the ten samples are arranged in order of decreasing reflectance, and the ranking of the samples by each observer is shown, together with the average of these rankings. Inspection of Table I readily suggests a correlation between the reflectance measurements and the appearance as judged visually. Correlation coefficients connecting reflectance and visual ranking were calculated (17) for each observer and for the average ranking by the seven observers, and are included in the table. The coefficient 0.84 for the average ranking indicates that a good correlation exists between the measured reflectances and the visual appearance of the sugar samples. With one exception the correlation coefficients for the individual observers are good or fair.

Effect of Grain Size and Coloring Matter on Reflectance of Sugars

The separate effect of grain size and coloring matter on the reflectance of sugars was studied by screening 24 samples of sugar through a set of sieves having Bureau of Standards sieve numbers 20, 30, 40, 50, and 70 with sieve openings 0.84, 0.59, 0.42, 0.30, and 0.21 mm., respectively. The average grain sizes of the various portions of the screened sugars were assumed to be 0.71 mm. for the sugar passing through No. 20 and retained on No. 30; 0.50 mm. for sugar passing through No. 30 and retained on No. 40; 0.36 mm. for that passing through No. 40 and retained on No. 50; 0.25 mm. for that passing through No. 50 and retained on No. 70; and 0.15 mm. for that passing through No. 70. The reflectances were measured for the various screened portions and are recorded in Table II. Transmittancy measurements were made in the photoelectric apparatus on solutions of the original unscreened sugars. The transmittancies for green and red light and the values for the apparent color index $I_c = 100(1 - T_g/T_r)$ are also given in Table II. The apparent color was assumed to be the same for all the screened portions of a given sugar.

Comparison of readings for individual samples of Table II shows that, in general, reflectance diminishes as grain size increases. It is also apparent from the data in Table II, especially that included in the last three columns, that the reflectance of a sugar decreases as the apparent color index of the sugar in solution increases. The data indicate definitely that the presence of coloring matter affects the reflectance, and hence the appearance, of a coarse-grained sugar more than that of a fine-grained sugar. For example, comparing samples 21 (color index 8.8) and 59 (color index 23.8), the larger amount of "color" in the latter sample is responsible for a per cent reflectance lower by 5.12 for the 0.71-mm. grain size but only 2.88 lower for the 0.36-mm. grain size.

A few irregularities or inconsistencies appear in Table II. For instance, in some cases the reflectance of the fraction of smallest grain size (column headed 0.15 mm.) is not as high as might be expected from examination of the data on

the fractions of larger grain size. This is probably due to accumulation of small particles of foreign matter in the fraction of smallest grain size during the screening process, which tends to lower the reflectance. Another type of inconsistency appears for sample 56, for which a high color index and high reflectance both occur. The solution of this sugar had a pronounced milky appearance not shown by the other solutions, and it was concluded that this solution contained an unusually large proportion of very small scattering particles and hence exceptional selectivity of scattering. In this particular case the apparent color index is probably not even an approximate indication of the true coloring matter in solution, since the high reflectances obtained would place it near the top of the table with sugars having an apparent color of about 6. However, a solution of this nature is only rarely encountered, and the consistency of the data for the rest of the samples of Table II indicates that the apparent color index used may be a suitable practical indication of color in unfiltered sugar solutions.

TABLE II. TRANSMITTANCY, APPARENT COLOR, AND REFLECTANCE OF VARIOUS GRANULATED SUGARS

Sample No.	Unfiltered Solutions of Sugars before Screening			Screened Fractions of Granulated Sugars ^b				
	Green light T_g	Red light T_r	Apparent color index ^a I_c	0.15 %	0.25 %	0.36 %	0.50 %	0.71 %
24	82.7	86.2	4.0	91.90	91.39	90.40	89.88	...
2	82.5	86.5	4.6	90.95	89.25	...
29	77.8	81.7	4.7	92.38	91.85	90.90	88.80	...
33	81.8	86.0	4.8	92.92	92.13	91.07	89.42	...
26	77.9	82.8	5.9	92.78	91.77	90.42	88.80	...
28	71.6	76.6	6.5	91.76	91.33	90.18	88.62	...
37	72.7	78.2	7.0	92.65	91.30	89.82	88.35	...
25	72.9	78.7	7.3	91.60	91.40	90.42	89.02	...
27	77.3	83.9	7.9	92.18	90.72	90.03	88.42	...
31	76.7	83.4	8.1	92.02	91.07	90.07	88.16	...
21	73.0	80.0	8.8	90.50	89.36	87.04
34	66.7	73.5	9.2	91.52	91.13	90.42	88.90	...
22	63.2	70.6	10.5	...	90.35	89.45	87.87	...
38	68.3	76.7	10.9	90.60	90.12	89.37	87.65	...
8	62.5	70.3	11.1	89.41	87.50	85.50
5	51.8	58.3	11.1	89.37	88.22	85.02
36	64.0	72.2	11.3	91.43	90.25	88.82	87.02	...
23	68.7	77.9	11.8	...	90.28	89.43	87.88	...
32	68.3	77.5	11.9	91.17	90.62	89.18	87.53	...
35	62.9	71.6	12.2	91.53	89.72	88.15	86.32	...
60	46.3	57.8	20.0	90.28	89.80	88.85	86.44	...
30	51.8	65.6	21.0	90.59	89.67	88.86	85.70	...
59	37.1	48.7	23.8	87.62	85.47	81.92
56	25.8	40.0	35.5	92.58	91.92	91.38	89.78	...

^a $I_c = 100(1 - T_g/T_r)$.

^b Reflectance of the fractions of graduated grain size, average diameter in mm.

Using the data of Table II (supplemented by data shown later in Table III) an attempt was made to formulate a relationship between the reflectance, R , of a sugar, its grain size, g , and the apparent color, I_c , of its solution. If sufficient data were available, a plot of reflectance against grain size would be expected to yield a family of curves, one curve for each value of apparent color. Sufficient data for accurate evaluation of these curves were not available, but an approximate expression was obtained by grouping all sugar samples of Tables II and III into three groups: (1) samples having $I_c < 6.0$ (average value 4.6), (2) samples having I_c between 6.0 and 11.5 (average 9.3), and (3) samples having $I_c > 11.5$ (average 13.2). Reflectance was then plotted against grain size (excluding as unreliable the data in Table II for the 0.15-mm. grain size) for the three color groups. Though the points in each group scattered considerably, three parallel straight lines, one for each group, appeared best to represent the trend. The approximate equation for the family of curves was found to be

$$R = -14.3g + R_0 \tag{1}$$

where R is the per cent reflectance of the sugar, g its grain size in millimeters, and R_0 the reflectance for zero grain size, which is different for different amounts of color. R_0 was

TABLE III. PHOTOELECTRIC ANALYSIS TO DETERMINE QUALITY OF COMMERCIAL GRANULATED SUGARS

Sample No.	Average Grain Size Mm.	Apparent Color Index ^a I _c	Turbidity Index ^b I _t	Reflectance			Sample No.	Average Grain Size Mm.	Apparent Color Index ^a I _c	Turbidity Index ^b I _t	Reflectance		
				Observed %	Calculated %	Difference %					Observed %	Calculated %	Difference %
1	0.300	15.8	36.3	90.03	89.48	+0.55	32	0.368	11.9	22.5	90.00	89.31	+0.69
2	0.308	4.6	13.5	91.54	91.67	-0.13	33	0.316	4.8	14.0	91.85	91.51	+0.34
3	0.293	9.5	21.4	90.37	90.88	-0.51	34	0.330	9.2	26.2	91.12	90.40	+0.72
4	0.310	7.1	14.3	90.82	91.13	-0.31	35	0.329	12.2	28.4	89.73	89.81	-0.08
5	0.425	11.1	41.7	88.35	88.63	-0.28	36	0.322	11.3	27.8	89.85	90.09	-0.24
6	0.338	10.9	22.5	90.38	89.94	+0.44	37	0.317	7.0	21.8	91.17	91.05	+0.12
7	0.343	15.4	28.6	88.54	88.95	-0.41	38	0.366	10.9	23.3	89.23	89.54	-0.31
8	0.446	11.1	29.7	87.80	88.36	-0.56	39	0.342	4.8	18.4	90.57	91.14	-0.57
9	0.291	13.4	27.2	91.70	90.10	+1.60	40	0.377	2.4	11.2	91.25	91.14	+0.11
10	0.391	7.8	18.1	90.55	89.72	+0.83	41	0.367	10.8	24.8	90.02	89.55	+0.47
11	0.369	11.5	42.5	90.72	89.34	+1.38	42	0.282	12.7	24.2	90.70	90.37	+0.33
12	0.391	8.6	20.0	89.60	89.66	-0.06	43	0.384	15.7	29.9	88.82	88.87	-0.05
13	0.344	11.7	30.1	90.72	89.70	+1.02	44	0.319	3.1	11.7	93.13	91.82	+1.31
14	0.312	4.2	11.4	93.45	91.59	+1.86	45	0.312	5.3	19.7	91.47	91.57	-0.10
15	0.311	14.1	34.8	89.55	89.67	-0.12	46	0.337	4.1	13.4	92.02	91.36	+0.66
16	0.301	3.7	11.1	92.45	91.96	+0.49	47	0.320	25.8	45.6	91.25	87.13	+4.12
17	0.383	8.5	35.8	88.93	89.79	-0.86	48	0.366	10.8	14.6	89.28	89.57	-0.29
18	0.312	10.0	27.2	91.37	90.50	+0.87	49	0.369	11.7	35.7	88.52	89.34	-0.82
19	0.358	14.0	48.2	88.37	89.02	-0.65	50	0.327	7.0	16.7	91.00	90.90	+0.10
20	0.307	15.0	21.1	89.25	89.50	-0.25	51	0.335	15.0	22.1	90.42	89.15	+1.27
21	0.445	8.8	20.0	89.25	88.95	+0.30	52	0.366	10.0	18.1	90.32	89.73	+0.59
22	0.312	10.5	29.4	90.50	90.40	+0.10	53	0.309	7.3	14.9	91.68	91.09	+0.59
23	0.335	11.8	22.1	89.83	89.80	+0.03	54	0.369	3.6	11.7	90.68	91.01	-0.33
24	0.338	4.0	13.8	91.30	91.37	-0.07	55	0.312	4.7	16.1	91.68	91.59	+0.09
25	0.352	7.3	21.3	91.28	90.49	+0.79	56	0.327	35.5	60.0	92.48	85.03	+7.37
26	0.326	5.9	17.2	91.27	91.14	+0.13	57	0.348	6.6	30.4	89.32	90.68	-1.36
27	0.318	7.9	16.1	90.96	90.84	+0.12	58	0.319	6.9	14.1	90.53	91.04	-0.51
28	0.301	6.5	23.4	91.18	91.38	-0.20	59	0.442	23.8	51.3	85.73	85.81	-0.08
29	0.339	4.7	18.3	91.62	91.20	+0.42	60	0.327	20.0	42.2	89.85	88.22	+1.63
30	0.293	21.0	34.4	89.60	88.50	+1.10	Av.	0.341	10.3	24.6	90.45	90.03	+0.42
31	0.338	8.1	16.6	90.75	90.52	+0.23							

^a I_c = 100 (1 - T_g/T_r).^b I_t = 100 (1 - T_r).^c From equation R = -0.206 I_c - 14.3g + 97.02.

evaluated by plotting the intercepts (reflectance extrapolated to zero grain size) of the three straight lines against the average value of I_c for each of the three groups. This gave the following expression relating R₀ and I_c:

$$R_0 = -0.206 I_c + 97.02 \quad (2)$$

Combining Equations 1 and 2 the complete relation is

$$R = -0.206 I_c - 14.3g + 97.02 \quad (3)$$

This expression predicts a maximum reflectance of about 97 per cent for a sugar free from coloring matter and having very small grain size. However, this limiting value is apparently somewhat low, as a finely pulverized sample of a highly purified sugar gave a measured reflectance of 97.3 per cent.

In 60 typical unscreened sugar samples examined (Table III), the average grain size ranged from 0.28 to 0.45 mm., and the apparent color ranged from about 2 to 24. By means of Equation 3 it is seen that for the extremes of grain size in this lot of typical samples the reflectance value is affected approximately 2.2 per cent, while for the extremes of apparent color it is affected twice as much, 4.4 per cent. The worst possible sugar in a group with these extremes would differ in reflectance from the best possible sugar by only 6.6 per cent. The magnitude of these changes in reflectance values produced by differences in grain size and differences in amount of coloring matter could be increased by using an effective wave length of light smaller than the mean wave length 590 mμ estimated for the present measurements.

Quality Analysis on Typical Sugars

In order to illustrate application of the photoelectric photometer to routine analysis of general quality of sugars, measurement of reflectance and determination of apparent color index and turbidity index were made on 60 samples of commercial granulated sugar. These values are given in Table III. The average grain size of each sample was calculated by use of grain-size distribution data available from previous screening and weighing of these sugars. The observed reflectance of each sample is compared with the value calculated from Equation 3.

The size of the differences in the last column indicates that Equation 3 expresses the relation between reflectance, grain size, and apparent color fairly satisfactorily. The average value of the observed minus the calculated reflectances for the 60 samples is 0.42 per cent. There are, however, some large discrepancies, notably for samples 47 and 56. (The latter sample was discussed in connection with Table II.) The turbidity index for these solutions is large, but, while no larger than, for example, samples 19 and 59, these solutions showed visually a milky appearance not possessed by the other samples of high turbidity. Solutions of this type, though not frequently encountered, will show a high apparent color index which may not be even an approximate indication of the true coloring matter in the solutions. Some difference between the apparent color and true color may exist for all the results reported, since the differences shown in Table III in many cases are larger than the precision of measurements of both reflectance and transmittancy. However, the error made in estimating color in the solutions by this method is believed to be not serious enough (except for occasional samples such as 47 and 56) to outweigh the advantage gained by eliminating filtration of solutions. It is possible that the color index would be more reliable if applied only on filtered solutions, but if this were done doubt would remain because of the possibility of loss of color in the filtration process. Some evidence for the reliability of the apparent color index, as determined on unfiltered solutions, for indicating true color is shown in the consistency of results in Table II (except for sample 56).

Further evidence is gained from Table III in the fact that the difference in observed and calculated reflectances averaged for the group of samples having high turbidity does not differ significantly from the differences averaged for the group of samples having low turbidity; the same is true for the group of samples having high apparent color as compared with the samples having low apparent color (omitting samples 47 and 56).

As mentioned previously, the specific absorptive index of the unfiltered solutions for red light should agree approximately with turbidity figures measured by Balch's method (2). In order to verify this, values of (-log T_r)/bc were

calculated from the red transmittancies T_r , measured on the photoelectric photometer for 10 unfiltered sugar solutions and these were compared with the specific absorptive index differences between the unfiltered and filtered solutions of the same samples as measured on a photoelectric spectrophotometer. Fair agreement for the 10 samples was obtained, the average numerical difference between the two methods being ± 0.005 at $560 \mu\mu$ and ± 0.003 at $650 \mu\mu$. A similar comparison of results for the 60 samples of Table III with results obtained previously by another observer on a visual spectrophotometer at $560 \mu\mu$ by Balch's method showed agreement to ± 0.004 .

The possibility of obtaining a color index for sugar by reflectance measurements on the sugar in granulated form was considered. Table IV shows the reflectances of three screened sugars, measured on the photoelectric photometer for green and red light. R_g is the reflectance measured with the blue-green filter (spectral centroid $535 \mu\mu$), R_r the reflectance measured with the red filter (spectral centroid $655 \mu\mu$), and the quantity $100(1 - R_g/R_r)$ is a convenient color index. The grain size of these three screened samples of sugar was 0.36 mm. and the apparent color as determined from transmittancy measurements (see Table II) on unfiltered solutions was low for sample 24 and high for sample 30. Sample 56 is the one which showed discrepancies in the results of Tables II and III. The reflectance color index of Table IV appears to place this sample among sugars of low color where it apparently belongs.

TABLE IV. REFLECTANCE MEASUREMENTS FOR GREEN AND RED LIGHT

Sample No.	R_g ($535 \mu\mu$)	R_r ($655 \mu\mu$)	$100(1 - R_g/R_r)$
30	86.3	90.2	4.3
56	90.1	92.6	2.7
24	89.2	91.4	2.4

While a measurement of the reflectance of granulated sugar for green (or blue) light and red light may provide a reliable index of the coloring matter present in sugars of equal grain size, such a method is considered not practical because it would require screening of all samples. Since grain size greatly affects the color of granulated sugars, the use of a reflectance method in obtaining an index of coloring matter for unscreened sugars is judged to be not as reliable as the method described for determining the apparent color using unfiltered solutions.

Certain possible improvements both in apparatus and method might be suggested at this point for further work.

1. Some advantage should be gained by using a "visibility" correcting filter with the photocell for the reflectance measurements. Results would then agree more nearly with data obtained by visual measurements or with other makes of photocells also having correcting filters, and would have a less arbitrary numerical value. Reflectances measured using such a filter would, however, be only slightly lower than those reported here and the conclusions reached would be the same.

2. Because of slight differences in spectral sensitivity for individual photocells and difficulty in reproducing identical color filters, readings obtained on a given series of samples on several similar instruments will not agree exactly, especially when using the blue-green filter. By compensating spectral response differences by thickness adjustment of the blue-green filters, it would be possible practically to eliminate such differences in readings. However, an easier way of bringing such results into agreement would be to use monochromatic light. For this purpose, use of sources such as

mercury, sodium, and cadmium arcs, with suitable filters, might be practicable with the present apparatus. The measurements would then be fundamental, and would be free from many sources of error present when using tungsten lamp illumination with arbitrary filters.

Summary

The reflectance of white sugars in granulated form, measured on a photoelectric apparatus using directional illumination, has been shown to be a practical method of evaluating the "appearance" of sugars. The variation of reflectance of such sugars with grain size and amount of coloring matter has been studied. A simple method of determining the "apparent color" and turbidity of sugar solutions by abridged spectrophotometry, without necessity for filtration of the solutions, is proposed for the purpose of practical quality evaluation. While the present investigation has been limited to white granulated sugars, it is believed that the apparatus and method might be used for measuring the reflectance of other sugars and for determining the "apparent color" and turbidity of other sugar products using less depth of solution and a suitable concentration.

Acknowledgment

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Literature Cited

- (1) Ambler, J. A., and Byall, S., *IND. ENG. CHEM., Anal. Ed.*, **3**, 135 (1931).
- (2) Balch, R. T., *Ibid.*, **3**, 124 (1931).
- (3) Bates, *Intern. Sugar J.*, **22**, 654 (1920).
- (4) Brewster, J. F., *J. Research Natl. Bur. Standards*, **16**, 349 (1936).
- (5) Brice, B. A., *Rev. Sci. Instruments* **7** (July, 1937); *J. Optical Soc. Am.*, **24**, 162 (1934).
- (6) Bruckner and Becker, *Deut. Zuckerind.*, **56**, 692 (1934).
- (7) Buse, H., *Centr. Zuckerind.*, **41**, 290 (1933).
- (8) Dawson, L. E., Beet Sugar Report, VI, Carbohydrate Division, Bureau of Chemistry and Soils, U. S. Dept. Agriculture, 1927.
- (9) Ganz, E., *Ann. Physik*, **26**, 331 (1936).
- (10) Gibson, K. S., *Natl. Bur. Standards, Letter Circ. LC-473* (July 9, 1936); *Instruments*, **9**, 309 (1936).
- (11) Gillett, T. R., and Holven, A. L., *IND. ENG. CHEM.*, **28**, 391 (1936).
- (12) Hardy, J. D., and Pfund, A. H., unpublished work.
- (13) Herke, T., and Rempel, N., *Deut. Zuckerind.*, **59**, 379, 397 (1934).
- (14) Heyden, E. v., *Ibid.*, **56**, 627 (1934).
- (15) Holven, A. L., and Gillett, T. R., *Facts About Sugar*, **30**, 169 (1935).
- (16) Jackuschoff, P., *Deut. Zuckerind.*, **56**, 859, 882 (1933).
- (17) Judd, D. B., *Paper Trade J.*, **103**, No. 8, 38 (1936).
- (18) Keane, J. C., and Brice, B. A., *Facts About Sugar*, **30**, 383 (1935).
- (19) Landt, E., *Z. Ver. deut. Zucker-Ind.*, **84**, 954 (1934).
- (20) Landt, E., and Witte, H., *Ibid.*, **84**, 450 (1934).
- (21) *Natl. Bur. Standards, Letter Circ. LC-395* (Jan. 20, 1936).
- (22) Peters, H. H., and Phelps, F. P., *Bur. Standards Tech. Paper* **338** (1927).
- (23) Sandera, K., *Z. Zuckerind. czechoslovak. Rep.*, **55**, 33 (1930).
- (24) Spengler, O., and Landt, E., *Z. Ver. deut. Zucker-Ind.*, **77**, 429 (1927); **81**, 13 (1931).
- (25) *Ibid.*, **83**, 223 (1933).
- (26) Weston Electrical Instrument Corp., *Tech. Bull.* (Photronic Cells).
- (27) Zerban, F. W., and Sattler, L., *IND. ENG. CHEM., Anal. Ed.*, **3**, 226 (1931); **8**, 168 (1936).
- (28) Zerban, F. W., Sattler, L., and Lorge, I., *Ibid.*, **6**, 178 (1934); **7**, 157 (1935).

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Direct Determination of Low Vapor Pressures

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THE boiling points under reduced pressure of various phlegmatic liquids have been determined by a number of methods during the past 7 years. The first measurements, made in 1930, on butyl phthalate in an apparatus of complicated design (4), were reliable over the limited range of 1.0 to 0.1 mm., but concordant readings were not obtained at lower pressures. The next measurements were made 4 years later in the apparatus shown in Figures 1, 2, and 3, which extended the readings to 0.03 mm.

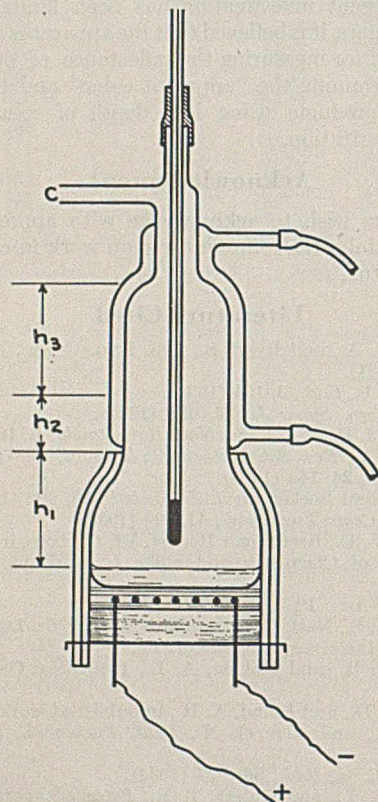


FIGURE 1. TENSIMETER-HYPSOMETER

In 1935 the ultimate vacuums producible at 20° C. by various phthalic acid esters (3) when boiled in condensation pumps were measured with the ionization gage (2). The earlier boiling points of butyl phthalate had been plotted on logarithmic paper against the inverse of the absolute temperature, in the usual manner, and, when the readings of the ionization gage were incorporated, it was found that an extrapolation of the earlier values met those from the ionization gage if a slight curvature (3) was introduced. Recently the apparatus shown in Figure 4 has been constructed, which provides direct readings of vapor pressure to 10^{-3} mm., possibly to 10^{-4} mm. These readings have been found to fall very nearly on the line connecting the early data with those from the ionization gage. The two direct methods for determining vapor pressure in the intermediate range—that is, between 5 and 10^{-4} mm.—are described below.

The equilibrium pressure of a gas may be assessed in terms of the random motion of its molecules. When vapor passes from the hot surface of a liquid to the cool surface of a condenser, the molecules possess an impressed velocity towards

the condenser which detracts from the random velocities. At high pressures, the effect of the forward motion of the vapor is infinitesimal and the temperature of a thermometer immersed in the stream of saturated vapor measures correctly the condensation temperature of the vapor. If the pressure is lowered, the forward velocity becomes comparable with the random velocity, and the thermometer records less accurately the condensation temperature of the saturated vapor. At low pressures (1, 6), the resistance of the tube connecting boiler and condenser produces a continuous change in pressure throughout the length, so that the orifices connecting the two regions must be large. At very low pressures, residual uncondensable gas (generally air) diffuses through the large orifice against the vapor and vitiates further the thermometer readings.

Apparatus

The tensimeter-hypsometers illustrated in Figures 1 and 3 were constructed so that the vapors pass the thermometer at low velocity and suffer the minimum obstruction. Most of the experiments have been done with the simpler form, having no vacuum jacket.

The tensimeter consists of a short, wide boiler connected with a water-jacketed condenser. The boiler is heavily insulated with felt and has fastened underneath a light-weight heating element protected by a few pieces of asbestos paper. Electricity

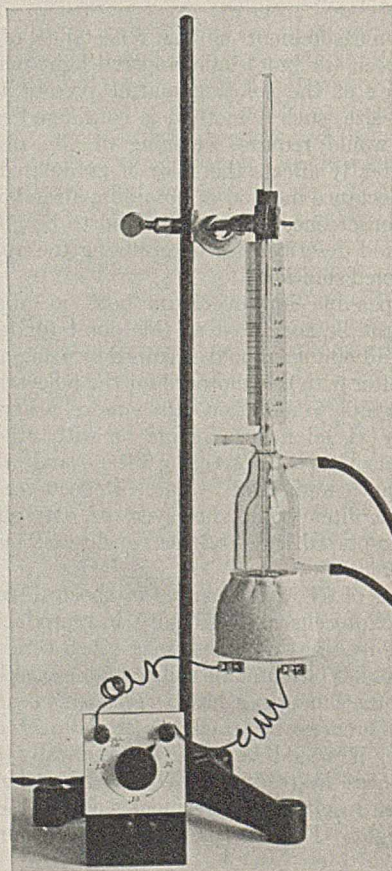


FIGURE 2. PHOTOGRAPH OF APPARATUS

is supplied through a variable resistance and a meter. The liquid to be tested is boiled with various pressures of residual air in the apparatus. The pressures, which may range from 0.01 to 0.10 mm., are conveniently measured with an oil manometer (5) attached directly to the tensimeter.

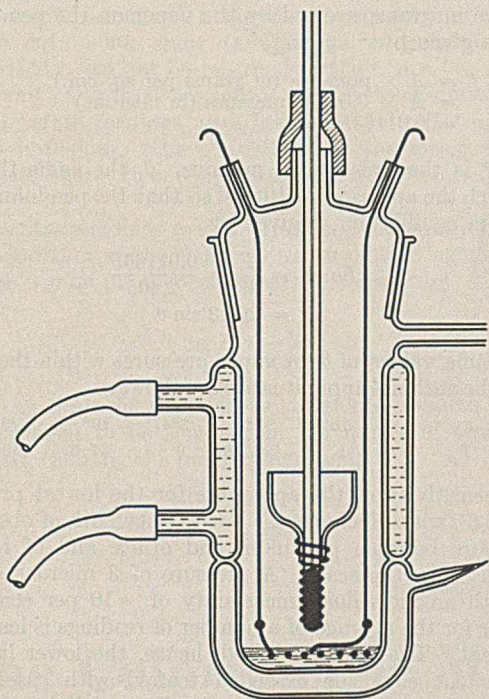


FIGURE 3. TENSIMETER-HYPSOMETER

At each steady pressure, the heat input is increased slowly, and the temperature recorded by the thermometer is plotted against the input. At pressures above 0.05 mm., the temperature remains constant over a wide variation of input. This constant temperature is regarded as the boiling point of the substance at the prevailing pressure. At pressures below 0.05, the thermometer assumes no steady state, thus demonstrating that substances have no fixed boiling points under high vacuum.

The tensimeter is not reliable for pressures above 5 mm. because the vapor is evolved, in a superheated condition, from a distilland which bumps and splashes onto the thermometer. The readings between 0.03 and 4 mm. are concordant and tally with those found by other means. The vapor pressures of butyl phthalate recorded with this apparatus for various inputs of heating current are shown in Figure 5. The horizontal lines show the variation of temperature with heat input at constant pressure. The vertical lines, *D* and *E*, show the limits of heat input permissible for each pressure. Line *C* shows the optimum heat input to which the tensimeter should be adjusted for final readings.

If the heat input is maintained at a constant value and the pressure of inert gas in the apparatus is raised, the thermometer adjusts itself to the new boiling point in a few seconds. When, however, the pressure is lowered, many minutes are required before the ther-

mometer assumes a steady lower temperature. The downward lag has been diminished by the construction shown in Figure 3. Here the heating coil is immersed in the operating liquid and a cup is placed on the thermometer so that on the occasions when the pressure is being lowered and a sudden rush of lower temperature vapor rises in the tensimeter, condensate trickles back over the thermometer, cooling it rapidly to the new temperature. This modified apparatus responds sufficiently quickly to be used as a hypsometer or secondary manometer. The sensitiveness of the scale remains constant throughout its useful range, which is in happy contrast to the scale of an oil manometer which becomes increasingly difficult to read at low pressures.

The hypsometer fails to work at low pressures because of interdiffusion between vapor and the residual gas, and because the random velocity is small compared with the forward velocity of the vapor molecules. Both defects could be cured by placing a flexible diaphragm across the junction between the boiler and condenser. Readings of the thermometer would correspond to the pressure above the diaphragm when this was accurately balanced by the pressure of vapor below. The flexible diaphragm is impracticable, but a substitute has been evolved, as in Figure 4, which operates satisfactorily.

Here the diaphragm is replaced by a disk forming the end of a long, light-weight pendulum, the disk swinging to close the orifice of the boiler, *A*. The substance is placed in the boiler and the assembly is immersed in a bath of oil. The bath is brought to various temperatures and is maintained constant by an electric heater, stirrer, etc., in the usual manner. The large side tube, *B*, is connected directly to a condensation pump, which is in turn connected to a mechanical oil pump. The tensimeter, condensation pump, and pipe line can be rotated around the axis of the side tube, *B*, by the gear wheels, *C*, which are carried by suitable supports. A pointer attached to the tensimeter records the angular deflection on a scale, *D*. The annulus, *E*, collects condensate from the upper parts of the tensimeter and returns it by a narrow tube to the boiler, *A*. The substance is placed in the tensimeter and a vacuum of 10^{-4} mm., as recorded by the Pirani gage, *F*, attached to *B*, is produced. The apparatus is tilted so that the pendulum just closes the orifice of the boiler. The temperature of the oil bath is raised, and presently the vapor from *A* blows the pendulum bob away from the orifice. The tensimeter is twisted until the pendulum again just closes the orifice. By comparing the position at low temperature with that at high, the deflection, produced by the pressure of the vapor when no vapor is flowing, is readily deducible.

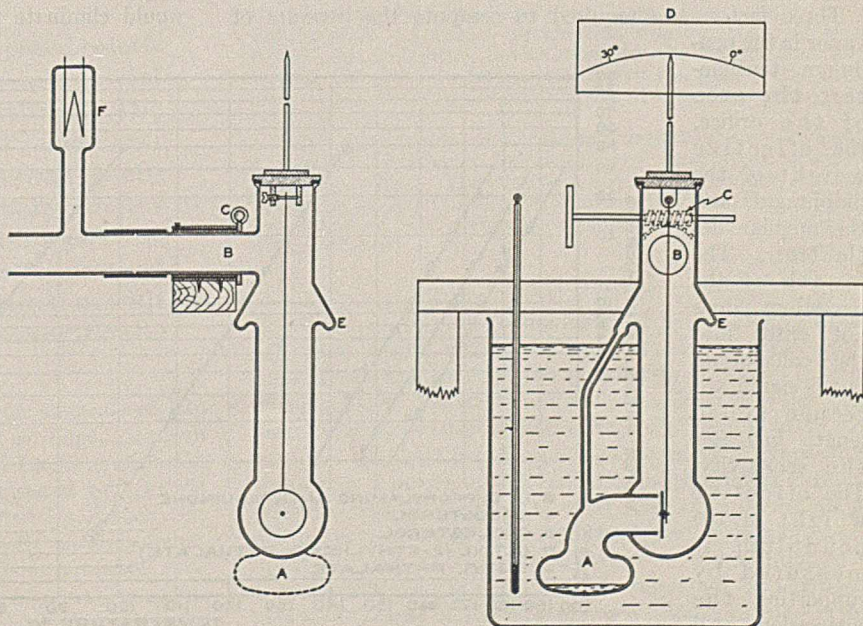


FIGURE 4. DIAGRAM OF APPARATUS FOR DIRECT DETERMINATION OF VAPOR PRESSURE

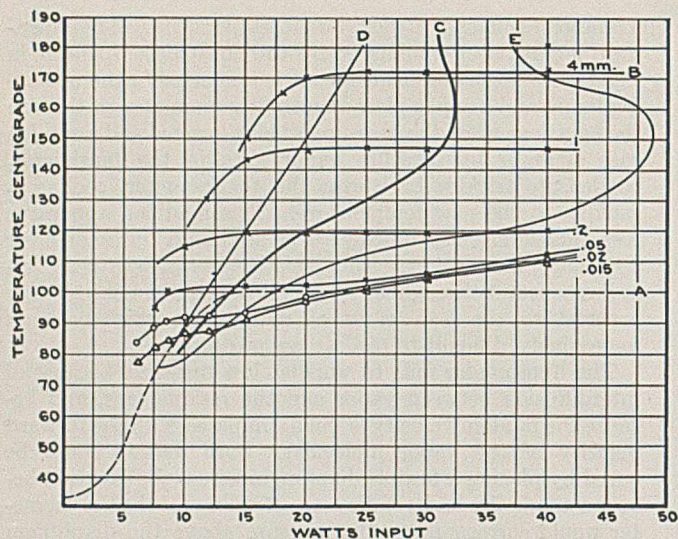


FIGURE 5. VAPOR PRESSURES OF BUTYL PHTHALATE

It is useful to allow vapor to stream by the open pendulum for some time before taking readings, in order that the material may become completely degassed.

The substance supplying the vapor is never entirely hermetically sealed in the boiler; there is always a slight leakage around the pendulum end through the tube by which the condensate returns. This tube can be closed with an iron ball and the pressures can be read with the tube closed or open and the temperatures varying in ascending or descending order. (A steel ball from a ball bearing can be placed in the annulus before sealing the apparatus. The ball is moved into or away from the tube by means of an external magnet.) The data recorded for each of the four variations prove to be the same within the limits of measurement, indicating that true equilibrium conditions obtain even with the open tube. It has been the authors' experience that, whenever measurements of low vapor pressures are made on compound substances hermetically sealed in measuring apparatus, a spurious pressure, which vitiates the lower readings, always develops after moderate exposure to heat. The devices described here are not open to this form of error.

Three factors are required to compute the pressure of vapor in the pendulum tensimeter: the area of the orifice, the effective weight of the diaphragm, and the angular deflection. The length of the pendulum does not enter into the calculation, but is significant because added length increases the sensitivity. The effective weight of the pendulum is measured by supporting the suspension end horizontally on

its fulcrum outside a balance and allowing the diaphragm to rest by its center point on the balance pan.

For the apparatus used in this work, A represents the area of the orifice, 8.553 sq. cm., and W represents the effective weight of the pendulum, 2.405 grams. The force in grams exerted by the vapor on the pendulum, f , is given by:

$$\begin{aligned} f &= A \times \text{pressure (in grams per sq. cm.)} \\ &= A \times 0.00136 \text{ pressure (in microns)} \\ &= 0.01163P \end{aligned}$$

P is the pressure in microns. θ , the angle through which the apparatus is turned so that the pendulum may be in equilibrium, is given by

$$\sin \theta = \frac{F}{W} = \frac{0.01163P}{2.405}$$

or

$$P = 206.3 \sin \theta$$

Some values of θ for vapor pressures within the range of the authors' apparatus are as follows:

θ	0	16'40"	1°	2°47'	10°	29°1'
P_{μ}	0	1	3.78	0	37.6	100

The sensitivity of the apparatus for the lowest pressure is about 6', which includes the uncertainty both of observing the closure between pendulum and orifice and of reading the pointer on the scale. A pressure of 3 microns can be read with an individual uncertainty of ± 10 per cent, but the error for the average of a number of readings is less than 5 per cent. The sensitivity and, hence, the lower limit of measurement could be extended tenfold with ease. The improvements would include lengthening and lightening the pendulum, observing the closure telescopically, and making the angular reading with a vernier. Also, the area of the orifice could be doubled without making the apparatus unwieldy. These improvements have not yet been made because there are other systematic errors which are less open to control. Undoubtedly there is an "edge effect" because the walls of the orifice are not indefinitely thin and the pendulum overlaps the outer edge. At low pressures there is probably a greater thrust than that calculated, owing to spread of the vapor at the edge of the orifice. This same spread may introduce a Bernoulli suction effect at higher pressures. Using a diaphragm that slides within the orifice would eliminate these errors, but would introduce others.

