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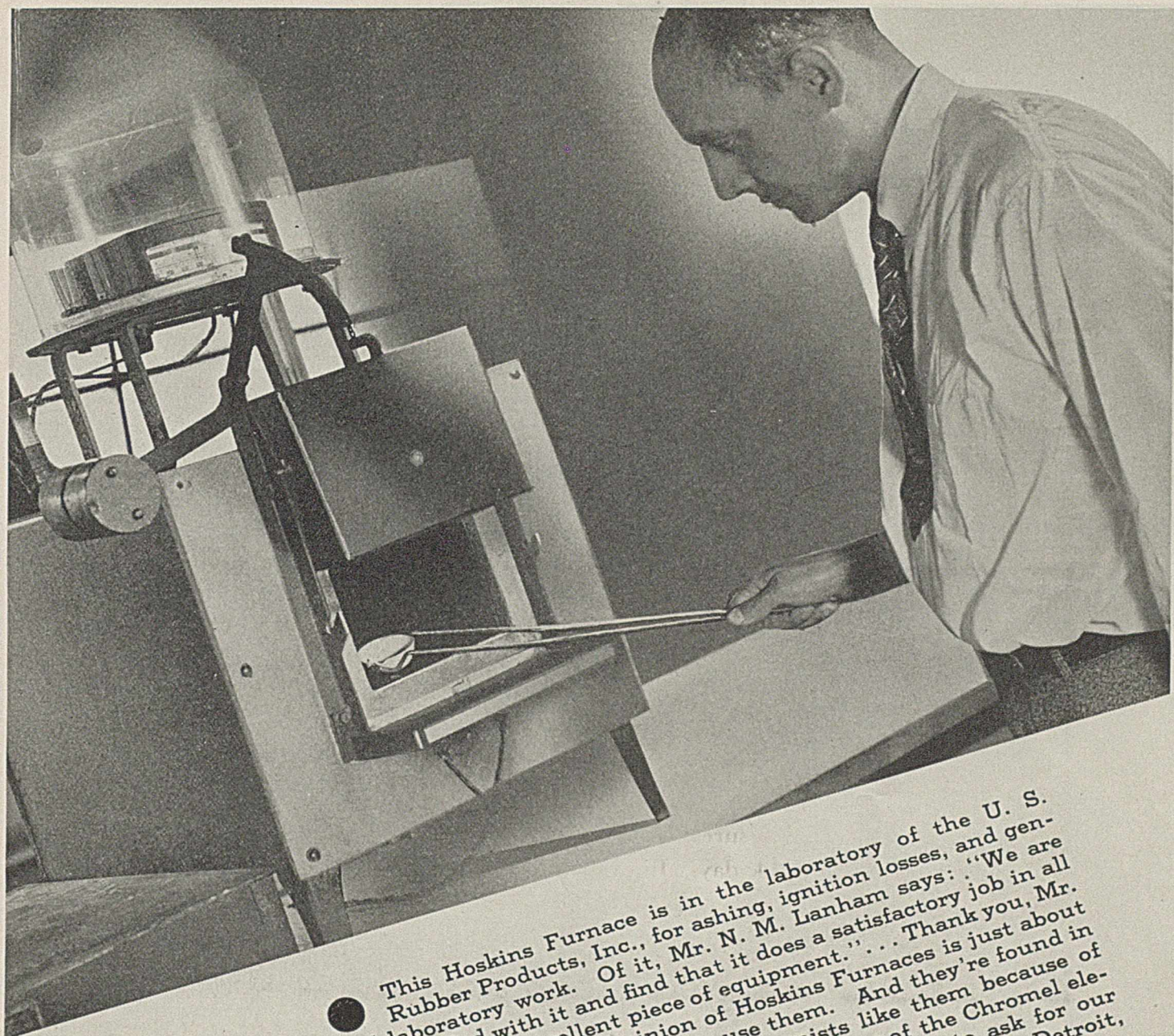


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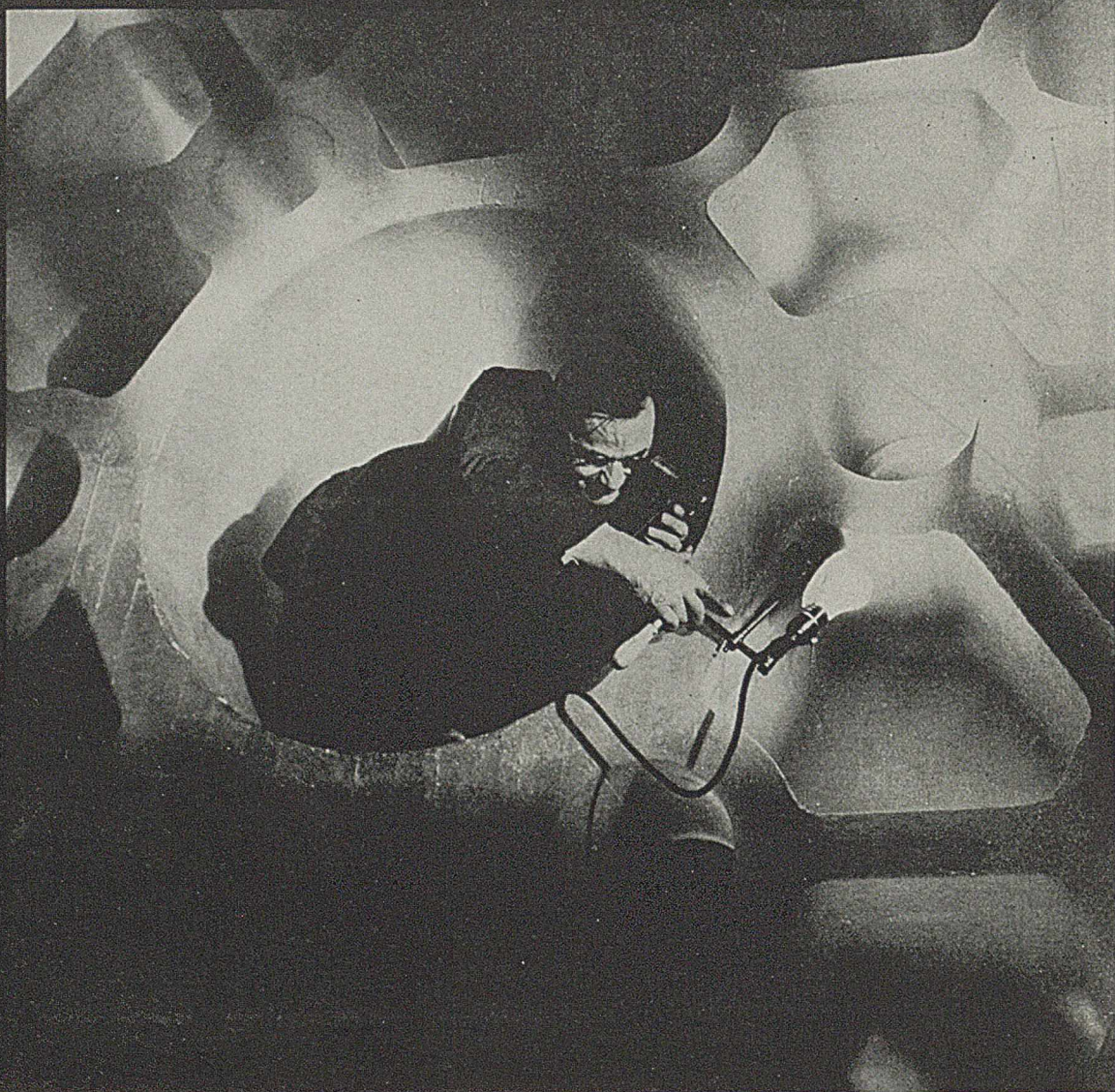
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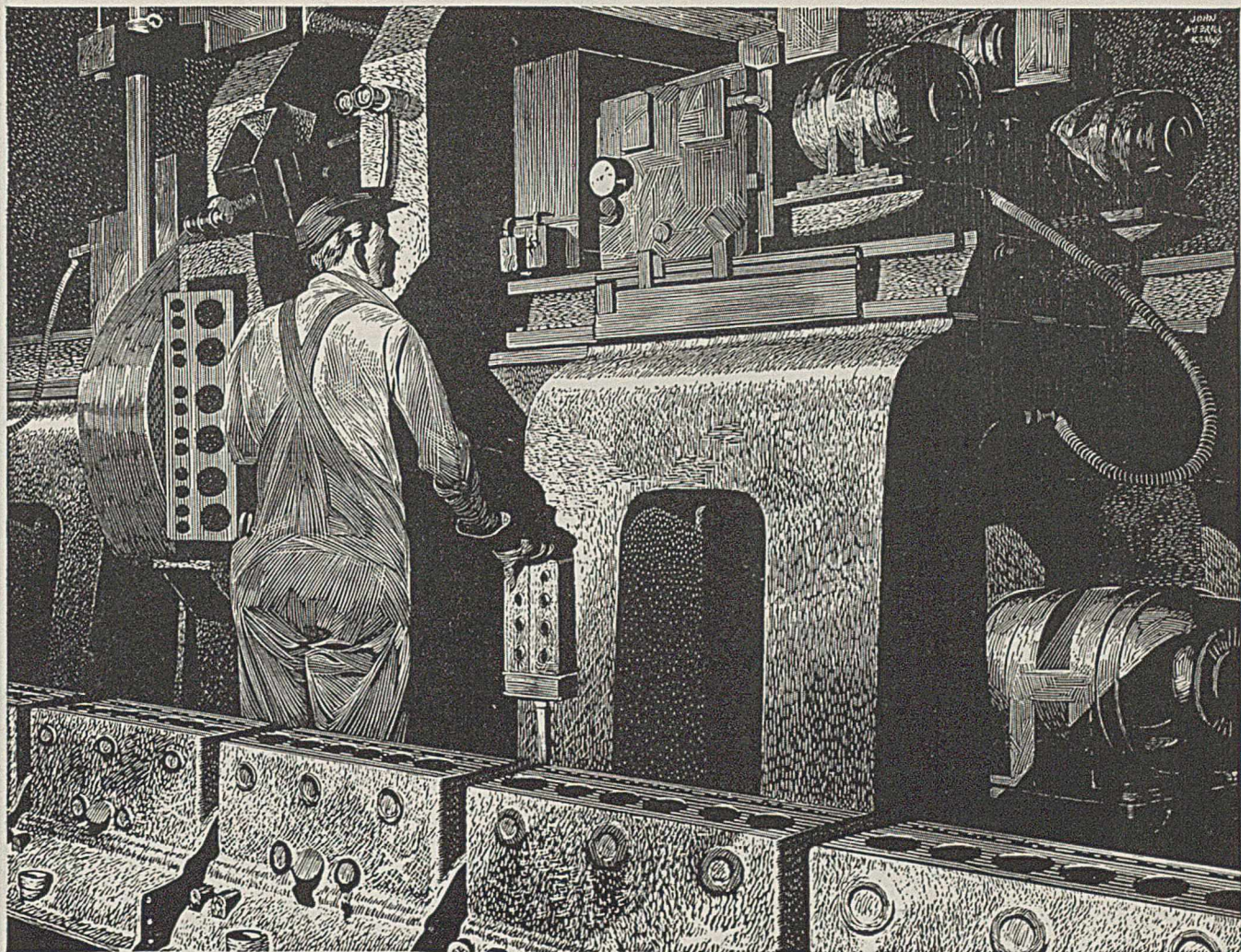
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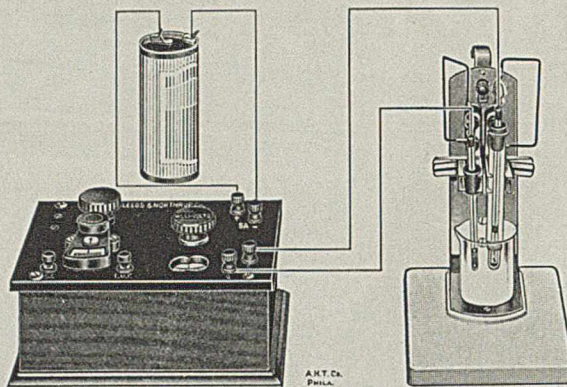
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INDUSTRIAL and ENGINEERING CHEMISTRY

Harrison E. Howe, Editor

Titration of Fluorine in Aqueous Solutions

R. J. ROWLEY AND H. V. CHURCHILL

Aluminum Company of America, New Kensington, Pa.

Fluorine may be titrated quantitatively with thorium nitrate (0.1 *N*) in an aqueous solution, instead of the 48 per cent ethyl alcohol solution recommended by Willard and Winter (4), by closely controlling the pH of the solution to be titrated. A pH of from 2.9 to 3.1 was found to be suitable, and is obtained by the use of monochloroacetic acid, half neutralized by sodium hydroxide. The end point is more definite in an aqueous solution than in a 48 per cent ethyl alcohol solution. When using a 48 per cent alcoholic solution and 0.1 *N* thorium nitrate, a fluorine content of approximately 20 mg. can be titrated to a fairly definite end point; if a greater amount of fluorine is present, the end point is indefinite. However, in an aqueous solution (using 0.1 *N* thorium nitrate) as much as 50 mg. of fluorine may be titrated to a definite end point.

WILLARD and Winter's volumetric method (4) for determination of fluorine consists of the titration of soluble fluorides or silico fluorides in a 48 per cent ethyl alcohol solution with a standard thorium nitrate solution, using zirconium nitrate-sodium alizarin sulfonate as an indicator. In their original article, Willard and Winter stated, "Since thorium fluoride is quite insoluble in a solution containing ethyl alcohol, an attempt was made to titrate fluoride solutions containing an equal volume of ethyl alcohol with standard thorium nitrate, using the zirconium-alizarin mixture to determine the point at which all of the fluorine was precipitated. The results with pure fluoride solutions were good." Armstrong (1) modified the method by eliminating the use of zirconium nitrate in the indicator, since thorium itself forms a pink lake with sodium alizarin sulfonate in acid solutions. He later found (2) that in determining very small amounts of fluorine in biological materials, an aqueous, rather than an alcoholic solution gave better results. If thorium fluoride so behaves in aqueous solutions that a satisfactory titration can be made when the amount present is only 0.001 mg., a titration of larger amounts of fluorine in aqueous solutions should be satisfactory.

This matter has been investigated. The effect of acid concentration (determined by pH measurements) was first studied.

A standard sodium fluoride solution containing 1 mg. of fluorine per cc. was made up and standardized by titration in a 48 per cent ethyl alcohol solution. Titrations were then made on aqueous solutions having a pH ranging from approximately 1.0 to 5.0. These values were obtained by adding standard *N* or 0.1 *N* hydrochloric acid solution in the correct amount to give the desired pH. All solutions were titrated in a volume of 100 cc., using 8 drops of 0.05 per cent aqueous sodium alizarin sulfonate as an indicator. After the titration had been made, the pH of the solution was determined with the glass electrode, using the Beckmann pH meter. The end points observed were as given in the following tables. The thorium nitrate used had a normality of 0.092, 1 cc. being equal to 0.00175 gram of fluorine.

TABLE I. EFFECT OF ACIDITY OF AQUEOUS SOLUTION

Volume Cc.	HCl Added Cc.	pH ^a	F Added Gram	Titra- tion Cc.	F Found Gram	End Point	
100	10	(<i>N</i>)	1.1	0.0100	?	?	Indistinct
100	1	(<i>N</i>)	2.1	0.0100	6.9	0.01208	Indistinct
100	0.1	(<i>N</i>)	3.15	0.0100	5.8	0.01015	Good
100	10	(0.1 <i>N</i>)	1.9	0.0100	7.9	0.01383	Indistinct
100	1	(0.1 <i>N</i>)	2.9	0.0100	5.8	0.01015	Good
100	0.5	(0.1 <i>N</i>)	3.4	0.0100	5.7	0.00998	Good ^b
100	0.25	(0.1 <i>N</i>)	4.1	0.0100	5.0	0.00875	Indistinct
100	0.10	(0.1 <i>N</i>)	4.7	0.0100	4.4	0.00770	Indistinct

^a pH values were obtained after titration was completed.

^b The end point obtained at this pH, while very good, is similar to that obtained when titrating in 48 per cent ethyl alcohol solution at approximately the same pH. The flashes of pink observed disappear upon stirring, although finally a distinct and permanent pink end point will be reached.

Table I shows that a pH of approximately 3.0 gives the most positive end point, and that a pH of 2.9 to 3.4 gives results which are stoichiometrically correct. Hoskins and Ferris (3) stated that monochloroacetic acid gives a pH of 2.8 in water and a pH of 3.5 in a 48 per cent ethyl alcohol solution, and they recommended that this buffer be used at half neutralization—i. e., at maximum buffering power. In this laboratory the authors had been using this buffer with satisfactory results. They have, however, found it convenient to make up the buffer in a single solution, somewhat more concentrated than that previously recommended, by dissolving 9.448 grams of monochloroacetic acid and 2.000 grams of sodium hydroxide in 100 cc. of water.

Varying amounts of this buffer were added to 100 cc. of water, and the pH was determined. Results obtained were as follows:

Volume Cc.	Buffer Cc.	pH	Volume Cc.	Buffer Cc.	pH
100	0.1	3.6	100	1.0	3.1
100	0.5	3.2	100	2.0	3.0

To determine the effect of varying amounts of buffer in the fluoride solutions, 10-cc. aliquots of the standard sodium fluoride solution (containing 1 mg. of fluorine per cc.) were made up to a volume of 100 cc. and titrated as before. After the solutions had been titrated the pH was determined.

TABLE II. EFFECT OF VARYING AMOUNTS OF BUFFER PER 100 Cc.

Buffer Added Cc.	pH	F Added Gram	Titration Cc.	F Found Gram	End Point
0.1	3.6	0.0100	5.6	0.0098	Fading
0.5	3.2	0.0100	5.75	0.01006	Good
1.0	3.1	0.0100	5.75	0.01006	Good
2.0	3.0	0.0100	5.75	0.01006	Good

The effect of varying amounts of fluorine was next studied to determine if the equivalence of the thorium nitrate solution is exact throughout the range of 1 to 50 mg. of fluorine. Varying amounts of the standard sodium fluoride solutions were made up to volumes of 50 and 100 cc., 1 cc. of the buffer solution and 4 or 8 drops of sodium alizarin sulfonate were added, and the solutions were titrated with 0.092 *N* thorium nitrate. After titration, the pH of each solution was determined. The end point was good in all cases.

TABLE III. EFFECT OF VARYING AMOUNTS OF FLUORINE

Volume Cc.	pH	F Added Gram	Titration Cc.	F Found Gram
100	3.1	0.0010	0.6	0.00105
100	3.1	0.0050	2.9	0.00508
100	3.1	0.0100	5.75	0.01006
100	3.1	0.0200	11.6	0.02030
100	3.1	0.0250	14.0	0.02450
100	3.0	0.0500	28.5	0.04988
50	3.0	0.0010	0.6	0.00105
50	3.0	0.0050	2.9	0.00508
50	3.0	0.0100	5.75	0.01006
50	3.0	0.0200	11.5	0.02013

It is evident from Table III that the equivalence of the thorium nitrate is uniform throughout the range, and that 1 to 50 mg. of fluorine may be quantitatively determined by titration with thorium (0.1 *N*) in an aqueous solution, thereby saving the expense of using ethyl alcohol. The authors also attain greater accuracy because the end point is more definite in the aqueous solution. Three analysts, who had had little, if any, experience with the method, had no trouble in observing the

correct end point in the aqueous solutions, although they experienced considerable difficulty when they tried titrating the alcoholic solutions.

It also appears that a larger amount of fluorine may be satisfactorily titrated in an aqueous than in an alcoholic medium.

In titrations of very small amounts of fluorine, when using 0.01 *N* instead of 0.1 *N* thorium nitrate, the titration is very sensitive with respect to the pH of the solution. Apparently there is some optimum pH for this titration of smaller amounts of fluorine in an aqueous solution that has not yet been definitely established. Further work is being done on this phase of the problem.

The method now recommended for the titration of fluorine when using 0.1 *N* thorium nitrate is as follows:

Prepare the buffer by dissolving 9.448 grams of monochloroacetic acid and 2.000 grams of sodium hydroxide in 100 cc. of water.

Take an aliquot of 50 or 100 cc., depending upon the amount of fluorine present. If 50 cc. are taken, dilute to 100 cc. with water. Add 8 drops of sodium alizarin sulfonate indicator. Adjust the acidity back and forth with 2 per cent sodium hydroxide and 1 to 200 hydrochloric acid, finally leaving the solution just acid and the pink color discharged. Add 1 cc. of the buffer solution and titrate with 0.1 *N* thorium nitrate to a permanent pink. A blank determination should be made.

Standardize the thorium nitrate by titration of the fluorine obtained by distillation of 100 per cent natural cryolite, fluorspar, or sodium fluoride.

The authors' method of titration in aqueous solution is applicable to the titration of fluorine when interfering substances are not present—for example, they have applied it with satisfactory results to the determination of fluorine in lithium fluoride and in sodium fluoride, without previous separation of the fluorine by distillation. The aqueous method has also been used successfully on many types of food.

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- (1) Armstrong, W. D., *IND. ENG. CHEM., Anal. Ed.*, 8, 384-7 (1936).
- (2) Armstrong, W. D., *J. Am. Chem. Soc.*, 55, 1741-2 (1933).
- (3) Hoskins and Ferris, *IND. ENG. CHEM., Anal. Ed.*, 8, 6-9 (1936).
- (4) Willard and Winter, *Ibid.*, 5, 7-10 (1933).

RECEIVED September 23, 1937.

The T-50 Test Applied to Zinc Oxide Compounds

GEORGE S. HASLAM AND CLARENCE A. KLAMAN

Research Division, The New Jersey Zinc Company, Palmerton, Pa.

The authors have adapted the T-50 test, as described by Gibbons, Gerke, and Tingey (1) in 1933, to a study of the curing rate of zinc oxides in rubber compounds. A new method of expressing results obtained in this test is used which condenses the data and renders comparisons relatively easy. The major variables in zinc oxide, particle size and chemical purity, have been studied with several accelerators and conclusions drawn as to the effectiveness of these variations in zinc oxide on curing rate in both gum stocks and loaded stocks.

Data on the reproducibility of the test and the effect of the freezing temperature and of shelf aging are also given.

THE function of zinc oxide in the vulcanization reaction and the effect of various modifications of zinc oxide on the curing rate of rubber compounds have received considerable attention. In the past few years, the development of a number of new grades of zinc oxide, having a wide range of chemical and physical properties, has served to increase the interest in this pigment and in methods of evaluating the effect of these several modifications in the laboratory.

Several methods of attack have been applied to studies of the effect of zinc oxide on the curing rate of rubber, ranging from the analytical determination of free and combined sulfur, through the conventional physical tests, to actual performance evaluation. This latter method is obviously the most satisfactory but is also the most costly and time-consuming. The use of physical measurements, such as stress-strain properties, has been the most widely used method of evaluating compounds, the principal objections being the inherent inaccuracies of rubber testing and the

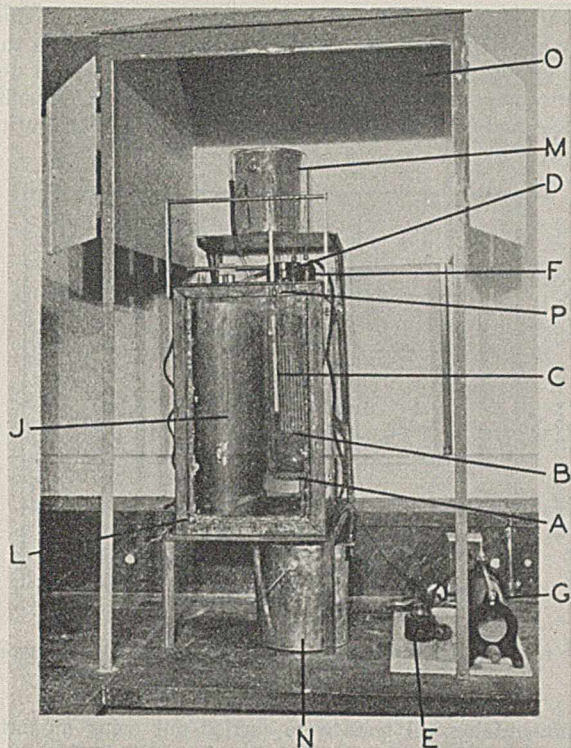


FIGURE 1. GENERAL ASSEMBLY OF APPARATUS

- | | |
|--------------------------|---------------------------|
| A. Testing Dewar flask | J. Insulated cooling tank |
| B. Specimen rack | L. Glass-windowed tank |
| C. Thermometer | M. Acetone reservoir |
| D. Stirrer | N. Acetone overflow |
| E. Stirrer speed control | O. Ventilated hood |
| F. Heater | P. Weights |
| G. Rheostat for heater | |

failure to differentiate between "state of cure" and the actual reinforcing value of the pigment.

In 1933, Gibbons, Gerke, and Tingey (1) published a discussion of a test method which they called the T-50 test. Since that time relatively little has been published, although it is known that the test is being used in a number of laboratories in a routine way. Inasmuch as this test is particularly sensitive to state of cure, following, in a general way at least, the combined sulfur analysis, it is obviously of real interest in studies of any factors affecting the curing rate. In this paper, the authors report their efforts to apply the T-50 test to a study of the effect of zinc oxide and zinc oxide variables on the curing rate of rubber compounds.

Discussion of Test Method

Briefly, the T-50 test consists of stretching a 1.5 by 0.075 inch strip of rubber to a predetermined elongation (500 per cent was used in all the tests reported in this paper); while in the extended position, the specimen is frozen at -70°C . in acetone, the temperature of which has been reduced by passing it through a coil immersed in solid carbon dioxide and acetone. The holder is released while the rubber is frozen, the acetone bath is allowed to heat up, and the temperature at which the rubber regains its elastic properties is observed. The temperature at which the rubber has retracted to 50 per cent of its original elongation is known as the T-50.

The apparatus used is essentially the same as that described by the above-mentioned investigators and is shown in Figures 1 and 2. Figure 3 shows the redesigned specimen clamp, which, by eliminating the necessity for screwing the test piece in place increases the ease and speed with which

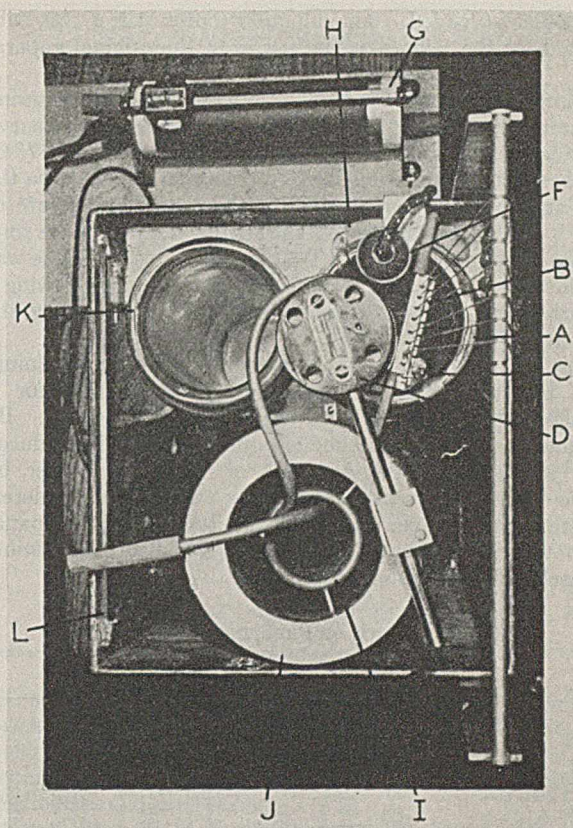


FIGURE 2. TOP VIEW OF APPARATUS

- | | |
|------------------------|-----------------------------|
| A. Testing Dewar flask | H. Siphon overflow |
| B. Specimen rack | I. Copper cooling coil |
| C. Thermometer | J. Insulated cooling flask |
| D. Stirrer | K. Conditioning Dewar flask |
| F. Heater | L. Glass-windowed tank |
| G. Rheostat for heater | |

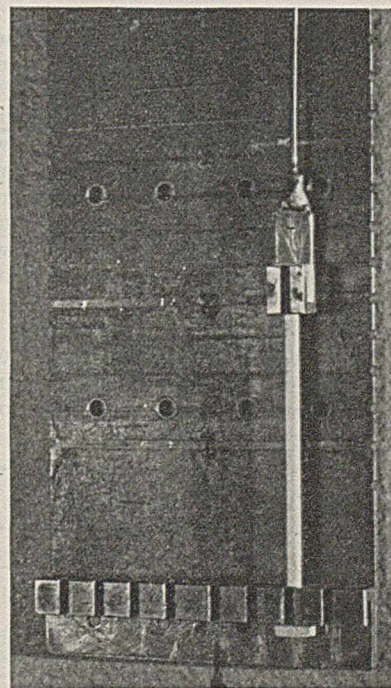


FIGURE 3. CLOSE-UP OF SPECIMEN HOLDER

the holder is loaded. An induction motor stirrer was substituted for the remote-driven stirrer of the original apparatus.

In order to obtain a satisfactory value to express curing rate, an extensive study of the time of cure versus T-50 curve was made. In all cases a compound having a T-50 of -7°C . was a satisfactorily cured stock. In order to condense the data and to use a single value for the expression of rate of cure, it was decided to express the results in terms of the time of cure in minutes to give a T-50 of -7°C . This value was obtained by plotting the T-50 for a range of cures, drawing a smooth curve through these points, and interpolating the time at -7°C .

This value should not be interpreted as the optimum cure, but rather as the length of time required for a specified stock to reach a definite state of cure. By this means, the curve of time of cure versus T-50 is reduced to a single value, the accuracy of which is greater by virtue of the fact that it is essentially an average of 6 determinations rather than one. Physical tests and performance evaluation will still have to be used to establish the optimum for each different compound.

TABLE I. EFFECT OF FREEZING TEMPERATURE

Cure at 30 lb.	-70°C .			-50°C .			
	1st test	2nd test	Av.	1st test	2nd test	Av.	
Compound containing 5 parts zinc oxide A	15 + 2.0	+ 1.0	+ 1.5	+ 2.5	-11.5	-11.5	-11.5
	30 -10.5	-11.5	-11.0	-11.5	-11.5	-11.5	-11.5
	45 -20.0	-18.5	-19.6	-21.0	-20.0	-20.5	-20.5
	60 -26.5	-25.0	-25.8	-26.5	-25.0	-25.8	-25.8
	90 -35.0	-31.0	-33.0	-33.0	-30.5	-31.8	-31.8
	120 -40.0	-33.5	-36.8	-35.5	-33.5	-34.5	-34.5
Time to T-50 of -7°C .	26.0	25.5	26.0	26.0	26.0	26.0	26.0
Compound containing 200 parts zinc oxide A	15 + 9.0	+ 8.5	+ 8.8	+ 9.0	+ 9.5	+ 9.3	+ 9.3
	30 + 1.5	+ 0.5	+ 1.0	0	+ 2.0	+ 1.0	+ 1.0
	45 - 7.0	- 7.5	- 7.3	- 7.0	- 7.0	- 7.0	- 7.0
	60 -12.5	-12.5	-12.5	-12.0	-12.0	-12.0	-12.0
	90 -20.0	-19.0	-19.5	-19.5	-19.5	-19.5	-19.5
	120 -23.0	-22.0	-22.5	-22.0	-21.5	-21.8	-21.8
Time to T-50 of -7°C .	45	44	44.5	45	45	45	45

* Unhook.

Some difficulty was encountered in reaching and holding a temperature of -70°C ., particularly on days when the laboratory temperature was high. As a matter of interest, a series of tests was carried out using freezing temperatures of -70° and -50°C . The data obtained are shown in Table I. As these data indicate that in the present investigation the starting temperature was not particularly important, a compromise was made. In every case the acetone temperature was reduced to at least -65°C ., but no effort was made to obtain exactly -70°C . as did the investigators mentioned above.

It was also desirable to determine what effect shelf aging over a period of a week or 10 days might have on the T-50 results. One compound was selected and run in duplicate with 3- or 4-day intervals between determinations. These

TABLE II. REPRODUCIBILITY OF RESULTS

Cure	Days of Shelf Aging										Av. of 10 Tests
	1		3		7		9		15		
5	+ 9.0	+ 9.5	+11.0	+10.3	+11.0	+10.3	+10.5	+10.3	+ 8.5	+ 7.5	+ 9.8
10	+ 1.0	+ 4.0	+ 6.0	+ 1.5	+ 2.8	+ 3.5	+ 3.0	+ 2.5	+ 2.0	+ 1.0	+ 2.7
15	- 3.5	- 3.0	- 2.0	- 3.5	- 2.5	- 3.3	- 2.5	- 4.0	- 4.3	- 5.2	- 3.4
30	-17.0	-17.0	-17.0	-17.3	-16.3	-17.0	-17.0	-17.5	-16.0	-18.0	-17.0
45	-24.5	-25.5	-26.5	-26.0	-25.5	-25.8	-25.8	-26.0	-25.8	-26.5	-25.8
60	-29.0	-29.0	-31.0	-30.0	-28.5	-32.3	-29.5	-30.0	-28.5	-30.0	-29.8
^a	16.5	-17.0	19.0	16.5	17.5	17.5	17.0	17.0	18.0	17.0	17.3

^a Time of cure (minutes) to T-50 of -7°C .

data are shown in Table II and indicate that the reproducibility between the first and after 14 days is as good as that obtained on any one day. All results herein reported were run on compounds which were cured at least 24 hours before the test and none was held more than a week after curing.

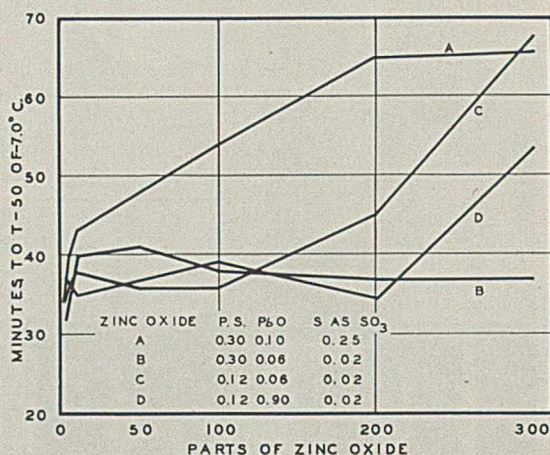


FIGURE 4. TESTS ON COMPOUND 1, CAPTAX

Summarizing, all tests were carried out using an initial elongation of 500 per cent, a freezing temperature of less than -65°C ., and a shelf-aging period of at least 1 day but not more than 7 days. All results wherever possible are expressed in terms of time of cure in minutes to give a T-50 of -7°C .

Discussion of Results

For this preliminary survey, 4 standard zinc oxides representing modifications of particle size, lead, and sulfur content were chosen. Zinc oxide A is a slow-curing oxide and zinc oxide B is a fast-curing oxide of essentially the same particle size. Zinc oxides C and D are oxides of fine particle size, the former being essentially lead-free and the latter containing approximately 1 per cent of lead as the oxide which has an accelerating effect particularly evident with certain accelerators. The particle sizes and chemical analyses of these oxides are given in Table III.

TABLE III. PROPERTIES OF ZINC OXIDES USED

Zinc Oxide	Particle Size Microns	Pb as PbO	S as SO ₃
A	0.30	0.10	0.25
B	0.30	0.06	0.02
C	0.12	0.06	0.02
D	0.12	0.90	0.02

The first series of tests was in a compound accelerated with mercaptobenzothiazole (Captax) and having the following base formula, hereafter referred to as compound 1:

Smoked sheet	100
Sulfur	3
Captax	1
Agerite powder	1
Stearic acid	3

The zinc oxide was varied from 2 to 300 parts on 100 parts of rubber. The results, expressed in the time required to reach a T-50 of -70°C ., are shown in Table IV and Figure 4.

