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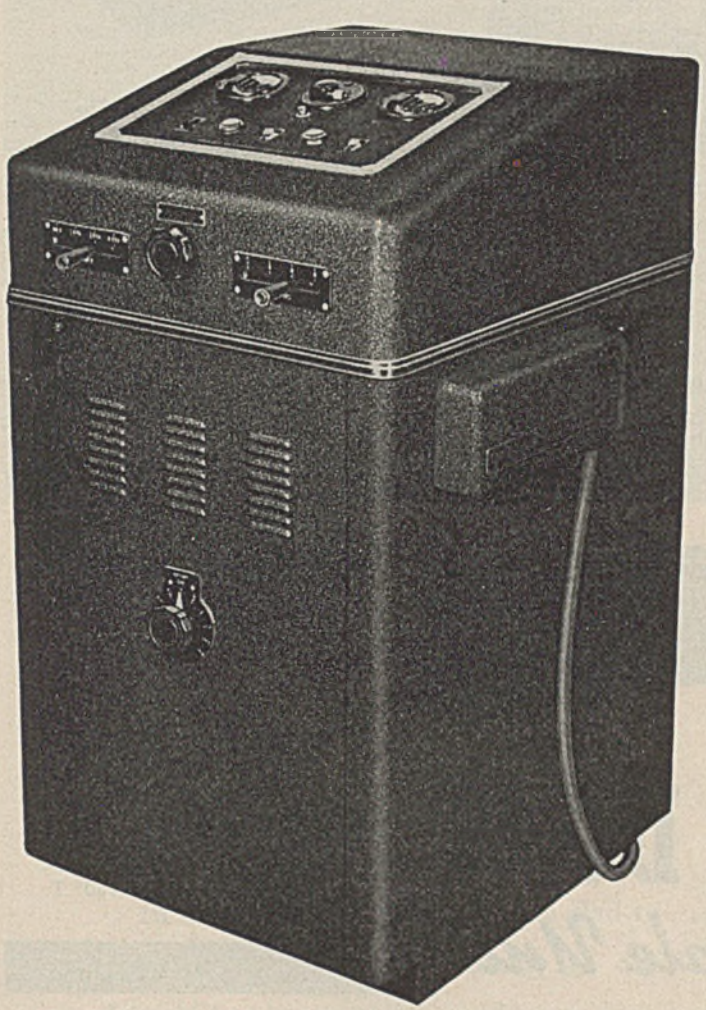

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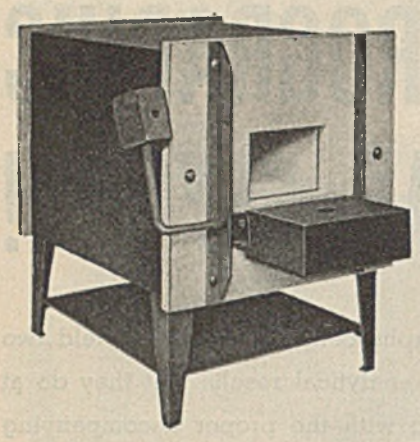

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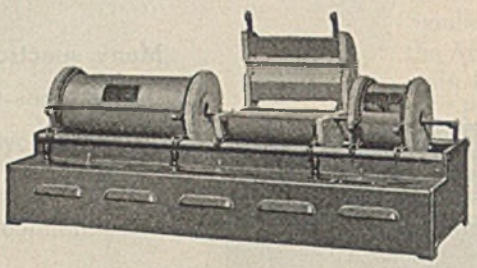

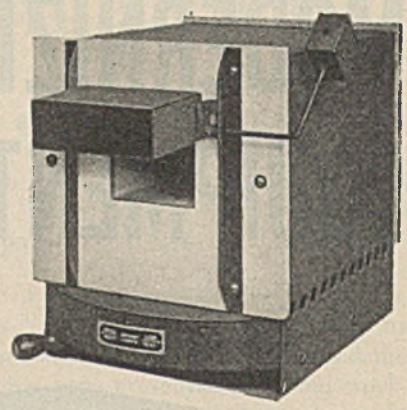

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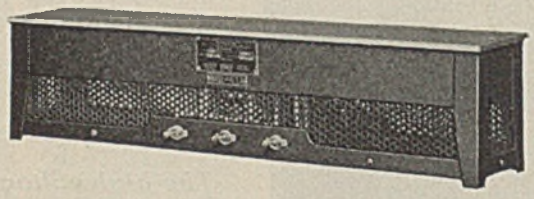

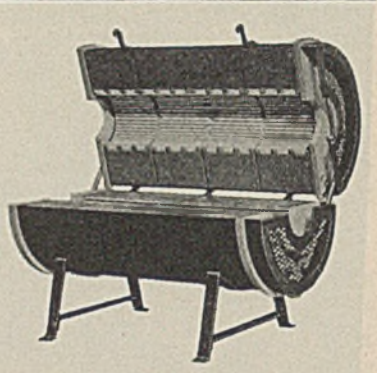

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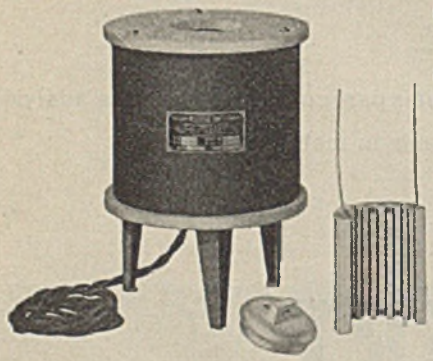

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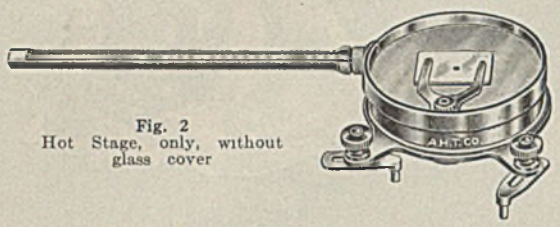


Fig. 2
Hot Stage, only, without glass cover

For determining corrected micro melting points on the microscope with samples as small as a single crystal

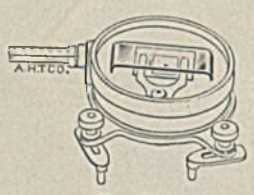


Fig. 3
Showing Glass Baffle D in position on Hot Stage

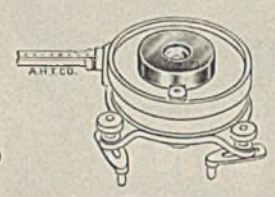


Fig. 4
Showing Type B Fischer Sublimation Block in position on Hot Stage

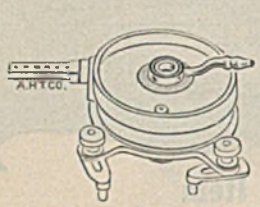


Fig. 5
Showing Kofler - Dernbach Vacuum Chamber in position on Hot Stage

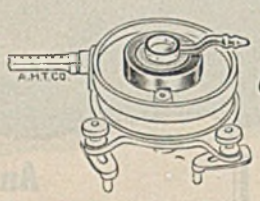
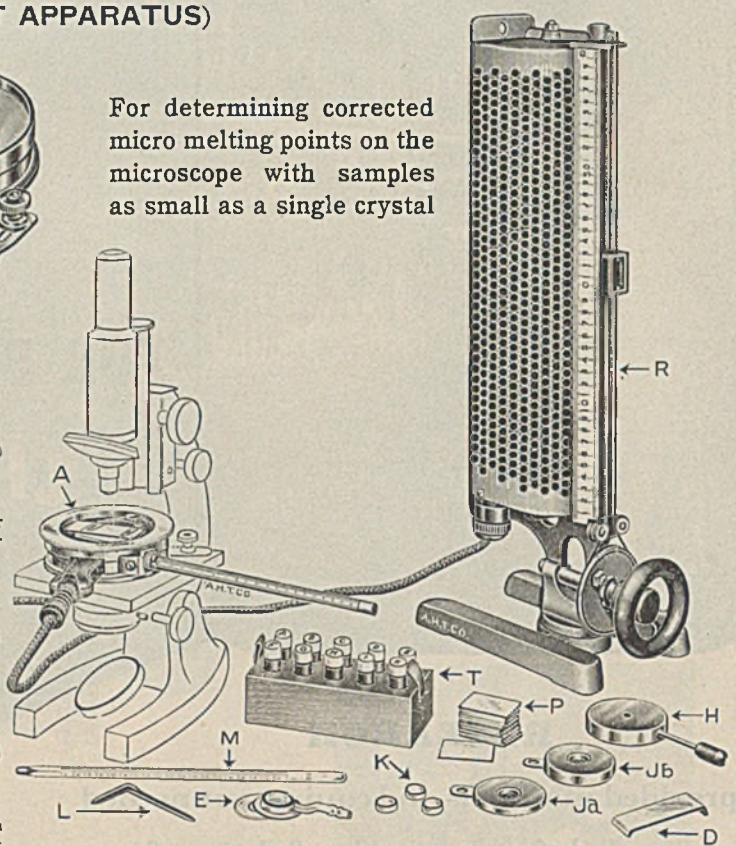


Fig. 6
Showing Kofler - Dernbach Vacuum Chamber in position on Fischer Block



6886-A — Fig. 1. Showing Complete Assembly

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6886-A. **Micro Hot Stage, Kofler,** as above described, complete outfit as shown in illustration, i.e., Hot Stage A, two calibrated thermometers M, cooling block H, Fischer sublimation blocks Ja and Jb, glass baffle D, three sublimation dishes K, Kofler-Dernbach vacuum sublimation chamber E, fork lifter L, twenty-four micro slides P, set of test reagents T, and vertical rheostat R; in case, with directions for use. For 115 volts, a.c. or d.c. 204.25

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Determination of *o*-Cresol in Phenol by a Cloud Point Method

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Calco Chemical Division, American Cyanamid Company, Bound Brook, N. J.

IN THE process of freeing phenol from *o*-cresol by distillation it is important to have an accurate method for determining low concentrations of the latter in the presence of the former, in order to evaluate the plate efficiency of the column. It is assumed from a knowledge of the compounds involved that only *o*-cresol is present with the phenol.

One method for *o*-cresol in phenol (*6*, *10*) is based upon the formation of a complex between *o*-cresol and cineole, followed by the determination of the freezing point of this complex. This seems to be more suitable for high concentrations of cresol. Another method which has been recommended by a number of authors (*3*, *7*, *8*, *11*) is based upon the lowering of the freezing point of phenol. Unfortunately, *o*-cresol freezes out with the phenol in a continuous series of mixed crystals (*3*). This would make it impossible to get very accurate values of *o*-cresol unless the degree of supercooling were rigidly controlled in relation to the concentration of *o*-cresol. The extent of this difficulty is obvious from an inspection of the divergent values reported for the lowering of the freezing point of phenol by *o*-cresol (*3*, *7*, *8*, *11*). At least one of these authors (*3*) recognized this difficulty, and so determined the temperature at which the last crystals melted, instead of the usual freezing point, in order to avoid the effects of supercooling. This would, however, make the procedure less adapted to routine use. Besides, the lowering of the freezing point for a given *o*-cresol content is considerably less than the corresponding lowering of the cloud point in the method reported below.

The statement (*1*) that 1 volume of cold liquefied phenol (rendered liquid by the addition of 8 per cent of water) forms, with 1 volume of glycerol, a clear liquid which is not rendered turbid by the addition of 3 volumes of water (absence of creosote and of cresol) suggested the possibility that a cloud point method could be developed for *o*-cresol in phenol. Dolique (*4*) has published a study of the systems phenol-water and phenol-glycerol-water, including the effects of a number of impurities. Other papers have also been published on the influence of impurities on the critical solution temperature of phenol-water (*2*, *5*, *9*), but in none did the authors find that *o*-cresol had been included.

The authors' first work was done with the system phenol-water-glycerol with additions of *o*-cresol, but this was abandoned in favor of the phenol-water system because the former involved some difficulties in the precise observation of the cloud point, and had no advantage over the simpler system. Working with mixtures of phenol and *o*-cresol containing up to 5.6 per cent cresol, and also containing water added in the ratio of 65 parts by weight to 35 parts by weight of the mixed phenol-cresol, the authors found that each addition of cresol increases the cloud point to an extent that can be expressed by two linear equations, one for concentrations from 0 to 3 per cent *o*-cresol and the other for concentrations from 3 to 5.6 per cent. The method has an accuracy for the lower concentration range which is expressed by a standard deviation of a single value from the true *o*-cresol content of ±0.07 per cent *o*-cresol and for the higher concentrations of ±0.09 per cent. The accuracy can obviously be increased by taking the average of more than one determination.

Method of Analysis

About 7 to 8 grams of the phenol sample are placed in a dry, tared test tube (2.5 × 15 cm.) and weighed to the nearest milligram. A number of milliliters of distilled water equal to 1.857 times the weight of the phenol sample (this makes a mixture of 35 per cent phenol sample and 65 per cent water) are added from a buret. The tube is placed in a water bath at 75° to 80° C. and its contents are mixed with a glass stirrer (looped to fit around the thermometer to be used later) until the mixture is clear. The tube is then centered by means of a cork in a larger test tube (3.25 × 17.5 cm., 1.5 × 7 inches) which serves as an air jacket and is kept in a water bath maintained at about 65° C. A thermometer with 0.1° divisions, calibrated for 7.5-cm. (3-inch) immersion, is placed in the solution, which is then stirred vigorously (about 80 to 100 strokes per minute).

As the solution cools, a turbidity sets in which serves as a warning of the approach of the cloud point. This turbidity starts at about 1° to 2° before the cloud point, starting sooner the greater the concentration of cresol, but its onset and the increase in its opacity are not sharp. Finally there is an abrupt increase in the opacity of the mixture. This is taken as the cloud point and the thermometer is read to the nearest 0.05° C. The tube may be reheated and the determination repeated at will if it is desired to increase the accuracy by taking a mean of several values.

For cloud points up to 70.25° C., the percentage of *o*-cresol is calculated by the equation

$$\%\ o\text{-cresol} = \frac{\text{cloud point (° C.)} - 66.40}{1.326} \qquad (1)$$

and for cloud points from 70.25° to 73.5° C. by the equation

$$\%\ o\text{-cresol} = \frac{\text{cloud point (° C.)} - 66.81}{1.167} \qquad (2)$$

Development of the Method

PHENOL was purified by distilling C. P. phenol through a packed column, redistilling the middle cut, redistilling the middle cut from this, and collecting three successive cuts which had freezing points of 40.94°, 40.93°, and 40.93° C., respectively. The freezing points were run in a magnetically stirred enclosed apparatus to protect the phenol from absorption of moisture from the air. There was no significant change in the freezing point when the phenol was boiled in the freezing point tube in order to remove possible traces of moisture.

TABLE I. DEVIATION OF CALCULATED CRESOL VALUES FROM TRUE VALUES

Cloud Point (Mean of 10 Values) ° C.	Cresol Calculated %	Cresol Actual %	Deviation % cresol
	By Equation 1		
66.39	−0.01	0.00	−0.01
66.41 (mean of 5 values)	0.01	0.00	+0.01
67.00	0.45	0.45	0.00
67.36 (mean of 5 values)	0.72	0.67	+0.05
67.70	0.98	1.03	−0.05
68.19	1.35	1.37	−0.02
68.33	1.46	1.46	0.00
69.18	2.10	2.08	+0.02
69.40	2.26	2.33	−0.07
70.23	2.89	2.83	+0.06
	By Equation 2		
70.77	3.39	3.43	−0.04
71.59	4.10	4.17	−0.07
72.34	4.74	4.71	+0.03
73.42	5.66	5.59	+0.07

o-CRESOL was prepared by diazotizing and decomposing with water *o*-toluidine which had in turn been prepared from *o*-acetotoluide that had been recrystallized to a constant melting point of 110.9–111.6° C. (corrected). The *o*-cresol was distilled under reduced pressure. The middle cut had a freezing point (run in the aforementioned closed apparatus) of 30.99° C. (corrected). The same freezing point was obtained upon redistilling this material under reduced pressure and taking a middle cut.

THERMOMETERS. The thermometers were calibrated at an immersion depth of 7.5 cm. (3 inches) by comparing with another thermometer certified by the National Bureau of Standards.

GLYCEROL-WATER-PHENOL-CRESOL MIXTURES. Choosing proportions of phenol, glycerol, and water on the basis of data reported by Dolique (*4*), a number of cloud points were determined for phenol-cresol mixtures containing up to 5.83 per cent *o*-cresol. The phenol-cresol samples were mixed with an aqueous glycerol solution having a specific gravity at $\frac{30° \text{ C.}}{30° \text{ C.}}$ of 1.0218, in the ratio of 87.80 ml. of the glycerol solution to 13 grams of the phenol-cresol mixture. It was possible to get cloud point values for the individual mixtures which agreed within 0.05° C., but when the cloud points were plotted against the cresol content, some of the points fell away from a straight line by as much as 0.2 per cent cresol. The difficulty was with the determination of the cloud point. This did not appear sharply enough, so that there was a lack of concordance between the point taken as the cloud point for one sample and that for another, although two successive readings on the same sample were concordant.

PHENOL-WATER-CRESOL MIXTURES. The first mixture which was tried consisted of 32.15 per cent water and 67.85 per cent phenol by weight. Repeated determinations of the cloud point on the same mixture resulted in successive values, each of which was lower than the previous value by about 0.2° C., the initial value being 33.75° C. According to Dolique's data (*4*) a change in the water content of the mixture of about 0.07 per cent (or for the size of sample used, about 0.004 ml. of water) would suffice to lower the cloud point by 0.2° C. It would seem most likely that such losses explained the difficulty with this mixture.

It was next decided to use a mixture of 35 per cent phenol and 65 per cent water which would be closer to the critical solution temperature of the system, because the system is much less sensitive to small changes in composition in that region.

The method proposed does not pretend to determine the critical solution temperature, which is the temperature at which the two liquid phases become equal in composition. What is determined is merely the temperature at which a definite clouding phenomenon appears. Because of this fact it is unnecessary for the use of the method to resolve the divergencies in the critical solution temperatures which have been reported in the literature.

A number of mixtures were made up of phenol and *o*-cresol, ranging from 0 to 5.6 per cent *o*-cresol, and the cloud points were determined. With each mixture ten separate determinations of the cloud point were made (five in two cases). When the average cloud points were plotted against the known cresol content, it was found that the relationships could be expressed most conveniently by two straight lines (Equations 1 and 2). Possibly the fundamental relationship could be expressed by a hyperbolic equation, but the use of two straight-line equations seems more practical. The equations were chosen in such a way that the percentages of *o*-cresol, calculated for each of the average cloud points from the equations, would, when compared with the actual percentages of *o*-cresol, give deviations such that the difference between the sum of the squares of the positive deviations and the sum of the squares of the negative deviations would be at a minimum. The data are given in Table I.

Precision and Accuracy

The precision of the method will be determined by the degree of agreement between individual cloud point values on a single mixture and the mean. This has been determined for each of the 14 mixtures by calculating for each mixture the average deviation of each value from its respective mean and then multiplying by a factor (1.49 for 5 values and 1.36 for 10 values) to convert to the standard deviation. (The calculation of the standard deviation by means of a factor is not so accurate as by means of the usual root mean square average of the deviations from the arithmetic mean, but it is felt that the difference in the two methods of calculation is not sufficient to affect the reported standard deviations in the one significant figure to which they have been calculated.) The latter is then calculated to per cent *o*-cresol, using Equation 1 or 2. The data are given in Table II.

The accuracy of a single value was determined by calculating by means of Equations 1 or 2 the cloud point value corresponding to each actual percentage of *o*-cresol, getting the average deviations of the individual determined cloud point

TABLE II. PRECISION OF CLOUD POINT DETERMINATION

Composition of Sample % *o-cresol*	Cloud Point (Mean of 10 Values) ° C.	Average Deviation from Mean ± ° C.	Standard Deviation from Mean ± ° C.	Standard Deviation from Mean ± % *o-cresol*
0.00	66.39	0.050	0.07	0.05
0.00	66.41 (mean of 5 values)	0.068	0.10	0.08
0.45	67.00	0.045	0.06	0.05
0.67	67.36 (mean of 5 values)	0.040	0.06	0.05
1.03	67.70	0.045	0.06	0.05
1.37	68.19	0.040	0.05	0.04
1.46	68.33	0.045	0.06	0.05
2.08	69.18	0.067	0.09	0.07
2.33	69.40	0.061	0.08	0.06
2.83	70.23	0.067	0.09	0.07
		Av.	0.07	0.05
3.43	70.77	0.052	0.07	0.06
4.17	71.59	0.050	0.07	0.06
4.71	72.34	0.046	0.06	0.05
5.59	73.42	0.065	0.09	0.08
		Av.	0.07	0.06

TABLE III. ACCURACY OF METHOD

Composition of Sample % *o-cresol*	Calculated Cloud Point ° C.	Deviation from Calculated Cloud Point Average ± ° C.	Average ± % *o-cresol*	Standard ± % *o-cresol*
0.00	66.40	0.070	0.053	0.07
0.00	66.40	0.055	0.041	0.06
0.45	67.00	0.045	0.034	0.05
0.67	67.29	0.066	0.050	0.07
1.03	67.77	0.065	0.049	0.07
1.37	68.22	0.046	0.035	0.05
1.46	68.34	0.045	0.034	0.05
2.08	69.16	0.068	0.051	0.07
2.33	69.49	0.107	0.081	0.11
2.83	70.15	0.080	0.060	0.08
			Av.	0.07
3.43	70.81	0.062	0.053	0.07
4.17	71.68	0.090	0.077	0.10
4.71	72.31	0.056	0.048	0.07
5.59	73.33	0.091	0.078	0.11
			Av.	0.09

values from their respective calculated values, recalculating the average deviation to per cent cresol, and converting to the standard deviation as per cent cresol. These data are given in Table III.

The values indicate that the precision is a little better than the accuracy. By taking the mean of a number of cloud point determinations the standard deviation may be improved by a factor equal to the reciprocal of the square root of the number of determinations.

Effect of Variations in Water Content

Since the sample must be made up by adding water, it is important to know how changes in the water content of the prepared sample will affect the cloud points. This is particularly necessary because of the hygroscopic nature of phenol. If the accuracy of the method were affected by small changes in water content, it would be difficult to use.

Dolique (*4*) published data on the change of the critical solution temperature of phenol-water with changes in composition:

Water %	Phenol %	Critical Solution Temperature ° C.
61.16	38.84	66.4
64.13	35.87	66.5
65.00	35.00	66.5
65.69	34.31	66.5
68.46	31.54	66.4

It is seen that near the region of concentrations with which this method is concerned, the cloud point of pure phenol is insensitive to small changes in water concentration.

To two mixtures of cresol in phenol, 1 per cent less and 1 per cent more, respectively, than the usual 65 per cent of water were added, with results as follows:

o-Cresol Content %	Water Content %	Cloud Point ° C.	*o*-Cresol Found %	Error % *o*-cresol
1.14	64	67.78	1.05	−0.09
	65	67.91 (calcd.)	..	....
	66	67.88	1.13	−0.01
2.63	64	69.61	2.46	−0.17
	65	69.88 (calcd.)	..	....
	66	69.84	2.62	−0.01

It can be seen that 1 per cent additional water causes a negligible error. If about 15 ml. of water are measured from a buret for a single mixture, an excess of even 0.2 ml. will cause an error of no more than 0.01 per cent *o*-cresol. A deficiency of water may be more serious, but that can be avoided with considerable certainty.

Summary

A method has been devised for the determination of *o*-cresol in phenol in concentrations up to 5.6 per cent, by measuring the cloud point of a mixture of the sample with water. The relationship between the cloud point and the *o*-cresol content is expressed by one straight-line equation up to 3 per cent and another from 3 to 5.6 per cent. The accuracy of the method is indicated by the standard deviation of a single value from the true *o*-cresol content; this equals ±0.07 per cent *o*-cresol up to 3 per cent and ±0.09 per cent from 3 to 5.6 per cent.

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A New Gas Generator

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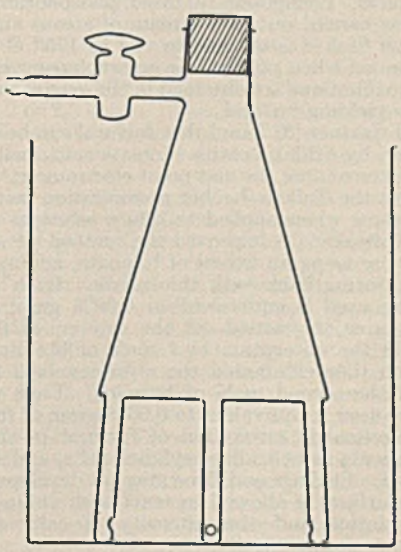
THE writer has frequently required a compact, portable form of gas generator. The instrument described here was finally adopted as being satisfactory from the standpoints of simplicity of manufacture and operation and ease of cleaning.



For ordinary operations, a 300-ml. Erlenmeyer flask was employed, to the base of which were sealed three 5-cm. lengths of 8- to 9-mm. tubing, as illustrated. These legs were sealed off and a small hole was blown into each of them near the base. A stopcock side arm was sealed to the neck of the flask, as shown, though in a simpler modification the stopcock was simply inserted in the stopper. The instrument fits nicely into a 1-liter beaker.

In operation, the solid reagent is placed in the flask, while the acid is poured into the beaker, to within an inch of the brim. Opening the stopcock admits acid through the legs of the flask, generating the gas. When the stopcock is closed, the gas pressure displaces the acid from the flask and the reaction ceases.

Determination of Furfural

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IN STUDYING methods and procedures for the preparation of hemicellulose from plant material many obstacles are encountered. One difficulty is the possible loss of hemicellulose as the steps in the preparation are carried out. A means of determining any change in the hemicellulose content would aid considerably, as the procedure could be modified to prevent this loss. With certain types of material, furfural may be determined at the various stages of extraction and purification to indicate whether there is a change in the hemicellulose content. With this in mind methods for determining furfural were examined, seeking an accurate and rapid method which is easily manipulated.

The method of Tollens and Kröber for the determination of furfural (*6*) is the one most commonly used. The pentoses, pentosans, etc., are converted into furfural by distillation with 12 per cent hydrochloric acid solution according to a standard procedure. After precipitation with phloroglucinol the weight of furfural, pentose, or pentosan corresponding to a given weight of phloroglucide may be obtained by reference to Kröber's tables.

Pentoses do not usually yield the theoretical quantity of furfural upon distillation with acids. Xylose gives about 90 per cent and arabinose about 75 per cent of theoretical. This has been explained as being due to a partial destruction of furfural. Pervier and Gortner (*3*) and Youngburg (*7*) suggested distilling in a current of steam to lessen the opportunity for decomposition. Others (Iddles and Robbins, *2*) found that passing steam into the solution during distillation gave little or no increase in furfural.

Instead of distilling pentoses or pentosans in the presence of hydrochloric acid, Youngburg (*7*) used phosphoric acid. The distillation was carried out in a stream of steam and the temperature in the flask was allowed to rise to 175° C. Good results were claimed when pure xylose or arabinose were distilled, but only approximations are obtained in the case of various complex materials yielding furfural.

Pervier and Gortner (*3*) found that furfural can be determined in acid solution by oxidation with bromate salts in the presence of bromides, determining the end point electrometrically. They also found that the Tollens-Kröber precipitation method was in considerable error when applied to dilute solutions of furfural. Powell and Whittaker (*4*) improved the method of determining the end point by using an excess of bromate, adding potassium iodide, and titrating back with thiosulfate. Each milliliter of 0.1 *N* bromate used is equivalent to 0.0024 gram of furfural. Hughes and Acree (*1*) carried out the reaction at 0° C. This procedure held the absorption to 1 mole of bromine per mole of furfural and thus eliminated the error involved in the slow absorption of the second mole of bromine. Each milliliter of 0.1 *N* bromate used is equivalent to 0.0048 gram of furfural.

For the colorimetric estimation of furfural in the distillate such color reagents as benzidine, xylidine salts, and aniline salts have been used. Stillings and Browning (*5*) developed a method in which the furfural is allowed to react with aniline acetate in acetic acid solution and the intensity of color produced is measured photocolorimetrically.

Experimental

Since it was desired to select a suitable method for determining furfural in plant material, some of the available methods were compared. As the Tollens and Kröber method has been shown to be in considerable error, particularly when applied to low concentrations of furfural, attention was turned to a volumetric or colorimetric procedure.

A study of the colorimetric method of Stillings and Browning (*5*) showed that fairly consistent results are obtained when the temperature, concentration of reagents, and freedom from light are carefully controlled. However, the method could be improved by reducing the time required for maximum color to develop and by stabilizing the color. With this in mind a number of substances were added to the furfural solutions prior to the addition of the color reagent. It was found that small amounts of a mixture of oxalic acid and disodium phosphate increased the rate of color development. In these trials 0.075 mg. of furfural, 25 ml. of glacial acetic acid containing 2.5 ml. of aniline, and varying amounts of the other reagents were used. The final volume was 50 ml. and the relative color intensities of the solutions were determined by means of a Kuder photoelectric colorimeter.

Table I. Effect of Oxalic Acid and Disodium Phosphate on Color of Furfural Solutions

Sample No.	Treatment		Kuder Readings[a] 30 min.	45 min.	1 hour	1.25 hours
	Grams					
1	1.0	NaCl	47.5	48.4	48.5	47.5
2	0.50	Na_2HPO_4	48.7	48.8	47.5	46.0
3	0.25	Na_2HPO_4	48.2	48.1	46.8	44.9
4	0.12	Na_2HPO_4	48.4	48.2	46.8	44.6
5	0.5 0.12	Na_2HPO_4 Oxalic acid	49.1	50.2	50.1	49.4
6	0.25 0.12	Na_2HPO_4 Oxalic acid	49.2	50.2	50.2	49.5
7	0.12 0.12	Na_2HPO_4 Oxalic acid	48.5	50.2	50.1	49.8
8	0.50 0.12	NaCl Oxalic acid	Cloudy			
9	0.25 0.25 0.12	NaCl Na_2HPO_4 Oxalic acid	48.9	50.0	50.7	50.2

[a] All values represent means of from 2 to 4 determinations. Kuder readings are directly proportional to color intensity of solutions.

The results given in Table I show that the addition of 0.12 to 0.50 gram of disodium phosphate to the color reagents increases the rate of color development, but did not improve the stability of the color. The addition of a mixture of 0.12 gram of oxalic acid and 0.12 to 0.5 gram of disodium phosphate increased the intensity of color as compared to the sodium chloride treatment, and the solutions were more stable than those containing disodium phosphate alone. The addition of 0.25 gram of sodium chloride to this mixture had little or no effect on the color. A mixture of oxalic acid and sodium chloride gave a cloudy solution after standing 30 to 45 minutes.

Twelve per cent hydrochloric acid is commonly employed in the distillation of pentoses, pentosans, etc., for the separation of furfural. Since Youngburg recommended phosphoric acid, it was decided to compare phosphoric and different concentrations of hydrochloric acid.

A xylose solution containing 0.25 gram of xylose per 25 ml. was used, and 25-ml. aliquots were placed in 500-ml. two-necked, round-bottomed flasks. Samples of arabinose, sweet clover, alfalfa, and crude hemicellulose were also distilled. Acids to give the following concentrations were added to the flasks: phosphoric acid, 57 per cent; hydrochloric acid, 12, 18.5, and 24 per cent. A steam inlet tube, which extended almost to the bottom of the flask, was placed through one opening, and the flask was connected through the other opening to a condenser by means of an adapter, provided with thermometer. All connections were interchangeable ground-glass joints. A steady stream of steam was passed into the flask, under which a small flame was placed. A vigorous boil was maintained throughout the distillation. The distillate was collected in 1-liter

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Table II. Determination of Furfural by Distilling in the Presence of Phosphoric and Hydrochloric Acids

Sample Material	Wt. of Sample	Acid Used H_3PO_4	Acid Used HCl	Temp. of Distn.	Time of Distn.	Furfural Found By titration	Furfural Found Colorimetrically
	Gram	%	%	° *C.*	*Hours*	%	%
Xylose	0.25	57	..	98–105	3	57.4, 57.4, 57.7	49.5, 49.5, 51.1
	0.25	57	..	110–12	2	55.3, 54.7	50.2, 51.0
l-Arabinose	0.25	57	..	110–12	1	44.4, 44.1, 44.7	37.0, 36.3, 36.9
Sweet clover	0.20	57	..	110–12	1	8.2, 8.2	5.1, 5.1
Alfalfa	0.20	57	..	110–12	1	9.3, 9.1	6.1, 6.1
Xylose	0.25	..	12	102–3	6	60.6, 60.8	55.1, 55.8, 54.9
	0.25	..	18.5	105	2.5	61.2, 61.0	54.8, 55.2, 54.8, 55.2
	0.25	..	24	105	2.5	60.8, 60.2	55.9, 54.8
Sweet clover	1.00	..	18.5	105	2.5	9.3, 9.0	6.0, 6.0, 5.9
Crude hemicellulose	0.10	..	18.5	105	2	33.2, 32.2	29.2, 29.2
Xylose	0.25	..	12	102–3	2	53.1	44.4
	0.25	..	12	102–3	3.5	58.0	51.1
	0.25	..	12	102–3	4.5	59.7	53.6
	0.25	..	12	102–3	6	60.8	54.9

volumetric flasks. The distillation is complete when several drops of the distillate placed in a test tube fail to give a color in 10 minutes when an equal volume of glacial acetic acid, containing 2.5 ml. of aniline per 25 ml., is added. The pH of the distillates was in the range of 3 to 5 and never failed to give a color test when furfural was present.

The furfural in the distillates was determined by both the titration procedure of Hughes and Acree (*1*) and the modified colorimetric method.

The results given in Table II show that higher furfural values were obtained when the distillations were carried out in the presence of hydrochloric acid as compared to phosphoric acid. Approximately equal values were obtained with 12, 18.5, and 24 per cent hydrochloric acid; however, 12 per cent hydrochloric acid required at least twice as long for the complete removal of furfural from the sample. The 18.5 and 24 per cent concentrations required about an equal length of time.

The titration procedure gave consistently higher values than the colorimetric procedure, but the reason for this was not clear. In an attempt to clarify this point it was decided to compare the results obtained by titration and colorimetrically when other sugars were distilled with 18.5 per cent hydrochloric acid. In addition, samples of xylose were reinforced with certain aldehydes and other compounds and distilled, and pure furfural was determined colorimetrically and by titration.

Table III. Titration and Colorimetric Values

[Distillates from rhamnose (methylpentose), levulose (hydroxymethylpentose), xylose, and xylose reinforced with 0.20 gram of aldehydes, etc.]

Substance Distilled	Wt. of Sample	Results Calculated as Furfural By titration	Results Calculated as Furfural Colorimetrically
	Gram	%	%
Rhamnose	0.17	29.6	0
Levulose	0.25	5.3	0
Xylose	0.25	58.3	55.6
Xylose + benzaldehyde	0.25	56.6	55.2
Xylose + vanillin	0.25	109.3	55.7
Xylose + quercitin	0.25	56.6	54.7
Xylose + salicylaldehyde	0.25	204.9	55.2
Furfural	1.000	98.7	98.7

Table III shows that methylpentose and hydroxymethylpentose gave a titration value but did not produce a color with the furfural color reagents. When xylose was reinforced with certain aldehydes the distillates gave higher titration values than xylose alone. The colorimetric procedure gave no higher values. Quercitin and benzaldehyde had no apparent effect on either the colorimetric or the titration procedure. Pure furfural gave almost theoretical values when titrated or measured colorimetrically. Samples of pure furfural (not shown) gave approximately 100 per cent recovery by steam-distillation. These results indicate that the colorimetric method is more accurate for the determination of furfural. Since plant materials probably produce certain reducing substances on distillation with acids, these might interfere with the bromate titration method, as pointed out by other investigators.

To obtain evidence as to the effect of substances distilled from alfalfa and sweet clover on the colorimetric method, spectrophotometric curves of the color produced from the distillates of alfalfa and sweet clover were compared with similar curves plotted from pure furfural color solutions of equal concentration. Within experimental error all the curves were similar, which indicated that no appreciable interfering substances were present in the alfalfa or sweet clover distillates.

Procedure

A sample of pentose, pentosan, or plant material having a furfural content between 1 and 15 mg. is placed in a 500-ml. two-necked round-bottomed flask. Hydrochloric acid and water in sufficient amount to give between 200 and 225 ml. of about 18.5 per cent hydrochloric acid (approximately 1 to 1 by volume) is added to the sample. A steam tube extending almost to the bottom of the flask is inserted through one opening, and the flask is connected to a condenser through an adapter containing a thermometer. A steady stream of steam is passed into the solution and a flame is placed under the flask. When the contents of the flask begin to boil vigorously the flame is adjusted to hold the temperature between 105° and 106° C., measured at the opening into the condenser. The distillate is allowed to pass through a small filter, as it comes from the condenser, and then into a 1-liter volumetric flask. If the liquid in the distilling flask is reduced to approximately 75 ml., the steam inlet tube is removed and hydrochloric acid (1 + 1) is added to bring the volume back to 200 to 225 ml. The distillation is usually complete in 2 or 2.5 hours. This is determined when a few drops of the distillate fail to give a color in 10 minutes with an equal volume of glacial acetic acid containing 2.5 ml. of aniline per 25 ml. of acid.

The solution is diluted to the mark, and mixed, and 10-ml. aliquots are pipetted into 50-ml. volumetric flasks. The solutions are made just alkaline to phenolphthalein with sodium hydroxide, and 5 ml. of a solution containing approximately 0.12 gram of oxalic acid and 0.25 gram of disodium phosphate per 5 ml. are added. The solution is diluted to approximately 25 ml. with distilled water and 25 ml. of glacial acetic acid containing 2.5 ml. of freshly distilled aniline are added. The acetic acid and aniline should be mixed and allowed to come to room temperature just before using. It is then diluted to the 50-ml. mark, mixed, placed in a water bath at 20° C., and covered so that almost all the light is excluded. After 45 minutes to 1 hour it is read in a photoelectric colorimeter. The concentration of furfural corresponding to a given colorimeter reading is obtained by reference to a calibration curve made by plotting a series of known furfural solutions against colorimeter readings. If a photoelectric colorimeter is not available, the unknown solution may be compared to known standards in any type of colorimeter in general use.

Summary and Conclusions

The steam-distillation of pentoses and plant material with hydrochloric acid resulted in higher yields of furfural than steam-distillation with phosphoric acid. The use of 12 per cent hydrochloric acid required at least twice as long as 18.5 or 24 per cent hydrochloric acid to remove all the furfural. The yield of furfural from xylose was approximately the same when the three concentrations were used.

In the application of the aniline acetate colorimetric method, the addition of small amounts of oxalic acid and di-

sodium phosphate to the color reagents resulted in increased color intensity and shortened slightly the time required for maximum color to develop. The colorimetric method was not affected by methyl furfural or hydroxymethyl furfural. The distillates from alfalfa or sweet clover produced colored solutions very similar to that produced with pure furfural, as shown by spectrophotometric curves. The titration method of Hughes and Acree (*1*) gave consistently higher results than the colorimetric method when applied to the distillates from pure sugars, alfalfa, or sweet clover. This may be due to the presence of reducing substances other than furfural in the distillates. For these reasons it is thought that the colorimetric method may be more accurate.

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Determination of Total Sulfur in Rubber and Rubberlike Materials

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A modification is presented of the oxidation procedure employed in the standard method for the determination of total sulfur in rubber and similar materials. The method is especially valuable for the analysis of vulcanized synthetic rubberlike materials. It is likewise applicable to a wide variety of sulfur-containing organic compounds.

THE determination of total or combined sulfur in vulcanized rubber and materials of similar type involves numerous difficulties. This fact is attested by the very large number of methods which have been proposed (*3*).

The most important methods all involve oxidation of the sulfur, in whatever form it may be present, to sulfate and weighing the latter as barium sulfate. The only essential differences lie in the methods of oxidation employed.

The methods which seem to be the most popular at the present time are (*a*) oxidation of the sample in a Parr bomb with sodium peroxide, potassium chlorate, and sugar (*5, 6, 8, 9*); (*b*) oxidation with perchloric acid and nitric acid (*12*), sometimes with the additional use of bromine (*4*); (*c*) oxidation with nitric acid and bromine, followed by sodium carbonate–potassium nitrate fusion (*1, 2, 11*); and (*d*) oxidation with nitric acid–zinc oxide mixture, bromine, and potassium chlorate (*1, 2, 7*).

Serious explosions have been known to occur with perchloric acid oxidations; hence this method is not so popular at present as the other three. The fusion methods are reliable, but they are time-consuming and therefore not convenient when large numbers of samples must be handled.

Methods (*c*) and (*d*) have been for a number of years the preferred procedures of the A. S. T. M. For several years the fusion method was the "recommended" one and method (*d*), commonly referred to as the "Kratz-Flower" method, was listed as the "alternate" method (*1*). In 1940 (*2*) the order of listing was reversed, with the Kratz-Flower method becoming the recommended and, at least inferentially, the preferred procedure.

This procedure involves a preliminary oxidation with nitric acid and bromine, following which the mixture is slowly evaporated to a foamy sirup. Then, if organic matter or carbon remains at this point, a few milliliters of fuming nitric acid and a few crystals of potassium chlorate are added and the solution is evaporated at a boil. The operation is repeated until all carbon is gone and the solution is clear, colorless, or light yellow. It is then evaporated and nitrates are decomposed by one of two alternate methods.

The analyst is cautioned to use care during the addition of potassium chlorate. This is a standard precaution, to be found in all analytical textbooks. That it is well founded is proved by the fact that explosions frequently occur when the addition is carried out in this manner.

An additional disadvantage of this standard procedure is the fact that the seemingly drastic conditions of oxidation are still not sufficient to effect the oxidation of many samples. Carbon black is oxidized in some samples, but not in others. Some of the synthetic rubbers prove especially troublesome, as the solution reaches a dark, nearly black color which is not destroyed by repeated treatment.

A somewhat unorthodox modification of the above procedure has been found to take care of these difficulties and to yield a clear, light-colored solution with considerably less trouble. The writer does not claim to have originated the method; in its present form it is an adaptation of a general procedure with which he came in contact a number of years ago and the exact origin of which is not known. In the meantime, the method has been extensively tested, in the hands of both experienced analysts and students who were completely unfamiliar with the procedure. A number of variables affecting the procedure have thus been studied in some detail, and the operating details as indicated here are believed to be general in their application.

Modified Method

In the standard method as modified, the nitric acid–bromine oxidation is carried out as usual. Then the resulting solution is evaporated slowly until no more nitrogen oxide or bromine fumes are visible, diluted with 10 to 15 ml. of concentrated nitric acid, and heated to boiling. To the vigorously boiling solution are added successively several 0.5-gram portions of potassium chlorate.

Contrary to what one might expect, no explosion occurs. This procedure has been employed in hundreds of analyses of

TABLE I. TYPICAL SULFUR DETERMINATIONS

Sample	Theoretical	Parr Bomb	Modified A. S. T. M.
Rubber stock A	...	2.42	2.50
		2.45	2.45
Rubber stock B	...	1.80	1.80
		1.85	1.84
Rubber stock C	...	3.05	3.10
		3.09	3.14
Hycar O. R. stock	...	2.76	2.80
		2.80	2.81
Buna S stock A	...	1.76	1.78
		1.80	1.78
Buna S stock B	...	1.42	1.37
		1.40	1.42
Thiokol stock	...	47.20	47.30
		47.38	47.42
Mercaptobenzothiazole	38.42	38.28	38.50
		38.42	38.40
Ethyl-*p*-toluenesulfonate	15.98	16.00	16.00
		15.98	15.95
Thiocarbanilide	14.04	14.17	14.10
		14.12	14.17
n-Butyl sulfite	16.48	16.32	16.40
		16.37	16.47

various types of rubber products and explosions have occurred only where the solution was allowed to cool and was no longer boiling vigorously.

Carbon black is oxidized readily by this method, and the dark-colored solutions obtained from vulcanized synthetic rubber samples are readily decolorized to yield usually straw-colored solutions. If the successive portions of chlorate are added too rapidly, foaming may result. An occasional sample foams when companion samples do not; this variance may be due to the presence of certain compounding ingredients. A little practice will enable the analyst to anticipate cases of bad foaming, and to control them by quickly removing from the heat during the early stages of foaming, and, if necessary, cooling under tap water.

The exact amount of chlorate necessary to effect the oxidation varies with the individual sample. This is particularly true of those containing carbon black. The relative ease of oxidation seems to be related to the type of black. In general, any unnecessary excess of chlorate should be avoided, to prevent contamination of the barium sulfate precipitate by other salts. A large excess of chlorate definitely tends to favor coprecipitation.

Since potassium chlorate is somewhat difficult to obtain in war time, a number of determinations have been made with an analytical grade of sodium chlorate. The sodium salt may be substituted for the potassium with no noticeable loss in efficiency, but where both are available, the potassium salt is preferred, as it can usually be obtained in a higher state of purity.

Following the chlorate treatment the normal procedure may be employed, with no additional modifications.

This general method for the determination of sulfur is also adapted for the analysis of various sulfur-containing compounds, especially organic ones. It is reasonably convenient and merits more attention than it has received in the past from those engaged in analyzing materials other than rubber. It has been used successfully by the writer in analyzing a wide variety of sulfur compounds; none of those investigated have failed to be oxidized by this method. However, it is not a completely universal method, and some judgment must be exercised in its use. In the case of long-chain organic sulfur compounds of very considerable molecular weight, and relatively high sulfur content (*10*), the recurrence of units in the chain of the type —RSR— is common and on oxidation can give rise to sulfones of such stability that even the sodium peroxide fusion method very frequently leads to low results. The only method that gives consistently accurate results in the case of this type of compound involves the practically instantaneous oxidation of the sample in a bomb under about 30 atmospheres of oxygen pressure.

Many organic compounds are completely oxidized by the nitric acid–bromine combinations and the chlorate is then unnecessary.

In Table I are listed a few of the more typical results obtained by this procedure. The Parr bomb fusion with sodium peroxide was chosen as a reference method for these samples. The agreement between these two methods is good and the analytical results for the pure compounds check well with the calculated values.

Complete Procedure

Place 0.5 gram of soft rubber or 0.2 gram of hard rubber in a 500-ml. Erlenmeyer flask of chemically resistant material (Pyrex, quartz, etc.), add 10 ml. of zinc oxide–nitric acid solution (containing 200 grams of zinc oxide to 1000 ml. of nitric acid, specific gravity 1.42), and moisten the sample thoroughly. Let stand at least 1 hour, overnight if convenient. The sample becomes partly decomposed; this permits the addition of fuming nitric acid with no danger of ignition of the sample. Add 15 ml. of fuming nitric acid and whirl the flask rapidly to keep the sample immersed to avoid ignition. With some samples it may be necessary to cool the flask under running water.

When the solution of the rubber appears to be complete, add 5 ml. of a saturated water solution of bromine and slowly evaporate the mixture until no more fumes of nitrogen oxide or bromine are visible. Dilute the solution with 10 to 15 ml. of concentrated nitric acid and heat to boiling. To the vigorously boiling solution add about 0.5 gram of potassium chlorate (or an analytical grade of sodium chlorate). If the solution is still dark in color, continue to boil and add another portion of chlorate. Continue the addition of successive portions of chlorate until all carbon is gone and the solution is clear, colorless, or light yellow. Do not use an excess of chlorate over the amount required to complete the oxidation. (Caution: Foaming may result if the portions of chlorate employed are too large or if the successive portions are added too rapidly.) If foaming starts, cool immediately, if necessary under running water.

Evaporate the mixture to dryness and bake at the highest temperature of a Tirrill burner until all nitrates are decomposed and no more nitrogen oxide fumes can be detected. Anneal the flask carefully to prevent cracking.

Add 50 ml. of hydrochloric acid (1 to 6) to the cooled flask and digest warm until solution is as complete as possible. Filter the solution, wash the filter, and dilute the solution to 300 ml. Add 10 ml. of saturated picric acid solution, precipitate with 10 per cent barium chloride, and allow the precipitate to stand overnight. Filter, wash with hot water until the filter paper is colorless, and determine the barium sulfate precipitate in the usual manner.

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Importance, Composition, and Analysis of Bolivian Tin Concentrates

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IT IS characteristic of all strategic metals, minerals, and ores that their domestic supply is inadequate and that there exists a marked inequality of distribution among producing and consuming countries. This is particularly true in the case of tin. This country, the world's largest consumer of tin (almost 50 per cent of the world output) is compelled, with the exception of some secondary recovery, to import all its tin from distant countries.

Prior to the present war, approximately 70 per cent of the total world production of tin ore, mostly from placer deposits, was produced in southeastern Asia (Malaya, China, Dutch East Indies) and about 20 per cent, mostly from lode deposits, in Bolivia.

Repeated attempts have been made to exploit small and low-grade deposits in this country, but there seems little hope that an appreciable output of tin ore can be developed, as known deposits are too small in size and too low in grade to justify work on a scale that would produce an output of appreciable magnitude (*14*).

Until recently, the smelting picture was not much brighter. The smelters in Malaya and the Dutch East Indies used to produce more than 60 per cent of the world's metallic tin; Bolivia, the world's second largest ore producer, does no smelting; and England, which is only a small ore producer (2 per cent of the world production), is the second largest smelter.

There have been only two noteworthy attempts in the past to operate smelters in the United States (with Bolivian ores), one in 1907, the other in 1916; both ended in utter failure, chiefly because of political and commercial control of the ore supplies. As tin is probably the most important strategic metal, Roush advised (*15*) a reserve stock pile containing enough metal to tide over anticipated needs for one or two years.

Therefore, early in the present crisis, the Government increased imports of tin from abroad and stepped up secondary recovery, particularly from tin plate scrap and very recently from used tin cans. In addition, and despite failures in the past and views of pessimistic observers, the Government, represented by the Metals Reserve Company, concluded, as early as November, 1940, five-year contracts with a number of Bolivian tin ore producers, providing for the annual delivery of many thousand tons of tin ores and concentrates. A new and impressive tin smelter has been built in Texas and is operated for the U. S. Government by the Dutch N. V. Billiton subsidiary, called the Tin Processing Corporation, a group which reportedly has had "more actual experience in smelting refractory Bolivian ores than any other available person or corporation" (*2*). It is hoped that the operation of this vital plant will go a great way toward establishing a permanent tin industry in this country. Since production and supply of tin are essential factors contributing to victory, the importance of the Bolivian tin concentrates (although of lower quality than the Malayan and East Indian concentrates) cannot be overestimated, particularly in the light of recent military events in the Far East.

TABLE I. COMPOSITION OF BOLIVIAN TIN CONCENTRATES

Grade	Sn	Pb	Cu	Sb	As	Bi	Zn	S	Fe	SiO_2	WO_3	Ti
	%	%	%	%	%	%	%	%	%	%	%	%
High	64.15	0.02	0.38	0.10	0.49	0.003	0.19	2.17	[a]	[a]	[a]	[a]
High	57.78	1.14	0.52	0.78	0.45	0.012	0.38	2.53	7.69	4.32	0.06	0.14
High	59.30	0.32	0.62	0.09	0.53	0.004	2.47	4.13	6.42	4.70	0.17	0.03
High	62.19	0.02	0.17	0.18	0.27	0.027	0.21	2.35	[a]	[a]	[a]	[a]
Medium	38.20	0.09	0.32	0.18	0.14	0.033	0.78	3.13	[a]	[a]	[a]	[a]
Medium	52.83	1.38	0.07	0.65	0.62	0.008	4.14	4.79	[a]	[a]	[a]	[a]
Medium	48.92	0.14	0.87	0.64	0.22	0.008	0.07	3.33	7.17	19.14	[a]	[a]
Medium	36.49	4.17	0.66	0.14	0.46	0.230	10.09	12.99	[a]	[a]	[a]	[a]
Low	19.07	0.33	0.54	0.57	0.58	0.131	0.24	2.63	[a]	[a]	[a]	[a]
Low	24.16	1.13	0.03	0.14	0.34	0.026	23.12	24.55	15.68	[a]	[a]	[a]
Low	22.16	0.92	0.96	3.48	0.56	0.074	0.37	8.19	19.57	22.91	0.75	1.21
Low	23.11	0.75	2.11	0.34	0.07	0.217	0.03	6.77	12.15	38.00	3.07	[a]

[a] Not determined.

Composition of Bolivian Tin Concentrates

The chemical analysis of the Bolivian tin concentrates presented a major problem to the laboratories entrusted with this task, as these concentrates are of widely varying grade and composition and the amount of impurities ranges from zero to many per cent.

The tin concentrates are of the cassiterite (SnO_2) type, stannite ($Cu_2S.FeS.SnS_2$) and thealite ($PbS.SnS_2$) being rejected by terms of the contract. They are delivered in 3 grades: high grade, over 55 per cent tin; medium grade, over 35 per cent tin; low grade, over 18 per cent tin.

Bolivian tin concentrates are contaminated by varying amounts of silica, iron, lead, copper, bismuth, antimony, arsenic, and zinc, mostly in the form of oxides and sulfides. Sometimes concentrates containing varying amounts of tungsten, titanium, aluminum, and calcium are encountered, as well as manganese, cadmium, molybdenum, vanadium, tantalum, columbium, silver, and indium, mostly in very small quantities. The contracts between the Metals Reserve Company and the Bolivian tin producers provide that more than small but defined amounts of lead, copper, bismuth, antimony, arsenic, zinc, and sulfur are objectionable, certain penalties and treatment charges being imposed for their presence. Some typical composition figures obtained in actual analysis (Table I) indicate some of the difficulties that analysts encounter in judging the approximate composition of the tin concentrates, and are helpful in choosing the proper analytical procedure to be followed.

As the writer has been engaged in the analysis of tin concentrates, he decided to test all methods mentioned in the literature that appeared to be suitable, to determine concisely their range of application, and to compile and present them in a form that may prove helpful not only to laboratories engaged in analysis of these particular concentrates, but also to chemists performing assays on similar material.

In some instances, a procedure incorporating the best features of several methods has been developed, which gives reliable results and is generally applicable to almost any

type of tin concentrate. In other cases, however, new suggestions and procedures had to be worked out and these have been included in the investigation reported here. Spectrochemical methods for the determination of impurities in tin concentrates are becoming more popular as methods are being perfected. One laboratory engaged in the analysis of Bolivian tin concentrates first identifies all samples spectroscopically, and unless the amount of the impurity exceeds a certain limit, it is quantitatively determined by spectrochemical analysis. The high cost of spectroscopic equipment, however, and its limited range of application for routine quantitative analysis caused this writer to omit a detailed description of such methods.

Preparation and Solution of Sample

Cassiterite is scarcely attacked by any acid, but some of the impurities present in the form of sulfide or oxide (arsenic, zinc, sulfur, copper) can be dissolved by proper acid treatment.

Other methods, applied in the procedures described below, are:

1. Fusion with a mixture of sodium peroxide and sodium carbonate in a nickel or iron crucible. The writer has carried out numerous tests to determine the most efficient and economical fusion mixture. Sodium peroxide alone, used by the majority of laboratories, though very effective with cassiterite and other ores, is extremely corrosive and readily attacks nickel and iron crucibles, frequently causing loss of money and time when fusions "melt through". However, a mixture of 1 part of sodium carbonate with 2 parts of sodium peroxide not only produces perfect decomposition of the sample but lessens the corrosive action of the sodium peroxide upon the crucible, considerably lengthening its life.
2. Cassiterite can be decomposed by fusion with a mixture of equal parts of sodium carbonate or potassium carbonate and sulfur. Tin, antimony, and arsenic (also any molybdenum, tungsten, and vanadium) are found in the water extract of the fusion, while iron, zinc, copper, lead, and bismuth (as well as any titanium, manganese, and cadmium) appear in the residue. This method of decomposing tin concentrates, however, should be avoided when the sample is high in iron or zinc.
3. Cassiterite is reduced to tin by ignition in a stream of hydrogen, most of the impurities also being found in the metallic residue. Fusion of the concentrate with potassium cyanide and other reducing fluxes will effect a similar reduction to the metal.
4. Fusion of cassiterite with certain oxidizing lead fluxes will result in its decomposition, tin and impurities passing into the slag and bismuth being collected in the lead button.

Determination of Tin (Routine Method)

Weigh 1 gram of low-grade tin or 0.5 gram of medium- or high-grade tin concentrate into a 50-ml. high-form iron or nickel crucible, add 4 grams of sodium carbonate, mix thoroughly, and cover with 8 grams of sodium peroxide. Heat the crucible and contents over a small Bunsen flame to expel any water in the flux and until the charge starts melting, then carefully finish fusion by holding and revolving the crucible around the outer edge of the flame until the mixture melts down quietly. When the contents are in quiet fusion, continue heating with the full flame of the Bunsen burner, while rotating the crucible, for about 2 minutes.

Let the melt solidify and cool, then place the crucible in a 400-ml. beaker, add 60 ml. of cold water, and allow the melt to disintegrate. Remove the crucible from the beaker with a glass rod, rinsing it thoroughly with warm water. Add 50 ml. of concentrated hydrochloric acid to the beaker, agitating the solution until all has dissolved, as indicated by the clear green color of nickel chloride or the brown color of ferric chloride. Clean the crucible with 50 ml. of hydrochloric acid and add to main solution.

Transfer the solution to a 500-ml. Erlenmeyer flask and dilute to 250 ml. Introduce a nickel strip or foil weighing about 5 grams and boil the solution gently for about 25 minutes until all ferric chloride has been reduced (if fusion of the sample was carried out in an iron crucible). Introduce a second nickel strip and close the flask with a rubber stopper containing a glass tube extending on the outside to the bottom of the flask. Boil the solution gently for 20 more minutes, then seal the end of the glass tube with a hot solution of sodium bicarbonate in a 250-ml. beaker, remove the flask from the hot plate, cool to below 15° C., and titrate with a 0.125 *N* iodine solution, using starch as indicator.

Strength of Iodine Solution. Weigh 160 grams of C. P. iodine and 320 grams of C. P. potassium iodide into a large beaker and cover with distilled water. Allow to stand for several days with occasional stirring, adding more water until all is dissolved, filter through asbestos into a dark bottle, and dilute with distilled water to approximately 10 liters. Allow to stand for about 2 weeks. The strength of the iodine solution is such that all low-grade tin concentrates (tin <35 per cent) and all high-grade concentrates (tin <78 per cent) can be run on the 1.0-gram or 0.5-gram basis, respectively, using in either case less than 50 ml. of the iodine solution. It is undesirable to reduce and titrate more than about 400 mg. of tin.

Standardization of Iodine Solution. 1. As stannous chloride is very unstable and the titer of the iodine solution changes somewhat with the concentration of acid and salts, it is best to use one of the standard tin concentrates made available by the National Bureau of Standards and fuse, reduce, and titrate it, as described above, simultaneously with the sample which is analyzed.

2. If a standard sample of a similar composition is not at hand, it may be replaced by finely rolled and cut tin foil, which is easily fused and decomposed in a nickel or iron crucible by the same fusion flux (Na_2CO_3 + Na_2O_2) used for cassiterite.

3. Adding to the hydrochloric acid solution of standard tin a "blank fusion" of sodium peroxide in an iron crucible, in order to introduce the same amount of salts and approximate conditions prevailing during the reduction of the solution of the sample, is a standardization procedure sufficient for routine work where extreme accuracy is not required but is inadequate when highly accurate results are expected. The sample has to undergo a number of manipulations during which it is subject to possible mechanical losses by spattering, volatilization, etc. On the other hand, by dissolving tin in hydrochloric acid and adding a blank fusion, the standard is not submitted to the same manipulations and possible mechanical losses as the sample. Consequently this standardization procedure produces somewhat low tin results.

4. One laboratory proposes the use of a "standard solder" of known tin content, which is dissolved in nitric acid (1 gram of the solder). Metastannic acid thus obtained is filtered off, ignited, and fused exactly like the sample. The writer believes that this standardization procedure is objectionable, not only as it raises the question of the reliability of the "standard solder", but also because any chemical or mechanical loss of metastannic acid would raise the titer of the iodine solution. The tendency of this procedure is to give high tin results.

Nature of Interference. Few of the elements found in Bolivian tin concentrates will interfere with the above method.

Most of the arsenic is expelled as trichloride, and most of the antimony precipitated by the nickel foil. Small amounts of arsenious and antimonious compounds are without effect if the solution contains sufficient acid. Larger amounts of antimony (>50 mg.) will obscure the end point and are best removed by treating the hydrochloric acid solution with iron nails and subsequently filtering it prior to the reduction with nickel. Small quantities of copper (<50 mg.) do not interfere as they are precipitated by the nickel, but larger amounts should be removed with iron. The small amounts of bismuth found in Bolivian tin concentrates are precipitated by the nickel and do not interfere. Tungsten is reduced to a lower oxide by the nickel, presumably to the blue tungsten pentoxide, which, however, does not consume any iodine. When much tungsten is present the blue color thus produced is apt to obscure the end point of the starch indicator. In such cases lead should be used instead of nickel to reduce the stannic chloride.

There are contradictory statements in the literature concerning the exact nature of interference of molybdenum, Mantell (*11*) asserting that molybdenum has no effect, while Scott (*16*) claims that it is reduced by the nickel (presumably to the trichloride) and is subsequently reoxidized by the iodine. Tests carried out by the writer would support this latter view. The reoxidation of the molybdenum trichloride, however, is not proportional to the amount of molybdenum present. According to Scott (*16*) reduction

with lead will obviate the above difficulties. Vanadium is also reduced by the nickel and partly reoxidized by the iodine solution, and in the presence of large amounts of vanadium reduction should be carried out with lead. Titanium chloride is reduced to titanous chloride by the nickel. The reduced compound, however, is oxidized only by an excess of iodine, and even then the action is extremely slow.

Modifications of the above method have been proposed.

Some analysts use iron, antimony, zinc, and aluminum instead of nickel, to reduce the stannic chloride. The method favored by many European laboratories (*4*) consists in removing copper, antimony, etc., by reducing the hydrochloric acid solution of the tin with "ferrum reductum" and subsequently filtering into a 750-ml. Erlenmeyer. The solution is then treated with aluminum, heated until both the aluminum and tin have dissolved, cooled, and titrated, after starch has been added, with a solution of iodine or of ferric chloride, using in the latter case an indicator of potassium iodide and cuprous iodide. During the entire procedure the air in the Erlenmeyer flask is replaced by carbon dioxide gas. The ferric chloride solution is made up by dissolving 144 grams of $FeCl_3.6H_2O$ or 86 grams of $FeCl_3$ in 300 ml. of concentrated hydrochloric acid and 1000 ml. of water. The solution is then diluted to 3000 ml. The indicator used for this titration is prepared by adding 50 grams of hydriodic acid (specific gravity 1.50) to 100 grams of potassium iodide and 25 grams of cuprous iodide. Next 50 ml. of warm water are added and the solution is stirred until the cuprous iodide has dissolved and then decanted into a stock bottle containing some copper wire. To the undissolved potassium iodide 50 ml. of hydriodic acid and 50 ml. of warm water are added and after all has dissolved this is added to the main solution. Carbon dioxide is passed in until the solution is colorless.

Potassium Iodate Method

As pointed out above, the chief difficulty in obtaining satisfactory tin results is that the reduced compound is extremely unstable and tends to reoxidize in contact with air.

Because of this instability of stannous chloride, most analysts try to reduce the time of titration (unless special precautions, such as eliminating admission of air by passing carbon dioxide over the surface of the solution, are employed during the titration) by running the assay with a small portion of the sample (0.25 to 0.5 gram) or by using for the titration a comparatively strong iodine solution, 1 ml. of which titrates 10 mg. of tin.