The refinements must await such investigation as future experience warrants.

The vapor pressures of various substances have been determined, and the pressure-temperature curves of a few are shown in Figure 6.

The points on the curve for 2-ethylhexyl phthalate (octoil) show poor alignment because the measurements were done in a rapid

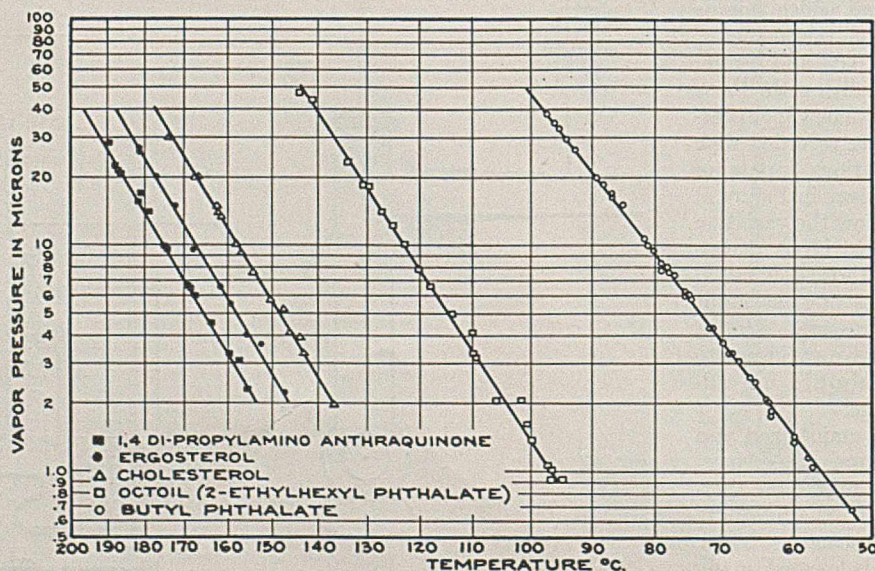


FIGURE 6. PRESSURE-TEMPERATURE CURVES

and preliminary manner, insufficient time being allowed for the attainment of equilibrium at each temperature.

Cholesterol (m. p. 148.5° C.), ergosterol (m. p. 160° C.), and 1,4-dipropylaminoanthraquinone (m. p. 155° C.) were solids at the temperatures of the cooler parts of the apparatus. Time for degassing and attainment of equilibrium was necessarily cut short, since the portion of substance which vaporized could not be returned to the boiler.

A wait of at least 5 minutes at each temperature was allowed before readings were taken of the vapor pressure of butyl phthalate. The consistency of the measurements in this case shows that equilibrium had been reached satisfactorily.

The straight lines drawn through the points representing the logarithm of the vapor pressure plotted against $1/T$ in Figure 6 may be expressed mathematically by

$$\log P = -\frac{A}{T} + B$$

If the heats of vaporization of the substances examined are assumed to be constant in the ranges of temperatures studied, then, by the familiar equation,

$$\log P = -\frac{\Delta H}{2.3RT} + \text{constant}$$

The heats of vaporization in calories per mole for these substances are equal to $2.3R$ times A . The constants A and B and the heats of vaporization are found to be as follows:

	A	B	ΔH
Butyl phthalate	4680	14.215	21,400
Octoil	5590	15.116	25,600
Cholesterol	6000	14.931	27,400
Ergosterol	6200	15.072	28,400
1,4-Dipropylaminoanthraquinone	6180	14.784	28,300

Summary

Two methods have been described for determining the vapor pressures of substances over the range 0.001 to 4.0 mm. The vapor pressures from 1 to 50 microns of mercury have been determined for two vacuum pump fluids, two sterols, and a dye.

Literature Cited

- (1) Dushman, S., "High Vacuum," Schenectady, N. Y., General Electric Review Press, 1922.
- (2) Dushman, S., and Found, C. G., *Phys. Rev.*, **17**, 7 (1921).
- (3) Hickman, K. C. D., *J. Franklin Inst.*, **221**, 215, 383 (1936).
- (4) Hickman, K. C. D., *J. Phys. Chem.*, **34**, 627 (1930).
- (5) Hickman, K. C. D., *Rev. Sci. Instruments*, **5**, 161 (1934).
- (6) Hickman, K. C. D., and Weyerts, W. J., *J. Am. Chem. Soc.*, **52**, 4714 (1930).

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The Colorimetric Method for Soft Resins of Hops

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Approximately 30 per cent of the world's hops are grown in the three Pacific Coast states, with Oregon producing two-thirds of the 30 per cent. Little use has been made of chemical methods for hop evaluation in the United States, because of the lack, until recently, of satisfactory methods of analysis and the time required by the gravimetric procedure.

A discussion of a recently proposed colorimetric procedure is undertaken and several suggested modifications are outlined. The modified method is applied to Pacific Coast hops and a comparison of the data so obtained with those from gravimetric determinations indicates that, while not extremely accurate, the colorimetric method may have a definite use in conjunction with physical examination in evaluating hops.

RECENTLY, in the course of work on methods of hop analysis and chemical evaluation of hops, occasion arose to employ the colorimetric method for determination of the soft resins of hops originally suggested by Guthrie and Philip (3) in 1930, and later modified by French (2), Guthrie and Philip (4), and Comrie (1). It was soon found that many data obtained through use of the published procedures were not in agreement with data obtained by gravimetric analyses. Further observation clarified some difficulties and suggested modification of the existing methods.

A discussion of some of these points may prove of interest to those engaged in chemical evaluation of hops. Particularly is this true since the investigation deals with Oregon-grown hops, which generally carry a somewhat higher soft-resins content and are employed to a greater extent by the brewing industry of the United States than the British or Continental hops worked with by the previously mentioned investigators.

Apparatus and Chemicals

A 5-cc. Bausch and Lomb colorimeter with all-glass cups was used exclusively. Readings to 0.1 mm. were possible on the vernier scale. Artificial illumination was by means of an enclosed electric lighting device made by the Bausch and Lomb Optical Company to fasten securely to the base of the instrument. A clear blue-glass disk was placed on the eyepiece to reduce the light intensity.

Ferric chloride, uranyl acetate, and uranyl nitrate were Baker's c. p. grade. Methanol, petroleum ether, and ether of suitable quality were used. The methanol, a synthetic product, was found to require no fractionation before use. Likewise, that recovered by distillation from previous use exhibited no color reaction with uranyl nitrate.

Experimental

COLOR STANDARDS. It was observed, as reported by Comrie (1), that uranyl nitrate and uranyl acetate were equally satisfactory for development of color in methanol solutions of pure α -resin. However, a precipitate formed in the uranyl acetate solution after standing for some days at room temperature in a dark cupboard. Because, in all attempts to use it directly in methanol extracts of hops, cloudiness developed which interfered with color matching, uranyl acetate was discarded in favor of uranyl nitrate for color development.

All attempts to utilize as a permanent color standard the 10 per cent ferric chloride solution suggested by Comrie (1) met with failure because the extreme density of color of such a solution rendered impossible accurate matching of color

with the colorimeter used. After a number of trials a 2.5 per cent ferric chloride solution containing 1 cc. of 1 *N* hydrochloric acid per 100 cc. was found to give a satisfactory color density when the blue-glass disk was used. Although no tests were made, it is considered advisable to employ an even more dilute ferric chloride solution if the blue-glass disk is not used on the eyepiece.

It was observed that the color intensity of a ferric chloride solution is not proportional to its concentration—for example, the color developed in a certain α -resin solution required 53.3 mm. of 2.5 per cent ferric chloride or 17.6 mm. of 10 per cent ferric chloride to effect a color match. If the color intensities were proportional to concentration, 53.3/4 mm. or 13.3 mm. of the 10 per cent ferric chloride should be required. It is therefore necessary actually to determine the color value in terms of α -resin for any strength of ferric chloride decided upon.

TABLE I. LOSS IN COLOR VALUE OF METHANOL EXTRACTS OF HOPS

Hop	Depth to Match Color of 30 Mm. of 2.5 Per Cent FeCl ₃ Solution						
	Immediately	1 hour	2 hours	18 hours	24 hours	42 hours	68 hours
	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
1	20.8	23.5	24.8	19.9	24.7	23.6	32.7
2	16.8	18.5	18.6	16.4	20.2	17.7	21.0

Two lots of α -resin lead salt were prepared from portions of the same sample of minced hops. In one case the preliminary ether extraction advised by Hastings and Walker (5) and referred to by Guthrie and Philip (3, 4) and Comrie (1) was carried out while in the other the ether extraction was omitted. The two compounds have been kept in weighing bottles in a desiccator in a well-lighted room for over 1.5 years without any apparent deterioration. Omission of the ether extraction of this particular hop, at least, did not produce an α -resin lead salt which differed from that obtained through use of ether extraction, as far as could be noted from the characteristics of the color standards prepared from them. These observations are contradictory to those of other workers, but, because of the limited nature of the tests, should not be considered conclusive until they have been verified on preparations from a number of hop samples.

The use of a dye mixture to compensate for the lack of chlorophyll in pure α -resin solutions is believed to be of questionable value, because the variation in a series of five or six readings on one solution is generally greater than the increase in color observed on an α -resin solution through the addition of the dye.

It was found that 1.0 cc. of a dye mixture (25 cc. of 0.1 per cent methanol solution of bromothymol blue, 1 cc. of 0.1 per cent methanol solution of xylene cyanol FF, and 40 cc. of methanol) diluted in α -resin solution to give 100 cc. of 0.01 per cent α -resin solution imparted a color approximating that of a 0.1 per cent hop extract. As nearly as could be determined on such weakly colored solutions, 1 cc. of the above dye mixture diluted to 100 cc. with methanol produced a color equivalent to that of 0.5 mm. of 2.5 per cent ferric chloride solution. Dye was not used in the work reported in this paper.

PERMANENCE OF α -RESIN SOLUTIONS. Although the stability of α -resin solutions is not of prime importance when ferric chloride solution is employed as a standard for color comparison, a few tests were made incidental to other experiments. There appeared to be a slight change immediately after preparation (as directed by Comrie, 1, except that a 0.01 per cent solution containing no dye was used) of the solution followed by stabilization within a few days. The α -resin solution was kept in a dark cupboard at room temperature

except as it was removed to withdraw aliquots for color development.

Experiments on the change in methanol solutions of α -resin showed that the depth to match the color of 30 mm. of 2.5 per cent ferric chloride solution was as follows: immediately, 13.6 mm.; after 24 hours, 14.5 mm.; after 4 days, 15.1 mm.; after 8 days, 15.0 mm.

In another test no change was noted in an α -resin solution in which the color had been developed for a period of 24 hours. This observation substantiates in a limited way that of Guthrie and Philip (4), who state that they noted no changes over a 12-month period in the colored solutions.

STABILITY OF HOP EXTRACTS AND MINCED HOPS. Contrary to Comrie's (1) experience and in accord with French's (2) findings, the color-producing value of methanol extracts of hops was found to decrease from the time they were prepared, and the loss of color-forming constituents was more rapid in 0.1 per cent than in 10 per cent extracts. Extracts from two different hop samples were prepared, using 5 grams of hops and 50 cc. of methanol (Table I). At the expiration of the indicated times, 1 cc. of the extract was placed in a 100-cc. flask, treated with uranyl nitrate, and diluted to 100 cc., and the color was immediately balanced against 30 mm. of 2.5 per cent ferric chloride. After the first two determinations the extracts were stored at approximately 0° C. (32° F.) except while removing aliquots. The average of 5 readings was chosen for each value.

TABLE II. EFFECT OF CONCENTRATION ON RATE OF CHANGE OF METHANOL EXTRACT OF HOPS

	Depth to Match Color of 30 Mm. of 2.5 Per Cent FeCl ₃ Solution			
	No. 1	No. 2	No. 3	No. 4
	Mm.	Mm.	Mm.	Mm.
Immediately	17.2	17.5	24.1	22.3
10 per cent extract after 5 days	20.5	20.1		
0.1 per cent extract after 5 days	30.7	26.9	35.0	34.8

The difference in rate of change of the 10 per cent extract and the 1 to 100 dilution of the 10 per cent extract is indicated by data from four lots of hops (Table II). Both solutions were stored at 0° C. (32° F.) for 5 days. One cubic centimeter of the 10 per cent extract was then taken and diluted to 100 cc. and the color developed; in case of the dilute extract, the color was developed directly. An average of 4 or 5 readings was taken for each determination.

Examination of Table I reveals some figures which appear to be at odds with the general behavior of the solutions. This disagreement has also been noted frequently when working with other hop solutions. However, the apparent increase in color value so often occurs between 18 and 24 hours after the hop extract is prepared that the coincidence seems more than accidental, and the method of storage of the hop extract suggested a possible explanation. To expedite determinations and to prevent evaporation errors introduced through filtration of extracts, the author has made it a practice to shake the minced hops and methanol in a stoppered centrifuge bottle, and then to centrifuge the mixture for about 5 minutes. Aliquots of clear extract may then be pipetted from the supernatant liquid without resort to filtration. If a series of tests was to be made over a period of time the centrifuge bottle containing the hops and supernatant extract was stored at 0° C. (32° F.) in a refrigerator. It was thought that the presence of the extracted hops might be responsible for the peculiar results noted, possibly through some adsorption and re-solution phenomena. To check the surmise, a one-to-ten hop extract was prepared as described above and, after centrifuging, part of the clear liquid was transferred to a clean flask. Aliquots from both the centri-

fuge bottle and flask were then tested at intervals. The results appear in Table III, and are averages of five settings for each determination.

The trend of these data is very similar to that of Table I figures although, in the absence of hops in contact with the stored solution, the color value did not return as near to the original value as was the case of the solution on the centrifuged hops. It would seem, therefore, that the suggested reason for the observed behavior of the solution is in part, at least, untenable. The questions raised by these observations remain, for the present, unanswered.

In connection with the discussion of hop extracts it may be of interest to record the differences in color value noted when the color was developed directly in the methanol extract and when the color was developed in a methanol solution of the material removed from the original methanol hop extract by shaking out with petroleum ether. The colorimetric procedure assumes that the color formation is brought about through the reaction of the uranium salt with the soft resins, and that petroleum ether extracts only the soft resins from a methanol hop extract. Therefore, the color value obtained on a hop by either procedure should be the same and Guthrie and Philip's (3) procedure indicates such to be the case. The data, however, did not substantiate the assumption when the method was applied to four hops treated in the manner indicated. One hop was 22 months old and the other three were 10 months old, and all had been kept in cold storage from the time they were baled. In one set of samples the colorimetric determination was made as usual, directly on the methanol extract; in the second set, aliquots of the methanol extracts were placed in separatory funnels with the proper amount of 1 per cent sodium chloride solution and extracted five times with petroleum ether. Aliquots of the petroleum ether extracts were evaporated to dryness in a vacuum oven at 40° C., the residues were dissolved in methanol, and the color was developed. An average of five readings was taken for each value recorded and comparisons were made against 30 mm. of 2.5 per cent ferric chloride.

TABLE III. EFFECT OF PRESENCE OF HOPS ON CHANGE IN COLOR VALUE OF THE METHANOL EXTRACT

Hop Extract	Depth to Match Color of 30 Mm. of 2.5 Per Cent FeCl ₃ Solution							
	Immediately	1 hour	3 hours	5 hours	7 hours	23 hours	47 hours	
	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
In contact with hops	11.5	12.0	12.1	15.2	14.7	12.5	14.6	
Free of hops	..	12.2	14.0	16.3	17.0	14.9	22.8	

If the precautions taken to prevent oxidation or loss of soft resins during extraction with and removal of petroleum ether may be considered effective, it would appear that a portion of the color must originate in constituents other than the soft resins, when the method is applied directly to the methanol extract. On the other hand, the preservative value calculated from the color value on methanol extracts more nearly agreed with that from gravimetric data than did that calculated from the color value of the petroleum ether residues. At any rate, the matter should be considered as yet open to question.

Minced hops, stored in a stoppered bottle at 0° C. (32° F.), were found to give the same colorimetric values after 2 weeks' storage as at the time of grinding.

COLOR DEVELOPMENT. Guthrie and Philip (3) recommended 10 cc. of 0.5 per cent uranyl acetate solution as sufficient to develop maximum color in a solution containing 0.01 gram of α -resin or in methanol extract equivalent to 0.1 gram of hops. In their second paper (4) the amount of uranyl acetate was doubled, 10 cc. of a 1.0 per cent solution being specified. French (2) and Comrie (1) chose uranyl nitrate

and used essentially 10 cc. of a 1.0 per cent methanol solution to develop the color in the amounts of α -resin or hops indicated by Guthrie and Philip (3), apparently with satisfactory results.

TABLE IV. EFFECT OF PETROLEUM ETHER EXTRACTION ON COLOR VALUE

	Depth to Match Color of 30 Mm. of 2.5 Per Cent FeCl ₃ Solution			
	No. 1	No. 2	No. 3	No. 4
	Mm.	Mm.	Mm.	Mm.
Methanol extract	18.3	19.0	21.7	18.2
Residue from petroleum ether extract	23.8	25.4	32.9	23.6

After obtaining some rather erratic results on both pure α -resin solutions and hop extracts, it was found that more uranyl nitrate was required to develop maximum color in α -resin solutions than had been previously supposed.

Two tests on α -resin lead salt were carried out: In the first, 1.0 per cent uranyl nitrate was used but, because the volume required was large, a 2.5 per cent solution was employed in the second test. The results are similar, so only the data of the second test are presented. The test solutions were prepared by decomposing 0.1580 gram of α -resin lead salt in 3 to 4 cc. of methanol with 2.5 cc. of 20 per cent sulfuric acid by grinding in a mortar, transferring to a separatory funnel, adding 50 cc. of aqueous 1.0 per cent sodium chloride, and extracting 5 times with petroleum ether. The petroleum ether was removed in vacuum at 40° C. and the residue dissolved in methanol and made to 100-cc. volume. Aliquots (5 cc., equivalent to 0.005 gram of α -resin) were placed in 50-cc. flasks with the indicated amounts of 2.5 per cent uranyl nitrate solution and made to volume. Comparison was against 30 mm. of 2.5 per cent ferric chloride. Averages of 5 settings of the colorimeter were taken for each result.

The depth to match the color of 30 mm. of 2.5 per cent ferric chloride solution, when the substance tested was 0.005 gram of α -resin in 50 cc., was found to be as follows:

2.5 per cent uranyl nitrate, cc.	2	3	4	5	6	7
α -resin solution, mm.	17.0	14.1	13.5	13.8	13.6	13.6

These data indicate that at least 4 cc. of the 2.5 per cent uranyl nitrate solution are required, which is equivalent to 20 cc. of 1.0 per cent solution, per 0.01 gram of α -resin. In order to ensure an excess of reagent, the writer uses 10 cc. of the 2.5 per cent solution for each 0.01 gram of α -resin or for methanol hop extract equivalent to 0.1 gram of hops. The extra color imparted by the uranyl nitrate solution itself is not significant, when compared to the magnitude of other errors inherent to the method.

Colorimetric Procedure

The following outline of the colorimetric procedure is a modification of that suggested by other workers and incorporates several changes which seem warranted from the observations and data presented in this paper.

REAGENTS. Synthetic methanol. Petroleum ether, b. p. under 60° C. Ethyl ether.

Pb(C₂H₃O₂)₂·3H₂O, c. p., 1 per cent methanol solution containing 1 cc. of glacial acetic acid per liter.

FeCl₃·6H₂O, c. p., 2.5 per cent aqueous solution containing 10 cc. of 1 N hydrochloric acid per liter. (A lower concentration of ferric chloride may be used if preferred.)

UO₂(NO₃)₂·6H₂O, c. p., 2.5 per cent methanol solution, stored in a brown bottle in the dark when not in use.

NaCl, 1 per cent aqueous solution.

PREPARATION OF α -RESIN LEAD SALT FOR STANDARDIZATION. A good quality of hop is passed through a food chopper fitted with a 12- to 16-point cutter. Twenty-gram samples are weighed into two 250-cc. capacity centrifuge bottles, 200 cc. of ethyl ether are added to each; they are shaken on a mechanical shaking

device for an hour, and centrifuged, and 200 to 300 cc. of clear extract, equivalent to 20 to 30 grams of hops, are evaporated to dryness in vacuum at 40° C. The residue is dissolved in methanol and filtered, and the filtrate is divided roughly into four portions which are placed in four 250-cc. separatory funnels, each containing 100 cc. of 1 per cent sodium chloride solution. Each portion is extracted five times with 40- to 50-cc. portions of petroleum ether which are passed through a filter paper. The combined petroleum ether extracts are evaporated to dryness in vacuum at 40° C., taken up in 160 to 240 cc. of methanol, depending upon the quantity of hops represented, and the α -resin lead salt is precipitated as described by Walker and Hastings (6) in their gravimetric method for α -resin determination. The precipitate is filtered on paper and washed thoroughly with methanol followed by ethyl ether, after which it is dried in vacuum at 40° C.

STANDARDIZATION OF 2.5 PER CENT FERRIC CHLORIDE SOLUTION. A 0.0158-gram sample of the α -resin lead salt (equivalent to 0.01 gram of α -resin) is ground in a mortar with 2 to 5 cc. of methanol and 0.5 cc. of 20 per cent sulfuric acid. The decomposed salt is washed with methanol into a separatory funnel containing 25 cc. of 1 per cent sodium chloride, and extracted with five 10- to 15-cc. portions of petroleum ether. After filtration the filtrate and washings are evaporated to dryness in vacuum at 40° C., taken up in methanol, and filtered into a 100-cc. flask. Ten cubic centimeters of 2.5 per cent uranium nitrate solution are added, and the flask contents are well mixed and made to volume with methanol. The color value is then compared to that of 2.5 per cent ferric chloride solution in a suitable colorimeter. Because the same depth of ferric chloride solution will be used against unknown hop extracts, it is convenient to select a suitable depth, say 20 or 30 mm. of ferric chloride solution, and adjust the α -resin standard against it rather than vice versa. Designate the α -resin color setting as *A*.

DETERMINATION OF PRESERVATIVE VALUE OF A HOP. Ten grams of ground hops and 100 cc. of methanol in a centrifuge bottle are shaken in a mechanical shaking machine for 15 to 20

minutes and centrifuged, and 1.0 cc. of clear extract is transferred to a 100-cc. flask, together with 10 cc. of 2.5 per cent uranyl nitrate solution and, after mixing, the flask is filled to the mark with methanol. The color is immediately compared to that of the same depth of 2.5 per cent ferric chloride as was used against the α -resin standard. (To economize on reagents one may use 0.5 cc. of hop extract plus 5 cc. of uranyl nitrate made to 50-cc. volume and obtain the same result.) Designate the color reading of the hop extract as *B*.

(In their broader interpretation the terms "preservative value" and "brewing value" are frequently used synonymously. In a strict sense "preservative value" is a measure of the inhibitory effect of the soft resins of hops on the growth of certain lactic acid-forming bacteria in beer or wort. The use of the formula $\alpha + \frac{\beta}{3}$ for "preservative value" in this paper does not necessarily

imply that it is the correct one, but that it furnishes as accurate a means as is at present available for the comparison of gravimetric and colorimetric data for soft resins of hops.)

CALCULATION OF PRESERVATIVE VALUE. Since the depth of ferric chloride solution is the same in both standardization and determination, it is eliminated from the calculation. The ratio of the setting for α -resin to the setting for an equal weight of hops then becomes $\frac{10A}{B}$, because 0.01 gram of resin per 100 cc. is compared to 0.1 gram of hops per 100 cc. and is comparable to Walker and Hastings' $\alpha + \frac{\beta}{3}$ derived from gravimetric data.

Or if it is wished to use $10\left(\alpha + \frac{\beta}{3}\right)$ as is commonly done to express the preservative value (*PV*) from gravimetric data, the equation for the corresponding colorimetric value becomes $PV = \frac{100A}{B}$.

To give an idea of the accuracy which may be expected of the colorimetric method in its present state of perfection, the data in Table V, calculated from both gravimetric and colorimetric determinations for 1936 crop Oregon-grown Fuggles and Late Cluster varieties of hops, are recorded.

TABLE V. ANALYSIS OF HOPS

Sample	Date of Analysis	α -Resin %	β -Resin %	$10\left(\alpha + \frac{\beta}{3}\right)$	Colorimetric $\frac{100A}{B}$	
Fuggles, 1936	10-19-36	3.98	7.94	66.3	65.3	
	10-7-36	4.32	8.32	70.9	74.7	
	10-19-36	4.10	7.82	67.1	68.3	
	10-7-36	3.83	8.44	66.4	75.6	
	10-19-36	4.26	7.74	68.4	76.3	
	10-19-36	3.98	7.65	65.3	76.3	
	10-19-36	4.70	8.47	75.2	80.9	
	10-7-36	4.49	8.35	72.7	78.1	
	11-4-36	4.81	8.09	75.1	85.5	
	11-4-36	4.59	8.03	72.7	89.3	
	11-20-36	3.93	7.87	65.5	71.5	
	11-20-36	3.81	7.66	63.6	71.6	
	11-20-36	4.22	8.10	69.2	75.6	
	11-20-36	4.15	7.89	67.8	71.9	
	11-20-36	3.81	7.62	63.5	67.0	
	11-20-36	3.94	7.03	62.8	74.7	
	11-27-36	4.58	7.13	69.6	88.9	
	11-27-36	5.02	6.64	72.3	92.6	
	Late Clusters, 1936	10-7-36	6.68	10.49	101.8	100.7
		10-29-36	6.25	11.25	100.0	118.3
10-7-36		6.94	11.18	106.7	108.7	
10-14-36		7.04	10.94	106.9	112.5	
10-29-36		6.37	11.17	100.8	103.1	
10-29-36		5.92	10.73	95.0	120.4	
10-29-36		6.92	11.08	106.1	110.4	
11-4-36		6.18	10.44	96.6	106.2	
11-4-36		5.77	10.67	93.3	100.0	
10-14-36		5.53	9.67	87.5	103.8	
11-4-36		5.43	9.37	87.5	105.2	
10-14-36		6.65	11.18	102.5	105.3	
10-14-36		6.74	11.34	105.2	111.5	
10-14-36		6.22	10.90	99.5	101.5	
11-17-36		6.34	10.84	99.5	112.3	
11-17-36		6.30	10.45	97.8	110.6	
11-17-36		4.44	10.16	78.3	93.2	
11-17-36		5.56	8.26	83.1	105.4	
11-17-36		7.05	10.95	107.0	118.2	
11-27-36		7.15	10.68	107.1	112.3	
11-27-36	6.32	10.01	96.6	99.2		
11-2-36	6.16	10.41	96.3	108.8		
12-9-36	6.40	10.35	98.5	99.2		
12-9-36	5.83	10.17	92.2	96.5		
12-9-36	7.04	10.66	105.9	103.7		
12-9-36	5.42	9.31	85.2	86.6		
12-9-36	5.23	9.12	82.7	89.9		
12-14-36	4.85	9.19	79.1	86.0		
12-14-36	4.75	8.89	73.8	85.5		
12-14-36	6.55	10.76	101.4	102.2		
12-14-36	6.75	10.85	103.7	103.1		
12-14-36	6.75	11.00	104.2	103.0		
12-21-36	6.19	10.79	97.9	110.6		
12-21-36	6.61	10.64	101.6	117.2		
12-21-36	6.80	11.10	105.0	115.4		
12-21-36	6.33	11.27	100.9	108.0		
12-21-36	6.98	11.41	107.8	116.2		

It requires no more than a glance at Table V to realize that the agreement between the two methods is in many cases far from satisfactory. Guthrie and Philip (3, 4) likewise obtained poorer correlation with the few Oregon hops they tested than with the English hops. In practically all instances the colorimetric result is higher than that obtained from the gravimetric method, although the reverse is true when compared to $10\left(\alpha + \frac{\beta}{3}\right)$ for most of the data published by other investigators.

Summary and Conclusions

A study of colorimetric methods proposed for determining the preservative value of hops suggests the need of some modification to make the methods suitable for application to Oregon-grown hops. Data relative to a number of controversial points are submitted and several minor changes are incorporated in the procedure as finally employed.

Comparison of results obtained by the method with those obtained from gravimetric analyses leads to the conclusion that the colorimetric method in its present form cannot be relied upon to yield a particularly accurate estimation of the preservative value of Oregon-grown hops. However, it is believed that its employment in conjunction with the commonly used physical tests offers a rapid and more accurate means of arriving at the quality of a hop than can be expected from physical examination alone. For exact data, the more tedious gravimetric methods are still to be preferred.

Literature Cited

- (1) Comrie, A. A. D., *J. Inst. Brewing*, 40, 420 (1934).
- (2) French, J. M., *Ibid.*, 37, 436 (1931).
- (3) Guthrie, J. M., and Philip, G. G., *Ibid.*, 36, 455 (1930).
- (4) *Ibid.*, 39, 220 (1933).
- (5) Hastings, J. J. H., and Walker, T. K., *Ibid.*, 34, 9 (1928).
- (6) Walker, T. K., and Hastings, J. J. H., *Ibid.*, 39, 509 (1933).

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Carotenoids in Yellow Corn

Quantitative Estimation from Modified Absorption Spectra Measurements of Carotenoids in Yellow Corn of Different Varieties and Qualities

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THERE are several pigments in yellow corn; all present to any extent may be classed as carotenoids. This classification includes hydrocarbons, alcohols, acids, and ketones. However, the three most important ones in corn are carotene, $C_{40}H_{56}$, a hydrocarbon, cryptoxanthin, $C_{40}H_{56}O$, and xanthophyll or zeaxanthin, $C_{40}H_{56}O_2$.

Early investigations pointed to a great difference in vitamin A content of white and yellow maize. Euler (1) limited the activity to the carotenes $C_{40}H_{56}$. The zeaxanthin, $C_{40}H_{56}O_2$, isolated by Karrer (3) was found to be completely without growth-promoting ability when fed to rats. Kuhn and Grundman (5) isolated cryptoxanthin, with the formula $C_{40}H_{56}O$, which does have growth-promoting ability.

The present work was undertaken in order to determine how carotene, cryptoxanthin, and xanthophyll contents might vary in different varieties of yellow corn; whether the ratio of carotene plus cryptoxanthin to xanthophyll content is constant; and how the carotenoid content differs between sound corn and damaged corn of the same variety. Since absorption spectra are the most important means of identification of these compounds, the method was adopted for these determinations.

Adaptation of Available Apparatus

The spectrograph available was a Bausch and Lomb medium-sized quartz spectrograph, fitted with a slit operated by a micrometer screw so that the slit width could be read directly in 0.01-mm. intervals and estimated to a micron. The procedure was to make a series of spectrograms, in which the slit width was decreased gradually, while the absorption cell filled with solvent was placed in the light path. This gave a set of reference spectra which could be used in evaluating intensities, I . The absorption cell was then emptied, filled with solution, and replaced in the light path, and the absorption spectrum was photographed. At this time the slit width

was usually equal to the maximum width employed in making the reference spectra. During a set of exposures all conditions were kept as constant as possible except for the variation of slit width. By putting such a series of reference spectra on each plate, any variation in general background fogging, variation in developing conditions, etc., would be without effect in interpretation of spectrograms.

The light source used in this work was an underwater spark described in a recent paper (2).

The most serviceable form of absorption cell was one whose body was a short length of 14-mm. Pyrex tubing with a side arm of 4-mm. Pyrex tubing and 60 mm. in length. The ends of the large Pyrex tubing were ground perpendicular to the longitudinal axis of the tubing. Plates of plane polished vitreous silica 1 mm. thick were then fixed on the open ends with molten silver chloride as adhesive. This cell had a length of 20.4 mm. between the inner surfaces of the silica plates.

Preparation of Samples for Analysis

The most satisfactory method for grinding the corn was with the use of a 20-cm. (8-inch) flint ball mill. A representative 50-gram sample was placed in the mill, and the air displaced by dropping in solid carbon dioxide and allowing it to vaporize. The sample was then ground for 12 to 20 hours, and the material screened with an 80-mesh screen. Alternate sieving and grinding of the coarse material were continued until the entire sample passed the sieve. The entire ground sample was then mixed, reweighed, and stored in carbon dioxide in the dark at 4° C. until used.

As carotenoid extraction was started, samples were weighed out equivalent to 10 grams of corn. Methanol was found most satisfactory to extract the color. Portions of methanol were added and centrifuged to facilitate removal of the liquid until extraction was complete. This usually required 120 cc., in five portions, per sample. Solid potassium hydroxide was added to the alcoholic extracts to make a 5 to 7 per cent solution. Saponification of any xanthophyll esters proceeded for 2 to 3 hours. Petroleum ether (low-boiling) was added to extract the carotenes and cryptoxanthin from the xanthophylls. The layers were separated and a fresh portion of petroleum ether was added.

This process was continued until extraction was complete. The combined petroleum ether fractions were then washed with 10 per cent potassium hydroxide-90 per cent methanol until any small amount of xanthophyll was removed. The petroleum ether fraction was then washed with water until the alkali was removed. The next steps were to evaporate the fraction to dryness in a vacuum desiccator at room temperature or lower to eliminate a possibility of an emulsion, and to add a given volume of petroleum ether (low-boiling) to the solid pigment. This solution containing the carotenes and the cryptoxanthin was then ready to use in production of an absorption spectrum.

Purification of the xanthophyll fraction was similar to that of the carotenes. The alkaline solution was diluted with two volumes of water, and cooled, and portions of diethyl ether were added and removed until no more color passed into the ether. The methanol-water layer, usually nearly colorless, was then discarded. The combined xanthophyll fraction was washed with water to free it of potassium hydroxide, and evaporated to dryness in a vacuum desicca-

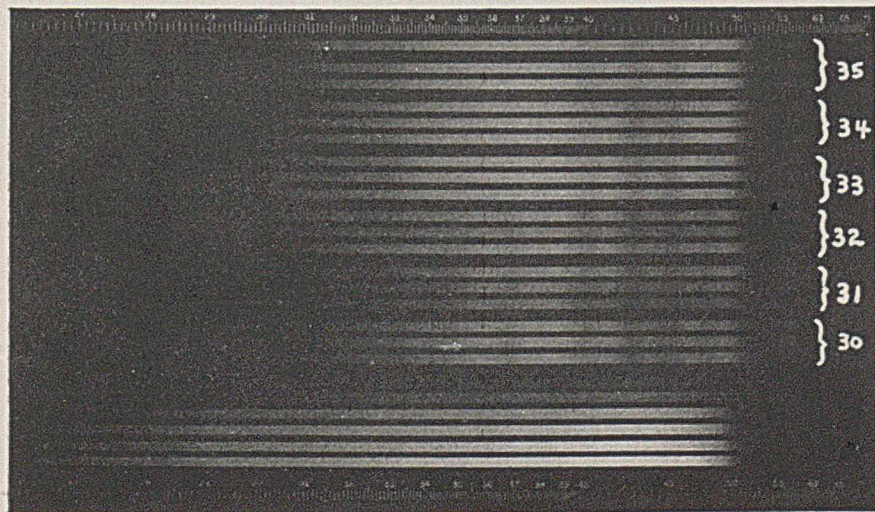


FIGURE 1. TYPICAL ABSORPTION SPECTRA OF CAROTENE-CRYPTOXANTHIN FRACTIONS IN YELLOW CORN

Standard continuous spectra (below) with varying slit widths (0.02 to 0.15 mm.)

tor; 95 per cent ethanol was added to dissolve the solid residue and the solutions were then ready for use in making an absorption spectrum.

The appropriately diluted solution was placed in the cell and duplicate or triplicate spectrographic exposures were made. Usually a solution representing the same sample was used at different concentrations in order to give a suitable spectrum.

TABLE I. RESULTS OF PHYSICAL TESTS

Variety	Pounds per Bushel	Per Cent of Cracked and Foreign Material	Per Cent by Weight of Damaged Corn	Number of Kernels per 100 Grams
Krug (sound)	58.4	0.150	2.03	461.8
Krug (damaged)	56.8	0.486	4.68	591.5
Funk Hybrid 214 (sound)	60.8	0.014	1.52	371.0
Funk Hybrid 214 (damaged)	58.4	0.081	9.07	515.0
Morgan 106 (sound)	59.7	0.239	3.46	322.6
Morgan 106 (damaged)	54.0	0.483	7.66	512.0
Indiana Hybrid 880 (sound)	58.57	0.453	0.24	810.0
Indiana Hybrid 880 (damaged)	42.39	0.268	55.95	750.0

Figure 1 is a print of the absorption spectra of the carotene fractions of Indiana Hybrid 880, together with a series of "standard" spectrograms.