TABLE IV. TESTS ON COMPOUND 1, CAPTAX

Zinc Oxide	Cure at 126° C. Min.	Parts of Zinc Oxide						
		2	5	10	50	100	200	300
A	15	+ 8.0	+10.5	+10.0	+12.5	+13.0	+13.7	+16.5
	30	- 4.0	- 1.0	+ 0.5	+ 2.0	- 2.5	+ 0.6	+ 1.0
	45	-13.5	-10.0	- 8.0	- 6.0	- 4.5	- 0.7	- 1.7
	60	-20.5	-15.5	-15.0	-12.5	- 8.5	- 5.5	- 4.5
	75	-25.0	-22.5	-20.5	-17.5	-15.0	- 9.3	- 8.8
B	10	+ 8.0	+10.5	+ 9.5	+10.0	+10.0	+13.0	+10.0
	15	+ 4.0	+ 6.5	+ 7.5	+ 7.0	+ 6.0	+ 7.0	+ 7.5
	30	- 7.0	- 4.0	- 2.0	- 2.0	- 3.0	- 3.0	- 2.5
	45	-13.5	-11.0	- 9.5	- 9.0	-10.0	- 9.0	- 8.5
	60	-19.5	-16.0	-15.0	-15.5	-15.5	-16.5	-17.0
C	10	+ 9.5	+10.5	..	+ 7.5	+ 8.5	+ 9.5	+11.0
	15	+ 6.5	+ 8.0	+ 6.5	+ 3.5	+ 3.0	+ 6.0	+ 8.0
	30	- 5.5	- 3.0	- 4.0	- 6.0	- 4.0	- 0.5	+ 4.0
	45	-12.0	-11.0	-10.5	-10.0	- 9.5	- 6.5	- 1.5
	60	-18.5	-17.0	-15.5	-14.0	-15.0	- 9.0	- 4.0
D	10	+11.0	+11.0	+ 9.0	+ 7.5	+ 8.0	+ 7.0	+10.5
	15	+ 8.5	+ 6.5	+ 5.0	+ 4.5	+ 5.0	+ 3.5	+ 7.5
	30	- 3.0	- 4.5	- 5.0	- 4.0	- 3.5	- 5.5	+ 0.5
	45	-10.5	-11.5	-11.5	-10.0	- 9.0	-10.0	- 3.0
	60	-17.5	-17.0	-16.0	-14.5	-14.0	-14.5	- 9.0
75	-22.0	-22.0	-20.5	-19.5	-18.5	-18.0	-12.0	
		Time of Cure (Minutes) to T-50 of -7.0° C.						
A		34	39.5	43.0	47.8	54.0	65.0	66.0
B		32	35	40	41	38	37	37
C		34.5	37	38	36	36	45	67.5
D		37.5	36	35	36.5	39	34.5	53.5

TABLE V. TESTS ON COMPOUND 2, 808

Zinc Oxide	Cure at 126° C. Min.	Parts of Zinc Oxide						
		2	5	10	50	100	200	300
A	10	+10.0	+ 9.5	+ 9.5	+ 8.0	+13.0	+21.0	No cure
	15	+ 8.0	+ 7.5	+ 8.0	+ 7.5	+12.0	+20.5	No cure
	30	+ 2.5	+ 2.0	+ 2.5	+ 4.0	+ 9.0	+17.5	+22.0
	45	- 1.5	- 2.5	- 3.0	+ 0.5	+ 4.5	+16.0	+20.0
	60	- 4.5	- 6.0	- 6.5	- 3.5	+ 2.0	+13.0	+15.5
B	10	+10.0	+10.5	+10.0	+ 9.5	+11.0	+15.5	+13.0
	15	+ 8.0	+ 7.5	+ 9.0	+ 7.0	+ 9.0	+13.5	+11.0
	30	+ 3.5	+ 2.0	+ 2.5	+ 1.0	+ 3.0	+ 5.0	+ 4.0
	45	- 1.5	- 2.0	- 3.5	- 2.5	- 3.0	- 1.0	- 2.5
	60	- 4.5	- 5.5	- 6.0	- 7.0	- 5.5	- 4.0	- 6.0
C	10	+10.0	+10.0	+12.0	+ 9.5	+ 8.5	+12.0	+15.0
	15	+ 8.0	+ 7.5	+ 7.5	+ 7.0	+ 6.0	+11.0	+13.0
	30	+ 1.0	+ 2.5	+ 2.0	+ 0.5	0	+ 3.0	+12.0
	45	- 3.5	- 3.0	- 4.0	- 4.5	- 4.0	0	+ 8.5
	60	- 7.0	- 7.5	- 7.0	- 8.0	- 7.5	- 3.0	+ 2.5
D	10	+ 9.0	+ 9.5	+ 9.0	+ 9.0	+10.0	+ 7.5	+14.5
	15	+ 7.5	+ 6.5	+ 6.0	+ 4.5	+ 5.5	+ 5.5	+12.5
	30	+ 2.0	0	- 0.5	- 0.5	+ 2.0	0	+ 5.0
	45	- 2.0	- 4.5	- 3.5	- 5.0	- 0.5	- 2.5	+ 2.5
	60	- 7.5	- 8.5	- 8.5	- 7.5	- 3.5	- 4.0	- 0.5
75	-11.0	-11.5	-11.5	-11.5	- 6.5	- 7.0	- 2.5	
		Time of Cure (Minutes) to T-50 of 0° C.						
A		41	36	36	46	75
B		42	37	39	34	38	45	40
C		34	35	35	32	31	45	79
D		38	30	30	28	38	31	58

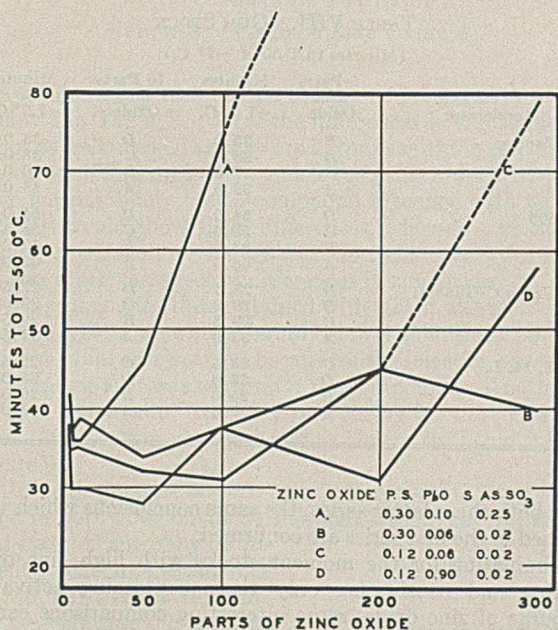


FIGURE 5. TESTS ON COMPOUND 2, 808

Zinc oxide A, the "slow-curing" zinc oxide, shows a progressive retardation of cure as the amount of zinc oxide is increased, for with each increase in oxide content the amount of chemical retardant is increased. Zinc oxide B, the relatively coarse "fast-curing" zinc oxide, gives a straight-line relation, indicating that when the vulcanization reaction reaches an equilibrium there is no change in curing rate with a change in the zinc oxide loading. Zinc oxide C, the fine "fast-curing" oxide, because of its increased surface shows a slightly increased activity and speeding up of the cure to a loading of 50 parts of zinc oxide, at which point the sulfur and accelerator absorption causes an unbalancing of the compound and retardation of cure results. Zinc oxide D, fine particle size and containing 1 per cent of lead as the oxide, shows a definite acceleration up to a loading of 200 parts of oxide, at which point the increase in the surface of oxide and the resulting sulfur and accelerator absorption overcome the accelerating effect of the litharge and retardation is observed.

The behavior of zinc oxides and the effect of these variations have been predicted and shown by various investigations, but to show all these changes in a single set of data, with a reasonable reproducibility, adds considerable weight to previous experiments and predictions.

As a further check on the properties of these oxides, three other sets of data were obtained. In Table V and Figure 5, the results with butyraldehyde aniline condensation product (808) are shown.

The base formula hereinafter referred to as compound 2 is as follows:

Smoked sheet	100
Sulfur	3.25
808	0.7
Neozone A	1.0
Stearic acid	1.0

In this case, owing to the selection of a curing temperature which was too low for the compound, it was necessary to make the comparison at a T-50 somewhat higher than was used in the previously discussed tests. The value of 0° C. was selected and the conclusions were essentially the same as were reached in the mercaptobenzothiazole stocks.

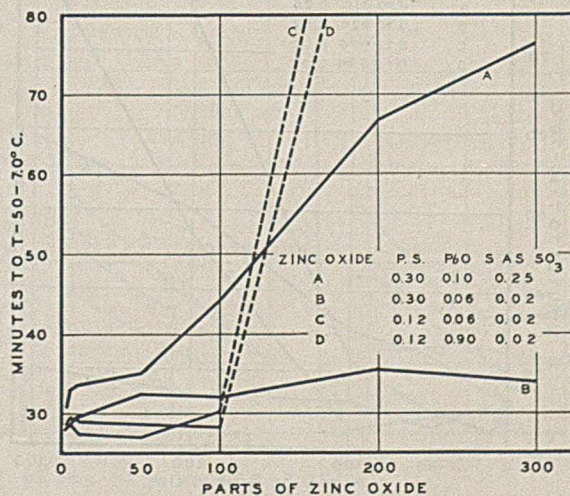


FIGURE 6. TESTS ON COMPOUND 4, UREKA C-GUANTAL

TABLE VI. TESTS ON COMPOUND 3, UREKA C-GUANTAL

Zinc Oxide	Cure at 130° C. Min.	Parts of Zinc Oxide						
		2	5	10	50	100	200	300
A	15	+ 6.0	+ 7.5	+ 6.5	+ 8.5	+10.0	+14.8	+16.5
	30	- 6.5	- 6.0	- 5.0	- 4.0	- 1.0	+ 4.5	+ 8.5
	45	-14.0	-13.5	-12.0	-11.5	- 6.3	- 1.3	+ 3.0
	60	-18.5	-18.5	-18.5	-16.0	-12.0	- 5.5	- 1.5
	75	-21.5	-22.0	-21.5	-19.5	-14.5	- 9.0	- 6.5
90	-23.0	-24.0	-24.0	-22.0	-17.0	-11.0	-11.5	
B	15	+ 6.0	+ 6.5	+ 5.0	+ 7.0	+ 8.0	+ 8.5	+ 6.5
	30	- 8.5	- 8.0	- 7.5	- 5.5	- 5.5	- 3.5	- 4.5
	45	-15.0	-15.5	-14.5	-13.0	-13.0	-12.0	-12.3
	60	-19.5	-19.5	-19.5	-18.0	-17.5	-18.5	-15.5
	75	-23.0	-23.0	-22.0	-20.5	-21.0	-19.5	-18.5
90	-24.5	-24.5	-23.5	-23.0	-22.5	-21.5	-22.0	
C	15	+ 3.5	+ 3.5	+ 3.0	+ 2.5	- 1.3	+ 8.5	+16.5
	30	- 7.5	- 7.8	- 7.5	- 8.5	- 8.3	+ 5.0	+13.0
	45	-15.5	-15.5	-15.5	-16.0	-12.3	+ 1.0	+10.5
	60	-19.8	-20.0	-20.8	-20.3	-16.0	- 1.0	+ 8.5
	75	-22.0	-23.5	-22.0	-22.0	-17.0	- 2.0	+ 7.5
90	-23.5	-25.0	-24.3	-23.8	-19.0	- 4.8	+ 6.0	
D	15	+ 4.8	+ 5.3	+ 2.0	+ 3.5	+ 1.0	+10.8	+14.5
	30	- 8.0	- 8.5	- 9.0	- 7.3	- 7.8	+ 6.0	+10.5
	45	-14.3	-15.8	-15.8	-14.0	-13.3	+ 1.5	+ 7.0
	60	-19.0	-20.5	-20.5	-18.5	-17.2	- 0.5	+ 3.0
	75	-22.3	-23.3	-22.0	-20.5	-19.3	- 3.0	+ 0.0
90	-23.3	-25.5	-23.8	-22.3	-21.0	- 4.3	- 2.3	
Time of Cure (Minutes) to T-50 of -7.0° C.								
A	31	33	33.5	35	44.5	67.0	76.5	
B	28	29	29.5	32.5	32.0	35.5	34.0	
C	28.5	28.5	27.5	27.0	30.0	
D	28.5	29.5	29	29.0	28.5	

TABLE VII. TESTS ON COMPOUND 4, Z. M. L.

Zinc Oxide	Cure at 135° C. Min.	Parts of Zinc Oxide						
		2	5	10	50	100	200	300
A	15	+ 3.5	+ 5.0	+ 4.5	+ 5.5	+ 5.0	+11.0	+16.5
	30	-10.0	- 9.5	- 8.5	- 6.0	- 4.5	+ 0.5	+10.0
	45	-21.0	-19.5	-18.0	-14.0	-12.0	- 4.5	+ 0.5
	60	-28.5	-25.0	-24.5	-21.0	-18.5	-10.0	- 5.5
	90	-38.5	-34.0	-31.0	-28.5	-25.5	-19.0	-18.0
120	-43.5	-37.0	-34.5	-31.0	-27.0	-20.5	-23.5	
B	15	0	+ 2.0	+ 2.0	+ 1.5	+ 3.0	+ 5.0	+ 1.0
	30	-12.0	-11.0	-10.5	- 9.5	-10.0	- 8.5	- 7.5
	45	-22.5	-20.5	-19.0	-18.5	-18.5	-16.0	-14.5
	60	-29.0	-26.5	-25.5	-23.5	-22.5	-19.5	-19.5
	90	-38.5	-34.0	-38.0	-28.5	-27.5	-25.0	-24.0
120	-37.0	-33.5	-30.5	-29.0	-27.5	-25.5	-25.5	
C	15	+ 0.5	+ 1.0	+ 0.5	+ 1.5	+ 2.0	+11.0	+14.0
	30	-11.5	-11.5	-12.0	- 8.5	- 6.0	+ 4.5	+10.5
	45	-19.5	-20.0	-18.0	-16.0	-13.5	- 0.5	+ 6.0
	60	-25.0	-26.0	-22.5	-20.5	-18.0	- 4.5	+ 5.0
	90	-30.5	-31.5	-29.0	-26.0	-23.5	- 9.5	- 1.5
120	-32.5	-34.0	-31.5	-29.0	-26.5	-15.0	- 5.0	
D	15	+ 3.5	+ 1.5	+ 1.5	- 0.5	- 1.0	+ 7.0	+10.5
	30	- 9.5	-12.0	-10.0	-11.0	-10.5	- 2.0	+ 4.5
	45	-19.0	-19.0	-18.5	-18.5	-15.5	- 6.0	+ 1.5
	60	-21.0	-24.0	-23.5	-22.5	-20.0	-10.0	- 2.5
	90	-33.0	-30.0	-28.0	-27.0	-25.0	-15.5	- 8.0
120	-35.5	-32.5	-30.0	-29.5	-26.5	-20.0	- 9.0	
Time of Cure (Minutes) to T-50 of -7.0° C.								
A	26	27.5	27.0	32.0	35.0	50.0	59.0	
B	23	25	26	23	26	27	30.0	
C	24	23.5	22.5	27.5	31.5	74	..	
D	27.5	24	25.5	24.0	22.5	47	82.0	

Table VI and Figure 6 show the results with a combination accelerator, in this case benzothiazyl thiobenzoate (Ureka-C) and 2 diphenylguanidine, 1 phthalic acid, 1/2 water (Guantal).

The base formula hereinafter referred to as compound 3 is as follows:

Smoked sheet	100
Sulfur	3
Ureka-C	0.45
Guantal	0.30
Stearic acid	1

Table VII and Figure 7 give the results with a thiazole zinc salt and Laurex (Z. M. L.).

The base formula hereinafter referred to as compound 4 is as follows:

Smoked sheet	100
Sulfur	3
Z. M. L.	1.95
B. L. E.	1
Laurex	0.5

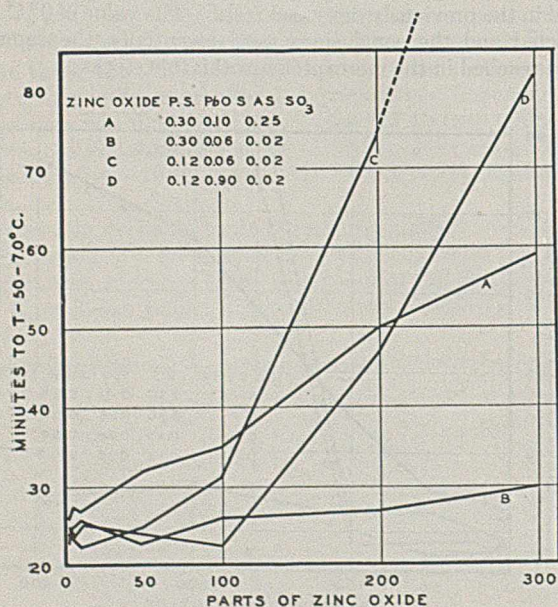


FIGURE 7. TESTS ON COMPOUND 4, Z. M. L.

TABLE VIII. GUM STOCK

(Minutes to T-50 of -7° C.)

Accelerator	5 Parts Zinc Oxide	Minutes to -7.0° C.	10 Parts Zinc Oxide	Minutes to -7.0° C.
Captax	B	35.0	D	35.0
	D	36.0	C	38.0
	C	37.0	B	40.0
	A	39.5	A	43.0
SOS	D	54.0	D	54.0
	C	58.0	C	54.5
	B	63.5	B	59.0
	A	66.5	A	62.0
Ureka C-Guantal	D	28.5	D	27.5
	B	29.0	C	29.0
	C	29.5	B	29.5
	A	33.0	A	33.5
Z. M. L.	C	23.5	C	22.5
	D	24.0	D	25.0
	B	25.0	B	26.0
	A	27.5	A	27.0

In both these latter series, the same conclusions which were reached in the first series are confirmed.

Eliminating for the moment stocks with high zinc oxide loading and considering only those containing activation amounts of zinc oxide, some interesting comparisons can be made. In the compounds containing 5 and 10 parts of zinc oxides, while the differences are small and probably of little commercial significance, these differences are consistent. In every case, the slow-curing oxide, A, has the slowest rate of cure as judged by the T-50 test, being 5 or 6 minutes slower than zinc oxide D, which generally gives faster curing compounds. The spread between the extremes is somewhat greater in the case of the alkaline accelerators. These data are shown in Table VIII.

This conclusion being true for gum stocks, it was of particular interest to determine what differences could be detected in a loaded compound such as a tread stock. In Table IX are shown the results obtained in a typical tread stock accelerated with Captax and containing 40 parts of carbon black. Here the differences in zinc oxide are much less marked; in the case of 5 parts of pigment, zinc oxides A, B, and C are essentially equal, and zinc oxide D is only slightly faster. With 10 parts of zinc oxide, differences are noted which are not consistent with the observations made with the gum stocks.

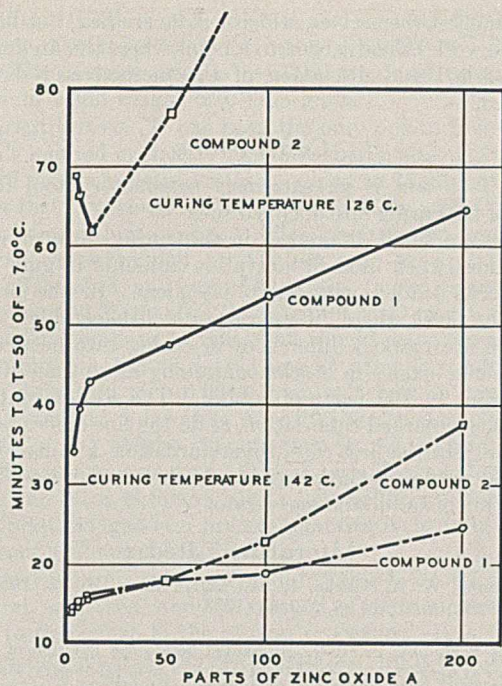


FIGURE 8. TESTS ON ZINC OXIDE A

A similar set of tests with a compound loaded with whiting is shown in Table X. Here the differences in zinc oxides are about as well marked as they are in the case of the gum stocks, the oxides lining up in very much the same order. It would seem entirely likely that a compound extended with an inert pigment would show these differences, whereas a stock containing a pigment of high absorption characteristics might entirely mask the effect of differences in zinc oxides.

In discussing the data obtained with 808, it was pointed out that the results were considerably slower than those obtained with the other accelerators, because of the selection of a curing temperature that was too low for the compound. Another set of data using zinc oxide A, but curing at 142°C. rather than 126°C., was obtained and is shown in Table XI and Figure 8.

Although the time of cure to a T-50 of -7°C. may be the same in both compounds at the higher temperature, the actual state of cure may be different. The interesting observation is that at this curing temperature the increase in zinc oxide content does not have the same retarding effect observed at the lower temperatures with either of these accelerators and it is only at the two higher loadings that any real differences can be observed.

A theoretical picture of the effect of the particle size of zinc oxide has been built up on the basis of accelerator and sulfur absorption. An extensive series of experiments has been carried out to demonstrate the correctness of these theories. By varying the accelerator and sulfur through a reasonable commercial range, the data

TABLE IX. TREAD STOCK

5 Parts Zinc Oxide	Minutes to -7.0°C.	10 Parts Zinc Oxide	Minutes to -7.0°C.
D	75.0	D	74.5
A	88.0	B	83.5
B	88.0	A	85.0
C	88.5	C	88.0

Formula

Smoked sheet	100
Stearic acid	4
Pine tar	3
Carbon black	40
Captax	1.25
Sulfur	3
Zinc oxide	5 and 10

TABLE X. COMPOUND LOADED WITH WHITING

5 Parts Zinc Oxide	Minutes to -7.0°C.	10 Parts Zinc Oxide	Minutes to -7.0°C.
D	32.5	D	29.0
C	33.5	C	34.0
B	35.0	B	34.0
A	39.5	A	40.5

Formula

Smoked sheet	100
Sulfur	3
Captax	1
Stearic acid	3
Agerite powder	1
Whiting	67
Zinc oxide	5 and 10

TABLE XI. EFFECT OF CURING TEMPERATURE

Curing Temperature °C.	Parts of Zinc Oxide A						
	2	5	10	50	100	200	
Compound 1	142	14.5	14.5	16.0	18.0	19.0	25.0
	126	34.0	39.5	43.0	47.8	54.0	65.0
Compound 2	142	14.0	15.0	15.5	18.0	23.0	38.0
	126	69.0	66.5	62.0	77.0	100.0	174.0

shown in Table XII and Figure 9 have been obtained. For this series of experiments, Captax acceleration was again used.

It will be noted that at a loading of 50 parts of zinc oxide, zinc oxide C, the fine fast-curing oxide, is faster than the coarse fast oxide B when 1 per cent of accelerator is used. With 200 parts of pigment, the fine oxide is slower because of absorption of accelerator and sulfur as pointed out earlier. When the accelerator is increased to 1.4 parts, the fine oxide regains

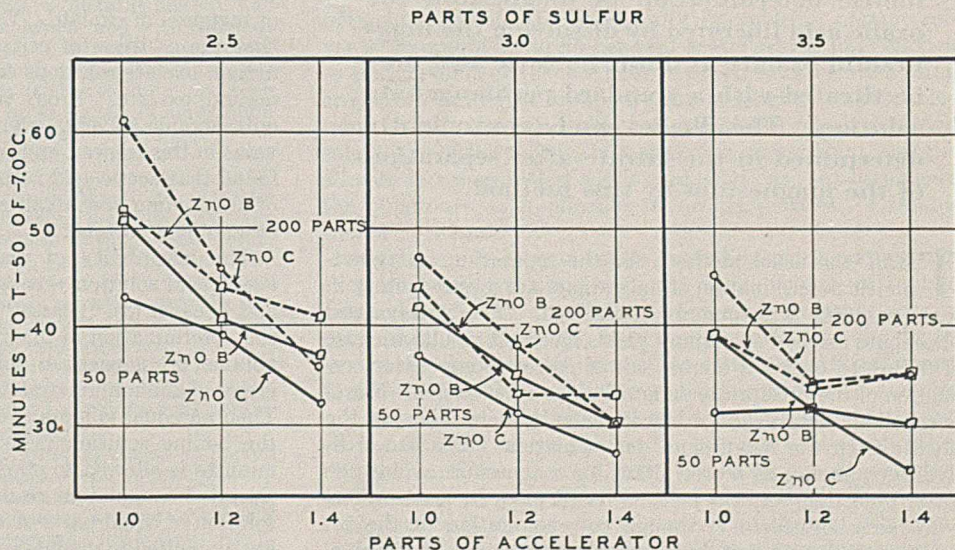


FIGURE 9. EFFECTS OF VARYING ACCELERATOR AND SULFUR

TABLE XII. EFFECT OF VARIATION OF SULFUR AND ACCELERATOR

(In compounds containing 50 and 200 parts of zinc oxides *B* and *C*)

Parts Sulfur	Parts Accelerator	Minutes to $-7.0^{\circ}\text{C. at T-50}$			
		50 parts zinc oxide		200 parts zinc oxide	
		<i>C</i>	<i>B</i>	<i>C</i>	<i>B</i>
2.5	1.0	43	51	61	52
	1.2	39	41	46	44
	1.4	32	37	36	41
3.0	1.0	37	42	47	44
	1.2	31	35	38	33
	1.4	27	30	30	33
3.5	1.0	31	39	45	39
	1.2	31.5	31.5	34	33.5
	1.4	25.0	30	35	35

Formula	
Rubber	100
Stearic acid	3
Sulfur	2.5-3.0-3.5
Captax	1.0-1.2-1.4
Zinc oxide	50 and 200

its faster curing rate. Increase in sulfur content has essentially the same effect to a less marked extent. When the amount of sulfur and accelerator is increased to an excess, the differences between the two oxides are masked.

In presenting the data in this paper, the authors do not pretend to have exhausted the possibilities of investigations by means of the T-50 tests. There are innumerable problems

which suggest themselves, which will be studied, but it is felt that the work has advanced to a point where the findings can be published and discussion of the method and data encouraged.

Conclusions

The T-50 test is an extremely satisfactory tool for the study of the curing rate of zinc oxides.

There are small differences in the curing rates of various zinc oxides when used in activation amounts in gum stocks and stocks loaded with inert extenders. In the presence of carbon black, these differences are not detectable.

There are marked differences in curing rate between the various zinc oxides in stocks containing more than 10 parts of pigment in 100 parts of rubber. The oxides containing sulfur show marked retardation, as do the fine oxides, at high loadings. In the first case, this retardation is caused by the chemical nature of the pigment; in the second case, by the absorption of sulfur and accelerator.

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Separation of Magnesium as Oxalate

By Precipitation in Concentrated Acetic Acid Solution

PHILIP J. ELVING AND EARLE R. CALEY

Frick Chemical Laboratory, Princeton University, Princeton, N. J.

Magnesium can be quantitatively precipitated as the oxalate in 85 per cent acetic acid solution. The precipitate may be ignited to oxide for the gravimetric determination of magnesium, or for the volumetric determination of magnesium the oxalic acid liberated by dissolving the magnesium oxalate in dilute sulfuric acid may be titrated with a standard permanganate solution. The alkalies can be conveniently determined in the filtrate after separation of the magnesium by this method.

THAT the usual methods for the separation and gravimetric determination of magnesium are unsatisfactory in some respects is commonly recognized. The widely used phosphate method sometimes yields incorrect results because of failure to obtain a double salt of correct composition, reduction of the precipitate on ignition, or other causes. Moreover, alkali metals cannot be conveniently determined in the filtrate from the magnesium determination. The use of 8-hydroxyquinoline as a precipitant for magnesium avoids the latter objection, and the method based upon its use is otherwise fairly satisfactory, though co-precipitation of the reagent with the precipitate is sometimes a source of trouble. In the method here described, which is based upon the insolubility

of magnesium oxalate in 85 per cent acetic acid, the precipitate is readily obtained in a pure state, and any of the alkalies can be conveniently determined in the filtrate from the magnesium determination.

Though magnesium oxalate is but slightly soluble in water, it has long been known that the addition of excess oxalate ion to dilute magnesium solutions does not produce a precipitate of magnesium oxalate. Various investigators have observed that the addition of certain organic solvents to such magnesium oxalate solutions causes the precipitation of the magnesium oxalate. From the practical analytical viewpoint only organic solvents completely miscible with water are of value in this respect, and from preliminary experiments it was found that acetic acid is the best of these, since the solubility of ammonium and alkali salts is too low in such solvents as ethanol and acetone.

The insolubility of magnesium oxalate in concentrated acetic acid solution was apparently first noticed by Souhay and Lensen (3). Classen (1) attempted to apply this fact to the determination of magnesium. In his procedure a 25-ml. volume of magnesium solution is treated with 1.5 to 2.0 grams of ammonium oxalate while the solution is being heated. Then an equal volume of 80 per cent acetic acid is added to the boiling solution, which after further boiling for a few minutes is allowed to stand for 6 hours at 50°C . The precipitated magnesium oxalate is filtered off, washed with a solution of equal parts of water, acetic acid, and alcohol, and finally ignited to magnesium oxide. Thirty-four experimental results given by Classen for amounts of magnesium oxide

ranging from 0.0377 to 0.2075 gram are, with but five exceptions, low, the range of error being +0.0008 to -0.0021 gram. The average error is -0.0007 gram on an average magnesium oxide weight of 0.1105 gram.

Apparently Nass (2) has been the only one to investigate Classen's method critically. In the experiments of Nass, 30 ml. of 85 per cent acetic acid were added to 25 ml. of boiling solution that contained 1.3232 grams of $MgSO_4 \cdot 7H_2O$ and 4 grams of ammonium oxalate. After precipitation under the conditions recommended by Classen, the precipitate was filtered off, washed, and ignited to oxide. In two experiments Nass obtained 0.2119 and 0.2117 gram of MgO from a sample weight of magnesium sulfate that should have given him 0.2164 gram on the basis of present atomic weights, an average difference of -0.0046 gram. It will be seen that Classen's method is far from quantitative, though Nass, on the basis of the atomic weights then in use, considered it satisfactory for routine work. The data in Table I show why Classen and Nass obtained such poor results in attempting to precipitate magnesium oxalate quantitatively from about 40 per cent acetic acid solution.

For the experiments represented in Table I, a total volume of 100 ml. was used, and the method of determination was similar to that given in the general procedure. It is evident that precipitation in 85 per cent acetic acid leads to quantitative results if sufficient reagent is present, and that with a considerable excess of reagent a medium of slightly lower acid concentration may be used. However, when large amounts of magnesium are to be precipitated, the relatively low solubility of ammonium oxalate in acetic acid solutions prevents the use of a large excess of reagent. Hence, in general, the use of a medium of the highest practical concentration in respect to acetic acid is necessary. Oxalic acid, though more soluble than ammonium oxalate, cannot be employed as a reagent because the increased hydrogen-ion concentration introduced by its use leads to increased solubility of the magnesium oxalate. From these solubility experiments and from systematic experiments on method of precipitation, time of standing after precipitation, technic of filtration, and treatment of precipitate for weighing, the following procedure was developed.

General Procedure

Concentrate the neutral solution containing magnesium, ammonium, and the alkali metals to a volume of 5 ml. or, preferably, evaporate it to dryness and dissolve the residue in 5 ml. of water. If less than about 40 mg. of magnesium as metal is present, add 85 ml. of glacial acetic acid, to this solution, and with constant stirring add slowly from a pipet 10 ml. of saturated ammonium oxalate solution. If a larger amount of magnesium is present, add 70 ml. of glacial acetic acid to the sample solution, and then slowly add 25 ml. of a solution made up of 1 gram of ammonium oxalate dissolved in a mixture of 15 ml. of acetic acid and 10 ml. of water. If both magnesium and sulfate are present in large amounts, first add the 25 ml. of special oxalate reagent, which should be warm in this case, and then add the 70 ml. of acetic acid. After precipitation by any of these methods allow the covered vessel to stand on the steam bath until the magnesium oxalate precipitate settles in a flocculent mass leaving the supernatant liquid clear. This should require from 30 to 60 minutes. Decant the supernatant liquid through retentive quantitative paper, such as Munktell's No. 00, and wash the precipitate once or twice by decantation using hot 85 per cent acetic acid. Finally, transfer the precipitate to the filter and wash with the hot acid solution which is preferably delivered from an all-glass wash bottle. Ordinarily a total of about 60 ml. of 85 per cent acid in three to five portions is sufficient for washing.

If accurate results are desired when both magnesium and alkali metal salts are present in large quantities, a double precipitation should be made. For this purpose dissolve the magnesium oxalate from the filter with the minimum necessary amount of hot 3 N hydrochloric acid and wash out the paper with hot water. Evaporate the solution to dryness and add 2 ml. of concentrated nitric acid and 5 ml. of concentrated perchloric acid to the residue.

Heat to destroy the oxalate, finally fuming off all the excess perchloric acid. Dissolve the residue in 5 ml. of water and precipitate as before.

For ignition, place the paper and precipitate in a weighed platinum crucible, heat gently at first to expel acetic acid and water, then char and burn off the paper in the usual way. Finally ignite in a covered platinum crucible at the highest temperature obtainable with a Méker burner or blast lamp. Cool in a desiccator containing an efficient desiccant and weigh as MgO . If a platinum crucible is not available, ignition may be made in porcelain, but it is difficult in this case to ignite the magnesia at a temperature high enough to render it sufficiently nonhygroscopic for accurate weighing and to burn off all carbonaceous matter. If a porcelain crucible is used it is therefore best to check the result by dissolving the magnesia in a slight excess of dilute sulfuric acid in the crucible, followed by evaporation to dryness, ignition at 400° to 500° C. and final weighing as $MgSO_4$.

For preparation of the filtrate from the magnesium determination for the determination of the alkalis, add 25 to 30 ml. of concentrated nitric acid and evaporate to dryness. Add 2 ml. of nitric and 5 ml. of perchloric acid to the residue and again evaporate to dryness. Finally fume off all excess perchloric acid. The residue may then be used for the systematic separation of the alkalis or for their direct or indirect determination by various procedures.

TABLE I. EFFECT OF COMPOSITION OF MEDIUM AND CONCENTRATION OF REAGENT ON COMPLETENESS OF PRECIPITATION OF MAGNESIUM BY AMMONIUM OXALATE IN ACETIC ACID SOLUTION

CH_3COOH Per Cent by Volume	Equivalents of $(NH_4)_2C_2O_4$ Present	Mg Taken Gram	Mg Found Gram	Difference, Error Gram
50	1	0.0100	0.0000	-0.0100
60	1	0.0100	0.0014	-0.0086
70	1	0.0100	0.0060	-0.0040
80	1	0.0100	0.0078	-0.0022
90	1	0.0100	0.0097	-0.0003
40	2	0.0100	0.0000	-0.0100
50	2	0.0100	0.0020	-0.0080
60	2	0.0100	0.0077	-0.0023
70	2	0.0100	0.0097	-0.0003
80	2	0.0100	0.0098	-0.0002
85	2	0.0100	0.0100	+0.0000
30	4	0.0100	0.0000	-0.0100
40	4	0.0100	0.0035	-0.0065
50	4	0.0100	0.0081	-0.0019
60	4	0.0100	0.0095	-0.0005
70	4	0.0100	0.0098	-0.0002
80	4	0.0100	0.0100	+0.0000
85	4	0.0100	0.0101	+0.0001

INTERFERING SUBSTANCES. Heavy metals and alkaline earth metals must be absent, since their oxalates are generally insoluble in concentrated acetic acid solutions. Magnesium, ammonium, and the alkali metals may be in the form of chlorides, nitrates, acetates, perchlorates, or sulfates, but for ease of separation of magnesium from the alkalis it is preferable to have them in the form of the first three. Though potassium perchlorate is generally insoluble in organic solvents, its solubility in 85 per cent acetic acid is high enough so that no difficulty should arise in practical cases when using analytical samples of around a gram in weight. Sulfate solutions are the least desirable because of the relatively small solubilities of the sulfates of magnesium, ammonium, and the alkalis in concentrated acetic acid solutions, but here again the procedure is applicable in ordinary cases. Oxalates should be absent.

Ammonium salts must not be present in such large amounts that they will not dissolve in the small volume of sample solution required in the method. Since magnesium is usually determined in the filtrate from the determination of calcium as oxalate, the excess of ammonium salts in this filtrate must first be destroyed by oxidation with nitric acid in the customary way, followed by removal of the oxalate with nitric and perchloric acids as described in the procedure. Various other reagents such as aqua regia, nitric and sulfuric acids, bromine, and ammonium persulfate were tested for their efficiency in removing oxalate, but the mixture of nitric and perchloric acids was found to be the best. The magnesium solution should be approximately neutral. If strongly acidic it should

TABLE II. DETERMINATION OF MAGNESIUM ALONE

Analysis No.	Mg Taken Gram	Mg Found Gram	Difference, Error Gram
1	0.0001	0.0002	+0.0001
2	0.0001	0.0002	+0.0001
3	0.0002	0.0001	-0.0001
4	0.0002	0.0002	±0.0000
5	0.0003	0.0002	-0.0001
6	0.0003	0.0004	+0.0001
7	0.0011	0.0011	±0.0000
8	0.0011	0.0011	±0.0000
9	0.0025	0.0026	+0.0001
10	0.0025	0.0025	±0.0000
11	0.0100	0.0100	±0.0000
12	0.0101	0.0101	±0.0000
13	0.1001	0.1006	+0.0005
14	0.1001	0.1007	+0.0006
15	0.0100	0.0098	-0.0002 ^a
16	0.0101	0.0101	±0.0000 ^a
17	0.1001	0.0998	-0.0003 ^a
18	0.1001	0.1002	+0.0001 ^a

^a Double precipitation in these cases.

be neutralized with ammonium hydroxide solution and then made just barely acid with acetic acid.

METHOD OF PRECIPITATION. Whenever possible the first method of precipitation should be used because the resulting precipitate is most easily filtered and washed. The second method is necessary in order to introduce sufficient reagent when precipitating the larger amounts of magnesium. The third variation is required because the direct addition of glacial acetic acid to concentrated magnesium sulfate solutions produces a precipitate of magnesium sulfate. Because of the large volume of magnesium oxalate precipitated in this way and because of the limits imposed by the low solubility of the reagent, precipitation of more than about 100 mg. of magnesium should not be attempted.

FILTRATION AND WASHING. Because of the irritating physiological action of acetic acid fumes, it is strongly recommended that these operations be performed under a good hood. The process of washing the bulky and finely divided magnesium oxalate precipitate will be unduly prolonged if the solution is not kept warm. The addition of paper pulp does not noticeably accelerate the process of filtration, since the acetic acid hardens the paper and prevents its proper dispersion. Attempts to use filtering crucibles met with little success, because with other than minute amounts of magnesium the somewhat gelatinous precipitate rapidly clogged the pores of glass or porcelain filter disks. The use of an all-glass wash bottle is almost a necessity because of the solvent action of hot concentrated acetic acid on rubber. For the same reason a rubber policeman cannot be used for transferring the precipitate. Small pieces of quantitative filter paper should be used for the removal of any small residues of magnesium oxalate that adhere to the walls of the precipitating vessel. When the maximum amount of reagent is used for the precipitation of only a few milligrams of magnesium, the excess of ammonium oxalate will frequently crystallize out in the filtrate on cooling. Since this salt is distinctly crystalline in appearance, it should not readily be mistaken for magnesium oxalate that has run through a defective filter.

IGNITION AND WEIGHING. Carbonaceous matter concealed in lumps of magnesium oxide after ignition is the most serious single cause of error in this method. Not only is the presence of this foreign material not easily evident from appearance, but it is sometimes not readily detected by weighing because it burns off very slowly when insulated from heat by the voluminous magnesium oxide. Therefore, the precipitate should be broken up and stirred at intervals during ignition. If any suspicion arises as to the presence of carbonaceous matter in the ignited precipitate, the magnesium oxide may be dissolved in dilute hydrochloric acid, and any carbonaceous matter that remains may be readily determined by filtering

it off on a filter crucible and weighing it after drying at about 100°. Even though conversion to sulfate involves an extra step, this is highly desirable when the ignition of precipitates weighing more than a few milligrams is done in porcelain, since only in this way can the carbonaceous matter be burned away in a conveniently short time.

Test Analyses

For the analytical experiments on pure magnesium solutions and on solutions containing magnesium and other metal ions, distilled magnesium metal, furnished by courtesy of the Aluminum Company of America, was used as the standard of reference. This was stated to contain 99.99 per cent of magnesium, and its high purity was confirmed by both chemical and spectroscopic examination. Standard magnesium solutions were prepared by dissolving accurately weighed quantities of the metal in the minimum necessary quantity of constant-boiling hydrochloric acid, followed by dilution in calibrated flasks. The concentration of each of these solutions was checked by adding a slight excess of sulfuric acid to a carefully measured volume, evaporating in a platinum dish, and weighing the residual magnesium sulfate.

In Table II are shown typical results from test determinations on pure magnesium chloride solutions. Numbers 13 and 14 may be taken as typical of the error that is caused by failure to burn off the last traces of carbonaceous matter. The last four determinations in the table show that no loss occurs when a double precipitation is made.

