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CONTENTS

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Direct Determination of Eleostearic Acid in Tung Oil	<i>P. S. Ku</i>	103	Detection of the Elements in Organic Compounds.	<i>Robert H. Baker and Charles Barkenbus</i>	135
The Fusibility of Coal Ash.	<i>J. J. Brennan, D. F. Mitchell, F. P. Tierney, and W. C. Thompson</i>	106	Determination of Potassium. By Means of an Aqueous Solution of Trisodium Cobaltinitrite in the Presence of Nitric Acid.	<i>L. V. Wilcox</i>	136
Separating Butenes from Butanes. Distillation of Azeotropic Mixtures with Sulfur Dioxide.	<i>M. P. Matuszak and F. E. Frey</i>	111	Physical Properties of Asphalt.	<i>Seward Mason, R. J. Loomis, S. D. Patterson, H. G. Nevitt, and L. C. Krchma</i>	138
Analysis of Sodium Acetate	<i>Charles B. Hurd and William Fiedler, Jr.</i>	116	A Simple Auto-Bubbler Pipet	<i>Milton Burton and Thomas W. Davis</i>	139
Physical Testing Procedure for Latex Stocks	<i>L. A. Wohler</i>	117	Carbonate Content of Oil Lye. Clarified by Centrifugation and Long Settling.	<i>John E. S. Han</i>	140
Effect of Temperature on the Consistency of Asphalts. Viscosity-Temperature Susceptibility Coefficient as an Index.	<i>H. G. Nevitt and L. C. Krchma</i>	119	Anhydrous Sodium Carbonate as a Standard of Reference in Acidimetry.	<i>G. Frederick Smith and G. F. Croad</i>	141
Areometric Estimation of Small Amounts of Sulfate as Barium Sulfate.	<i>V. R. Damerell and P. Spremulli</i>	123	MICROCHEMISTRY:		
Rare Earth Salts. Precipitation and pH Studies with the Glass Electrode	<i>J. A. C. Bowles and H. M. Partridge</i>	124	The Living Cell. Physical Properties of and Microchemical Reactions	<i>Robert Chambers, M. J. Kopac, and C. G. Grand</i>	143
A Dithizone Method for Measurement of Small Amounts of Zinc.	<i>P. L. Hibbard</i>	127	Colorimetric Microdetermination of Cobalt and Potassium.	<i>C. P. Sideris</i>	145
Refractometric Determination of Fat in Chocolate.	<i>Joseph Stanley</i>	132	Micromethod for Determining Viscosity of Lubricating Oils.	<i>Harry Levin</i>	147
			Microchemical Analysis of Pigments. Used in the Fossae of the Incisions of Chinese Oracle Bones.	<i>A. A. Benedetti-Pichler</i>	149

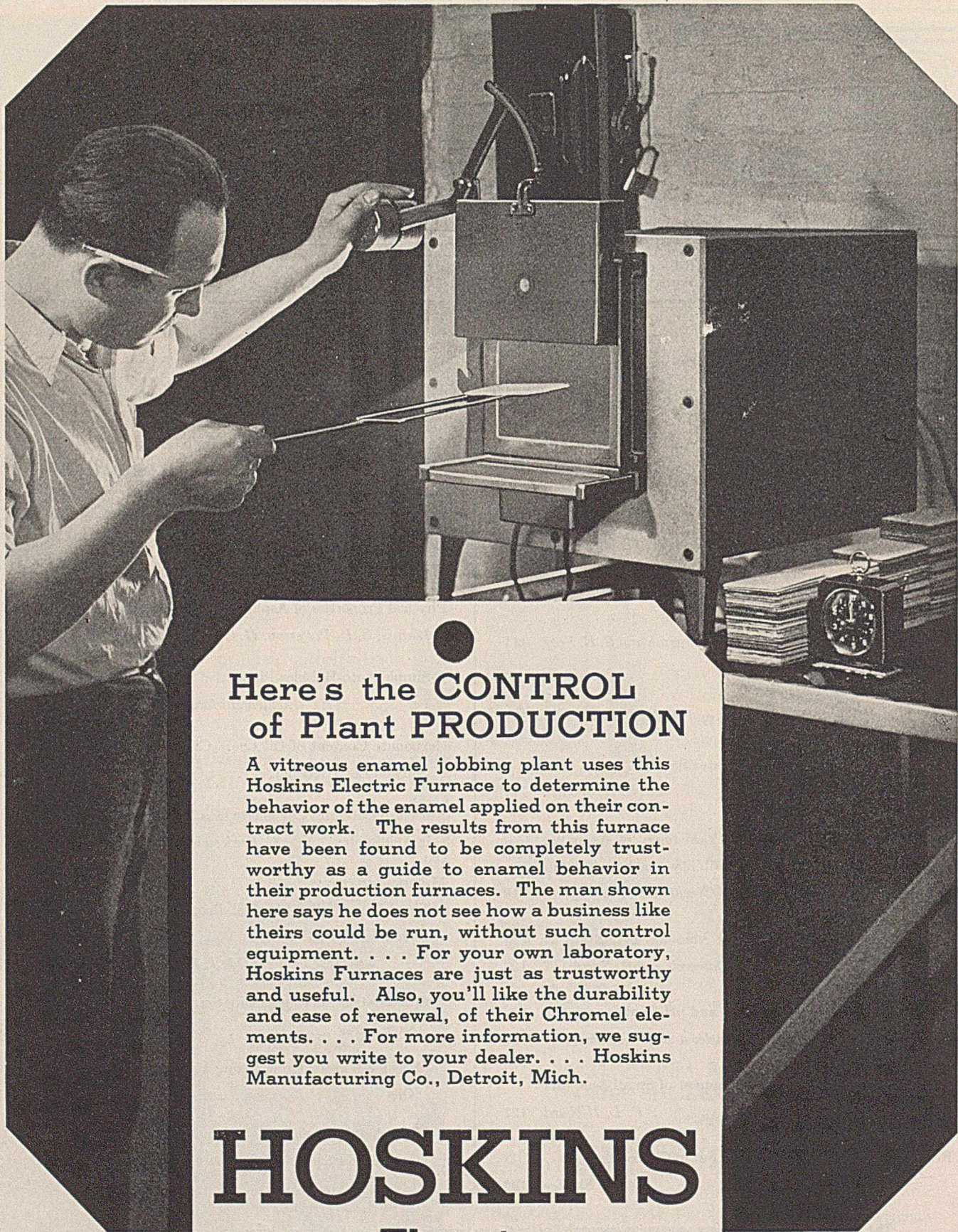
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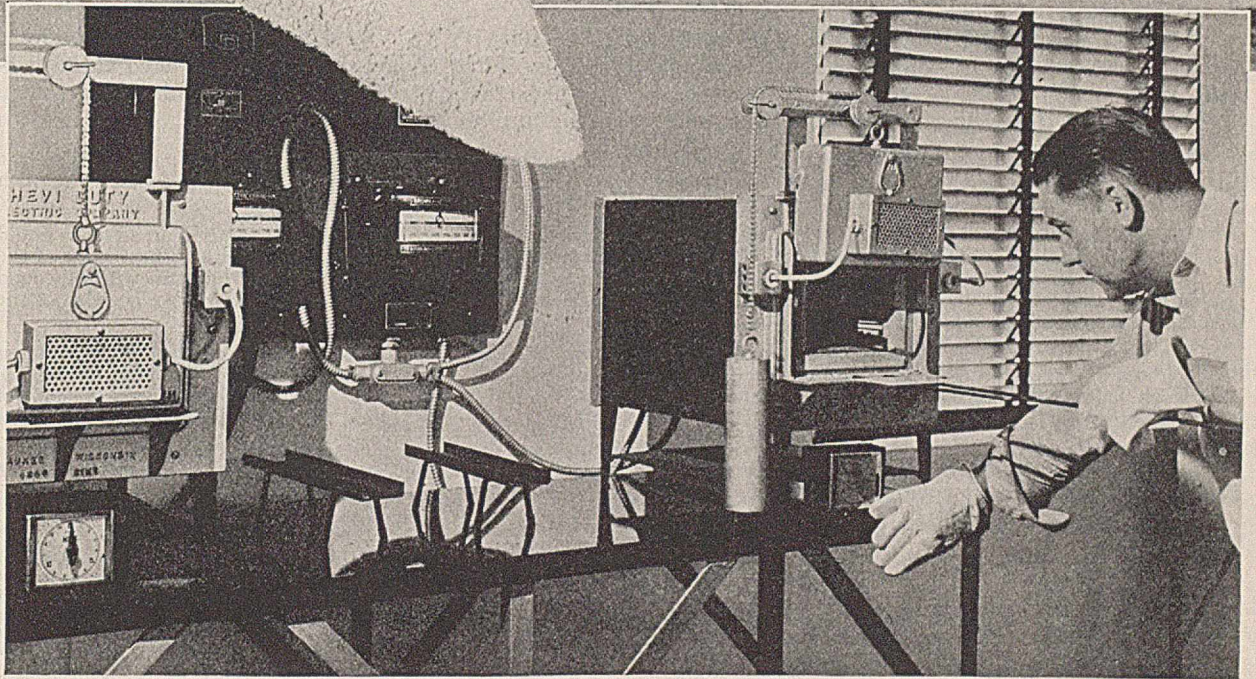
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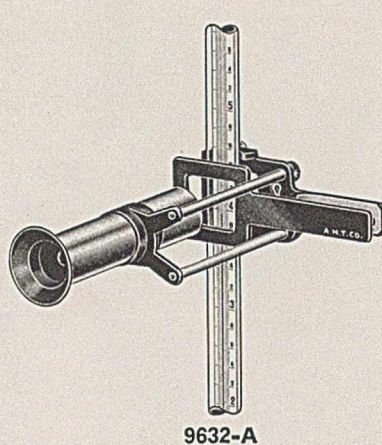
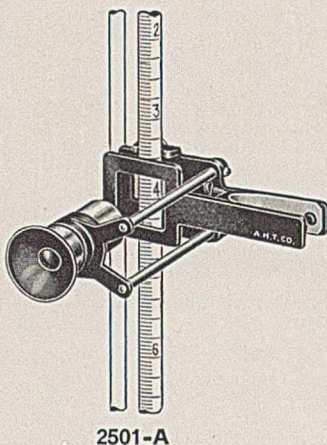
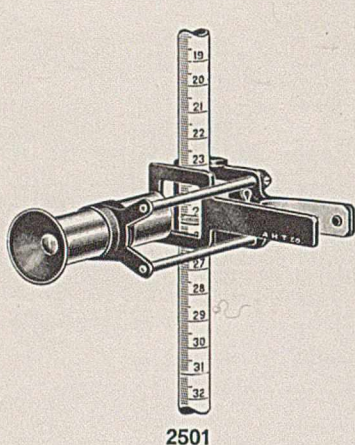
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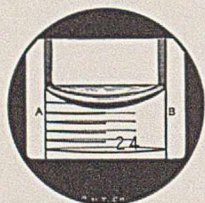
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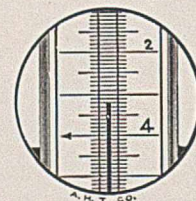
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INDUSTRIAL and ENGINEERING CHEMISTRY

Harrison E. Howe, Editor

Direct Determination of Eleostearic Acid in Tung Oil

P. S. KU

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METHODS hitherto proposed for estimating eleostearic acid in tung oil are mostly based upon calculations from unsaturation values. Thus in Kaufmann's method (6) eleostearic glyceride is calculated from the bromine number and the thiocyanogen number; in Toms' method (17), from iodine numbers by Wijs' method, and by his bromine vapor methods; and in Bolton and Williams' method (2), from the so-called "instantaneous iodine number." All these methods are indirect and hence their validity is limited by the faults of the methods for halogen values and also by the weak assumptions involved in their calculations. Instead of the calculation methods, Bolton and Williams (2), however, suggested another method to determine eleostearic glyceride by estimating the "polymerizable matter" of the oil (1). But the assumption on which this method was based seems to be inconsistent with Rhodes and Welz's theories of head gelatinization of tung oil (11), and experimentally Gardner (3) showed this method to be not dependable unless modified.

It seems that no direct method is yet available for determining eleostearic acid itself or its glyceride in tung oil. As the drying property of tung oil is chiefly due to its eleostearic acid content, it appears that a direct determination of it would give a better commercial evaluation of the oil than any consideration of constants or variables (3).

Separation of Eleostearic Acid

Two ways to separate eleostearic acid from the other fatty acids had been tried: by precipitation with catalysts and by suitable solvents. In the methods usually employed for determining tung oil in varnishlike products, such as those of Goldsmith (4), Scheiber (12), von Reibnitz (10), and Marcusson (8), the oil is separated out through precipitation with catalysts such as halogens, nitrites, stannic chlorides, etc. Such precipitation reactions are probably due to polymerization, and it appears possible then, to utilize these reactions for the determination of eleostearic acid in tung oil. Comparative tests on these catalysts showed that a solution of iodine in petroleum

ether is most suitable because it gives a slow precipitation and a noncolloidal precipitate.

From 0.5 to 1.0 gram of pure dried eleostearic acid (prepared in this laboratory) was dissolved in 15 cc. of petroleum ether. The solution was ice-cooled and 5 cc. of cooled iodine reagent were added. It was allowed to stand in a cool place until precipitation was complete. The precipitates were filtered on a Gooch crucible, washed free from iodine, dried at 30° C. in a vacuum oven, and then weighed. In a test experiment three duplicates using the same sample of eleostearic acid gave the following percentages of precipitates: 83.03, 73.96, and 80.31. The inherent errors of the various procedures are too great to give concordant results.

Since the results of the precipitation method did not justify further study, the author turned to separation by suitable solvents. Before attempts were made to separate fatty acids, separation of their lead and magnesium soaps with both ether and petroleum ether as solvents had been tried. The results were unsatisfactory and hence the other way of separation was resorted to.

Unfortunately the literature gives only a few data on solubilities of eleostearic and oleic acids. The data collected from the literature and those obtained in this laboratory are given together in Table I.

A glance at Table I will show that the solvents listed would not permit very sharp separation. A study of the available solubility data of tung-oil acids in aqueous alcohol solutions, however, reveals that the separation of eleostearic acid from the other acids can be accomplished in alcohol solutions of proper strength at low temperatures. The solubilities of these acids in aqueous alcohol solutions of different strengths at 0° C. were carefully investigated. The

results are given in Table II and plotted in Figure 1.

Figure 1 shows clearly that the complete separation of stearic and palmitic acids from eleostearic acid is impossible. The solubility difference between oleic and eleostearic acids is greatest as the percentage of alcohol increases

TABLE I. SOLUBILITIES OF THE FATTY ACIDS OF TUNG OIL

Solvent	Stearic Acid	Palmitic Acid	α -Eleostearic Acid	Oleic Acid ^b
Acetone	4.73 at 25° ^a	Soluble ^b	Very soluble ^b	Very soluble
Amyl acetate	11.19 at 25° ^a	16.6 at 25° ^c	Very soluble ^b	Very soluble
Carbon disulfide	19.20 at 25° ^a	Very soluble ^b	Very soluble ^b	Very soluble
Carbon tetrachloride	10.25 at 25° ^a	Soluble ^b	Very soluble ^b	Very soluble
Chloroform	15.54 at 25° ^a	Very soluble ^b	Very soluble ^b	Very soluble
Ether (absolute)	20.04 at 25° ^a	32.8 at 25° ^c	Very soluble ^b	Very soluble
Ethyl acetate	7.36 at 25° ^a	10.7 at 25° ^c	Very soluble ^b	Very soluble
Nitrobenzene	0.067 at 0° ^a	0.14 at 0° ^c	3.75 at 0° ^c	Soluble
Toluene	13.61 at 25° ^a	Soluble ^b	Very soluble ^b	Very soluble
Petroleum ether	Very soluble ^b	Soluble ^b	Very soluble ^b	Very soluble

^a Solubilities in grams per 100 grams of solution.

^b Results of author's investigation. Others were quoted from Seidell (14).

^c Solubilities in grams per 100 grams of solvent.

to 76 per cent by volume or 68.98 per cent by weight. This particular strength of alcohol is, therefore, chosen for the separation.

Development of the Method

As early as 1915 Schumann (13) described a method to determine the "oleomargaric acid" in tung oil by means of an alcohol solution which was found also to contain about 76 per cent of alcohol by volume. But unfortunately the original procedure gave too few details and the results of more than twenty trials made by the author showed that it was far from being a quantitative method.

Based upon the same principle, a new procedure was then worked out. A 2-gram sample was saponified with 20 cc. of 5 per cent alcoholic potassium hydroxide and then acidified with 25 cc. of 2*N* sulfuric acid. The solidified fatty

TABLE II. SOLUBILITIES OF TUNG-OIL ACIDS IN AQUEOUS ALCOHOL AT 0° C.

(Grams per 100 grams of saturated solution)				
Alcohol by Volume at 15.56° C. %	Oleic Acid	α -Eleostearic Acid	Stearic Acid	Palmitic Acid
54.84	0.20	0.023	0.048	0.027
59.61	0.42	0.047	0.070	0.041
70.19	1.82	0.267	0.113	0.054
71.87	2.44
73.93	4.06
75.07	7.06
76.05	28.00	0.614	0.22	0.105
80.33	...	0.983	0.37	0.165
90.14	...	3.28	0.88	0.449

acid was dissolved in 25 cc. of 76 per cent alcohol (by volume) and the solution was allowed to cool for crystallization. The following conditions were found to be optimum: (a) saponification with 90 per cent alcoholic potassium hydroxide; (b) a temperature of 41° ± 1° C. for acidification with a duration of 10 minutes; (c) strength of alcohol for crystallization, 76.0 to 76.1 per cent by volume; (d) temperature of cooling bath, 0° C.; (e) washing the acid once with 60 per cent alcohol.

Reagents

POTASSIUM HYDROXIDE. A 5 per cent solution of potassium hydroxide in 90 per cent alcohol (by volume) containing 5 grams of E. Merck's reagent potassium hydroxide per 10 cc. of alcohol. The alcohol used for this purpose should be previously treated with potassium hydroxide and silver nitrate, allowed to stand for a few days, and then distilled and diluted. Solutions made in this way will not readily turn yellow on standing.

DILUTE SULFURIC ACID. A 2*N* solution made by diluting to 300 cc., 16 cc. of the c. p. acid of specific gravity 1.84.

ALCOHOL FOR CRYSTALLIZATION. About 80 volumes of purified alcohol (95 per cent), less if absolute alcohol is used, are diluted with water to 100 volumes. The volume percentage of alcohol at 15.56° C. is determined by the pycnometer method, and the strength adjusted so that it is between 76.00 and 76.10 per cent. It is advisable to make up a large volume of solution at start and check its alcohol strength from time to time.

ALCOHOL FOR WASHING. A 60 per cent alcohol solution made by diluting with water 64 volumes of purified alcohol to 100 volumes and adjusting the strength to 60 per cent alcohol by volume.

STANDARD SODIUM HYDROXIDE. A solution of 0.2*N* sodium hydroxide standardized against c. p. benzoic acid or standard sulfuric acid, using phenolphthalein as indicator.

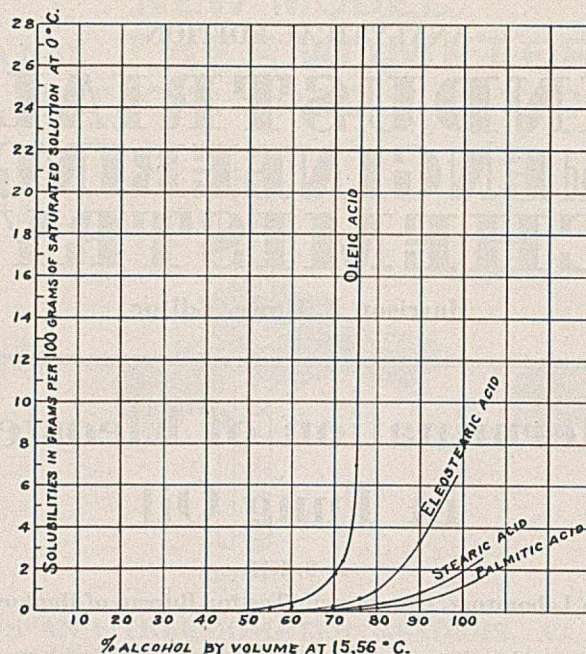


FIGURE 1. SOLUBILITIES IN AQUEOUS ALCOHOL SOLUTIONS

down and drain as dry as possible. Press the filter paper dry between sheets of absorbent paper. Then dry the flask and the filter paper at room temperature (about 20° C.) in a vacuum desiccator under a vacuum of 10 to 20 mm. of mercury for just 30 minutes. There should be now no water visible on its wall or on the surface of the cake. Open the desiccator and dissolve the fatty acids in the flask and those on the filter paper in exactly 25 cc. of 76 per cent alcohol by pouring the warmed alcohol through the filter paper into the flask. Gently warm the flask, if necessary, to dissolve any undissolved cake, then cork, and immerse the flask in a bath of ice and water. Put the bath in the specially constructed refrigeration box, or an electric refrigerator, maintained between -3° and 0° C. and allow to stand overnight. The temperature of the bath next morning should be between 0° and 1° C.

Fit up a jacketed Büchner funnel 5 to 6 cm. (2 to 2.5 inches) in diameter and surround the funnel with ice and water. Filter

PHENOLPHTHALEIN INDICATOR. One gram of phenolphthalein dissolved in 100 cc. of neutralized 95 per cent alcohol.

Procedure

Saponify from 2.00 to 2.05 grams of oil with 20 cc. of alcoholic potassium hydroxide in an Erlenmeyer flask by refluxing on a water bath for 1 hour. Allow the flask to stand for a few minutes in a water bath kept at 41° ± 1° C. Then add slowly 25 cc. of dilute sulfuric acid and maintain the temperature inside and outside the flask at 41° ± 1° for just 10 minutes, rotating the flask occasionally. Then take out the flask, add 25 cc. of water, and cool in ice water until the fatty acids are solidified to a cake. Filter by decantation on a small filter paper about 7 cm. in diameter, applying suction if necessary. Then, keeping most of the cake in the flask, wash the flask and filter paper thoroughly until free from sulfate ion. Carefully turn the flask with the cake in it upside

TABLE III. ANALYTICAL CONSTANTS^a OF TUNG OIL

	Ta Mee Tung	Shiao Mee Tung	Tsai Tung
Specific gravity, 15.5° C.	0.9415	0.9415	0.9416
Acid value	1.5	3.6	1.2
Saponification value	191.9	191.8	192.0
Refractive index, 25° C	1.5181	1.5183	1.5178
Iodine number (Wijs) ^b	168.7	170.1	168.2
Worstall's test	5' 28"	5' 28"	5' 42"

^a Analyses done according to the methods of this bureau, which are essentially the same as A. S. T. M. methods.

^b Values corrected to standard conditions proposed by Ho, Wan, and Wen (5).

TABLE IV. PRECISION OF THE METHOD

Experiment Number	Shiao Mee Tung		Ta Mee Tung		Tsai Tung	
	Eleostearic acid, uncorrected %	Deviation from arithmetical mean %	Eleostearic acid, uncorrected %	Deviation from arithmetical mean %	Eleostearic acid, uncorrected %	Deviation from arithmetical mean %
1	76.0	0.02	76.5	0.10	75.9	0.10
2	77.0	0.07	76.4	0.06	75.8	0.01
3	77.0	0.05	76.5	0.13	75.8	0.07
4	76.9	0.06	76.3	0.07	75.6	0.12
5	77.1	0.13	76.2	0.14	75.9	0.11
6	76.9	0.10	76.5	0.10	75.8	0.06
7	77.0	0.00	76.3	0.12	75.7	0.08
8	76.9	0.12	76.3	0.09	75.6	0.13
		Av. 0.07		Av. 0.10		Av. 0.09
Arithmetical mean	77.0		76.4		75.8	
Average deviation/arithmetical mean	0.9 part per 1000		1.3 parts per 1000		1.3 parts per 1000	

the creamlike crystals on the cooled funnel and suck the eleostearic acid dry with a vacuum pump. Wash first the flask and then the acid with 15 cc. of 60 per cent alcohol which has been previously cooled overnight in the refrigeration box. Suck again with pump until no liquid drops. Dissolve the crystals in warmed redistilled alcohol and wash the top and tip of the funnel thoroughly, using a total volume of about 65 cc. of alcohol. Titrate the acid with 0.2*N* sodium hydroxide, using phenolphthalein as indicator. 1 cc. of 0.200*N* sodium hydroxide = 0.05566 gram of eleostearic acid.

Precision

Three genuine and pure specimens of tung oil known as "Ta Mee Tung," "Shiao Mee Tung," and "Tsai Tung" in native terms were used to test the precision of the proposed method. These specimens were expressed from seeds of *Aleurites fordii* bought in Szechuan in January, 1935. Their analytical constants are given in Table III.

A series of eight determinations was made on each specimen, following strictly the procedure described above. No result was rejected unless the difference between the doubtful determination and the arithmetical mean of the other determinations was four times or more the average deviation of the other determinations, because it can be shown from the theory of probability that such a determination is 99 per cent the result of accidental errors (9). The results given in Table IV show the concordance of checks by careful workers. The precision of the method was found to be from 0.9 to 1.5 parts per 1000. Unnecessary exposure to air, warmth, and light of both the crude and crystallized eleostearic acid should be avoided as much as possible. Experience shows that it is advisable not to carry out this procedure in places where the temperature is above 25° C.

Constant Error of the Method

The acid crystals finally obtained in this method were found to have usually a melting point of 46–47.5° C. (m. p. of pure α -eleostearic acid, 48.0°) and a Wijs iodine number in 1-hour contact of about 175–183. These constants definitely show that the crystals are mainly α -eleostearic acid but slightly adulterated with palmitic and stearic acids and traces of oleic acid, as is to be expected from solubility considerations. It is evident that the presence of palmitic, stearic, and oleic acids will raise the result, while the eleostearic acid which is inevitably present in the mother liquor and in the washings will cause a lowering in the result. The sum of these errors makes the constant error of this method.

To test this error, control experiments were made in which mixtures of pure eleostearic acid and other tung-oil acids were employed, but for reasons mentioned above the author did not use the halogen methods to test the proposed method.

The pure α -eleostearic acid used was prepared by a modified procedure of Thomas and Thomson (16) without the use of carbon dioxide.

Reflux 75 grams of pure tung oil for 1 hour with 300 cc. of 10 per cent potassium hydroxide in 90 per cent alcohol. Decompose the soap with 400 to 450 cc. of 3*N* sulfuric acid warmed to 45° C. and keep the mixture at 40° C. for 10 minutes, stirring occasionally. Add 200 cc. of cold water and cool in ice until the acids solidify to a cake. Decant off the acid and wash the cake until free from sulfate ion. Drain and then dissolve in 300 to 350 cc. of warmed 90 per cent alcohol, and allow to stand overnight at 0° C. Filter in an ice-cooled funnel and wash three times with 30 to 35 cc. of cooled 90 per cent alcohol. Recrystallize twice in 150 and 130 cc. of 90 per cent alcohol, using each time a shorter period of cooling. For use in control experiments, a portion of crystals may be now taken out, dried in vacuum, and recrystallized twice in 76 per cent alcohol.

Solutions of eleostearic acid in 76 per cent alcohol were then prepared with these crystals and their strengths adjusted to proper values by titration with 0.2*N* sodium hydroxide. For solubility determinations the crystals after being recrystallized thrice in 90 per cent alcohol were subjected to a fourth recrystallization in 90 per cent alcohol and then dried at about 20° C. under high vacuum. The final products from either procedure were found to have a melting point of 48.0° C.

Six kinds of solutions of eleostearic acid were freshly prepared and standardized, containing from 1.276 to 1.554 grams of this acid in each 25.0 cc. These correspond to from 65 per cent to 78 per cent of eleostearic acid in 2 grams of oil, which will nearly cover the range of percentages in ordinary tung oil. According to van Loon and Steger (7, 15) tung oil contains about 13.6 per cent of oleic acid, 3.7 per cent of palmitic acid, and 1.2 per cent of stearic acid. To imitate this composition approximately on the basis of a 2-gram sample, 0.27 gram of oleic acid, 0.074 gram of palmitic acid, and 0.024 gram of stearic acid were mixed and dissolved by warming below 40° C. in 25-cc. portions of the six standard solutions of eleostearic acid and then the mixtures were allowed to stand overnight at 0° C. The eleostearic acid in each mixture was determined by the procedure proposed for tung oil. By analysis of six mixtures, the constant error of this method for a 2.00- to 2.05-gram sample was found to be from 20.6 to 25.0 parts per 1000 and the percentage of eleostearic acid found experimentally was lower than the theoretical value by approximately 1.6 per cent. Hence a correction of 1.6 per cent should be added to the experimental values. However, this correction is by no means very accurate, since the true percentages of oleic, palmitic, and stearic acids in tung oil have not yet been accurately determined.

Application of Method to Commercial Samples

As this method was developed and tested on genuine oils only, it is interesting that when applied to commercial samples it was found in general equally satisfactory. For use in test experiments, several samples with good analytical data were chosen from the exported oils which this bureau had examined during the period from May to November, 1935. In Table V there are given percentages of eleostearic acid and the analytical constants of the oils. It is important to note the consistent relationship between these percentages

TABLE V. APPLICATION TO COMMERCIAL SAMPLES

Oil No.	Refractive Index at 25° C.	Iodine No. (Wijs)	Acid Value	Saponification Value	Worstall's Test	Eleostearic Acid (Corrected) %	Mean	Average Deviation from Mean
2918	1.5169	166.8	2.9	191.3	6' 32"	76.14	76.13	0.08
						76.24		
						76.16		
						75.96		
2926	1.5172	166.7	3.2	191.8	6' 25"	76.55	76.56	0.14
						76.29		
						76.80		
						76.51		
2983	1.5173	167.1	2.6	191.5	6' 23"	76.70	76.67	0.21
						76.78		
						76.95		
						76.26		
3030	1.5165	167.8	2.9	191.3	6' 52"	75.51	75.48	0.10
						75.63		
						75.33		
						75.43		
3032	1.5166	167.9	2.4	192.0	6' 52"	75.78	75.67	0.12
						75.65		
						75.80		
						75.46		
3263	1.5176	167.8	1.3	190.8	6' 23"	77.19	77.08	0.10
						77.11		
						77.13		
						76.87		
3284	1.5179	167.6	1.4	191.7	6' 17"	77.55	77.50	0.12
						77.67		
						77.43		
						77.33		

and the analytical constants, particularly the refractive indices, as this clearly shows the validity of the method.

Application to Adulterated Tung Oil

Before being applied to adulterated samples, the method had been tested on different vegetable oils commonly used as adulterants in tung oil. It was found that under the same treatment these oils yielded less than 10 per cent of residue insoluble in 76 per cent alcohol, except rapeseed and cottonseed oils which gave 28.6 per cent and 29.2 per cent, respectively. However, the melting point and iodine number of the crystals of pure tung oil are sufficient to show the identity of α -eleostearic acid, while the residues of other vegetable oils, including rapeseed and cottonseed oils, all behaved like mixtures upon heating, were incapable of being dried, had no definite melting points, but generally had very low iodine numbers. All these facts serve to distinguish clearly the fairly pure crystals of tung oil from the impure residues of other vegetable oils.

The applicability of this method to adulterated tung oil was tested on mixtures of pure tung oil with 2.5 per cent of six common adulterants. The eleostearic acids content of these mixtures were determined by the proposed method. They were found to be 1.70 to 1.98 per cent lower than that of the pure sample and by calculation this lowering would be about 1.3 per cent to 1.58 per cent for mixtures containing 2.0 per cent of adulterant. In the test experiments here described only mixtures with 2.5 per cent of adulterant were studied, for a further study on adulteration problems had been planned. However, the results thus far obtained (Table VI) show that this method is applicable to adulterated tung oil and that by means of it it is possible to detect adulterants in tung oil adulterated with 2.0 per cent or more of other vegetable oils. The precision of the method will be reduced when applied to adulterated samples.

Summary

From the study of solubilities of the fatty acids of tung oil, a method based upon the separation of eleostearic acid in 76 per cent alcohol at 0°C. has been developed for its direct determination in tung oil.

To make the method quantitative, the control of its variable factors was investigated in detail. The precision and constant error of this method were estimated and the necessary correction was ascertained.

The method has been found satisfactory with commercial samples on the market as well as with genuine and pure samples. The percentages of eleostearic acid are generally consistent with the important analytical constants which usually serve to indicate the quality of this oil.

TABLE VI. APPLICATION OF METHOD TO ADULTERATED TUNG OIL

Mixture No.	Composition (by Parts)	Refractive Index at 25° C.	Eleostearic Acid of Pure Tung Oil %	Eleostearic Acid of Mixture %	Lowering %
10	Pure tung oil Stillingia oil 2.5	97.5 1.5169	77.35	75.37	1.98
20	Pure tung oil Poppyseed oil 2.5	97.5 1.5168	77.35	75.43	1.92
30	Pure tung oil Soybean oil 2.5	97.5 1.5168	77.35	75.47	1.88
40	Pure tung oil Rapeseed oil 2.5	97.5 1.5168	77.35	75.55	1.80
50	Pure tung oil Cottonseed oil 2.5	97.5 1.5168	77.35	75.65	1.70
60	Pure tung oil Sesame oil 2.5	97.5 1.5167	77.35	75.42	1.93

The method is also applicable to adulterated tung oil and may be used to detect 2 per cent or more of common adulterants in tung oil.

Acknowledgment

The author is greatly indebted to K. Ho and C. S. Wan for their valuable advice which has been very helpful to this investigation.

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The Fusibility of Coal Ash

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THE gas-furnace method for the determination of the fusibility of coal ash was adopted as a standard by the A. S. T. M. in 1924 (2). This method requires molded cones of the ash to be subjected to increasing temperatures. The fusing point usually reported is the softening temperature (3) recorded when the ash cone has fused down to a condition as shown by either cone 2 or cone 3 (Figure 1). The standard method permits a tolerance of 54° F. for the same laboratory and 90° F. for different laboratories.

Because of the difficulty of coordinating the softening

temperature determined by the standard method and clinker formation, the time required to make the test, the tolerance permitted in duplicate determinations, and the difference in the results obtained by different laboratories (1, 6), the present investigation was undertaken.

Ten samples of coal ash, the softening temperatures of which had been reported by the Bureau of Mines in 1930 (9), were formed into cones and photographed to show their condition at various temperatures. The ten samples of ash were divided into two series: five with low softening temperature (series A) and five with high softening temperatures (series B). A plaque bearing

series A cones, which had been heated to 1800° F. in accordance with the standard method, was removed from the furnace and photographed. Another similar plaque was removed at 1850° F. and photographed, another at 1900° F., and so on for each 50° F. up to 2500° F. The photographs of these plaques are assembled in Figure 2. The cones of series B were treated in the same manner as series A cones for a temperature range of 2300° to 2850° F., as shown in Figure 3.

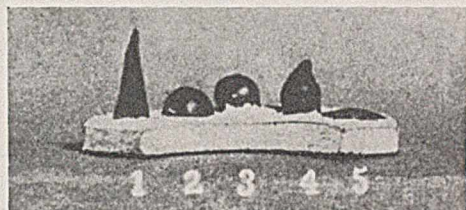


FIGURE 1

It is possible to decide on the softening points of these ashes by referring to the photographs and to the definition of the softening point, as explained previously in connection with Figure 1. It is unfortunate that the standard method permits the recording of the softening temperature when the cone has fused down to the condition as shown by either cone 2 or cone 3 (3). These cones are evidently not in the same condition in regard to fusion, since they differ in height and shape. The authors' interpretations of the softening points, guided by the condition of cone 2, Figure 1, are shown in Table I with the softening temperatures of these same ashes as determined and published by the Bureau of Mines (9).

With the exception of the softening points on ash 11 and ash 14, the results as shown by the photographs and as given by the Bureau of Mines are within the tolerances permitted

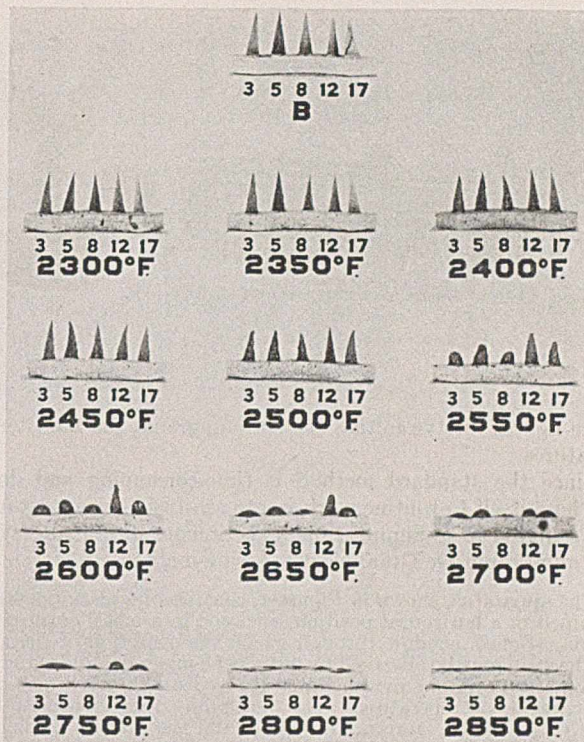


FIGURE 3

TABLE I. COMPARISON OF GAS-FURNACE SOFTENING TEMPERATURES OF COAL ASH

(As shown by photographs and as given by the Bureau of Mines)

Series	Ash No.	Softening Temperature		Difference ° F.
		From photo- graphs ° F.	By Bureau of Mines ° F.	
A	7	2025	2055	30
	9	2275	2275	0
	11	2300	2195	105
	14	2350	2200	150
	19	1975	2040	65
B	3	2600	2595	5
	5	2625	2615	10
	8	2575	2605	30
	12	2725	2705	20
	17	2650	2665	15

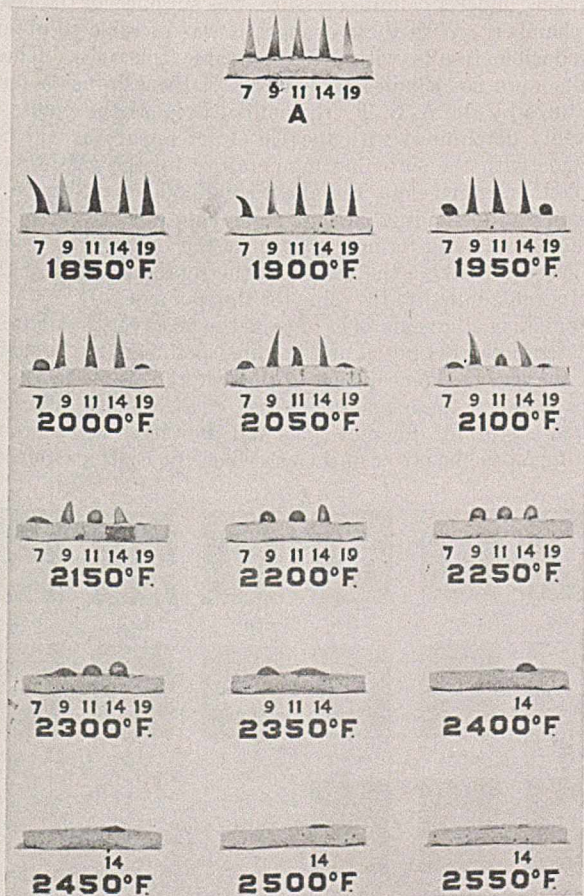


FIGURE 2

under the A. S. T. M. standard method. There is very close agreement between the softening points as shown by the photographs and as determined by the Bureau of Mines for the higher fusing ash represented by series B.

Attention should be called to the condition of cone 11. In making a fusion test of this ash by the standard method, it can be seen from Figure 2 that the condition defined as the softening point persists from 2150° to 2300° F. This appears to be due to peculiar characteristics of this ash, as will be shown below.

The value of ash-fusion tests depends not only on the accuracy of the method employed but also on the degree to which the results can be correlated with the behavior of the coal under furnace conditions. Heavy clinkers have been encountered throughout the ash-softening temperatures from 2200° to 2815° F. and no clinker trouble has been experienced with certain coals having ash-softening temperatures as low as 2388° F. (5). There appears to be a general relationship between the softening temperature and clinking in the furnace (4), yet it is practically impossible to predict the behavior of ash in coals having softening temperatures in the neighborhood of 2400° to 2600° F. In many cases clinking characteristics are not represented by the

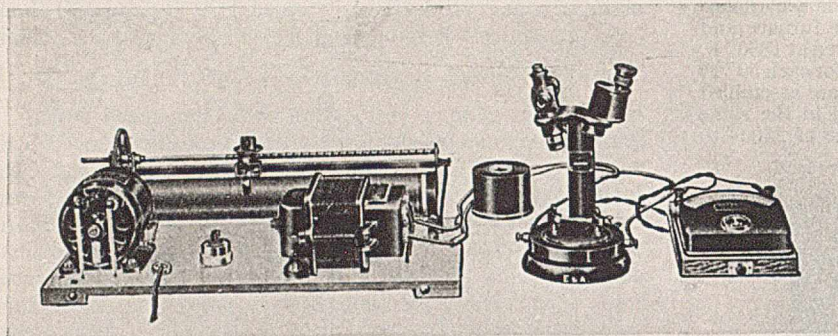


FIGURE 4

mere figures for the initial, the softening, and the fluid temperatures.