Interpretation of Spectrograms

To interpret the spectrograms, relative intensities of the standard spectrograms and of the absorption spectrograms at a desired wave length must be measured accurately. For this purpose a microphotometer was employed. In using this instrument the spectrographic plate is conveyed transversely across the spectrograms at a uniform rate while perpendicular to a light beam which, after transmission through the plate, is focused on a thermopile. Variations in the intensity of the beam incident on the thermopile cause an electromotive force of corresponding variations to be produced, which is recorded by a light reflected from the swinging mirror of a sensitive galvanometer. Since the variations in the light incident on the thermopile are caused by differences in blackening of the photographic emulsion on the spectrographic plate, the microphotometer trace can then be correlated with intensities of the spectrogram.

Figure 2 is a reproduction of microphotometer traces of the absorption spectrograms of the carotene-cryptoxanthin fractions of Indiana Hybrid 880, sound corn; and of standard reference spectra for different slit widths of the spectrograph photographed on the same plate. The *b*-level is used as a base line for making other measurements. Tracings at the *b*-level were made when there was no light whatever falling on the microphotometer thermopile, and correspond to the rest point of the galvanometer. The *f*-level is reached while the light is passing through a region of general fogging (background) on the spectrographic plate. The *s*-level is produced while a spectrogram is intercepting the light beam directed onto the thermopile of the microphotometer. Except for adjustments made on the microphotometer, the *b*-level and *f*-level should remain practically constant. The *f*-level will be changed if there is a change in the amperage passing through the illuminating bulb. This current is supplied by storage batteries to increase its constancy. Variations in the *s*-level then correspond to variations in blackening of the spectrograms. The distances *s* to *f* and *b* to *f* were measured directly from the microphotometer traces. The ratio $(s-f)/(b-f)$ was then calculated in all cases. The less absorption the higher will be this ratio and vice versa. In order to correlate this ratio with actual light

intensities, the standard reference spectra were employed. The standard spectrogram produced with the same maximum slit width (0.15 mm.) as was used for all the absorption spectrograms, was assigned an arbitrary I_0 (initial intensity) value of 10; others photographed with narrower slits were assigned correspondingly smaller I_0 values, as, for example, $0.06/0.15 \times 10$ for the 0.06-mm. slit width.

Figure 3 shows a plot as obtained from data of the microphotometer traces shown in Figure 2 (standard spectrograms). From this curve, the value of the intensity, *I*, corresponding to a ratio of $(s-f)/(b-f)$ measured for an absorption spectrogram of an unknown can be evaluated at once. Then values for $\log I_0$ (where I_0 is usually 10) and $\log I$ can be obtained and substituted in the formula $\log I_0 - \log I = ksc$, where *k* is the extinction coefficient, *s* is the cell thickness, and *c* is the concentration of the solution. If the absorption spectrogram corresponds to a solution of known concentration, *c*, the extinction coefficient, *k*, can be determined; if *k* is known, *c* can be calculated if the spectrogram is of an unknown.

Experimental Calculation and Results

All the samples with the exception of one, a white corn sample, were supplied by George Dungan of the University of Illinois Agronomy Department. In Table I are listed the results of physical tests on these specimens. Absorption spectra were also made of solutions of α -carotene, β -carotene, and xanthophyll, which were purchased ready prepared, in order to determine values of *k*, the extinction coefficient, at any wave length desired.

The following positions of maximum absorption were determined (corrected wave lengths):

α -Carotene	$\lambda\lambda 4730, 4440, 4240, 2660 \text{ \AA.}$
β -Carotene	4820, 4490, 4240, 2700
Xanthophyll (leaf)	4730, 4430, 4200

These data compare favorably with those of other investigators. Corn xanthophyll (zeaxanthin) and cryptoxanthin in benzene apparently both have absorption bands at $\lambda\lambda 4850$ and 4530 \AA.

The wave length 4500 \AA. was found to be the most suitable in the carotene spectrum to determine the extinction coefficient.

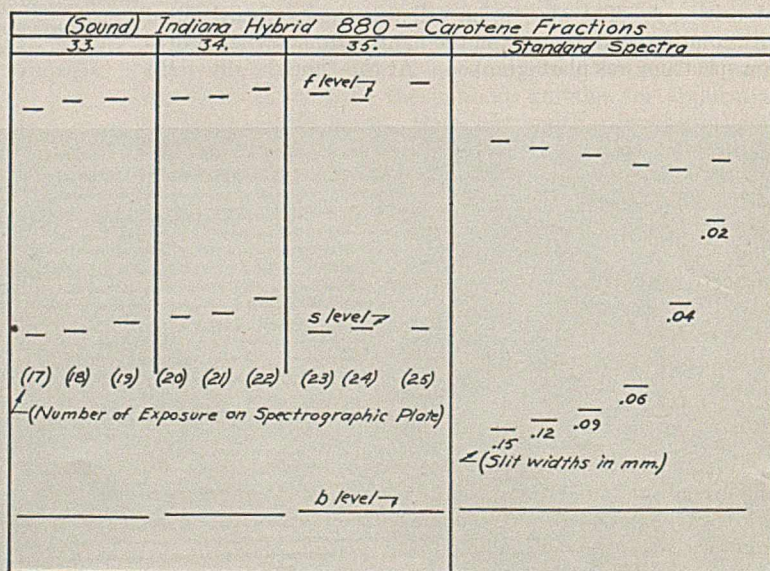


FIGURE 2. MICROPHOTOMETER TRACES OF SPECTRUM INTENSITIES LEADING TO DIRECT MEASUREMENT OF RATIO $(s-f)/(b-f)$

b, base line. *f*, general background fogging. *s*, blackening of photographic emulsion across spectrogram
Left, typical absorption spectra (Figure 1) of carotene-cryptoxanthin fractions. Right, standard spectra at various slit widths (*s*-levels)

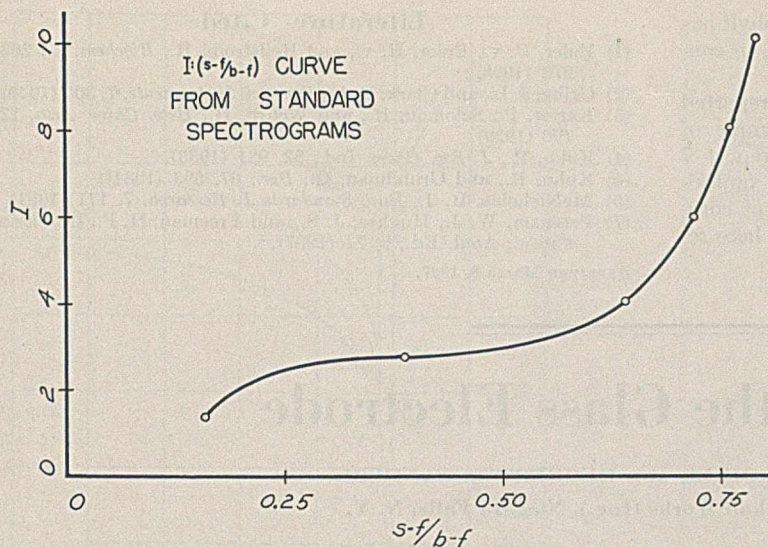


FIGURE 3. CURVE OBTAINED BY PLOTTING $(s-f)/(b-f)$ VALUES MEASURED FOR STANDARD SPECTRA IN FIGURE 2, AGAINST INTENSITIES AS A FUNCTION OF SLIT WIDTH

I for maximum width used for absorption spectra is arbitrarily given value 10. From this curve I values are determined for absorption spectra of unknowns.

cient and make subsequent measurements on absorption spectra. In the formula, $\log I_0 - \log I = ksc$, it was found most convenient to have k evaluated when s , cell thickness, was expressed in millimeters and c , concentration, in gamma (gamma = 10^{-6} gram) per cubic centimeter. Thus k for β -carotene at $\lambda 4500 \pm 10 \text{ \AA}$. was found equal to 2.1×10^{-2} ; k for xanthophyll at $\lambda 4500 \pm 10 \text{ \AA}$. was 6.4×10^{-3} . New values for extinction coefficients for β -carotene have been published recently by Peterson, Hughes, and Freeman (?).

The averaged results of quantities are tabulated in Table II. In these calculations the extinction coefficient for carotene is used for the petroleum-phasic fraction containing both carotene and cryptoxanthin since the coefficient for the latter is not known.

The carotene-cryptoxanthin fraction of a sample of Indiana Hybrid 880 sound corn was chosen for purposes of illustrating the method of calculation. A print of the absorption spectrum of this particular sample is shown as No. 35 in Figure 1. Figure 2 shows the microphotometer trace made across this plate at $\lambda 4500 \text{ \AA}$. Figure 3 shows a graph of the ratio $I:(s-f)/(b-f)$ as obtained from this same microphotometer trace of the "standard" spectrograms. Measurements of the three traces from absorption spectrograms of sample 35 give $(s-f)/(b-f)$ values of 0.57, 0.55, and 0.57. These are evaluated in terms of I from the graph shown in Figure 3. Then values for $(\log I_0 - \log I)$ are obtained equal to 0.48, 0.49, and 0.48, respectively. Substituting the value of k as 2.1×10^{-2} , and s as 20.4, and v as 10 cc. in $\log I_0 - \log I = ksc/v$, values of 11.3, 11.6, and 11.3 gamma per 10 grams of corn are obtained, giving an average result of 11.4 for the three analyses of this sample.

Conclusions

An inspection of column 2, Table II, shows that with the one exception of Krug corn, more carotene (and cryptoxanthin) was obtained from the damaged samples of corn than from the corresponding sound varieties. This result was quite unexpected. The same is found to hold true for the xanthophyll content. This led to a calculation of the ratio of carotene content to xanthophyll content, which result is shown in column 4. In every case there is a definitely higher ratio in the tests on the sound corn, which would indicate, as would be expected, that there is an oxidation of carotene as

decay takes place. An examination of carotenoids previously listed would indicate that an oxidation of carotene would not be unexpected. In fact, numerous investigators have taken precautions to keep their carotene from being oxidized. McNicholas (6) shows that there is only a slight change within a period of 55 days.

Why there should be more carotenoids from the damaged corn than from the sound is without good explanation. To investigate the possibility of a modified cell structure which allowed more complete extraction in the former case, a portion of the extracted residues was examined under a microscope and no evidence of color could be seen in any case. A similar examination of the unextracted sample easily disclosed highly pigmented particles. As another check, a sample extracted according to the method described was placed in a small steel ball mill and ground while under alcohol. The alcohol was found colorless when centrifuged from the solid residue. Extended extraction of other samples for a period of a week yielded no more carotenoids. Therefore, it seems that there are actually more carotenoids in the damaged corn. Possibly a synthesis of carotenoids is aided by conditions of decay. Kuhn (4) states that when tomatoes are plucked green and allowed to ripen, the carotenoid content increases to a value greater than would be obtained from a simple direct combination of any molecules already present at the time of picking. This indicates a synthesis within the fruit itself, when isolated from the plant.

A comparison of one variety with another indicates that the contents are not at all constant. The authors have also made a few isolated analyses on very fresh corn from which more carotenoids could be extracted than from the samples used in this set, all of which were more than one year old at the time of analysis. Therefore, the interval of time between harvesting and testing is another factor to be considered.

All of the samples, with the exception of the Krug sample, were of hybrids, whose properties are often erratic.

TABLE II. AVERAGED RESULTS

Variety	Petroleum-Phasic Fraction (Carotene-Cryptoxanthin)		Ratio 1:2	Ratio 2:1
	Xanthophyll Content (1)	Xanthophyll Content (2)		
	Gamma per 10 grams of corn			
Krug (sound)	7.2	240	0.030	33.3
Krug (damaged)	4.0	200	0.020	50.0
Funk Hybrid 214 (sound)	3.3	50	0.066	15.0
Funk Hybrid 214 (damaged)	5.7	130	0.044	22.8
Morgan 106 (sound)	1.0	22	0.045	22.0
Morgan 106 (damaged)	4.3	190	0.023	44.2
Illinois Hybrid 168 (sound)	1.4	97	0.014	69.2
Indiana Hybrid 880 (sound)	11.1	330	0.034	29.7
Indiana Hybrid 880 (damaged)	11.3	640	0.018	56.7
A white corn	None	None

Attention should also be called to the fact that the carotenoids are distributed near the surface of corn kernels. Therefore, the greater the surface area, the greater the quantity of carotenoids to be expected. A comparison of grain size with carotenoid content shows an inverse ratio holding true with the exception of the Krug variety.

The ratio of xanthophyll content to carotene content, as shown in Table II, indicates the overwhelming preponderance

of xanthophyll. This is of interest because xanthophyll has been shown to be without growth-promoting ability, in contrast to carotene.

One other set of analyses on carotenoids in corn is reported by Kuhn and Grundman (5), who analyzed a sample of Italian corn and two of Hungarian corn. They report 7 gamma or less of carotene present per 10 grams and xanthophyll contents of 170 to 210 gamma per 10 grams of corn, which is in satisfactory concordance with the results here reported.

Literature Cited

- (1) Euler, B. v., Euler, H. v., and Hellström, H., *Biochem. Z.*, **203**, 270 (1928).
- (2) Gring, J. L., and Clark, G. L., *Rev. Sci. Instruments*, **7**, 305 (1936).
- (3) Karrer, P., Salomon, H., and Wehrli, H., *Helv. Chim. Acta*, **12**, 790 (1929).
- (4) Kuhn, R., *J. Soc. Chem. Ind.*, **52**, 981 (1933).
- (5) Kuhn, R., and Grundman, C., *Ber.*, **67**, 593 (1934).
- (6) McNicholas, H. J., *Bur. Standards J. Research*, **7**, 171 (1931).
- (7) Peterson, W. J., Hughes, J. S., and Freeman, H. F., *IND. ENG. CHEM., Anal. Ed.*, **9**, 71 (1937).

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Errors of the Glass Electrode

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It has been found that at temperatures above 30° C. the glass electrode is not in agreement with the hydrogen electrode, exhibiting deviations not only in the alkaline but also in the neutral and acid ranges. The magnitude of these deviations is greatly influenced by temperature changes and by the sodium-ion concentration. These departures are entirely reproducible, however, and correction curves have been furnished for use with two commercial types of glass electrode. The theory of these errors is briefly reviewed.

MOST of the pioneer work on the behavior of the glass electrode stressed its usefulness rather than its limitations. When it became increasingly obvious that deviations from ideal behavior were occurring in alkaline solution, attention was turned in this direction. Of the large number of investigations on the so-called "alkaline errors," that of Dole (3) is the most complete. Even this was not carried out under those extreme conditions which are so often encountered in industrial work, and it became desirable to learn the limitations of the electrode as a research and control tool in working with saturated sodium chloride solutions at room temperatures and higher.

Experimental Procedure

Since the object of this work was essentially practical—viz., to provide a set of correction curves for use with glass electrodes in industrial applications—it was thought best to use standard commercial equipment in the study.

Two types of commercial apparatus were used. One was a Leeds & Northrup No. 7685 glass-bulb type of electrode, made from Corning 015 glass of the approximate composition Na₂O 22 per cent, CaO 6.0 per cent, and SiO₂ 72 per cent. The diameters of the bulbs were 24 ± 2 mm., and the thickness was 0.025 to 0.06 mm. They were on a stem 125 mm. long and 16 mm. in diameter. Their low resistivity (about 8 megohms) enables measurements to be made with a fairly sensitive galvanometer and a potentiometer. This is especially true above room temperature, for the resistivity of the glass falls rapidly as its temperature rises. For the inner reference electrode a special form of quinhydrone electrode is supplied, and its tip is immersed in a hydrochloric acid solution of pH 1.00. Measurements were

also made with a commercial vacuum-tube outfit known as the Coleman pH electrometer, which is equipped with special glass electrodes, having as inner reference a Pb-PbCl₂ electrode in 0.2 N hydrochloric acid. The glass electrodes with this equipment had a glass bulb 18 ± 2 mm. in diameter made of the same type of glass. These electrodes have a resistance between 75 and 120 megohms.

Two Leeds & Northrup and three Coleman electrodes were used in the same solution. The average correction for each type of electrode was determined.

All measurements were made under equilibrium conditions in an oil bath with the temperature constant to ±0.1° C.

The solutions measured were buffers of constant sodium-ion content (and, in one case, of potassium-ion), since this was the factor of most interest here. The actual system used was as follows:

A 0.1 N solution of "Prideaux-Ward universal buffer" (1) was made up with a certain concentration of sodium chloride. To this was added 0.2 M sodium hydroxide containing the same concentration of sodium chloride. In this way the sodium-ion content was maintained constant as the pH increased. The value of the pH after 5 cc., 10 cc., etc., of base had been added was found in a separate hydrogen-electrode experiment. In this way the pH as found by the glass electrode in such a solution can be compared with that given by the hydrogen electrode. Such comparisons were carried out, and correction curves plotted, at 30°, 50°, 60°, and 65° C., and in buffers 0.5, 2.0, and 5.0 M in sodium chloride (and also 0.2 M in potassium chloride for 30° C.). In experiments with 5.0 M sodium chloride phenylacetic acid was "salted out" from the universal buffer; so it was replaced by acetic acid, which has almost the same dissociation constant.

In order to take account of the drift in the electrode systems, the electrodes were calibrated each day in a 0.5 M potassium acid phthalate solution at the temperature under investigation. The

TABLE I. EXPERIMENTAL RESULTS

(Leeds & Northrup electrodes in 5.0 M sodium ion at 30° C.)

True pH	Mean Observed pH	L1 Correction	L2 Correction	Mean Correction
1.04	1.07	-0.03	-0.03	-0.03
1.36	1.40	-0.06	-0.02	-0.04
2.16	2.10	-0.01	+0.12	+0.06
3.87	3.88	-0.03	+0.02	-0.01
4.57	4.55	+0.01	+0.03	+0.02
5.16	5.12	+0.03	+0.05	+0.04
7.38	7.30	+0.06	+0.11	+0.08
9.03	8.72	+0.28	+0.34	+0.31
11.20	9.76	+1.40	+1.48	+1.44
Check Run				
1.04	1.09	-0.05	-0.05	-0.05
1.36	1.41	-0.04	-0.07	-0.05
3.87	3.88	-0.01	-0.02	-0.01
7.38	7.31	+0.08	+0.07	+0.07
9.03	8.72	+0.31	+0.32	+0.31
11.55	9.79	+1.74	+1.79	+1.76

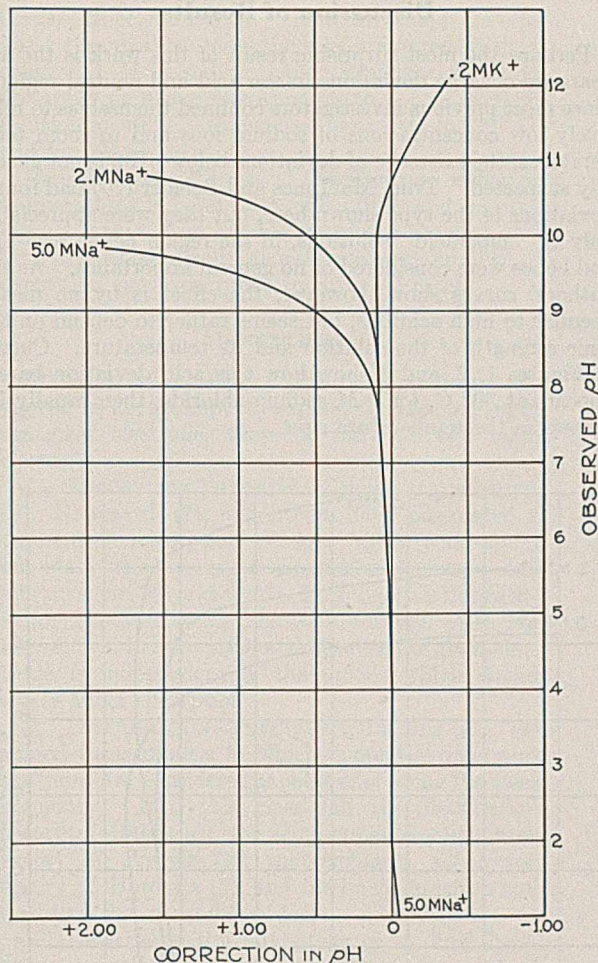


FIGURE 1. LEEDS & NORTHRUP ELECTRODE CORRECTIONS UNDER CONSTANT-TEMPERATURE CONDITIONS AT 30° C.

Add correction to observed pH as found from Leeds & Northrup tables or graph in Figure 6.

pH of this solution was 3.97 at 30° C., 4.00 at 50° C., and 4.02 at 60° and 65° C. The Coleman electrometer is adjustable, so that the dial would read correctly in the biphthalate solution. The potential of a Leeds & Northrup electrode was measured and converted to pH by means of a chart (Figure 6) based on Leeds & Northrup tables. Any difference between this and the correct pH was added to subsequent determinations. This method of calibration takes care of errors of the inner electrodes or the calomel half-cell. The temperature of the calomel half-cell is immaterial, so long as it is constant, because the thermal e. m. f. in the salt bridge was found to be reproducible.

Experimental Results

On account of the large number of readings involved it is not practical to present results in tabular form, but Table I is given in order to show the order of reproducibility to be expected.

Figures 1, 2, and 3 give the corrections for the Leeds & Northrup electrodes. Figures 4 and 5 give the corrections for the Coleman electrodes. Figure 6 is an extrapolation of the Leeds & Northrup conversion tables for the glass electrode. These graphs are constructed from averaged data, and individual electrodes may show small departures from them. Deviations up to 0.05 pH unit are not considered serious, since industrial requirements rarely exceed an accuracy of 0.1 pH unit. These correction curves apply only to measurements made after equilibrium has been reached. In some cases—e. g., 5.0 M sodium ions at 50° C.—initial equilibrium

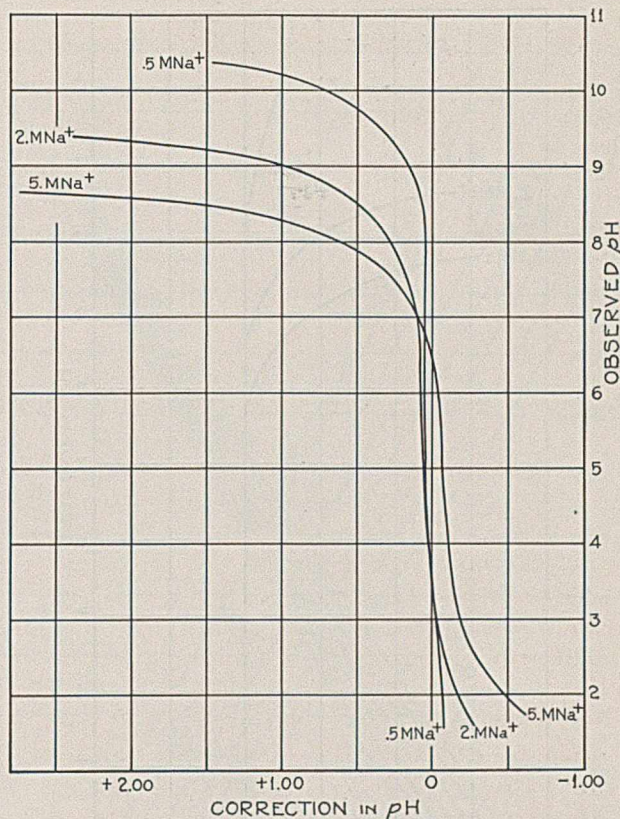


FIGURE 2. LEEDS & NORTHRUP ELECTRODE CORRECTIONS UNDER CONSTANT-TEMPERATURE CONDITIONS AT 50° C.

Add correction to observed pH as found from Leeds & Northrup tables or graph in Figure 6.

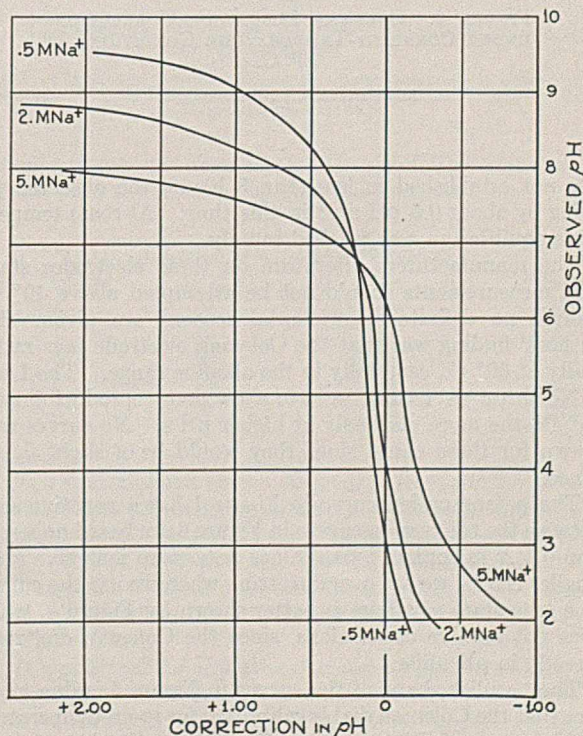


FIGURE 3. LEEDS & NORTHRUP ELECTRODE CORRECTIONS UNDER CONSTANT-TEMPERATURE CONDITIONS AT 60° C.

Add correction to observed pH as found from Leeds & Northrup tables or graph in Figure 6.

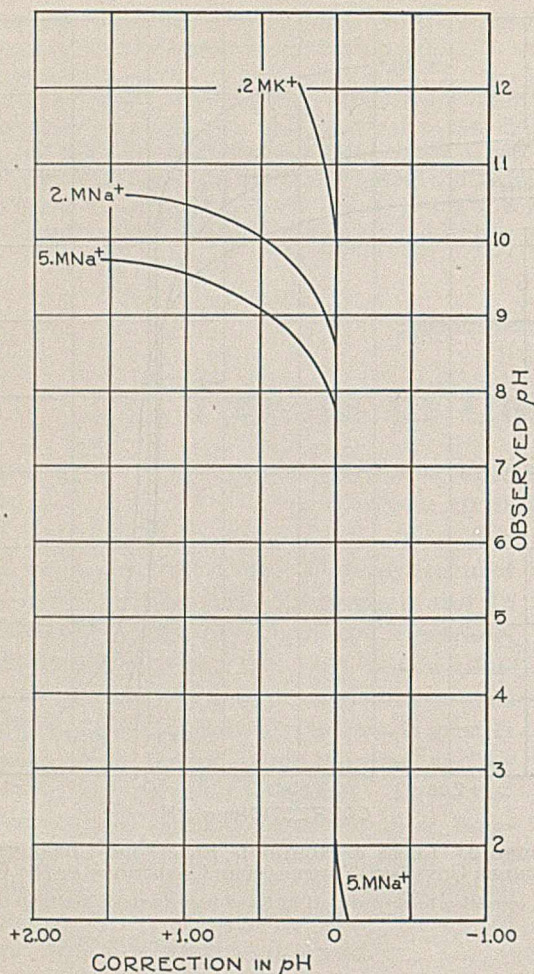


FIGURE 4. COLEMAN ELECTRODE CORRECTIONS UNDER CONSTANT-TEMPERATURE CONDITIONS AT 30° C.

Add correction to observed pH.

was not established in less than 3 hours, the observed pH rising by about 0.5 pH unit in this time. At room temperatures equilibrium was reached rapidly.

The manufacturers' literature on these electrodes states that measurements should not be attempted above 40° C., though no definite experimental reasons are given. The authors' finding was that the Coleman electrode fails rather badly at 60° C., especially in the alkaline range. The Leeds & Northrup electrodes begin to show poor reproducibility at 65° C., the more markedly at higher pH's. No curves were drawn for these cases, since they would be of slight significance.

The potassium-ion curve in Figure 1 has a negative slope because the conversion curves in Figure 6 are based on a solution 0.1 *N* in sodium ions. Since potassium ions give much smaller errors, we are overcorrecting when we use the curves. The true state of affairs is better shown by Figure 4, which does not involve conversions, since the Coleman dial reads directly in pH units.

The peculiar shape of the curves in Figure 5 is due to the fact that the Coleman dial is calibrated for room temperature, and hence an additional source of error is involved in measurements at 50° C. These curves apply only if the calibrating solution is about pH 4.00, as with the authors' biphthalate solution.

Discussion of Results

Perhaps the most surprising result of this work is the appearance of large deviations in the acid and neutral regions. Since most previous investigators confined themselves to relatively low concentrations of sodium ions and to room temperatures, the existence of deviations below pH 9 is not generally suspected. True, MacInnes and Belcher (10) had found deviations of the type shown here, but they were appreciable only in "superacid" solutions, in the region below zero pH, and hence were considered of no general importance. As the authors' curves show, however, the effect is by no means peculiar to high acidities, but seems rather to depend on the ionic strength of the solution and its temperature. Curves in Figures 1, 2, and 3 show how this acid deviation barely appears at 30° C. for 5 *M* sodium chloride, then rapidly increases as the temperature rises.

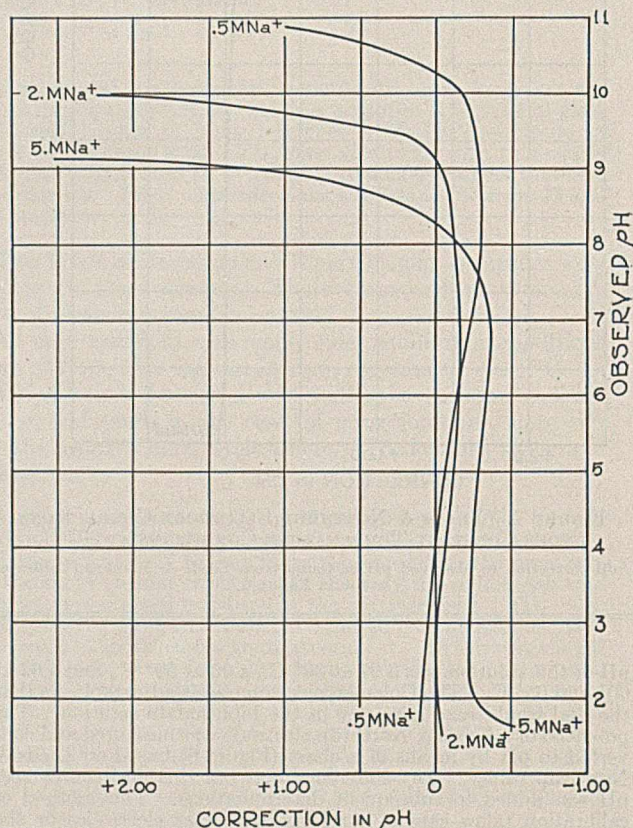


FIGURE 5. COLEMAN ELECTRODE CORRECTIONS UNDER CONSTANT-TEMPERATURE CONDITIONS AT 50° C.

Add correction to observed pH.

The alkaline errors have been recognized for several years, but their rapid increase with temperature has apparently never been studied. At 60° C. the error begins about pH 5 and the curves are so steep as to preclude any measurements above a true pH of 10. In all the cases studied (except 0.2 *N* potassium) measurements above pH 12 were not practicable. This would seem to rule the glass electrode out of consideration as an instrument for use in highly alkaline solution. It was found that at pH 11.0 at 50° C. the potential of the glass was independent of the pH, but changed linearly with the pNa of the solution. Thus the hydrogen-electrode function of the glass is destroyed at a lower pH, the higher the temperature and the higher the sodium-ion concentration.

This work indicates the necessity for a greater number of correction curves. Although we have the corrections for

0.5 M, 2 M, and 5 M sodium we would have to guess the alkaline corrections if presented with a solution 1 M in sodium ions. Similarly, we could not apply an accurate correction to a 5 M sodium solution at 40° C., though we have data for 30° C. and for 50° C.

In brief, then, the use of the electrode at higher temperatures is beset with difficulties, and necessitates a rather exact knowledge of the amount and kind of cations present, as well as a large number of correction curves in order to cover all cases.

Theoretical

Although a variety of theories has been advanced in an attempt to explain the mechanism of the glass electrode, these all fall into two main classes:

1. ADSORPTION THEORIES. Schiller (11), Lengyel (9), Haugaard (?), and others have postulated a differential adsorption of ions at a solid-liquid boundary which causes a separation of charges and sets up a sort of condenser. This theory is not satisfactory because ionic migration through glass has been shown to take place and because the glass electrode is independent of the anions which would surely affect adsorption.

2. DISTRIBUTION THEORIES. In this are included those models in which "potential-determining" ions are considered capable of crossing the glass boundary. Into this class fall the distribution theory of Haber (6), the semipermeable membrane theory of Cremer (2), the exchange adsorption theory of Horovitz (3), and the liquid-junction and quantum theory models of Dole.

All these have the advantage of lending themselves to rational thermodynamic treatment, and seem in many respects much more satisfactory than the rather vague adsorption theories. The general idea underlying them is that only those ions that can actually pass to and fro across the boundary play any part in determining the potential.

A number of workers have attempted a mathematical treatment of the alkaline error of the glass electrode, but the present discussion is limited to Dole's results, since the others are similar in form.

Starting with the idea that the glass-electrode potential is due to the fact that certain ions (hydrogen and sodium) can pass from energy levels in the glass to other levels in the solution across a potential barrier, thus setting up a distribution potential, Dole (5) has applied statistical mechanics to the problem and found the following expression for the error of the glass electrode in alkaline solutions containing sodium ions:

$$E = \frac{RT}{F} \ln \frac{C_{H^+} + C_{Na^+} e^{\frac{-A}{RT}}}{C_{H^+}} \quad (1)$$

where A was at first supposed to be a constant related to the energies of the lowest quantum levels of hydrogen or sodium ions on the glass surface.

Equation 1 may be rearranged into the form

$$\text{Log} \left(e^{\frac{FE}{RT}} - 1 \right) = \text{log} C_{Na^+} \cdot e^{\frac{-A}{RT}} + \text{pH} \quad (2)$$

By plotting the left-hand side of this equation against pH, a straight line with unit slope should result. Dole (4) tested this for a number of solutions and found that the slopes of the lines were less than unity, so concluded that A is not a con-

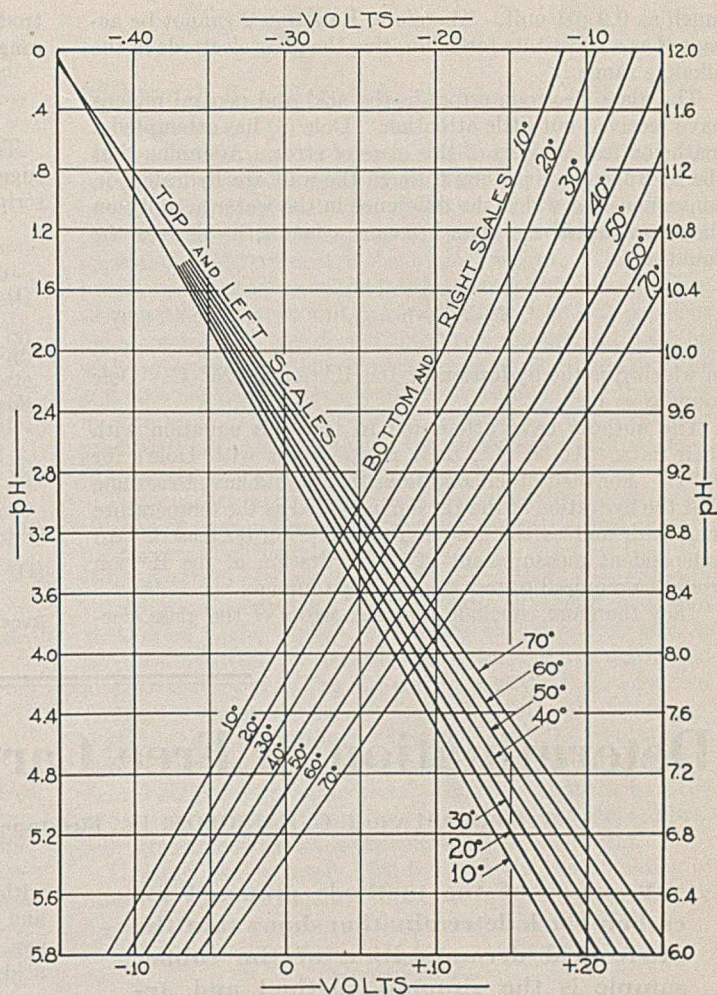


FIGURE 6. CONVERSION OF GLASS ELECTRODE-SATURATED CALOMEL VOLTAGES TO pH

Both electrodes at same temperature. When the calomel electrode is negative, the voltage is negative. Drawn and extrapolated from the pamphlet "Leeds & Northrup Standard 1203 2-1133."

stant but depends on the pH. He also found that the slope of the lines varied with the Na⁺-ion concentration.