TABLE III. DETERMINATION OF MAGNESIUM IN PRESENCE OF LITHIUM

Li Present Gram	Mg Taken Gram	Mg Found Gram	Difference, Error Gram
0.0100	0.0011	0.0011	±0.0000
0.0100	0.0011	0.0011	±0.0000
0.1000	0.0010	0.0012	+0.0002
0.1000	0.0010	0.0011	+0.0001
0.0100	0.0100	0.0101	+0.0001
0.0100	0.0100	0.0100	±0.0000
0.0500	0.0102	0.0106	+0.0004
0.0500	0.0102	0.0104	+0.0002
0.1000	0.0100	0.0108	+0.0008
0.1000	0.0100	0.0109	+0.0009
0.0010	0.1001	0.1000	-0.0001
0.0010	0.1001	0.1000	-0.0001
0.0100	0.1001	0.1005	+0.0004
0.0100	0.1001	0.1003	+0.0002
0.0100	0.0010	0.0009	-0.0001 ^a
0.0100	0.0010	0.0009	-0.0001 ^a
0.1000	0.0011	0.0010	-0.0001 ^a
0.1000	0.0011	0.0008	-0.0003 ^a
0.0100	0.0100	0.0100	±0.0000 ^a
0.0100	0.0100	0.0099	-0.0001 ^a
0.1000	0.0100	0.0101	+0.0001 ^a
0.1000	0.0100	0.0102	+0.0002 ^a
0.0010	0.1000	0.1000	±0.0000 ^a
0.0010	0.1000	0.1001	+0.0001 ^a
0.0100	0.1000	0.0999	-0.0001 ^a
0.0100	0.1000	0.1000	±0.0000 ^a
0.0100	0.1001	0.1004	+0.0003 ^a
0.0100	0.1000	0.0998	-0.0002 ^a

^a Double precipitation.

Tables III, IV, and V show the effect of the presence of individual alkalis on the accuracy of the magnesium determination. Chloride solutions were used in all these experiments. It will be noted that in certain cases both lithium and sodium cause a noticeable positive error when only a single precipitation is made, lithium having the most serious effect. On the other hand, as shown by the results in Table V, potassium causes no error when present in the same proportions. It is also evident that the error introduced by the tendency of lithium or sodium compounds to be adsorbed on or co-precipitated with the magnesium oxalate can be avoided by double precipitation. However, very large amounts of sodium, such as might be present after a sodium carbonate fusion, cannot be separated conveniently.

TABLE IV. DETERMINATION OF MAGNESIUM IN THE PRESENCE OF SODIUM

Na Present Gram	Mg Taken Gram	Mg Found Gram	Difference, Error Gram
0.1000	0.0011	0.0010	-0.0001
0.1000	0.0010	0.0011	+0.0001
0.0100	0.0100	0.0101	+0.0001
0.0100	0.0100	0.0100	±0.0000
0.1000	0.0100	0.0101	+0.0001
0.1000	0.0100	0.0103	+0.0003
0.0100	0.1003	0.1009	+0.0006
0.0100	0.1003	0.1007	+0.0004
0.1000	0.0010	0.0010	±0.0000 ^a
0.1000	0.0010	0.0010	±0.0000 ^a
0.1000	0.0100	0.0099	-0.0001 ^a
0.1000	0.0100	0.0101	+0.0001 ^a
0.0100	0.1001	0.1003	+0.0002 ^a
0.0100	0.1001	0.0998	-0.0003 ^a

^a Double precipitation.

TABLE V. DETERMINATION OF MAGNESIUM IN THE PRESENCE OF POTASSIUM

K Present Gram	Mg Taken Gram	Mg Found Gram	Difference, Error Gram
0.1000	0.0010	0.0011	+0.0001
0.1000	0.0010	0.0011	+0.0001
0.1000	0.0100	0.0101	+0.0001
0.1000	0.0102	0.0101	-0.0001
0.0100	0.1003	0.1004	+0.0001
0.0100	0.1003	0.1002	-0.0001
0.1000	0.0010	0.0009	-0.0001 ^a
0.1000	0.0010	0.0009	-0.0001 ^a
0.1000	0.0100	0.0098	-0.0002 ^a
0.1000	0.0100	0.0100	±0.0000 ^a
0.0100	0.1001	0.0998	-0.0003 ^a
0.0100	0.1001	0.1004	+0.0003 ^a

^a Double precipitation.

In Table VI are shown results that were obtained on the determination of both magnesium and individual alkalis after separation by single precipitation. In all these experiments the filtrates from the magnesium determinations were treated with nitric and perchloric acids as described in the general procedure. Lithium was determined by converting the perchlorate residue into sulfate for weighing. For the determination of sodium or potassium these were weighed either as perchlorates or as sulfates. Here also lithium causes the most error, whereas in the other experiments the results are satisfactory for both magnesium and the alkalis.

TABLE VI. DETERMINATION OF MAGNESIUM AND INDIVIDUAL ALKALIES IN THE SAME SAMPLE

Alkali Present	Alkali Taken Gram	Alkali Found Gram	Difference, Error Gram	Mg Taken Gram	Mg Found Gram	Difference, Error Gram
Li	0.0101	0.0101	±0.0000	0.0102	0.0102	±0.0000
	0.0250	0.0250	±0.0000	0.0102	0.0101	-0.0001
	0.0251	0.0246	-0.0005	0.0102	0.0103	+0.0001
	0.499	0.0493	-0.0006	0.0102	0.0106	+0.0004
Na	0.0255	0.0255	±0.0000	0.0102	0.0101	-0.0001
	0.0250	0.0251	+0.0001	0.0102	0.0101	-0.0001
	0.0500	0.0503	+0.0003	0.0102	0.0103	+0.0001
	0.0500	0.0499	-0.0001	0.0102	0.0101	-0.0001
K	0.0446	0.0447	+0.0001	0.0102	0.0102	±0.0000
	0.0510	0.0512	+0.0002	0.0102	0.0099	-0.0003
	0.1000	0.1003	+0.0003	0.0102	0.0101	-0.0001
	0.1005	0.1005	±0.0000	0.0102	0.0101	-0.0001

The method was further tested by the determination of magnesium in two standard samples issued by the Bureau of Standards—namely, argillaceous limestone No. 1a and dolomite No. 88.

In analyzing the argillaceous limestone, the dried and weighed samples were first strongly ignited in platinum. Then the major part of the silica was removed by the usual hydrochloric acid method. The aluminum, iron, and accompanying constituents were removed by double precipitation with ammonium hydroxide. In samples 4, 5, and 6 bromine water was added prior to precipitation. Calcium was separated as oxalate, but in samples 1, 2, and 3 the precipitation was performed by the slow addition of dilute ammonium hydroxide to the acidified solutions, and a

double precipitation was made, whereas in the other three samples the calcium was precipitated once by the urea method of Willard and Chan. The oxalate and the excess of ammonium salts were removed from the calcium filtrates by the use of nitric and perchloric acids, and the residual salts were dissolved in dilute hydrochloric acid. After filtration to remove dust and silica, these solutions were evaporated to dryness, and the residues were each dissolved in 5 ml. of water for the precipitation of the magnesium by the first method given in the general procedure. On ignition, the precipitates from samples 1, 2, and 3 turned dark gray, evidently because of the presence of oxides of manganese and carbonaceous matter. In order to remove both contaminants, the impure oxides were treated with dilute nitric acid which dissolved only the magnesium oxide. The nitric acid solutions were then filtered, but instead of drying and weighing the impurities to obtain a correction to apply to the weights of the impure oxides, which is perhaps the more convenient method, the filtrates were evaporated and the magnesium was redetermined to obtain the second and more exact set of results shown in Table VII.

The precipitates of Nos. 4, 5, and 6 were also gray after the first ignition, but on evaporation with dilute sulfuric acid and conversion to sulfate, the carbonaceous matter responsible for the discoloration burned off, leaving pure residues of magnesium sulfate, the weights of which were used for obtaining the final results on these samples. It will be seen from Table VII that the final results obtained by either variation of the method agree well with the established percentage of magnesium in this sample. Apparently if even small amounts of manganese are not removed prior to the determination of magnesium by this method, the manganese will be precipitated and weighed with the magnesium. Therefore, in such a case the weights of the magnesium oxide should be corrected for the presence of oxides of manganese either by the methods mentioned here or from the results of colorimetric determinations of the manganese in the ignited magnesium oxide or the original material.

TABLE VII. DETERMINATION OF MAGNESIUM IN STANDARD ARGILLACEOUS LIMESTONE SAMPLE

Analy- sis No.	Sample Taken Grams	MgO Found on First Precipitation		MgO Found on Second Precipitation		MgO Weighed as Sulfate	
		Gram	%	Gram	%	Gram	%
1	1.3605	0.0317	2.33	0.0303	2.21
2	1.3674	0.0320	2.34	0.0302	2.19
3	1.3055	0.0296	2.27	0.0286	2.23
4	1.2495	0.0294	2.35	0.0274	2.20
5	1.3258	0.0298	2.25	0.0290	2.19
6	1.3777	0.0301	2.19	0.0292	2.12
Av.			2.29		2.21		2.17
Stated MgO percentage, U. S. Bureau of Standards							2.19

In analyzing the dolomite, the silica, the aluminum and iron, and the calcium were all separated by the conventional procedure for the analysis of carbonate rock, the oxalate and ammonium salts being removed from the calcium filtrates by the use of nitric and perchloric acids. The residual salts were dissolved in dilute hydrochloric acid, and after filtration the solutions were evaporated to dryness. Then each of the residues was dissolved in 5 ml. of water, and the magnesium was precipitated by the second method given in the general procedure. The oxides from the first precipitation were found to contain calcium, as would be expected from the fact that calcium is imperfectly separated by the oxalate method in the presence of disproportionate amounts of magnesium. In order to remove the calcium, the ignited precipitates were each dissolved in a slight excess of dilute sulfuric acid, and the calcium was precipitated as sulfate from a small volume of solution by the addition of nine volumes of methanol, a method that was shown by an independent investigation to give a sharp separation. After removal of the calcium sulfate by filtration, the filtrates were evaporated to dryness and magnesium determinations were repeated with the results shown in Table VIII.

After this redetermination the ignited precipitates evidently contained slight amounts of carbon or carbonaceous matter. Instead of removing this by prolonged ignition, the precipitates were dissolved in dilute sulfuric acid, and the impurities were filtered off on filter crucibles and weighed, these weights then being applied as a correction to obtain

the final results shown in Table VIII. These results, with the exception of No. 2, agree well with the established percentage. It is likely that mechanical loss caused the slightly low results on the second sample.

TABLE VIII. DETERMINATION OF MAGNESIUM IN STANDARD DOLOMITE SAMPLE

Analy- sis	Sample Taken Gram	MgO Found on First Precipitation		MgO Found on Second Precipitation		MgO Found after Final Correction	
		Gram	%	Gram	%	Gram	%
1	0.3395	0.0747	22.00	0.0737	21.71	0.0732	21.56
2	0.5741	0.1258	21.91	0.1229	21.42	0.1222	21.29
3	0.6137	0.1354	22.06	0.1323	21.56	0.1321	21.53
4	0.8057	0.1775	22.03	0.1739	21.58	0.1736	21.54
Av.			22.00		21.57		21.48
Stated MgO percentage, U. S. Bureau of Standards							21.49

From these experiments on actual samples it was found, therefore, that this method for the separation and determination of magnesium could be fitted into the ordinary analytical scheme with little difficulty. Other experiments indicated that it also could be used in systematic qualitative analysis.

Indirect Volumetric Determination of Magnesium

Instead of converting the precipitated magnesium oxalate to oxide for weighing, the determination may be completed by dissolving the precipitate in dilute sulfuric acid and titrating the liberated oxalic acid with standard permanganate. However, if this is done a modification in procedure is desirable, chiefly because the complete removal of the reagent from filter paper by washing with 85 per cent acetic acid is too time-consuming a process. It was found much more satisfactory to separate and wash the precipitate by means of the centrifuge according to the following method:

VOLUMETRIC PROCEDURE. Transfer the 5 ml. of magnesium sample solution to a conical centrifuge vessel of about 125-ml. capacity, using glacial acetic acid for rinsing out the original vessel. Add glacial acetic acid to the contents of the centrifuge vessel until the total volume is 90 ml. Precipitate the magnesium by the slow addition of 10 ml. of saturated ammonium oxalate solution and coagulate the precipitate by placing the centrifuge vessel on a steam bath for about an hour. Then centrifuge at high speed until the precipitate packs at the bottom of the vessel. This should require less than 10 minutes. Carefully decant or siphon off as much supernatant liquid as possible without disturbing the precipitate and add 15 to 25 ml. of hot 85 per cent acetic acid. After shaking to distribute the precipitate in the wash liquid, and washing down any precipitate that has collected on the sides of the vessel above the level of the liquid, centrifuge again. Repeat the washing process until a sample of the supernatant liquid fails to produce a precipitate when tested with calcium chloride solution. Ordinarily three washings will be sufficient. Dissolve the washed precipitate, together with the remaining few milliliters of wash liquid that cannot be safely removed, in 5 per cent sulfuric acid. After washing out this solution into the titrating vessel with additional 5 per cent sulfuric acid, titrate the oxalic acid with standard permanganate solution in the usual way. One milliliter of 0.1 *N* permanganate solution is equivalent to 0.001216 gram of magnesium.

A stoppered centrifuge vessel with a stem into which the precipitate can be centrifuged is the most satisfactory type. In order to prevent troublesome adherence of the precipitate to the walls of the vessel it is necessary to clean it thoroughly with dichromate cleaning solution before use.

The principal source of error is mechanical loss of fine particles of precipitate in the process of removing supernatant liquid. This usually occurs if an attempt is made to drain off the last few milliliters of liquid. The residual acetic acid left in and above the precipitate after the final washing does not react with the permanganate solution under the conditions of the titration.

By reason of the volume of the precipitate, especially after

washing, it is inconvenient to determine more than about 25 mg. by this procedure.

EXPERIMENTAL RESULTS. In Table IX are shown results from a series of determinations by this volumetric procedure. In determinations 7 and 8, where some slight mechanical loss of precipitate was suspected, the decantations and washings were filtered for gravimetric determination of the suspended matter by ignition to magnesium oxide. In both cases the weights of oxide corresponded exactly to the deficiencies in the volumetric results. Hence, by avoidance of mechanical loss during washing, exact results should be obtained by this procedure. It becomes rapid if a multiple-head centrifuge is used for making a number of determinations simultaneously.

TABLE IX. VOLUMETRIC DETERMINATION OF MAGNESIUM

Analysis No.	Mg Taken Gram	0.0515 <i>N</i> KMnO ₄ Required Ml.	Mg Found Gram	Difference, Error Gram
1	0.0010	1.60	0.0010	±0.0000
2	0.0010	1.53	0.0010	±0.0000
3	0.0025	3.91	0.0024	-0.0001
4	0.0025	3.93	0.0025	±0.0000
5	0.0102	15.92	0.0100	-0.0002
6	0.0102	15.93	0.0100	-0.0002
7	0.0102	15.90	0.0100	-0.0002
8	0.0102	15.88	0.0099	-0.0003
9	0.0252	40.21	0.0252	±0.0000
10	0.0252	40.13	0.0251	-0.0001

Attempts to determine magnesium by measuring the volume of precipitate in a graduated centrifuge tube were not successful because reproducible results could not be obtained.

General Remarks

Because of the bulk of magnesium oxalate precipitated in acetic acid solution and the attendant difficulties in filtering and washing, both the gravimetric and volumetric procedures are most satisfactory in practice when applied to the separation and determination of amounts of magnesium not exceeding 25 mg., though as much as 100 mg. can be handled by the gravimetric procedure. From the standpoint of speed, this method is superior to the phosphate method and compares favorably with the 8-hydroxyquinoline method. When magnesium must be separated prior to the determination of the alkalies and platinum ware is not available, this method has the peculiar advantage that the separation is carried out in acid solution so that introduction of alkalies from the glass or porcelain becomes a negligible source of error. Another distinct advantage is the ease with which impurities in the ignited precipitate, whether oxide or sulfate, can be tested for and removed. The chief inconvenience of the method, working with hot concentrated acetic acid solutions, is not serious in practice if a good hood is available.

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Arsenate Method for Determination of Zirconium

The article entitled "The Arsenate Method for the Determination of Zirconium," by W. C. Schumb and E. J. Nolan [*IND. ENG. CHEM., Anal. Ed.*, 9, 371 (1937)] was based largely on work supported by a J. T. Baker Chemical Company Fellowship awarded to E. J. Nolan for the year 1934-35.

Determination of the Stain Number of Asphalts

H. E. SCHWEYER¹ AND H. C. HOWELL, The Barber Company, Inc., Maurer, N. J.

To determine the staining propensity of asphalt, the sample is placed between pads consisting of 16 sheets of a special grade of paper under a given load at 54.4° C. (130° F.), and the staining is evaluated by the number of sheets discolored by the exuded oil. The stain number (number of sheets discolored) gives a direct measure of the staining propensity which may be used to compare asphalts from various sources.

LABORATORY evaluation of asphalts used as plying adhesives in the manufacture of waterproof wrapping papers and cartons requires a rapid method for determining the staining propensity of such materials. Several different methods are employed by manufacturers of paper products to determine this characteristic of asphalt, but most of these tests have the disadvantage of requiring the use of a standard asphalt. The degree of staining is usually evaluated by comparing the color of a stain made on filter paper under given conditions, by the standard and unknown samples, or by determining the relative length of time required for the asphalts to give an appreciable stain to a piece of filter paper. The results obtained by these methods are dependent upon the personal element in rating the samples because they are influenced by the amount of saturation of the paper by the asphalt and by the color of the oil exuded by different asphalts.

The slight but undesirable discoloration of paper plied together with certain asphalts is caused by the exudation of some part of the oily phase from the colloidal asphalt (3, 4). The degree to which the asphaltene are dispersed determines in part the "stability" of this colloidal system, and therefore how well it will retain the oily material. Comparative solubilities in partial solvents cannot be used to evaluate the staining propensity of different asphalts, since the amount of dispersed material thereby indicated does not determine the "stability" of the colloidal system. The physical chemical composition of an asphalt and the changes in internal structure which occur with time probably determine its staining propensity. Asphalts processed in different ways and from different crude oils show varying degrees of staining.

The method described below for evaluating the staining of paper in contact with asphalt has been successfully used in this laboratory for the past 18 months. It was adopted after a study of more elaborate methods, such as photoelectric measurement of light transmitted through stained and unstained paper, and comparative reflection of light from stained and unstained paper. While these latter methods are probably more sensitive than the test described, they have the disadvantage of requiring special apparatus and a technically trained operator.

Stain Number

The procedure for determining the "stain number" of an asphalt is as follows:

One gram of the cold asphalt, weighed to the nearest 0.02 gram, is cut from below the surface of the sample and is made into a flat disk about 1.5 cm. in diameter. This disk is then placed

between two pads, clipped together at one end, each consisting of 16 sheets (10 by 8 cm.) of a special paper.²

The pads and asphalt are placed in an oven at 54.4° C. (130° ± 1° F.) for about 1 hour to soften the asphalt; a weight is then placed on top of the upper pad. The weight used consists of a circular tin box filled with lead shot to weigh either 50 or 400 grams. (The 3-ounce Gill style deep-pattern ointment box specified by A. S. T. M. Method D5-25 serves very well for this purpose. If the ring and ball softening of the asphalt is less than 76.7° C. (170° F.), the 50-gram weight is used; otherwise the 400-gram weight is used.) The diameter of the circular base of this tin is 5.6 cm. (2.188 inches). When the weight is placed on the upper pad, care is taken that the layers of paper lie as smoothly as possible; the samples are then allowed to remain undisturbed for 5 days at 54.4° C. (130° F.). At the end of this time the stain number is obtained by recording the average of the number of sheets stained above and below the sample, counting the sheets next to the asphalt as No. 1. Duplicate tests should check to within one-half a stain number. The test should not be run on a sample that has been previously overheated and thereby subjected to decomposition.

Discussion

It will be found, with asphalts showing a high stain number, that the last sheets are stained over a smaller area than those closer to the samples. The last sheet will occasionally show a very small stain, but should be counted only when the diameter of the spot is greater than 1.6 mm. (0.0625 inch). This limit has been arbitrarily established because cases have been found where a minute hole in the paper allowed a small amount of the staining oil to pass to the next succeeding sheet. Experience in running the test will develop judgment in evaluating such cases.

TABLE I. STAIN NUMBERS FOR ASPHALTS

[About 20 penetration at 25° C. (77° F.), 100 grams, 5 seconds]

Method of Processing	Ring and Ball Softening-Point Range	Stain Numbers	
		5 Days at 54.4° C. (130° F.)	50 grams 400 grams
Steam refined	Below 65.6° C. (150° F.)	1 or less ^a
Slightly blown	65.6-76.7° C. (170° F.)	1 to 2
Semiblow	76.7-87.8° C. (190° F.)	1 to 5
Fully blown	87.8-98.9° C. (210° F.)	2 to 9
Fully blown	Above 98.9° C. (210° F.)	3 or more

^a If the asphalt does not stain more than one sheet, its staining propensity is too small to evaluate in 5 days and a longer time must be used.

Frequently the asphalt will stain more sheets above than below, or vice versa. When this occurs the difference is rarely more than one and the resulting stain number—i. e., the average—is not an integer but is reported to a half number.

The approximate range of stain numbers for different asphalts of about 20 penetration at 25° C. (77° F.), 100 grams, 5 seconds, and different softening points is shown in Table I.

² This special paper was selected after tests on many kinds of thin paper. In order to get a maximum number of sheets stained in a short time, the paper must be very thin. Further, it must not be too dense or it will prevent passage of the oily phase of the asphalt which is responsible for the staining. (Condenser paper about 0.010 mm. thick was found to be too dense to allow staining of more than one sheet.) Finally, it must not be too porous and absorbent or the asphalt will saturate it, resulting in the spreading of the staining oil throughout the sheet horizontally instead of vertically through successive sheets.

The paper used is 0.015 mm. thick, shows a densimeter (1) reading (100) of 800 to 1000 seconds, and weighs about 7 pounds per 2880 square feet. The paper is the regular 4-pound "Washington" grade (cigarette paper) manufactured by Peter J. Schweitzer, Inc., Elizabeth, N. J. It can be obtained in a 5-pound nubbins roll 26 inches wide, which is sufficient for about 600 tests, for \$5.00 per roll. A 50-cm. (about 18-inch) length of this paper is folded double five times, clipped at one end, and trimmed down to 10 by 8 cm. If this folding is done properly, two separate pads are obtained composed of 16 sheets each, between which the asphalt disk can be placed.

¹ Present address, Columbia University, New York, N. Y.

In general, the stain number of a particular asphalt is greater if the test is run at a higher temperature. However, if the temperature of test is too near the softening point, the asphalt becomes more nearly a true solution of the asphaltenes in the petrolenes or malthenes. In this condition the oily material tends to be retained, resulting in low stain numbers. This effect is more pronounced in the slightly oxidized asphalts. Further, as the temperature of test approaches the softening point, the asphalt becomes more fluid (2) and spreads out between the pads beyond the periphery of the bottom of the tin. In such a case the weight is not distributed uniformly over the surface of the asphalt. Considering the above factors and the desirability of using one temperature of test, an optimum temperature of 54.4° C. (130° F.) was selected as being most satisfactory. Using this temperature and two optional loads, it is possible to evaluate simultaneously the staining propensities of most plying asphalts over a wide range of softening points.

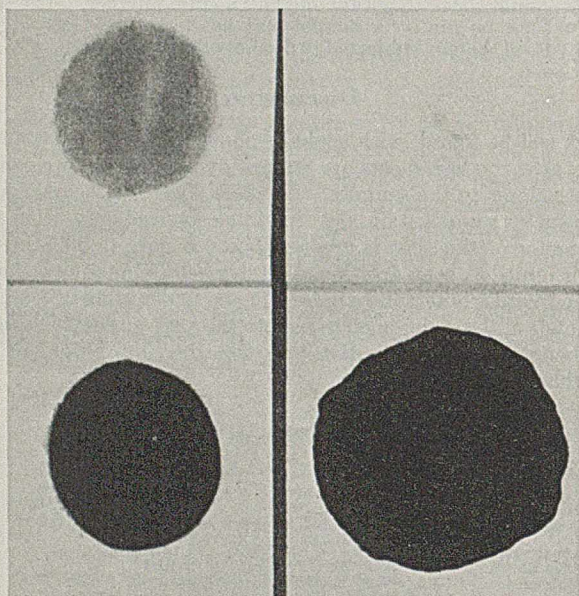


FIGURE 1. TYPICAL STAIN NUMBER RESULTS, SHOWING RELATIVE SIZE OF ASPHALT DISKS

The stain number usually increases as the weight applied is increased. In the case of asphalts with softening points below 76.7° C. (170° F.) and low loads (such as 50 to 400 grams), this increase is not appreciable and the results obtained for a 50-gram load on these asphalts may be compared with those obtained for asphalts of higher softening points under a 400-gram load. (A few experiments have indicated that there is a linear relation between the stain number and high applied loads, such as 400 to 2700 grams, for asphalts showing a high staining propensity.) Asphalts having high softening points will give a smaller surface exposed to a given weight, and consequently the weight per unit area will be greater than for asphalts of lower softening point. However, the increase in the stain number caused by the greater load per unit area for the former can be neglected because the effect on the stain number is about the same as would result from raising the temperature of test so as to obtain the same weight per unit area used with the asphalts of lower softening point.

The relative size of the asphalt disks for two asphalts is shown in Figure 1. The asphalt on the left had a ring and ball softening point of 93.3° C. (200° F.) and showed a stain number of 5.5 in 5 days, under a 400-gram load at 54.4° C. (130° F.). The asphalt on the right had a ring and ball softening point of 75° C. (167° F.) and showed a stain number of 1.5 in 5 days under a 50-gram load at 54.4° C. (130° F.).

Most asphalts show a relatively large proportion of their

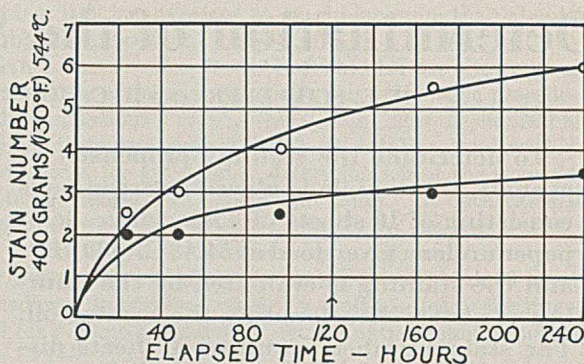


FIGURE 2. TYPICAL STAIN NUMBER-ELAPSED TIME CHART

staining in the first 75 to 100 hours of the test. This is illustrated in Figure 2. After about 120 hours the rate tends to slow down and the curve flattens out, except for asphalts which show stain numbers above about 8. The length of time for a rapid evaluation of staining propensity has therefore been set arbitrarily at 5 days (120 hours). In general there is sufficient difference between the stain numbers of asphalts at 5 days to evaluate their staining propensity. The difference in stain numbers is accentuated by using a longer time, such as 10 days, for the test, but this length of time is recommended only for asphalts that show a stain number of less than one. The asphalts continue to stain indefinitely; two samples that have been at room temperature under a 400-gram load for one year still show evidence of increased staining but the rate is very slow, as shown in Table II. Asphalts A and B showed a stain number of 3.5 and 5.5, respectively, for a 5-day test at 54.4° C. (130° F.).

The staining propensity as measured by the stain number is definitely a time function and cannot be accelerated; subjecting disks of asphalts, between various types of paper, to high pressures for a short time did not give the desired information.

Interpretation of the Stain Number

The determination of the stain number is not greatly influenced by the personal element. Although it is not a true quantitative measure of staining, it is more than a qualitative test. When two asphalts C and D have stain numbers of 6 and 3, respectively, C is definitely more staining than D. However, C does not necessarily exude twice as much oil as D, since the sixth sheet of C may show only a small stain while the third sheet of D may show a large stain.

TABLE II. STAIN NUMBERS

(Asphalts A and B at room temperature under 400-gram load)

Elapsed Time, Days	Sheets Stained	
	Asphalt A	Asphalt B
45	3.5	5.5
51	4	6
70	5	7
114	5	8
194	6	10
258	6	10.5
303	7	11.5
365	7	12.5

Although the stain number measures the rate of staining, it is apparently related to the total amount of oil exuded. The results in Table II indicate that there is more staining oil in asphalt B than in A because the stain number of A is increasing at a much slower rate than that of B and appears to be approaching a constant.

When two asphalts are within one-half a stain number they must be considered as having the same staining propensity, since this is the limit of accuracy of the test as determined by duplicate runs.

Acknowledgment

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An Electrometric Method for the Determination of Silver

H. ROBINSON AND H. HUGG, Tiffany & Co., Newark, N. J.

IN THE potentiometric determination of silver, using potassium iodide as the precipitant, the end-point error due to adsorption of the reagent by the precipitated silver iodide has been eliminated by the method of Lange and Berger (1). However, the length of time required renders the method unsuitable for industrial analysis.

The method described here eliminates this error, and is fast and accurate. The silver, in solution as nitrate, is titrated with potassium iodide, using a pair of electrodes which are connected to a microammeter. One electrode is gold, the other is carbon saturated with nitric acid. The first excess of potassium iodide generates sufficient current through oxidation by the nitric acid-carbon electrode to read directly on the microammeter, neither amplifier nor balancing circuit being required.

Apparatus and Reagents

A microammeter with a range of 0 to 100 microamperes is required, preferably with a zero center scale.

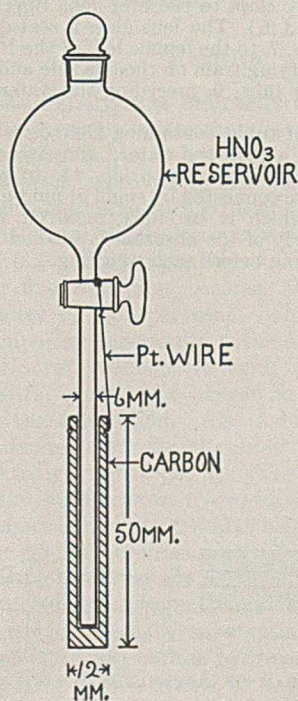


FIGURE 1. CARBON ELECTRODE

The gold electrode may be of any convenient size. The one used by the authors is 2 mm. square by 100 mm. long. Larger gold electrodes allow a larger current flow at the end point, but one of shorter duration. The metal should be well annealed, and cleaned by rubbing with moist pumice powder.

The carbon electrode may consist of a piece of coreless arc-light carbon 12 mm. in diameter. However, if much work is to be done by this method, an electrode may be constructed as illustrated in Figure 1.

The carbon electrode is saturated with nitric acid which has been treated with nitrogen peroxide, made by passing nitric oxide through concentrated nitric acid in an open vessel. Potassium iodide (0.1 *N*) is used for the titration.

Procedure

The carbon electrode, if solid, should be allowed to soak in nitric acid containing dissolved oxides of nitrogen for about 5 minutes. If the hollow electrode is used, the stopcock from the nitric acid reservoir is opened until the electrode is saturated. In either case, the electrode is prepared for 20 sterling silver assays without further treatment with nitric acid.

The carbon electrode may be saturated with ammonium persulfate instead of nitric acid. Crystallization of the salt renders it less desirable.

The electrodes are connected directly to the microammeter, the carbon electrode being positive at the end point.

One gram of the silver alloy is weighed and placed in a 250-cc. beaker with 5 cc. of 1 to 1 nitric acid, and heated until the metal has dissolved and oxides of nitrogen have been expelled. An excessive amount of nitric acid must be avoided. After cooling, the solution is diluted to 120 cc. and placed under the electrodes. At first a momentary current of 100 μ a is generated, the meter rapidly returning to zero and remaining there. The mechanical stirrer is started and the titration is begun by allowing the 0.1 *N* potassium iodide solution to run at the rate of 0.5 cc. per second into the beaker.

The microammeter will not start to fluctuate until the titration has proceeded to within 1 cc. of the end point. At this stage, the addition of each drop will cause the needle to fluctuate, but after each fluctuation it will return to zero, until 0.05 cc. of 0.1 *N* potassium iodide solution in excess has been added. At this point the meter will indicate about 40 μ a. This flow of current will be constant for 4 minutes with the gold electrode 2 mm. square immersed 50 mm. in the solution. An excess of 0.1 cc. will generate 120 μ a, increasing with added potassium iodide until at 0.7 cc. excess the current generated is 1000 μ a. Further addition of the precipitant will produce increasing current flow, but with decreasing gain in proportion to reagent added.

Interfering Elements

Lead, copper, cadmium, nickel, cobalt, and zinc in concentrations as high as 55 per cent have been found not to interfere with the end-point potential nor the accuracy of the method. Suspended metastannic acid, and traces of antimony, aluminum, and colloidal gold have no effect. The presence of iron does not lower the accuracy or sensitivity, but in solution as ferric nitrate it will cause a current flow in the same direction as that generated at the end point, and proportional to the amount of iron present. However, when iron is present the needle of the microammeter may be returned to zero by a balancing current and the titration carried out as usual. Palladium must be absent, as this element is precipitated as iodide in weak acid solutions and is precipitated completely before the end point.

The presence of sulfates renders the end point indefinite. If the sample consists of sulfates or if the sample has been dissolved in concentrated sulfuric acid, the carbon electrode must be saturated with 0.1 *N* ceric nitrate. Results will be satisfactory if the concentration of sulfuric acid is about 2 *N*.

Accuracy

The results obtained by this method were checked by the gravimetric chloride method, using 1-gram samples of sterling silver. Some typical results are given.

Gravimetric Chloride %	Electrometric Method %
92.99	93.00
93.01	93.04
93.00	93.03

The method is accurate up to 50° C. Above this temperature the rapid oxidation produces violent fluctuation of the microammeter at the end point, with consequent shortening of the duration of the current flow at the end point. At temperatures below 25° C. the end-point reading of 40 μ a will remain for 4 minutes.

Summary

A new method for the determination of silver incorporates the following features: It is accurate, precise, and rapid. With the exception of palladium none of the usual elements present in silver alloys interferes.

No amplifier, balancing circuit, nor reference cell is required. (In the exceptional case where iron is present, the balancing circuit must be used.)

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Determination of Carbon and Hydrogen Content by Combustion

MARY W. RENOLL, THOMAS MIDGLEY, JR., AND ALBERT L. HENNE
Ohio State University, Columbus, Ohio

THE purpose of the present paper is to show that carbon and hydrogen determinations by combustion can be performed with a degree of accuracy considerably higher than that which is generally obtained. These improved results are obtained by slight modifications of the ordinary combustion setup, and above all by adequate technic in the burning of the sample.

Apparatus

The equipment used in this laboratory (see Figure 1) follows the design of that described by Smith, Taylor, and Wing (3). It has no rubber connections, only three ground joints, and is made entirely of glass. The purifying train consists of tubes sealed in series and containing, 1, copper oxide heated by an external electric resistance; 2, concentrated sulfuric acid acting as a bubble counter; 3, Ascarite; 4, Dehydrite; and 5, phosphorus pentoxide. This train ends in a male half of a 20-mm. standard Pyrex ground-glass joint, 6, and it is mounted on a board to permit its connection to the combustion tube by sliding it in place as one unit. The air which it purifies is received through a calcium chloride tower from a 20-liter bottle from which it is displaced by water. Up to the purifying train, rubber connections are used, but not beyond it.

The combustion tube, 8, is of the shape described by Smith (3) but is of Jena Supremax glass (obtained from the Fish-Schurman Co., New York, N. Y.). It contains plain copper oxide held between two rolls of copper gauze. The reason for this change is that combustions are always better regulated with air than with oxygen; however, when air is used, a higher temperature is needed to burn completely the high molecular weight

materials used in this laboratory. At the high temperature needed, the life of a Pyrex tube is only one or two combustions, and it frequently adheres to the heating units, thereby ruining them. (New Pyrex glass No. 172 has recently become available; its specifications are very close to those of Jena Supremax, but the authors have not tried it.) The Jena glass is sealed by means of a ring of uranium glass, 7, to the female half of the Pyrex joint, 6, connecting to the purifying train on the one side and to the U-shaped water-condensing tube, 9, preceding the water absorber, 10, on the other.

The absorbers are light tubes containing Dehydrite and phosphorus pentoxide, 10, to absorb the water; and Ascarite with a little Dehydrite and phosphorus pentoxide, 11, to absorb the carbon dioxide. They are connected by small ground-glass joints, coated with vaseline, which is carefully removed with ether before weighing; the body of the absorber is washed with ether and wiped with a clean rag before each weighing.

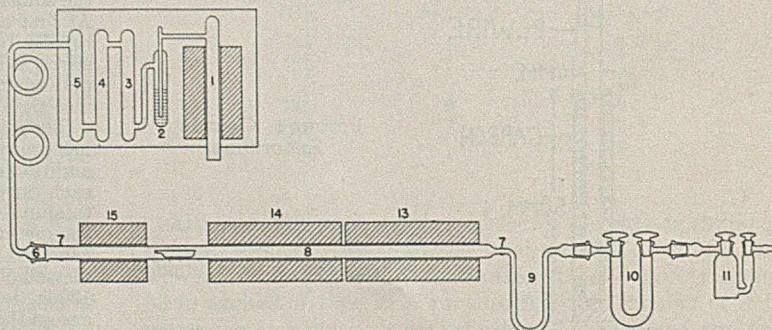


FIGURE 1. DIAGRAM OF APPARATUS

As a final precaution, the effluent gases are always bubbled through white concentrated sulfuric acid. This serves as a measurement of the combustion speed and as a check on the completeness of the combustion, since incompletely burned materials color the acid, thus warning that the results are incorrect and to be discarded. If oxygen is used instead of air, the acid invariably becomes colored.

Procedure

The combustion procedure itself aims essentially at causing as slow and steady a combustion as possible. Volatile samples are slowly evaporated, and nonvolatile samples are charred progressively without inflammation. The following procedure generally gives the desired results:

The two long electric units of the combustion furnace, 13 and 14, are heated until the tube is red hot. Air is passed at a speed of about 2 bubbles per second, maintained during the whole procedure. After about 15 minutes the absorbers are attached; air is passed during half an hour (or a whole hour if the absorbers have been freshly refilled); the absorbers are then removed, cleaned, weighed, and reattached. The sample, weighed in an ignited platinum boat, is introduced into the cold end of the furnace in the empty space between the long heating units, 13 and 14, and the short electric unit of the furnace, 15. The hot section should now be white hot.

The sample is heated gently with a Bunsen burner to cause evaporation or carbonization; the gas burner is used because it is impractical to supply heat gently enough at this stage by means of the short electric unit of the furnace. This phase of the combustion requires considerable patience, but its correct manipulation is essential for accurate results; it usually takes from 60 to 90 minutes. When only carbonaceous material remains, the short electric unit is heated and progressively brought over the sample. Intense heating is continued for 1 to 2 hours. During this time air is passed through the tube at the same steady rate, and causes the water (partially condensed in the U-shaped end of the combustion tube) to be carried over into the drying agent. This transfer of water must not be accelerated by heating the U-end of the tube, since the steam thus generated can cause a leak through the vaseline of the ground joint and carry vaseline into the absorbent.