Both procedures will meet routine requirements, but are not adequate if extremely accurate results are expected. For, if the assay is run with 0.5 or 0.25 gram of the sample, any plus or minus error in the manipulation will be doubled or quadrupled in the final calculation. On the other hand, if the analysis is carried out with 1 gram of the sample and titration is performed with an iodine solution, 1 ml. of which oxidizes 10 mg. of tin, in order to obtain extremely accurate results an agreement of 0.1 ml. or less in the titration must be reached.

A method, recently worked out by this writer and described below, successfully obviates the difficulties attending the usual procedures. It is not intended for routine work, as the approximate tin content of the sample must be known or first be determined by another method. However, it gives excellent results and makes it possible to take for one tin determination 2 grams or more of high-grade cassiterite. The procedure was originally intended and may be highly recommended for determination of tin in pig tin and tin-bearing alloys by dissolving 2 to 5 grams of the sample in hot concentrated sulfuric acid and proceeding as described below.

PROCEDURE (Example, N. E. I. tin concentrate, tin = 75 per cent). Weigh 2-gram portions of tin concentrate, and 2 grams of a standard sample containing approximately the same amount of tin, into nickel crucibles and fuse with 5 grams of sodium carbonate and 10 grams of sodium peroxide. Acidify, reduce, and cool along the lines indicated in the regular iodine method, described above, using a 750-ml. Erlenmeyer flask.

Weigh in 0.8800-gram portions of potassium iodate if the sample contains 75 to 78 per cent of tin, or 0.8500-gram portions of potassium iodate if the sample contains 73 per cent of tin, add about 0.5 gram of sodium bicarbonate and about 1 gram of potassium iodide, and dissolve in 75 ml. of cold water. (As 0.9 gram of potassium iodate oxidizes approximately 1.50 grams of tin, the amount of potassium iodate weighed in as directed above is sufficient to oxidize approximately 96 to 97 per cent of the stannous chloride present. 0.6010 gram of $KIO_3 \simeq 1.0000$ gram of tin.)

Remove the stopper with the glass tube from the Erlenmeyer flask containing the reduced tin solution and add at once quantitatively the potassium iodate solution, washing the beaker with cold water. Add starch solution and titrate immediately with a potassium iodate solution, 1 ml. of which contains 0.0030 gram of potassium iodate.

Prepare the potassium iodate solution by dissolving 3.0000 grams of potassium iodate and about 3 grams of sodium bicarbonate in cold water. Transfer to a 1000-ml. volumetric flask, fill up to the mark, and shake.

CALCULATION

Standard Sample Containing 75.93% Sn		N. E. I. Tin Concentrate
KIO_3 added, gram	0.8800	0.8800
Iodate titrated, ml.	12.2	11.0
	12.3	11.0
		10.95
12.25 ml. of $KIO_3 \simeq$ 36.75 mg. of KIO_3		10.99 ml. of $KIO_3 \simeq$ 32.97 mg. of KIO_3
0.8800 gram of KIO_3		0.8800 gram of KIO_3
0.03675 gram of KIO_3		0.03297 gram of KIO_3
0.91675 gram of KIO_3		0.91297 gram of KIO_3

$$\text{Sample contains } 75.93 \times \frac{0.91297}{0.91675} = 75.62\ \%\ \text{Sn}$$

NOTES. 1. If a standard sample is not at hand, standardization may be carried out by fusing 1.5000 grams of finely cut C. P. tin foil in a nickel crucible with sodium carbonate and sodium peroxide.

2. As the oxidation value of the potassium iodate differs only very slightly from its theoretical titer, it is adequate for routine analysis of samples of approximately known tin content to establish an empirical factor.

3. Instead of the potassium iodate solution a weak (0.075 *N*) iodine solution may be used to carry out the end titration. To carry out the standardization of this iodine solution, a certain measured amount of this solution and a certain weight of potassium iodate (which is dissolved in water and acidified with hydrochloric acid, and to which some potassium iodide solution is added) are both titrated with an approximately 0.1 *N* sodium thiosulfate solution. Thus the strength of 1 ml. of the iodine solution and also the amount which was required to carry out the end titration can be expressed in grams of potassium iodate. This weight, in turn, is added to the weight of potassium iodate which originally had been added to oxidize the bulk of the stannous chloride.

Determination of Copper, Lead, and Antimony

The determination of copper in cassiterite has been the cause of some controversy between the laboratories involved, as one side has insisted that methods based on acid decomposition of the sample, although rapid and easy of manipulation, are in most cases insufficient and will invariably produce low copper results, while the other side insists that acid decomposition is adequate.

The writer supports the former view and bases this opinion on an extensive investigation which is recorded in Table II.

In 2 series of tests copper was thus determined in a large number of samples both by the two regular methods (described

TABLE II. RELIABILITY OF ACID DECOMPOSITION

Type of Tin Concentrate	Copper Found by Acid Decomposition		Copper Found by Sulfur Soda Fusion		Copper Found by Na_2O_2 Fusion	
	Original	Duplicate	Original	Duplicate	Original	Duplicate
	%	%	%	%	%	%
High grade	0.57	0.58	0.69	0.70	0.71	0.69
	0.18	0.20	0.36	0.34	0.37	0.36
	0.08	0.08	0.08	0.08	0.09	0.07
	0.43	0.44	0.57	0.59	0.60	0.58
Medium grade	0.72	0.69	0.91	0.89	0.90	0.90
	0.35	0.35	0.40	0.42	0.43	0.40
	1.19	1.23	1.44	1.46	1.45	1.43
	0.68	0.64	0.71	0.69	0.68	0.68
Low grade	0.75	0.76	0.94	0.95	0.88	0.90
	0.24	0.27	....	....	0.33	0.33
	2.21	2.18	2.37	2.38	2.39	2.40
	1.53	1.48	1.57	1.60	1.61	1.61

below) and by decomposing the sample with aqua regia and sulfuric acid. The results definitely show that acid decomposition is not sufficient and will not give the full copper content. However, duplicate results obtained by this method are generally in good agreement, thus misleading some analysts to the belief that they are reliable.

Warmbrunn (*3*) arrived at a similar conclusion, although the material that he analyzed was somewhat different.

METHOD I. This method is applicable to all grades of cassiterite, although Method II, described below, has advantages under certain defined conditions.

PROCEDURE. Weigh 1.0 gram of cassiterite into a 50-ml. iron crucible, mix with 4 grams of sodium carbonate, cover with 8 grams of sodium peroxide, and fuse as for tin. Transfer the crucible, when cool, to a 400-ml. beaker, add 100 ml. of water, and allow the melt to disintegrate. Remove the crucible and wash with hot water. Add just enough hydrochloric acid to give a clear solution, but disregard undissolved iron scale. Rinse the crucible with dilute hydrochloric acid and add to main solution. Pass in sulfur dioxide for about 5 minutes to reduce the ferric chloride, then expel excess sulfur dioxide by gentle boiling. Neutralize the warm (but not hot) solution carefully with about 6 *N* ammonia until a permanent deep green precipitate forms, then add 6 *N* hydrochloric acid drop by drop until the precipitate turns white, and finally an excess of 6 ml. of the same acid. Dilute to 250 ml., pass in hydrogen sulfide for about 20 minutes, dilute to 325 ml., and continue passing in hydrogen sulfide for 10 more minutes.

Allow the precipitate to settle, filter on 12.5-cm. No. 40 Whatman filter paper, and wash 6 times with warm 1 per cent sulfuric acid wash solution containing hydrogen sulfide. Wash the precipitate back into the original beaker and place the latter under a funnel. Pour 60 ml. of potassium sulfide solution (prepared by dissolving 75 grams of potassium hydroxide and 20 grams of sodium sulfate in 500 ml. of water, saturating the solution with hydrogen sulfide, and diluting to 1000 ml.) over paper. Warm on a hot plate until the soluble portions have been extracted. Filter through the original paper into a 500-ml. Erlenmeyer flask and wash with warm dilute potassium sulfide solution. Save the filtrate for the antimony determination.

Place the precipitate and paper in the original beaker and fume with 20 ml. of nitric acid and 8 ml. of sulfuric acid, adding, if necessary, more nitric acid to destroy all carbonaceous compounds. Finally fume strongly to expel excess nitric acid. Dilute the cool solution with 75 ml. of water and heat to boiling. Cool the solution for 2 hours to below 15° C., filter off lead sulfate on a 9-cm. No. 42 Whatman filter paper, and wash 5 times with cold one per cent sulfuric acid. Save filtrate for the copper determination.

Wash the lead sulfate back into the original beaker and place the latter under the funnel. Pour 30 ml. of ammonium acetate solution (300 grams of the salt in 1000 ml. of solution) over paper. Warm on a hot plate until lead sulfate has dissolved, then filter through the original paper, receiving the filtrate in a 250-ml. beaker and washing with hot dilute ammonium acetate solution. Add 5 ml. of 12 *N* hydrochloric acid and heat to boiling. (The addition of hydrochloric acid instead of acetic acid tends to prevent the precipitation of basic lead chromate upon the addition of ammonium chromate.) Add to the boiling solution 20 ml. of 20 per cent ammonium chromate solution and continue with the boiling until the precipitate has turned to a shade of orange. Filter on a tared Gooch crucible, dry at 105° C., and weigh as lead chromate.

To the filtrate of the lead sulfate add 10 ml. of 50 per cent tartaric acid and make the solution slightly ammoniacal, then slightly acid with hydrochloric acid. Add 20 ml. of strong sulfur dioxide water and 2 ml. of 10 per cent ammonium thiocyanate solution. Stir the solution vigorously to accelerate coagulation of copper thiocyanate, filter on 11-cm. No. 42 Whatman paper, and wash the precipitate once with cold water. Place the precipitate in the original beaker and take to fumes with nitric acid and 5 ml. of sulfuric acid until all the carbonaceous compounds are destroyed and heavy fumes of sulfur trioxide escape. Dilute with 300 ml. of water, add 5 ml. of ammonia and 3 ml. of nitric acid, and determine the copper electrolytically.

Acidify the potassium sulfide extract containing the antimony with 75 ml. of 9 *N* sulfuric acid, warm until the precipitate has settled, and filter on 12-cm. No. 40 Whatman paper, washing the precipitate with dilute sulfuric acid containing hydrogen sulfide. Place the precipitate and paper in the original Erlenmeyer flask. Take to fumes with 1 gram of potassium bisulfate, 3 grams of ammonium sulfate, and 30 ml. of 36 *N* sulfuric acid by heating, first cautiously, then with the full heat, on a very hot plate until all carbon is destroyed.

Add to the cool solution 75 ml. of strong sulfur dioxide water and 100 ml. of 12 *N* hydrochloric acid and boil down on a hot plate to 85 ml. to expel all arsenic as trichloride. Dilute with 250 ml. of water, cool to below 15° C., and titrate with 0.05 *N* potassium permanganate solution which has been standardized with C. P. antimony.

If titration with potassium bromate is preferred, add 120 ml. instead of 100 ml. of 12 *N* hydrochloric acid, boil down to a volume of about 100 ml., add 100 ml. of hot water, and titrate with 0.02 *N* potassium bromate solution, using methyl orange as indicator.

METHOD II. This method is very rapid, accurate, and well suited for the determination of lead and copper in high-grade cassiterite. Considerable difficulties are, however, encountered when applying it to low-grade concentrates high in iron, and, to a lesser degree, to those concentrates high in zinc. This is due to the tendency of iron sulfide to enter into soluble complex compounds with sodium sulfide, while the filtration of zinc sulfide from alkaline solution is difficult. This method is also well adapted for the determination of antimony in cassiterite provided that the amount of the latter does not exceed a few milligrams. With a higher antimony content slightly low results will be obtained with this procedure, and preference should be given to Method I.

Procedure. Weigh 1 gram of cassiterite into a 150-ml. tall-form porcelain beaker, mix thoroughly with 4 grams of sodium carbonate and 5 grams of sulfur, and cover with 3 grams of potassium carbonate. Heat the beaker with the full flame of a Bunsen burner until the charge has melted down quietly, keeping the beaker covered with a watch glass. Allow the melt to cool, then add 3 grams of sodium sulfite and 120 ml. of water and heat on a hot plate to effect disintegration of the melt and extraction of the soluble portions. Filter on 11-cm. No. 40 Whatman filter paper, receiving the filtrate in a 500-ml. Erlenmeyer flask and washing the precipitate with warm dilute potassium sulfide solution. Proceed with the antimony determination as in Method I. For the determination of lead and copper, place the precipitate in a 250-ml. beaker, and clean the porcelain beaker with a little nitric

TABLE III. ACCURACY OF METHODS I AND II

Type of Tin Concentrate	Found by Method I			Found by Method II			Reputed Pb, Cu, Sb Content		
	Pb	Cu	Sb	Pb	Cu	Sb	Pb	Cu	Sb
	%	%	%	%	%	%	%	%	%
High grade	0.41	0.17	0.42	0.44	0.19	0.40	0.40	0.15[a]	0.38
	1.14	0.52	0.78	1.17	0.51	0.73	1.18	0.40[a]	0.73
	0.02	0.17	0.18	0.05	0.17	0.20	0.06	0.15[a]	0.19
	0.14	0.08	0.09	0.14	0.09	0.12	0.10	0.09a	0.10
Medium grade	0.09	0.32	0.18	0.12	0.29	0.15	0.12	0.23[a]	0.14
	1.38	0.07	0.65	1.36	0.09	0.62	1.32	0.08[a]	0.61
	0.14	0.87	0.64	0.15	0.88	0.61	0.15	0.66[a]	0.60
	0.23	0.45	0.02	0.20	0.49	0.00	0.25	0.36[a]	0.00
Low grade	0.75	2.11	0.34	0.73	2.15	0.29	0.77	1.98[a]	0.36
	0.92	0.96	3.48	0.93	0.99	3.38	0.97	0.86[a]	3.43
	0.68	0.36	0.63	0.64	0.40	0.59	0.71	0.30[a]	0.59

[a] Copper determined by acid decomposition.

acid which is then added to the 250-ml. beaker. Add 20 ml. of 16 *N* nitric acid and 8 ml. of 36 *N* sulfuric acid, and proceed as in Method I.

Some results of actual copper, lead, and antimony determinations are given in Table III.

Determination of Arsenic

Weigh 1.0 gram of cassiterite into a 250-ml. beaker, add 20 ml. of 16 *N* nitric acid and 15 ml. of 36 *N* sulfuric acid, and evaporate slowly on a hot plate to strong fumes of sulfur trioxide. When cool, add 15 ml. of strong sulfur dioxide water and take again to fumes, repeating the evaporation once more with 10 ml. of distilled water.

Transfer the solution to a distilling flask, using the least amount of water possible. Add 45 ml. of hydrazine sulfate solution (10 grams of hydrazine sulfate and 20 grams of potassium bromide in 1000 ml. of solution) and 70 ml. of concentrated hydrochloric acid. Immerse the outlet of the condenser beneath the surface of 250 ml. of cold water in a 600 ml. beaker. Distill until the volume in the flask has been reduced to 75 ml., then add 40 ml. more of hydrochloric acid and distill again to 75 ml.

Remove the beaker from under the condenser, washing the latter with distilled water and allowing washings to run into the distillate. Make the solution alkaline with ammonia, using methyl orange as indicator, then just acid with hydrochloric acid. Cool to below 15° C., add 8 grams of sodium bicarbonate, and titrate with 0.03 *N* iodine solution, using starch as indicator.

Standardize the iodine solution by dissolving a weighed amount of arsenic trioxide in a little sodium hydroxide (0.5 to 1 gram) and 10 ml. of water, dilute to 250 ml., add 100 ml. of concentrated hydrochloric acid, neutralize with ammonia, acidify with hydrochloric acid, cool, and proceed with the titration as for the sample.

TABLE IV. APPLICATION RANGE OF TWO ZINC METHODS

Type of Tin Concentrate	Reputed Zinc Content	Zinc Found by Method I		Zinc Found by Method II	
		Original	Duplicate	Original	Duplicate
	%	%	%	%	%
High grade	...	0.10	0.12	0.09	0.13
	...	0.70	0.70	0.73	0.70
	2.47	2.49	2.45	2.44	2.47
Medium grade	1.12	1.12	1.09	1.10	1.08
	4.73	4.76	4.78	4.73	4.75
	2.47	2.40	2.45	2.50	2.46
Low grade	0.99	0.99	0.98	0.99	0.96
	12.89	12.81	12.78	12.91	12.88
	16.64	16.52	16.50	16.62	16.64
	23.98	23.88	23.88	24.00	23.96

Determination of Zinc

In contrast to copper which is found chemically combined with cassiterite and other tin ores (stannite!), zinc seems not to have entered into such combinations, but merely accompanies the other impurities of tin concentrates. Hence, there have been very few instances where the writer in determining zinc in tin concentrates has had cause to distrust results obtained by Method I which is based on acid decomposition. This procedure, which is very rapid and accurate, can be used as long as the amount of zinc does not materially exceed 10 per cent. Method II should be preferred for tin ores of poor quality which occasionally contain up to 25 per cent of zinc, although this method is more lengthy and not so easy of manipulation as Method I. Preference should also be given to Method II whenever doubts arise as to whether or not acid decomposition is sufficient. Results which indicate the range of application of both methods are given in Table IV.

METHOD I. Weigh 2.0 grams of cassiterite into a 250-ml. beaker, add 25 ml. of 16 *N* nitric acid and 15 ml. of sulfuric acid, and evaporate on hot plate until heavy fumes of sulfur trioxide escape. Take up the cold solution with 100 ml. of water, add 3 grams of ammonium sulfate, and heat to boiling. Pass in hydrogen sulfide for about 5 minutes to precipitate arsenic, copper, antimony, bismuth, etc., and the small amounts of tin which have been brought into solution. (If the sulfide precipitate is large, indicating that the sample consists largely of stannite or other tin sulfides, it is advisable to discard this procedure and start another portion of the sample using Method II.) Filter on 9-cm. No. 2 Whatman filter paper and wash the precipitate 5 times with warm 3 per cent sulfuric acid containing hydrogen sulfide. Receive the filtrate in a 400-ml. beaker, heat to boiling to expel hydrogen sulfide, then oxidize the solution with hydrogen peroxide. Add 12 *N* ammonia until the solution is strongly alkaline. Heat to boiling, filter off ferric hydroxide on 12-cm. No. 2 Whatman filter paper, receiving the filtrate in a 600-ml. beaker, and wash 4 times with hot water. Wash the precipitate back into the original beaker and redissolve iron hydroxide in a little sulfuric acid and hydrogen peroxide. Repeat the ammonia separation, filter through the original paper into the original filtrate, and wash the precipitate 4 times with hot water. Discard the precipitate.

Evaporate the filtrate to approximately 250 ml., cool to below 20° C., add 3 drops of methyl orange, then 9 *N* sulfuric acid, drop by drop, until the yellow color just turns red, then add 2 drops of the same acid in excess. Pass in hydrogen sulfide for half an hour, allow zinc sulfide to settle, filter on 11-cm., No. 42 Whatman paper, and wash the precipitate 3 times with warm water. Ignite zinc sulfide and paper in a clay or porcelain crucible, first at a low heat, then with the full flame of a Bunsen burner, and for 5 minutes with a blast lamp, raising the heat to approximately 900° C. Cool in a desiccator and weigh as zinc oxide.

TABLE V. DETERMINATION OF ZINC

Zinc Found as Zinc Oxide	Zinc Found Electrolytically	Zinc Found by Titration
%	%	%
0.38	0.34	...
0.64	0.59	...
0.80	0.76	0.73
1.29	1.22	1.20
3.77	3.66	3.70
5.12	5.02	5.00
8.83	8.72	8.74
13.01	....	12.89
18.38	....	18.24
24.27	....	24.14

The results are usually slightly high, owing to incomplete oxidation of the sulfide. Hence it is advisable to verify the results by one of the two following procedures:

Procedure for Less Than 100 Mg. of Zinc. This procedure is based on the electrolytic deposition of zinc from sodium hydroxide solution, a method that is not particularly in vogue in this country, even though extremely accurate, if properly executed.

Transfer the zinc oxide to a 250-ml. beaker, add 15 ml. of 18 *N* sulfuric acid, and evaporate to fumes of sulfuric acid. Take the solution up with 100 ml. of water and add solid sodium hydroxide until just alkaline, then about 4 grams in excess. Filter off, if necessary, any iron hydroxide, cadmium hydroxide, or sulfur present, through a small paper into a 250-ml. electrolytic beaker and wash the paper with hot water containing some sodium hydroxide. Dilute to approximately 250 ml. and electrolyze the zinc from this solution with 2 volts and 0.5 ampere on a platinum cathode which has previously been coated with not more than 20 mg. of copper.

Titration with Potassium Ferrocyanide. Transfer the zinc oxide to 600-ml. beaker and dissolve in 15 ml. of 6 *N* hydrochloric acid. Add 5 grams of ammonium chloride and dilute to 250 ml. Pass in hydrogen sulfide for 2 minutes, heat the solution to boiling, and titrate with a weak solution of potassium ferrocyanide (9 grams of $K_4Fe(CN)_6$ in 1000 ml. of solution), using uranyl acetate as an external indicator. Standardize with C. P. zinc.

Results obtained by these two procedures are usually in good agreement, although slightly lower than those calculated from the weight of the zinc oxide (Table V).

METHOD II. Method II is more time-consuming and its execution more exacting than Method I. Its application should therefore be confined to tin ores high in zinc or containing acid-insoluble zinc.

Procedure. Fuse 1.0 gram of cassiterite in a nickel crucible, as for tin. Place the cool crucible in a 400-ml. beaker and add 100 ml. of water and 60 ml. of concentrated hydrochloric acid. Remove the crucible and rinse with dilute hydrochloric acid. Heat

the solution to boiling to expel chlorine, then adjust the acidity to 25 ml. of hydrochloric acid in 250 ml. of solution. Pass in hydrogen sulfide for 15 minutes, dilute to 350 ml., and continue passing in hydrogen sulfide for 10 more minutes.

Allow the precipitate to settle, filter on 11-cm., No. 40 Whatman filter paper, receiving the filtrate in a 600-ml. beaker, and wash 5 times with warm 3 per cent sulfuric acid containing hydrogen sulfide. Wash the precipitate back into the original beaker, add 10 ml. of hydrochloric acid and 3 grams of potassium chlorate, and heat on a hot plate until the sulfides have dissolved and chlorine has been expelled. Dilute to 100 ml., pass in hydrogen sulfide for 15 minutes, dilute to 150 ml., and continue passing hydrogen sulfide for 15 more minutes. Let the precipitate settle and filter through the original paper into the original filtrate containing the bulk of the zinc. Wash the precipitate 4 times with 3 per cent sulfuric containing hydrogen sulfide. Discard the precipitate.

Heat the filtrate to boiling to expel hydrogen sulfide, then oxidize with hydrogen peroxide and proceed as in Method I.

Note. If the final zinc sulfide precipitate appears discolored, indicating that some nickel sulfide had been coprecipitated, dissolve the zinc sulfide in hot dilute hydrochloric acid, add 2 ml. of 36 *N* sulfuric acid, and evaporate to fumes of sulfur trioxide. Take the solution up with 200 ml. of water and render it just alkaline with ammonia, using methyl orange as indicator. Then render it acid with 9 *N* sulfuric acid, adding an excess of 2 drops of the latter. Pass in hydrogen sulfide for half an hour and proceed as in Method I.

TABLE VI. INFLUENCE OF TIN

Tin Present	Expected Weight of $BaSO_4$	Actual Weight of $BaSO_4$
Gram	*Grams*	*Grams*
0.24	0.3284	0.3254
0.37	0.2917	0.2911
0.26	0.7426	0.7405
0.26	1.6893	1.6878
0.55	0.3645	0.3629

Determination of Sulfur

Good sulfur results are frequently the product of a number of compensating plus and minus errors. For instance, many analysts (*6*, *13*), find that the plus error due to coprecipitation of barium chloride and the minus error caused by the solubility of barium sulfate in water generally balance each other, if some precautions are observed. Mellon (*12*) speaks of entrainment of barium chloride as a minus error when precipitating barium sulfate by adding sulfuric acid to a solution containing barium chloride.

There are, however, a number of other factors which may largely influence the determination of sulfur in tin ores, necessitating more or less tedious purification or correction procedures. Some of the more important factors causing low sulfur results are:

1. Precipitation of barium sulfate in the presence of sodium, potassium, and ammonium chloride causes coprecipitation of sodium, potassium, and ammonium sulfate, instead of barium sulfate; these are of lower molecular weight, hence producing low sulfur results. In the presence of ammonium chloride this minus error is greater, because of the volatility of ammonium sulfate.
2. Precipitation of barium sulfate in the presence of the same salts also causes coprecipitation of bisulfates of sodium, potassium, and ammonium, of lower molecular weight than barium sulfate, and decomposition at high temperatures, changing first into the pyrosulfates and then into the normal sulfates. In the case of ammonium chloride this minus error is greatest because of the volatility of all ammonium sulfate salts.

$$2NaHSO_4 \rightarrow Na_2S_2O_7 + H_2O$$
$$Na_2S_2O_7 \rightarrow Na_2SO_4 + SO_3$$

3. Precipitation of barium sulfate in the presence of ferric salts causes coprecipitation of ferric sulfate, of lower molecular weight than barium sulfate, and decomposition into ferric oxide and sulfur at 480° C.
4. Precipitation of barium sulfate in the presence of nitrates causes entrainment of barium nitrate by the barium sulfate, producing high sulfur results. This tendency is lessened, eliminated, or even reversed in the presence of alkali or ammonium salts, because of their tendency to produce low sulfur results.
5. Precipitation of barium sulfate in the presence of even large amounts of tin will produce satisfactory sulfur results (Table VI).

With the above cited defects and sources of error in mind, let us consider the pros and cons of those procedures that seem to have possibilities for the determination of sulfur in tin ores and concentrates.

METHOD I. FUSION WITH SODIUM PEROXIDE. Fusion of tin ores requiring sodium peroxide as flux eliminates the use of platinum crucibles and necessitates the employment of nickel crucibles, thus introducing large amounts of nickel salts, which are without any influence upon the precipitation of barium sulfate.

Procedure. Weigh 1.0 gram of tin concentrate into a nickel crucible and fuse as for tin. When the fusion is cool, place the crucible in a 600-ml. beaker, add 75 ml. of water, and allow the melt to disintegrate. Add 70 ml. of hydrochloric acid and agitate until all is in solution. Remove the crucible and wash it with dilute hydrochloric acid. Evaporate the solution to dryness on a water bath or hot plate and dehydrate the silica by heating the residue for half an hour at about 105° C. Add 5 ml. of concentrated hydrochloric acid and 200 ml. of water, heat to boiling, filter on 11 cm. No. 42 Whatman filter paper, receiving the filtrate in a 600-ml. beaker, and wash with hot water. (Hold the precipitate for possible test for barium sulfate.)

Dilute the solution to 500 ml., heat to boiling, then add slowly with the help of a pipet or a precipitating cup (*8*) enough 10 per cent barium chloride solution to precipitate the sulfate ion and provide an excess of about 5 ml. Allow barium sulfate to settle overnight and filter on 11-cm. No. 42 filter paper. Wash the precipitate 3 times by decantation with hot water, transfer it to the paper, and continue the washing until the test for chloride ion fails. Dry the wet paper in a clay or porcelain crucible and ignite carefully in a good oxidizing atmosphere, finally raising the heat to about 900° C. Cool in a desiccator and weigh as barium sulfate.

In order to demonstrate the application range of this method and its remarkable merits, unfortunately restricted, however, to certain types of samples, it has been applied in the analysis of a large number of tin ores of reputed sulfur content. Minus errors due to coprecipitation of sodium sulfate and sodium bisulfate (*7*), ferric sulfate and tin sulfate were accurately determined (Table VII).

TABLE VII. ACCURACY OF METHOD I, BASED ON FUSION

Reputed Sulfur Content	Sulfur Found, Uncorrected	Sulfur Found, Corrected	Na_2SO_4	$NaHSO_4$	$Fe_2(SO_4)_3$	$Sn(SO_4)_2$
%	%	%	+%	+%	+%	+%
2.11	2.08	2.13	0.02	0.01	0.01	0.01
2.87	2.83	2.89	0.02	0.02	0.02	...
3.46	3.39	3.46	0.02	0.02	0.02	0.01
4.55	4.47	4.57	0.03	0.02	0.04	0.01
7.68	7.56	7.67	0.03	0.02	0.04	0.02
10.24	10.10	10.26	0.05	0.04	0.04	0.03
13.72	10.55	10.74	0.06	0.06	0.04	0.03
18.93	18.66	18.95	0.11	0.10	0.05	0.03
23.37	23.02	23.38	0.16	0.13	0.04	0.03

The data in Table VII clearly indicate that Method I, although subject to many sources of error, gives excellent results as long as the sulfur content does not exceed a certain percentage (5 to 8 per cent). As the uncorrected sulfur figures of samples in this category deviate only slightly from the true sulfur content, and the split agreed upon by the Metals Reserve Company and the Bolivian tin processors, is 0.25 per cent, it would represent a major waste of time to execute the corrections mentioned above for every sulfur determination.

On the other hand it is apparent that with increasing amounts of sulfur the reliability of this method undergoes

TABLE VIII. ACCURACY OF METHOD II

Sulfur Found, Method I (Corrected)	Sulfur Found, Method II	Sulfur Found in Residue of Method II
%	%	%
2.13	2.02	0.09
2.89	2.73	0.11
3.46	3.28	0.15
4.57	4.39	0.14
7.67	7.49	0.15
10.26	10.02	0.18
13.74	13.50	0.18
18.65	18.39	0.20
23.38	23.12	0.22

a marked decline. For tin ores containing as much as 25 per cent of sulfur, there is scarcely any certainty that results obtained by this method represent the true sulfur content, even if all plus and minus errors have been corrected. One source of a minus error, coprecipitation of ferric sulfate, could be eliminated by prior reduction of the ferric to the ferrous ion with aluminum, zinc, or iron, since ferrous sulfate is not coprecipitated with barium sulfate. As this procedure would eliminate only one source of error and still would necessitate corrections of the remaining discrepancies, it seems safer, more accurate, and more economical to have recourse to a correction procedure, similar to that proposed by Hillebrand and Lundell (*8*). A correction graph is prepared, based on the analysis of a great number of tin ores of known sulfur content, covering the whole range of the regular samples, by preparing the solution containing the sulfate ion and precipitating the barium sulfate under exactly the same conditions and in the presence of the same impurities as in the regular routine samples.

METHOD II. SULFUR DETERMINATION BASED ON ACID DECOMPOSITION. A survey of the methods for the determination of sulfur, in use at the present time in various laboratories engaged in the analysis of tin ores and concentrates, disclosed that the majority of chemists prefer methods based on acid decomposition of the sample, frankly admitting, however, various discrepancies and uncertainties encountered in the execution of all such procedures. Procedures based on acid decomposition more or less follow the line of operation used for pyrite samples (*1*, *17*).

Procedure. Treat 1 gram of the sample either with a mixture of bromine and carbon tetrachloride followed by nitric and hydrochloric acids (*1*), or with a mixture of 3 parts of nitric acid and 1 part of hydrochloric acid containing a little bromine (*17*). Subsequently evaporate the solution on the water bath to dryness, add hydrochloric acid, and repeat the evaporation. Dehydrate silica by heating at approximately 100° C., take up the dried mass in 5 ml. of concentrated hydrochloric acid, and warm until solution of the soluble parts is complete, then treat with aluminum or zinc until colorless, filter, and wash the precipitate with hot water. Dilute the solution to about 500 ml., heat to boiling, and precipitate barium sulfate as usual.

In order to determine the accuracy and application range of this method, it was applied by the writer to the determination of sulfur in a great number of tin ores of known sulfur content; it became apparent that these methods in their original form are incompatible with accuracy, mostly because of incomplete decomposition of the sample and failure to recover the sulfur in the undecomposed residue (Table VIII).

Methods for the determination of sulfur in pyrites and other sulfides, based on acid decomposition of the sample, usually result in complete decomposition of the sample, leaving very little, if any, undecomposed residue. But this is different in the case of most tin ores, and particularly with cassiterite. The preponderance of stannic oxide causes partial envelopment of the sulfide particles, with incomplete decomposition of the sample, and thus very often produces irregular, erratic, and always low sulfur results; hence it is imperative to determine sulfur also in the residue from acid decomposition. This, however, involves lengthy procedures. As ignition of the filter paper containing the undecomposed residue would cause certain loss of the sulfide sulfur, one of the two following procedures may be used:

1. Wash the residue into a nickel crucible, evaporate to dryness on a water bath, mix with sodium carbonate and sodium peroxide, and proceed as in Method I, which is based on immediate fusion of the sample.
2. Dry the paper and residue for 3 hours in an electric oven at approximately 70° C., brush the residue into a nickel crucible, and proceed as in Method I.

METHOD III. The writer recently succeeded after many fruitless attempts and with the defects of the above methods in mind, in developing a method, also based on acid decomposition, which is easy of manipulation and gives good results (Table IX).

It is based on the strong oxidizing power of 70 per cent perchloric acid at its comparatively high boiling point of approximately 200° C. Preliminary treatment of the sample prior to the addition of perchloric acid consists in oxidizing the bulk of the sulfide sulfur to the sulfate ion by a mixture of bromine and acetic acid, followed by nitric and hydrochloric acids. The excess of the acids is expelled by perchloric acid, which in its turn readily attacks the residue, oxidizing any remaining sulfur to the sulfate ion. To prevent a loss of sulfuric acid during this evaporation, a little calcium nitrate is added (*5*).

The new procedure has been applied to all types of tin concentrates, regardless of their sulfur content, and is very rapid, as it does not involve corrections of plus and minus errors or the preparation of a correction graph as in Method I or the lengthy treatment of the residue as in Method II.

Procedure. Weigh 1.0 gram of tin ore into a 250-ml. beaker, add 10 ml. of a mixture of 3 parts of acetic acid and 1 part of bromine (each 100 ml. of which contain 10 grams of calcium nitrate or an equivalent amount of zinc nitrate), and add 3 ml. of bromine. Allow to stand at room temperature for about 15 minutes, then add 8 ml. of nitric acid and 8 ml. of hydrochloric acid and warm gently until action ceases. Add 15 ml. of perchloric acid and evaporate slowly on a hot plate to fumes of perchloric acid, then heat strongly for about 3 minutes. Allow the solution to cool, add 120 ml. of water, and 10 ml. of concentrated hydrochloric acid, and heat to boiling. Reduce with zinc or aluminum until the solution is colorless. Filter on 11-cm. No. 42 Whatman filter paper into a 600-ml. beaker and wash with hot water. Dilute the filtrate to about 500 ml., heat to boiling, and add 10 per cent barium chloride solution with the help of a pipet or a precipitating cup. Determine and weigh as barium sulfate.

TABLE IX. ACCURACY OF METHOD III

Sulfur Found, Method I (Corrected Results)	Sulfur Found, Method III	
	Original	Duplicate
%	%	%
2.13	2.10	2.14
3.46	3.47	3.44
10.26	10.22	10.23
23.37	23.40	23.42

Determination of Bismuth

Bolivian tin concentrates generally are low in bismuth, most of them containing less than 0.03 per cent. In some instances, however, bismuth was found to be as high as 0.5 per cent.

The dissolving of samples with such small amounts of bismuth is rather a difficult task, as acid decomposition is insufficient, fusion with a mixture of sodium carbonate and sulfur causes great losses of bismuth, and fusion with sodium

peroxide in an iron or nickel crucible is confined to the opening of small portions of cassiterite. The following procedure enables the handling of 5 to 10 grams of tin concentrate by collecting the bismuth by lead in a furnace fusion, while tin and the remaining impurities pass into the slag.

PROCEDURE. Weigh 5 grams of high-grade concentrates or 10 grams of medium- or low-grade concentrates into 30-gram clay crucibles, containing 75 grams of flux No. 1 (No. 1 flux consists of: litharge 15,000, pearl ash 1000, soda ash 2500, borax glass 1500, silica 500, flour 500), mix thoroughly, and add 75 grams of flux No. 2 (No. 2 flux consists of: litharge 10,000, pearl ash 3000, soda ash 2000, borax glass 5400, silica 2000, argols 800), cover with borax glass, and fuse in a muffle furnace. When fusion is complete, remove from the furnace and pour into an iron mold. When cool, clean the lead button by hammering, add enough test lead to give 65 grams (combine at this point two or more lead buttons if the sample is extremely low in bismuth), place in 7.5-cm. (3-inch) scorifiers, and scorify down to a button weighing between 18 and 25 grams.

To continue, modifications of two reliable procedures may be used.

METHOD I. AMMONIUM FORMATE METHOD (*9*). Flatten the lead button, place in a 600-ml. beaker, add 200 ml. of water, and 45 ml. of concentrated nitric acid, and warm to complete solution. Neutralize the warm solution with 8 *N* ammonia until further addition would cause precipitation of lead and bismuth. The solution should be definitely clear at this point, but the acidity should not exceed 2 ml. of 16 *N* nitric acid in 300 ml. of solution. Add 8 ml. of 40 per cent ammonium formate solution. Allow to stand warm for 1 hour, when as little as 1 mg. of bismuth has settled. Filter off the precipitate on 11-cm. No. 42 Whatman paper and wash 8 times with hot water. Dissolve the precipitate in warm 4 *N* nitric acid, evaporate to dryness on a water bath, and take up with 1 ml. of hydrochloric acid (1 to 9), 2 grams of ammonium chloride, and 5 ml. of hot water. Warm to complete solution, then dilute to approximately 500 ml. and allow bismuth oxychloride to settle. Filter and wash with hot water. Dry at approximately 105° C. and weigh as bismuth oxychloride.

If only minute amounts of bismuth are present, dissolve the bismuth formate in hot (6 *N*) sulfuric acid and determine bismuth colorimetrically with potassium iodide.

METHOD II. LEDOUX'S METHOD (*10*). Dissolve the lead button in nitric acid as in the preceding method. Add carefully to the warm solution 8 *N* ammonia until the excess acid is neutralized and a faint cloud but no permanent precipitate forms. Now add 1 ml. of hydrochloric acid (1 to 9). The solution will clear for a moment, then bismuth, when present in appreciable amounts, will precipitate and coagulate rapidly as a white crystalline precipitate. Allow it to settle on the hot plate until the supernatant solution appears clear. Filter on No. 42 Whatman filter paper and wash with hot water. Dissolve the precipitate, which contains only small amounts of lead, in hot dilute nitric acid and proceed as in Method I.

Other Impurities

A complete discussion of methods dealing with the determination of other impurities is not attempted. A short outline of the more important determinations follows.

DETERMINATION OF SILICA. Fuse 1 gram of cassiterite in a nickel crucible with sodium carbonate and sodium peroxide. Leach with water in a nickel dish. Pour the solution into a casserole or a beaker containing enough hydrochloric acid to render the solution acid. Evaporate to dryness and dehydrate the silica by heating at 105° C. Take up with 10 ml. of hydrochloric acid and 200 ml. of water. Heat to boiling, filter off silica, ignite in a platinum crucible, weigh, expel the silica with hydrofluoric acid and a drop of sulfuric acid, reignite, and weigh.

DETERMINATION OF TUNGSTEN. Fuse 1 gram of the sample as for silica. Transfer the crucible to a 600-ml. beaker and leach fusion with water. Acidify with hydrochloric acid and evaporate the solution to dryness, then take it up with 10 ml. of hydrochloric acid and 200 ml. of warm water, and heat it to boiling. Add 5 ml. of cinchonine solution, and allow to stand overnight. Filter off the precipitate and wash with 10 per cent cold hydrochloric acid. Wash the precipitate back into the original beaker, which is then placed under the funnel. Pour 40 ml. of 6 *N* ammonia over the paper, warm the solution on a hot plate, filter through the original paper into a 400-ml. beaker, and wash with 10 per cent ammonia. Dilute the solution to 200 ml., and expel ammonia by boiling, acidify with 5 ml. of hydrochloric acid, dilute to 200 ml., add 5 ml. of cinchonine solution, and allow to stand overnight. Filter, wash the precipitate with dilute cinchonine solution, ignite in a tared platinum crucible, expel the silica with hydrofluoric acid and a drop of sulfuric acid, reignite, and weigh as tungsten trioxide.

DETERMINATION OF IRON, ALUMINUM, TITANIUM, CALCIUM, AND MAGNESIUM. Use the filtrate from the silica determination or fuse 1 gram of the sample in a nickel crucible with sodium carbonate and sodium peroxide. Leach the fusion with 100 ml. of water in a 400-ml. beaker, add 65 ml. of concentrated hydrochloric acid, remove the crucible, and rinse it with dilute hydrochloric acid. Heat the solution to expel chlorine, then adjust acidity to 15 ml. of hydrochloric acid in 300 ml. of solution. Pass in hydrogen sulfide for half an hour and allow the precipitate to settle. Filter, receiving the filtrate in a 600-ml. beaker and washing the precipitate with warm 3 per cent sulfuric acid containing some hydrogen sulfide. Discard the precipitate, expel the hydrogen sulfide by boiling, then oxidize the solution with hydrogen peroxide.

Render the solution ammoniacal, heat to boiling, filter off, precipitate, and wash with 5 per cent ammonia containing some ammonium chloride. Dissolve precipitate in hydrochloric acid and repeat the ammonia separation, filtering into the main filtrate.

In the filtrate calcium may be precipitated as the oxalate and in the filtrate of the calcium oxalate the magnesium as magnesium ammonium phosphate.

Dissolve the precipitate containing the iron, aluminum, etc., in dilute hydrochloric acid, adjust the acidity to 5 ml. of hydrochloric acid in 150 ml. of solution, add 2 grams of tartaric acid, and pass in hydrogen sulfide for 20 minutes. Filter off any precipitate and wash with 1 per cent sulfuric acid, containing hydrogen sulfide and a little tartaric acid. Discard the precipitate. Render the solution ammoniacal, adding an excess of 5 ml. of ammonia. Pass in hydrogen sulfide for 5 minutes, filter off precipitate immediately, and wash it with an ammonium sulfide solution containing tartaric acid.

Transfer precipitate to the original beaker and take to fumes with nitric and sulfuric acids until all carbonaceous matter has been destroyed. To expel any nitric acid, take the solution twice to fumes with water. Finally determine the iron by reducing it either with stannous chloride or by the Jones reductor and subsequent titration with potassium permanganate.

Boil the filtrate containing the titanium and aluminum to expel ammonium sulfide, add 40 ml. of hydrochloric acid and again boil to expel all hydrogen sulfide, add 30 ml. of hydrogen sulfide, and again boil to expel excess peroxide. Dilute to 300 ml. cool, add a 6 per cent cupferron solution until no further precipitate forms. Filter, using pulp, and wash with cold water containing 100 ml. of hydrochloric acid per liter. The precipitate contains the titanium which may be contaminated by zirconium (quantitatively) and by some columbium and tantalum. Ignite the precipitate in a platinum crucible, fuse with bisulfate, take up with 150 ml. of about 3 *N* sulfuric acid, add 5 ml. of 3 per cent hydrogen peroxide, and compare the color with that produced by a standard solution of titanium. If larger amounts of titanium are present than can be accurately determined by this colorimetric procedure, pass the solution through a Jones reductor, receive it in a solution of ferric sulfate, and titrate with potassium permanganate.

If zirconium has to be determined, it may be precipitated with diammonium phosphate in the presence of hydrogen peroxide after the colorimetric titanium determination.

Add 25 ml. of sulfuric acid and 40 ml. of nitric acid to the filtrate of the cupferron precipitate and boil down to incipient fumes on a hot plate, adding more nitric acid from time to time until all organic matter has been oxidized. Take the solution up with 150 ml. of water, heat to boiling, filter off any silica, and wash with dilute sulfuric acid. Precipitate aluminum in the filtrate with ammonia, filter off, and wash with hot water containing ammonium nitrate. If chromium and beryllium are absent, ignite the precipitate in a tared platinum crucible and finally weigh as aluminum oxide.

If chromium is present (indicated by the color of the precipitate), dissolve into a 400-ml. beaker with hot dilute hydrochloric acid (1 to 1), add 25 ml. of perchloric acid, and boil till the chromium appears to be oxidized, and then for 5 more minutes. (If a chromium determination is required, use dilute nitric acid, instead of hydrochloric acid, to dissolve the hydroxide precipitate.) Cool, take up with 200 ml. of water, and neutralize with ammonia until distinctly ammoniacal. Heat to boiling, filter (through asbestos, if a chromium determination is required), and wash with hot water containing ammonium nitrate. In the absence of

beryllium, ignite the precipitate in a tared platinum crucible and finally weigh as aluminum oxide. In the presence of beryllium, separate aluminum using 8-hydroxyquinoline.

Acknowledgment

The writer must give due credit to Walker & Whyte, Inc., New York, N. Y., where he carried out part of the above investigation while he was associated with Herbert H. White, now chief chemist of the Tin Processing Corporation, Galveston, Texas. To him and to W. C. Bowden, L. Cudroff, and E. H. Turner, all of Ledoux & Co., 155 Sixth Ave., New York, N. Y., the writer expresses grateful appreciation for valuable suggestions in connection with the preparation of this paper.

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Determination of Iodate in the Presence of Bromate and Chlorate

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THE method of van der Meulen (*2*) for the volumetric determination of iodate in the presence of bromate, while accurate, involves a long and rather complicated procedure. It has been found that by carefully buffering the reaction mixture it is possible to determine iodate by means of an ordinary iodometric titration without interference from bromate or chlorate. After the titration of iodate, bromate can be titrated in the same mixture by adding an adequate amount of hydrochloric acid and a few drops of a molybdate solution as a catalyst (*1*).

Preliminary experiments indicated that the reaction between iodate and iodide was rapid and complete in phthalate buffers between pH 4 and 5. Under the same conditions the reaction between bromate and iodide is slow. At pH 5 it is slow enough to be disregarded during the time required for a titration unless the concentration is high. The rate of the reaction is more rapid at pH 4. By proper choice of buffer it is possible to have all the iodate present in a mixture react without appreciable interference from the bromate. The buffer added has two functions. It supplies the hydrogen ions necessary for the iodate-iodide reaction. It also adjusts the pH of the medium to a value at which the iodate reaction is rapid, whereas the bromate reaction is slow, though measurable. The pH of the buffered solution increases during the reaction between iodate and iodide, since hydrogen ions are used up. Thus the pH is raised to a value at which the rate of reaction between bromate and iodide is negligibly small.

Table I. Titration of Iodate

(Titration of 25.00-ml. samples of 0.1 *N* KIO_3 with 0.09791 *N* $Na_2S_2O_3$)

0.1 *N* $KBrO_3$ Added *Ml.*	Biphthalate *Grams*	$Na_2S_2O_3$ Used[a] *Ml.*	Error %
..	2	25.54	+0.04
..	2	25.54	+0.04
..	3	25.55	+0.08
..	3	25.53	0.00
..	1.5	25.53	0.00
..	1.5	25.54[b]	+0.04
25	2	25.55	+0.08
25	2	25.53	0.00
25	2	25.56	+0.08
25	6	25.60	+0.27
25	6	25.60	+0.27
[c]	2	25.71	+0.7
[c]	2	25.80	+1.1

[a] Theoretical 25.53.
[b] Stood 5 minutes before titration.
[c] 1 g. of $KBrO_3$ present.

Table II. Titrations of Iodate-Bromate Mixtures with 0.09713 *N* Sodium Thiosulfate

0.1 *N* KIO_3 *Ml.*	0.1 *N* $KBrO_3$ *Ml.*	Biphthalate *Grams*	$Na_2S_2O_3$ Used *Ml.*	$Na_2S_2O_3$ Theoretical *Ml.*	Error %
25	100	2.0	25.75[a]	25.74	+0.04
25	100	2.0	25.75[a]	25.74	+0.04
50	25	4.0	51.45	51.48	−0.06
50	25	4.0	51.48	51.48	0.00
5	25	2.0	5.210	5.148	+1.2
5	25	2.0	5.240	5.148	+1.9
5	25	0.5	5.153	5.148	+0.1
5	25	0.5	5.153	5.148	+0.1
5[b]	0	0.5	5.148	5.148	0.00
10[c]	0	1.0	10.30	10.30	0.00
10	10	1.0	10.30	10.30	0.00
10	10	1.0	10.30	10.30	0.00
25	0[d]	2.0	25.74	25.74	0.00
25	0[d]	2.0	25.74	25.74	0.00

[a] End point tended to drift slightly.
[b] 20 ml. of H_2O added.
[c] 10 ml. of H_2O added.
[d] 10 ml. of 1 *N* $KClO_3$ added.

Experimental

Aliquot portions of a standard 0.1 *N* potassium iodate stock solution were treated with various amounts of solid potassium biphthalate. Potassium iodide was added and the mixtures were titrated with standard sodium thiosulfate. In each case the major portion of the thiosulfate was added from a pipet and the titration was finished with a microburet. This technique

Table III. Titrations with 0.01 *N* Solutions in Presence of 1 Gram of Potassium Biphthalate

0.01 *N* KIO_3	0.1 *N* $KBrO_3$	0.009713 *N* $Na_2S_2O_3$	$Na_2S_2O_3$ Theoretical	Error
Ml.	*Ml.*	*Ml.*	*Ml.*	%
25	0	25.71	25.74	−0.12
25	0	25.70	25.74	−0.16
25	5	25.77	25.74	+0.12
25	5	25.77	25.74	+0.12
25	1	25.75	25.74	+0.04
25	0[a]	25.71	25.74	−0.12
25	0[a]	25.70	25.74	−0.16
10	1	10.34	10.30	+0.40
10	1	10.31	10.30	+0.10

[a] 2 ml. of 1.0 *N* $KClO_3$ present.

permitted reproducibility to about 0.05 per cent in titrations requiring approximately 25 ml. of solution. Titrations were made also with varying amounts of potassium bromate or chlorate present. The following procedure was found to give excellent results.

To 25 to 50 ml. of solution (containing about 2 to 3 milliequivalents of iodate) 2 grams of potassium biphthalate are added and the mixture is swirled until solution is effected. Three grams of potassium iodide are added and the mixture is allowed to stand for 3 minutes. The liberated iodine is then titrated with standard 0.1 *N* sodium thiosulfate to a starch end point.

The amount of biphthalate added supplies a threefold excess of hydrogen for the iodate-iodide reaction. The pH of a pure biphthalate solution is 4.0, but the reaction between iodate and iodide removes sufficient hydrogen ions to raise the pH to 5.0 (with 2.5 milliequivalents of iodate). This is important, as the iodate reaction thus takes place within a few seconds at the higher acidity and automatically reduces the hydrogen-ion concentration to a level at which the bromate reacts very slowly. If a much larger excess of biphthalate were to be added, a drifting end point and high results would be obtained.

Analytical Results

The data in Table I show that the conditions of the procedure permit an accurate titration of iodate and that the amount of biphthalate used is not critical. Tables I and II show that a fourfold excess of bromate or chlorate does not interfere.

The approximate ratio of 2 grams of biphthalate to 2.5 milliequivalents of iodate is necessary if results accurate to 0.1 per cent or better are desired. The above ratio of biphthalate to iodate is not critical, but large excess of biphthalate gives results accurate to only 0.25 or 2 per cent if bromate is present in equal or greater amounts. If the order of magnitude of the iodate concentration is not known, a preliminary titration permits estimation of the proper amount of biphthalate to be added for the exact determination. The determination gives high results when very large concentrations of bromate are encountered. Thus, titration of 0.1 *N* iodate to which sufficient solid potassium bromate had been added to make its concentration 1.8 *N* gave results about 1 per cent high.

In titrations with 0.01 *N* solutions the reaction between iodate and iodide was found to be inconveniently slow unless the ratio of biphthalate to iodate was increased considerably. By using 1 gram of biphthalate for 0.10 to 0.25 milliequivalent of iodate in 10 to 30 ml. of solution, fairly accurate results were obtained (Table III).

Acknowledgment

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Vacuum Desiccator for the Synthetic Organic Laboratory

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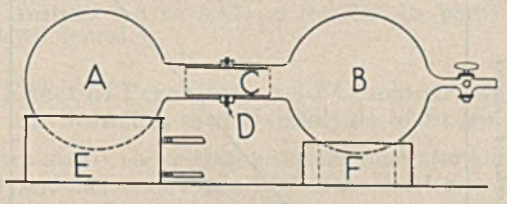
THE conventional form of a vacuum desiccator has limitations and disadvantages which render its use impracticable. In organic syntheses, whenever sharp drying of larger batches is required, the following simple adaptation of standard equipment has proved useful in this laboratory.



One of two similar round-bottomed flasks, *B*, is provided with a side arm for connection to the vacuum pump. (A glass stopcock in this place is desirable but not necessary. Its presence enables the flask to be used as a large separatory funnel.)

A not too loosely fitting glass sleeve, *C*, serves as a guide for the union between flasks *A* and *B*. The sleeve carries a rubber gasket, *D*, conveniently cut from an old inner tube. The gasket seals the vacuum, while the sleeve prevents the side-slipping of the contact surfaces. Without the guiding sleeve, the assembly is not safe. Special guiding clamps could be used, but they have no particular advantages in this case.

When in use, *A* contains the product, and *B*, the drying agent; *E* is a steam bath, and *F*, any convenient support. The apparatus, assembled at random from stock flasks of 5-liter capacity, will hold a vacuum of 2 mm. for 24 hours (with the aid of a high grade vacuum grease).

The following features make the "dumb-bell desiccator" particularly desirable for synthetic work: (1) Frequently one operation may be saved, since a round-bottomed flask in which the reaction or process of concentration was carried out may be attached to the drying bulb without the need of a transfer. (2) Within limits, the desiccator may be made as large or as small as desired. With reasonable precaution, flasks up to 24 liters may presumably be used. (The author has found it useful to coat evacuated vessels on the outside with a thin film of a soluble plastic. The shattering hazards seemed to be greatly reduced and experimentally induced implosions proceeded with not much more than a dull thud.) (3) While being dried the product may be readily heated on a steam bath and may be stirred by rotating the assembly. This also exposes a new surface of drying agent at each turn, thus hastening the process.

A comparative test with a highly hygroscopic sirup has shown that the dumb-bell desiccator works about twice as fast as the conventional model under comparable circumstances (such as equal amounts of desiccant). With gentle warming, the rate of drying was increased fourfold or better.

Communication No. 904 from the Kodak Research Laboratories.

Rapid Determination of Starch

An Index to Maturity in Starchy Vegetables

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IT IS well known that in certain vegetables such as peas, corn, and lima beans, the starch content of the seed tends to increase as the plant matures. This increase in starch is usually associated with a decrease in total sugar, tenderness, and general food quality of the vegetables.

Since the increase of starch is one of the major changes that occur during the maturing of these vegetables, it seemed logical that the estimation of starch should serve as an index of maturity and quality. This idea was supported by the fact that alcohol-insoluble solids, which give a rough measure of starch, correlate well with quality in green peas (*2*, *4*).

Common methods of starch analysis (*1*, *3*, *5*) usually involve drying the sample and grinding in a ball mill or other device for disintegrating the tissues. The material is then extracted with alcohol and suspended in water, the starch is brought into solution with acid, after which it is hydrolyzed with an enzyme or acid, the resulting product is clarified, and the sugar is determined by some conventional method. Some methods include an additional step for separating dextrins, either by different solubility in various concentrations of alcohol or by a precipitation of the starch with iodine, after which the starch is determined by hydrolysis or colorimetrically with iodine (*5*). Hassid and coworkers (*3*) combine the alcohol extraction and acid solubilization by adding a small amount of acid to the alcohol and refluxing.

The above procedures require a good deal of time-consuming manipulation and they increase considerably the chances of loss of starch. Most methods do not attempt to remove dextrins and other polysaccharides, which are determined along with starch upon hydrolysis. Pucher and Vickery (*5*) by a long procedure do remove most of the interfering substances.

A determination by any of the above methods will require at least a day and sometimes several days. If a large number of samples are run together a considerable amount of equipment is required. The method presented in this paper was developed mainly for speed without appreciable sacrifice in accuracy. Since manipulation is greatly reduced, errors from that source are minimized. The starch is estimated colorimetrically with iodine, using a red filter, which decreases considerably the error due to dextrins. Interfering glucosides and alkaloids are shown to be absent from the products examined. However, a rapid procedure for their removal is given, in case they are present in the sample to be analyzed. A single sample can be carried through the whole procedure, including preparation, in 20 to 30 minutes. Forty to 50 samples can be analyzed in a day.

Perchloric acid is unique, in that practically all its inorganic compounds are soluble in water. In order to ascertain whether this "solubilizing" effect might occur in organic combinations, various concentrations of perchloric acid were mixed with raw potato starch. It was found that after a certain normality was reached, which was well below the concentration of hydrochloric acid used for the same purpose, the starch granules lost their form and passed into solution in 3 to 4 minutes.

This acid "solubilization" has now been applied to vegetable material disintegrated in a Waring Blendor. As a result, a rapid procedure has been devised for the extraction of starch, which can then be estimated by the starch-iodine colorimetric method as suggested by Pucher and Vickery (*5*).

Reagents and Equipment

Photoelectric colorimeter. For rapid work the colorimeter should have a test tube adaptor and at least a dozen matched test tubes. A red filter is necessary for maximum sensitivity.

Disintegrator, a Waring Blendor or any similar instrument.

Perchloric acid, 72 per cent reagent grade solution; acetic acid, 2 *N* solution; sodium hydroxide, 6 *N* solution; potassium iodide, 10 per cent solution; and potassium iodate, 0.01 *N* solution.

Procedure

A 100-gram sample of the fresh, frozen, or canned vegetable is placed in the disintegrator cup with an equal weight of water, and the instrument is allowed to run at the high-speed position for 3 to 4 minutes. Two grams of the ground sample are weighed directly into a 30- or 50-ml. beaker on a torsion balance sensitive to 0.01 gram, 2 ml. of water are added, and then exactly 2.7 ml. of 72 per cent perchloric acid are slowly added with thorough stirring, so that there will not be momentary high concentrations of the acid in any portion of the sample. The mixture is allowed to stand with occasional stirring for about 10 minutes.

After standing, the mixture is made up to 25 or 50 ml. with distilled water, depending on the starch content, and then poured into a suitable test tube to settle. A 1-ml. aliquot of the supernatant liquid is pipetted into a 100-ml. beaker and 6 ml. of water are added. A drop of phenolphthalein is added and the solution is brought to a pink color with a few drops of 6 *N* sodium hydroxide. Now 2 *N* acetic acid is added until the pink color disappears, 2.5 ml. are then added in excess, 0.5 ml. of 10 per cent potassium iodide and 5 ml. of 0.01 *N* potassium iodate are accurately added, and the solution is allowed to stand at least 5 minutes. If the solution is relatively pale bluish-green, it should now be made up to 25 ml., and if it is dark bluish-green, it should be made up to 50 ml. The color is estimated in a photoelectric colorimeter using a red filter having a transmission range from 640 to 700 millimicrons. The colorimeter should be set at zero absorption or the readings corrected, with

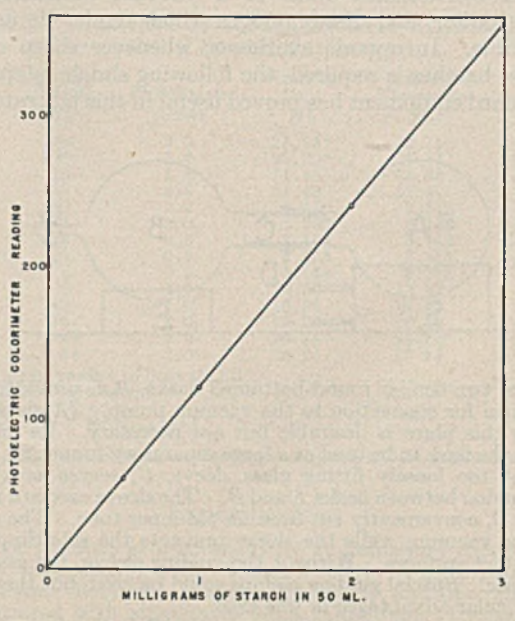

FIGURE 1. ABSORPTION OF LIGHT BY STARCH-IODINE SOLUTIONS, RED FILTER

Table I. Effect of Perchloric Acid Concentration on Solution and Hydrolysis of Potato Starch

Treatment	Weight of Starch	Molality of Acid	Starch Recovery
Min.	*Mg.*		%
10	35	12.0	11.0
10	35	8.0	16.2
10	35	6.0	89.8
10	35	4.8	100.0
10	35	3.4	87.5
10	35	2.7	67.8
15	35	12.0	4.1
15	35	8.0	12.4
15	35	6.0	80.0
15	35	4.8	100.0
15	35	4.0	100.0
15	35	3.4	94.5

a blank containing all of the reagents. If the filtrate used in developing the starch-iodine color is turbid, an extra blank correction should be made if precise results are desired. This can be done by discharging the blue color with a few drops of 0.1 *N* sodium thiosulfate and comparing the turbid solution against water.

Standardization

The percentage of starch is calculated from a curve prepared from the colorimeter readings of a known range of starch concentration. For solution depths of about 1.25 cm. (0.5 inch), the best range of starch concentrations is from 0 to 3 mg. per 50 ml. Figure 1 shows a typical standardization curve with the Klett-Summerson photoelectric colorimeter.

Soluble starch cannot be used for standardization. If absolute results are desired, starch prepared from raw, unblanched material similar to that which is to be analyzed should be used. Equal weights of starch from different products, such as potatoes and peas, do not give the same amount of color with iodine; therefore one type of starch cannot be used as a standard for all products. Perhaps if factors were established between the various starches, a single standard such as potato starch would suffice. If a series of analyses is to be carried out on a given product and only relative results are desired, potato starch, which is easily prepared, could be used to prepare a standard curve.

To obtain starch for standardization, disintegrate raw, unblanched material in a Waring Blendor type of disintegrator with an equal weight of water. Separate the fibrous material by washing the ground pulp through a 100- to 200-mesh screen, place the material that passed through the screen in a large beaker or pan, and stir with a large volume of water. Allow the starch to settle and decant off the water. Repeat this process until the starch is free of extraneous material. Now wash the starch with alcohol and ether and dry in an oven at 70° to 80° C. for 30 minutes. This should give a starch that is reasonably pure. Analyses can be made to establish its purity if such accuracy is desired.

Effect of Perchloric Acid Concentration on Solution and Hydrolysis of Starch

It was stated above that a certain concentration of perchloric acid had to be reached before the starch granules went into solution. To study this further and to ascertain the hydrolytic effect of the acid, samples of potato starch were treated with known concentrations of acid for two different periods. The data in Table I indicate that a concentration near 4 molal is necessary to bring the starch into solution and that this range can extend to at least 4.8 molal without hydrolysis of the starch when held at room temperature for 15 minutes. A similar experiment carried out on corn as shown in Table II placed the lower limit slightly higher, probably because of the buffering effect of the sample. In a third experiment on lima beans (Table III), little hydrolytic effect was shown even after 30 minutes.

Effect of Filtration on Solubilized Starch

A Whatman No. 1 filter paper can be used to filter the sample after it has been solubilized and made up to volume. Curiously enough, a Whatman No. 2 paper, which is a good deal heavier, removes about 20 per cent of the starch from the solution. For this reason the method was devised so as to involve no filtration and thus eliminate any chance of absorption of starch by filter paper. Turbid solutions which had settled for only a few minutes were sampled and compared with some of the same solution which had been centrifuged. Starch results by the two procedures were identical.

Stability of Starch-Iodine Color

If the sample is immediately made up to volume after the preparation of the starch-iodine color, a slow upward drift in colorimeter reading will be observed. However, if the sample is allowed to stand in the concentrated state for 5 minutes, this drift occurs to only a very limited extent. Twelve samples prepared by the latter procedure had an average upward drift of 1 division, equivalent to 0.008 mg. of starch in 40 minutes.