TABLE II. ALKALINE ERROR

NaCl Molarity	T ° C.	A	Slope
2.0	30	35340	0.552
5.0	30	29700	0.440
0.5	50	32500	0.533
2.0	50	33000	0.533
5.0	50	33800	0.533
0.5	60	21800	0.404
2.0	60	24270	0.404
3.0	60	24900	0.404

The authors have plotted their data from pH 7.5 to pH 11 for the Leeds & Northrup electrodes in this form and obtained straight lines. However, they found that the slope of the lines did not vary with the Na⁺-ion concentration, but at 50° and 60° C. the slope was characteristic of the temperature. The values for A were not constant. This is shown in Table II.

It was hoped the Equation 2 could be used to calculate the temperature coefficient of the alkaline error. In Table II, the values for the slope and A appear to be characteristic of the temperature at 50° and 60° but show no agreement at 30° C. The authors tried to use the average of values of the slope and A to calculate the alkaline error at pH 10. The difference between the observed and calculated values was as

much as 0.9 pH unit. Therefore, Equation 2 cannot be accepted as a substitute for calibrating the glass electrode in the alkaline range.

The glass electrode errors in the acid and neutral regions have received but little attention. Dole (4) has attempted a mathematical analysis of this class of error. Assuming that the hydrogen ions passing through the wall are hydrated, in consequence of which the difference in the water activity on the two sides of the glass becomes a factor, he derives the equation

$$E = S \frac{RT}{F} \ln a_{H^+} \quad (3)$$

in which S is the hydration of the H^+ ion at 25° C. Dole found $S = 1$.

The authors have attempted to test this equation with their data. At 30° C., their results agree with Dole's for 25° C. For their other conditions they would have to assume that the hydration of the H^+ ion increased as the temperature increased, and as the Na^+ ion and H^+ ion decreased. An independent measurement of the hydration of the H^+ ion would be required to test this equation further.

They therefore conclude that the errors of the glass elec-

trode cannot yet be calculated with sufficient precision for all ranges within which the glass electrode is a useful tool.

Acknowledgment

The authors are indebted to Malcolm Dole for helpful suggestions in the early stages of the preparation of the manuscript.

Literature Cited

- (1) Britton, H. T. S., and Robinson, R. A., *J. Chem. Soc.*, 1931, 458.
- (2) Cremer, M., *Z. Biol.*, 47, 562 (1906).
- (3) Dole, M., *J. Am. Chem. Soc.*, 53, 4260 (1931).
- (4) *Ibid.*, 54, 3095 (1932).
- (5) Dole, M., *J. Chem. Phys.*, 2, 862 (1934).
- (6) Haber, F., and Klemensiewicz, Z., *Z. physik. Chem.*, 67, 385 (1909).
- (7) Haugaard, G., *Ibid.*, 160, 279 (1932).
- (8) Horovitz, K., *Z. Physik*, 15, 369 (1923).
- (9) Lengyel, B., *Z. physik. Chem.*, 154, 371 (1931).
- (10) MacInnes, D. A., and Belcher, D., *J. Am. Chem. Soc.*, 53, 3315 (1931).
- (11) Schiller, H., *Ann. Physik*, 74, 105 (1924).

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Determination of Free Carbon in Rubber Goods

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A survey of the methods proposed for carbon black determination shows that the nitric acid decomposition of the rubber sample is the simplest method and accurate enough for technical purposes.

The following improvements upon this method are recommended: decreasing the size of the sample; omitting the preliminary extraction of the sample; using an intermediate wash of acetic acid, acetone, and chloroform between the nitric acid and acetone and chloroform; and correcting the results when clay is present.

THIS paper is presented with the aim of rendering more accurate and simple the difficult analytical determination of carbon black in rubber.

A survey of the methods proposed for this determination reveals that they are not as short, easy, or accurate as might be desired. Smith and Epstein (5) have discussed what is probably the most widely used method, nitric acid decomposition of the rubber sample. In its essentials, this is the method recommended to the AMERICAN CHEMICAL SOCIETY in 1922 by the Committee on Methods of Analysis of the Rubber Division (1), and was recommended (6) to German chemists with the variation of making the filtration through hardened filter paper. Another variation, recommended by the Research Association of British Rubber Manufacturers (2), calls for filtration through a thick layer of kieselguhr, using carbon tetrachloride in the nitric acid. In addition, two unique methods have been recommended (4), which call, respectively, for decomposition of the sample in hot molten paraffin

with subsequent centrifuging of benzene and ether solutions and for distillation of the rubber in an atmosphere of nitrogen. The consensus of opinion seems to be that the nitric acid decomposition is the simplest method and accurate enough for technical purposes. This paper will be confined to improvements upon this method.

Procedure

Weigh samples of such size that the amount of carbon black does not greatly exceed 75 mg. and place in a 250-cc. beaker. Add 10 to 15 cc. of concentrated nitric acid and allow to stand at approximately 60° C. until the rubber is disintegrated. Add 50 cc. more of concentrated nitric acid, taking care to wash down the sides of the beaker, and heat on the steam bath for 1 hour. Filter before it is cool with moderate suction through ignited Gooch crucibles having a medium layer of asbestos, and wash well with hot concentrated nitric acid. It is essential that all the black be rinsed from the beaker at this stage. Turn off the suction when the carbon in the crucible is still covered with a small amount of the last nitric acid wash.

Empty the filter flask (this is important), pour into the crucible a hot mixture of equal parts of acetic acid, acetone, and chloroform, and continue the filtration. Wash the black with a warm 50-50 mixture of acetone and chloroform until the filtrate is colorless. Wash with hot 10 per cent sodium hydroxide until three washings have come through colorless. Wash three times with 15 per cent by volume of hot hydrochloric acid and once with 5 per cent by volume of warm hydrochloric acid. Remove the crucibles and clean the outside with a cloth moistened with the acetone-chloroform mixture. Dry in the 110° C. oven for 2 hours. Cool in a desiccator and weigh rapidly. Burn off the carbon and reweigh. The difference in weight, corrected for clay if present, represents approximately 105 per cent of the carbon black originally present. To obtain the correction factor for clay, multiply the amount of clay present in the sample by 14 per cent, or multiply the sum of SiO_2 and R_2O_3 weights in the sample by 16.3 per cent, and subtract this figure from the total ignition loss.

It seems to be important that the carbon black should not dry during filtration. Drying in the nitric acid wash seems

to pack the layer of carbon and thus slow the filtration. Small particles of black will not be retained on the filter if the nitric acid is completely filtered through before the addition of the acetone-acetic acid-chloroform mixture. Drying of the black during the later washings seems to have no effect beyond reducing the effectiveness of the wash solutions.

Discussion

It has been the authors' experience that when more than 75 mg. of carbon black are to be filtered from a nitrated rubber solution, the filtration usually becomes extremely slow. Rubber goods, as, for instance, tread stocks (3), now contain increased amounts of carbon black as compared with those used when the nitric acid method was first devised. Therefore, in the analysis of stocks containing over 15 per cent black, the authors recommend the use of a sample smaller than the 0.5 gram originally specified. For rapid determinations on tread stocks containing in the neighborhood of 30 per cent black, the sample size should not exceed 0.25 gram.

The standard practice of extracting samples with acetone and chloroform is unnecessary. This is shown by analyses of the same tread stock extracted and not extracted:

	Carbon Black %		Carbon Black %
Extracted sample	31.28	Unextracted sample	31.28
	31.12		31.32
	31.72		31.28

In the change of wash solutions from hot nitric acid to acetone and chloroform, small particles of black are frequently lost, acetone having a more detrimental effect than the mixture of acetone and chloroform. Whether this difficulty is encountered because of the wetting tendency of acetone or because of the charge upon the particles is not known. The authors' experiments have shown that an intermediate wash of equal parts of acetone, chloroform, and acetic acid has less tendency to disperse the black than immediate washing with either acetone or acetone and chloroform, as recommended in prior methods.

A common type of rubber stock for mechanical goods is a carbon black-clay mix. Clays have an ignition loss and give too high a value to the carbon black determination of such a stock. The Committee on Methods of Analysis of the Rubber Division of the AMERICAN CHEMICAL SOCIETY has recommended (1) treating the clay residue with sodium hydroxide. The authors have found that such treatment is futile. An analysis of an average clay showed that 85 per cent was insoluble in alkali, and the component showing ignition loss was the insoluble portion. Since they know of no way to remove this insoluble clay prior to the ignition, it is fortunate that the ignition loss for practically all silicates used in the rubber industry is in the neighborhood of 14 per cent, and a correction factor can therefore be applied. Knowing the amount of clay in the sample, we can subtract 14 per cent of this value from the ignition loss. If the original clay content is not known, we can subtract from the ignition loss 16.3 per cent of the sum of SiO_2 and R_2O_3 weights in the sample. The authors recommend this method of correction as fairly accurate. The correction so applied may amount to 2 or 3 per cent. Slight differences in composition of clays will affect the correction factor only to a small degree.

Washing the black with sodium hydroxide is still necessary, however, to remove part of the mineral rubber not removed by nitric acid or acetone and chloroform, as well as other material adsorbed from the nitric acid solution of the rubber sample. Analyses were made of the following stocks by the method here recommended; analyses were also made by the same method, omitting only the sodium hydroxide and subsequent washes.

	Without NaOH Wash %	With NaOH Wash %		Without NaOH Wash %	With NaOH Wash %
30% black	31.16	30.84	30% black,	33.28	30.72
	31.04	30.48	10% mineral rubber	33.68	30.24

The reaction product of nitric acid upon carbon black is probably some stable form of graphitic acid (5). It cannot be reduced by formaldehyde. Smith and Epstein have stated (5) that carbon black is recovered from nitric acid in an amount approaching 105 per cent of the original weight. The authors have found that unless washed with water or sodium hydroxide, the reaction product will have approximately a 2 per cent higher weight. They do not, however, recommend washing with water, since sodium hydroxide serves the same purpose and does not have water's tendency to cause loss of the black in filtration. The water-soluble portion of this oxidation product is believed to be gases adsorbed from the nitric acid. These must be washed out.

The authors have found in a large number of determinations of carbon black in rubber by the nitric acid decomposition method that the results were slightly higher than the theoretical 105 per cent, and that carbon black does not gain weight when treated with hydrochloric or acetic acids and then dried. The higher results are therefore not due to adsorbed hydrochloric or acetic acids, but may be attributed to the difficulty of freeing the carbon particles from adsorbed material contained in the average rubber mix.

It has been the authors' experience that the results vary but little whether the nitric acid solution of rubber is filtered immediately or allowed to cool. Allowing the black to settle apparently does not hasten the filtration; therefore, filtration is recommended while the solution is at least warm.

Although lead is rarely used today in the compounding of rubber, it must be removed if present (1). A negligible error is caused by the presence of barium and calcium sulfates.

Summary

The carbon black analysis should not be made without a consideration of the nature of the original stock. The size of the sample must be related to the black content. To lessen time consumed in this analysis, preliminary extraction of the sample should be omitted. The correction factor for clay must be applied. By the revised method greater accuracy is obtained, although there is still a tendency for the results to be higher than calculated. Precision in this method seems to depend mainly upon accuracy of weighing and avoiding the loss of small particles of black.

Acknowledgment

The authors gratefully acknowledge the permission of The Firestone Tire and Rubber Company to publish this paper. They wish to thank the Physical Testing and Research Departments of the Firestone Company and L. M. Baker for their kind assistance.

Literature Cited

- (1) Am. Chem. Soc., Committee on Methods of Analysis, Rubber Division, *IND. ENG. CHEM.*, 15, 308 (1923).
- (2) Dawson, T. R., and Porritt, B. D., "Rubber: Physical and Chemical Properties," p. 535, Croyden, England, Research Association of British Rubber Manufacturers, 1935.
- (3) Park, C. R., *IND. ENG. CHEM., News Ed.*, 11, 343-6 (1933).
- (4) "R", *Gummi-Ztg.*, 50, 178 (1936).
- (5) Smith, A. H., and Epstein, S. W., *J. IND. ENG. CHEM.*, 11, 33-6 (1919).
- (6) Zilchert, P., *Gummi-Ztg.*, 50, 778 (1936).

Apparatus for Precise Plasticity Measurements at High Temperatures

Data on Coal Plasticity

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An instrument for precise measurements of plasticity at elevated temperatures is described. Adequate apparatus is included for avoiding eccentric loading.

Measurements made on Pittsburgh and Alma seam coals show that the truly plastic properties of these coals are very transient, the life period being of the order of 1 minute at 460° C. Measurements of deformations proportional to the load were obtained at 410° C. An analysis of these data indicates that the deformations are elastic rather than plastic in character. Measurements on the deformation of the solid plus oily bitumen (obtained by benzene extraction) of Pittsburgh seam coal at 120° C. show that this is a truly plastic material.

THE rheologists' concept called plasticity has certain close analogies to the viscosity, or more accurately, to the fluidity (the reciprocal of viscosity) of liquids. It is common knowledge that a liquid yields permanently under a shearing stress, no matter how small, and that the yielding increases linearly with increasing shearing stress. The coefficient of viscosity is by definition the ratio of shearing stress to rate of shear; or the fluidity, a term which perhaps conveys to the mind a more concrete picture of the consistency of the liquid, is the rate of shear per unit shearing stress. It is constant, so long as the conditions tacitly involved in its definition are fulfilled, for any one liquid at a given temperature, regardless of the rate of shear. If, for the case of a liquid, a plot be constructed of the rate of shear against shearing stress or quantities proportional thereto, respectively—as, for example, the volume rate of flow against the pressure for liquid flow through a capillary tube—the result will be a straight line through the origin, the slope of which is by definition the viscosity of the liquid.

Certain materials, some of which appear to be liquids and others definitely solids, behave in a fashion exactly similar to liquids in all respects except one—namely, that no permanent shear results until the shearing stress surpasses a certain value, which varies from one material to another. For shearing stresses greater than that required to start permanent shear, the rate of shear is proportional to the excess of pressure over the threshold value. For such materials the flow-pressure diagram, in the case where the stress distribution is uniform throughout the volume of material under stress, is a straight line intersecting the pressure axis at some positive value. The slope of such a line is a measure of the plasticity of the substance being tested. Plasticity is therefore analogous to the fluidity of a viscous liquid; dimensionally it is identical with it.

Very few plastic solids behave precisely in accordance with this description of plasticity. Nevertheless the definition

given above has been found useful and sufficient to specify the behavior of plastic materials.

Coal "Plasticity"

When certain bituminous coals, particularly coking coals, are heated in the absence of air, some of the components of the coal soften or become incipiently or completely molten. The mass of coal as a whole becomes so soft that it is capable of being deformed under load. Such behavior is believed to be essential for coke formation. In the coke oven the pressure of the overburden probably aids the softened individual lumps to flow together, while the evolution of gases tends to knead the mass into a more or less homogeneous whole.

American coking coals are reported to be "plastic" within the temperature interval 375° to 475° C. Close to the latter temperature the coal hardens rapidly, so that it can no longer be readily deformed; and in commercial practice, heating is continued to various higher temperatures, up to perhaps 1100° C., depending upon the use for which the coke is designed.

A considerable number of investigators have made laboratory studies of the (so-called) plastic characteristics of American coals (see literature cited by Brewer and Atkinson, 1). However, little work has been done by methods such that the magnitude and distribution of the shearing stresses in the coal specimen were known. A notable exception is the work (in England) of Seyler (2, 3), who used specimens in the form of cylinders 6.1 mm. in diameter and 20 mm. in length made by briquetting powdered coal. The cylinders were loaded uniformly across the section, and the plasticity was measured by the time rate of deformation (decrease in length) under the applied load when the specimens were brought rapidly to predetermined temperatures.

Because an absolute method often yields more information than methods involving other variables, and because it

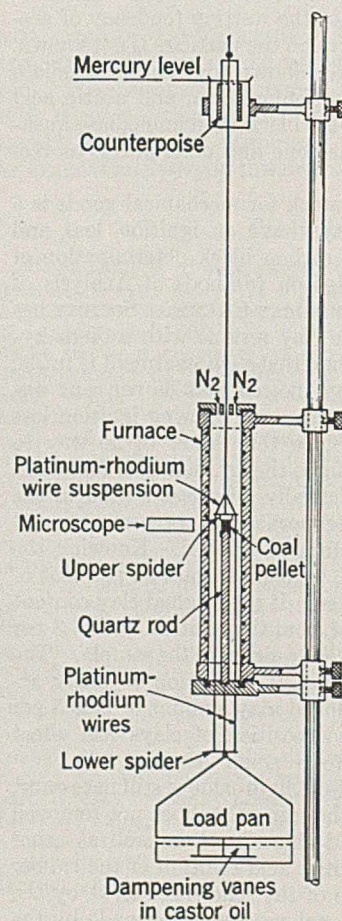


FIGURE 1. DIAGRAM OF PLAS-TOMETER ASSEMBLY

was, judging by Seyler's (2, 3) work, possible to obtain reproducible and precise measurements of the response of such coal specimens to known shearing stresses, it was considered desirable to study some American coals by a similar method. The apparatus used by Seyler, while correct in principle, does not preclude the possibility of eccentric loading. The authors' loading device (described below) was designed to eliminate such eccentricity.

Description of Plastometer

In most previous work on coal plasticity it has been the practice to heat the specimen at some predetermined temperature rate, more or less simulating those commonly used in coke-oven practice. Because of certain known variables in the problem, in particular, change in the consistency of the coal with time, at constant temperature, and the obvious effect of temperature gradients in the specimen if the consistency is a rapidly changing function of the temperature, it was considered desirable to provide as well for what is termed "instantaneous" heating of the specimen, thus minimizing the effect of both variables mentioned. This was accomplished by bringing the furnace to a predetermined temperature, with the loaded specimen exterior thereto, then dropping the furnace instantaneously over the specimen.

A diagram of the complete assembly of the plastometer drawn to scale, a detailed drawing with dimensions, and a photograph of the entire apparatus are given in Figures 1, 2, and 3.

The large (19-mm.) rod of a heavy workshop microscope stand was fitted with a heavy brass arm which carried at its outer end a brass disk of the required geometry and dimensions. The coal specimen rested on the top of a silica post, rising from the center of the brass disk. Metal pieces were attached to each end of the silica post by means of a refractory cement. The piece on the lower end carried a relatively wide flange, and a thread on the exterior portion below such flange. The threaded portion passed through a neat-fitting hole in the disk of the post support arm and was held in position by a nut below the disk. The upper metal piece was plain cylindrical on the exterior, to take neat-fitting caps, counterbored on their top faces, to various diameters, and to a depth of 0.39 mm., thus providing for accurate centering of specimens of several diameters. The top metal piece and caps were made of 18-8 chromium-nickel alloy. Final machine cuts on the metal pieces were made after they were cemented to the quartz post, with the whole running between centers on a precision lathe. Accordingly, the perfection of alignment of the parts constituting the supporting post was limited only by the accuracy of the lathe.

The literature supplied little information regarding the pressures likely to be required to produce measurable deformation rates under the proposed conditions. In fact, the sole example was the work of Seyler (2, 3) who obtained sizable apparent deformations under pressures of a fraction of a gram per square centimeter. Accordingly, the authors' apparatus was designed to eliminate to a high degree all forces on the specimen other than that of the net load to

be applied. Also, because an eccentric load, very small in absolute value, would, because of the small size of specimen, cause large variations in the lateral distribution of shearing stress, provision was made to center the load very accurately.

Although, because of the high pressures found necessary during the experiments, the refinements used to minimize undesired forces were not essential for the work on coal, they were found to function satisfactorily and hence may merit description because they were useful in the experiments on coal bitumens; and will probably be of interest to experimenters in measuring deformations of highly plastic materials.

The loading arrangement comprised (1) the loading system proper and (2) a device for counterbalancing the entire arrangement.

The loading arrangement consisted of a nickel-chromium "spider," in the form of a thin disk and short concentric cylinder, the two being turned integrally from one piece of metal. This spider was arranged for placement on top of the coal specimen, the cylindrical portion being in contact with the coal. Three No. 70 holes were drilled through the disk portion of the spider at equal angular distances of 120°; they were each given a slight (but accurately the same for each) countersink on the upper side of the disk.

A platinum-rhodium (20 per cent rhodium) wire with a spherical bead on its upper end was passed through each of the three holes in this upper spider. The beads were formed, all to the same diameter, by fusing the requisite length of the wire. Resting in the countersinks, they centered the wires in the holes and carried the load. After the wires were passed through the upper spider similar beads were formed on the lower ends of the wires. The three wires were then brought to the same length by stretching the necessary ones the correct amount.

The beads on the lower ends of the wires supported a lower spider similar to the one resting on the specimen, except that it was a plain disk only, and the countersinking of the holes was done on the lower face. Also, to permit placing the wires in the holes of the lower spider after the lower beads were made, a cut with a fine jeweler's saw was made from the edge of the spider into the respective holes.

A loading pan was suspended from the bottom of the lower spider, at its mid-point. To prevent appreciable shift of the center of gravity of the loading system on change of weight on the load pan, the joint between scale pan and spider was a flexible one of minimum friction, and the load pan was recessed for the various weights in such fashion, that weights were always distributed symmetrically about the axis of the loading system.

The counterbalancing device comprised a steel well containing mercury and a steel float immersed therein, together with arrangements for guiding the float accurately in one line and means for attaching it to the loading system.

A drilled and reamed post was attached to the base of the well as its mid-point and passed throughout the well length. The float was in the form of a hollow, thick-walled cylinder of suitable dimensions attached to and guided by a polished hollow rod of such diameter as to move up and down in the hollow post of the well with a minimum of friction and play. Attachment between the float and its guide was a skeleton one made by cutting away as much as was allowable of the thin-walled hollow cylinder from which it was constructed. A cross section of this skeleton cylinder is given in Figure 2, which shows the dimensions of the various parts of the apparatus.

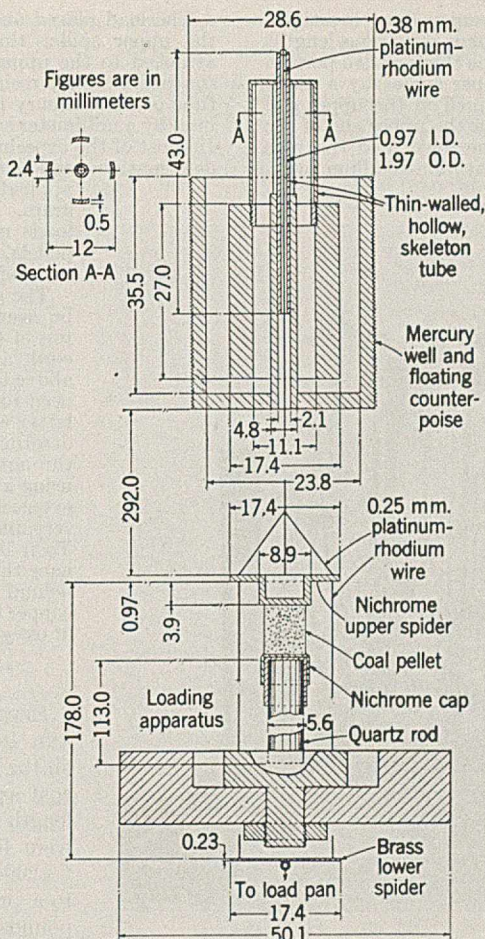


FIGURE 2. DETAILED DRAWING

The mercury well was arranged to screw up or down in a tight-fitting thread, permitting the use of specimens of various lengths and complete immersion at all times of the thick-walled portion of the float, which was attached to the upper spider by a platinum-rhodium wire. A spherical bead formed on the upper end of such wire rested in a slight countersink in the upper end of the hollow rod attached to the float. At the lower end the wire was fused to a tripod, also made of platinum-rhodium wire,

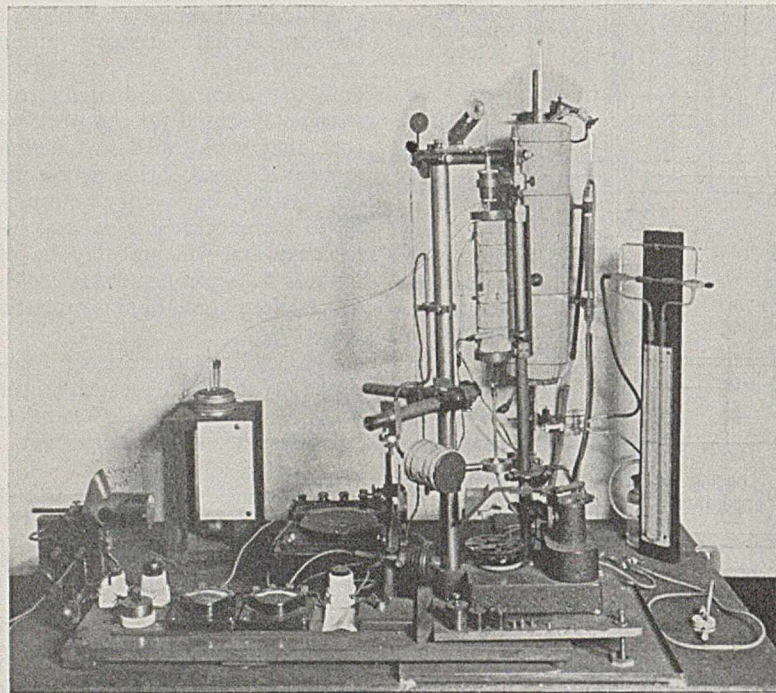


FIGURE 3. PHOTOGRAPH OF APPARATUS

the three legs of which were in turn fastened to the upper spider at points 120° apart near its circumference. Such attachment was done, as previously described, by wires with spherical beads on the ends passing through the holes in the spider, the beads resting in slight countersinks. Final adjustment of the three legs of the tripod to equal length again was made by stretching the wires slightly.

Obviously, the counterbalance wire and the three load wires had to pass through the top and bottom of the furnace, respectively. The former passed through a No. 50 hole drilled through the transite piece closing the top of the furnace. The brass disk of the post support arm formed the bottom closure of the furnace, and the three load pan wires passed through No. 56 holes drilled through the disk. In order to avoid friction and interference with alignment of the loading arrangement with the specimen, it was necessary for all wires to pass free through the holes. Accordingly provision was made for removing any torsion from the counterbalance wire after assembly by arranging to turn the rod of the counterbalance float to the required azimuth, with a simple friction device to hold the adjustment.

It is apparent that the entire loading apparatus was suspended from the bead on the platinum-rhodium wire resting on the guide tube of the steel float in the mercury well. Since this arrangement formed a perfectly good pendulum, suitable dampening vanes immersed in castor oil were attached to the under side of the loading pan. Before loading a pellet, the lower surface of the upper spider was brought very close to, but not in contact with, the upper surface of the pellet by raising or lowering the mercury well, using the fine screw thread on the outside of the well for this adjustment. Since the mercury level was always kept above the heavy-walled portion of the float, and since the skeleton tube of the float displaced only 0.007 cc. per mm. of immersion, this counterpoise system was very sensitive, and was found to be accurate to ± 0.02 gram.

The load placed on the pan was transmitted to the pellet by the upper spider through the three platinum-rhodium wires attached to the upper and lower spiders. Any deformation of the pellet would result in a greater immersion of the skeleton tube of the mercury float. This increased immersion was measured by a millimeter scale etched on one leg of the skeleton tube. In most of the experiments described in this paper the maximum deformation was less than 1 mm., and hence the correction to be applied to the apparent load was less than 0.035 gram. This correction was negligible for the high loads necessary for the deformation of the coal pellets, but was of significance in the measurement of the plasticity of the coal bitumens.

The general appearance of the apparatus may be seen in Figure 3. The two pulleys near the top of this picture were used to conduct a light cord attached to the platinum-rhodium wire above the counterpoise attachment; this cord was used to support the loading apparatus when the latter was not in use. For measurement of the deformations, the top of the pellet was sighted through a 3×10 mm. hole in the furnace wall, using a low-power microscope with a micrometer eyepiece. The top closure of the furnace is observable at the extreme right of the photograph. To it is attached a tube for leading into the furnace the oxygen-free nitrogen. The large furnace behind the plastometer was used to heat a mass of copper turnings to 500° C., so as to remove traces of oxygen from the nitrogen gas.

Slow Heating

EFFECT OF LOAD ON MAXIMUM EXPANSION AND INITIAL CONTRACTION TEMPERATURE. In all the experiments reported in this paper the coal specimen was cylindrical, 7.5 mm. in length and 6.4 mm. in diameter. These pellets were formed by compressing the powdered (-200-mesh) coal in a mold kept at 300° C., to a pressure of 7050 kg. per sq. cm. (100,000 pounds per sq. inch). Apparent densities computed from the dimensions and weight of the specimens varied from 1.27 to 1.29.

Figure 4 summarizes experiments in which the heating schedule was about 7° C. per minute up to 350° C. and about 1° C. per minute thereafter. The pellets were loaded before the heating was begun, and the same load was maintained throughout the experiment. A stream of oxygen-free nitro-

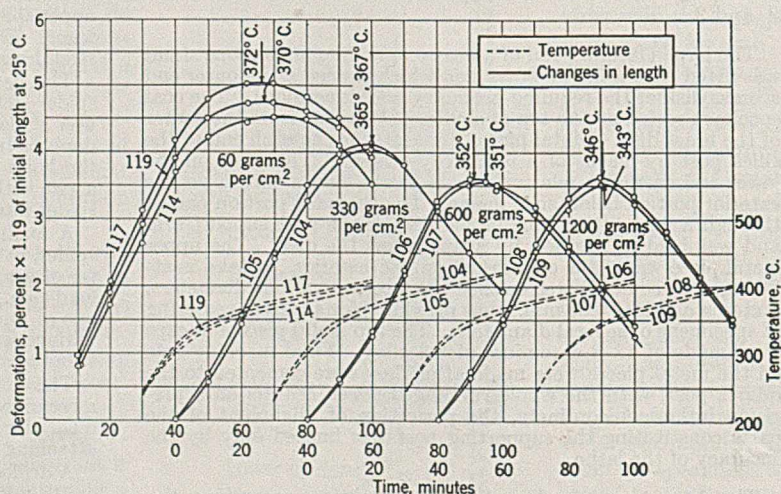


FIGURE 4. HEATING EXPERIMENTS WITH COAL 30

gen gas was passed through the furnace during all experiments. The coal used was a mixture of 80 per cent of Pittsburgh seam, Warden coal, and 20 per cent of Summerlee, Sewell bed coal, and was designated as coal 30 in the U. S. Bureau of Mines investigation of gas-, coke-, and by-product-making properties of American coals.

Length measurements and temperature readings were made once per minute, but only the 10-minute points are shown in Figure 4. The most striking facts about the curves are: (1) The temperature of initial contraction decreases with increasing load. (2) The maximum increase in length decreases with increasing load up to 600 grams per sq. cm. and appears to be independent of loads greater than 600 grams per sq. cm. (3) The slope of the time vs. changes in length curves before and after the maximum length has been reached is about the same for all loads.

Thermal expansion causes increase in length until the "plastic" range is reached.

Subsequently thermal expansion is accompanied by contraction due to filling of voids and to shrinkage due to structural changes accompanying chemical decomposition. The decrease in maximum expansion with load may be due to an increased rate of filling of voids by closer packing of wetted grains of solid material. Beyond about 600 grams per sq. cm. the frictional resistance accompanying such closer packing may become sufficiently great to make further deformation almost independent of load.

The approximate equality of the slopes of the curves immediately before and after maximum length has been reached shows that continuous deformation proportional to load does not exist under the conditions of these experiments.

Since the pellets were restrained by metal caps, it appeared possible that the effect of load on the initial contraction tem-

TABLE I. DEFORMATION RATES AT 410° C.

Coal No.	Experiment Nos.	Load G./sq. cm.	Time Min.	Maximum Expansion Per cent (× 1.19) of initial length at 25° C.	Deformations per Minute for Stated Time Intervals after Maximum Length Is Reached (in Per Cent, × 1.33 ^a of Maximum Length at 410° C. and Zero Load)					
					As Observed			Corrected for Change in Maximum Expansion with Load		
					2 min.	10 min.	20 min.	2 min.	10 min.	20 min.
16	173-176	0	6.0	13.8	0.100	0.075	0.061	0.10	0.075	0.061
16	170-171	330	4.0	7.75	0.380	0.239	0.156	2.68	0.700	0.385
16	177-178	720	3.5	6.10	0.600	0.385	0.280	2.90	0.960	0.568
16	283-284	1200	3.0	7.10	0.780	0.625	0.370	3.08	1.32	0.715
16	287-288									
16	274-279	1800	2.5	6.06	1.00	0.708	0.435	3.30	1.51	0.837
16	252-256	2400	2.25	4.66	1.43	0.975	0.543	3.73	1.84	0.975
16	284-285									
16	259	3000	2.25	4.85	1.68	1.17	0.709	3.98	2.04	1.14
16	296-300									
16	280-282	3600	2.25	4.97	1.80	1.23	0.738	4.10	2.10	1.17
16	292-295									
30	151	330	4.0	8.05	0.300	0.150	0.091	2.60	0.610	0.320
30	148	600	4.0	7.55	0.360	0.168	0.198	2.66	0.630	0.380
30	149	1200	4.0	6.76	0.600	0.377	0.234	2.96	0.860	0.480

^a All the coal pellets used in the experiments of Table I were of the same length—namely, 7.5 mm. or 119 turns of the micrometer screw on the eyepiece. The units used for all deformations of Table I are in turns of this screw. For conversion to per cent of the initial length at 25° C. the figures given must be divided by 1.19. For conversion to per cent of maximum length at 410° C. and zero load the deformations must be divided by 1.33.

perature might be caused by better thermal contact with increasing load, with a resultant decrease in such temperature gradient as might exist in the coal pellet. To vary this experimental condition within wide limits, accurately ground cylinders of Pyrex glass, approximately 4.7 mm. thick, were placed above and below the coal pellet in the plastometer. The effect of load was quantitatively the same for either arrangement. With coal specimens between metal caps the initial contraction temperatures were 371°, 366°, 351°, and 344° C. for pressures of 60, 330, 600, and 1200 grams per sq. cm., respectively. With the Pyrex cylinders inserted the temperatures were 368° and 341° C. for respective pressures of 60 and 1200 grams per sq. cm.

In a few cases the temperature gradient across the diameter of the pellet was directly measured by inserting a thermocouple in a fine hole drilled along the axis of the cylindrical specimen. This gradient for the slow heating schedule was never greater than 2° C. and averaged closer to 1° C. For the rapid heating schedule (described below) the gradient was about 10° C. during the first 2 minutes, after which it dropped rapidly to 1° to 2° C.

To obtain larger deformations and to measure these at constant temperature, a large number of experiments were made in which the specimen was heated very rapidly to 410° C. and measurements were made at that temperature.

Rapid Heating

DEFORMATIONS PROPORTIONAL TO LOAD. In a large number of preliminary experiments in which the loaded pellet was rapidly (within 3 to 4 minutes) heated to temperatures of 410° to 475° C. it was found that when plastic deformation occurred it was almost always too fast to be measurable, the loaded coal pellet being squashed out of range of the microscope in a few seconds after the maximum temperature was reached. The final thickness of the material remaining between the loading caps was apparently limited only by the downward distance which the movable upper cap was free to travel. When it was sought to avoid this very rapid deformation by using much smaller loads, measurements were made impossible by swelling and irregular distortion due to gas evolution.