Since the standard method is time-consuming and does not lend itself to routine work where ash-fusion temperatures are required in minimum time, experiments were made with the more rapid De Graaf electric fusing method.

The apparatus, shown in Figure 4, consists of a platinum strip clamped in a horizontal position, enclosed in a metal cover containing a glass window through which the condition of the ash on the strip may be observed by means of a magnifier and through which the radiation pyrometer is focused on the strip so as to indicate the temperature. The platinum strip is heated by passing an electric current through it and the rate of heating is controlled by mechanical movement of contacts on the rheostat. Tubes at the base of the instrument permit the introduction of an oxidizing, neutral, or reducing atmosphere within the heating chamber.

In making the first experiments with the apparatus the instructions furnished by the manufacturer (?) were followed, but the results were not reliable. There was considerable

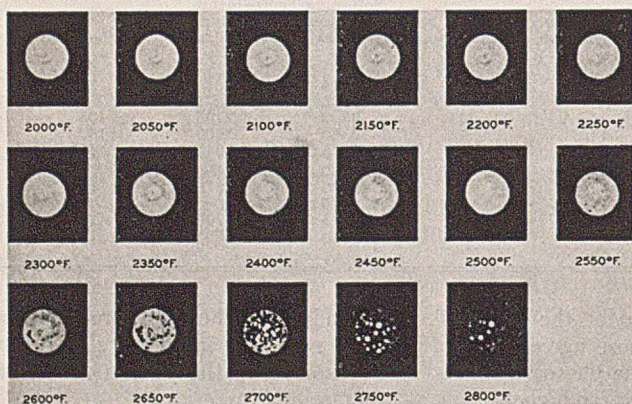


FIGURE 5

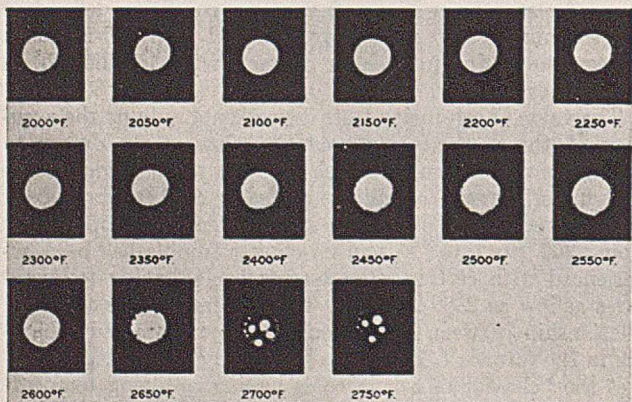


FIGURE 6

confusion in regard to the meaning of the initial and the final points determined by the De Graaf apparatus when compared with the initial deformation, the softening, and the fluid temperatures by the gas-furnace method.

In 1930 the Bureau of Mines (9) reported the results of an investigation of the De Graaf apparatus in which four laboratories using it made determinations of the initial and the final points of nineteen samples of coal ash which were furnished by the Bureau of Mines. The results obtained in the four laboratories showed such decided discrepancies, not only in the results with

the De Graaf apparatus but also between these results and those of the Bureau of Mines, determined by the gas-furnace method, that the De Graaf apparatus was not considered satisfactory for the determination of ash fusibility. Other tests were made (8) in various laboratories which indicated the possibility of the usefulness of the method, provided a modified procedure could be developed to correct some of the variables encountered in its use.

It was decided not to abandon the method and further experiments were carried on after making certain changes, particularly with regard to the manner in which the ash was applied to the platinum strip and the atmosphere supplied to the furnace. A small but definite amount of finely ground ash was thoroughly mixed with a definite quantity of liquid (preferably glycerol) and a small globule of this mixture was transferred to the platinum strip by means of a ball point. The glycerol was vaporized at a low temperature, leaving a uniform layer of ash in intimate contact with the platinum. Nitrogen, under a definite pressure, was supplied to the heating chamber. With these changes it was possible to obtain reproducible results within a reasonable tolerance. These results were not significant in terms of the ash-fusion temperatures by the A. S. T. M. method because the points of fusibility determined with the De Graaf apparatus did not coincide with the softening temperature by the gas-furnace method. Nevertheless, the altered method proved to be of great value in grading current shipments of coal as to the clinkering and slag-forming characteristics of the ash. Both the speed of making the tests and the reproducibility of the results contributed to its value for this purpose.

In making a large number of tests the observer, in addition to determining the initial and the final points, noted progressive changes in the condition of the ash at various temperatures between these points. These changes have different characteristics for different coals and they have considerable bearing on the behavior of the ash when the coals are burned

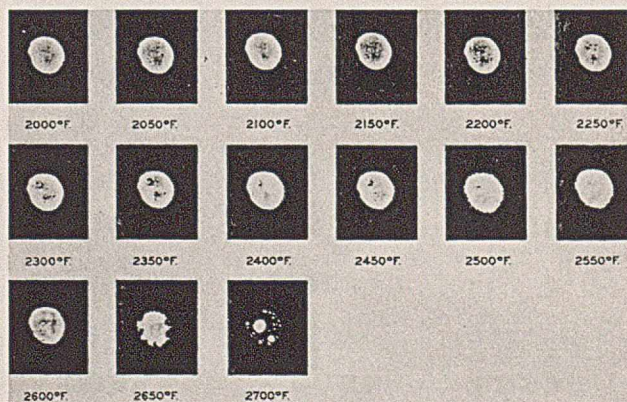


FIGURE 7

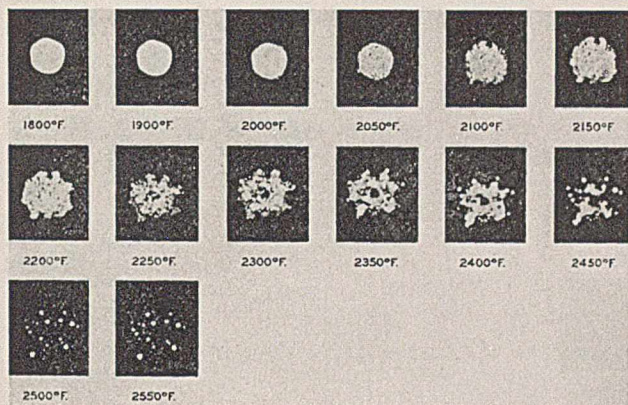


FIGURE 8

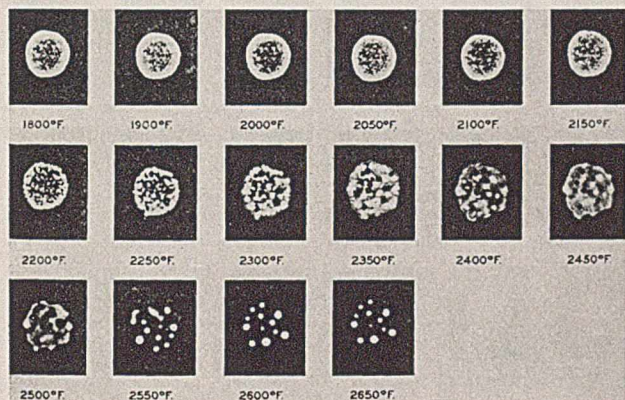


FIGURE 9

in various types of equipment. Unfortunately, only one observer could watch the progress of the change in the nature of the ash, and it was difficult for him to describe the appearance and extent of these changes throughout any particular temperature range. It was thought that a series of photographs of the progressive changes furnished more information concerning the fusing characteristics of ash and permitted a better understanding of the relation between clinker formation and fusibility than did the mere record of empirical points, such as the initial and the final points by the original De Graaf method or the initial deformation, the softening, and the fluid temperature by the gas-furnace method. Therefore the apparatus was remodeled so as to permit taking photographs of the ash sample on the platinum strip at various temperatures throughout the test.

Photographs taken by this procedure are presented to show the difference in behavior, within the fusibility range, of ash from various coals. Figures 5 to 10, inclusive, represent three kinds of coal with which the authors have had experience in regard to burning and clinker-forming characteristics. The photographs show two ashes from bituminous coals from the Appalachian Field (Figures 5 and 6), two semibituminous coals from the Appalachian Field (Figures 7 and 8), and two bituminous coals from the Eastern Interior Field (Figures 9 and 10). The photographs of these six coals illustrate the following points: that ashes from different coals do not exhibit the same progressive changes throughout the fusibility range, and that the interpretation of empirical points such as initial softening, softening, and fluid, by any method, is greatly supplemented by the information to be gained from a study of the photographs.

In the interpretation of the fusibility range from the photographs of the ash, the initial softening point has been defined

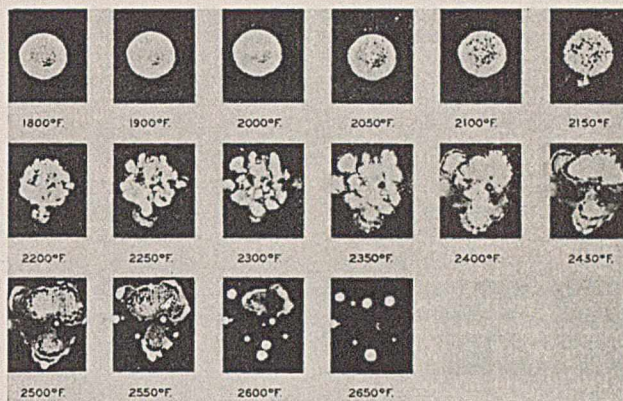


FIGURE 10

as the temperature at which there is the first visible indication of coalescence of the ash particles (see 2400° F., Figure 5) and the final point as the temperature at which the ash is formed into globules (see 2750° F., Figure 5).

The series of photographs of Figure 5 shows the fusing characteristics of the ash from a high-volatile, noncoking coal which has a fusibility range of 2400° to 2750° F. The gas-furnace softening temperature was 2725° F. This coal has been burned without the formation of clinker in a furnace equipped with a V-type overfeed stoker. Serious clinker trouble was experienced on this same equipment when burning coal mined from the same seam. The photographs of the ash from the troublesome coal (Figure 6) show different characteristics within its fusibility range of 2150° to 2700° F. The initial point was accompanied in this case by the formation of a ghostlike ring or halo encircling the main mass of the ash (see 2150° F.). The gas-furnace softening temperature was 2510° F.

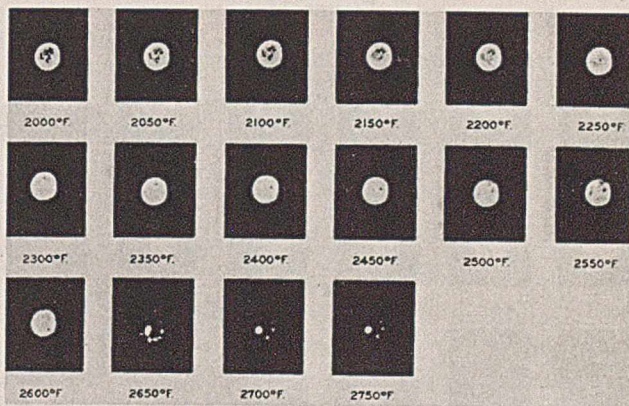


FIGURE 11

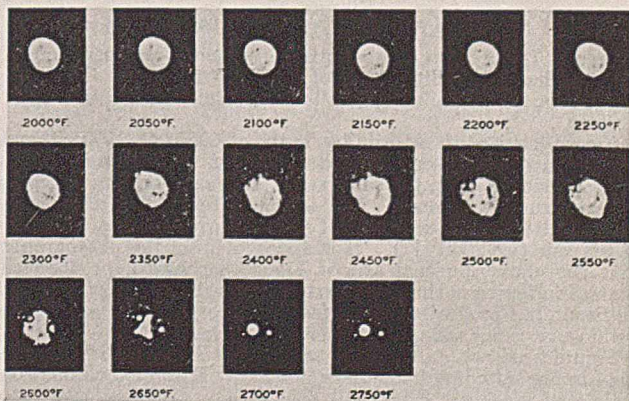


FIGURE 12

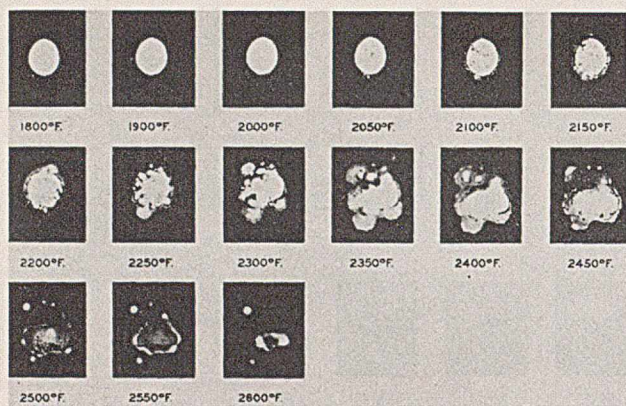


FIGURE 13

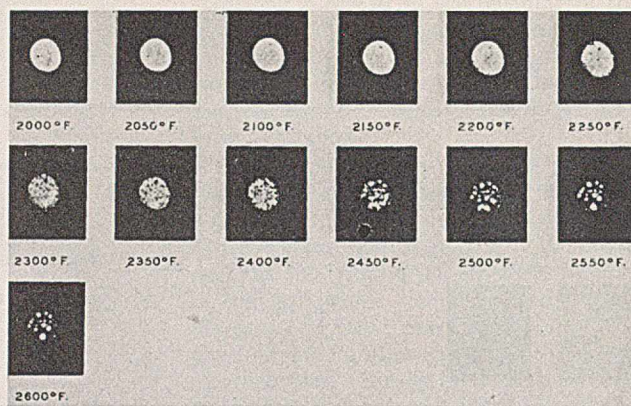


FIGURE 16

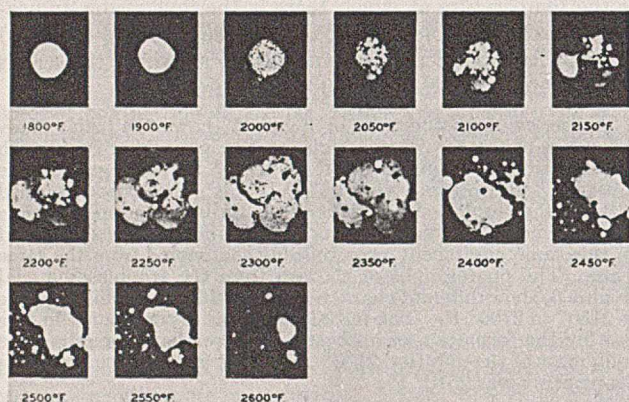


FIGURE 14

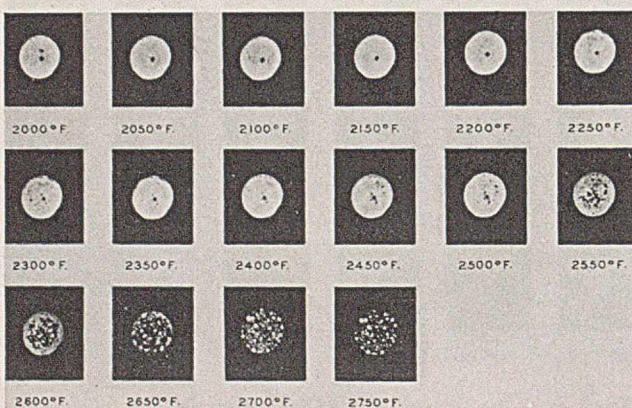


FIGURE 15

Figure 7 ash with a gas-furnace softening temperature of 2550° F. has a fusibility range of 2250° to 2700° F. This ash, which is a low-volatile coal, caused no clinkering on underfeed stokers.

Figure 8 ash with a fusibility range of 2000° to 2500° F. and a gas-furnace softening temperature of 2090° F., also a low-volatile coal but not from the same seam, did cause serious clinkering on the same equipment. The initial softening in this case is accompanied by an extrusion of softened matter from the body of the ash (see 2000° F.). It is apparent from the photographs that the clinkering coal ash of Figure 8 shows a pronounced general softening in the lower part of the fusibility range and that its fusion has progressed much farther at any given temperature within that range than has that of Figure 7 ash.

Figure 9 ash with a fusibility range of 2150° to 2550° F. and a gas-furnace softening temperature of 2185° F. formed clinkers on underfeed stokers. Figure 10 ash with a range of 2050° to 2650° F. and a gas-furnace softening temperature of 2040° F. is from a coal from the same field, but not the same seam as Figure

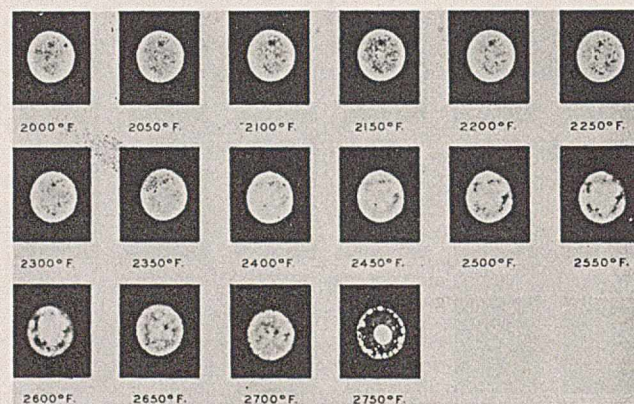


FIGURE 17

9 ash. Figure 10 ash clinkered readily when the coal was burned on underfeed stokers.

Some coal-ash samples of like A. S. T. M. gas-furnace softening temperatures evidence entirely different characteristics by the photographic method. Two pairs of photographic series illustrate this: Figures 11 and 12 (U. S. Bureau of Mines samples 11 and 14, respectively), and Figures 13 and 14 (Bureau of Mines samples 7 and 19, respectively).

Figure 11 ash with a gas-furnace softening temperature of 2195° F. shows a fusibility range of 2150° to 2650° F. plus in the photographs. This ash is the Bureau of Mines sample 11, to the unusual behavior of which attention has been called. It will be noted in Figure 2 that sample 11 cone appears to have reached its softening temperature at about 2150° F. and that it changes but little in appearance with increasing temperature up to about 2300° F. This ash exhibits the same characteristic when studied by the photographic method (see Figure 11). The initial point is reached at 2150° F.; a gradual change follows up to about 2500° F., and then a rapid change occurs up to the final point at 2650° F. plus.

Figure 12 ash with a gas-furnace softening temperature of 2200° F. and a fusibility range of 2150° to 2650° F. plus shows a tendency to spread out on the strip early in its fusibility range. These last two plates show ashes with essentially the same empirical points, but quite different in their fusibility progressions.

Figures 13 and 14 with gas-furnace softening temperatures of 2055° and 2040° F. and with like fusibility ranges from the photographs (2000° to 2600° F.) are the second series to illustrate that coal ash of like gas-furnace softening temperatures may exhibit different characteristics when studied by this photographic method.

From the empirical points, these coals might be expected to have like clinkering characteristics, but it is apparent from the photographs that their fusibility progressions are quite different. The ash of Figure 14 is similar to that of Figure 10 which formed troublesome clinker. The appearance of these plates suggests the formation of extremely free-flowing slag, a characteristic which is shown to a lesser degree in Figure 13.

Figures 15 and 16 show the fusing characteristics of ash from

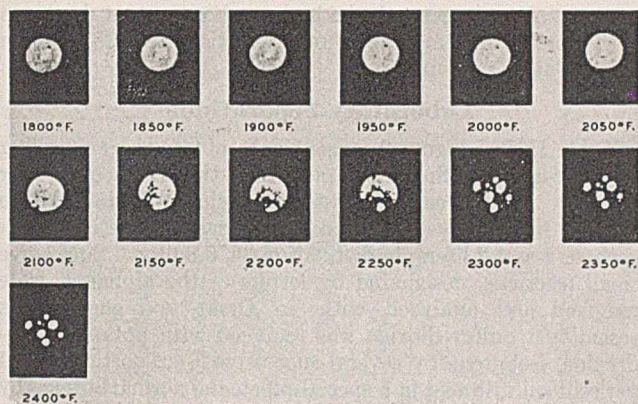


FIGURE 18

two low-volatile, semi-bituminous coals from the Appalachian Field. The coal in Figure 15 with an ash-fusibility range of 2250° to 2700° F. has been burned on underfeed stokers without the formation of objectionable clinkers. This ash exhibits only gradual changes in its condition up to 2500° F. and shows a rapid change above that temperature. The coal in Figure 16 with a fusibility range from 2200° to 2500° F. when burned on the same equipment produced troublesome clinkers. Ash from this coal shows more rapid progression of fusion than is shown by the ash of Figure 15.

The fusibility progression of ash from a high-volatile, coking, bituminous coal from the Appalachian Field is shown in Figure 17. It is difficult to select the fusibility range of this ash because it shows only slight changes at the lower temperatures. However, an abrupt change occurs between 2700° and 2750° F. The slow progression of the fusion in the case of this ash is significant in that the coal has been burned on a variety of equipment without the formation of troublesome clinkers.

Figure 18 shows the fusing characteristics of ash from lignite coal, indicating a fusibility range of 2000° to 2300° F. with distinct progression from the initial point to the final point. This

coal cannot be burned on certain types of equipment, particularly underfeed stokers, without the formation of troublesome clinker, as might be expected from the low fusibility range and the low final point of 2300° F.

It is hoped that the information presented in this paper will stimulate further study of the fusibility of coal ash and its relation to clinker formation. The photographic method should be particularly useful because of the permanent records that are made and the comparatively short time that is required for each test. An extended study of the relation between ash fusibility and clinkering must necessarily involve a number of factors, such as chemical composition of the ash, effect of fluxing agents, viscosity and surface tension of the slag formed, size and association of particles, furnace temperature, surrounding atmosphere, and length of time the ash is subjected to temperature. It is possible that the method may be of value in studying the effect of addition of various materials to coal in order to alter the fusing characteristics of the ash.

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Separating Butenes from Butanes Distillation of Azeotropic Mixtures with Sulfur Dioxide

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It has been found that four-carbon hydrocarbons form minimum-boiling azeotropic mixtures with sulfur dioxide. The order of the azeotropes with respect to boiling point is different from that of the hydrocarbons, for both butane azeotropes have lower boiling points than any of the

butene azeotropes. This permits practical separation into a butene and a butane fraction. Vapor pressures and equilibrium compositions of both liquid and vapor phases at various temperatures have been determined for mixtures of sulfur dioxide and four-carbon refinery gas fractions.

PRACTICAL separation of mixtures of hydrocarbons having four carbon atoms to the molecule, such as certain gas fractions from modern cracking operations, into a butene part and a butane part by simple fractional distillation is very difficult because of the small boiling point range:

	° C.		° C.
Isobutane	-12.4	n-Butane	-0.6
Isobutene	-6.7	2-Butene (trans)	1.0
1-Butene	-6.7	2-Butene (cis)	3.7

Moreover, the order or arrangement of the hydrocarbons with respect to boiling point necessitates obtaining four fractions instead of only two.

Separation can be more readily accomplished by distillation in the presence of sulfur dioxide, which forms azeotropic mixtures with the following approximate boiling points at atmospheric pressure:

	° C.
Azeotrope of isobutane	-24
Azeotrope of n-butane	-18
Azeotrope of 1-butene	-16
Azeotrope of isobutene	-14
Azeotrope of 2-butene (trans)	-14
Azeotrope of 2-butene (cis)	-13

The order of the azeotropes with respect to boiling point differs from that of the hydrocarbons themselves, for both

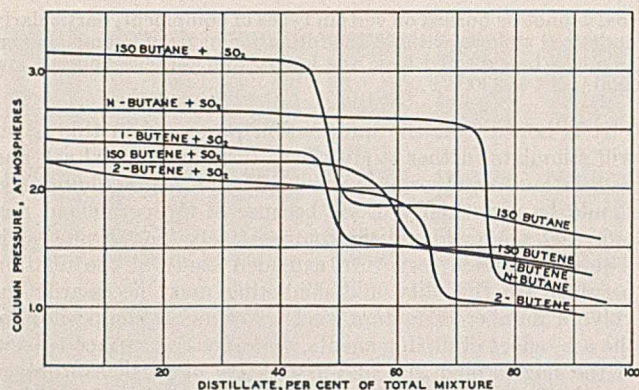


FIGURE 1. DISTILLATION CURVES FOR BINARY MIXTURES OF SULFUR DIOXIDE AND EXCESS FOUR-CARBON HYDROCARBONS AT 3° C.

butane azeotropes have lower boiling points than any butene azeotrope. This change is evident in Figure 1, which shows typical isothermal distillation curves obtained with binary mixtures containing excess hydrocarbon (except No. 27, which had an excess of sulfur dioxide) in a laboratory vacuum-jacketed (unsilvered) glass gas-analytical column. The reflux condenser was cooled with an ice-water mixture and the distillation was followed by reading the column pressure. Total gas volumes of only 1 to 2 liters were used. Whereas *n*-butane has a position between 1-butene and 2-butene, its azeotrope has one between isobutane and 1-butene.

TABLE I. BINARY AZEOTROPIC MIXTURES OF SULFUR DIOXIDE AND FOUR-CARBON HYDROCARBONS

Hydrocarbon	Number	Distillation		Mole Per Cent Hydrocarbon	Mole Per Cent Sulfur dioxide
		Temp. ° C.	Pressure Atm.		
Isobutane	30	3	3.17	45.1	54.9
	11	-35	0.46	40.5	59.5
	22	-18	0.99	39.3	60.7
	8	-18	0.99	38.9	61.1
	20	-19	0.99	39.7	60.3
n-Butane	21	-5	1.89	36.9	63.1
	10	-5	1.89	36.6	63.4
	23	3	2.65	35.6	64.4
	40	-16	0.99	41.7	58.3
	38	3	2.37	40.7	59.3
1-Butene	19	-30	0.46	46.0	54.0
	16	-14	0.99	44.2	55.8
	17	0	1.88	46.6	54.4
	18	0	1.88	46.4	53.6
	26	3	2.24	36	64
Isobutene	27	3	2.40	37.5	62.5
	14	-29	0.46	32.5	67.5
	12	-14	0.99	31.6	68.4
	2	.	0.99	30.3	69.7 ^a
	5	-13	0.99	31.0	69.0 ^b
2-Butene	13	1	1.88	27.8	72.2
	24	3	2.05	27.7	72.3

^a Absorption with potassium hydroxide gave 69.4 per cent.

^b Absorption with potassium hydroxide gave 66.8 per cent.

If sulfur dioxide is added to a mixture of four-carbon hydrocarbons in an amount equivalent to the azeotropes of the butanes present and if the resulting mixture is then fractionally distilled, the butanes can be separated from the butenes, for there is a difference of over 11° C. between the boiling points of the highest boiling paraffin azeotrope and the lowest boiling of the olefins.

Composition of Azeotropes

Table I indicates the composition of the azeotropes when distilled in a laboratory gas-analytical column. The percentages have been calculated from the position of the breaks in the distillation curves and from the over-all composition. The temperature figures are approximate only, but are believed to be correct to about 1° C.

The sulfur dioxide content differs with the hydrocarbon concerned, being smallest for isobutane and largest for 2-

butene. Also, in general, the hydrocarbon content decreases with increase in temperature of distillation, or with increase in distillation pressure.

Laboratory Separations

Table II and Figure 2 present data obtained by distilling two four-carbon refinery gas fractions in the presence of sulfur dioxide. In each case the total gas volume of the mixture was 2.0 liters. In distillation 35 the gas volume of hydrocarbons was 1.2 liters; in distillation 36, 0.8 liter. Successive small fractions, designated by letters of the alphabet, were removed and analyzed with an Orsat-type gas-analysis assembly. Sulfur dioxide was removed with potassium hydroxide, isobutene by several successive 1-cc. portions of 64 per cent sulfuric acid in a special pipet, and normal butenes by 1-cc. portions of 95 per cent sulfuric acid in an empirically determined procedure that gave accurate results. Precautions were observed to eliminate errors caused by solution of sulfur dioxide in moisture contained in the buret and connections, by desiccation of the sample by sulfuric acid, by incomplete absorption due to establishment of equilibrium, and by solubility of hydrocarbons in the absorption products.

The hydrocarbons in fraction A of distillation 35 consisted chiefly of isobutane; in B, of both butanes. The latter contained considerable butenes, owing to too rapid distilling. Still more butenes appeared in fraction C; in D, they predominated, revealing a depletion of the butanes. Since analyses continued to show the presence of paraffins in subsequent fractions and since their percentage increased at the end of the distillation, it is believed that some pentane was present in the original refinery gas fraction. The sulfur dioxide became practically exhausted in fraction E, causing a sudden drop in distillation pressure from 2.2 to 1.5 atmospheres.

In distillation 36, it had been planned to use an excess of sulfur dioxide; but its low content in the residual gas in the column and kettle (fraction K) indicates that scarcely enough was present. The sulfur dioxide content of the earlier or butane-rich fractions was practically constant at 62 to 65 per cent, which is comparable with 64.4 obtained for the azeotrope of *n*-butane in distillation 23 of Table I. For the butene-rich fraction J it increased to 71.8 per cent, which agrees with 72.3 found for the azeotrope of 2-butene in distillation 24 of Table I. With respect to the hydrocarbon content, the first several fractions contained mainly *n*-butane and the last two mainly butenes. The butane became exhausted with fraction I, causing the pressure to drop suddenly from 2.4 to 1.85 atmospheres. This fraction contained a mixture of butane and butenes, with the butane predominating. Fraction J contained practically no butane. The slight increase in paraffin content shown by the last fraction, K, is attributed to the presence of a trace of pentane.

The summary given in Figure 2 shows that in distillation 35 the first composite fraction, A-B, containing 31.4 per cent of all the hydrocarbons, contained 65.5 per cent of all the paraffins at an average concentration of 93.5 per cent and 3.7 per cent of all the butenes at an average concentration of 6.5 per cent. All

TABLE II. LABORATORY SEPARATIONS OF FOUR-CARBON REFINERY GAS FRACTIONS

Distillation	Fraction	Distn. Time Min.	Mole Per Cent Distilled	Sulfur dioxide	Analysis, Mole Per Cent		
					Hydrocarbons, SO ₂	Free-Paraffins	n-Butenes
35	Original	23.0	35.5	41.5
	A	25	18.0	43.9	0.7	2.3	97.0
	B	15	39.1	51.2	0.9	8.9	90.2
	C	35	54.1	58.0	1.8	23.3	75.0
	D	65	64.0	55.0	23.7	56.5	19.9
	E	25	70.4	32.7	44.8	49.1	6.1
	F	43	87.9	0.7	45.0	50.1	5.0
	G	30	96.4	0.6	25.2	48.8	25.9
	H	..	100.1	0.9	21.0	48.8	30.1
36	Original	1.2	18.5	80.3
	A	15	9.5	62.6	0.2	1.2	98.5
	B	15	19.1	62.4	0.1	0.4	99.6
	C	11	29.8	63.0	0.0	0.3	99.6
	D	15	39.4	63.1	0.1	1.5	98.5
	E	16	48.4	62.5	0.0	0.6	99.4
	F	15	56.1	65.0	0.0	0.9	99.1
	G	23	65.8	62.7	0.2	1.7	98.1
	H	18	74.5	61.9	0.2	5.6	94.2
	I	15	82.5	64.4	3.4	36.4	60.3
	J	34	91.9	71.8	3.4	96.0	0.6
K	..	99.8	59.4	2.4	93.3	4.3	

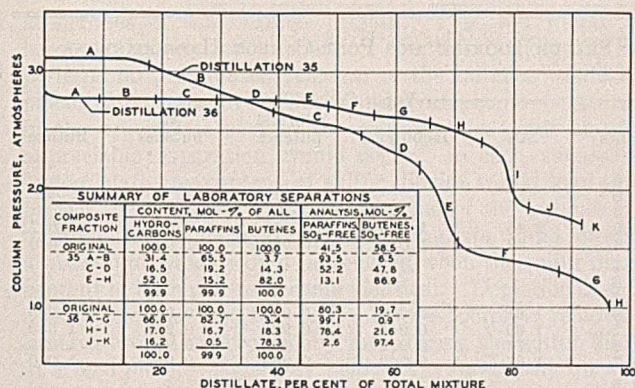


FIGURE 2. DISTILLATION CURVES FOR MIXTURES OF SULFUR DIOXIDE AND FOUR-CARBON REFINERY GAS FRACTIONS AT 30°C.

concentration figures for the hydrocarbons are on a sulfur dioxide-free basis. The last composite fraction, E-H, containing 52.0 per cent of all the hydrocarbons, contained 15.2 per cent of all the paraffins at an average concentration of 13.1 per cent and 82.0 per cent of all the butenes at an average concentration of 86.9 per cent. If pentane had been absent from the original refinery gas fraction, the concentration of butenes would have been much higher than 86.9 per cent.

In distillation 36 the first composite fraction, A-G, containing 66.8 per cent of all the hydrocarbons, contained 82.7 per cent of all the paraffins at an average concentration of 99.1 per cent and 3.4 per cent of all the butenes at an average concentration of 0.9 per cent. The last composite fraction, J-K, containing 16.2 per cent of all the hydrocarbons, contained 0.5 per cent of all the paraffins—principally pentane—at an average concentration of 2.6 per cent and 78.3 per cent of all the butenes at an average concentration of 97.4 per cent. On a pentane-free basis and on the assumption that the average butane content was that found in fraction J, the concentration of butenes in this composite fraction was 99.4 per cent.

The data show an excellent separation. It is true that the intermediate composite fractions, C-D and H-I, contained both olefins and paraffins, at concentrations not greatly different from those present in the original material, but these fractions were small and passed overhead only when the butane was becoming exhausted. The data were obtained with small samples having total gas volumes of only 2.0 liters and with a laboratory gas-analytical column. It is clear that with larger samples and with more efficient distilling equipment the intermediate fractions would become relatively negligible or disappear entirely.

Vapor-Liquid Equilibria Data

A study was made of the equilibrium composition, at various temperatures, of both liquid and vapor phases of a number of complex mixtures of sulfur dioxide and four-carbon hydrocarbons. A 250-cc. steel bomb, always more than half filled with the liquid phase, was used. It was brought to a predetermined temperature in a water bath, with occasional vigorous shaking to ensure establishment of equilibrium conditions. Samples of both vapor and liquid phases—the latter after inverting the bomb—were removed by cracking open a needle valve fitted to the top of the bomb. These were run directly into the buret of an Orsat-type gas-analysis assembly and analyzed for sulfur dioxide, isobutene, and normal butenes. In order to have a volume of hydrocarbons of 75–95 cc., it was necessary to take a total sample of 100 to 300 cc., depending on the sulfur dioxide content.

The data are arranged in Table III in groups, designated by letters of the alphabet, in the order of increasing concentration of sulfur dioxide in the liquid phase. Within each group the determinations of the liquid phase are given first and then those of the vapor phase arranged in the order of increasing temperature.

Empirical Vapor-Liquid Relationships

A striking phenomenon indicated by group A of Table III is the pronounced difference in sulfur dioxide content of the two phases. As is shown by the vapor-to-liquid ratios in the eighth column, the vapor had well over twice as high a concentration as the liquid. The same phenomenon is exhibited, in successively decreasing degree, by groups B, C, D, E, and F. This is more clearly evident from Figure 3, which shows that the vapor-to-liquid ratio decreased in a uniform but nonlinear manner from a value of about 3 for a liquid-phase sulfur dioxide content of about 5 mole per cent to one of unity at 66 mole per cent. The value of 66 mole per cent doubtless represents approximately an average or over-all concentration of sulfur dioxide for all of the several possible azeotropic mixtures. Above 66 mole per cent, the vapor-to-liquid ratio continued to decrease, indicating that the concentration of sulfur dioxide in the vapor was less than in the liquid. In other words, as was to be expected for an azeotropic mixture of minimum boiling point, there was a strong tendency for the vapor phase to approach the sulfur dioxide content of the over-all azeotropic mixture both when too little and when too much was present in the liquid phase.

The significance and importance of this tendency becomes evident from inspection of the vapor-to-liquid ratios for butenes and butanes in the last two columns of Table III. Since both ratios were very close to unity in group A, scarcely any separation of butanes from butenes occurred when the sulfur dioxide content of the liquid was only about 11 mole per cent. (Since at the same time there was a marked concentration of the sulfur dioxide in the vapor phase, this fact indicates that a minimum-boiling azeotropic mixture does not consist of a single chemical compound or of definite aggregates of loosely bound molecules.) But in group B the ratios definitely diverged from unity, showing that appreciable separation took place when the sulfur dioxide content in the liquid was about 25 mole per cent, which was approximately the same concentration as in the vapor for group A. As the ratio for butenes was smaller than unity and that for butanes was larger than unity, the former tended to concentrate in the liquid phase and the latter in the vapor phase. Still greater divergence from unity was shown in group C, the liquid phase for which contained approximately the same concentration of sulfur dioxide as the vapor phase in group B, about 41 mole per cent. This increase in the effectiveness of the separation with increase in sulfur dioxide content is clearly indicated by all groups of Table III.