Table II. Influence of Perchloric Acid Concentration on Extraction of Starch from Corn

Sample No.	Molality of Acid	Starch Found in Sample
		%
73	4.8	5.20
	2.4	2.52
74	4.8	4.03
	4.0	3.41
	3.4	3.30
30	6.0	4.25
	4.8	4.83
31	6.0	2.83
	4.8	3.46
37	6.0	2.58
	4.8	3.20
45	6.0	3.13
	4.8	3.83

Table III. Influence of Time in 4.8 Molal Perchloric Acid on Per Cent of Starch Found in Lima Beans

Sample No.	Time in 4.8 *M* $HClO_4$	Starch Found in Sample
	Min.	%
66	5	7.34
66	10	7.25
66	15	7.17
66	30	7.15

Effect of Alcohol Extraction

Most of the procedures that have been proposed for starch involve drying the starch-containing material, grinding in a ball mill, and then extracting for several hours with alcohol. This serves to remove sugars which would interfere in a hydrolysis procedure for starch. According to Pucher and Vickery (*5*), it also removes certain compounds which give a blue color similar to that produced by starch with iodine. Since the method developed did not involve the determination of sugar produced by the hydrolysis of starch, the removal of sugars was of no concern. However, it is necessary to remove any compounds other than starch which would give a blue color with iodine.

To check this point, 20-gram samples of the disintegrated material from several different varieties of frozen corn, lima beans, and peas were each mixed with 200 ml. of alcohol and reground in the disintegrator for several minutes. A 25-ml. aliquot of this mixture was then filtered through a Whatman No. 1 paper in a Gooch crucible and washed several times

TABLE IV. INFLUENCE OF PRELIMINARY ALCOHOL EXTRACTION ON THE DETERMINATION OF STARCH

Sample No.	Product	Starch	Starch after Alcohol Extraction
		%	%
86	Corn	2.43	2.45
87	Corn	1.45	1.46
36	Corn	3.86	3.91
30	Corn	4.83	4.86
31	Corn	3.46	3.52
37	Corn	3.20	3.28
45	Corn	3.83	3.91
51	Lima beans	9.35	9.30
882	Lima beans	12.12	11.85
877	Lima beans	12.42	12.52
874	Lima beans	11.91	12.00
3	Soybeans	2.43	2.50
57	Peas	7.90	7.62
10	Peas	9.30	9.10
36	Peas	7.92	7.94
5	Peas	7.80	7.58
59	Peas	10.90	10.50
65	Peas	9.35	9.13
27	Peas	6.65	6.50

with alcohol. That the extraction was complete was indicated by the pure white residue left on the filter paper. This residue was then suspended in 4 ml. of water and starch was determined by the procedure given above. Table IV shows that there were no interfering compounds in the products studied.

Influence of Dextrin

The method herein described does not attempt to separate dextrins from starch. It is not necessary in most cases and to do so would greatly lengthen the procedure. There was no indication of the presence of dextrins in the peas, soybeans, or lima beans used for the experiments. However, in corn an occasional sample had a slightly brownish color when iodine was added. To determine the influence of the red color of dextrins in the colorimeter reading using a red filter, a sample containing 125 mg. of bacteriological dextrin was analyzed. This sample gave an apparent starch content of 22 mg. or between one fifth and one sixth as much absorption of light as would the same amount of starch. This means that the error due to dextrins is much less than in a hydrolysis procedure for starch where the dextrins are not removed.

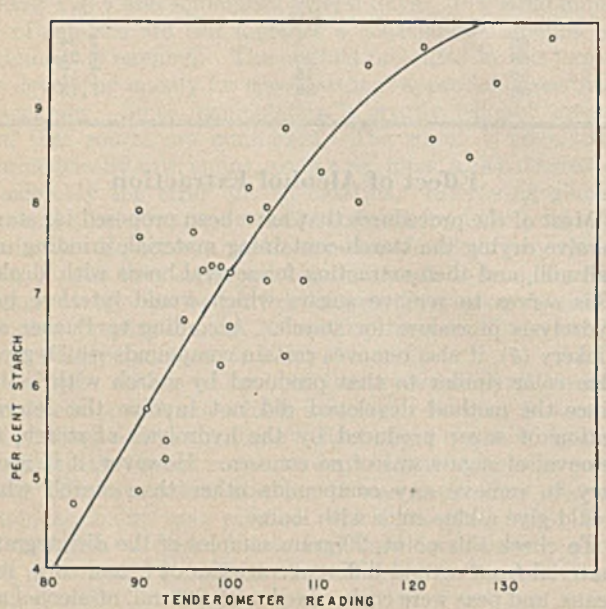

FIGURE 2. RELATIONSHIP OF PER CENT STARCH TO TENDEROMETER READING IN RAW PEAS
Curve drawn by inspection

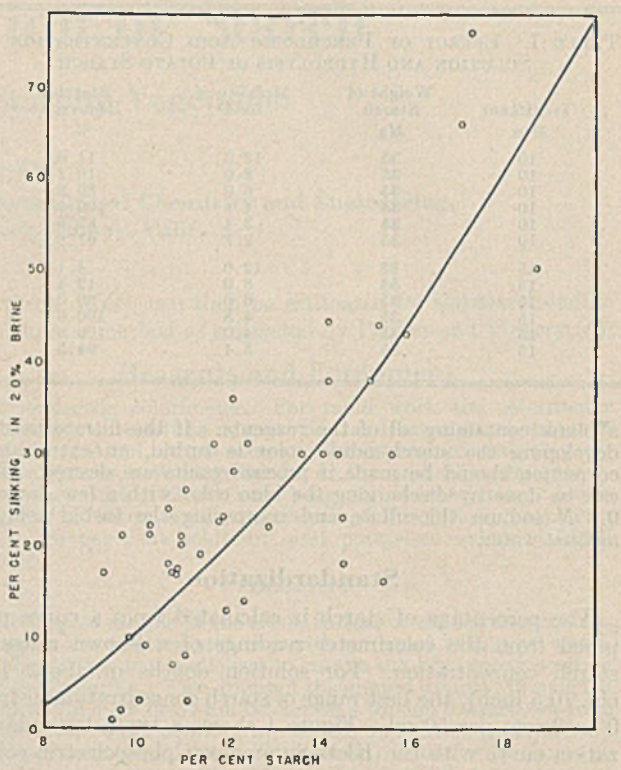

FIGURE 3. BRINE FLOTATION OF BABY LIMA BEANS *vs.* PER CENT STARCH
Curve drawn by inspection

Recovery Experiments

A known quantity of potato starch was added to samples of lima beans and soybeans whose starch contents had been previously determined. Table V indicates that the starch added can be determined within less than 3 per cent, which is a good recovery for most starch methods.

TABLE V. RECOVERY OF ADDED POTATO STARCH

Product	Starch Added	Starch Found	Recovery
	Mg.	*Mg.*	%
Soybeans	0	25.6	
	49.3	74.2	98.6
Lima beans	0	109.6	
	49.3	158.0	98.2
	0	69.5	
	49.3	117.5	97.4

Discussion

Since the vegetables are to be analyzed for a constituent which is not in solution, great care should be taken to keep the disintegrated material well mixed as it is being weighed out. Care should also be taken not to add an excess of perchloric acid to the sample, since a few tenths of a milliliter of acid will cause a considerable increase in the final molality.

Perchloric acid develops some heat of solution. The rise in temperature brought about when the acid is added to extract the starch facilitates its solution. Cold 4.8 molal perchloric acid, however, will dissolve starch in 15 to 30 minutes. If the time period suggested in this paper is adhered to, 72 per cent acid must be used in order readily to get a sufficient rise in temperature to dissolve the starch in 5 to 10 minutes.

Complete extraction of the starch is indicated by recovery experiments, the ability to duplicate results closely, and the check of results on samples reground and extracted with alcohol with those obtained directly determined without extraction. Other evidence is that a reextraction of the residue on the filter paper after the extraction of starch gave a negligible starch content. A starch determination on material left on a 40-mesh screen after grinding the sample in the disintegrator and washing through the screen also gave a negligible result.

Further evidence of the reliability of the method has been obtained in its application. A group of raw pea samples were graded for quality with a tenderometer and then analyzed for starch. Figure 2 shows the relationship between these two factors.

Fifty samples of frozen lima beans were graded for quality organoleptically and by brine flotation. Starch analyses on these samples correlated very well with both the organoleptic and brine flotation grading. The relationship between proportion of sinkers in 20 per cent brine and percentage of starch in lima beans is shown as an example in Figure 3.

Rapidity of the Method

Starch in a single sample can be determined in 20 to 30 minutes if the reagents have been previously prepared. Forty to 50 samples can be analyzed for starch in an 8-hour day if a routine is established.

Perchloric Acid Hazards

There is no danger whatsoever from the 72 per cent perchloric acid itself, other than the usual hazards of strong acids. The cold diluted acid is a very poor oxidizing agent, as is evidenced by the fact that it will not release iodine from iodide ion. Hot perchloric acid, however, forms unstable compounds with organic material and for this reason the treated samples should never be heated. Samples have been allowed to stand in the laboratory at room temperature and to dry on filter paper for several days without accident.

Summary

A very rapid and reasonably accurate method for the determination of starch in certain vegetables has been developed. It includes grinding the fresh sample in a Waring Blendor-type disintegrator, extracting the starch with 4.0 to 4.8 molal perchloric acid, and estimating by photoelectric colorimeter the dissolved starch indicated by the blue color produced with iodine. Alcohol extraction of the products studied was found to be unnecessary. The use of a red filter in the colorimeter considerably reduces the error produced by dextrins when present.

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Separation of Carotenes from Xanthophylls

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THE methods which have been most generally used for the separation of xanthophylls from carotenes in provitamin A analysis suffer from certain disadvantages. The separation by extraction of petroleum ether solutions with 85 to 90 per cent methanol and the separation on various adsorption columns are time-consuming. The obvious advantages of the chromatographic method for routine work are offset by the difficulties in obtaining adsorbents of uniform performance, and by the fact that there always appears to be some loss of provitamin A material on the columns.

It was known that compounds containing conjugated double bond systems such as occur in the azulenes (*6*) react with 85 per cent orthophosphoric acid to form blue substances which are extracted from petroleum ether by the acid. It was thought that this reaction might be applied to carotene separations.

Petroleum ether solutions of the mixed pigments of canned pineapple, which were obtained by saponification of the solid material with 30 per cent potassium hydroxide in methanol for 12 hours at 3° C. and extraction with petroleum ether (60 to 70°), were treated with phosphoric acid; 25-ml. portions of the petroleum ether solution, which does not need to be dried, were shaken with 4 to 5 ml. of 85 per cent phosphoric acid in a 25-ml. glass-stoppered graduate. The acid layer became blue-green in color. The absorption curve for the pigment remaining in the petroleum ether solution was essentially the same as those obtained with carotene solutions which had been purified by the methanol separation and by passage through magnesia and calcium phosphate columns. Figure 1 shows a group of such curves compared with that of pure β-carotene (S. M. A. β-carotene).

The xanthophyll fraction obtained from a sample of these mixed pigments by the methanol separation was transferred into petroleum ether and this solution was treated with 85 per cent phosphoric acid. All the pigment was removed from the petroleum ether phase and converted into blue-green substances in the acid layer. On the other hand, carotene extracts, purified both by the methanol separation and by passage through magnesia or calcium phosphate columns, gave no apparent reaction when treated in the same manner with 85 per cent phosphoric acid. The absorption curves of such extracts were not appreciably altered by the phosphoric acid treatment (Figure 2). The deviation of the curve of a sample of phosphoric acid–treated β-carotene from that of the untreated carotene is similar to that obtained with extracts of natural materials. This change in the absorption of the pigments is undoubtedly due to isomerization of the type first observed by Gillam and El Ridi (*3*, *4*) and extensively studied by Zechmeister and his co-workers (*5*, *7*, *8*, *9*), and by Beadle and Zscheile (*2*).

Using this shortened method, results were obtained on canned pineapple which were in satisfactory agreement with those of biological assays (Table I). In this case the results can be expressed as units of vitamin A, since chromatographic adsorption on magnesia showed the pigment to be homogenous, and the absorption curve checked that of β-carotene which had been treated with phosphoric acid.

A comparison was made of the A. O. A. C. method (*1*) and the phosphoric acid method, and since carotene has a slight solubility in 90 per cent methanol the results are as might be expected (Table II). In each case the phosphoric acid method gave results which were slightly higher than those of the A. O. A. C. method.

TABLE I. COMPARISON OF PHOSPHORIC ACID METHOD AND BIOLOGICAL ASSAY FOR VITAMIN A ACTIVITY OF FIVE BRANDS OF CANNED PINEAPPLE

(International units per 100 grams)

Brand	H_3PO_4 Method	Rat Assay U. S. P.
A	135	145
B	106	125
C	129	143
D	134	138
E	135	147

TABLE II. COMPARISON OF PHOSPHORIC ACID AND A. O. A. C. METHODS

Sample	H_3PO_4 Method γ/100 g.	A. O. A. C. Method γ/100 g.
1	75.6	66.0
2	111.5	99.5
3	103.9	97.3
4	66.0	58.1
5	99.5	90.0
6	97.3	87.6
	Av. 92.3	83.1

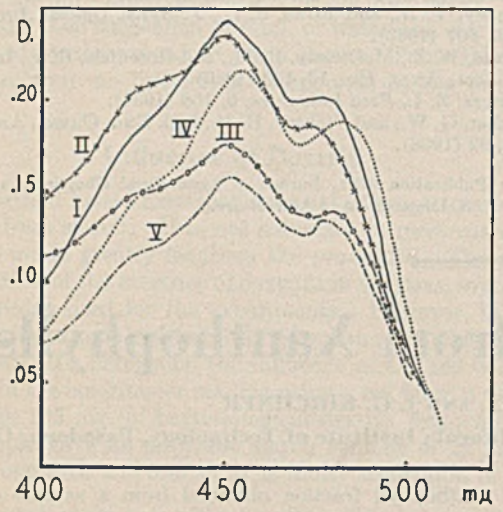

FIGURE 1. COMPARISON OF ABSORPTION CURVES OF β-CAROTENE OBTAINED BY VARIOUS SEPARATION METHODS AND OF PURE β-CAROTENE

I. Adsorbed on Micron Brand magnesia
II. Separated with phosphoric acid reagent
III. Partition between petroleum ether and 90 per cent methanol
IV. Pure β-carotene
V. Filtered through dicalcium phosphate column

As a further check on the method, samples of mixed poultry feeds were saponified and extracted by the A. O. A. C. procedure. These extracts were treated with 85 per cent phosphoric acid and the absorption curves of the remaining pigments in the petroleum ether solution were measured. The curves were the same as those obtained for extracts separated by the use of 90 per cent methanol, and the concentrations of carotene calculated from the absorptions at 450 mμ were in agreement (Table III).

Summary

A new method which has been applied to the purification of carotene extracts in the determination of carotenes in foods, etc., makes use of the reaction between xanthophylls and 85 per cent orthophosphoric acid to separate the latter from carotene. Results agreed satisfactorily with the biological assays and also with the A. O. A. C. method. It is more rapid than the A. O. A. C. method and probably more accurate for analysis of material of low or average carotene content. This is due to the loss of carotene in the A. O. A. C. method occasioned by the residual solubility of carotene in 90 per cent methanol.

When the spectrophotometer is used it is preferable to make the measurements in the range of 440 to 450 mμ, since the absorption values of the extracts do not deviate greatly from those of β-carotene. As in all analytical methods, this method must be used with discretion, as, for example, phosphoric acid will not remove lycopene. It will not separate α- and β-carotene, and in such cases the method would yield the crude carotene content.

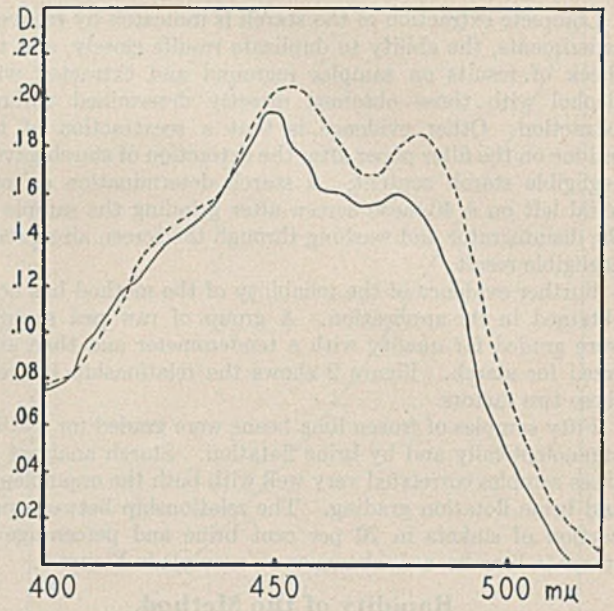

FIGURE 2. ABSORPTION CURVE OF β-CAROTENE BEFORE AND AFTER TREATMENT WITH PHOSPHORIC ACID

– – – Pure β-carotene
——— Pure β-carotene after shaking with phosphoric acid

TABLE III. COMPARISON OF PHOSPHORIC ACID AND A. O. A. C. METHODS ON MIXED POULTRY FEEDS

Sample	H_3PO_4 Method γ/g.	A. O. A. C. Method γ/g.
1	13.3	11.0
2	15.3	12.4
3	13.8	11.5

Acknowledgment

The authors wish to acknowledge with thanks the Pineapple Producers Cooperative Association's financial support for the research program of which this investigation is a part.

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Chromogenic Reagent for Vitamin C Determinations

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RECENT studies in this laboratory have shown that ferridipyridyl sulfate may be used as a reagent for spectrophotometric determination of vitamin C. The reagent cannot be prepared directly by reacting dipyridyl with ferric sulfate, but a yellow-brown solution of the complex compound may be obtained by oxidizing ferrodipyridyl sulfate with ceric sulfate. Ferridipyridyl ion is fairly stable, and on reduction with vitamin C forms the extremely stable pink or deep red ferrodipyridyl ion. With ferridipyridyl in excess, the ferrodipyridyl formed is proportional to the amount of vitamin C. Beer's law is followed over a wide range, permitting accurate spectrophotometric determination of the vitamin.

The reagent oxidizes ascorbic acid (molecular weight 176.12) in two stages, corresponding to equivalent weights of 88.06 and 44.03, at widely different reaction velocities. It may thus be possible to determine vitamin C in the presence of other reducing substances, by suitable control of temperature, time, and concentration of the reagent. This possibility is to be investigated in an extension of the present work in which the new method is being compared with other methods for ascorbic acid in analyzing a series of increasingly complex systems.

Preparation of Reagents

SULFUR DIOXIDE SOLUTION. Pass washed tank sulfur dioxide into a weighed portion of distilled water, reweigh, and dilute to obtain a 1 per cent solution.

CERIC SULFATE SOLUTION. Add 28 ml. of 36 *N* sulfuric acid to 500 ml. of water. Add 40 grams of commercial ceric sulfate, stir until dissolved, filter after standing, and dilute to 1000 ml.

AQUA AMMONIA. Bubble commercial anhydrous ammonia into distilled water until a 4 *N* to 6 *N* solution is obtained. Ordinary aqua ammonia is not suitable even when distilled, as it contains reducing impurities. Commercial synthetic anhydrous ammonia produced by the National Ammonia Co. of Philadelphia was found satisfactory.

FERRODIPYRIDYL SOLUTION. Dissolve 1.76 grams of ferrous ammonium sulfate hexahydrate (Mohr's salt) in a little water and add 10 ml. of 1 per cent sulfur dioxide solution. Make to about 800 ml., add 2.50 grams of α,α'-dipyridyl (2,2'-bipyridine) and stir until this has dissolved. Heat to boiling (or allow to stand overnight) to complete the reaction, cool, and make to 1000 ml. The clear red ferrodipyridyl solution is very stable, and may be used as a stock solution for preparing the ferridipyridyl reagent in smaller portions.

FERRIDIPYRIDYL REAGENT. Heat 200 ml. of ferrodipyridyl solution to 80° C. and titrate with ceric sulfate solution until the color changes from red to yellow; about 11 ml. of 0.08 *N* ceric sulfate are required. The end point is sharp but slow. Back-titrate with 1 per cent sulfur dioxide solution to restore a pink color.

With the aid of a pH meter adjust the solution to a pH of 3.6 by addition of aqua ammonia, avoiding even a temporary excess, which may cause ferric hydroxide to precipitate. The solution darkens as it is neutralized. Finally make to 400 ml. and if a precipitate forms allow it to settle out overnight and use the clear supernatant solution as the reagent. If necessary, add sulfur dioxide from time to time to maintain a small amount of ferrodipyridyl in the reagent. The effect of the ferrodipyridyl will be eliminated by use of a suitable blank as a reference solution in the transmittance measurements, whereas if it is absent an error may result. A check on this adjustment is provided by the blanks, which should be faint pink in color rather than yellow. The blanks prepared as described below are usually stable and each one may be used for all transmittance measurements made over a period of 2 or 3 days.

ACETATE BUFFER. Make 60.0 ml. of glacial acetic acid and 10.00 grams of recrystallized and suitably dried sodium acetate trihydrate to 1 liter, and adjust to a pH of 3.6 by further small additions of acid or salt.

Analytical Procedure

The following procedure is general, and may easily be adapted to meet particular requirements. The essential accuracy is between 0.5 and 2 per cent, but much larger errors may result from sampling difficulties, oxidation of the vitamin, and the presence of interfering substances.

The solution used in the transmittance measurements must be clear. Clarification may be effected by filtration through Pyrex or platinum filter crucibles, by centrifuging, or sometimes simply by allowing suspended or colloidal material to settle out. This may be done either before or after color formation; once the color has been fully developed it remains constant for days, in most cases.

SPECTROPHOTOMETRIC PROCEDURE. Add a small piece of Congo red paper to an aliquot portion of the analytical solution containing not more than 0.40 mg. of ascorbic acid. The volume of the aliquot should be such as to permit addition of reagents without exceeding the specified final volume, and should preferably be small, since dilution decreases the velocity of the analytical reaction.

Add aqua ammonia until the color of the indicator paper is the same as that of a similar piece in a buffer of pH 3.6. The pH is not critical, but should probably not be less than 2.5 or more than 4.0.

Next add 10 ml. of acetate buffer and 20 ml. of ferridipyridyl reagent and eventually (see below) make the solution to a volume of exactly 100 ml. The four critical amounts above may be halved or quartered without changing the transmittance-concentration curve, as a matter of convenience or economy: α,α'-dipyridyl is somewhat expensive. Moreover, the ferridipyridyl reagent addition specified represents a fivefold excess over the maximum ascorbic acid concentration measurable with 1.308-cm. cuvettes and might be reduced in some cases, the blank being changed accordingly.

Constant color may be attained to permit readings within 30 to 60 minutes by heating the solution between 70° and 80° C. for at least 25 minutes before cooling and dilution to final volume. Some systems—often those in which the reagent has been considerably diluted by the aliquot—become cloudy if heated too long or at too high a temperature, but usually give correct results after clarification. Alternatively, constant color may be developed by allowing the solution to stand at room temperature for 12 to 48 hours before dilution to final volume; this period of standing may conveniently be used to remove suspended or colloidal material. In either case the vitamin is oxidized to threonic acid and oxalic acid.

Transmittance readings made between 10 and 40 minutes after adding the chromogenic agent, with solutions kept at room temperature, indicate in many cases that the analytical reaction has proceeded almost exactly to the dehydroascorbic acid stage. This suggests that dehydroascorbic acid is formed rapidly and later oxidized more slowly to the other acids. Several interesting and perhaps useful implications of this observation are more or less evident.

When constant color has been attained, make duplicate transmittance readings with two successive portions of the solution at a wave length of 510 millimicrons. Use as a reference solution a blank containing 5 ml. of the buffer and 10 ml. of the reagent per 50 ml. Using the median transmittance found, read the result of the analysis from a previously prepared graph.

In the present work calibration data were obtained with a Coleman Model 10-S-30 spectrophotometer equipped with square cuvettes 1.308 cm. in depth, using freshly prepared standard solutions made at separate times over an extended period with

pure crystalline ascorbic acid from three different sources. An independent and most accurate calibration was derived by calculating the transmittance-concentration curve for ascorbic acid as ferrodipyridyl from an accurately established transmittance-concentration curve for iron as ferrodipyridyl, through the iron equivalent of ascorbic acid. All measurements were made at temperatures between 28° and 32° C.

The various calibrations in which the ascorbic acid was oxidized to threonic and oxalic acids are best represented by a straight line passing through the points (T = 100.0, C = 0.000) and (T = 10.0, C = 0.400) where T is the percentage transmittance of the solution relative to the blank plotted on a logarithmic scale, and C is the ascorbic acid concentration in milligrams per 100 ml., plotted on an arithmetical scale. The less well established line for oxidation to the dehydroascorbic acid stage passes through the point (T = 10.0, C = 0.80).

Colorimetric Procedure. Colorimetric measurements may be made by comparing analytical solutions obtained as described above with standards of similar composition prepared in the same manner and at the same time.

Applications of the Reagent

So far the new reagent has been used mainly in assaying commercial ascorbic acid, citrus fruit juices, and dried foods for ascorbic acid. It doubtless may also be used in determining other substances capable of reducing it quantitatively. However, both large and small concentrations of such common reducing agents as arsenious acid, formaldehyde, acetaldehyde, methyl alcohol, and formic acid do not reduce the reagent, either in hot or cold solution, and 0.4 mg. of oxalic acid dihydrate or 200 mg. of citric acid per 100 ml. have little or no effect on the reagent even in systems heated to 80° C. Sulfur dioxide reduces the reagent rapidly, but in small concentrations does not produce equivalent quantities of ferrodipyridyl when treated by the procedure used for ascorbic acid.

Photometric Determination of Reduced and Total Ascorbic Acid

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THE most widely used procedures for the determination of reduced ascorbic acid depend on its oxidation to dehydroascorbic acid. Rapid titration of an acid extract with a standardized solution of the sodium salt of 2,6-dichlorophenolindophenol yields accurate values for products rich in ascorbic acid and relatively free from interfering reducing substances. The photometric method (*2*, *3*, *15*) has made possible analyses of colored or turbid solutions even in the presence of other reducing substances. This procedure involves measurement in a photoelectric colorimeter of the progressive reduction of an excess of the dye.

Dehydroascorbic acid, the biologically active, reversibly oxidized form of the vitamin, must be reduced before it can be determined by any of the dye methods. Hydrogen sulfide is usually used. A microbiological reduction of dehydroascorbic acid employing a suspension of *Bacterium coli* has been described (*5*). However, this fails for some food materials.

In this report, a modification of the photoelectric colorimetric methods of Bessey (*2*) and Evelyn, Malloy, and Rosen (*3*) is presented. Fundamental studies of the applicability of the method to the determination of reduced and dehydroascorbic acids in a variety of biological materials were carried out. Evidence is submitted for the superiority of the photometric method over the visual, the necessity for including dehydroascorbic acid in the estimation of "vitamin C", and the proper procedures which should be observed in partitioning vitamin C between the reduced and dehydro forms.

Ascorbic Acid Determination, Biological Materials

Apparatus. A direct-reading photoelectric colorimeter with a 520-millimicron filter. (A null-point instrument cannot be used. The direct reading galvanometer must be critically damped and have a short period. The time required to swing from 0 to 100 and become stable should not be more than 3 seconds. An Evelyn photoelectric colorimeter, manufactured by the Rubicon Co., Philadelphia, Penna., has proved very satisfactory.)

Interchangeable test tubes for the colorimeter.

A pipet delivering exactly 5 cc. of an aqueous solution in less than 1 second. This is easily constructed from a 5-cc. transfer pipet as illustrated in Figure 1.

Reagents. The metaphosphoric acid and citrate solutions described by Bessey (*2*, *16*).

A stock 2,6-dichlorophenolindophenol reagent containing approximately 10 mg. per 500 cc. The photometric density of 5 cc. of the dye plus 5 cc. of the citrate–metaphosphoric acid buffer at pH 3.5 is adjusted to read exactly 0.398 (transmission = 40.0 per cent) by dilution of the dye with water. (The galvanometer is first set at 0.0 for zero transmission, and 100.0 for a solution containing 5 cc. of the buffer at pH 3.5 and 5 cc. of dye, to which a crystal of ascorbic acid is added for complete decolorization.)

Procedure. All manipulations are conducted under an atmosphere of nitrogen, and all extractions and dilutions are made with solutions previously deaerated with a stream of nitrogen. This precaution is necessary if reduced ascorbic acid is to be determined but not if only the total vitamin C content is of interest.

A representative sample is dropped into an equal weight of 6 per cent metaphosphoric acid solution, and macerated mechanically. (A Waring Blendor has proved most satisfactory. One minute at high speed gives an excellent homogeneous mixture of most food substances.) For complete inhibition of the oxidase in some vegetables, it is necessary to add large segments of the sample directly to boiling 6 per cent metaphosphoric acid. (Boiling converts metaphosphoric acid in part to orthophosphoric acid, the latter solution having a lower pH. This, however, has little effect on the final pH, for subsequent dilutions are made with fresh metaphosphoric acid.) In such a medium the action of oxidative enzymes is inhibited. After boiling for 5 minutes, the contents are cooled, transferred to a Waring Blendor, and then macerated.

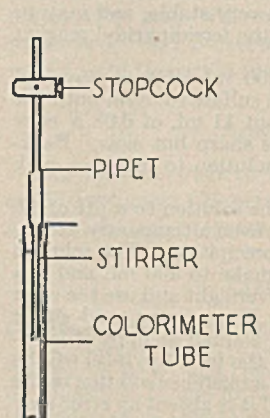

Figure 1. Pipet Used for Addition of Ascorbic Acid Extract to Dye Solution

By use of this technique as much as 150 grams of material may be taken for analysis. The desirability, and in many cases the necessity, of using such large quantities for proper sampling are obvious. This procedure is better than averaging a series of replicate tests on very small portions of the test material (*7*).

An aliquot of the uniform suspension is drawn off and diluted with 3 per cent metaphosphoric acid until the total solids content of the sample in suspension is 10 per cent or less. The samples are shaken mechanically for 15 minutes and then centrifuged. The extract is then buffered at pH 3.5 by adding 14 cc. of the citrate solution to 50 cc. of extract. Using graduated pipets, a rough visual titration is made to determine the volume of extract necessary to decolorize 5 cc. of the dye. Diluting this volume to 10 cc. with citrate–metaphosphoric acid buffer generally gives the optimal concentration for measurement in the photoelectric colorimeter. A testing range of 2 to 6 micrograms per cc. is considered optimal. Smaller concentrations cause insufficient reduction of the dye and hence give less precise results. Larger concentrations are to be avoided because the quantity of dye becomes a limiting factor and also because accurate galvanometer readings at the 5-second point are difficult when the transmission values are increasing rapidly.

Total ascorbic acid (reduced plus dehydro) is determined by a slight modification of Bessey's procedure (*2*). To 25 cc. of an extract buffered at pH 3.5, 6 drops of caprylic alcohol are added, and the solution is treated with a slow stream of hydrogen sulfide for 20 minutes. After 2 hours' standing in the closed system, the excess hydrogen sulfide is removed by streaming wet nitrogen through the solution for 2 hours.

For the photometric measurement the colorimeter tube is placed in the instrument and 5 cc. of the standard dye solution are introduced. The special pipet is filled with buffered extract, and with stirrer lowered, the assembly is placed on the tube as shown in Figure 1. The stopcock is opened, and 2 seconds later the assembly is lifted out of the tube. Galvanometer readings are taken exactly 5 and 10 seconds after the stopcock is opened. The absorption of the reaction mixture due to extraneous pigments and turbidities (the blank) is then obtained by adding a crystal of ascorbic acid to complete the decolorization of the dye.

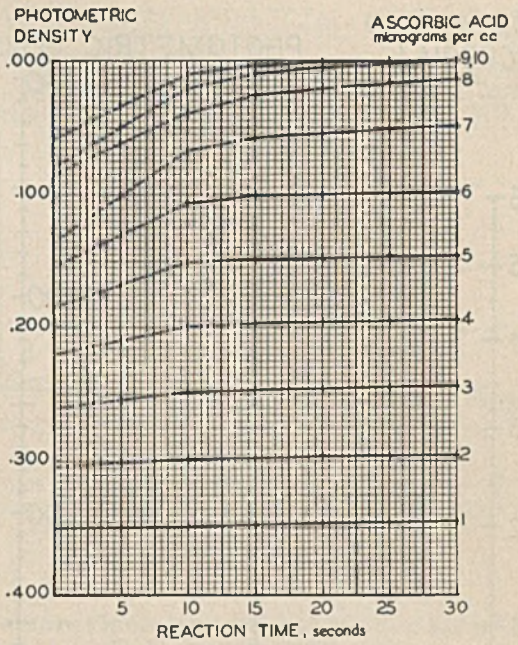

FIGURE 2. PROGRESSIVE DECOLORIZATION OF DYE WITH INCREASING CONCENTRATIONS OF ASCORBIC ACID

REACTION RATE BETWEEN DYE AND ASCORBIC ACID. Figure 2 shows the rate of fading of the standard dye when it is mixed with solutions of ascorbic acid containing 1 to 10 micrograms per cc. Readings were also taken beyond 10 seconds for study of the reaction rate. In solutions containing less than 2 micrograms of ascorbic acid per cc., the reaction with the dye is almost instantaneous—i. e., complete in 5 seconds. Between 2 and 5 micrograms the reaction is incomplete at the end of 5 seconds but is complete at 10 seconds. For 6 micrograms fully 15 seconds are required for completion of the reaction, and concentrations from 7 to 8 micrograms fail to react completely within the 30-second observation period. Thus a concentration of ascorbic acid of 8 micrograms per cc., theoretically capable of completely reducing the dye, fails to do so after 30 seconds. Only when an excess of the vitamin is present, at least 9 micrograms per cc., is complete reduction of the dye observed during this period.

In the absence of the vitamin, the fading rate of the dye at pH 3.5 is approximately one tenth of a "per cent transmission unit" per 5 seconds. Accordingly, the reaction with the vitamin is considered complete when the rate of fading is equal to or less than this. In that case the extent of decolorization of the dye is observed to be proportional to the concentration of ascorbic acid in the extract (from 0 to 6 micrograms per cc. during the 30-second period).

In the equation

$$A = CD$$

where A is the concentration of ascorbic acid in the buffered extract, and D is the decrease in photometric density of the dye at the completion of the reaction, C is found to be 19.9 micrograms per cc. per unit of photometric density. Thus from a measurement of the decrease in the photometric density at any given instant, it is possible to calculate the extent of reaction at that time.

The reaction rate constant, k, for a second order reaction may be expressed by the equation

$$k = \frac{1}{(A - B)t} \log_{10} \frac{[B(A - X)]}{[A(B - X)]}$$

where A is the initial concentration of ascorbic acid in the reaction solution, B is the initial dye concentration also in the reaction solution, and X is the total decrease in concentration of each of the reacting components at any instant. From the data used in plotting Figure 2, the value of k may be calculated for each of the concentrations tested. Expressing the concentration of the dye, B, in terms of its ascorbic acid equivalent in micrograms per cc., A and X also in micrograms per cc., and t in seconds, the value for k is found to be 0.099 ± 0.015 at 25° C. and pH 3.5. This constant is confirmed by measurements with dye solutions of one third, one half, and twice the concentrations of the standard dye. (Because of the nature of the data the reaction constant is subject to much greater error than the ascorbic acid concentration calculated from the same data. The average deviation of the value for k was ±10 per cent, and k may be in error by 15 per cent; this value, however, is considered uniform for a reaction rate constant of the type measured here.)

The results of the study plotted in Figure 2 and supported by the reaction constant calculated therefrom constitute good evidence that the reaction between ascorbic acid and the dye is not instantaneous as has been claimed (*7*), and that the observed drift in galvanometer readings is due to incomplete reaction at the time of recording.

To avoid the complications arising from the fact that the reaction between dye and ascorbic acid is not instantaneous, two procedures were adopted by previous investigators for the measurement of the vitamin in biological extracts. One technique (*2*, *15*) involves taking readings at 15 and 30 seconds, neglecting the course of the reaction up to the first 15-second reading. However, results presented below indicate that many nonspecific reducing substances react to a considerable extent in 15 seconds, so that extrapolation of the 15- and 30-second readings obtained with extracts containing such substances yields erroneously high "ascorbic acid" values. A second alternative has been to take readings every 5 seconds (*3*) and to correct for the nonspecific reductants by extrapolation of the curve to zero time. This is a highly questionable procedure, for theoretically all curves should extrapolate to zero concentration of ascorbic acid at zero time because the reaction is not instantaneous.

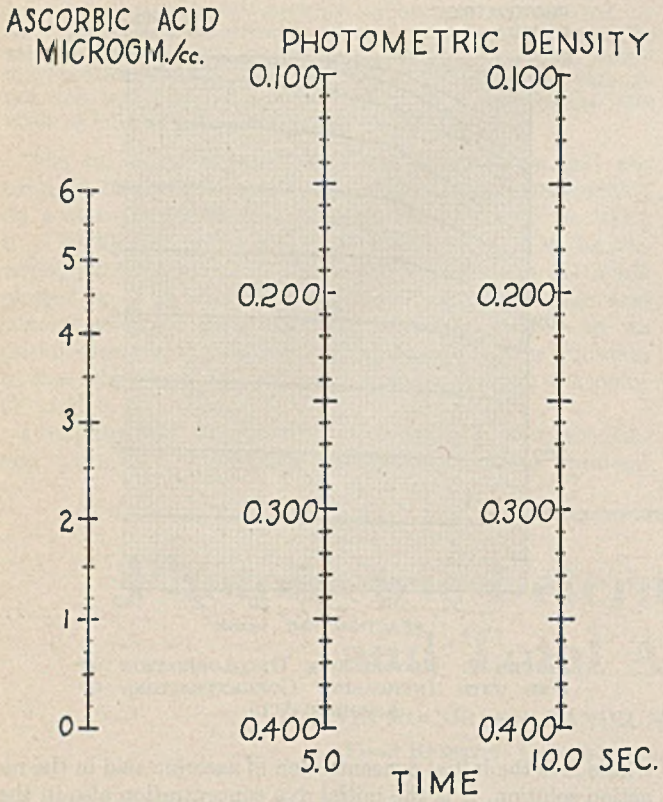

FIGURE 3. NOMOGRAM FOR ESTIMATION OF ASCORBIC ACID CONCENTRATION OF EXTRACT

Photometric density of blank is subtracted from those of test solution at 5 and 10 seconds. Straight-line extrapolation of corrected photometric densities gives vitamin concentration.

CALCULATION OF RESULTS. Anomogram (Figure 3) has been constructed to facilitate the estimation of the concentration of ascorbic acid in an extract. From the photometric densities of the test solutions at 5 and 10 seconds is subtracted that of the blank, and a straight-line extrapolation of the corrected photometric densities gives the vitamin concentration.

The nomogram was calibrated using the 0-, 5-, and 10-second values in Figure 2. This nomogram is merely illustrative and is not intended to be universally applicable. Each analyst should construct such a nomogram from data obtained in his own laboratory.

The extrapolation assumes that when two or more reducing substances are present their reaction curves (the residual photometric density of the dye plotted against time) are additive. If other reducing substances are present which react bimolecularly with the dye, as ascorbic acid does, the rate of disappearance of the dye is given by

$$\frac{-d\,[Dye]}{dt} = \sum K_i\,[R_i]\,[Dye]$$

where $[Dye]$ is the concentration of the dye at any instant, $[R_i]$ is the concentration of each reducing substance, and K_i is its bimolecular reaction constant. The rate of reaction in a complex mixture is thus a function of the concentrations of both the reducing substances and the dye. If a very large excess of dye were present, the reaction rate of each constituent in the mixture would be unaffected by the reaction of the other constituents; but with only a small excess of dye, the reaction of each reducing agent decreases the dye concentration sufficiently to affect significantly the reaction rates of the other constituents. Actual tests have been conducted on mixtures of ascorbic acid and other reducing substances, using the procedure described in this report and reported more fully below. These indicate that the negative error in the calculated ascorbic acid values arising from this cause is of the order of only a few per cent and is usually masked by the small positive error due to these interfering substances.

Comparison of Photometric and Titrimetric Determinations

The photometric method described above was compared with visual titration of 8 per cent acetic plus 2.5 per cent metaphosphoric acid (*8*) extracts of biological materials. The results are given in Table I. Agreement between the two methods is excellent for fresh orange juice, fresh tomato juice, and a pharmaceutical vitamin tablet. These products contain no appreciable amounts of nonspecific indophenol-reducing substances. For the other samples, however, the results differ considerably. Large discrepancies in the ascorbic acid values of the dehydrated products are noted. The vitamin capsule was manufactured 6 months before analysis and at the time of manufacture contained 35 mg. of ascorbic acid and 15 mg. of iron as ferrous sulfate. The results obtained with the capsule and the control solutions do not support the finding of Harris and Olliver (*7*) of no reduction of the dye by ferrous ion. In the photometric method extrapolation of the 5- and 10-second values reduces the interference of ferrous ion to one tenth of that evident in the visual titration. Woessner, Elvehjem, and Schuette (*21*) state "the ferrous ion reacts instantaneously with indophenol". However, in that study readings were taken only at 15 and 30 seconds. From the reaction curves for ferrous sulfate in Figure 4, it is apparent that a similar conclusion might be drawn from the authors' data if the 5- and 10-second readings were omitted. Ferrous

TABLE I. COMPARISON OF REDUCED ASCORBIC ACID VALUES AS DETERMINED PHOTOMETRICALLY AND TITRIMETRICALLY[a]

Material	Photometric	Titrimetric[b]
	Mg.	*Mg.*
Fresh orange juice, per 100 grams	49	48
Fresh tomato juice, per 100 grams	17	17
Vitamin tablet, per tablet	17	18
Canned tomato soup, per 100 grams (after 1 + 1 dilution)	2.0	3.5
Experimental dehydrated tomato soup, per 100 grams		
Fresh sample	26	30
After storage[c]		
No. 1	9	24
No. 2	7	24
No. 3	10	23
No. 4	8	22
Vitamin capsule containing $FeSO_4$, per capsule	21	45
$FeSO_4$ solution (10 mg. as Fe^{++}), per sample	1.5	15[d]
Ascorbic acid:$FeSO_4$ solution (10 mg.:10 mg. as Fe^{++}), per sample	11	24.5

[a] Using 2,6-dichlorophenolindophenol dye.
[b] Solvent = 8 per cent acetic acid, 2.5 per cent metaphosphoric acid.
[c] One week at 37° C. at 90 per cent humidity.
[d] This figure was also obtained using 5 per cent metaphosphoric acid as solvent.

TABLE II. REDUCED ASCORBIC ACID IN EXPERIMENTAL DEHYDRATED TOMATO SOUPS BY PHOTOMETRIC METHOD[a]

Sample	Initial Test	Incubated 1 Week, 37° C., 90% Humidity	Incubated 2 Weeks, 37° C., 90% Humidity
	Mg. per 100 grams		
1	26.2	8.7	1.2
2	28.4	7.1	2.1
3	21.3	9.8	0.3
4	27.2	7.7	1.2

[a] These samples had been judged by visual titration to be stable during the periods of storage, the ascorbic acid values approximating 30 mg. per 100 grams. However, organoleptic and colorimetric tests supported the conclusions drawn from the photometric values. Discrepancies in the figures obtained by the two assay procedures were not so great when the tests were conducted on subsequent products of improved stability in vitamin content and palatability.

iron is oxidized by atmospheric oxygen much more readily than ascorbic acid in the dilute solution used for photometric measurement. Therefore, in order to demonstrate the interference of ferrous iron, it is essential to exclude air from all solutions.

Visual titration with 2,6-dichlorophenolindophenol is frequently used to follow the fate of ascorbic acid in foods during processing and storage. The assumption is made that the concentration of interfering reducing substances is small, and is constant in the consecutive analyses. In the early stages of the development of a dehydrated tomato soup, visual titrations were used for control purposes for estimating reduced ascorbic acid. The results indicated the vitamin to be stable during the holding tests. When the photometric method was employed, very rapid destruction of the vitamin was observed. Typical values are listed in Table II. Apparently, other dye-reducing substances were formed during the storage period, and these were estimated as ascorbic acid by the titrimetric method. The same conclusion was reached in studies conducted by others (*12A*, *19A*) on dehydrated potatoes.

Importance of Including Dehydroascorbic Acid in Determining Vitamin C Content

Total ascorbic acid of the dehydrated soups was also determined by the photometric method. The results in Table III indicate that failure to determine dehydroascorbic acid causes the apparent loss of the vitamin to be much greater than that which actually occurred. The reaction curves for these samples have been plotted in Figure 5, after calculations to eliminate the effects of the ascorbic acid present. This allows graphic presentation of the progressive formation of other dye-reducing substances on storage. These compounds react slowly with the dye to give falsely high visual titrations. This interference is even greater after the hydrogen sulfide treatment.

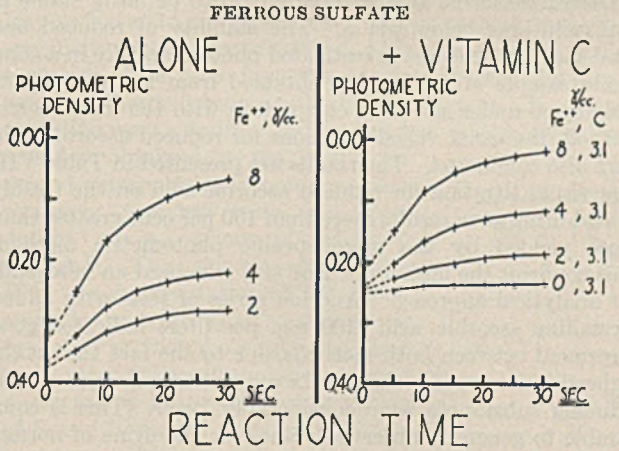

FIGURE 4. REACTION RATE CURVES FOR DYE AND FERROUS ION

With and without added ascorbic acid. Initial photometric density of dye is 0.398.

In Table III ascorbic acid analyses of a number of other foods by the photometric method are also presented. In the canned grapefruit juice, canned pineapple juice, and vitamin tablet, very little dehydroascorbic acid was found. The same was true of the tomato juice and orange juice when fresh, but after processing, appreciable amounts of the oxidized form of the vitamin appeared. After 2 weeks' storage at 37° C., 85 per cent of the ascorbic acid in the two dehydrated tomato soups and 26 per cent of that in the concentrated orange juice were in the biologically active, oxidized form.

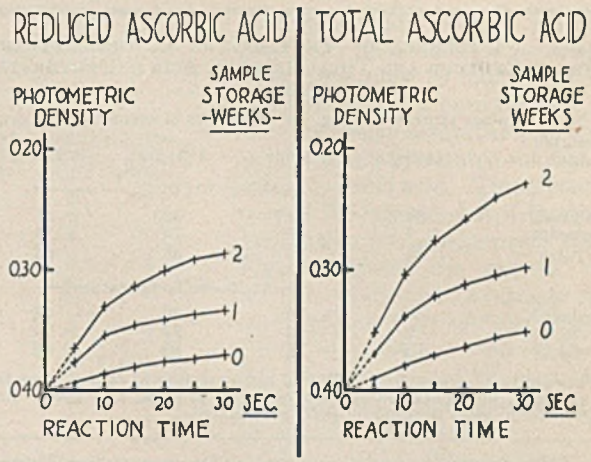

FIGURE 5. DEVELOPMENT OF DYE-REDUCING SUBSTANCES IN DEHYDRATED TOMATO SOUP DURING HOLDING TESTS

Initial photometric density of dye is 0.398.

Factors Operating to Convert Reduced to Dehydroascorbic Acid

Dehydroascorbic acid may be present in foods at the time of analysis, as shown in Table III, or it may arise in the course of analysis from oxidation of reduced ascorbic acid. A fundamental precaution in the analysis, if a reliable value for reduced ascorbic acid is to be obtained, is the prevention of atmospheric oxidation which is accelerated by oxidases and copper, especially with increasing temperature. Preparations of composite samples and of extracts are sometimes lengthy procedures, so that considerable oxidation of reduced ascorbic acid may occur if precautions are not taken.

In the analysis of a composite of a daily diet, the constituents were mixed with solid carbon dioxide, and the mixture was ground several times to produce a homogeneous semisolid mass. The manipulations required 2 hours, but at all times the temperature was maintained at less than 0° C. Photometric analysis for

TABLE III. REDUCED, DEHYDRO, AND TOTAL ASCORBIC ACID IN BIOLOGICAL MATERIALS DETERMINED BY THE PHOTOMETRIC METHOD

Material	Ascorbic Acid Reduced	Dehydro	Total
	Mg.	*Mg.*	*Mg.*
Canned grapefruit juice, per 100 cc.	40	1	41
Canned pineapple juice, per 100 cc.	35	0	35
Vitamin tablet, per tablet	17	1	18
Fresh tomato juice, per 100 grams	17	1	18
Fresh orange juice, per 100 grams	49	0	48
Raw, fresh string beans, per 100 grams	17	6	23
Orange sirup 2, per 100 grams	30	4	34
Stored 2 weeks, 42° C., per 100 grams	23	8	31
Experimental dehydrated tomato[a], per 100 grams	02	11	73
Experimental dehydrated tomato soup[b] (No. 1), per 100 grams	26	6	32
Stored 1 week, 37° C.	9	6	15
Stored 2 weeks, 37° C.	1	6	7
Experimental dehydrated, tomato soup[b] (No. 2), per 100 grams	27	5	32
Stored 1 week, 37° C.	8	6	14
Stored 2 weeks, 37° C.	1	6	7
Dehydrated potato, per 100 grams	0	0	0
Dehydrated banana, per 100 grams	2.5	0.8	3.3
Potato chips[c], per 100 grams	11	5	16
Pasteurized milk, per quart	0	3.6	3.6
Evaporated milk, per quart	0	0	0
Milk powder, per 100 grams	2.3	0	2.1
Composite diet, freshly prepared at less than 0° C. under CO_2, per 2710 calories	0	115	115

[a] Represents 12-fold concentration of tomato solids.
[b] Represents 5-fold concentration of tomato solids.
[c] In preparation of potato chips a 3.5-fold concentration of solids occurred. Thus, actual loss of ascorbic acid in making this product is calculated to be approximately 80 per cent.

TABLE IV. INFLUENCE OF TEMPERATURE IN THE DETERMINATION OF REDUCED AND TOTAL ASCORBIC ACID IN DEHYDRATED TOMATOES[a]

(Values expressed in mg. per 100 grams of sample)

Ascorbic Acid	Initial	1 Hour	3 Hours	5 Hours
		At 0° C.		
Reduced	54	54	52	51
Dehydro	9	9	13	14
Total	63	63	65	65
		At Room Temperature		
Reduced	54	46	40	38
Dehydro	9	12	22	24
Total	63	58	62	62

[a] This product, representing a 12-fold concentration of tomato, was free from enzymes, but contained approximately 50 p. p. m. of copper. Acid extracts were allowed to stand for periods indicated.

TABLE V. INFLUENCE OF ATMOSPHERIC OXYGEN IN THE DETERMINATION OF REDUCED AND TOTAL ASCORBIC ACID IN DEHYDRATED TOMATO SOUPS

Sample No.	Experiment	Ascorbic Acid Reduced	Dehydro	Total
		Mg. per 100 grams		
A-1	Extracting buffer saturated with air; analysis under air	27	16	43
A-2	Extracting buffer saturated with nitrogen; analysis under air	32	12	44
A-3[a]	Extracting buffer saturated with nitrogen; analysis under nitrogen	36	7	43
B-1	Same as A-1	23	11	34
B-2	Same as A-2	27	8	35
B-3[a]	Same as A-3	31	3	34

[a] Tests involving addition of 3 mg. of ascorbic acid to 10 grams of these samples gave recovery values of 92 and 98 per cent, respectively, as reduced ascorbic acid.

reduced ascorbic acid showed none to be present. However, after the hydrogen sulfide treatment, 115 mg. of total ascorbic acid were found. Calculation of the ascorbic acid content from published data on the component foods indicated this finding to approximate the expected value. The ascorbic acid was supplied mainly by fresh, uncooked fruits and vegetables; these included 150 cc. of orange and 75 cc. of tomato juice. From the nature of the foods in the diet, it was obvious that the dehydro was formed from reduced ascorbic acid (through the action of ascorbic acid oxidases) in the course of preparing the sample, despite the presence of carbon dioxide and maintenance of the low temperature. The dehydroascorbic acid apparently was stable under these conditions.

In an accurate measurement of reduced ascorbic acid, it is desirable to complete the analysis as soon as possible after extraction is effected. If delay is unavoidable, especially when a large series of analyses is being conducted, immersion of the samples in an ice bath inhibits oxidative changes. In Table IV values are given for reduced and total ascorbic acid in an acid extract (buffered at pH 3.5) of dehydrated tomatoes which was allowed to stand in air at room temperature and at 0° C. for various periods. Progressive decrease of reduced ascorbic acid was observed in the extract at room temperature with little change at 0° C. However, the values for total ascorbic acid were not affected by the preliminary oxidation. (These measurements were made immediately after removal of the excess hydrogen sulfide by nitrogen aeration.) The material analyzed was free from enzymes but contained an appreciable amount of copper (*13*).

The influence of atmospheric oxygen upon the oxidation of reduced ascorbic acid at room temperature is shown in Table V. In the first solution the extracting buffer was saturated with air and the analysis conducted in air. In the second the extracting buffer was saturated with nitrogen and the analysis conducted again in air; and in the third the extracting buffer was saturated with nitrogen and the analysis conducted under nitrogen. A progressive increase in reduced ascorbic acid was noted with the elimination of oxygen from the atmosphere. It is significant that here again the figures for total ascorbic acid were not affected by the partial oxidation.

In the analysis for reduced ascorbic acid in cooked and uncooked vegetables, the figures for the cooked products are frequently higher than those for the uncooked. This has been attributed by some (*17*) to the presence of bound ascorbic acid, which is released on cooking. Others (*12*) have ascribed the observation to the presence of active enzymes in the raw samples, which are inactivated during cooking. In Table VI are presented the results of some analyses on string beans, a product rich in ascorbic acid oxidase. Sample 1 was prepared in a Waring Blendor by a 1-minute, high-speed maceration of the raw beans with water under carbon dioxide. Sample 2 was homogenized with 6 per cent metaphosphoric acid instead of water. Sample 3 was blanched for 5 minutes in boiling water, cooled, and then macerated in the cooking water. The results of this study, summarized in Table VI, emphasize the precautions which must be observed to prevent enzymic oxidation of the ascorbic acid. The thermal inactivation of the enzymes by boiling in 6 per cent metaphosphoric acid appears to be the preferred method. Use of 5 per cent sulfuric–2 per cent metaphosphoric acid as the extracting solvent (*14*), with no preliminary blanching of the beans, yielded essentially the same results for the reduced and dehydroascorbic acid content. Extraction with the stronger acid is not so desirable, since subsequent pH adjustment cannot be made so readily as in the procedure recommended in the present report. It is significant that the figures for total ascorbic acid in all samples were the same. These observations support Harris and Olliver's criticism (*7*) of the bound ascorbic acid theory (*17*), since the total ascorbic acid content of the unblanched beans is not increased on cooking. The enzymic oxidation taking place in the uncooked product accounts for an apparent increase in "ascorbic acid" after cooking when reduced ascorbic acid alone is measured.

Applicability of Photometric Method to Urine Analysis

Dehydroascorbic acid is reported (*1*) to be fairly stable in pure solutions below pH 5. The stability of reduced and total ascorbic acid was investigated photometrically in a composite sample of fresh urine obtained from twelve subjects and stored under air. For comparison with the photometric method, the usual visual titrations for reduced ascorbic acid were also conducted. The results are presented in Table VII. The visual titration for reduced ascorbic acid on the freshly voided urine gave results more than 100 per cent greater than those yielded by the more specific photometric method. This confirms the findings of Roe (*19*) who used an independent analytical approach. Another series of tests with added crystalline ascorbic acid (100 mg. per liter) indicated good agreement between both methods, due to the fact that at the higher dilutions used in the test the concentrations of nonspecific reducing substances were considerably lower. (This is comparable to generally observed values for the urine of normal subjects following oral administration of a 300-mg. test dose.)

TABLE VI. INFLUENCE OF ASCORBIC ACID OXIDASE IN THE DETERMINATION OF REDUCED AND TOTAL ASCORBIC ACID IN RAW STRING BEANS

(Values expressed in mg. per 100 grams of beans)

Sample No.	Preparation of Sample[a]	Ascorbic Acid Reduced	Dehydro	Tota
1	Raw, macerated with equal weight of H_2O	4	19	23
2	Raw, macerated with equal weight of 6% HPO_3 solution	14	9	23
3	Boiled with H_2O 5 minutes, then macerated	16	7	23
4	Boiled with 6% HPO_3 solution 5 minutes, then macerated	17	6	23

[a] All manipulations were carried out under an atmosphere of carbon dioxide.

Table VII. Stability of Ascorbic Acid and Other Dye-Reducing Substances in Urine

(Values expressed in mg. per liter)

Preservative per Liter	Form	Ascorbic Acid before and after Storage: Initial Photometric	Initial Titrimetric	After 24 Hours Photometric	After 24 Hours Titrimetric	After 48 Hours[b] Photometric	After 48 Hours[b] Titrimetric	After 120 Hours Photometric	After 120 Hours Titrimetric
None	Reduced	8	19[a]	3	13	0	4	0	0
	Dehydro	9	..	3	..	1	..	4	..
	Total	17	..	0	..	1	..	4	..
30 cc. of 3.5 *N* H_2SO_4	Reduced	11	23	9	19	3	13	0	6
	Dehydro	5	..	4	..	4	..	6	..
	Total	16	..	13	..	7	..	6	..
10 grams of HPO_3	Reduced	8	20	4	13	2	13	0	6
	Dehydro	10	..	4	..	3	..	0	..
	Total	18	..	8	..	5	..	0	..
10 grams of HPO_3 and storage at 5° C.	Reduced	9	20	8	23	1	14	1	12
	Dehydro	9	..	8	..	11	..	9	..
	Total	18	..	16	..	12	..	10	..

[a] Comparisons should be made between only reduced ascorbic acid values in evaluating degree of nonspecificity of titrimetric method. Total ascorbic acid values, obtained by titrimetric method, are greater, but such analyses of urine are practically never made.

[b] Ascorbic acid values obtained after this period of storage lack precision because of lowered concentration of vitamin in presence of large amounts of interfering reducing substances in urine. This is particularly true of dehydroascorbic acid figures which are obtained by difference.

The ascorbic acid in the samples containing the larger quantities appeared to be appreciably more stable. This is in agreement with frequent observations (*4*) that the oxidative destruction of ascorbic acid is more nearly absolute than proportional to the concentration of the vitamin. Storage of the urine sample at 5° C. with added metaphosphoric acid was the most effective means for preservation. A consideration of the data compiled indicates that the nonspecific reducing substances in urine are also unstable but not to the same extent as ascorbic acid.

Extrapolation of Photometric Densities at Five and Ten Seconds

Linear extrapolation of the photometric density at 5 and 10 seconds gives ascorbic acid values considerably lower than extrapolation at 15 and 30 seconds. This may arise from greater specificity of the former method, or from a possible early retardation of the rate of reaction between the dye and ascorbic acid by other substances in biological extracts. If such a retardation were a reality, low recoveries of added ascorbic acid would be obtained by the 5- and 10-second extrapolation procedure. Accordingly, recovery tests were conducted on a variety of biological materials. The values shown in Table VIII are representative of the differences in ascorbic acid values to be expected in the photometric method using the two extrapolation procedures, and indicate that extrapolation of 5- and 10-second readings furnishes a more specific index of ascorbic acid content.

Compounds Interfering with the Photometric Method

The use of hydrogen sulfide for the determination of dehydroascorbic acid has been criticized (*6, 9, 10, 11, 14*). It has been asserted (*8, 14*) that nitrogen aeration fails to remove the last traces of hydrogen sulfide, which in turn could be responsible in part for increased "ascorbic acid" figures. Under the conditions of test described here, there is insufficient residual hydrogen sulfide to cause any photometrically measurable dye reduction even after only 20 minutes of nitrogen aeration of a pure buffered solution previously saturated with the gas, or of a similarly treated solution with added ascorbic acid. This is confirmatory of the experiments of Hamburger and Joslyn (*6*). Reference is made to Figure 6 giving the reaction curves for two solutions of hydrogen sulfide (not subjected to nitrogen aeration) which were able to decolorize the dye. By using the 5- and 10-second extrapolation this interference is reduced by more than 70 per cent.

It has further been suggested (*6, 9, 10, 14*) that the hydrogen sulfide is loosely combined in biological extracts or is responsible for the formation of nonvitamin dye-reducing substances. However, alleged interferences from these causes were based for the most part upon titration values without extrapolation to zero time.

In the present study tests were conducted with three of the compounds which have been reported (*20*) to react with hydrogen sulfide to yield indophenol-reducing substances. The reaction curves for these are also plotted in Figure 6. In these graphs, the "ascorbic acid" concentration is 0.0 microgram per cc. at a photometric density of 0.398, and 4.0 at a photometric density of 0.200. The solid curves represent reaction curves after hydrogen sulfide treatment (with subsequent removal of the gas). The values at 5 and 10 seconds are extrapolated to zero time by means of a straight line as on the nomogram. (The dotted curves obtained prior to hydrogen sulfide reduction indicate that these compounds cause no decolorization of the dye.) The results show that except for 2-methyl-1,4-naphthoquinone, the interferences following the hydrogen sulfide treatment are much greater in the visual titration (single value at the 15-second or 30-second point) than in the photometric method. In fact, pyruvic acid shows no interference, for its curve extrapolates linearly to a photo-

Table VIII. Justification for Extrapolation of Photometric Densities at 5 and 10 Seconds in Preference to 15 and 30 Seconds

Test Material	Ascorbic Acid from Extrapolation of Photometric Densities at 5 and 10 seconds (*a*)	Ascorbic Acid from Extrapolation of Photometric Densities at 15 and 30 seconds (*b*)	Value[a] for $\frac{(b)-(a)}{(a)} \times 100$	Recovery of Added[b] Ascorbic Acid from Extrapolated Photometric Densities at 5 and 10 Seconds
	Micrograms per cc. of extract			%
Dehydrated tomato soup A-3	2.93	3.80	30	104
Dehydrated tomato soup B-3	2.34	2.81	20	93
Dehydrated banana	1.63	2.61	60	93
Dehydrated potato	0	0	...	96
Pasteurized milk	0.91	1.15	26	105
Evaporated milk	0	0	...	90
Milk powder	1.07	1.39	30	103
Urine, composite of 12 subjects	1.81	2.15	20	94
Ferrous sulfate, 5 micrograms of Fe^{++} per cc.	0.74	2.25	204	97[c]
Orange, fresh	4.18	4.18	0	No recovery tests
Tomato, fresh	5.62	5.94	6	conducted on
Urine	2.32	3.22	39	these samples
Urine during vitamin C saturation test	2.97	3.14	6	
Pineapple pie	0.60	1.83	205	
Pumpkin pie	0.59	1.49	153	

[a] Per cent difference in ascorbic acid values obtained by two methods of extrapolation.

[b] Except where indicated, amount of ascorbic acid added for recovery experiment was approximately equal to amount believed to be originally present as determined from data in literature, or by previous analysis of same or similar samples. For recovery test, vitamin was added to original material and carried through entire analysis.

[c] For recovery test on this sample, 3.05 micrograms of ascorbic acid were added to each 1.00 cc. of test solution.