Samples to be burned should weigh between 0.1 to 0.2 gram, determined to 0.01 mg. The absorbed water and carbon dioxide are weighed with the same accuracy. The whole procedure takes from 6 to 8 hours. For a series of combustions, it is convenient to keep the furnace and purifying train warm day and night.

Results

Combustion analysis as ordinarily reported seldom yields results of an accuracy better than 0.2 per cent. The typical results given in Table I demonstrate how greatly the accuracy has been improved by the method herein described. Investigation has demonstrated that this accuracy is limited only by the errors which occur in weighing. Hence, with a sample of 0.2 gram weighed to ± 0.01 mg. the maximum error with five weighings becomes 0.025 per cent with a probable error of 0.01 per cent. This estimation is borne out by comparing the results with calculations in the cases of synthetic rubber, benzoic acid, and triphenylcarbinol. The unknown quantity of oxygen in natural rubber interferes with the correlation. Also a higher hydrogen-carbon ratio is indicated for natural rubber than C_5H_8 , which has been repeatedly verified (2, 3). The same high hydrogen-carbon ratio holds true in hydro-rubber. Sucrose is a material in which dehydration starts before desiccation is complete; the results obtained thus indicate an excessive removal of water in drying the particular sample.

The close checking of several runs should be noted.

This degree of accuracy substantially permits the determination of one more or less hydrogen atom in a molecule containing 1000 carbon atoms.

Results are almost uniformly good, after the operator has gained some practice. For routine analyses which are regularly carried out by students, the same technic is used but weighings are done to only 0.2 mg.

TABLE I. TYPICAL RESULTS

	Calculated		Measured	
	C	H	C	H
Synthetic rubber (C_5H_8) _n	88.16	11.84	88.17 88.17 88.17 88.07	11.82 11.83 11.83 11.86
Natural rubber (C_5H_8) _n O?	88.16	11.84	88.07 85.59 85.58	11.86 14.39 14.40
Hydro-rubber (C_5H_8) _n	85.62	14.37	85.58 68.84 68.83	14.39 4.94 4.95
Benzoic acid	68.84	4.95	68.84 42.17 42.16	4.94 6.49 6.50
Sucrose	42.10	6.48	42.16 87.63	6.50 6.20
Triphenylcarbinol	87.65	6.20		

No sulfur compounds have been tried. Some chlorinated materials have been successfully analyzed with the use of electrolytic silver wool, supplied by Dr. McNevin of this department. This phase of the work will be presented by Dr. McNevin in the near future; the authors' own experience should still be regarded as limited.

Discussion

In beginning this work the then conventional atomic weights of O = 16.000, C = 12.00, and H = 1.008 were adopted. Experimental data indicated a uniform and average deficiency of total recovery of 0.03 per cent. Likewise the hydrogen-carbon ratios were inclined to be high. A careful recapitulation of possible errors failed to disclose any cause. It was then recognized that the value 12.00 for carbon was less accurate, by a decimal point, than the check results obtainable. It was therefore held proper to assume a value for carbon which would yield consistent results. Table II gives the results of computations on the data derived from synthetic rubber. It will be seen that C = 12.005 corrects the previously observed deficiency. This value has been used in all the results reported herein.

TABLE II. SYNTHETIC RUBBER

	Hydrogen		Carbon		Total (Average)
C = 12.000	11.82	11.82, 11.83	88.14, 88.14	88.14	99.97
C = 12.005	11.82	11.83, 11.83	88.17, 88.17	88.17	100.00
C = 12.010	11.82	11.83, 11.83	88.19, 88.19	88.20	100.02

No contention is made that this value of 12.005 is a determination of the atomic weight of carbon. It may well be that it is merely a correction factor for some regular, but not recognized, error. On the other hand, the newer experimental values for carbon reported during the past 2 years indicate 12.007, while Baxter and Hale (1) report 12.009 measured by much this same combustion method on much larger samples.

Summary

This paper shows that by simple improvements of the customary combustion apparatus, and patient burning of the sample in air instead of oxygen, results are obtained for carbon and hydrogen which are accurate to 0.01 per cent.

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Determination of Moisture in Wood Chips, Sawdust, and Pulp

A. J. BAILEY, Agricultural Experiment Station, University of Minnesota, St. Paul, Minn.

A COMMON and standard method (3) of determining moisture in wood and similar plant material consists of refluxing with toluene, the toluene returning to the distilling flask and the water being retained in a trap. By employing a noninflammable liquid of higher boiling point, safety and speed may be increased, while the method is suitable for routine work in the hands of an unskilled worker.

Apparatus and Reagent

Tetrachloroethylene is admirably suited to this determination, having a boiling point of 118.5° C. and being noncombustible. The apparatus and technic of the determination with this liquid are only slightly modified from the standard procedure. The proposed method consists of boiling the wet material in tetrachloroethylene, condensing the vapors in a reflux condenser and returning them to a trap from which the tetrachloroethylene is drained to the distilling flask, leaving the water layer in the graduated trap.

The apparatus (Figure 1) consists of a wide-necked flask, a Liebig condenser, a moisture trap, and a drying tube. The size of the flask depends on the bulkiness of sample used, but should preferably be of 500- to 1000-ml. capacity. The moisture trap follows the general plan of that proposed by Dean and Stark (2) and Bidwell and Sterling (1), but the total capacity should be 50 to 100 ml. instead of the usual 10 ml. The exact size of the trap is not important as only its lower, narrow portion need be graduated. The side tube of the trap is bent parallel and close to the trap body, on the bottom of which a stopcock is sealed.

A two-hole rubber stopper connects the stopcock and vapor tube to the distilling flask. Because of the high specific gravity of the tetrachloroethylene (1.608), the water layer floats; hence, the necessity of draining the tetrachloroethylene to the flask to trap the water. A drying tube at the top of the condenser prevents moisture condensation from atmosphere of high relative humidity. The interior of the condenser tube should be cleaned with hot chromic-sulfuric acid cleaning solution before use to minimize the retention of water drops after the distillation.

Procedure

After the sample has been added to the flask, the trap and condenser are attached, and tetrachloroethylene is poured down the condenser until a normal space is left above the floating sample for vapor disengagement. A drying tube and electric heater are attached, and a constant rate of boiling is established. The stopcock is then opened slightly to return the tetrachloroethylene to the flask as fast as it distills, in order to keep the lighter water from running back down the vapor tube. All water is usually driven off in 0.5 to 0.75 hour. After the boiling is stopped, the condenser is wiped with a tube brush on a ramrod, while simultaneously a small quantity of tetrachloroethylene is poured down to remove adhering drops of water. By opening the stopcock, all tetrachloroethylene is returned to the flask, and the volume of water is read directly and calculated to percentage moisture content.

Precision

The method was checked against moisture contents determined by oven drying and by the standard toluene method. Values obtained by the proposed method and the toluene method on wood chips, wood sawdust, and wood pulp were practically the same. The differences between the values obtained by the proposed method and by oven drying were in close agreement with the differences between the toluene method and oven drying. Hence, in accuracy and precision the new method is equivalent to the toluene method. On the

basis of a sample of 100 grams dry weight and duplicate water volumes in the trap agreeing to within 0.1 ml., a precision of about one part in a thousand was indicated. With the material examined, no interfering substances were found; turpentine, resin, and volatile oils were soluble in the tetrachloroethylene. Naturally, the precision is dependent upon the moisture content and size of sample.

Discussion

The proposed method is handicapped by slightly higher reagent cost, although the difference is minor, especially when nearly complete recovery can be effected. Presence of some water-soluble volatile liquids, such as ethanol and glycerol, if the method were applied to material containing these, would result in error, but of less magnitude than with toluene. It would appear that water of crystallization would be driven off as in the toluene method.

The technical skill required for the determination is the same as that required for the toluene method. As far as is known, decomposition of carbohydrates, involving either liberation or imprisonment of water, does not occur. Owing

to the high density of the tetrachloroethylene, samples are not exposed to the superheating that occurs in the toluene distillation; hence, there is no possibility of the sample's sinking to the bottom where burning (and water formation) are likely to occur. The method is more accurate than the usual oven drying, which measures volatile substances such as turpentine and volatile oils by loss of weight, whereas the proposed method measures water directly. The time required is a little less than that using toluene.

In view of the absence of oxidation or other detrimental effects on the sample, the method should be applicable to a wide variety of biological and organic materials. The simple apparatus and manipulation should recommend its adoption for control work by laboratory assistants. Emphatic recommendations for its general adoption are the complete freedom from the fire hazard that is encountered in using toluene, turpentine, naphtha, etc., and the ease of reading the meniscus, since only

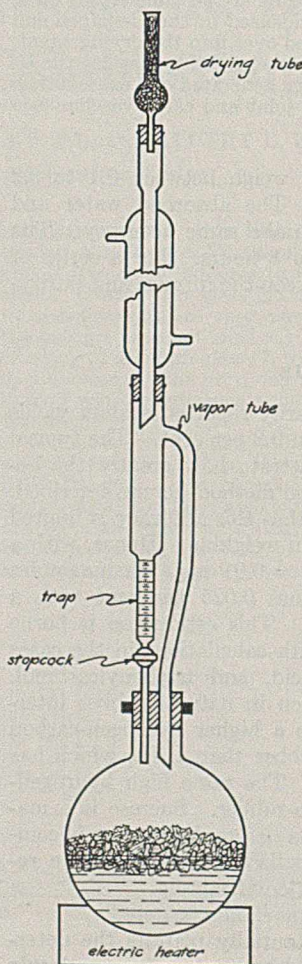


FIGURE 1. APPARATUS

a water-air meniscus is read, obviating the necessity of recalibrating the graduated trap for a water-toluene meniscus.

Summary

A method of determining the moisture in wood and pulp by distilling with tetrachloroethylene substituted for toluene is proposed. Common apparatus suffices, only a slight modification of the standard equipment being necessary, while the simplicity of the technic of the determination lends itself to routine work. The accuracy and precision of the method are

nearly identical with the toluene method, while time is reduced and fire hazard is completely eliminated.

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Determination of Small Quantities of Arsenic in White Metals

A Bromate Titration Method

C. W. ANDERSON, Continental Can Company, Inc., Chicago, Ill.

IN MOST established methods for the determination of arsenic in metals and alloys the sample is dissolved in concentrated hydrochloric acid with the addition of potassium chlorate. The arsenic is then separated by adding to the solution sodium hypophosphite (1) or stannous chloride (4), and determined by dissolving in an excess of standard iodine solution and titrating the excess with a standard sodium arsenite solution. Calcium hypophosphite (3) is also being used for the separation of arsenic. The time required for an analysis by these methods is indicated to be at least 2 hours.

In the present method calcium hypophosphite is used to separate the arsenic from a bromine-hydrochloric acid solution of the metal. The arsenic is then dissolved in hot concentrated sulfuric acid and reduced with sodium sulfite, the excess sulfur dioxide is expelled, and the solution, containing arsenious acid, is titrated with standard potassium bromate solution. The time required for a tin or bearing metal analysis is less than 1 hour, and for a lead analysis, less than 2 hours. Concurrent results are obtainable when two or more analyses are carried through on the same metal. Experimental analyses performed with metals of known arsenic content, to which various amounts of pure arsenic are added, yield recoveries which are in accord with those obtainable by established methods. Calcium hypophosphite is an excellent reducing agent for separating arsenic in white metal analyses. Table I gives the experimental data obtained in determining the arsenic content of a sample of antimony. These analyses show that in the presence of large amounts of antimony, there is no interference by this metal when using calcium hypophosphite for arsenic separations.

Solutions and Reagents Required

BROMINE SOLUTION. Dissolve 12 ml. of pure bromine in 100 ml. of concentrated hydrochloric acid by shaking vigorously in a glass-stoppered bottle.

CALCIUM HYPOPHOSPHITE SOLUTION. Dissolve 15 grams of calcium hypophosphite in 100 ml. of water to which has been added 5 to 10 ml. of concentrated hydrochloric acid.

Cuprous chloride and anhydrous sodium sulfite.

METHYL ORANGE INDICATOR. Dissolve 0.1 gram of methyl orange powder in 100 ml. of hot water and filter.

POTASSIUM BROMATE SOLUTION, 0.015 N; 1 cc. = 0.5622 mg. of arsenic. Weigh 0.4175 gram of the salt, dissolve in water, and make up to volume in a liter flask. This solution should be standardized against pure arsenic trioxide. A quantity of the trioxide, 0.01485 gram, is weighed, then dissolved in 2 or 3 drops

TABLE I. ARSENIC DETERMINATIONS ON A SAMPLE OF ANTIMONY

Weight of Sample Gram	Arsenic Originally Present Mg.	Arsenic Added Mg.	Total Arsenic Present Mg.	0.015 N KBrO ₃ ML.	Arsenic Found Mg.
0.30	0.55	0.309
0.30	0.55	0.309
0.30	0.309	0.50	0.809	1.45	0.815
0.50	0.515	0.675	1.19	2.15	1.209

of a saturated solution of sodium hydroxide, water and sulfuric acid are added, and the titration is carried out as in the regular analysis. This quantity of the trioxide requires 20 ml. of the bromate solution.

GOOCH MICROCRUCIBLES of about 1.5-ml. capacity (Gooch microcrucibles can be purchased from the Wilkens Anderson Company, or the Central Scientific Company, Chicago, Ill.).

SPECIALLY PREPARED ASBESTOS (2) for the Gooch crucibles for filtering the arsenic. Medium-fiber asbestos is shaken in a bottle with a solution of one part of the bromine-hydrochloric acid mixture and seven parts of water. It is allowed to stand a few hours and diluted with an equal volume of water. When used in the Gooch crucible the excess bromine is washed out by one or two washings with water. High and erroneous results are obtained if ordinary asbestos is used without this treatment.

Procedure for Tin and Bearing Metals

Weigh a 1.0-gram sample of filings into a 100-ml. beaker. With a cover glass over the beaker, add a mixture of 5 ml. of 1 to 1 hydrochloric acid and 12 to 15 ml. of the bromine-hydrochloric acid solution. Allow to stand 1 or 2 minutes and then place over a small flame to complete solution of the metal. Add 0.3 to 0.5 gram of cuprous chloride, and after it is dissolved add 5 to 10 ml. of calcium hypophosphite solution and place the beaker over the small flame again. A brownish black suspension of finely divided arsenic will form after a few seconds. Cuprous chloride acts as a catalyzer in the precipitation of the arsenic.

Continue heating, finally allowing the solution to boil gently for 10 to 15 minutes to cause the precipitate to become coarser for more convenient filtration. Filter the solution through a Gooch microcrucible, using an aspirator or the vacuum line. Wash the beaker twice with a little concentrated hydrochloric acid, allowing it to flow through the crucible. Follow this by two or three washings with water. Transfer the crucible to a Pyrex test tube of about 1.8 cm. inside diameter and 15 cm. in length. Add 3 ml. of concentrated sulfuric acid and shake carefully to loosen the asbestos layer holding the arsenic. Insert the test tube into the flame of a Méker burner and hold there 10 to 15 seconds or until all the arsenic is dissolved. Allow to cool, add a few milliliters of water, and mix the contents by shaking. Cool again and wash the

TABLE II. RESULTS OF EXPERIMENTAL ANALYSES

Sample	Arsenic Originally Present		Arsenic Added Mg.	Total Arsenic Present Mg.	0.015 N KBrO ₃ Ml.	Arsenic Found Mg.	Error Mg.	Per Cent Recovery
	Grams	Mg.						
Pure Arsenic	{	1.25	...	2.25	1.265	+0.015	101.2
	{	1.50	...	2.60	1.462	-0.038	97.5
Bureau of Standards sample No. 54, tin-base bearing metal	{ 1.0	0.50	0.90	0.506	+0.006	101.2
	{ 1.0	0.50	0.25	0.75	1.35	0.759	+0.009	101.2
	{ 0.5	0.25	0.275	0.525	0.95	0.534	+0.009	101.7
	{ 0.5	0.25	0.40	0.65	1.20	0.675	+0.025	103.8
	{ 0.5	0.25	0.75	1.00	1.80	1.012	+0.012	101.2
Continental Can Company, tin No. 1	{ 1.0	0.95	0.534
	{ 1.0	0.534	0.30	0.834	1.45	0.815	-0.019	97.7
Another tin sample, No. 2	{ 1.0	0.85	0.478
	{ 1.0	0.478	0.50	0.978	1.75	0.984	+0.006	100.6
Continental Can Company lead	{ 2.0	0.40	0.225
	{ 1.0	0.112	0.30	0.412	0.70	0.394	-0.018	95.6

contents of the test tube into a narrow-form 180-ml. Pyrex beaker, diameter 3.5 to 4.0 cm., and wash the last traces of solution from the tube with water.

To the solution and crucible in the beaker, volume 15 to 20 ml., add 10 mg. of anhydrous sodium sulfite. Mix by a gentle shaking or swirling, cover with a watch glass, and place over a small flame until gentle boiling begins. Now allow a fairly rapid stream of air, three or four bubbles per second, to pass through the solution for 1 minute. Wash off the cover glass and sides of the beaker, add a drop of methyl orange indicator, and titrate with 0.015 N potassium bromate solution. Add the bromate drop by drop from a 10-ml. buret, graduated in 0.05-ml. divisions, to the disappearance of the pink color of methyl orange. From the final buret reading deduct 0.10 ml., this being the amount of the blank titration for the reagents used. It is advisable to determine the reagent blank occasionally.

Procedure for Lead Analysis

Weigh a 2-gram sample of 80-mesh filings into a 150-ml. beaker. Add the bromine-hydrochloric acid alone without any dilution with water or hydrochloric acid, the solution of this metal pro-

ceeding somewhat slowly even when this most reactive solution is used. The time required for solution of 2 grams of the metal is about 1 hour. Care must be exercised to maintain some excess of free bromine during the process of solution to avoid loss of arsenic by the formation of the volatile trichloride. From this stage the process is continued as given above for tin and bearing metals. When the arsenic has been precipitated, the solution is filtered while hot to avoid difficulty caused by the crystallization of lead chloride.

Bureau of Standards sample No. 54, a tin-base bearing metal containing tin 88.24, antimony 7.33, copper 3.75, lead 0.56, bismuth 0.05, and arsenic 0.05 per cent, was used as a

sample for reference in the development of this method. In the experimental analyses the arsenic added was taken from a solution prepared from Bureau of Standards arsenic trioxide. In the two experiments using pure arsenic alone, the regular course of analysis was followed. The larger deviation in the second experiment is an amount of arsenic less than that to which 0.10 ml. of the bromate solution is equivalent. In all the other experimental analyses the error is less than the arsenic value of 0.05 ml. of the bromate solution.

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Cellulose Analysis

A Comparison of Three Principal Methods

J. DAVID REID AND D. F. J. LYNCH

U. S. Agricultural By-Products Laboratory, Iowa State College, Ames, Iowa

THE cellulose work of this division is concerned with the utilization of fibrous farm by-products as a source of cellulose. An accurate method of estimating cellulose, as well as a comparison of the values obtained by analysts using different methods, is desired. The present investigation was accordingly carried out in the following manner: Four representative farm wastes—namely, wheat straw, rye straw, bagasse and cornstalks, and spruce wood of 40- to 60- and 60- to 80-mesh fineness—were analyzed for cellulose by three different methods and the resulting crude celluloses were analyzed for pentosan, lignin, ash, and alpha-cellulose.

The numerous methods of cellulose analysis need not be critically reviewed here. This has been thoroughly and capably done by Renker (16) and others. These methods fall mainly into two groups: those which hydrolyze cellulose leaving the accompanying substances, and those which oxidize and remove the associated substances leaving cellulose. Since this division is interested in the preparation of cellulose, particularly alpha-cellulose, the first group was not considered. A review of these methods, particularly that of Kiesel and Semiganovsky (7, hydrolysis of cellulose and titration of the resulting glucose) is given by Kalomanovitch and Kalotireva (6).

On the basis of Renker's (16) critical investigation, The International Commission on Applied Chemistry (1909) recognized the methods of Cross and Bevan (4) and of Müller (13) as being the most accurate.

The greater convenience of the former method over the latter has established it or one of its numerous modifications as practically a standard method. Three promising methods, as to accuracy and rapidity of manipulation, for determining cellulose in fibrous materials have been developed since the original Cross and Bevan method was published. They are as follows:

The chlorine dioxide method of Schmidt (17); this method was not used in the present studies for the reason that the explosive nature of chlorine dioxide renders its use undesirable for routine analyses in the laboratory.

The Norman and Jenkins (14) method which involves the use of sodium hypochlorite solution.

The Kürschner and Hoffer (9) method which is based upon the use of nitric acid and alcohol as a reagent.

The latter two methods and the Cross and Bevan method, with certain modifications, were selected for study in this investigation.

Experimental

SAMPLES. Bagasse, cornstalks, rye straw, wheat straw, and spruce wood were selected as representative materials. They were ground in a Wiley mill (21) to pass through a 40-mesh sieve and be retained on a 60-mesh sieve. An additional sample of spruce wood flour was prepared to pass through a 60-mesh sieve and be retained on an 80-mesh sieve. Since wood of the latter size is usually taken for analysis, it was felt that both sizes should be used. (The results did not vary greatly for the two sizes.) The spruce samples were given a preliminary extraction with benzene-alcohol (60-40) mixture to remove resins. Every effort was made to obtain uniform samples. The cornstalks were particularly difficult to handle because of sand embedded in the stalks.

The samples are not truly representative of the plant material selected. For example, the bagasse had received a mechanical cleaning treatment with sieving and the fiber portion was further segregated by the grinding in the Wiley mill and sieving again to obtain the selected samples. This is evidenced by the abnormally high cellulose and lignin contents of the bagasse samples.

The sieved material was kept in sealed mason jars until it was required. Then thirty-five samples, a number sufficient for the entire analysis, were prepared and stored in weighing bottles until used.

PROCEDURE. Jena fritted-glass crucibles (No. 1-G3), capacity 30 cc., were used. The disks had pores ranging from 20 to 30 microns in diameter. An average loss of about 0.0020 gram per crucible per determination was noted in the Cross and Bevan and Norman-Jenkins methods, due, probably, to solvent action of the hot alkaline liquors on the glass. No correction was made for this loss (about 0.2 per cent) as was done by Menon (12). Oven-dried samples were not used for analysis, the moisture contents being determined on separate samples. Six to eight 2-gram samples were weighed out and the cellulose was determined by one of the three methods given below. The pentosan content was determined on three of these samples as well as on the original material by the official A. O. A. C. (1) 12 per cent hydrochloric acid method. Ash was determined on one sample at low red heat. (Two samples were used if the ash were high.) Lignin determinations were made on one or two samples by the fuming hydrochloric acid method (2) but no correction was made for nitrogen.

The average of these impurities (ash, lignin, pentosans) was calculated and subtracted from the crude cellulose value to give the value designated as "pure cellulose." It was necessary to treat large samples (5 to 6 grams of material in each case) so that an alpha-cellulose determination could be made on one portion and a moisture determination on another portion. Special apparatus was used in the case of the large Cross and Bevan samples. Alpha-cellulose determinations were made on the resulting celluloses according to the method described by Schorger (18), except that fritted-glass crucibles were used instead of the aluminum ones recommended. Practically no loss due to the action of the sodium hydroxide solution on the glass was found in these alpha-cellulose determinations, probably because the solution was cold and was in contact with the crucible for only a very short time.

DEFINITIONS. The terms used in this paper are defined as follows:

"Crude cellulose" is that portion of the plant material remaining after treating according to one of the above-mentioned methods of cellulose analysis in each case.

"Pure cellulose" is the crude cellulose after correction for its ash, pentosan, and lignin content.

"Alpha-cellulose" is that portion of the "crude cellulose" remaining after treatment in the prescribed manner with 17.5 per cent sodium hydroxide solution and correcting for ash content.

Methods and Apparatus

CROSS AND BEVAN. The apparatus used for the 2-gram sample was a slight modification of that used by Sieber and Walter (19) as described by Phillips (15). The procedure was that described by Phillips, except that no permanganate after-bleach was used and the cellulose was not given a final

wash with alcohol, because of the strong adsorptive power of cellulose for alcohol (20), but it was removed from the crucible and digested thoroughly with 100 cc. of water in a beaker. Otherwise, the method was the usual one of alternate chlorination and extraction with 2 per cent sodium sulfite solution.

The final filtration of the Cross and Bevan cellulose as well as each of the Norman-Jenkins filtrations, using the fritted-glass crucible, gave considerable trouble unless the suspension was stirred well and poured into the crucible, allowing it to settle a little before turning on the suction. This forms a mat, preventing the fine material from clogging the fritted-glass filter. No trouble was encountered in the filtration of Kürschner-Hoffer cellulose.

A special apparatus, which proved very satisfactory, was developed for the analysis of the large 6-gram samples, as shown in Figure 1.

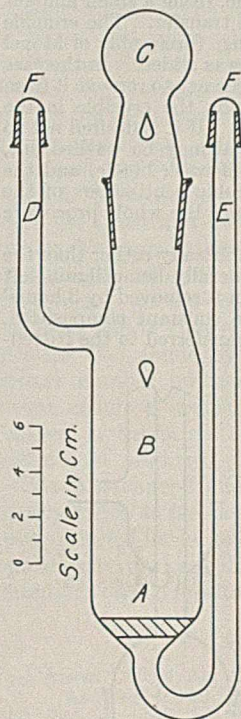


FIGURE 1. APPARATUS FOR LARGE SAMPLE CROSS AND BEVAN DETERMINATIONS

The apparatus is useful because large samples up to 10 grams in weight may be treated at one time. The apparatus consisted of a sintered-glass disk, A, sealed into a glass tube, B, which is 45 mm. in diameter and 145 mm. long. The top, C, was made from a 29/42 standard ground-glass joint and was held on by springs hooked to small glass lugs. Two tubes, D and E, were sealed on as shown. Two caps, F and F', were ground onto the arms, D and E, so that the apparatus could be made airtight for weighing. A piece of Nichrome wire was put around the tube in such a way as to support the long arm and also serve as a sling for weighing.

The sample was weighed into the flask and wetted. Chlorine was introduced at D and suction applied at E. Alternatively, chlorine may be introduced at E and drawn up through the sample. The springs holding the top, C, should be weak, so that if chlorine pressure develops inside, the top will not crack when it snaps back into place. A drop of glycerol should be used as lubricant for the ground-glass joints. This is easily washed out before weighing. The sample was washed and heated in sodium sulfite solution in the usual manner. Liquids were drawn off by attaching a suction flask to E by means of an L-shaped glass tube and a small piece of rubber tubing and applying suction. Large samples were weighed in the apparatus by using a balance of suitable capacity. The 6-gram samples were generally reduced in size by the pulping action so that they could be removed quantitatively and weighed in the fritted-glass crucibles used for the smaller determinations.

Except for the correspondingly larger amounts of solutions, the same procedure was used on both large and small samples.

NORMAN-JENKINS METHOD. The Norman-Jenkins (14) method was used with the following slight modifications:

Sets of four samples were boiled for 30 minutes in 2 per cent sodium sulfite solution, maintaining the volume with hot water, and using a four-spindle motor stirrer to avoid bumping.

For the two alkaline chlorinations, the material was suspended in 90 cc. of water and 14 cc. of sodium hypochlorite (5.3 per cent available chlorine) were added. The 5.3 per cent solution was substituted for the 15 per cent recommended because it was found that the strong commercial hypochlorite (15 per cent available chlorine) obtained from laundry supply companies in gallon lots decomposed rather rapidly even in the cold. It was more satisfactory to buy pint bottles of the more dilute hypochlorite (5.3 per cent available chlorine) sold in grocery stores. Similar solutions were found by Cooper (3) to lose about 0.09 per cent of their original available chlorine content per day. The hypochlorite

was diluted to 3 per cent available chlorine content and 5 cc. were mixed with 2 cc. of 20 per cent sulfuric acid in 100 cc. of water for the acid chlorinations.

KÜRSCHNER-HOFFER METHOD. The Kürschner-Hoffer method (9) was modified and carried out as follows:

The special apparatus shown in Figure 2 was made by sealing off the outer portion of a 50/50 interchangeable ground-glass joint and sealing the inner portion to a Pyrex condenser as shown. A trace of glycerol was used as lubricant in the seal. For large samples, a 66/60 joint was used, the lower part of it measuring about 60 × 200 mm. A 2-gram sample was weighed into the flask, 100 cc. of reagent (made by adding 20 cc. of concentrated nitric acid, specific gravity 1.4, to 80 cc. of 95 per cent ethyl alcohol) were added, and the mixture was refluxed for 1 hour. A small constant-level boiling water bath was constructed. The opening of the cover should be of such diameter that it will act as a support for the flask, fitting just under the bulge found in the glass joints.

After 1 hour's refluxing, the mixture was emptied into a beaker and then filtered in a fritted-glass crucible, using a small amount of alcohol from a wash bottle to aid the transfer. The crucible was placed in the flask using a pair of tongs (preferably of Monel metal or stainless steel) and the reagent was added. In the case of dense material such as wood, it was necessary to remove it from the crucible with a spatula before placing the crucible in the flask in order to assure good penetration. (If it is desired not to put the crucible in the flask, the material may be washed out, using exactly 80 cc. of alcohol in a small wash bottle, and the acid added afterward.) One hundred cubic centimeters of the nitric acid-alcohol reagent were added and the whole procedure was repeated a third time.

Three 1-hour refluxes were selected empirically rather than the usual test for lignin because there is generally some lignin left after two refluxes, while most of the lignin is removed by 3 hours' refluxing, thus giving a sample of more constant composition. After the third reflux the cellulose was transferred to the fritted-glass crucible by using a rubber policeman and alcohol from a wash bottle. The cellulose must be carefully washed with alcohol, preferably by letting each portion of alcohol remain in contact with the cellulose a short time before removing by suction. It is dried in the oven at 105° C. and weighed with the crucible in a weighing bottle. Care should be taken not to allow the alcohol in the filter flask to evaporate to dryness, as some of the nitrated material may be explosive. Crude alcohol may be recovered by neutralizing with technical sodium hydroxide and distilling.

Results and Discussions

The results of the analyses are given in Table I. A comparison of the figures on "crude cellulose, corrected for ash" shows that the Cross and Bevan and Norman-Jenkins results are approximately the same, while the Kürschner-Hoffer figures are about 85 to 95 per cent of the Cross and Bevan values. This difference is less, however, when the resulting celluloses are corrected for impurities. The figures "pure cellulose in original" show the Kürschner-Hoffer cellulose to be about 95 per cent as large as that of the Cross and Bevan cellulose.

The Kürschner-Hoffer figures for "crude cellulose, corrected for ash" are closer to the Cross and Bevan "pure cellulose" figure than are either the Cross and Bevan or Norman-Jenkins "crude cellulose, corrected for ash." That this may be a fortuitous circumstance is possible. These

analyses show that the "pure cellulose" obtained from the Kürschner-Hoffer process is 0.7 to 10.6 per cent, averaging about 4 per cent lower than that obtained by the Cross and Bevan method—that is, if the "pure cellulose" figure of the Kürschner-Hoffer pulp is subtracted from the Cross and Bevan "pure cellulose" and then divided by this figure, the percentage loss of cellulose (about 4 per cent) due to the more drastic conditions of the Kürschner-Hoffer method over that of the Cross and Bevan method is found. This loss, combined with the naturally smaller pentosan and lignin content, makes the Kürschner-Hoffer "crude cellulose, corrected for ash" figure considerably closer to the Cross and Bevan "pure cellulose" than the Cross and Bevan "crude cellulose, corrected for ash" figure.

A further examination of the table with relation to the alpha-cellulose figures and an application of calculations similar to those above reveal that while the average loss of "pure cellulose" is 4 per cent, the Kürschner-Hoffer alpha-cellulose is 15 to 24 per cent (average about 20 per cent) lower than the Cross and Bevan alpha-cellulose. Since the alpha-cellulose determination is entirely empirical, it is probable that the alpha-cellulose analyses of Kürschner-Hoffer and Cross and Bevan celluloses are not strictly comparable. (The alpha-cellulose determinations on the Cross and Bevan and Norman-Jenkins celluloses are apparently more comparable.)

This difference of the Kürschner-Hoffer cellulose may be due to either physical or chemical differences in the pulp or both. Korsheniovsky (8) found that cotton linters lost their fibrous structure when treated by the alcohol-nitric acid reagent. He stated that this was probably due to the fact that the cellulose was not sufficiently protected by encrustants. This decomposition was not found in the present samples. Instead, the encrustants were apparently dissolved out in such a way that the fibrous particles retained their shape. Under the microscope the particle appears to be a translucent bundle of fibers. This structure would give the particle greatly increased surface. Lynch (11) has shown that the state of division makes considerable difference in the solubility of cellulose in hot 7.14 per cent sodium hydroxide, but that the difference is small, though constant, with 17.5 per cent sodium hydroxide solution. In this case it is possible that the greatly increased surface may have increased the solubility of the cellulose but probably not as much as 20 per cent.

Lewis and Laughlin (10) have also criticized the Kürschner-Hoffer method and found 0.25 to 0.5 per cent of nitrogen in the cellulose. However, these investigators found little drop in the copper number, thus indicating that not much oxycellulose was formed. On the other hand, they found that the viscosity of Kürschner-Hoffer cellulose was considerably lower than that of Cross and Bevan cellulose. In the light of the recent researches of Farr (5), this latter fact may mean only that a greater portion of the pectin-containing cementing substance has been removed by the nitric acid than by chlorination. This would explain the decrease in viscosity, since Farr claims that viscosity is due almost entirely to the pectin substance and not to the size of the cellulose molecule. Since nitric acid may hydrolyze the pectin or form soluble nitropectin, or the oxalic acid formed in the reaction may react with the pectin, it might thus very well remove some of the cementing substance. One is then inclined to speculate on whether this removal may then affect the alpha-cellulose results, causing them to be so low. Thus, the increased solubility of the Kürschner-Hoffer cellulose may be due either to physical differences, such as increased surface or removal of the protective coating, or to chemical changes such as actual degradation or nitration of the cellulose molecule.

The Cross and Bevan and Norman-Jenkins methods are

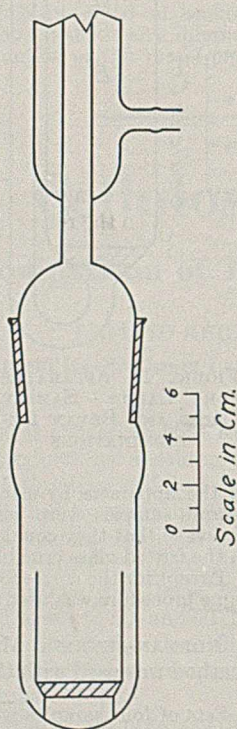


FIGURE 2. APPARATUS FOR KÜRSCHNER-HOFFER DETERMINATIONS

approximately equal, in the authors' opinion, as far as convenience is concerned. Both, exclusive of weighing, require about 2.25 hours' manipulation time. It is, however, considerably more convenient to use sodium hypochlorite solution instead of gaseous chlorine. The Kürschner-Hoffer method is very much more convenient to use than either of these methods. Manipulation time is about 1 hour or less than half that required for either of the other methods. The cost of reagents for the Kürschner-Hoffer determination is greater than that for the others, but this cost is so small that the time and labor saved greatly overbalance it.

TABLE I. DATA OBTAINED BY SUBJECTING PLANT MATERIALS TO ANALYSIS

	(Cross and Bevan, Norman-Jenkins, and Kürschner-Hoffer methods, respectively ^a)					
	Wheat Straw, 40-60 Mesh %	Rye Straw, 40-60 Mesh %	Bagasse, 40-60 Mesh %	Corn-stalks, 40-60 Mesh %	Spruce Wood, 40-60 mesh %	Wood, 60-80 mesh %
	Original					
Moisture	7.84	6.33	4.45	7.64	Nil ^b	Nil ^b
Pentosan	19.8	20.5	17.7	19.6	12.1	12.0
Ash	4.89	6.30	0.82	7.58	0.90	0.74
Lignin	17.2	13.3	24.0	15.7	28.0	27.7
	Cross and Bevan					
Crude cellulose	55.4	48.5	64.5	40.5	52.4	51.4
Ash in crude cellulose	2.00	1.83	1.30	2.20	1.80	1.28
Crude cellulose corrected for ash	54.3	47.6	63.7	39.6	51.5	50.8
Pentosan in crude cellulose	26.5	25.1	25.7	23.7	8.90	8.85
Lignin in crude cellulose	1.90	2.37	1.80	1.27	0.11	0.20
Pure cellulose in original material	38.6	34.3	46.0	29.5	46.8	46.1
Alpha-cellulose in crude cellulose	71.8	72.7	83.3	76.4	75.8	76.5
Alpha-cellulose calcd. on original material	39.8	35.3	53.7	30.9	39.7	39.3
	Norman-Jenkins					
Crude cellulose	55.3	49.7	63.6	41.8	50.6	51.6
Ash in crude cellulose	0.70	0.88	0.50	1.11	1.10	1.17
Crude cellulose corrected for ash	54.9	49.3	63.3	41.3	50.0	51.0
Pentosan in crude cellulose	30.3	31.5	26.9	28.1	7.84	7.92
Lignin in crude cellulose	1.46	1.66	4.06	6.62	0.07	0.13
Pure cellulose in original material	37.4	32.8	43.6	26.8	46.0	46.8
Alpha-cellulose in crude cellulose	71.7	74.5	76.6	72.1	72.6	71.6
Alpha-cellulose calcd. on original material	39.6	37.0	48.7	30.1	36.7	36.9
	Kürschner-Hoffer					
Crude cellulose	48.2	42.5	55.0	40.4	49.2	49.0
Ash in crude cellulose	5.50	2.80	0.80	9.50	0.20	0.23
Crude cellulose corrected for ash	45.6	41.3	54.6	36.6	49.1 ^c	48.9 ^c
Pentosan in crude cellulose	16.8	20.3	19.9	16.3	7.07	5.95
Lignin in crude cellulose	1.01	0.49	4.59	0.73	0.39	1.20
Pure cellulose in original material	37.0	32.5	41.1	29.7	45.4	45.4
Alpha-cellulose in crude cellulose	67.5	70.7	74.4	63.9	66.5	61.0
Alpha-cellulose calcd. on original material	32.6	30.0	40.9	25.8	32.7	29.9

^a All results except moisture are given on a moisture-free basis.

^b Previously extracted by alcohol and benzene.

^c Faintly yellow.

This alcoholic-nitric acid reagent has been criticized by Lewis and Laughlin (10) because it is injurious to the hands, desk, and clothing and also because it fumes violently when the alcohol and nitric acid are mixed. Ordinary care will prevent its being dropped on hands or clothing and the simple precaution of adding the acid to the alcohol, rather than the reverse, prevents fuming. Addition of alcohol to acid will cause bumping and explosions similar to that occurring when water is added to sulfuric acid. An odor of sweet spirits of niter is noticeable during the refluxing process. No noticeable effects have been incurred from this odor during use of the reagent over a period of 2 years. No loss in weight of the fritted-glass crucibles is found as with the other two methods. The precision of the Norman-Jenkins method is very good, the average deviation from the mean being less than 0.1 per cent. The Cross and Bevan and Kürschner-Hoffer methods are less precise, their average deviation being about 0.2 and 0.3 per cent, respectively.