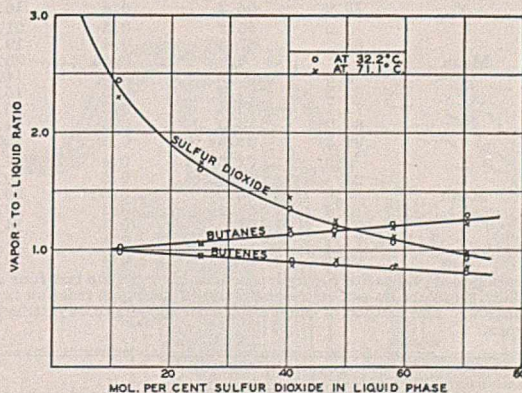


FIGURE 3. DEPENDENCE OF VAPOR-TO-LIQUID RATIOS ON SULFUR DIOXIDE CONTENT OF LIQUID PHASE

From Figure 3 it is evident that the relationships between sulfur dioxide content in the liquid phase and vapor-to-liquid ratios for butenes and butanes are virtually linear in the range covered. The two straight curves begin with a common value

TABLE III. VAPOR-LIQUID EQUILIBRIA DATA FOR MIXTURES OF SULFUR DIOXIDE AND FOUR-CARBON HYDROCARBONS

No.	Phase	Temp., °C.	Composition, Mole Per Cent				Vapor Concn./Liquid Concn. ^a				
			Hydrocarbons, SO ₂ -Free				SO ₂	Isobutene	Normal butenes	All butenes	Butanes
			SO ₂	Isobutene	Normal butenes	Butanes					
A-47	L	35	11.6	21.8	36.6	41.6
50	L	67	10.9	22.5	36.5	41.0
	Mean		11.25	22.15	36.55	41.3
48	V	32.2	27.6	22.3	35.7	42.0	2.45	1.008	0.976	0.988	1.017
49	V	71.1	26.1	22.6	36.1	41.3	2.32	1.020	0.988	1.000	1.000
B-43	L	65	25.3	22.4	35.5	42.1
44	L	25	25.2	22.1	35.6	42.3
	Mean		25.25	22.25	35.55	42.2
46	V	0.0	41.7	20.2	33.9	45.9	1.61	0.909	0.954	0.937	1.088
45	V	32.2	42.5	21.0	34.3	44.7	1.69	0.945	0.965	0.957	1.060
41	V	71.1	43.7	21.2	34.2	44.6	1.74	0.954	0.962	0.959	1.058
42	V	97.5	47.1	20.9	34.4	44.7	1.87	0.940	0.968	0.957	1.060
C-2	L	32.2	41.1	22.2	35.0	42.8
4	L	32.2	41.1	22.2	35.4	42.4
8	L	71	40.7	22.4	35.4	42.1
10	L	85.3	40.4	22.4	35.5	42.1
12	L	7	...	23.0	35.9	41.0
13	L	23.4	39.3	22.5	35.5	42.0
	Mean		40.5	22.45	35.45	42.1
11	V	5.3	52.5	18.9	32.7	48.4	1.297	0.842	0.922	0.892	1.148
1	V	32.2	55.4	18.8	32.8	48.4	1.368	0.837	0.925	0.892	1.148
3	V	32.2	54.5	19.1	32.9	48.0	1.346	0.851	0.928	0.899	1.140
6	V	53.0	57.3	18.0	31.9	50.2	1.415	0.802	0.900	0.860	1.190
5	V	71.1	58.0	18.7	32.5	48.8	1.432	0.833	0.917	0.885	1.159
7	V	71.1	59.5	18.4	32.1	49.5	1.470	0.819	0.906	0.873	1.175
9	V	84.8	59.8	18.8	32.3	48.9	1.477	0.837	0.911	0.883	1.160
D-16	L	32.2	48.1	22.5	35.5	42.0
18	L	73	48.3	22.8	35.2	42.0
	Mean		48.2	22.65	35.35	42.0
14	V	1.8	55.2	17.0	31.4	51.6	1.146	0.751	0.888	0.834	1.230
19	V	7.0	54.1	18.5	32.6	48.9	1.121	0.817	0.922	0.881	1.164
15	V	32.2	57.1	18.7	32.5	48.8	1.185	0.826	0.919	0.883	1.161
17	V	73.2	60.3	19.2	32.9	47.9	1.250	0.848	0.930	0.899	1.140
E-22	L	24	58.0	22.9	35.2	41.9
27	V	0.0	57.9	16.1	30.8	53.1	0.998	0.703	0.875	0.807	1.269
20	V	0.7	58.2	14.9	30.0	55.1	1.002	0.651	0.853	0.790	1.315
21	V	1.3	58.2	16.2	31.1	52.7	1.002	0.708	0.883	0.814	1.259
24	V	30.0	61.2	17.6	31.8	50.6	1.056	0.769	0.903	0.850	1.210
23	V	32.2	61.5	17.2	31.7	51.1	1.060	0.751	0.900	0.842	1.220
25	V	71.0	64.6	17.6	31.9	50.5	1.114	0.769	0.906	0.852	1.206
26	V	72.0	64.7	17.6	32.0	50.4	1.116	0.769	0.909	0.854	1.201
F-29	L	0.0	70.9	23.4	36.3	40.3
32	L	64	70.2	22.5	35.7	41.8
	Mean		70.55	22.95	36.0	41.05
28	V	30.0	61.9	14.5	29.2	56.3	0.877	0.632	0.811	0.742	1.370
30	V	32.2	65.7	16.2	30.8	53.0	0.931	0.706	0.855	0.793	1.290
31	V	71.0	69.1	17.5	31.8	50.7	0.980	0.763	0.883	0.836	1.234
G-34	L	31	78.1	31.4	41.0	27.6
37	L	22.7	78.3	31.5	41.1	27.4
	Mean		78.2	31.45	41.05	27.5
33	V	33.8	70.0	24.0	37.2	38.8	0.895	0.763	0.906	0.844	1.411
35	V	74.0	73.6	25.5	37.9	36.6	0.941	0.811	0.923	0.875	1.331
36	V	90.0	75.0	26.7	38.8	34.5	0.959	0.849	0.945	0.904	1.254
H-52	L	0.0	23.0	0.6	20.0	79.4
56	L	86	24.2	0.5	20.0	79.5
	Mean		23.6	0.55	20.0	79.45
51	V	0.0	49.8	0.4	17.6	82.0	2.11	0.7	0.880	0.875	1.032
53	V	32.3	49.0	0.5	17.8	81.7	2.08	0.9	0.890	0.890	1.029
54	V	71.1	46.7	0.5	18.4	81.1	1.98	0.9	0.920	0.920	1.021
55	V	87.0	47.4	0.5	18.5	81.0	2.01	0.9	0.925	0.925	1.020
I-58	L	0.0	46.4	0.5	20.3	79.2
61	L	66	48.2	0.5	19.8	79.7
	Mean		47.4	0.5	20.05	79.45
57	V	0.0	58.1	0.3	15.9	83.9	1.228	0.6	0.793	0.783	1.056
59	V	32.2	61.0	0.4	16.0	83.6	1.289	0.8	0.798	0.798	1.052
60	V	73.0	63.2	0.4	16.3	83.3	1.334	0.8	0.813	0.812	1.048
J-63	L	0.0	56.2	0.5	21.3	78.2
67	L	65	57.6	0.4	19.9	79.7
	Mean		56.9	0.45	20.6	78.95
62	V	0.0	60.7	0.3	14.3	85.4	1.068	0.7	0.694	0.694	1.081
64	V	32.2	63.9	0.3	15.3	84.4	1.122	0.7	0.743	0.742	1.070
65	V	71.1	65.8	0.3	16.3	83.5	1.157	0.7	0.791	0.784	1.058
66	V	86.0	68.2	0.3	14.9	84.8	1.199	0.7	0.724	0.723	1.074
68	V	99.3	68.5	0.4	15.4	84.2	1.204	0.9	0.748	0.751	1.068
K-70	L	0.0	71.2	0.4	21.0	78.6
74	L	25	70.6	0.5	20.9	78.5
	Mean		70.9	0.45	20.95	78.55
69	V	0.0	64.9	0.2	12.4	87.4	0.916	0.4	0.592	0.588	1.112
71	V	32.2	68.0	0.3	14.0	85.7	0.960	0.7	0.668	0.667	1.091
72	V	71.1	71.1	0.4	14.7	84.9	1.003	0.9	0.702	0.705	1.080
73	V	99.4	72.7	0.3	15.1	84.6	1.026	0.7	0.720	0.719	1.078

^a The vapor-to-liquid ratios for hydrocarbons given in the last four columns were calculated from the sulfur dioxide-free mole percentages of columns 5, 6, and 7. They therefore do not represent ratios of the mole fraction in the vapor phase to the mole fraction in the liquid phase, since they ignore the presence of sulfur dioxide. The method of calculation used appears to be justified because it brings out sharply the effect of the sulfur dioxide on the separation of butanes from butenes.

of unity at about 10 mole per cent of sulfur dioxide—that is, detectable separation of butanes from butenes occurs only if the concentration of sulfur dioxide in the liquid phase exceeds about 10 mole per cent. The linear relationship continues even when the content exceeds that of the over-all azeotropic mixture—that is, the tendency for butenes to remain in the liquid phase and for butanes to pass into the vapor phase becomes greater the higher the concentration of sulfur dioxide.

The empirical relationships just discussed elucidate the action taking place in a fractionating column. Three cases are possible—namely, those in which the over-all concentration of sulfur dioxide is less than, equal to, or greater than that required to form azeotropic mixtures with all of the hydrocarbons present.

The first case would yield a kettle product containing little or no sulfur dioxide if the amount used is equivalent to the

azeotropes of the butanes present. The feed would thus have a relatively low proportion of sulfur dioxide. At first, perhaps no preferential removal of the butanes would take place. But the sulfur dioxide would soon become concentrated in the uppermost part of the column to a point at which appreciable separation would occur. In each successively higher plate the content of sulfur dioxide would tend to approach that required for the azeotropes of the butanes. Simultaneously, the effectiveness of each plate would approach a maximum which would be reached when the sulfur dioxide content of both phases became identical. Depletion of sulfur dioxide by the first few plates before complete removal of butanes would be avoided by introducing the sulfur dioxide at a feed plate considerably below that for the hydrocarbon mixture.

In the second case, since all plates would have approximately the same concentration of sulfur dioxide, neglecting the fact that the azeotropes of the different hydrocarbons contain different amounts of sulfur dioxide, all would be of approximately equal effectiveness. The fractionating tower could operate with a smaller number of plates than that necessary for the preceding case. Also, there would not be the same necessity for introducing the hydrocarbons and the sulfur dioxide at different feed plates.

In the third case, an excess of sulfur dioxide is used. Since from Table III and Figure 3 the effectiveness of a plate increases linearly with the sulfur dioxide content of the liquid phase even when the concentration exceeds that required to form the azeotropic mixtures, the fractionating tower would not need to have as many plates as in the first two cases.

From the vapor-to-liquid ratios in the ninth and tenth columns of Table III, it is evident that there was a better separation of butane from isobutene than from normal butenes. It is believed that the normal butenes in this case consisted principally of 1-butene, whose azeotrope has a higher vapor pressure than the azeotrope of isobutene.

Although the foregoing has been written with reference to the data of groups A to F of Table III, which were obtained with one four-carbon liquefied-gas fraction, the principles discussed appear to be of general application. The data of groups H to K, obtained with a different liquefied gas fraction containing much more *n*-butane, no isobutane, and much less isobutene, are very similar to those of groups A to F and, if plotted, give curves similar to those of Figure 3. The concentrating of sulfur dioxide in the vapor phase was more rapid for this fraction than for the first, probably because of the absence of isobutane, whose azeotrope contains less sulfur dioxide than the azeotrope of *n*-butane. Also, the vapor-to-liquid ratio for the *n*-butane present was uniformly smaller than for the mixture of butanes, for the azeotrope of *n*-butane has a lower vapor pressure than that of isobutane. The data of group G, obtained with a mixture relatively poor in butane, are also similar to those already discussed.

Temperature and Pressure

The data of Table III indicate two effects attributable to temperature. First, with one or two exceptions, within any one group of data, the mole percentage of sulfur dioxide in the vapor phase increased in a practically linear manner with the temperature. This is in harmony with the experimental fact that the azeotropes decrease in hydrocarbon content with increase in temperature. Second, with a few exceptions, the ratios for the hydrocarbons became somewhat less favorable to separation as temperature increased.

From the absolute pressure measurements presented in Table IV, it appears that at still-head temperatures ranging from 50° to 75° C. the pressure in a fractional distillation column used for separating butanes from butenes in the presence of sulfur dioxide would range from about 9 to 18 atmospheres.

To this range the phase composition data of Table III are applicable.

TABLE IV. VAPOR PRESSURE DATA FOR MIXTURES OF SULFUR DIOXIDE AND FOUR-CARBON REFINERY GAS FRACTIONS

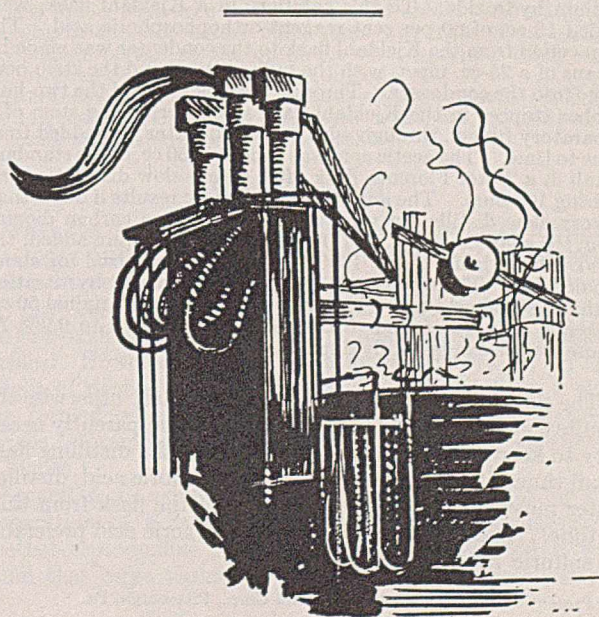
Absolute Pressure of Mixture Left from:							
G-37		B-46		I-61		K-72	
° C.	Atm.	° C.	Atm.	° C.	Atm.	° C.	Atm.
51	9.8	39.0	6.3	48.0	9.0	33.5	6.3
53.0	10.5	50.0	8.4	51	9.8	41	7.7
56.5	11.1	53.5	9.0	53	10.5	47	9.0
59	11.8	61.2	11.1	58.7	11.7	52	10.5
62.5	12.9	64.2	11.8	60.8	12.5	56.8	11.8
66	13.6	69.5	13.3	63.0	13.3	61.0	13.3
66	13.9	71.0	13.9	65	13.9	65	14.6
67.2	14.6	74.1	14.6	67	14.6	69	16.0
69	15.3	79.0	16.0	69.5	15.3	73	17.4
72	16.0	80.2	16.7	71	16.0	76.2	18.8
73	16.7	81.2	17.4	73	16.7	79.3	20.2
75	17.4	75	17.4	83.0	21.6
80	19.5	85	22.9
81.7	20.2	89	24.4
83.8	20.9	92	25.7
85.0	21.6	94	27.2
88.0	22.9	97.7	28.5
						98.5	29.2

Since data on the thermodynamic properties of sulfur dioxide-hydrocarbon mixtures are far from complete, a thermodynamic analysis has not been attempted. Intermolecular cohesive forces in the liquid state between sulfur dioxide molecules and between hydrocarbon molecules can be considered to be greater than those existing between molecules of sulfur dioxide and hydrocarbon, and this accounts for a boiling point of the mixture lower than that of either component. That simple paraffins and olefins in admixture exhibit partial vapor pressures closely proportional to their molar concentration and vapor pressures has been well established. The data presented show a boiling point depression on mixing butanes with sulfur dioxide markedly greater than in the case of butene-sulfur dioxide mixtures, after making due allowance for boiling point differences, and this difference parallels the familiar difference in mutual solubility. Thus *n*-butane and sulfur dioxide will separate into two liquid phases at -5° C. and below (1), while isobutene and sulfur dioxide remain in a single phase down to the freezing point of sulfur dioxide (-73° C).

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The Analysis of Sodium Acetate

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IN A RECENT study in this laboratory of certain phenomena occurring during the setting of gels of hydrated silica (1, 2), the authors found it necessary to make numerous analyses of sodium acetate, particularly in solution. The method ordinarily recommended for the determination of this substance involves ignition to the carbonate, which may be followed by a titration of the carbonate with standard dilute hydrochloric acid (3, 5).

Very little information could be found concerning the accuracy of this determination. Unfortunately the salt sodium acetate, which crystallizes with three molecules of crystal water, is efflorescent; hence no dependence may be placed upon it as a standard.

A study of the literature yielded only two methods of analysis which appeared worth serious investigation. The first was the pyrolytic method mentioned above. The second consisted of the distillation of the acetic acid from the sodium acetate solution, to which a nonvolatile acid such as phosphoric acid had been added (4). The acetic acid was caught in standard alkali. The following account will illustrate the procedures and one typical set of results.

Standard Acetic Acid Solution

An approximately normal solution was prepared from reagent-grade glacial acetic acid and recently boiled distilled water, and was standardized against an approximately normal standard sodium hydroxide solution which contained enough barium hydroxide to remain free from carbonate. This was kept in a Squibb automatic buret assembly, protected by fresh tubes of soda-lime. This base had been standardized against a standard 0.75 *N* hydrochloric acid, prepared by dilution of constant-boiling acid and standardized against sodium carbonate.

This particular acetic acid was titrated with the standard sodium hydroxide, using phenolphthalein. Values of 0.967 *N* and 0.968 *N* were obtained.

DISTILLATION METHOD. A solution of sodium acetate was prepared by neutralizing 50 cc. of the 0.968 *N* acetic acid with sodium hydroxide. To this solution, in a Kjeldahl flask, were added 15 cc. of 60 per cent reagent orthophosphoric acid. The connection from the Kjeldahl flask to the condenser was made by means of a 25-cc. pipet, with the bulb vertical and the stem bent to go into the condenser. Through the other hole of the two-hole rubber stopper in the Kjeldahl flask was inserted the stem of a separatory funnel, through which distilled water was added from time to time. The acetic acid was caught in 50 cc. of the standard alkali in a 2-liter Florence flask after a very slow distillation, requiring 10 hours. The authors found erratic results if other than a very slow distillation were used. To remove carbon dioxide from the solution, 50 cc. of 1.088 *N* sulfuric acid were added, the total volume being about 1300 cc. This was refluxed for about a half hour. The excess acid was then determined by titration with the standard base. The concentration of the original 50 cc. of acetic acid was found to be 0.967 *N*, compared to 0.968 *N*. These results can be easily duplicated.

The slow distillation appears to be essential; otherwise the results come out much too high. Also, it is apparently necessary to keep at least 200 cc. of solution in the distilling flask at all times during distillation with phosphoric acid; distilled water must be added to the contents of the flask from time to time. The authors have found phosphoric acid preferable to sulfuric acid.

By this method, a solution of reagent-grade sodium acetate from a freshly opened bottle, prepared by weight to be exactly 1 *N*, was found to be 0.995 *N*. The method, while reliable, is very time-consuming.

It would have been interesting, from the point of view of the method, to study carefully the high results obtained when the distillation was not carried out slowly. Since, however, the authors were trying to develop a satisfactory method of analysis to assist in carrying out a long-delayed study of the setting of the silicic acid gels they avoided rather than studied these deviations. Results nearly 1 per cent high were obtained with rapid distillation. The trouble was caused by phosphoric acid carried over, apparently as spray. It is the authors' opinion that a more suitable trap could be devised, which would permit much more rapid distillation. This method was of use in determining the acetate in the presence of silicate, where the pyrolytic method was not suitable.

PYROLYTIC METHOD. The same solution of sodium acetate prepared from reagent sodium acetate was analyzed by this method. Exactly 10 cc. of the solution were measured into a weighed platinum crucible, using a specially calibrated 10-cc. buret. The solution was evaporated on a steam bath, heated in an air bath, and finally heated carefully over a burner at dull redness until all carbon particles had disappeared. The residue, weighed as pure anhydrous sodium carbonate, gave 0.997 *N* for the sodium acetate solution, as compared to 0.995 *N* by the distillation method.

The authors have found it desirable not to heat the materials above low redness, although the removal of the carbon particles requires a little more time.

The literature suggests that the sodium carbonate formed be titrated with standard hydrochloric acid; the authors have found practically the same results, whether weighed as sodium carbonate or titrated. The statement is made in the literature that sodium carbonate undergoes slight decomposition if heated much above 300° C., and the temperature recommended in textbooks on quantitative analysis for heating sodium carbonate to prepare a primary standard is 270° to 300° C. During the pyrolysis, the material is carried for some time considerably over 300° C. and the titration method might be considered preferable.

The authors were unable to determine differences in the two procedures greater than their experimental error and have preferred to weigh the carbonate because it proved easier and more rapid.

PRECISION AND ACCURACY. After making a number of determinations by both methods, the authors are satisfied that each yields satisfactory results when carried out as described. The pyrolytic method is much more rapid and will be preferred.

The statement will be found that the distillation method gives low results. In the authors' experience, using the slow distillation described, duplicate determinations have agreed within 2 parts in 1000. About 1 part in 1000 lower than the pyrolytic method appears to be the average.

LIMITATIONS. Since the authors have been interested in the determination of sodium acetate only in solutions containing sodium acetate alone or sodium acetate and sodium silicate, they are prepared to say little about the limitations of the methods. While for them both methods have given satisfactory results on the solutions of sodium acetate

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alone, only the distillation method is suitable where the solution contains both sodium acetate and silicate.

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RECEIVED August 28, 1936.

Physical Testing Procedure for Latex Stocks

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ALTHOUGH procedures for the preparation of physical testing slabs from milled rubber stocks have been standardized, no such specifications are available for latex stocks. Test slabs from latex require special treatment and, if certain conditions are not fulfilled, erratic results will be obtained. The term "physical testing" as used here means the elongation modulus and tensile readings usually determined on the Scott testing machine. The procedure herein described is not set up as a complete specification, but it does give a method by which accurate and reproducible results have been obtained in this laboratory. It further calls attention to the fact that a latex stock containing more or less standard compounding ingredients (of which some are water-soluble) may be greatly altered in its physical properties by a variation in the humidity conditions under which it is being tested. All tests in this investigation were made on pure gum stocks, which experience has shown to give the most erratic results. While it is true that test strips made from factory-produced articles may give sufficient information for factory control, it is also considered essential to have available a test method for use in obtaining basic information on accelerator-sulfur ratios and general compounding ingredients.

Two methods have been proposed in the literature. One (2) recommends drying the latex test film on a glass plate placed in an oven at 45° C. The other (3) recommends drying the test films on unglazed tile, the edges of which have been built up with strips of paraffined paper to form a tray for drying the latex mix. In this investigation the glass-plate method was adopted in preference to the porous-tile method, in order to eliminate any loss of water-soluble substances originally contained in the latex or added during compounding.

In making a latex mix to be used in forming a test slab, three conditions must be considered—namely, proper viscosity of the mix, uniform fine dispersion of the pigments, and a perfectly smooth surface on the dried slab. The viscosity of the mix must be high enough to prevent settling of the pigments during drying, yet low enough to allow all air bubbles trapped during mixing to rise to the surface in a reasonable length of time before the slabs are poured. The dried surfaces of the slabs must be entirely free from ridges, cracks, or other blemishes.

All compounding ingredients used were made up in the form of water dispersions or solutions before being added to the latex. The zinc oxide and sulfur dispersions were of 40 and 50 per cent concentrations, respectively, and were prepared in a ball mill in which they were ground for 48 hours. The zinc oxide was dispersed in a 2 per cent Saprotin solution and the sulfur was dispersed in a 10 per cent glue solution. The basic test formula was of 50 per cent total solids content as follows:

	Grams
60% centrifuged latex	166
40% zinc oxide dispersion	2.5
50% sulfur	3
Piperidine pentamethylene dithiocarbamate (Pip-Pip)	0.75
10% ammoniacal casein	10
Water	26.25

The test mix was prepared by adding first the casein and then the pigments to the latex. The mix was stirred for 10 minutes at 350 r. p. m. with a single-blade mechanical stirrer and then strained through fine jersey knit rayon cloth. The strained mix was placed in a special buret and allowed to stand for 0.5 hour before the slabs were poured. During this time the air bubbles rose to the surface.

The above-mentioned burets were constructed from 71-cm. (28-inch) lengths of 29-mm. (1.125-inch) glass tubing, graduated into 25-cc. divisions and fitted at the bottom with stopper, tube, and screw clamp. The slabs were formed and dried in plate-glass trays having inside dimensions of 175 × 175 × 6 mm. (6.875 × 6.875 × 0.25 inch). These trays were constructed by cementing, with sodium silicate solution, 13-mm. (0.5-inch) wide strips of 6-mm. (0.25-inch) plate glass about the perimeter of 187-mm. (7.375-inch) squares of the same material.

The mix was flowed into these trays by placing the buret tube close to the bottom of the tray and allowing the compounded latex to flow slowly into the cavity. The amount of the mix used was determined by the total solids content of the compound and the desired thickness of the dried slab. With the above mix 75 cc. produced a dried slab of 1.27-mm. (0.050-inch) thickness. This was the thickness of all slabs tested in this experimental work. The filled glass trays were placed upon a level surface and allowed to dry overnight at room temperature. The slabs were then removed from the trays and after 48 hours' further drying were cured by hanging individually in an oven at 100° C. If any moisture remained in the slabs after this drying period, it was removed during the air cure which followed. It was found that even with substantial amounts of water remaining in the slab before cure, there was little effect on the physical properties at the optimum cure, provided other conditions to be discussed later were fulfilled.

After the cure, test strips were cut out with a standard A. S. T. M. die 11.1 cm. (4.375 inches) long with a 2.5-cm. (1-inch) construction and tested on the Scott machine.

Experimental

When the first slabs were prepared using the given formula, the upper surface of the dried slabs was found to be covered with a network of fine surface cracks which would invalidate any physical tests made with them. By process of elimination the zinc oxide was found to be the pigment causing the cracked surface. However, when 1 per cent of Aquarex D, on the weight of rubber, was added as additional stabilizer, a slab was formed which when dry had a smooth and flawless surface. Examples of the two types of surfaces are shown in Figure 1.

Several tests using the procedure outlined above for the preparation of a satisfactory slab were made to determine whether reproducible results could be obtained, but it was found that large variations occurred when the test was re-

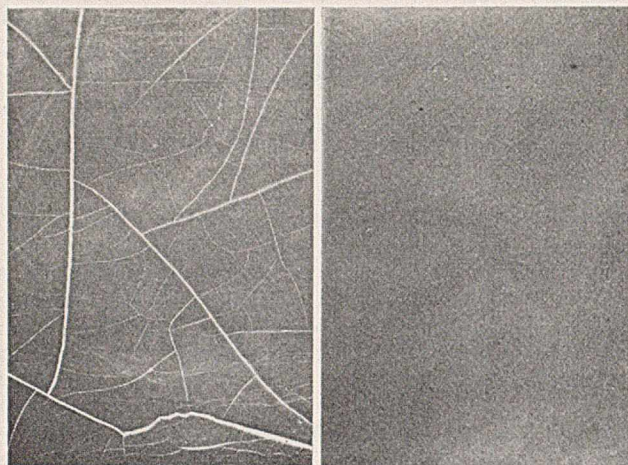


FIGURE 1. TWO TYPES OF SLAB SURFACES

peated over several days. The results of a series of this kind are shown in Table I. The slabs for this series were prepared from separate mixes on successive days using identical compounding ingredients. These slabs were also given identical drying and curing treatments. The tensile strength varied up to 25 per cent and the modulus at 600 per cent elongation varied 50 per cent.

TABLE I. RESULTS WITH TEST SLABS

Test	Elongation %	Modulus at 600 Per Cent		Tensile	
		Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.
1	910	500	35	4200	295
2	910	450	32	4090	288
3	870	750	53	4530	318
4	900	680	48	4570	321
5	910	620	44	4450	313
6	880	950	67	5360	377

Cure, 45 minutes at 100° C. 4 strips pulled on each test.

The well-known water-absorbing properties of latex stocks suggested that the cause of this variation might be changes in humidity which normally occur at room conditions. Therefore, tests were run in which the strips were conditioned at controlled humidities until tested. Controlled humidities were maintained in desiccators in which were placed the proper substances to give the desired moisture contents. In the examples reported, 50 per cent relative humidity was obtained over a saturated solution of sodium dichromate, while 0 per cent humidity was obtained over calcium chloride.

The test strips, which had been cured, gaged, and benchmarked, were individually hung in a desiccator and conditioned for 48 hours, and were removed from the desiccator only as they were pulled. Table II and Figure 2 show the effect of variation in relative humidity from 0 to 50 per cent. The modulus at 800 per cent elongation and the tensile strength were both reduced approximately 30 per cent when the relative humidity was increased from 0 to 50 per cent. Elongation increased slightly with increased relative humidity.

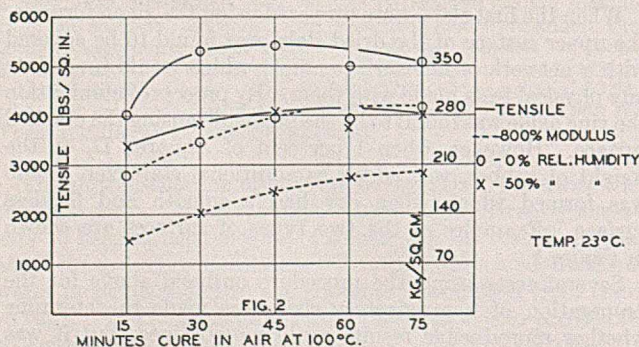


FIGURE 2. EFFECT OF HUMIDITY ON LATEX STOCK

TABLE II. EFFECT OF HUMIDITY ON LATEX STOCK

Cure at 100° C. in Air	Elongation		Modulus at 800 Per Cent				Tensile			
	0%	50%	0%	50%	0%	50%	0%	50%	0%	50%
Min.	%	%	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.
15	900	990	2820	1440	198	101	4010	3400	282	239
30	920	930	3420	2070	240	146	5360	3870	377	272
45	900	900	3980	2490	280	175	5460	4100	384	288
60	870	850	3900	2800	274	197	4980	3850	350	271
75	850	870	4150	2880	292	202	5080	4030	357	283

3 strips tested for each cure. Thoroughly dried strips were conditioned for 48 hours at indicated humidity before testing.

TABLE III. CONSISTENCY COMPARISON OF LATEX STOCKS vs. MILL-MIXED PURE GUM STOCK

Test	Elongation %	Modulus at 800 Per Cent		Tensile	
		Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.
Latex Stock ^a					
1	870	3980	280	5380	378
2	880	3680	259	5180	364
3	880	3860	271	5140	361
Mill-Mixed Stock ^b					
Modulus at 600 Per Cent					
1	780	940	66	3080	217
2	800	810	57	3060	215
3	800	850	60	3010	211

^a Cure, 45 minutes at 100° C. 4 strips pulled on each test. 0% humidity; 23° C.

^b Cure, 45 minutes at 127° C. Tested at room conditions, 23° C.

This reduction in tensile and modulus values with an increase in relative humidity showed that consistent results could be obtained only when the humidity was controlled up until the time of testing. Conover and Depew (1) recommend that regular mill-mixed stocks be conditioned at 0 per cent relative humidity before pulling. While these recommendations are not generally followed on mill-mixed stocks, it is most important that constant and preferably 0 per cent relative humidity be maintained when testing latex stocks.

In order to determine the reproducibility of results by this method (using 0 per cent humidity) the test was repeated three times, the compounding ingredients being identical in each case. A comparison was made with a mill-mixed pure gum stock of the following formula:

Smoked sheets	100
Sulfur	3
Zinc oxide	4
Mercaptobenzothiazole	1

This stock was tested by regular methods. A comparison of the consistency of results from the two types of stocks is shown in Table III. It will be seen that the percentage deviation from batch to batch in the latex stock is favorably comparable to that of the mill-mixed variety.

Summary and Conclusion

Adjustment of stabilizers may be necessary in order to produce a smooth surface on an air-dried latex test slab. A combination of 1 per cent of casein and 1 per cent of Aquarex D on the rubber gave a satisfactory dried slab.

Reproducible results cannot be obtained unless the test strips are conditioned at controlled relative humidity conditions. Zero per cent humidity gave highest tensile and modulus figures.

Batch-to-batch accuracy of latex stocks using methods described herein was comparable to that of mill-mixed pure gum stock.

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Effect of Temperature on the Consistency of Asphalts

The Viscosity-Temperature Susceptibility Coefficient as an Index

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Since the absolute measure of consistency is viscosity, the authors point out that the change of consistency of an asphalt with temperature would be more logically measured as the change of viscosity with temperature. The objections to the usual empirical susceptibility indexes are discussed and the requirements of a satisfactory index outlined.

The viscosity-temperature susceptibility coefficient is presented as a more fundamental viscosity-temperature index based on the A. S. T. M. viscosity-temperature formula and is mathematically represented as

$$S = 0.221 \frac{\text{Log} \left(\frac{\text{Log} (\mu_1 + 0.8)}{\text{Log} (\mu_2 + 0.8)} \right)}{\text{Log} \frac{T_2}{T_1}}$$

where S is the viscosity-temperature susceptibility coefficient and μ_1 and μ_2 are the kinematic viscosities at absolute temperatures T_1 and T_2 . Graphically S would be the slope of a straight line connecting the two points obtained by plotting the viscosities of an asphalt, as obtained at two temperatures, on the A. S. T. M. chart D-341-32T. Data presented indicate that the viscosity-temperature susceptibility coefficient is applicable to a wide range of temperatures and viscosities.

THE consistency characteristics of bitumens—i. e., softening points, floats, penetrations, etc.—have been of general interest. The rate of change of consistency with temperature has received particular attention and many noteworthy contributions have been made, such as the thorough reviews presented by Holmes, Collins, and Child (3) and Traxler and Schwyer (7).

An examination of the various susceptibility factors that have been proposed indicates that they are either empirical indexes based on measurements of certain properties, or, although on a more fundamental basis, are limited to only carefully defined temperature and viscosity ranges. The selected tests may be functions of more than the flow characteristic, in which case the interrelation between the tests at different temperatures will not entirely be dependent upon the flow characteristics; or the relationship, while involving only flow characteristics, may not disclose the constancy of the susceptibility under a practically convenient definition.

The indexes suggested by Holmes, Collins, and Child, based on results obtained on a pressure-still residuum and a Mexican asphalt, have satisfactorily eliminated the large and erratic variations found so objectionable in some "susceptibility factors." However, the results are relative and, as mentioned above, based on a combination of tests that may not measure the change of consistency with temperature under similar conditions. The results are given in units which do not characterize the material except relative to some other. The various indexes are not consistent and therefore cannot be conveniently used together. Finally, they are limited to asphaltic systems on which the penetration can be determined with reasonable accuracy—i. e., they are confined to asphalts in a limited consistency range. Hence such indexes are not entirely satisfactory when the analysis of viscosity-temperature phenomena is the only or primary purpose of their use.

Recognizing the logical tendency to measure consistency in absolute viscosity units (evidenced by recent publications, 5-7, as well as foreign specifications based on absolute viscosity units) the susceptibility of the consistency of asphalts to temperature change can also be logically evaluated by expressing the viscosity as a function of the temperature, thus placing viscosity-temperature characteristics on a more scientific basis. An index is required that evaluates the susceptibility in basic terms that have physical as well as mathematical significance independent of any variables except the rate of change of the viscosity with temperature.

The asphalt viscosity index (7) is one of this nature and in general meets all the requirements with the exception of the last—namely, it is not satisfactorily independent of the defining temperatures or as to the extent of the viscosity range.

Although the viscosity of asphalt will eventually be determined in absolute units at the usual room temperatures in the general asphalt laboratory, most of the present asphalt laboratories are not equipped either as to personnel or equipment to make such viscosity measurements. Hence some fundamental index of the viscosity-temperature characteristics that can be evaluated using the present equipment is necessary. However, the index should be such that, irrespective of the equipment used or the temperature range involved, it will have the same significance as long as the data can be expressed in terms of absolute viscosity units.

Viscosity-Temperature Susceptibility Coefficient

On the basis of the above requirements and conditions, the viscosity-temperature susceptibility coefficient (V. T. S.) first proposed by Nevitt (4) is presented as a possible index most satisfactorily meeting these requirements.

The viscosity-temperature susceptibility is based on the present A. S. T. M. chart and the equation (2)

$$\text{Log } A (\mu + 0.8) = KT^c \quad (1)$$

which has been accepted by the American Society for Testing Materials as the formula which most satisfactorily represents the viscosity of petroleum products as a function of

TABLE I. MIDCONTINENT ASPHALT TEST DATA AND CALCULATED VISCOSITY-TEMPERATURE INDEXES

Sample numbers	1	2	3	4	5	6	7	8	9	10
Saybolt Furol viscosity:										
98.89° C. (210° F.)	6683	2785	1858	1217	810	580	223	93	45.5
135° C. (275° F.)	597	365	270	199	143	109	50
148.89° C. (300° F.)	318
Saybolt Universal viscosity:										
98.89° C. (210° F.)	242
135° C. (275° F.)	251	140	92
Penetration:										
100-5-25	35	59	89	154	232
200-60-0.0	9	15	25	42	68	115
Softening point (ball and ring):										
° C.	58	51.4	46.4	43.0	36.2	32.3
° F.	136.3	124.5	115.5	109.5	97.1	90.1
Viscosity-temperature susceptibility, 98.89° to 135° C. (210° to 275° F.)	0.690	0.635	0.632	0.625	0.630	0.634	0.66	0.66	0.686	0.70
Fluidity factor	197	180	161	69	-206
Fluidity index (S)	100	96	98	104	107
Softening point-penetration index (S)	80	78	77	100	10-40
Asphalt viscosity index (S)	6.4	5.5	5.2	5.0	4.7	4.2	4.1	3.5	3.1	2.9

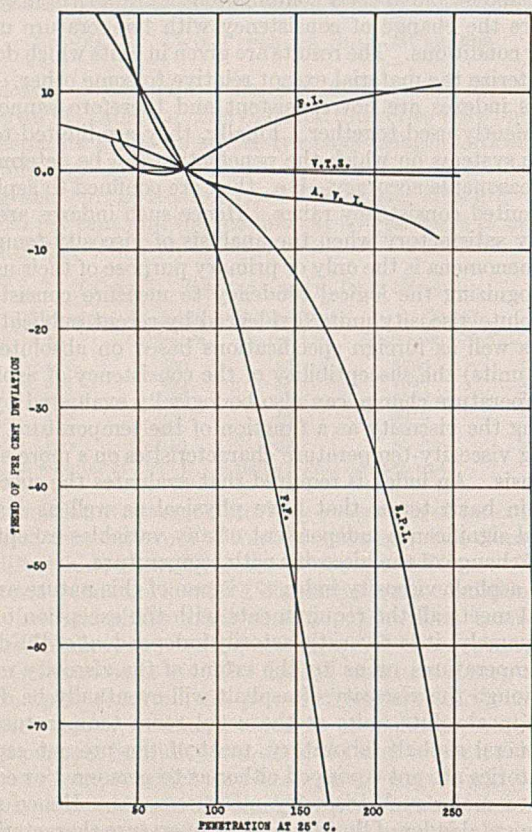


FIGURE 1. TREND OF DEVIATION OF VARIOUS VISCOSITY-TEMPERATURE INDEXES WITH CHANGE OF PENETRATION OF A MIDCONTINENT ASPHALT

temperature. Graphically the viscosity-temperature susceptibility can be defined as the slope of a straight line passing through the points obtained by a plot of two viscosities versus the corresponding two temperatures on the regular A. S. T. M. Tentative Standard D-341-32 T chart. Mathematically it may be defined as:

$$S = K \frac{\text{Log} \left(\frac{(\text{Log } \mu_1 + B)}{(\text{Log } \mu_2 + B)} \right)}{\text{Log} \frac{T_2}{T_1}} \quad (2)$$

where S is the viscosity-temperature susceptibility coefficient; μ_1 and μ_2 being the absolute viscosities at the absolute temperatures T_1 and T_2 ; K and B being constants. The accepted A. S. T. M. value for B is 0.8 and for the present A. S. T. M. chart $K = 0.221$. (Viscosities are expressed in centipoises, or in practical use with asphalts in centistokes.)

For the evaluation of the viscosity-temperature susceptibility coefficient it is necessary to have the absolute viscosities of the material at the two temperatures. The Saybolt instrument was used for the measurement of the necessary viscosities, and by applying the American Petroleum Institute viscosity conversion (1) the necessary kinematic viscosities were obtained. Saybolt viscosities at 98.89°, 135°, and 149.89° C. (210°, 275°, and 300° F.), with the aid of the three interchangeable (Universal, Furol, and road oil) tips, proved to be feasible for the usual range of viscosities encountered up to approximately 20 penetration asphalt. The data presented compare the viscosity-temperature susceptibility coefficient with the asphalt viscosity index (7), the fluidity factor [(Saybolt Furol viscosity at 275° F. - penetration at 77°) / 100 = fluidity factor], the

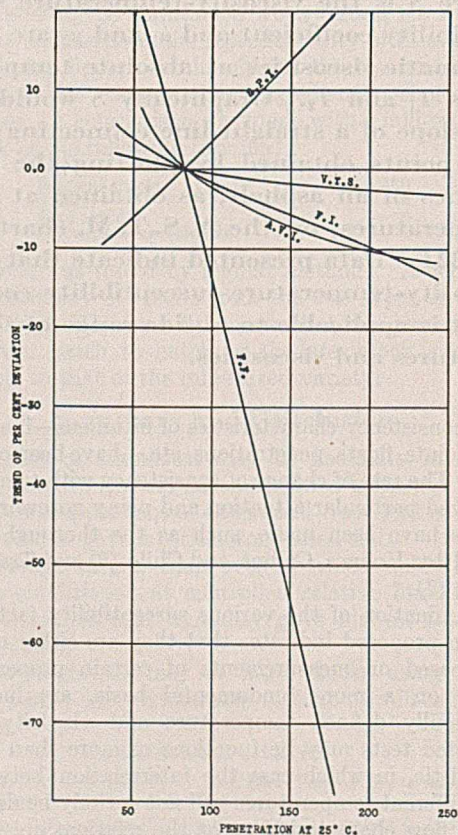


FIGURE 2. TREND OF DEVIATION OF VARIOUS VISCOSITY-TEMPERATURE INDEXES WITH CHANGE OF PENETRATION OF AN OXIDIZED ASPHALT

TABLE II. OXIDIZED ASPHALT TEST DATA AND CALCULATED VISCOSITY-TEMPERATURE INDEXES

Sample numbers	1	2	3	4
Saybolt Furol viscosity:				
98.89° C. (210° F.)	17900	5440	2210	1452
135° C. (275° F.)	945	422	214	165
Penetration, 100-5-25	47	91	185	225
Softening point (ball and ring):				
° C.	67.22	57.78	50.56	46.11
° F.	153.0	136.0	123.0	115.0
Viscosity-temperature susceptibility, 98.89° to 135° C. (210° to 275° F.)	0.780	0.767	0.769	0.753
Fluidity factor	422	301	53.7	-132
Fluidity index (β)	128	118	115	112
Softening point-penetration index (β)	140	157	191	200
Asphalt viscosity index (β)	7.8	6.8	6.3	5.9

fluidity index, and the softening point-penetration index. To ascertain the latter two, the charts developed for this purpose by Holmes, Collins, and Child (3) were used.

The susceptibility characteristics of three asphalts as a function of the penetration were investigated in this respect and the data are summarized in Tables I, II, and III. The trends of results are graphically shown as the per cent deviation of the various indexes from their respective values at

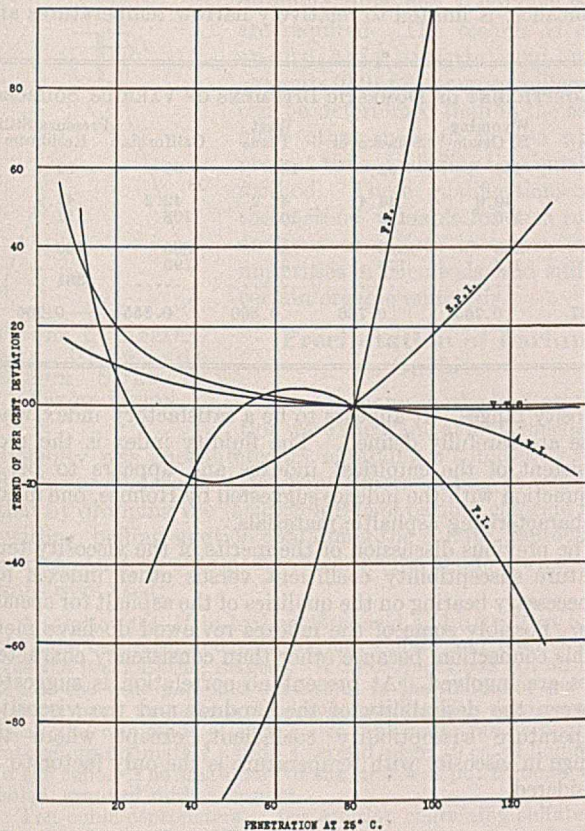


FIGURE 3. TREND OF DEVIATION OF VARIOUS VISCOSITY-TEMPERATURE INDEXES WITH CHANGE OF PENETRATION OF A PRESSURE-STILL RESIDUUM

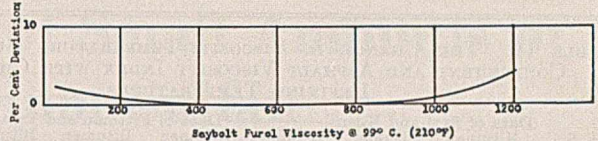


FIGURE 4. TREND OF DEVIATION OF VISCOSITY-TEMPERATURE SUSCEPTIBILITY COEFFICIENT WITH THE VISCOSITY OF A MIDCONTINENT ASPHALT

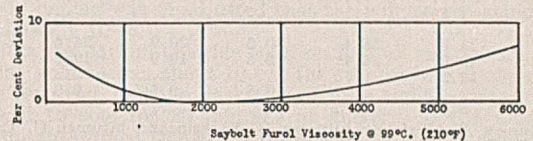


FIGURE 5. TREND OF DEVIATION OF VISCOSITY-TEMPERATURE SUSCEPTIBILITY COEFFICIENT WITH THE VISCOSITY OF A PRESSURE-STILL RESIDUUM

80 penetration, plotted against penetration, in Figures 1, 2, and 3, which represent results for a Midcontinent asphalt, an oxidized asphalt, and a pressure-still residuum, respectively. Eighty penetration was chosen as the reference point as it approximates the middle (2×10^8 centistokes) of the 25° C. viscosity range (approximately 2×10^7 to 2×10^9 centistokes) of the asphalts considered.