These difficulties were almost completely avoided by working at the lowest temperature consistent with measurable deformations under loads of 100 to 3600 grams per sq. cm.; and by adding 20 per cent of -200-mesh + 220-mesh electrode

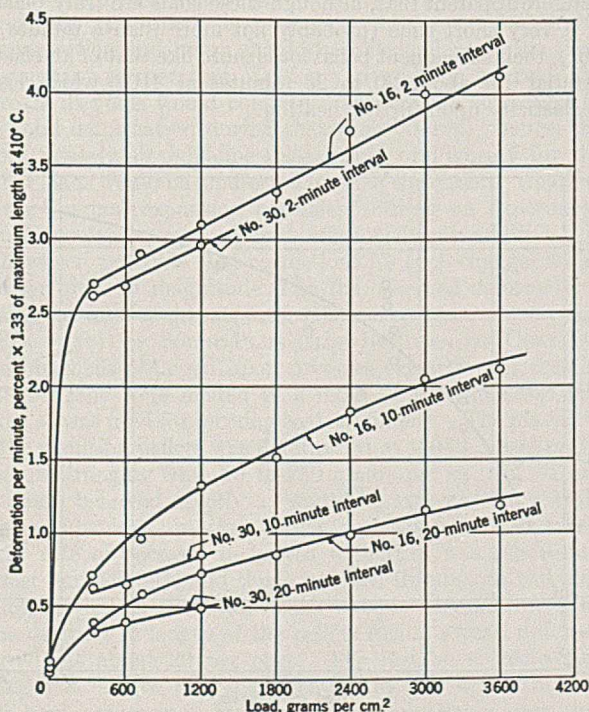


FIGURE 5. DEFORMATION RATES AT 410° C.

Coals 16 and 30 plus 20 per cent electrode carbon

carbon to the coal. Measurable deformation rates proportional to the load were obtained at 410° C. during the first 20 minutes after maximum length had been reached. During the 20- to 40-minute interval the deformation rates were only 10 to 20 per cent of those measured during the first 20 minutes. The 20- to 40-minute rates were independent of load for loads greater than about 800 grams per sq. cm.

The data for deformations during the first 20 minutes are given in Table I and Figure 5. Coal 16 was Alma seam (West Virginia) coal. The experiments listed in Table I were reproducible to within 10 per cent of the deformation values given. From the fifth column of Table I it will be observed that the maximum expansion of the coal pellet decreases very rapidly in going from a load of zero to one of 330 grams per sq. cm., but the decrease thereafter with load is relatively small, and the maximum expansion is practically constant for loads greater than about 1800 grams per sq. cm. These facts are consistent with the behavior of pellets of No. 30 coal (containing no electrode carbon) given in the preceding section of this paper. Such behavior is more characteristic of an elastic material than of a plastic one. The time

necessary to reach maximum expansion decreases with the load, in the range from zero to 1800 grams per sq. cm., but beyond 1800 grams per sq. cm. it is constant; hence, variations in this time cannot explain the apparent constancy of the initial deformations at the higher loads.

The deformation-rate curve for coal 16, for the 2-minute interval (beyond the time of maximum expansion) of Figure 5, shows a very large deformation rate for relatively small loads. The curve then changes its slope very markedly. Beyond 330 grams per sq. cm. the curve is practically a straight line. This abrupt change in slope is of course due to the large correction made necessary by the change in maximum expansion with load.

This correction was made as follows: It was assumed that the expansion of 13.8 turns (see footnote to Table I) in 6 minutes for coal 16 at zero load occurred at the uniform rate of 2.3 turns per minute, and that the same expansion rate existed in all of the experiments of Table I. Then, for example, at 330 grams per sq. cm. for coal 16, since maximum expansion was reached in only 4 minutes, the deformation rate due to the increased load must have just equaled the expansion rate at this time, and hence during the subsequent 2 minutes a deformation of 2.3 turns per minute (in addition to the apparent rate of 0.380 turn per minute of column 6) occurred but was obscured by the expansion. The corrected deformation rate is therefore $2.30 + 0.380$ or 2.68, as given in column 9 of Table I. For the 10- and 20-minute intervals at 330 grams per sq. cm. for coal 16, 4.6 turns are added to the total expansion during 10 and 20 minutes and the sums divided by 10 and 20, respectively, to obtain the figures in columns 10 and 11 of Table I.

The physical significance of this abrupt change in slope is not obvious. If the explanation (given above) concerning an exponential falling off in the rate of filling of voids due to frictional resistance to closer packing were

correct, then one would expect that the portion of the curve for the higher loads would parallel the pressure axis. While the change in slope is admittedly large, there is, nevertheless, a positive and precisely measurable slope for the curve beyond 330 grams per sq. cm. This fact indicates that the deformations are elastic rather than plastic in character. When a given load was abruptly replaced by a lighter load at any time within the 10-minute interval (after maximum length was reached), the pellet expanded by an amount such that its length was close to what it would have been if under the lighter load from the beginning of the experiment. This behavior was also observed by Seyler (2, 3).

The rapid change in deformation rates with time is easily seen by comparing the three curves for coal 16 in Figure 5.

The rates decrease rapidly during the 2- to 10-minute interval and more slowly during the next 10 minutes. Since a plastic material has a constant deformation rate at a given temperature under constant load, it is apparent that both Alma seam and Pittsburgh seam coals are in this respect not truly plastic materials. That both coals are nevertheless capable of extensive deformation under small loads was shown by the authors' preliminary experiments with 100 per cent coal pellets at 450° to 475° C., where the "squashing" (described

at the beginning of this section) was observed within a few seconds after maximum temperature was reached. It is therefore apparent that, although these coals are truly plastic for a very short time (probably not more than a minute at 460°), their subsequent behavior is more like that of an elastic material (for about 20 to 25 minutes at 410°) which loses its elasticity upon further heating.

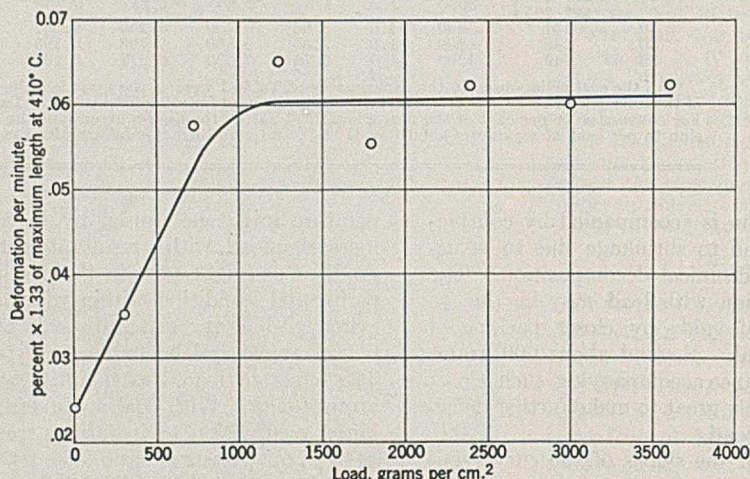


FIGURE 6. DEFORMATION RATES AT 410° C.

Coal 16 plus 20 per cent electrode carbon, 22- to 40-minute interval

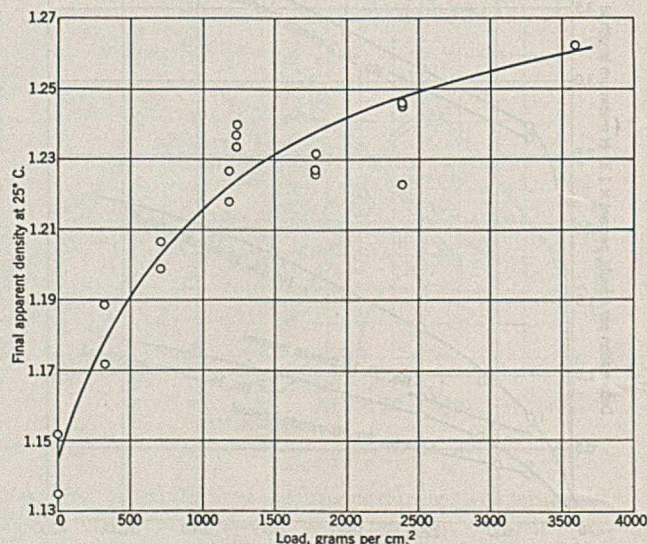


FIGURE 7. VARIATION IN APPARENT DENSITY

Coal 16 plus 20 per cent electrode carbon, instantaneous heating to 410° C. Total time at 410° C. about 40 minutes

The intercepts of the curves of Figure 5 indicate a small deformation at zero load. This is consistent with the extensive squashing at very low loads and 460° C. It is, however, possible that a portion of this deformation at zero load is due to shrinkage caused by chemical changes.

In Figure 6 the deformation rates in the second 20-minute interval are plotted against the load. It is apparent that the rate is practically constant for loads greater than about 800 grams per sq. cm. This fact is perhaps more closely analogous to the behavior of coal 30 described in Figure 4 (slow heating and no electrode carbon) than is the abrupt change in slope of the 2-minute interval curve of Figure 5. The deformation rates represented in Figure 6 are probably combinations of the rate of filling of voids (slippage of wetted grains of solid into a more closely packed formation), the rate of shrinkage due to chemical decomposition, and the rate of creation of new voids due to gas evolution.

The variation in apparent density as measured at 25° C., after 40 minutes under load at 410° C., with the load is shown in Figure 7. Here the curve does not flatten so sharply as in Figure 6, but there is nevertheless a marked decrease in slope at loads higher than about 800 grams per sq. cm. The only apparent explanation for the differences in shape between the curves of Figures 6 and 7 is that the coefficient of thermal expansion increases with the apparent density (and hence with the load). This would cause the curve of Figure 6 to flatten more conspicuously than that of Figure 7.

Some incidental data may be noteworthy concerning the increase in voids during an experiment at 410° C. for 40 minutes. The voids increased from 15 to 24 per cent. The weight loss was about 7 per cent. The increase in voids during an experiment is unquestionably due to chemical decomposition and hence should be independent of the load. At constant temperature and for a given time interval, the increase in voids would constitute an additive correction to the total deformation during that time interval; hence, the approximately straight-line relationship of Figure 5 for the higher loads would be unaffected by such correction. Changes in the thermal expansion coefficient during an experiment would involve corrections that are not simply additive. It is, however, probable that corrections for such changes are of a lower order of magnitude than the observed deformations during the first 20-minute interval.

PLASTICITY OF SOLID PLUS OILY BITUMEN OF COAL 30. The bitumens obtained upon pressure extraction of coal 30 with benzene were melted in a mold of the same size and shape as was used for forming coal specimens. The plasticity of the resulting pellets was determined at 120° C., and under pressures ranging from 20 to 250 grams per sq. cm. These bitumens behaved exactly as would be expected for a truly plastic substance, in that under each load an accurately linear rate of decrease in length with time was established almost immediately, and this continued throughout the time of application of the load, usually about 10 minutes. The total decrease in length of the pellets (using several different loads) was about 20 per cent. The results, corrected for changes in length and diameter during the application of each load, are given in Figure 8. A straight line intercepting the pressure axis at a small positive value represents the data very well.

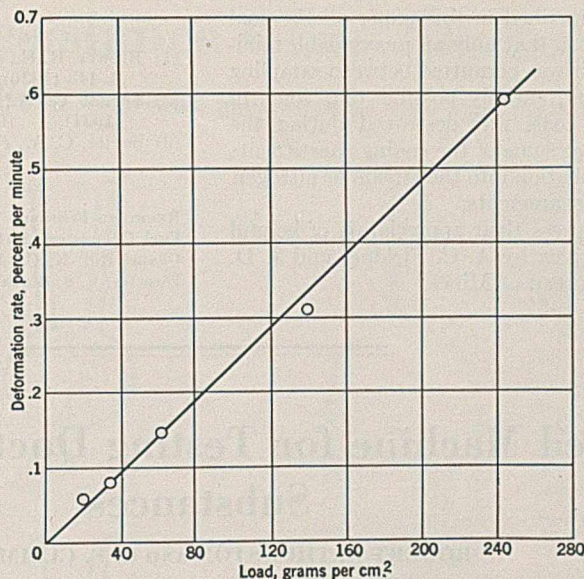


FIGURE 8. PLASTICITY OF SOLID PLUS OILY BITUMEN OF COAL 30 AT 120° C.

Discussion

Although the bitumen obtained from Pittsburgh seam coal by pressure extraction with benzene is a truly plastic substance, the coal itself does not, under any of the conditions used in this work, yield an accurately linear deformation-time curve under load. Seyler (2, 3) obtained initial deformation rates proportional to the load at 361° C. with Busty-Vitrain. These rates were not constant, but decreased rapidly with time. Seyler's explanation is as follows:

Whereas a substance like pitch at its softening point will deform continuously at the same rate at a constant pressure, the rate of deformation of coal decreases until it finally becomes zero and the flow ceases. This occurs at greater final contractions, the greater the pressure. What is the explanation of this? It is not due to loss of the property of deformation, for if the pressure is increased the movement is resumed. It does not appear to be related to the duration of the heating or to progressive decomposition. It seems to be due to an increase of the resistance to deformation which increases with the total extent of the contraction. It is of the nature of a back pressure acting in the opposite direction to the load and tending to produce expansion. If, for instance, the load is diminished, temporary expansion takes place until the total contraction is reduced to something like that corresponding to the reduced load. It can only be due, I think, to the pressure of the gases evolved by the decomposition of the coal. If these gases are developed faster than they can escape, they must tend to cause expansion and exert a vertical pressure in the opposite direction to the load.

While the phenomena observed by Seyler are consistent with those recorded in this paper, the authors prefer to place more emphasis than he does upon the very transient nature of the truly plastic properties of bituminous coking coals. In fact, these are so short-lived that none of their measurements are really plasticity measurements (except those for the benzene-extracted bitumens). They choose rather to characterize the measurable deformations as being those of an elastic solid whose elasticity is being rapidly destroyed by chemical decomposition.

Seyler's "plasticity" constant for Busty-Vitrain at 361° C. is about 0.013 per cent contraction per minute per gram per sq. cm. load. The same constant for Alma coal plus 20 per cent electrode carbon at 410° C. is 0.006, using the first 2-minute interval deformation rate at 330 grams per sq. cm.

The results obtained in this paper show that coal 16 is definitely more deformable at 410° C. than coal 30. This is in qualitative agreement with the data obtained by other investigators (1) who used the Davis plastometer.

A logical extension of the work described in this paper would be to attempt to measure the very rapid deformations at temperatures well within the plastic range. These were mentioned in connection with coals 30 and 16 at about 450° C. in the opening paragraph of the "rapid heating" section of this paper. Using small loads, and a rotating photographic film, it should be possible to obtain deformation rates in the temperature range where coking coals are known to be very fluid.

Throughout the work described in this paper all the coal samples used were "fresh," in that only an unavoidable minimum time of exposure to air was permitted between sampling and testing. It is, however, entirely possible that some of the coking power of the coals was destroyed during the briquetting process, and that some of the coking constituents may have been lost by distillation into the stream of nitrogen during the deformation measurements.

The authors wish to express their appreciation of helpful suggestions and criticism given by A. C. Fieldner and J. D. Davis, both of the U. S. Bureau of Mines.

Literature Cited

- (1) Brewer, R. E., and Atkinson, R. G., *IND. ENG. CHEM., Anal. Ed.*, 8, 443 (1936).
- (2) Seyler, C. A., *Colliery Guardian*, 142, 401-4, 488-90, 577-9 (1931).
- (3) Seyler, C. A., *Proc. S. Wales Inst. Engrs.*, 47, 9-14 (1931).

RECEIVED February 18, 1937. Presented before the Division of Gas and Fuel Chemistry at the 93rd Meeting of the American Chemical Society, Chapel Hill, N. C., April 12 to 15, 1937. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

An Improved Machine for Testing Ductility of Bituminous Substances

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THE ductility of a bituminous material is measured by the distance to which it will elongate before breaking, when two ends of a briquet of the material are pulled apart at a specified speed and temperature. The accepted procedure for conducting this test is outlined in Method D-113-35 of the American Society for Testing Materials, and specifies that a brass mold of definite dimensions shall be used for holding the specimen to be tested so that a cross section of material 1 cm. square can be elongated. The usual rate of elongation is 5 cm. per minute, and the customary temperature of the water bath in which the test is carried out is 25° C. (77° F.), although other speeds and temperatures are frequently used.

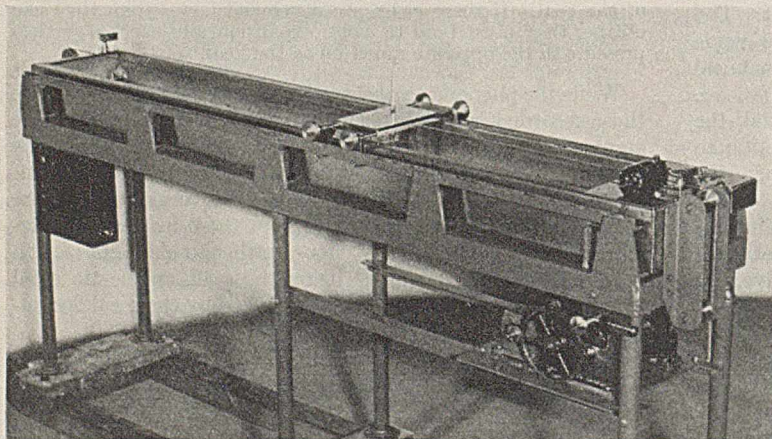


FIGURE 1. IMPROVED DUCTILITY MACHINE

The machine by which this test is accomplished is not described or specified by the A. S. T. M., but the usual machines available on the market are constructed of stone and permit a total elongation of the specimen of from 100 to 200 cm. The driving mechanism is ordinarily a screw which is submerged in the liquid and consequently disturbs the placidity of the bath during testing. This construction not only interferes with complete visibility of the specimens under test, but also fails to provide for constant temperature control.

An improved ductility machine has been developed at The Texas Company's Research Laboratories.

The bath itself is a Monel metal tank, placed inside a sheet-steel tank, provided with circulating liquid between the tanks. The liquid is preferably water, which is maintained automatically at a constant temperature by means of a cold-water coil and an electric heating element actuated by the mercury temperature control shown at the far corner of the bath. The motor shown on top of the machine at the near corner of the bath drives a paddle by means of a vertical shaft which keeps the water in the jacket circulating from end to end around a long vertical baffle between the inner and outer tanks. By setting the thermoregulator for the desired temperature, the water in the jacket is maintained constantly at this temperature and the bath inside the inner tank is thereby also held at this temperature without agitation.

The test is conducted in the inner bath; a white porcelain plate in the bottom makes readily visible the fine black threads of bituminous material, which are formed during the test. The carriage, shown midway between the ends of the bath, is made of Monel metal and rides on rails by means of grooved wheels mounted on ball bearings. It is moved at the required speed by means of a 0.3-cm. (0.125-inch) flexible stainless-steel continuous cable which is wound on a grooved drum and draws the carriage the entire length of the bath at the required speed. Lugs attached to this carriage support the moving end of the molds containing the specimens under test which are beneath the surface of the water. This eliminates all agitation of the bath in which the test is being made and provides for maximum visibility of the specimens during testing. The stationary end of the molds, which are pulled apart by means of the carriage, can be placed at either end of the bath underneath the water level. The supports for two molds can be seen at the far end of the bath. Similar supports are attached to the carriage. The machine can be made in different widths to accommodate one, three, or five specimens. The photograph shows a machine built for testing five samples at once.

The driving mechanism shown in the foreground provides for four speeds, any one of which is occasionally required by purchasing specifications for asphalt: 0.25, 1, 5, and 10 cm. per minute.

The usual centimeter scale is provided for reading the distance to which the specimens are pulled out before breaking. The entire machine is mounted on a pipe frame and is so installed that it is accessible from all sides. The electrical control panel for the motors and automatic controls for the bath are shown in the photograph; they are mounted underneath the driving mechanism attached to the frame in the foreground. When the molds are in place, the test can be started by a clutch which engages the driving mechanism. An automatic electric stop switch stops the driving mechanism when the carriage reaches the end of the bath and the clutch is released to enable the carriage to be moved back to the starting position by hand.

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Low-Resistance Glass Electrodes

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THE many improvements in design, the universal use of special glass, and the increased simplicity and reliability of electronic instruments, all have contributed to the present-day popularity of the glass electrode.

The greatest obstacle in successfully designing such an electrode is the inherent high resistance of the glass membrane, as well as its essentially fragile nature. Any successful model must be a compromise between these two practical factors. Most of the electrodes now commercially available have sufficient mechanical strength, but their electrical resistance is of the order of 10^7 ohms and there is no practical model with a resistance below one megohm. This relatively high resistance creates inconveniences, the most obvious of which are (1) the imperative use of a sensitive electrical measuring instrument such as a quadrant electrometer or vacuum-tube voltmeter, (2) the necessity of shielding, and (3) the need of special precautions in insulation. Although these difficulties are not insuperable, the errors caused by deviation films on the glass electrode itself are not always so easy to control (1).

The type of glass electrode described here is sturdy enough for all practical purposes and yet has an electrical resistance ranging from 10^4 to 10^5 ohms. This relatively low resistance overcomes most of the inconveniences inherent in the older models.

This new type of electrode can be made in quantities, easily and rapidly; and no special glass-blowing skill is required. Although at first it is best to practice with a few pieces of ordinary glass, the low-resistance electrode must be made from special low-resistance glass tubing (Corning No. 015, 5- to 10-mm. bore, is convenient).

Starting with two pieces of tubing about 10 cm. long, a small sturdy bulb is blown at one end of each tube (bulbs should be about twice the diameter of the tube bore). The two tubes are inserted in a two-hole stopper, which is mounted on a blowing tube as shown in Figure 1, A, making it easy to blow equally into both tubes. The two bulbs are then heated as uniformly as possible, allowing them to touch and fuse together at one point. A final blow will cause the point of contact to expand into a thin plane membrane (Figure 1, B)—so thin that a few faintly colored interference rings should appear near the center of the membrane. If a gray or black spot appears, the blowing has been too prolonged; on the other hand, if the exterior hemispheres expand excessively, the pressure has been applied too suddenly; in either case the electrode will be excessively fragile.

A small hole near the bottom of one of the hemispheres (not too near the membrane) is necessary for drainage (Figure 1, C). It is made while the glass is still hot and before removing from the mounting, by using a narrow pointed flame and blowing gently as the glass softens in the flame.

Several other precautions may prove useful. Since the No. 015 glass tends to crystallize, only fresh tubing should be used and the number of reheatings kept to a minimum. If, on cooling, the electrodes tend to crack into two halves, the tubes should be mounted in the blower at a greater angle to each other. This will place the tubes farther away from the membrane. Finally,

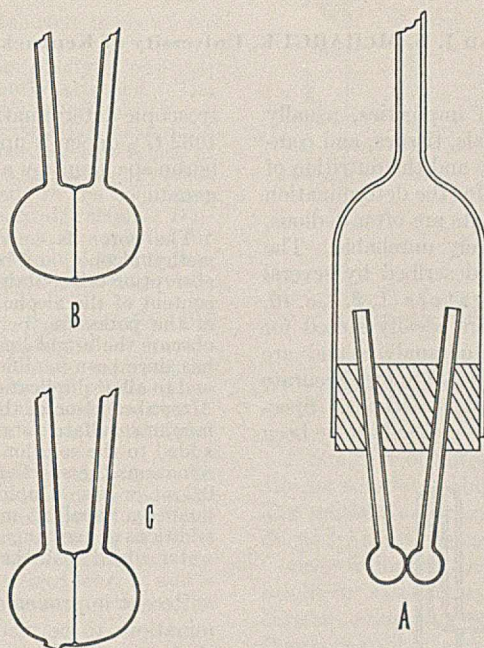


FIGURE 1

the outside of the electrodes may be given a light coat of paraffin wax to prevent creeping of solutions.

Obviously, the method of forming the glass membrane is the essential feature, and other constructional details lend themselves to many variations. For example, if the initial bulbs are blown in the center of one or both tubes, two or more side tubes can be kept on either side or both sides of the membrane. These membranes may also be used in making an all-glass compensated manometer. In order to make this instrument capable of standing considerable abuse and yet retaining its sensitivity near zero, three membranes intersecting in a common line may be formed by blowing simultaneously on three Pyrex glass bulbs.

The details of setting up the electrode for actual use can also be varied considerably. In this laboratory, the stopper used in the original mounting is kept on the finished

electrode in order to facilitate subsequent clamping; then by means of a capillary pipet the intact hemisphere is filled with a reference solution; finally, the whole electrode is placed in a stoppered wide-mouthed bottle containing enough of the same reference solution to cover the membrane on the side of the pierced bulb. When required for use, two saturated calomel half-cells are introduced into the circuit and the asymmetry potential of the electrode system is determined. The calomel half-cells and glass electrode are easily mounted on a single stand by means of three buret clamps, and the unknowns substituted for the reference solution on the pierced side by placing the liquids in a small beaker which can be raised or lowered around the glass electrode. A short piece of tubing drawn to a capillary on one end can be attached to one of the calomel cells in order to make contact with the solution on the reference side of the electrode.

A precision better than one millivolt or 0.02 pH unit is easily obtainable with electrodes having a resistance of 10^5 ohms used in conjunction with a Leeds & Northrup enclosed lamp and scale portable galvanometer. In the range usually considered valid for glass electrodes, repeated experiments have shown that the accuracy is at least as good as this. Some of these electrodes have been used successfully in this laboratory for a period of over 6 months.

Summary

Procedure for making a low-resistance glass electrode is given. Electrodes made in this manner are fully as satisfactory as the traditional types, with the additional advantage that the measurements may be made with the ordinary potentiometer and a portable galvanometer of medium sensitivity.

Literature Cited

- (1) Kahler, H., and DeEds, F., *J. Am. Chem. Soc.*, **53**, 2998 (1931).

RECEIVED March 4, 1937.

Optical Spectroscopic Determination of Boron

Polarizing Attachments

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THE exact measurement of certain impurities, usually present in minute quantities in metals, tissues, and compounds, is often important in metallurgy and the nutrition of plants and animals. Chemical methods for the determination of minute quantities of the minor elements are often tedious, complicated, and, in many cases, entirely unreliable. The quantitative spectroscopic methods as described by several

investigators (1, 2, 6, 8, 10, 11, 12) are ideally suited for this type of analysis and are considered (5) more accurate than chemical methods. Spectrographic methods have been

troscopic determination of boron, described by the authors in 1932 (?), depends upon the absorption of certain lines of the boron spectrum by a standard solution of potassium permanganate.

The boron is converted to methyl borate, volatilized with methyl alcohol, and burned in an atmosphere of oxygen before an absorptor cell containing the permanganate solution. The boron content of the alcohol solution is estimated from the normality of the potassium permanganate solution added to the cell to obscure the bright lines of the boron spectrum. (This procedure has since been modified to check the absorption of the spectrum and to allow duplicate readings to be made on the same solutions. After absorption of the boron spectrum a solution of ferrous ammonium sulfate, standardized against the permanganate, is added to the solution in the cell. In properly conducted determinations the spectrum will be discernible upon the addition of 0.2 ml. or less. Duplicate readings are made by adding a definite quantity, usually 5 ml., and again absorbing the bright lines by additions of permanganate solution. A correction is made for the water added with the ferrous ammonium sulfate.)

Recent improvements in this method, which allow determinations to be made at more efficient light intensities, include a tube for saturating natural gas with a solution of methyl borate in methyl alcohol, ignition in an oxygen blast, a standard boron spectrum for comparison, and polarizing accessories for measuring differences in light intensities.

A New Procedure

The optical system is shown in Figure 1.

The transmission of light is represented by dotted lines. Light originating at burner 1 is plane-polarized by plate 2, and is reflected by a small mirror, 4, through the lower half of slit 5. Light originating at burner 3 passes over the mirror, 4, and through the upper half of slit 5. Lenses 6, 8, and 10 invert the spectra and retain proper focus on the compound prism, 7. The analyzing plate, 9, is mounted on a movable scale. A standard boron solution is burned at 1 and the sample solution is burned at 3. Rotation of plate 9 changes the intensity of the spectrum originating from burner 1, leaving that from 3 unchanged, thus allowing the intensities of the two to be matched and the unknown to be measured in terms of the known.

A glass burner as shown in Figure 2 is used for exciting the spectrum. Connections with oxygen and gas are made at 1 and 2, respectively. The orifice at the lower end of tube 2 is neces-

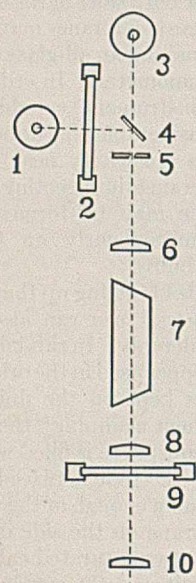


FIGURE 1. OPTICAL SYSTEM

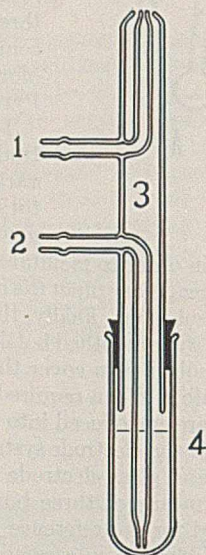


FIGURE 2. OXYGEN BLAST TUBE

For burning and saturating natural gas with an alcoholic solution of methyl borate

applied successfully for the control of industrial processes (4) in alloy analysis and for the classification of steels, as well as test methods (13) and color measurements in textile fabrics (9). Spectroscopic methods of analysis are also applicable to samples of biological material (3).

Photographic methods of spectrum analysis have been developed to a much greater extent than optical methods. In many instances the wave lengths of lines most accurately measured are beyond the range of visible light. A permanent record of the chemical constituents of matter can also be obtained by photographic methods.

Most optical methods have been based upon systematic observation and dilution of a solution of some compound of an element until certain lines are no longer visible in the spectrum. Since the end point of such a method occurs under conditions of low instrument efficiency, a high degree of accuracy is impossible. A quantitative optical method for the spec-

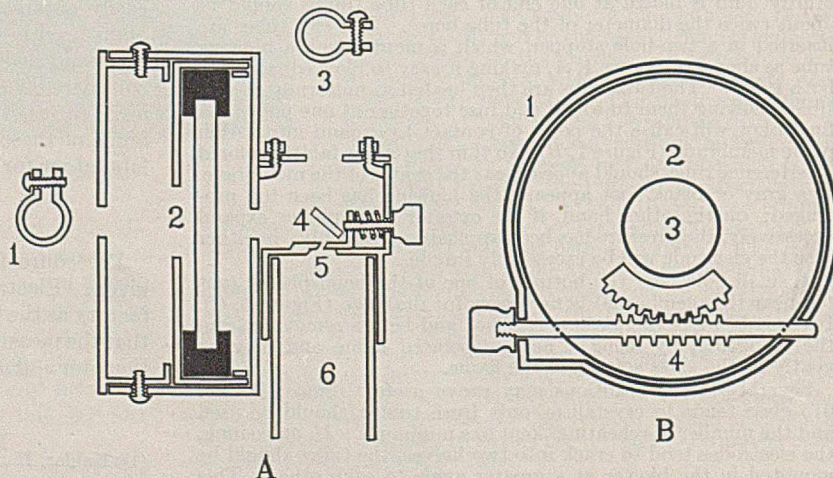


FIGURE 3. CONSTRUCTION DETAILS OF POLARIZING COLLIMATOR ATTACHMENT

sarily very small, to produce a fine stream of bubbles which is essential for a steady flame and the most efficient saturation of the gas with the solution. The oxygen and gas tubes are permanently adjusted and sealed to tube 3. Tube 4 is graduated to hold 2 ml. and is detachable to facilitate the changing of solutions. Constant gas pressures are maintained by the use of glass stopcocks.

The construction of the collimator attachment is shown by diagram *A*, Figure 3.

The clamps, 1 and 3, support the burners rigidly in position; they are accurately aligned and permanently attached. The polarizing plate is held in the cylinder, 2, by a brass spring. A slight degree of rotation is provided for accurate adjustment of the zero point on the scale. The mirror, 4, is permanently sealed in proper position. The slit, 5, is adjustable, as indicated, by means of a screw and spring. Attachment is made to the collimator tube, 6, of the spectroscope by means of a removable clamp. Diagram *B*, Figure 3, shows the worm and pinion, 4, provided for rotation of the polarizing plate. Caps are bolted on for protection and support of working parts. The attachment is constructed of brass.

The analyzing head, shown in Figure 4, is attached to the telescope tube of the spectroscope. In the horizontal section, *A*, 1 represents the lightproof housing, 2 is a plate carrying the scale, and 3 is the case containing the analyzing plate. A reducing-gear system, 2 to 1, was used between 2 and 3 to obtain greater sensitivity in rotation of the analyzing plate and wider spacing on the scale.

The side elevation, *B*, shows the assembly of the parts. In this diagram 1, 2, and 3 are as represented in *A*, but are shown in section. The knob, 4, is the exterior means of rotation of the movable parts. Case 3, containing *D*, the analyzing plate, is supported in place by short sections of tubing projecting into the telescope tubes, which serve as bearings. A fixed lens, *L*, and a movable lens, *L'*, are provided to obtain proper focus on the spectroscopic prism.

The polarizing plates used in this instrument consisted of a film or matrix for submicroscopic dichroic crystals mounted between glass disks. The crystals, about 1×10^{12} per square inch (manufacturer's specifications), were accurately oriented, so that the whole film functioned as a single crystal. The structure is invisible at 1100 magnifications. Practically complete polarization of visible light obtains, except at the extremities of the spectrum where the sensitivity of the eye is less efficient.

The crystals effect polarization by splitting light rays into two oppositely polarized beams, one being transmitted parallel to the main axis, and the other reflected at right angles.

The greatest accuracy in matching boron spectra was obtained after an initial rotation of 30° . Other factors, such as

reflection, diffusion, etc., resulted in losses of light, further reducing the transmission efficiency.

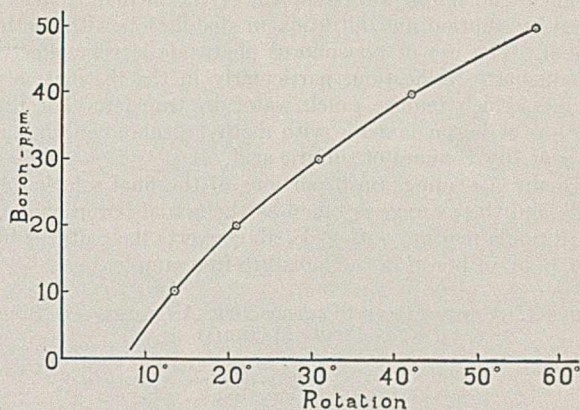


FIGURE 5. CALIBRATION CURVE OF BORON

A quantity of boron slightly less than 1 p. p. m. in methyl alcohol was detectable at a saturation temperature of 35°C . The greatest accuracy was obtained in matching spectra produced by solutions containing from 5 to 35 p. p. m. of boron. Concentrations much above 50 p. p. m. produced spectra too bright for satisfactory comparison. The portion of the scale corresponding to a 60° rotation from zero transmission was therefore calibrated from 0 to 50 p. p. m. It was found experimentally that about 30 per cent of the light available, calculated from the quantity of boron in solution, was lost in the polarizing system. A further loss of approximately 20 per cent resulted from the utilization of less than 60° of the total rotation to maximum transmission. It was found more practical, considering instrument design and a greater accuracy in the preparation of standardized solutions, to increase the boron content of the solution than to concentrate the light by a lens system. A standard containing 100 p. p. m. was used.

Figure 5 shows the calibration curve obtained experimentally. Each point is the average figure of triplicate determinations on five solutions, representing about 150 instrument readings. The instrument scale was converted from degrees to parts per million of boron in the alcoholic solution.

Because of the pronounced effect of temperature changes on the cubical expansion of methyl alcohol, it was found advantageous to correct all volumetric solutions to the capacity at 0°C . For this correction the formula $V_t = V_0(1 + t 1.1856 \times 10^{-3} + t^2 1.5649 \times 10^{-6} + t^3 0.9111 \times 10^{-8})$ was used to prepare a curve giving the corrections for temperatures from 15° to 35°C .