If the cellulose produced is to be examined for alpha-cellulose either the Cross and Bevan or Norman-Jenkins method is satisfactory. However, on the basis of their analyses, the authors believe that if an alpha-cellulose or viscosity determination is not to be made, and if convenience and time are factors, the Kürschner-Hoffer method may well be used, particularly on farm wastes. The crude cellulose obtained by this method contained less pentosan and lignin than did the crude cellulose obtained by either of the other two methods.

Summary

Wheat straw, rye straw, bagasse, cornstalks, and two samples of spruce wood, one of 40- to 60- and one of 60- to 80-mesh fineness, have been analyzed by each of the three methods, Cross and Bevan, Norman and Jenkins, and Kürschner and Hoffer for cellulose content. The resulting crude cellulose was corrected for ash and analyzed for pentosan, lignin, and alpha-cellulose. The results have been calculated as "pure cellulose" and alpha-cellulose in the original material. Based on the weights of ash-free cellulose found, the Cross and Bevan and Norman-Jenkins results were shown to be practically the same but the Kürschner-Hoffer yields were 10 to 15 per cent lower. However, the Kürschner-Hoffer cellulose was considerably lower in pentosans and lignin and the calculated "pure cellulose" only averaged about 4 per cent lower than the Cross and Bevan "pure cellulose" and about equal to the Norman-Jenkins "pure cellulose." The Kürschner-Hoffer alpha-cellulose determinations show a decrease of about 20 per cent. In the light of recent research on the viscosity of cellulose, and in view of the fact that Kürschner-Hoffer cellulose has been found by other investigators to have an equal copper number but much lower viscosity than Cross and Bevan cellulose, it is suggested that this drop may be due to removal of the pectic layer, by the nitric acid used and the oxalic acid produced during the Kürschner-Hoffer reaction.

The Kürschner-Hoffer method was found to be approximately twice as fast as either of the other methods. It is recommended for large numbers of routine cellulose analyses, particularly on agricultural wastes where no further determinations on the resultant cellulose is contemplated.

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Development of Acidity in Certain Lubricating Oils on Use or Oxidation

A. R. RESCORLA, F. L. CARNAHAN, AND M. R. FENSKE

Petroleum Refining Laboratory, The Pennsylvania State College, State College, Pa.

Increases in viscosity, sludge content, and carbon residue value of lubricating oils subjected to oxidation at elevated temperatures are in many instances accompanied by development of acidity. In such cases the acid content as indicated by an electro-metric method is a convenient means of following these changes and of furnishing additional data on the general problem of oil deterioration. Some of the oil samples studied were obtained from engine tests, the remainder from a laboratory oxidation procedure.

ALUBRICATING oil undergoes complicated changes when it is subjected to oxidation at elevated temperatures. Whatever the nature of these changes, they are evidenced by variation in one or more of the following properties: viscosity, carbon residue, sludge content, and acidity. It is not implied that acid formation is either the cause or the effect of the other changes mentioned, but the data presented for the oils studied indicate that the acidity increases in a more or less regular way with these other indications of deterioration. The iron content of these oils in service also rises, but it is difficult to estimate the relative proportions of iron resulting from mechanical abrasion and chemical attack.

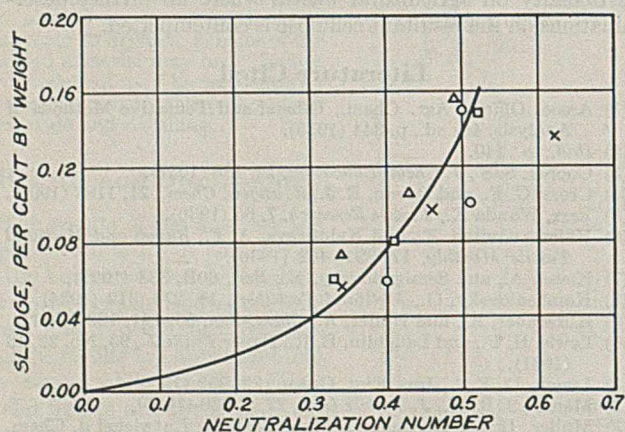


FIGURE 1. RELATION OF SLUDGE CONTENT AND ACIDITY FOR OIL 1 IN SEVERAL ENGINE TESTS

It should not be inferred that the relationships found in the case of these particular oils and conditions are general features for all oils and all types of oxidation treatment. Many exceptions will probably be evident when the problem has been studied more completely. While the data presented here show a reasonable correlation, other results (5) on different types of oil present such exceptions. Undoubtedly correlations of acidity with other properties will be affected by the type of crude and refining methods used to furnish the oil and also by the conditions employed in the oxidation or deterioration of the lubricant. For a given lubricant and test

method, correlations as shown by the present data are possible.

Analytical Methods

The acid contents of oils were determined by an electro-metric method previously described (6). Tungsten-platinum electrodes were used together with a vacuum-tube amplifying system and a milliammeter. The oil was dissolved in a mixture composed of equal parts of isoamyl alcohol, benzene, and carbon tetrachloride and saturated with lithium chloride; sodium isoamylate was used as the base.

TABLE I. PROPERTIES OF ORIGINAL OILS USED IN ENGINE TESTS

Oil number	1	2	3	4
Gravity, ° A. P. I.	28.6	29.6	29.5	30.8
Flash point, ° F.	450	415	405	425
Fire point, ° F.	505	470	465	490
Pour point, ° F.	+30	-10	-5	+25
Color, A. S. T. M.	7	3½	3½	4
Carbon residue	0.60	0.08	0.09	0.01
Acid number	0.02	0.08	0.08	0.00
Viscosity:				
Centistokes at 210° F.	10.9	5.73	5.69	5.80
Centistokes at 100° F.	99.8	38.1	36.3	38.55
Saybolt at 210° F.	61.6	44.2	44.0	44.4
Saybolt at 100° F.	460	178	169	179.6
Viscosity index	103	99	106	101

Viscosity was determined by means of modified Ostwald pipets (2); viscosity indexes were calculated using the data of Hersh, Fisher, and Fenske (4). The engine oil samples were not freed of dilution or sludge prior to ascertaining viscosity. Carbon residues were found by the A. S. T. M. method (1). Sludge was estimated by a procedure developed by this laboratory (3). A photometric analysis (7) for iron was utilized.

Description of Oils

Inspection data for the oils used in this investigation are shown in Table I. Oil 1 is a conventionally refined Pennsylvania oil in the S. A. E. 30 range. Oil 2 is a neutral; oil 3 is composed of 95 per cent oil 2 and 5 per cent sperm oil. Oil 4 is an unfiltered Pennsylvania neutral.

Engine Tests

Oils 1, 2, and 3 were used under carefully controlled conditions (3) in four 1933 Dodge 6-cylinder motors by the Depart-

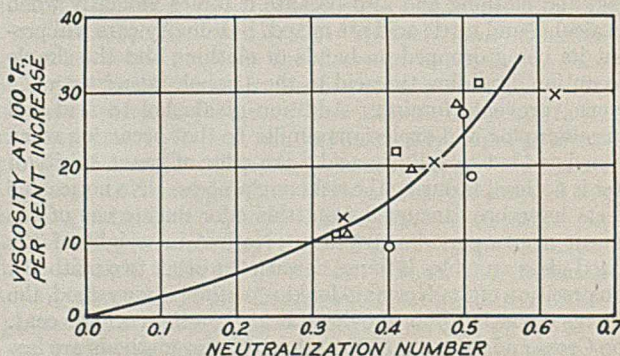


FIGURE 2. RELATION BETWEEN PER CENT VISCOSITY INCREASE AND ACIDITY OF OIL 1 IN SEVERAL ENGINE TESTS

ment of Mechanical Engineering. The engines were operated at 3250 r. p. m. to deliver 48 brake horsepower. The air-fuel ratio was 14 to 1; a nonleaded gasoline was used. The temperature of the oil entering the bearings was 121.11° C. (250° F.). Water entered the cooling system at 71.11° C. (160° F.) and left at 82.22° C. (180° F.). Samples for testing were removed from the oil circulation line at regular intervals.

Laboratory Oxidation

In laboratory oxidations, 150 cc. of oil were heated at 171.69° C. (341° F.) with 5 liters of air per hour passing through it. These conditions are essentially the same as those of the Indiana oxidation test developed by Rogers and Shoemaker (8). However, the procedure was modified in some instances by the presence of copper or other metals. In certain cases also, oxidation inhibitors were added to the oil being tested; the action of these materials will be discussed fully in another publication. During the progress of oxidation, the sludge content, the viscosity (usually taken on desludged oil), and the neutralization number were found.

Results and Discussion

ENGINE RUNS. The relation between sludge content and acidity for oil 1, a conventionally refined S. A. E. 30 Pennsylvania oil, is shown in Figure 1. The results are from four different engine tests, in each of which a battery of four engines was run for 24 hours; closer correlation may be obtained if a separate curve is drawn for each test.

In general, lubricating oils increase in viscosity on oxidation, more viscous oils being more susceptible to this type of deterioration; on the other hand, lighter oils blended from the same stocks tend to form a greater proportion of sludge.

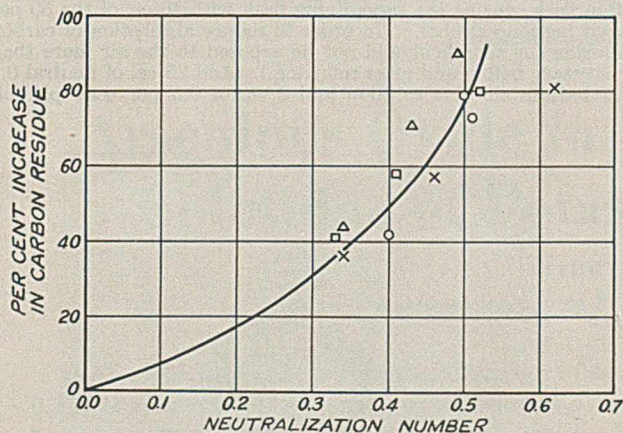


FIGURE 3. ACIDITY AND INCREASE OF CARBON RESIDUE FOR OIL 1 IN SEVERAL ENGINE TESTS

Viscosity increase in oils is probably due to both sludge formation and polymerization, though the latter process alone results in considerable viscosity increases in certain heavy oils which produce little or no sludge on oxidation. However, for the oils studied in this work, acid formation seems to be related to viscosity increase as well as to sludging; data for oil 1 are given in Figure 2.

When an oil is used in an engine, its carbon residue value increases; this circumstance is probably associated with the formation of sludge, the production of large molecules by polymerization, and the action of high temperatures in certain portions of the motor. Under such conditions that carbon residue value increases, the acid content of an oil frequently becomes larger. In the present instance, a rather definite relationship exists, as the data of Figure 3 show. The initial carbon residue value for oil 1 as determined by the A. S. T. M. method was 0.6 per cent.

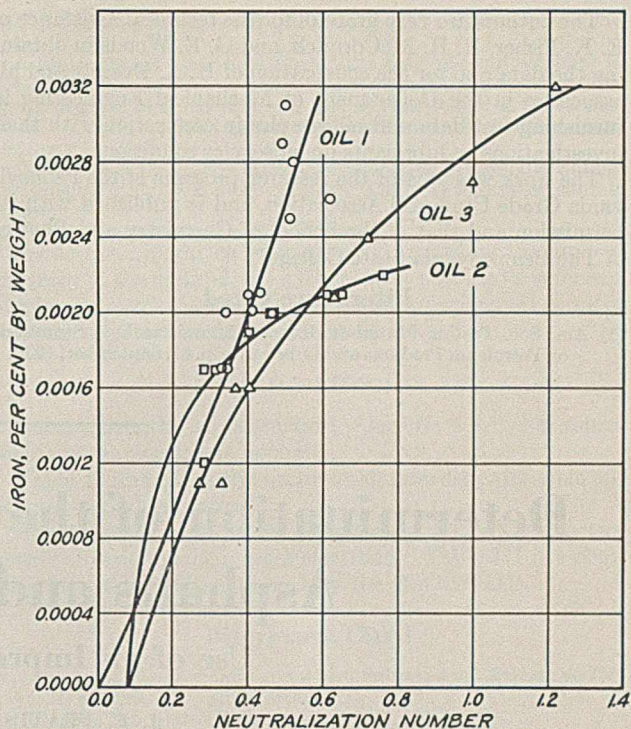


FIGURE 4. IRON CONTENT AND ACIDITY FOR SEVERAL OILS

Oils in internal combustion engine service gain a certain amount of iron, most of it probably from abrasion of ferrous surfaces but possibly some from the chemical attack of combustion products or acids in the oil. Though the iron contents of certain oils show a correlation with neutralization numbers, the role of petroleum acids in increasing the amount of iron in crankcase oils is not at all clearly defined. Some of the available data on acid and iron contents of used oils are presented in Figure 4.

LABORATORY OXIDATIONS. The deterioration of oils is generally accelerated by the presence of copper, other factors being the same. In regard to acid content, this circumstance is illustrated by Figure 5; the neutralization number for an unfiltered Pennsylvania neutral oil at the end of 48 hours' oxidation was about three times as great when copper was present.

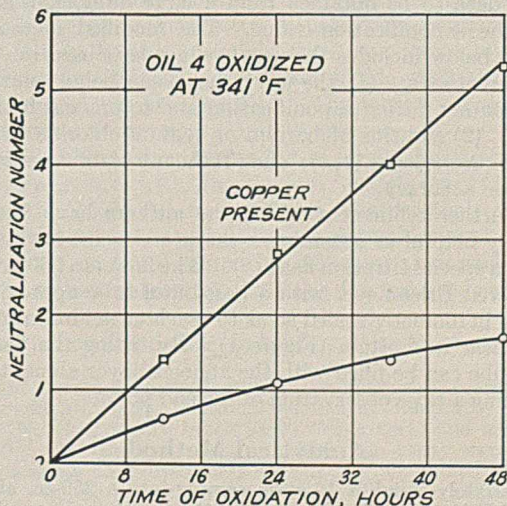


FIGURE 5. EFFECT OF COPPER ON ACID FORMATION

The authors are very grateful for the technical assistance of E. K. Fisher, R. H. McCormick, and G. E. Woods in obtaining the data and for the cooperation of H. A. Everett and his associates in the Department of Mechanical Engineering in furnishing test data and oil samples in connection with their investigations on lubricants under service conditions.

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Determination of the Saponification Value of Asphalts and Asphaltic Oils

Use of an Improved Titration Flask

J. E. FRATIS AND D. H. CONDIT

Standard Oil Company of California, San Francisco, Calif.

A simple and rapid method for determining the saponification value of asphalts and asphaltic oils, based upon standard methods and the use of a special titration flask, is described. Data are presented to demonstrate the accuracy and usefulness of the method.

THE natural characteristics of asphalts have always been an obstacle to the accurate determination of their saponification value. Despite the fact that numerous investigators have contributed to the literature concerned with this subject, the most widely recognized methods fail to give sufficiently rapid and accurate results for control work.

Recent investigations in this laboratory have included a study of the saponifiable constituents of asphalt. Among other data to be obtained from a large number of samples was the saponification value. The modified method presented below includes the usual refinements used in conventional methods: (1) the use of benzene-alcohol solutions to give contact during saponification and to prevent hydrolysis (1, 4); (2) addition of barium or sodium chloride to give a clear aqueous layer (1, 2); and (3) the use of dilute reagents to increase accuracy.

A further refinement which the authors have found extremely helpful in obtaining a sharp end point has been the use of a special titration flask (3). The flask is a 250-cc. glass-stoppered Erlenmeyer with a horizontal tube approximately 5 mm. in diameter sealed so as to reach one-third around the flask near its bottom (Figure 1). By tilting the flask, the side tube can be filled with the aqueous layer alone, thereby affording a close observation of the end point.

Analytical Method

Accurately weigh a 10-gram sample into a 250-cc. alkali-resistant Erlenmeyer flask. Dissolve the sample in 50 cc. of a mixture of 50 per cent benzene and 50 per cent of 95 per cent neutral

ethyl alcohol and add 25 cc. of 0.05 *N* potassium hydroxide in 50 per cent aqueous alcohol.

Reflux for 1 hour and transfer while hot to the special titration flask, rinsing the saponifying flask with 10 cc. of the 50 per cent benzene-alcohol. (In order to reduce absorption of carbon dioxide the sample should not be exposed to the air more than necessary before and after refluxing.) Add 25 cc. of neutral 0.1 *M* barium chloride solution and 3 cc. of 0.5 per cent phenol-

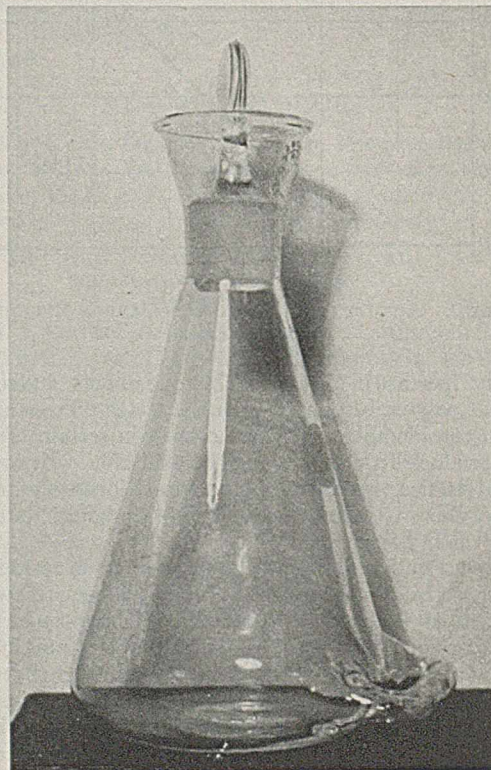


FIGURE 1. TITRATION FLASK

TABLE I. SAPONIFICATION VALUES

Petroleum Asphalts	Saponification Value Mg./gram	Natural Asphalts	Saponification Value Mg./gram
Arkansas	0.68	Bermudez (Lake)	6.20
California	0.50-3.25	Bermudez (fluxed)	11.30
Mexico	1.05-1.30		
Russia	0.99	Road Oils	
Texas	0.46	California	0.75-2.75
Venezuela (Quire Quire)	5.70	Midcontinent	0.40
Venezuela (Lake)	1.04	Oklahoma	1.04
West Virginia	0.56	Pennsylvania	0.42
Wyoming	0.36		

TABLE II. ACCURACY

Asphalt	Operator 1	Operator 2	Operator 3
A	1.56-1.56	1.58-1.56	1.54-1.55
B	3.12-3.08	3.06-3.09	3.07-3.05
C	0.81-0.83	0.79-0.83	0.81-0.84
D	0.14-0.17	0.13-0.17	0.15-0.16

TABLE III. COMPARISON OF RESULTS

Asphalt	Saponification Value Indicator method	Glass electrode method
California (A)	1.56	1.73
California (B)	3.08	3.38
Bermudez	11.30	11.27

phthalein. Titrate immediately against 0.05 *N* aqueous hydrochloric acid.

Add the acid rapidly without shaking the flask until the indicator begins to fade in the water layer. As the end point is approached, shake the flask after each addition of acid and tilt so that the side tube is downward. Touch the corner of the tube to a hot plate for a moment. This breaks any emulsion and cleans the walls of the tube, permitting observation of the aqueous layer.

The last trace of pink in the side tube should be taken as the end point.

A blank should always be run on the reagents and solvents to determine the amount of caustic lost during the process. This blank usually amounts to 3 or 4 mg. of caustic and is fairly constant. Duplicate determinations should be made where greater accuracy is desired.

When determining the saponification value of asphalts having an unusually high value (Bermudez, Table I) a smaller sample is used.

While there might be some question regarding the limit of accuracy of the method, the authors have obtained a sufficient number of check results to indicate an experimental error of 0.05 mg. of potassium hydroxide per gram.

Analytical Results

Table I lists the saponification values for a series of representative paving grade asphalts.

Table II illustrates the accuracy obtained by different operators using the method.

The accuracy of the method was also checked by electro-metric titration using a glass electrode. Table III is a comparison of the results obtained by the two methods.

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Arsenious Oxide in the Standardization of Solutions of Potassium Permanganate

HARRY A. BRIGHT

National Bureau of Standards, Washington, D. C.

Values obtained in the standardization of 0.1 *N* potassium permanganate solutions by National Bureau of Standards' arsenious oxide No. 83, using potassium iodide or potassium iodate as a catalyst (Lang's procedure), have been compared to those obtained with sodium oxalate by the method of Fowler and Bright. The normalities found agreed to within one part in 3000, which demonstrates the suitability of arsenious oxide as a direct primary standard in permanganimetry.

IT IS WELL known that the direct titration of trivalent arsenic with permanganate in dilute acid solutions is unsatisfactory because the reaction does not proceed according to stoichiometric relations. Lang (3) has stated that a very small amount of potassium iodate or iodide acts as a catalyst to complete the reduction of manganese to the divalent state. His data show satisfactory precision, and he apparently

checked the accuracy of the procedure by means of iodine (through permanganate-iodide and thiosulfate), though this is not stated clearly. Kolthoff, Laitinen, and Lingane (2) compared the normality of 0.5 *N* potassium permanganate determined by Lang's procedure with that found by direct potentiometric titration of potassium iodide with permanganate in very dilute acid solution. The factors obtained by the two methods agreed within 0.03 per cent.

Recently the author has made a careful comparison of Lang's procedure with the sodium oxalate procedure of Fowler and Bright (1) to determine whether the former is sufficiently accurate to permit the use of the National Bureau of Standards' standard sample No. 83 of arsenious oxide (now issued as an iodometric standard) as a fundamental standard in permanganimetry.

The experimental details, in brief, were as follows:

Weight burets were used, and all weights were corrected to the vacuum standard. National Bureau of Standards' sodium oxalate No. 40c (purity taken as 99.95 per cent) and arsenious oxide No. 83 (purity taken as 99.98 per cent) were used. Both materials were dried for 1 hour at 105° C. immediately before use. In the potentiometric titration the usual bright platinum-calomel electrode arrangement was used. Standardization with sodium oxalate was done as described by Fowler and Bright.

With arsenious oxide Lang's procedure, as described below, was used except that 0.3- to 0.6-gram samples were taken.

Procedure for Standardizing 0.1 *N* Potassium Permanganate with Arsenious Oxide

Accurately weigh approximately 0.25 gram of the dried oxide and transfer to a 400-ml. beaker. Add 10 ml. of a cool 20 per cent solution of sodium hydroxide, free from oxidizing or reducing substances. Let stand for 8 to 10 minutes, stirring occasionally. When solution is complete, add 100 ml. of water, 10 ml. of hydrochloric acid (sp. gr. 1.18), and 1 drop of 0.0025 *M* potassium iodate or potassium iodide. The titration can be followed potentiometrically or visually.

POTENTIOMETRICALLY. Titrate with the permanganate solution to the maximum value of the ratio, $\Delta E/\Delta V$, change in potential per unit volume of solution added. Add the last 1 to 1.5 ml. dropwise, allowing equilibrium to be reached before the ΔE reading is taken. In the potentiometric titration the blank is negligible, provided the reagents are free from interfering substances.

VISUALLY. Titrate with the permanganate solution until a faint pink color persists for 30 seconds. Add the last 1 to 1.5 ml. dropwise, allowing each drop to become decolorized before the next is introduced. Determine the volume of permanganate required to duplicate the pink color of the end point. This is done by adding permanganate to a solution containing the same amounts of alkali, acid, and catalyst as were used in the test. The corrections should not amount to much more than 0.03 ml. The end point can also be taken with ferrous phenanthroline indicator. In this case, add 1 drop of a 0.025 *M* solution of the indicator as the end point is approached. Then add permanganate slowly until the pink color of the indicator changes to a very faint blue. The blank correction should average about 0.02 ml.

The normalities indicated for two approximately 0.1 *N* solutions of potassium permanganate are shown in Table I. The data indicate that the recommended procedures yield results of a very satisfactory order of precision and that the standardizations of permanganate solutions by the use of the

TABLE I. NORMALITY OF POTASSIUM PERMANGANATE

(Comparison of the normality of approximately 0.1 *N* KMnO_4 as indicated by titration of As_2O_3 and $\text{Na}_2\text{C}_2\text{O}_4$)

Normality by As_2O_3	Number of Determinations	Average Deviation from Mean %	Difference from $\text{Na}_2\text{C}_2\text{O}_4$ Value %		Catalyst
			Value	%	
Series 1. Normality by $\text{Na}_2\text{C}_2\text{O}_4 = 0.10015^a$					
0.10016	3	0.022	0.01		KIO_3
0.10018 ^b	3	0.029	0.03		KIO_3
0.10019	2	0.002	0.04		KIO_3^c
0.10019	3	0.028	0.04		KI
Series 2. Normality by $\text{Na}_2\text{C}_2\text{O}_4 = 0.10391^a$					
0.10387	1	...	0.04		KIO_3^d
0.10388	1	...	0.03		KI ^d
0.10390	4	0.015	0.01		KIO_3
0.10389	2	0.015	0.02		KI

^a Normality as indicated by Fowler and Bright's method. In the first series the value is the average of 8 determinations (average deviation from mean = 0.014 per cent), and in the second, the average of 7 determinations (average deviation = 0.010 per cent).

^b 0.6000 gram of arsenious oxide used, all others 0.3000 gram.

^c KMnO_4 added slowly, about 7 ml. per minute.

^d End point with *o*-phenanthroline.

National Bureau of Standards' standard samples of sodium oxalate No. 40c and arsenious oxide No. 83 should agree within one part in 3000.

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RECEIVED October 21, 1937. Published by permission of the Director, National Bureau of Standards, U. S. Department of Commerce.

A Simple Electrodialyzer

DOUGLAS B. ROXBURGH AND MARSHELLE H. POWER

The Mayo Foundation, Rochester, Minn.

IN THE course of certain investigations in this laboratory involving the purification of serum proteins, a simple and fairly easily constructed electrodialyzer has been developed. It is similar in some respects to that described recently by Bartell (1) but seems to offer advantages as regards ease of construction and use.

The apparatus used is illustrated in Figure 1. It consisted of a central glass cylinder, *a*, 46 mm. in outside diameter and 60 mm. in length, and two glass cylinders, *b*, each 49 mm. in inside diameter and 60 mm. in length. These cylinders were cut with a rotary saw from thick-walled Pyrex glass tubing; the ends were carefully ground and then fire-polished. The cylinders, *b*, were closed with No. 11 soft-rubber stoppers each carrying a glass tube, *f*, into which was sealed a coil of platinum wire, and small glass tubes, *g* and *h*, for inflow and outflow of distilled water.

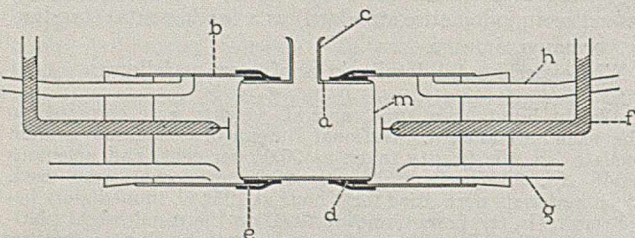


FIGURE 1. DIAGRAM OF ELECTRODIALYZER

The glass tubes, *f*, were bent as shown and filled with mercury, into which wires leading from a bank of B batteries were inserted.

The apparatus is assembled and prepared for use as follows: A square of Cellophane (du Pont No. 300, plain transparent) is placed over each end of cylinder *a* and held in place by gathering the edges under the rubber band, *d*. The end of the cylinder is dipped into water and the moistened paper then is adjusted until it is smooth and tight. The excess paper can be trimmed off even with the rubber band. The cylinders, *b*, are now forced carefully over the ends of the smaller cylinder and the joints made water-tight by means of a second rubber band, *e*. The rubber bands, *d*, 10 mm. in width, and *e*, 20 mm. in width, were cut from ordinary Gooch crucible tubing having a flat outside diameter of 3.1 cm. (1.25 inches). With the Cellophane membranes, *m*, in place, the capacity of *a* was about 100 cc.

With this apparatus it was found that a sodium sulfate solution of protein which had previously undergone simple dialysis, could be electrodialyzed, in 6 to 8 hours at 220 volts, to the point at which the specific conductivity was of the order of 1×10^{-5} , as determined by a standard method. When the conductivity was of this order a milliammeter inserted in the circuit indicated the passage of a current of 0.5 to 1.0 milli-ampere through the apparatus.

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Apparatus for Freezing Point Determinations

D. QUIGGLE, C. O. TONGBERG,¹ AND E. M. FRY,¹ The Pennsylvania State College, State College, Pa.

THE value of freezing point determinations as an aid in ascertaining the purity and establishing the identity of substances, particularly of hydrocarbons isolated from petroleum, is well known (2, 3, 5-7). For determining definite values of purity, particularly for substances freezing at low temperatures, it is obvious that a careful, standardized, and reproducible procedure is necessary.

In order that the usual observations of temperature as a function of time may be used to the best advantage and that results may be reproducible, it is essential that the rate of heat withdrawal from the cooling liquid as well as the freezing mass be at a substantially constant rate. This may best be accomplished by maintaining a constant temperature difference between the sample and its surroundings.

It is important in working with substances which freeze at low temperatures to exclude air from the sample. This eliminates any possibility of condensation of moisture in the air, and solution not only of it but also of the air, in the freezing liquid, with possible lowering of the freezing point due to such contamination.

Also, it is desirable in obtaining freezing points of inflammable materials such as hydrocarbons, when liquid air is used as the cooling medium, that the apparatus be fabricated of metal. The possibility of an explosion or a fire inherent in a glass apparatus if breakage should occur, allowing the sample to come into contact with the high oxygen concentration present in liquid air, is thus done away with (4). In order to approximate the foregoing conditions as closely as possible, the freezing point apparatus shown in Figure 1 has been constructed.

Apparatus

The apparatus consists of three concentric brass tubes, *C*, *D*, and *E*, soft-soldered to a common brass top. The innermost tube, *E*, is 2.9 cm. in outside diameter (1.125 inches, No. 20 Stubs gage) and 15.9 cm. long (6.25 inches). This tube is open at the top and closed at the bottom and is the container for the sample. The middle tube, *D*, is 4.4 cm. in outside diameter (1.75 inches, No. 18 Stubs gage) and 17.2 cm. (6.75 inches) long. It also is closed on the bottom. Since these two cans are soldered to the common brass top, the annular space existing between them is shut off entirely from the outside air. The lengths of the inner and middle tubes, *E* and *D*, are such that a 1.3-cm. (0.5-inch) space is left between the two bottoms.

Fastened to the outside of the inner tube, *E*, and to the inside of the middle tube, *D*, with the tips properly insulated, are two sets of opposing asbestos-covered copper-constantan thermocouples, *G*, to determine the temperature difference between these two surfaces. One set of thermocouples leads directly through a switch to the potentiometer, while the other set goes to a photoelectric-cell control device for maintaining the desired temperature difference. The leads are brought out through a tube, *M*, in the top of the can, the connection being made air-tight by a special packing arrangement. Before this annular space was closed off, it was first evacuated and then filled with dry nitrogen. In this way the medium between the tubes is always constant and unaffected by the sucking in of air and condensation of moisture on the cold surfaces which would change the heat transfer coefficient and hence the rate of heat withdrawal.

The third and outer tube, *C*, is 5.7 cm. in outside diameter (2.25 inches, No. 17 Stubs gage) and 18.1 cm. (7.125 inches) long. There is an 0.8-cm. (0.31-inch) hole in the bottom of this can and two 0.3-cm. (0.125-inch) nickel tubes, *L*, protrude from the top cover between it and the middle can. This unit made up of the three tubes is kept in a silvered Dewar, *B*, 11.4 cm. (4.5 inches) in inside diameter by 38 cm. (15 inches) deep, with a 1.9-cm. (0.75-inch) unsilvered strip running from top to bottom to allow the depth of liquid air, which is used as the cooling

medium, to be observed. A cork ring, *K*, holds the brass freezing point unit centered in the thermos bottle. The joint between the cork ring and the brass unit is made tight by rubber cement, and that between the cork ring and the bottle, by a piece of rubber automobile inner-tube, some wire, and paraffin wax. These seals prevent the liquid air, which is vaporized by a heater, *A*, made of two concentric coils of asbestos-covered chromel resistance wire (1.1 ohms per foot, total resistance 6 ohms) located at the bottom of the thermos bottle, from taking any path other than that through the hole in the bottom of the outer brass can, *C*, into the annular space between the outer and middle tubes, *C* and *D*, and out through the exit tubes, *L*, at the top.

Temperatures of the freezing liquid are obtained by means of a thermocouple unit, *U*, made of No. 30 B and S gage constantan wire and No. 36 B and S gage copper wire, both double silk-covered. This unit consists of five thermocouples connected in series with leads taken off in such a way that the temperature may be measured by two, three, or five thermocouples in series. This allows a greater accuracy in temperature reading to be obtained than is possible with a single thermocouple. The lower the temperature level at which the substance freezes, the less the accuracy with which the temperature may be read, because of the gradual decrease in the millivolt change per degree of temperature—for example, at 0° C. the millivolt change per degree is twice that at -171° C. (and three times that at -218° C.). The tips of the thermocouple unit are soft-soldered and insulated from one another with a cellulose acetate coating.

To keep the unit out of direct contact with the sample and at the same time allow the minimum of temperature drop between

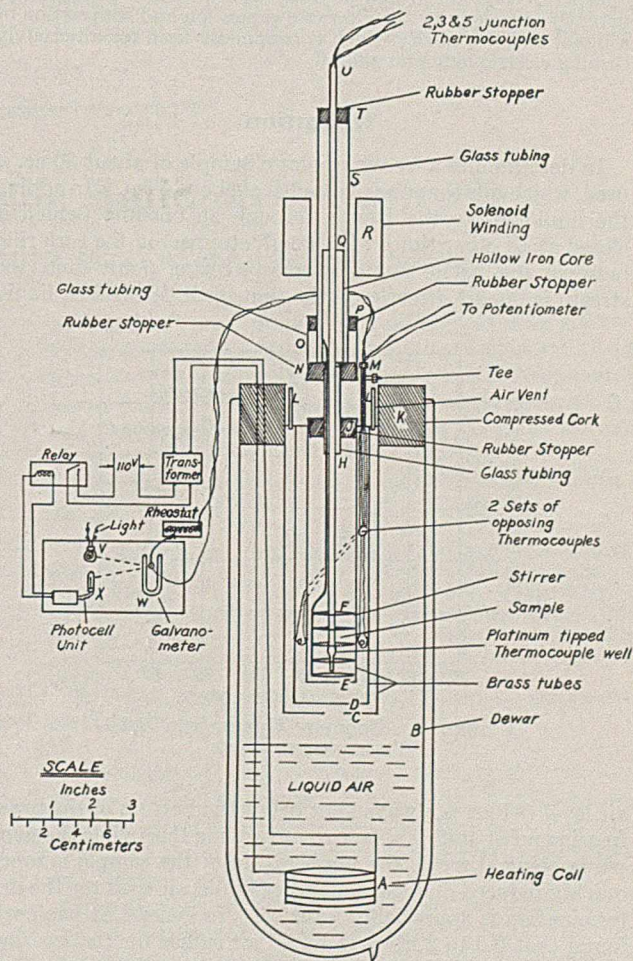


FIGURE 1. FREEZING POINT APPARATUS

¹ Present address, Esso Laboratories, Elizabeth, N. J.

the thermocouples and the sample, the former are placed in a protecting tube made of soft-glass capillary tubing into the end of which a thin-walled platinum tube 3 mm. in outside diameter (0.125 inch) by 3.5 cm. (1.375 inches) in length is sealed. The tips are placed in the platinum end of the tube, which is flattened out over them in such a way that it is in direct contact with their cellulose acetate insulation. The end of the platinum tube is closed off with soft solder, while Picein (Central Scientific Co.) cement holds the thermocouples in place at the top of the glass capillary and effectively prevents condensation of moisture in the tube. This thermocouple unit is made of constantan wire from the same spool as that used in the Cryoscopic Laboratory at the Pennsylvania State College. In addition, the thermocouple unit has been checked against one of the Cryoscopic Laboratory's thermocouples which has been accurately calibrated down to temperatures of 12° K. (1). Additional checks have been obtained at the freezing point of mercury, the sublimation point of carbon dioxide, and the boiling point of oxygen.

Temperatures are measured by means of a Leeds & Northrup Type 8662 portable, precision potentiometer, and the readings are accurate to within $\pm 0.02^{\circ}$ to $\pm 0.05^{\circ}$ C., depending upon the number of thermocouples used in measuring the temperature and the temperature level at which the substance freezes.

To exclude air from the sample a stirrer actuated by a solenoid is used. The stirrer, *F*, is made of several loops of 1.6-mm. (0.083-inch) brass rod fitting closely against the sides of the tube, but still allowing free up and down motion. These loops are brazed on one side, and at right angles, to the handle of the stirrer which is fastened at its upper end to a hollow iron core, *Q*. This core is about 1.3 cm. (0.5 inch) in outside diameter and 7.1 cm. (2.8 inches) long (weight 41 grams) with an inside diameter sufficiently large to allow it to slip up and down over the thermocouple tube. The iron core with attached stirrer is raised every time an outside coil, *R*, 4.5 cm. (1.75 inches) long containing about 800 grams of No. 26 B and S gage enameled copper wire is energized, and dropped when the coil is deenergized. The current through this coil, which is normally controlled by a Variac transformer (General Radio Co.), is made and broken 30 times a minute by a "flasher" (from the 5 and 10 cent store). This "flasher" apparently functions by the alternate expansion and contraction of a metal and is a device which is commonly used for alternately turning electric lights on and off.

Operation

In determining a freezing point a sample of about 30 cc. is used, which fills the tube to a depth of about 5 cm. In adding the liquid air to the Dewar through an opening (which is closed at all other times with a cork stopper) in the cork ring between the bottle and the brass freezing point unit, the stream is played directly on the unit until the desired liquid

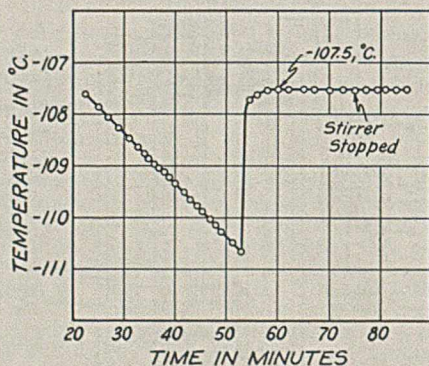


FIGURE 2. COOLING CURVE FOR 2,2,4-TRIMETHYLPENTANE

air level (which is always kept below the bottom of the brass freezing point unit) is attained. By doing this (while the sample is being stirred), the temperature of the sample is more quickly reduced and the amount of liquid air used for the determination is appreciably lessened. In general, it has been found that 0.5 to 2 liters of liquid air suffice for the freezing point determination of a hydrocarbon, depending on the skill of the operator and the temperature level at which the sub-

stance freezes. The temperature is then further reduced to within a few degrees of the freezing point of the sample by vaporizing the liquid air by means of the heater, *A*, located in the liquid air at the bottom of the thermos bottle. The rate of evaporation is then regulated so that approximately the desired temperature difference between the inner and middle tubes is maintained. A temperature difference of 10° to 15° C. seems suitable for most hydrocarbons.