Figures 4 and 5 are similar plots of the midcontinent and pressure-still residuum, over an extended viscosity range varying from extremely hard asphalts to heavy road oils. This deviation is plotted using the Saybolt Furol viscosity at 98.89° C. (210° F.) of 80 penetration asphalt as the reference point.

Discussion

The results consistently show the fluidity factor (F. F.) to be erratic, and the softening point-penetration index (S. P. I.) comparatively erratic, while the fluidity index (F. I.) is much more consistent, but approaches constancy only over a relatively small range of consistencies. The asphalt viscosity index (A. V. I.) is constant, but only over a small range of consistencies. The viscosity-temperature susceptibility coefficient (V. T. S.), except for extremely hard asphalts, is satisfactorily independent of the consistency; it appears to offer a characterization index for asphalts, having a practically constant value for each source. Its increase at low penetration may be characteristic of the material at this viscosity (the order of magnitude is 10^{10} centipoises at 25° C.), or may be due to the failure of the basic A. S. T. M. equation to apply satisfactorily to such extremely viscous systems.

The viscosity-temperature susceptibility coefficient as defined is applicable to any two specified temperatures or viscosity range. Similarly the asphalt viscosity index can be calculated for any two temperatures. The effect of changing the definition temperatures and hence the viscosity merits some attention. If all asphalts plotted as a straight line on the A. S. T. M. viscosity-temperature chart, there would be no

TABLE III. PRESSURE-STILL RESIDUUM TEST DATA AND CALCULATED VISCOSITY-TEMPERATURE INDEXES

Sample numbers	1	2	3	4	5	6	7	8	9
Saybolt Furol viscosity:									
98.89° C. (210° F.)	4550	2360	1350	1023	704	472	418	294	246
135° C. (275° F.)	170	108	88	77	62	50	47	38	35
Penetration, 100-5-25	4	8	16	18	26	44	63	90	116
Softening point (ball and ring):									
° C.	61.11	60.0	55.0	54.44	53.33	48.89	45.56	43.33	41.67
° F.	142.0	140.0	131.0	130.0	128.0	120.0	114.0	110.0	107.0
Viscosity-temperature susceptibility, 98.89° to 135° C. (210° to 275° F.)	1.075	1.07	1.000	1.025	0.970	0.935	0.925	0.920	0.905
Fluidity factor	6.64	8.0	11.5	10.6	9.4	2.6	-10.0	-46.8	-94.0
Fluidity index (β)	10	12	16	14	10
Softening point-penetration index (β)	-60	-17	-12	-6	13	14	8	9	10
Asphalt viscosity index (β)	9.0	8.6	7.3	6.9	6.5	6.0	5.9	5.6	5.3

TABLE IV. THE CHANGE IN VISCOSITY-TEMPERATURE SUSCEPTIBILITY COEFFICIENT AND ASPHALT VISCOSITY INDEX WITH CHANGE OF DEFINING TEMPERATURES

V. T. S., ° C.	Data of Saal and Koens		Data of Pittman and Traxler ^a				
	Bitumen A	Bitumen B	Bitumen A	Bitumen B	Bitumen C	Bitumen D	Bitumen E
15-35	1.16	1.08	0.753	0.797	0.930	0.720	0.762
25-50	1.14	1.123	0.790	0.881	0.902	0.835	0.832
25-60	1.147
70-100	0.759	0.782	0.861	0.764	0.699 ^b
75-100	1.141
A. V. I.							
15-35	24.3	28.4	20.6	20.9	24.6	19.9	20.0
25-50	19.0	24.4	18.5	19.9	19.7	18.6	18.8
25-60	12.2
70-100	9.8	9.5	9.9	9.4	9.3
75-100	8.1

^a Bitumen A, Mexican; bitumen B, Venezuelan; bitumen C, Trinidad; bitumen D, Bermudez Lake; bitumen E, Trinidad Lake.

^b Calculated on the basis of the 70°-90° C. viscosities. Erratic viscosity at 100° C. possibly due to rapid settling of inherent mineral matter.

variation as the temperatures changed. Actually not all asphalts do give an exactly straight line. Typical values of the viscosity-temperature susceptibility coefficient and the asphalt viscosity index over various temperature ranges from the data of Saal and Koens (6) and Pittman and Traxler (5)

values for the usual straight-run asphalts vary from 0.73 for Midcontinent and Illinois asphalt to 0.85 for Californian asphalts. The pressure-still residuum, as would be anticipated, has a relatively high viscosity-temperature susceptibility coefficient as represented here by 0.966. However, as these products vary considerably, the coefficient of pressure-still residua will vary from 0.95 to 1.1. Although insufficient data are available, coal-tar pitches have a viscosity-temperature susceptibility coefficient of approximately 1.1 to 1.5.

Conclusions

In general the viscosity-temperature susceptibility coefficient appears best to meet the technical and practical requirements of fundamentally defining the viscosity-temperature characteristics for a wide range of consistencies and temperatures, which was not heretofore practical with the usual empirical consistency index. The asphalt viscosity index, although having fundamental significance, is limited to relatively narrow temperatures and

TABLE V. TEST DATA AND VISCOSITY-TEMPERATURE SUSCEPTIBILITY COEFFICIENT OF DOMESTIC BITUMENS OF VARIOUS SOURCES^a

	Midcontinent Oklahoma	Illinois	Wyoming B. Crude	Smackover	West Texas	Californian	Pressure Still Residuum
Penetration, 25° C. (77° F.), 100 grams 5 seconds	82	106	133	92	102	96	89
Softening point (ball and ring):							
° C.	45.6	46.1	40.6	44.4	42.2	42.2	43.9
° F.	114	115	105	112	108	108	111
Saybolt Furol viscosity:							
98.9° C. (210° F.)	1620	1670	890	1520	790	880	363
135° C. (275° F.)	188	191	112	179	95	90
Saybolt Universal viscosity, 135° C. (275° F.)	381
Viscosity-temperature susceptibility, 98.9° to 135° C. (210° to 275° F.)	0.732	0.737	0.765	0.766	0.800	0.855	0.966

^a From data collected at the Montana Highway Commission Laboratories.

are shown in Table IV. The data as presented indicate that the asphalt viscosity index is dependent on the defining temperature; hence in this respect, if it is used as an index for temperature susceptibility at any temperature other than those originally defined, the results rapidly lose significance, as large deviations occur between the normal room temperature-viscosity ranges and viscosity ranges in the neighborhood of 100° C.

The change in the viscosity-temperature susceptibility coefficient with change in determining temperatures is small in most instances as compared to the relatively large changes in the asphalt viscosity index. However, to eliminate all question along this line it is recommended that the viscosity-temperature susceptibility coefficient be determined from two standardized temperatures such as 98.9° and 135° C. (210° and 275° F.), since at present at these temperatures the generally accepted Saybolt instrument can be conveniently used. Possibly at a later date it will be found better to use other temperatures. However, this is a minor point and has no great practical importance in connection with either the use of the viscosity-temperature susceptibility coefficient or its relative merits as a temperature-susceptibility index as here discussed.

Table V represents the viscosity-temperature susceptibility coefficient of several domestic asphalts in order of their viscosity-temperature susceptibility, as determined between the temperatures of 98.9° C. (210° F.) and 135° C. (275° F.) using the commercially available Saybolt viscometer. The

viscosity ranges. It appears to be a satisfactory index when these are carefully defined. The fluidity index is the most consistent of the empirical indexes and appears to be, in conjunction with the indexes suggested by Holmes, one means of characterizing asphaltic materials.

The previous discussion of the merits of the viscosity-temperature susceptibility coefficient versus other indexes has no necessary bearing on the qualities of the asphalt for specific uses. Possibly some of the indexes reviewed do have merit in this connection, because other than consistency characteristics are involved. At present no correlation is suggested between the desirability of the product and the viscosity-temperature susceptibility coefficient, except where the change in viscosity with temperature is the only factor to be considered.

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Areametric Estimation of Small Amounts of Sulfate as Barium Sulfate

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RECENTLY a method was published for the estimation of small amounts of heavy precipitates by measuring the apparent area of the spot formed when the precipitate was gathered to the center of the flask bottom (2). The present authors have used a similar technic in the case of barium sulfate, and have succeeded in working out a method which for certain types of analyses not requiring great accuracy has several advantages over methods in use at present (3).

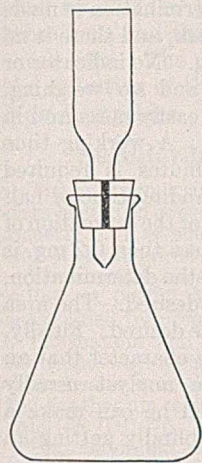


FIGURE 1. APPARATUS USED FOR BARIUM SULFATE PRECIPITATION

The apparatus is simpler than that used for any of the present comparable methods, including the centrifugal (1), since only a 50-cc. Erlenmeyer flask, a dropping tube, and a millimeter rule are required. The technic is correspondingly simple, and smaller amounts (0.01 to 4 or more milligrams) can be determined than in the case of most other methods in use at the present time, including the centrifugal method. These qualifications make the method valuable for such routine analyses as sulfate in water, sulfate impurities in chemicals, and sulfur in certain organic materials.

Precipitation of Barium Sulfate

A great many methods of precipitation were tried, and at first considerable difficulty was encountered in obtaining a sufficiently reproducible crystal size. After some experimenting, it was found that by dropping the (acid) solution of barium chloride into a swirling, boiling solution containing the sulfate, reproducible results could be obtained. Accordingly, the following directions were used:

A solution 0.1 *M* in hydrochloric acid and 0.01 *M* in barium chloride was saturated with barium sulfate and filtered. This was the precipitating reagent. A 25-cc. pipet was cut off at the top of the wide part and drawn out in the middle of the lower narrow part, to make a dropping funnel. The opening at the small end was made of such a size that water ran through at a rate of approximately a drop a second when 10 cc. of liquid were in the tube. The small part of the tube was put through a one-holed, grooved rubber stopper.

Ten cubic centimeters of the solution containing sulfate were put in a 50-cc. Pyrex Erlenmeyer flask. The solution had been made neutral by adding very dilute sodium hydroxide and hydrochloric acid until phenolphthalein just turned colorless. The stopper containing the dropping tube was put in the flask (Figure 1) and the whole was held by a test-tube holder and swirled over a small flame until boiling started. Then 10 cc. of barium chloride-hydrochloric acid solution were put in the dropping tube, and the flask was swirled and the contents were boiled while the barium chloride solution dropped in. The

rate of boiling was so adjusted that the volume remained at approximately 10 cc.

After the barium chloride solution had all run in and the resulting volume was about 10 cc., the stopper and dropping tube were removed, and the flask was at once tightly stoppered and allowed to cool for 30 minutes or longer. If the amount of precipitate formed was about 0.2 mg. or more, it could be measured after 30 minutes. For smaller amounts than this, the authors allowed the flask to stand overnight.

Measurement of Precipitates

The flask bottom was first cleaned and dried, and the flask was swirled twenty or thirty times, to bring most of the precipitate to the center of the flask. Then, after allowing a minute or two for settling, the flask was tipped, so that the edge of the liquid crept across the flask bottom nearly to the center, or to the edge of the spot of precipitate. This movement, to sweep the remaining precipitate to the center, was repeated about ten times to the left, ten times to the right, and ten times each backwards and forwards, although occasionally a precipitate adhered to the flask bottom so tightly that more tipping was necessary.

When the precipitate was essentially all in the center of the flask bottom, the flask was swirled gently. In this operation the bottom of the flask was kept against a piece of black, glazed paper, and the flask was moved in small circles. This caused the precipitate to form a cone with steeper sides than could normally exist when the flask was not in motion, so that when rotating was stopped (after fifteen or twenty circles) the precipitate flowed outward from the pile, automatically adjusting the height of the pile and producing sharp, smooth edges. Infrequently a precipitate of such character was obtained that this rotation produced a scattering, and then the earlier vibration technic had to be used (2). The average diameter of these spots was estimated to the nearest 0.1 mm. with a transparent millimeter rule against a white background. For the smaller spots a standard spot card, described earlier (2), was used, although this was not indispensable. The areas were rapidly obtained from the

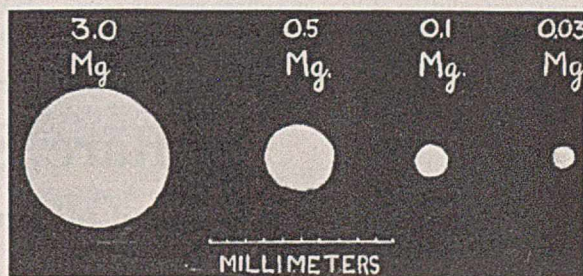


FIGURE 2. PHOTOGRAPHS OF BARIUM SULFATE SPOTS

TABLE I. REPRESENTATIVE RESULTS USING POTASSIUM SULFATE SOLUTIONS WITH AND WITHOUT IMPURITIES

Sulfate Present Mg.	Impurity Present	Sulfate Found Mg.	Sulfate Present Mg.	Impurity Present	Sulfate Found Mg.
0.01	None	0.01	0.30	1 gram MgCl ₂	0.31
0.03	None	0.04	0.50	1 gram MgCl ₂	0.45
0.08	None	0.08	0.01	1 gram KCl	0.03
0.10	None	0.11	0.50	1 gram KCl	0.53
0.30	None	0.27	2.0	1 gram KCl	1.9
0.50	None	0.45	2.0	1 gram CaCl ₂	2.3
0.70	None	0.72	0.03	1 gram NH ₄ Cl	0.05
1.0	None	0.9	0.08	1 gram NH ₄ Cl	0.06
2.0	None	1.9	0.10	1 gram NH ₄ Cl	0.14
3.0	None	3.0	0.70	1 gram NH ₄ Cl	0.59
4.0	None	4.0	3.0	1 gram NH ₄ Cl	2.9
0.30	1 gram NaCl	0.40			
0.70	1 gram NaCl	0.50			
2.0	1 gram NaCl	1.9			
3.0	1 gram NaCl	2.8			

diameters by a numerical table. The diameters themselves could have been used instead of the areas, but in view of the possibility of an occasional irregular spot the areas were considered more trustworthy. The areas so obtained were then compared to those produced by known amounts of barium sulfate, completing the analysis.

Examples of spots obtained are given in Figure 2, and representative results are given in Table I, including results obtained in the presence of large amounts of sodium, calcium, magnesium, potassium, and chloride ions. Average areas, corresponding to various weights of precipitates, are shown by the curve in Figure 3. However, for the best results, individual flasks should be calibrated with known amounts of barium sulfate, since with the swirling technic different flasks gave somewhat different areas for the same weight of barium sulfate, particularly with the larger amounts.

Discussion

Errors in the method are chiefly due to differences in crystal size and possibly in shape and not to errors in measurement, as good checks could be obtained on the latter for an indefinite number of times with any given sample. The authors believe that the point to watch most carefully in the entire procedure is the first addition of barium chloride solution, since this governs the number of crystal nuclei formed, which in turn governs the number and size of those eventually formed.

The solution was boiled down to the volume occupied by the (barium sulfate-saturated) barium chloride solution. In this way any solution of barium sulfate was overcome. Actually there was a small blank, about 0.005 mg., probably

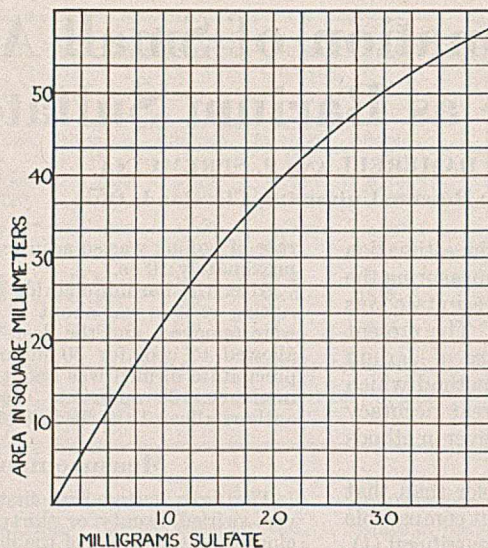


FIGURE 3. AVERAGE AREAS OF BARIUM SULFATE PRECIPITATES

due to the volatilization of a small amount of hydrochloric acid in the boiling, with resulting decreased solubility of the barium sulfate.

The flask was tightly stoppered at once after boiling the solution, because this seemed largely to eliminate the formation of precipitate on the surface of the liquid.

For very small amounts (0.1 to 0.01 mg.) it was not necessary to use such care in the addition of the barium chloride solution, because the main portion of the precipitate did not form until after the solution had cooled.

The method has several advantages besides requiring a very simple apparatus and technic. The determination is made in the precipitation flask, and there is no transferring or filtering. No indicator or titration is required, and no weighing. The spot size can be easily measured in a colored solution. A working time of only about 15 minutes is required

for a determination. This, added to a standing time of half an hour makes a total time of 45 minutes for the estimation of 0.2 mg. or more. The standing time for less than 0.2 mg. is longer. The precipitate is not destroyed in the determination, and may be used later in another way, if desired. The area of the spot can be checked as many times as desired. Finally, if an occasional precipitate forms of such a character that an inaccurate measurement will result, the analyst usually becomes aware of this in handling it, and he can make a correction or discard the sample without blindly getting an erroneous result.

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Rare Earth Salts

Precipitation and pH Studies with the Glass Electrode

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THE pH values at which some of the rare earth salts are precipitated from their solutions by alkalis have been investigated to some extent by Hildebrand (4) and Britton (2) with the use of the hydrogen electrode.

The present pH investigation was done by use of the glass electrode on solutions of the sulfates of lanthanum, cerous and ceric cerium, praseodymium, neodymium, ytterbium, and thorium, also the chlorides of neodymium and lanthanum.

Since most methods for the separation of cerium from the other rare earths depend upon the oxidation of the cerium to the ceric state and the ultimate precipitation of the element as a basic ceric salt (nitrate or sulfate), and since this salt is sparingly soluble even in a fairly strong acid solution, a method for separating cerium by simply controlling the pH suggested itself.

The changes in potential at the surface of the glass cell were measured by a vacuum-tube null-indicator used and described by the authors (6) in an investigation of the pH of normal and malignant tissues.

In this work the ordinary saturated calomel electrode was used as the reference electrode. A potassium chloride agar-agar bridge connected this electrode to the solution being measured. Any contact potentials developed were not a source of error, because the whole system was calibrated at constant temperature before and after a series of measurements with buffers of known pH values. The buffer solutions were those of Clark and Lubs (3) and were compared with the quinhydrone and two hydrogen electrodes. The two calibrations, even after a titration lasting 18 hours, were never found to vary by more than two or three hundredths of a pH unit and this difference was in the low and high pH regions.

The solutions were titrated in an air chamber whose temperature was $25^{\circ} \pm 0.3^{\circ} \text{C.}$, using a Beaver regulator in con-

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junction with a mercury-alcohol regulator. The heat was furnished by a nichrome resistance and was circulated throughout the bath by a small electric fan.

The volume of the titration vessel was approximately 125 ml. and the volume of the solution titrated was 50.00 ml. in all cases, with the exception of the thorium and ceric salts where 45.00 ml. were used. The solutions were titrated against sodium hydroxide and were stirred by tank nitrogen.

Sources of Salts Investigated

The cerium was procured from Oscar T. Coffelt of Jackson, Mich. The thorium was kindly furnished by H. C. Fogg of the University of New Hampshire. All the salts used were spectroscopically pure, with the exception of the neodymium sulfate which contained a few tenths of 1 per cent of praseodymium. The neodymium, titrated as chloride, was spectroscopically pure and was loaned by C. J. Rodden. The praseodymium and ytterbium sulfates were the identical samples used by Rodden (7) in his work on the paramagnetism of these ions, and the authors are very grateful for the loan of these salts. The remainder of the salts was procured from the collection of the late Charles James of the University of New Hampshire.

Standardization of Solutions at 25° C.

The anhydrous sulfates of lanthanum, cerium, and neodymium were heated to constant weight at a temperature of about 600° C. Exactly 0.01 *M* solutions were prepared at 25° C. by the addition of the required volume of carbon dioxide-free distilled water.

The thorium sulfate was prepared by dissolving the anhydrous sulfate in 0.0792 *N* sulfuric acid. The molarity was 0.00975, ascertained by precipitating as oxalate and igniting to oxide.

Lanthanum and neodymium chlorides were standardized in the same way as the thorium sulfate, but in this case the hydrated salts were dissolved in distilled water. The molarity of the lanthanum chloride was 0.01128, and of the neodymium chloride, 0.01076.

Praseodymium and ytterbium sulfates were weighed directly as their octohydrates. The molarity of the former was 0.01298 and of the latter, 0.01108.

The anhydrous ceric sulfate was dissolved in 0.1418 *N* sulfuric acid. Because this salt hydrolyzes in sulfuric acid of this concentration, the solution was standardized as soon as it was prepared and titrated immediately against a freshly prepared solution of Mohr's salt of exactly 0.01 *M* strength. The indicator was orthophenanthroline ferrous complex and the titrations were carried out in the manner of Walden, Hammett, and Chapman (8). The molarities of three different solutions were, respectively, 0.007828, 0.01119, and 0.01134.

The ceric ammonium sulfate was dissolved in 0.0792 *N* sulfuric acid and standardized in the same manner as the simple sulfate. The molarity was found to be 0.01048. Although this ceric salt was dissolved in a much less concentrated acid, the solution remained clear for nearly 2 weeks, whereas the anhydrous ceric sulfate solution remained clear for only 5 to 8 hours.

Titration of Salts

LANTHANUM SULFATE. This solution was titrated against 0.1029 *N* sodium hydroxide. After a few tenths of a milliliter of alkali had been added and until practically all of the cation had been removed from solution by further addition of alkali, an apparent equilibrium was attained within a minute or two. The titration curve shows that after about one-half the equivalents necessary for complete precipitation as hydroxide had been added, a further addition of alkali, after a few minutes, gave a potential that indicated that the solution had become more acid.

It is difficult to say just what precipitate was formed, but along with the formation of a basic salt, there is evidence of a reaction between the sodium sulfate (formed from the reaction of the alkali and the simple sulfate) and the simple sulfate. This appeared probable because the cerite members of the rare earths form sparingly soluble double sulfates with alkali sulfates. Furthermore, ytterbium gave no such break in its curve and ytterbium sulfate forms no insoluble double sulfates with alkali sulfates. If some double salt of lanthanum

was formed, it appeared to be stable for some time in a solution of pH about 8.5. The bulk of the precipitate was probably a basic salt which reacts with alkali even after all of the cation has been removed from solution. As the time required for the complete conversion of this basic salt appeared to be indefinite, to obtain the point where precipitation was complete, potential readings (toward the end of the titration) were taken soon after the addition of alkali.

In three titrations the first indications of a visible precipitate were at pH 7.59, 7.62, and 7.62, respectively. At these points 0.31, 0.30, and 0.31 ml., respectively, of alkali had been added; with the further addition of alkali the solution became increasingly turbid, and opaque after 5 ml. had been added.

LANTHANUM CHLORIDE. The titration of lanthanum chloride proved to be very different from the sulfate. At no time during the titration was a steady potential reached soon after the addition of alkali; even at the beginning about 15 to 60 minutes were required to lapse after each addition of the alkali. About 5 hours were taken for the first milliliter. The precipitate was not dense and opaque as was the sulfate, but gave to the solution a thin bluish opalescence until within about 2 ml. of the total volume necessary for complete precipitation. The precipitate did not coagulate until after the end point. This point of coagulation was definite, occurring on duplicates within 0.1 ml. of added precipitant.

Precipitation in the two titrations began at pH 8.04 and 8.02 upon the addition of 0.48 and 0.42 ml. of alkali, respectively. The titration curve shows that the pH changes were smaller, even after the addition of a large volume of alkali, than in the case of the sulfate, and that 2.76 equivalents of the necessary 3 were required for complete precipitation.

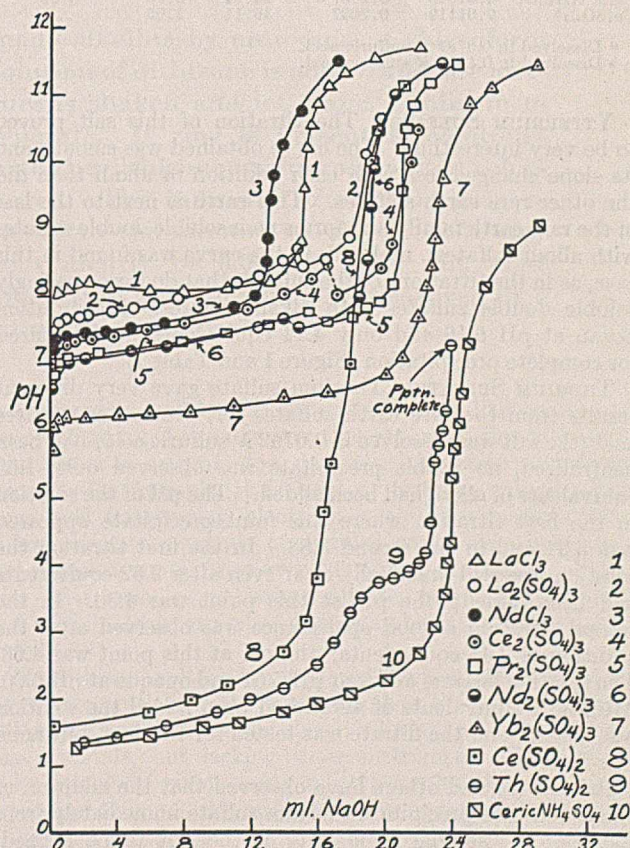


FIGURE 1. PRECIPITATION OF THORIUM AND RARE EARTHS

Curves 1 to 8, inclusive, represent 50 ml. of solution titrated against 0.1029 *N* sodium hydroxide. Curves 9 to 10, inclusive, represent 45 ml. of solution titrated against 0.2037 *N* sodium hydroxide. In curve 8 add 22.33 ml. to obtain the amount of alkali actually used.

CERIOUS SULFATE. The titration of this salt resulted in a curve very similar to that of lanthanum sulfate. Again, a steady potential was obtained within 2 minutes after each addition of alkali until the point for complete precipitation was approached. Precipitation began at pH 7.07 after the addition of 0.19 ml. of alkali.

NEODYMIUM SULFATE AND PRASEODYMIUM SULFATE. The titration of these salts resulted in curves similar to those of lanthanum and cerous sulfates. Neodymium precipitation began at pH 6.72 and praseodymium at pH 6.98.

NEODYMIUM CHLORIDE. A smooth curve was obtained in the titration of this salt, but the point at which precipitation began was difficult to ascertain, owing to the combined effect of the pink color of the solution and the colloidal nature of the precipitate—the curve indicates a pH of 7.1, but a visible precipitate was not observed until the solution had a pH of 7.4. From the curve complete precipitation resulted when 2.57 equivalents had been added. Britton (2) found 2.53 for the chloride at 17° C., with which this work is in fair agreement, but he observed the formation of a precipitate at pH 7.00.

TABLE I. PRECIPITATION OF RARE EARTHS
(Temperature 25° C.)

Soln. Titrated, 50 ml.	Molarity	NaOH Normality	Precipitation Began		Equivalent NaOH for Complete Precipitation
			ml. of NaOH	pH	
La ₂ (SO ₄) ₃	0.01000	0.1029	0.31	7.61	3.89
LaCl ₃	0.01128	0.1029	0.45	8.03	2.76
Ce ₂ (SO ₄) ₃	0.01000	0.1029	0.19	7.07	4.32
Nd ₂ (SO ₄) ₃	0.01000	0.1029	0.15	6.73	3.75
NdCl ₃	0.01076	0.1029	0.42	7.40	2.57
Pr ₂ (SO ₄) ₃	0.01298	0.1029	0.38	6.98	3.33
Yb ₂ (SO ₄) ₃	0.01108	0.1029	0.35	6.16	4.14
45 ml.					
Th(SO ₄) ₂ ^a	0.00975	0.2037	21.99	3.91	3.02
Ceric NH ₄ SO ₄ ^a	0.01048	0.2037	22.14	2.75	2.69
Ce(SO ₄) ₂ ^b	0.01119	0.2037	36.11	2.65	...

^a Dissolved in 0.0792 *N* sulfuric acid.

^b Dissolved in 0.1418 *N* sulfuric acid.

YTTERBIUM SULFATE. The titration of this salt proved to be very interesting. The curve obtained was smooth and its slope changed less with each addition of alkali than did the other rare earth sulfates. This earth is next to the last of the rare earth family and forms no insoluble double sulfates with alkali sulfates; no break in the curve was found in this case, as in the titrations of the sulfates that do form sparingly soluble double sulfates with alkali sulfates. Precipitation began at pH 6.16 and only 4.14 equivalents were required for complete precipitation (Figure 1 and Table I).

THORIUM SULFATE. Thorium sulfate gave very different results from the rare earth sulfates for, even after the free acid (the salt was dissolved in 0.0792 *N* sulfuric acid) had been neutralized, no visible precipitate was observed until 1.63 equivalents of alkali had been added. The pH of the solution in the first titration where this faint precipitate appeared was 3.94 and in the second 3.88. In the first titration the solution was still practically clear even after 2.32 equivalents had been added; the pH at this point was 4.30. In the second titration a good opalescence was observed after the addition of 2.48 equivalents; the pH at this point was 4.66. The solution became milky at pH 5.51 and opaque at pH 6.00. After 3.01 equivalents of alkali had been added the solution was filtered and the filtrate was tested for thorium, but none was found.

Britton (1) and others have observed that the addition of alkali does not precipitate thorium sulfate immediately from solution; a "soluble basic salt" is thought to be formed. Britton observed a precipitate at pH 3.53 at 15° C.

CERIC AMMONIUM SULFATE. This salt was dissolved in 0.0792 *N* sulfuric acid. The solution was a brownish yellow and remained clear for 2 weeks. Its molarity was 0.01048,

and as in the case of thorium, 45 ml. were titrated against 0.2037 *N* sodium hydroxide.

The cerium remained in the colloidal state at the beginning, for after the free acid had been neutralized no precipitation was observed in three titrations until 1.94, 1.96, and 2.12 equivalents of alkali had been added. The pH's of the above solutions, where precipitation began, were 2.71, 2.72, and 2.82, respectively. The average number of equivalents required for complete precipitation in these three titrations was 2.69. The average pH for complete precipitation was 4.50.

In the third titration the solution had a pH of 5.84 after the addition of 2.90 equivalents of the necessary 4 required for complete precipitation as pure ceric hydroxide. After filtering the solution the filtrate was tested for cerium, but none was found.

CERIC SULFATE. This salt was dissolved in 0.1418 *N* sulfuric acid, standardized, and used immediately. The molarities of the three ceric solutions used were, respectively, 0.007828, 0.01119, and 0.01134; they were titrated against 0.2037 *N* sodium hydroxide. Before titrating solutions 2 and 3, 10 ml. of 0.4550 *N* sodium hydroxide were added; a precipitate formed, but the solutions became clear again within a few minutes. The color of the original solution was a brownish yellow which changed to a pale greenish yellow after the addition of the 10 ml. of 0.4550 *N* sodium hydroxide. Solution 3 was allowed to stand for 1.5 hours after the addition of the concentrated alkali; it became opaque and its pH was 1.60.

Solutions 1 and 2 were titrated immediately and after the free acid had been neutralized a precipitate was observed when the solutions had a pH of 2.64 and 2.65, respectively. At these two pH's, 1.72 and 1.95 equivalents of alkali had been added. The precipitate in the second case apparently remained longer in the colloidal state. The average pH for complete precipitation was 4.64.

The pH at which ceric sulfate precipitates from solution was not as definite as in the case of ceric ammonium sulfate, for a noticeable precipitate occurred in stock solutions 1 and 2, 5 hours after their preparation and standardization. Very likely because of this, the titrations were less satisfactory than those of ceric ammonium sulfate.

Separation of Cerium from Lanthanum

In view of the results obtained with ceric sulfate, it was thought that by simply controlling the pH of a solution containing ceric cerium and other rare earths, a good separation of cerium could be realized.

To a solution containing 30 ml. of 0.01134 *M* ceric sulfate in 0.1418 *N* sulfuric acid and 30 ml. of 0.01 *M* lanthanum sulfate, sodium hydroxide solution was added until the resultant pH was 5.78. At this pH all of the ceric cerium should have been precipitated. (Lanthanum sulfate in preceding work was found not to precipitate until pH 7.62.) The same amount of standard sodium hydroxide used to obtain the desired pH was added to three samples identical with the above test solution. The precipitate formed was filtered and washed with distilled water. To the filtrate was added oxalic acid and the resultant precipitate was filtered, washed, and ignited in an electric muffle furnace to about 900° C. The results shown in Table II were obtained.

TABLE II. SEPARATION OF LANTHANUM

Sample	Lanthanum Present	Lanthanum Found
	Gram	Gram
1	0.0978	0.0971
2	0.0978	0.0971
3	0.0978	0.0976

The oxides from the ignition of the oxalates were dissolved in hydrochloric acid and tested for cerium by the delicate peroxide test. In all cases a very faint yellow color was observed, showing the presence of a very small amount of cerium.

Comparing the weights of lanthanum recovered with the weights of lanthanum present, the above separation may be considered satisfactory. The amount of cerium in the lanthanum precipitates as observed from the yellow color was minute, and its presence may be attributed to reduction of the ceric sulfate stock solution (5). Cerous sulfate was previously found not to precipitate until pH 7.07.

Summary

Titrimetric and pH studies with the glass electrode and vacuum-tube null-indicator of some rare earth salts and thorium sulfate at 25° C. have been made. The order of increasing basicity and likewise the order in which the salts studied precipitated were found to be as follows: ceric cerium, thorium, ytterbium, neodymium, praseodymium, cerous cerium, and lanthanum.

Precipitates formed during titration of the rare earth chlorides remained colloidal until a slight excess of sodium hydroxide (necessary for complete precipitation of the cation) had been added.

The rare earth sulfates precipitated from solution upon the

addition of sodium hydroxide at a lower pH than did the chlorides.

The work shows more clearly than ever the impracticability of separating the rare earths by fractional precipitation with hydroxides (except ceric cerium), as there is only a pH difference of 1.46 between lanthanum and ytterbium, which includes 14 of the 15 rare earth elements.

A method for separating cerium from lanthanum by simply controlling the pH of the solution is suggested.

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A Dithizone Method for Measurement of Small Amounts of Zinc

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The dithizone method is a means for very quickly measuring to 5 to 10 per cent the small amounts of zinc commonly present in animal, vegetable, and many other substances. Qualitatively it appears to be the quickest and most sensitive test for zinc ion now known. It is accurate enough for most purposes.

The zinc must first be brought into solution by suitable means. The solution is

made alkaline by ammonia, a chloroform solution of dithizone is added, and the mixture is shaken and let stand a minute to separate. If zinc is present it combines with the dithizone in chloroform and colors it red. The intensity of color is proportional to the amount of zinc, which may conveniently be 0.001 to 0.020 mg. The amount of zinc may be also measured by a titration procedure.

THE speed, convenience, high sensitivity, simplicity, cheapness, and ease of performance of the dithizone method for zinc are reasons for this presentation of this method, not yet entirely perfected although readily usable. The spectrograph or the polarigraph, both expensive and requiring experience for successful operation, are the only other means for detection and estimation of the small amounts of zinc for which the dithizone method is especially suitable. Recent recognition of the importance of zinc in plant, and perhaps also animal, nutrition has created a demand for a simple means for estimating the small amounts of this metal almost universally present in everything about us.

Dithizone, diphenylthiocarbazone, forms colored complexes with many metals, as shown by Fischer (10) and others. Chloroform or carbon tetrachloride dissolves these colored complexes out from an alkaline or sometimes acid aqueous solution, thus isolating the metal from other substances. The amount of the metal in the chloroform extract may be estimated by colorimetry or by titration. The dithizone method is conveniently applicable only to estimation of amounts of 0.001 to 0.100 mg. of zinc or other metal. In the technical literature 0.001 mg. is commonly expressed as

one gamma, γ , and is thus designated here. This method is very well adapted to show that the amount of zinc in watery solutions or in reagents does not exceed a certain very small amount—for example, it is used to test the culture solutions used for growing plants in a zinc-free medium. In a few minutes a sample of distilled water may be tested and found to contain not over 0.005 p. p. m. of zinc. Likewise salts such as potassium nitrate, magnesium sulfate, and calcium hydrogen phosphate may be easily and quickly tested.

The dithizone method is not offered as a complete substitute for or as equivalent to the spectrograph or the polarigraph for estimating small amounts of zinc in solutions containing other heavy metals, but lacking those instruments of precision it is capable of giving fairly reliable results at a minimum expense of time, money, and laboratory equipment. Though it may not be considered a precision method, it is doubtful whether much more precise results are obtainable by any other known method for estimating such small quantities of zinc.

The great advantages of the method are its speed, simplicity, and inexpensiveness. A disadvantage is that it is

not specific for zinc when several other metals are present. However, good methods of separation are available.

The chemistry of the dithizone metal complexes is discussed by Fischer (5, 8), White (16), and others. The details of procedure have been worked out by the writer, aided by suggestions from the work of Fischer (5, 8), Winter, Robinson, et al. (20), Winkler (19), Wilkins, Willoughby, et al. (17), Heller, Kuhla, and Machek (12), and others. The methods described in a previous paper (14) by the writer have a sensitivity about one-tenth that of the method here described.

A dithizone method described by Deckert (4) was not found satisfactory. So far as is known to the writer, no published dithizone method for estimation of these micro amounts of zinc is very good.

Preparation of Solutions of Analysis

Organic substances, vegetable or animal, in general may be burned, preferably below red heat, and the ash extracted with dilute hydrochloric or sulfuric acid. If the material is difficult to burn white, or has an easily fusible ash, addition of a little magnesium nitrate before burning is helpful. Combustion by wet methods with nitric or perchloric acids is likely to cause loss of zinc by volatilization; moreover, the oxidizing agent must be entirely removed (which may not be easy) before the dithizone test is applicable to the solution. Hydrogen peroxide may be used to remove small amounts of interfering organic matter, but the excess hydrogen peroxide must be entirely removed. In many cases a small amount of organic matter in the solution does not interfere seriously in applying the dithizone test for zinc. Solutions of water-soluble salts require no further preparation. If the solution contains Ca^{++} , Fe^{+++} , PO_4^{---} , or other ions which produce precipitates when the solution is made alkaline with ammonia, ammonium citrate should be added to prevent this precipitation. Solutions of alloys which cannot be prevented from precipitating when ammonia is added cannot well be tested directly by the dithizone method.

Precautions and Preliminary Tests

Since small amounts of zinc are present in nearly every material about us in everyday life, great care is necessary to avoid introducing it from some other source into the material to be tested. Most mineral salts contain zinc, sometimes as much as several parts per million. Organic reagents such as acetic or citric acids may have still more, while others are nearly zinc-free. Distilled water, as well as ordinary water as it comes from service pipes, contains some zinc. All kinds of rubber so far examined contain zinc. Everything used in the analytical operations of testing for zinc should be tested before it is used. A blank test should be frequently made on all materials used. It is ordinarily simpler to apply a correction for the amount of zinc found in the blank test than to try to obtain and use zinc-free reagents. The amount of this correction should be minimized by using reagents and apparatus as nearly as possible free of zinc.

Reagents

1. **DITHIZONE** (diphenylthiocarbazon). Fifteen milligrams in 100 cc. of chloroform. Other proportions optional. The usual (Eastman) commercial reagent is not always found satisfactory. It may be purified as described by Clifford and Wichmann (3), Wilkins et al. (17), or Winkler (19).