The recommended procedure for the preparation of the sample is for the most part that previously described (7). The sample should contain between 0.025 and 0.50 mg. of boron for quantitative determination. Organic material is ignited in the presence of sodium carbonate. Brines and waters are made alkaline before concentration, and soils and minerals are fused with sodium carbonate. In the analysis of brines, large organic samples, and materials requiring fusion with sodium carbonate, it is of considerable advantage to acidify the aqueous extract of the residue

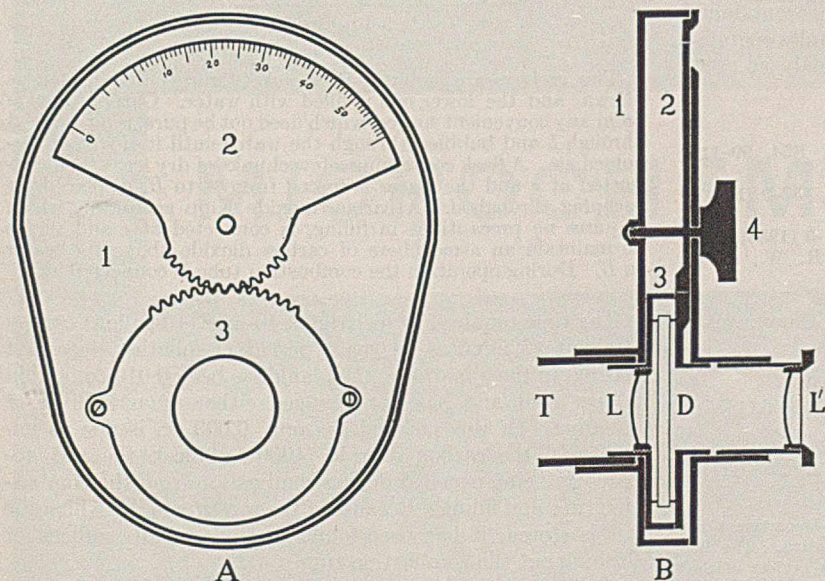


FIGURE 4. CONSTRUCTION OF ANALYZING TELESCOPE ATTACHMENT

with dilute sulfuric acid and precipitate the halides with a solution of silver sulfate. Excessive quantities of sodium sulfate are then removed by dehydration with ethyl alcohol and filtration. The boron after removal of the alcohol is concentrated by solution and filtration or distillation with methyl alcohol. The use of phosphorus pentoxide is very effective in inducing esterification, particularly in the distillation of residues which require much water to transfer. The final solution of boron is made with methyl alcohol containing 5 per cent (by volume) of sulfuric acid.

Usually 5 readings on 3 portions of the final solution are made and the average is taken as the actual boron content. The formula $p. p. m. = R \times V_0/W$ converts the scale reading to p. p. m. of boron in the moisture-free sample.

TABLE I. COMPARATIVE SPECTROSCOPIC ANALYSES FOR BORON IN PLANT MATERIAL

Sample	Boron	
	Permanganate method P. p. m.	Polarization method P. p. m.
Carrot (leaves)	7.4	7.1
Carrot (tuber)	5.1	5.0
Sweet potato	2.75	2.0
Tomato (fruit)	9.0	9.0
Tomato (fruit)	8.5	8.5
Tomato (fruit)	10.1	9.8
Tomato (vines)	5.3	5.0
Tomato (vines)	5.5	5.6
Cabbage	8.0	8.2
Lettuce	19.0	18.6

The equipment and procedure described have been in use for about 6 months. Analyses compare very favorably with values obtained by the previously published method (7). Individual readings are much closer to the average, smaller samples are permissible, and the analytical procedure is much shorter. Data on a few samples of plant material analyzed by both methods are given in Table I.

Summary

Polarizing attachments and an oxygen-methane blast burner for the spectroscopic determination of boron are described. Natural gas saturated with methyl borate in methyl alcohol is ignited in an oxygen blast to excite the spectrum. A standard solution on ignition and polarization produces a reference spectrum in juxtaposition to the spectrum of the sample. The degrees of rotation of the analyzing plate are read on a scale in terms of parts per million of boron in the solution upon matching the intensities of the spectra. Recommendations are given for the treatment of samples containing halides and large amounts of sodium salts. Samples containing from 1 to 600 p. p. m. of boron have been analyzed.

Literature Cited

- (1) Breckpot and Mevis, *Ann. soc. sci. Bruxelles*, B54, 99-119 (1934).
- (2) Brode and Steed, *IND. ENG. CHEM., Anal. Ed.*, 6, 157-9 (1934).
- (3) Drea, W. F., *J. Nutrition*, 8, 229-34 (1934).
- (4) Dreblow and Harvey, *IND. ENG. CHEM.*, 25, 823-5 (1933).
- (5) Duffendack, O. S., Wolfe, R. A., and Smith, R. W., *Ibid.*, Anal. Ed., 5, 226-9 (1933).
- (6) Kreamer, W., *Z. anal. Chem.*, 97, 89-93 (1934).
- (7) McHargue, J. S., and Calfee, R. K., *IND. ENG. CHEM., Anal. Ed.*, 4, 385-94 (1932).
- (8) Nitchie, C. E., *Ibid.*, 1, 1-7 (1929).
- (9) Nutting R. D., *Textile Research*, 5, 391-400 (1935).
- (10) Schubert, H., and Cruse, *Z. physik. Chem.*, A172, 143-55 (1935).
- (11) Smith, D. M., *J. Inst. Metals*, 55, 417-25 (1934).
- (12) Triche, Henry, *Compt. rend.*, 199, 419-21 (1934).
- (13) Waldbauer and Gantz, *IND. ENG. CHEM., Anal. Ed.*, 5, 311-13 (1933).

RECEIVED February 25, 1937. Contribution from the Department of Chemistry of the Kentucky Agricultural Experiment Station. The investigation reported in this paper is in connection with a project of the Kentucky Agricultural Experiment Station and is published by permission of the director.

Storage of Carbon Dioxide from Dry Ice for Dumas Determinations

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DRY ICE is a convenient source of pure carbon dioxide and the following method of storage makes it readily available for Dumas nitrogen determinations with less effort and in purer form than is ordinarily possible with double Kipp generators.

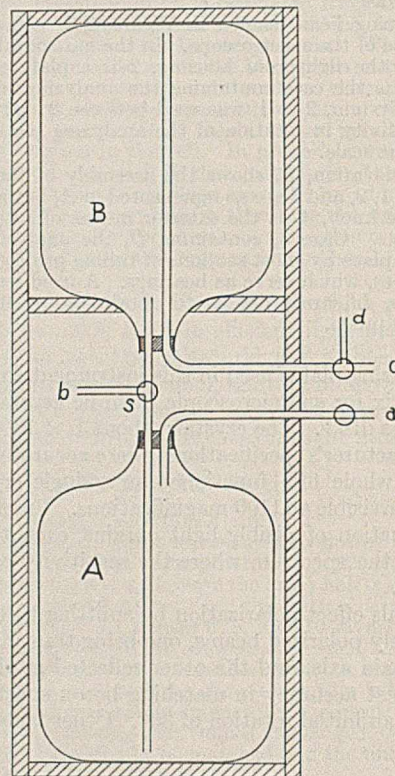


FIGURE 1

Two carboys are mounted in a rack (Figure 1), connected as shown, and the lower one is filled with water. Carbon dioxide from any convenient source, which need not be pure, is introduced through *b* and bubbled through the water until it is free of dissolved air. A flask containing a few chunks of dry ice is then connected at *a* and the water is forced from *A* to *B*, displaced air escaping through *d*. A carbon dioxide Kipp generator, which requires no precautions in filling, is connected at *c* and serves to maintain an atmosphere of carbon dioxide above the water in *B*. During operation the combustion tube is connected at *a*.

The time required to recharge a 40-liter (10-gallon) carboy is about 15 minutes. Over a period of months, since first setting up the apparatus, the blank has been 0.010 cc. within 10 per cent and has not changed either upon refilling or standing. Of this residual gas only 0.003 cc. is due to impurity in the carbon dioxide (1000 bubbles), the rest apparently being expelled during combustion from the combustion tube and filling. Because of the pressure under which the gas is stored, it has been found that one minute suffices for flushing out the combustion tube.

RECEIVED May 19, 1937.

A black and white micrograph showing numerous star-shaped or radiating crystals of Vitamin B1 Hydrochloride. Each crystal consists of many fine, needle-like or fibrous structures radiating from a central point, creating a starburst appearance. The crystals are scattered across a dark, almost black background, with some overlapping. The overall effect is a dense field of these intricate, radiating structures.

MICROCHEMISTRY

Prepared by Leopold R. Cerecedo and Frank Kaszuba
and photographed by Leo K. Yanowski and
Walter A. Hynes, Fordham University

Crystals of Vitamin B₁ Hydrochloride
from Brewer's Yeast

Microdetermination of Density by the Falling-Drop Method

SEYMORE HOCHBERG AND VICTOR K. LA MER, Columbia University, New York, N. Y.

BARBOUR and Hamilton describe an ingenious method (1) for the microdetermination of the density of an aqueous solution, based upon the rate of fall of a minute drop of the solution through an immiscible liquid of low viscosity and volatility. Using bromobenzene-xylene mixtures they obtained densities of 0.01 cc. of solution to an accuracy of ± 0.0001 . Recently, Fenger-Ericksen, Krogh, and Ussing (2) applied the method to the determination of the deuterium content of heavy water. Using an elaborate apparatus and timing by stop watch to ± 0.02 second, they claim that the method is capable of an accuracy of ± 0.000001 in the density. Their method of calculation, however, involves an error of principle, which produces an error of 0.000022 in the numerical example they cite.

In this paper is described a simpler form of apparatus and technic which is capable of determining rapidly the density of water solutions to ± 0.00001 using 2 drops of solution, each of 0.001- to 0.01-cc. volume. The time required for a drop of solution of unknown density to fall through 15 cm. of a bromobenzene-xylene mixture is compared with the time required by similar drops of solutions of known density.

For spheres of equal size, of densities d_1 and d_2 , respectively, falling through a medium of density d' , the times of fall, t_1 and t_2 , respectively, are related as follows:

$$\frac{t_2}{t_1} = \frac{d_1 - d'}{d_2 - d'} \quad (1)$$

For any given medium and a given drop size it follows that for spherical drops

$$d = \frac{k}{t} + d' \quad (2)$$

where d is the density of a drop, t is its time of fall over a fixed distance, and k is a constant depending upon the viscosity and density of the medium and the distance over which the drop is timed.

Equation 2 is obeyed even though the drop is distorted slightly, provided an accuracy of only ± 0.0001 is desired (1). However, to attain an accuracy of ± 0.00001 , it is necessary in making interpolations to apply a correction, the magnitude of which is determined by the velocity differences—and hence by the density differences—over which one interpolates.

Experimental

For the determination of densities of water solutions ranging from 0.997 to 1.110 at 25° C., master solutions of potassium chloride (0 to 17 per cent separated by differences of 1 per cent) are made by weight (3). From these a series of solutions separated by steps of 0.250 per cent of potassium chloride is prepared by dilution, and preserved in glass-stoppered bottles.

A series of fifteen glass tubes (35 cm. long, 7 mm. in inside diameter) containing solutions of bromobenzene and xylene graded in density between 0.996 and 1.108 is set up in a thermostat (with glass window) regulated to $\pm 0.002^\circ$ C. The drops are timed between marks 10 cm. and 25 cm., respectively, below the surface of the bromobenzene-xylene mixture.

To avoid undue waste of valuable solution, an orienting determination of the density is made by employing a more viscous medium, prepared from light petrolatum and dibutyl phthalate of such proportions that a drop (0.005 to 0.01 cc.) of distilled water requires 2 minutes to fall 15 cm. through the mixture. From the preliminary result one selects the proper tube of bromobenzene-xylene to give the most accurate density

determination. That tube of bromobenzene-xylene mixture is used in which drops of the unknown and of the standards for comparison require between 25 and 70 seconds to fall between marks—the longer the time the more sensitive the method.

The capillary pipet (Figure 1) is made from glass tubing 3 mm. in inside diameter and a glass rod selected to fit the tubing with very little clearance. The dimensions are not critical. The plunger is given a thick, uniform coating of a grease made by melting together, in equal proportions, powdered resin and ordinary stopcock grease. Care is taken to prevent large air bubbles in the mercury column or between the plunger and the

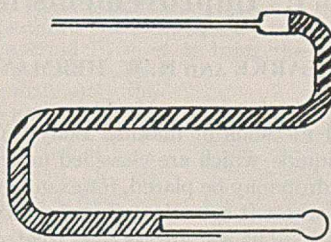


FIGURE 1

mercury. Exact reproducibility of the drops is obtained by measuring their volume between two marks, approximately 9 cm. apart on the capillary. The drops are forced out of the pipet under the surface of the bromobenzene-xylene solution. Upon raising the pipet out of the medium the drops are broken off by the surface tension. The drops were timed by a stop watch accurate to ± 0.2 second.

Corrections

A single rinsing, using approximately 0.001 cc. of solution, is sufficient to clean the pipet.

When interpolating between standard solutions differing by 0.250 per cent in potassium chloride, the maximum density correction to Equation 2 is -0.00002 at a density approximately midway between those of the standards, and decreases to zero as the density of either standard is approached.

Difference between Interpolated Density and Density of Closest Standard	Correction
0 - 0.00030	0.00000
0.00030 - 0.00060	-0.00001
0.00060 - 0.00080	-0.00002

Precision and Method of Calculation

Potassium chloride solutions of the densities shown in Table I were dropped through the same solution of bromobenzene and xylene.

TABLE I. MICRODETERMINATION OF DENSITY

Solution number:	I	II	III	IV	V
Density at 25,000° C.:	0.99707	0.99866	1.00025	0.99787	0.99946
	Sec.	Sec.	Sec.	Sec.	Sec.
Time, t	55.0	29.0	20.6	37.6	24.0
	55.2	29.0	20.6	37.6	24.0
	55.2	29.0	20.6	37.6	24.0
	55.2	29.0	20.6	37.6	24.0
Mean, $1/t$	0.0181	0.0345	0.0485	0.0266	0.0417

Calculating the density of IV from I and II we have:

$$d = \frac{0.0266 - 0.0181}{0.0345 - 0.0181} (0.99866 - 0.99707) + 0.99707 = 0.99789$$

Correction -0.00002

0.99787

The density of V, calculated from II and III by applying the correction as above, is $d = 0.99745$, which checks the result by weight to 0.00001.

Fenger-Ericksen, Krogh, and Ussing interpolate as though the d vs. t curve were linear. A considerable error should often result. For example, using the data on page 1267 of

their article and interpolating the density as a linear function of $1/t$, we obtain for the deuterium concentration in their sample 2.667 per cent rather than 2.645 per cent. The correction over such a short interpolation is negligible compared with the error of the incorrect interpolation.

Conclusions

A simple apparatus and technic are described with which the density of water solutions may be measured rapidly to ± 0.00001 , using for each determination 2 drops of solution

each containing 0.001 to 0.01 cc. For heavy water this corresponds to an accuracy of ± 0.01 per cent calculated as D_2O .

Literature Cited

- (1) Barbour and Hamilton, *J. Biol. Chem.*, **69**, 633 (1926).
- (2) Fenger-Ericksen, Krogh, and Ussing, *Biochem. J.*, **30**, 1264 (1936).
- (3) International Critical Tables, Vol. III, p. 87, New York, McGraw-Hill Book Co.

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Paper as a Medium for Analytical Reactions

I. Improvements in the Spot Test Technic

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FEIGL (1) has described methods of making analytical tests on single drops of liquids, which are classified under the term "spot tests." The drop may be placed, for example, on suitable absorbent paper, where it spreads uniformly until the surface forces are balanced. The wet area is then treated with a drop of the reagent, and the reaction produces an identifiable colored product. A variation is to place the two drops side by side on the paper, so that reaction occurs along a line formed where the spreading boundaries meet.

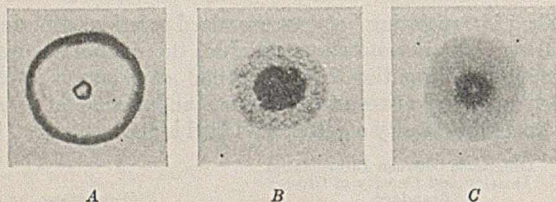


FIGURE 1. THREE TYPES OF SEPARATIONS BY CAPILLARY SPREADING

- A. Separation by precipitation of one component
Ions separated: Fe (2 γ) and Ni (5 γ)
Paper impregnant: BaCO₃
Fe(OH)₃ precipitated at center. Ni washed to periphery and detected by immersing paper in dimethylglyoxime solution
- B. Separation based on difference in solubility of reaction products
Ions separated: Ag (2 γ) and Cu (3 γ)
Paper impregnant: CdS
Black Ag₂S precipitates at center; brown CuS, having higher solubility product, precipitates in outer zone
- C. Separation based on difference in colloidal behavior
Ions separated: Cu (5 γ) and Fe (3 γ)
Paper impregnant: Zn₂Fe(CN)₆
Red Cu₂Fe(CN)₆ fixed strongly at center; Fe₄[Fe(CN)₆]₃, not readily fixed, diffuses outward with solution, giving blue peripheral zone

Because the sensitivity of such a test, with a given reaction, is determined by the smallest quantity of reaction product per unit paper area that the observer can just detect, any modification in the technic that tends to concentrate this product by restricting the area of reaction will lead to increased sensitivity. Thus Hahn (3) points out the advantage gained when the solution under test is introduced into the paper through the fine tip of a capillary tube. The test drop then enters at a single point, precipitation or adsorption of the reaction product taking place in the immediately surrounding region, where it remains fixed in the fibers while the clear liquid spreads radially outward by capillarity. A concentration of the colored product, which would otherwise be spread over the whole area originally wetted by the test drop, is obtained, rendering minute quantities distinctly visible.

The present article deals with improvements in both sensitivity and reproducibility brought about by the use of a capillary buret and thin, close-textured papers impregnated with reagents having low solubility in the liquids under test. To afford better control of the conditions of test, a special buret assembly is described, which permits delivering to a small area of the reagent paper, through a capillary orifice, a measured microvolume of solution, at a controllable rate of flow.

The slow capillary spreading of the solution from a central point in the meshes of an impregnated paper, combined with differences in solubility, reaction rate, and colloidal properties, may work to effect the separation of two or more substances. Elementary reasoning would lead one to expect that, of several substances precipitable in a given paper, the most insoluble would be the first to form around the point where the liquid is introduced, the other products precipitating concentrically around this in the inverse order of their solubilities. Experimentally this is not always attainable because of numerous interfering effects, but when conditions are favorable the process of simultaneously detecting two or more ions is a simple one.

In some cases the separation is better accomplished by precipitating only one of the substances, at the point of introduction, by the fixed impregnant. The other remains in solution and diffuses outward. After drying, a small quantity of wash liquid, again introduced at the center, carries any of the soluble ion remaining in the central portion of the spot to the concentric peripheral ring and there concentrates it. By dipping the dried spot in a second reagent the color reaction characteristic of this substance is brought about. Colloidal properties may aid in effecting separations, as, for example, when one of two substances precipitated is strongly adsorbed by the fibers and therefore fixed near the point of precipitation, while the other diffuses outward with the liquid.

Regardless of the factors on which a given separation depends, the effect is enhanced by reducing to a minimum the area over which the solution enters the paper. In many cases, control of the rate of spreading, possible with the capillary buret, aids materially. Figure 1 shows a photograph of capillary separations using the technic herein described. Figure 2 shows a comparison of effects with and without the buret.

Thus the localization of reaction products through the action of capillarity makes possible the attainment of increased sensitivity as well as the simultaneous recognition of substances. However, if the precipitating reagent contained in

the paper is soluble in the solution under test, effective, uniform fixation of the reaction product is often delayed or entirely prevented. As the solution flows into paper so impregnated, the first portions react with the soluble reagents, producing a small quantity of colored product. The clear

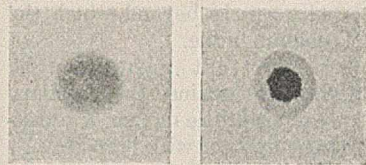


FIGURE 2. COMPARISON OF CAPILLARY BURET AND DROP METHODS IN SEPARATIONS

Composition of solution, 25 γ Cu and 25 γ Fe per cc.
A. 0.005 cc. added to Zn₂Fe(CN)₆ paper as single drop from glass rod
B. 0.005 cc. added from capillary buret

liquid, its reactive ion or ions thus removed, spreads outward carrying with it much if not all of the impregnant, depleting the area around the point of entrance. Hence the next portions of solution will remain unprecipitated until they are brought into contact with the reagent, concentrated by evaporation, at the periphery of the wet area. A further disadvantage of many soluble impregnants is their instability. Many soluble alkali salts decompose rather easily in paper, while less soluble salts of other metals keep reasonably well.

These objections point to the desirability of papers containing reagents not readily soluble in water but still capable of furnishing the small necessary concentration of the precipitating ion to react with the substance under test. As a matter of fact, the concentration of the reactive ion can be regulated automatically by proper selection of the impregnating salt, and the specificity of the test greatly improved by thus restricting the number of possible reactions. For example, potassium xanthate has little value as an impregnating reagent in test papers. It decomposes readily and the paper is useless after a few days. It precipitates practically all of the heavy metals, several of which give colored compounds. When cadmium xanthate is used, however, a paper is obtained which gives sensitive reactions only with copper and molybdenum and will keep for months. The colorless cadmium and zinc ferrocyanides afford similar advantages as sources of ferrocyanide ion.

Figure 3 shows a comparison of the effects produced when iron is tested for by the buret method, using potassium ferrocyanide and zinc ferrocyanide papers.

The use of an alkali sulfide as a source of the sulfide ion in test papers is entirely unsatisfactory, since it permits of no control of the concentration of that ion. Furthermore, alkali sulfides are highly soluble and unstable. When zinc, cadmium, or antimony sulfide is used, however, stable papers result, each of which has its own maximum sulfide-ion concentration and hence precipitates only those metals whose sulfide solubility products are sufficiently low. Antimonous sulfide paper, for example, precipitates copper, silver, and mercury in the presence of zinc, cadmium, lead, tin, iron, nickel, and cobalt. Precipitated red silver chromate is ordinarily encountered in analysis as a reaction product. In paper, conditions may be reversed, silver chromate serving to detect halides.

Such test papers are prepared by direct precipitation of the reagent substance on the paper fibers. The preparation of each reagent paper presents its peculiar problems (which will be dealt with in a future article in this series), but in general the method is as follows:

The paper is first soaked in a solution containing one of the ions to be precipitated, dried, then immersed quickly in a solution containing the other ion, washed thoroughly, and dried. For example, cadmium sulfide paper is prepared using a 10 per cent solution of cadmium acetate, followed by precipitation with

5 per cent sodium sulfide. Final washing is done with weak acetic acid to remove any remaining traces of sodium sulfide.

It might be supposed that the use of "insoluble" reagents would slow up the reaction rate. In paper, however, this retardation is not serious because of the state of fine division and the great surface available. Reduction in sensitivity becomes appreciable only when the solubility products of the reagent and reaction product approach the same order. This is naturally avoided in the selection of the reagent.

It is the belief of the authors that the use of reagents of low solubility is somewhat novel in analysis, and that it is rendered practicable through the use of paper as the reaction medium.

Apparatus

The apparatus shown in Figure 4 consists essentially of a microburet, A, constructed of thermometer tubing. It has a capacity of 0.05 cc. and is graduated in thousandths. The delivery end is drawn out to a capillary tube which is bent in the form of an inverted U, so as to bring the tip at right angles to the buret

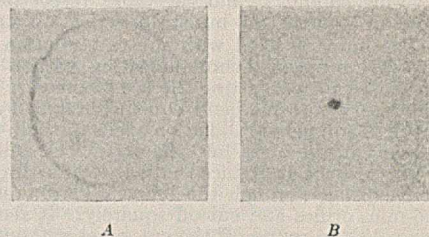


FIGURE 3. COMPARISON OF EFFECTS WITH SOLUBLE AND FIXED REAGENTS

0.1 γ Fe contained in 0.01 cc. added from capillary buret
A. To K₄Fe(CN)₆ paper
B. To Zn₂Fe(CN)₆ paper

axis and in approximately the same plane. The buret is mounted on a panel, B, of phenol fiber or similar material, which, in turn, is inclinable, on a suitable stand, at any desired angle from the horizontal to the vertical. A graduated circle shows this inclination. A tightening nut, C, secures the panel in the position desired.

The panel is held against the buret tip by an adjustable table, D, of phenol fiber or hard rubber. A central opening in the table accommodates the wet area of the paper, the buret tip being centered over it. On the underside, a shallow recess surrounding the opening seats a glass capsule, E, which is held in place by a spring clip. By this means gaseous reagents or vapors can be applied conveniently to the paper as the test solution is introduced. The table swings on a pivoting member, F, to which it is attached by phosphor-bronze spring straps, G. These straps provide the pressure necessary to ensure good contact between the buret

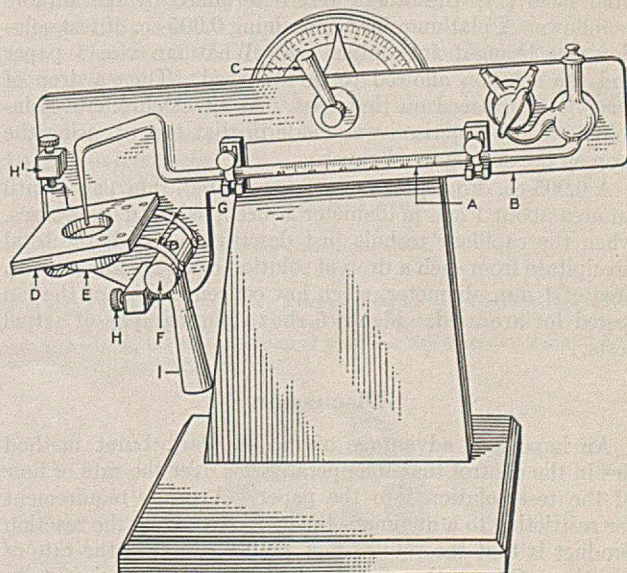


FIGURE 4. CAPILLARY BURET ASSEMBLY

TABLE I. COMPARISON OF SENSITIVITIES OF SPOT TEST BY FEIGL AND CAPILLARY BURET METHODS

Reagent Group or Ion	Ion Detected	Drop Method		Capillary Buret Method	
		Reagent solution	Limit of detectability	Impregnated paper	Limit of detectability
Ferrocyanide	Cu	Potassium ferrocyanide	0.5	Zinc ferrocyanide	0.05
Ferrocyanide	Fe	Potassium ferrocyanide	0.1 ^a	Zinc ferrocyanide	0.02
Xanthate	Mo	Potassium ethyl xanthate	0.2	Zinc xanthate	0.01
Dimethylglyoxime	Ni	Dimethylglyoxime	0.16 ^a	Dimethylglyoxime	0.005
Chromate	Ag	Potassium chromate	2.0 ^a	Zinc chromate	0.1
Diethyldithiocarbamic acid	Cu	Sodium diethyldithiocarbamate	0.2	Zinc diethyldithiocarbamate	0.002
Silver chromate	Cl	Silver chromate paper	0.5	Silver chromate	0.05
Sulfide	Cd	Sodium sulfide	6.3	Zinc sulfide	0.05
p-Dimethylaminobenzalrhodanine	Ag	p-Dimethylaminobenzalrhodanine	0.02 ^a	p-Dimethylaminobenzalrhodanine	0.004

^a Taken from Feigl (1).

tip and the paper, while the nonrigid method of support prevents breaking the tip through jamming the paper against it. The height to which the table can be swung upward is controlled by the adjusting screws, *H* and *H'*, acting against the arm of the pivoting handle, *I*, and the table, respectively. Regulation of pressure against the buret tip is thus obtained.

The buret is filled with the test solution through the tip, a two-way stopcock, communicating with a small bulb at the opposite end, permitting the use of pressure or suction from the laboratory outlets when frequent filling and emptying are necessary. A stoppered tubulation opens the bulb to the air for normal delivery of the buret into the paper. Cleaning liquids and wash water may be introduced into the bulb through the tubulation and expelled through the buret. The buret tip is drawn to a 0.5-mm. orifice and cut off squarely. It should receive a slight fire-polish to round off the cut edges without constriction of the bore.

USE OF CAPILLARY BURET. The impregnated reagent paper is placed over the opening in the table, and this is raised until the previously adjusted contact is made with the buret tip. The panel holding the buret, which has previously been filled to the zero mark with the solution under test, is then inclined to the angle that has been experimentally determined to give the optimum rate of flow for the particular test. A measured volume is then allowed to flow from the buret into the paper.

Experimental

Table I shows that the capillary buret method, in combination with the use of paper impregnated with reagents of low solubility, has an increased sensitivity over the drop method of from fivefold to one hundred fold. In Table I the limits of detectability by the drop method in four cases are taken from Feigl (1); the others were determined by the authors as follows: A platinum loop containing 0.005 cc. of test solution was brought in contact with Whatman No. 1 paper and the solution allowed to be absorbed. Then a drop of reagent was placed on that spot. As silver chromate is insoluble, the comparison was made in that test by using the loop on the impregnated paper.

A 0.005-cc. drop spreads, in fine-textured, thin paper until an area about 1 cm. in diameter is occupied. In most cases, when the capillary technic just described is used, the total precipitate from such a drop of solution can be confined to an area of 1 mm. diameter, when low concentrations of the ion tested for are used. Figure 5 shows photographs of actual tests.

Discussion

An important advantage of the capillary buret method lies in the control that the operator has over the rate of flow of the test solution into the paper. A prime requirement for restricting to a minimum the area covered by the reaction product is that the rate of flow shall not exceed the rate of reaction. The optimum rate of flow can be experimentally determined for a given test. For the tip orifice and papers

used in the authors' experiments, this rate was variable between 10^{-3} cc. per second for the vertical downward position and 5×10^{-5} cc. per second for an upward inclination of 50° , the angle beyond which the column broke.

The test paper can be brought against the capillary tip with little danger of breakage and yet with pressure sufficient to ensure continuous, uniform reproducible flow and freedom from any tendency for the paper to shift. Treatment with various vapors, or even warming of the paper during the test, is facilitated. Finally, the tediousness and uncertainty of carrying out such tests with the unaided hand are avoided. This is particularly desirable in capillary separations.

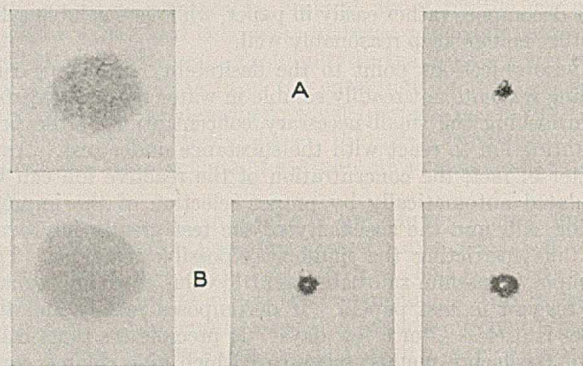


FIGURE 5. COMPARISON OF SPOTS BY DROP METHOD AND CAPILLARY BURET METHOD

- A. 0.005 cc. containing 0.1% Cu on zinc diethyldithiocarbamate paper
Left, drop method
Right, buret method
- B. 0.005 cc. containing 0.1% Ni on dimethylglyoxime paper
Left, drop method
Center, buret method, axis inclined 10° upward
Right, buret method, axis inclined 60° downward

The increased sensitivity of spot tests and the separability of substances by capillary flow through paper and fixation of the products therein have been mentioned by Feigl (2). No one seems, however, to have fully appreciated the possibilities offered by the use of relatively insoluble reagents precipitated on the paper fibers, or by the precise control of the rate of flow. The authors feel that the improved technic here reported, consisting essentially of the control of variables, lays the groundwork for advancing the qualitative spot test to the status of a method of quantitative microanalysis. In the succeeding papers in this series the subject will be developed in this direction, among others.

Literature Cited

- (1) Feigl, F., "Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 2nd ed., Leipzig, Akademische Verlagsgesellschaft M. B. H., 1935.
- (2) Feigl, F., and Kapulitzus, H. J., *Mikrochemie*, 8, 239 (1930).
- (3) Hahn, F. L., *Ibid.*, 10, 319 (1931).

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Determination of Carbon and Hydrogen

An Electrically Heated, Thermostatically Controlled Constant-Temperature Device for the Pregl C-H Determination

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IT IS well known that in the microanalytical determination of carbon and hydrogen, the lead peroxide portion of the combustion tube filling must be kept at a constant temperature, which must be over 170° or under 200° C. It has been found (1) that the higher its temperature, the more rapidly the lead peroxide gives up its retained water, provided that the temperature never exceeds 200° C.

the liquid in the system and minimizes leakage at the junction between the double-walled vessel and condenser. The tendency to gum is lessened (gumming is retarded, although not eliminated), since the metallic surfaces, which apparently catalyze the polymerization, are eliminated. However, this device still requires careful regulation of the gas flame and necessitates the use of bits of porous tile, etc., to ensure quiet boiling.

The authors have attempted to overcome these difficulties by electrical heating and thermostatic control of the electric current.

Their apparatus consists of a double-walled tube of glass, as in the Schoebel device. The condenser is replaced by a three-way stopcock and capillary tube, as shown in Figure 1. The double-walled tube is filled with mercury through tube B, the mercury acting both as heating medium and as its own thermoregulator. Contact is made and broken in capillary tube A, as in the familiar thermoregulator. Tubes A and B are fitted with hard-rubber stoppers, the one in A carrying a screw attached to the platinum wire contact for fine adjustment of temperature. The circuit is completed by means of a platinum wire fused into the tube.

The double-walled tube is wrapped with asbestos paper and then wound with about 6.5 meters (20 feet) of No. 24 Nichrome wire and the whole is encased in refractory cement. The tube, thus insulated, together with an external resistance, relay, and light bulb, is enclosed in an asbestos board case.

The function of the external resistance is to slow down the rate of heating. The refractory cement retains the heat so well that, if the heating circuit is connected directly to the winding on the double-walled tube, the temperature continues to rise for a time even after the current has been cut off. This prevents sharp control of the temperature.

The lamp, which is placed in series with the magnet circuit of the relay, acts as a resistance and indicates that the apparatus is functioning.

A Dunco Midget relay is used, since both the magnet and heating circuits operate on 110 volts and its compactness allows it to be easily fitted into the asbestos case.

The apparatus may be set for any temperature desired, as suggested by Saschek, and will easily maintain that temperature within $\pm 0.5^\circ \text{C}$. It is entirely automatic and needs only to be plugged into the 110-volt line.

Since the boiling liquid has been eliminated, all the disadvantages encountered in the previous types of apparatus have been overcome.

Literature Cited

- (1) Saschek, William, private communication.
- (2) Verdino, *Mikrochemie*, 4, 123 (1931).

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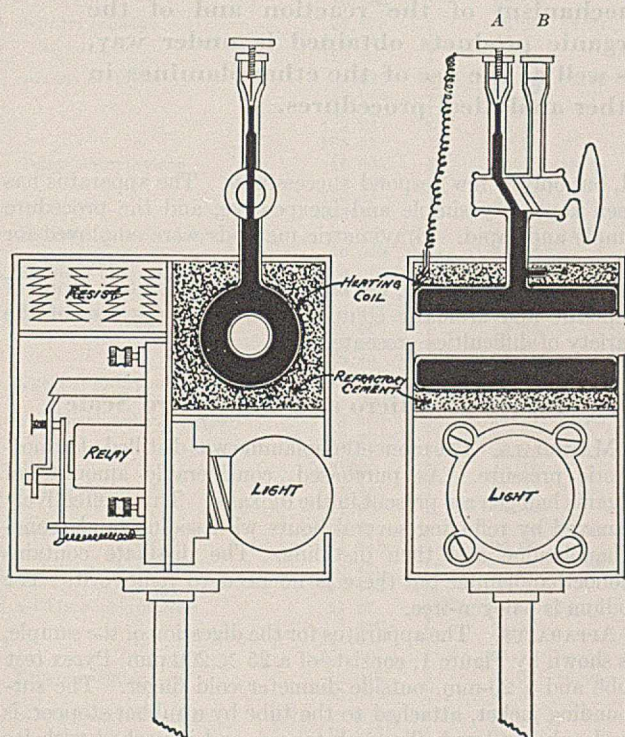


FIGURE 1. DIAGRAM OF APPARATUS

The usual devices employed for this purpose consist of a double-walled metallic or glass tube, the space between the walls being filled with a liquid whose boiling point lies within the range of 170° to 200° C. To this double-walled tube is attached a reflux air condenser. The temperature inside the tube is maintained constant by keeping the liquid boiling by means of a small gas flame.

This type of apparatus has numerous disadvantages. There is first the mechanical difficulty of making the apparatus leakproof, which has been overcome to some extent by the constant-temperature device of Verdino (2).

Another difficulty arises from the fact that cymene and decalin, usually employed as boiling liquids, always polymerize and form gummy deposits that prevent proper heat transfer from the flame to the liquid and make frequent adjustments of the gas flame necessary. They also cause superheating. Moreover, it is impossible to determine the amount of liquid remaining in the all-metal apparatus and to observe if even boiling is being maintained.

The all-glass device of Schoebel makes it possible to observe



Micro-, Semimicro-, and Macro-determination of Halogens in Organic Compounds

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A qualitative test to distinguish between reactive and unreactive halogen in organic compounds has been developed.