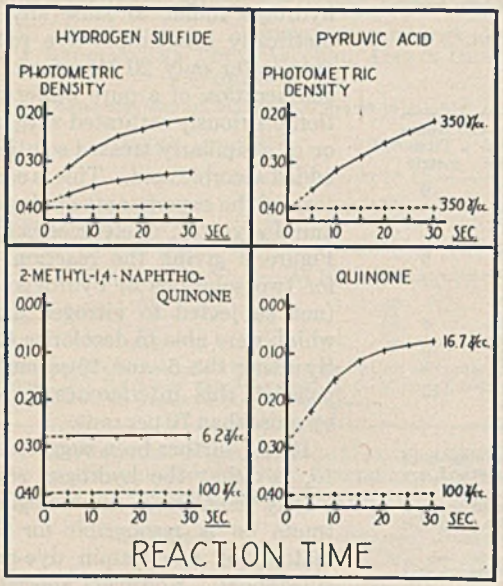

FIGURE 6. REACTION CURVES FOR SUBSTANCES ALLEGED TO INTERFERE IN DETERMINATION OF ASCORBIC ACID

Before (dotted lines) and after (solid lines) hydrogen sulfide treatment. Initial photometric density of dye is 0.398.

metric density of 0.398. For the others, the concentrations normally found in biological materials are not sufficient to interfere in the determination of total ascorbic acid. Thus, the objections to the use of the hydrogen sulfide reduction procedure in titrimetric or photometric methods previously published are minimized in the procedure described in the present report.

Discussion

In titrimetric methods in general, as the titration progresses the concentration of at least one of the reactants decreases. Thus, from kinetic theory the reaction rate must decrease. The behavior of the sulfhydryl compounds on dye titration reported by King (*11*) is entirely analogous to that noted in this laboratory with ferrous sulfate. Indeed, at the concentrations used in the photometric method, the reaction rate between ferrous sulfate and the dye becomes easily measurable (see Figure 4). As a consequence of this slower reaction, the interference of ferrous sulfate is reduced by 90 per cent in the photometric method (see Table I). Other interferences may be similarly minimized.

The results presented here impose serious limitations on the use of the visual titration. The method of "reversed titration" (*7*), titrating the dye with the extract, is inadvisable, for many of the interfering reducing substances added to the dye during the early part of the titration are given an ample period for reaction. The interference is thus much greater than in the normal titration where the dye is removed as it is added, chiefly by the more rapidly reacting ascorbic acid. The question of duration of the end point is controversial, for with a 5-second end point the ascorbic acid may not react completely, and with a 30-second end point, many interfering substances may react. In this laboratory, interfering reducing substances have been encountered in such a wide variety of samples that the photometric method has replaced visual titration. Only in the routine testing of pharmaceutical products shown by the photometric reaction curve to be free from interfering compounds is visual titration used.

The data presented in this paper on the occurrence of dehydroascorbic acid in biological materials and on the necessity for its determination are contrary to the conclusion of Harris and Olliver (*7*), who state, "The amount of vitamin C present in foodstuffs in the form of dehydroascorbic acid, even during aging and in stale foods, is generally so small as to be of little or no practical significance." However, their conclusion was based on analyses of a limited variety of foods by the "reversed titration" method, involving also an obviously faulty procedure for the conversion of reduced to dehydroascorbic acid, particularly with reference to pH adjustment (*14*).

Summary

Reduced and total ascorbic acid in biological materials have been determined by a modification of published photometric methods based on the rate of decolorization of the dye 2,6-dichlorophenolindophenol. A nomogram has been presented to facilitate the estimation of the ascorbic acid concentration from the residual photometric densities of the dye at the end of 5 and 10 seconds of reaction. The reduction of the dye by the vitamin was found to be a reaction of the second order; the rate constant was calculated for 25° C. and pH 3.5. The photometric procedure has a much greater degree of specificity than the visual titration, and allows determinations to be made on extracts containing small amounts of ascorbic acid, even in the presence of relatively large amounts of other substances which reduce the dye. Evidence has been obtained stressing the importance of determining dehydroascorbic acid, initially present in some materials and produced in others when proper analytical precautions are not taken. The photometric method is applicable to analyses of urine before and after the administration of test doses. Proof is presented of the greater specificity of the improved photometric method, as compared with the various titrimetric and photometric procedures.

Acknowledgment

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Determination of Ferrous Iron in Difficultly Soluble Materials

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THE determination of ferrous iron in materials containing both ferrous and ferric iron presents several difficulties when the material to be analyzed is difficultly soluble, as is the mineral chromite. Not only is it difficult to get the ore into solution, but the solvents oxidize the ferrous iron, usually without liberating another material which can be determined.

The method herein described indirectly determines ferrous iron by titrating the sulfur dioxide liberated when sulfuric acid oxidizes ferrous oxide.

Various methods have been proposed, but for one reason or another none has proved entirely satisfactory.

As early as 1860, Mitscherlich (*11*) determined ferrous oxide in chrome ore by decomposing the ore with medium strength sulfuric acid in a bomb tube at 250° to 290° C. The decomposition required about 8 hours, and precautions were taken to prevent oxidation by the air. Similar results were obtained by Jannasch and Vogtherrr (*8*), using hydrochloric acid–ammonium chloride solutions in a bomb tube. Not all chrome ores respond to this treatment, however.

Fusion with boric acid and treatment with a mixture of sulfur and hydrofluoric acid have also been tried (*7*). Decomposition with concentrated sulfuric acid has been found to be incomplete (*2, 15*), and treatment with acid sulfates such as potassium bisulfate oxidizes the chrome ore completely (*1, 6, 12*), as is the case also with Usatenko's phosphoric-sulfuric acid method (*18*). Treatment with oxidizing acids such as nitric acid is impracticable (*4, 10, 19*).

Alkaline fusions, using sodium carbonate or borax (*3, 5, 13, 14*), absorb oxygen from the air rapidly at the high fusion temperature required.

Schein (*16*) measures the increase in weight of the ferrous oxide on heating in oxygen, making allowance for the loss of water and carbon dioxide in the process. The unusually high calculating factor, 9, is an objection to this method. The author has determined the oxidizable materials in the ore by first finding the loss on ignition in an atmosphere of nitrogen and the subsequent gain when heated in oxygen. The results agree very closely with those obtained by the procedure described in this paper.

Methods recently proposed depend upon solution of the ore in phosphoric acid, the ferrous iron in the solution being then determined by titration with potassium permanganate. Konopicky and Caesar (*9*) dissolve 0.2 gram of powdered ore in 16 to 20 ml. of phosphoric acid of specific gravity 1.92 in a wide test tube. The test tube is heated on an air bath to 300° to 320° C. and carbon dioxide is passed through it during the reaction. The cooled solution is diluted with air-free water and titrated with permanganate to a gray color. In the author's experience this method gives results which are not only much too low but incapable of being duplicated. This is true because any sulfur trioxide present is reduced to sulfur dioxide which is lost, and at high temperatures phosphine may be lost. By this method duplicate results cannot be consistently obtained on magnetite of known ferrous oxide content.

Stevens (*17*) describes a method in which a 0.3-gram sample of ore is placed in a glass tube about 20 cm. long, 11 mm. in inside diameter, and 1 mm. in wall thickness. Five milliliters of 85 per cent phosphoric acid are added, the air in the tube is displaced by carbon dioxide, and the tube is sealed off by drawing it out in the form of a hook, at a point about twice the height of the phosphoric acid. The tube is then suspended about 1.25 cm. (0.5 inch) above the bottom of a metal crucible which is heated just strongly enough to keep the phosphoric acid gently boiling until the sample is dissolved. This may take anything up to 24 hours. After cooling, the tube is opened and the contents are washed into distilled water containing 10 ml. of sulfuric acid. This solution is then titrated with 0.05 *N* potassium permanganate to a gray color. (Incidentally, none of the authors mentioned seems to have made use of *o*-phenanthroline–ferrous sulfate complex as indicator in this titration.) This method has the same objectionable features as the Konopicky and Caesar method described above.

It has been found possible to obtain consistent results by this method, but they are again too low, and the correction to be applied, as determined by experiments with magnetite, is so large as to preclude use of the method for materials containing low percentages of ferrous oxide. Another disadvantage is the length of time required for a determination.

Stevens notes that the need for a correction factor is due to the reduction of some of the phosphoric acid and consequent oxidation of some of the ferrous oxide. The extent of this oxidation probably depends on the time of heating and on the amount of ferrous oxide present, and since these factors vary with different ores, a single correction factor cannot very well serve for all ores. Sulfur trioxide and other impurities in the phosphoric acid yield gaseous reducing reaction products which are partially lost. If the product of reduction is phosphorous acid, as assumed, the amount of the latter formed should be equivalent to the amount of ferrous oxide oxidized. Phosphorous acid, however, is not oxidized by permanganate solutions in the cold under these conditions, and thus cannot be determined by titration with permanganate.

In order to eliminate the large factor involved in the Stevens method, by estimating the phosphorous acid formed as well as the ferrous iron in solution, an iodometric method was tried. Theoretically, either ferrous or ferric iron may be determined iodometrically in a solution containing both, in accordance with the reversible equation

$$2Fe(OH)_2 + I_2 + 2H_2O \rightleftharpoons 2Fe(OH)_3 + 2HI$$

In strongly acid solution (hydrochloric acid) the reaction proceeds toward the left. In the presence of a small amount of sodium bicarbonate, which keeps the pH of the solution constant, the reaction proceeds toward the right, and should, therefore, constitute a method for the determination of ferrous iron. Tests were carried out using the methods, the phosphoric acid solution of the ore being neutralized by adding sodium hydroxide solution until nearly neutral and then adding solid sodium bicarbonate. An excess of standard iodine solution was then added, and the excess was titrated with sodium thiosulfate. The results obtained were still too low, and it was found that phosphoric acid could not be effectively neutralized with sodium bicarbonate.

Phosphorous acid decomposes on heating, phosphoric acid being formed and phosphine liberated in accordance with the equation

$$4H_3PO_3 = 3H_3PO_4 + PH_3$$

Assuming that acid solutions of phosphates behave in the same way, the reaction between ferrous oxide and phosphoric acid might take place in the following stages:

1. The ferrous oxide dissolves in the phosphoric acid, forming ferrous phosphate

$$3FeO + 2H_3PO_4 = Fe_3(PO_4)_2 + 3H_2O$$

2. The ferrous phosphate reacts with a further quantity of phosphoric acid, forming ferric phosphate, ferric phosphite, and phosphorous acid

$$8Fe_3(PO_4)_2 + 11H_3PO_4 = 15FePO_4 + 9FePO_3 + 3H_3PO_3 + 12H_2O$$

TABLE I. DETERMINATION OF FERROUS IRON

Weight Taken Mg.	Found by Operator A Mg.	Found by Operator B Mg.
Estimation of Fe in Iron Wire		
25	25.4	26.7
50	50.3	51.1
75	74.8	75.8
100	99.3	101.4
125	123.9	125.7
150	149.9	149.9
Estimation of FeO in Cuban Chromite		
200	8.4	9.0
300	8.6	9.0
400	8.8	8.9
500	8.8	8.9
600	8.7	8.9
Estimation of FeO in Magnetite		
200	25.6	26.4
400	25.9	26.4
600	25.6	26.4
800	25.7	26.0

	Weight Taken Mg.	Found by Operator A Mg.	Found by Operator B Mg.
Determination of FeO in Chromites			
Cuban	500	8.2	8.2
	500	8.9	9.0
Transvaal	500	16.9	16.7
	500	16.8	16.7
Low-grade Philippine	500	8.3	8.5
	500	8.3	8.5
High-grade Philippine	500	10.8	11.2
	500	10.8	11.3
Rhodesian	500	10.4	10.7
	500	10.5	10.8
Turkish	500	8.9	8.6
	500	9.0	8.6
Blanks, Determination of FeO in C. P. Fe_2O_3			
	500	0.0	0.0
	500	0.0	0.0
	500	0.0	0.0
	500	0.0	0.0

3. The ferric phosphite–phosphorous acid mixture decomposes under the influence of heat, giving ferric phosphate and phosphine

$$3FePO_3 + H_3PO_3 = 3FePO_4 + PH_3$$

These equations may be combined and the net result of the reactions expressed as

$$8FeO + 9H_3PO_4 = 8FePO_4 + PH_3 + 12H_2O$$

Phosphine is oxidized by potassium dichromate, giving phosphoric acid

$$PH_3 + 2O_2 = H_3PO_4$$

It was decided to attempt the determination of ferrous oxide on these lines. The sample was heated strongly with phosphoric acid in a stream of carbon dioxide, and the gaseous products of the reaction were passed into standard 0.1 *N* potassium dichromate solution. From the amount of dichromate reduced, the ferrous oxide was calculated, using the last two equations. Any unchanged ferrous phosphate was determined by titrating the phosphoric acid solution with potassium permanganate.

At the time these experiments were started no pure phosphoric acid was available and C. P. phosphoric acid of specific gravity 1.57 was used. With this acid, the method was found to give excellent results with Cuban chrome ore containing about 9 per cent of ferrous oxide, but with a magnetite of known ferrous oxide content low results were obtained (Table I). Moreover, in the case of chrome ore the amount of residual ferrous iron in the phosphoric acid solution was found to be so small that the permanganate titration could be omitted, but with magnetite this titration amounted to 4 ml. or more, using a 0.5-gram sample. When the experiments were repeated later, using pure phosphoric acid, no reduction of the dichromate took place, but titration of the phosphoric acid solutions with permanganate gave results averaging 22.3 per cent ferrous oxide with a magnetite of 26.3 per cent ferrous oxide content, and 7.2 per cent ferrous oxide with a chrome ore containing 9.2 per cent ferrous oxide.

The reduced dichromate solutions obtained when C. P. phosphoric acid was used were analyzed for phosphates, and showed a phosphate content equivalent to only 0.26 per cent of ferrous oxide calculated on the phosphine theory. This amount of phosphoric acid could easily have been carried over mechanically into the dichromate. Furthermore, when chrome ore or magnetite was heated with either pure or C. P. phosphoric acid in a stream of carbon dioxide, and the gaseous reaction products were passed into mercuric chloride solution, a slowly forming white precipitate of calomel was obtained which contained no phosphorus. There was no trace of the light brown chloride-phosphide precipitate which forms in large quantities in the mercuric chloride when a small quantity of phosphorous acid is heated strongly with phosphoric acid under similar conditions.

It was, therefore, concluded that the reduction of the dichromate when C. P. phosphoric acid was used was caused by a gaseous product formed by the reaction of the ferrous oxide with some impurity in the acid rather than with the acid itself. Analysis of the C. P. phosphoric acid showed that, among other impurities, sulfates were present in considerable quantity. At high temperatures and in the presence of phosphoric acid the reaction between ferrous oxide and sulfuric acid may be represented by the equations

$$FeO + H_2SO_4 = FeSO_4 + H_2O$$

$$2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + SO_2 + 2H_2O$$

or simply

$$2FeO + 4H_2SO_4 = Fe_2(SO_4)_3 + SO_2 + 4H_2O$$

The sulfur dioxide passes into the dichromate and is oxidized to sulfuric acid. The amount of dichromate reduced, for the same amount of ferrous oxide, is the same whether the gas formed is phosphine or sulfur dioxide. Chrome ore was dissolved in C. P. phosphoric acid and the gases were passed into neutral dichromate solution. The sulfate content of the reduced dichromate solution was estimated gravimetrically as barium sulfate, and calculated to ferrous oxide. The results obtained were all high, owing to a small amount of sulfur trioxide carried over, but were in proportion to the results calculated from the titration of the reduced dichromate.

It was thus proved that the reduction of the dichromate was due to sulfur dioxide formed by the reduction of sulfuric acid by ferrous oxide, and that this reaction was quantitative.

The amount of sulfate in the C. P. phosphoric acid used was insufficient to oxidize all the ferrous oxide in a 0.5-gram sample of magnetite and this probably accounts for the low results obtained. A mixture of 1 part of sulfuric acid and 4 parts of phosphoric acid was found to give excellent results with all ores, including magnetite, and the resultant solution contained no ferrous iron. This mixture was, therefore, used in all subsequent experiments.

Chromium may also be determined in the phosphoric acid solution. The chromium is oxidized with ammonium persulfate in the presence of a silver salt, and the resulting chromate determined by titration.

Apparatus and Procedure

Reducing agents, such as ferrous iron, carbides, and sulfides, react at high temperatures (350° C.) and under low pressures with sulfuric acid in phosphoric acid to form sulfur dioxide, which is distilled into an excess of 0.1 *N* potassium dichromate. The excess potassium dichromate is determined and the reducing agent is calculated.

Chemicals Required for Ferrous Oxide Determination. Phosphoric-sulfuric acid mixture, 4 parts of 85 per cent phosphoric acid to 1 part of concentrated sulfuric acid; potassium dichromate, 0.1 *N* containing 50 ml. of sulfuric acid per liter; sodium thiosulfate, 0.1 *N;* potassium iodide, 40 per cent solution; and starch solution.

Apparatus. The apparatus used is shown in Figure 1. The sample and acid are contained in the 200-ml. round-bottomed reaction flask, *A*. A round-bottomed flask is necessary not only because the system is under a partial vacuum during the determination, but also because it is much more difficult to get chromium ores into solution in a flat-bottomed flask, the ore collecting around the bottom edge of the flask.

The reaction flask rests on the electrically heated air bath, *B*. The heating element is covered by an iron plate, and the heater supports an iron ring, which in turn supports a cover made of thick asbestos board. The cover has two holes for each flask, one of which is actually above the air bath, whereas the other is used to hold the flask while it is cooling after the reaction. The holes are tapered to fit the flask, and, using a 200-ml. flask and a a 1000-watt heater, should be 6.56 cm. (2.625 inches) in diameter at the bottom. The iron ring is made of such depth that there will be 2.5 cm. (1 inch) of space between the iron plate covering the heating element and the cover of the air bath. The temperature of the bath is controlled by a rheostat and ammeter, and is measured by a thermometer passing through a hole in the cover and suspended from a stout wire bent as shown.

The stopper of the reaction flask carries two tubes, one of which is connected with a supply of carbon dioxide contained in the large aspirator bottle, *C*. Prior to the determination the aspirator is completely filled with air-free water, which is then displaced by carbon dioxide from bottle *C*, and forced over into the other large bottle, *D*. Carbon dioxide of the highest purity should be used and it is recommended that the carbon dioxide be generated by adding cold freshly boiled dilute sulfuric acid to a strong solution of sodium bicarbonate which has been previously boiled and cooled. Cylinder carbon dioxide of the highest purity may be used, but it is not recommended because of the wide variation in the purity of different cylinders of gas. During the determination a slow stream of carbon dioxide is drawn from *C* by way of tube *E* through the whole apparatus. (Two tubes *E* are shown in the diagram, but only one is necessary.) *E* contains water and is of help in adjusting the rate of flow of the carbon dioxide.

The other tube leading from the reaction flask is connected with the absorption tubes, *F* and *G*, which contain the standard dichromate solution. These tubes are immersed in a vessel through which passes a stream of water for cooling purposes. The gaseous products of the reaction, together with carbon dioxide, bubble through the dichromate, which absorbs any reducing agent. Trap *H* is inserted as a precaution against the loss of dichromate by splashing, which may occur if too rapid a stream of carbon dioxide is passed.

The whole system is under a vacuum of some 680 mm. of mercury throughout the determination, and any possibility of the entry of air is precluded by the insertion of the Bunsen valve, *J*, in the line.

If the equipment is available, the rubber-stoppered reaction flask can be replaced by one having a ground-glass stopper with glass inlet and outlet tubes, and glass stopcocks can be used wherever metal pinchcocks are indicated in the drawing. The Bunsen valve can likewise be replaced by a glass float valve. Precautions, however, must be taken to avoid sticking of the ground-glass joints.

Preparation of Sample. Since all reducing agents, such as metallics, carbides, sulfides, etc., react with phosphoric acid, the preparation of the sample is important. Many chromites, after heat-treating, are magnetic and, therefore, removal of iron by a magnet is precluded.

The sample is crushed carefully in hardened steel, then ground in a porcelain ball mill with nonmetallic balls until all passes 100 B. S. mesh. A 10-gram sample is ground to pass through a 325-mesh Bureau of Standards screen in an agate or mullite mortar. Fine grinding is essential because of the time of solution.

Procedure. Twenty-five milliliters of the phosphoric-sulfuric acid mixture are placed in flask *A*, and 0.5 gram of the 325-mesh ore is introduced on top of the acid. When the sample has become wetted, the liquid is swirled in the flask until all small lumps have been broken up. Fifteen milliliters of 0.1 *N* potassium dichromate are placed in absorption tube *F* and 5 ml. in *G*, diluted with 10 ml. of water. Clamp *K* and stopcock *L* are then closed, and the apparatus is connected as shown in the diagram, *A*, resting in the cooling hole of the air bath for the time being. The vacuum pump is then started and *L* opened slowly, care being taken to avoid excessive splashing in the absorption tubes as the evacuation of the apparatus proceeds. When the stopcock is fully open and bubbling in the tubes has ceased, *K* is opened carefully and carbon dioxide is allowed to pass at the rate of about one bubble per second, as observed in *E*. *A* is then placed in the hole over the air bath, and is held in position by inverted U-shaped wire supports which stand in holes drilled

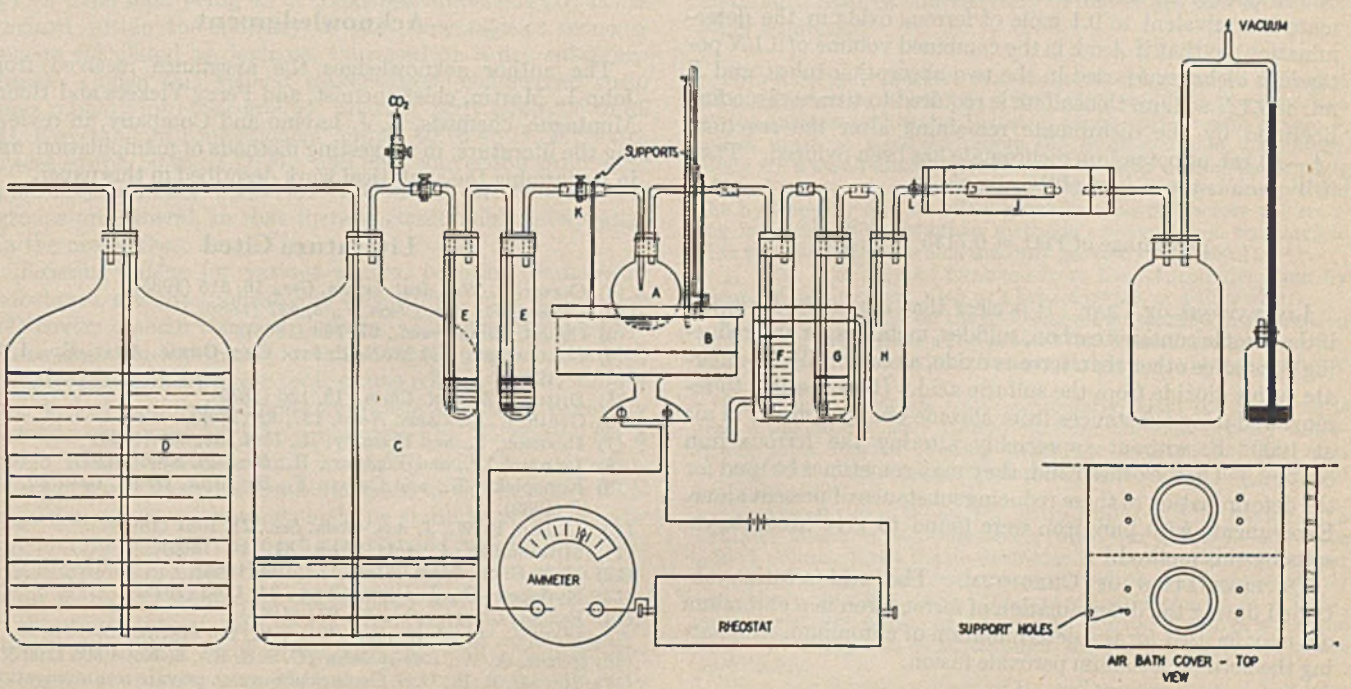

Figure 1. Apparatus for Determining Ferrous Iron

in the air bath cover. The bath is maintained at a temperature of 360° to 380° C.

Little or no solution of the ore takes place until all the water has evaporated from the acid mixture, after which the ore dissolves fairly rapidly. The time required for completion of the reaction varies from 35 to 90 minutes, depending on the ore. With some ores it is necessary to raise the temperature of the bath somewhat, but this should be avoided if possible, as the silica liberated from the glass of the flask coats the remaining particles of ore, rendering solution even more difficult. The reaction is complete at the point when bubbles cease to form in the acid mixture, but heating is continued for about 10 minutes after this point is reached.

The flask is then removed to the cooling hole of the air bath and the rate of flow of carbon dioxide is increased somewhat in order to avoid sucking back of the liquid in the absorption tubes and to ensure complete reaction between the sulfur dioxide and the potassium dichromate. After about 5 minutes L is closed and more carbon dioxide is admitted until the pressure has reached equilibrium throughout the system.

The absorption tubes are disconnected and the contents poured into a 500-ml. Erlenmeyer flask. The tubes and connections are carefully washed and the washings added to the main solution. Five milliliters of 1 to 1 sulfuric acid are added and the solution is diluted to about 250 ml. An excess of 0.05 N ferrous sulfate solution is added, using *o*-phenanthroline as an indicator. Not less than 10 ml. is added, and the excess is titrated, using 0.05 N potassium permanganate solution.

Alternate. Two milliliters of 40 per cent potassium iodide solution are added, and the liberated iodine is titrated against 0.1 N sodium thiosulfate to a green color having a faint yellow tinge. Starch solution is added and the titration completed, the end point being reached when the solution loses its blue color and becomes a pale apple green. This end point is sharp.

Since phosphoric acid varies considerably in impurities, it is necessary to determine the blank which must be deducted from each determination. The blank includes impurities in the acid and the amounts of standard solutions used to indicate the end point, and in no case should exceed 0.5 ml. If the solvent, consisting of 4 parts of phosphoric acid and 1 part of sulfuric acid, is fumed for 30 minutes at atmospheric pressure, the blank to be deducted from the determination approaches zero very closely. Boiling the solvent is considered good practice.

CALCULATION. The equation

$$2FeO + 4H_2SO_4 = Fe_2(SO_4)_3 + SO_2 + 4H_2O$$

shows that 2 moles of ferrous oxide liberate 1 mole of sulfur dioxide, which is equivalent to 0.5 mole of oxygen or 2 liters of 1 N potassium dichromate. Hence 1 liter of 0.1 N dichromate is equivalent to 0.1 mole of ferrous oxide in the determination, so that if A ml. is the combined volume of 0.1 N potassium dichromate used in the two absorption tubes, and B ml. of 0.1 N sodium thiosulfate is required to titrate the iodine liberated by the dichromate remaining after the reaction, $(A-B)$ ml. of potassium dichromate has been reduced. Then if W gram is the weight of the sample

$$\text{Percentage of FeO} = 0.7185 \times \frac{A - B}{W}$$

LIMITATIONS OF TEST. It is clear that the method will fail if the sample contains carbon, sulfides, metallics, or any reducing substance other than ferrous oxide, as these will also liberate sulfur dioxide from the sulfuric acid. (It is possible to remove reducing substances from chrome ore by ignition in air at 1000° F. without appreciably altering the ferrous iron content.) On the other hand, they may sometimes be used for the determination of these reducing substances if present alone. Experiments with pure iron were found to give accurate results by this method.

DETERMINATION OF CHROMIUM. The acid solution obtained during the determination of ferrous iron in a chromium ore may be used for the determination of chromium, eliminating the need for a sodium peroxide fusion.

Water is added to the flask while still hot. If the phosphoric acid solution is allowed to cool too much it becomes very thick and viscid, and is difficult to dissolve. The solution is washed into a 600-ml. beaker and diluted to 200 ml., 25 ml. of 1 to 1 sulfuric acid, 1 ml. of 1 per cent silver nitrate (catalyst), 50 ml. of 40 per cent ammonium persulfate, and at least 5 or 6 drops of strong potassium permanganate solution (2.5 per cent) are added, and the solution is boiled for 10 minutes. The presence of manganese is necessary to obtain complete oxidation of the chromium during this operation. The amount of manganese in most chrome ores is insufficient. Two milliliters of 1 to 1 hydrochloric acid are then added and the boiling is continued for a further 5 minutes, precipitating the silver and destroying any permanganate that may have been formed from manganese present in the ore.

The cooled solution is diluted to 350 ml. and 6 drops of *o*-phenanthroline indicator are added. Standard ferrous sulfate (approximately 0.2 N) is added from a buret, with stirring, until the liquid turns red, and then about 10 ml. more. The excess of ferrous sulfate is found by titration with 0.1 N potassium permanganate until the solution assumes a clear green color.

Alternate. The solution is cooled, 2 ml. of 40 per cent potassium iodide are added, and the iodine liberated is titrated against 0.1 N sodium thiosulfate. The thiosulfate titration is directly proportional to the chromium content of the ore.

The equation

$$2Cr_2O_3 + 3O_2 = 4CrO_3$$

shows that 12 liters of 1 N permanganate are equivalent to 304 grams of chromium trioxide, so that 1 ml. of 0.1 N potassium permanganate is equivalent to 0.002533 gram of chromium trioxide. If the amount of ferrous sulfate added is equivalent to A ml. of 0.1 N potassium permanganate and the final titration is B ml. of 0.1 N potassium permanganate, the chromium trioxide in the sample is equivalent to $(A - B)$ ml. of 0.1 N potassium permanganate. Hence, if the weight of the sample of chrome ore is W gram

$$\text{Percentage of } Cr_2O_3 = 0.2533 \times \frac{(A - B)}{W}$$

Summary

The method outlined is not perfect, but it gives the most accurate results of any method which has come to the author's attention. It is satisfactory for control. Boiling the solvent, 4 parts of phosphoric acid and 1 part of sulfuric acid, for 30 minutes decreases the blank to an exceedingly low value.

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Baumé–Dextrose Equivalent–Dry Substance Tables for Corn Sirup and Corn Sugar

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Tables covering the Baumé–dextrose equivalent–dry substance relationship for corn sirup and corn sugar sirup are presented. These are based on extensive research on a method (previously presented) for determination of dry substance. Dry substance for a given Baumé increases with increasing dextrose equivalent. Commercial Baumé is defined as Bé. = Bé. 140°/60° F.+1.00°. The tables have been accepted by the Corn Industries Research Foundation for use by its member companies, all refiners of the corn wet-milling industry.

APPROXIMATELY 1,500,000,000 pounds of corn sirup and 125,000,000 pounds of crude corn sugar are produced annually in the United States. The confectioners' industry is the largest consumer of corn sirup, although substantial quantities are used by the baking, canning, preserving, mixed table sirups, and ice cream industries. Crude sugars in either billet or chipped form—No. "70" and No. "80"—are used in the manufacture of rayon, leather, caramel color, and tobacco.

Corn sirup is the thick, viscous, substantially colorless sirup obtained from the incomplete hydrolysis of starch. It is sold on the basis of Baumé and dextrose equivalent and in the trade is often referred to as corn sirup unmixed or, more simply, C. S. U. The Baumé (commercial) will run from 42° to 47°, the bulk being 43°. Dextrose equivalent (D. E.) is defined within the industry as the percentage of reducing sugars calculated as dextrose, expressed on a dry substance basis. Under this general classification, commercial sirup falls roughly into four groups: brewers' body sirup, 25 to 35 D. E.; standard confectioners' sirups, 40 to 45 D. E.; extra sweet sirups, 50 to 57 D. E.; and dual conversion sirup (acid plus enzyme), 60 to 70 D. E. The names for the first three groups are general, in that there is considerable interchange in the use of these sirups.

Existing tables for various sugars, covering Baumé–dry substance, are not applicable to corn sirup. One publication (*7*) covers a small range of Baumés. Various references are to be found in the trade journals covering a specific Baumé, usually based on a private table of one refiner. The industry has lacked uniform Baumé–dry substance tables primarily for two reasons: (1) The amount of dry substance for a given Baumé increases with increasing dextrose equivalent, and (2) there was considerable dispute in the industry itself regarding moisture methods and the stability of the specific product on drying. Through an extended research program, the questions of methods and stability have been solved and these methods accepted by the industry and published (*3–8*).

Since commercial corn sirups are extremely viscous, it is difficult to obtain satisfactory readings with a Baumé hydrometer at ordinary temperatures. To eliminate this difficulty an arbitrary method was adopted years ago and is still in use. It consists of making the determination at 140° F. (60° C.) using a hydrometer standardized at 60° F., adding the arbitrary correction of 1.00° Baumé to the observed reading. The application of this correction approximately corrects to the reading at 100° F. The hydrometer used is that based on 145 modulus, 60° F. (the standard in the United States for liquids heavier than water). Thus commercial Baumé, the basis for sale, is designated as Baumé = Baumé 140°/60° F. + 1.00. The use of a hydrometer at 80° F. above the temperature of standardization requires special considerations which will be discussed in detail.

When the temperature of observation differs from that at which the hydrometer was standardized—i. e., the normal reading—the observed reading is not the true specific gravity according to the basis of the instrument, but a figure which differs from the normal reading by an amount depending upon the difference in temperature and the relative thermal expansion of the instrument and of the particular liquid. A table of temperature corrections of considerable precision may be determined, provided subsequent hydrometers are made with glass of the same thermal expansion and of the same physical dimensions as the primary standard. The Baumés in the following tables are based on readings made with the so-called "streamlined" type hydrometers, having a range of 10.00° Bé. graduated to 0.1° Bé. Hydrometers of such simple design have definite advantages when used at temperatures higher than that of standardization, particularly in viscous liquids.

Determination of Baumé

The procedure for determination of Baumé on corn sirup requires that the test be made at 140° F. This temperature materially reduces the viscosity of the sirup, but introduces other troubles.

EVAPORATION. Surface evaporation is the principal difficulty. At a temperature of 140° F., water is lost rapidly by evaporation at the surface. As water is lost, a tough surface skin develops, which must be removed before the hydrometer is introduced. Even so, a small amount of skin will develop during the reading of the hydrometer. This exerts a drag on the free movement of the hydrometer and its effect must be removed before the reading is made. Two common methods are employed to alleviate this trouble, both of which are only partially successful:

1. The skin may be removed from the hydrometer stem by means of a thin straw, such as a broom straw, or a thin wire.
2. The skin effect on the hydrometer is retarded or minimized by diluting the surface sirup around the stem of the hydrometer. A capillary tube is used to place small drops of water around the stem.

While these methods help, particularly when the meniscus is read from above, they cause striations through density differences, or a blurred reading when the hydrometers are read through the glass at plane surface level, as is required for more accurate work.

CONDENSATION. When the sirup under test is placed in a cylinder which is not completely filled (in order to allow for added volume when the hydrometer is immersed), water vapor condenses on the inner surfaces of the cylinder and subsequently runs down into the sirup. This produces a change in density, causing density striations which give blurred readings when the hydrometer scale is read through the glass cylinder at plane surface line.

TIME FOR SIRUP TO ATTAIN BATH TEMPERATURE. A correct Baumé reading is obtainable only after the temperature of the

sirup and hydrometer equals that of the bath—that is, 140° F. An error is often introduced by reading the Baumé before sufficient time has elapsed for the temperature of the sirup and hydrometer to attain bath temperature. A study has been made of the time necessary (for sirup at 70° F.) to attain bath temperature. The results are shown in Table I. When glass cylinders are used, a longer time is required.

Effect of Air. The presence of air in corn sirup or corn sugar sirup results in too low a Baumé reading. A serious error is often introduced, as the observer fails to recognize the importance of air on the reading. Sirup must be free of air before an accurate reading can be obtained. The time required to remove all the air is longer than generally assumed, and in the case of copper cylinders is difficult to observe. In order to obtain a measure of the time necessary to remove all the air from the sirup in a cylinder, the following experiment was made:

Corn sirups (42 D. E.) of different Baumés were poured with average care into glass cylinders 2 inches in inside diameter and the cylinders were placed in a water bath at 140° F. The observed time required for all the air trapped in the pouring operation to float to the surface where it could be removed by skimming was as follows:

° Bé.	Hours
42	1
43	3.5
44	6
45	24
46	95

The effect of small residual quantities of trapped air is too often discounted as insignificant. In order to determine the magnitude of this effect, the following test was made:

Corn sirups (42 D. E.) of different Baumés were poured into glass cylinders, which were placed in a water bath at 140° F. When the temperature in all the cylinders reached 140° F., a stream of air was introduced through a capillary for an equal period of time in all cylinders, after which the Baumé was read at stated intervals and the amount of deviation between the observed reading and that on the final air-free sirup determined. (Table II).

These data show the danger of introducing errors through occluded air, since an analyst, noting that the reading on the 46° Bé. sirup had been constant for 60 minutes, would assume constancy and report a false reading. Apparently in sirups of such high viscosity, the effect of small amounts of residual air is more slowly transmitted to the hydrometer, for in cross checks between laboratories on such samples there is always better agreement, although the data are invariably low.

Effect of Grease, etc., on Hydrometer Reading. Very small traces of grease, etc., have a noticeable effect on the hydrometer position, particularly in the range of 35° to 43° Bé. Errors caused by surface effects can be eliminated in many liquids through the use of an overflow (*2*) which renews the surface of the liquid, but this is not practical in the case of corn sirup. At least, the cylinder and hydrometer used can be thoroughly cleaned by sulfuric acid–sodium bichromate mixture, and the hydrometer can be kept clean and free from grease by touching only the portion of the stem above the scale during manipulation.

Table I. Time to Attain Bath Temperature

Copper Cylinder	Commercial Baumé of Corn Sirup 42°	43°	44°	45°	46°
	Time to Reach 140° F.				
Inches	*Minutes*				
2	55	70	80	90	100
2.25	72	86	98	111	124
2.5	90	107	120	136	152
3	130	155	180	205	240

Table II. Deviation

Time	Deviation from True Baumé Reading 42°	43°	44°	46°
Min.	° *Bé.*	° *Bé.*	° *Bé.*	° *Bé.*
10	−0.14	−0.16	−0.28	−0.15
30	−0.07	−0.07	−0.17	−0.15
60	−0.02	−0.05	−0.07	−0.15
120	−0.00	−0.01	−0.02	−0.07
1010	....	....	....	−0.03

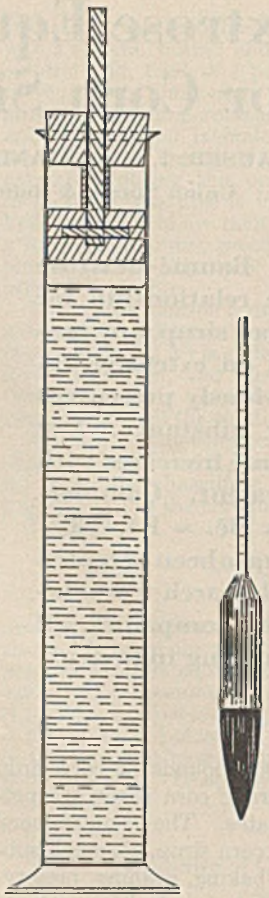

Figure 1. Hydrometer and Special Cylinder

Although the difficulties in the accurate determination of Baumé in corn sirup are many, it is believed that the official referee method adopted by the Corn Industries Research Foundation overcomes them to a large extent.

C. I. R. F. Official Referee Method for Baumé

The necessary equipment is shown in Figure 1. The important step in the procedure is the method of sealing the sample in the cylinder, during the period of heating to 140° F. and of removing all the air. The equipment for this consists of two rubber stoppers which fit snugly in the cylinder, and are separated on a metal rod by approximately 3 inches. The rod is fixed in the bottom stopper, but does not extend through it. The top stopper is free to move on the rod, although sufficiently tight to maintain a predetermined position. Through the use of these stoppers, little or no water evaporates from the surface and cool air does not reach the inner walls of the cylinder, thus enabling a given sample of sirup to remain in the bath without the difficulties previously mentioned.

Apparatus. Water bath, 32-gallon capacity, lagged, equipped with stirrer and metastatic mercury regulators with sensitivity of 0.02° C., set at 100° and 140° F. The bath was further equipped with a live steam inlet to raise the temperature rapidly from 60° to 100° to 140° F.

Vacuum ovens, Weber, with Cenco Megavac pumps, producing an oven pressure of less than 1 mm.

Distillation apparatus, as described (*5*, *7*, *9*). Moisture apparatus, as described (*3*). Pycnometers, as shown. Hydrometer cylinders, 15 × 2.25 inch, Pyrex, without lip. Hydrometers, 10.00° Bé., graduated to 0.1° Bé.

The Corn Industries Research Foundation has adopted specifications for referee hydrometers to be used by the industry in the sale of corn sirup. These specifications conform to those of the hydrometers used in the preparation of the tables appearing here and are as follows:

The hydrometers shall be the streamlined type, 145 modulus, standardized at 60° F., with a range of 10.00° Bé., graduated to 0.1° Bé., manufactured from Kimble flint glass with a linear coefficient of expansion of 0.0000092.

The over-all length of the hydrometer shall be not more than 13 or less than 12 inches. The diameter of the body at the center shall be not more than 0.790 or less than 0.770 inch.

For 35° to 45° Baumé hydrometers, the scale length for 10 Baumé degrees shall not be more than 155 mm. or less than 147 mm. For other hydrometers, the scale length for 10 Baumé degrees shall not be more than 140 mm. or less than 130 mm. Hydrometers to these specifications are made and stocked by Wm. Hiergesell & Sons, New York, N. Y., as C. I. R. F. hydrometers.

Procedure. Pour the sirup under test into the cylinder within 4 inches of the top, taking care that the sides are free of sirup. Seal the cylinder with the dual stoppers, the bottom stopper being placed within 0.5 inch of the sirup surface and the top stopper closing the cylinder. Place the cylinder in the water

TABLE III. EXPANSION OF WATER

Temperature, ° C.	Specific Gravity of Water, $T°/4°$ C.	Specific Gravity of Water, $T°/15.56°$ C.	Baumé of Water, $T°/15.56°$ C.
15.56	0.99904	1.00000	0.000
37.78	0.99307	0.99402	−0.872
60.00	0.98324	0.98418	−2.331

TABLE IV. SPECIFIC GRAVITIES

Temperature, ° C.	Specific Gravity Apparent	Specific Gravity Corrected	Baumé, Pycnometer 6 Apparent	Baumé, Pycnometer 6 Corrected
15.56/15.56	1.00000	1.00000	0.000	0.000
37.78/15.56	0.99423	0.99402	−0.842	−0.872
60.00/15.56	0.98465	0.98424	−2.260	−2.322
			Pycnometer 7	
15.56/15.56	1.00000	1.00000	0.000	0.000
37.78/15.56	0.99423	0.99402	−0.842	−0.872
60.00/15.56	0.98457	0.98415	−2.272	−2.335

bath so that the water extends to within 1 inch of the top. At the same time, run distilled water into a second cylinder, place the test hydrometer in it, and place in the water bath. When the sirup is free of air, place the cylinder on a higher shelf, so that the surface of the sirup will extend about 0.5 inch above the water after immersing the hydrometer. Remove dual stoppers from the cylinder. Remove test hydrometer by contact with top of the stem, dry quickly with clean towel, and immerse in the sirup.

In approximately 10 minutes read the hydrometer at intervals of 2 minutes through the cylinder, taking every care to avoid parallax. Read until two or more readings are identical. Watch carefully that the sirup meniscus is uniform around the hydrometer stem. Usually it is necessary to add a very small drop of water at the stem meniscus. To the observed reading of the hydrometer add any correction found necessary from the previous standardization against a Bureau of Standards hydrometer.

Baumé by Pycnometers

In the initial work Baumés were determined by hydrometers as given above. Hydrometers were compared with an instrument certified by the Bureau of Standards at five points. The Baumé reading on distilled water was −0.71° at 100° F., and −2.01° at 140° F. The Baumé on a given sirup was the average of the readings of two or more observers. In view of the large amount of data necessary for complete tables, this method was so laborious and tedious that the determination of Baumé was transferred from hydrometers to pycnometers, whereby two or more could be employed on a single sirup by one analyst, and greater accuracy could be obtained.

The initial work was started with the usual type of flat-bottomed pycnometers, but it was found that when used at elevated temperatures, each expanded differently according to some small change in design. Accordingly, a new type of pycnometer was designed in the form of a sphere with standard taper joints of Pyrex, as shown in Figure 2.

These pycnometers agreed among themselves when used at elevated temperatures, and specific gravities at 100°/60° F. and 140°/60° F. were close to the true specific gravity after correction for the expansion of glass, as will be seen from the following tables. Table III gives the theoretical expansion of water itself, specific gravity being calculated on the basis of grams per milliliter.

Table IV gives the data obtained by two typical pycnometers, showing the specific gravities, as is or apparent, and after correction for the cubical expansion of Pyrex (0.0000096 per ° C.).

The Baumé readings obtained by the Pyrex pycnometers did not check the values of hydrometers for distilled water at 37.78° and 60.00° C. As the glass in the two instruments was different, this was at first explained on the basis of difference in thermal expansion.

A formula was developed whereby the apparent specific gravity of pycnometers could be translated to hydrometer readings. The basis for the formula was the hydrometer readings in distilled water at 37.78° C. (−0.71° Bé.) and 60.00° C. (−2.01° Bé.), as follows:

$$H = \frac{W_2 + (A \times V \times C)}{W_1}$$

when

H = specific gravity at $T°/15.56°$ C. (in vacuum) corresponding to hydrometer reading at $T°$
W_2 = weight of liquid in pycnometer at $T°$, corrected to vacuum
W_1 = weight of water in pycnometer at 15.56° C., corrected to vacuum
$A = \frac{W_2}{W_1}$ apparent specific gravity
V = volume of pycnometer at 15.56° C.
C = correction

or

$$C = \frac{W_1 H - W_2}{AV}$$

The seven pycnometers used had an average capacity of 80 ml. The average value for C at 37.78° C. was 0.00089 and at 60° C. was 0.00175.

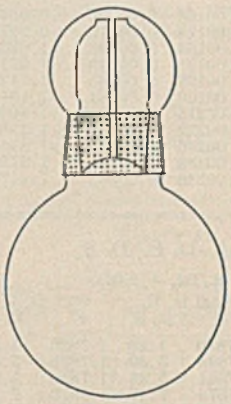

FIGURE 2. PYCNOMETER

The apparent specific gravities by pycnometers on various concentrations of corn sirup, employing the correction as indicated above, were compared with actual readings by hydrometers in the same sirup and found to agree within 0.01° Bé. The same relationship was found true, employing sulfuric acid solutions at the temperatures indicated.

In Tables V to XVI, the Baumé recorded is in all cases the hydrometer reading at the temperature indicated. The specific gravity in air is the corresponding value of the Baumé. In the case of the 60°/60° F. tables, the Baumé reading is true, as is also the specific gravity in air. However, in the tables at 100°/60° F. and 140°/60° F., the Baumé reading and the assigned specific gravity are apparent. True specific gravity—vacuum—can be obtained for Baumé readings at the three table temperatures by means of Table V, which covers the corrections to be subtracted from the assigned specific gravity in air.

Determination of Moisture

Corn sirup is extremely stable at the temperatures encountered in the usual moisture determination methods. It can be dried without decomposition as high as 112° C., if the pH of the product is within the range of 4.5 to 5.5. The basis for this statement is that identical values can be obtained by benzene distillation (80–81° C.), vacuum oven drying (100° C.), and toluene distillation (112° C.), and the results of these determinations can be correlated to others obtained at much lower temperatures through special methods (*3*, *8*).

In a moisture determination, the problem involved is that of spreading the corn sirup over a sufficiently large surface so that the moisture can be removed quickly and completely (*3*, *7*, *8*, *9*).

Crude corn sugars, in contrast to corn sirups, are more variable among manufacturers, and are marketed with several dextrose equivalents and ash contents. They are more sus-

TABLE V. CORRECTIONS

Hydrometer Reading	Assigned Specific Gravity, Air	Corrections to Be Subtracted: Air to vacuum	Expansion of glass	Hydrometer correction	Total	True Specific Gravity Vacuum
		60°/60° F.				
0.00	1.0000	0.00000	.....	.....	0.0000	1.0000
5.00	1.0358	0.00005	.....	.....	0.0001	1.0357
10.00	1.0742	0.00012	.....	.....	0.0001	1.0741
15.00	1.1156	0.00019	.....	.....	0.0002	1.1154
20.00	1.1602	0.00025	.....	.....	0.0002	1.1600
25.00	1.2086	0.00031	.....	.....	0.0003	1.2083
30.00	1.2612	0.00037	.....	.....	0.0003	1.2609
35.00	1.3186	0.00043	.....	.....	0.0004	1.3182
40.00	1.3815	0.00050	.....	.....	0.0005	1.3810
45.00	1.4506	0.00056	.....	.....	0.0006	1.4500
		100°/60° F.				
−0.71	0.9951	−0.00001	0.00021	0.00085	0.00105	0.9940
0.00	1.0000	0.00000	0.00021	0.00090	0.00111	0.9989
5.00	1.0358	0.00005	0.00022	0.00093	0.00120	1.0346
10.00	1.0742	0.00012	0.00023	0.00095	0.00130	1.0729
15.00	1.1156	0.00019	0.00024	0.00100	0.00143	1.1142
20.00	1.1602	0.00025	0.00025	0.00104	0.00154	1.1587
25.00	1.2086	0.00031	0.00026	0.00108	0.00165	1.2069
30.00	1.2612	0.00037	0.00027	0.00113	0.00177	1.2594
35.00	1.3186	0.00043	0.00028	0.00117	0.00188	1.3167
40.00	1.3815	0.00050	0.00030	0.00120	0.00200	1.3795
45.00	1.4506	0.00056	0.00031	0.00124	0.00211	1.4485
		140°/60° F.				
−2.01	0.9864	−0.00002	0.00042	0.00166	0.00206	0.9843
0.00	1.0000	0.00000	0.00042	0.00174	0.00216	0.9978
5.00	1.0358	0.00005	0.00044	0.00184	0.00233	1.0335
10.00	1.0742	0.00012	0.00046	0.00191	0.00249	1.0717
15.00	1.1156	0.00019	0.00047	0.00199	0.00265	1.1129
20.00	1.1602	0.00025	0.00050	0.00206	0.00281	1.1574
25.00	1.2086	0.00031	0.00052	0.00215	0.00298	1.2056
30.00	1.2612	0.00037	0.00055	0.00222	0.00314	1.2581
35.00	1.3186	0.00043	0.00057	0.00230	0.00330	1.3153
40.00	1.3815	0.00050	0.00059	0.00238	0.00347	1.3780
45.00	1.4506	0.00056	0.00061	0.00246	0.00363	1.4470

ceptible to decomposition because of a larger protein, acid, and ash content. Further, as the dextrose equivalent of the starch hydrolysate increases, the material retains its water more tenaciously. This appears to reach a peak at about 82 D. E. Thus the problem of drying has been to remove these last traces of residual moisture, without resorting to high temperatures which lead to decomposition. Occasionally with some lots of crude sugar, the vacuum oven procedure described gave results which made the distinction between the last traces of water removal and decomposition a difficult decision. In such cases benzene distillation was employed as confirmative. The basis for this conclusion is described elsewhere (*5*, *6*).

The determination of moisture in corn sirup and corn sugar is discussed fully elsewhere (*3–9*). The methods used were as follows:

CORN SIRUP. Filter-Cel method (diatomaceous silica, Johns Manville Hy-Flo), vacuum oven at 100° C.; alternative methods, toluene distillation and benzene distillation.

CORN SUGAR. For 80 to 92 D. E., Filter-Cel method, vacuum oven at 80° C.; alternative, benzene distillation.

PREPARATION OF SAMPLE. The sirups used for the tables were from two factories. The heavy sirups or solid sugars were diluted with distilled water, refined with activated carbon, and either diluted further or concentrated under vacuum to the desired density. The warm sirup was run into a 2-liter round-bottomed flask fitted with rubber stopper and stopcock. The flask was then evacuated to a pressure of 70 to 75 mm. (mercury) by a water pump and slowly cooled to 80° to 90° F. During the cooling process the sirup was constantly stirred by rotating the flask. A homogeneous cooled sample substantially free from dissolved air was obtained by this procedure. The cold sample was transferred carefully to 4-ounce glass bottles, fitted with

TABLE VI. EXPERIMENTAL BÉ.–D. E.–D. S.

(140°/60°. F = Factor = D. S./Bé. + 2.01)

Baumé	42.00 D. E. F	42.00 D. E. D. S.	55.00 D. E. F	55.00 D. E. D. S.	89.00 D. E. F	89.00 D. E. D. S.	90.7 D. E. F	90.7 D. E. D. S.
−1.00	1.7469	1.76	1.7553	1.78	1.7830	1.80	1.7823	1.80
0.00	1.7479	3.51	1.7566	3.53	1.7845	3.59	1.7838	3.59
1.00	1.7489	5.26	1.7579	5.29	1.7861	5.38	1.7854	5.37
2.00	1.7499	7.02	1.7593	7.06	1.7876	7.17	1.7870	7.17
3.00	1.7510	8.77	1.7607	8.82	1.7893	8.96	1.7886	8.96
4.00	1.7521	10.53	1.7619	10.59	1.7909	10.76	1.7901	10.76
5.00	1.7532	12.29	1.7633	12.36	1.7925	12.57	1.7917	12.56
6.00	1.7543	14.05	1.7647	14.14	1.7942	14.37	1.7934	14.37
7.00	1.7554	15.82	1.7661	15.91	1.7959	16.18	1.7951	16.17
8.00	1.7565	17.58	1.7675	17.69	1.7977	18.00	1.7968	17.99
9.00	1.7577	19.35	1.7689	19.48	1.7994	19.81	1.7985	19.80
10.00	1.7589	21.12	1.7704	21.26	1.8012	21.63	1.8003	21.65
11.00	1.7601	22.90	1.7719	23.05	1.8031	23.46	1.8021	23.42
12.00	1.7614	24.68	1.7733	24.84	1.8050	25.29	1.8040	25.28
13.00	1.7627	26.46	1.7749	26.64	1.8070	27.12	1.8058	27.11
14.00	1.7640	28.24	1.7764	28.44	1.8090	28.96	1.8077	28.94
15.00	1.7654	30.03	1.7780	30.24	1.8110	30.80	1.8097	30.78
16.00	1.7668	31.82	1.7796	32.05	1.8131	32.65	1.8117	32.63
17.00	1.7682	33.61	1.7813	33.86	1.8152	34.51	1.8138	34.48
18.00	1.7697	35.41	1.7830	35.68	1.8174	36.37	1.8159	36.34
19.00	1.7711	37.21	1.7847	37.50	1.8196	38.23	1.8181	38.20
20.00	1.7727	39.02	1.7865	39.32	1.8220	40.10	1.8203	40.06
21.00	1.7742	40.82	1.7883	41.15	1.8244	41.98	1.8227	41.94
22.00	1.7758	42.64	1.7902	42.98	1.8268	43.86	1.8250	43.82
23.00	1.7775	44.46	1.7921	44.82	1.8294	45.75	1.8275	45.71
24.00	1.7793	46.28	1.7940	46.66	1.8320	47.65	1.8300	47.60
25.00	1.7810	48.10	1.7960	48.51	1.8347	49.56	1.8326	49.50
26.00	1.7829	49.94	1.7981	50.37	1.8375	51.47	1.8354	51.41
27.00	1.7848	51.78	1.8003	52.23	1.8404	53.39	1.8382	53.33
28.00	1.7867	53.62	1.8025	54.09	1.8433	55.32	1.8411	55.25
29.00	1.7887	55.47	1.8048	55.97	1.8464	57.26	1.8441	57.19
30.00	1.7908	57.32	1.8071	57.85	1.8496	59.21	1.8472	59.13
31.00	1.7930	59.18	1.8095	59.73	1.8529	61.16	1.8505	61.09
32.00	1.7952	61.05	1.8120	61.63	1.8563	63.13	1.8538	63.05
33.00	1.7975	62.93	1.8146	63.53	1.8598	65.11	1.8572	65.02
34.00	1.7999	64.81	1.8173	65.44	1.8634	67.10	1.8607	67.00
35.00	1.8024	66.71	1.8201	67.36	1.8672	69.11	1.8644	69.00
36.00	1.8051	68.61	1.8231	69.30	1.8710	71.12	1.8681	71.01
37.00	1.8078	70.52	1.8261	71.24	1.8750	73.14	1.8720	73.03
38.00	1.8107	72.45	1.8293	73.19	1.8791	75.18	1.8760	75.06
39.00	1.8137	74.38	1.8326	75.16	1.8834	77.24	1.8801	77.10
40.00	1.8169	76.33	1.8361	77.14	1.8877	79.30	1.8845	79.17
41.00	1.8202	78.29	1.8397	79.13	1.8922	81.38	1.8890	81.25
42.00	1.8237	80.26	1.8436	81.14	1.8968	83.48	1.8935	83.33
43.00	1.8273	82.25	1.8477	83.17	1.9017	85.60	1.8982	85.44
44.00	1.8311	84.25	1.8518	85.20	1.9066	87.72	1.9030	87.56
45.00	1.8350	86.26	1.8562	87.26	1.9116	89.86	1.9079	89.69
46.00	1.8391	88.30	1.8609	89.34	1.9168	92.03	1.9130	91.84

TABLE VII. EXPERIMENTAL BÉ.–D. E.–D. S.

(100°/60°. F = Factor = D. S./Bé. +0.71)

Baumé	42.00 D. E. F	42.00 D. E. D. S.	55.00 D. E. F	55.00 D. E. D. S.	89.00 D. E. F	89.00 D. E. D. S.	90.7 D. E. F	90.7 D. E. D. S.
0.00	1.7544	1.25	1.7680	1.26	1.7927	1.27	1.7898	1.27
1.00	1.7555	3.00	1.7692	3.03	1.7943	3.07	1.7914	3.06
2.00	1.7567	4.76	1.7704	4.80	1.7959	4.87	1.7931	4.86
3.00	1.7579	6.52	1.7716	6.57	1.7976	6.67	1.7948	6.66
4.00	1.7591	8.29	1.7729	8.35	1.7993	8.47	1.7966	8.46
5.00	1.7604	10.05	1.7741	10.13	1.8010	10.28	1.7984	10.27
6.00	1.7617	11.82	1.7755	11.91	1.8028	12.09	1.8002	12.08
7.00	1.7630	13.59	1.7768	13.70	1.8046	13.91	1.8020	13.89
8.00	1.7643	15.37	1.7782	15.49	1.8065	15.73	1.8039	15.71
9.00	1.7657	17.15	1.7796	17.28	1.8084	17.56	1.8058	17.53
10.00	1.7671	18.93	1.7810	19.07	1.8104	19.39	1.8078	19.36
11.00	1.7685	20.71	1.7825	20.87	1.8125	21.22	1.8098	21.19
12.00	1.7699	22.50	1.7840	22.67	1.8145	23.06	1.8119	23.03
13.00	1.7713	24.28	1.7855	24.48	1.8165	24.90	1.8140	24.87
14.00	1.7728	26.08	1.7871	26.29	1.8187	26.75	1.8162	26.72
15.00	1.7743	27.88	1.7888	28.10	1.8209	28.61	1.8184	28.57
16.00	1.7759	29.68	1.7904	29.92	1.8231	30.47	1.8207	30.42
17.00	1.7775	31.48	1.7921	31.74	1.8254	32.33	1.8230	32.28
18.00	1.7791	33.29	1.7939	33.56	1.8278	34.20	1.8253	34.15
19.00	1.7808	35.10	1.7957	35.39	1.8302	36.07	1.8277	36.02
20.00	1.7825	36.92	1.7975	37.22	1.8327	37.96	1.8302	37.90
21.00	1.7843	38.74	1.7994	39.06	1.8353	39.85	1.8328	39.79
22.00	1.7861	40.56	1.8014	40.91	1.8379	41.74	1.8354	41.68
23.00	1.7879	42.39	1.8034	42.76	1.8407	43.64	1.8381	43.58
24.00	1.7898	44.23	1.8055	44.61	1.8435	45.55	1.8409	45.49
25.00	1.7918	46.07	1.8077	46.47	1.8464	47.47	1.8437	47.40
26.00	1.7938	47.91	1.8099	48.34	1.8494	49.40	1.8466	49.32
27.00	1.7960	49.77	1.8122	50.22	1.8525	51.33	1.8497	51.25
28.00	1.7982	51.63	1.8146	52.10	1.8556	53.27	1.8528	53.19
29.00	1.8005	53.49	1.8171	53.99	1.8589	55.23	1.8560	55.14
30.00	1.8028	55.36	1.8196	55.88	1.8623	57.19	1.8593	57.10
31.00	1.8052	57.24	1.8223	57.79	1.8658	59.16	1.8626	59.06
32.00	1.8077	59.13	1.8250	59.70	1.8694	61.15	1.8661	61.04
33.00	1.8104	61.03	1.8279	61.62	1.8731	63.14	1.8697	63.03
34.00	1.8131	62.93	1.8308	63.55	1.8769	65.15	1.8735	65.03
35.00	1.8159	64.85	1.8338	65.49	1.8809	67.17	1.8774	67.04
36.00	1.8189	66.77	1.8370	67.44	1.8850	69.20	1.8814	69.07
37.00	1.8219	68.70	1.8403	69.40	1.8893	71.25	1.8855	71.10
38.00	1.8251	70.65	1.8438	71.37	1.8936	73.30	1.8898	73.15
39.00	1.8283	72.60	1.8474	73.36	1.8981	75.37	1.8943	75.22
40.00	1.8317	74.57	1.8512	75.36	1.9028	77.46	1.8990	77.31
41.00	1.8353	76.55	1.8552	77.38	1.9078	79.57	1.9038	79.41
42.00	1.8391	78.55	1.8594	79.41	1.9129	81.70	1.9088	81.53
43.00	1.8430	80.56	1.8637	81.46	1.9182	83.84	1.9140	83.67
44.00	1.8470	82.58	1.8682	83.53	1.9236	86.00	1.9194	85.82
45.00	1.8512	84.62	1.8728	85.61	1.9292	88.18	1.9250	87.99
46.00	1.8556	86.68	1.8776	87.70	1.9350	90.38	1.9307	90.18
47.00	1.8602	88.75	1.8826	89.82	1.9410	92.61	1.9367	92.40

TABLE VIII. EXPERIMENTAL BÉ.–D. E.–D. S.

(60°/60°. F = Factor = D. S./Bé.)