2. **CHLOROFORM**. Ordinary U. S. P. grade is found suitable. It should dissolve dithizone easily, and produce a dark green solution. When greatly diluted, the dithizone solution must still have the same green tint, not soon changing to yellow which would indicate presence of some oxidizing agent that makes it useless. Impure or used chloroform may be recovered by distillation. A small amount of sodium thiosulfate with very little sodium hydroxide dissolved in water is added to the flask containing the chloroform before distilling. No previous washing is necessary. For good purification it is again distilled with a

similar cover of water containing sodium thiosulfate. The water in the distillate is separated by freezing it out in a refrigerator.

Another method was proposed by Bidle (1), who washed the impure chloroform with sulfuric acid and distilled over lime.

3. **AMMONIA**, free of zinc. The usual strong reagent, specific gravity 0.9, is diluted with water, 1 to 4, or to other desired concentration.

4. **WATER**, free of zinc. Best obtained by distilling ordinary distilled water from a Pyrex apparatus fitted with an efficient spray trap. The distilling flask should be frequently cleaned out, so that there will be little accumulation of zinc or other metals in it. A less effective method for preparing zinc-free water consists in extracting zinc and other metals from it by shaking out with chloroform and dithizone repeatedly, until no more zinc is removed.

5. **AMMONIUM CITRATE**, free of zinc. A 10 per cent solution of citric acid is made alkaline with ammonia and repeatedly shaken out with dithizone and chloroform until no more zinc is extracted.

6. **HYDROCHLORIC ACID**, as nearly free of zinc as possible. This cannot be freed of zinc by distillation, as the zinc passes over with the acid at ordinary pressure. Nearly zinc-free acid may be prepared by slowly running ordinary c. p. hydrochloric acid into concentrated sulfuric acid, and absorbing the hydrochloric acid gas in pure water. No heat is required.

Apparatus

No unusual apparatus is needed. The most used are conical separatory funnels of 60-, 125-, and 500-cc. capacity with well-fitting stoppers and stopcocks, preferably of Pyrex glass. A glass containing zinc (Jena or other) is not permissible. No grease or lubricant other than water is used on stopcocks. All brass, copper, or zinc apparatus should be avoided. It is easy to introduce enough zinc from the fingers to ruin results after handling a brass stopcock. The small quantities (5 to 10 cc.) of chloroform constantly required are most conveniently delivered from a 200-cc. separatory funnel with a very short stem.

A supply of small (15 to 20 cc.) shell vials or sample tubes with flat clear bottoms is most convenient for containing the pink chloroform-dithizone-zinc extracts till the analyst is ready to make color readings on them. These tubes should be closed with good smooth corks, never with rubber stoppers.

For titrations of zinc dithizone solutions with bromine, glass-stoppered 60-cc. narrow-mouthed bottles are most convenient. Burets of 5-cc. capacity divided in 0.05 cc. are used for measuring the titrating solutions.

Extracting Zinc from Solution by Dithizone

Place the solution in a conical separatory funnel large enough to hold as much more as the volume of the solution and add dilute ammonia till alkaline. If a precipitate is produced, add hydrochloric acid till it dissolves, then 1 to 2 cc. of reagent 5, and again make the solution alkaline with ammonia. It must remain clear. Add several drops of reagent 1 and 5 cc. of chloroform, and shake somewhat vigorously for a few seconds. Let stand a minute to separate. In the absence of zinc or other heavy metal the chloroform remains green, and the water is brownish yellow from dithizone dissolved in the alkaline solution, except that if the solution contains much ammonium salts the excess dithizone produces very little color in it. If zinc is present the chloroform is colored some shade of red, the more zinc the redder. Add more dithizone, again shake the mixture, and repeat this treatment until the chloroform becomes purplish or bluish from excess dithizone and the watery layer is yellow from the excess dithizone except in presence of much ammonium salts. Other metals if present may modify the color of the chloroform. When it is judged that excess dithizone is present, draw off the chloroform layer into another separatory funnel, add more chloroform and dithizone to the watery mixture in the first separatory funnel, shake out again, and draw off the chloroform layer into the second separatory funnel. This second extract should be green, or only slightly reddish, indicating that practically all the zinc was obtained in the first extraction. In this process amounts of dithizone, chloroform, water, and ammonia may vary considerably without much effect on the final result, provided that excess of dithizone is used so that all zinc is extracted. The second separatory funnel contains the zinc-dithizone complex with an excess of dithizone, which is removed by shaking out two or three times with three times its volume of slightly ammoniacal

water, about 0.02 *N*. Very strong ammonia decomposes the red zinc complex and causes low results. Each time after the chloroform settles the watery layer is siphoned off, more water is added, and it is shaken again. Only 5 to 10 seconds of vigorous shaking is necessary each time to produce adequate washing. When the watery layer is colorless and the chloroform is some shade of red, washing is sufficient. If copper or some other metal that reacts other than zinc is present, the chloroform may have some other color than the bluish red of pure zinc alone. The chloroform is now drawn off into a suitable container for estimation of the zinc, as described below. The red complex of zinc dithizone is so nearly insoluble in the ammoniacal wash water that it is scarcely possible to detect any loss of zinc in the normal washing process, which is necessary to remove the excess dithizone so that the chloroform remains pink or red, not modified by uncombined dithizone. Excessive washing tends toward low results.

The effects of variations in washing and some other variations in treatment were as given in Table I. For each test 10 γ of zinc were taken, and usually about 10 cc. of chloroform were used. For each washing 20 to 30 cc. of 0.02 *N* ammonia were used, and the mixture was shaken vigorously about 5 seconds, then let stand a few minutes till the aqueous layer was nearly clear. This was siphoned off and the washing repeated.

TABLE I. EFFECTS OF VARIATIONS

	No. of Washings	Zinc Found
	3	10.0
	3	10.0
	6	10.0
	6	8.9
With large excess of dithizone	3	11.0
	6	10.8
Washed with water only	3	10.0
	3	10.0
With 7 cc. of chloroform	5	10.3
With 20 cc. of chloroform	5	7.7
With 20 cc. of chloroform	3	10.0

Measurement of Zinc in Chloroform Extract

The amount of zinc in the red chloroform-dithizone extract is proportional to the intensity of color for amounts of 0 to 10 γ of zinc. Much larger amounts of zinc are difficult to compare. Carbon tetrachloride acts like chloroform, except that the color is about one-fifth less in tetrachloride. The color may be measured by any of the usual colorimetric methods. However, this tint of red is difficult to compare. The standard cup may contain 10 γ of zinc, or for very small amounts of zinc 5 γ of zinc are better. A blue light filter in the eyepiece of the comparator produces a tint easier to compare.

Since the solutions of the unknown are frequently not clear and are sometimes off color for various reasons, it is often difficult to make an accurate measure of the amount of zinc by means of the usual comparator. A good approximation may be made by matching the unknown against known amounts prepared in the same manner, using smaller flat-bottomed tubes similar to Nessler tubes. Because the color fades and changes tint somewhat with time, it is necessary to prepare the standard comparison tubes, containing known amounts of zinc, anew every day or two. For ordinary use a set of tubes containing 1, 2, 4, 6, and 10 γ of zinc in 10 cc. is satisfactory. Rough estimates may be made by comparing with pieces of pink Cellophane which have been calibrated against known amounts of zinc. A number of dyes and colored solutions were tried as color standards. The only one found which closely matches the zinc-dithizone color and has any permanence in water solutions is Amaranth 107, of the National Aniline and Chemical Company, which does very well for amounts up to 5 γ of zinc in 10 cc. But no watery solution can match closely the appearance of the zinc-dithizone complex in chloroform because of the great difference in density and

refractive index of water and chloroform. No colored glass which nearly matches the color has been found.

Measurement by Titration with Bromine

Several oxidizing agents destroy the red color of zinc-dithizone in chloroform, probably by breaking some bond in the dithizone molecule. A solution of bromine in carbon tetrachloride of such strength that 1 cc. equals about 10 γ of zinc has been found very good for estimating amounts of zinc from 5 to 30 γ . The solution has a pale yellow color similar to that produced by 2 drops of methyl orange in 50 cc. of alkaline solution. It is prepared by dissolving bromine in carbon tetrachloride and determining its strength relative to zinc by titrating against known amounts of zinc which have been separated by dithizone as above described. This bromine solution is nearly equal in strength to 0.001 *N* thiosulfate. A solution of bromine in chloroform changes in strength so rapidly that it is not reliable after several hours; therefore carbon tetrachloride is used. The chloroform solution of dithizone and zinc to be titrated is placed in a 60-cc. glass-stoppered narrow-mouthed bottle, and the bromine solution is added slowly with frequent vigorous shaking of the bottle until the red color fades to colorless, or yellowish when much zinc is present. The end point is not distinct; therefore some excess of bromine is added, and after a minute about 1 cc. of 20 per cent potassium iodide in water followed by a little starch solution and 5 cc. of water containing 1 per cent sodium bicarbonate. The excess bromine liberates iodine which is titrated to colorless with 0.001 *N* thiosulfate. This method is applicable to amounts of zinc from 3 to 30 γ ; for smaller amounts the color comparison method is better.

Difficulties

Some of the difficulties likely to be met are lack of a more positive and exact means for measuring the minute amounts of zinc (this lack is common to other methods for measuring such small amounts); presence of lead, copper, or other metals, which if not removed may be estimated as zinc; formation of emulsions difficult to separate; presence of solids which tend to occlude zinc during the extraction process; formation of precipitates, which occlude zinc during the extraction process; and absorption of zinc by filter media.

EMULSIONS. Emulsions are likely to form during shaking of chloroform with watery solutions, especially if some organic matter or finely divided solid such as clay is present. The extraction and washing of the chloroform extract are carried out as usual until the excess dithizone is removed, and then the emulsion is run slowly through a tube closed at one end by a piece of bolting silk or other firm fine-meshed fabric. This breaks up the emulsion, which is then returned to the separatory funnel to separate the water from the chloroform. Formation of emulsions is minimized by avoiding violent shaking. In many cases the emulsion is most easily broken by addition of more chloroform, after removal of the separated water and gentle mixing, so that water and chloroform in the emulsion separate.

PRECIPITATES. Another difficulty which is likely to cause low results in estimation of zinc by the dithizone method is caused by any substance in the solution which produces a precipitate when the solution is made alkaline. The most common are Fe^{+++} , Ca^{++} , and PO_4^{---} . Addition of 1 to 2 cc. of a 10 per cent solution of ammonium citrate usually prevents formation of a precipitate and permits complete extraction of the zinc. Insoluble solid matter such as clay may be precipitated under the conditions of the dithizone test and carry with it some of the zinc. The only known remedy for this is removal of the solid matter by sedimentation or centrifuging before making the test.

ABSORPTION BY FILTER MEDIA. No sort of filter has been

found suitable for filtering out solid matter. Filter paper or pulp, absorbent cotton, asbestos, and apparently any kind of porous absorbent material take up small amounts of zinc from a solution passing through them. Subsequent extraction of the filter with dilute acid removes part of the zinc. If the same filter is used repeatedly, it may absorb zinc from one solution and permit some of the absorbed zinc to go into the next solution. When the solution contains only 1 to 2 γ of zinc, the whole of it may be retained, by the filter, so that no zinc is detectable in the filtrate. Since the acid used to extract the zinc from the filter is itself not free of zinc, a correction must be made for it, and since the correction may sometimes be larger than the zinc in the sample, the corrected result is of uncertain value. This difficulty is avoided by sedimentation or centrifuging instead of filtering out solid matter.

For means of avoiding difficulty due to oxidation of dithizone by F^{+++} by use of hydroxylamine, see Wilkins et al. (17).

In all cases where volumes of 200 cc. or more of water and considerable amounts of reagents which are not zinc-free must be used in a determination of a few gammas of zinc in a sample, the result found may be in error to the extent of 10 to 50 per cent. The only remedy for this difficulty is to use zinc-free reagents.

Interference by Other Metals

Some 15 to 20 metal ions are extracted from slightly alkaline water solutions by a chloroform solution of dithizone. The same reagents extracts several of them from more or less acid solutions, so that by appropriate regulation of pH and by addition of some other reagent it is possible to isolate most of them. Before undertaking such separations one should look over the papers by Fischer and collaborators (7, 8, 16). Fischer has described procedures for many separations.

The scheme for separations shown in Table II is based on Fischer's statements, with some suggestions from others. Great excess of one metal may hinder or prevent complete separations.

Mn, unless present in large amounts, is separated along with Fe^{+++} by the same treatment.

A satisfactory separation of Zn from Co and Ni by means of dithizone seems yet to be unknown.

Fe^{++} and Sn^{++} are rendered inactive by changing to the higher state of oxidation. Bi is separated from Cu by addition of tartaric acid.

For more precise description of separations see: for silver, Fischer et al. (11); mercury, Winkler (19) and Fischer (6); lead, Clifford and Wichmann (3); zinc, Fischer and Leopoldi (10); bismuth, Willoughby and associates (18); copper, Fischer and Leopoldi (9); by polarigraph, Heller, Kuhla, and Machek (12); separations in general, Fischer (8), and White (16). The dithizone method for lead has been thoroughly studied in a model way by Clifford and Wichmann (3). White (16) gives an informative article on "Dithizone as an Analytical Reagent" with a bibliography of about 40 references.

Zinc along with other metals extracted by the dithizone method may be estimated by means of the polarigraph of Heyrovsky (13) without separation of the other metals if they do not greatly exceed the zinc in amount. The procedure is described by Heller, Kuhla, and Machek (12). This is perhaps the neatest available method for estimating zinc in presence of lead, copper, and several other metals.

TABLE II. SCHEME FOR SEPARATIONS

pH of Aqueous Solution	Metal Ions Extracted by Dithizone in Chloroform
Less than 2	Nobel metals plus Hg
2 to 3	Cu, Bi, Sn^{++}
4 to 7	Zn, Cd, Pb, Tl, and all the above
7 to 10	All the above. Washing with 0.04 N ammonia removes Sn^{++} . Addition of KCN leaves only Pb, Tl, or Bi if not previously removed
Above 11	Cd remains, Zn is removed

Effect of pH on Partition of Zinc

Fischer (10) implies that zinc is completely extracted from an acetate solution at pH 4 by dithizone in carbon tetrachloride, thus making possible its separation from lead. The writer has not been able to verify this. Instead there is a partition of the zinc between the aqueous and the chloroform or carbon tetrachloride, the amount in each solution depending on the pH of the aqueous solution. Fischer used carbon tetrachloride which permits a better, though not complete, separation of lead and zinc than chloroform. With chloroform as solvent lead begins to be extracted at about pH 5 and is completely separated at pH 7. Portions of 10 gammas each of zinc in water were extracted by chloroform dithizone with following results: At pH 3, 0; pH 4, 1; pH 5, 4; pH 6, 7; pH 7 to 10, 10; pH 11, 2.5 γ . So it appears that zinc and lead overlap and are therefore not separable at any certain pH. A simple and exact method depending on the use of potassium thiocyanate has been worked out as follows:

Separation of Zinc from Lead

Make the solution alkaline with ammonia and extract with dithizone in chloroform as usual. After washing out the excess dithizone, add 2 cc. of a 5 per cent water solution of potassium thiocyanate, shake, and separate. The lead remains in the chloroform, which is washed with a little water and separated. Add the wash to the aqueous solution of potassium thiocyanate which now contains the zinc. Run this into a dish, acidify with hydrochloric acid, and evaporate to dryness on the steam bath to remove CN^- . Add to the dry residue 1 to 2 cc. of N hydrochloric acid and water enough to cover it all, and heat a few minutes. Cool and test the solution for zinc with dithizone as usual.

TABLE III. SEPARATION OF ZINC FROM LEAD

Amounts Taken		Found ^a
Pb	Zn	Zn
γ	γ	γ
50	0	3
10	2	1.4
10	10	9.8
50	0	3.1
10	2	2.6
10	10	9.6

^a The blank on reagents was so small that no correction for it was made.

Separation of Zinc and Copper

First, extract from the solution both zinc and copper by the usual dithizone procedure as if only zinc were present, and wash out most of the excess with 0.02 N ammonia as usual. This separation removes the zinc and copper from iron, calcium, and other substances which might later interfere.

Second, shake out the dithizone-chloroform solution of zinc and copper with about 5 cc. of 0.5 N hydrochloric acid. Draw off the chloroform layer into another separatory funnel. Wash the acid with a little chloroform and add this to the other chloroform solution. Shake this out with another 5 cc. of 0.5 N hydrochloric acid. Now draw off the chloroform layer, which contains the copper, and add the acid solution to the first acid extract. This solution contains the zinc, which may be separated by the usual dithizone procedure. The chloroform extract contains the copper with excess dithizone which may be removed by washing with 0.02 N ammonia. The copper in the purified extract may be estimated by the same methods used for zinc or by McFarlane's method (15).

This separation is not exact. A trace of zinc seems to remain with the copper and a little copper with the zinc. No means of making it more exact was found.

A less exact separation may be made in absence of iron, etc., by bringing the solution to pH 3, then adding 2 cc. of sodium acetate (25 per cent solution in water) of pH 3 and shaking out 3 or 4 times successively with dithizone in chloroform which removes the copper, leaving the zinc in the aqueous solution.

Corrections for blank in reagents were made on all these separations. More exact results could be obtained if purer reagents were available.

ACCURACY AND REPRODUCIBILITY OF RESULTS. The accuracy of results is of the same order as that of ordinary

TABLE IV. SEPARATION OF ZINC AND COPPER

Amount Taken		Found
Cu	Zn	Zn
γ	γ	γ
0	10	9.7
10	10	9.7
50	0	0
0	0	2.0
50	10	9.0
10	5	5.4
10	2	2.2
10	10	9.8

After correction
for blank
Blank on re-
agents

Plant ash extract = 1 gram of original material	15.2 15.8	}	Also contains about 10 γ of Cu
HCl extract of soil = 0.06 gram of original material	28 29 29 31	}	Contains much Fe, Al, Ca, etc., and about 40 γ of Cu
Same plus 10 γ of Zn, corrected for added Zn	24 26		

precision would be attainable by use of a suitable photoelectric color comparator.

The bromine titration method, not sensitive enough for less than 3 γ of zinc, usually is reproducible within 5 to 10 per cent on amounts of 5 to 20 γ of zinc.

Tables V and VI show the amounts of zinc found in some manures and soils and indicate something in regard to reproducibility of results. Certain discrepancies in the figures given are attributed to impurities in reagents, to faulty technic, and to the very small amounts of zinc extracted in many cases. Other results indicating the reliability of the methods are presented above.

Summary

A simple, convenient, quickly performed dithizone test for estimating amounts of zinc of 0.001 to 0.100 mg. is described. The method is not well adapted to measurement of amounts much greater than 0.1 mg.

Qualitatively the dithizone test for zinc is probably the most sensitive known. After isolation of the zinc by means of dithizone, the amount of zinc in the red-colored chloroform extract may be measured by color comparison or by titration with bromine. Means are discussed for overcoming several difficulties which may appear.

Many other metals besides zinc produce colored complexes with dithizone. By means of suitable solvents, the use of which is described, zinc is separated from other metals which are most likely to interfere in estimation of the zinc.

TABLE V. ZINC FOUND BY BROMINE TITRATION METHOD

	Zn Found, γ
1 gram of sheep manure, water extract	19.2 20.0 20.8
Same + 10 γ of zinc	28.0 - 10 = 18.0 30.4 - 10 = 20.4
1 gram of chicken manure, water extract	21.6
Same + 10 γ of zinc	31.2 - 10 = 21.2
1 gram of cow manure, water extract	16 16 16
Same + 10 γ of zinc	25 - 10 = 15 25 - 10 = 15

TABLE VI. ZINC EXTRACTED FROM SOILS BY VARIOUS REAGENTS

Soil No.	Water (1:5)	CO ₂ water (1:10)	HCl to pH 5 (1:10)	1 N HCl (1:2)	Total by Fusion ^a
<i>P. p. m. in air-dry soil</i>					
1	0.21	0.42	3.9	200	326
59	0.11	0.20 0.25	0.51 0.60	17	24
80	0.05	0.00	0.20	13	22
89 (con- tains CaCO ₃)	0.02	0.03	0.25	15	46
	0.01	0.00	0.06 0.12	6	
112	..	0.02 0.03	0.00 0.05	5	26
127	0.02	0.02	0.04 0.02	3	192
103	0.01	0.05	0.06	4	20
	0.05	0.03	0.07	6	

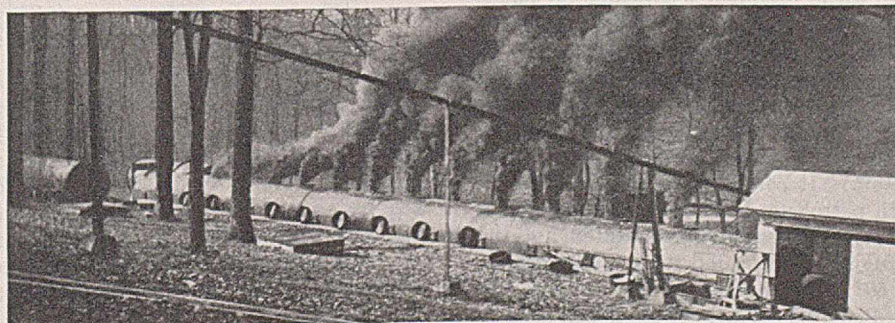
^a Total zinc found by the fusion method described by Boggs and Alben (2).

colorimetric work, 5 to 10 per cent, limited by the accuracy of the instruments used in making the comparisons. In absence of interfering substances, results are reproducible as nearly as can be estimated by the eye. It may be that greater

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Courtesy, U. S.
Bureau of Mines

IGNITION OF COAL DUST IN TEST

Refractometric Determination of Fat in Chocolate

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A rapid refractive method for determining total fat in chocolate has been devised. A refractometer of the Abbé or butyro type is used in conjunction with tricresyl phosphate, dibutyl phthalate, or diethyl phthalate as solvent. The method should prove especially useful to chocolate plants for control purposes. The results obtained check the official extraction method satisfactorily.

THE fat content of chocolate is an important factor in the cacao industry, and particularly in the manufacture of coatings has a great bearing on the properties of the chocolate. It became even more important with the introduction of vegetable lecithin in the chocolate industry. As is well known, a few tenths of a per cent of vegetable lecithin can thin down a chocolate coating to an extent equivalent to the addition of some 5 per cent of cocoa butter. The two prime factors in chocolate technology are therefore fat content and viscosity, which are standardized and controlled for each coating in all modern chocolate plants. The viscosity of the melted chocolate is rapidly ascertained by means of the MacMichael viscometer, but unfortunately no equally rapid and accurate method has been available for determining the fat content.

In the plant the fat content and viscosity must be determined while the batch is running, and adjustments made with the cocoa butter and lecithin to conform to established standards. It is clear, therefore, that a rapid method for fat is most essential in the chocolate industry. Viscosity (16), fat content, and lecithin content are so closely interrelated that a rational discussion of one must include the other two also (Table I).

TABLE I. INTERRELATIONSHIP OF FAT, LECITHIN, AND VISCOSITY

	Fat, %	MacMichael Viscosity
Heavy chocolate	33.80	1360
Same chocolate, with 4 per cent of cocoa butter	37.80	213
Same chocolate, with 0.25 per cent of lecithin	33.80	205

This investigation was undertaken to devise a rapid and safe refractometric method for the determination of fat in chocolate. A number of the newer solvents were investigated and finally tricresyl phosphate, dibutyl phthalate, and diethyl phthalate were chosen as most satisfactory.

The official method of the Association of Official Agricultural Chemists (2) for fat in cacao products is satisfactory, but is much too long for control purposes and requires extensive apparatus and skilled personnel for its proper execution. To get around these disadvantages some use a centrifugal method which in the hands of experienced operators has been found to yield good results. (This centrifugal method is used in a number of plants, but to the writer's knowledge it has never been published in detail.) It consists in mixing a weighed portion of sample with petroleum ether in a weighed centrifuge tube and centrifuging. The solvent is decanted, and the extraction and centrifuging are repeated twice. The residue is then dried at 40° to 50° C. for 30 minutes, and weighed, the loss in weight being calculated to fat. A good densimetric method was invented by Harris (8), involving the use of an adjusted proprietary solvent (largely *o*-dichlorobenzene) as

the extractant. The sample is extracted with the solvent and filtered, and the density of the filtrate is ascertained with a hydrometer which reads directly in percentage of fat. The refractive method described in this paper is faster and more accurate than either the centrifugal or the densimetric method referred to previously.

Chiefly on account of their speed and convenience, refractive methods are coming to the fore. We find them in use for the determination not only of fat, but of total solids in liquid eggs (1, 3) and even of hygroscopic moisture in seeds, using glycerol as the solvent (15). The author has developed a rapid refractometric method for the determination of sucrose, lactose, and dextrose in chocolate to be published later.

One of the earliest to do work in this field was Richter (13), who used a mixture of ethyl ether and ethyl alcohol as the solvent. Hasse and Bake (9) used a mixture of ethyl ether and ethyl acetate as the solvent. The chief disadvantages of these methods are the expense and volatility of the solvents used. Wesson (14) succeeded in partially overcoming the disadvantage of volatility by using as the solvent a technical grade of monochloronaphthalene commonly known as Halowax. But Halowax is far from a perfect solvent for this purpose. It has an obnoxious and persistent odor, and it irritates the skin. Operators who have to use Halowax continually complain that it acts somewhat as an asphyxiant. In spite of these disadvantages and its high price, it has found some use as a solvent for the refractometric (4, 5) determination of oil in oil-bearing materials.

Leithe (11, 12) has done considerable work on the refractometric analysis of cacao products. For the fat determination he uses a specially manufactured petroleum ether (b. p. 90-100° C.) as the solvent, and the immersion refractometer. For control purposes the use of so volatile and inflammable a solvent as petroleum ether and the immersion refractometer is considered impractical. A prolonged period of extraction will extract all the fat, but cacao beans and cocoa shells generally require some sort of heat treatment (10). A rapid refractometric fat test must therefore preferably involve heating with the solvent, and for this purpose the solvent must be practically involatile and non-inflammable. More recently Demkovskii (6) suggested the use of chlorobenzene as a refractometric extractant. This solvent is rejected on account of its volatility. At about the same time Ermakov (7) recommended the use of α -bromonaphthalene for the same purpose. But this solvent is the bromine homolog of Halowax and was condemned *a fortiori* for similar reasons.

Refraction of Solvents

A solvent suitable for this purpose should first of all have an index of refraction differing from that of cocoa butter to an extent consistent with accuracy—that is, it should differ sufficiently in index to allow duplicate tests to check one another within 0.1 per cent. Such a solvent should be as cheap as possible. In addition, it must be a good solvent for cocoa butter,

odorless, non-inflammable, and easily secured. Moreover, it must not affect the operator's health, and must have a very high boiling point and low viscosity. Different batches of solvent should not differ materi-

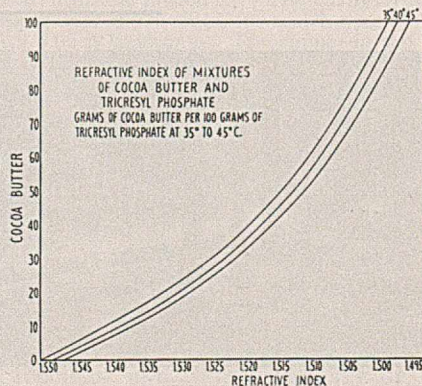


FIGURE 1

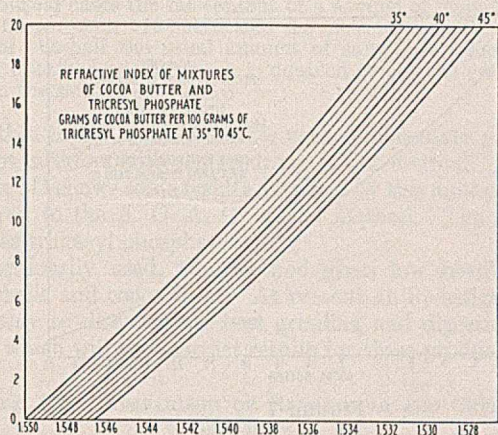


FIGURE 2

ally in index of refraction, so that a single graph can be used permanently. These specifications are met by tricresyl phosphate, diethyl phthalate, and dibutyl phthalate (furnished by the American-British Chemical Supply Co., Inc., 180 Madison Ave., New York, N. Y.). The tricresyl phosphate used was the C grade, which consists of a mixture of the meta and para isomers practically free from the ortho. As the meta and para isomers of tricresyl phosphate present in grade C have the same density and index of refraction, this mixture may be regarded as a single entity as far as this test is concerned.

The indices of refraction at 40° C. of the fats encountered in the chocolate industry are: cacao fat 1.4573; butter fat 1.4547; and coconut oil 1.4484. From these indices it is seen that the presence of butter fat in milk chocolates (which might run as high as 20 per cent of the total fat) does not influence the accuracy of the refractometric method. The presence of coconut oil would give high results. Very occasionally one may come across a sample containing coconut oil to which this refractive method is inapplicable, but for the general run of chocolates, and especially for control purposes, the probable presence of coconut oil need give us little concern.

The index of refraction and boiling point of the above solvents are as follows:

Solvent	Index of Refraction at 40° C.	Boiling Point, 760 Mm. ° C.
Tricresyl phosphate	1.5486	420
Dibutyl phthalate	1.4855	340
Diethyl phthalate	1.4948	295

It was considered advisable to work with the phthalates as well, since these can be used with the narrow-range butyrorefractometer. The dispersion of the ordinary butyrorefractometer is not corrected for the phthalates with the same exactness as it is for oils, but by using twice the sample as indicated in Figures 7 and 8 this difficulty can be reduced to a minimum. In the case of tricresyl phosphate an equal weight of sample and solvent is satisfactory, since not only can the dispersion be corrected by means of the Amici prisms, but the refraction of tricresyl phosphate is higher than either phthalate.

To facilitate the use of this method in the plant it was decided to do away with the analytical balance, by using a

large sample weighed on a rough balance sensitive to 0.05 gram. In addition the chocolate and solvent are warmed together and stirred, producing a perfectly homogeneous mixture. The tests were always carried out using at least 10 grams of chocolate and 10 grams of either phthalate. If the balance used is not of suitable accuracy, twice the above quantities can be used. Using the above weights of solvent, the loss due to warming can be neglected. For tricresyl phosphate a digestion temperature as high as 75° C. can be used, whereas for the phthalates the temperature should not exceed 50° C. In fact, it was found that the digestion with tricresyl phosphate can be left overnight in an oven at 100° C. without loss in weight exceeding a few milligrams, which is entirely negligible. As the digestion period used in the analysis is 10 to 15 minutes, no difficulty can arise from this point. The temperature used is also limited by the nature of the sample examined—for example, milk chocolates should not be heated beyond 40° C. but dark chocolates can be heated higher, say to 75° C. The reason for this is that milk chocolates tend to coagulate and subsequently filter slowly.

Graphs and Tables

In constructing the curves for tricresyl phosphate, known mixtures of cocoa butter and solvent were weighed out on the analytical balance, and refracted at 35° to 40° C., using a Valentine refractometer reading to five decimal places. For this purpose the Abbé refractometer can be used with equal accuracy, despite the fact that it reads to four decimal places only.

Table II was constructed using filtered pure prime pressed cocoa butter. The figures in the first column show grams of cocoa butter per 100 grams of tricresyl phosphate. The figures of Table II were plotted in Figure 1 on a small scale, and in Figures 2 to 4, inclusive, on a large scale, interpolating between 35° and 45° in degree intervals. (Large-sized graphs are available from the American Lecithin Co., Elmhurst, N. Y.) Thus in an actual analysis, if one uses an equal weight of solvent and chocolate, the percentage of fat can be read directly from Figures 2 to 4, inclusive, provided one has ascertained the index of refraction of the filtered mixture at any temperature between 35° and 45° C.

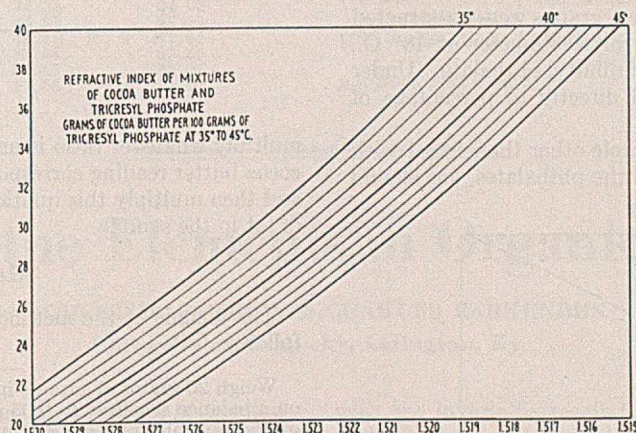


FIGURE 3

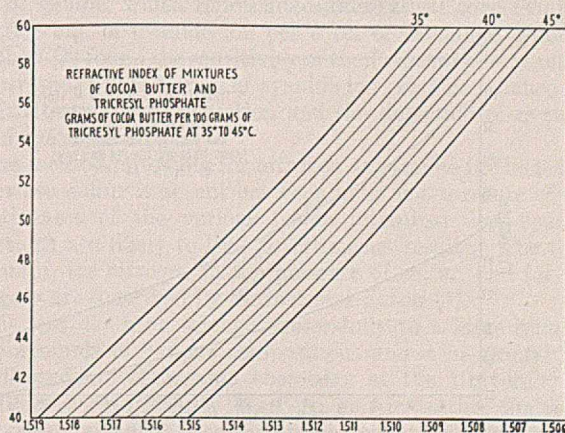


FIGURE 4

TABLE II. REFRACTIVE INDEX OF COCOA BUTTER AND TRICRESYL PHOSPHATE

(Concentration of cocoa butter is expressed as grams of fat per 10,000 grams of solvent.)

Cocoa Butter per 10 Grams of Solvent	Refraction		
	35° C.	40° C.	45° C.
0.000	1.55039	1.54841	1.54659
0.250	1.54772	1.54563	1.54380
0.500	1.54498	1.54283	1.54115
0.750	1.54243	1.54031	1.53823
1.000	1.53892	1.53774	1.53593
1.250	1.53765	1.53533	1.53343
1.500	1.53547	1.53336	1.53167
1.750	1.53348	1.53150	1.52940
2.000	1.53146	1.52950	1.52700
2.250	1.52943	1.52738	1.52548
2.500	1.52774	1.52560	1.52400
2.750	1.52613	1.52445	1.52213
3.000	1.52434	1.52223	1.52049
3.250	1.52283	1.52076	1.51900
3.500	1.52148	1.51953	1.51778
3.750	1.52026	1.51814	1.51649
4.000	1.51856	1.51695	1.51524
4.250	1.51740	1.51540	1.51380
4.500	1.51649	1.51444	1.51253
4.750	1.51515	1.51307	1.51130
5.000	1.51358	1.51177	1.50997
5.250	1.51261	1.51081	1.50921
5.500	1.51185	1.50960	1.50819
5.750	1.51049	1.50906	1.50723
6.000	1.50967	1.50775	1.50619
6.500	1.50825	1.50615	1.50448
7.500	1.50495	1.50309	1.50110
8.500	1.50196	1.50014	1.49828
9.500	1.49950	1.49772	1.49570
10.000	1.49804	1.49627	1.48450

The graphs with the phthalates were constructed in a similar manner, and are shown in Figures 5 and 6. The graphs for dibutyl phthalate actually used in an analysis are shown in Figures 7 and 8. These graphs were constructed from readings taken on the butyrefractometer at 48° C., using 2 parts of sample to 1 part of dibutyl phthalate. Under these conditions the graphs read directly in percentage of fat in sample.

In using ratios of solvent to sample other than 1 to 1 with tricresyl phosphate, or 1 to 2 with the phthalates, one should

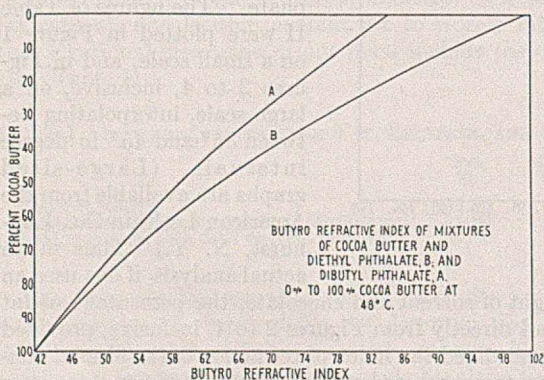


FIGURE 5

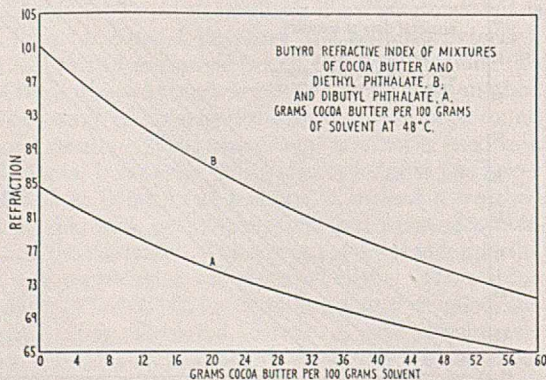


FIGURE 6

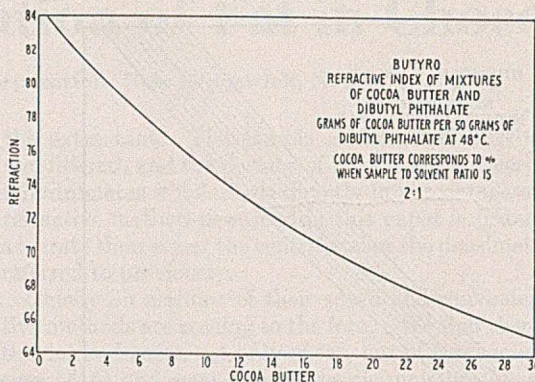


FIGURE 7

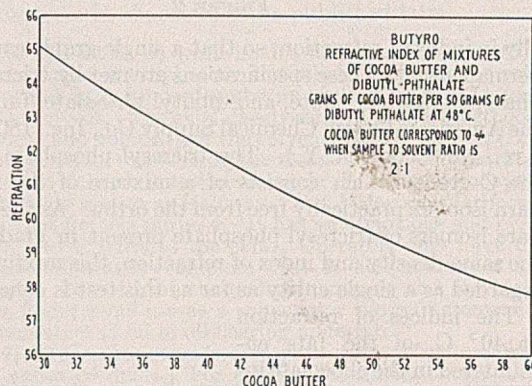


FIGURE 8

multiply whatever ratio is used by 100, divide this into the cocoa butter reading corresponding to the index of refraction, and then multiply this quotient by 100 to get the percentage of fat in the sample.

Method

The technic of the method using tricresyl phosphate is as follows:

Weigh 20 grams of sample in a 100-cc. low-form, lipped beaker on a balance sensitive to 0.05 gram, and then weigh in 20 grams of tricresyl phosphate. Set in a warm place until the chocolate has melted, stir thoroughly, then set again in the warm place for 10 minutes. The temperature can be as high as 75° C. but for milk chocolates it should not exceed 40° C. At the end of this time stir thoroughly and filter. The filtration is best accomplished without using a funnel, as follows: Open a 24-cm. fluted No. 1 Whatman or similar filter paper in a 100-cc. tall-form, unlippped Pyrex beaker so that the apex of the filter paper touches the bottom of the beaker. Pour the sample into the paper and set the beaker in the same warm place.

By using this technic one can obtain in a few minutes 5 to 10 cc. of filtrate, which are certainly enough for a determination of refractive index. Refract between 35° and 45° C., noting the exact temperature. Look up the percentage of fat in Figures 2 to 4, inclusive. By preference the author uses an Abbé refractometer whose temperature is controlled thermostatically at 40° C. In getting the zero point for the solvent, run a blank without, of course, using any sample, but going through the same heating period, filtration, etc. The difference between this blank reading and its supposed reading as obtained from Figure 2 constitutes the correction to be used in the analysis, and rarely exceeds a few units in the fourth decimal place. Its variation is due not only to slight differences in the composition of the solvent but to slight shifts in the zero point of the instrument itself.

If the reader is equipped with only a butyrefractometer, he must use dibutyl phthalate as the solvent. In this case he must add only one-half the weight of solvent, and warm the mixture of solvent and sample to a temperature not to exceed 50° C. for the digestion. He must also refract the filtrate at 48° C. in order to use the curves of Figures 7 and 8. Under the above conditions these curves read directly in percentage of fat in the samples.

In unusual cases the fat content of a sample of chocolate will exceed 60 per cent. In such cases the method can still be used, provided one-half the usual amount of sample is taken. The reading obtained on the graph is doubled to get the percentage of fat in the sample.

Lecithin in the small amounts used in chocolate products does not interfere with the accuracy of this method.

Table III shows some results obtained by this method when compared to the A. O. A. C. official method. The solvent used was tricresyl phosphate.

As ordinarily used, this method gives low results with cocoa shells and cocoa itself. At present an investigation is under way to discover the best grinding and digestion procedure which will give correct results for these products also.