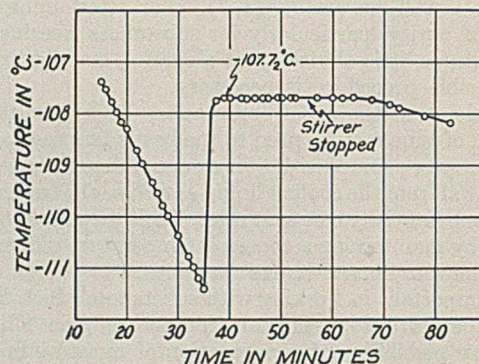


FIGURE 3. COOLING CURVE FOR 2,2,4-TRIMETHYLPENTANE CONTAINING 0.9 MOLE PER CENT OF NORMAL HEPTANE

The temperature difference existing is determined by the opposing set of thermocouples which is connected directly to the potentiometer. At this point, the set of opposing thermocouples connected to the photoelectric-cell temperature-control device is brought into operation by closing a switch. The principal features of this device are a relay to turn the current on and off in the heater which vaporizes the liquid air, a photoelectric-cell unit, *X*, and a galvanometer, *W*. If less than the desired temperature difference between the sample tube, *E*, and the middle tube, *D*, exists, the galvanometer mirror is at such an angle that it causes a beam of reflected light from *V* to fall at some position other than on the photoelectric cell and in this position the relay is closed, allowing current to pass through the heater with consequent evaporation of liquid air. When the temperature difference tends to get too great, owing to the cooling effect of the vaporized liquid air, the galvanometer mirror swings to such an angle that the beam of reflected light shines on the photoelectric cell which causes the relay to open, thus shutting off the current and stopping the vaporization of liquid air. This causes the temperature difference to decrease, the beam of light to be thrown off the cell, the relay to be closed, the liquid air to be vaporized again, etc. Thus a constant temperature difference is always maintained.

A rheostat in series with the pair of opposing thermocouples and the galvanometer of the photoelectric-cell control device makes it easy to control the current passing through the thermocouple circuit, so that the right deflection of the galvanometer mirror may be maintained to give the desired temperature difference. It is unnecessary to change the setting of this rheostat once the position for the desired temperature difference has been found. The mirror deflection may also be regulated, though less readily, by turning the knob attached to the mirror suspension.

In some instances the operator may find it unnecessary to use the photoelectric-cell control device for maintaining a substantially constant difference in temperature between the can containing the sample and the surroundings. When sufficient technic has been acquired, it is possible so to adjust the amount of current going through the heating coil that just sufficient liquid air is evaporated to maintain the desired difference in temperature. The considerable mass of the freezing point unit is an important factor in making this possible.

While this extra mass may require the use of more liquid air, it is believed that the benefits derived from such uniform and definite control over the freezing behavior are far more important than a small economy of liquid air. It is obviously impossible to have optimum conditions for every phase of the operation, and for this apparatus the emphasis has been placed on reproducibility, reliability, and accuracy with the minimum of special detailed or skilled technic.

It is realized that the solenoid stirrer is not the most powerful device that may be used for stirring, and other stirring means may be used. However, this stirrer is adequate for all the ordinary cases of freezing point measurement where a liquid is frozen under definite and controlled conditions. True, thermal and molecular equilibrium between the solid and liquid phases is not a condition that is readily attained, and yet it is a fundamental requisite for correct freezing point data. It is obvious that this condition can be more readily attained if the liquid phase, rather than the solid phase, predominates. Under such conditions the stirrer described here is ample. It may not be adequate where a considerable mass of solid needs to be broken up while at the same time intimately maintaining contact with the liquid phase. But, as indicated, it is believed that the more reliable freezing point measurements are made under conditions where a large mass of solid is not present. Otherwise a mechanically driven stirrer is advisable.

Results

Typical time-temperature freezing point curves obtained with this apparatus are shown in Figures 2 and 3. Figure 2 gives the results obtained with a mixture of substantially pure 2,2,4-trimethylpentane. The freezing point of -107.5_1°C . obtained indicates a purity of 99.6 mole per cent when the value

of -107.41°C . is taken as the correct freezing point of the pure substance (2). Figure 3 shows the freezing point of the same material, when 0.9 mole per cent of pure normal heptane is added to be -107.7_2°C . Calculations on the purity of this mixture from the freezing point depression (2) indicate a purity of 98.8 per cent, which checks very well with the known amount of normal heptane added. These results indicate that where the simple relationships concerning freezing point depression and mole per cent purity are valid, the apparatus and procedure outlined should be useful in determining the purity of materials, especially in cases where the freezing point depression might otherwise be difficult to determine.

Acknowledgment

The authors are indebted to M. R. Fenske for his suggestions and help, and to J. G. Aston and G. H. Messerly for their assistance in calibrating the thermocouple unit.

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RECEIVED July 28, 1937. References 5 and 6 list all papers published to June, 1935, by A. P. I. Research Project 6 at the National Bureau of Standards on the chemical constitution of the gasoline fraction of petroleum.

A Glass-Enclosed Metallic Reference Electrode

OLUS J. STEWART AND WILLIS L. CARRUTH, University of Kentucky, Lexington, Ky.

AN ELECTRODE was constructed by drawing a short length of Corning No. 015 glass tubing to the proportions of a fine knitting needle, closing one end of the thin-walled tube in a flame, and introducing sufficient mercury to provide a depth of 1 or 2 inches at the closed end. Metallic contact with the mercury was effected by inserting a fine wire of iron or platinum.

The potential of this glass electrode, whether open to the air and charged with mercury or closed and charged with a liquid amalgam of sodium, potassium, lithium, copper, cadmium, bismuth, or tellurium, was found to be unaffected by the oxidizing character of the solution into which it dipped. The device, therefore, may serve as a reference electrode in oxidation-reduction potentiometric titrations. As a hydrogen electrode, however, it has not yielded satisfactory pH values in buffered solutions. This problem will be the subject of a later study.

In order to ascertain the serviceableness of the instrument as a reference electrode, a number of titrations were conducted in a vessel provided with both the glass electrode and a calomel half-cell of the usual type, together with a stout platinum wire which served as the indicator electrode. After each addition of the reagent, the measuring electrode was alternately connected in series with the glass and with the calomel electrode through an amplified circuit, and the potentials were recorded. The vacuum-tube circuit used was that described

by Elder (2) and the potential differences were read with a Leeds & Northrup student-type potentiometer. In several instances the results were verified by more refined measurements made with the vacuum-tube circuit employed by Amis and Gabbard (1) and by them kindly placed at the authors' disposal.

The following types of potentiometric titrations were studied:

A. Ferrous solutions acidified with sulfuric acid and titrated with ceric sulfate solution, acidified with sulfuric acid and titrated with permanganate solution, or acidified with hydrochloric acid and titrated with dichromate solution in the presence of mercuric chloride, mercurous chloride, stannic chloride, and phosphoric acid, the last-named compound serving to render the end point sharp.

B. Hypochlorite solutions, buffered with sodium bicarbonate, and titrated with arsenite solution.

When the volumes of reagents used were plotted against the corresponding potential readings, the resulting curves for the two electrode systems were parallel in A but were not parallel in B. The two electrodes, however, yielded identical end points.

The stability of the glass electrode was further compared with that of the calomel electrode by placing the two reference electrodes in opposition during the titration of an acidified ferrous solution with a dichromate solution. The potential

difference remained constant throughout the operation, even though the end point was finally considerably overrun.

Several years ago Stewart (3) operated a sodium coulometer in such a manner that sodium was electrolytically removed from the sodium amalgam with which the cell was charged. On one occasion electrolysis was inadvertently continued after the supply of sodium had been exhausted, with the result that the glass of the cell became permanently discolored. If this discoloration was the result of mercury ions entering the glass, it seems reasonable to suppose that the mercury-filled glass electrode described in this paper functions as a metallic electrode, the glass wall acting in the capacity of an electrolytic medium through which mercury ions tend to migrate.

The electrode described in this paper possesses such advantages as simplicity of construction, sturdiness, convenience, immunity to attack by reagents and "poisons," impenetrability, suitability for semimicro work, and adaptability for insertion into living tissue.

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RECEIVED June 24, 1937. Based upon the thesis presented to the faculty of the Graduate School of the University of Kentucky by Willis L. Carruth in partial fulfillment of the requirements for the degree of master of science.

The Goodrich Flexometer

E. T. LESSIG, Physical Research Laboratory, The B. F. Goodrich Company, Akron, Ohio

A new form of hysteresis test has been developed in this laboratory and used for a number of years in the study of heat generation and fatigue of both rubber and rubber-fabric compositions at ordinary and elevated temperatures. It involves applying a definite compressive load to a test piece through a lever system having high inertia, imposing on the sample an additional high-frequency cyclic compression of definite amplitude, and measuring with a thermocouple the temperature rise at the base of the test piece. Because of the high inertia and low natural period of the lever

system, practically none of the high-frequency vibration is transmitted to the loading lever, although the lever does move to compensate for slow changes in the sample caused by permanent set and other structural changes. The machine may be used to study the effects of the time of cure, the magnitude of the applied load, changes in pigmentation, and variations caused by anisotropy in rubber compounds on the heat generation during flexure. It is so designed that structural changes such as softening or stiffening may be followed during the period of flexure.

THE service of rubber compounds often is limited by the heat generated during the flexing of the rubber and several types of flexing machines have been developed to study this factor.

In one of the first tests (14) devised, a spherical test piece was rotated under compression between two parallel plates until rupture occurred. Vogt (20) described the use of the Shields rotary machine. In this test bands are stretched radially over lubricated pins on a vertical rotating disk. The center pins are on an eccentric so that the bands are alternately stretched and relaxed. The hysteresis is measured by the throw of a pendulum which measures the torque produced. Later Abbott (1) arranged test pieces between two horizontal plates. The loaded top plate was then oscillated in the horizontal plane. The flexure-set, temperature rise, and time of failure were observed. Depew and Snyder (8) subjected rubber cylinders to a specified number of hammer blows per minute in order to study heat generation and breakdown.

In 1933, Cooper (5) reported a new compression flex test in which the test piece was held between two loaded, eccentric horizontal plates, one of which was rotated usually until the sample ruptured or blew out. (For those unfamiliar with the terminology of the rubber industry it should be stated that blow-outs in solid masses of rubber are caused by the development of high temperatures at the center of the mass, causing decomposition, the formation of liquid and gaseous compounds, and finally rupture of the solid walls of the mass by the expansion of these decomposition products. In large masses under heavy loads the temperatures attained have been so high that ignition of the gases has occurred spontaneously.) The changes in the test piece dur-

ing the test were followed by measuring the permanent set. Havenhill and MacBride (11) in 1935 described an improved compression flexometer fundamentally similar to Cooper's machine, but so designed that the horizontal forces necessary to displace or maintain the lower plate in a given off-center position could be measured at any time. With this arrangement certain structural changes during flexure could be followed. In later experiments Havenhill (10) showed that rubber test pieces stiffened during flexure and in some instances exhibited an anisotropic structure.

The development of these tests has moved in the direction of smaller and more conveniently prepared test pieces, but none of them has reached the stage where the test pieces were small enough to be cut from finished products such as pneumatic tire treads, nor could they be used very effectively with rubber-fabric compositions. In the tests which employ the off-center rotation, large horizontal forces are encountered which act in opposite directions at the two plates and large loads are required to keep the test pieces from slipping. For this reason the specimens usually develop very high temperatures and blow out in a very short time. Apparently none of the tests has been used generally to measure the temperature rise at equilibrium under less severe flexing conditions, nor have the machines so far described been equipped for work at elevated temperatures.

The study of ply separation or the separation of fabric from rubber has been confined, for the most part, to the study

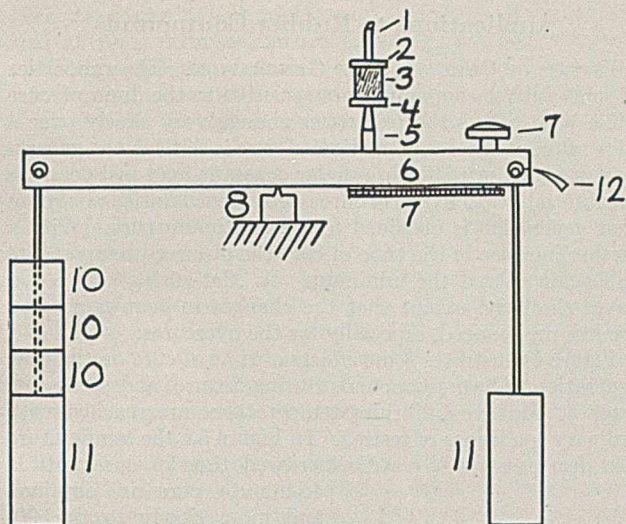


FIGURE 1. DIAGRAM OF FLEXOMETER

of belts (12, 16) driven under load or to strips of plied, calendered fabric subjected to a reciprocating motion (7, 9, 13, 18) over a pulley. Flex tests designed to test tread-cracking have been used to some extent to evaluate ply separation in plied fabric samples (17, 19). The essential characteristics of the different types of flex tests have been summarized in several publications (2, 3, 6, 15).

A new form of hysteresis test has been developed in this laboratory and used for a number of years here and in several other laboratories in the study of both rubber and rubber-fabric compositions at ordinary and elevated temperatures. It involves applying a definite compressive load to the bottom face of a test piece through a lever system having a high inertia, imposing on the upper face of the sample an additional high-frequency cyclic compression of a definite amplitude, and measuring with a thermocouple the temperature rise at the base of the sample. Because of the high inertia and low natural period of the lever system, practically none of the high-frequency vibration is transmitted to the loading lever, although the lever does move to compensate for the slow changes in the sample caused by permanent set and other structural changes. Light loads and high-frequency vibrations of low amplitude cause the temperature to rise to some equilibrium value; heavier loads and larger deflections produce a complete breakdown on the sample. Samples may be tested under a constant applied load, a constant initial compression, or at constant deflection during the test. The change in height of the test piece can be measured continuously during flexure and the degree of softening or stiffening, the effect of anisotropic differences in structure or modulus changes over a range of temperatures can also be observed. The test piece is of a convenient size so that test specimens may be obtained directly from manufactured articles.

Description of the Machine

The assembled machine¹ is shown in Figure 2 and the essential parts of the system are sketched in Figure 1 and may be described briefly as follows:

The test piece, 3, is placed between anvils covered with hard rubber, 2 and 4. The top anvil, 2, is connected through 1 to an adjustable eccentric usually driven at 1800 r. p. m. The load, 10, is applied by means of the lever, 6, resting on knife-edge 8. The moment of inertia of the lever system is increased and its

¹ These machines may be obtained from the Ferry Machine Co., Kent, Ohio.

natural frequency reduced, by suspending the equal weights, 11, 11, at each end of bar 6 at positions equidistant from the knife-edge. Anvil 4 can be raised and lowered to bar 6 by means of a calibrated micrometer device, 7, 7. With this device the bar may be maintained in a horizontal position during a test, as indicated by pointer 12 and a reference mark on the bar. The dimensions indicated in the legends of Figures 3 and 4 have proved satisfactory for tests on rubber samples of any Shore durometer hardness from 20 to 80 and also on rubber-fabric samples.

The temperature rise at the base of the sample is determined by means of a thermocouple placed at the center of the bottom anvil as illustrated in position 6, Figure 4, Section A.A. To keep the sample in contact with the insulated anvils during the entire compression cycle, the total length of the compression stroke must be less than about twice the initial compression of the test piece. The length of the compression stroke is adjusted by means of the vernier and scale on the eccentric shown in position 8, Figure 3.

The machine is equipped with an oven shown in position 1 in Figure 3. The base of the oven is permanently fastened to the frame, as shown in position 8 of Figure 4. The top or oven proper slides in place and can be removed in an instant when not in use. The oven is insulated with 0.5-inch asbestos board and is equipped with two 125-watt heaters, a thermoregulator, a squirrel-cage fan for circulating the air, and a small light that is automatically turned on when the oven door is open.

The dimensions of the machine have been selected to accommodate cylindrical rubber test pieces 1 inch high and 0.7 inch in diameter. These may be conveniently cut from larger blocks or from manufactured articles, using a cylindrical cutting tool either in a drill press or lathe. Laminated test pieces also may be built up without the use of adhesive from thin disks 0.7 inch in diameter arranged horizontally in the machine. Smaller or larger test pieces may be used if necessary. When testing rubber-fabric compositions it is sometimes more convenient to use rectangular samples.

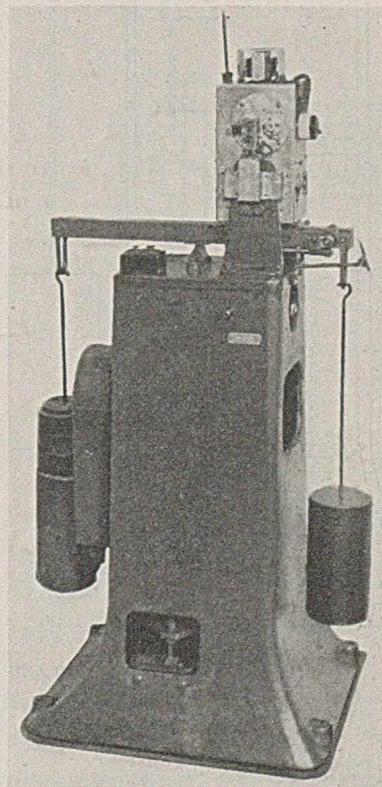


FIGURE 2. PHOTOGRAPH OF ASSEMBLED MACHINE

To adjust the micrometer device before starting a test, the top anvil is raised as far as the eccentric will permit and a piece of brass 1 inch high is inserted between the plates. The calibrated micrometer is set at zero and the pointer, 12 (Figure 1), is set on

a mark on the end of the lever bar to locate the zero position. When the test piece is inserted and the load applied the bar is again returned to its zero position by turning the micrometer mechanism. The static compression under load is then read directly on the micrometer scale to 0.001 inch.

The lever bar is adjusted to zero position at intervals to determine the change in the mean height of the sample during flexure. The permanent set is taken as the per cent difference in height between the original unstressed test piece at room temperature and the height of the unstressed test piece at room temperature after flexure, referred to the original height.

The temperature rise, measured at the base of the sample, depends not only upon the heat generated, but also upon the conductivity and emissivity of the test piece, the conductivity of the insulators, etc. If necessary, the observed temperatures may be corrected for differences in conductivity, but in practice this and other corrections may be neglected and the stocks compared on a basis of actual temperature rise at the base of the test piece. The amount of heat lost through the insulators varies with the temperature, but this factor does not change the relative characteristics of compounds when tested at any given oven temperature.

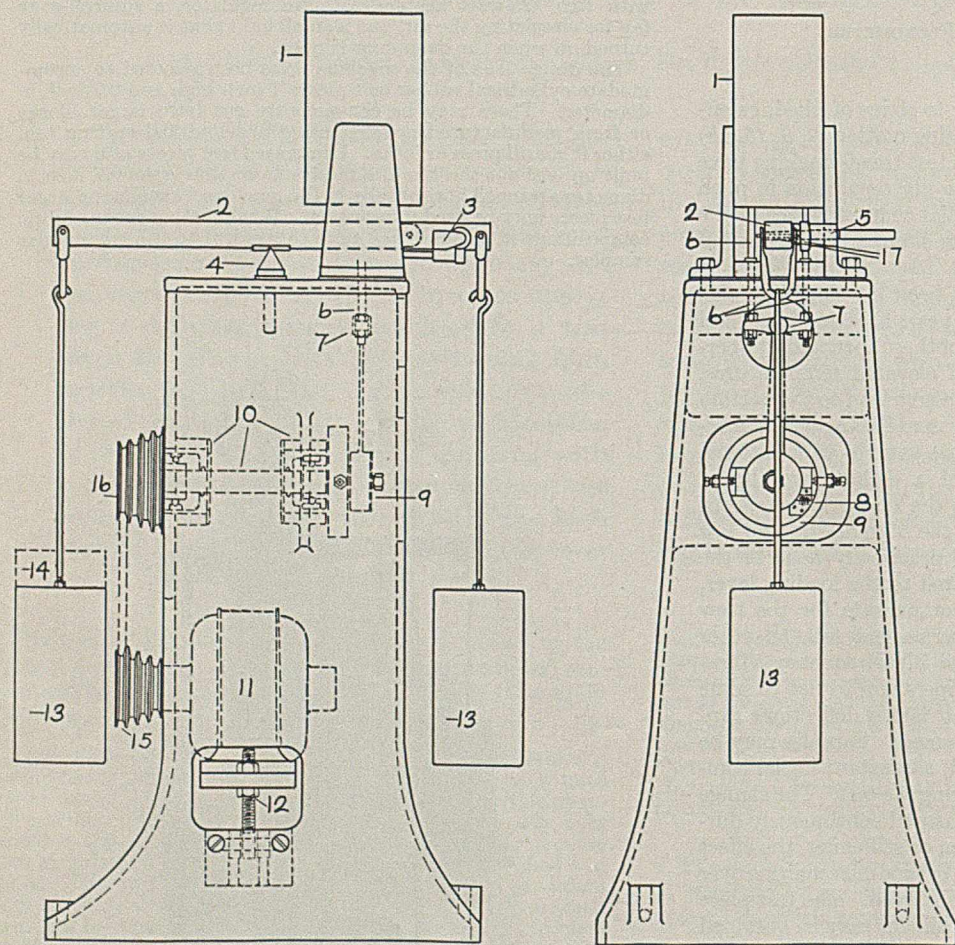


FIGURE 3. SIDE AND FRONT VIEWS

1. Oven, thermostatically controlled
 2. Balance bar, 24 × 1.5 × 1.5 inches
 3. Mechanism for raising and lowering bottom anvil with accessory mechanism to read this movement to 0.001 inch
 4. Fulcrum, a knife-edge on which 2 is balanced
 5. Tapered rod by means of which 2 may be held in position to avoid initial impulse when motor is started
 6. Rods connecting upper anvil to driving mechanism
 7. Bearing and connecting rod to eccentric
 8. Vernier and scale for gaging eccentricity
 9. Housing for eccentric
 10. Shaft for eccentric
 11. Motor
 12. Mechanism for adjusting height of motor and tension on belt
 13. Inertia weights (50 lb.)
 14. Load
 - 15, 16. Pulleys arranged to give four speeds
 17. Calibrated mechanism for reading height of bottom anvil relative to a reference point
- Distance between points of suspension of inertia weights and fulcrum is 11.35 inches and distance between loading platform and fulcrum is 5 inches.

Applications to Rubber Compounds

EFFECT OF CURE ON HEAT GENERATION. The properties of some rubber compounds are sensitive to the time of cure while with others the properties change very slowly over a wide range of cures. If the time of cure is critical, the generation of heat during flexure under constant load will decrease substantially as the time of cure is lengthened until a minimum heat generation is obtained for the optimum cure. With a further increase in the time of cure the observed temperature will again exceed the minimum. A "flat-curing" stock behaves similarly, except that the changes in heat generation are less pronounced, especially for the overcures.

Figure 5 illustrates some effects of time of cure on the heat generation of two compounds during flexure, and shows the rates at which equilibrium temperatures are reached with ordinary conditions of testing. In Figure 5A the temperature rise decreases rapidly with increased time of cure until a 45-minute cure is obtained and more slowly to the 90-minute cure. In Figure 5B the heat generation for compound B increases as the time of cure is increased from 30 to 90 minutes, probably because of reversion.

The time of cure that is necessary to obtain the minimum heat generation may vary with the applied load used in the test. When Figures 5B and 5B-1 are compared, it will be noted that the relative positions of the graphs for the 30- and 45-minute cures are reversed when the applied load is increased. The compound requires a longer cure for the minimum heat generation at the higher load. Not all stocks show the reversal illustrated in Figures 5B and 5B-1. The behavior of two different compounds over a range of applied loads is shown in Figure 6. The relative differences between the heat generated for the different cures increase as the load is increased but the relative order is unchanged. For these compounds the temperature rise for the overcure is only slightly higher than for the optimum cure.

EFFECT OF PIGMENTATION. The graphs in Figure 7 illustrate the nature of the temperature curves obtained with stocks containing 0 to 30 parts by volume of carbon black on 100 of rubber with 3.5 parts of sulfur and 6.0 parts of litharge, cured 75 minutes at 280° F. Litharge was used as an accelerator because it gives the same rate of cure with different amounts of black.

The test pieces, 1 inch high by 0.7 inch in diameter, were flexed at room temperature under an applied load of 140 pounds per square inch and a compression stroke of 0.175 inch. The temperature rise varied from 27° F. for the gum stock to 90° F. for the 30-volume gas black stock. Although the flexure was continued for 80 minutes in order to show the types of graphs obtained, a practical differentiation may be obtained in 25 minutes.

Changes in the formulation of a compound that do not appreciably change the hardness may cause substantial changes in heat generation—e. g., for a group of compounds differing only in acceleration and all having an initial compression of 24 to 25 per cent under the same load, the temperature rise varied from 13° to 52° F. For another group differing in pigmentation and having an initial compression of 15 to 17 per cent, the temperature rise during flexure varied from 98° to 165° F.

CHANGES IN MODULUS OR STRUCTURE DURING FLEXURE. Some rubber compounds may stiffen as the temperature rises during flexure, others may remain unchanged, and some may soften. These effects may be caused by thermal expansion, or by phenomena associated with the Joule effect or changes in structure. They may be detected by observing the change in height of the test piece during flexure and comparing this figure with the permanent set of the test piece after it is removed from the machine and cooled. If the decrease in sample height during flexure is greater than the permanent set the sample softens during flexure—i. e., there is a reversible decrease in modulus. If the height of the test piece increases during flexure, or if the decrease in height is less than the permanent set, the compound stiffens during flexure.

TABLE I. EFFECT OF CARBON BLACK LOADING ON STRUCTURE AND HEAT GENERATION DURING FLEXURE

Compound	Volume Loading of Gas Black	Temperature Rise during Flexure ° F.	Change in Height during Flexure % ^a	Permanent Set % ^a	Increase in Height Caused by Reversible Structural Changes
					% ^a
A	0	27	+1.0	1.1	2.1
B	10	37	+0.6	1.4	2.0
C	20	56	-1.0	3.1	2.1
D	30	89	-6.2	8.8	2.6

^a Based on initial height of test piece.

The changes in height during flexure observed for the carbon black stocks mentioned above are graphed in Figure 8 and are compared to the permanent set in Table I. All the data are expressed as per cent change based on the initial height of the uncompressed test piece. For compound D in Table I, the permanent set is 8.8 per cent, while the recorded decrease in height during flexure is only 6.2 per cent. The height during flexure was, therefore, 2.6 per cent greater because of a reversible increase in modulus.

All these compounds stiffen slightly. By way of further illustration these effects may be noticed for the several compounds listed in Table II.

BREAKDOWN TESTS. If the load applied during flexure is increased sufficiently, the test piece may be made to blow out or fracture. Figure 9 represents the behavior of two different rubber compounds under identical testing conditions. Compound A blew out in 60 minutes, while compound B was in excellent condition even after 150 minutes of flexure. The primary inflection point observed for compound A has been

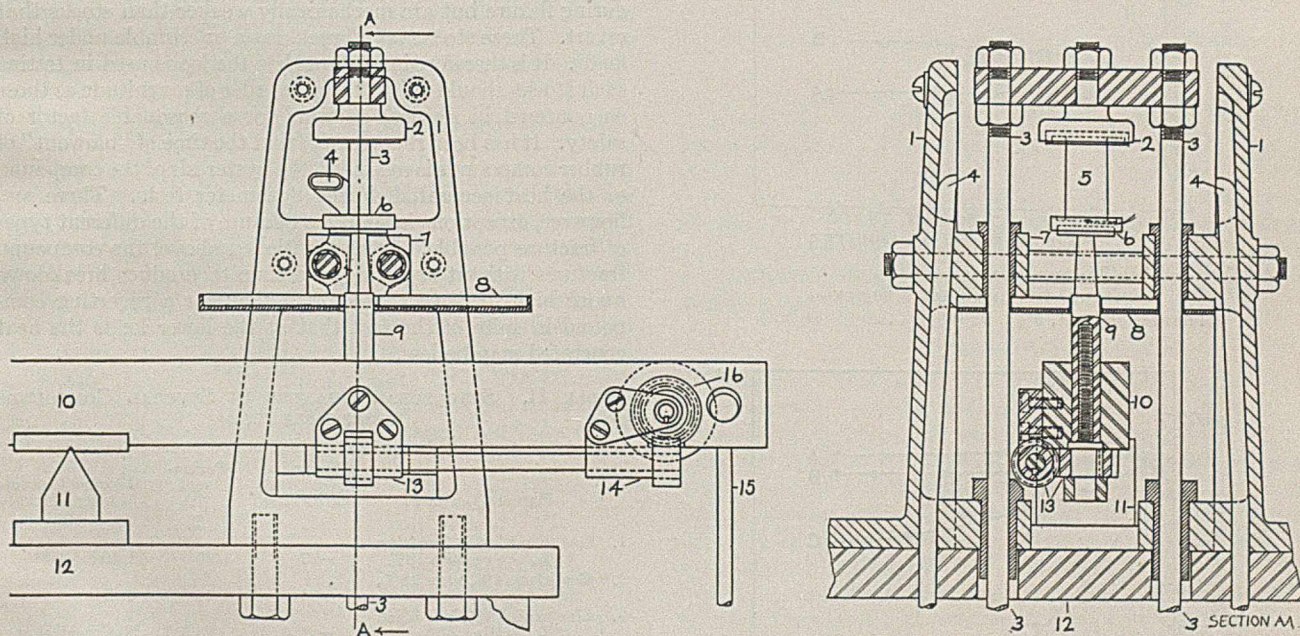


FIGURE 4. SIDE AND FRONT VIEWS WITH OVEN OMITTED

1. Frame holding bearings and oven
2. Upper anvil driven through rods, 3; hard-rubber insulation 0.1 inch thick
3. Rods connected to eccentric as shown by 6 and 7 in Figure 3
4. Concealed air vent for producing windage or cooling when desired
5. Test piece (Section AA)
6. Lower anvil showing hard-rubber insulator 0.1 inch thick and showing position of thermocouple (Section AA)
7. Bearing
8. Base of oven. Entire oven can be lifted from base at any time.
9. Support for lower anvil. Anvil is raised or lowered by screw and gears 13, 14.
10. Inertia bar
11. Fulcrum
12. Frame
- 13, 14. Gears by means of which vertical position of 9 or 6 is adjusted
15. Rods supporting inertia weights
16. Mechanism for turning gears 13 and 14. Calibrated to read height of sample to 0.001 inch from zero point level of bar. Zero point indicator omitted here is shown, 12, in Figures 1 and 2.

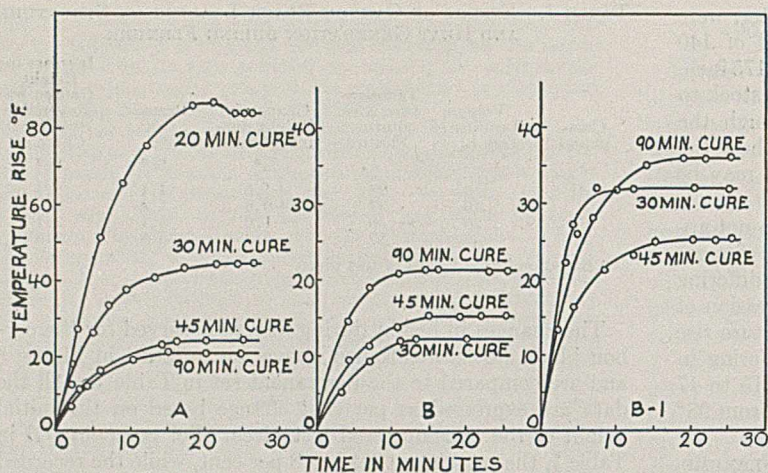


FIGURE 5. VARIATION IN TEMPERATURE RISE WITH CURE AND LOAD

A. D. P. G., 9 carbon black, 15% ZnO. Applied load of 62 lb./sq. inch
 B. High gum-Captax stock. Applied load of 62 lb./sq. inch
 B-1. High gum-Captax stock. Applied load, 122 lb./sq. inch. Compression stroke, 0.25 inch

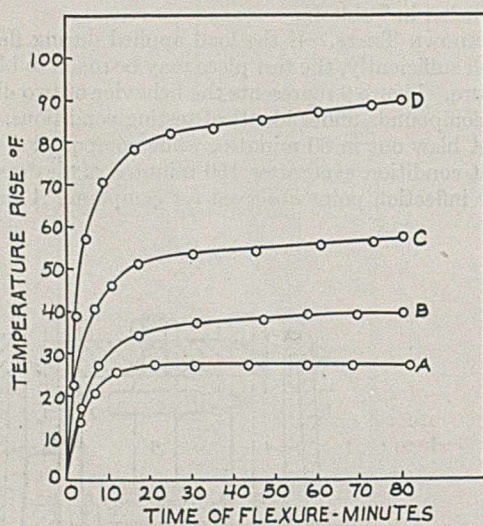


FIGURE 7. TEMPERATURE RISE USING VARIOUS PERCENTAGES OF CARBON BLACK

Volume loading: A, 0%; B, 10%; C, 20%; D, 30%

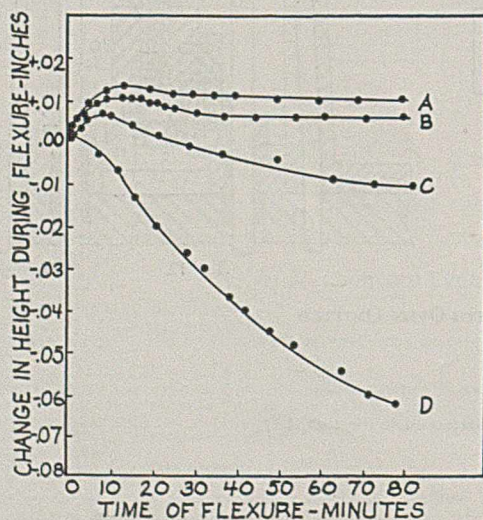


FIGURE 8. CHANGE IN HEIGHT OF FLEXURE USING VARIOUS PERCENTAGES OF CARBON BLACK

Volume loading: A, 0%; B, 10%; C, 20%; D, 30%

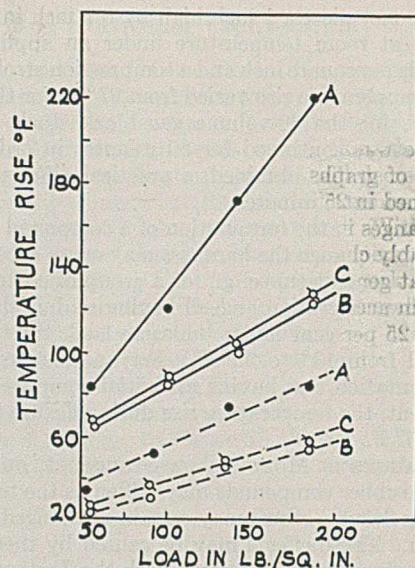


FIGURE 6. EFFECT OF APPLIED LOAD ON TEMPERATURE RISE

A, 60-minute cure; B, 110-minute cure; C, 160-minute cure
 — 50% carbon black stock
 - - - 5% zinc oxide stock

of no practical importance for comparing breakdown characteristics of rubber compounds and may be entirely absent when the test is greatly accelerated or when reversion does not occur.

Some types of pigmentation produce stocks that run cooler during flexure but are mechanically weaker than stocks that revert. These stocks may break down or crumble under high loads. It is therefore important that the loads used in testing such stocks should be of the same order of magnitude as those encountered in service, allowing for a reasonable factor of safety. It has been reported (4) that the time of "blowout" of rubber compounds is related to the hysteresis of the compound or the heat generated during flexometer tests. There are, however, exceptions in practice because of the different types of fracture possible. If, as mentioned above, the compound fractures without reverting, the time to produce breakdown under high load may be shorter than for a reverting compound in spite of the fact that at the lower loads the heat generated may be less.

TABLE II. STRUCTURAL CHANGES IN SEVERAL COMPOUNDS DURING FLEXURE

(Flexed 75 minutes under an applied load of 155 pounds per square inch)

Pigment Loading	Change in Height during Flexure %	Permanent Set %	Modulus Changes during Flexure
1. Gas black 20%, whiting 15%, tire reclaim 18%	-25	20	Softens
2. Gas black 4%, clay 28%, reclaim 20%	-34	46	Stiffens
3. Zinc oxide 19%, soft black 16%, whiting 37%	-2.5	3.7	Not much change
4. Zinc oxide 4%	+2.5	0.0	Stiffens

ANISOTROPY. Havenhill (10) has shown that anisotropy in rubber compounds can be detected by means of flexometer tests. When the length of a pigment particle is greater than the other two dimensions, or when two dimensions are much larger than the third dimension, it has a tendency to orient itself in the rubber during mixing and calendering with the long axis or plate surface parallel to the direction of rotation of the mill or calender rolls. It has been found that when this pigment orientation is retained in the cured rubber, the heat generation obtained during flexing will be greater if the

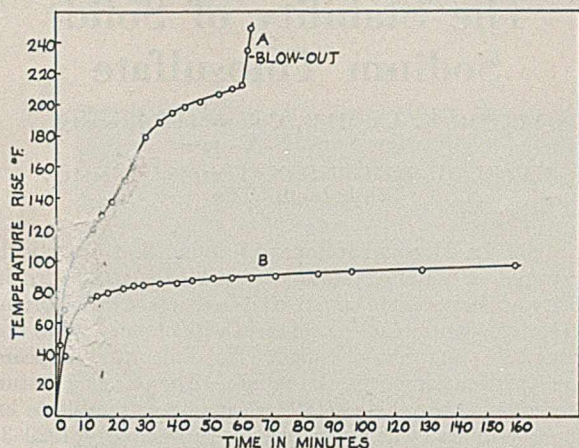


FIGURE 9. FATIGUE TEST

A. Loaded with channel black, 25 parts, and zinc oxide, 132 parts
 B. Loaded with soft black, 51 parts, and zinc oxide, 10 parts.
 Applied load: 180 lb./sq. inch. Compression stroke, 0.25 inch

between cord and rubber. This type of test piece is useful in studying the resistance to cord separation in compositions having similar cord structures. On the other hand, since the tendency for the cord separation is diminished for the type B test piece, this type is more useful for the study of differences in heat generation in such structures.