Baumé	42.00 D. E. F	42.00 D. E. D. S.	55.00 D. E. F	55.00 D. E. D. S.	89.00 D. E. F	89.00 D. E. D. S.	90.7 D. E. F	90.7 D. E. D. S.
0.00		0.00		0.00		0.00		0.00
1.00	1.7358	1.74	1.7407	1.74	1.7670	1.77	1.7638	1.76
2.00	1.7371	3.47	1.7425	3.48	1.7690	3.54	1.7658	3.53
3.00	1.7385	5.21	1.7443	5.23	1.7710	5.31	1.7678	5.30
4.00	1.7399	6.96	1.7462	6.98	1.7730	7.09	1.7699	7.08
5.00	1.7413	8.71	1.7480	8.74	1.7750	8.87	1.7720	8.86
6.00	1.7427	10.46	1.7499	10.50	1.7771	10.66	1.7742	10.64
7.00	1.7441	12.21	1.7518	12.26	1.7793	12.46	1.7764	12.43
8.00	1.7456	13.96	1.7537	14.03	1.7816	14.25	1.7787	14.23
9.00	1.7471	15.72	1.7557	15.80	1.7838	16.05	1.7810	16.03
10.00	1.7487	17.48	1.7577	17.58	1.7861	17.86	1.7833	17.83
11.00	1.7503	19.25	1.7597	19.36	1.7885	19.67	1.7857	19.64
12.00	1.7519	21.02	1.7617	21.14	1.7909	21.49	1.7881	21.46
13.00	1.7536	22.80	1.7638	22.93	1.7934	23.31	1.7907	23.28
14.00	1.7553	24.58	1.7659	24.72	1.7959	25.14	1.7933	25.11
15.00	1.7571	26.36	1.7680	26.52	1.7985	26.98	1.7959	26.94
16.00	1.7589	28.14	1.7701	28.32	1.8011	28.82	1.7986	28.78
17.00	1.7608	29.93	1.7723	30.13	1.8038	30.66	1.8013	30.62
18.00	1.7627	31.73	1.7746	31.94	1.8066	32.52	1.8040	32.47
19.00	1.7646	33.53	1.7769	33.76	1.8094	34.38	1.8068	34.33
20.00	1.7666	35.33	1.7792	35.58	1.8123	36.25	1.8097	36.19
21.00	1.7687	37.14	1.7816	37.41	1.8153	38.12	1.8127	38.07
22.00	1.7708	38.96	1.7840	39.25	1.8184	40.00	1.8158	39.95
23.00	1.7730	40.78	1.7865	41.09	1.8215	41.89	1.8189	41.83
24.00	1.7752	42.60	1.7890	42.94	1.8247	43.79	1.8221	43.73
25.00	1.7775	44.44	1.7916	44.79	1.8281	45.70	1.8254	45.64
26.00	1.7799	46.28	1.7943	46.65	1.8315	47.62	1.8288	47.55
27.00	1.7823	48.12	1.7970	48.52	1.8350	49.55	1.8323	49.47
28.00	1.7848	49.97	1.7998	50.39	1.8387	51.48	1.8360	51.41
29.00	1.7874	51.83	1.8027	52.28	1.8424	53.43	1.8397	53.35
30.00	1.7901	53.70	1.8057	54.17	1.8464	55.39	1.8435	55.31
31.00	1.7929	55.58	1.8088	56.07	1.8504	57.36	1.8474	57.27
32.00	1.7958	57.47	1.8119	57.98	1.8545	59.34	1.8515	59.25
33.00	1.7987	59.36	1.8152	59.90	1.8588	61.34	1.8557	61.24
34.00	1.8018	61.26	1.8186	61.83	1.8633	63.35	1.8601	63.24
35.00	1.8051	63.18	1.8221	63.77	1.8679	65.38	1.8646	65.26
36.00	1.8084	65.10	1.8258	65.73	1.8727	67.42	1.8692	67.29
37.00	1.8119	67.04	1.8296	67.70	1.8775	69.47	1.8740	69.34
38.00	1.8155	68.99	1.8335	69.67	1.8825	71.54	1.8790	71.40
39.00	1.8192	70.95	1.8377	71.67	1.8877	73.62	1.8841	73.48
40.00	1.8231	72.92	1.8420	73.68	1.8931	75.73	1.8893	75.57
41.00	1.8272	74.92	1.8466	75.71	1.8987	77.85	1.8946	77.68
42.00	1.8314	76.92	1.8514	77.76	1.9045	79.99	1.9002	79.81
43.00	1.8359	78.94	1.8564	79.83	1.9105	82.15	1.9061	81.96
44.00	1.8406	80.99	1.8616	81.91	1.9167	84.33	1.9121	84.13
45.00	1.8456	83.05	1.8670	84.01	1.9229	86.53	1.9183	86.32
46.00	1.8509	85.14	1.8726	86.14	1.9293	88.75	1.9246	88.53
47.00	1.8564	87.25	1.8784	88.28	1.9359	90.99	1.9310	90.76
48.00	1.8621	89.38	1.8843	90.45	1.9426	93.24	1.9375	93.00

screw tops. Ten bottles were so prepared. One bottle was used for each Baumé and each moisture determination. The specific gravity determination was the average of two or three tests, the variation never being more than one in the fourth decimal place. The moisture determinations were the average of two to six tests by different methods and carried out by two analysts. The maximum variation between analysts was 0.03 per cent with an average of 0.015 per cent.

Dextrose Equivalent and Ash

Dextrose equivalent is the amount of reducing sugars, determined by the Lane-Eynon (*10*) method, expressed as dextrose on the dry substance obtained. The ash, largely sodium chloride, was determined by ashing at dull red heat according to the A. O. A. C. procedure (*1*). The results were in agreement with direct determination of chlorides by the Volhard titration.

PROCEDURE. In this work one chemist determined all the specific gravities; one or two, the moistures. With sirups which would crystallize, tests were started as soon as the samples were prepared. The dextrose equivalent was the average of tests made by at least two chemists.

The Baumé–dry substance correlation was made on four sirups as follows:

D. E.	Ash, D. S. B.
42.00	0.28
55.00	0.30
89.00	0.61
90.7	1.22

The first two corn sirups are typical for all manufacturers in dextrose equivalent, specific rotation, and ash content. The latter two are typical of two general types of crude sugar manufactured in the industry—a low-ash sugar of approximately 89 D. E. maximum and a high-ash sugar of approximately 92 D. E. maximum.

The complete range of Baumé 0 to 47° was covered at three temperatures—60.0°, 100.0°, and 140.0° F. The points were determined every 5° Bé. in the lower ranges and every 2° Bé. in the higher ranges. The average number of points for each curve was nineteen. The method of plotting used at first was Baumé against dry substance. The paper chosen was millimeter paper, each millimeter equaling 0.10° Bé. and 0.10 per cent dry substance. The second decimal place was plotted on the paper by the fine point of the drawing instrument and a hand lens. Although this was satisfactory for the Baumé, the length of the curve for dry substance was so great that it did not sufficiently show up small variations in dry substance. The method was changed to one of factors against Baumé. The factors were determined as follows:

$$\text{At } 60^\circ\text{F., factor } 60^\circ\text{F.} = \frac{\text{D. S.}}{\text{Baumé}}$$

$$\text{At } 100^\circ\text{F., factor } 100^\circ\text{F.} = \frac{\text{D. S.}}{\text{Baumé} + 0.71}$$

$$\text{At } 140^\circ\text{F., factor } 140^\circ\text{F.} = \frac{\text{D. S.}}{\text{Baumé} + 2.01}$$

The use of these factors shortened the ordinate and amplified the experimental variation. Thus at 5° Bé. each millimeter equaled 0.0090 per cent D. S. The curve was drawn through the points by means of a steel ferule and a very fine-pointed hard pencil. From the curve so drawn, the factors were read for each Baumé and, in turn, the dry substance value was obtained. The values so obtained were in excellent agreement with experimental results.

The computed data for the three temperatures appear in Tables VI, VII, and VIII.

TABLE IX. EXPANDED BÉ.–D. E.–D. S.

(140°/60°)

D. E.	30.00	42.00	55.00	82.00	87.00	89.00	91.2	90.7
Ash	0.28	0.28	0.30	0.41	0.61	0.61	0.61	1.22
Baumé	Per Cent Dry Substance							
−1.00	1.75	1.76	1.78	1.80	1.80	1.80	1.80	1.80
0.00	3.49	3.51	3.53	3.58	3.58	3.59	3.59	3.59
1.00	5.23	5.26	5.29	5.36	5.37	5.38	5.39	5.37
2.00	6.98	7.02	7.06	7.15	7.17	7.17	7.18	7.17
3.00	8.72	8.77	8.82	8.94	8.96	8.96	8.97	8.96
4.00	10.47	10.53	10.59	10.73	10.76	10.76	10.77	10.76
5.00	12.22	12.29	12.36	12.53	12.56	12.57	12.58	12.56
6.00	13.97	14.05	14.14	14.33	14.36	14.37	14.39	14.37
7.00	15.73	15.82	15.91	16.13	16.17	16.18	16.20	16.17
8.00	17.48	17.58	17.69	17.94	17.98	18.00	18.02	17.98
9.00	19.24	19.35	19.48	19.75	19.79	19.81	19.83	19.80
10.00	20.99	21.12	21.26	21.56	21.61	21.63	21.65	21.62
11.00	22.76	22.90	23.05	23.38	23.44	23.46	23.48	23.45
12.00	24.52	24.68	24.84	25.20	25.26	25.29	25.31	25.27
13.00	26.29	26.46	26.64	27.02	27.09	27.12	27.15	27.10
14.00	28.06	28.24	28.44	28.85	28.93	28.96	28.99	28.94
15.00	29.83	30.03	30.24	30.69	30.77	30.80	30.84	30.78
16.00	31.61	31.82	32.05	32.53	32.62	32.65	32.69	32.63
17.00	33.39	33.61	33.86	34.38	34.47	35.41	34.55	34.48
18.00	35.17	35.41	35.68	36.23	36.33	36.37	36.41	36.34
19.00	36.95	37.21	37.50	38.08	38.19	38.23	38.28	38.20
20.00	38.74	39.02	39.32	39.94	40.05	40.10	40.15	40.06
21.00	40.53	40.82	41.15	41.81	41.93	41.98	42.03	41.94
22.00	42.33	42.64	42.98	43.68	43.81	43.86	43.92	43.82
23.00	44.13	44.46	44.82	45.56	45.70	45.75	45.81	45.71
24.00	45.92	46.28	46.66	47.44	47.60	47.65	47.71	47.60
25.00	47.73	48.10	48.51	49.34	49.50	49.56	49.62	49.50
26.00	49.55	49.94	50.37	51.24	51.40	51.47	51.54	51.41
27.00	51.37	51.78	52.23	53.15	53.32	53.39	53.47	53.33
28.00	53.19	53.62	54.09	55.07	55.25	55.32	55.40	55.25
29.00	55.02	55.47	55.97	56.99	57.18	57.26	57.34	57.19
30.00	56.84	57.32	57.85	58.93	59.13	59.21	59.30	59.13
31.00	58.68	59.18	59.73	60.87	61.08	61.16	61.25	61.09
32.00	60.52	61.05	61.63	62.82	63.04	63.13	63.23	63.05
33.00	62.37	62.93	63.53	64.79	65.02	65.11	65.21	65.02
34.00	64.23	64.81	65.44	66.76	67.00	67.10	67.21	67.00
35.00	66.10	66.71	67.36	68.75	59.00	69.11	69.22	69.00
36.00	67.97	68.61	69.30	70.75	71.01	71.12	71.24	71.01
37.00	69.85	70.52	71.24	72.75	73.03	73.14	73.26	73.03
38.00	71.75	72.45	73.19	74.77	75.06	75.18	75.31	75.06
39.00	73.65	74.38	75.16	76.81	77.12	77.24	77.37	77.10
40.00	75.57	76.33	77.14	78.86	79.17	79.30	79.44	79.17
41.00	77.50	78.29	79.13	80.92	81.25	81.38	81.53	81.25
42.00	79.44	80.26	81.14	83.00	83.34	83.48	83.63	83.33
43.00	81.39	82.25	83.17	85.10	85.46	85.60	85.75	85.44
44.00	83.36	84.25	85.20	87.21	87.58	87.72	87.88	87.56
45.00	85.34	86.26	87.26	89.33	89.71	89.86	90.03	89.69
46.00	87.35	88.30	89.34	91.47	91.87	92.03	92.20	91.84

TABLE X. EXPANDED BÉ.–D. E.–D. S

(100°/60°)

D. E.	30.00	42.00	55.00	82.00	87.00	89.00	91.2	90.7
Ash	0.28	0.28	0.30	0.41	0.61	0.61	0.61	1.22
Baumé	Per Cent Dry Substance							
0.00	1.24	1.25	1.26	1.27	1.27	1.27	1.27	1.27
1.00	2.98	3.00	3.03	3.06	3.07	3.07	3.07	3.06
2.00	4.73	4.76	4.80	4.85	4.87	4.87	4.88	4.86
3.00	6.48	6.52	6.57	6.65	6.66	6.67	6.68	6.66
4.00	8.24	8.29	8.35	8.44	8.46	8.47	8.48	8.46
5.00	9.99	10.05	10.13	10.25	10.27	10.28	10.29	10.27
6.00	11.75	11.82	11.91	12.05	12.08	12.09	12.10	12.08
7.00	13.51	13.59	13.70	13.86	13.90	13.91	13.92	13.89
8.00	15.28	15.37	15.49	15.68	15.71	15.73	15.75	15.71
9.00	17.05	17.15	17.28	17.50	17.54	17.56	17.58	17.53
10.00	18.81	18.93	19.07	19.32	19.37	19.39	19.41	19.36
11.00	20.58	20.71	20.87	21.14	21.20	21.22	21.24	21.19
12.00	22.36	22.50	22.67	22.98	23.04	23.06	23.09	23.03
13.00	24.13	24.28	24.48	24.81	24.87	24.90	24.93	24.87
14.00	25.91	26.08	26.29	26.65	26.72	26.75	26.78	26.72
15.00	27.69	27.88	28.10	28.50	28.58	28.61	28.64	28.57
16.00	29.48	29.68	29.92	30.35	30.44	30.47	30.51	30.42
17.00	31.26	31.48	31.74	32.20	32.29	32.33	32.37	32.28
18.00	33.06	33.29	33.56	34.06	34.16	34.20	34.24	34.15
19.00	34.85	35.10	35.39	35.93	36.03	36.07	36.12	36.02
20.00	36.65	36.92	37.22	37.81	37.92	37.96	38.01	37.90
21.00	38.46	38.74	39.06	39.68	39.80	39.85	39.90	39.79
22.00	40.26	40.56	40.91	41.56	41.69	41.74	41.80	41.68
23.00	42.07	42.39	42.76	43.45	43.59	43.64	43.70	43.58
24.00	43.89	44.23	44.61	45.35	45.49	45.55	45.61	45.49
25.00	45.71	46.07	46.47	47.26	47.41	47.47	47.54	47.40
26.00	47.53	47.91	48.34	49.18	49.34	49.40	49.47	49.32
27.00	49.37	49.77	50.22	51.10	51.26	51.33	51.40	51.25
28.00	51.21	51.63	52.10	53.03	53.20	53.27	53.35	53.19
29.00	53.05	53.49	53.99	54.97	55.16	55.23	55.31	55.14
30.00	54.89	55.36	55.88	56.92	57.11	57.19	57.28	57.10
31.00	56.75	57.24	57.79	58.87	59.08	59.16	59.25	59.06
32.00	58.61	59.13	59.70	60.85	61.06	61.15	61.24	61.04
33.00	60.49	61.03	61.62	62.83	63.05	63.14	63.24	63.03
34.00	62.36	62.93	63.55	64.82	65.06	65.15	65.25	65.03
35.00	64.26	64.85	65.49	66.82	67.07	67.17	67.28	67.04
36.00	66.15	66.77	67.44	68.84	69.10	69.20	69.31	69.07
37.00	68.05	68.70	69.40	70.87	71.14	71.25	71.37	71.10
38.00	69.97	70.65	71.37	72.91	73.19	73.30	73.42	73.15
39.00	71.89	72.60	73.36	74.96	75.25	75.37	75.50	75.22
40.00	73.83	74.57	75.36	77.03	77.34	77.46	77.60	77.31
41.00	75.78	76.55	77.38	79.12	79.44	79.57	79.71	79.41
42.00	77.75	78.55	79.41	81.23	81.57	81.70	81.85	81.53
43.00	79.72	80.56	81.46	83.35	83.70	83.84	83.99	83.67
44.00	81.71	82.58	83.53	85.49	85.85	86.00	86.16	85.82
45.00	83.71	84.62	85.61	87.65	88.03	88.18	88.35	87.99
46.00	85.74	86.68	87.70	89.83	90.22	90.38	90.55	90.18
47.00	87.76	88.75	89.82	92.04	92.45	92.61	92.79	92.40

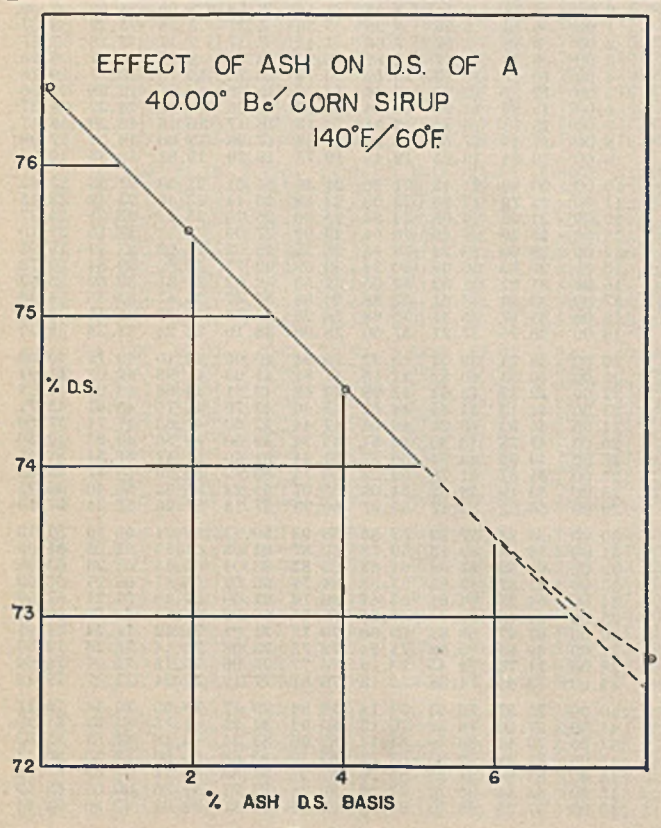

FIGURE 3

TABLE XI. EXPANDED BÉ.–D. E.–D. S.

(60°/60° F.)

D. E.	30.00	42.00	55.00	82.00	87.00	89.00	91.2	90.7
Ash	0.28	0.28	0.30	0.41	0.61	0.61	0.61	1.22
Baumé	Per Cent Dry Substance							
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	1.73	1.74	1.74	1.77	1.77	1.77	1.77	1.76
2.00	3.45	3.47	3.48	3.53	3.54	3.54	3.54	3.53
3.00	5.18	5.21	5.23	5.30	5.31	5.31	5.31	5.30
4.00	6.93	6.96	6.98	7.07	7.08	7.09	7.10	7.08
5.00	8.67	8.71	8.74	8.85	8.86	8.87	8.88	8.86
6.00	10.41	10.46	10.50	10.63	10.65	10.66	10.67	10.64
7.00	12.15	12.21	12.26	12.42	12.45	12.46	12.47	12.43
8.00	13.89	13.96	14.03	14.21	14.24	14.25	14.27	14.23
9.00	15.63	15.72	15.80	16.00	16.04	16.05	16.07	16.03
10.00	17.38	17.48	17.58	17.80	17.84	17.86	17.88	17.83
11.00	19.14	19.25	19.36	19.61	19.65	19.67	19.69	19.64
12.00	20.90	21.02	21.14	21.42	21.47	21.49	21.51	21.46
13.00	22.67	22.80	22.93	23.23	23.29	23.31	23.33	23.28
14.00	24.44	24.58	24.72	25.06	25.12	25.14	25.17	25.11
15.00	26.20	26.36	26.52	26.89	26.95	26.98	27.01	26.94
16.00	27.97	28.14	28.32	28.72	28.79	28.82	28.85	28.78
17.00	29.74	29.93	30.13	30.55	30.63	30.66	30.69	30.62
18.00	31.52	31.73	31.94	32.40	32.49	32.52	32.55	32.47
19.00	33.31	33.53	33.76	34.25	34.35	34.38	34.42	34.33
20.00	35.10	35.33	35.58	36.11	36.21	36.25	36.29	36.19
21.00	36.89	37.14	37.41	37.97	38.08	38.12	38.17	38.07
22.00	38.69	38.96	39.25	39.85	39.96	40.00	40.05	39.95
23.00	40.49	40.78	41.09	41.73	41.84	41.89	41.94	41.83
24.00	42.30	42.60	42.94	43.61	43.74	43.79	43.85	43.73
25.00	44.12	44.44	44.79	45.51	45.65	45.70	45.76	45.65
26.00	45.94	46.28	46.65	47.42	47.56	47.62	47.68	47.54
27.00	47.76	48.12	48.52	49.34	49.49	49.55	49.61	49.47
28.00	49.58	49.97	50.39	51.26	51.42	51.48	51.55	51.41
29.00	51.42	51.83	52.28	53.19	53.36	53.43	53.50	53.35
30.00	53.27	53.70	54.17	55.14	55.32	55.39	55.47	55.31
31.00	55.13	55.58	56.07	57.09	57.28	57.36	57.44	57.27
32.00	56.99	57.47	57.98	59.06	59.26	59.34	59.43	59.25
33.00	58.85	59.36	59.90	61.05	61.26	61.34	61.43	61.24
34.00	60.73	61.26	61.83	63.04	63.27	63.35	63.45	63.24
35.00	62.62	63.18	63.77	65.05	65.29	65.38	65.48	65.26
36.00	64.51	65.10	65.73	67.07	67.32	67.42	67.53	67.29
37.00	66.42	67.04	67.70	69.11	69.37	69.47	69.58	69.33
38.00	68.34	68.99	69.67	71.16	71.43	71.54	71.65	71.40
39.00	70.27	70.95	71.67	73.23	73.51	73.62	73.74	73.48
40.00	72.20	72.92	73.68	75.31	75.61	75.73	75.86	75.57
41.00	74.16	74.92	75.71	77.41	77.73	77.85	77.99	77.68
42.00	76.14	76.92	77.76	79.53	79.86	79.99	80.13	79.81
43.00	78.12	78.94	79.83	81.67	82.01	82.15	82.30	81.96
44.00	80.14	80.99	81.91	83.83	84.19	84.33	84.49	84.13
45.00	82.16	83.05	84.01	86.01	86.38	86.53	86.70	86.32
46.00	84.21	85.14	86.14	88.21	88.60	88.75	88.92	88.53
47.00	86.29	87.25	88.28	90.45	90.84	90.99	91.16	90.76
48.00	88.39	89.38	90.45	92.67	93.08	93.24	93.42	93.00

TABLE XII. TEMPERATURE CORRECTIONS

(Standard hydrometer, range 10° Bé.)

Observed Bé.	140° to 100° F.	140° to 60° F.	100° to 60° F
	42.00 D. E. C. S. U.		
−2.01	1.30	2.01	
−0.71	1.29	2.02	0.71
0.00	1.29	2.02	0.72
5.00	1.26	2.04	0.77
10.00	1.23	2.06	0.82
15.00	1.19	2.06	0.86
20.00	1.15	2.03	0.88
25.00	1.10	1.99	0.89
30.00	1.04	1.93	0.89
35.00	0.97	1.83	0.87
40.00	0.89	1.70	0.83
45.00	0.79	1.53	0.75
	55.00 D. E. C. S. U.		
−2.01	1.30	2.01	
−0.71	1.29	2.02	0.71
0.00	1.29	2.03	0.72
5.00	1.25	2.06	0.79
10.00	1.22	2.07	0.84
15.00	1.18	2.06	0.87
20.00	1.14	2.04	0.90
25.00	1.09	2.00	0.91
30.00	1.03	1.93	0.90
35.00	0.96	1.83	0.88
40.00	0.88	1.69	0.83
45.00	0.79	1.52	0.75
	89.00 D. E. Sugar		
−2.01	1.30	2.01	
−0.71	1.30	2.03	0.71
0.00	1.29	2.03	0.72
5.00	1.26	2.06	0.79
10.00	1.23	2.08	0.84
15.00	1.18	2.08	0.89
20.00	1.14	2.06	0.91
25.00	1.09	2.01	0.92
30.00	1.03	1.93	0.91
35.00	0.96	1.82	0.88
40.00	0.87	1.68	0.82
45.00	0.77	1.50	0.74

TABLE XIII. TEMPERATURE CORRECTIONS

(In Baumé to be added or subtracted to observed Baumé to reduce to 100° F.)

Temperature, ° F.	Observed Baumé 0.0	5	10	15	20	25	30	35	40	45
	Subtract from Observed Baumé									
60	0.72	0.79	0.84	0.87	0.90	0.91	0.90	0.88	0.84	0.77
65	0.64	0.70	0.75	0.77	0.79	0.80	0.79	0.77	0.73	0.66
70	0.56	0.61	0.65	0.67	0.69	0.69	0.68	0.67	0.63	0.57
75	0.48	0.52	0.55	0.57	0.58	0.58	0.57	0.56	0.52	0.48
80	0.39	0.43	0.44	0.46	0.47	0.47	0.46	0.45	0.42	0.39
85	0.30	0.33	0.34	0.35	0.36	0.36	0.35	0.33	0.31	0.29
90	0.21	0.23	0.23	0.24	0.24	0.24	0.24	0.22	0.21	0.19
95	0.11	0.12	0.12	0.12	0.13	0.12	0.12	0.11	0.10	0.09
	Add to Observed Baumé									
105	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.10	0.10
110	0.24	0.24	0.25	0.25	0.25	0.25	0.24	0.23	0.21	0.19
115	0.37	0.38	0.39	0.39	0.39	0.38	0.36	0.35	0.32	0.29
120	0.51	0.52	0.53	0.54	0.53	0.51	0.49	0.46	0.43	0.39
125	0.66	0.68	0.69	0.69	0.67	0.65	0.62	0.58	0.54	0.49
130	0.84	0.84	0.85	0.84	0.82	0.79	0.75	0.71	0.65	0.59
135	1.05	1.04	1.03	1.01	0.98	0.94	0.89	0.83	0.76	0.69
140	1.29	1.26	1.23	1.19	1.14	1.09	1.03	0.96	0.88	0.79

TABLE XIV. TEMPERATURE CORRECTIONS

(In Baumé to be added to observed Baumé to reduce to 60° F.)

Temperature, ° F.	Observed Baumé 0.0	5	10	15	20	25	30	35	40	45
60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
65	0.08	0.09	0.09	0.10	0.11	0.11	0.11	0.11	0.11	0.10
70	0.16	0.18	0.19	0.20	0.21	0.22	0.22	0.21	0.21	0.19
75	0.24	0.27	0.29	0.30	0.32	0.33	0.33	0.32	0.31	0.28
80	0.33	0.36	0.40	0.41	0.43	0.44	0.44	0.43	0.41	0.37
85	0.42	0.46	0.50	0.52	0.54	0.55	0.55	0.55	0.52	0.47
90	0.51	0.56	0.61	0.63	0.66	0.67	0.66	0.66	0.62	0.56
95	0.61	0.67	0.72	0.75	0.77	0.79	0.78	0.77	0.73	0.66
100	0.72	0.79	0.84	0.87	0.90	0.91	0.90	0.88	0.83	0.75
105	0.84	0.91	0.96	0.99	1.02	1.03	1.02	1.00	0.93	0.85
110	0.96	1.03	1.09	1.12	1.15	1.16	1.14	1.11	1.04	0.94
115	1.09	1.17	1.23	1.26	1.29	1.29	1.26	1.23	1.15	1.03
120	1.23	1.31	1.37	1.41	1.43	1.42	1.39	1.34	1.25	1.13
125	1.39	1.47	1.53	1.56	1.57	1.56	1.52	1.46	1.36	1.23
130	1.57	1.64	1.69	1.71	1.72	1.70	1.65	1.59	1.47	1.33
135	1.78	1.84	1.87	1.88	1.88	1.85	1.79	1.71	1.58	1.42
140	2.03	2.06	2.07	2.06	2.04	2.00	1.93	1.83	1.69	1.52

TABLE XV. ASH CORRECTION FOR 40.00° BÉ. (140°/60° F.)

Ash %	Decrease in Dry Substance %
1.0	0.51
2.0	1.01
3.0	1.51
4.0	2.00
5.0	2.50
6.0	2.98
7.0	3.41
8.0	3.76

The ash content of a sirup affects the dry substance for a given Baumé. Of the four sirups used, the first three have ash contents essentially in proportion to the dextrose equivalent, thus permitting a cross plot wherein coordinates dry substance and dextrose equivalent are plotted for the corresponding values for each Baumé.

In this plot each millimeter equaled 0.10 per cent D. S. and 0.10 D. E. The curve for each Baumé was found to fit a straight line within the experimental error of 0.01° Bé. or 0.02 per cent D. S. This observation was checked by a number of points at 32.8, 36.5, 82.0, and 83.6 D. E. with sirup prepared or obtained for this particular purpose. The data obtained by extrapolation and interpolation for the usual dextrose equivalents at 60.0°, 100.0°, and 140.0° F. are shown in Tables IX, X, and XI.

As noted, the ash content of a given sirup changes the dry substance for a given Baumé—that is, the addition of ash lowers the dry substance for a given Baumé. This ash effect becomes very important in the manufacture of refined sugar, where second and third corn sugar sirups and hydrol are obtained with increasing amounts of ash, up to 8 per cent. Thus a table of ash corrections is most important. In Tables IX, X, and XI, the last two columns are headed D. E. 91.2, ash 0.61 per cent, and D. E. 90.7, ash 1.22 per cent. If these dextrose equivalents are reduced to an ash-free basis they are the same. Thus the difference between these dry substance values for all Baumés becomes a measure of the effect of 0.61 per cent ash. This is 0 at 0° Bé. and increases as the Baumé is increased. Thus it would be possible to prepare a series of such curves for different amounts of ash, provided a cross curve for a given Baumé was obtained—that is, a curve showing the effect of increasing amounts of ash on the dry substance in a given sirup having a constant dextrose equivalent (carbohydrate solids basis) and a constant Baumé.

TABLE XVI. COMMERCIAL TABLE

(Bé. = Bé. 140° F./60° F. + 1.00°)

Baumé	Specific Gravity[a]	Pounds per Gallon[a]	Dextrose Equivalent and Ash 30.00 0.28	42.00 0.28	55.00 0.30	82.00 0.41	87.00 0.61	89.00 0.61	91.2 0.61	90.7 1.22
			Per Cent Dry Substance							
0.00	1.0000	8.328	1.76	1.77	1.78	1.80	1.80	1.80	1.80	1.80
1.00	1.0069	8.386	3.50	3.52	3.53	3.58	3.59	3.59	3.59	3.59
2.00	1.0140	8.445	5.24	5.27	5.29	5.36	5.38	5.38	5.38	5.37
3.00	1.0211	8.504	6.98	7.02	7.06	7.15	7.17	7.17	7.18	7.17
4.00	1.0285	8.565	8.72	8.77	8.82	8.94	8.96	8.96	8.97	8.96
5.00	1.0358	8.626	10.47	10.53	10.59	10.73	10.76	10.76	10.77	10.76
6.00	1.0433	8.689	12.22	12.29	12.36	12.53	12.56	12.57	12.58	12.56
7.00	1.0508	8.751	13.97	14.05	14.14	14.33	14.36	14.37	14.39	14.37
8.00	1.0585	8.815	15.73	15.82	15.91	16.13	16.17	16.18	16.20	16.17
9.00	1.0663	8.880	17.48	17.58	17.69	17.94	17.98	18.00	18.02	17.99
10.00	1.0742	8.946	19.24	19.35	19.48	19.75	19.79	19.81	19.83	19.80
11.00	1.0822	9.013	21.00	21.13	21.26	21.56	21.61	21.63	21.65	21.62
12.00	1.0903	9.081	22.76	22.90	23.05	23.38	23.44	23.46	23.48	23.45
13.00	1.0986	9.150	24.52	24.68	24.84	25.20	25.26	25.29	25.31	25.27
14.00	1.1071	9.220	26.29	26.46	26.64	27.02	27.09	27.12	27.15	27.11
15.00	1.1156	9.291	28.06	28.24	28.44	28.85	28.93	28.96	28.99	28.94
16.00	1.1242	9.362	29.83	30.03	30.24	30.69	30.77	30.80	30.84	30.78
17.00	1.1330	9.436	31.61	31.82	32.05	32.53	32.62	32.65	32.69	32.63
18.00	1.1419	9.510	33.39	33.61	33.86	34.38	34.47	34.51	34.55	34.48
19.00	1.1510	9.586	35.17	35.41	35.68	36.23	36.33	36.37	36.41	36.34
20.00	1.1602	9.662	36.95	37.21	37.50	38.08	38.19	38.23	38.28	38.20
21.00	1.1696	9.741	38.73	39.01	39.32	39.94	40.05	40.10	40.15	40.06
22.00	1.1791	9.820	40.52	40.82	41.15	41.81	41.93	41.98	42.03	41.94
23.00	1.1888	9.900	42.32	42.63	42.98	43.68	43.81	43.86	43.92	43.82
24.00	1.1986	9.982	44.12	44.45	44.82	45.56	45.70	45.75	45.81	45.71
25.00	1.2086	10.065	45.92	46.27	46.66	47.44	47.60	47.65	47.71	47.60
26.00	1.2188	10.150	47.73	48.10	48.51	49.34	49.50	49.56	49.62	49.50
27.00	1.2291	10.236	49.54	49.93	50.37	51.24	51.40	51.47	51.54	51.41
28.00	1.2396	10.324	51.36	51.77	52.23	53.15	53.32	53.39	53.47	53.33
29.00	1.2503	10.413	53.19	53.62	54.09	55.07	55.25	55.32	55.40	55.25
30.00	1.2612	10.504	55.02	55.47	55.97	56.99	57.18	57.26	57.34	57.19
31.00	1.2723	10.596	56.85	57.33	57.85	58.93	59.13	59.21	59.30	59.13
32.00	1.2836	10.690	58.69	59.19	59.73	60.87	61.08	61.16	61.25	61.09
33.00	1.2950	10.785	60.53	61.06	61.63	62.82	63.04	63.13	63.22	63.05
34.00	1.3067	10.883	61.39	62.94	63.53	64.79	65.02	65.11	65.21	65.02
35.00	1.3186	10.982	64.25	64.83	65.44	66.76	67.01	67.10	67.21	67.00
36.00	1.3307	11.083	66.11	66.72	67.36	68.75	69.01	69.11	69.22	69.00
37.00	1.3430	11.185	67.99	68.62	69.30	70.75	71.01	71.12	71.24	71.01
38.00	1.3556	11.289	69.88	70.54	71.24	72.75	73.03	73.14	73.26	73.03
39.00	1.3684	11.396	71.77	72.46	73.19	74.78	75.07	75.18	75.31	75.06
40.00	1.3815	11.505	73.66	74.39	75.16	76.82	77.12	77.24	77.37	77.10
41.00	1.3947	11.615	75.58	76.34	77.14	78.86	79.18	79.30	79.44	79.17
42.00	1.4083	11.729	77.51	78.30	79.13	80.92	81.25	81.38	81.52	81.25
43.00	1.4221	11.844	79.45	80.27	81.14	83.00	83.35	83.48	83.63	83.33
44.00	1.4361	11.961	81.39	82.25	83.17	85.10	85.46	85.60	85.75	85.44
45.00	1.4506	12.081	83.36	84.25	85.20	87.21	87.58	87.72	87.88	87.56
46.00	1.4652	12.202	85.34	86.26	87.26	89.33	89.71	89.86	90.03	89.69
47.00	1.4802	12.328	87.33	88.29	89.34	91.47	91.87	92.03	92.21	91.84

[a] In air.

The ash encountered in this industry is largely sodium chloride formed from the neutralization of the hydrolyzing acid (hydrochloric) by soda ash. This ash is increased automatically as crystalline dextrose is withdrawn from the massecuite. The method chosen for establishing a cross curve was as follows:

It was assumed that the ash effect would be essentially independent of dextrose equivalent—that is, dependent upon a ratio of carbohydrate to salt. Since corn sirup is more easily dried than sugar and free from the criticism of instability on drying, the test was made with corn sirup. A 5-gallon conversion was made in pilot plant equipment to approximately 42 D. E., using sulfuric acid for hydrolysis and barium carbonate for neutralization. This was refined in the usual manner, and concentrated to 40° Bé. at 140° F. (41° Bé. commercial). This sirup was substantially ash-free (0.07 per cent). To this was added sodium chloride in amounts to make 1.00, 2.00, 4.00 and 8.00 per cent (dry substance basis). Sirups were made above and below 40° Bé. (140°/60° F.) and specific gravity and dry substances were obtained. Since the Baumé range was small, a straight line was drawn between the two points, the values being plotted on a scale which was five times that previously used, and the exact values for 40.00° Bé. (140°/60° F.) were obtained for each of the salt concentrations.

The data obtained together with the calculated ash-free point appear in Figure 3. The specific values are shown in Table XV.

The curve obtained is a straight line up to 6 per cent and bends slightly thereafter. For commercial work the salt correction may be taken as a straight line. Thus a cross curve for salt effect has been obtained for a heavy Baumé, and the data, together with the data for salt effect for 0.61 per cent ash for all Baumés, enable a family of curves to be drawn of high precision and of greater accuracy than is generally required for factory work.

Attention was called above to the commercial method of determining Baumé—namely, the reading at 140° F. plus 1.00° Bé. or Bé. = Bé. 140°/60° F. + 1.00. All sirups are sold in the industry on this basis. Table XVI is the commercial table that has been accepted by the Corn Industries Research Foundation for its member companies for use in the sale of its products. The specific gravities and the weights per gallon are those in air. This method of assignment was suggested by the National Bureau of Standards for use in the preparation of a commercial table.

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(7) Evans, J. W., and Fetzer, W. R., *Ibid.*, 7, 41 (1935).
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Pressure Stopcock

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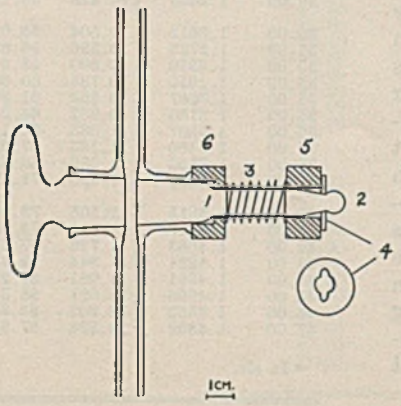
WITH present laboratory techniques it is frequently necessary to employ for gas absorption, gas analysis, solvent extraction, and the like, glass systems which operate under superatmospheric pressures. As far as this writer is aware only special, commercially manufactured pressure stopcocks operate reliably. Rubber bands and metal clips either impede the operation of the stopcock or do not prevent lifting of the plug, thereby causing escape of the confined material.

The design of the commercially available stopcock requires special glass-drilling equipment and is, therefore, not well adapted to duplication at the laboratory. A pressure stopcock which can be adapted from the generally stocked glass stopcock, with ordinary glass-blowing skill and at insignificant cost should, therefore, prove of help to the laboratory worker.

The pressure stopcock presented here has been designed to fill this gap. Depending upon spring strength and the type of stopcock lubricant pressures of 30 pounds or more may be applied. The stopcock has proved its worth in various apparatus.

The drawing illustrates a standard 4 mm. Pyrex stopcock. It is recommended that stopcocks made from Pyrex be used in the assembly of the pressure stopcock. Only those possessing a protruding portion of the barrel for a rubber ring should be selected. As an added precaution against damage, during sealing, the ground portion of the barrel may be protected by a moist strip of asbestos paper. Stopcocks made from soft glass could probably be used only if reground after the sealing operation.



1 is a solid glass rod of slightly smaller diameter than that of the plug body, sealed to the latter without undue heating of the ground portion of the plug. This seal should be carefully annealed. The rod is drawn out in the shape indicated by 2 and the rounded portion is flattened with forceps or pliers to fit through the elongated portion of the hole in the washer. Part 6 is machined from a metal bar of suitable size or a nut may be adapted. It rests against the evenly ground reinforced rim of the stopcock shell and fits rather loosely over the extension of the stopcock plug. 5 designates a metal bar with a hole of about the same diameter as part 6. Spring 3 should be of suitable strength and its ends should preferably be squared to ensure proper seating against 5 and 6.

The stopcock is assembled by inserting the properly lubricated plug (*1*) into the stopcock shell, slipping cap 6, spring 3, and part 5 over the plug extension, and securing these parts by locking plate 4, which is turned 90 degrees after insertion.

Exact dimensions depend on the stopcock size applied, but the proportions of the various component parts are apparent from the drawing.

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Analysis of the Thixotropy of Pigment-Vehicle Suspensions

Basic Principles of the Hysteresis Loop

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THIXOTROPIC systems have been studied in numerous ways, but an investigation of the subject by means of the hysteresis loop—one of the most fruitful methods—seems to have been neglected. Very few references to the loop occur in the literature. An early paper by Hatschek (*9*, 1913) shows data that if replotted would give the loop. Ostwald (*11*), much later, observed thixotropic hysteresis behavior and would have obtained the characteristic loop if he had plotted his data in the necessary manner. Reiner (*14*) lists non-Newtonian types giving hysteresis loops. Pryce-Jones (*12*) shows a graph of a hysteresis loop and at the same time states a cardinal rheological principle: Thixotropy cannot be determined from a single consistency curve. The importance of the Pryce-Jones principle has not been universally recognized by rheologists.

To learn something of the extent and nature of thixotropic change in breakdown or buildup, it is necessary to have data that cover both the before and after states. This requires at least two curves. The hysteresis loop, obtained by means of the rotational viscometer (described by one of the authors in a recent paper, *6*) is the graph of both states. The loop is obtained by plotting both curves together—i. e., the upcurve, demonstrating breakdown, and the downcurve, showing the particular state of equilibrium to which the material has been brought. Instead of the loop, two downcurves obtained at two different thixotropic levels can be employed. In either case two curves are always necessary.

The Criterion of Thixotropy

A true sol has been defined as a colloidal suspension that has zero yield value. Freundlich (*3*) describes a thixotropic material as one that will undergo isothermally a gel/sol/gel transformation, but is very careful to qualify this definition by pointing out that the conversion to a complete sol is "a specially characteristic and limiting case of thixotropy". This qualification permits such suspensions as paints and printing inks to be classified as thixotropic. Freundlich further adds that suspensions not truly colloidal but containing particles of microscopic size such as "pastes of clay, etc.", "show extremely pronounced thixotropic behavior". He also includes under the phenomenon of thixotropy—and this is important—materials like gelatin, which "become less viscous and elastic on shaking or stirring but assume the original values of viscosity and elasticity when left to rest". Since elasticity is associated with the presence of yield value, it is evident that a material that only becomes "less elastic" (in addition to a decrease in viscosity) might still possess yield value. In other words, a complete transformation from a gel to a true sol is not a prerequisite for thixotropy. A partial transformation is all that is necessary. This is the attitude taken by Goodeve (*4*) and it is the one that will be used here.

Controversial Issues

There are four controversial points involved in the rheology of thixotropic systems. It is necessary that the authors' position in regard to them be made clear.

1. THE NONLINEARITY OF THE LOWER END OF THE CONSISTENCY CURVE. One of the primary causes of this curvature has been shown to arise from the gradual change of plug to laminar flow (*7*, *8*). Buckingham (*2*) showed that this condition occurs in capillary tube viscometers because the shearing force decreases from the capillary wall inward. Reiner (*13*) proved that this same condition exists in rotational viscometers and furthermore indicated that this curvature must become shorter when the distance between the bob and cup is decreased. Laboratory experiments have confirmed this conclusion. Hence the curvature, so far as actually known at present, could be entirely due to an instrumental effect and does not necessarily have to arise from any change in the structure of the material under low shearing stresses. If the distance between the bob and cup were infinitesimally small, there probably would be no curvature under such a condition. The authors realize, however, that Reiner's deductions are based on an entirely stable system and that thixotropy and pseudoplasticity might easily increase the length of the nonlinear portion of the curve beyond the amount predicted by Reiner.

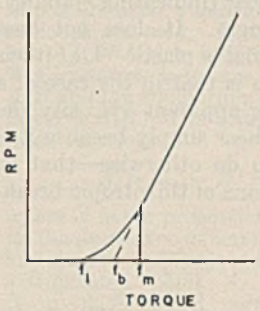

FIGURE 1

2. THE THREE DIFFERENT YIELD VALUES. Houwink (*10*) defines three types of yield values (Figure 1). The lower yield value is the intercept f_l where the first evidence of flow occurs. This is known to be where the outer layer of the "plug" begins to shear (*2*, *7*, *8*). The maximum yield value, f_m, is where the curve becomes linear (*7*, *13*). This is where plug flow is completely gone and the entire flow is laminar. Buckingham (*2*) shows that for capillary viscometers this state is attained only at infinite rates of shear and f_m is the intercept of the asymptote. The intercept, f_B, is the Bingham yield value. The authors' viewpoint is that these three intercepts are not three different yield values but three different functions of one and the same yield value. Reiner (*13*) has shown for rotational viscometers, where thixotropy and pseudoplasticity are not involved, that

$$f_l = 2\pi R_b^2 hf \quad (1)$$

$$f_m = 2\pi R_c^2 hf \quad (2)$$

$$f_B = [4\pi hf \ln (R_c/R_b)]/[1/R_b^2 - 1/R_c^2] \quad (3)$$

where R_c = radius of the cup
R_b = radius of the bob
h = depth of immersion of the bob
f = the real yield value

3. THE APPARENT VISCOSITY. This is a variable quantity depending on the rate of shear. It is obtained by dividing the ordinate (rate of flow; r. p. m.) by the abscissa (force; torque) and multiplying the product by an instrumental constant. It is obvious that apparent viscosity is not the coefficient of viscosity, which by definition is the number of

dynes per sq. cm. that will give a velocity gradient of 1 cm. per second. Other than being the ratio of force to rate of flow it is not "apparent" what it is; hence, it is something of a misnomer and perhaps an unfortunate one.

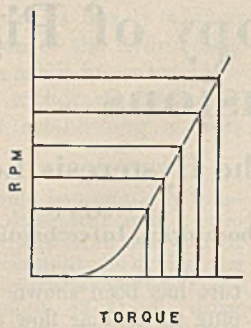

FIGURE 2

An inspection of Figure 2 will show that the ratio of torque—to r. p. m. must decrease with increasing rate of shear—i. e., the apparent viscosity decreases as the speed of the agitation or stirring increases. Unfortunately this reaction is an isothermal one and reversible; hence, any investigator who considers apparent viscosity to be a substitute for coefficient of viscosity will erroneously classify the material giving the consistency curve in Figure 2 as thixotropic. Now all that can be said about the curve is that except for its lower end it is linear (indicating stability) and does not pass through the origin. It does not pass through the origin because the material is plastic—i. e., it has a yield value. The authors' opinion is that in the case of a curve like the one in Figure 2, the apparent viscosity decreases with an increase of rate of shear simply because it is mathematically impossible for it to do otherwise—that is, it is a question of geometry and not one of thixotropic breakdown of the sample during testing.

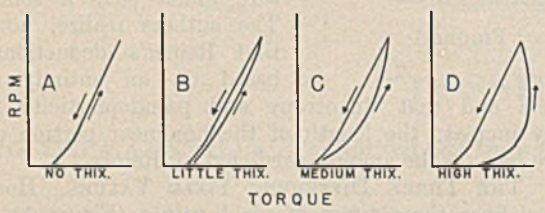

FIGURE 3. THIXOTROPY

Time of measurement constant

4. PLASTIC FLOW WITHOUT LIQUEFACTION. There is a widespread belief that certain suspensions, like finely divided quartz in carbon tetrachloride, are highly thixotropic. If such a suspension, of the right consistency, is put into a test tube and inverted it will not flow out because of its high yield value. If the thumb is placed over the end of the tube and the tube is shaken, it can be observed that the material flows. If the thumb is suddenly removed immediately after shaking has ceased, the material will not flow out. The customary argument is that the material would not flow during shaking if it did not first liquefy—i. e., turn into a sol. When a metal, many degrees below its melting point, is drawn through a die the metal is easily visualized as undergoing plastic flow. In other words, it is a solid before it enters the die, while it passes through the die, and after it is drawn from the die. At no time is the metal considered to be liquid because at no time is it above its melting point. If consistency curves could be obtained for metals like steel, bronze, copper, etc., it seems obvious that they would not be Newtonian. They would all possess intercepts, such as that shown in Figure 3, *A;* yet no one has classified these metals as thixotropic. However, when soft mushy materials of the quartz-carbon tetrachloride suspension type are considered, it is often assumed that flow takes place only when preceded by an intermediate state of liquefaction.

This is an important point, for if it should be true—and the authors believe it is not—then the quartz-carbon tetrachloride type of suspension would be thixotropic in spite of the fact that it gives no hysteresis loop. If such a non-loop-forming material (see also Figure 12) must be accepted as highly thixotropic, a conflict is introduced in our reasoning, for it would mean that at both ends of our series of loops (Figure 3) a high state of thixotropy would exist. In other words, no hysteresis loop *A* and a large hysteresis loop *D* would both indicate a high state of thixotropy. Any investigator examining a series of thixotropic materials like those represented in Figure 3 would unhesitatingly say that *D* was more thixotropic than *C*, and *C* more thixotropic than *B*. It therefore seems unreasonable that there should be a sudden increase in thixotropy in going from *B* to *A*. Consequently the authors have adopted the viewpoint that curve *A* indicates plasticity with no thixotropy. By so doing confusion is eliminated and a large part of the theory of thixotropy becomes rationalized.

The Hysteresis Loop

The method of making the loop has been described in detail in a previous paper (*6*).

Briefly, it is obtained with a rotational viscometer of special design. This instrument is operated through a Graham continuously variable transmission (Briggs and Stratton Mfg. Co.) which enables the investigator to change the r. p. m. without stopping the rotation of the cup. The procedure commences with the upcurve, starting at the lowest practical r. p. m. The speed is increased continuously and rapidly while noting the change in torque induced. At some specified upper limit the speed is reversed and the downcurve taken. If the material is thixotropic, the up- and downcurves when plotted together will not coincide, thus forming the loop (Figure 3, *B, C, D*).

THE TIME ELEMENT IN THIXOTROPIC BREAKDOWN. If restraints could be placed on the thixotropic material at the beginning of the upcurve so that it could not break down, the consistency curve would follow a straight path, such as T_2A (Figure 4). If the restraints should then be removed and the r. p. m. at *B* maintained, the torque would decrease from T_A until a state of equilibrium is reached at some point T_{An}. Since the product of the two coordinates (r. p. m. × torque) gives a quantity with the dimensions of power, it is evident that the area of the parallelogram OT_AAB must be the minimum power that will break down the material from the thixotropic level T_2A to the thixotropic level T_2A_n using the velocity gradient given at *B*. In actual practice restraints cannot be employed and so the material continuously breaks down as the upcurve is taken. The real upcurve follows a path such as T_2CA_1. If on reaching A_1 the r. p. m. is kept constant and sufficient time is allowed for equilibrium to be attained, the torque will drop from T_{A1} to T_{An}. The downcurve A_nT_2 will be linear, if not too much time is consumed in running it.

As the time taken for the upcurve is increased, the curve moves in the direction of the curve T_2DA_n. If equilibrium points are run—i. e., if sufficient time is allowed at each successive r. p. m. for the thixotropic buildup to equal the thixotropic breakdown—then the upcurve will follow the path T_2DA_n and not the straight path T_2A_n. This means that after equilibrium has been attained

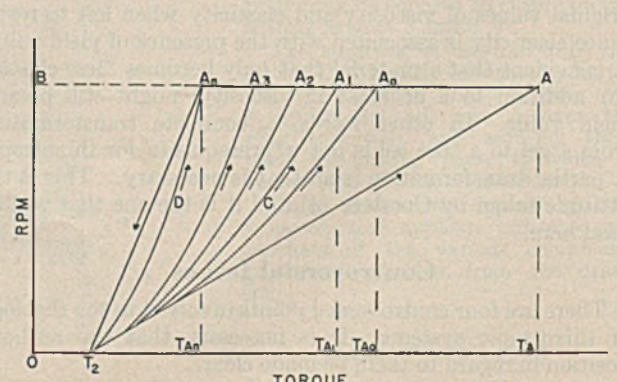

FIGURE 4. EFFECT OF TIME

for any given r. p. m. further breakdown can be had only by increasing the velocity gradient—i. e., by using a higher r. p. m. (more power).

There are two methods then for breaking down thixotropic structure: by increasing the velocity gradient, and by prolonging the time of the applied force. When the time used in taking the measurements for the upcurve is decreased—i. e., when the time during which each successive r. p. m. is allowed to operate is lessened—then the upcurve is displaced in the direction of the curve T_2A. A hypothetical curve run in such a short time that breakdown resulting from the time element is negligible would occupy some position as T_2A_0, where point A_0 would fall between the theoretical point A and the last (fastest) experimentally determinable point, A_1. The curve T_2A_0 should not coincide with curve T_2A because the former is run without restraints while the latter is run with them.

Any curvature of T_2A_0 must result from thixotropic breakdown; but this breakdown has taken place simultaneously with the commencement of flow. In other words the curvature of T_2A_0 arises only from velocity gradient, because the time element is in this case negligible. Such a model of flow would necessitate exceedingly short nondistensible bonds.

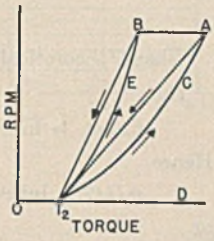

FIGURE 5

When the downcurve is commenced as soon as the maximum r. p. m. is reached, the loop will be referred to simply as a hysteresis loop—e. g., Figure 5, loop T_2CAT_2. When the maximum r. p. m. is applied over a time interval sufficient to attain a state of equilibrium, the loop will be called an equilibrium hysteresis loop—e. g., Figure 5, loop T_2CABT_2. When every point on the upcurve is an equilibrium point, the loop will be called the minimum equilibrium hysteresis loop—e. g., Figure 5, loop T_2EBT_2. The consistency of the material at point A is given by its plastic viscosity, derived from the angle DT_2A; its yield value is obtained from the torque T_2. When the material is broken down further by the prolonged application of the maximum r. p. m. until equilibrium is reached at B, it will have a plastic viscosity derived from the angle DT_2B, and a yield value again obtained from torque T_2. The equations for calculating these consistency factors are derived from Reiner's work (*6*, *13*):

$$\text{Plastic viscosity, } U = (T - T_2)\,S/\omega \qquad (4)$$

$$\text{Yield value, } f = T_2C \qquad (5)$$

$$S = (1/R_b^2 - 1/R_c^2)/4\pi h \qquad (6)$$

$$C = S/\ln(R_c/R_b) \qquad (7)$$

where

ω = angular velocity

Unlike "apparent viscosity", plastic viscosity has a definite meaning. It is the number of dynes per sq. cm. in excess of the yield value that will produce a velocity gradient of 1 cm. per second. Yield value is the dynes per sq. cm. that will just cause flow. These quantities are given by Equations 4 and 5.

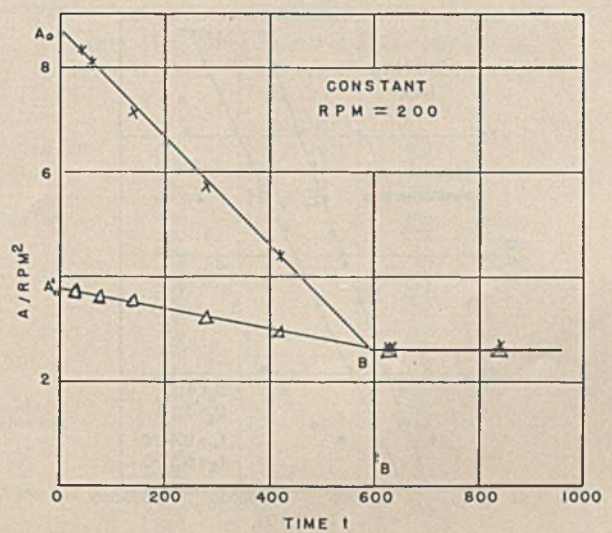

FIGURE 6. EFFECT OF TIME

TABLE I. EXPERIMENTAL DATA FOR FIGURE 6, GIVING EQUATION 8

A = area of hysteresis loop in (gram-cm.) r. p. m.
$A_{eq.}$ = area of equilibrium hysteresis loop. Its dimensions are those of A.
t = time of upcurve in seconds
RPM is constant = 200.

t	$A/(RPM)^2$	$A_{eq.}/(RPM)^2$
31.5	3.7	...
44	...	8.3
61	...	8.1
75	3.6	...
140	3.5	7.1
280	3.2	5.7
420	2.9	4.4
630	2.6	2.6
840	2.6	2.7
1570	...	2.6
2520	2.6	2.6

If experimentally determined areas like the diagrammatic ones in Figure 4, $T_2A_1A_nT_2$, etc., are plotted against their respective times (in seconds), a linear relationship results. This relationship is obtained whether hysteresis loops or equilibrium hysteresis loops are used. Data of this type are plotted in Figure 6, but $A/(RPM)^2$ is used instead of area. The hysteresis loops are given in curve $A_0'B$ and the equilibrium hysteresis loops in curve A_0B. The general formula for these curves is

$$A = A_0 - Nt \;(t \leqq t_B) \qquad (8)$$

where N is the proportionality constant, t is the time taken in making the upcurve, and A_0 is the intercept at zero time. The extrapolated point A_0 times its top (r. p. m.)^2 should correspond to the area of the hypothetical equilibrium loop $T_2A_0A_nT_2$ given diagrammatically in Figure 4. Similarly the extrapolated point A_0' times its top (r. p. m.)^2 should correspond to the area of its hypothetical hysteresis loop.

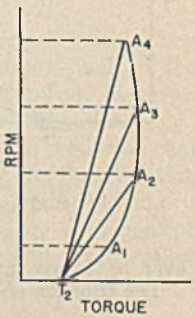

FIGURE 7

TABLE II. EXPERIMENTAL PROOF OF EQUATION 9

		Experimentally Determined Loop Area, A	$(RPM)^2$	$Q = A/(RPM)$
Yellow ink	1	1.61×10^4	1×10^4	1.61
		6.40	4	1.60
		10.0	9	1.11
		26.6	16	1.66
	2	2.64	1	2.64
		10.25	4	2.56
		26.06	9	2.78
		44.17	16	2.76
Red ink	1	1.5	1	1.50
		5.0	4	1.25
		12.9	9	1.43
		22.4	16	1.40
	2	3.63	1	3.63
		14.3	4	3.58
		32.0	9	3.55
		55.0	16	3.44
Blue ink		0.41	1	0.41
		1.82	4	0.45
		3.46	9	0.38
		7.6	16	0.47
White ink		0.54	1	0.54
		2.15	4	0.54
		5.00	9	0.55

THE VELOCITY GRADIENT ELEMENT IN THIXOTROPIC BREAKDOWN. If the time of application of each r. p. m. is maintained constant and the top or maximum r. p. m. is varied, a series of hysteresis loops such as those shown in Figure 7 occurs. The area of these loops plotted against the square of their respective top r. p. m. gives the linear equation

$$\text{(Area) } A = Q(RPM)^2 \qquad (9)$$

where Q is the proportionality constant and (RPM) is the top r. p. m. Equations 8 and 9 constitute the two basic principles involved in the subject of thixotropy. The existence of both principles—breakdown by time, and breakdown by velocity gradient—has been recognized by most investigators of thixot-

ropy; but they probably have not been expressed previously in the form of the equations given here.

The Upcurve

THIXOTROPIC BREAKDOWN. Let a be any point above T_2 on the upcurve (Figure 8). At point a the material has a viscosity given by the cotangent of TT_2a. If upon increasing ω to $\omega + d\omega$ there is no further thixotropic breakdown, the torque would increase from T to T_3. There is breakdown, however, and the torque is increased from T only to T_1; hence, the loss in torque resulting from breakdown is $(T_3 - T_1)$ or bc.

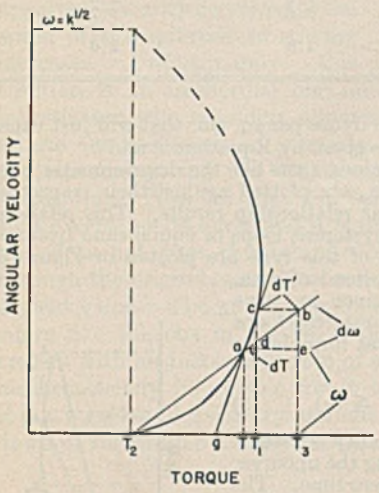

FIGURE 8

Let the total thixotropic loss in torque acquired in going from $\omega = 0$ to $\omega = \omega$ be equal to some quantity in excess of the yield value, such as $(T' - T_2)$. Also let it be assumed that $(T' - T_2)$ is proportional to the velocity gradient. Then

$$T' - T_2 = Z\omega/2\pi R^2hS \quad (10)$$

and

$$dT'/d\omega = Z/2\pi R^2hS \quad (11)$$

where Z is the proportionality constant, $\omega/2\pi R^2hS$ the velocity gradient at radius R, and dT' is the loss of torque resulting from breakdown when ω is increased by the amount $d\omega$. However, bc is also equal to this loss: hence $bc = dT'$.

The triangles abc and aT_2g are similar; consequently,

$$dT'/d\omega = (g - T_2)/\omega \quad (12)$$

From Equation 11 it follows that

$$g - T_2 = Z\,\omega/2\,\pi\,R^2hS \quad (13)$$

From Equations 10 and 13 it follows that

$$T' = g$$

and that the loss in torque from thixotropic breakdown, when ω is increased from $\omega = 0$ to $\omega = \omega$, is equal to $(g - T_2)$. In other words, the tangent at point a gives an intercept g on the torque axis from which the total breakdown (in loss of torque) up to point a can be determined.

EQUATION OF THE UPCURVE. In Figure 8 it can be seen that the net change in torque for an increase in angular velocity of $d\omega$ is ad. Then from the similar triangles bae and aT_2T,

$$dT'/d\omega + dT/d\omega = (T - T_2)/\omega \quad (14)$$

Substituting from Equations 12 and 13 and making the constant $Z/2\pi R^2h$ equal to $2/m$ gives

$$dT/d\omega - T/\omega + T_2/\omega = -2/mS \quad (15)$$

TABLE III. PRINTING INK DATA FOR FIGURE 10

RPM	Upcurve Torque	Downcurve Torque	Equilibrium Downcurve Torque
11	114 × 10⁴	49 × 10⁴	37 × 10⁴
14	136	66	45
21	161	88	67
26	182	106	76
33	196	120	87
42	205	133	98
48	216	151	111
55	225	160	121
62	233	174	128
69	236	193	139
76	244	202	150
83	248	214	162
90	253	230	168
97	262	240	180

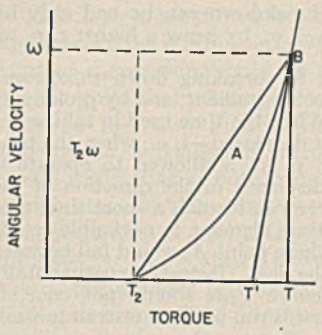

FIGURE 9

Multiplying by $\omega d\omega/\omega^2$ gives

$$\omega dT/\omega^2 - Td\omega/\omega^2 + T_2d\omega/\omega^2 = -2d\omega/mS \quad (16)$$

Then

$$d\,[(T - T_2)S/\omega] = -2d\omega/[m\omega \quad (17)$$

or

$$dU = -2d\omega/m\omega \quad (18)$$

Integrating and multiplying by $m/2$

$$mU/2 = -\ln\,\omega + \text{const.} \quad (19)$$

When U theoretically $= 0$, let ω have the value $k^{1/2}$ (see Figure 8). Then

$$\text{Const.} = \ln k^{1/2} \quad (20)$$

Hence

$$mU/2 = \ln(k^{1/2}/\omega) \quad (21)$$

or

$$e^{mU/2} = k^{1/2}/\omega \quad (22)$$

Squaring puts Equation 22 into a more useful form, as will appear later.

$$e^{mU} = k/\omega^2 \quad (23)$$

Upon substituting $(T - T_2)S/\omega$ for U, the equation of the upcurve is obtained.

$$T = \omega \ln k/mS - 2\omega \ln \omega/mS + T_2 \quad (24)$$

From Equation 23

$$mU = \ln k + \ln (1/\omega^2) \quad (25)$$

Hence, if experimentally determined U is plotted against experimentally determined $(1/\omega^2)$ on semilogarithmic paper a linear relationship should result. This is what happens, as shown in the section on experimental results. Equations 23 and 24 are thus confirmed.