TABLE III. COMPARISON OF REFRACTIVE AND OFFICIAL METHODS

Sample	(Using tricresyl phosphate as solvent)	
	Refractive Method %	Official A. O. A. C. Method %
Chocolate liquor	53.54	53.20
	50.22	50.02
	51.60	51.92
Dark chocolate	39.05	39.23
	41.15	40.82
	36.88	36.93
	40.00	39.89
	37.85	38.17
	38.40	38.37
Skim-milk chocolate	39.00	38.80
	38.80	38.83
	34.80	35.22
	35.21	35.02
Whole-milk chocolate	32.75	33.09
	34.28	34.08
	26.81	27.19
Light chocolate	31.37	31.64
	33.34	33.50
Eskimo pie coating	52.35	52.06
	51.85	51.59

Acknowledgment

The author wishes to thank the American-British Chemical Supply Company for its assistance and courtesy in furnishing samples of various solvents. In addition thanks are due John Ritchie, chief chemist, Loft, Inc., and Benjamin Zenlea, chief chemist, Walter Baker and Co., for their counsel and criticism of this method. Thanks are also due to William A. Cleary, vice president, and Joseph Eichberg, president of the American Lecithin Company, Inc., who inspired and directed this research to a successful conclusion.

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Detection of the Elements in Organic Compounds

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A PRELIMINARY detection of the elements is essential to the rapid identification of an organic compound and, although the sodium fusion method has been widely used, it is well known that nitrogen often escapes detection.

Graebe (4) attributes the frequent failure of the method to the easy formation of nitrogen gas, and Feist (2) adds that highly volatile compounds often escape detection. Although Kehrler (6) states that the detection is infallible if the vapors are repeatedly passed over the hot sodium, no practical method for carrying out this operation has been found. After this manuscript had been submitted to the editor there appeared an article by Miceli (8) which is essentially a simplification of Kehrler's method. Many special tests have been described, such as those of Zenghelis (10) and Högl (5), but most of them are impractical and applicable only to nitrogen.

Castellana (1) dropped the organic material into an ignited mixture of potassium carbonate and magnesium, but Flieringa (3) found that this procedure often assimilated enough nitrogen from the air to give a positive test; hence, the original objection of Graebe is overcome and it is merely necessary to remove the air from the tube. Flieringa accomplished this by incorporating hydrated sodium carbonate in the mixture, but the authors find that the sensitivity of the reaction is reduced. They created inert atmospheres by adding such solids as sodium acetate, naphthalene, and paraformaldehyde,

with the invariable result that the sensitivity was reduced, probably because of dilution of the vapors of the organic material. Ether is superior to these materials, for the reason that it is completely vaporized before it is necessary to heat the organic material. Back-diffusion of the air is prevented by means of the glass-wool plug, and increased sensitivity is assured by passing the vapors over the ignited mixture.

The test as described below is positive for as little as 0.46 mg. of aniline, which represents a theoretical concentration of 0.032 mg. of cyanide ion per 5 cc. of leachings, whereas Kolthoff (7) found the sensitivity of the Prussian blue reaction to correspond to 0.01 mg. of cyanide ion per 5 cc.; hence the sensitivities of the production and the detection of cyanide are of the same order.

The method of testing for nitrogen as cyanide in the leachings when sulfur is absent has been used as a measure of the effectiveness of the various fusion mixtures; less specific directions are likely to lead to erroneous results. The tests for sulfur, for nitrogen in the presence of sulfur, and for the halogens are described by Shriner and Fuson (9).

The test has been applied successfully to a large number of compounds of various compositions and is in general use by all students of organic chemistry at the University of Kentucky. No difficulty has been met in testing the nitro compounds, although according to Shriner and Fuson (9) they

often escape the sodium fusion. One compound—namely, diazobenzene sulfonic acid—failed to give the expected result because of the violence of the detonation. Many compounds containing no nitrogen have been tested and in no case has a nitrogen test been obtained.

Procedure

The fusion mixture is prepared by grinding to a fine powder two parts of anhydrous potassium carbonate and one part of magnesium powder. It retains its usefulness over a long period and may be easily dispensed from the bottle by means of a spoon shaped to contain approximately 0.2 gram of the mixture.

FILLING THE TUBE. Place 2 drops of liquid or the equivalent weight of solid in the bottom of a 75-mm. soft-glass test tube, being careful that the liquid has not wet the sides of the tube. Then, holding the tube at an angle about 30° from the horizontal, allow to slide down it, to within about 1 cm. of the substance, about 0.2 gram of the magnesium-potassium carbonate mixture. This should extend about 3 cm. up the tube. Allow 2 drops of ether to run down onto the mixture, and plug the mouth of the tube tightly with glass wool.

THE IGNITION. Holding the tube at the same angle with forceps, heat in the hottest portion of the Bunsen flame, beginning directly under the mixture and nearest the mouth of the tube. When the mass begins to glow, bring the lower end of the tube into the flame so as to distill the substance over the glowing mass. Continue the heating so as to keep the mass glowing and the substance distilling, finally turning the burner up and heating the full length of the tube to dull redness. Then carefully drop it into a 15-cm. (6-inch) test tube containing 20 cc. of water, shake vigorously to break up the ignition tube, filter, and use the filtrate for the various tests.

The compound to be tested must not be heated until the reac-

tion between the carbonate and the magnesium has started. Failures by those unfamiliar with the test have been traced to the omission of this precaution.

TEST FOR NITROGEN IN THE ABSENCE OF SULFUR. To 5 cc. of the filtrate add 5 drops each of 10 per cent sodium hydroxide, 4 per cent ferrous ammonium sulfate, and 20 per cent potassium fluoride. Allow the tube to stand in boiling water for 3 minutes, then cool by shaking in cold water. Add a drop of 5 per cent ferric chloride and acidify by the addition of 6 *N* sulfuric acid until the precipitated hydroxides just dissolve. The appearance of the blue coloration is indicative of the presence of nitrogen.

Conclusions

The magnesium-potassium carbonate method of fusion of organic compounds has been studied and found to be superior to the older sodium fusion. The test materials are more easily prepared, preserved, and handled than is metallic sodium. The method of fusion is equally as rapid, more reliable, and less dangerous than the sodium fusion.

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RECEIVED October 23, 1936. Contribution from the Chemical Laboratory of the University of Kentucky.

Determination of Potassium

By Means of an Aqueous Solution of Trisodium Cobaltinitrite in the Presence of Nitric Acid

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An aqueous solution of trisodium cobaltinitrite replaces the familiar two-solution reagent. Nitric acid, rather than acetic acid, is used as the acidifying agent to maintain the nitrate-nitrite equilibrium and thereby prevent nitrite decomposition. The resulting precipitate is granular, heavy, and easily filtered and washed. The gravimetric and volumetric procedures for the determination of potassium by this new method are described. The normality of the oxidizing solution bears a stoichiometric relation to the potassium of the precipitate and the equation for the reaction is shown. The absolute accuracy as well as the reproducibility appears to be within ± 0.05 mg. expressed as potassium.

THE cobaltinitrite reaction has been studied by a large number of workers and its application to the quantitative determination of potassium forms the subject matter of an already voluminous literature. Almost without exception, the two-solution reagent of Adie and Wood (1) has been used, resulting in an extremely fine precipitate, difficult to filter, of variable composition, and bearing no evident stoichiometric relation to a volumetric solution used in its estimation. As a result of a theoretical consideration of this reaction, another reagent is suggested which overcomes the difficulties mentioned above.

In the method here described, use is made of an aqueous solution of trisodium cobaltinitrite as the precipitating reagent and the reaction is carried out in the presence of nitric acid. Trisodium cobaltinitrite has been used extensively as a qualitative reagent for potassium, but its use with nitric acid in the quantitative determination of potassium is thought to be an innovation. The following advantages result: (1) The precipitate is crystalline and heavy, comparing favorably with barium sulfate in ease of filtering and washing; (2) the composition appears to be constant and practically

independent of the Na^+ concentration; (3) the determination can be completed either gravimetrically by drying and weighing the precipitate or volumetrically by titration with potassium permanganate in acid solution.

TABLE I. GRAVIMETRIC AND VOLUMETRIC DETERMINATION OF POTASSIUM AS DIPOTASSIUM SODIUM COBALTNITRITE

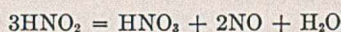
Potassium Present	Gravimetric		Volumetric	
	Weight of precipitate	Potassium found	KMnO_4 0.0514 N	Potassium found
Mg.	Mg.	Mg.	Cc.	Mg.
2.00	11.5	1.98	5.46	1.99
2.00	11.5	1.98	5.41	1.97
3.00	17.4	3.00	8.28	3.02
3.00	17.5	3.01	8.36	3.05
4.00	22.7	3.91	10.88	3.97
4.00	23.0	3.96	10.96	4.00
5.00	29.0	4.99	13.68	4.99
5.00	29.1	5.01	13.66	4.99
10.0	58.4	10.0	27.14	9.91
10.0	58.2	10.0	27.22	9.94

^a Standardized by means of sodium oxalate. 1 cc. = 0.365 mg. of potassium.

While the author has not attempted to include a bibliography, the number of papers published currently evidences a keen interest in, and a need for, a more satisfactory method for potassium in small quantities, especially in waters, soil extracts, and plant materials.

It is the experience of the writer that the cobaltinitrite method, as usually applied, gives high results, which appear to be due to the occlusion of material from the precipitating medium. The Adie and Wood reagent obtained by mixing a solution of cobaltous acetate in acetic acid with a solution of sodium nitrite may contain, in addition to the trisodium cobaltinitrite, cobaltous acetate, sodium acetate, sodium nitrite, and acetic acid, and approaches saturation with the oxides of nitrogen. Obviously, a reagent containing less extraneous material would be desirable. Trials were made with an aqueous solution of trisodium cobaltinitrite, the sample being acidified in this case with acetic acid. The results were more nearly quantitative but still slightly high. There was also some decomposition of the reagent during precipitation, as evidenced by the evolution of gas.

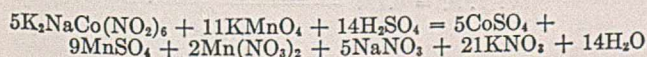
Nitrous acid or nitrites in acid solution are unstable and the decomposition can be represented by the equation:



The equilibrium constant for this reaction is given by Latimer and Hildebrand (2) as $K=30$, which indicates that it might be rather easily reversed, or, stated in another way, the addition of nitric acid should retard the decomposition of nitrite. Accordingly, nitric acid was substituted for acetic acid. The results were so satisfactory that these reagents were made the basis for the quantitative methods herein described.

It has been the practice, in the volumetric determination of potassium, to use an arbitrary factor for the oxidizing solution. In the procedure developed by the writer, this is not necessary; in fact, a stoichiometric relation exists between the potassium in the precipitate and the normality of the potassium permanganate solution. It is suggested that the permanganate be standardized by the use of pure sodium oxalate and the value in terms of potassium be calculated on the basis of the oxidation-reduction reaction given below.

The volumetric determination depends upon the oxidation of the nitrite of the precipitate with permanganate in acid solution. It has not been emphasized that the cobalt, present as Co^{+++} , under these conditions is a strong oxidizing agent equal to potassium permanganate and that it therefore oxidizes an equivalent amount of nitrite. The reaction can be represented by the following equation:



Here, 30NO_2 or 60 reducing equivalents are balanced by 11KMnO_4 or 55 oxidizing equivalents plus 5 oxidizing equivalents from the cobaltic-cobaltous couple.

Therefore, 11KMnO_4 or 55 equivalents are required for 10K or:

$$\frac{10\text{K}}{55} = \frac{390.96}{55} = 7.1084 \text{ grams of K per equivalent of } \text{KMnO}_4$$

Then, cc. of $\text{KMnO}_4 \times$ normality of $\text{KMnO}_4 \times 7.1084 =$ milligrams of K in the sample titrated.

Gravimetric Determination of Potassium

REAGENTS. Trisodium cobaltinitrite solution. Prepare an aqueous solution containing 1 gram of the salt of reagent quality in each 5 cc., allowing 5 cc. for each determination. Filter before use. The solution is stable for some time, but the writer prefers to make up a fresh lot before each set of determinations. Nitric acid, approximately normal and 0.01 N. Ethyl alcohol, 95 per cent.

PROCEDURE. The aliquot for analysis should contain between 2 and 15 mg. of potassium in a neutral aqueous solution of 10-cc. volume. Add 1 cc. of 1 N nitric acid and 5 cc. of the sodium cobaltinitrite solution, mix, and allow to stand for 2 hours. Filter in a porous-bottomed porcelain filtering crucible, the tare weight of which is known, using 0.01 N nitric acid in a wash bottle to make the transfer. Wash 10 times with 2-cc. portions of the dilute nitric acid and 5 times with 2-cc. portions of alcohol. Evacuate until quite dry. Wipe the outside with a cloth, dry for 1 hour at 110°C ., cool in a desiccator, and weigh.

The composition of the precipitate can be represented by the formula $\text{K}_2\text{NaCo}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$. K = 17.216 per cent.

Volumetric Determination of Potassium

REAGENTS. In addition to the reagents listed under the gravimetric procedure, except 95 per cent ethyl alcohol, the following will be required: sodium hydroxide, approximately 0.5 N, sulfuric acid, concentrated; potassium permanganate solution, standard 0.05 N; sodium oxalate solution, standard 0.05 N.

PROCEDURE. Follow the gravimetric procedure through the precipitation and washing with nitric acid. Omit washing with alcohol. Wash the precipitate into a 250-cc. beaker, place the crucible in the beaker, and make to about 100 cc. with water. Add 20 cc. of 0.5 N sodium hydroxide and boil for 3 minutes. Withdraw into another beaker a slight excess of standard potassium permanganate, make to 50 cc. with water, and add 5 cc. of concentrated sulfuric acid. Pour the hot potassium cobaltinitrite solution into the cold potassium permanganate solution, transfer the crucible, and wash the beaker with a small amount of water. Add an excess of standard sodium oxalate solution, heat to boiling, and complete the titration with potassium permanganate.

Cc. of $\text{KMnO}_4 \times$ normality of $\text{KMnO}_4 \times 7.1084 =$ milligrams of K in sample titrated.

Table II shows the effect of a number of cations. The volume in each case was 10 cc., so that the concentration of Na^+ in sample 2 is approximately 1 N, in addition to the Na^+ of the reagent. Ca^{++} and Mg^{++} in concentrations to 0.2 N appear to have little effect (samples 4 and 7) and likewise 0.1 N Ba^{++} (sample 9). The high result shown as

TABLE II. EFFECT OF VARIOUS CATIONS ON THE GRAVIMETRIC DETERMINATION OF POTASSIUM

(In each case, 5.00 mg. of potassium were present.)

Sample	Salt Added Formula	Weight of Potassium Precipitate Found		
		Mg.	Mg.	Mg.
1	NaNO_2	340	29.0	4.99
2	NaNO_2	850	29.3	5.04
3	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	118	28.9	4.98
4	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	236	28.8	4.96
5	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	472	27.9	4.80
6	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	128	28.7	4.94
7	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	256	29.0	4.99
8	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	512	28.4	4.89
9	$\text{Ba}(\text{NO}_3)_2$	130	28.8	4.96
10	$\text{Ba}(\text{NO}_3)_2$	325	38.4	6.61
11	NH_4NO_2	2	30.2	5.20
12	NH_4NO_2	5	32.5	5.60

TABLE III. GRAVIMETRIC DETERMINATION OF POTASSIUM IN PLANT MATERIAL

Sample	1		2	
Alfalfa sample, grams	1.1403		0.9987	
Potassium chloride added, grams	0		0.0961	
Potassium found, entire sample, mg.	52.0	52.0	96.2	96.4
Potassium referred to 1 gram of sample, mg.	45.6	45.6	96.3	96.5
Potassium added to 1 gram of sample 2, mg.	50.4	50.4
Theoretical weight of potassium sample 2 (1-gram basis), mg.	(45.6 + 50.4)		96.0	96.0
Total potassium found in 1 gram of sample 2, mg.	96.3	96.5
Recovery of total potassium, per cent	100.3	100.5

sample 10 resulted from the use of 325 mg. of barium nitrate or approximately 0.25 *N* Ba ammonium must be absent.

Silica in small amounts, as silicate, causes no difficulty, but the hazard that it will separate as silica gel when acidified warrants its removal. Sulfate and chloride in large amounts tend towards low results, the error being in the order of 1 to 2 per cent. Acetate will produce correspondingly high results.

The volume of 1 *N* nitric acid used can vary from 0.5 to 5 cc. without measurable effect. The temperature of the solution during precipitation should be about 20° C. Lower temperatures give high values—e. g., 10° C. gave a positive error of 2 per cent while at 25° to 30° C. the result was low or the error was -2 per cent. The time allowed for precipitation was chosen arbitrarily. At the end of 1 hour, the results

are slightly low, while at 7 hours they average about 2 per cent high. The temperature at which the precipitate is dried may vary from 80° to 120° C.

Table III presents the results of an analysis of plant material for potassium by the gravimetric procedure. In this case the potassium was separated directly from an acid solution of the plant ash. The sample analyzed was the above-ground portion of alfalfa grown in sand culture with a nutrient solution. Duplicate samples were weighed into platinum dishes. To sample 2 a known amount of potassium chloride was added. The samples were dried and ignited in the presence of sulfuric acid. The white ash was digested with water containing 2 cc. of 1 *N* nitric acid, filtered, and made to 100 cc. Duplicate 10-cc. aliquots were taken for analysis.

Consideration of the tables here presented and experience with the method over a period of approximately 1 year seem to justify the statement that the reproducibility and absolute accuracy fall within the limits of ±0.05 mg. of potassium.

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RECEIVED September 28, 1936.

Physical Properties of Asphalt

Viscosity-Temperature Susceptibility

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PREVIOUS papers, such as those of Holmes, Collins, and Child (2), Traxler and Schweyer (5), and Nevitt and Krehma (4), have discussed indexes for the rates of change of viscosity of asphalts with temperature, but very few references are available that discuss this question with respect to several asphalts, particularly domestic asphalts, over the usual penetration range. Holmes, Collins, and Child carefully made the necessary analysis and comparisons on the basis of the available indexes but, as pointed out by Traxler and Schweyer and by Nevitt and Krehma, the indexes employed were for a good part empirical. The asphalt viscosity index (A. V. I.) and the viscosity-temperature susceptibility coefficient (V. T. S.) were suggested as indexes of fundamental physical significance which would more logically indicate the rates of change of the viscosities with temperature.

On the basis of a comparison of the most acceptable indexes made by Nevitt and Krehma, it appeared that the viscosity-temperature susceptibility coefficient was most suitable because of its relative independence of the consistency and the temperature ranges over which it is to be determined. Accordingly in the present investigation the viscosity-temperature characteristics of several domestic asphalts and one Mexican asphalt have been studied over the usual penetration ranges, using the viscosity-temperature susceptibility coefficient as the index.

Standard A. S. T. M. procedures were employed wherever possible. The penetrations were determined at 25° C. exactly following the A. S. T. M. procedure. The viscosities

were determined at 98.89° C. (210° F.) and 135° C. (275° F.), using a thermostatically controlled Saybolt viscometer with interchangeable Universal, Furol, and asphalt orifices (3).

A special thermometer which met the Saybolt thermometer requirements for the 135° C. viscosities was used; for the 98.89° C. viscosities the usual Saybolt thermometer was used.

The results reported are an average of at least three independent determinations of the viscosity. Times of efflux appreciably below 50 seconds were avoided, or usually checked using the next smaller orifice. Similarly times of efflux more than 600 seconds were run on the next larger orifice whenever possible.

The A. P. I. Saybolt viscosity conversion (1) was used to convert Saybolt viscosities to kinematic units. The viscosities determined by the "asphalt tip" were multiplied by 10 to convert to Saybolt Furol viscosities. This conversion is believed to be within the limits of the errors inherent in the determinations of Saybolt viscosities at these elevated temperatures.

The viscosity-temperature susceptibility coefficient was calculated from the formula given by Nevitt and Krehma (4) where μ_1 and μ_2 are the kinematic viscosities at absolute temperatures T_1 and T_2 .

$$V. T. S. = 0.221 \frac{\text{Log} \left(\frac{(\text{Log } \mu_1 + 0.8)}{(\text{Log } \mu_2 + 0.8)} \right)}{\text{Log} \frac{T_2}{T_1}}$$

TABLE I. VISCOSITY-TEMPERATURE SUSCEPTIBILITY COEFFICIENT OF TYPICAL COMMERCIAL ASPHALTS

Type	Manufacture	Penetration At 25° C.	Viscosity		V. T. S.
			At 98.89° C.	At 135° C.	
Mexican	Steam	24	1152 ^a	78 ^a	0.736
		97	221 ^a	245 ^b	0.717
		213	111 ^a	150 ^b	0.707
Smackover	Steam	21	687 ^a	535 ^b	0.739
		55	209 ^a	235 ^b	0.720
		92	152 ^a	179 ^b	0.732
		149	105 ^a	136 ^b	0.726
		231	783 ^b	112 ^b	0.722
Illinois	Vacuum-steam and air	44	349 ^a	298 ^b	0.769
		75	218 ^a	233 ^b	0.731
		106	167 ^a	191 ^b	0.737
		179	96 ^a	127 ^b	0.732
		257	67 ^a	98 ^b	0.731
Midcontinent	Vacuum-steam	27	439 ^a	360 ^b	0.756
		82	162 ^a	188 ^b	0.732
		142	102 ^a	124 ^b	0.759
		188	76 ^a	110 ^b	0.722
Wyoming	Vacuum-steam	32	339 ^a	292 ^b	0.770
		69	184 ^a	174 ^b	0.765
		100	125 ^a	142 ^b	0.767
		150	857 ^b	106 ^b	0.774
		197	674 ^b	88 ^b	0.781
		309	442 ^b	67 ^c	0.753
		Soft	266 ^b	462 ^c	0.759
		Wyoming	Steam	23	480 ^a
41	259 ^a	241 ^b	0.769		
78	146 ^a	164 ^b	0.755		
133	89 ^a	112 ^b	0.765		
180	70 ^a	95 ^b	0.766		
222	541 ^b	77 ^b	0.770		
West Texas	Vacuum-steam	30	224 ^a	204 ^b	0.790
		102	79 ^a	95 ^b	0.798
		134	61 ^a	81 ^b	0.786
		207	408 ^b	61 ^b	0.782
California	Vacuum-steam	20	270 ^a	207 ^b	0.840
		96	88 ^a	90 ^b	0.855
		156	57 ^a	67 ^b	0.854
		207	454 ^b	58 ^b	0.842
300	334 ^b	48 ^b	0.836		
Montana	Pressure still	28	138 ^a	111 ^b	0.902
		80	61 ^a	64 ^b	0.899
		122	467 ^b	541 ^c	0.876
		194	322 ^b	420 ^c	0.875
283	248 ^b	362 ^c	0.907		

^a Viscosity expressed in seconds using asphalt tip.

^b Viscosity expressed in Furol seconds.

^c Viscosity expressed in Universal seconds.

TABLE II. VISCOSITY-TEMPERATURE SUSCEPTIBILITY COEFFICIENT OF TAR

Type of Tar	Sample No.	V. T. S.
Vertical retort	1-V	1.13
	2-V	1.16
By-product coke oven	3-C	1.29
	4-C	1.19
	5-C	1.20
	6-C	1.24
	7-C	1.19
Horizontal retort	8-H	1.155
	9-H	0.956

The results, summarized in Table I, are on Mexican, Smackover, Illinois, Midcontinent, Wyoming, West Texas, California, and Montana asphalts of the usual penetration ranges. The materials are listed roughly in order of their viscosity-temperature susceptibility coefficient; the Mexican asphalt has the lowest by a small margin, while of the straight-run asphalts the California has the highest. The material of highest viscosity-temperature susceptibility coefficient listed in Table I is a pressure-still residue of Montana crude. Examination of the pressure-still residuals data of Nevitt and Krchma (4) indicates that these products may have a still higher viscosity-temperature susceptibility coefficient of 0.9 to 1.0. Tars (unfiltered) have a coefficient of 1.1+, as is indicated by calculations based on the data of Volkmann, Rhodes, and Work (6), summarized in Table II.

Judging from the available recent data covering the viscosity-temperature characteristics of bituminous materials, the values for the coefficient vary from 0.7 for straight-run low-temperature susceptibility asphalts to 1.2+ for tars.

The uniformity over the consistency range of the various asphalts investigated confirms the conclusion that the viscosity-temperature susceptibility coefficient is a suitable index and, using the Standard Saybolt viscometer, it is an index readily applicable at the present stage of asphalt technology.

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RECEIVED November 27, 1936. Laboratory tests were made at the Montana Highway Commission Materials Laboratory.

A Simple Auto-Bubbler Pipet

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THE writers have recently required in some gas analyses a small auto-bubbler pipet which would permit the complete and ready removal of contained liquid for subsequent analysis. The Francis auto-bubbler (1) was not suited to this requirement. The Matuszak bubbler (2) also has a region from which liquid is not readily removable and, in addition, is rather difficult for even the competent amateur to construct. The design indicated in Figure 1 obviates these difficulties. During use, the lower part of the unit shown is dipped into an Erlenmeyer flask.

The bead, A, is of Jena glass specially selected for roundness. The rest is Pyrex. The tube, B, is ground smooth on emery cloth where the bead is to rest and then the bead is ground in with a few easy turns, using emery powder. No special care need be taken with this latter operation. Tube B is now sealed off at its lower end and one side is blown out into a thin bubble which is contacted to a thinned portion of tube C. The hole at D is then blown out in the flame. The order of construction of the rest of the apparatus is obvious. Care should be taken in preparing the inner seal at E to pull out tube C so that hole D comes directly below the inner seal. This will eliminate all dead space. Tube C should be large enough to permit free movement of the bead. Accurate centering of tube B is then not essential.

The operation of the pipet is self-evident.

Literature Cited

- (1) Francis, U. S. Patent 1,850,499 (1932).
- (2) Matuszak, U. S. Patent 2,001,581 (1935).

RECEIVED January 21, 1937.

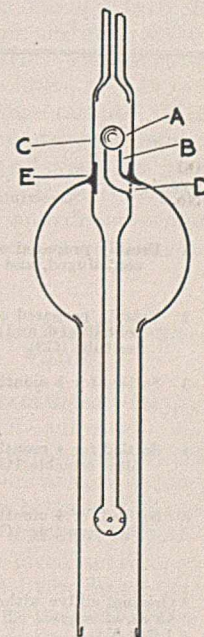


FIGURE 1. AUTO-BUBBLER PIPET

Carbonate Content of Oil Lye

Clarified by Centrifugation and Long Settling

JOHN E. S. HAN, Shanghai, China

THE small amount of carbonate remaining in volumetric sodium hydroxide solutions after different treatments for carbonate removal has been determined by Han and Chao (3). Although the "oil lye" method does not remove carbonate as completely as precipitation with barium salts, yet it has the decided advantage of not introducing foreign ions into the solution. The long time required for the solid carbonate to settle out is sometimes a disadvantage.

Han and Chao found that when settling was hastened by heating as recommended by Pregl (4), the oil lye contained 0.09 to 0.19 per cent of carbonate. (The carbonate content was expressed in terms of total alkali. Thus on an average 0.15 per cent of the Na₂O present was in the form of Na₂CO₃.) Allen and Low (1) shortened the time of settling by centrifuging oil lye at 2200 to 2300 r. p. m. for 30 minutes. Their data were obtained by a volumetric procedure somewhat different from that of the author and were not checked against a standard method. The centrifuge method, however, has a distinct advantage over that of Pregl in not requiring heating which might increase the solubility of sodium carbonate. The author considered it worthwhile to redetermine the carbonate content of centrifuged oil lye by both gravimetric and volumetric methods.

The author prepared oil lye by dissolving sodium hydroxide (reagent quality) in an equal weight of water, allowing it to cool, and centrifuging four 250-cc. portions in closed tubes at 2000 to 2300 r. p. m. for 30 minutes. The lye became perfectly clear and most of the solid matter packed tightly on the bottom of the tubes. A small amount of solid matter, however, remained floating on the surface of the lye and could be easily disturbed on the introduction of a siphon.

For volumetric analysis the simplified procedure of the author (2) was used. An Erlenmeyer flask was freed from carbon dioxide, filled with oil lye, and attached to the buret as shown in Figure 1. The buret was filled with *N* hydrochloric acid in the absence of carbon dioxide. No titration head was used, as entry of carbon dioxide was prevented by soda-lime guard tubes.

The carbonate content of the siphoned lye was slightly higher than that of the filtered lye; on an average they amounted to 0.11 and 0.10 per cent, respectively. Neither the siphoned nor filtered lye was perfectly clear, because of the presence of minute quantities of solid particles which had passed through. (The carbonate contents were slightly lower than the average value of oil lye clarified by heating, which also became slightly turbid on cooling.)

The author also examined a number of long-settled oil lyes; some had been settled for 1 to 5 months, and others for 2 to 2.5 years. Their carbonate contents seem to depend primarily on the temperature at which they were settled. Lyes 1 to 5 months old, which were settled and siphoned (or filtered) at temperatures not higher than 18° C., contained 0.07 per cent of carbonate, while three lots of lyes 2 to 2.5 years old all contained 0.09 per cent. The lyes 2 to 2.5 years old had been settled for much longer periods and were siphoned or filtered at temperatures not higher than 19° C., but they had passed two successive summers (with maximum temperature of 38° C.) in contact with solid sodium carbonate. Apparently the redissolved sodium carbonate formed supersaturated solutions.

Experimental data for the centrifuged lyes and settled lyes 4 to 5

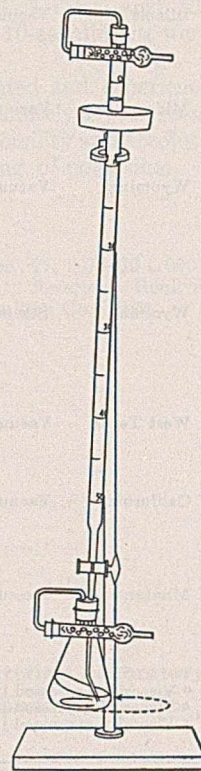


FIGURE 1

TABLE I. COMPARISON OF GRAVIMETRIC AND VOLUMETRIC METHODS

Oil Lye No.	Description of Oil Lye	Gravimetric Method				Volumetric Method				Na ₂ O in Form of Carbonate		
		Vol.	Total Na ₂ O	CO ₂ found	Na ₂ O in form of carbonate	1st End Point		2nd End Point		Direct calculation	Corrected (-0.02)	
						N HCl	N HCl	N HCl	N NaOH			%
		Cc.	Grams	Gram	Gram	%	Cc.	Cc.	Cc.	Cc.	%	%
1	Freshly prepared oil lye, cooled to 17° C., centrifuged, and siphoned	45	25.66	0.0193	0.0272	0.11	42.80	0.64	2.10	0.67	0.124	0.10
		45	25.66	0.0194	0.0273	0.11	42.80	0.76	1.68	0.28	0.129	0.11
		(0.11)	42.81	0.86	2.38	0.84	0.131	0.11
											(0.11)	(0.11)
2	Freshly prepared oil lye, cooled to 17° C., centrifuged, and filtered through Jena filter tube (G3)	90	51.18	0.0370	0.0521	0.10	42.68	0.80	1.88	0.50	0.123	0.10
		90	51.18	0.0372	0.0524	0.10	42.68	0.84	2.38	0.94	0.119	0.10
		90	51.18	0.0370	0.0521	0.10	42.68	0.48	1.62	0.32	0.119	0.10
						(0.10)					(0.10)	(0.10)
3	Settled for 5 months, siphoned	90	51.42	0.0264	0.0372	0.07	41.90 ^c	0.52	2.02	0.84	0.096	0.08
		90	51.42	0.0266	0.0375	0.07	41.90 ^c	0.90	1.84	0.74	0.090	0.07
		90	51.42	0.0272	0.0383	0.07	41.90 ^c	0.50	1.54	0.48	0.092	0.07
						(0.07)					(0.07)	(0.07)
4	Settled for 4 months, filtered through Jena filter crucible 1G3	90	50.59	0.0256	0.0361	0.07	41.22 ^c	0.64	1.54	0.50	0.091	0.07
		90	50.59	0.0250	0.0352	0.07	41.22 ^c	0.33	1.42	0.40	0.091	0.07
		90	50.59	0.0246	0.0347	0.07	41.22 ^c	0.46	1.47	0.42	0.094	0.07
						(0.07)					(0.07)	(0.07)
5	Settled for 4 months, filtered through Jena filter crucible 1G4	90	52.23	0.0245	0.0345	0.07	42.56 ^c	0.68	1.14	0.08	0.099	0.08
		90	52.23	0.0242	0.0341	0.07	42.56 ^c	0.15	1.29	0.28	0.090	0.07
		90	52.23	0.0248	0.0349	0.07	42.56 ^c	0.48	1.54	0.38	0.102	0.08
						(0.07)					(0.08)	(0.08)

^a Original oil lye without dilution, prepared by dissolving sodium hydroxide in an equal weight of water.

^b 45 cc. of original oil lye diluted to 871 cc. and 45 cc. of the solution obtained used for each titration.

^c 1.022 *N*.

Figures in parentheses are averaged values.

months old are given in Table I. All filtrations were carried out by gravity, without suction and without access of carbon dioxide. Pressure was obtained by maintaining a fairly high column of lye over the filtering medium.

Oil lye can be conveniently settled and stored in paraffin-lined bottles until needed. Preference should be given to the centrifuge method rather than the heating method, when oil lye must be clarified in a short time.

The author is indebted to K. F. Tseng and M. I. Okada

for permission to use the laboratories of the Shanghai Science Institute for part of the experiments.

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RECEIVED November 10, 1936.

Anhydrous Sodium Carbonate as a Standard of Reference in Acidimetry

Stability of Sodium Carbonate in the Temperature Range 300° to 400° C.

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THE generally accepted procedure for the preparation of anhydrous sodium carbonate by the conversion of pure sodium bicarbonate calls for decomposition at 300° C. Waldbauer, McCann, and Tuleen (3) state that this conversion can be carried out at temperatures from 102° to 450° C. The wide difference between the previously accepted maximum temperature of 300° C. and the findings of Waldbauer and collaborators (3) has led to the present investigation.

Preparation of Materials

CONSTANT-BOILING HYDROCHLORIC ACID. This was made by the process described by Foulk and Hollingsworth (1), and the distillation flask and condenser as well as the pressure-regulating apparatus were exact duplicates of those which they described. Since but two fractions of distilled acid were desired, the receiver was modified as shown in Figure 1. By its use the first 400 ml. of distillate were collected with the receiver in position as shown in Figure 1. The last portion of distillate, 50 ml. of constant-boiling acid, was collected in the smaller of the two receivers after the receiving flasks had been inverted without discontinuing the process of distillation. The constant-boiling hydrochloric acid was taken at 750-mm. pressure, after correcting the existing barometric reading with the pressure-regulating system as shown. A 5000-ml. flask was placed between the acid receiver from the still and the pressure-regulating device to minimize fluctuations in the water manometer shown. Ten grams of platinum scrap were used in the distilling flask to prevent bumping, the distillate was collected at a rate of 4 to 5 ml. per minute as recommended, and 50 ml. of undistilled acid were left in the still.

ANHYDROUS SODIUM CARBONATE. Pure sodium bicarbonate was dissolved in pure water to make a saturated solution at 80° C., which was filtered and allowed to cool. The sodium bicarbonate thus obtained was centrifuged and dried at approximately 50° C. Qualitative tests showed the absence of chloride, sulfate, potassium, etc. Anhydrous sodium carbonate was prepared from the bicarbonate by the process described by Smith and Hardy (2). The sodium bicarbonate was dissociated at 290° C. at 1- to 4-mm. pressure during a period of 1 hour and stored in glass-stoppered bottles in a desiccator over anhydrous magnesium perchlorate. The apparatus assembly for this preparation is shown in Figure 2.

APPROXIMATELY 0.2 N HYDROCHLORIC ACID. Portions of constant-boiling hydrochloric acid were weighed from weight burets, transferred to calibrated volumetric flasks, and diluted to volume.

Experimental Procedure

The purity of the anhydrous sodium carbonate was first experimentally demonstrated. Weighed portions of anhydrous sodium carbonate (corrected to the vacuum basis) were weighed into 400-ml. beakers, dissolved in water, and titrated, using the standard hydrochloric acid and Bureau of Standards calibrated burets. The agreement between the calculated normality of hydrochloric acid and the values found by this method, assuming the anhydrous sodium carbonate to be pure, is indicated by the following series of results:

0.2320	0.2320	0.2322	0.2319	Av. 0.2320	(calcd. 0.2318)
0.2005	0.2003	0.2000	0.2002	Av. 0.2002	(calcd. 0.2002)

The results show an agreement to within less than 0.01 per cent of theory, and are typical of results obtained from 10 different solutions of standard hydrochloric acid from different samples of prepared constant-boiling acid. The indicator used in these titrations was an aqueous solution of 0.10 per cent methyl orange and 0.25 per cent indigo carmine. The color change is from green in basic solution to gray at the end point and violet in acid solution. It is concluded that the anhydrous sodium carbonate was pure as prepared.

Change in Alkaline Value

Samples of the same preparation of anhydrous sodium carbonate were heated for 4 hours at various temperatures between 300° and 390° C. and used to standardize a given solution of standard hydrochloric acid made from constant-boiling material as described.

The results, shown in Table I, are averages from at

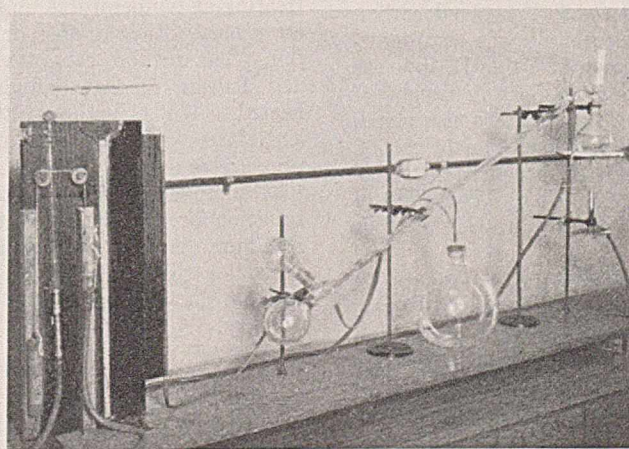


FIGURE 1. APPARATUS FOR PREPARATION OF CONSTANT-BOILING HYDROCHLORIC ACID

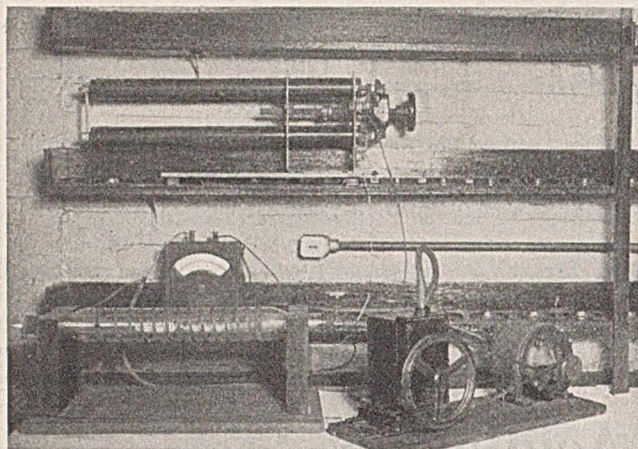


FIGURE 2. APPARATUS FOR PREPARATION OF ANHYDROUS SODIUM CARBONATE FROM BICARBONATE

least two closely agreeing duplicates. At 390° C. the error in the determination of acid normality is 3 per cent for the 4-hour time of decomposition. By plotting the data of Table I with temperature on one axis and acid normality on the other, it is seen that an approximate straight-line relationship is involved. There is no reason to believe that at 475° C. the error involved in a 4-hour treatment would not double the inaccuracy to approximately 6 per cent or more.

TABLE I. INFLUENCE OF TEMPERATURES BETWEEN 300° AND 390° C. ON ALKALINE VALUE OF ANHYDROUS SODIUM CARBONATE (Time of heating 4 hours at indicated temperature. Normality of HCl used on weight basis, 0.2121)

Temperature ° C.	Normality of HCl Found	Change in HCl Normality
300	0.2121	0.0000
330	0.2097	0.0024
370	0.2075	0.0046
380	0.2070	0.0051
390	0.2061	0.0060

Determination of Decomposition

The experiments of Table I are repeated at a temperature of 390° to 400° C. with intervals of 0.25 to 3 hours. In this case a stream of dry, carbon dioxide-free air was passed over the sample and the evolved gases containing carbon dioxide of decomposition were then passed through ascarite and anhydrous in a weighed Turner tube to absorb evolved carbon dioxide. The loss in weight of the sample was also determined as a check. The results, shown in Table II, indicate a fair degree of agreement between the loss in weight of samples and the recovered weight of carbon dioxide evolved. With longer time intervals the rate of evolution of carbon dioxide seems to accelerate, possibly because of the effect of accumulation of sodium oxide as impurity. The time of reaction was not sufficiently extended to substantiate this point.

STUDIES IN CLOSED SYSTEM. The experiments of Table II were repeated with the changed condition that the system was kept closed until the end of the time interval involved and was then flushed out with a stream of dry, carbon dioxide-free air, and the carbon dioxide evolved was then absorbed and weighed. The rate of decomposition would in this case be expected to diminish as the accumulation of carbon dioxide increased. This was found to be the case, as shown in Table III.