Two procedures for the quantitative determination of organic halogen have been developed. Method I is general for all types of organic chlorides, bromides, or iodides with the exception of the very low-boiling compounds with firmly held halogen. Method II is, in general, suitable only for the aliphatic or reactive compounds. Either method may be used on a micro,

AS A MODIFICATION of the Stepanow method for the determination of halogens in organic compounds (12), several investigators (5, 6, 7, 11) have suggested the substitution of higher boiling alcohols for the ethyl alcohol used by Stepanow and by others (1-4, 13) who have extended his method. Other workers (8, 9, 10) recommend diluting the alcohol with benzene, xylene, kerosene, or other inert solvent to avoid loss of volatile compounds such as carbon tetrachloride.

It occurred to the author that one of the ethanolamines might be used as a high-boiling alcohol in a Stepanow method for the determination of organic halogen. The ethanolamines are not only high-boiling, but readily soluble in water, cheap, and easily purified for the purpose at hand. Monoethanolamine, because of its lower viscosity, was chosen for investigation. It reacts at a slow rate with sodium in the cold, and the rate of reaction is increased very materially by raising the temperature. The reaction rate may be made moderate at high temperature by dilution with dioxane, which is soluble in both water and ethanolamine. Monoethanolamine will dissolve aliphatic halogen compounds, at least in the amounts required for the analytical procedure which has been developed, but it has an inferior solvent action on the aromatic halogen derivatives. Dioxane is very useful here for bringing the aromatic substance into solution. In addition monoethanolamine itself was found to be a powerful reagent for converting halogen in aliphatic combination to the ionic form, whereas it is entirely without action on the usual type of aromatic halogen derivative. Activated aromatic halogen, such as that found in 2,4-dinitrochlorobenzene is, however, easily converted to the ionic form.

It has been found possible to develop a simple qualitative test to distinguish aliphatic or reactive halogen from aromatic or firmly bonded halogen using monoethanolamine, and to develop general methods for the quantitative determination of halogens in many types of organic compounds on a micro, semimicro, and macro scale. Two methods have been developed. By Method I all halogen compounds investigated, with the exception of the low-boiling *s*-dichloroethylene, can be readily analyzed on any of the above-mentioned scales. Method II is satisfactory only for the aliphatic or activated halogen derivatives. By this second method even the very volatile aliphatic compounds, such as *s*-dichloroethylene, may be analyzed with ease on any of the above-mentioned scales. Some aromatic compounds may also be analyzed by Method

semimicro, or macro scale. There is no essential difference in method, regardless of scale.

The author is extending the method to include the determination of fluorine in organic combination and the estimation of aliphatic halogen in the presence of aromatic halogen. Investigation of the mechanism of the reaction and of the organic products obtained is under way, as well as the use of the ethanolamines in other analytical procedures.

II, but only a few respond successfully. The apparatus has been kept very simple and inexpensive, and the procedure simple and rapid. Gravimetric methods were employed for all analyses.

As shown by Table I, the method was applied to a group of aliphatic and aromatic compounds selected because of the variety of difficulties presented.

Method I. Micro and Semimicro Scale

MATERIALS. The monoethanolamine was distilled at atmospheric pressure. As purchased, considerable amounts of organic halogen are present in the dioxane. This is effectively removed by refluxing several hours with sodium and monoethanolamine and then distilling. The distillate contains monoethanolamine but there is no need to remove it. The sodium is halogen-free.

APPARATUS. The apparatus for the digestion of the sample, as shown by Figure 1, consists of a 25 × 200 mm. Pyrex test tube and a 20-mm. outside diameter cold finger. The surrounding jacket, attached to the tube by a rubber stopper, is used only for low-boiling substances, and is packed with ice and salt.

An alternative apparatus, which is also very satisfactory and simple, is a 50-ml. pear-shaped Pyrex acetylation flask and condenser tube with a 24/40 F ground joint. The condenser tube is provided with a Liebig jacket.

For some high-boiling liquids and solids, which form no volatile partially dehalogenated products, the condenser in Figure 1 may be omitted if the process is carefully watched.

METHOD OF WEIGHING SAMPLES. Nonhygroscopic solids and high-boiling liquids are weighed in small open bottles made by cutting down specimen vials 8 to 10 mm. in diameter. Solids are introduced into the weighing bottle by means of a small spatula. Liquids are introduced by means of a capillary pipet made by drawing down capillary tubing of 1-mm. inside diameter. Liquids boiling from 75° to 120° C. are best weighed in glass-stoppered vials of about 0.25-ml. capacity, such as are used in the Victor Meyer method for molecular weights. These are supported on the balance pan by a frame made from sheet aluminum. Substances boiling below 75° C. are weighed in the same vials containing about 0.1 ml. of monoethanolamine. Substances boiling as low as 38° C. may be handled thus.

TABLE I. RESULTS BY MICRO-, SEMIMICRO-, AND MACROMETHODS

Compound	Sample Mg.	Method	Halogen		Compound	Sample Mg.	Method	Halogen	
			Found %	Theory %				Found %	Theory %
Ethyl bromide	21.014	I	73.21	73.35	<i>p</i> -Phenylphenacyl bromide	12.400	I	29.00	29.06
	25.224	I	73.25			13.416	II	28.88	
	178.70	I	73.43			14.762	II	28.95	
	160.25	I	73.34						
<i>s</i> -Dichloroethylene	14.239	II	73.24	73.16	Chlorobenzene	25.187	I	31.56	31.52
	9.384	II	73.16			28.044	I	31.50	
	164.70	II	73.14			138.20	I	31.40	
	204.05	II	73.18			150.65	I	31.49	
Chloroform	14.315	I	88.96	89.10	Bromobenzene	20.197	I	50.85	50.92
	8.801	II	89.11			31.048	I	50.86	
	164.75	I	88.99			143.80	I	50.86	
	141.20	II	89.08			185.70	I	50.97	
Carbon tetrachloride	14.010	I	92.07	92.20	<i>o</i> -Chlorotoluene	18.603	I	27.95	28.03
	25.739	I	92.25			15.550	I	27.92	
	153.80	I	92.33		Iodobenzene	25.143	I	62.29	62.22
	145.25	II	92.00			18.263	I	62.16	
Ethyl iodide	16.159	II	81.46	81.38	181.35	I	62.32		
	21.082	II	81.48		260.85	II	62.21		
Ethylene chloride	28.305	I	71.72	71.67	205.35	II	62.03		
	27.730	I	71.60		<i>o</i> -Chloroaniline	28.925	I	27.87	27.81
Propylene chloride	14.796	II	62.74	62.78		26.865	I	27.80	
	16.206	II	62.70		<i>o</i> -Iodotoluene	16.269	I	58.38	58.23
<i>n</i> -Butyl bromide	22.673	I	58.23	58.34		19.841	I	58.30	
	115.75	II	58.29		α -Bromonaphthalene	17.137	I	38.60	38.61
	122.20	I	58.36			24.111	I	38.56	
<i>n</i> -Amyl bromide	9.519	I	52.99	52.92		183.35	I	38.61	
	15.050	I	52.87		182.05	I	38.69		
	109.70	I	52.94		181.45	II	38.62		
	178.35	I	53.04		<i>p</i> -Bromodimethylaniline	16.187	I	40.03	39.96
	203.65	II	52.86			22.200	I	39.87	
Tetrachloroethylene	15.998	II	85.70	85.53	19.129	I	39.98		
	6.826	I	85.62		<i>p</i> -Bromotoluene	19.467	I	46.70	46.74
	136.25	I	85.65			24.256	I	46.80	
	252.45	II	85.46		2,4-Dinitrochlorobenzene	30.726	I	17.38	17.51
Ethylene chlorohydrin	29.200	I	44.11	44.05		36.786	I	17.38	
	16.050	I	44.06			45.44	I	17.53	
Ethylene bromide	6.099	I	85.17	85.08	2,5-Dichloroaniline	19.526	I	43.74	43.78
	24.590	I	85.28			21.725	I	43.70	
Acetylene tetrachloride	4.773	I	84.46	84.50	<i>p</i> -Dichlorobenzene	22.183	I	48.28	48.26
	10.069	I	84.55			6.512	I	48.19	
	208.95	I	84.41			197.95	I	48.27	
	119.40	II	84.52		155.00	I	48.21		
Cyclohexyl bromide	33.190	I	49.13	49.03	Picryl chloride	28.621	I	14.29	14.33
	24.020	I	49.00			19.975	I	14.26	
β,β' -Dichlorodiethyl ether	18.860	II	49.47	49.60	<i>p</i> -Dibromobenzene	28.030	I	67.77	67.77
	22.201	II	49.59			33.999	I	67.62	
	117.75	I	49.38		152.80	I	67.70		
	121.00	I	49.55		148.55	I	67.63		
<i>n</i> -Heptyl bromide	5.955	I	44.62	44.64	Tribromoaniline	20.165	I	72.52	72.70
	21.940	I	44.44			14.467	I	72.70	
Benzyl chloride	27.591	I	27.99	28.03		12.943	I	72.62	
	25.245	I	28.09		Tetrachlorophthalic anhydride	12.677	II	49.50	49.62
α -Butylene bromide	10.430	II	73.94	74.03		29.286	I	49.40	
	18.433	II	73.90		Hexachlorobenzene	13.894	I	74.61	74.74
γ -Chlorobutyronitrile	22.27	II	34.24	34.25		4.597	I	74.51	
	1.440	I	34.20			140.10	I	74.71	
	215.60	I	34.22		133.60	I	74.65		
	173.60	I	34.21		<i>p</i> -Bromoacetanilide	26.315	I	37.34	37.34
Ethylene iodide	15.946	I	89.96	90.06		27.752	I	37.38	
	36.043	I	90.33		<i>o</i> -Chlorodiphenyl	10.060	I	18.77	18.81
<i>p</i> -Nitrobenzyl bromide	43.904	I	89.96	37.00		160.20	I	18.78	
	19.943	I	37.06		<i>p</i> -Bromodiphenyl	5.596	I	34.37	34.30
	Iodoform	11.960	I	96.79		96.70	4.276	I	34.24
		36.470	I	96.61		109.50	I	34.37	
Hexachloroethane	0.465	I	89.90	89.86	Sodium <i>p</i> -chlorobenzenesulfonate	10.099	I	16.54	16.53
	1.560	I	89.88			88.35	I	16.48	
	24.401	II	89.74		Sodium <i>p</i> -chlorotoluenesulfonate	20.621	I	15.65	15.51
	7.150	II	89.85			104.20	I	15.62	
	229.10	I	89.93		<i>p</i> -Chlorobenzonitrile	3.756	I	25.90	25.87
133.90	II	89.80		52.50		I	25.84		
Hexabromoethane	23.136	I	95.34	95.23	α -Ethyl- α -phenyl- γ -chloro- butyronitrile	1.216	I	17.17	17.08
	11.178	I	95.34			10.402	I	17.13	
	12.504	I	95.19						

PROCEDURE. The weighing bottle containing the sample is allowed to slide gently down the side of the inclined 25 × 200 mm. test tube or acetylation flask, after first removing the glass stopper, if a glass-stoppered vial is used. A volume of 3 to 4 ml. of monoethanolamine is added and, if necessary, enough dioxane to bring the sample into solution. As much as 3 ml. of dioxane has been used in some cases, although this is more than is needed to dissolve the sample. One-half to 1 ml. of dioxane is desirable in any case to retard the action of the sodium and to provide a low-temperature reflux to keep the condenser washed down. A 0.2-gram piece of clean sodium is added and the condenser is attached.

If the sample is a high-boiling liquid or a solid, the contents of the tube or flask are heated rapidly to boiling with a microburner flame, the tip of which just touches the vessel to be heated.

Currents of hot air along the test tube can be deflected by placing a disk of asbestos paper at about the level of the bottom of the cold finger. Refluxing is continued for 30 minutes, with frequent shaking. The surface of the ethanolamine usually becomes covered with a fairly tough froth which is not easily broken by shaking. If all the sodium disappears during the half-hour reflux, another piece of the same weight is added. For low-boiling liquids, the tube contents are heated only enough to cause the sodium to react moderately with the ethanolamine. The reaction is allowed to proceed at this moderate rate for about 15 minutes, and then the contents are refluxed for another 15 minutes or longer as desired. Solids and some high-boiling liquids, both aromatic and aliphatic, may be decomposed without using the condenser.

At the end of the half-hour heating period, the tube is allowed

to cool well below 100° C. before adding a few drops of water to decompose excess sodium. The condenser is then washed down with about 5 ml. of water. The tube is further cooled in running tap water by placing it in a beaker through which a current of water is passing. The ethanolamine and sodium compounds are then neutralized with concentrated nitric acid added drop by drop from a buret, using litmus as an outside indicator. During the neutralization the tube may be left immersed in a beaker of cold water to aid in the absorption of the large heat of neutralization. More care must be exercised with bromides and iodides. A large excess of nitric acid should be avoided if heat coagulation of the silver halide is to be employed. After neutralization, the tube is examined for turbidity due to insoluble reduction products such as are obtained from halogen derivatives of naphthalene, diphenyl, and similar compounds.

If heat coagulation is not to be used, the turbidity may be brought into solution by the use of alcohol or other organic solvents. When heat coagulation of the silver halide is to be employed, the presence of alcohol or other low-boiling solvent is very undesirable. If heat coagulation is to be used, or in any case if desired, the turbidity is removed by filtration. For very rapid filtration without loss of material a microhalogen filtration tube with a thick asbestos mat is placed through one hole of a two-holed rubber stopper in another 25 × 200 mm. test tube. By using the siphon tube of the standard Pregl filtration apparatus and applying suction to the other hole of the rubber stopper, the filtration may be carried out with rapidity and with minimum rinsing of the digestion tube, siphon, and filter tube. Water or 1 to 100 nitric acid is used for rinsing. When acetylation flasks are used for the digestion and it is necessary to remove turbidity by filtration, it is best to filter into a 25 × 200 mm. test tube. Filtration and rinsing can be done in about 2 minutes.

An excess of 10 per cent silver nitrate solution is added drop by drop to the filtrate and the silver halide is then coagulated by heating in boiling dilute permanganate solution according to the standard procedure. It was found, however, that coagulation could be brought about very rapidly and thoroughly in the cold by spinning for a few minutes. The spinning was accomplished by clamping a stirring motor to a stand so that the shaft was vertical, and placing a one-hole rubber stopper of proper size on the shaft. The test tube was hung from the stopper and guided at its lower end by a small clamp with cork-covered jaws slightly moistened with oil. The speed of the motor, which was controlled by a slide-wire rheostat, was such that the forced vortex was kept well below the rubber stopper. Even 1 mg. of silver halide may be coagulated effectively in a few minutes in this manner. Any particles of silver halide left sticking to the upper wall of the test tube are easily washed down with alcohol before filtration. The pear-shaped acetylation flasks may likewise be spun, but are best guided and braked with the fingers.

After coagulation and cooling (if necessary) filtration is performed immediately, using the usual Pregl procedure. No trouble is experienced in removing silver halide found inside the weighing bottles. The alcohol and dilute nitric acid washing removes these particles very effectively. All weighing vials used were of such diameter that the siphon tube may be slipped inside them. Quickest results are obtained in weighing the filter tubes if they are thoroughly wiped before the drying process and then not wiped again before weighing. Otherwise static charges from the wiping are very troublesome.

Where no sodium is used in the treatment of the sample, considerable trouble with bumping of the ethanolamine can be expected. The use of three to four platinum tetrahedra, as recommended by Pregl for his ebullioscopic molecular weight micromethod, is surprisingly effective for preventing this bumping.

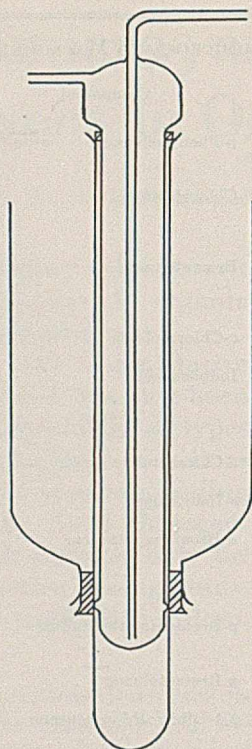


FIGURE 1. DIGESTION APPARATUS

Method I. Macro Scale

MATERIALS. Exactly the same materials are used as in the micro- and semimicromethod.

APPARATUS. Pear-shaped Pyrex acetylation flasks of 125- to 250-ml. capacity with condenser tube and 24/40 $\frac{1}{2}$ ground joint are used.

METHOD OF WEIGHING SAMPLES. The samples are weighed in the same weighing bottles as in the micromethod. Light, bulky, powdery solids are best handled on the macro scale in the form of pellets. These are easily made and handled in glass tubing of 4-mm. inside diameter using two tightly fitting glass rods with square-cut ends to press the powder into the form of pellets. Very firm pellets may be made in this way without the use of an expensive pellet press. After forming the pellet in the tube, the outside of the tube is wiped off and the pellet pressed into the weighing bottle with one of the glass rods. Liquids are handled exactly as in the micro-method.

PROCEDURE. The same general procedure is followed as in the micro work. A volume of 10 ml. of ethanolamine and 5 to 10 ml. of dioxane are used. The amount of sodium is increased to 2 grams, and this is added in two portions of several pieces each. In general, the total reaction time is extended to 1 hour. Turbidity on neutralization is removed as in the previous method. Either type of coagulation procedure may be employed. The silver halide may be automatically transferred to a crucible as in the micromethod. Glass crucibles with 1G3 sintered-glass disks and thick asbestos mats are very satisfactory. Figure 2 shows the filtering device by which the silver halide is rapidly and automatically transferred to the crucible. The alcohol and dilute nitric acid washing is very effective in removing the last trace of precipitate from the walls of the acetylation flask. The usual drying procedure is followed. In both the micro- and macroprocedures brownish colors appear with some compounds, but do not affect the analyses.

Method II. Micro and Semimicro Scale

All aliphatic compounds may be analyzed by a second procedure which is particularly valuable for the very volatile compounds, but only a few aromatic compounds were successfully treated by this procedure. It involves heating the sample with a solution of sodium in monoethanolamine in small sealed tubes.

MATERIALS. A solution of 1.5 grams of sodium in 50 ml. of monoethanolamine. Commercial, unpurified diethanolamine.

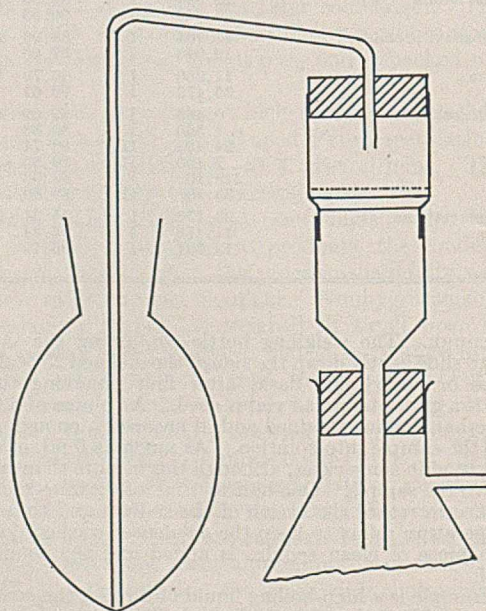


FIGURE 2. FILTERING DEVICE

APPARATUS. The bomb tubes used are 3×0.375 inch bacteriological weight culture tubes or 10×75 mm. Pyrex test tubes. Both are perfectly satisfactory, although the Pyrex tubes are more troublesome to open. The bomb tubes are heated in a bath of boiling diethanolamine contained in a 32×300 mm. Pyrex test tube; smaller test tubes for heating baths can be used, if it is desired to heat only one bomb tube at a time. For protection in case of failure of a bomb tube, the bath tube is wrapped in wire gauze and asbestos paper. The bomb tubes are placed in the heating bath in a Nichrome or nickel-gauze cylindrical basket which slides readily into the bath tube. This basket is raised and lowered by a Nichrome wire and the boiling diethanolamine is condensed by a cold finger. Figure 3 illustrates the apparatus.

METHOD OF WEIGHING SAMPLES. All samples are weighed directly into the bomb tube, which is suspended from the hook of the microbalance by means of a cork and aluminum wire hook thrust through the cork. The bomb tubes weigh approximately 5 grams. Liquids are allowed to drop directly from the previously described micro-pipets onto the bottom of the tube. Solids are introduced most easily in the form of pellets prepared as previously described. For microsamples the diameter of the pellet tube may be reduced to any desired size.

PROCEDURE. After the sample is weighed, 1 ml. of the sodium in ethanolamine solution is added from a 1-ml. Mohr pipet. The tube is next sealed as in the Carius method; the sealing is very easy and should require little practice. The culture test tubes are thick-walled and of small diameter and may be sealed with great ease. A fairly good capillary is desirable but not essential. After cooling, the tube is placed in the wire basket which is slipped into the bath tube. The heating bath liquid is commercial diethanolamine, boiling at about 268°C . The bath may be boiling when the basket of tubes is inserted, although it is much safer if it is at room temperature. The bomb tubes are heated for 0.5 hour after the diethanolamine has been brought to boiling, after which the cold finger is raised and the basket lifted from the bath liquid for about 10 minutes in order to cool. It is then removed from the bath tube by the wire, placed in a towel-lined beaker, and allowed to cool another 10 minutes. A towel may be thrown over the basket as it comes out of the bath tube to protect the operator against tube failure. A failure has never occurred, however, following the above procedure. The basket is finally cooled in running tap water in a beaker if the work is to be continued immediately, or the tubes may be allowed to stand indefinitely. If desired the tubes may be allowed to cool to room temperature in the bath tube, but this takes considerable time.

After thorough cooling, the tube is opened. The very end of the tube is warmed slightly to drive down any ethanolamine, and then, by applying a very small flame from the blast lamp to the tip of the capillary, the moderate pressure in the tube is allowed to release itself gently by blowing out the glass. The tube is next cut off about 1.5 cm. from the end, using a hot rod. This is exceedingly simple with the culture tube, as the glass cracks easily. The upper portion is placed on a piece of paper until it is rinsed out. During the opening process the bomb tube may be wrapped in a towel to avoid danger of failure, although failure has never occurred. The contents of the bomb tube are next transferred to a 25×200 mm. Pyrex test tube. This is most satisfactorily done by the filtration method used to remove insoluble material

described in Method I. The bomb tube is nearly filled with water, which is sucked over into the test tube, and the tube and siphon are washed with three 1-ml. portions of water. The tip, which had been cut from the bomb tube, is likewise rinsed out, the hole in the capillary causing no loss of wash liquid. The filter tube is finally washed with 1 ml. of water. The total volume is thus kept small. About 2 minutes are required for the transfer. Glass splinters which might be formed in cutting the tube are removed in the filtration. From this point the procedure exactly follows Method I.

The use of a stronger solution of sodium in ethanolamine is not recommended, as enough pressure often develops in the tubes to cause failure when in the boiling bath. For many and perhaps all, aliphatic compounds, ethanolamine alone may be used. Such compounds as chloroform, carbon tetrachloride, acetylene tetrachloride, tetrachloroethylene, *s*-dichloroethylene, and even hexachloroethane have been successfully analyzed without use of sodium. No pressure is found in the bomb tubes after cooling to room temperature; in fact a slight negative pressure is usually observed.

Various colors develop with different compounds in the bomb tube method. These may change with acidification, but never cause trouble.

Macromethod II

The procedure is exactly the same as that used in the micro-method except that 13×100 mm. Pyrex test tubes are used for the bombs, and the amount of sodium in monoethanolamine solution or monoethanolamine is increased to 4 ml., and the heating time to 1 hour. Test tubes (25×200 mm.) are always used for the coagulation of the silver halide, even on the macro scale. The total volume may be kept not greater than 30 ml. In many cases the microfiltration tubes may be used on the macro scale if the amount of silver halide is not over 100 to 150 mg.

Qualitative Test for Reactive Halogen

To about 0.1 gram of the substance in a 25×200 mm. test tube add 1 to 2 ml. of monoethanolamine. Boil over a burner for about 2 minutes with constant shaking to avoid bumping. Allow the contents to cool, dilute with about 4 ml. of water, and carefully neutralize with concentrated nitric acid. If a turbidity appears, dissolve it in a little alcohol after cooling again. Add silver nitrate solution. The amount of compound to be tested should be kept down to 0.1 gram, as a vigorous reaction generating enough heat to throw out the contents of the tube may result with some compounds.

Literature Cited

- (1) Bacon, *J. Am. Chem. Soc.*, **31**, 49 (1909).
- (2) Cook and Cook, *IND. ENG. CHEM., Anal. Ed.*, **5**, 186 (1933).
- (3) Drogin and Rosanoff, *J. Am. Chem. Soc.*, **38**, 711 (1916).
- (4) Duin, van, *Rec. trav. chim.*, **45**, 363 (1926).
- (5) Favrel and Bucher, *Ann. chim. anal. chim. appl.*, **9**, 321 (1927).
- (6) Kimura, *J. Soc. Chem. Ind. Japan, Suppl. binding*, **37**, 589 (1934).
- (7) Kimura, *Ibid.*, **37**, 590 (1934).
- (8) Landis and Wickmann, *IND. ENG. CHEM., Anal. Ed.*, **2**, 394 (1930).
- (9) Maryott, *Chem. News*, **103**, 1 (1911).
- (10) Miller and Johnson, *J. Colo.-Wyo. Acad. Sci.*, **1**, No. 1, 55 (1929).
- (11) Palfray and Sontag, *Bull. soc. chim.*, **47**, 118 (1930).
- (12) Stepanow, *Ber.*, **39**, 4056 (1906).
- (13) Walker and Rae, *J. Am. Chem. Soc.*, **33**, 598 (1911).

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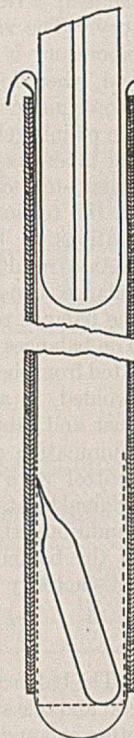


FIGURE 3

A Microchemical Balance Room

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The construction of the microchemical balance room of the Coal Research Laboratory of the Carnegie Institute of Technology is described, as well as the methods used for dust removal, vibration-free mounting of the balances, heat-free illumination, and humidity and temperature control. Microbalances installed in this way in such a room need to be cleaned and serviced less frequently and have a longer life. Zero-point changes (at least in case of the Starke-Kammerer balance used by the author) are small (about 5γ) in the interval from morning to night. Weighings can be made with higher precision and accuracy, with less difficulty, and hence with greater speed.

SINCE its inception, over 5 years ago, the balance room of the microanalytical laboratory of the Coal Research Laboratory of the Carnegie Institute of Technology has undergone a gradual evolution. This article, describing the balance room as it now exists, is written with the hope that other microanalysts may find some of the features described here of use in connection with their balance rooms.

When this microanalytical laboratory was first organized, the single Kuhlmann balance then in use was merely placed in one corner of the laboratory. It was mounted on a heavy, solid balance table with a 2.5-cm. (1-inch) Transite top fitted with gas-pipe legs which stood on the floor and away from the wall; the entire top of the table was covered with a steel cabinet provided with glass top, sides, and a counter-weighted sliding-front glass door which could be moved up and down smoothly without setting up excessive vibrations. By use of this type of table the balance was well protected from dust. However, after the balance had been in use about a year and a half it began to exhibit signs of failure; successive readings showed considerable damping and even zero-point readings were no longer reproducible, so that the balance finally had to be returned to its maker for repairs.

The above experience is not unlike that reported by Furter (4) who found that vibrations set up by a street car, passing outside the laboratory in Utrecht, caused the failure of a Kuhlmann balance after only 4 weeks' use and just after having been completely overhauled, including a repolishing of the knife edges by Kuhlmann. The vibrations in this case must have been unusually severe to cause failure after so short a time. A support, such as described below, would undoubtedly have greatly ameliorated the difficulty.

After receiving the author's balance for repairs, Kuhlmann, in a private communication, remarked on the fact that the metal parts of the balance were covered with a black "coal dust" deposit and that the knife edges needed sharpening. Presumably, the abrasive character of the deposit, coupled with the considerable vibration always present in the laboratory, led to a rapid deterioration of the sensitive parts of the balance. The black "coal dust" deposit found on the balance is characteristic of the atmosphere of industrial localities, particularly during the winter months. It might also be due to finely divided cinder particles, since there is a cinder road

and parking lot just outside the laboratory window; in the summer each automobile passing over this road on a dry day sends up a cloud of this dust, some of which enters the laboratory. The vibration problem is also serious; the analytical laboratory is located on a reinforced concrete-steel balcony and, when doors are slammed, shop motors are running, or people mount the stairs outside the laboratory, the vibrations are plainly felt. In addition to this there is a materials-testing laboratory in a large room adjoining the laboratory in which steel, concrete, and other building materials are broken on the testing machines with the production of strong vibrations.

As a result of the failure of the author's first Kuhlmann balance, considerable thought was given to the question of the balance room so as to avoid a repetition of this trouble. The balances were, first of all, placed in a separate room isolated from the general laboratory and means were found which avoided, to a large extent, the difficulties due to abrasive dust and vibration. At the same time suitable methods of illumination as well as constant temperature and humidity control were developed which were entirely absent in the original location of the balance. Despite the severity of local conditions, the three microbalances now on hand and housed in the balance room described below continue to function satisfactorily after from 3 to 4 years of constant use.

The Balance Room

The balance room proper is a room $10 \times 6 \times 11$ feet. One end and one side are made up of solid concrete walls, while the other end and side are of steel construction with glass windows with a 27-inch door entering at one end and a 3-foot door at the center of one side. The doors are provided with pneumatic door checks so that they close silently, gently, and without slamming and hence do not cause any appreciable vibrations. The steel and glass portions of the room are tightly fitted and calked so that, with the doors closed, there are no openings into the laboratory, other than through the ventilating system and perhaps in the small spaces around the doors. Two balances are mounted on a table like that already described, which occupies a place near the side concrete wall, while the third balance is placed on a similar table near the end concrete wall. Suitable small tables are placed adjacent to the balance tables to hold absorption tube stands, chamois and flannel dishes, sample tubes, and similar accessories.

Dust Removal

Since the failure of the Kuhlmann balance can be more or less directly ascribed to the action of abrasive dust on the knife edges and agate bearings, it was necessary to remove this hazard as completely as possible. This was done by filtering the air which enters the balance room. A small electrically operated air blower was installed in the end of the balance room just below the ceiling. The air from the laboratory which passed through the blower and into the balance room was made to traverse a cylindrical filter, 45 cm. long \times 25 cm. in diameter (18×10 inches) filled with sections of cotton separated from each other by layers of wire gauze and cheesecloth. The volume of air which enters is not sufficient to create noticeable drafts but puts the air in the balance room under a slight pressure, so that leakage of air tends to be out of the room rather than into it. Since the installation of this

filtering device, the improved cleanliness of the balance room has been marked. The cotton filter is renewed about every 6 months and the amount of dust and dirt removed from the air is clearly shown by the contaminated condition of the filter sections.

Vibration Absorption

With the major part of the dust removed from the balance room atmosphere, the next problem was to find a method of mounting the balance so as to absorb most of the vibrations within the room.

The question of a proper mounting for a microchemical balance seems to have received relatively little attention. Pregl (9) stresses the importance of the proper setting up of the balance, but both he and Emich (2) merely recommend mounting it on a marble slab which is supported by iron brackets attached to the wall, with lead sheet as vibration insulation between the iron bracket and the slab. Such a device might suffice for relatively vibration-free locations, but it is of little help in locations subjected to strong vibrations. Weygand (12) states that a mounting just as good as a marble, wall-supported table consists in standing the balance on any solid wooden table, provided the floor boards of the room do not vibrate. (From the author's experience, such a setup, at least on a concrete floor, is likely to lead to trouble.) He, as well as Friedrich (3), cautions against setting up the balance in the vicinity of vibrating machines. Besides using Pregl's lead-sheet insulators, Boëtius (1) recommends putting a rubber stopper 1 cm. thick under each of the metal disks in which the feet sit. Gorbach (5), in an excellent and very complete summarizing article dealing with the microbalance, adds little to the above information regarding the proper vibration-free mounting of the balance. In the case of concrete buildings, Roth (10), commenting on the use of wall supports, points out that vibrations caused by machines are transmitted through the walls and, if a Pregl-Emich type of mounting is used, into the iron wall support and thence to the balance. He claims that such vibrations are completely avoided by supporting the balance on a table which is not in contact with the wall. The legs of the table are made of two heavy concrete pillars (25 cm. wide \times 60 cm. deep) mounted on masonry foundations. Between the floor and the foundations, as well as between the concrete supports and the marble top, are placed several thicknesses of 1.5- to 2-mm. lead sheet. Roth claims that such a support has most excellently protected the balance against vibrations of all sorts. He cautions against using rubber or cork insulators in place of lead sheet, because one then has a support unstable to pressure or nonuniform loading which may cause zero-point changes.

In this laboratory attempts were first made to mount the entire balance table on a rubber vibration-free supporting system, but such a system was found to be too unstable. It became obvious that a practical mounting would have to be a compromise between complete vibration absorption and a stable system. A system which would completely absorb all

vibrations—e. g., a Julius suspension—becomes too unstable for use under the conditions imposed—namely, the necessity of releasing and arresting the balance while on the suspension. On the other hand, too stable a system permits too much vibration to be imparted to the balance.

The answer to the problem was found in an article by Howard (8) in which various supporting and suspension systems were constructed and both the imparted horizontal and vertical vibrations were measured by means of a seis-

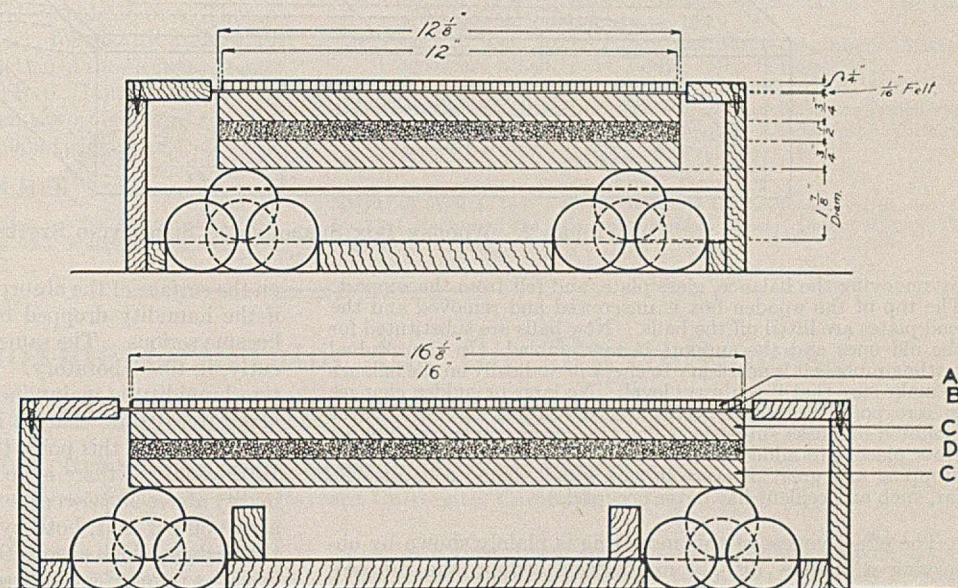


FIGURE 1. SYSTEM USED TO SUPPORT MICROBALANCES

Above, section through A-A'
Below, section through B-B'

mographic instrument and recorded on a kymograph. The effectiveness of the various systems in absorbing vibrations is clearly shown by the kymograph records. In the case of simple layers of insulators such as rubber, felt, and cork only qualitative comparisons were made by noting the degree of agitation of a mercury surface, but Howard states that "it is certain that these materials are much inferior to rubber balls as vibration absorbers." He found that the most effective, stable supporting system was obtained by arranging small rubber balls in the form of a tetrahedron and placing four such tetrahedra at the four corners of the apparatus to be supported. To obtain the necessary stability the system is heavily loaded.