AREA OF THE LOOP. The area, A, of the loop (Figure 9) is

$$A = \int_0^\omega Td\omega - T_2\omega - (T - T_2)\omega/2 \quad (26)$$

Substituting the value of T given in Equation 24 and integrating gives

$$A = \omega^2 \ln k/2mS - \omega^2 \ln \omega/mS + \omega^2/2mS - (T - T_2)\omega/2 \quad (27)$$

From Equation 24

$$\omega^2 \ln k/2mS = \omega^2 \ln \omega/mS + (T - T_2)\omega/2 \quad (28)$$

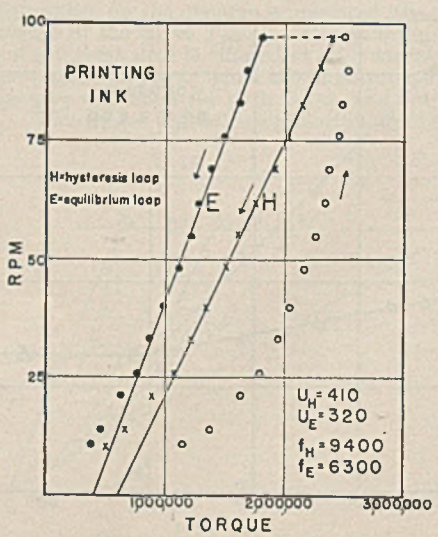

FIGURE 10

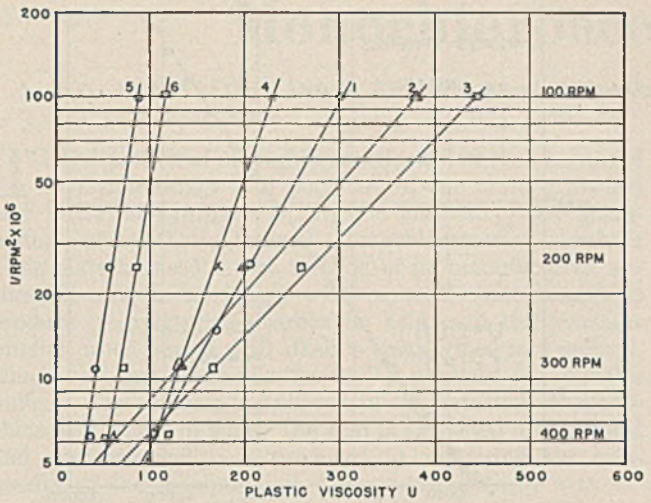

FIGURE 11

Substituting in Equation 27 gives

$$A = \omega^2/2mS \tag{29}$$

which shows that A is directly proportional to ω^2. This is confirmed by the empirical relationship given in Equation 9.

Other important relationships derived from the preceding equations are

$$A = Z\omega^2/8\pi R^2hS \tag{30}$$

$$dT'/d\omega = 4A/\omega^2 \tag{31}$$

$$A = {}^1/_2 \text{ area } \Delta\, T'T_2B \text{ (Figure 9)} \tag{32}$$

$$e^{mU} = k/2mSA \tag{33}$$

$$2/m = M = Z/2\pi R^2h = 2(U_1 - U_2)/\ln(\omega_2^2/\omega_1^2) \tag{34}$$

The proportionality constant, Z, is the loss in torque per unit increase in velocity gradient for the arbitrarily selected time employed in making the upcurve. Z depends on the instrument used in so far as the torque depends on the instrumental dimensions. However, m is independent of the instrument. Therefore $2/m$, or M, will be called "the coefficient of thixotropic breakdown". It is defined as the loss in shearing force per unit area per unit increase in velocity gradient for the arbitrarily selected time employed in making the upcurve.

Experimental Results

In a previous paper (*6*) a number of experimental flow curves were given showing loops of various sizes; consequently, in order to avoid unnecessary repetition only one experimental hysteresis loop is presented here (Figure 10 and Table III). Most pigment suspensions of the printing ink type give loops of this kind. The loop area is best obtained with a planimeter. This area must be multiplied by the proper conversion factors, so that the dimensions are correct for substituting in the various equations given here.

It was found empirically that a linear relationship is obtained by plotting plastic viscosity U against ln $(1/RPM^2)$ when the "time" is maintained constant (Figure 11, Table IV). By "time" is meant the time interval during which the shearing force is allowed to operate for each experimental point on the curve. This interval is regulated and controlled by the operator, who measures a predetermined number of points per minute. Each succeeding point is separated by exactly the same number of r. p. m. The results of the above work lead to the following empirical equation.

$$e^{mU} = \frac{\text{const.}}{RPM^2} \tag{35}$$

This checks the theoretical Equation 23, which was derived on the assumption that when the "time" is maintained constant the loss in torque resulting from thixotropic breakdown is directly proportional to the velocity gradient. Since the empirical and theoretical equations check, this assumption is probably correct.

Goodeve and Whitfield (*5*) use a similar hypothesis. They state that "the rate of breakdown is proportional to the shear". They develop and use this conception, however, in a different manner from that employed in this paper.

Equation 8 is empirical. No theoretical equation has been derived so far that corresponds to it. In this equation the top r. p. m. is maintained constant while the time is changed for each different curve (see Figure 6). In Equation 9 the opposite plan is followed. Time, here, is constant while the top r. p. m. is varied (see Table II). This equation

TABLE IV. EXPERIMENTAL DATA FOR FIGURE 11

[$RPM = 9.55\,\omega$, $Z = 4\pi R^2h/m$, $R = (R_c + R_b)/2$]

	RPM	$1/(RPM)^2$	Plastic Viscosity, U	Z
Yellow ink	100	100×10^{-6}	300	1.07×10^4
	200	25	205	
	260	15	172	
	400	6.3	104	
Red ink 1	100	100	380	1.42
	200	25	198	
	300	11	132	
	400	6.3	60	
2	100	100	447	1.80
	200	25	261	
	300	11	166	
	400	6.3	119	
3	100	100	255	0.74
	200	25	173	
	300	11	132	
	400	6.3	100	
Blue ink	100	100	82	0.21
	200	25	57	
	300	11	44	
	400	6.3	38	
White ink	100	100	115	0.27
	200	25	88	
	300	11	72.5	
	400	6.3	53.5	

TABLE V. QUARTZ IN NUJOL DATA FOR FIGURE 12

RPM	Upcurve Torque	Downcurve Torque
9	161×10^3	145×10^3
13	179	163
20	196	196
27	214	216
34	232	232
40.5	245	247
49	259	261
55	273	273
62	283	288
70	294	296
77	304	308
84	314	319
92	325	332
98	337	340

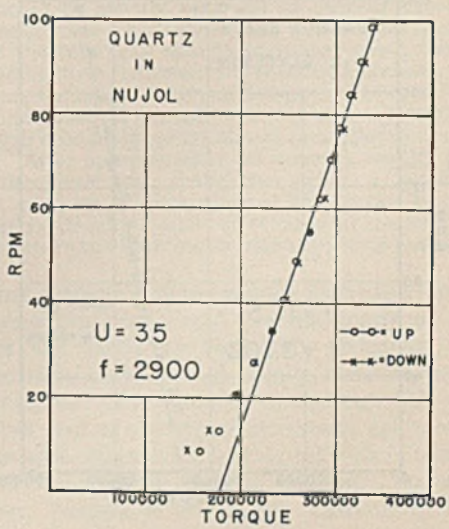

FIGURE 12

TABLE VI. CARBON BLACK IN GLYCEROL DATA FOR FIGURE 13

RPM	Upcurve Torque	Downcurve Torque
9	...	198 × 10³
13	...	210
20	238 × 10³	226
26	235	232
33	238	241
41	244	244
48	254	254
55	260	256
62	275	260
69	275	269
76	275	272
83	275	278
90	278	281
97	281	284
104	284	286
116	286	290
131	299	305
144	308	308
158	314	318
177	324	324
196	336	339

is empirical but it corresponds to the theoretically derived Equation 29.

In deriving Equation 17, m is treated as a constant. Equations 29 and 30 give the relation between A and ω for any single substance, m (or Z) being a constant for a given material. For different substances m (or Z) varies and the relationship between m (or Z) and A is expressed by Equation 33.

It is difficult to find pigment suspensions that give no loops. They can be made, however, and three of them are shown in Figures 12, 13, and 14 (Tables V, VI, and VII). The microscopic glass spheres used in Figure 14 were made in the Interchemical Research Laboratories by a method similar to the one developed by Bloomquest (*1*).

From the authors' viewpoint these non-loop-forming materials are plastic without being thixotropic. The more general conception is that such materials are so highly thixotropic that no apparatus built so far is quick enough to record either the breakdown or the buildup. Obviously, then, this breakdown or buildup is entirely conjectural, for its existence has not been proved experimentally. If conjecture is acceptable, it seems far more reasonable to say that the absence of a loop indicates the absence of thixotropy.

Conclusion

The authors have treated the subject here only in its elemental form—i. e., where the primary change occurring upon agitating a thixotropic suspension is a decrease in plastic viscosity. This treatment is sufficient for many cases. In a later paper an analysis will be given of materials involving a double change—i. e., in both plastic viscosity and yield value.

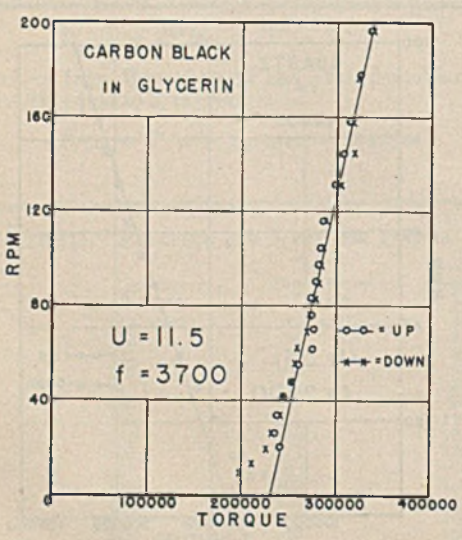

FIGURE 13

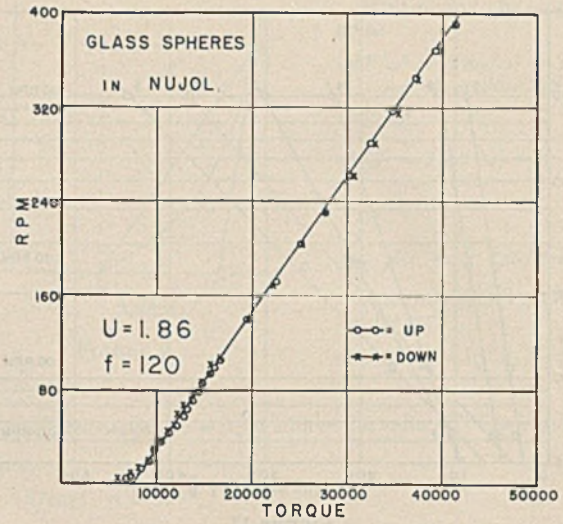

FIGURE 14

TABLE VII. GLASS SPHERES IN NUJOL DATA FOR FIGURE 14

RPM	Upcurve Torque	Downcurve Torque
5	67.7 × 10³	59.8 × 10³
8	70.2	72.8
15	83.2	80.5
21	91.0	91.0
30	96.2	98.8
37	104	104
45	112	110
51	120	117
59	128	122
65	132	128
72	138	135
79	143	140
87	148	146
94	156	156
101	161	156
107	166	166
141	195	195
174	226	223
204	252	252
234	278	278
264	301	307
291	325	330
319	349	354
345	372	375
369	393	398
392	414	414

Acknowledgment

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Monochloroacetic Acid in Wine

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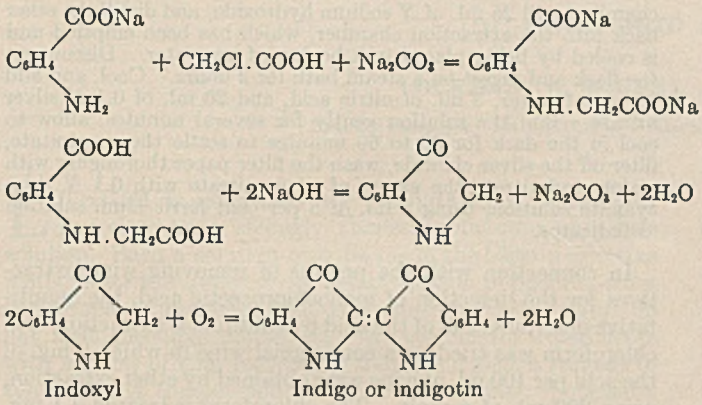
THE detection of monochloroacetic acid in the analysis of beverages brings into play one of the most renowned and historical syntheses of organic chemistry, the manufacture of synthetic indigo. Monochloroacetic acid is a basic material used in one method of its manufacture; anthranilic acid is condensed with monochloroacetic acid to produce phenylglycine-*o*-carboxylic acid, and the resultant product when heated with alkali is transformed into indoxyl, which on being made alkaline in the presence of air yields indigo. This process is followed in the detection of monochloroacetic acid in wine; the acid is extracted and purified and synthetic indigo is produced. Considering the complexity of the manipulation, the results obtained with exceedingly small quantities of the acid are excellent. At the present writing, indigo has been produced from 4.2 grams of the acid in 100 liters of wine or 42 parts per million by the use of a 200-ml. sample.

The steps in the formation of indigo from monochloroacetic acid are (*1*)



Methods for both the qualitative and quantitative determination of monochloroacetic acid in wine seem to be lacking, but Wilson (*3*) has developed a quantitative method for nonalcoholic beverages, and Chernoff (*2*), one for its qualitative detection in salad dressing. These were used as a basis for the method for its detection in wine.

In order to determine whether or not Wilson's method is applicable to wine, more than 100 authentic samples of wine were analyzed and in none of them was a trace of chlorine or chlorine compound extracted. Known quantities of monochloroacetic acid were then introduced into some of the samples and the chlorine compounds which were extracted corresponded to 94 per cent or more of the acid added.

The qualitative analysis of wine containing monochloroacetic acid is much more difficult than the quantitative determination. In extracting the very small quantities of the acid which may be present, there are also extracted wine congenerics which contaminate the acid to such an extent that Chernoff's method cannot be successfully followed without removing the interfering substances.

In the procedure outlined, the conditions of evaporation and heating of the residue at a high temperature for a few seconds which are prescribed permit attainment of consistent results when small quantities of the acid are present.

Detection of Monochloroacetic Acid in Wine

REAGENTS. Anthranilic acid reagent. Dissolve 1 gram of anthranilic acid in 50 ml. of water containing 0.3 gram of sodium hydroxide (7.5 ml. of *N* sodium hydroxide + 42.5 ml. of water).

Caustic soda solution. Dissolve 10 grams of caustic soda in 10 ml. of water.

Anhydrous sodium carbonate, C. P.; ether, C. P.; and benzene, thiophene-free, which meets A. C. S. specifications.

A dropper, 20 cm. (8 inches) long, with orifice 2 mm. in diameter. Rubber bulb, 2-ml. capacity.

METHOD. Place 200 ml. of sample, to which have been added 2 ml. of concentrated sulfuric acid in a continuous extractor and extract rapidly with ether for 2 hours, using a 500-ml. round-bottomed flask for the receiver, and preferably heating on a water bath over an electric heater. Pour the ether from the extraction chamber through a dry filter paper into the round-bottomed flask by tilting the extractor to drain as much of the ether as possible into the flask without contamination by the wine solution. Discard the wine and clean the extraction chamber. Add 5 ml. of distilled water to the ether in the flask, shake vigorously, and distill the ether back into the extraction chamber, which is cooled by being placed in a beaker of ice water. This usually leaves 30 to 35 ml. of alcoholic solution in the flask.

Place the alcoholic solution in a 15-cm. (6-inch) porcelain evaporating dish and evaporate it in the cold by use of an electric fan until approximately 10 ml. of liquid remain. Place the liquid in a separatory funnel, add 25 ml. of ether, shake vigorously for 5 minutes, allow to settle for 5 minutes, draw off the aqueous solution, and decant the ether into a 150-ml. beaker. Evaporate the ether in the cold by use of an electric fan, to the residue add 25 ml. of benzene, stir, and pour into a 50-ml. glass-stoppered Erlenmeyer flask, washing out traces of the residue by pouring back the benzene several times from the flask. Add 3 drops of water to remove the last remaining portions of residue and add them to the flask. Shake vigorously for 5 minutes, allow to settle for 5 minutes, decant the benzene into a 150-ml. beaker, evaporate in the cold by the use of an electric fan, and to the benzene-free residue add 2 ml. of the anthranilic acid reagent and 0.03 gram by actual weight of anhydrous sodium carbonate, and stir. This solution should be alkaline; if it is not, add another 0.03 gram of the sodium carbonate. No more than 0.06 gram of sodium carbonate should be added and the second portion should not be added unless absolutely necessary.

Pour the liquid into a 15 × 1.56 cm. (6 × 0.625 inch) test tube having a fully rounded bottom and heat in a boiling water bath for 30 minutes. Place in a drying oven at 120° to 130° C., with the test tube reclining at a 45° angle, and evaporate nearly to dryness or until only 1 drop of liquid remains. With the long dropper, add 2 drops of the caustic solution and replace in the oven to dry, keeping the contents in one spot of the test tube, which is inclined at a 45° angle. Dry at 120° to 130° C. for approximately 60 minutes, remove from the oven, and without cooling, plunge the test tube into a molten solder bath maintained at 305° to 312° C. for approximately 30 seconds. The temperature of the solder bath and the time of heating for this reaction should be strictly observed to prevent decomposition of the phenylglycine-*o*-carboxylic acid. As the alkali melts, the contents of the tube may assume an orange color, the depth of color depending upon the amount of reacting materials. Remove the tube from the bath, cool immediately, add at once 8 to 10 ml. of water, and shake in contact with the air. A green to deep blue color will become apparent almost immediately if indigo has developed. After approximately 10 minutes, acidify the liquid with *N* hydrochloric acid, shake thoroughly to subdivide the precipitate, and pour through a folded filter paper, washing with approximately 100 ml. of water to remove all the acid. Dry at room temperature the filter paper which contains the indigo.

In the first extraction of the sample with ether, in addition to any monochloroacetic acid present, many of the wine congenerics are partly or completely extracted, such as glycerol, tartaric acid, alcohol, higher alcohols, esters, and coloring material. The second extraction with ether removes 80 per cent of any monochloroacetic acid present and some of the wine congenerics, leaving the bulk of them behind in the small amount of aqueous solution. To purify the acid further, benzene is employed. Chloroform was tried as a solvent, but it removed too many impurities to give

Table I. Determination of Monochloroacetic Acid

Wine	Date of Analysis	Size of Sample	Alcohol	Monochloroacetic Acid
		Ml.	%	*P. p. m.*
Sauterne	June 13, 1942	200	13	90.0
	July 27, 1942	200		90.0
	January 4, 1943	200		90.0
Dry white	June 5, 1942	200	13	230.0
	January 5, 1943	100		226.8
Champagne dosage solution	August 13, 1942	200	14	406.0
	August 20, 1942	25		411.0
	January 5, 1943	50		396.8

satisfactory results. Benzene removed small amounts of the acid in a fairly pure state, the main deterrent to extraction being the presence of water. The importance of having as little water as possible present at this point in the procedure is shown by the fact that when a sample containing 20 mg. and one containing 40 mg. of the acid are extracted with benzene, 26 per cent of it is removed in each case, whereas if 7 ml. of water are present only 5 per cent of the acid is extracted with benzene. When as little as 2 mg. of the acid is separated from the wine in a fairly pure state for the final reactions, positive results are obtained with the test.

To obtain consistent results in the detection of minute quantities of monochloroacetic acid in wine, the method must be carefully followed in several details—the test tube kept at a 45° angle at all times, so that the residue is concentrated in one small spot; the initial evaporation in the test tube continued until only 1 drop of liquid remains; and the solid alkaline mass heated for 1 hour or more for complete desiccation, so that the final reaction at 305° to 312° C. may be obtained in the required time of approximately 30 seconds. Occluded moisture causes the compact mass to swell and allow too much air to take part in the reaction, and prevents the sudden reaching of the reaction temperature, resulting in prolonged heating and destruction of the phenylglycine-*o*-carboxylic acid.

In some of the wine, an emulsion formed during the first extraction with ether. Since no way was found to prevent it, the procedure was to continue the extraction for the required time, allowing the emulsion to be carried over into the receiver. The ether was distilled off as usual, and the solution containing the monochloroacetic acid was made up to the original volume with acidified water and reextracted with ether. This time no emulsion formed or not enough to be carried into the receiver.

Results so far obtained in this laboratory show that the presence of sulfur compounds in wine as normally used for preservative purposes has no effect on the determination of monochloroacetic acid and the presence of the acid does not interfere with the quantitative determination of sulfur dioxide therein.

In addition to various types of wine, the juice expressed from unripe grapes was analyzed. Samples of 175 ml. of juice from each of two varieties were analyzed by the qualitative method and in both cases the results were negative.

The chlorine compounds naturally present in normal wines are not extracted by ether; therefore any chloride in the ether extract must come from foreign material added to the wine.

Quantitative Determination

The following method is that of Wilson (*3*), with a few minor changes necessary to make it applicable to the small quantity of the acid found in wine.

Place 200 ml. of wine and 2 ml. of concentrated sulfuric acid in a continuous extractor and extract with ether for 2 hours. Disconnect the apparatus and drain through a dry filter paper into the flask as much of the ether as possible from the extraction chamber, add 25 ml. of *N* sodium hydroxide, and distill the ether back into the extraction chamber, which has been emptied and is cooled by being placed in a beaker of ice water. Disconnect the flask and digest on a steam bath for 2 hours. Cool, and add 50 ml. of water, 8 ml. of nitric acid, and 20 ml. of 0.1 *N* silver nitrate. Boil the solution gently for several minutes, allow to cool in the dark for 30 to 60 minutes to settle the precipitate, filter off the silver chloride, wash the filter paper thoroughly with water, and titrate the excess of silver nitrate with 0.1 *N* thiocyanate solution, using 5 ml. of 8 per cent ferric alum solution as indicator.

In connection with the process of removing wine extractives for the detection of monochloroacetic acid, the quantitative determination of the acid by continuous extraction with chloroform was tried on a commercial wine in which 9 mg. of the acid per 100 ml. of wine were obtained by ether extraction, using 200 ml. of sample. The chloroform extracted 7.1 mg. of the acid during the first 1.5 hours and 11.3 mg. during a further 1.5-hour extraction, making a total of 18.4 mg. from 200 ml. of sample. However, no advantage was gained by the use of chloroform instead of ether.

The range of quantities of monochloroacetic acid so far

Table II. Analyses of Wines and Champagnes

Mfg.	Wine	Alcohol	Storage	Monochloroacetic Acid	SO_2 Free	SO_2 Total	Indigo Produced	Chlorine Due to $CH_2ClCOOH$	Chlorine Due to Wine	Chlorine Total
		%		*P. p. m.*	*P. p. m.*	*P. p. m.*		*Gram/100 ml.*		
A	Sweet white	13	Tank	230	...	66.0	Yes	0.0085	0.0053	0.0138
	Sweet white	13	Tank	270	...	...	Yes	0.0101	0.0059	0.0160
	Sweet red	13	Tank	230	...	87.0	Yes	0.0085	0.0053	0.0138
	Sauterne	13	Bottle	90	...	209.9	Yes	0.0034	0.0030	0.0064
B	Sauterne	13	Bottle	90	...	74.2	Yes	0.0034	0.0059	0.0093
	Claret	13	Bottle	90	...	...	Yes	0.0034	0.0076	0.0110
C	Medium dry	12	Bottle	None	...	...	No	0.0000	0.0039	0.0039
	Sweet white	13	Bottle	None	26.0	256.0	No	0.0000	0.0057	0.0057
D	Dry white	..	Tank	None	...	...	No	0.0000	0.0036	0.0036
	Dry red	..	Tank	None	...	...	No	0.0000	0.0046	0.0046
E	Chateau type	..	Tank	None	253.6	771.8	No	0.0000	....	....
	Sauterne	12	Bottle	None	126.5	289.3	No	0.0000	....	....
F	Champagne	12	Bottle	187	...	...	Yes	0.0071	....	....
	Champagne	12	Bottle	137	...	...	Yes	0.0052	....	....
	Wine dosage solution	14		406	...	...	Yes	0.0153	....	....
	Sparkling wine	13	Bottle	230	...	...	Yes	0.0085	....	....
G	Dry white (6 samples)	13	Tanks	42 on each	...	...	Yes	0.0016	....	....

extracted from commercial wines and champagnes in this laboratory extends from 42 to 400 parts per million, which have fallen into four average groups: 42, 90, 150, and 250 parts per million.

To determine whether or not monochloroacetic acid is decomposed in wine on long standing, three samples were analyzed at various intervals of time. The results given in Table I not only show that the acid is stable in wine, but also check the accuracy of the method, since consistent figures were obtained with varying amounts of sample.

Table II contains some of the results of the analysis of various wines and champagnes made during the course of the work.

The total chlorine was determined by the official A. O. A. C. method for chlorine in wines, by the addition of sodium carbonate and evaporation to dryness. Two hours or more are required for the determination and Wilson has shown that monochloroacetic acid is completely hydrolyzed in that length of time, according to the equation $2CH_2Cl.COOH + Na_2CO_3 + H_2O = 2CH_2OH.COOH + 2NaCl + CO_2$. Therefore the figure for total chlorine in the wine includes that derived from any monochloroacetic acid present.

The chlorine due to monochloroacetic acid was determined by Wilson's method and that due to the wine was found by difference. The chlorine content due to the wine itself, as shown in Table II, is normal for the types of wine represented.

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A New Selective Reagent for Lithium

Application to the Rapid Volumetric Estimation of Lithium in the Presence of Potassium and Sodium

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LITHIUM is quantitatively precipitated as a complex periodate by a strongly alkaline potassium periodate solution. Such a solution may be made the basis of selective methods for the detection or determination of lithium, since with proper adjustment of alkalinity the other alkali metals do not form insoluble periodates. By systematic experiments with a series of trial reagents it was found that a reagent of the following composition gave the best results: potassium hydroxide, 24 grams; potassium metaperiodate, 10 grams; water, 100 ml.

The potassium hydroxide is first dissolved in the water, and after the solution has become nearly cool the potassium metaperiodate is dissolved. Simultaneous dissolution of the two solids is not a satisfactory procedure, since slight decomposition of the periodate then often occurs, apparently as a consequence of heat developed by the dissolution of the potassium hydroxide. The reagent undergoes slight decomposition by the action of light and should preferably be kept in a dark bottle. Because of its high alkalinity it should be placed in a paraffined container unless all of it is to be used within a very short time. When properly prepared and bottled, this reagent is stable for at least a month.

Qualitative Behavior

For delicate results in the detection of lithium, both the volume of test solution and the volume of reagent must be properly restricted. The test solution should be reduced to a volume of 1 ml. or less, and an equal volume of reagent should be added. With 1 ml. of each, 0.5 mg. of lithium present as chloride yields a distinct precipitate in one minute in the cold, and if the mixture is warmed to about 70° C., a distinct precipitate is produced by 0.1 mg. of lithium. The delicacy of the test is but little reduced by the use of larger volumes of reagent up to 5 ml., but is greatly reduced by the use of larger volumes of test solution.

As much as 50 mg. of sodium or ammonium, or 100 mg. of potassium, present as chloride does not yield a precipitate when the volume of test solution and reagent is each 1 ml. The presence of potassium, sodium, or both does not reduce the sensitivity of the test, but the presence of ammonium in appreciable concentration does. For example, in the presence of 50 mg. of ammonium no precipitate is produced when 1 ml. of reagent is added to 1 ml. of test solution containing 0.5 mg. of lithium. For best results, therefore, ammonium should be removed before testing for lithium with this reagent. Excess ammonium may be readily removed by boiling the test solution with a slight excess of concentrated potassium hydroxide solution, and the test may be made directly on the boiled solution, since some potassium hydroxide in the test solution does not interfere with the lithium reaction.

Because of the nature of the reagent, metals other than alkali metals must obviously be absent. Common anions such as chloride, nitrate, or sulfate do not interfere. Moreover, free strong or weak acids, when not present in high concentration, do not interfere, though when such acids are present some free iodine may be liberated on the first addition of the reagent to the test solution, but this disappears when the solution becomes basic. It is better in practice, however, to neutralize any free acid with potassium hydroxide solution before adding the reagent. Numerical data on interference are given under the discussion of the quantitative application of this reagent.

Properties and Composition of the Precipitate

The precipitate formed by this reagent is finely divided but may be separated by filtration without much difficulty, especially when the precipitation is performed slowly at an elevated temperature. It is soluble in water, in acid

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TABLE I. ANALYSES OF PRECIPITATES FORMED BY ADDITION OF PERIODATE REAGENT TO SOLUTIONS OF LITHIUM CHLORIDE

Preparation	Average Lithium Content	Average Iodine Content	Atomic Ratio of Lithium to Iodine
	%	%	
I	11.13	46.62	4.37
II	12.27	49.10	4.57
III	11.87	47.01	4.62
IV	12.42	48.34	4.70

Key to preparations:
I. Precipitated cold and dried in air at room temperature.
II. Precipitated cold and dried at room temperature over P_2O_5.
III. Precipitated hot and dried in air at room temperature.
IV. Precipitated hot and dried in air at 90° C.

solutions, or in weakly alkaline solutions. Only in strongly alkaline solutions does it have a low solubility in aqueous media. However, when precipitated in and washed with a strongly alkaline solution, considerable alkali is firmly retained by the precipitation, probably in large part by adsorption. Though but slightly soluble in the common organic solvents miscible with water, most of these react with it to an appreciable extent. Hence, it is difficult to isolate this precipitate in a pure state for the purpose of studying its composition. By precipitating a large enough quantity and washing it sparingly with small portions of distilled water, enough to provide samples for analysis may be isolated.

Actually, in preparing the four samples for the analyses shown in Table I, 200-mg. quantities of lithium were precipitated with 40 ml. of reagent. The precipitate separated by filtration was transferred to a centrifuge, and washed with 10 successive 5-ml. portions of distilled water. Lithium was determined either gravimetrically as the sulfate or volumetrically by the method described below. Iodine was determined by titration with standard arsenite solution after adding potassium iodide to the properly prepared solutions of the samples.

There are not only differences in the percentage composition of these samples, but no integral stoichiometric relationship exists between the proportions of lithium and iodine. The differences in composition are evidently due in part to differences in the extent to which the samples were dried, but all differences in composition cannot be ascribed to differences in the method of drying. It is not unlikely that some alteration of the original composition of the precipitates occurred on washing them with water, and this may account in part for the observed differences in composition. However, neither the method of drying nor the method of washing can account for the lack of integral stoichiometric ratio between the proportions of lithium and iodine, since the same lack of integral ratio was found to exist in precipitates which had neither been washed with water nor dried. Moreover, as indicated by Table I and as established definitely in the development of the volumetric method described below, the atomic ratio of lithium to iodine is lower in precipitates formed at room temperature than in precipitates formed at higher temperatures. Evidently, the precipitate produced by this reagent is a mixture of lithium periodates and does not consist of a single compound. However, as shown by the quantitative studies described below, this mixture is so constant in composition when formed under fixed conditions that its lithium content may be accurately determined from a measurement of its iodine or periodate content. The ratio of lithium to iodine in the precipitate is much more variable after washing with water and drying than in the wet precipitate separated from solution and washed with strong alkali solution. Because of the difficulty of washing and drying this precipitate and because of its uncertain composition when washed and dried, it apparently is useless for the gravimetric determination of lithium. It may, however, be made the basis of a rapid and satisfactory empirical method for the volumetric estimation of this element.

Quantitative Application

By properly restricting the volume of the solution in which lithium is to be determined and the volume of reagent used, quantities of lithium as small as 0.1 mg. may be quantitatively precipitated, and for convenience in manipulation 50 mg. is about the maximum amount that should be precipitated, though somewhat greater amounts may be precipitated and successfully determined. After precipitating, filtering, and washing in the manner detailed in the procedure, the precipitate is dissolved in dilute sulfuric acid and the liberated periodate is determined by titration, which may be done in several different ways. For example, potassium iodide may be added to the acid solution, and the liberated iodine may be determined by titration with a standardized 0.1 *N* thiosulfate solution. Because of the very large ratio between volume of thiosulfate solution and weight of lithium in the precipitate, this method of titration is unusually suitable for the determination of amounts of lithium not exceeding 10 mg., but is not suitable for the determination of larger amounts of lithium. For such determinations it is better to buffer the acid solution of the precipitate with an excess of borax or sodium bicarbonate, add potassium iodide, and then titrate with a standardized 0.1 *N* sodium arsenite solution. The solution of the precipitate may also be titrated with arsenite by adding the potassium iodide first to the acid solution and afterward adding the buffer. In this way the ratio of volume of titrating solution to weight of lithium is as favorable as in a thiosulfate titration. The validity of this variation in the usual method of titrating periodate with arsenite solution was established by appropriate experiments. Thus a single standardized arsenite solution may be used for the titration of both large and small amounts of lithium in the range in which this method is applicable.

TABLE II. TRIAL DETERMINATIONS WITH LITHIUM ALONE

Lithium Present	Volume of 0.1040 *N* Arsenite Solution Required	Lithium Found	Error
Mg.	*Ml.*	*Mg.*	*Mg.*
Cold Precipitation and Titration with Standard Arsenite Solution			
0.5	0.25	0.4	−0.1
1.0	0.55	0.9	−0.1
5.0	3.00	5.0	±0.0
10.0	6.02	9.9	−0.1
20.0	12.32	20.2	+0.2
25.0	15.26	25.0	±0.0
50.0	30.70	50.3	+0.3
50.0	30.40	49.7	−0.3
Hot Precipitation and Titration with Standard Arsenite Solution			
0.5	0.27	0.4	−0.1
1.0	0.55	0.9	−0.1
2.0	1.17	2.0	±0.0
5.0	2.93	5.0	±0.0
10.0	5.93	10.1	+0.1
20.0	11.87	20.2	+0.2
25.0	14.84	25.3	+0.3
50.0	29.34	50.0	±0.0

TABLE III. TRIAL DETERMINATIONS WITH LITHIUM ALONE

(Hot precipitation and titration with standard thiosulfate solution)

Lithium Present	Volume of 0.1034 *N* Thiosulfate Solution Required	Lithium Found	Error
Mg.	*Ml.*	*Mg.*	*Mg.*
0.1	0.12	0.05	−0.05
0.2	0.43	0.2	±0.0
0.5	1.12	0.5	±0.0
1.0	2.34	1.0	±0.0
2.0	4.70	2.0	±0.0
5.0	11.85	5.0	±0.0

TABLE IV. TRIAL DETERMINATIONS OF LITHIUM IN THE PRESENCE OF SODIUM

Volume of Reagent	Volume of Test Solution	Sodium Present	Lithium Present	Lithium Found	Error
Ml.	*Ml.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
		Cold Precipitation			
1	1	50	0.5	0.3	−0.2
2	2	150	0.5	0.3	−0.2
1	1	50	5.0	5.2	+0.2
1	1	50	5.0	5.1	+0.1
5	1	50	5.0	5.0	±0.0
2	2	100	5.0	5.0	±0.0
3	3	150	5.0	5.0	±0.0
10	2	200	5.0	6.1	+1.1
5	1	50	50.0	49.7	−0.3
10	2	150	50.0	50.5	+0.5
		Hot Precipitation			
1	1	10	0.5	0.5	±0.0
2	2	30	0.5	0.5	±0.0
1	1	50	0.5	1.0	+0.5
1	1	10	5.0	4.9	−0.1
1	1	20	5.0	8.0	+3.0
2	2	20	5.0	4.9	−0.1
1	1	30	5.0	9.9	+4.9
2	2	30	5.0	4.9	−0.1
1	1	40	5.0	10.4	+5.4
5	1	50	5.0	4.9	−0.1
5	1	50	50.0	49.5	−0.5
2	2	100	5.0	25.0	+20.0
3	3	150	5.0	35.0	+30.0

Procedure

From the chloride, nitrate, perchlorate, or sulfate solution containing not more than 50 mg. of lithium remove all metals except those of the alkali group. Remove ammonium also, if more than a few milligrams are present. Reduce the volume of the solution to 2 ml., finally placing it in a beaker of not more than 50-ml. capacity. Immerse the bottom half of the beaker in a water bath maintained at 60° to 70° C., and after a few minutes add the special periodate reagent dropwise with constant swirling at a rate not exceeding one drop every 5 seconds until 2 ml. have been added. If a heavy precipitate forms add 3 ml. more of reagent in the same way. If the precipitate is very heavy, as shown by the formation of a mixture that does not flow freely, add another 3 to 5 ml. of reagent. Allow the precipitated solution to digest at 60° to 70° C. for 20 minutes and then filter through a Gooch crucible fitted with a moderately thick asbestos pad. Wash the precipitate with 4 successive 2-ml. portions of 3 to 5 *N* potassium hydroxide added slowly from a pipet. If more than 20 mg. of sodium is present, precipitate, filter, and wash in the same way but at room temperature. Transfer the pad and precipitate to a 250-ml. beaker with the aid of distilled water, and add 5-ml. of *N* sulfuric acid in order to ensure complete solution of the precipitate.

Titrate the periodate in the solution by means of a standardized sodium thiosulfate or arsenite solution. If thiosulfate is used adjust the acidity, add potassium iodide, and titrate in the usual way. If arsenite is used and the amount of lithium is relatively high, add an excess of borax or sodium bicarbonate as a buffer before adding the potassium iodide and titrating. If the amount of lithium is low, add the potassium iodide before the buffer and then titrate. Standardize the titrating solution on a known amount of lithium by exactly the same procedure as used in the determination.

In Tables II and III is shown the degree of accuracy obtainable when this procedure is applied to pure lithium chloride solutions. The results of Table II are based upon the results for the 50-mg. quantity taken as a standard. For those of Table III, the 5-mg. quantity was taken as the basis. Although the accuracy is not high, it is satisfactory from the standpoint of practical analysis. The results in these tables illustrate well the different volumes of the same titrating solution required for a given quantity of lithium when the precipitation is made at different temperatures, and also the different volumes of arsenite and thiosulfate solution required for a given quantity of lithium.

The results in Table IV indicate the effect of sodium on the accuracy of the determination. These results were also obtained on chloride solutions. It is evident that when precipitation is done at room temperature interference occurs only with the largest amounts of sodium that may possibly be present, whereas at an elevated temperature interference occurs with much smaller amounts of sodium. The reason for this difference apparently is that a periodate containing sodium precipitates out at the elevated temperature. When more than a decigram or two of sodium is present it is advisable to precipitate at room temperature. Precipitation at an elevated temperature produces a precipitate that may be filtered and washed more easily and rapidly, but, to avoid gross errors, precipitation should always be made at room temperature whenever doubt exists as to the amount of sodium present.

As shown by Table V, considerable amounts of ammonium lead to low results, apparently because ammonium in high concentration increases the solubility of the lithium precipitate. However, relatively small amounts do not cause an appreciable error. Table VI indicates that lithium may be successfully determined by this method in the presence of various substances, some of which will commonly be present in the solution in which the lithium is to be determined when this solution is a filtrate from other determinations or separations.

In spite of the empirical nature of the method lithium may be successfully determined by its use in the presence of sodium and certain other substances which ordinarily interfere with the quantitative determination of this element. As far as the authors are aware, this is the only method by which lithium may be determined in the presence of sodium with rapidity and satisfactory accuracy.

TABLE V. TRIAL DETERMINATIONS OF LITHIUM IN THE PRESENCE OF AMMONIUM

Volume of Reagent	Volume of Test Solution	Ammonium Present	Lithium Present	Lithium Found	Error
Ml.	*Ml.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
1	1	50	5.0	4.8	−0.2[a]
3	1	50	5.0	5.1	+0.1[a]
2	2	100	5.0	4.8	−0.2[a]
3	3	150	5.0	3.7	−1.3[a]
2	2	50	5.0	5.1	+0.1[b]
3	1	50	5.0	4.9	−0.1[b]
5	1	50	5.0	5.0	±0.0[b]
3	1	100	5.0	4.1	−0.9[b]

[a] Hot precipitation.
[b] Cold precipitation.

TABLE VI. TRIAL DETERMINATIONS OF LITHIUM IN THE PRESENCE OF VARIOUS SUBSTANCES

Substance Added to Test Solution	Volume of Reagent	Volume of Test Solution	Lithium Present	Lithium Found	Error
	Ml.	*Ml.*	*Mg.*	*Mg.*	*Mg.*
0.05 ml. of concentrated HCl	3	1	10.0	10.1	+0.1
	3	1	10.0	9.9	−0.1
0.1 ml. of 60% $HClO_4$	3	1	10.0	10.0	±0.0
	3	1	10.0	10.0	±0.0
1.0 gram of KNO_3	9	3	10.0	9.9	−0.1
	9	3	10.0	10.0	±0.0
0.3 gram of K_2SO_4	9	3	10.0	10.0	±0.0
	9	3	10.0	10.0	±0.0

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The Rolling Ball Viscometer

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A study of the system of the inclined tube and rolling ball as applied to the measurement of viscosity is described. Dimensional analysis was used to derive general relations between the variables involved and the simple calibration for the rolling ball viscometer in the streamline region of fluid flow. The coefficient of the calibration equation may be calculated from the dimensions of the instrument with the aid of an experimentally determined empirical factor. By using the equations given, the useful range of the rolling ball viscometer may be predicted without experimental calibration or an instrument may be designed for measurements over any desired range of viscosity. An empirical correlation is given which allows viscosity to be estimated from data taken on the viscometer in the turbulent region of fluid flow. The effect of temperature changes on the viscometer and its calibration is discussed.

FOR many years the system of the inclined tube and rolling ball has been used as an empirical instrument for viscosity measurement without complete knowledge of the general relations existing between the variables involved. The instrument has been used because it is more easily adaptable for measurements in enclosed systems. It has many advantages, which may be listed as follows:

1. The apparatus can be extremely simple.
2. Only a small sample of material is required.
3. Visual observation in glass apparatus is possible even with opaque liquids, since the ball is in contact with the tube at one point.
4. The system possesses great flexibility, with the opportunity of changing one or more of the variables: tube diameter, ball diameter, angle of inclination, ball density, and rolling distance of ball.

The use of the system of the inclined tube and rolling ball as a viscometer was first suggested by Flowers (*7*) and was studied by Hersey (*8*), who evolved by dimensional treatment the manner of correlation of the variables involved. A calibration first used by Hersey and Shore (*9*) consisted of a plot of the equation

$$\beta \frac{\mu}{\rho\sqrt{\frac{\rho_s}{\rho} - 1}} = z\sqrt{\frac{\rho_s}{\rho} - 1} \qquad (1)$$

Except at high rolling velocities this relation was linear, and the line extended passed through the origin.

Sage (*13*) described the use of the system in measuring the viscosity of hydrocarbon solutions. He used a calibration of the form

$$\mu = b\, z\, (\rho_s - \rho) \qquad (2)$$

which may readily be derived from Equation 1. This relation also departed from the linear function through the origin, but only for viscous fluids and low rolling velocities.

Sage and Lacey (*14*) measured the viscosity of hydrocarbon gases in a similar apparatus and worked in the turbulent region of flow to a large extent. The value of constant b in Equation 2, which represented the calibration in the streamline region only, was obtained from observations on known liquids. Using other fluids for the turbulent region, but still calculating viscosity by Equation 2, a viscosity-ratio correction factor obtained for each fluid was plotted against a function proportional to Reynolds number. By use of this plot applicable to the one instrument only, the viscosity of fluids flowing with turbulence was calculated by the method of successive trials.

Block (*5*) has recently suggested the addition of a term containing an empirically derived exponent to the calibration Equation 1 to effect agreement of the equation with experimental results in the turbulent region.

Hoeppler (*10*) reported the results of experimental work on the eccentric fall of large spheres in a tube inclined at an angle of 80°. In suggesting that this arrangement of the inclined tube and rolling ball be used as a viscometer, he too employed Equation 2 as a calibration. The commercial instrument bearing his name uses a short, nearly vertical glass tube of large diameter (16 mm.) and close fitting balls of either glass or steel.

No general study of the system of the inclined tube and rolling ball has been reported. An experimental investigation of the system was therefore made on tubes from 6 to 10 mm. in diameter with balls of aluminum, steel, and brass ranging in size from 85 per cent to the full tube diameter. The general correlation obtained verified the viscometer calibration, Equation 2, and in addition indicated a method by which the unknown coefficient, b, could be calculated from the dimensions of the apparatus with the aid of an empirical correlation.

Nomenclature

b, c = proportionality constants
C = coefficient, defined by Equation 15
d = diameter of ball, cm.
D = diameter of tube, cm.
f = resistance factor = $R/(h^2\,\rho\,u^2)$, dimensionless
f_c = resistance factor at critical velocity
F = force, gram cm. per second^2
g = acceleration of gravity = 980 cm. per second^2
h = equivalent diameter of annular space between ball and tube, defined by Equation 7, cm.
K = correlation factor, dimensionless
L = length, a fundamental dimension, cm.
M = mass, a fundamental dimension, grams
R = driving force on ball or resistance of fluid to motion of ball, defined by Equation 8, gram. cm. per second^2
Re = Reynolds number = $(h\,u\,\rho)/\mu$, dimensionless
Re_c = Reynolds number at critical velocity
t = temperature, ° C.
T = time, a fundamental dimension, seconds
u = average fluid velocity through annular space between ball and tube, cm. per second
V = terminal rolling velocity of ball, cm. per second
z = time of roll, seconds
α_b = linear coefficient of thermal expansion of ball material, per ° C.
α_t = coefficient of expansion of tube, per ° C.
β = coefficient in Equation 1
δ = prefix indicating derivative
Δ = increment of change of variable
θ = angle of inclination of tube to the horizontal
μ = viscosity of fluid, grams per cm. per second
μ_0 = viscosity of fluid calculated when Equation 14 is used in the turbulent region, gram per cm. per second
π = 3.1416
ρ = density of fluid, grams per cc.
ρ_s = density of ball, grams per cc.
ϕ = symbol for "is function of"
o = subscript denoting value at temperature of calibration of viscometer

Dimensional Analysis

There are seven variables to be considered in the analysis of the rolling ball viscometer. In addition to the fundamental units—length, L; mass, M; and time, T—force, $F = MLT^{-2}$, is considered a unit of its own kind. This can

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be done because the system is in equilibrium and in unaccelerated motion, and no use is made of the fact that where there happens to be accelerated motion, force is equal to mass times acceleration. The seven variables with symbols and dimensions are:

Variable	Symbol	Dimension
Diameter of tube	D	L
Diameter of ball	d	L
Velocity of motion	V	LT^{-1}
Density of ball	ρ_s	ML^{-3}
Density of fluid	ρ	ML^{-3}
Viscosity of fluid	μ	$FL^{-2}T$
Acceleration of gravity	g	FM^{-1}

The dimensional formula of viscosity is obtained directly from its definition of force per unit area per unit velocity gradient. The intensity of gravity is taken with the dimensions FM^{-1} because the equations of motion in this case will not use the accelerating aspect of gravitational motion but only the intensity of the force exerted by gravity upon unit mass. Because of the inclination of the tube at the angle θ to the horizontal, the effective acceleration of gravity is $g \sin \theta$.

There are seven variables and four kinds of units; therefore three dimensionless products or groups of variables must be found. Two of these groups, the ratios d/D and ρ_s/ρ, may be written immediately by inspection. The third dimensionless product, obtained by the method of Bridgman (*6*), includes five variables in the form $V^{-1}\,\mu^{-1}\,d^2\,\rho\,g \sin\theta$. The final general relation is

$$\phi\,(V^{-1}\,\mu^{-1}\,d^2\,\rho\,g \sin\theta)\;\phi'\left(\frac{\rho_s}{\rho}\right)\phi''\left(\frac{d}{D}\right) = 0 \qquad (3)$$

The velocity of the ball rolling down an inclined tube is given by the equation

$$V = c\,\frac{d^2\,\rho\,g \sin\theta}{\mu}\,\phi'\left(\frac{\rho_s}{\rho}\right)\phi''\left(\frac{d}{D}\right) \qquad (4)$$

The viscosity of the fluid is expressed as a function of all the variables by the relation

$$\mu = c\,\frac{d^2\,\rho\,g \sin\theta}{V}\,\phi'\left(\frac{\rho_s}{\rho}\right)\phi''\left(\frac{d}{D}\right) \qquad (5)$$

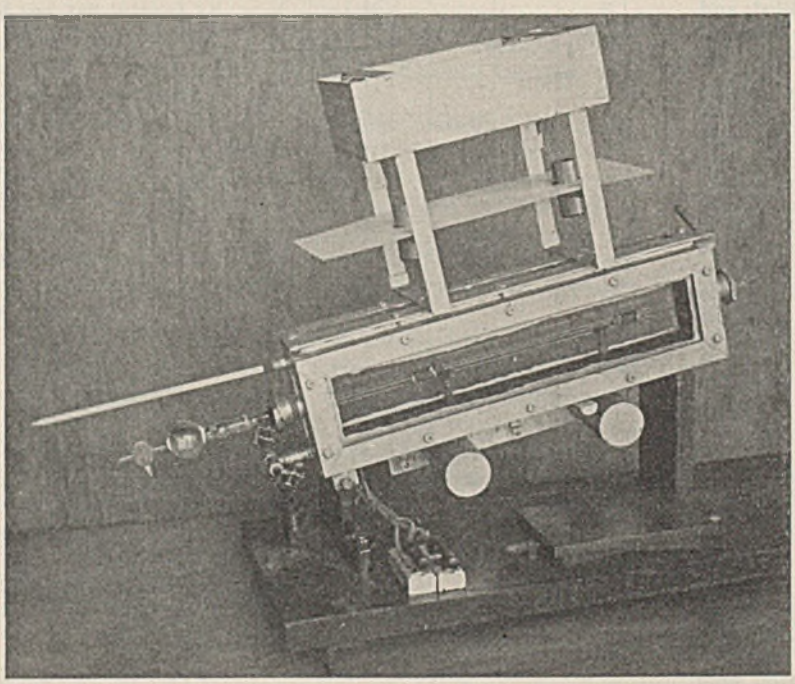

FIGURE 1. EXPERIMENTAL APPARATUS, ROLLING BALL IN INCLINED TUBE

The solution of the entire problem is obtained if the unknown functions are evaluated.

The resistance to the motion of the ball is developed by the fluid in being accelerated and decelerated in passing through the constriction between the ball and tube. The average fluid velocity through this space is related to the ball velocity by the equation

$$\frac{u}{V} = \frac{d^2}{D^2 - d^2} \qquad (6)$$

The linear dimension commonly employed in hydraulics for noncircular channels is the equivalent diameter, equal to four times the hydraulic radius, which is defined as the cross-sectional area of the channel divided by the wetted perimeter. In this system the equivalent diameter of the crescent-shaped space is theoretically

$$h = 4\,\frac{\pi}{4}\,\frac{D^2 - d^2}{\pi\,(D + d)} = D - d \qquad (7)$$

The dimensional analysis can be simplified by combining the factors d, ρ_s, ρ, and θ into a force term, the driving force on the ball, equal to the resisting force of the fluid since the ball rolls with unaccelerated motion. This term is represented by the equation

$$R = \frac{5}{7}\,g \sin\theta\,\frac{\pi d^3}{6}\,(\rho_s - \rho) \qquad (8)$$

The coefficient 5/7 is that fraction of the effective force of gravity that causes translational motion of the rolling sphere.

In the dimensional treatment of a similar problem, Awberry and Griffiths (*1*) included Reynolds number as one of the dimensionless products. In a second application of dimensional analysis to the present system, the variables used are:

Variable	Symbol	Dimension
Driving force	R	MLT^{-2}
Equivalent diameter	h	L
Density of fluid	ρ	ML^{-3}
Viscosity of fluid	μ	$ML^{-1}T^{-1}$
Velocity of fluid	u	LT^{-1}

There are now five variables and three kinds of fundamental units; therefore two dimensionless products must be found. If the Reynolds number, $(h\,u\,\rho)/\mu$, is assumed to be one dimensionless product, the other is shown to be $R/(h^2\,\rho\,u^2)$, which group will now be called the resistance factor. A general relation having only one unknown function and whose terms are capable of evaluation by experiment is written

$$\frac{R}{h^2\,\rho\,u^2} = \phi\,\frac{h\,u\,\rho}{\mu} \qquad (9)$$

Apparatus and Experimental Methods

In order to evaluate the functions of Equations 5 and 9, experimental equipment designed to permit variation of all factors was constructed.

The apparatus consisted of a precision-bore glass tube (procured from the Fish-Schurman Corp., New York, N. Y., and also available from the Fischer and Porter Co., Hatboro, Penna.) in an isothermal water bath and an automatic photoelectric device for recording the time required for a rolling ball to traverse a known distance in the tube. A photograph of a tube in its bath is shown in Figure 1.

TABLE I. SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS

Tube	Tube Diameter Cm.	Ball Diameter Cm.	Diameter Ratio	No. of Experimental Points	Range of Reynolds No.	Critical Reynolds No.	Correlation Factor, K Calculated	Graphical
I	0.5994	0.5951	0.9928	38	0.31–18.0	..	6.22×10^{-7}	.....
		0.5937	0.9905	45	0.43–32.6	..	1.16×10^{-6}	.....
		0.5861	0.9778	37	1.8–135	21.5	7.13×10^{-6}	.....
		0.5785	0.9650	38	5.1–236	18.0	.....	2.00×10^{-5}
		0.5709	0.9523	21	35–330	(15.5)	.....	4.00×10^{-5}
		0.5556	0.9269	107	8.2–511	13.0	.....	1.06×10^{-4}
		0.5144	0.8581	37	32–505	(9.8)	.....	4.17×10^{-4}
II	0.6485	0.5951	0.9177	33	20–270	(12.0)	.....	1.54×10^{-4}
		0.5785	0.8921	33	30–344	(11.0)	.....	2.78×10^{-4}
		0.5556	0.8568	99	15–448	(10.0)	.....	4.60×10^{-4}
III	0.8014	0.7950	0.9921	23	0.97–13.1	..	6.84×10^{-7}	.....
		0.7938	0.9905	61	1.03–65	..	1.02×10^{-6}	.....
		0.7525	0.9390	62	0.036–705	13.0	7.36×10^{-6}	.....
		0.7144	0.8914	237	0.0046–806	10.6	2.62×10^{-4}	.....
IV	0.9997	0.9906	0.9909	51	1.5–122	35.0	1.13×10^{-6}	.....
		0.9830	0.9832	20	18–263	24.0	.....	3.94×10^{-5}
		0.9754	0.9756	40	12–406	20.0	.....	7.15×10^{-5}
		0.9677	0.9680	21	63–537	(18.5)	.....	1.59×10^{-4}
		0.9525	0.9527	109	13–916	17.5	.....	4.65×10^{-4}
		0.9112	0.9115	31	60–936	(11.5)	.....	1.67×10^{-4}
		0.8731	0.8734	44	38–383	(10.0)	.....	3.45×10^{-4}

Values in parentheses obtained by extrapolation.

Light from two lamps was focused onto the upper surface near the ends of the glass tube. Light passing through the tube was conducted through quartz tubes to two gas-filled photoelectric cells. These cells were part of circuits which, through sensitive relays, controlled an electric chronoscope. When the light to the first photocell was interrupted by a ball rolling down the inclined tube, time measurement by the chronoscope was started. Similarly, the ball stopped the time measurement in passing through the second light beam.

The inclination of the tube and the distance traversed by the balls were measured with a cathetometer. The roll distance between the light beams was measured as the distance between the positions of stationary balls placed in each light beam at the point at which they just caused the relays to operate the chronoscope. The inclination of the tube was varied from 4° to 25° from the horizontal. The distance between the light beams was about 17 cm.

The glass tube was carefully cleaned before use. Water maintained at a constant temperature was circulated through the jacket by a pump. After the water jacket attained the desired temperature, the tube and reservoir at its lower end were filled with the liquid used. At each inclination about ten balls of each size and material were introduced into the open end and successively rolled down the tube. The balls were removed from the receiver at the lower end of the tube, the tube was refilled, and the procedure was repeated at another inclination. The roll velocity was calculated from the known distance and the average of the values of roll time.

Four Jena KPG glass tubes were used in this work. Their inside diameters were measured with plug gages. Seventeen different ball sizes were used. Steel balls are manufactured to a high degree of precision and were assumed to be their nominal diameter. Close fitting aluminum balls were specially measured by the manufacturer (Hoover Ball and Bearing Co., Ann Arbor, Mich.). Table I gives the diameter of the tubes and balls used.

Sixteen fluids were used. Except for air, water, ethyl alcohol, and solutions of ethanol and sucrose, which are accepted as standards for viscometer calibration, the viscosity of the fluids was measured in Bingham (*3*) or Ostwald capillary tube viscometers. The density of all fluids was measured experimentally. The viscosity of the fluids varied from about 0.23 to 144 centipoises, the density from 0.62 to 1.61 grams per cc. The measurements were made to an estimated precision as follows:

Tube diameter	0.08 per cent
Ball diameter	0.01 to 0.05 per cent
Ball density	0.03 per cent
Fluid density	0.02 per cent
Roll distance	0.1 per cent
Roll time	0.2 per cent
Inclination of tube	0.05 to 0.1 per cent

The major source of error was the change in viscosity of the fluid with slight changes in temperature, caused by contact of the fluid with the rolling balls. Most of the work was conducted at room temperature. At other temperatures the balls were brought to operating temperature in a separate container jacketed with the circulating water. An over-all precision in calculated rolling velocity from 0.5 to 1 per cent was obtained on measurements made under similar conditions at different times.

Experimental Results

The conditions used in the experimental work more than covered the useful range for viscosity measurement. The streamline region of fluid flow, which is the region having characteristics suitable for viscosity measurement, was covered over its most useful range. The turbulent region of flow, often used but not as advantageous for viscosity measurement, was also covered.

The turbulent region was characterized by a deviation from the relations existing in the streamline region of flow. The deviation is probably due to the inertia of the fluid, to the formation of eddy currents in the flowing fluid, or to a combination of these causes. Block (*5*) has expressed the opinion that inertia and not turbulence accounts for the deviation. No attempt was made in this work to determine the causes and only an empirical correlation was obtained.

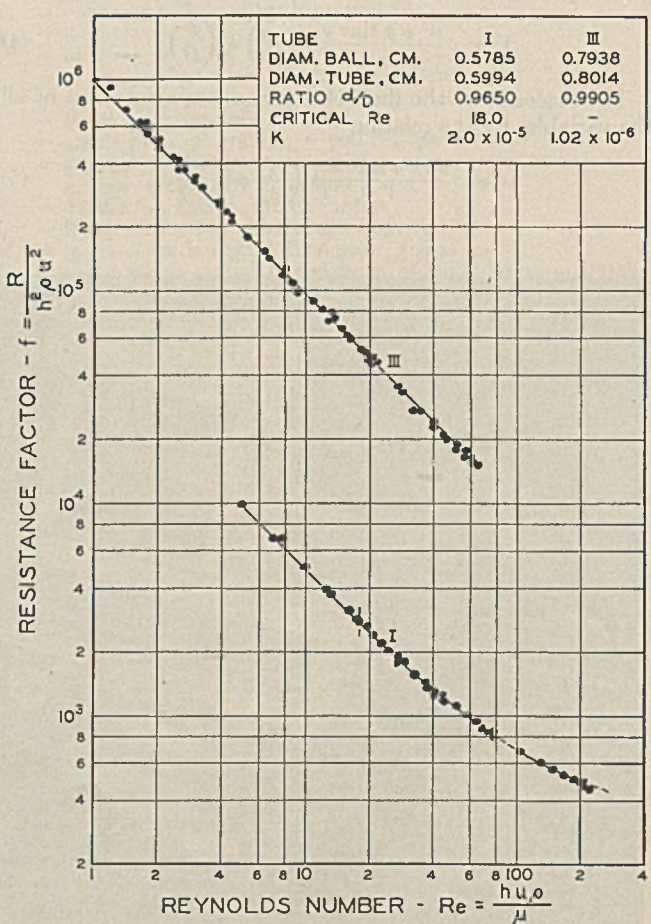

FIGURE 2. TYPICAL CORRELATION FOR SYSTEM ROLLING BALL IN INCLINED TUBE

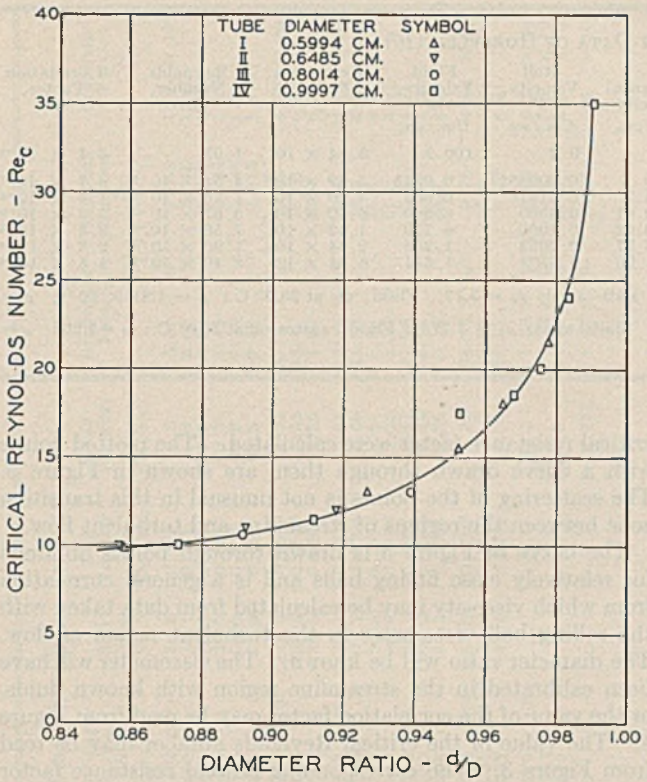

FIGURE 3. CRITICAL REYNOLDS NUMBER FOR ROLLING BALL VISCOMETER

The observed motion of the ball was fundamentally a steady rolling motion at constant velocity. Block (4) observed and measured the extent of sliding motion in combination with rolling in more viscous fluids at angles above 13°. Sliding was observed in this work with viscous oils at higher inclinations. With the least viscous fluids sliding was not apparent. The critical velocity at which the fluid flow changed from streamline to turbulent could not be determined by direct observation of the rolling balls. To a large extent the motion of the ball in both the streamline and turbulent regions was uniform and the data were reproducible. The limit of usefulness of the viscometer was reached before the motion of the ball became visibly irregular.

The experimental data were grouped according to ball and tube size or ratio of diameter of ball to diameter of tube, d/D. For each combination the values of Reynolds number and the resistance factor were calculated and plotted on logarithmic coordinate paper. The twenty-one plots obtained were similar in every respect to the fluid friction plot for flow through pipe. Two representative curves are shown in Figure 2.

In the region of streamline flow the experimental data fell on a straight line of slope −1 (upper curve of Figure 2). The turbulent region was represented by a smooth concave curve as shown by the lower curve. Within the limits of the experimental data all curves had the same shape. Regardless of the values of ball and tube diameter, the location of the curve on the coordinate system was dependent only on the ratio d/D.

For streamline flow the equation of the straight line through the plotted data was expressed as

$$\log \frac{R}{h^2 \rho u^2} = -\log \frac{h u \rho}{\mu} + \log \frac{1}{K} \tag{10}$$

which became Equation 11.

$$\frac{R}{h^2 \rho u^2} = \frac{1}{K} \frac{\mu}{h u \rho} \tag{11}$$

After substituting the values of the equivalent diameter, h, and the driving force, R, given by Equations 7 and 8, respectively, Equation 11 was written

$$\mu = \frac{5\pi}{42} K \frac{d^2 \rho g \sin\theta}{u} \frac{\rho_s - \rho}{\rho} \frac{d}{D - d} \tag{12}$$

By expressing the fluid velocity in terms of the ball velocity, V, the above relation became

$$\mu = \frac{5\pi}{42} K \frac{d^2 \rho g \sin\theta}{V} \frac{\rho_s - \rho}{\rho} \frac{D + d}{d} \tag{13}$$

Equation 13 is dimensionally correct and similar to Equation 5. The correlation factor, K, must be included with the term $(D + d)/d$ as a part of the function ϕ'', since it is shown to be a function of the ratio d/D.