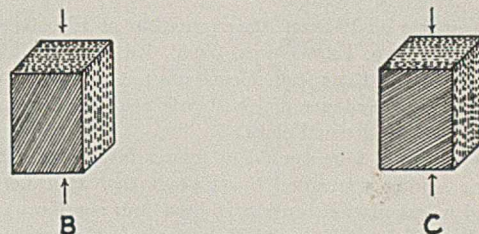
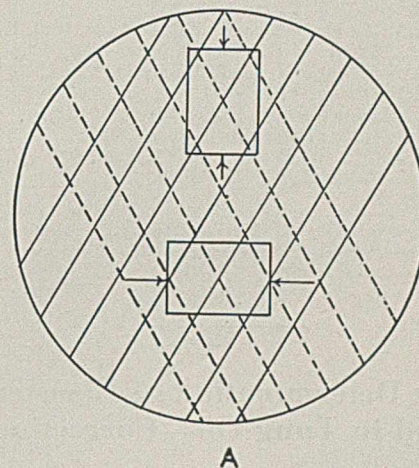


FIGURE 11. APPLICATION TO RUBBER-FABRIC COMPOSITIONS

flexure is directed parallel to the long axis of the pigment particles or parallel to the plate surface than when flexure is directed parallel to the short axis of the pigment particles. Havenhill kindly donated for this test compounds containing oriented particles of Suprex clay and asbestine. The results obtained from the flexure of these compounds are graphed in Figure 10.

Anisotropy can sometimes be detected in high-gum stocks, especially when the stock is calendered in thin sheets at comparatively low calender temperatures. The effect, however, is usually small and may be eliminated by holding the stocks at an elevated temperature before they are cured, for a time dependent upon the degree of anisotropy that may occur.

Applications to Rubber-Fabric Compositions

When rubber-fabric compositions are constructed so that a definite angle is obtained between cords in alternate plies, test pieces may be cut from the cured composition in two directions as indicated in Figure 11A. The flexure characteristics of these test pieces may then be compared for different rubber compounds. If any cord angle other than 90° is chosen, one test piece may be obtained having cord angles of less than 90° as in Figure 11B, and another may be obtained having cord angles greater than 90° as in Figure 11C. The tendency for cord separation in the type C test piece is greater than for type B because the compressive force causes a greater strain

The study of rubber-fabric compositions may follow the same procedure as for rubber compounds. Tests may be made to produce equilibrium temperatures or the load may be increased to produce breakdown. The test pieces may be subjected to a constant applied load, or, when comparing a series of compositions, the load may be adjusted from one composition to the other in order to obtain compressions of similar magnitude.

Summary

The Goodrich flexometer is of simple design and is easily operated at ordinary or elevated temperatures. Test pieces procured from laboratory specimens or from finished rubber or rubber-fabric products may be tested, using moderate loads that produce equilibrium temperatures during flexure or larger loads that rupture the test piece. This machine may be used to study the effects on heat generation of the time of cure, the magnitude of the applied load, changes in pigmentation, and variations caused by anisotropy in rubber compounds. It is so designed that the structural changes such as softening or stiffening may be followed during the period of flexure.

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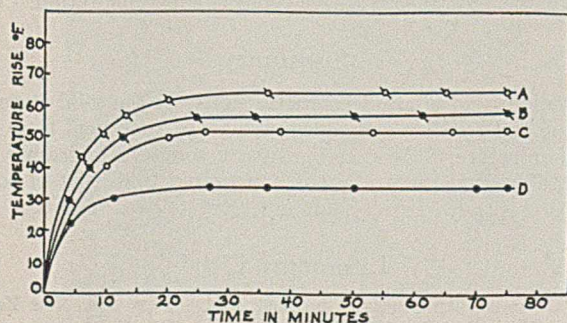


FIGURE 10. ANISOTROPY

A. Suprex-clay filler. Flexure parallel to plate surface of pigment
 B. Suprex-clay filler. Flexure normal to plate surface of pigment
 C. Asbestine filler. Flexure parallel to long axis of pigment
 D. Asbestine filler. Flexure normal to long axis of pigment
 Applied load, 143 lb./sq. inch. Compression stroke, 0.25 inch.
 Filler, 25.6 volumes

The Stability of Solid Sodium Thiosulfate

VICTOR K. LA MER, Columbia University,
New York, N. Y., and
HAZEL M. TOMLINSON, Temple University,
Philadelphia, Pa.

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Direct Determination of Eleostearic Acid in Tung Oil—Correction

In the article on "Direct Determination of Eleostearic Acid in Tung Oil" [*IND. ENG. CHEM., Anal. Ed.*, 9, 103 (1937)] in Table IV the deviations from means are not in accord with the corresponding percentages of eleostearic acid, which have been rounded off to one decimal place.

The retention of four significant figures in the percentages of eleostearic acid is warranted by the fact that all experimental data used in calculation contain at least four significant figures. The results of Table IV serve to show not only the precision ratio but also the concordance between the percentages of the acid determined in different runs. On this account these percentages and the deviations as listed in this table carry two decimal places, so as to show the degree of concordance and the magnitude of deviations better than the numbers with one decimal place would do. The average deviations from means thus contain one or two significant figures. The arithmetical mean when introduced in the calculation of the precision ratio may therefore be rounded off to two significant figures. It need not, however, be rounded off before calculation. Table IV should read as follows:

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	76.99	0.02	76.48	0.10	75.85	0.10
2	77.04	0.07	76.44	0.06	75.76	0.01
3	77.02	0.05	76.51	0.13	75.82	0.07
4	76.91	0.06	76.31	0.07	75.63	0.12
5	77.10	0.13	76.24	0.14	75.86	0.11
6	76.87	0.10	76.48	0.12	75.81	0.06
7	76.97	0.00	76.26	0.12	75.67	0.08
8	76.85	0.12	76.29	0.09	75.62	0.13
	Av. 0.07		Av. 0.10		Av. 0.09	
Arithmetical mean	76.97		76.38		75.75	
Average deviation/arithmetical mean	0.9 part per 1000		1.3 parts per 1000		1.2 parts per 1000	

P. S. KU

IN 1932, La Mer and Kamner (3) found that a particular sample of sodium thiosulfate yielded steadily drifting velocity constants when employed as a reactant in the bromoacetate thiosulfate reaction, whereas with other samples non-drifting constants were obtained. The difficulty disappeared on recrystallization of the thiosulfate. The puzzling feature, however, was that this particular sample of thiosulfate had been recrystallized with considerable care previously (1929-31) by La Mer and Fessenden (2), who obtained excellent kinetic results with the sample at that time. La Mer and Kamner, accordingly, suggested that sodium thiosulfate in the solid phase probably undergoes a slow decomposition into sulfur and sodium sulfite. Such instability would not ordinarily be detected in analytical work, but would, of course, seriously interfere with the kinetics of a reaction presumed to involve only bromoacetate and thiosulfate.

In resuming the kinetic studies of this reaction (1937), the authors have had occasion to use a thiosulfate sample twice recrystallized from water below 60° C. by Percival (4) in 1933. This sample proved entirely satisfactory in his work on the *N*-chloroacetanilide rearrangement. Four years later, this solid sample forms cloudy aqueous solutions which give positive tests for sulfite (1). When a portion was once recrystallized, the clear aqueous solution was sulfite-free. Moreover, when a solution of Percival's thiosulfate was used (1937) in kinetic studies of the bromoacetate-thiosulfate reaction, reproducible velocity constants were obtained but they exhibited almost identical drifts with time, the puzzling behavior encountered by Kamner in 1932.

Approximately 0.01 *M* solutions were prepared from the previously and newly purified crystals using identical treatment of containers, carbon dioxide-free water, and protection from light. Aliquot portions of both solutions were titrated frequently against the same iodine solution, using the same indicator solution, after the same time intervals over a period of 2.5 summer months. From thirteen such titrations, the average titer remained constant over this period to within one part per thousand both for old and recrystallized salt.

Although the investigation is incomplete, these findings are submitted for their analytical interest, since it appears that the constancy of the titer of a thiosulfate solution is not a sufficiently adequate criterion of its stability for application to kinetic and other sensitive types of experimentation.

Summary

Sodium thiosulfate decomposes slowly in the solid state to sulfur and to some substance giving the analytical tests for sodium sulfite. The deterioration of solutions of freshly recrystallized thiosulfate is not more rapid than that of solutions prepared from crystals not recrystallized recently.

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RECEIVED October 20, 1937.

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MICROCHEMISTRY



Courtesy, J. R. Rachele and J. T. Bryant

Azoxybenzoate in Polarized Light

Qualitative Separations on a Micro Scale

III. Analysis of the Selenium Group of Noyes and Bray

A. A. BENEDETTI-PICHLER AND JULIAN RICHARD RACHELE
Washington Square College, New York University, New York, N. Y.

A procedure for the qualitative micro-analysis of the selenium group of Noyes and Bray has been carried out, permitting the isolation and approximate estimation of selenium, germanium, and arsenic when starting with a solid sample of 1-mg. weight. Five micrograms of any of the three elements can safely be detected, even when accompanied by a hundredfold excess of the other two elements of this group. A screw clamp for microcones enables the simple performance of pressure digestions. A buzzer is used to accelerate the formation of precipitates.

IN THE development of a general scheme for the inorganic qualitative analysis of milligram samples (3), it was necessary to provide for the separation, isolation, and estimation of the elements of the selenium group of Noyes and Bray—namely, selenium, arsenic, and germanium. The plan adopted is, in general, that given by Noyes and Bray in their well-known book (7), but several changes had to be made in its application to small samples. In the selenium group, the outline of separation is practically the only part of the original scheme which is retained.

of sodium germanate were used. If the volumes of stock solutions necessary to give the required amounts of the metals became too large, the mixtures were evaporated to dryness in the distilling tube previous to the treatment with hydrobromic acid and bromine.

The isolation of the selenium group is performed according to the directions given in a previous paper (1). The distillation is carried out at 95° to 100° C. until a dry residue is obtained. The fractions collected are combined in a microcone (4) and considered as distillate D4.

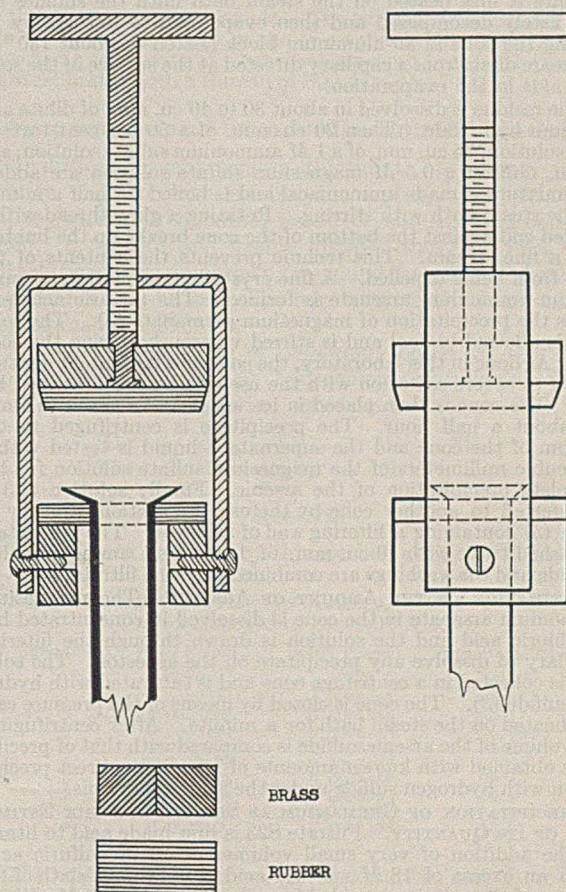


FIGURE 1. PRESSURE CAP FOR MICROCONES

ISOLATION OF SELENIUM. A 3 M solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$ is added to distillate D4 in portions of approximately 1 cu. mm. with the use of a capillary pipet, until the solution becomes colorless—i. e., until the bromine is reduced. Then a 5 cu. mm. excess of the reagent is added. The cone is closed with a small brass pressure cap (Figure 1) and then placed in a steam bath for 5 minutes. The use of the pressure cap prevents the loss of germanium and arsenic.

The selenium is deposited as a fine red precipitate which, on prolonged heating, is converted to a more compact black form. The time required for the conversion depends on how closely the red selenium is packed. However, it is immaterial whether or not the conversion is allowed to take place. The precipitate and the solution are separated in the usual way with the use of centrifuge and capillary pipet (2). The precipitate is washed twice with 10 cu. mm. of water and the washings are combined with the filtrate.

ESTIMATION OF SELENIUM. The elementary selenium, P21, is dissolved by warming with 5 cu. mm. of fuming nitric acid.

Procedure

HBr solution S2 containing Se, As, and Ge is distilled

Distillate D4: Contains the bromides of Se, As, and Ge, and of some of the Sn and Sb + $\text{NH}_2\text{OH}\cdot\text{HCl}$

Residue R4: Contains the rest of the cations

Precipitate P21: Elementary Se + concd. HNO_3 + H_2O + $\text{Hg}_2(\text{NO}_3)_2$ reagent

Solution S21: Strongly acid solution is treated with H_2S

Hg_2SeO_2

Precipitate P22: As_2S_3 and GeS_2 . Treated with fuming HNO_3 , evaporated to dryness, dissolved in NH_4OH + tartaric acid + $(\text{NH}_4)_2\text{SO}_4$ + MgSO_4

Solution S22: Sn and Sb. Combined with R4

Precipitate P23: $\text{Mg}(\text{NH}_4)\text{AsO}_4\cdot 6\text{H}_2\text{O}$ + concd. HCl + H_2S

Solution S23: + H_2SO_4 + H_2S

As_2S_3

GeS_2

The numbers of the precipitates and filtrates coincide as far as possible with the corresponding paragraph numbers of the scheme of Noyes and Bray.

The hydrobromic acid-bromine solution, S2, is prepared according to the directions of Noyes and Bray (7), and should have a volume between 20 and 30 cu. mm. In the work described in this paper, mixtures of 1 per cent and 5 per cent solutions of selenium dioxide and of sodium arsenate, and a 1 per cent solution

Another portion of the acid is added if solution is not complete. The solution is diluted with 0.1 ml. of water. Then 2-cu. mm. portions of mercurous nitrate reagent are added until no more precipitate forms on further addition. The reagent is prepared according to Denigès (6) by dissolving 10 grams of mercurous nitrate in 10 ml. of nitric acid (sp. gr., 1.39) and 100 ml. of water. The precipitate of mercurous selenite is collected by centrifuging, and its volume is compared with that of precipitates obtained by direct precipitation of known amounts of selenite.

SEPARATION OF ARSENIC AND GERMANIUM FROM TIN AND ANTIMONY. Solution S21 is made 6 *M* with respect to H⁺ by the addition of concentrated hydrochloric acid. The solution is treated at room temperature with hydrogen sulfide (2) until precipitation of the sulfides of arsenic and germanium is complete. The precipitate is digested for a few minutes by heating the sealed cone in a steam bath. Solution and precipitate are separated by centrifuging and the solution containing tin and antimony is first heated to expel the hydrogen sulfide and then combined with residue R4 of the distillation.

SEPARATION OF ARSENIC AND GERMANIUM. Sulfide precipitate P22 is treated with 20 cu. mm. of fuming nitric acid and the mixture is first heated on the steam bath until the sulfides are completely decomposed and then evaporated to dryness by inserting the cone in an aluminum block heated to about 130° C. A stream of air from a capillary directed at the surface of the solution aids in the evaporation.

The residue is dissolved in about 30 to 40 cu. mm. of dilute ammonium hydroxide. Then 20 cu. mm. of a 50 per cent tartaric acid solution, 25 cu. mm. of a 1 *M* ammonium sulfate solution, and 25 cu. mm. of a 0.5 *M* magnesium sulfate solution are added. The mixture is made ammoniacal and is boiled for half a minute on the steam bath with stirring. Rotating a glass thread with a beaded end against the bottom of the cone breaks up the bubbles into a fine stream. This technic prevents the contents of the cone from being expelled. A fine crystalline precipitate of magnesium ammonium arsenate is formed. The tartaric acid prevents the precipitation of magnesium germanate (5). The solution is allowed to cool and is stirred vigorously during the cooling. As done in this laboratory, the cone and its content are subjected to severe agitation with the use of a buzzer described below. The cone is then placed in ice water and allowed to stand for about a half hour. The precipitate is centrifuged to the bottom of the cone and the supernatant liquid is tested with a few cubic millimeters of the magnesium sulfate solution for the complete precipitation of the arsenic. Finally solution S23 is transferred to another cone by the use of a suction capillary siphon (4) containing a filtering wad of asbestos. The precipitate is washed twice with 10 cu. mm. of 1 per cent ammonium hydroxide and the washings are combined with the filtrate.

ESTIMATION OF THE AMOUNT OF ARSENIC. The magnesium ammonium arsenate in the cone is dissolved in concentrated hydrochloric acid and the solution is drawn through the filtering capillary to dissolve any precipitate on the asbestos. The solution is collected in a centrifuge cone and is saturated with hydrogen sulfide (2). The cone is closed by means of the pressure cap, and heated on the steam bath for a minute. After centrifuging, the volume of the arsenic sulfide is compared with that of precipitates obtained with known amounts of arsenic by direct precipitation with hydrogen sulfide under the same conditions.

PRECIPITATION OF GERMANIUM AS SULFIDE AND THE ESTIMATION OF ITS QUANTITY. Filtrate S23 is first made acid to litmus by the addition of very small volumes of 18 *M* sulfuric acid. Then an excess of 18 *M* sulfuric acid equal to one-sixth of the volume of the solution is added to make the solution 3 *M* with respect to sulfuric acid and approximately 6 *M* with respect to hydrogen ion. The solution is then saturated with hydrogen sulfide. The cone is closed with the pressure cap and its contents are digested on the steam bath for a few minutes.

The estimation of the amount of germanium is based on the volume of the centrifuged germanium sulfide precipitate and is carried out as in the case of arsenic.

The formation of a white sulfide is a sufficient confirmatory test for germanium.

Discussion of Experiments

The method outlined above gave satisfactory results with solutions of known composition which contained the elements selenium, arsenic, and germanium in the following extreme ratios:

Se:As = 1:100 and 100:1
Ge:As = 1:100
Ge:Se = 1:100

In all the mixtures 5μg. of the minor component were present.

A deviation from the procedure of Noyes and Bray was necessary in the isolation of the selenium group. Their method consists of distilling the sample with 10 ml. of 9 *M* hydrobromic acid containing some bromine until the volume of the residue is 3 ml. The exact reproduction of this procedure on the milligram scale is not feasible, since the proper time for the interruption of the distillation cannot be perceived with sufficient accuracy. If the distillation is stopped too early, complete separation of the germanium is not assured, and if the distillation is continued beyond a certain point, appreciable quantities of tin and antimony go into the distillate. It was decided to continue the distillation until a dry residue was obtained—i. e., to a stage that can be definitely recognized. In this way, a large part of the tin and a considerable amount of antimony volatilize. However, no appreciable amount of mercury was found to distill.

As to the analysis of the distillate, the original scheme of Noyes and Bray did not permit a good separation of germanium from arsenic on the micro scale or the detection of germanium even when present as high as 10 to 20 per cent of the sample weight. These authors base the separation on the precipitation of arsenic sulfide from an ammoniacal solution of the thio complexes of arsenic and germanium by the addition of hydrofluoric acid. The germanium should be retained in solution as the fluoro complex. The procedure was tried on the milligram scale with the use of centrifuge cones and capillary siphons made of platinum. The use of platinum apparatus for handling small volumes of solutions and precipitates introduces technical difficulties. In addition, it was found that some germanium precipitates with the arsenic sulfide and that large amounts of germanium were lost in the subsequent evaporation of the filtrate with sulfuric acid, probably through the formation of the volatile fluoride.

The following schemes for the separation of arsenic and germanium were tried on the micro scale without success:

Cathodic reduction of germanium to gaseous GeH₄ and subsequent combustion to a metallic germanium mirror.

Reduction of arsenic to the elementary form with stannous chloride-hydrochloric acid reagent.

Precipitation of the arsenic as the uranyl ammonium arsenate.

Distillation of germanium tetrachloride in the presence of chlorine from potassium chlorate in the acid solution, the arsenic being kept in the pentavalent state.

With the procedure finally adopted, it was found that the separation with magnesia mixture in a tartrate solution cannot be applied directly to hydrobromic acid solution S21. The bromide ion apparently reduces the arsenate ion in the ammoniacal solution, thus interfering with the precipitation of the magnesium ammonium arsenate. The bromine formed is removed by reaction with the ammonia or the hydroxylamine present, favoring the conversion of the arsenate to arsenite. Therefore, it is necessary to remove the bromide by evaporation with fuming nitric acid in cases where the absence of tin and antimony makes the preliminary separation of the arsenic and germanium as sulfides unnecessary.

BUZZER. Mention may be made here of a special use of a commonplace device. The interrupter of an electromagnetic door buzzer is fastened down so that it cannot make and break. When the buzzer is connected to the 110-volt alternating current line through a transformer, the interrupter vibrates with an almost imperceptible motion. If a centrifuge cone is held against the oscillating arm, vibrations are set up in the contents of the cone. The device has been used for the more rapid attainment of a complete precipitation of magnesium ammonium arsenate and for the acceleration of the flocculation of germanium sulfide which tends to be colloidal, especially when present in small amounts.

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RECEIVED August 5, 1937. Presented in preliminary form before the Microchemical Section at the 93rd Meeting of the American Chemical Society, Pittsburgh, Pa., September 7 to 11, 1936. Abstracted from a thesis to be submitted by J. R. Rachele to the faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of doctor of philosophy.

An Improved Method for the Determination of Iodates

VICTOR J. ANHORN AND H. HUNT, Purdue University, West Lafayette, Ind.

STARCH used as an indicator in the determination of iodine does not give a reproducible end point which warrants the determination of a fraction of a milligram of potassium iodate. The physical condition of starch solutions or their absorptive power varies and this causes the sensitivity of the end point to fluctuate. Extraction methods do not place all the iodine in a nonaqueous solution free from optically interfering aqueous layers; besides, there are extra steps involved in an extraction process. Therefore, the authors found it expedient to develop a more convenient and accurate procedure for the determination of iodine than they could find in the literature.

This paper describes inexpensive apparatus and an accurate method for determining as little as 0.3 mg. of potassium iodate. The method involves titration, with weight burets, using the color of free iodine as the indicator.

Apparatus and Procedure

A weight buret of 1-ml. capacity and weighing about 6 grams was constructed as shown in Figure 1. It was possible to regulate the flow to 0.1 mg. of solution delivered. Delivery was made below the surface of the liquid being titrated. The titrating vessel, shown in Figure 1, had a capacity of about 15 ml. The observation tube was 40 cm. in length, its sides were painted black, and the bottom was illuminated with a 150-watt blue Mazda bulb. As little as 0.0000003 gram of iodate gave a pronounced color.

The solution was stirred with compressed nitrogen, using the gas lift principle. (About 15 to 30 minutes were used for a determination.)

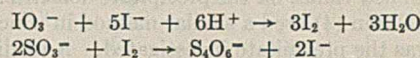
A blank was run with each determination. The blank contained the same concentration of acid and iodide, and was stirred

at the same rate as the sample. The titration was stopped when the colors were identical in the two tubes. The analytical balance had a sensitivity of three divisions per 0.1 mg. The weights were calibrated with a Bureau of Standards set.

Preparation and Standardization of Solutions

Analytical reagent sodium thiosulfate, potassium iodate (purity checked with electrolytic copper), and potassium iodide (with no free iodine) were recrystallized and carefully dried. c. p. acids and freshly distilled water (4) were used. All solutions were prepared by weighing the calculated amount of reagents and water. The normality of the solutions was approximately 0.015.

A 2 per cent solution of potassium iodide (5) was found most satisfactory; 0.01 *N* hydrochloric or sulfuric acid (2) gave optimum hydrogen-ion concentration for reactions



Results

Typical data obtained by this method are given in Table I.

TABLE I. DETERMINATION OF IODATE, USING 2 PER CENT IODIDE SOLUTIONS AND 0.01 *N* ACID

Sample No.	KIO ₃ Found Gram	KIO ₃ Present Gram	Percentage Error
1	0.0002866	0.0002853	+0.5
2	0.0003654	0.0003650	+0.1
3	0.0003144	0.0003143	+0.031
4	0.0003862	0.0003854	+0.2
5	0.0003474	0.0003488	-0.5
6	0.0003464	0.0003460	+0.1
7	0.0003393	0.0003393	0.0
8	0.0001954	0.0001947	+0.4
9	0.0003100	0.0003128	-0.9

This method has proved more accurate and more convenient than the starch indicator (3) method or the iodine-cyanide (1) procedure.

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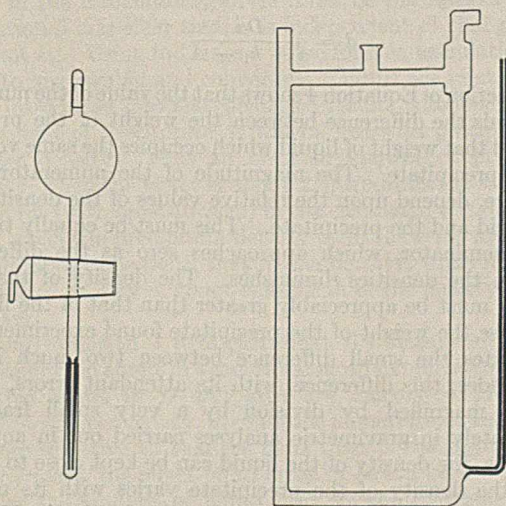


FIGURE 1. WEIGHT BURET (LEFT) AND TITRATION CELL (RIGHT)

The observation tube at right of titration cell had an approximately optically plane bottom and was open at the top.

CORRECTION. In the article on "Quantitative Determination of Arsenic in Small Amounts in Biological Materials" [*IND. ENG. CHEM., Anal. Ed.*, **9**, 448 (1937)] the figure "6100" in line 4, paragraph 2, of "Development of Color" should have been "610."

HERBERT O. CALVERY

A New Method in Pycnometric Analysis

Preliminary Report

W. WALKER RUSSELL, Metcalf Laboratory, Brown University, Providence, R. I.

A simple and rapid method of pycnometric analysis is provided, in which a purified precipitate is quantitatively transferred to a very small pycnometer and weighed in the presence of a liquid of known density. Analyses involving such physically different precipitates as silver chloride, barium sulfate, and ferric hydroxide indicate that the method is capable of good accuracy.

THE determination of the density of solid substances by means of a pycnometer has long been recognized as a standard method and has been shown to be capable of considerable precision (3). Conversely, a pycnometric procedure has been used as a means of determining the weights of precipitates of known densities in a unique method of gravimetric analysis. Thus in 1877 Popper (5) transferred such precipitates as aluminum hydroxide, barium sulfate, ferric hydroxide, mercuric sulfide, nickel hydroxide, and lead sulfate to a pycnometer of some 30-cc. capacity, along with some of the supernatant liquid, and weighed them. Then having determined the densities of the supernatant liquids, he calculated the weights of the precipitates present using previously determined values for the precipitate densities.

Recently Oknin (4) used a similar method in which barium chromate was the precipitate investigated. A modified Popper method has been proposed by Chatelet (1) in which the precipitation is carried out in the pycnometer itself, thereby avoiding transfer of the precipitate. After weighing, a sufficient amount of the supernatant liquid is removed for a density determination. In this laboratory Gruntfest (2) found considerable difficulty in obtaining acceptable results by such methods as the aforementioned, and the procedures proved tedious and exacting.

The pycnometric method of gravimetric analysis, however, has a number of important advantages and if its disadvantages can be eliminated or sufficiently minimized, should take its proper place among quantitative methods of analysis. The pycnometric method eliminates the necessity of isolating the precipitate and thereby avoids some of the most tiresome and uncertain operations in gravimetric analysis. Transfer of the precipitate to the filtering medium becomes unnecessary. Washing of the precipitate has frequently been omitted. Any drying, heating, or ignition of the precipitate is entirely eliminated. This last advantage is probably the most important. In many gravimetric analyses the isolation of the precipitate in a final form which is highly pure, of perfectly definite composition, and capable of accurate weighing is exceedingly difficult. This is true largely because of the deleterious action of filter paper, dust, and organic matter in general during ignitions, because of the rather narrow high-temperature range in which many precipitate transformations are strictly quantitative, and because of the rather general hygroscopicity of ignited materials. Furthermore, the pycnometric method makes possible in principle the use of precipitates which, being otherwise suitable, fail because they cannot be isolated without indefinite change in composition. Some of the newer organic precipitants which possess such valuable properties as good specificity, low precipitate solubility, high equivalent weight, and the like, may well fall into

this class. These advantages of the pycnometric method appear to make worth while an effort to reduce its complexity and associated errors.

Theory

If a vessel of accurately defined capacity, such as a pycnometer, is weighed when it contains a precipitate insoluble in the liquid which fills the vessel, we have the following expressions relating measurable properties of the system:

$$A = a + b + c \quad (1)$$

$$A = a + b + W - Dv \quad (2)$$

$$A = a + b + VD - Da/d \quad (3)$$

$$a = \frac{b + VD - A}{(D/d - 1)} \quad (4)$$

A = weight of pycnometer in grams plus precipitate plus liquid necessary to fill pycnometer

a = weight of precipitate

b = weight of dry, empty pycnometer

c = weight of liquid necessary to fill pycnometer when it also contains the precipitate

W = weight of liquid held by the pycnometer

D = density of liquid in grams per cc.

v = volume of precipitate

V = capacity of pycnometer in grams per cc.

d = density of precipitate

Units are grams and cubic centimeters.

With a given precipitate, using a given pycnometer and a liquid of known density, Equation 4 will contain only one experimental variable to be determined—namely, A

$$a = \frac{k_1 - A}{k_2} = k_3 - A/k_2 \quad (5)$$

where

$$k_1 = b + VD, \text{ and } k_2 = (D/d - 1), \text{ and } k_3 = k_1/k_2$$

From Equation 3, it follows also that

$$d = \frac{Da}{a + b + VD - A} \quad (6)$$

With a given pycnometer and a liquid of known density Equation 6 becomes

$$d = \frac{Da}{a + k_1 - A} \quad (7)$$

Inspection of Equation 4 shows that the value of the numerator equals the difference between the weight of the precipitate and that weight of liquid which occupies the same volume as the precipitate. The magnitude of the numerator will, therefore, depend upon the relative values of the densities of the liquid and the precipitate. This must be equally true of the denominator, which approaches zero as the difference between the densities diminishes. The density of the precipitate must be appreciably greater than that of the liquid; otherwise the weight of the precipitate found experimentally constitutes the small difference between two much larger magnitudes, this difference, with its attendant errors, being greatly magnified by division by a very small fraction. Fortunately in gravimetric analyses carried out in aqueous solutions, the density of the liquid can be kept close to unity while the density of the precipitate varies with its nature between 2 and 10. Assuming unit density for the liquid, over this range of precipitate densities, therefore, the value of the denominator varies from -0.5 to -0.9 ; for unit volume of precipitate, the value of the numerator varies from -1 to -9 .

Sources of Error in a Pycnometric Method of Analysis

In order to make a pycnometric method precise and accurate, it is necessary to recognize and effectively deal with its sources of error. As ordinarily carried out, pycnometer determinations suffer from those errors characteristic of methods which depend upon a small difference between much larger magnitudes. Furthermore, because of the relatively large thermal expansion coefficients of useful liquids, very exact thermostating is required for any considerable volume of liquid. Also the considerable surface of most pycnometers may be a source of error in weighings. Solubility of the precipitate in the liquid, and deviations of the densities of the precipitate and liquid from their calculated values, also are sources of error. Errors of large magnitude can arise from pycnometers of unsuitable design, especially those with defective closure which do not contain and maintain a constant volume of liquid during the weighings. Finally, there are mechanical losses if the precipitate is transferred.

For pycnometric gravimetric analysis, ideally the pycnometer should be just large enough to hold the precipitate plus a minimum of liquid. Because of the relatively large volumes of liquid required for successful gravimetric precipitations, it is obvious, therefore, that some means of quantitative transfer of the precipitate must be devised. If precipitates can be tightly packed, the volume occupied by 0.5 gram of solid will vary roughly between 0.3 and 0.1 cc. except for some very voluminous precipitates which may require up to 5 cc. A complete, charged pycnometer of 1- to 5-cc. capacity need not weigh over 10 to 15 grams and will possess about the same surface as an ordinary analytical crucible. Furthermore, the weight of the pycnometer when filled will vary by only 0.02 to 0.03 mg. per 0.1° C. per cc. of water near room temperatures. Regulation of the temperature bath, therefore, becomes extremely simple, especially as but a few minutes are required to reach temperature equilibrium. Unless the pycnometer stopper is flat and optically plane (3), this vessel is probably best equipped with a ground-in stopper provided with a central capillary exit. If, by means of a scratch or otherwise, the liquid level in the capillary can be read to 0.1 mm., the error in level adjustment will amount to 0.08 mg. with a 1-mm. capillary, or to 0.02 mg. with a capillary 0.5 mm. wide.

The densities of the precipitate and of the pycnometer liquid are seen to be involved in every calculation of precipitate weight. If the density of either varies from the value used in the calculations, errors must be introduced. From Equation 5 it is clear that k_1 is independent of changes in d , but not k_2 . Using too large a value for d in calculations will lead to low results, and conversely. While the relative error thus introduced into the calculated results is independent of the weight of precipitate, it will be less with precipitates of greater density. Thus an error in knowing a precipitate density, when the latter is about 2, introduces the same relative error (with opposite sign) in the calculated result. However, when the precipitate density is 10 the error introduced is only about one-tenth that in the density, while for a precipitate of density 5, about one-fourth of the density error so appears.

From Equation 4 it is clear that the density of the pycnometer liquid enters in a somewhat more complicated manner. Positive errors in D will give low calculated precipitate weights, and conversely, because the numerator of Equation 4 is more sensitive to changes in D than is the denominator. Furthermore, the effect of an error in D will be the less, the smaller the amount of liquid held by the pycnometer, the larger the weight of precipitate involved, and the greater the density of the precipitate. Thus with 1 gram of precipitate of density 2 in a pycnometer of 1-cc. capacity, a 0.1 per cent

positive error in D (which is usually near unity) produces a 0.1 per cent negative error in a . This error is increased to -0.5 per cent if a pycnometer of 3-cc. capacity is used. However, if with the larger pycnometer 2 grams of a precipitate of density 6 are employed, the error in a is reduced to -0.15 per cent.

From Equation 6 it is clear that if the value of the liquid density varies from the true value, the determined value of the density of the precipitate will be affected. Positive errors in D will produce negative errors in d , and conversely, because the numerator is less sensitive to changes in D than is the denominator of Equation 6. Also the effect of an error in D will be the less, the smaller the amount of liquid held by the pycnometer, the larger the weight of precipitate involved, and the smaller the density of the precipitate. Thus with 1 gram of precipitate of density 2 in a pycnometer of 1-cc. capacity, a 0.1 per cent positive error in D (which is usually near unity) produces a 0.1 per cent negative error in d . This error is increased to -1.1 per cent if a pycnometer of 2-cc. capacity and a precipitate of density 6 are involved. However, if at the same time the weight of the precipitate used is made 3 grams, the error in d is reduced to -0.3 per cent. ▽

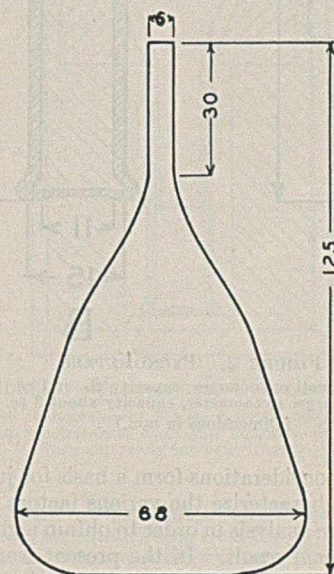


FIGURE 1. PRECIPITATION FLASK
(Dimensions in mm.)

No error is introduced into a pycnometric analysis if an arbitrary value is assumed for the density of the standardizing liquid—e. g., unit density for distilled water, provided that the density of the pycnometer liquid, the density of the precipitate, and the capacity of the pycnometer are all referred to this same standard liquid.

If the densities of the precipitates involved in pycnometric analyses are determined by the same experimental procedures to be used later in analyses, a considerable compensation of experimental errors may be achieved. Thus, if the value of a used in computing the density of a precipitate differs from the amount of precipitate actually present during the experimental determination of d , the value of d is incorrect as an absolute value, but if this incorrect value of d is then used in computing an analysis in which the amount of precipitate present differs in the same relative degree from the amount that theoretically should be present, no error is introduced into the pycnometric analysis. A complete compensation of errors of this type requires that the same fraction of a be always lost (or always gained) in the experimental manipulations. In practice this probably will be most nearly the case

when similar amounts of precipitates are involved, at least as regards precipitate losses in transfer and those due to solubility. It also follows from the above discussion that assuming an incorrect factor for converting a sample constituent to the precipitate form, or vice versa, introduces no error into a pycnometric analysis, provided of course that the same assumption is made in the experimental determination of precipitate density. This is a fact of considerable importance, as the exact composition of the precipitation form may be in doubt, especially as regards its degree of solvation.

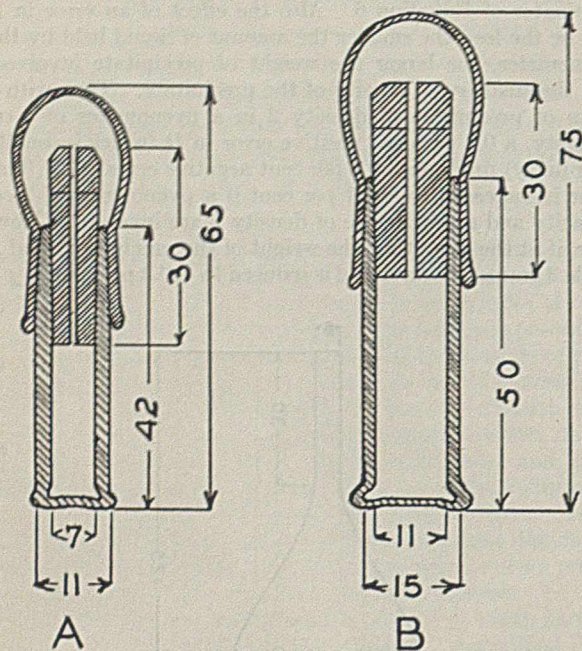


FIGURE 2. PYCNOMETERS

- A. Small pycnometer, capacity about 1 cc.
 B. Larger pycnometer, capacity about 3 cc.
 (Dimensions in mm.)