An examination of Table III and comparison with Table II show that the rate of decomposition in a spacious closed system is about equal to that in a system in which the evolved carbon dioxide is removed rather than allowed to accumulate. Only at the 3-hour period of heating is the rate lessened. A graph of these data shows a rapid decrease in the change of evolution of carbon dioxide with increase in time, indicating that the vapor pressure of sodium carbonate at 400° C., which results in the evolution of carbon dioxide, does not appreciably retard the rate of decomposition until sufficient has accumulated. This effect is governed by the volume of the decomposition chamber.

TABLE II. DECOMPOSITION OF SODIUM CARBONATE AT 390° TO 400° C. AT VARIOUS TIME INTERVALS

(As determined by loss in weight and weight of CO₂ evolved.)

Weight of Na ₂ CO ₃ , gram	0.7569	0.7564	0.7107	0.9116	0.7414
Time heated, min.	15	30	60	180	360
Weight of Na ₂ CO ₃ after heating, gram	0.7552	0.7534	0.7070	0.9064	0.7285
Weight loss, gram	0.0017	0.0030	0.0037	0.0052	0.0129
Weight of CO ₂ found, gram	0.0017	0.0032	0.0036	0.0063	0.0117
Av. per cent decomposition	0.23	0.40	0.51	0.63	1.66

TABLE III. DECOMPOSITION OF SODIUM CARBONATE AT 390° TO 400° C. AT VARIOUS TIME INTERVALS IN A CLOSED SYSTEM

(As determined by loss in weight and the weight of CO₂ evolved.)

Weight of Na ₂ CO ₃ , gram	0.5733	0.6687	0.6590	0.7744	0.8902
Time heated, min.	15	30	60	180	360
Weight of Na ₂ CO ₃ after heating, gram	0.5716	0.6654	0.6552	0.7688	0.8831
Weight loss, gram	0.0017	0.0030	0.0038	0.0056	0.0071
Weight of CO ₂ found, gram	0.0015	0.0032	0.0046	0.0062	0.0072
Av. per cent decomposition	0.28	0.46	0.64	0.76	0.80

The experiments of Table II were repeated at a temperature of 310° to 315° C., to test the possibility of heating sodium carbonate at a temperature above 300° C., which is the upper limit permissible according to Smith and Hardy (2) and many other investigators. Samples of approximately 1 gram lost in weight 0.0012 and 0.0015 gram, and the carbon dioxide evolved weighed 0.0014 and 0.0016 gram, respectively. A solution of 0.2120 N hydrochloric acid was restandardized, using these samples, and the values 0.2096 and 0.2091 N were found.

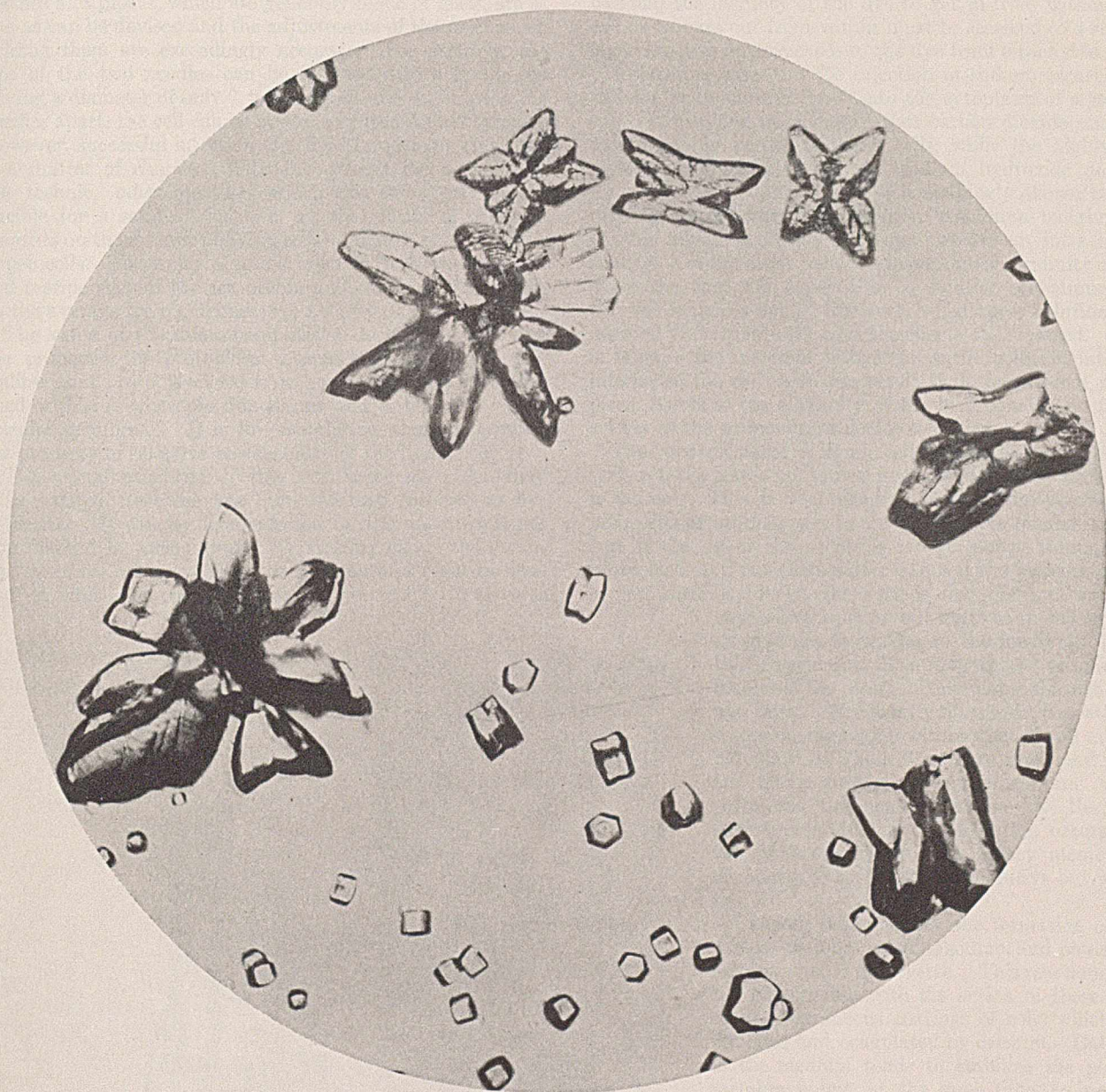
Conclusions

From the experimental evidence it is to be concluded that anhydrous sodium carbonate dissociates to give off carbon dioxide gas at temperatures above 300° C. Heating for 1 hour at 310° to 315° C. results in an error of more than 1 per cent in the alkaline value of the sodium carbonate so treated. Heating at temperatures up to 400° C. greatly increases the error, using either an open or closed vessel for the decomposition. The authors cannot agree with Waldbauer, McCann, and Tuleen (3) that anhydrous sodium carbonate can be heated to 475° C. without alteration in neutralization equivalent. The dynamic method of determining the carbon dioxide pressure of sodium carbonate heated above 300° C. proves that there is an appreciable decomposition and that the resulting product is not suitable for use as an acidimetric standard. Anhydrous sodium carbonate, such as that prepared for this investigation from sodium bicarbonate with vacuum dissociation at 300° C., is suitable for use in acidimetry.

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MICROCHEMISTRY



Photomicrograph
by courtesy of
A. A. Benedetti-Pichler

Bismuth
Cobalticyanide

The Living Cell

Physical Properties of and Microchemical Reactions

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THE micromanipulative technic depends upon a mechanical contrivance to manipulate microneedles and pipets in the field of the compound microscope. The tips of the needles and pipets, which are generally made of glass, are as fine as can be devised and the adjustments of the mechanism holding them are exceedingly accurate. For example, the tips of the two needles can be inserted into a living cell having a diameter of only 7 to 8 microns and, by moving the needles apart, the cell can be stretched without destroying it. However, successful injection of a fluid into such a small cell is a matter of chance. With the present development of the technic, microinjections which are sufficiently reproducible for a serious study—e. g., the effects of chemical reagents on the interior of living cells—must be done on much larger cells. Examples of these are the fresh-water ameba and marine eggs of the sea urchin and starfish. These cells on the average have a diameter of about 0.01 cm.

The value of the micromanipulation technic for studying the properties of protoplasm becomes evident when one realizes that protoplasm exists as such only when it is confined within microscopic dimensions and is bounded by its peculiar membrane. It is this membrane which determines the property of selective permeability of the living cell.

The actual existence of this membrane as a definitely differentiated structure has been regarded hitherto as hypothetical. It can be demonstrated by the micromanipulation method in various ways. A striking one is the microinjection into a living cell of the solution of a nontoxic dye-stuff to which the cell is normally impermeable. The color

of the injected solution quickly diffuses through the interior of the cell and stops on reaching the cell boundary. Evidently the interior of the cell is freely permeable to the dye and the inability of the dye to get in from without the cell or to pass out from within must be ascribed to a surface layer which is impermeable to the dye from either side.

Interesting cases are the injection of sodium bicarbonate and the ammonium chloride into the cytoplasm of a starfish egg. It has long been known that carbon dioxide and ammonia readily penetrate living cells, while the highly dissociated hydrochloric acid and sodium hydroxide do not. This selective action of the cell is strikingly shown by immersing starfish eggs in a solution of sodium bicarbonate. In this alkaline solution the eggs develop an intracellular acidity. On the other hand, an intracellular alkalinity occurs when the eggs are exposed to a solution of ammonium chloride which is acid. However, when these solutions are injected directly into the eggs the effects are reversed. This is because the injection brings the entire solution into the interior of the cell, with the result that the internal protoplasm reacts to the alkalinity of the bicarbonate and to the acidity of the ammonium chloride solutions.

The protoplasm of a living cell is able to repair a torn surface if the tear is not too extensive, and if the environment is normal. This is well illustrated in microdissection experiments on starfish eggs in sea water. No breakdown occurs if the tip of the needle is moved slowly through the protoplasm and out of its surface; but if the piercing action is performed suddenly, the surface film disrupts and the exposed cytoplasm will begin to spread out and its granules to scatter in the medium. While this is occurring, films may appear around the masses of the disorganizing material which swell and burst. Frequently films form beneath the disorganizing region within what is still normal cytoplasm. These films may unite and reach the intact, original plasma membrane which surrounds the healthy portion of the egg. After this no further disintegration occurs and the protoplasm, with its intact membrane, rounds up to constitute a diminutive but viable egg.

Calcium salts enhance the formation of the plasma membrane, while sodium and potassium salts tend to do the reverse. This reaction must not be confused with the action of these salts on the extraneous coatings of cells which are stiffened and coagulated by calcium. Calcium in the medium tends to stabilize the plasma membrane but, at the same time, to increase its fluidity.

Microinjection experiments present strong evidence that water forms a continuous phase in protoplasm. Aqueous solutions diffuse readily through the cytoplasm of such diverse types of cells as protoplasts of root-hair cells, amebas, various ova, muscle fibers, nerve cells, and ciliated epithelial cells. To ensure success the injection must be performed gradually; otherwise a localized disintegration may occur,

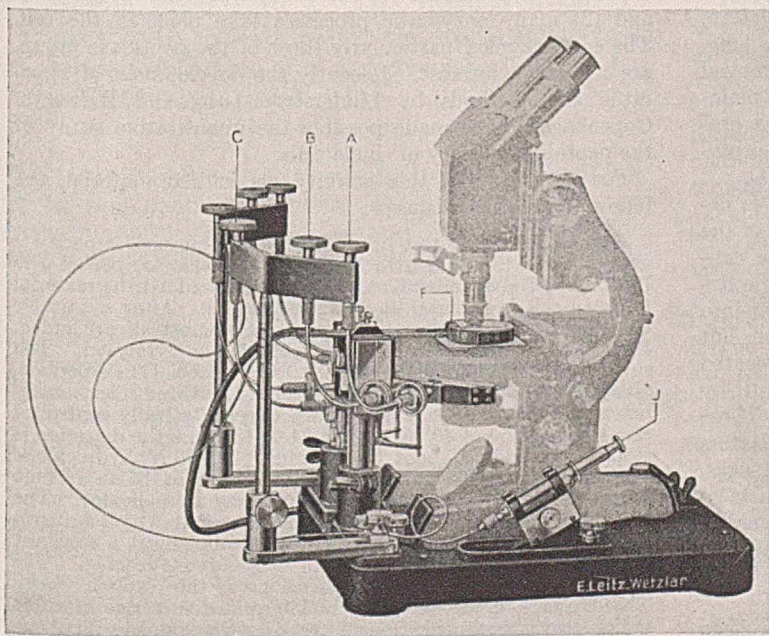


FIGURE 1. MICROMANIPULATOR WITH MICROSCOPE IN POSITION FOR OPERATION

Screw heads A, B, and C by means of flexible shafts control the movements of the microneedles which extend horizontally into the moist chamber, F, below the objective of the microscope. A and B control the two horizontal movements; C, the vertical. J is the plunger of the syringe which controls the pressure through a long, coiled copper capillary tube for the microinjections.

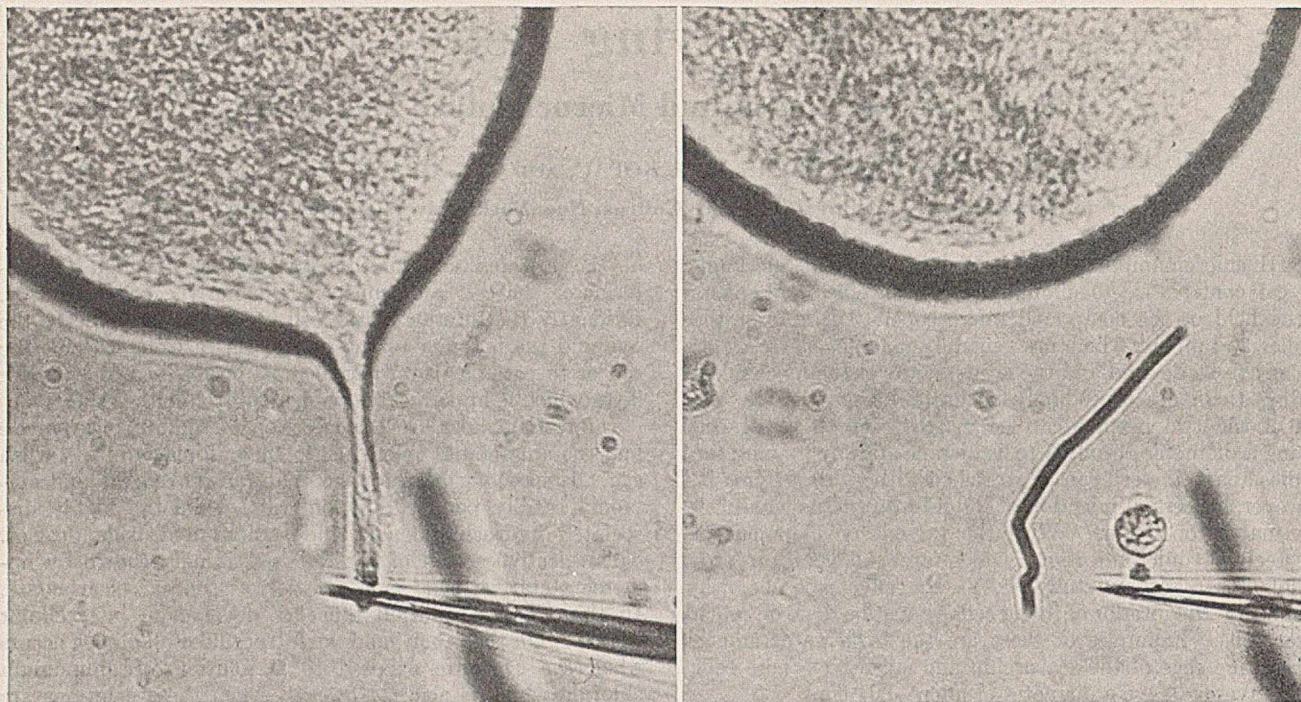


FIGURE 2. HIGHLY MAGNIFIED PHOTOGRAPH OF PART OF STARFISH EGG, SHOWING SEMIFLUID NATURE OF PROTOPLASM

Left, strand of protoplasm drawn out with the tip of a microneedle
Right, this strand on being released immediately flows back into the egg

and the resulting injury may spread and produce complete cytolysis. Frequently, however, a membrane may form around the disintegrating region to constitute a vacuole while the rest of the protoplasm remains unaffected.

The water within the cytoplasm freezes readily. To demonstrate this, the interior of the subcooled cell must be inoculated with an ice crystal, since the plasma membrane tends to obstruct the spread of freezing from outside the cell. In the amoeba, the freezing is in the form of feathery ice crystals which spread in all directions from the site of inoculation. In the case of the muscle fiber of a frog, the ice forms long, slender columns between denser longitudinally arranged constituents of the fiber. If the frozen condition is maintained for more than a few minutes, the ice columns progressively enlarge and the ensuing dehydration of the protoplasm becomes irreversible.

Since protoplasm is an organized structure which is destroyed by crushing, it is obvious that a determination of the hydrogen-ion concentration of extracts of crushed tissue cannot be a reliable clue to the intensity of acidity within the living cell. The microinjection of lipoid-insoluble indicators into the protoplasm has given results least open to question, but even then the color tends to be more or less rapidly segregated in vacuoles. Values obtained for the intracytoplasmic pH by the best available methods lie between 6.8 and 7.2. These values have been obtained by injecting a series of indicators of overlapping ranges into such cells as echinoderm eggs, various somatic cells of vertebrates and the protoplasts of plant cells and of amoebas. In Metazoa the cell nucleus has been found to be consistently more alkaline than the cytoplasm, the colorimetric value from injected indicators being in the neighborhood of pH 7.6 to 7.8.

The relatively neutral reaction of the internal protoplasm suggests that much of the protein present is on the alkaline side of its isoelectric point. This is borne out by the ease with which coagulation occurs when salts of polyvalent cations, even in very dilute concentrations, are injected into such cells as echinoderm eggs, amoebas, and the protoplasts

of plant cells. For example, calcium chloride in all concentrations down to 0.005 *M* and mercuric chloride in very low concentrations produce a coagulating effect which is either restricted or extensive according to the amount injected. The injection of sodium and potassium chlorides has no such effect, presumably because they form soluble salts of the majority of proteins present.

To the enzyme chemist the living cell is an important object of study because (1) the cell is a producer of enzymes and (2) many enzymatic processes take place in the cell. The endoenzymes, particularly those of the peptidase group, are of extreme interest. Recently the development of apparatus and methods by Linderström-Lang and Holter, of Copenhagen, have made possible the quantitative study of the peptidase activity of single cells.

For the study of this activity on cellular material, the following procedure is used:

A small Jena-glass test tube of about 250-cu. mm. capacity is used as a reaction and titration vessel. In this are placed 4 to 7 cu. mm. of glycerol and water, to which is added the material (cells or cell fragments) under investigation. After a suitable time (usually 30 to 60 minutes) 7 cu. mm. of substrate are added. By this time the cell should be completely cytolized. The substrate most commonly used is a 0.2 *M* solution of the dipeptide, alanyl-glycine. The resulting mixture is stirred electromagnetically and placed in a water bath thermostatically controlled at a temperature of 40° C. After 24 to 48 hours the digestion is stopped by adding about 30 cu. mm. of 0.05 *N* hydrochloric acid in acetone. To this are added 150 cu. mm. of an acetone solution of naphthyl red which is used as an indicator. The titration is completed by adding known amounts (with a microburet) of 0.05 *N* hydrochloric acid in alcohol until a constant pH value as indicated by the color of the dye is reached. The color standard has the same dimensions as the reaction vessel. The cleavage of the substrate is determined in terms of cubic millimeters of hydrochloric acid necessary to complete the titration.

Holter and Kopac performed the following experiments on amoebas to determine what role, if any, the various granules (particularly the neutral red and Janus B staining) and crystals play in the peptidase activity.

The amebas are transferred to small centrifuge tubes which are previously half-filled with a 2 per cent solution of Zulkowsky's soluble starch, which because of its density serves as a pycnotic cushion for the amebas while they are centrifuged. It has been found that stratification of the various inclusions can be accomplished by centrifuging at 2000 r. p. m. for 5 minutes and then at 7500 r. p. m. for 10 minutes. The amebas become essentially ellipsoidal and all granules, crystals, and other dense components collect at the centrifugal pole. Lipid components collect at the centripetal pole.

The centrifuged amebas are cut with two microneedles to separate the centrifugal and centripetal portions. The two fragments are transferred to separate reaction vessels to which 7 cu. mm. of phosphate buffer (pH 7.4) have previously been added. One hour later, 7 cu. mm. of substrate are added, the contents of each vessel are thoroughly mixed, and finally the vessels are placed in a water bath at 40° C. The period of digestion was varied between 18 and 24 hours. The amount of splitting of the substrate was determined by titrating with hydrochloric acid.

In a similar manner the peptidase activity of normal and denucleated amebas were compared. The nucleus of the ameba can be easily removed with a microneedle without causing the loss of any cytoplasm. Denucleated amebas were kept living for 24 hours before their enzymatic activity was determined. The results of these investigations on the peptidase activity of amebas are being published elsewhere.

In some experiments the successive changes in a cell are too rapid to be studied properly. However, a motion-picture film of these changes may be repeatedly reviewed. Photographs of microdissection experiments have been taken usually at 24 frames per second, making possible a record, for the duration of each exposure, of $1/24$ th second.

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Colorimetric Microdetermination of Cobalt and Potassium

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The amount of potassium in the potassium-sodium cobaltinitrite precipitate is obtained indirectly by determining colorimetrically the cobalt in the acid solution of the precipitate with the use of nitroso R-salt (disodium salt of 1-nitroso-2-hydroxy-3,6-naphthalenedisulfonic acid). It is shown that the cobaltinitrite precipitate contains potassium and cobalt in the atomic ratio 1 to 2. The nitroso R-salt gives with cobalt solutions an intensely colored solution of a red dye which is extremely stable.

IN 1921 van Klooster (3) suggested the nitroso R-salt for the qualitative identification of cobalt, but no one seems to have adopted this reagent for the colorimetric determination of cobalt or the indirect determination of the potassium in the cobaltinitrite precipitate. Nitroso R-salt, disodium salt of 1-nitroso-2-hydroxy-3,6-naphthalenedisulfonic acid, may be obtained from the Eastman Kodak Company, or prepared in the laboratory following van Klooster's directions (3). This reagent gives colorations with nickel ion (brownish yellow) and with ferrous ion (green). The intense red coloration with cobalt ion develops rapidly in solutions buffered by the addition of acetate.

For the colorimetric determination, 10-ml. portions of acidified cobalt chloride solutions are measured off into test tubes. Each portion is treated with 2 ml. of sodium acetate solution and 1 ml. of the nitroso R-salt reagent, and the mixture is agitated for 5 seconds. The red coloration, which appears immediately, is very stable and may be used for colorimetric comparison either immediately or in the course of a few hours or even 2 or 3 days.

Table I shows that accurate results are obtained if the quantity of cobalt lies between 0.025 and 0.25 mg. The validity of Beer's law within this range is further borne out

by the fact that identical results are obtained with standard solutions containing from 0.025 to 0.100 mg. of cobalt. In order to avoid the use of a calibration curve, it is therefore recommended to adjust the concentration of cobalt solution so that it lies between the limits of 0.0025 and 0.025 mg. of cobalt per ml. before proceeding to the colorimetric estimation. The volumes of the reagents should be increased proportionately if more than 10 ml. of the cobalt solution are used for the colorimetric determination.

Determination of Potassium

The methods based on the precipitation of the potassium as cobaltinitrite and known previous to 1932, such as that of Jacobs and Hoffman (2), have been discussed by Peters and Van Slyke (5). Since 1932 a few other modifications (4, 6, 7, 8, 9) have been published which offer certain distinct advantages. Except for the gravimetric and electrolytic methods, all depend on the determination of the nitrite content of the precipitate, either volumetrically with permanganate or colorimetrically by the formation of azo dyes. The permanganate titration presents difficulties in the determination of very small quantities of potassium, since the recognition of the end point lacks precision. The colorimetric determination of nitrite, although highly sensitive, is not very reliable on account of the instability of the azo dye. The colorimetric method of Morris and Gerdel

TABLE I. CONTROLS FOR THE COLORIMETRIC DETERMINATION OF COBALT WITH THE USE OF NITROSO R-SALT

(The standard solutions contained the following quantities of cobalt: A, 0.100 mg.; B, 0.050 mg.; C, 0.025 mg.)

μ Cobalt Given	Cobalt Found			Mean	Error %
	Stand-ard A	Stand-ard B	Stand-ard C		
μ	μ	μ	μ	μ	
500	267	266	265	266	-48
250	250	250	250	250	0
200	200	200	200	200	0
125	125	125	123	124	- 0.8
100	100	100	100	100	0
75	75	77	75	76	+ 1.3
50	50	50	50	50	0
25	25	25	25	25	0
10	8	7	5	7	-30

(4), read by the writer after the nitroso R-salt method had been developed and extensively used, possibly offers advantages similar to the one discussed in this paper.

TABLE II. CONTROLS FOR DETERMINATION OF POTASSIUM BY COLORIMETRIC DETERMINATION OF THE COBALT CONTENT OF THE POTASSIUM COBALTINITRITE PRECIPITATE

K Given Mg.	Number of Determinations	K Found, Arith- metical Mean Mg.	Average Deviation of Mean, = Mg. K	Coefficient of Vari- ability %
2.000	2	1.950	35	1.8
1.000	5	1.000	0	0
0.750	1	0.750	.	..
0.500	5	0.490	7	1.4
0.250	5	0.251	5	2.0
0.125	2	0.118	5	4.2
0.094	3	0.092	1	1.1
0.063	2	0.068	3	4.4
0.047	3	0.047	2	4.2
0.032	3	0.031	4	13
0.016	1	0.012	.	..
0.008	1	0.006	.	..

The procedure for the determination of potassium is described below as it has been developed for the analysis of the ash of biological (plant) materials.

A quantity of organic matter or ash is taken that is expected to contain from 0.04 to 0.1 mg. or more of potassium. The ash is dissolved in 5 ml. of 1 per cent hydrochloric acid. Without filtering off the insoluble material, the solution is made alkaline to phenolphthalein by the addition of sodium hydroxide and boiled for 15 minutes in order to remove any ammonia. The precipitate formed with sodium hydroxide will contain any ions which, if not precipitated at this stage, might interfere with the determination. The solution is filtered, and the precipitate washed with hot water. As a rule 20 ml. of hot water will be sufficient for washing. The combined filtrate and washings are acidified to a pH of 3 to 6 by the addition of hydrochloric acid.

The rest of the procedure varies according to the quantity of potassium expected. If less than 1 mg. of potassium is present, the precipitation of the cobaltinitrite is carried out in a centrifuge tube (A); with larger quantities of potassium, the usual laboratory technic may be used (B).

A. If the amount of potassium does not exceed 1 mg., the entire filtrate is transferred to a centrifuge tube of 15-ml. capacity, which must have been thoroughly cleaned beforehand. The centrifuge tube is placed in a steam bath and its contents are evaporated to a volume of 0.5 ml. or less. If the volume of the solution should exceed 0.5 ml. to any appreciable extent, the following precipitation of the potassium cobaltinitrite may not be complete. The contents of the centrifuge tube are cooled, and then 5 ml. of the alcoholic sodium cobaltinitrite reagent are added slowly. The contents are mixed thoroughly with gentle agitation, and the centrifuge tube is placed for 4 hours, or preferably overnight, in a refrigerator. It is then centrifuged for 5 minutes with 5000 r. p. m., or for 7 minutes with 1350 r. p. m., and the supernatant liquid to a distance of 5 mm. above the precipitate is removed by means of a capillary siphon of approximately 1-mm. bore, as described by Peters and Van Slyke (5). The siphon is fixed in a 3-hole stopper, and operated by controlled suction. Care must be taken not to remove floating particles of the precipitate.

The washing of the precipitate is performed as follows: First 10 ml. of water are allowed to flow down the sides of the centrifuge tube and to mix with the residual fluid above the precipitate without disturbing the latter. After centrifuging 5 minutes, the liquid is removed as described above. Now 5 ml. of acetone are added, the precipitate is agitated slightly with a pointed glass rod, and centrifuged, and the liquid is removed with the capillary siphon. The treatment with 5-ml. portions of acetone is repeated until the washings no longer show a yellow coloration; three washings with acetone are usually sufficient.

To effect the solution of the cobaltinitrite precipitate, 5 ml. of 1 M sulfuric acid are added, and the centrifuge tube is placed in a water bath. Heating for 5 to 10 minutes will give a complete solution of the precipitate. The solution is diluted to a definite volume chosen so as to obtain a potassium concentration between 0.003 and 0.035 mg. of potassium per ml. (corresponding to 0.0023

and 0.026 mg. of cobalt per ml.), and the determination of cobalt is carried out as described above.

B. If from 1 to 100 mg. of potassium are present, the entire filtrate from the sodium hydroxide precipitate, which may have a volume from 50 to 100 ml., is received in a 200-ml. beaker and evaporated on a water bath to a volume of 1 ml. or less. It is cooled, and then 20 ml. of the alcoholic sodium cobaltinitrite reagent are added slowly. It is mixed thoroughly with gentle agitation, the beaker is placed for 4 hours, or preferably overnight, in a refrigerator, and the solution is then filtered with the use of suction through a filter tube with a very compact layer of thoroughly washed asbestos. The beaker and precipitate are washed repeatedly with water until the washings no longer show a yellow coloration. The filter tube is connected to a clean suction flask, and the precipitate is treated in the tube with 10 ml. of hot 1 M sulfuric acid. Without applying suction, it is allowed to stand for 5 to 10 minutes until no more yellow particles can be seen. Suction is applied, and the precipitate is washed with distilled water to collect all the cobalt of the precipitate in the suction flask. If the precipitate resists solution, the entire contents of the filter tube may be transferred into a beaker containing 10 ml. of 1 M sulfuric acid and 10 to 20 ml. of water. The mixture is heated on a water bath and filtered through filter paper. In either case, the filtrate is finally diluted to a known volume, so as to obtain a potassium concentration between 0.003 and 0.035 mg. of potassium per ml. before proceeding to the colorimetric determination.

Table II presents the results of the application of the method to the analysis of solutions of known potassium content. The precision of the method is indicated by listing the absolute average deviation of the mean, and the coefficient of variability (relative average deviation). The accidental deviations are due mostly to mechanical loss of precipitate, incomplete washing of precipitate, or the introduction of potassium by the glass or by soaps employed in the cleaning of the centrifuge tubes.

As to methodical errors, Peters and Van Slyke (5) and Bonneau (1) are of the opinion that variations in the weight of the cobaltinitrite precipitate are in part due to variations in the state of hydration of the precipitate, but that aside from the water of hydration the precipitate has the constant composition $K_2NaCo(NO_2)_6$, providing the precipitate forms in a solution in which the ratio Na to K exceeds 22; the sodium of the reagent was included in calculating the Na to K ratios. If the above ratio was smaller than 22, the precipitate tended more towards the composition $K_3Co(NO_2)_6$, and when the Na to K ratio was lowered to 1, the precipitate was almost entirely $K_3Co(NO_2)_6$. The directions given above for the precipitation of the cobaltinitrite possibly assure the composition $K_2NaCo(NO_2)_6$ of the precipitate. The data of Table II, which have been obtained by determining the cobalt content of the precipitates by comparison with known quantities of cobalt (cobalt standard solutions), indicate that the ratio K to Co is actually 2 to 1 and not 3 to 1. Finally, interferences with the colorimetric determination of the cobalt are prevented in the determination of potassium, as the procedure takes care of the eliminations of ions (Ni, Fe) which interfere with the nitroso R-salt reaction of the cobalt.

Reagents

STANDARD COBALT SOLUTION. Dissolve 3.043 grams of $CoCl_2 \cdot 6H_2O$ in water, add 5 ml. of 13 M hydrochloric acid, and dilute with water to 1 liter. One milliliter of this solution contains 0.7537 mg. of cobalt, which is equivalent to 1.000 mg. of potassium. This standard is relatively concentrated, and aliquots taken for comparisons must be diluted from 100 to 500 times.

NITROSO R-SALT REAGENT. Dissolve 0.5 gram of nitroso R-salt in 100 ml. of water. The solution should be kept in the refrigerator to prevent spoilage.

SODIUM ACETATE SOLUTION. Dissolve 100 grams of sodium acetate by heating with 200 ml. of water. Filter.

SODIUM COBALTINITRITE REAGENT. Dissolve 25 grams of sodium cobaltinitrite in 200 ml. of water, place in the refrigerator for 24 hours, and then filter. Immediately before use, mix portions of this solution with equal volumes of 95 per cent ethyl

alcohol. The alcoholic mixture should be discarded if it cannot be used immediately.

Acknowledgment

The author wishes to express his appreciation to R. Tam for his assistance.

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Micromethod for Determining Viscosity of Lubricating Oils

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A method is described for the determination of viscosity of a few milligrams of petroleum lubricating oils. It is based on the rate of rise of the sample into a clean fine vertical capillary. In the known samples examined, it has been found that this rate of rise is directly related to the absolute viscosities of the samples.

WITHOUT being habitually concerned with micro quantities of sample as are those engaged in biological sciences, even in industrial oil laboratories one has frequent need for information as to viscosity of very small samples. As a result a method has been developed for determining absolute viscosity on about 15 mg. of material which has found application in numerous instances where small amounts of material were available, such as oil left in sprayed cotton and textiles, unsaponifiable of fatty oils, oil films, and components separated in the usual chemical analysis of oil sludges.

The method is based on the rate of rise of the oil into a fine vertical capillary, the actuating force being surface tension, and is preferably used with only a few milligrams of material.

Viscosity measurements based on the rate of rise into a capillary have long been made in the petroleum industry on kerosenes by means of the Saybolt thermoviscometer; but here the actuating force is the head of oil, not its surface tension, and the sample needed is approximately a pint.

Small sample viscometers have recently been described by Lidstone (1) and by Schneider and McConnell (2). In the former, the liquid is sucked up into a capillary tube above the height to which it would rise because of its surface tension, and then allowed to fall back under gravity, the time being taken for the passage of the meniscus between any two points, and corrections being made for capillary rise and for drainage. Lidstone mentions as drawbacks to his method the large capillary rise and the somewhat doubtful drainage correction. The method

of Schneider and McConnell employs 0.5 to 2 ml. of oil, in a "falling ball-inclined tube" type of viscometer.

Since the author's method is based on the rate of rise into a clean tube, drainage errors, which are large when efflux from fine capillaries is measured, are obviated, and a few milligrams of sample suffice.

A very detailed treatment has been given by Washburn (3), who has calculated the rate of advance of the meniscus of a liquid into horizontal and vertical capillaries.

Apparatus

Delivery pipet: a 20-cm. length of heavy-walled 1-mm. capillary glass tubing, one end ground to a cone. A line is etched around the tube at a point 25 mm. from the ground end, and another 6 mm. above that. (The capacity to the first mark is 0.02 ml. at 25° C.)

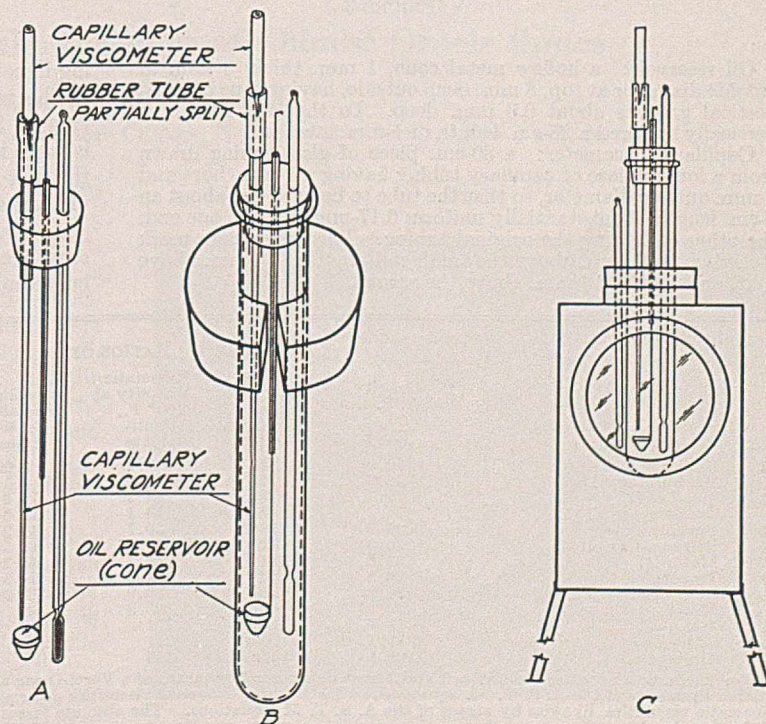


FIGURE 1. DIAGRAM OF APPARATUS

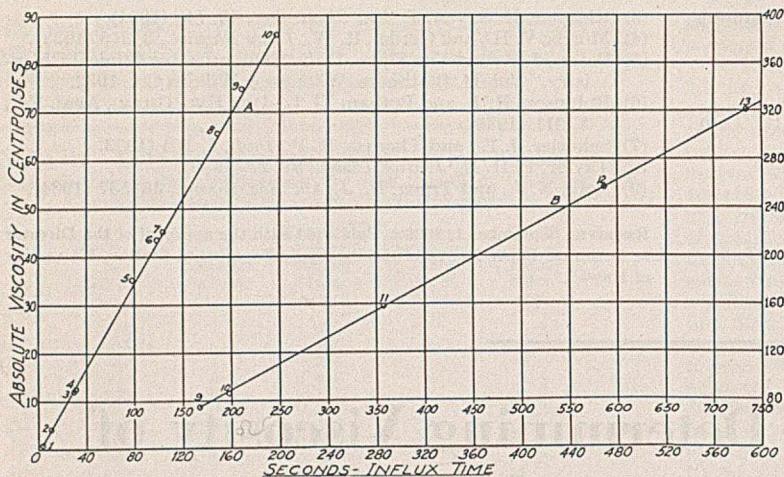


FIGURE 2

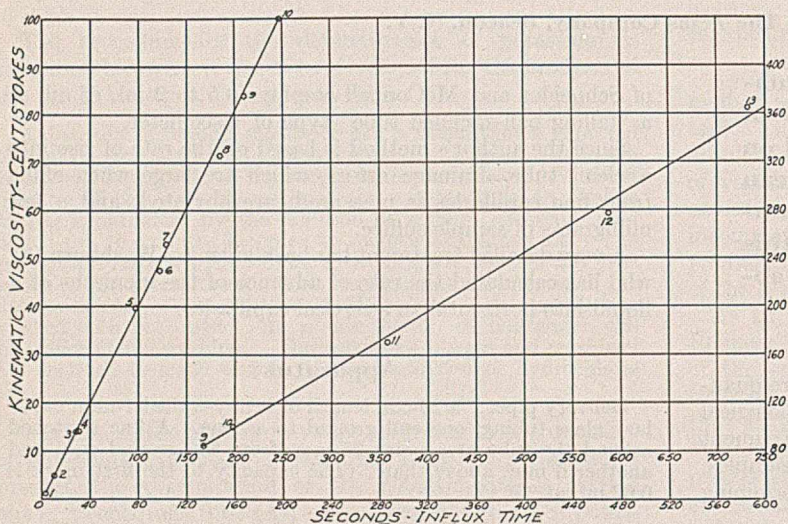


FIGURE 3

Oil reservoir: a hollow metal cone, 1 mm. thick, 8 mm. in outside diameter at top, 8 mm. deep outside, having four internal vertical grooves about 0.3 mm. deep. To the side of this is vertically soldered a 25-cm. length of 1-mm. steel rod.

Capillary viscometer: a 30-cm. piece of glass tubing drawn from a longer piece of capillary tubing having a 1-mm. bore and 5-mm. outside diameter, so that the tube to be used has about an 8-cm. length of substantially uniform 0.17-mm. bore at one end, the other end being the original tubing. This tube has a mark etched on it 25 mm. above the small end, another 13 mm. above that, and a third 13 mm. above the second.

Thermostat: a Vogel-Ossag viscometer water bath was found very satisfactory.

Miscellaneous: a test tube, 200 × 25 mm. (air bath); viscosity thermometers, A. S. T. M. type; rubber tubing 0.32-cm. (0.125-inch) bore; corks; and a stop watch.

Procedure

The sample to be examined is drawn into the delivery pipet to a point between the two marks and as close to the lower one as possible. Holding it vertically, the oil is allowed to drain to the lower mark, the sides and bottom of the pipet being wiped clean with a lintless cloth. The sample is then transferred from the delivery pipet to the oil reservoir, which should be in its place in the cork assembly as shown in Figure 1, A. Transfer is effected by bringing the end of the pipet into light contact with the inside of the cone, warming the pipet to assist very viscous oils, and forcing out the final portions by gently blowing into the top of the pipet through a tube filled with cotton. The cork assembly is then inserted into the test tube, B, which in turn is installed in the water bath, as in C.

The bath temperature and the air temperature inside the test tube should be within 0.06° C. (0.1° F.) of the desired test temperature throughout the test. This is easily accomplished with the Vogel-Ossag bath.