When D, d, θ, and K are constant, Equation 13 reduces to

$$\mu = C \frac{\rho_s - \rho}{V} \tag{14}$$

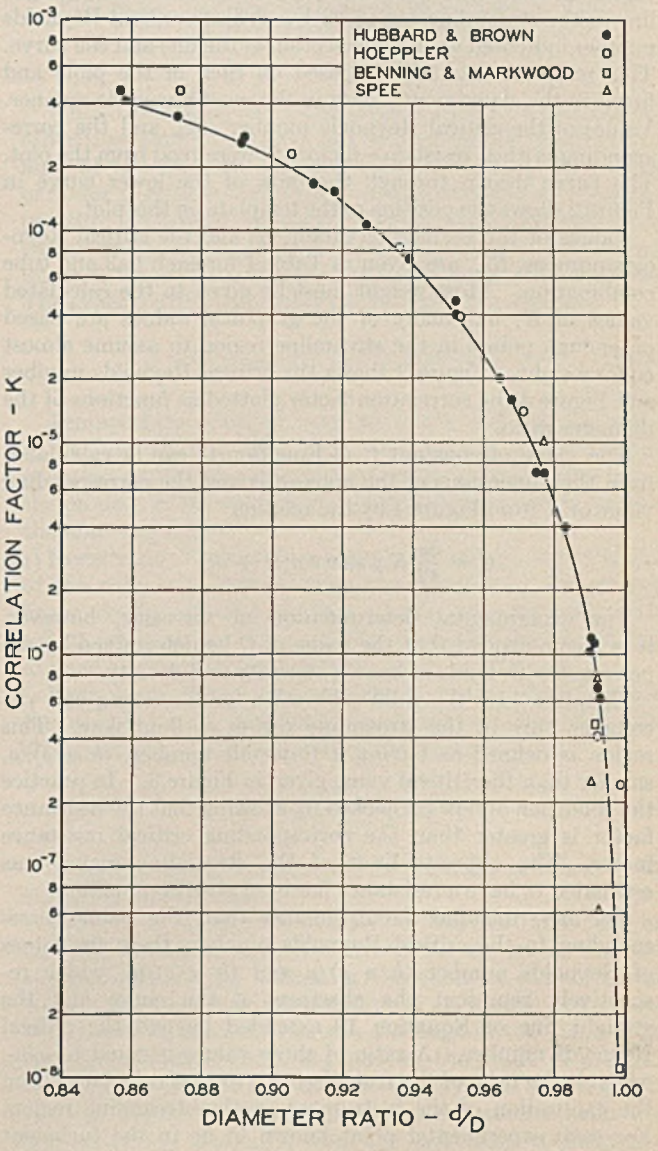

FIGURE 4. CORRELATION FOR ROLLING BALL VISCOMETER

TABLE II. CALCULATIONS FROM DATA OF HOEPPLER (*10*)

Fluid	$\left(\frac{\text{Radius of Tube}}{\text{Radius of Ball}}\right)^2$	Diameter Ratio, d/D	Ball Diameter, d	Driving Force, R	Reciprocal Velocity	Roll Velocity, V	Fluid Velocity, u	Resistance Factor, f	Reynolds Number, Re	Correlation Factor, K
		Cm.	*Cm.*	*Gm. cm./sec.²*	*Sec./cm.*	*Cm./sec.*	*Cm./sec.*			
Air[a]	1.002	0.9990	1.5984	11.46×10^3	.....	0.2	100.2	3.84×10^8	1.07	2.4×10^{-7}
Castor oil[b]	1.016	0.9921	1.5874	9.844×10^3	1810	0.000552	0.0345	5.39×10^{10}	4.54×10^{-5}	4.1×10^{-7}
	1.06	0.9713	1.5541	9.235	54.7	0.01828	0.305	4.90×10^7	1.46×10^{-3}	1.4×10^{-5}
	1.10	0.9535	1.5256	8.736	20.01	0.0500	0.500	6.60×10^6	3.87×10^{-3}	3.9×10^{-5}
	1.14	0.9366	1.4986	8.280	9.92	0.1008	0.720	1.62×10^6	7.50×10^{-3}	8.3×10^{-5}
	1.22	0.9054	1.4486	7.479	3.77	0.2653	1.205	2.34×10^5	1.90×10^{-2}	2.3×10^{-4}
	1.31	0.8737	1.3979	6.722	1.96	0.5102	1.644	6.34×10^4	3.46×10^{-2}	4.6×10^{-4}

[a] Tube: diameter = 1.600 cm. assumed; inclination = 80°; sine θ = 0.9848. Ball: steel; ρ_s = 7.77. Fluid: air at 20.0° C.; $\mu = 1.81 \times 10^{-4}$; $\rho = 0.0012$; $\rho_s - \rho = 7.769$.

[b] Tube: diameter = 1.600 cm. assumed; inclination = 80°; sine θ = 0.9848. Ball: steel; ρ_s = 7.775. Fluid: castor oil at 20.0° C.; $\mu = 9.204$; $\rho = 0.960$ (assumed); $\rho_s - \rho = 6.815$.

which is equivalent to Equation 2, most generally used to calculate viscosity from experimentally determined values of roll time or velocity.

Values of K were calculated from the experimental data by the method of least squares for 8 out of the 21 cases. For the remaining cases K was determined by inspection of the data. Since all the curves had the same shape, they could be superimposed by transposition. An aid to this process was a template made in the form of an average curve in the turbulent region and placed in proper relation to the straight line in the streamline region with a definite critical Reynolds number indicated at the intersection of the line and the curve. This template was superimposed on each of the plots and fitted to the experimental data in the most favorable manner. Values of the critical Reynolds number, Re_c, and the corresponding critical resistance factor, f_c, were read from the plot. The curve drawn through the data of the lower curve in Figure 2 shows the position of the template on this plot.

Values of the correlation factor, K, and the critical Reynolds number, Re_c, are given in Table I for each ball and tube combination. Most weight must be given to the calculated values of K, but many of the graphical values are based on enough points in the streamline region to assume almost equal weight. Figure 3 shows the critical Reynolds number and Figure 4 the correlation factor plotted as functions of the diameter ratio.

The value of constant C of Equation 14 can be calculated from the dimensions of the apparatus and the corresponding value of K from Figure 4 by the relation

$$C = \frac{5\pi}{42} K g \sin\theta\, d(D + d) \qquad (15)$$

For experimental determination of viscosity, however, it is recommended that the value of C be determined by experiment with fluids of known viscosity and density.

Equation 14 is the valid calibration for the rolling ball viscometer only in the streamline region of fluid flow. This region is defined as having a Reynolds number, $(h\ u\ \rho)/\mu$, smaller than the critical value given in Figure 3. In practice the condition of flow is checked by showing that the resistance factor is greater than the corresponding critical resistance factor. The opposite limit of the streamline region was estimated to have a resistance factor of about ten million.

For any resistance factor smaller than the value corresponding to the critical Reynolds number, there are values of Reynolds number $(h\ u\ \rho)/\mu$ and $(h\ u\ \rho)/\mu_0$, which respectively represent the abscissas of the curve and the straight line of Equation 10 extended beyond the critical Reynolds number. A ratio of these values is equal to μ/μ_0, which is the ratio of the true viscosity to that calculated from the calibration of the instrument in the streamline region. For each experimental point known to lie in the turbulent region, this ratio and the ratio of the resistance factor to the critical resistance factor were calculated. The plotted points with a curve drawn through them are shown in Figure 5. The scattering of the points is not unusual in this transition zone between the regions of streamline and turbulent flow.

The curve of Figure 5 is drawn through points obtained for relatively close fitting balls and is a general correlation from which viscosity may be calculated from data taken with the rolling ball viscometer in the turbulent region of flow. The diameter ratio will be known. The viscometer will have been calibrated in the streamline region with known fluids, or the value of the correlation factor may be read from Figure 4. The value of the critical Reynolds number may be read from Figure 3. The corresponding critical resistance factor is then calculated by substituting these values in Equation 11. Corresponding values of the resistance factor, f, and the Reynolds number, Re, may be calculated from the experimental roll velocity and the known driving force by means of Equation 11. If the resistance factor, f, is smaller than the critical resistance factor, f_c, the data were taken in the turbulent region of flow. Nevertheless the viscosity, μ_0, is calculated from Equation 14. Corresponding to the ratio of the resistance factors f/f_c, the ratio of the true viscosity to the viscosity just calculated is read from Figure 5.

The experimental work done in the turbulent region was very extensive and reached the point at which the rolling motion of the ball ceased to be uniform. The absolute limit of applicability of the instrument as a viscometer is a Reynolds number of about 800. Since the instrument loses its sensitivity in the turbulent region, its use is not recommended when ratio f/f_c is less than 0.25.

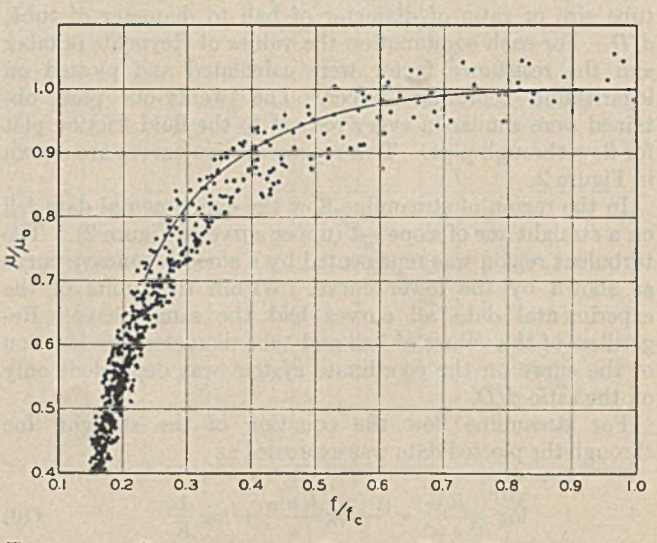

FIGURE 5. CORRECTION FOR ROLLING BALL VISCOMETER IN REGION OF TURBULENT FLOW

TABLE III. CALCULATIONS FROM DATA OF BENNING AND MARKWOOD (2) AND SPÉE (16)

Fluid	Tube Diameter, D	Ball Diameter, d	Diameter Ratio, d/D	Temp.	Fluid Viscosity, μ	Ball Density, ρ_s	Fluid Density, ρ	$\rho_s - \rho$	Driving Force, R	Roll Time	Roll Velocity V	Fluid Velocity, u	Resistance Factor, f	Reynolds Number, Re	Correlation Factor, K
	Cm.	Cm.	Cm.	° C.	G./cm. sec.	G./cc.	G./cc.	G./cc.	G. cm./sec.²	Sec.	Cm./sec.	Cm./sec.			
Air[a]	1.5934	1.5905	0.9982	1.4	1.715×10^{-4}	2.405	0.0013	2.404	3.492×10^{3}	36.0	0.278	76.0	5.59×10^{2}	1.652	1.084×10^{-3}
				1.7	1.717	2.405	0.0013	2.404	3.492	36.1	0.277	75.8	5.60	1.643	1.087
				30.7	1.859	2.404	0.0012	2.403	3.491	38.3	0.261	71.5	6.98	1.298	1.105
				40.0	1.904	2.403	0.0011	2.402	3.489	39.0	0.256	70.2	7.49	1.205	1.110
				49.7	1.949	2.403	0.0011	2.402	3.489	39.6	0.253	69.2	7.93	1.125	1.121
				79.5	2.086	2.402	0.0010	2.401	3.488	41.6	0.240	65.8	9.59	0.915	1.140
Water[a]	1.5934	1.5805	0.9919	0.5	17.63×10^{-3}	2.403	1.000	1.403	2.00×10^{3}	144.9	0.0690	4.21	67.8×10^{3}	3.08	4.79×10^{-7}
				30.0	8.00	2.402	0.996	1.406	2.005	65.4	0.1530	9.34	13.8	15.00	4.81
				59.6	4.73	2.401	0.983	1.418	2.020	38.5	0.260	15.85	4.92	42.5	4.79
Chloroform[a]	1.5934	1.5805	0.9919	29.67	5.12×10^{-3}	2.402	1.4079	0.9311	1.327×10^{3}	63.4	0.1578	9.61	5.88×10^{2}	35.6	4.78×10^{-7}
				0.46	6.97	2.4026	1.5256	0.8770	1.250	91.1	0.1096	6.69	11.00	18.9	4.81
				29.67	5.12	2.4017	1.4709	0.9308	1.328	63.4	0.1578	9.61	5.88	35.6	4.78
				59.36	3.92	2.4008	1.4142	0.9866	1.406	46.0	0.2174	13.25	3.37	61.6	4.81
				0.46	6.97	2.4026	1.5256	0.8770	1.250	95.1	0.1052	6.41	11.98	18.1	4.61
				30.91	5.07	2.4017	1.4683	0.9334	1.330	64.6	0.1548	9.44	6.11	35.2	4.64
				29.93	5.12	2.4013	1.4702	0.9315	1.328	65.2	0.1534	9.36	6.18	34.7	4.66
Freon-113[a]	1.5934	1.5805	0.9919	0.48	9.28×10^{-3}	2.4026	1.6202	0.7824	1.228×10^{3}	141.5	0.0707	4.32	24.35×10^{2}	9.75	4.21×10^{-7}
				29.88	6.19	2.4017	1.5534	0.8483	1.221	86.9	0.1150	7.02	9.58	22.8	4.58
				0.47	9.28	2.4026	1.6202	0.7824	1.228	141.2	0.0708	4.32	24.35	9.75	4.21
Air[b]	2.012	1.997	0.9925	19.5	1.813×10^{-4}	1.174	0.001	1.173	4.379×10^{3}	...	....	99.1	1.65×10^{2}	9.85	6.2×10^{-3}
	1.281	1.271	0.9922	19.8	1.815	1.1646	0.0012	1.1634	1.122	...	....	471.	4.22×10^{1}	31.0	7.6×10^{-3}
	2.017	1.997	0.9901	19.5	1.813	1.174	0.001	1.173	4.379	...	....	294.3	1.09×10^{2}	37.0	2.5×10^{-7}
Water[b]	1.301	1.271	0.9769	12.0	12.78×10^{-3}	1.1646	0.9995	0.1651	159.0	...	....	4.151	1.03×10^{2}	9.75	1.0×10^{-5}

[a] From Benning and Markwood: tube inclination = 80°; sine θ = 0.9848; roll distance = 10.00 cm.
[b] From Spée: tube inclination = 66°; sine θ = 0.9136.

Effect of Temperature Changes

The effect of temperature changes on the rolling ball viscometer is appreciable when high temperatures are employed or when materials with high coefficients of thermal expansion are used. The effect is greater if the ball and tube are of different material and when the ratio of diameters approaches unity.

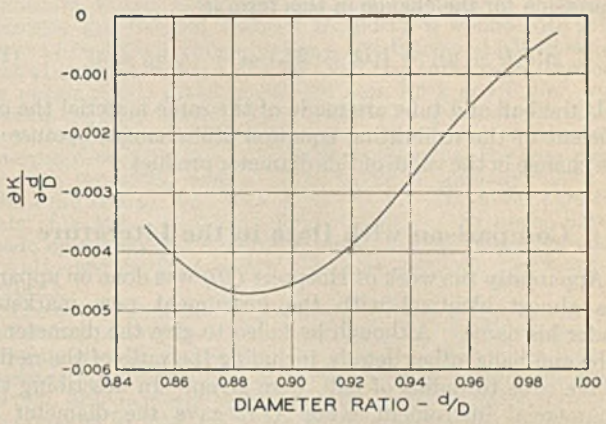

FIGURE 6. RATE OF CHANGE OF CORRELATION FACTOR WITH DIAMETER RATIO

When the rolling ball viscometer is used at a temperature other than that at which it was calibrated, the density of the fluid at the temperature used must be known. The value of factor C of Equation 14 will change as the operating temperature is changed, and the direction and magnitude of the change may be calculated from a knowledge of the average linear coefficients of expansion of the tube and ball materials. The general calibrating equation is written in the form

$$\mu = \frac{5\pi}{42} g \sin\theta \frac{\rho_s - \rho}{V} K\, d(D + d) \qquad (16)$$

Temperature changes have an effect only on the terms ρ_s, K, and $d(D + d)$. The coefficient of the calibrating equation must be estimated at each temperature and is the product of the numerical factor and the variable terms of the above equation.

EFFECT ON TUBE. The increase in length and diameter of the tube is calculated from the dimensions and average linear coefficient of expansion of the tube material. The rolling velocity is obviously the calculated length of tube divided by the observed roll time.

EFFECT ON BALL. An increase in temperature increases the diameter and decreases the density of the ball. The change in ball density is given by the relation

$$\Delta\rho_s = \frac{-3\alpha_b \Delta t}{1 + 3\alpha_b \Delta t} \rho_{s0} \qquad (17)$$

The term $(\rho_s - \rho)$ in Equation 16 is mainly affected by the change in fluid density.

EFFECT ON DIAMETER RATIO. If the ball and tube are made of the same material there is no change in the ratio of diameters and no change in the value of the correlation factor, K, when the temperature is increased. A change in the ratio of diameters causes a change in the value of the correlation factor which depends on the value of d/D and the rate of change of K with d/D. This rate is shown graphically in Figure 6. The change in the diameter ratio with temperature is estimated from the individual coefficients of expansion and the relation shown in Equation 18.

$$\Delta \frac{d}{D} = \frac{(\alpha_b - \alpha_t)\ \Delta t}{1 + \alpha_t\ \Delta t}\left(\frac{d}{D}\right)_o \qquad (18)$$

The rate of change of K from Figure 6 is then multiplied by the change in d/D from the equation above to obtain the estimated change in the correlation factor.

Effect on Diameter Product. The linear dimensions of the apparatus combine in the term $d(D + d)$ to affect the calibration when the temperature is changed. A general expression for the change in this term is

$$\Delta[d(D + d)] = [(D_o + 2d_o)\ \alpha_b + D_o\ \alpha_t]\ d_o\ \Delta t \qquad (19)$$

If the ball and tube are made of the same material the coefficient of the calibrating equation still changes because of the change in the value of this diameter product.

Comparison with Data in the Literature

Apparently the work of Hoeppler (*10*) was done on apparatus almost identical with the instrument now marketed under his name. Although he failed to give the diameter of tube and balls, other details, including the ratio of the radius of the tube to radius of ball, were given. In describing the commercial instrument Knop (*12*) gave the diameter as 1.5985 cm. and Schrader (*15*) gave 1.5987 cm. Using the data of Hoeppler on air and castor oil, the values of the resistance factor and Reynolds number were calculated for seven ball sizes. The correlation factor, K, was calculated from the single values for each condition. The detailed calculations are given in Table II and the calculated values of K are plotted on Figure 4.

Four out of six values of K calculated from these data check the present work, and the remaining two values are within about 40 per cent of the corresponding values read from the curve. Hoeppler's instrument was almost twice as large in diameter and inclined at an angle of 80° from the horizontal. Since sliding motion of the balls was probably more pronounced with this instrument, the agreement of these data with the present work is unexpectedly good. The values of Reynolds number limiting the streamline region cannot be applied to this instrument.

Benning and Markwood (*2*) used a modified Hoeppler instrument to measure the viscosity of gases and liquids. They derived a calibration equation for the ball and tube combination used on gases from an interpolated value of roll time in air at 20° C. Measurements in air were made at temperatures from 1.4° to 79.5° C., and the viscosity was calculated from the experimental values. The calculated viscosity did not check the critical values (*11*) for air and the deviation from the critical values was greater than the normal dispersion of data for air. Using the original data and the viscosity of air from International Critical Tables, the correlation factor, K, was calculated at seven temperatures. There was a definite trend of the values with changing temperature.

Apparently the ball used in this work was of glass. If it is assumed that the ball and tube material were the same, the diameter ratio and correlation factor would not change with temperature. The increase in diameter product in the temperature range used was small and did not account for the change indicated. It is concluded that the ball and tube were not made of material having the same coefficient of thermal expansion.

The ball and tube combination used on liquids and vapors was calibrated with water and two other known liquids at temperatures from 0° to 60° C. A definite trend in the calculated correlation factor was not evident, but in this case the diameter ratio was smaller and the apparatus was not so sensitive to temperature changes. The calculated values agree well with themselves but are 40 per cent smaller than the values found in the present work. The detailed calculations on the data of Benning and Markwood are given in Table III and the values of the correlation factor calculated from their data are plotted in Figure 4.

Spée (*16*) described experimental measurements of the fluid velocity required to suspend spheres in inclined tapered glass tubes. The full effective force of gravity was used in maintaining the position of the ball against the flowing fluid. In four cases of streamline flow values of the resistance factor, Reynolds number, and correlation factor were calculated. The detailed calculations are given in Table III. The points plotted on Figure 4 agree with the present work in two out of four cases, but the other values are of the right order of magnitude.

Summary

By the use of dimensional analysis, the variables involved in the calibration of the rolling ball viscometer have been combined in the Reynolds number containing the variable viscosity and a resistance factor proportional to the driving force on the ball. A general equation showing the relation between all variables was obtained from a correlation of these factors.

The usual calibration of the instrument in the streamline region of fluid flow was readily obtained from the general equation. The coefficient of this viscometer calibration can now be predicted from the dimensions of the instrument.

When data are taken with the rolling ball viscometer in the turbulent region of flow, the true viscosity can be estimated by applying an empirical correction to the viscosity calculated from the calibration valid only for the streamline region of flow.

A study of the effect of a change in operating temperature on the calibration has been made for the first time. The effect of temperature is appreciable when the coefficients of expansion are different, when temperature changes are large, and when close-fitting balls are used.

Because of the greater sensitivity to viscosity in the streamline region of fluid flow, best results as a viscometer are obtained when the instrument is used in this region. The relations presented have practical value in allowing the viscometer to be designed for a specific purpose or in allowing its range in the more applicable streamline region to be determined. A study of the variables involved will indicate the best design which should result in experimental measurements of greater reliability.

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An Electrically Heated Melting Point Apparatus

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AN ELECTRICALLY heated melting point apparatus with which it is possible to determine the melting point of substances in strict accordance with the heating rates prescribed by the United States Pharmacopoeia (*1*) is described. The relative simplicity and ease of operation make the apparatus very satisfactory for routine laboratory testing where a high degree of reliability is essential.

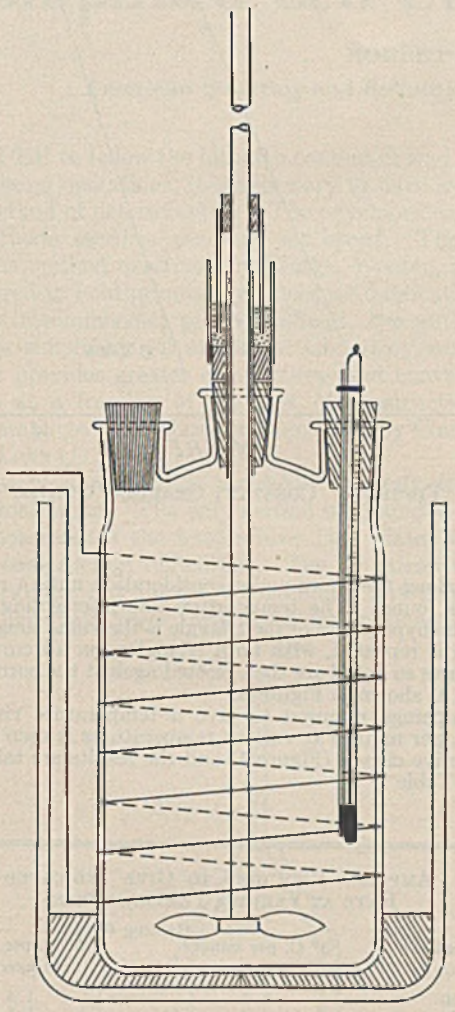

FIGURE 1. MELTING POINT APPARATUS

The volume of the bath used, 450 ml., while appreciably larger than those ordinarily employed for melting point determinations, is of the minimum size consistent with close temperature control. Most textbooks do not sufficiently emphasize the necessity for decreasing the rate of rise in temperature to 0.5° C. per minute at a point 3° or 4° below the supposed melting point of the material being tested. The authors feel that this is a serious oversight, for, unless this is done, high results are almost always obtained.

Because of the nature of the bath used, the apparatus should not be heated above 280° C. If it is to be used at higher temperatures, an adequate quantity of potassium sulfate or other suitable salt should first be dissolved in the sulfuric acid.

Apparatus

A thin-walled, three-necked (16, 19, and 16 mm. in inside diameter) Woulff bottle (Figure 1), approximately 75 mm. in diameter and 130 mm. high (to shoulder), is wound with seven turns of Nichrome ribbon having a resistance of 1.656 ohms per foot (1.5 × 0.125 mm.), the first and last turns being anchored by means of two metal bands, 0.6 mm. thick and 6 mm. wide, passing entirely around the bottle. To prevent the short-circuiting of a portion of the ribbon, a thin sheet of asbestos is interposed between the metal surfaces wherever the wire passes beneath the metal bands. (The bottle is specially blown by The Emil Greiner Co., New York, N. Y. The lower part consists of a 500-cc. tall-form Pyrex beaker. The upper part is made by cutting down a second beaker, to the bottom of which are attached the three necks. The two parts are then fused together.)

The bottle, thus wound, is set into a Pyrex battery jar (standard Pyrex battery jar, 116 × 225 mm. cut down to size) approximately 116 × 140 mm., and is held in place by a layer of asbestos fiber 20 mm. thick having a central depression about 10 mm. deep in which the bottle rests. This asbestos layer may be prepared by moistening long asbestos fiber with water, molding into shape, and then drying slowly at a moderate temperature.

The position of the bottle is so adjusted that the three necks lie in a direct line with the observer. An Anschütz thermometer of appropriate range is placed in the opening nearest the observer and held by means of a molded asbestos stopper. The hole in the stopper is cut slightly elliptical, so that both the thermometer and melting point capillary may be passed through it. A short section of rubber tubing serves to hold the capillary in place as well as to prevent the thermometer from falling into the bottle.

In order to assure atmospheric pressure in the bottle and at the same time prevent the escape of sulfur trioxide fumes due to the gradual decomposition of sulfuric acid at the higher temperatures, a "breather" consisting of a loose roll of thin asbestos sheeting is set in the opening farthest from the observer. A

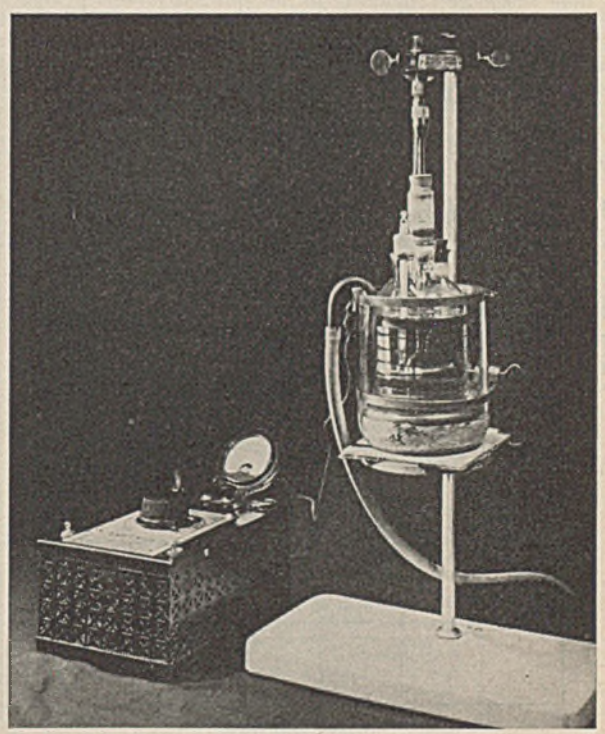

FIGURE 2. MELTING POINT APPARATUS

small motor-driven stirrer, fitted with a mercury seal, completes the setup.

The electrical input to the heating coil is controlled by means of a variable-voltage transformer—similar to the "Voltrol", Type T 1404—having a capacity of at least 6 amperes at 110 volts. The current is measured by an ammeter having a range of 0 to 6 amperes in 0.2-ampere divisions.

After using, the apparatus may be cooled quickly by blowing a current of air through the space between the bottle and the jar. Figure 2 shows the arrangement used by the authors, the air being distributed by means of a perforated brass ring made of 6.25-mm. tubing, set on the asbestos layer.

Calibration

No claim is made for the originality of this method. Credit, however, is given to Leo A. Flexser as the first to employ the method in this laboratory.

Having assembled the apparatus as indicated above, 450 ml. of sulfuric acid (specific gravity 1.84) are introduced and the speed of the stirrer is adjusted to a rate sufficiently high to assure effective distribution of heat. A current is then made to flow through the heating coil by closing the circuit, and is then adjusted to a definite value by applying the necessary potential across the unit by means of a variable voltage transformer. The temperature of the acid is noted periodically by means of a thermometer having a range from 0° to 300° C. In this work the authors found it best to make runs between 1.5 and 6 amperes in 0.5-ampere steps.

The temperatures so recorded are plotted as shown in Figure 3, and the point at which the slope of each curve is 0.5 and 3 (corresponding to a temperature rise of 0.5° and 3° C. per minute) is approximated graphically. This may easily be done by cutting two small right triangles, from a file card or other similar paper, having side ratios of 0.5 and 3. To determine the temperature at which a given amperage will give the desired heating rate, the base of the triangle is set horizontally and the triangle

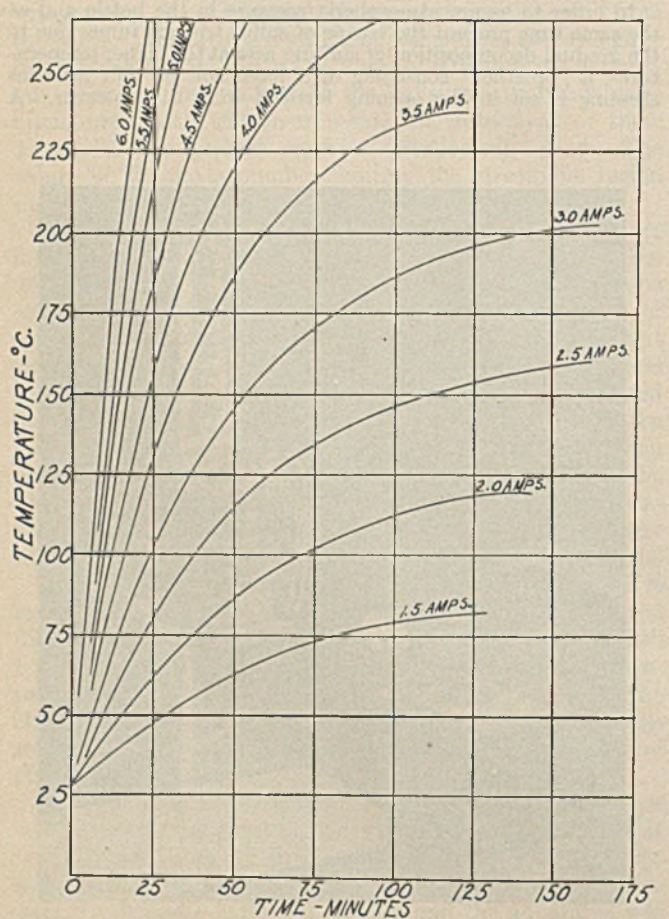

Figure 3. Time-Temperature Curves

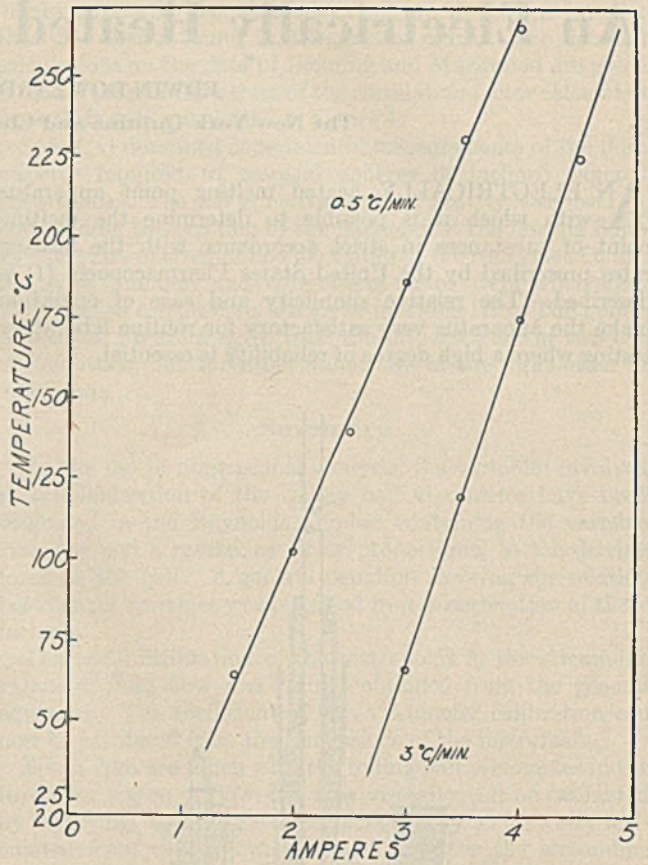

Figure 4. Constant Gradient Curves

is moved along the curve under consideration until a reasonably good fit is found. The temperature line intersecting the midpoint of the hypotenuse of the triangle is the value sought. This procedure is repeated, with both triangles, on all curves. The temperatures so noted are then plotted against the corresponding amperage as shown in Figure 4.

The amperage required to give a temperature rise of 0.5° and 3° C. per minute at various temperatures is then read from the respective curves (Figure 4) and the results are tabulated as shown in Table I.

Table I. Amperes Required to Give Indicated Heating Rate at Various Temperatures

Temperature	Heating Rate 3° C. per minute	0.5° C. per minute
° C.	*Amperes*	*Amperes*
50	2.8	1.4
60	2.9	1.5
70	3.0	1.6
80	3.1	1.7
90	3.2	1.8
100	3.3	2.0
110	3.4	2.1
120	3.5	2.2
130	3.6	2.3
140	3.7	2.4
150	3.8	2.6
160	3.9	2.7
170	4.0	2.8
180	4.1	2.9
190	4.2	3.1
200	4.3	3.2
210	4.4	3.3
220	4.4	3.4
230	4.5	3.5
240	4.6	3.7
250	4.7	3.8
260	4.8	3.9

Operation

After calibration, the apparatus is ready for use. The speed of the stirrer is adjusted to such a value that thorough mixing of the bath is assured without undue agitation. The capillary tube containing the material, the melting point of which is to be determined, is attached at its uppermost end to an Anschütz thermometer of appropriate range. The thermometer and capillary are then inserted in the asbestos stopper previously described, and put into the bath in such a position that both the material being tested and the thermometer graduations within the suspected melting point range are clearly visible.

The initial current to be used will depend upon the melting point of the substance, as much as 6 amperes being used for the higher temperatures. The temperature of the bath is raised rapidly to a point approximately 30° C. below the supposed melting point of the material. At this point the amperage is reduced to the value required for a temperature rise of 3° per minute. This heating rate is continued until the substance softens. The amperage is then further reduced to the value required for a temperature rise of 0.5° per minute, which rate is maintained until the substance melts.

Literature Cited

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Simplified Cell Unit for Internal Electrolysis

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American Smelting and Refining Company, Central Research Laboratory, Barber, N. J.

IN ORDER to follow the bismuth content of lead in certain processing operations, it is necessary to have a rapid, accurate method of determination. The oxychloride and other older methods sacrifice accuracy for speed. The internal electrolysis method described by Clarke, Wooten, and Luke (*1*) appeared to hold promise, but because duplication of the apparatus recommended proved difficult, the authors constructed a simplified cell unit from laboratory stock parts. This unit provides greater compactness and convenience of operation at a fraction of the cost of construction. The methods employed were those recommended by Clarke, Wooten, and Luke (*1*).

The design illustrated is assembled entirely from inexpensive stock items. The only section not found in any laboratory stock room is the hard-rubber base plate, which presents no construction difficulties. The air stirrer shown in the illustrations not only is economical, but eliminates a source of accidental error through contamination of the electrolyte during electrolysis, by copper salts from the electric motor. It also permits more compact assembly of the unit.

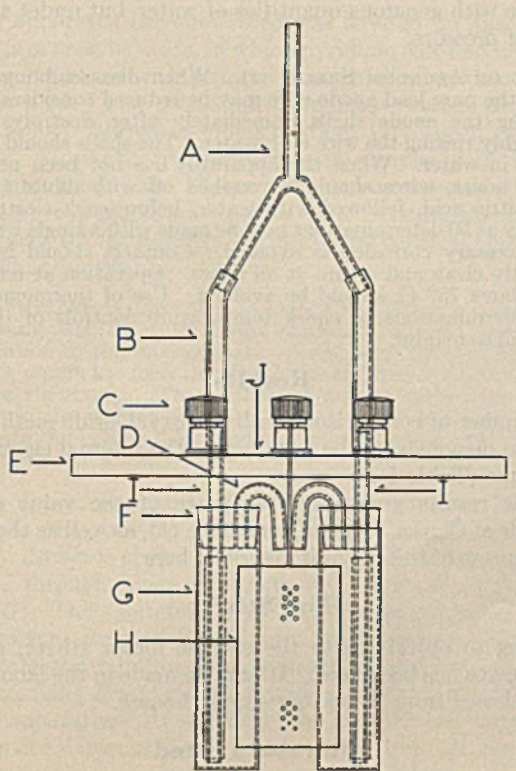


FIGURE 1. ANODE CONSTRUCTION

The cell consists of a hard-rubber or similar electrode support with three hard-rubber binding posts connected together on the upper side with a thin copper strip. Other parts of the cell—flushing tubes, anodes and shells, and the cathode—are attached to the hard-rubber base, which rests on the rim of a beaker during electrolysis with anodes and cathode suspended from it into the electrolyte. At completion of deposition, the unit is disconnected from the anolyte reservoir by one rubber tube connection, and lifted from the electrolyte with simultaneous flushing of the cathode. The continuance of the e. m. f. prevents resolution.

Figure 1 shows details of the anode construction. The flushing tubes serve as the anode cores, and the method by which the anodes are supported by the flushing tubes and rubber tubing above the plate should be noted. The binding posts are attached by tapped holes, but do not continue through to the under side. It is important to have no metals exposed on the under side. This design necessitates bending the cathode stem to avoid a hole through the plate, as shown in Figure 2. Figure 3 shows the relative positions of anodes and cathode and the extension of the cathode position for the introduction of the stirrer through the center.

Figure 4 shows the unit on an ordinary ring stand with all parts in place, exactly as it appears in operation. A small hot plate with high-, medium-, and low-temperature adjustments will be found satisfactory for this purpose. One valve, not two, in the previously designed apparatus is used for anode flushing. The plainly visible outlet tubes make this feature practicable.

A. Stock tubing. 0.25 inch in outside diameter
B. Short length of rubber tubing connecting flushing tubes to Y-tube, 6 to 7 cm. long
C. Binding posts, 3; one in center, outer ones 2.5 cm. from center, in line, on either side
D. Overflow tubes, same size as flushing tubes, bent U-shaped, inverted in use. These must turn to drain in opposite direction from cathode. A drop of anolyte might otherwise accidentally fall on cathode during removal (Figures 2 and 3)
E. Hard-rubber, Bakelite, or similar material plate, 13 cm. long, 0.7 to 1.0 cm. thick, 3 cm. wide. Slight variations in dimensions are permissible
F. Rubber stoppers with two holes to accommodate tubing (flushing and overflow tubes), also a very small hole to permit passage of anode leads
G. Alundum shells covering anodes, Norton Co.'s RA360, 2 × 9 cm. These are cut down to 7-cm. length to fit standard 400-ml. beaker
H. Platinum cathode, 5.5 cm. long, 3 cm. in diameter, stem bent as shown in Figure 2. Clearance of cathode and anode shells should be at least 1.5 cm. Cathode must extend beyond edge of hard-rubber base to permit stirrer operation through center (Figure 3)
I. Anode flushing tubes serving also as core for anode wire winding. They extend close to bottom of anode shells, and upwards through hard-rubber plate to 1.5 to 2.0 cm. above upper surface. Lead wire winding begins at extreme lower end of these tubes and continues upward to as close as possible to rubber stopper. Length of tubes will determine clearance of overflow tube from bottom of plate
J. Copper strip, 6.5 × 1.0 cm. connecting bases of all binding posts. After insertion should be greased lightly to minimize corrosion

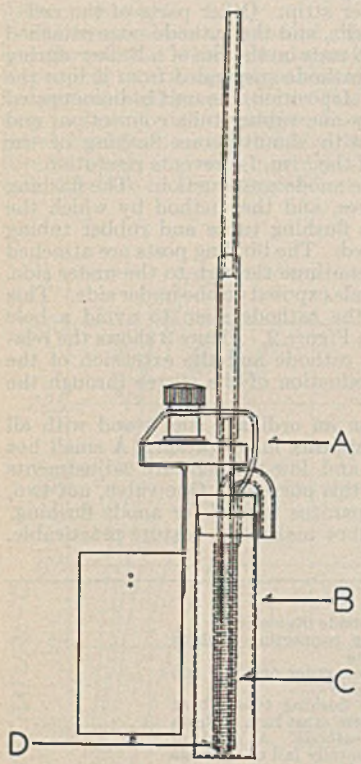
TABLE I. DETERMINATION OF BISMUTH

Sample No.	Bismuth Found: Internal electrolysis	Bismuth Found: Oxychloride
314	0.083	0.080
316	0.073	0.071
318	0.084	0.082
319	0.036	0.036
320	0.039	0.039
321	0.087	0.084
326	0.129	0.136
H4456	0.022	0.023
H4470[a]	9.20	9.20
352	0.099	0.099
H168	0.018	0.018
H4792	0.019	0.017
H92	0.016	0.016

[a] By aliquoting equivalent of 0.2 gram of sample.

Operation and Care of Cell Unit

As will be seen from Figure 4, a compact series of these units may be easily arranged. The method (*1*) stresses the use of the cell for the determination of small amounts of copper and/or bismuth. However, considerably larger amounts may be safely handled by reducing the weight of the sample used, either by direct weight or by diluting and aliquoting. The limiting factor is the amount of bismuth which will form an adherent deposit. On perforated cathode used, this is approximately 30 mg. Beyond this point difficulty will be experienced in washing and handling because of the powdery characteristics. By starting electrolysis at from 40° to 50° C. and gradually raising the temperature to 70° C., some slight improvement in adherence may be noted when working in the maximum weight range. Considerable improvement in this respect will occur in the presence of copper, which may be added in known amounts for this purpose, if desired. Washing of the cathode during removal from the electrolyte should be done with generous quantities of water, but under a minimum of pressure.



A. Anode lead through small hole in rubber stopper to outside binding posts. Anode wire is high-purity lead of No. 12–16 B. & S. gage
B. Anode shell
C. Flushing tube serving as lead anode wire core
D. Relative positions of lower edge of cathode and anode

FIGURE 2

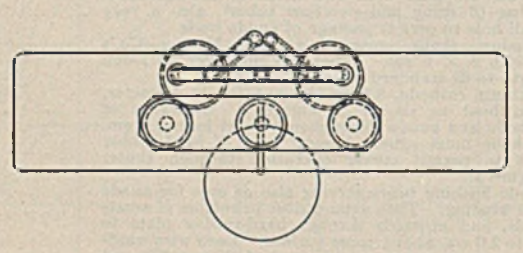


FIGURE 3. TOP VIEW

Shows clearance of cathode and anode shells as well as extension of cathode position to accommodate centrally positioned stirrer. Note location and direction of overflow tubes.

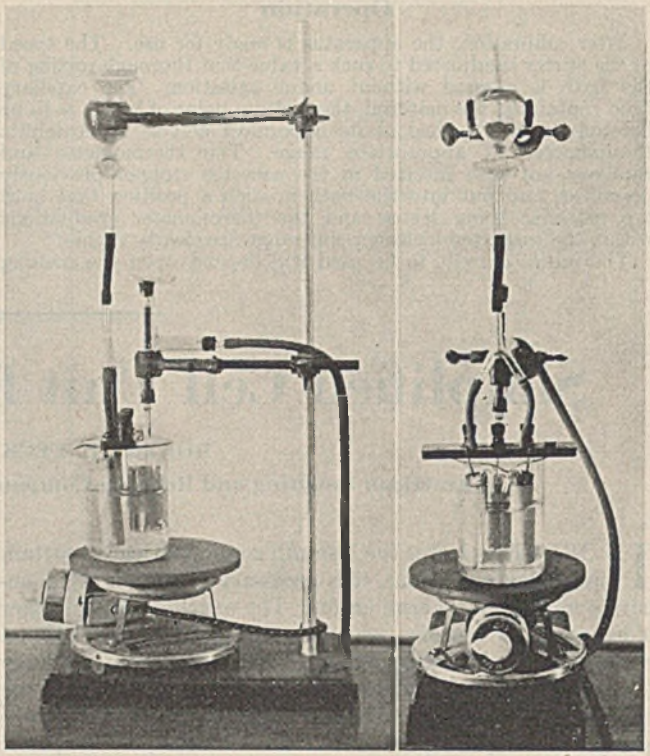


FIGURE 4. CELL UNIT

CARE OF ALUNDUM SHELLS (*1*). When disassembling, solution of the pure lead anode wire may be reduced considerably by removing the anode shells immediately after electrolysis and thoroughly rinsing the wire with water. The shells should be immersed in water. When the apparatus has not been used for several hours, wires should be washed off with dilute (10 per cent) nitric acid, followed with water, before each electrolysis. As many as 50 determinations may be made with a single winding, if unnecessary corrosion is avoided. Contacts should be kept efficiently clean and secure at all times. Operation at temperatures above 75° C. should be avoided. Use of thermometer in trial determinations to check temperature controls of the hot plate will be helpful.

Results

A number of comparisons with the oxychloride method are given to demonstrate the accuracy of the internal electrolysis technique (Table I).

These results give ample evidence of the value of the methods of Clarke, Wooten, and Luke (*1*), as well as the practical aspects of the cell unit described here.

The Stirrer

Owing to objections to the electric motor stirrer, an all-glass device has been used. It may be made in the laboratory or purchased from laboratory supply houses.

Literature Cited

(1) Clarke, Wooten, and Luke, IND. ENG. CHEM., ANAL. ED., 8, 411 (1936).

A Continuous Liquid-Liquid Extractor

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LIQUID-liquid extraction can be an extremely tedious and time-consuming operation, particularly when the two liquids tend to emulsify. Most commercial laboratory continuous extractors, though labor-saving, are expensive and very slow in operation. Hossfeld (*1*) describes an apparatus which is a considerable improvement over previous extractors, but which requires a motor and moving glass parts, always a potential source of trouble in careless or inexperienced hands.

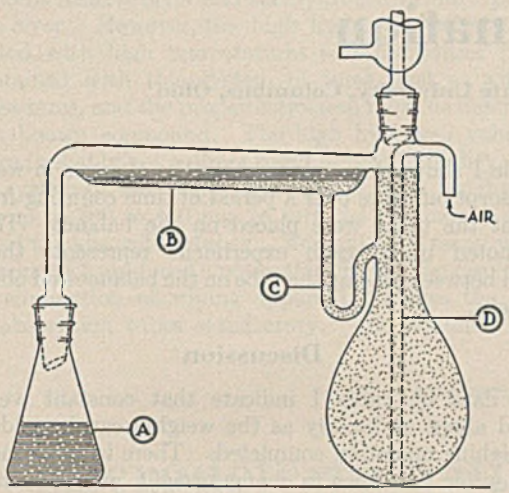

FIGURE 1. EXTRACTOR

The apparatus here described was devised for the routine analysis of cresylic acids, in which pyridine, oils, and naphthalene are extracted with benzene from an alkali solution of the cresylic acid. The potassium phenolates present ordinarily cause a high degree of emulsification. By use of this apparatus, a quantitative extraction is completed in 1 hour, as against more than 12 hours for a commercial extractor dispersing the solvent by means of a fritted-glass bubbler. The apparatus is relatively compact, inexpensive, and simple to build and operate.

The extractor is illustrated in Figure 1. Benzene passes from the boiling flask, *A*, to the reflux condenser, whence it drips into the solution in the mixing flask. Air passing through the inner tube, *D*, enters the flask in a fine jet at the bottom, agitating the mixture vigorously. The mixture of extract and solution overflows into the settling chamber, *B*, from which the extract overflows into the boiling flask, and the solution returns via the trap, *C*, to the mixing flask.

This design represents a simplification of an attempt to eliminate the moving parts in Hossfeld's extractor. The original design is shown in Figure 2. In this case, the reflux was led through inner tube *E* to the intake, *F*, of the aspirator, *G*. The aspirator, operated by a jet of air, circulated fresh solvent through the mixture, while the air served also to agitate the mixture. Surprisingly enough, it was found that removing *E* and closing *F* had no effect on the efficiency of the apparatus. Accordingly, the simpler and more compact device shown in Figure 1 was constructed. In operation, there was no measurable difference in efficiency between these two designs.

There are two possibly undesirable features inherent in the design of the extractor. One is that a long and efficient reflux condenser is necessary to prevent the loss of solvent vapor entrained in the stream of air. However, using a 50-cm. West-type condenser, this loss is negligible in routine work for the 1-hour period of operation. The other disadvantage lies in the fact that the stream of air may oxidize the material being extracted. An inert gas could, of course, be used to obviate this difficulty.

Details of Construction and Operation

The specifications for the extractor are fairly flexible. It was designed to contain approximately 1 liter of liquid, but there is no apparent reason why the flask could not be altered to any desirable shape and capacity. In this case, an 800-ml. Kjeldahl flask with a 24/40 standard-taper neck was used as the mixing flask, and a side arm approximately 25 cm. long was constructed of 3-cm. tubing. The seals at both ends of this arm were made at the top, to allow a maximum amount of space for the separation of the liquids. These openings must be at least 1 cm. in diameter to permit the flow of liquid and vapor in opposite directions. However, the opening at the flask end should not be larger than necessary, lest the turbulence of the contents of the mixing flask be carried into the settling chamber. In order to permit the extracted liquid to flow back to the drain, *C*, the side arm should be sealed on at a slight upward angle. The inner tube, *D*, was a length of 8-mm. tubing, whose lower end was drawn down to an opening of about 0.25 mm. It was sealed through the wall of the flask at the top, to prevent the loss of liquid when the air was turned off.

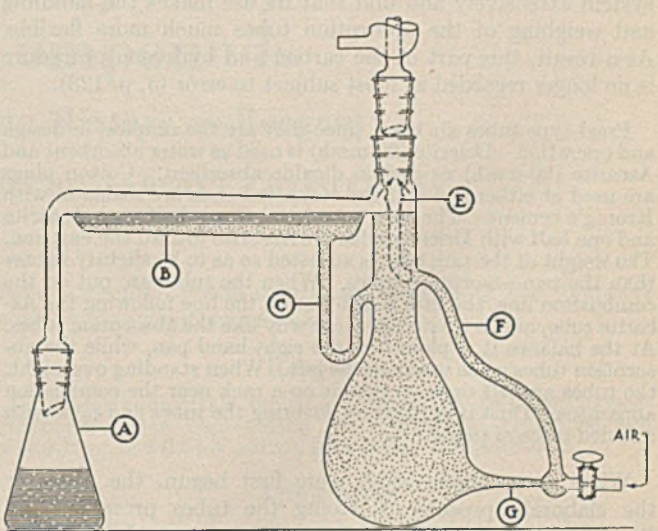

FIGURE 2. ORIGINAL DESIGN

In operation, the flask is filled with the liquid to be extracted to a point just below the bottom of the side arm, *B*. The volume of the air bubbles and solvent brings the level to the overflow. The stream of air should be regulated to the minimum required to give thorough mixing, as indicated by the homogeneity of the contents of the flask. Where colored material is being extracted, completion of extraction is easily estimated by the appearance of the extract in the settling chamber.

Literature Cited

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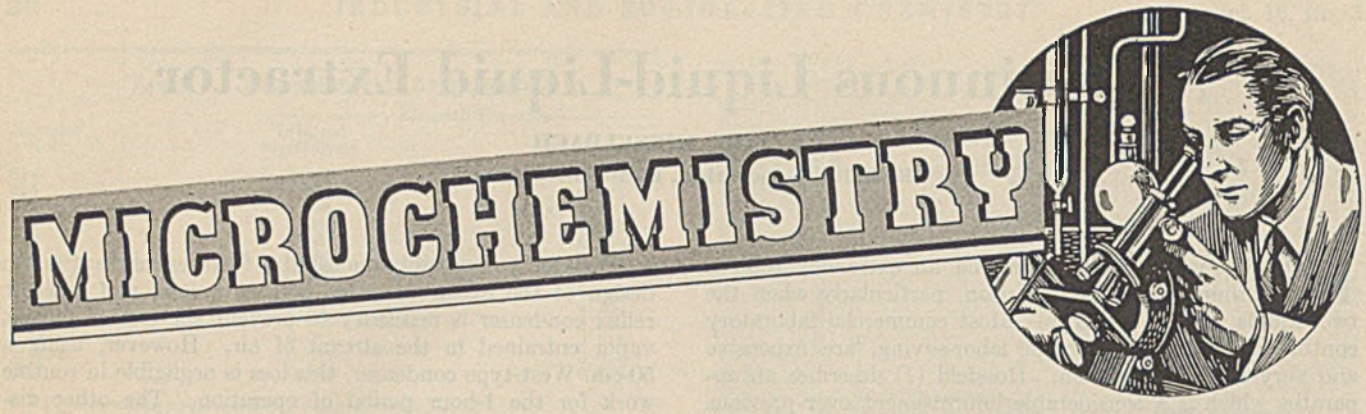

Absorption Tube Tares in Carbon and Hydrogen Microdetermination

W. M. MACNEVIN AND J. E. VARNER, Ohio State University, Columbus, Ohio

THE microdetermination of carbon and hydrogen as described by Pregl makes use of two absorption tubes, one for water and the other for carbon dioxide. Glass vessels containing lead shot are used as tares. The use of a third absorption tube as a control was described by Friedrich (*2*), who used specially designed tubes that could be closed for weighing. Niederl and Niederl (presumably using Pregl tubes) have suggested the use of a third tube not only as a control but as a tare in order to overcome the effects of high humidity (*3*, p. 114). However, the performance of their absorption system using Pregl type tubes has not been described in the literature. The authors have studied this system extensively and find that its use makes the handling and weighing of the absorption tubes much more flexible. As a result, this part of the carbon and hydrogen procedure is no longer regarded as most subject to error (*3*, p. 123).

Pregl-type tubes are used, since they are the simplest in design and operation. Drierite (20-mesh) is used as water absorbent and Ascarite (20-mesh) as carbon dioxide absorbent. Cotton plugs are used at either end and the stoppered ends are sealed in with Kronig's cement. The tare tube is filled one half with Ascarite and one half with Drierite, with the Ascarite toward the exit end. The weight of the tare tube is adjusted so as to be slightly lighter than the two absorption tubes. When the tubes are put on the combustion line, the tare is also put on the line following the Ascarite tube, and is treated in every way like the absorption tubes. At the balance it is placed on the right-hand pan, while the absorption tubes go as usual on the left. When standing overnight, the tubes are left open to the air on a rack near the combustion apparatus. Dust is kept off by covering the tubes and rack with a folded piece of paper.

When these observations were first begun, the need for the elaborate process of wiping the tubes prescribed by Pregl (*5*) was questioned. It quickly appeared, as Royer (*6*) has also observed, that wiping did not improve the results and often resulted in a drift in the apparent weight, thus requiring a longer waiting period. When the wiping was omitted the tubes became constant within 2 to 3 minutes of putting them on the balance—that is, as soon as the weighing could be completed—and remained constant over a relatively long period of time. The only wiping is given the outside of the tips of the capillaries between the thumb and first finger of the gloved hand, and the inside with a "pipestem" cleaner. A pair of clean white cotton gloves is worn when handling the tubes. The omission of wiping makes possible the use of absorption tubes made of Pyrex despite the statement of Niederl and Niederl (*3*, p. 136).

Table I shows data representing the changes in weight of the absorption tubes over a period of time counting from the moment the tubes were placed on the balance. The first time noted under each experiment represents the time elapsed between placing the tube on the balance and observing its weight.

Discussion

The data of Table I indicate that constant weight is reached about as rapidly as the weights can be added and the weighing operation completed. There is no pronounced tendency for the tubes to change weight, as has been found for other absorption systems (*1*). Thus it is not necessary to have a weighing time schedule. This makes the procedure flexible and therefore advantageous for beginners in the technique, whose working speed may be unusually slow. The greatest change noted in the water tube after 1-hour standing is +0.019 mg. For the four observations, the average change is +0.008 mg. For the carbon dioxide tube the corresponding values are noticeably less. This means that the operation of running carbon and hydrogen

TABLE I. CONSTANCY OF ABSORPTION TUBE WEIGHTS USING A THIRD TUBE AS CONTROL AND TARE

Expt.	H_2O Tube Elapsed time	H_2O Tube Change	CO_2 Tube Elapsed time	CO_2 Tube Change
	Min.	*Mg.*	*Min.*	*Mg.*
1	3		3	
	5	−0.002	5	−0.001
	8	−0.006	8	−0.005
			15	−0.008
2	3		3	
	5	−0.001	5	−0.001
	8	−0.003	8	−0.002
3	8		12	
	30	0.006	24	−0.002
4	8		12	
	60	0.019	64	0.000
5	8		12	
	60	0.007	64	−0.004
6	8		12	
	60	0.002	64	0.012
7	8		12	
	60	−0.003	64	0.007
8	8		12	
	90	0.013	94	0.004
9	8		12	
	90	0.024	94	0.014
10	8		12	
	20 hours	−0.020	20 hours	0.010
11	8		12	
	20 hours	−0.038	20 hours	0.015

analyses may, so far as the absorption tubes are concerned, be interrupted without affecting the results. Thus it is not always necessary to have a continuous period of several hours in order to perform carbon and hydrogen analyses. This is of some importance to students whose time is likely to be interrupted. (While such interruptions do not affect the tube weights, some combustion tube fillings, especially those containing lead dioxide, must be conditioned immediately before running an analysis.) The relative constancy of the tubes over a period up to 20 hours indicates the definite absence of any trend in the weight of the tubes. It also indicates that the Pregl tubes may safely be left open to the air for several hours without protecting them with rubber caps.

A great many analyses of research compounds prepared in this laboratory have been run with the absorption system described. The carbon values have agreed regularly within 0.3 per cent relative error and the hydrogen within 1 per cent relative error. However, the high hydrogen values usually associated with high temperatures and humidities (*4*) are still obtained with this system of tares, just as with the lead shot tares, and the proper correction must be determined using a known compound. The high hydrogen values are therefore probably not a direct result of high humidity.

This system of tare requires the use of extra weights from the set up to 300 to 400 mg. to tare the continuous gain in weight of the absorption tubes. The use of so many weights as a tare has not produced a noticeable error in the results.

The elimination of wiping apparently makes the use of Pyrex absorption tubes satisfactory. The omission of the waiting period shortens the total time for the analysis by at least 10 minutes.

Summary

The behavior of a carbon and hydrogen absorption system, in which a third Pregl-type tube is used both as a control and tare, is described.

If the tubes are not wiped, they are constant in weight as soon as they can be weighed. Thus they may be weighed without the usual waiting period.

The tubes remain fairly constant in weight up to periods of 1 hour and show only slight variations over much longer periods. Hence, a rigid weighing program is not required.

The omission of wiping makes possible the use of Pregl tubes made of Pyrex.

The use of a third tube as tare and control does not eliminate the high hydrogen values usually obtained at high atmospheric humidities with other absorption systems.

The use of extra weights to tare the gain in weight of the absorption tubes does not introduce a noticeable error.

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Microdetermination of Hydroxyl Content of Organic Compounds

Acetic Anhydride–Pyridine Mixture as Reagent

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THE simplest procedures for the determination of the hydroxyl content of organic compounds are those based on esterification. As yet little attention has been given to their application on a micro scale, a field in which they would be especially useful.

Several macro- and semimicromethods (*1*, *2*, *4*, *5*, *7*) employing both acetic anhydride and acetyl chloride have been described in the literature. Extensive esterification experiments with acetyl chloride have been reported recently from this laboratory (*1*). Attempts to use this reagent on a micro scale, however, have led to several other limitations besides those already mentioned (*1*).

Attention was therefore directed to a study of the esterifications with acetic anhydride–pyridine mixture. Both Peterson and West (*4*) and Verley and Bölsing (*7*) have published methods based on the use of this reagent. Stodola (*6*) has reduced the procedure to a micro scale. Since extensive testing of this mixture has not been previously reported, the behavior of a large number of typical alcohols and phenols treated with acetic anhydride–pyridine solutions was studied. As a result of this work a simple microchemical technique based on the use of a hermetically sealed tube has been developed in this laboratory which gives fairly satisfactory results for the microdetermination of the hydroxyl content of organic compounds.

Reagents

C. P. acetic anhydride, redistilled and acetate-free, kept in well-stoppered (screw cap) bottle; C. P. pyridine, redistilled and water-free; and 0.04 *N* sodium hydroxide, carbonate-free.

Apparatus

The reaction vessel consists of a melting point tube, 3 mm. in diameter and 6 cm. in length, made from a soft-glass test tube.

Three medicine droppers, for the delivery of alcohol, acetic anhydride, and pyridine, respectively, are made by drawing one end of a 6-mm. soft-glass tubing to a fine capillary and equipping the other end with a rubber policeman.

Glass plungers, 1.0 mm. × 0.5 cm., are made from soft-glass rod.

A microcentrifuge.

Analytical Procedure

Introduce 2 to 10 mg. of the compound into a weighed reaction tube by means of the dropper, or, in the case of solids, employ the technique described by Niederl for filling Rast tubes (*3*).

Centrifuge and again reweigh the tube. Using the same technique, add approximately 20 to 25 mg. (4 to 5 drops) of pure acetic anhydride from the second dropper, recentrifuge, and weigh

TABLE I. ACETYLATION WITH ACETIC ANHYDRIDE–PYRIDINE MIXTURES

Primary and Secondary Alcohols	No. of Determinations	OH Theory %	OH Found (Average) %	Average Deviation *Parts per 1000*
γ-Phenyl-*n*-propyl	2	12.4	12.3	0
Butyl	2	22.9	22.7	5
Isoamyl	2	19.3	19.25	8
Allyl	2	29.3	29.15	2
Cyclohexanol	2	17.0	16.90	6
Octanol-2	2	13.1	12.95	4
Hexanol	2	16.6	15.45	15
Benzyl	2	15.7	15.85	10
sec-Butyl	1	22.9	22.4	..
Cinnamyl	2	12.7	12.25	4
Diethylcarbinol	2	19.3	18.4	5
2-Ethylbutanol	2	16.6	15.9	12
Polyhydric alcohols				
Ethylene glycol	4	54.6	54.0	20
Propylene glycol	6	44.7	41.0	29
Diethylene glycol	4	32.1	30.1	4
Mannitol	2	56.1	56.15	1
Sorbitol	2	56.1	54.7	0
Substituted alcohols				
Ethylene chlorohydrin	4	21.1	20.0	3
1,3-Dichloropropanol-2	2	13.1	12.8	0
Terpenes				
Borneol	2	11.0	11.1	0
Menthol	2	11.0	10.9	9
Geraniol	2	11.0	9.9	0
Eugenol	2	10.4	10.55	5
Isoeugenol	4	10.4	9.75	7
Citronellol	4	10.9	9.45	28
Miscellaneous				
Benzoin	..	8.0	8.11	0
Cholesterol[a]	2[a]	4.4	4.5	11
Phenols				
Phenol	2	18.1	17.65	3
o-Cresol	2	15.7	15.55	10
p-Cresol	2	15.7	15.7	22
m-Cresol	2	15.7	15.35	3
α-Naphthol	2	11.8	11.55	4
β-Naphthol	2	11.8	11.65	4
Resorcinol	2	30.9	30.8	6
Hydroquinone	2	30.9	30.7	3
Orcinol	2	27.4	26.9	4
Catechol	2	30.9	31.05	5
2-Hydroxy-1,4-dimethylbenzene	2	13.9	13.8	8
Pyrogallol	3	40.5	40.0	17
Substituted phenols				
Vanillin	2	11.2	10.85	4
p-Hydroxy-benzaldehyde	2	13.9	13.65	4
Gallic acid	2	27.1	27.3	4
Thymol	2	11.0	11.15	4
Guaiacol	2	13.7	13.65	4
o-Chlorophenol	2	13.2	13.1	0
p-Chlorophenol	2	13.2	13.0	0
Methyl salicylate	2	11.2	11.35	4
Salicylic acid	2	12.3	12.35	4
m-Hydroxybenzoic	2	12.3	12.2	9
p-Hydroxybenzoic	2	12.2	12.25	4
4-Hydroxy-1,2-dimethyl benzene	2	13.9	14.15	4
m-Nitrophenol	2	12.2	12.1	9
p-Nitrophenol	2	12.2	11.35	4
o-Nitrophenol	2	12.2	11.45	2
p-Aminophenol	2	15.6	15.05	1
2-Hydroxy-1,4-dimethylbenzene	2	13.9	13.8	7
Sugars				
Sucrose[b]	4	39.8	39.9	5
Xylose	2	45.5	45.55	3

[a] Hydrolyzed in usual way, then 10 ml. of 95% ethanol added to dissolve ester before titration.
[b] Ran 48 hours.

again. In order to ensure the quantitative conversion of the alcohol to the ester, a ratio of at least 2 moles of anhydride per equivalent of hydroxyl should be maintained.