The foregoing considerations form a basis for judging what accuracy should characterize the various factors which enter into a pycnometric analysis in order to obtain a given order of accuracy in the final result. In the present work, using an ordinary analytical balance and weighing to the nearest 0.1 or 0.05 mg., a maximum error of about 1 mg. has been found, as would be estimated. The much smaller errors frequently found probably can be attributed to the operation of some of the compensation effects previously discussed.

Apparatus

Precipitation is carried out in special flasks designed to facilitate the transfer of the precipitate to the very small pycnometer used. The precipitate transfer is aided by the use of a centrifuge which not only conveys the precipitate more rapidly and completely, but also packs the precipitate tightly into the pycnometer. To obtain sufficient weights of very voluminous precipitates, close packing is necessary.

A precipitation flask can be made by drawing down the neck of a 125-cc. Pyrex Erlenmeyer flask and sealing to the portion so constricted a narrow piece of thin-walled Pyrex tubing. Pains should be taken to draw down the flask uniformly, and to attach the neck tube without producing irregularities on the inner flask surface on which precipitate particles can lodge. For a like reason the end of the neck tube should be fire-polished with care not to constrict it at all.

In Figure 1 a precipitation flask so prepared is shown. This flask, which has a neck tube 30 mm. long, 1 mm. in wall thickness, and 6 mm. in outside diameter, is suitable for use with the small pycnometer shown in Figure 2A. With the larger pycnometer

shown in Figure 2B, a precipitation flask with a neck tube 10 mm. in outside diameter can be used.

The size of the pycnometer will vary with the weight and bulkiness of the precipitate which it is desired to handle. In the present work pycnometers of about 1-cc. capacity mainly have been used. Such vessels will easily hold up to 1 gram of silver chloride or barium sulfate, or about 50 mg. of ferric hydroxide. The design of the pycnometer will be dictated also by the necessity of obtaining a highly accurate closure and by the type of centrifuge employed. In the present work an electrically driven centrifuge, Type SB, was used. (Centrifuge and cups are made by the International Equipment Company, Boston, Mass.)

Figure 2 shows two types of pycnometers drawn to scale. The pycnometer in A will fit into the lower chamber of centrifuge cup No. 395, while that in B requires a larger centrifuge cup—for example, No. 373. The pycnometers can be made from Pyrex tubing of about 2- to 3-mm. wall thickness, and as shown the smaller vessel has an outside diameter of 11 mm. while the larger is 15 mm. wide. The stoppers, which can be made from thick-walled capillary of 0.5- to 1-mm. bore, should be very carefully ground in, so that the pycnometer volume will be very accurately and reproducibly defined. A scratch encircles the capillary stopper in order to aid in defining the pycnometer volume. The pycnometer is completed by a cap with a ground-glass joint, which is necessary in order to prevent any slight evaporation of the enclosed liquid. The capacity of the pycnometer is determined at the temperature of use—e. g., 30° C.—which in any case should be above the highest balance room temperature that will be encountered. This precaution prevents the pycnometer from overflowing at any time through the capillary, which would cause a loss of liquid. The calibration liquid should be pure and preferably of accurately known density, conveniently pure water. The capacity of the pycnometer should be known to about 1 part in 10,000.

Figure 3 shows the small pycnometer of Figure 2A, attached to the precipitation flask of Figure 1 by means of a short piece of heavy-walled rubber tubing, the latter vessel being inverted to a position ready for centrifuging. The pycnometer rests on a small rubber disk, while the precipitation flask is supported in the centrifuge cup by rubber form No. 598 designed for use with the Goetz tube.

Figure 4 shows the larger pycnometer of Figure 2B, attached, in position for centrifuging, to a precipitation flask with a wider neck and a narrower base. This base is made just small enough to fit into centrifuge cup No. 373. By inserting the flask in an upright position into this cup and centrifuging, it becomes practical to wash by decantation, prior to transfer, those precipitates which normally settle very slowly. As shown in Figure 4, the precipitation flask is supported by the Goetz tube rubber form, which in turn is held by a cupped wooden form bored to hold the pycnometer. This wooden form should be well paraffined. A rubber form molded to the dimensions of centrifuge cup No. 373 and all in one piece is to be preferred.

Washing Media

The present method employs relatively large amounts of washing media of carefully determined density. It is convenient, therefore, to prepare several gallons of a given washing medium at one time, and to determine its density carefully, using a standard pycnometer of some 25- to 100-cc. capacity. A precision of at least 1 part in 10,000 is thus attainable. In the present work the following washing media were required: for barium sulfate, 0.03 N sulfuric acid plus 10 cc. of ethyl alcohol per liter, with a density at 30° C., of 0.99518; for silver chloride, 0.01 N nitric acid, with a density at 30° C., of 0.99601; for ferric hydroxide, ammonium nitrate solution, 10 grams per liter, with a density at 30° C., of 0.99932.

The Method

The precipitation is carried out in a precipitation flask similar to that shown in Figure 1. The introduction of the sample, solvent, reagent, etc., is accomplished by the use of a thistle tube whose exit end will just pass through the neck of the precipitation flask. It is usually convenient to dilute the solution to some 75

cc. and then to add the precipitating agent in a volume of about 25 cc. During precipitation the flask contents are readily agitated by shaking. When precipitation is complete, the precipitate is allowed to settle and to digest if desirable.

The washing of precipitates is carried out by decantation, using a siphon which will pass through the neck of the precipitation flask. The intake end of the siphon has its opening on the side, 1 to 2 mm. from a closed end. By placing the flask in an inclined position during the settling of the precipitate, the precipitate is kept to one side, so that even though the siphon end rests upon the bottom of the flask it contacts no precipitate. If any precipitate particles float upon the surface of the liquid, it is wise to stop the siphon just before it empties, thereby avoiding any chance of loss of traces of precipitate. The washing medium should not only be one in which the precipitate is highly insoluble, but also one which keeps the precipitate well coagulated and in a form which settles quickly.

When the precipitate has been washed sufficiently and the original supernatant liquid has been completely replaced by the standard washing medium, the volume of the latter is increased to about 100 cc. in the precipitation flask. Should any bits of precipitate cling to the inner side walls of this flask, they are easily displaced by a bit of rubber threaded onto a thin, stiff, curved wire which is inserted through the flask neck and used as a policeman. Now the pycnometer and the rubber connecting tubing are rinsed with the standard washing medium. Holding the pycnometer firmly, the rubber tubing is forced just over the edge of the ground-glass portion. By completely filling with the standard washing solution and pinching shut the end of the rubber, the latter is readily forced down into place.

The precipitation flask is now carefully inclined until its liquid almost emerges, and the liquid-filled pycnometer is slipped on far enough so that when the whole is centrifuged, the two vessels will separate slightly. When inverted, the precipitate falls into the pycnometer which has remained completely filled with liquid. By giving a rotary motion to the inverted precipitation flask, the transfer of precipitate is aided. Particles of silver chloride must be broken up by shaking, either during or after precipitation, if they are to pass readily through the neck of the flask used with the small pycnometer (Figure 2A). A rubber cap about 3 to 4 mm. thick is put under the bottom of the pycnometer before it is placed in the centrifuge cup. The cup is filled with water during centrifuging, as this prevents any tendency of the liquid within the glass vessels to escape. Now two cups are centrifuged for from 1 to 3 minutes at from 1200 to 2000 r. p. m., then removed and inspected. If any traces of precipitate cling to the inner walls of the flask, they are displaced by shaking. The packed precipitate shows little tendency to be disturbed, even though the flask

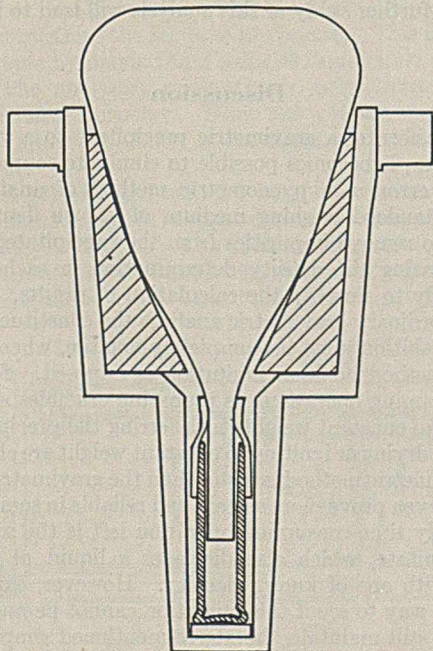


FIGURE 3. CENTRIFUGE CUP ASSEMBLY

Small pycnometer of Figure 2-A, attached to inverted precipitation flask and mounted in centrifuge cup ready for centrifuging

liquid is violently shaken. After again centrifuging, the precipitate transfer is generally complete.

Holding the pycnometer in an upright position the flask neck is carefully withdrawn, and the rubber connection eased off. The ground pycnometer stopper is first wet with some standard washing solution and then carefully though firmly inserted in place. The pycnometer is immediately immersed up to the ground joint in a liquid bath—e. g., in a Dewar vessel of water—which is maintained at the calibration temperature to within a tenth of a degree. After about 10 minutes the liquid level in the

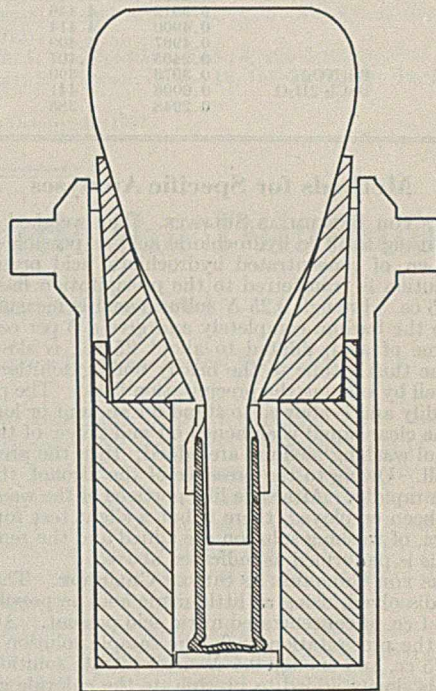


FIGURE 4. CENTRIFUGE CUP ASSEMBLY

Larger pycnometer of Figure 2-B, attached to inverted precipitation flask and mounted in centrifuge cup ready for centrifuging

capillary is adjusted to the scratch with tightly twisted wisps of filter paper. After withdrawing from the bath the pycnometer is carefully wiped—e. g., with filter paper—giving special attention to the ground joint. If this joint is defective in construction, the liquid level in the capillary may fall when the water is removed around the joint during the wiping. The dry cap is now put on and the pycnometer allowed to stand for 10 minutes in the balance case before weighing. During the next 10 minutes its weight will usually change less than 0.1 mg. A pycnometer is easily moved about by tightly grasping the protruding ends of a strip of tough paper which is bent around the vessel near its base.

Calculations

Equation 5 can be used to calculate the results of analyses. For a given precipitate, washing medium, and pycnometer, the values of k_1 and k_2 need be evaluated but once. The value of k_1 involves the weight of the empty pycnometer in grams, the volume of the pycnometer in cubic centimeters, and the density of the standard washing medium in grams per cc. The value of k_2 involves again the value of D and also the density of the precipitate. This latter value may be obtained by the analysis of known substances by the pycnometric method already outlined and the use of Equation 7. If any considerable change is made in a pycnometric method of analysis, its possible effect upon the value of d should be ascertained. Having determined the values of the constants in Equation 5, the computation of results becomes as easy as in ordinary simple gravimetric analysis.

TABLE I. PRECIPITATE DENSITIES

Precipitate	Original Material	Sample Weight Gram	Density at 30° G./cc.	Density, Mean Value
AgCl	NaCl	0.2555	5.460	...
		0.2023	5.465	...
		0.2052	5.462	5.463
Fe(OH) ₃	Fe	0.0222	2.644	...
		0.02045	2.636	...
		0.02145	2.652	2.644
BaSO ₄	BaCO ₃	0.5033	4.441	...
		0.5071	4.431	...
		0.5012	4.446	...
		0.4900	4.414	...
		0.4967	4.409	...
		0.2465	4.407	...
	Ba(NO ₃) ₂	0.3076	4.390	...
	BaCl ₂ ·2H ₂ O	0.6006	4.441	...
		0.2948	4.385	4.418

TABLE II. RESULTS OF PYCNOMETRIC ANALYSES

Sample	Precipitate	Weight of Precipitate		Relative Error %
		Present Gram	Found Gram	
NaCl	AgCl	0.6264	0.6263	-0.01
		0.4960	0.4960	0.00
		0.5031	0.5031	0.00
Fe	Fe(OH) ₃	0.0424	0.0424	0.00
		0.0391	0.03905	-0.20
		0.04105	0.0411	+0.20
BaCO ₃	BaSO ₄	0.5953	0.5962	+0.15
		0.5998	0.6003	+0.09
		0.5928	0.5939	+0.18
		0.5795	0.5794	-0.02
		0.5874	0.5871	-0.06
		0.2915	0.2913	-0.07
Ba(NO ₃) ₂	BaCl ₂ ·2H ₂ O	0.2747	0.2742	-0.19
		0.5739	0.5747	+0.15
		0.2816	0.2810	-0.22

Methods for Specific Analyses

ANALYSIS FOR BARIUM AS SULFATE. The weighed sample is dissolved, using as little hydrochloric acid as possible and so as to have 1 cc. of concentrated hydrochloric acid present. The sample solution is transferred to the precipitation flask and diluted to 75 cc. Enough 0.25 *N* sulfuric acid is measured out to precipitate the barium completely and give a 5 per cent excess. This volume of acid, diluted to about 25 cc., is slowly added through the thistle tube to the nearly boiling solution which is agitated well by shaking the precipitation flask. The precipitate settles readily and is allowed to stand for an hour or longer if desired. The clear liquid is siphoned off and 25 cc. of the sulfuric acid-alcohol washing medium are added; then the precipitate is shaken well. Owing to the presence of the alcohol, the precipitate settles rapidly. After five like portions of the washing solution have been employed, there is but a slight test for chloride. Now 100 cc. of washing solution are added and the remainder of the analysis is performed as indicated above.

ANALYSIS FOR CHLORIDE AS SILVER CHLORIDE. The weighed sample is dissolved, using as little nitric acid as possible and so as to have 1 cc. of concentrated nitric acid present. After transferring to the precipitation flask, the sample solution is diluted to about 75 cc. and enough 0.5 *N* silver nitrate solution (diluted to 25 cc.) is slowly added to precipitate the chloride completely and allow about a 5 per cent excess. During precipitation the flask contents are well shaken. When precipitation is complete, the mixture is heated to boiling and then allowed to stand for an hour or longer if desired. During the washing, which requires about five 25-cc. portions of the 0.01 *N* nitric acid, care is taken to shake the precipitate hard enough to break up any particles large enough to clog the neck of the precipitation flask during centrifuging. The analysis is completed as outlined above.

ANALYSIS FOR IRON AS FERRIC HYDROXIDE. The weighed sample (not over 25 mg. of iron) is dissolved and the iron is oxidized to the ferric state with nitric acid, hydrogen peroxide, or bromine, then transferred to the precipitation flask. Enough nitric acid is added to have about 1 to 2 cc. of the concentrated acid present and the sample is diluted to about 75 cc. About 3 cc. of filtered concentrated ammonium hydroxide are diluted to 20 cc. and slowly added to the nearly boiling solution, which is constantly shaken, until a slight excess of ammonia is present. The mixture is heated to boiling for 1 minute. After standing a half hour or longer if desired, the precipitate may be washed, using the prepared ammonium nitrate solution. Because of the bulky nature of the precipitate, it is particularly desirable here to settle the precipitate while the flask is inclined. Because some bits of precipitate tend to float on the liquid surface, the siphon is best stopped just before it empties itself. By heating the mixture just to boiling after the addition of each 50 cc. of washing medium, the ferric hydroxide settles rapidly. About 4 portions of washing solution are used.

Results

In Table I are shown the densities of the three precipitates studied, calculated from the pycnometric analyses of several simple substances of good purity by means of Equation 7. By the usual gravimetric procedures it was ascertained that the barium carbonate used contained 69.15 per cent of barium; the BaCl₂·2H₂O contained 56.13 per cent of barium; the barium nitrate contained 52.30 per cent of barium; the iron wire contained 99.85 per cent of iron; and the sodium chloride contained 60.63 per cent of chloride. From these

results the amount of precipitate present was calculated, using the simplest formula for the precipitate. In the case of ferric hydroxide this precipitate is undoubtedly hydrated. As has already been pointed out, assuming a simpler formula for the calculation of the precipitate density to be used in pycnometric analysis introduces no error, provided the same assumption is made there and the precipitate composition remains constant. The average density values in Table I differ somewhat from those recorded in the literature, and should be regarded primarily as apparent densities more or less characteristic of the method by which they were obtained.

Table II shows the results of the pycnometric analyses of the substances used in the density determinations of Table I, these substances now being treated as unknowns. The calculations are made with Equation 5, using the average values of the densities given in Table I. In Table II the weights of "precipitate present" are calculated by assuming the simplest formula for the precipitate, and correcting, on the basis of ordinary gravimetric analyses, for the purity of the substances analyzed. The chloride and iron analyses in particular indicate that the foregoing method is capable of considerable accuracy. The barium analyses are less accurate on the basis of absolute error, yet their average relative error is but slightly greater than 0.1 per cent, and there is reason to believe that further study of this analysis will lead to improved accuracy.

Discussion

By transferring a gravimetric precipitate to a very small pycnometer, it becomes possible to eliminate sources of considerable error in a pycnometric method of analysis. By using a standard washing medium of known density, it is possible to remove impurities from the precipitate, to eliminate repeating the density determination in each analysis, and greatly to simplify the calculation of results. Furthermore, in ordinary gravimetric analysis the constituents of the washing solution must be completely volatile, whereas in the present method no such limitation is imposed. Since such time-consuming operations as preparing crucibles and bringing them to constant weight, transferring the precipitate to a filter, and drying or igniting to constant weight are eliminated, the pycnometric method is faster than the gravimetric method and may even prove more certain and reliable in some cases.

The only time-consuming operation left is the washing of the precipitate, which also displaces a liquid of unknown density with one of known density. However, experiments are under way to see if this operation cannot be much shortened and still maintain the above-mentioned simplifications inherent in the use of a known constant-density pycnometer liquid. If so, the pycnometric method should compete with certain volumetric methods in rapidity. Although the centrifuge has been used in the analyses here reported, there is

evidence that it may be unnecessary with heavier and denser precipitates, and this possibility is being investigated.

Any pycnometric method is obviously dependent upon accurate knowledge of precipitate density. The values of precipitate density here reported differ in some degree from those reported elsewhere. It is proposed, therefore, to study the factors which particularly affect precipitate density, in order to ascertain in which parts of a pycnometric analysis particular care is needed. Such a study should also throw light upon certain fundamental characteristics of gravimetric precipitates.

The precision and accuracy obtained in the analyses here reported indicate that the present method of pycnometric analysis should compare favorably with good macrogravimetric procedures. In cases in which a precipitate acts

badly during drying or ignition, the pycnometric method may offer considerable advantages. It is proposed to extend this study to other conditions, including especially the effects of foreign ions, and to other precipitates, including organic compounds, in order to evaluate better the possibilities of this method of analysis.

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Microgasometric Analysis with the Dilatometer

Determination of the Carbonate Radical

BEVERLY L. CLARKE AND H. W. HERMANC, Bell Telephone Laboratories, New York, N. Y.

GASOMETRIC methods are particularly desirable in microanalysis because of the relatively large volume of the measured product, compared to the mass of the sample. Several procedures are available. The gas may be evolved against the pressure of a column of mercury and its volume determined from the measured increase in pressure. Such a manometric method requires that the free space in the apparatus be precisely known. To ensure accuracy of reading, the measured pressure difference must be reasonably great and the reaction must therefore be such as to proceed to completion at pressures above atmospheric. In addition to the difficulties imposed by such conditions, it is obvious that there is danger of leakage through rubber or ground-glass connections from a system under pressure. Further, the solubility of the gas in any liquid present increases with pressure.

Another procedure is to evolve the gas under constant pressure and measure the increase in volume. This is most commonly done by displacing a suitable liquid from a calibrated tube. The necessary apparatus is rather cumbersome for microchemical purposes. When the volume of gas is small, errors due to its solubility in the displaced liquid are likely to be serious.

Nernst (2) used the mercury bead dilatometer to measure small volume increases in vapor density determinations by the Victor Meyer method. The dilatometer consists of a graduated horizontal tube of small bore, closed by a droplet of mercury which is free to move until the internal and external pres-

ures are equalized. This movement, over the graduated scale, indicates the sense and the magnitude of the volume change. Applied to micromethods, such an arrangement possesses particular merit. Its construction is simple, permitting a reduction of the apparatus capacity to a point commensurate with the small volumes dealt with. Errors attendant upon measurement of the evolved gas by liquid displacement are not present in the dilatometer method.

The authors have applied such a dilatometer to the determination of carbon dioxide in samples of corrosion product weighing only a few milligrams. Because of the high solubility of carbon dioxide in most liquids, low results were obtained when acids, either dilute or concentrated, were used to liberate the gas, even when the volume of acid did not exceed 0.2 cc. Release of dissolved carbon dioxide by boiling the acid introduced complications in the construction of the apparatus and was not completely effective in the closed system because of the re-solution of the carbon dioxide by the condensed film on the walls. A method was therefore devised in which the carbon dioxide is liberated by a fused acid salt, potassium pyrosulfate, in which its solubility is negligible. The need for condensation chambers, moisture traps, and special arrangements for introducing the sample is thus eliminated. A simply constructed microretort for carrying out the fusion and the dilatometer constitute the assembly.

Apparatus

The apparatus shown in Figure 1 has two essential parts, the gas measuring buret, *A*, and the retort, *B*. The buret is constructed of thermometer tubing having a bore of approximately 2 mm. and a capacity of 2 cc., graduated in 0.01-cc. divisions. By means of a reading lens, tenths of a division may be estimated. A funnel-shaped opening at the outer end facilitates cleaning, and also serves to receive the mercury droplet when the gas volume accidentally exceeds the capacity of the buret. An interchangeable (No. 5) ground joint connects the retort with the dilatometer. The droplet of mercury used in the buret should not be too large. Its length should be about two and one-half times the bore of the tube. A tapper, *C*, made from an electric bell, helps to overcome the resistance opposing the movement of the mercury.

The retort unit, constructed of quartz glass, consists of a heavy-walled, conical bulb of about

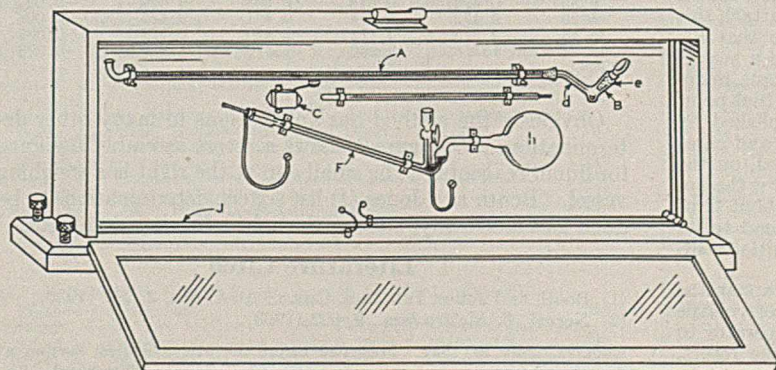


FIGURE 1. DILATOMETER

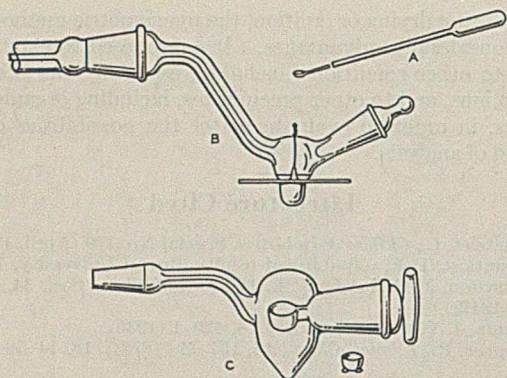


FIGURE 2. DETAILS OF RETORT ASSEMBLY

1-cc. capacity joined to which are two tubes: *e*, for the introduction of the sample, and *d*, communicating with the dilatometer. These tubes make an angle of about 45° with the axis of the retort bulb. Tube *d* has a capillary bore, 1 to 1.5 mm. in diameter, and is about 10 cm. long. Close to the retort, two or three small dilations in the tube bore serve to entrap any sulfur trioxide that may be accidentally given off or any pyrosulfate that may be spattered. The narrow bore of the tube reduces the dead space in the apparatus and its length decreases the heat transmission to the buret. The tube terminates in the male member of the ground joint connecting the retort unit with the dilatometer. Tube *e* is approximately 4 cm. long and has a bore of about 5 mm. It is provided with a ground-in stopper terminating in a solid process which extends downward and substantially fills the space within the tube, thus reducing unnecessary volume. A mica disk, about 4 cm. in diameter, perforated at the center, fits over the retort bulb (*B*, Figure 2) and protects tubes *d* and *e* from excessive heating. It is held in place by wires, looped over the tubes as shown.

The apparatus is mounted on a wooden panel which forms the back of a box, as shown in Figure 1. The box, the front panel of which is a detachable glass window, constitutes an air thermostat. The heater is a Nichrome wire, *J*, strung around the interior of the box as indicated. The thermoregulator, *F*, employs a glass vessel, *h*, blown with extremely thin walls, containing air as the expansion fluid. This type of regulator was found most satisfactory for the purpose.

Reagent

POTASSIUM PYROSULFATE. In a porcelain evaporating dish, heat gently 50 grams of c. p. potassium pyrosulfate until it no longer effervesces. Then slowly raise the temperature until sulfur trioxide fumes just commence to be evolved. Discontinue the heating, and pour the molten pyrosulfate out onto a porcelain plate, previously heated in an oven. Break up the solidified cake immediately and grind to about 10-mesh in a porcelain mortar. Preserve in a tightly stoppered bottle.

Procedure

Adjust the thermoregulator to maintain the temperature, in the closed box, 2° or 3° above that of the room.

Thoroughly clean the retort unit with hot chromic-sulfuric acid mixture, rinse with water and acetone, and dry in an oven. Introduce sufficient pyrosulfate reagent to fill about three-fourths of the retort bulb, and heat gently until it has melted and the air bubbles have been completely expelled. After cooling, attach this part of the apparatus to the microburet, taking care that the ground joint is lubricated with a minimum quantity of a heavy-bodied grease. With the cap removed from the sample introduction tube, gently force the mercury bead to the initial point on the buret scale, this operation being best accomplished by attaching a rubber tube to the open end of the buret and carefully blowing into it. Replace the cap, also lubricated, on the sample tube; replace the front panel of the box and allow the apparatus to stand undisturbed for 5 minutes to bring about temperature equilibrium. Finally, bring the mercury bead to its position of rest by means of the tapper and take the initial reading on the scale as well as the temperature of the box.

Before the actual determination, make a trial of the apparatus as a check on the tightness of the joints, the absence of volatile impurities in the pyrosulfate, and the ability of the operator to carry out the fusion without softening the wall of the retort. Gently heat the retort bulb until the pyrosulfate again fuses, taking care in this operation not to concentrate the flame at one

spot on the glass, but rather to use an even rotary motion, heating the upper part of the bulb as well as the lower. The temperature should not reach a point beyond that at which a faint red glow may just be detected in a darkened room. Failure to observe these precautions may result in the softening of the bulb with alteration of its shape and a change in the volume of the apparatus. Maintain the pyrosulfate in a fused condition for 5 minutes, then close the box and allow the apparatus to cool to the temperature of the thermostat. Now take readings of the position of the mercury bead at 1-minute intervals until three successive readings agree. If the details of the procedure have been carefully followed out and the apparatus was correctly constructed, the change in the volume of the gas in the apparatus should not exceed 0.005 cc.

When it has been established that the apparatus is working properly, weigh from 5 to 50 mg. of the finely ground sample, depending on the amount of carbon dioxide expected, and introduce into the retort bulb. This operation is most conveniently carried out by means of a small metal spoon with a detachable handle long enough to permit its introduction into the retort (*A*, Figure 2). Weigh the spoon, together with a small capsule containing the previously dried and finely ground sample, attach the handle and scoop up a portion of the sample, the excess material clinging to the bottom and edges of the spoon being jarred off by tapping against the edge of the capsule. Then transfer contents of the spoon to the surface of the pyrosulfate in the retort by rotating the handle. Detach the spoon, return to the balance pan, and obtain the sample taken as the loss in weight.

Adjust the mercury bead to the initial position in the buret and place the cap tightly on the sample introduction tube. Make three readings of the position of the bead at 1-minute intervals, using the vibrator each time. If there is no change, commence the heating of the retort, slowly bringing the pyrosulfate to a completely fused condition and maintaining it thus until there is no further evolution of gas and all the bubbles have escaped. (Often the heat of the hands in manipulating the apparatus preparatory to making the determination will raise the temperature of the air within by 3° or 4°. Hence it is not safe to start immediately without observing the precaution mentioned.) If particles of sample remain clinging to the upper wall of the retort chamber and have not come into contact with the pyrosulfate, this can usually be remedied by gently shaking the apparatus.

Replace the front panel and allow the apparatus to return to the temperature of the thermostat. Read the position of the bead at 1-minute intervals until 3 consecutive readings agree.

Calculation

The volume of carbon dioxide evolved is given by the difference in the positions of the bead.

1 mg. of CO₂ at 0° C. and 760 mm. ≈ 0.509 cc.

$$\text{Hence, weight of CO}_2 = \frac{(V_1 - V_2)}{0.509} \times \frac{760}{P} \times \frac{t + 273}{273}$$

where $V_1 - V_2$ is the observed volume increase; P , the barometric pressure in mm.; and t , the temperature of the thermostat in °C.

TABLE I. DETERMINATION OF CARBON DIOXIDE IN CERUSSITE

Sample Taken	Equivalent Volume of CO ₂ at 25° C.	Buret Reading		Volume of CO ₂ at 25° C. Found	Error
		Initial	Final		
Mg.	Cc.	Cc.	Cc.	Cc.	Cc.
a	...	0.075	0.072	...	-0.003
a	...	0.010	0.010	...	0.000
a	...	0.0130	0.0135	...	+0.0005
a	...	0.090	0.091	...	+0.001
5.70	0.516	0.150	0.661	0.511	-0.005
6.85	0.622	0.048	0.668	0.620	-0.002
5.20	0.472	0.014	0.491	0.477	+0.005
25.15	2.275	0.172	2.450	2.278	+0.003
12.23	1.118	0.260	1.370	1.110	-0.008

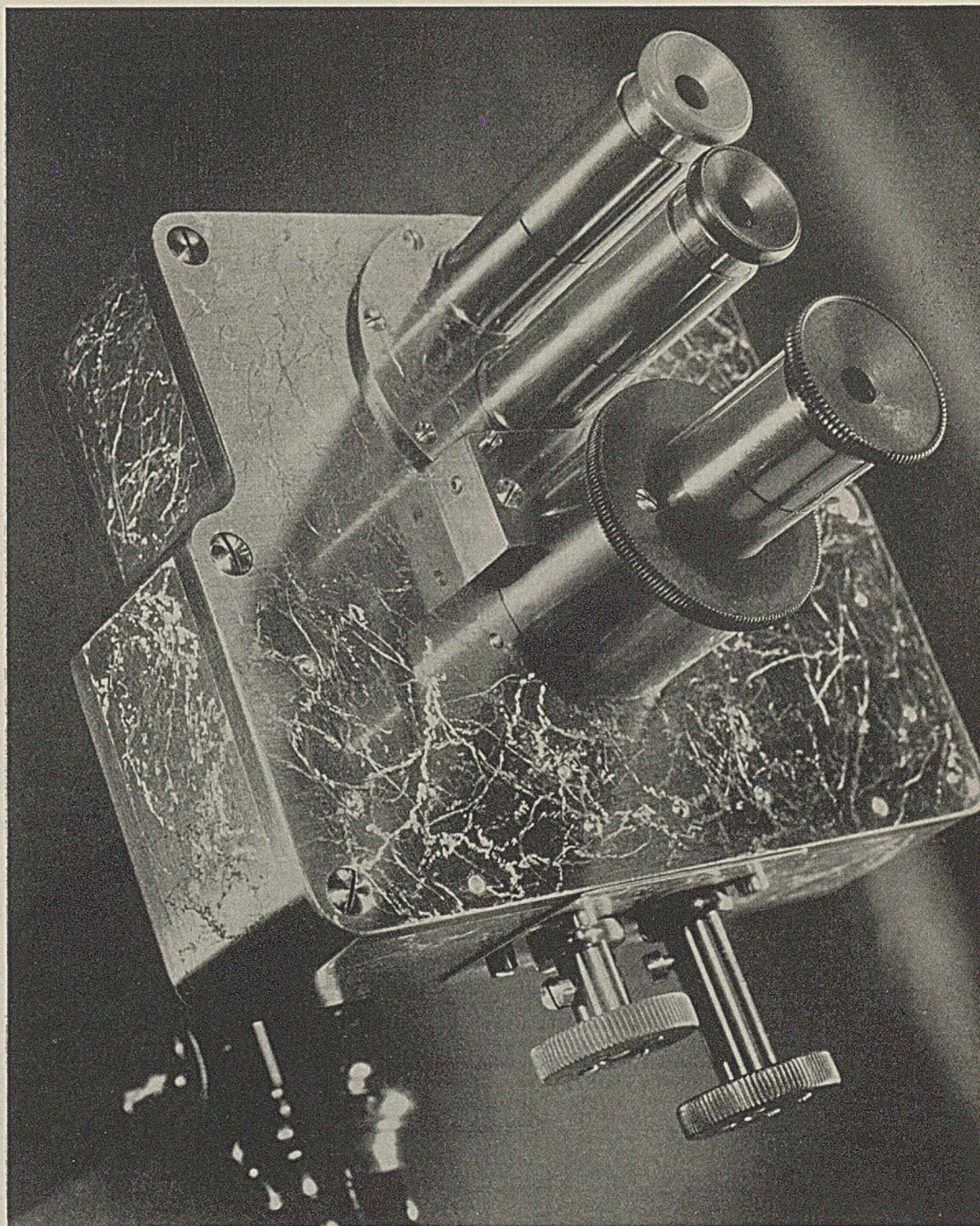
a Control experiments.

Obviously the method has applications to many other determinations. *C*, Figure 2, shows a retort assembly designed for liquid reagents. The small cup at the right is a weighing vessel. Booth and Jones (*1*) list sixteen determinations to be done gasometrically, stating that their list is incomplete.

Literature Cited

- (1) Booth and Jones, *IND. ENG. CHEM., Anal. Ed.*, 2, 237 (1930).
- (2) Nernst, *Z. Elektrochem.*, 9, 622 (1903).

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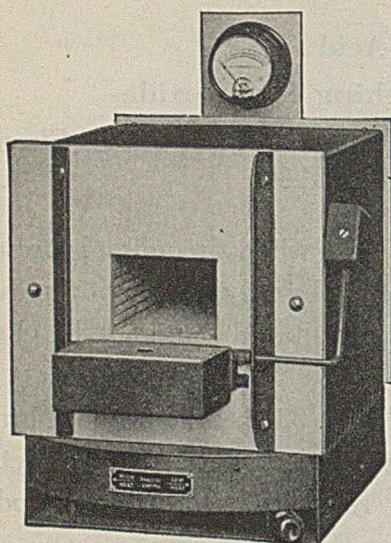
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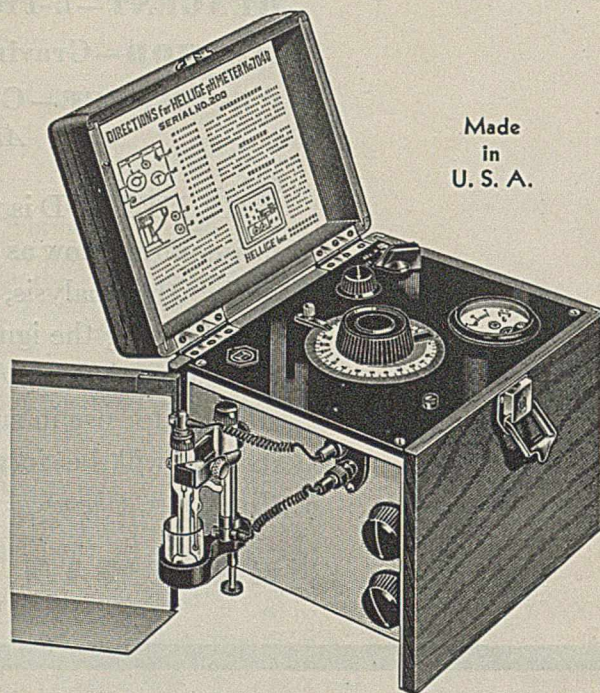
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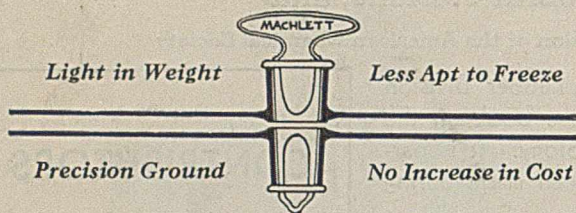
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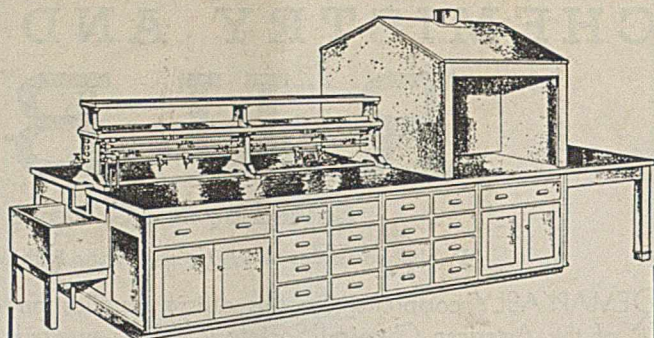
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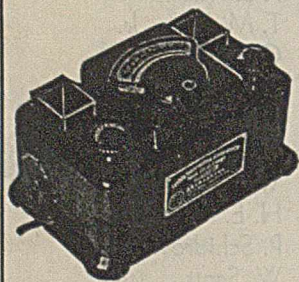
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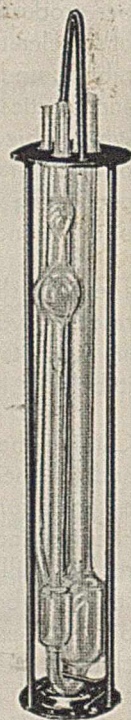
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