When the thermometer in the test tube has been at the desired temperature for 5 minutes, the actual viscosity measurement can be started by lowering the capillary viscometer into the oil reservoir and at the same moment starting the stop watch. The periods in seconds are then recorded as the oil rises by capillarity to the first, second, and third lines.

The time in seconds required for the sample to reach the middle line is used to obtain the absolute viscosity in centipoises, by reference to a curve based on data obtained with samples of known viscosity. For the author's capillary viscometer the curve shown as Figure 2 applies. It will be noted that there is a straight-line relationship between seconds of influx time and absolute viscosity in centipoises, the B curve being a continuation of the A curve to a different scale, for convenience, and both curves having in common the 74.7- and 86-centipoise points.

The relationship to kinematic viscosity is not so direct (Figure 3). The relationship to Saybolt Universal viscosity is more irregular still, as can be seen from Figure 4, despite the fact that it is drawn to a rather coarse scale to accommodate all the samples on one curve.

A curve established for liquids of one type will not be accurate for others having a very different surface tension. The curve must be based on samples of the type of the unknown.

TABLE I. RATIOS OF LINE TIMES

No.	Product	Gravity A. P. I. at 60° F.	Saybolt Universal Viscosity at 100° F.	Kinematic Viscosity at 100° F., Centi- stokes	Absolute Viscosity, Centi- poises	Influx Time in Seconds,			Influx Ratios		
						Mark 1, a	Mark 2, b	Mark 3, c	$\frac{c}{a}$	$\frac{c}{b}$	$\frac{b}{a}$
1	Kerosene	50.2	33	1.4	1.06	1.3	3	7.5	6.0	2.50	2.40
2	300 burning oil	36.9	42	5.0	4.1	3.5	10.5	24	6.9	2.29	3.0
3	Spindle oil	29.4	74	14.1	12.2	10.5	29.5	67	6.3	2.25	2.8
4	Transformer oil	24.1	74	14.1	12.6	11	31	70	6.4	2.26	2.8
5	Turbine oil	26.9	134	39.7	35.2	27.5	78	173	6.3	2.22	2.8
6	Refrigerating oil	20.9	219	47.6	43.5	34.5	98	223	6.5	2.27	2.8
7	Motor oil	31.8	244	53.1	45.2	38	103	232	6.1	2.25	2.7
8	Turbine oil	20.5	327	71.5	65.5	53.5	148	335	6.3	2.26	2.8
9	Heavy red paraffin oil	24.9	383	83.9	74.7	59	168	375	6.4	2.23	2.8
10	Motor oil	30.2	457	100.2	86	71	198	2.8
11	Motor oil	19.7	779	171	157	131	358	807	6.2	2.25	2.7
12	Bus oil	19.4	1260	277	256	214	587	1308	6.1	2.23	2.7
13	Airplane oil	26.6	1672	365	321	267	732	1606	6.0	2.19	2.7

The kinematic viscosities of samples 1 and 2 were determined by means of a Vogel-Ossag apparatus, the equivalent Saybolt Universal viscosities being calculated by means of the A. S. T. M. equations. The Saybolt Universal viscosities determined on samples 3 through 13 were converted to their equivalent kinematic viscosities, likewise by means of the A. S. T. M. equations. The absolute viscosities were calculated from the kinematic viscosities and densities of the samples.

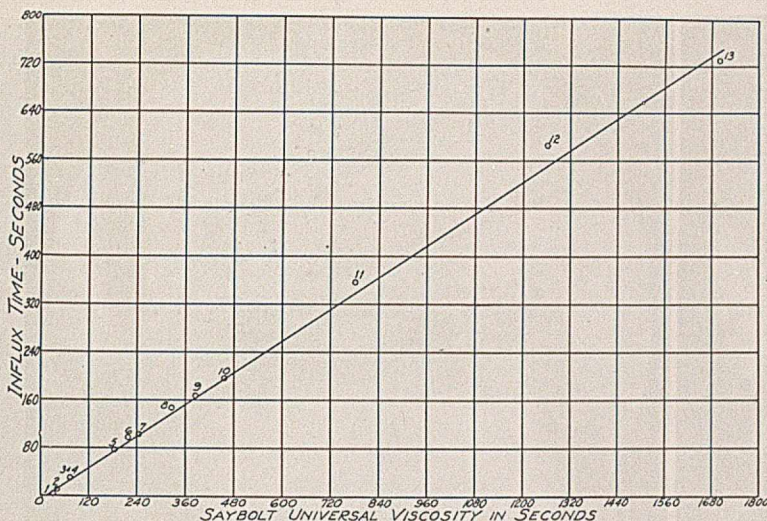


FIGURE 4

As the actual capacity of the capillary viscometer to the top mark is 1.1 cu. mm., 5 mg. of oil in the oil reservoir would be ample for a test, if the apparatus were so calibrated. To check a determination, it is only necessary to clean the viscometer and return it to the oil left in the reservoir. The removal of the 1 mg. of sample contained in the viscometer has no appreciable effect on the depth of oil left in the conical reservoir, and the check test may therefore be made without the necessity of cleaning the reservoir and replenishing the oil. When not actually in use, the capillary viscometer is held above the oil reservoir by means of a piece of partially split rubber tubing (Figure 1, A).

When the capillary viscometer is clean and all conditions

are correct, there is a definite relationship between the three line times, and when this relationship exists for the sample it is known that conditions were right. The time of rise to these three points is noted only for a check on conditions. Table I shows the ratios of line times for the author's particular capillary viscometer, as well as the data on which his curves are based. They can be determined for another by using a series of oils of known viscosities, as he did.

It was not the author's experience that many difficulties were caused by dirt clogging or lodging in so fine a tube as this capillary viscometer. The apparatus was promptly cleaned after each test; the oil reservoir by rinsing in hot benzene, followed by acetone, and blowing with air to dryness; the capillary viscometer by immersing the narrow end in a test tube of hot benzene, drawing the liquid through by application of vacuum to the other end, following with a wash of clean benzene, then with acetone, and finally sucking air through to dryness. When not in use, the apparatus is protected from dust.

Acknowledgment

The author wishes to acknowledge his appreciation of the helpful criticisms of Louis C. Roess.

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Microchemical Analysis of Pigments

Used in the Fossae of the Incisions of Chinese Oracle Bones

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THE chief find of archeological excavation at the Yin Hsü site near Anyang, in northern Honan province, consists of a mass of inscriptions incised upon turtle plastrons and bovine scapulas, ascribed to the Shang epoch which is conventionally dated from 1766 to 1122 B. C. Turtle plastrons and bones were used in divination. The omens were read from cracks made by scorching pits in the bone or shell. Shoulder-blade divination was widespread in Asia, but the use of turtle shell represents a special development, and the engraving of the oracular reports upon the oracular bone and shell seems to be distinctive of the royal court of Shang. Many of the specimens still retain black or red color pigments in the fossae of the incisions.

The pigments of two specimens belonging to the Princeton University collection were investigated on request of Roswell S. Britton of the Department of Mathematics, Washington Square College, who pointed out that the red pigment is assumed to consist of cinnabar while the black pigment is thought to be the blood of animals used in divination.

To obtain samples of the pigments without damage to the objects, the oracle bones were mounted on the stage of a binocular microscope (40X total magnification), and a Leitz

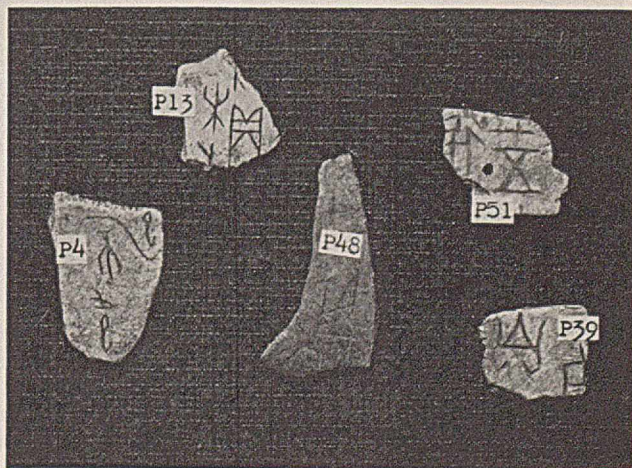


FIGURE 1. CHINESE ORACLE BONES OF THE PRINCETON UNIVERSITY COLLECTION, $\frac{3}{4}$ NATURAL SIZE

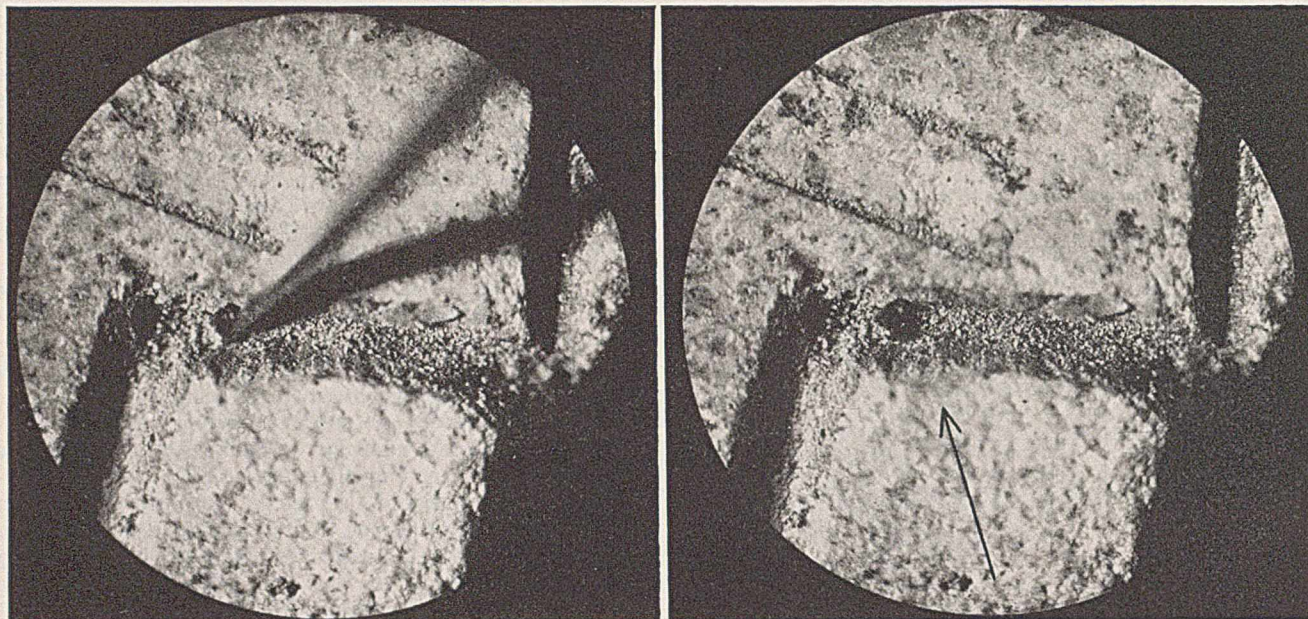


FIGURE 2. LOOSENING OF RED PIGMENT, 20X

Left, steel needle prying pigment loose
Right, loosened pigment indicated by arrow

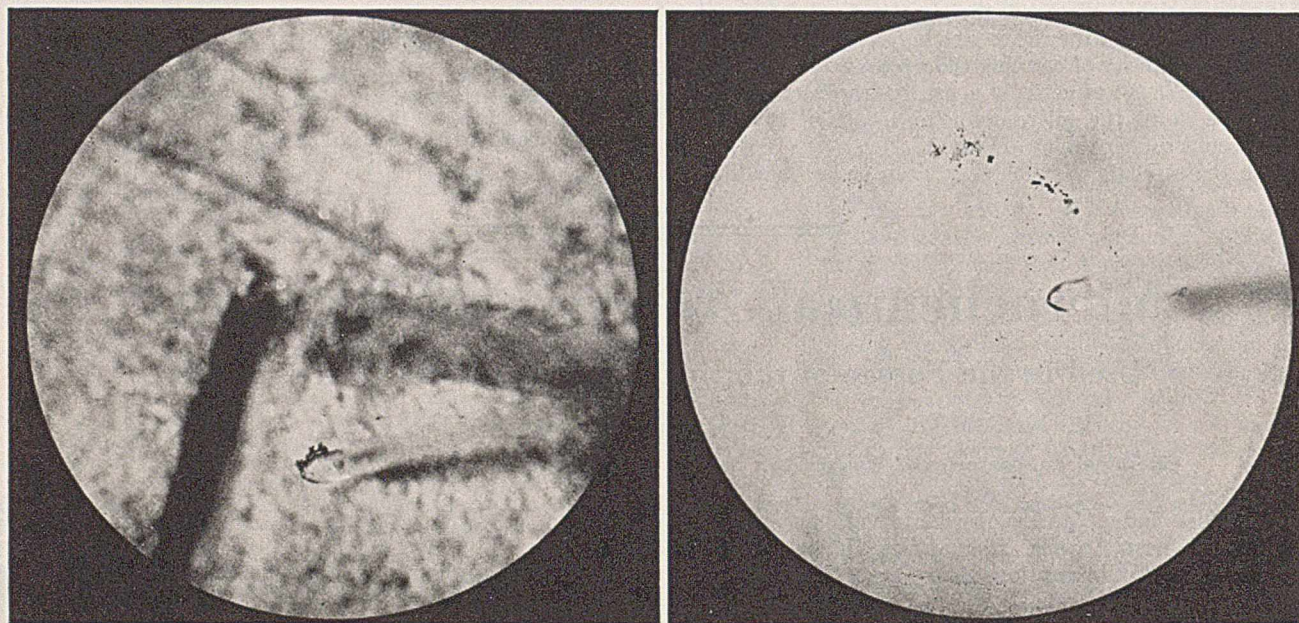


FIGURE 3. MANIPULATION OF RED PIGMENT, 20X

Left, pigment attached to glass thread visible above surface of oracle bone
Right, pigment collected in drop of water

simplified manipulator, allowing motions in the three directions with the use of rack and pinion, was used to remove small quantities of the pigment. The analysis of the red pigment will be used to give a detailed account of the procedure.

Analysis of Red Pigment

Specimens P39 and P51 (Figure 1) showed this red pigment of the characteristic color of cinnabar in the incisions. The sample for analysis was taken from specimen P39 from the first horizontal bar just below the label. Comparison of Figures 1 and 2 will permit the determination of the exact location.

First, a steel needle mounted in the manipulator was used to break loose a small amount of the pigment (Figure 2, left). Figure 2, right, shows the small cluster of pigment particles loosened by the needle. The microscope is focused on the pigment in the incision and not on the surface of the bone. The steel needle was then exchanged for a glass thread, the point of which was treated with a trace of glycerol so as just to give a surface film (1, 3). On touching the loose pigment particles with the point of the glass thread, they become attached to the latter and can be safely removed. Figure 3, left, shows the point of the glass thread with particles of pigment attached to it. Now the specimen was removed from the stage of the microscope, and a glass slide carrying a drop of 0.3 cu. mm. of water was put in its place. After focusing on the drop, the point of the glass thread was lowered into the drop. Contact of the thread with

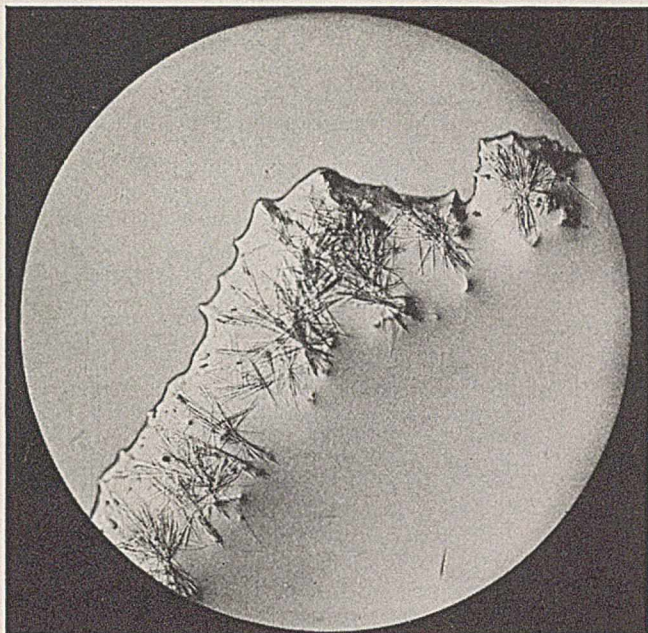


FIGURE 4. CRYSTALLIZATION OF CALCIUM SULFATE, 100 \times

the water caused the particles of pigment to float off (Figure 3, right).

Microscopic examination (80 \times) of the pigment showed that it consisted of a mixture of red particles and of colorless to yellowish particles which latter showed distinct birefringency. Neither kind of particle was attacked by cold hydrochloric acid. This test was carried out by inverting the slide and placing it on the opening of a bottle containing 13 *M* hydrochloric acid in such a way that the droplet with the particles in it could absorb hydrogen chloride from the gas space of the bottle.

Since color and solubility of the red pigment pointed toward cinnabar, it was decided to apply a confirmatory test without fur-

ther preliminaries. To this end the droplet containing the pigment particles was allowed to evaporate, after covering the slide with a larger beaker to protect it from dust. A drop of 1 cu. mm. of 1 per cent calcium chloride solution was then added to the particles, which remained behind collected in a circular area of approximately 2-mm. diameter. The slide was inverted and placed upon the opening of a bromine water bottle, so that the droplet of calcium chloride solution with the pigment particles hung into the gas space of the bottle. After 5 minutes the drop assumed a brown coloration due to an excess of bromine dissolved.

The slide was removed from the bromine water bottle, and the preparation examined under the microscope. All of the red pigment particles had disappeared, while the yellowish and colorless particles remained unchanged by the action of the bromine. These latter birefringent particles are probably quartz or silicate minerals. After a short time crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ appeared along the edge of the droplet. Figure 4 shows the appearance of this test. However, this photomicrograph was taken from a test made for the purpose of comparison on a small particle of elementary sulfur. The crystallization of calcium sulfate after oxidation and solution of the red pigment by bromine indicates the presence of sulfur in the pigment (2).

The test drop was allowed to evaporate completely. For the detection of mercury according to Emich (3), the residue was dissolved in 2 cu. mm. of 3 *M* hydrochloric acid, the solution taken up in a capillary, and there treated with a 1-mm. length of fine copper wire. After heating in the water bath for 5 minutes, the amalgamation of the copper wire was noticeable with the unaided eye. The wire was removed from the capillary, placed on a piece of filter paper, and there washed with a few drops of water. The washings were absorbed by the filter paper used to support the wire. Finally the wire was dried by pressing between filter paper, and then transferred into a dry capillary tube. Application of heat caused the mercury to distill off the wire. The condensate of mercury droplets obtained in the finely drawn-out part of the capillary tube was inspected under the microscope. Figure 5, left, shows the distillate obtained in the actual test by illumination with transmitted light while Figure 5, right, shows the same portion of the capillary tube in reflected light over a black background.

The characteristic hue of the red pigment, its insolubility in strong hydrochloric acid, and the detection of approximately equivalent quantities of sulfur and mercury in the bromine water solution prove beyond doubt that the red pigment consists of mercuric sulfide.

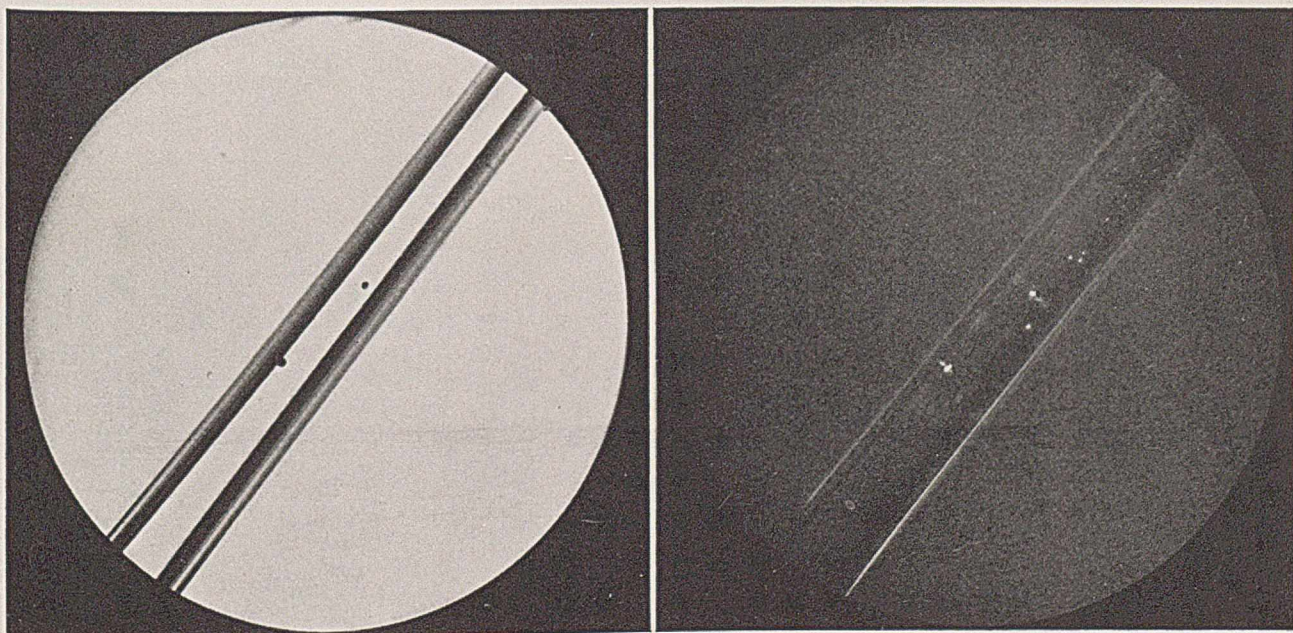


FIGURE 5. DISTILLATE OF MERCURY, 50 \times

Left, transmitted light
Right, reflected light and black background

Analysis of Black Pigment

The black pigment employed on specimens P4, P13, and P48 (Figure 1) was analyzed with the use of the technic described above. The black pigment, like the red pigment, appears mixed with the same colorless anisotropic matter, quartz or silicate, possibly loess in which the fragments have been buried for centuries. The black pigment seems to have been partially destroyed, since the content of black pigment particles varies considerably in the different specimens. The pigment of P13 appeared distinctly black, while the pigment of P48 should have been designated rather as grayish white. The difference is apparent in Figure 1. Specimen P13 was selected for the analysis of the pigment, and samples were taken from the large symbol in the right-hand corner of the specimen.

One sample was transferred into a droplet of water and treated with hydrochloric acid and bromine; these reagents were without action. After evaporation of the test droplet, the material was again carefully examined under the microscope and then ignited. On ignition the color of the black particles changed to white. A test for sulfur tried on another sample gave a negative result. Other samples were treated with sodium hydroxide solution and with glacial acetic acid; neither reagent had any solvent action on the black pigment.

According to these findings it may be assumed that the black pigment consists of some carbonaceous matter. Nega-

tive results with the hemin test of Teichman are not conclusive as far as the origin of this carbonaceous matter is concerned.

Value of Microchemical Method

The above report on the analysis of the pigments found in the incisions of Chinese oracle bones, Yin bones, may serve to demonstrate the use of those microchemical methods which have been termed classical. The amount of material required for such simple analysis may be judged from Figure 3. For the case under discussion, the claim can be made without hesitation that so little material was used for chemical analysis that even microscopic inspection of the specimens would be unable to prove that such an analysis had ever been carried out.

Literature Cited

- (1) Benedetti-Pichler, A. A., and Spikes, W. F., "Introduction to the Microtechnique of Inorganic Qualitative Analysis," Douglaston, N. Y., Microchemical Service, 1935.
- (2) Emich, F., *Z. anal. Chem.*, 32, 163 (1893).
- (3) Emich, F., and Schneider, F., "Microchemical Laboratory Manual," New York, John Wiley & Sons, 1932.

RECEIVED January 5, 1937. Presented before the New York Section of the American Chemical Society, December 11, 1936.

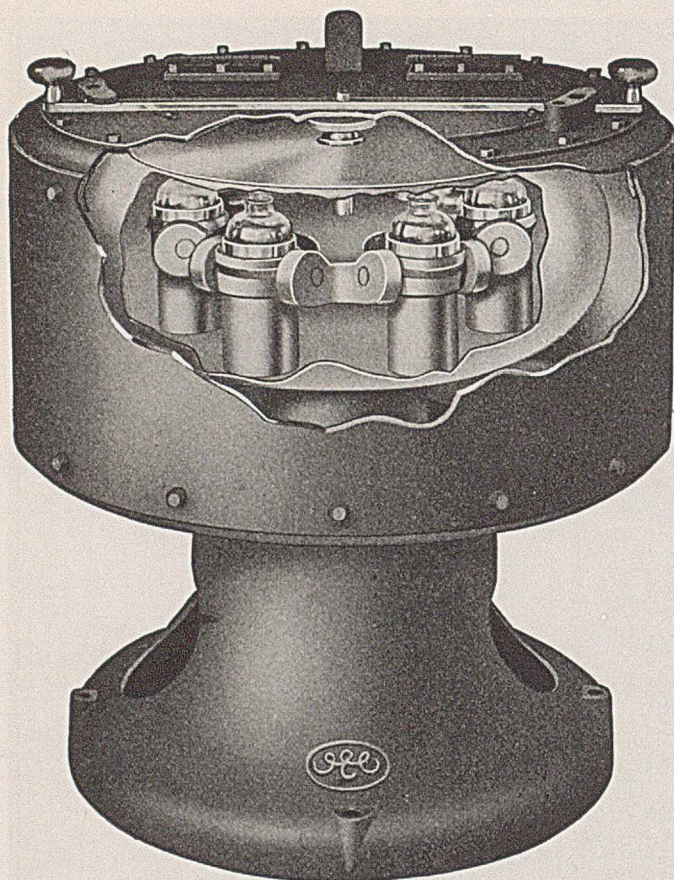
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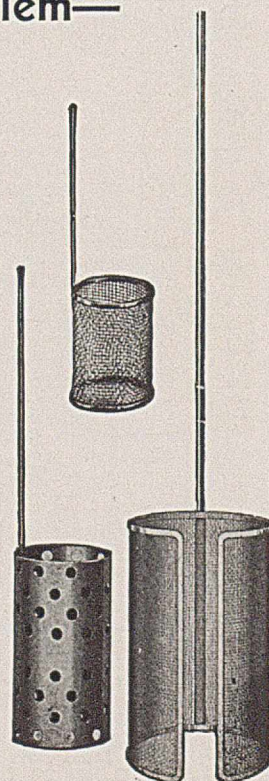
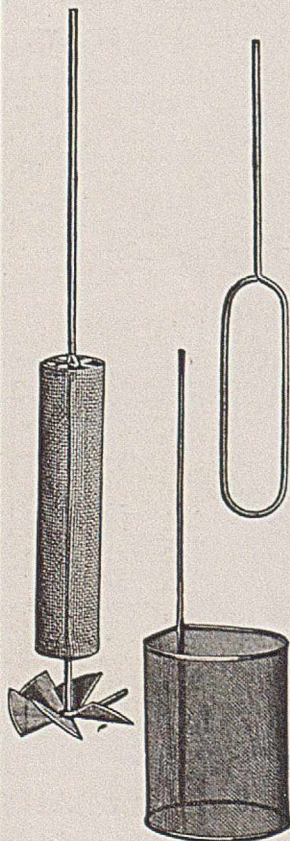
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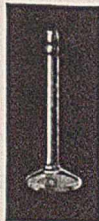
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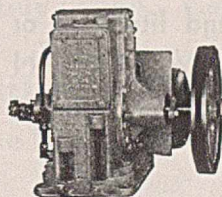
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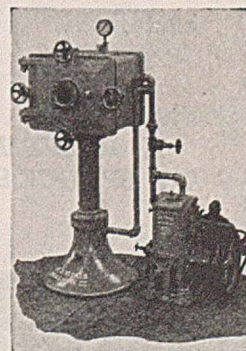
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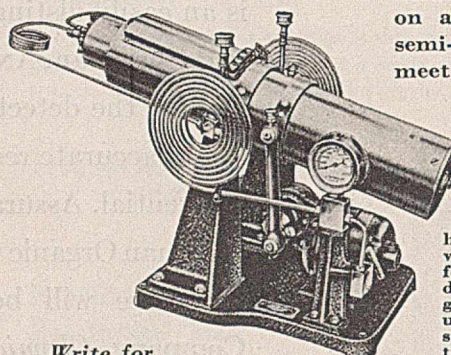
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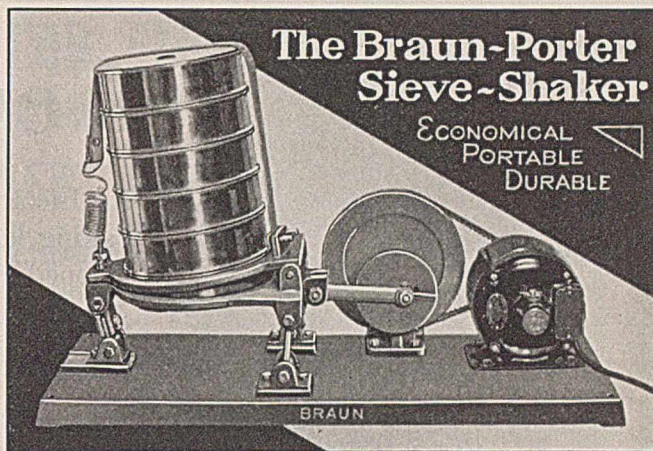
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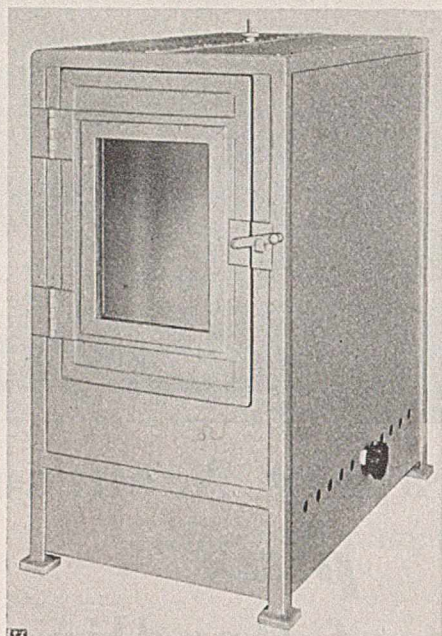
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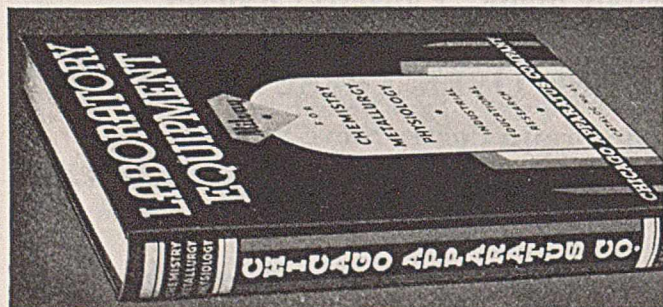
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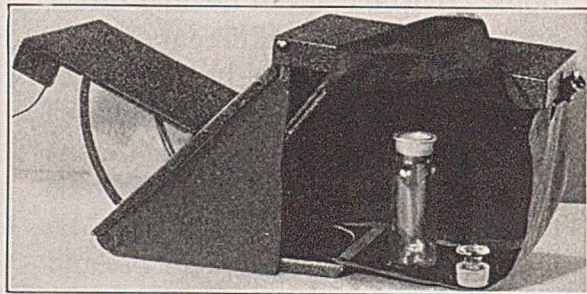


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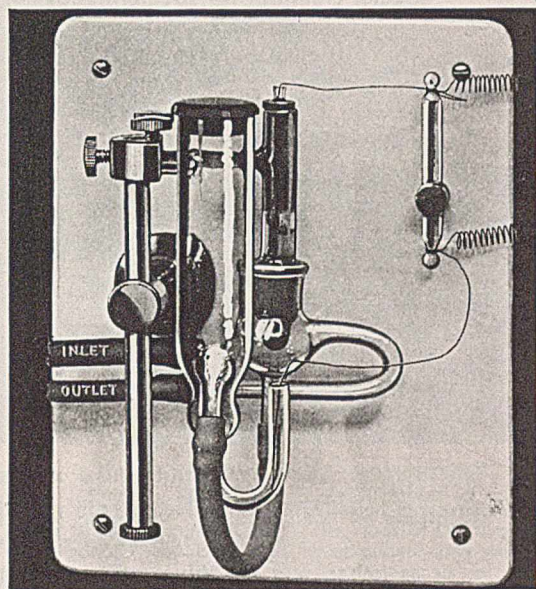


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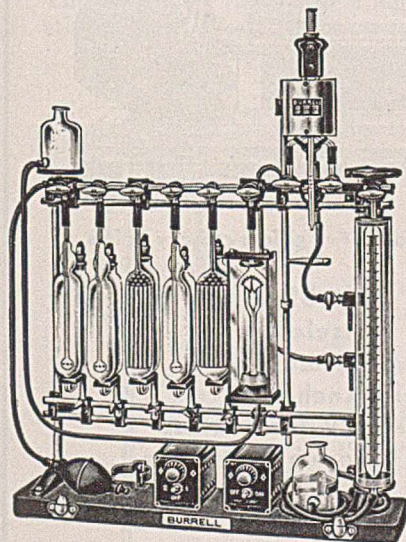
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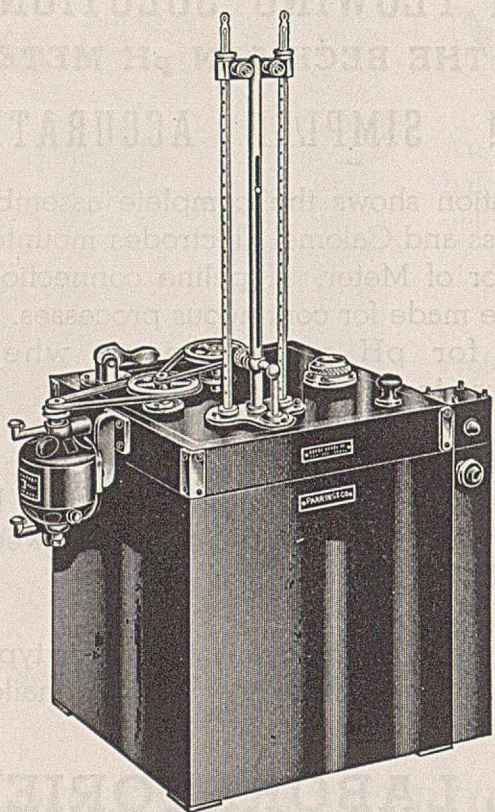
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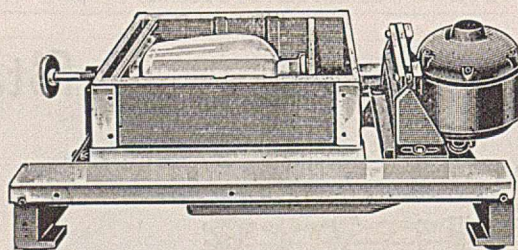
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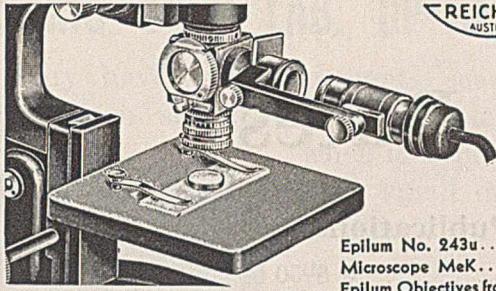
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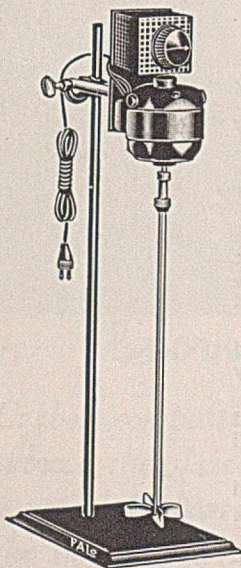
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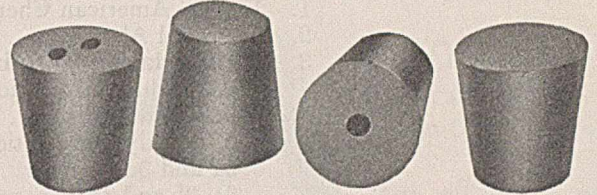
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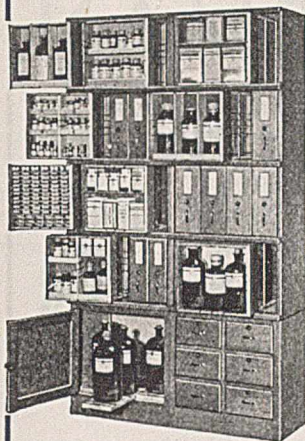
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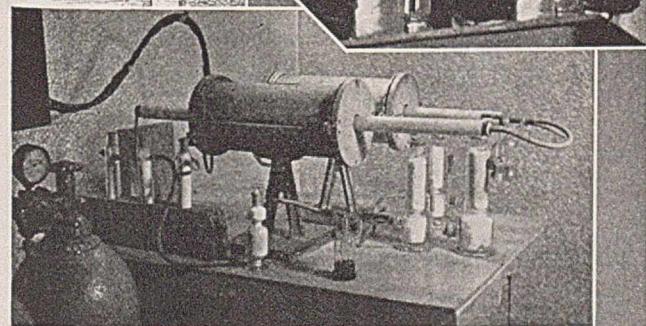
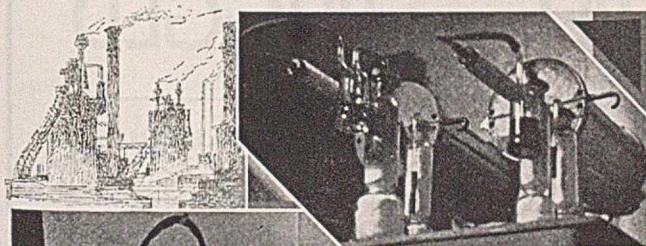
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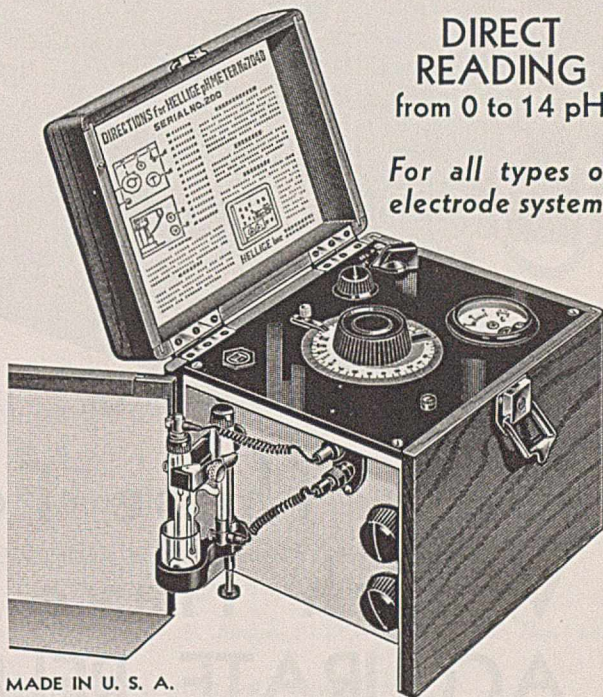
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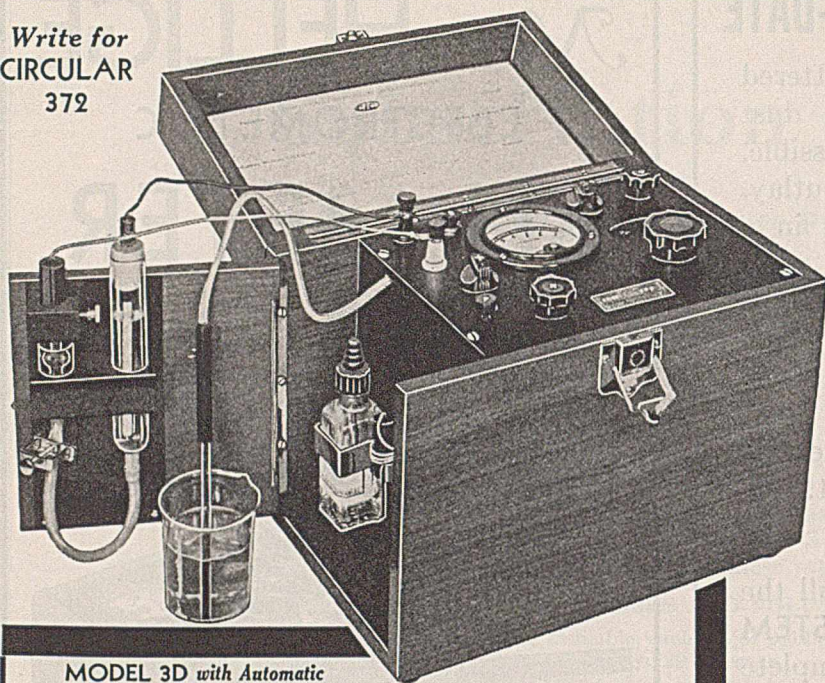


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