Figure 1 indicates the system which is in use for supporting the microbalances. The rubber balls are standard "hand balls" and the weight consists of two 1.9-cm. (0.75-inch) thick lead slabs, C (each weighing about 27 kg., 60 pounds), separated from each other by a 1.25-cm. (0.5-inch) thick sheet of sponge rubber, D. Figure 2 indicates the wooden box which surrounds the supporting system. The box not only serves to hold the hand balls in place, but also protects the entire system from accidental touching. The hand balls may rest either in a circular hole, as shown in Figure 2, or in a triangular hole with rounded corners. The height of the box is made so that with new balls in use, the piece of felt, B, just makes contact with the upper edge of the four sides of the rectangular opening. The felt tends to act as a slight brake on horizontal motion imparted by touching the balance and still it does not transmit any appreciable vibrations to the system. On top of the felt is placed a sheet of 0.6-cm. (0.25-inch) plate glass, A, to which the balance feet sockets are cemented with Krönig's cement. The rubber balls are deformed considerably by the weight on them and are not actually spherical as shown in the figure. They gradually assume a permanent deformation and the height of the support gradually decreases until finally the felt will no longer make contact with the edges of the box. When this occurs, usually after about 6 months, it is best to renew the balls. This is done

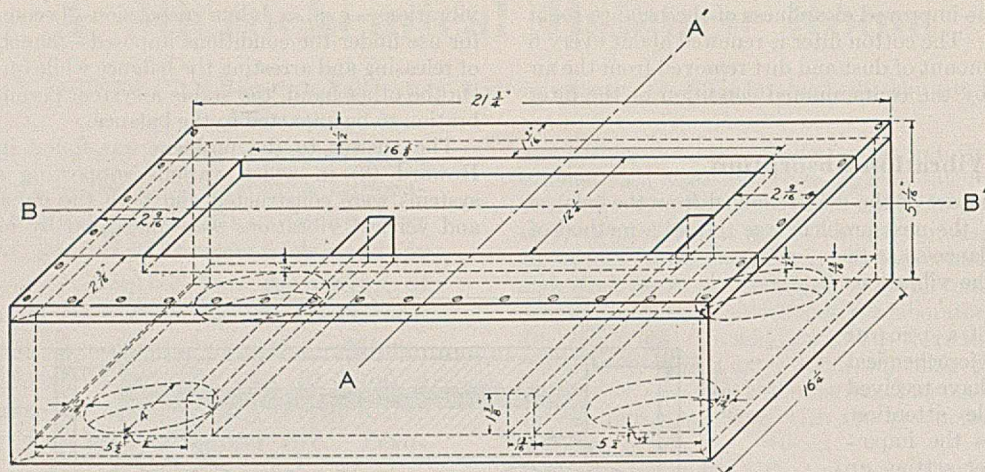


FIGURE 2. WOODEN BOX SURROUNDING SUPPORTING SYSTEM

by removing the balance, glass plate, and felt from the support. The top of the wooden box is unscrewed and removed and the lead plates are lifted off the balls. New balls are substituted for the old ones and the support is reassembled. In the gradual settling process it is necessary to check periodically on the balance to make sure that it is always level. No large or sudden changes in zero point have ever been observed on any of the balances mounted on these supports. The two lower transverse wooden cross pieces are added to the box to prevent the balance from dropping any great distance in case a ball should collapse. So far, such an accident has never occurred.

The effectiveness of this mounting is plainly shown by observing a shallow dish of mercury placed on the support. With the normal vibrations present in the room there is no noticeable motion of the mercury surface and even with severe vibrations set up by pounding the balance table with the fist, jumping up and down on the balance room floor, roughly sliding the outer balance case window up and down, etc., there is only a faint rippling of the mercury surface. However, with the dish of mercury on the balance table the normal vibrations present cause the surface to be in a constant state of motion and the strong production of vibration, by the methods just mentioned, causes violent agitation of the mercury surface.

Illumination

With the type of balance table and case in use it is possible to illuminate the scale of the balance sufficiently and at the same time prevent excessive heat from reaching the balance. This is accomplished by placing a large shallow beaker filled with distilled water on the top of the external balance case and placing a 100-watt bulb and shade just over the top of this beaker, which is carefully centered over the balance. The rays from the bulb pass through a 10-cm. (4-inch) column of water which absorbs practically all the heat, so that the underside of the glass barely becomes warm even if the light is left on continuously. The bulb is at a distance of about 37.5 cm. (15 inches) from the top of the balance. For safety's sake, wire glass is used in the top of the outside balance case, so that if this glass should crack the beaker of water could not fall onto the balance.

Humidity

Hernler (7) first pointed out that a relative humidity of 60 to 70 per cent seemed most favorable for carrying out carbon-hydrogen determinations and mentioned that a 45 per cent humidity was too low. Recently, Hayman (6) found that if the relative humidity was maintained above 45 per cent little difficulty was encountered with static charges being developed

on the surface of the absorption tubes during wiping, but that if the humidity dropped below 40 per cent these difficulties became serious. The same observation was made, independently, in this laboratory. The author found that if the relative humidity is maintained above 50 per cent no difficulty arises from static charges in weighing the absorption tubes, but that below this point the weighing becomes troublesome. In the summer there is no difficulty in maintaining the humidity above 50 per cent. In the winter the humidity is kept above 50 per cent, both by the water which evaporates from the beakers which absorb the heat from the lights and also by having a round Cenco, three-heat electrical water bath (110 or 220 volts, 50 to 600 watts) in the balance room. This adds moisture to the atmosphere but apparently adds relatively little heat. A satisfactory control of the humidity can be thus obtained with little effort. Daily records are kept of the humidity and it has been found that the maximum change in humidity in the balance room over a 7- to 8-hour interval is less than 5 per cent.

Temperature

The importance of careful temperature regulation of the balance room has been stressed by all microchemical authorities. There appears to be general agreement with Schwarz-Bergkamp (11) that in order to weigh to an accuracy of 2γ the balance must be set up in a room in which daily temperature fluctuations are less than 1°C . and the temperature should be maintained above 20°C ., so that the body temperature of the operator has less influence.

The laboratory surrounding the author's balance room is kept at an approximately constant temperature in the winter by means of a unit gas heater suspended from the ceiling and operated by an electrically controlled thermostat. The primary function of this heater is to maintain the laboratory room at constant temperature during the night when the steam heat is turned off. During the day time a fairly constant temperature is maintained in the laboratory by manual adjustment of the steam radiator. The temperature of the balance room itself is maintained at 24° to 25°C . and held constant, within the limits mentioned above, by means of an electrical heater placed in one corner of the room and operated manually. A recognized improvement would be the use of an automatic thermostatically controlled electrical heater such as is described by Furter (4).

With the progress constantly being made in air conditioning it is probably safe to predict that in the not far distant future, small, relatively inexpensive units will be available which would be adequate for a balance room such as that

under discussion. The problems of dust removal, temperature control, and proper humidification would all be simultaneously solved by the use of such a unit, which would be especially important in the summer time. In the balance room above described there is, at present, no attempt made to control the temperature and humidity during the hot, humid summer months. The temperature of the balance room during these months sometimes rises as much as 4° to 5° C. from morning to night and relative humidities of 80 to 90 per cent are not uncommon.

Grateful acknowledgment is hereby made to J. A. Thompson, chief mechanic of the laboratory, for making and installing the air filter and for the construction of the electrical heater and the three balance supports; to H. C. Howard for directing attention to his paper on vibration absorbers; and to other members of the laboratory for valuable suggestions.

Literature Cited

- (1) Boëtius, M., "Über die Fehlerquellen bei der mikroanalytischen Bestimmung des Kohlenstoffes und Wasserstoffes nach der

Methode von Fritz Pregl," p. 18, Berlin, Verlag Chemie, 1931.

- (2) Emich, F., "Lehrbuch der Mikrochemie," 2nd ed., p. 76, Munich, J. F. Bergmann, 1926.
- (3) Friedrich, A., "Die Praxis der quantitativen organischen Mikroanalyse," p. 12, Leipzig and Wien, Franz Deuticke, 1933.
- (4) Furter, M., *Mikrochemie*, 18, 1-10 (1935).
- (5) Gorbach, G., *Ibid.*, 20, 254-336 (1936).
- (6) Hayman, D. F., *IND. ENG. CHEM., Anal. Ed.*, 8, 342-3 (1936).
- (7) Hernler, F., *Mikrochemie*, Emich Festschrift, 148-51 (1930).
- (8) Howard, H. C., *J. IND. ENG. CHEM.*, 13, 231-5 (1921).
- (9) Pregl, F., "Quantitative organische Mikroanalyse," 3rd ed., p. 13, Berlin, Julius Springer, 1930.
- (10) Pregl, F., and Roth, H., "Quantitative organische Mikroanalyse," 4th ed., p. 11, Berlin, Julius Springer, 1935.
- (11) Schwarz-Bergkamp, E., *Z. anal. Chem.*, 69, 321-41 (1926).
- (12) Weygand, C., "Quantitative analytische Mikromethoden der organischen Chemie," p. 8, Leipzig, Akademische Verlagsgesellschaft, 1931.

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Carbon Dioxide Generator for the Micro-Dumas Determination of Nitrogen

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COMMERCIAL solid carbon dioxide has attained widespread use as a convenient source of the gas and two generators utilizing this material have been described (1, 2).

The generator described below was designed specifically for use in the micro-Dumas determination of nitrogen according to Pregl, for which purpose it has been found very satisfactory and convenient. The gas delivered is of uniformly high purity, and where intermittent service is required the generator seems to be superior to those of the chemical type because of its simplicity and the ease of refilling. Once the air is displaced by the heavier gas, the generator gives a constant flow of pure carbon dioxide at a pressure fixed by the overflow valve, until the charge is exhausted.

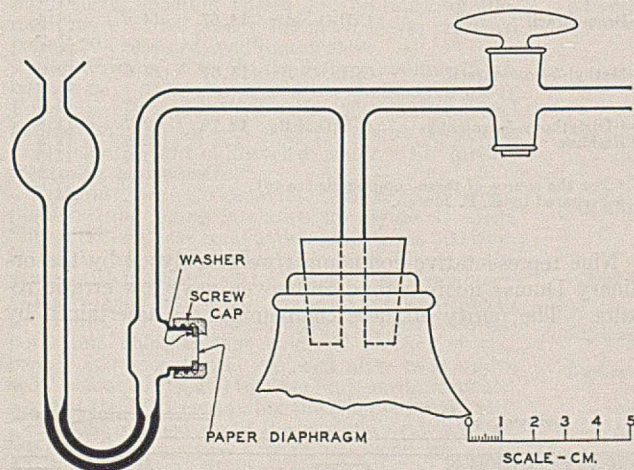


FIGURE 1. DIAGRAM OF APPARATUS

A commercial vacuum bottle (narrow-mouthed, 0.5-liter, 1-pint size) is nearly filled with finely crushed solid carbon dioxide and fitted with a one-holed rubber stopper carrying a T-tube, one side of which is sealed to the delivery stopcock and the other to a pressure-regulating valve (Figure 1). Two types of valve have been used; the first a simple all-glass mercury trap con-

sisting of a tube drawn to a 0.5-mm. capillary dipping under 3 to 4 cm. of mercury. Although this gave satisfactory service, the continuous escape of gas bubbling through mercury constitutes a possible health hazard, and a second valve was designed which overcomes this objection. This valve is illustrated in Figure 1 and consists of a mercury manometer actuated by the gas pressure, the mercury uncovering a paper diaphragm to release the excess gas. The best regulation is obtained by selecting a hardened filter paper (Carl Schleicher and Schüll, No. 575, hardened paper) of such porosity that a portion of the diaphragm remains uncovered by the mercury column. The trap is of soft glass, permitting the use of a short portion of a 15-mm. diameter vial with a perforated screw cap for the diaphragm holder. A washer of Neoprene is inserted between the glass and the paper to make a seal. If this order is reversed and the paper placed in contact with the glass, the gas leaks out too rapidly and causes oscillation of the mercury column. When properly adjusted, the fluctuation is less than 1 mm. of mercury.

After filling, the generator is allowed to stand for several hours before use, preferably overnight. The escaping gas sweeps out all the air and the resulting microbubbles fulfill the requirements (3, 4). A volume of approximately 30 cc. of gas absorbed in alkali in a microazotometer, at the rate of 2 bubbles in 3 seconds for a period of 0.5 hour, left a residue of 2 to 3 cu. mm. Charged with 450 grams of solid carbon dioxide, the generator delivered 3.4 grams of gas per hour at the start and 2.5 grams per hour after 100 hours. This rate will of course vary with different vacuum bottles. For continuous operation, the generator may be recharged every fourth or fifth evening and then is ready for use on the following morning.

Literature Cited

- (1) Conard, *J. Chem. Education*, 13, 539-40 (1936).
- (2) McIntosh, *Proc. Trans. Nova Sectian Inst. Sci.*, 17, Pt. 1, 71-8 (1927).
- (3) Pregl, "Quantitative Organic Microanalysis," 2nd ed., tr. by E. Fyfe, pp. 91, 102, Philadelphia, Pa., P. Blakiston's Son & Co., 1930.
- (4) Trautz, *Mikrochemie*, 9, 300 (1931).

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Nitrogen Determination in Refractory Substances

By a Modification of the Dumas Micromethod

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CERTAIN organic compounds, including derivatives of pyrimidine, purine, and chlorophyll (2, 4), give low erratic values for nitrogen by the Dumas micromethod. This difficulty often occurs with compounds which carbonize on heating to yield particles of "nitrogenous charcoal," or material only partly burned by oxygen supplied by the adjacent copper oxide. When this source of oxygen is exhausted, complete combustion cannot be accomplished even by heating at a high temperature. To obviate this lack of oxygen it has been recommended that potassium chlorate be mixed with the sample along with the fine copper oxide. This procedure is not satisfactory, presumably because of the low temperature (400° C.) at which potassium chlorate gives up its oxygen (1, 4). The oxygen is liberated and passes on before the compound has completely burned. Other suggested methods involving the use of potassium dichromate or lead chromate, which decompose at higher temperatures, are discussed by Friedrich (1). He concludes, however, that the results are not entirely satisfactory and should be confirmed by the Kjeldahl method. Milner and Sherman (2) draw a similar conclusion. Weidemann (4) recommends allowing the tube to cool after the combustion is first carried out in the normal way. The region in which the unburned residue may be found is then tapped to bring fresh copper oxide in contact with the nitrogen-containing residue, and the tube is reheated. This procedure has given good results with chlorophyll derivatives (4).

A modification of the Dumas micromethod leading to wider applicability provides advantages in determining empirical formulas of naturally occurring nitrogenous compounds and their derivatives. The authors' procedure obviates the need for confirmatory Kjeldahl determinations and results in economy of time, particularly for compounds requiring reduction prior to Kjeldahl digestion.

Modified Method

The essential features of the modified method are as follows: Pure potassium chlorate is used to supply oxygen. To overcome the objectionable low decomposition point, the potassium chlorate is not mixed with the sample but is placed in a porcelain boat in the unoccupied portion of the combustion tube following the copper oxide. The organic compound is burned in the usual manner and the evolved nitrogen is swept out with carbon dioxide until the approach of microbubbles. The carbon dioxide flow is then stopped and the portion of the tube including the sample and intervening distance to the furnace is heated with a wing-tipped burner while the chlorate is slowly decomposed by heating with another burner. In

this way the nitrogenous residue is subjected to an atmosphere of oxygen at a temperature of about 600° C. The copper adjacent to unburned particles is alternately oxidized and reduced until combustion is complete. To protect the reduced copper oxide in the permanent filling, a 10- to 15-mm. section of coarse reduced copper oxide is placed in the temporary filling of the combustion tube. Rate of gas flow into the azotometer is controlled by stopcock *b*, Figures 1 and 2, during the sweeping-out processes. This prevents the sudden compression of gas in the combustion tube which occurs at the outset of the scavenging period when regulation of gas flow is accomplished by stopcock *a*. This point is important, particularly following the decomposition of the chlorate, to prevent too rapid passage of oxygen into the heated copper section of the tube.

TABLE I. NITROGEN CONTENT BY THE KJELDAHL AND UN-MODIFIED DUMAS MICROMETHODS

Compound	Formula	Nitrogen		
		Calcd. %	Kjeldahl %	Dumas %
2-Hydroxy-6-aminopurine ^a	C ₅ H ₅ N ₃ O	46.34	46.4	43.8
			46.3	44.8
				39.4
				45.6
			44.8	
Cytosine	C ₄ H ₅ N ₃ O	37.83	37.8	36.2
				36.1
				36.6
1-Methyleytosine	C ₅ H ₇ N ₃ O	33.59	33.6	33.6
				33.8
				33.9
				33.6
			33.6	
2-Hydroxy-6-aminopurine- <i>d</i> -ribose ^a	C ₁₁ H ₁₃ O ₅ N ₅	24.73	24.7	22.8
				22.4
				24.3
				23.8
Thymine ^b	C ₅ H ₈ N ₂ O ₂	22.22	22.0	22.1
				22.3
				22.2
5-Bromocytosine	C ₄ H ₄ N ₃ OBr	22.12	22.2	21.1
				21.0
				21.2
5-Bromouracil	C ₄ H ₃ O ₂ N ₂ Br	14.67	14.6	14.4
				14.3
				14.4
1-Methyl-5-bromouracil	C ₅ H ₃ O ₂ N ₂ Br	13.67	13.6	12.9
				13.0
				13.2
2-4-Dimethoxy-5-bromopyrimidine	C ₈ H ₇ O ₂ N ₂ Br	12.79	12.7	11.8
				12.8
				11.5
				12.7

^a For the source of these compounds see (5).

^b Prepared by E. F. Jansen.

Nine representative compounds were analyzed by the ordinary Dumas micromethod and seven gave low erratic results. The purity of these compounds was ascertained by

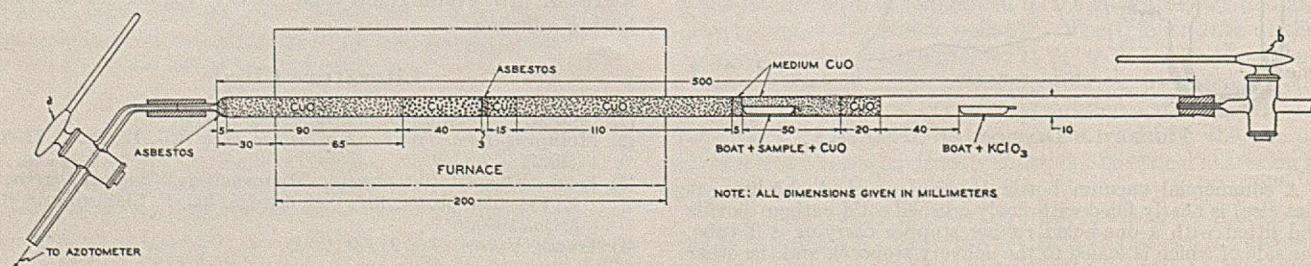


FIGURE 1. COMBUSTION TUBE FILLING

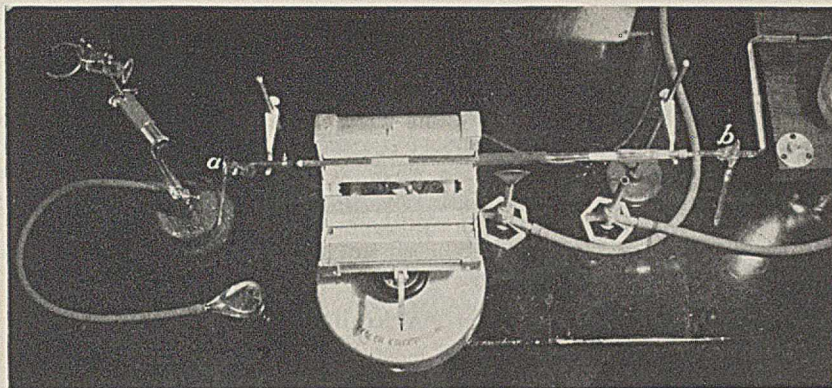


FIGURE 2. PHOTOGRAPH OF APPARATUS

analysis by the Kjeldahl micromethod. In some of the analyses as much as 14 per cent of the nitrogen was not obtained. Several of the compounds analyzed by the authors were reported by Milner and Sherman (2), who also obtained low results. Table I gives a summary of the results obtained by the Kjeldahl and the unmodified Dumas method. It is interesting that 1-methylcytosine and thymine could be analyzed correctly by the usual method.

The authors' modified Dumas method gave consistently correct values on all seven of the compounds which could not be analyzed by the regular method. More than 99 per cent of the nitrogen can be obtained by this modification. Detailed results of these analyses are given in Table II. The analyses reported are unselected and include all those made after the method was perfected. The amount deducted from the volume of nitrogen gas has been the subject of considerable investigation by others (5). The authors have chosen the 2 per cent correction because it gave satisfactory results with their modification.

Experimental

REAGENTS. Reagent grade potassium chlorate is used. Three additional recrystallizations made no apparent difference in the results obtained. Whether further purification of the potassium chlorate is necessary should be determined by analysis of a compound of known purity.

Copper oxide: coarse passes 20-, retained by 40-mesh sieve; medium passes 40-, retained by 100-mesh sieve; fine passes 100-mesh sieve; reduced passes 20-, retained by 40-mesh sieve.

Carbon dioxide is obtained from sodium bicarbonate in a generator similar to that described by Poth (3). Potassium hydroxide solution is prepared by dissolving 85 per cent stick potassium hydroxide in an equal weight of distilled water. No further treatment is necessary.

FILLING THE COMBUSTION TUBE. The combustion tube filling is shown in Figure 1. Jena Supermax or Pyrex combustion glass tubes 500 mm. in length are used. The permanent filling is the same as that described by Pregl. The temporary filling is made as follows: reduced copper oxide, 10 to 15 mm., to take care of excess oxygen from the potassium chlorate (the oxidized portion of this copper is removed and replaced after each analysis); coarse oxide, 100 to 110 mm.; medium oxide, 5 mm.; the boat containing the sample mixed with fine oxide, pushed up to the medium oxide with an ignited platinum wire and enough medium oxide poured in to surround it, making a section at least 55 mm. in length; coarse oxide, 20 mm.; and powdered potassium chlorate, 100 to 125 mg., in a 30-mm. porcelain boat, pushed into the tube to within 40 mm. of the final coarse copper oxide. An electric furnace is used to heat the tube in place of the gas long-burner.

WEIGHING AND PREPARATION OF THE SAMPLE. The sample is spread in a thin line along the length

of a 30-mm. porcelain boat and weighed on the microchemical balance. The boat is then half-filled with fine copper oxide and the sample and oxide are mixed thoroughly by careful stirring with a 25-mm. length of 30-gage platinum wire which is slightly flattened on one end. The wire is then laid on the oxide and the boat is filled with fine oxide. This method of mixing sample and oxide has given satisfactory results with a variety of compounds and obviates objectionable features of Pregl's method of introducing the sample.

GENERAL PROCEDURE. The apparatus used is shown in Figure 2. After inserting the boat containing the sample, the combustion tube should be inclined at an angle of about 45 degrees while sufficient medium copper oxide is poured in to surround it, care being used that the sample and fine oxide remain distributed over the full length

of the boat. Precaution should be taken in handling and connecting the filled combustion tube, so that the copper oxide remains tightly packed around the boat. The tube is evacuated (5) and the preliminary sweeping-out process and combustion are carried out in the usual way. All regulation of gas flow is accomplished by stopcock *b*, the plunger of which is notched to facilitate regulation.

The end of the carbon dioxide inlet tube, where it passes through the combustion-tube stopper, is melted down to a fine capillary opening as an additional aid to control of gas flow. The size of the orifice is such that 30 to 45 seconds are required for the evacuated tube to become filled with carbon dioxide when the pressure in the generator is about 40 mm. of mercury. This prevents any considerable volume of gas from passing through the tube if stopcock *b* is accidentally opened too far. Stopcock *a* is used solely to maintain vacuum in the tube while it is being connected to the azotometer.

After the combustion, when the sweeping-out process is almost completed, stopcock *b* is closed, and the lighted wing-tipped burner is gradually put in place. The other lighted burner is also gradually put in place between the boat containing chlorate and the combustion tube stopper. Stopcock *a* is open during

TABLE II. NITROGEN CONTENT BY MODIFIED DUMAS METHOD

Compound	Formula	Sample Mg.	Nitrogen			Difference %	Devia- tion of Average from Theory %
			Found ^a %	Calcd. %	Av. %		
Acetanilide ^b	C ₈ H ₉ NO	4.920	10.44	10.37	10.47	+0.10	+0.96
		4.803	10.50				
2-Hydroxy-6-amino- purine	C ₄ H ₅ N ₃ O	3.041	46.31	46.34	45.98	-0.36	-0.78
		3.049	45.90				
		3.137	45.75				
		2.789	45.94				
		1.890	46.06				
Cytosine	C ₄ H ₅ N ₃ O	1.867	45.91				
		1.977	46.22				
		2.251	45.75				
		2.306	37.77	37.83	37.85	+0.02	+0.05
		2.622	38.06				
1-Methylcytosine ^b	C ₅ H ₇ N ₃ O	3.700	37.76				
		3.844	37.81				
		4.540	33.47	33.59	33.74	+0.15	+0.45
		4.447	33.59				
2-Hydroxy-6-amino- purine- <i>d</i> -riboside	C ₁₀ H ₁₃ N ₅ O ₅	3.077	34.04				
		3.629	33.87				
Thymine ^b	C ₅ H ₈ N ₂ O ₂	2.781	24.78	24.73	24.85	+0.12	+0.49
5-Bromocytosine	C ₄ H ₄ N ₃ OBr	2.587	24.91				
		3.912	22.29	22.22	22.29	+0.07	+0.31
5-Bromouracil	C ₄ H ₃ N ₂ O ₂ Br	3.623	22.01	22.12	22.08	-0.04	-0.18
		3.817	22.15				
		4.563	14.95	14.67	14.74	+0.07	+0.48
1-Methyl-5-bromouracil	C ₅ H ₅ N ₂ O ₂ Br	4.083	14.78				
		4.186	14.49				
		4.296	13.77	13.67	13.68	+0.01	+0.07
2,4-Dimethoxy-5- bromopyrimidine	C ₆ H ₇ N ₂ O ₂ Br	3.993	13.59				
		4.054	12.59	12.79	12.64 ^c	-0.15	-1.17
		3.622	12.57				
		3.653	12.77				

^a Although in most cases the volume of nitrogen could be read only to three significant figures, the calculation was carried to four places for purposes of comparison with the theoretical value.

^b These compounds give correct nitrogen values by the unmodified method and therefore serve as controls for the modified method.

^c The low result is accounted for by the fact that this compound sublimes easily and probably some of the sample is lost in evacuating and sweeping out the combustion tube.

this time, so that heating up the combustion tube must be gradual to prevent undue increase in the rate of gas flow into the azotometer. The potassium chlorate is then decomposed, using a low flame, by advancing the burner a few millimeters at a time. The rate of gas flow should at no time exceed two bubbles in 3 seconds. Fifteen to 25 minutes are usually required for this operation. When all the potassium chlorate is decomposed, the mercury sucks back from the azotometer as oxygen is taken up by the copper. The combustion tube is then swept out until microbubbles are attained. Heating with the wing-tipped burner is continued while oxygen remains in the tube. The electric furnace must be left in place until just prior to disconnecting the azotometer to prevent passage of oxygen due to cooling of the copper. The filling surrounding the boat, after an analysis using potassium chlorate, should show only copper oxide.

An ignited 3-mm. brass rod is used to aid in removing the slightly fused temporary filling after each analysis. If the combustion tube is of sufficiently large diameter, no trouble will be experienced in removing the boat which contained potassium chlorate. Combustion tubes become discolored after twenty to thirty analyses and it becomes difficult to see into them when filling. Discolored tubes may be cleaned by removing the filling and washing with water, followed by aqua regia if necessary.

Used copper-copper oxide is recovered by washing out the potassium chloride with distilled water, drying, sieving, and igniting in a nickel crucible.

The amount of nitrogen obtained in the second phase of the combustion, during which the chlorate is decomposed, ranges from about 0.01 to 0.05 cc.

Summary

A modification of the Dumas micromethod for nitrogen is described which gives satisfactory results with compounds

which are resistant to combustion by the ordinary method. The method involves the use of potassium chlorate to supply oxygen. To overcome the objectionable low decomposition point of the chlorate, it is decomposed after the combustion of the organic compound while the site of the unburned residue is heated to about 600° C., thereby subjecting the nitrogenous residue to an atmosphere of oxygen at high temperature. Seven compounds, which include derivatives of pyrimidine and purine, were used for this study and it seems reasonable to expect that all refractory compounds of this type can thus be analyzed.

Acknowledgment

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Literature Cited

- (1) Friedrich, P. A., "Die Praxis der quantitativen organischen Mikroanalyse," pp. 74-5, Leipzig and Vienna, Franz Deuticke, 1933.
- (2) Milner, R. T., and Sherman, M. S., *IND. ENG. CHEM., Anal. Ed.*, 8, 331 (1936).
- (3) Poth, E. J., *Ibid.*, 2, 250 (1930).
- (4) Pregl, F., "Quantitative Organic Microanalysis," edited by H. Roth, tr. by E. B. Daw, 3rd English ed., pp. 85-6, Philadelphia, P. Blakiston's Son & Co., 1936.
- (5) *Ibid.*, pp. 70-2.
- (6) Spies, J. R., and Drake, N. L., *J. Am. Chem. Soc.*, 57, 774 (1935).

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The following is suggested as a general outline to be followed in preparing analytical methods for this edition:

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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

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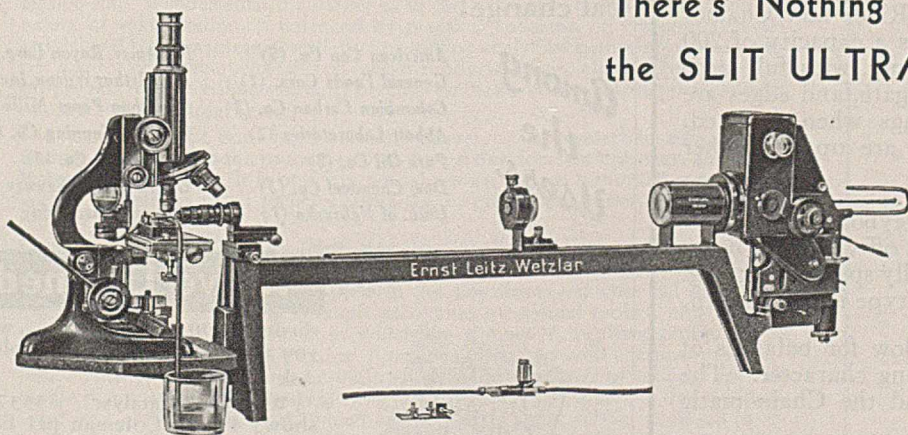
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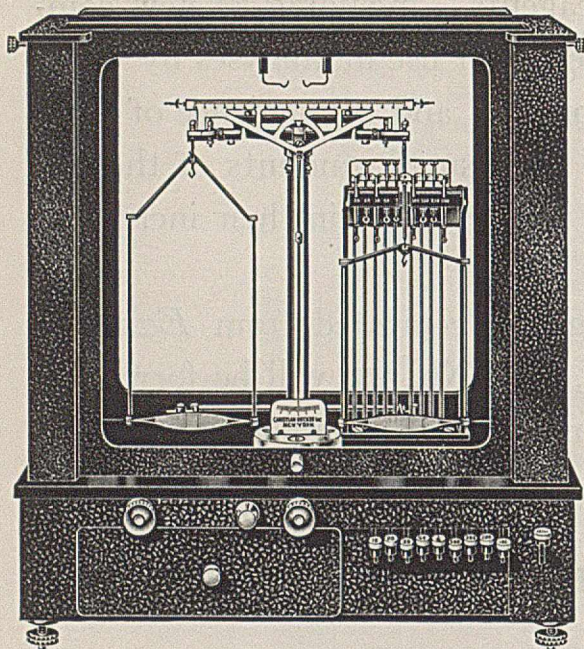
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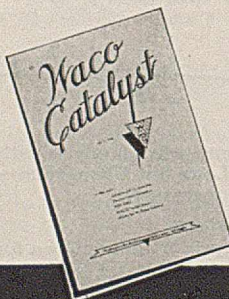
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Edited by: **Carroll C. Davis and John T. Blake, and**
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REMARKABLY comprehensive in its scope, this official publication of the A.C.S. Rubber Division has at last provided an authoritative reference book on both the theoretical and practical aspects of rubber technology. The fact that each chapter has been contributed by an expert or group of collaborators, especially eminent in their own particular fields, gives the book an authority, and a compelling interest, obtainable in no other way. For each special subject great care has been exercised to furnish adequate historical perspective for the most significant presentation of recent developments. Other attractive features are extensive bibliographies conveniently placed at the end of each chapter, and an unusually complete index, particularly emphasizing cross-references. A final chapter devoted to concise discussion of the literature of rubber chemistry also increases the utilitarian character of this volume.

In view of the notable advances in rubber manufacture during the past two decades, the appearance of this monograph is especially timely. Although there are several contributions from renowned Europeans and Canadians, this is essentially a treatise by American experts on current practice in the American industry. While adequately covered, the production of crude rubber and liquid latex is not unduly stressed. Rather emphasis is placed on the latest technical developments in the manufacturing industry, which have grown out of such research achievements as the x-ray study of the configuration of the rubber molecule; a more complete understanding of the behavior of rubber in liquids; and the growing realization of the basic changes in physical structure developed during reinforcement loading and vulcanization.

The special value of this book lies in the fact that the exposition of these recondite theoretical studies is well balanced by the comprehensive discussion of up-to-date manufacturing practice. The exhaustive treatment of the mechanism of the ageing, oxidation, and deterioration of rubber on exposure to light and heat, for example, is supplemented by a complete list of commercial anti-oxidants and age-resisters, and by a detailed description of the beneficial effect of other compounding ingredients in this respect. The fundamental, mathematical physics of vulcanized rubber, is offset by a chapter on current standard test methods and physical testing equipment. Fundamental theorizing as to the mechanism of acceleration, or the nature of vulcanization, is balanced by practical comments on compounding materials, and by a complete compilation of routine analytical methods for crude rubber and for commercial, vulcanized rubber products. Specialized subjects such as rubber reclaiming; balata and gutta percha; synthetic rubber and rubber substitutes receive adequate treatment.

The result is that the book has a universal appeal, to the research investigator and student, as well as to the routine analyst, to the development engineer, and to the factory compounder. It is both a practical manual and an authoritative reference work. It belongs in all technical libraries, in plant laboratories, and in factory offices.

Outside the rubber industry itself, this monograph will prove invaluable to research and development men in the numerous industries supplying materials for use in rubber compounding. Engineers in the petroleum and chemical industries, which are now considering synthetic substitutes for natural rubber, also will be much stimulated by the manner in which the distinctive, resilient properties of rubber are correlated with physical structure rather than with chemical composition. Finally, this book will be indispensable for consumers of rubber; for the textile plants which are now employing liquid latex very extensively; for the footwear and clothing industries which are constantly using rubber products to an increasing extent; for automotive and other mechanical design engineers interested in the dampening of vibration and the elimination of noise; and for industrial maintenance engineers everywhere, who are increasingly using rubber mechanical goods for factory and field installations, as for instance the growing use of rubber containers.

Although there are several contributions from renowned Europeans and Canadians, this is essentially a treatise by American experts on current practice in the American Industry

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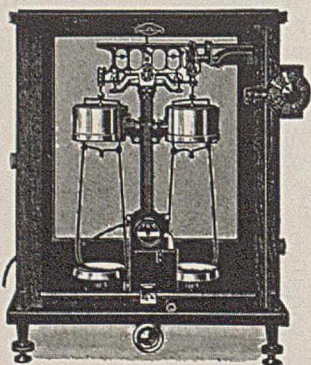
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Air-Damped Balance D3 "Proja"

FOR rapid weighings. Exact readings from 0 to 10 mg. with accuracy of .1 mg. on large projection scale. No eye strain from prolonged observations. All optical components are fixed to the pillar.

The damping device stops the balance after a single oscillation. Weights from 10–990 mg. are placed on right side of beam by rotating two dials. Direct readings eliminating errors. Zero point adjustment from outside of cabinet. Automatic light switch.

Particulars on request

Pfaltz & Bauer, Inc.
EMPIRE STATE BUILDING, NEW YORK

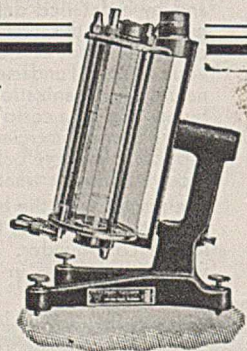
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Direct readings in Centipoises.
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Results consistent and reproducible.
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Bulletin HV 251 available on request.



Model B

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For micro-filtration according to the workings of Pregl, Emich, Lieb, Chamot and others. These filters possess numerous advantages. They are not attacked by such liquids as Fehlings Sol., alkali hydroxide, sulphuric acid, etc.; allow complete visibility during filtration, and can easily be cleaned. Available in various forms and porosities.



Immersion



Pregl

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