Add 4 to 6 drops of pure pyridine and again centrifuge. The amount of pyridine does not appear to be critical except in a few cases involving solubility. Insert a small glass rod in the tube, seal, then shake well to ensure complete mixing, and set aside for 24 hours. At the same time run a blank to determine the volume of standard base required to neutralize the acid derived from 1 mg. of acetic anhydride.

Place the reaction tube in a 50-ml. Erlenmeyer flask, add 5 ml. of water, and then break the tube by means of a stout stirring rod. Titrate released acid with 0.04 *N* sodium hydroxide. The per cent hydroxyl can then be calculated by means of the formula:

$$\%\,(OH) = \frac{(\text{m. e. of anhydride used} - \text{m. e. of acid found}) \times 1700}{\text{mg. of sample}}$$

where m. e. of acid found = ml. × normality, m. e. of anhydride used = mg. of anhydride × ratio × normality, and ratio = ml. of base required to neutralize acid derived from 1 mg. of anhydride.

Results and Discussion

The results obtained with this procedure are given in Table I. In most cases they are the average of duplicate determinations.

This method is not applicable to the determination of tertiary alcohols. Ethyl citrate, *t*-amyl, and *t*-butyl alcohol gave very low results which confirm the observations of others.

Although all experiments were extended over a period of 24 hours at room temperature, these conditions are not to be considered as well-established optima. Since the reaction mixture is hermetically sealed, experiments can be conducted with equal ease at elevated temperatures. Several compounds have been reported to acetylate in 15 minutes at 100° C. in acetic anhydride and pyridine. In this laboratory borneol has been quantitatively acetylated in 35 minutes at 100° C. On the other hand a number of alcohols give poor results at higher temperatures, possibly because of decomposition.

The authors' experience indicates that the ease of acetylation varies with the individual compounds. The ratio of acetic anhydride to alcohol has been found to be somewhat critical and should not fall below 100 mole per cent excess per equivalent of hydroxyl. Since the hydroxyl is determined by difference, it is not a good policy to employ too large an excess for accurate work.

Care should be exercised in the selection of acetic anhydride. It is essential that pure redistilled anhydride (from a good fractionating column) be used to obtain the best results. In some of the initial work erratic results were traced to the presence of a considerable quantity of acetic acid in the acetic anhydride. As soon as this was remedied the results were nearer the theoretical values and were much more reproducible. In later experiments the acetic anhydride was redistilled in a 7-plate column. The titer of this anhydride agreed perfectly with the theoretical value.

The experiments with sugars were performed merely to ascertain the possibilities of a micromethod in this field. As indicated, the results are satisfactory and are in agreement with the data of Peterson and West (*4*).

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Qualitative Analysis of Microgram Samples

Separation, Estimation, and Identification of the More Common Ions of the Hydrogen Sulfide Group

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The technique of working in the capillary cone has been applied to analyses requiring lengthy separations followed by sedimetric estimations and confirmatory tests. Various improvements have been made in the performance of manipulations, and a method for fractional distillation has been developed, which may be applied to liquids of approximately 0.1- to 0.01-cu. mm. volume.

The complete analysis of a particle of Wood's alloy of 1-microgram mass required approximately 12 hours. Such efficiency can be expected only after a period of training. Manual dexterity is perhaps of less importance than methodical organization of work. Proper design of work bench and the use of microprojection will considerably reduce fatigue, if work of this kind has to be performed for any length of time.

THE technique described in preceding papers of this series (*1, 3*) was tested by application to the analysis of rather complex mixtures containing ions of the hydrogen sulfide group. To make the test more severe a scheme of macroanalysis was chosen, which emphasizes quantitative separations and estimation of the amount of the ions.

Technique

The experience gained led to various improvements and extensions of the techniques employed in the transfer of solutions to capillary cones and in the mixing, stirring, and heating of the contents of such cones. These, as well as the procedure for distillation from one capillary cone to another, have been described in detail (*2*). Some advice may be added.

TRANSFER OF SOLIDS TO CAPILLARY CONES. When a sample is selected for analysis, it is desirable to have the material spread for microscopic inspection. The procedure described for the transfer of solid reagents (*2*) has the disadvantage that the use of an inclined slide does not permit a sharp focus for the entire field of vision. If the microscope slide with the material is placed level on top of the chamber containing the capillary cone, a suitable needle for the transfer of particles is obtained by sealing the tip of a micropipet and bending it through an angle of 30 degrees (*4, 9*). The shank of the pipet is then inserted into the holder, so that the tip points downward. When the selected particle has been picked up with the needle, the clamp of the manipulator is released for a moment, and the pipet holder is rotated to bring the tip of the needle into a horizontal plane. It is then easy to introduce the particle into the capillary cone. The procedure is illustrated by Figure 1. Filings of Wood's alloy (specific gravity 7) are first shown on a microscope slide. An approximately spherical particle, 66μ in diameter, which may be expected to have a mass of 1 microgram, has been brought into the center of the field and is just being touched with the point of the needle. On the right is the same particle just before it is deposited inside the capillary cone.

ESTIMATION OF THE QUANTITY OF PRECIPITATES. Figure 2 (left) shows a sulfide precipitate containing 0.1 microgram of antimony and 0.01 microgram of bismuth. Figure 2 (right) shows the same precipitate after whirling in the centrifuge. Obviously, it is collected in the point of the cone, but inspection under higher magnification would conclusively demonstrate that the point of the taper is free from precipitate. Neither base nor top of the truncated cone filled by the precipitate presents a plane surface. Since some arbitrary lines must be drawn when the calculation of the volume of precipitate is based on the assumption of a truncated cone, it seemed well to imagine a sphere containing the precipitate, and to base the estimation on the diameter of this imaginary sphere (*1*). It is understood that a definite amount of centrifugal force was applied for a certain time when collecting precipitates for the purpose of estimation. As a rule, 1 minute of centrifuging with a relative centrifugal force equal to 500 times gravity gave satisfactory results.

USE OF TEST PAPER. Spot tests on paper may be performed in a very simple manner. The paper is cut into strips approximately 3 mm. wide and 20 mm. long. Whenever needed, a strip is placed on the carrier so that it lies flat and parallel to the capillary cones and reagent cones. Approximately one third of the strip projects beyond the edge of the carrier, and this part of the paper is bent downward, so that the opening of the micropipet makes contact with the paper. Test solutions and reagent solutions are transferred from capillary cones or reagent containers to the paper by means of the micropipet. The colorations produced are best observed with low magnification and reflected light of low intensity.

The technique was employed when testing the acidity of solutions with litmus paper and in the confirmatory tests for cadmium (cadion) and tin (molybdenum blue).

PROJECTION OF MICROSCOPIC IMAGES. The operations performed under the microscope are just as easily controlled by observation of a projected image as by viewing through the eyepiece. The glare sent out by the illuminated apparatus on the stage is not very bothersome when the intensity of the light is decreased to that required for a screen image of 10- to 20-cm. diameter. Under this condition, the use of projection will reduce eyestrain, and the operator will be able to assume a more restful posture.

Scheme of Analysis

The scheme of Swift (*12*) was adopted with some modifications. The return, in a sense, of the mercury to the copper

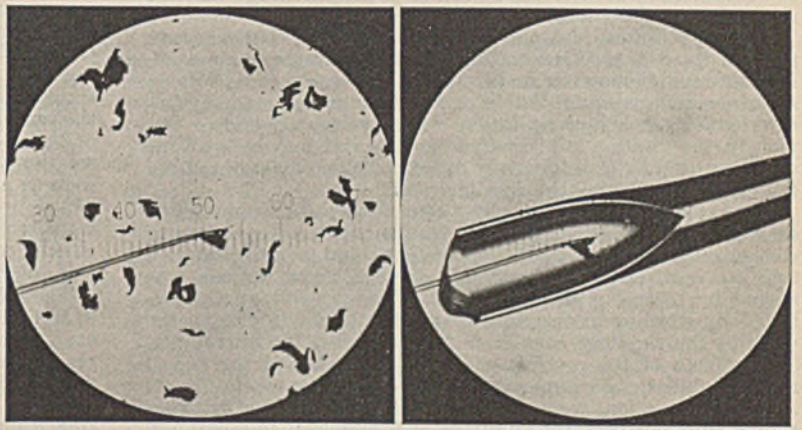

FIGURE 1. TRANSFER OF A PARTICLE OF WOOD'S ALLOY OF APPROXIMATELY 1-MICROGRAM MASS FROM A SLIDE TO CAPILLARY CONE
One division of micrometer scale corresponds to 22 microns. Magnification, × 46

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group probably is the most pronounced deviation, and it was introduced when it was found (*5*, *10*) that the extraction of mercuric sulfide from the sulfide precipitate remained incomplete when medium to large quantities of mercury were present. Various minor changes had to be made because of the substitution of sedimetric estimations followed by confirmatory tests for the titrimetric determinations employed by Swift.

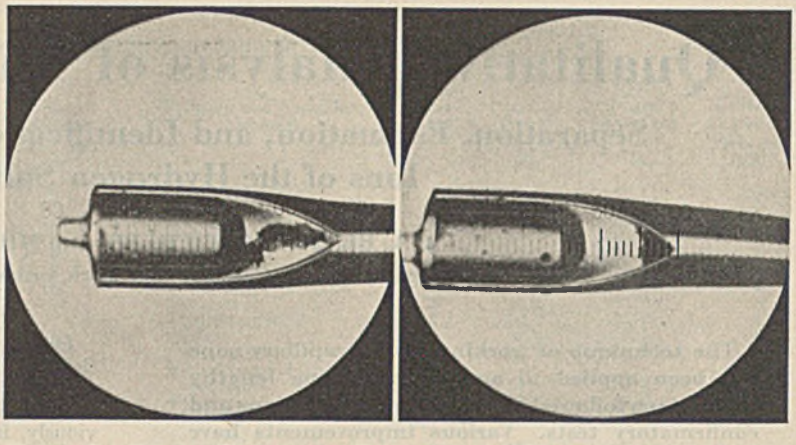

FIGURE 2. SULFIDE PRECIPITATE CONTAINING 0.1 MICROGRAM OF ANTIMONY AND 0.01 MICROGRAM OF BISMUTH

One division of eyepiece micrometer is equal to 21 microns. Magnification, × 48
Left. Contents of capillary cone after treatment with hydrogen sulfide
Right. Precipitate collected in point of cone by means of centrifuge. Estimated that precipitate would fill a sphere of 63-micron diameter, 3 divisions of the scale

PREPARATION OF SOLUTION. In the analysis of Wood's alloy a particle of approximately 1 microgram mass was treated in the capillary cone with 0.01 cu. mm. of 16 *M* nitric acid. Reaction with evolution of gas and separation of a white precipitate started immediately. The mixture of solution and precipitate was evaporated almost to dryness by heating on the steam bath, and the residue was taken up with 0.007 cu. mm. of 12 *M* hydrochloric acid. Most of the residue dissolved, and the mixture was treated with 0.1 cu. mm. of water previous to saturating with hydrogen sulfide.

Known solutions were prepared on a large scale and made approximately 4 *M* with respect to acid. Of these solutions 0.01 cu. mm. was taken for analysis, transferred to the capillary cone, and diluted with 0.1 cu. mm. of water. Precipitates separating because of hydrolysis appear brown in transmitted light and white in reflected light. They were left in suspension for the treatment with hydrogen sulfide.

PRECIPITATION OF THE HYDROGEN SULFIDE GROUP. The solution or mixture of solution and precipitate was saturated with hydrogen sulfide, as described in an earlier communication (*1*). The reaction mixture was heated at 60° to 70° C. for half a minute and then allowed to stand for 1 hour at room temperature. The precipitate was collected by means of the centrifuge and its volume was estimated. Another portion of 0.1 cu. mm. of water was added, and saturation with hydrogen sulfide, heating, standing, centrifuging, and estimation of volume were repeated. The solution was removed, and the precipitate was washed once with 0.01 cu. mm. of 0.12 *M* nitric acid.

SEPARATION OF THE COPPER AND ARSENIC GROUPS. The sulfide precipitate was immediately treated with 0.02 cu. mm. of sodium sulfide–hydroxide reagent (*8*, 48 grams of sodium sulfide novahydrate and 4 grams of sodium hydroxide in 100 ml. of solution). The capillary cone was sealed into a capillary and inserted in a water bath at 60° to 80° C. for one minute. The capillary was withdrawn from the bath a few times, and its contents were stirred by means of the buzzer (*2*). The extraction was repeated with a 0.02-cu. mm. portion of a 1 to 1 dilution of the reagent. The volume of the residual sulfides was estimated before removal of the second extract. The extracts were combined, and the residue was washed with 0.01 cu. mm. of water by stirring and centrifuging.

DISSOLVING THE SULFIDES OF THE COPPER GROUP. The residue from the extraction with sodium sulfide was immediately treated with 0.02 cu. mm. of 3 *M* nitric acid, sealed into a capillary, and heated in steam until solution of the sulfides appeared complete when observed under the microscope. A small residue of white sulfur was collected by means of the centrifuge, and the clear solution was transferred to another cone.

If the precipitate did not dissolve completely, 0.01 cu. mm. more of the 3 *M* acid was added and the heating was repeated. Mercuric sulfide may remain behind with the sulfur. Its volume may be estimated immediately or after solution in nitric-hydrochloric acid and reprecipitation with hydrogen sulfide. Obviously, the solution in nitric-hydrochloric acid may be set aside and later used for dissolving any mercuric sulfide separating from the extract containing the arsenic group.

ISOLATION OF MERCURY. The cone with the sodium sulfide extract was transferred to a dry chamber with a large drop of concentrated ammonia on the bottom plate and then treated with 0.03 cu. mm. of 3 *M* ammonium acetate. The mixture was stirred by means of the buzzer (*2*). The precipitate was collected by whirling in the centrifuge. Particles adhering to the walls of the capillary cone were loosened with the micropipet. The volume of the precipitate was estimated, and the supernatant solution was immediately transferred to another cone. All these operations were performed without delay, for evaporation of ammonia from the capillary cone may lead to separation of the sulfides of arsenic, antimony, and tin from the solution of their thio complexes.

Confirmatory Test for Mercury. The precipitate of mercuric sulfide was washed once with 0.01 cu. mm. of water, then treated with 0.01 cu. mm. of nitric-hydrochloric acid (1 to 1). The mixture was evaporated to dryness on the steam bath. The residue was either dissolved in 0.01 cu. mm. of 0.12 *M* nitric acid and the solution used for the diphenylcarbazide test (*3*), or it was dissolved in 0.005 cu. mm. of water and treated with 0.01 cu. mm. of 1 per cent stannous chloride. The whitish gray precipitate produced by the latter reagent is easily observed with reflected light after collection in the point of the capillary cone by means of the centrifuge.

PRECIPITATION OF THE ARSENIC GROUP. The centrifugate from the mercuric sulfide precipitate, which may contain thio complexes of arsenic, antimony, and tin, was treated with 1 *M* sulfuric acid. Approximately 0.2 cu. mm. of this acid are required, but the relatively large volume is of little consequence. Stronger acid reacts so violently that some of the reacting matter may be ejected from the cone as a consequence of the rapid liberation of hydrogen sulfide.

The sulfuric acid was added in small portions while stirring with the micropipet until the mixture became just acid. For testing, small portions of the solution were transferred to litmus paper. Flocculation of the precipitate was finally made complete by heating in a sealed capillary for a few minutes at 80° to 90° C. The mixture was centrifuged and the solution removed and rejected.

If there is reason to believe that too much acid had been added, one may test for absence of tin from the centrifugate by diluting it with 0.05 cu. mm. of water, saturating with hydrogen sulfide, heating, and stirring by means of the buzzer. An estimation of the volume of the sulfides of the arsenic group requires subtraction of the volume of the sulfur contained in the precipitate. The volume of the sulfur left behind when the sulfides are dissolved allows a crude approximation.

ISOLATION OF ARSENIC. The sulfides of the arsenic group were treated with 0.03 cu. mm. of 12 *M* hydrochloric acid. The mixture was warmed for 15 seconds in a water bath and then thoroughly agitated by means of the buzzer. The capillary cone was then returned to the dry chamber, and its contents were inspected under the microscope. If any sulfide was discovered, the mixture was treated with potassium bromate. One particle of the potassium bromate was added at a time, whereupon the solution was stirred. The addition of bromate was stopped as soon as all the sulfide was dissolved. The sulfur was then collected by means of the centrifuge, and the clear solution was transferred to another capillary cone. The residue of sulfur was washed with 0.03 cu. mm. of 12 *M* hydrochloric acid, and this acid was then added to the solution of the sulfides.

The solution of the sulfides was treated with 0.01 cu. mm. of 9 *M* hydrochloric acid and 0.02 cu. mm. of 3 *M* phosphorous acid. The cone was sealed into a capillary, immersed for 5 to 10 seconds in water at 80° to 90° C., and cooled in a stream of tap water. After insertion of the capillary cone into a distilling capillary (*2*), the distillation was started (Figure 3), and continued until the volume of the residue in the capillary cone was reduced to 0.015 or 0.01 cu. mm. The residue of the distillation was treated with 0.01 cu. mm. of 12 *M* hydrochloric acid, and the

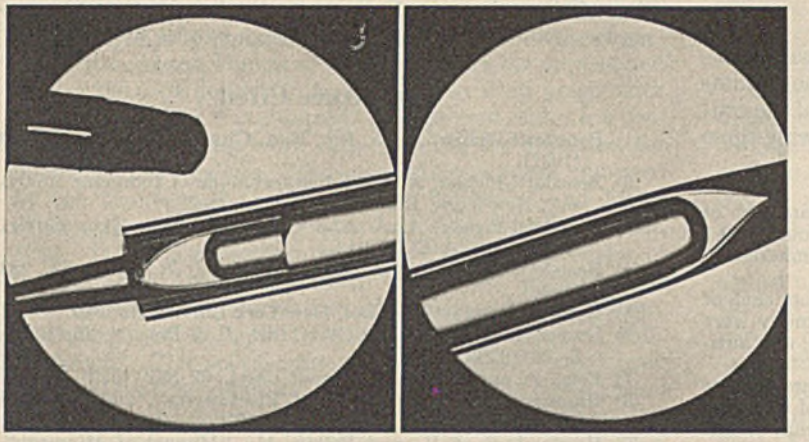

FIGURE 3. DISTILLATION FROM ONE CAPILLARY CONE TO ANOTHER

Photomicrographs show two halves of same distilling capillary. Magnification, × 30
Left. Start of distillation. Heating element is visible above opening of distilling capillary containing capillary cone with liquid to be distilled
Right. Close of distillation. Distillate collected at sealed end of distilling capillary

distillation was repeated until again a residue of the above indicated volume remained behind.

The distillate (Figure 3, right) was transferred to a capillary cone of the standard type, diluted with water to a volume of approximately 0.1 cu. mm., treated with 0.04 cu. mm. of 12 *M* hydrochloric acid, and saturated with hydrogen sulfide. Flocculation of the precipitate was brought about by heating for 30 to 45 seconds at 60° to 70° C. and agitation by means of the buzzer. The volume of the precipitate was estimated after centrifuging.

Confirmatory Test for Arsenic. The supernatant solution was removed, and the yellow precipitate of arsenic sulfide was washed once with approximately 0.03 cu. mm. of water and then dissolved in 0.01 cu. mm. of 6 *M* ammonia. The solution was evaporated almost to dryness by heating in steam, the residue was treated with approximately 0.05 cu. mm. of 16 *M* nitric acid, and the mixture was evaporated to dryness. The residue was extracted with a volume of 1 *M* nitric acid to give an approximately 1 per cent solution of arsenic. Part of this solution was treated on the plateau of the condenser rod with silver nitrate in acetate buffer solution (*3*).

ISOLATION OF ANTIMONY. The residue from the distillation was treated with 0.02 cu. mm. of 3 *M* sulfuric acid and 0.01 cu. mm. of 6 *M* hydrochloric acid, and water was added to bring the total volume to 0.075 cu. mm. Finally 5 cu. mm. of phosphoric acid, obtained by mixing 1 volume of sirupy acid with 4 volumes of water, were added, and the antimony sulfide was precipitated by saturating with hydrogen sulfide, and heating at 60° to 70° C. as described. The precipitate was collected by means of the centrifuge, and its volume was estimated. The solution containing the tin was transferred to another capillary cone. The precipitate was washed with 0.01 cu. mm. of 1.2 *M* hydrochloric acid, which was then combined with the centrifugate.

Confirmatory Test for Antimony. The antimony sulfide was dissolved by heating with 0.02 cu. mm. of 12 *M* hydrochloric acid. Part of the clear solution was transferred to the plateau of the condenser rod and tested with the quinine reagent (*3*).

ISOLATION OF TIN. The centrifugate containing the tin was treated by the addition of small portions of concentrated ammonia until test with litmus paper indicated alkaline reaction. The solution was then saturated with hydrogen sulfide and briefly heated at 60° to 70° C. After the capillary cone had been placed in a dry chamber, 0.005 cu. mm. of 3 *M* sulfuric acid was added to the contents. The precipitate of tin sulfide formed slowly. It could not be readily seen in transmitted light, but was visible in reflected light. Stirring with the pipet hastened flocculation. Precipitate and solution were again saturated with hydrogen sulfide, and the mixture was allowed to stand for at least a few hours. It was then centrifuged, and the volume of the stannic sulfide was estimated.

Confirmatory Test for Tin. The centrifugate was removed from the yellow stannic sulfide, the precipitate was washed once with 0.015 cu. mm. of 1 *M* ammonium chloride, and the sulfide was dissolved by heating in steam with 0.02 cu. mm. of 6 *M* hydrochloric acid. After addition of 0.01 cu. mm. of 12 *M* hydrochloric acid and centrifuging, parts of the clear solution were used for confirmatory tests. Since the crystals of the cesium chlorostannate are very small and difficult to identify, performance of a spot test was preferred. A small particle of magnesium metal, obtained by scraping with a razor on the edge of magnesium ribbon, was introduced into the acid solution. A small portion of the reduced solution was immediately transferred to a strip of ammonium phosphomolybdate test paper (*7*). The blue spot was observed with the use of the general room illumination and a magnification of 28 diameters.

ISOLATION AND CONFIRMATION OF LEAD. The nitric acid solution of the sulfides of the copper group was evaporated to dryness on the steam bath, the residue was treated with 0.015 cu. mm. of 6 *M* sulfuric acid, and the volume of the lead sulfate was estimated. The solution was transferred to another centrifuge cone, and the precipitate was washed once with 0.005 cu. mm. of 0.6 *M* sulfuric acid, which was then added to the centrifugate containing bismuth, copper, and cadmium.

The lead sulfate was dissolved by adding 0.02 cu. mm. of 3 *M* ammonium acetate and stirring. To the solution was added 3 *M* sodium chromate in small portions until yellow coloration of the solution indicated an excess of the reagent. The lead chromate was collected by means of the centrifuge, and its volume was estimated.

ISOLATION OF BISMUTH. The capillary cone with the centrifugate from the lead sulfate was transferred to a dry chamber, and the solution was treated with small portions of concentrated ammonia until a white precipitate could be perceived with reflected light. Then 0.005 cu. mm. more of the ammonia was added, and the mixture was heated for 15 seconds at 90° C. after being sealed into a capillary. After centrifuging, the capillary cone was transferred to a moist chamber for the determination of the volume of bismuth hydroxide.

Because of the transparent appearance of the precipitate, the removal of the supernatant solution and washing of the precipitate with 0.01 cu. mm. of 1 *M* ammonia were observed with reflected light. The washing was combined with the centrifugate containing copper and cadmium.

Confirmatory Test for Bismuth. The bismuth hydroxide was dissolved in 0.005 cu. mm. of 3 *M* hydrochloric acid. Parts of the solution were used for performance of the cesium and quinine iodobismuthite tests (*3*) on the plateau of the condenser rod.

ISOLATION OF COPPER. The copper may be separated from cadmium by precipitation as cuprous thiocyanate. This method was successfully applied to the analysis of centigram and milligram samples (*5*, *10*). In the experiments on the microgram scale copper never occurred with cadmium, and it could be isolated as the sulfide. The volume of the sulfide precipitate served for estimation of the quantity of copper.

Confirmatory Test for Copper. The copper sulfide was treated with 0.02 cu. mm. of 3 *M* nitric acid, the mixture was evaporated to dryness, and the residue was stirred with 0.015 cu. mm. of water. After centrifuging, half of the clear solution was transferred to the plateau of a condenser rod and tested with salicylaldoxime (*3*). The rest of the solution was treated on a plateau with a somewhat larger volume of a saturated solution of potassium ferrocyanide. The brown precipitate of copper ferrocyanide was observed with a magnification of 60 diameters.

ISOLATION OF CADMIUM. The ammoniacal centrifugate from the bismuth hydroxide was treated with 0.005 cu. mm. of 10 per cent potassium cyanide. The clear solution was then saturated with hydrogen sulfide, heated at 65° C. for about 20 seconds, agitated with the buzzer, and centrifuged. The volume of the yellow cadmium sulfide was determined.

Confirmatory Test for Cadmium. After removal of the centrifugate the cadmium sulfide was washed once with 0.02 cu. mm. of water and then dissolved in 0.015 cu. mm. of 6 *M* sulfuric acid. The mixture was briefly heated on the steam bath. After centrifuging, the clear solution was transferred to another capillary cone and treated with an approximately equal volume of buffer solution containing 10 grams of Rochelle salt and 0.1 ml. of glacial acetic acid in 100 ml. Homogeneity was obtained by stirring with the pipet. Approximately 0.015 cu. mm. of the solution was transferred to a strip of paper treated with Cadion 3B reagent (*2*, *6*). After the solution had evaporated on the paper, 0.01 cu. mm. of a solution consisting of 4 volumes of 2 *M* sodium hydroxide and 1 volume of ethyl alcohol was added. The pink coloration produced by the lake of the dye with the cadmium hydroxide was distinctly visible with reflected light.

Results

Application of the technique and scheme of analysis to samples of approximately 1-microgram mass revealed the qualitative composition in each instance. The reliability of the estimation of quantities may be derived from the following three examples.

In 0.01 cu. mm. of a solution containing 0.1 microgram each of the ions copper, arsenic, antimony, and tin were found: 0.1 microgram of copper, 0.06 microgram of arsenic, 0.1 microgram of antimony, and 0.24 microgram of tin.

In 0.01 cu. mm. of a solution containing 0.1 microgram each of mercuric mercury, lead, bismuth, cadmium, and antimony were found: 0.1 microgram each of mercury, lead, bismuth, and antimony, and 0.8 microgram of cadmium.

In 1 microgram of Wood's alloy containing 0.5 microgram of bismuth, 0.2 microgram of lead, 0.125 microgram of tin, and 0.125 microgram of cadmium were found: 10 microgram of bismuth, 0.4 microgram of lead, 0.1 microgram of tin, and 0.1 microgram of cadmium.

The most glaring mistakes were committed in the estimations of bismuth and cadmium, and in both instances the reason must be sought in the poor reproducibility of the volumes of gelatinous precipitates of bismuth hydroxide and cadmium sulfide. The trouble might be overcome by converting the bismuth hydroxide to metallic bismuth and the cadmium sulfide to cadmium-thiourea Reineckate (*11*). The determination of the volume and consequently the mass of the alloy may easily be affected with an uncertainty of ±50 per cent.

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(12) Swift, E. H., "System of Chemical Analysis for the Common Elements", New York, Prentice-Hall, 1939.

Presented in part before the Division of Microchemistry at the 100th Meeting of the American Chemical Society, Detroit, Mich. Abstracted from part of the thesis submitted by Michael Cefola to the faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of doctor of philosophy.

Report on Recommended Specifications for Microchemical Apparatus

SULFUR AND HALOGENS

G. L. ROYER, *Chairman* L. T. HALLETT
H. K. ALBER J. A. KUCK, *Secretary*

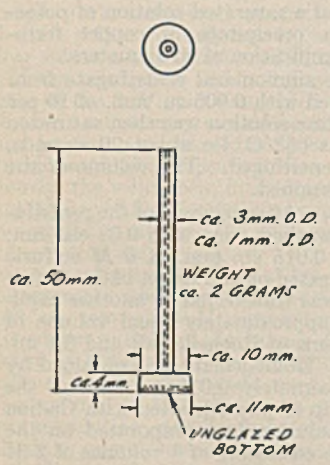

Figure 1. Porcelain Filter Stick

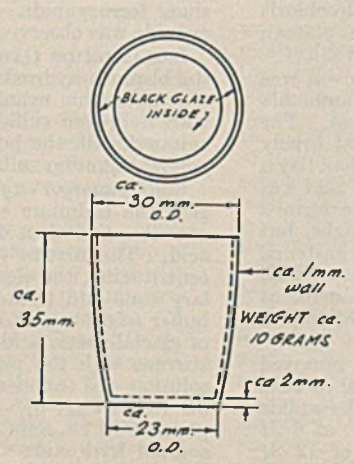

Figure 2. Porcelain Crucible

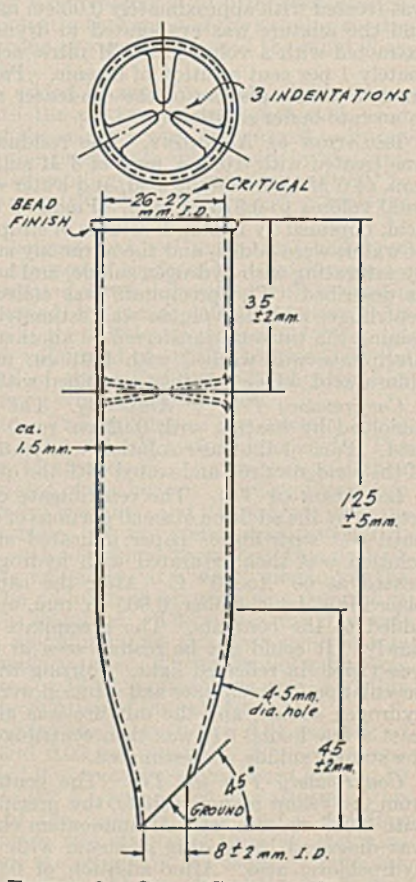

Figure 3. Glass Crucible Holder for Water Bath

A PREVIOUS report covering the recommended specifications for the apparatus for the determination of carbon-hydrogen and Dumas nitrogen (*1*) states the purpose and aims of the work and gives the bibliography from which much of the information was obtained. The present report is a continuation of the same work with regard to the apparatus for microchemical analysis. This present report was approved by the members of the Division of Analytical and Micro Chemistry after its presentation at Buffalo in September, 1942. It has also been approved by a special committee of the Scientific Apparatus Makers of America, appointed by John M. Roberts, president, which consisted of J. J. Moran, chairman, A. A. Kelm, L. D. Wilson, W. B. Warren, and J. E. Patterson. The specifications reported here, having been approved by this committee, have thus received the approval of the Scientific Apparatus Makers. With the acceptance of these recommended specifications by this organization and with the approval of the Division of Analytical and Micro Chemistry, the Committee on Standard Apparatus of the AMERICAN CHEMICAL SOCIETY advocated their publication.

An examination of the drawings shows that certain of the dimensions are theoretically and experimentally critical, while others could be varied over wide limits. However, many of these dimensions, which may not in themselves be critical, can be accurately controlled in the manufacturing process without inconvenience. For this reason, all the dimensions on the drawings are given with specified limits which have been agreed upon by both the manufacturers and the microchemists. We have been unable to describe specifically certain factors, such as the porosity of the sintered porcelain and glass apparatus. Therefore, we must rely upon the manufacturers to control these within the limits necessary to be satisfactory.

The drawings which accompany this report are not reproduced here in full size. Copies of the full-size drawings may be obtained at a nominal cost from the office of the Scientific Apparatus Makers of America, 20 North Wacker Drive, Chicago, Ill.

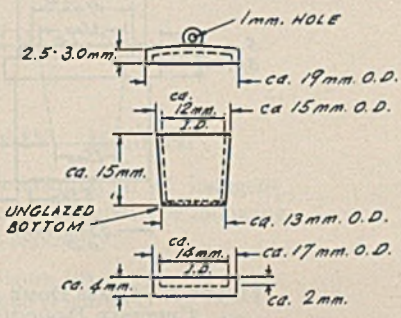

FIGURE 4. PORCELAIN FILTER CRUCIBLE AND IGNITION DISH

Part III. Sulfur

The following units were considered by the committee as requiring specifications:

Filter stick (Figure 1)
Crucible (Figure 2)
Glass crucible holder (Figure 3)
Filter crucible and ignition dish (Figure 4)
Crucible filter assembly (Figure 5)
Siphon, receiver, and inner container for barium sulfate filtration (Figure 6)
Glass dome and metal crucible desiccator (Figure 7)
Micro evaporating dish for sulfur bomb determination (Figure 8)
Platinum microware for both halogen and sulfur determinations (Figure 9)

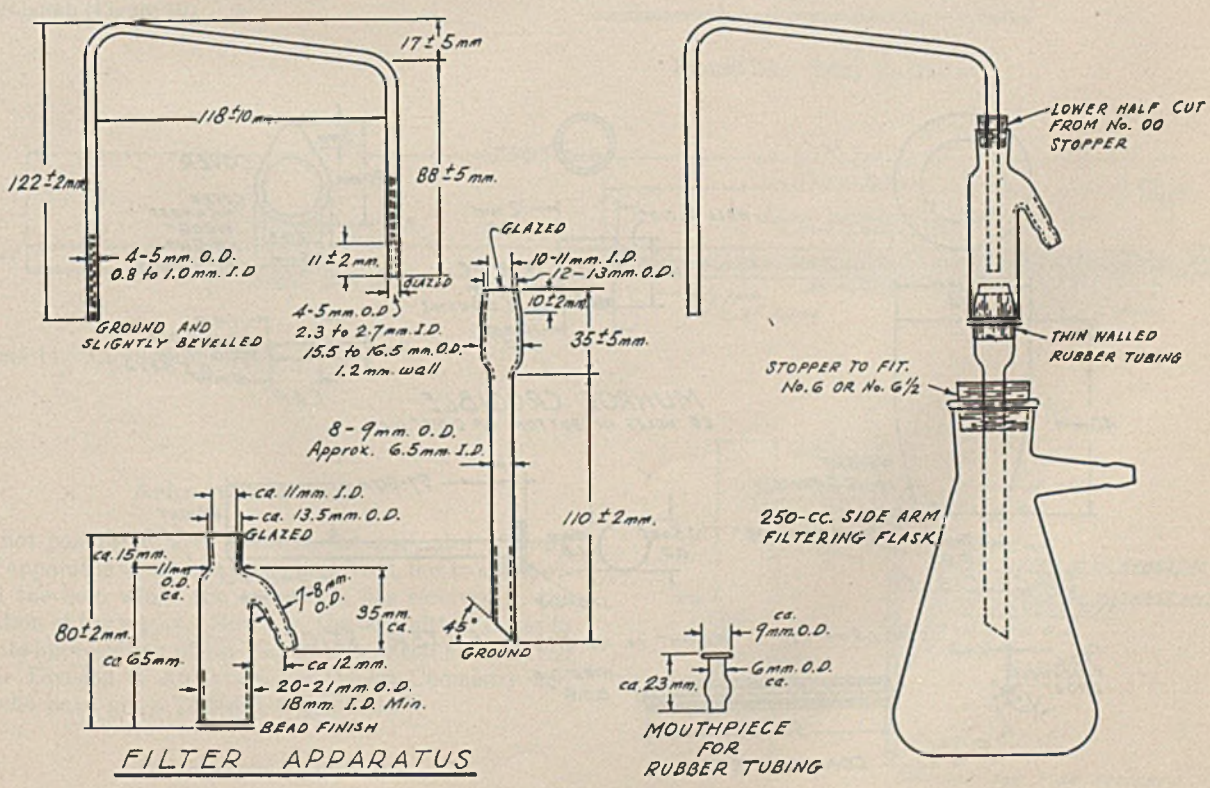

FIGURE 5. CRUCIBLE FILTER ASSEMBLY

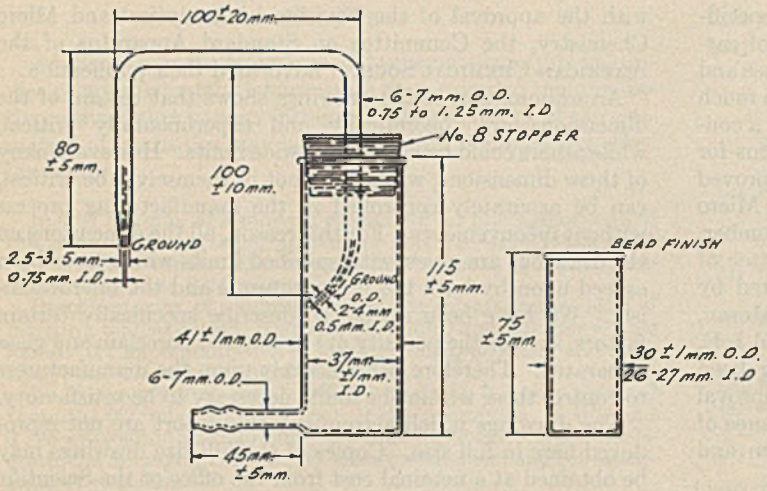

FIGURE 6. SIPHON, RECEIVER, AND INNER CONTAINER FOR BARIUM SULFATE FILTRATION

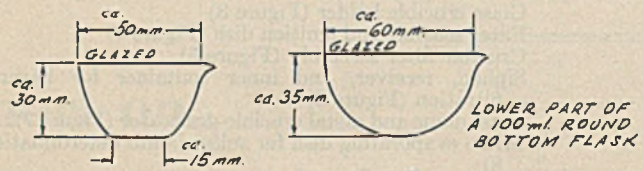

FIGURE 8. MICRO EVAPORATING DISH FOR SULFUR BOMB DETERMINATION

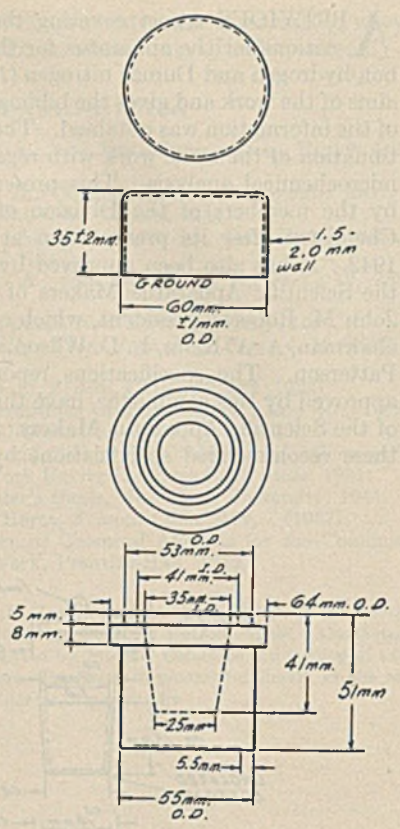

FIGURE 7. GLASS DOME AND METAL CRUCIBLE DESICCATOR

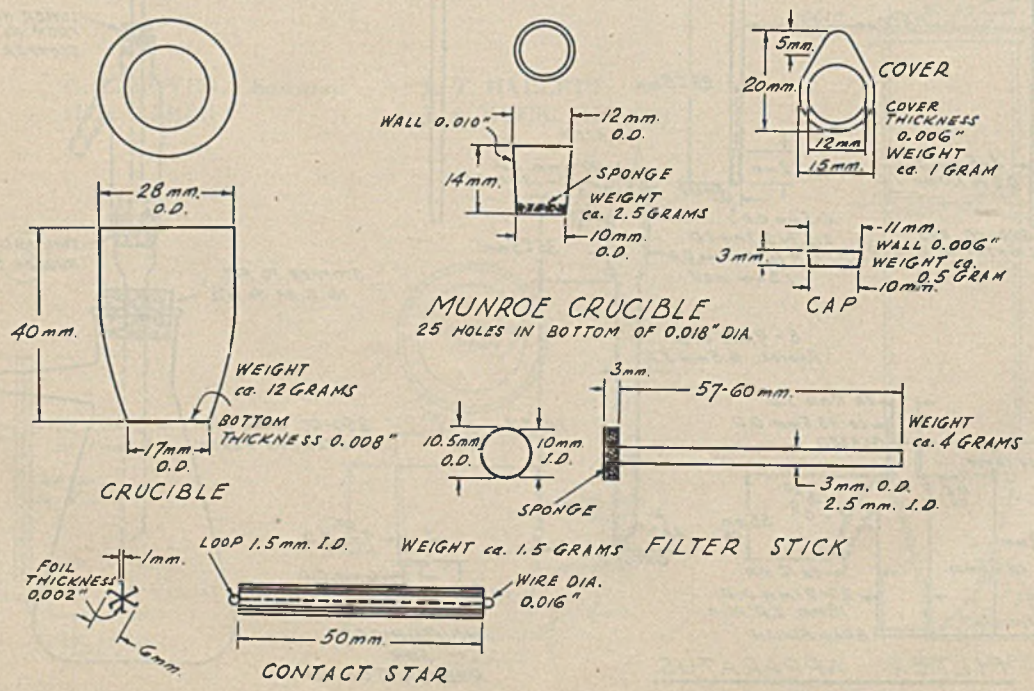

FIGURE 9. PLATINUM MICROWARE FOR HALOGEN AND SULFUR DETERMINATIONS

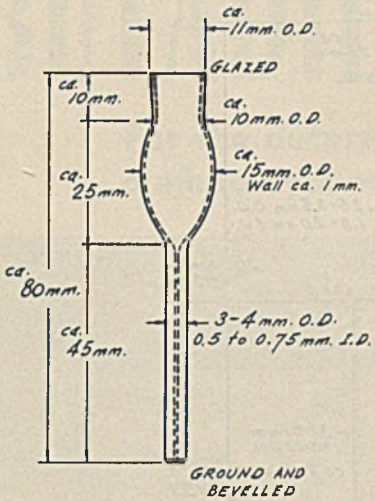

FIGURE 10. AIR FILTER

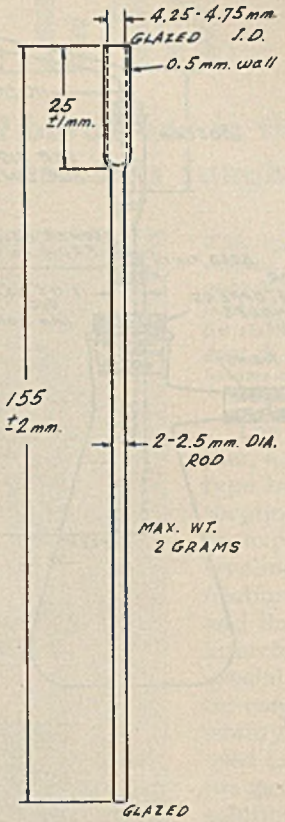

FIGURE 11. WEIGHING TUBE

Tube for Carius like above, except 200 mm. over-all

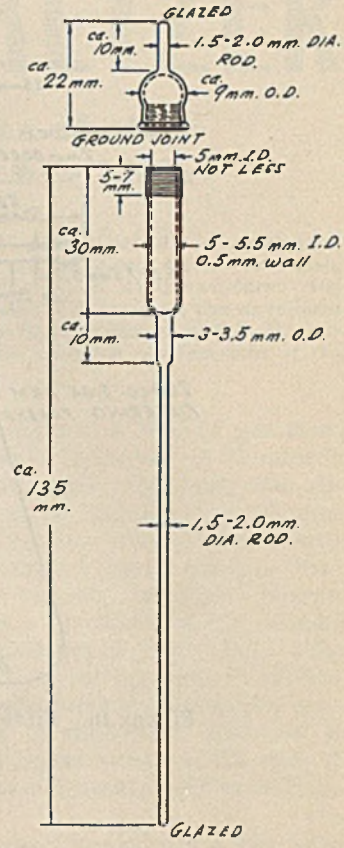

FIGURE 12. WEIGHING TUBE WITH CAP

Part IV. Halogen

For the determination of halogens, the committee considered the following specifications necessary:

Air filter (Figure 10)
Weighing tube (Figure 11)
Weighing tube with cap (Figure 12)
Snipe feather (Figure 13)
Combustion tube (Figure 14)
Filter tube (Figure 15)
Filtration assembly (Figure 16)
Graduated wash bottle (Figure 17)
Sintered-glass funnel (Figure 18)
Large-size glass test tube for metal microbomb (Figure 19)

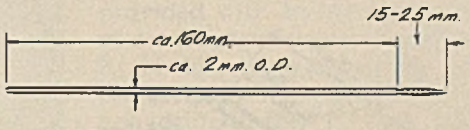

FIGURE 13. SNIPE FEATHER

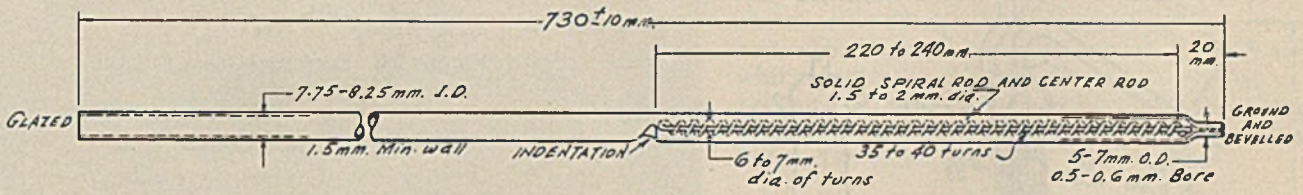

FIGURE 14. COMBUSTION TUBE

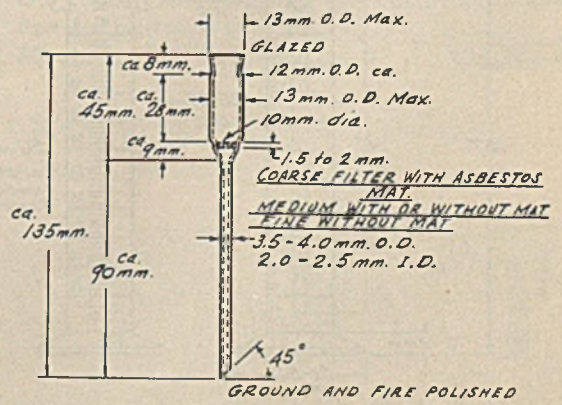

FIGURE 15. FILTER TUBE

Acknowledgment

It is not possible to give credit to the originator of every piece of apparatus which has been considered, nor to acknowledge all the help which the committee has received in the formulation of the report. However, the committee wishes to express its appreciation of the help and financial aid received from the Division of Analytical and Micro Chemistry and others who have given personal suggestions.

Literature Cited

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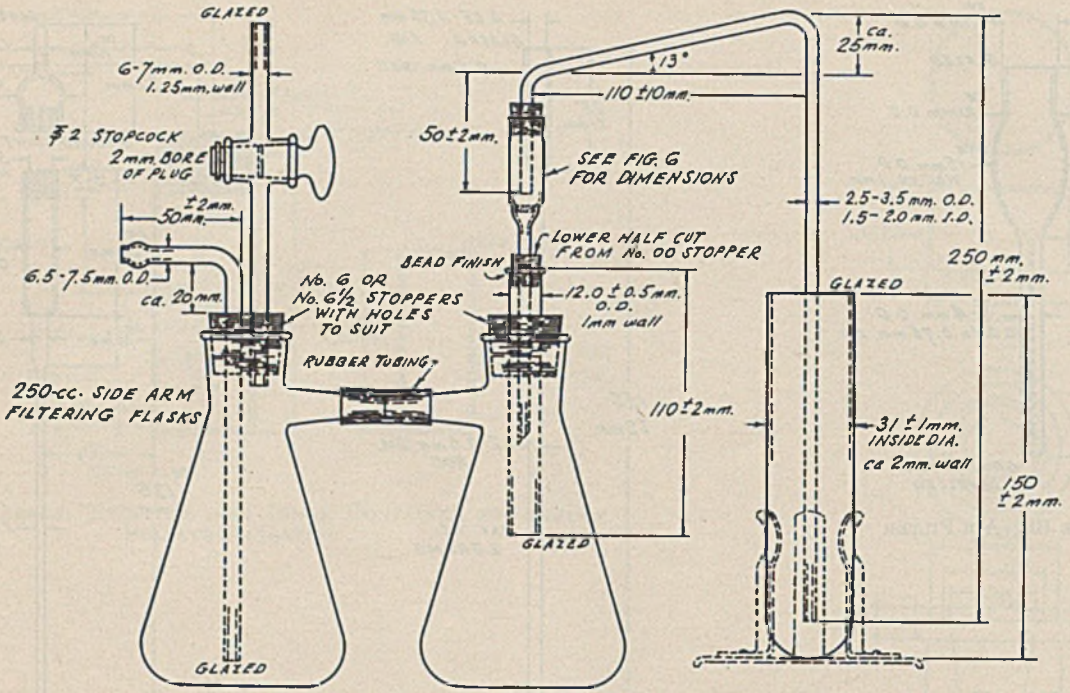


FIGURE 16. FILTRATION ASSEMBLY

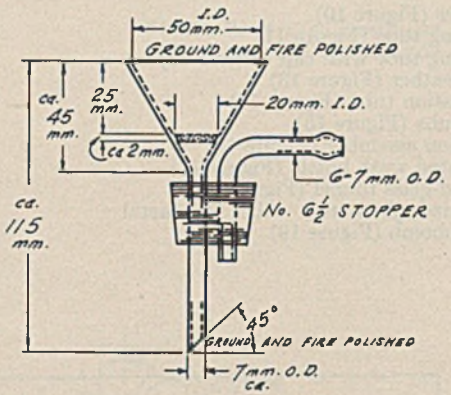


FIGURE 18. SINTERED-GLASS FUNNEL

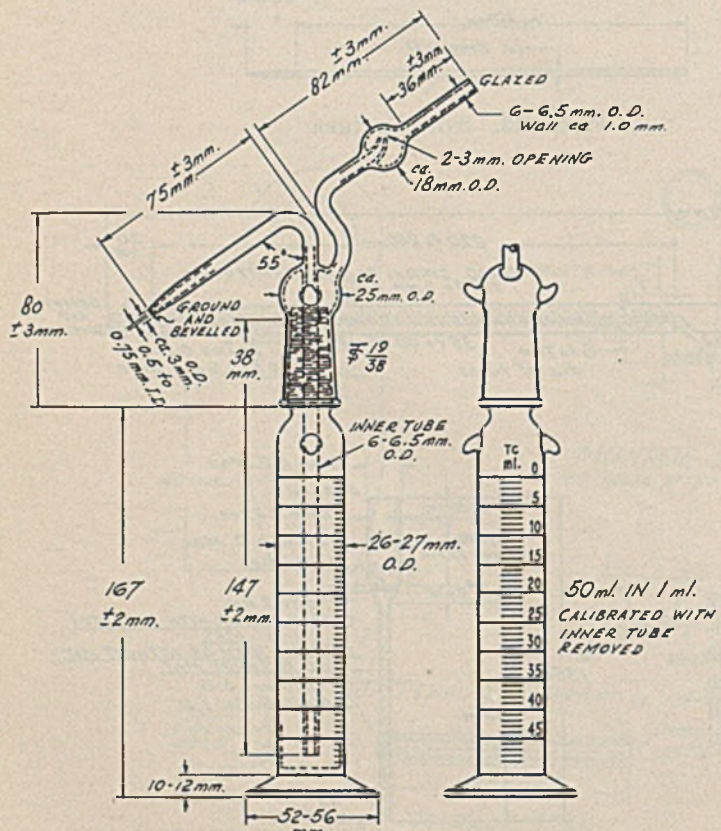


FIGURE 17. GRADUATED WASH BOTTLE

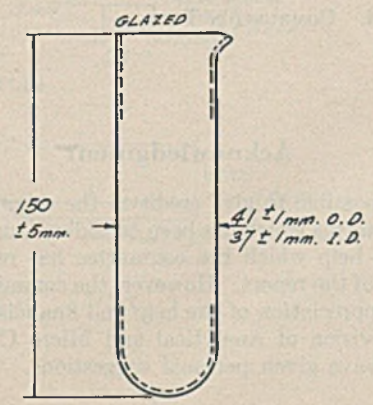
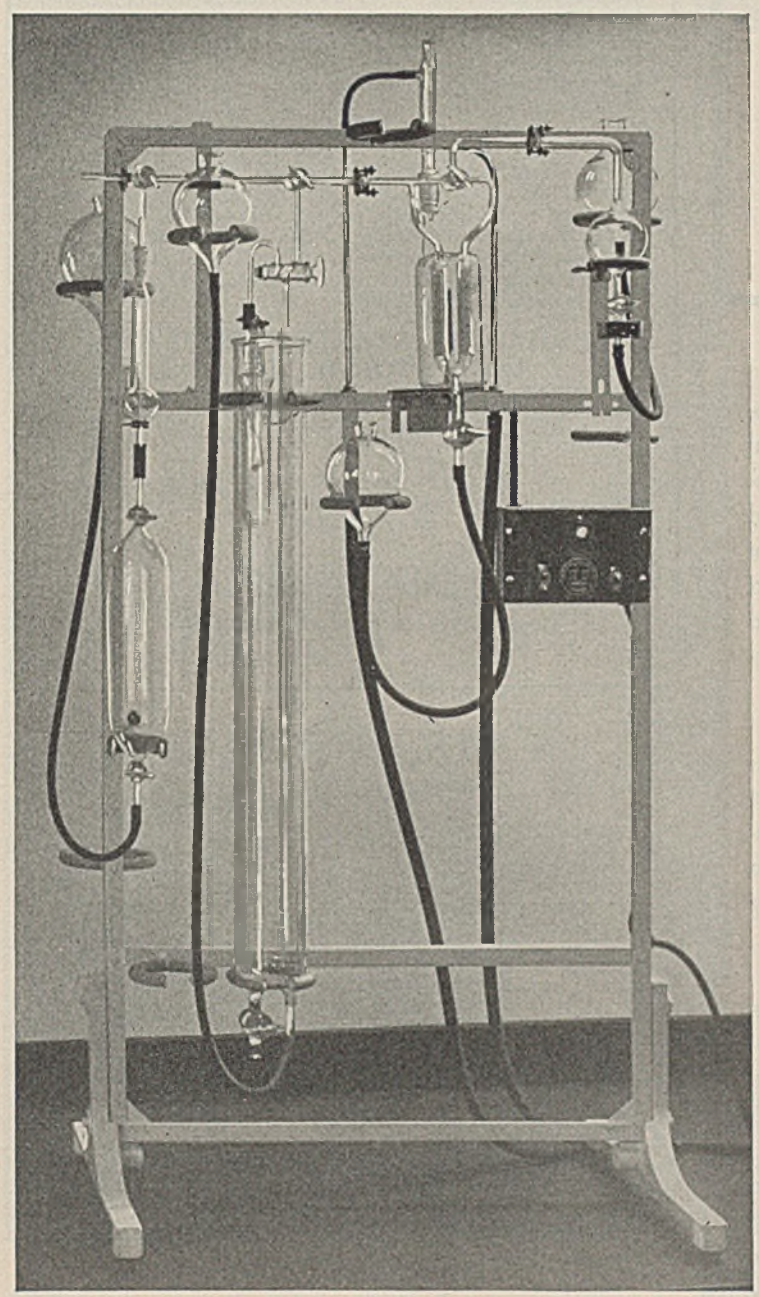


FIGURE 19. LARGE-SIZE GLASS TEST TUBE FOR METAL MICRO-BOMB

BUTADIENE GAS ANALYZER

For the determination of butadiene in the presence of other olefinic hydrocarbons in amounts ranging from 0.2 to 100%



This apparatus is based on the Diels-Alder reaction involving the addition of a conjugated olefine to maleic anhydride with the formation of a six-membered ring containing one double bond. The analyzer was developed by the Universal Oil Products Company and E. H. Sargent & Co., in accordance with the specifications of the former company.

The apparatus consists of a 500 ml gas sampler, a drying tube, an U. S. Bureau of Standards type burette and compensator assembly, the absorption pipette containing maleic anhydride and an expansion bulb, together with the necessary leveling bulbs for passage of the gas sample. Connections between the burette, absorption pipette and the expansion bulb are made with spherical interchangeable ground joints firmly held with special clamps providing considerable flexibility for connections and thus reducing materially possibility for breakage of glassware. Mercury is used as the confining liquid except in the case of the gas sampler where a saturated sodium sulfate solution is used.

The absorption pipette consists of a "U" tube filled with glass beads of 5 mm diameter to present a large surface for the absorption of butadiene by the maleic anhydride. The "U" tube is ring sealed into a cylindrical glass jacket which is provided with an inverted well for the insertion of a cartridge heater of sufficient heating capacity to raise the water in the cylindrical jacket to the boiling temperature in order that the maleic anhydride in the "U" tube may be kept molten. Steam generated in the water jacket is condensed by a 4-inch reflux condenser. The apparatus is also provided with a control panel containing a switch controlling the heater and another switch and neon light for actuating the compensator which indicates the attainment of atmospheric pressure in the system. All glass parts are mounted on adjustable supports on a sturdy steel frame finished in white enamel.

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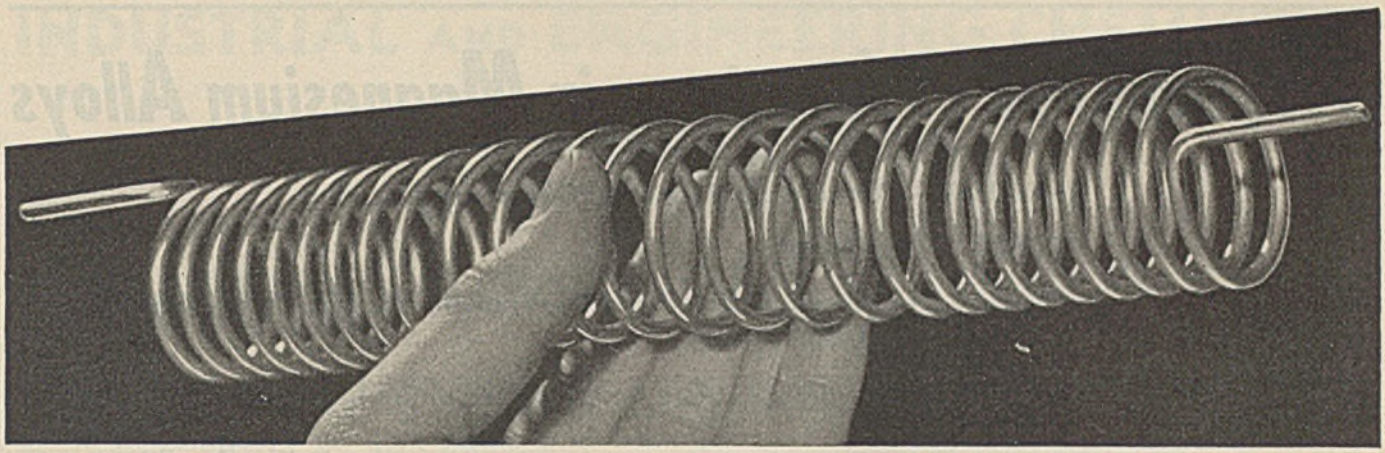

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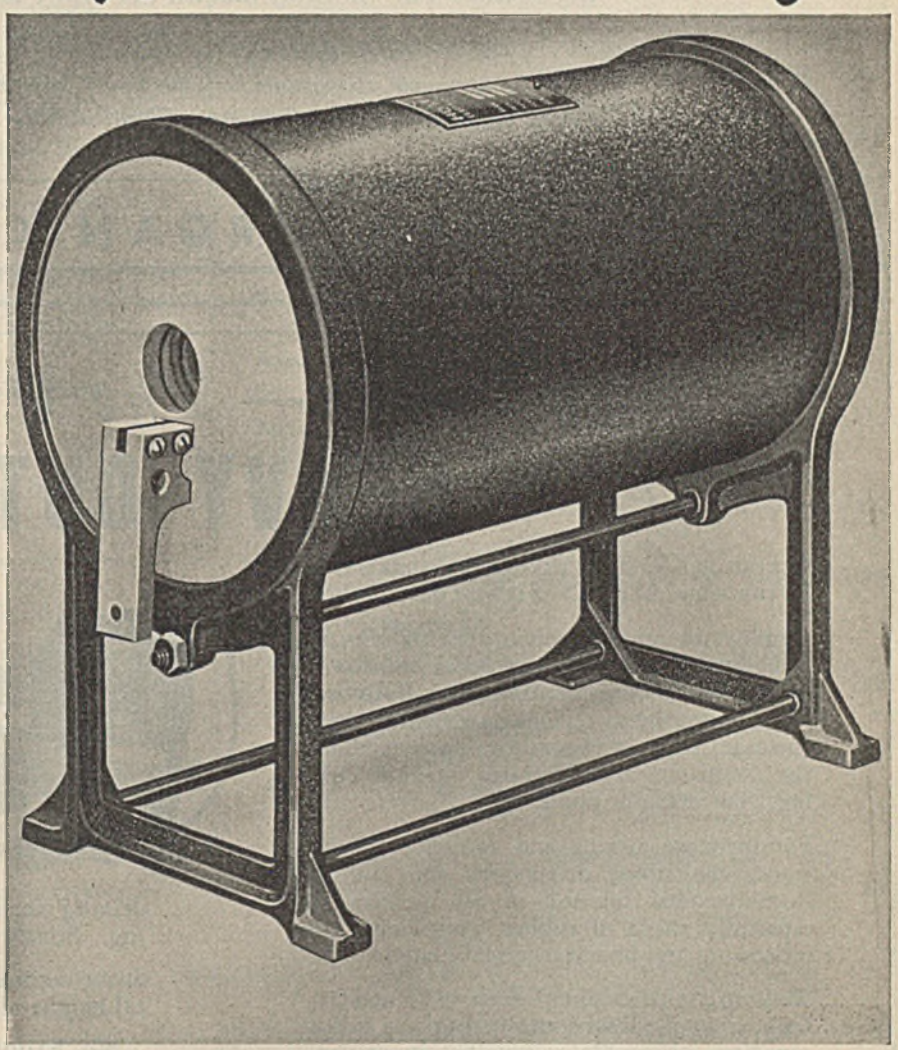

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