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DETERMINATION OF CHLORATE IN CAUSTIC SODA SOLUTIONS

By Reduction with Ferrous Sulfate

DWIGHT WILLIAMS

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The chlorate content of cell liquor from chlorine-caustic soda cells and of commercial 50% caustic soda is determined by reduction with excess ferrous sulfate in a sulfuric acid solution. The excess ferrous sulfate is titrated with potassium dichromate using diphenylamine sulfonic acid as indicator. The method is free from constant errors. The limit of uncertainty of the method under the best conditions (LU_1) is $\pm 0.0023\%$ sodium chlorate for a sample of 50% caustic soda analyzing 0.067%. The limit of uncertainty for the same sample under routine conditions (LU_2) is $\pm 0.0046\%$ and the average analysis was also 0.067%.

SODIUM chlorate is an important impurity in electrolytic caustic soda and, as a result, several methods have been developed for its determination in caustic soda solutions. The relatively large amounts of chlorate which are found in chlorine-caustic soda cell liquor and in commercial-grade 50% caustic soda are determined by reduction with ferrous sulfate. However, the precision of this method is such that it does not give useful results at the low concentrations which occur in high-purity, rayon-grade caustic soda. Chlorate in the latter is determined iodometrically, or colorimetrically by means of *o*-tolidine. This paper describes the determination of chlorate by reduction with ferrous sulfate and the two following papers describe the iodometric and colorimetric methods, respectively. The ferrous sulfate reduction method gives useful results at concentrations down to about 0.01%. The iodometric and colorimetric methods are applicable at concentrations of only 2 or 3 parts per million.

Boyle *et al.* (1) recently described the determination of chlorate in chlorine-caustic soda cell liquor by reduction with excess ferrous sulfate in relatively concentrated hydrochloric acid using ammonium molybdate as a catalyst. The ferrous sulfate reduction method which is used in this plant is somewhat different from that described by Boyle and his co-workers. The reduction is carried out either in sulfuric acid solution or in a mixture of sulfuric acid and phosphoric acid, and no catalyst is used.

As would be expected, the time required to complete the reduction depends upon the acid concentration, the ferrous sulfate concentration, the chloride-ion concentration, and the temperature. The effect of these factors has been evaluated and, from the resulting experimental data, conditions have been chosen which permit analyses to be made with the minimum number of manipulations and hence the minimum operating time. The number of

reagents has been reduced to a minimum and conditions have been chosen so that, with the exception of standard solutions, the measurement of the exact volume of reagent is not required. A large number of samples of cell liquor, 30 or more, are commonly analyzed at one time. The sample bottles and reaction flasks are arranged in several rows, one in front of the other, to permit their orderly manipulation. Reagents are dispensed with pipets which have been cut off just below the bulb, so that they can be discharged in 1 or 2 seconds and fill automatically when returned to the reagent bottle. An experienced analyst can analyze 150 samples of chlorine-caustic soda cell liquor per 8-hour day, including making all calculations and washing all glassware. This amounts to about 3 minutes per analysis.

The method has been applied to the determination of chlorates in commercial 50% caustic soda. A somewhat longer time is required to make this analysis, since the sample must be weighed.

REAGENTS

Potassium dichromate, 0.1 *N*.
Ferrous sulfate or ferrous ammonium sulfate, 0.1 *N* in 4 *N* sulfuric acid.
Sulfuric acid, 12 *N*.
Phosphoric acid, 1 to 1.
Diphenylamine sulfonic acid, 0.01 *M*.

PROCEDURE

CAUSTIC SODA, 50%. Take a 5-gram sample of 50% caustic soda for analysis and dilute with 25 ml. of water. Add 20 to 25 ml. of 1 to 1 phosphoric acid and swirl to mix. Add 10 ml. of 0.1 *N* ferrous sulfate and 45 to 50 ml. of 12 *N* sulfuric acid. Allow to stand 10 minutes or longer. Add approximately 0.5 ml. of 0.01 *M* diphenylamine sulfonic acid and titrate the excess ferrous sulfate with 0.1 *N* potassium dichromate solution. The end point should be taken when the maximum purple color develops.

Normally 10 ml. of 0.1 *N* ferrous sulfate are sufficient to complete the reduction in 10 minutes. However, if less than 5 ml. of potassium dichromate is required for the titration the analysis must be repeated using a larger amount of ferrous sulfate.

Standardize the ferrous sulfate each time it is used. Use the same amount of ferrous sulfate, phosphoric acid, sulfuric acid, and diphenylamine sulfonic acid for the standardization as for the sample.

$$\frac{(\text{Ml. of } K_2Cr_2O_7 \text{ standard} - \text{ml. of } K_2Cr_2O_7 \text{ sample}) \times N \ K_2Cr_2O_7 \times 1.774}{\text{grams of sample}} = \% \ NaClO_3$$

CELL LIQUOR. Measure 25 ml. of the sample for analysis, add 20 to 25 ml. of 1 to 1 phosphoric acid, 25 ml. of 0.1 *N* ferrous sulfate, and 20 to 25 ml. of 12 *N* sulfuric acid, and allow to stand 5 minutes or longer. Titrate the excess ferrous sulfate in the same manner as for 50% caustic soda. Standardize the ferrous sulfate, using the same amounts of reagents and the same conditions as in titrating the sample.

$$\frac{(\text{Ml. of } K_2Cr_2O_7 \text{ standard} - \text{ml. of } K_2Cr_2O_7 \text{ sample}) \times N K_2Cr_2O_7 \times 17.74}{\text{ml. of sample}} = \text{grams per liter of } NaClO_3$$

EXPERIMENTAL

The sodium hydroxide used for experimental work was prepared by dissolving c.p. sodium hydroxide pellets in water. Weighed portions of a 50% solution or pipetted portions of a 100-gram-per-liter solution were used for experimental purposes. Synthetic cell liquor was prepared by dissolving 100 grams of c.p. sodium hydroxide pellets and 150 grams of c.p. sodium chloride in sufficient water to make 1 liter of solution. Measured volumes of a standard solution of c.p. sodium chlorate (or the equivalent amount of c.p. potassium chlorate) were pipetted into each portion of sodium hydroxide solution or cell liquor prior to analysis.

The minimum sulfuric acid concentration required to reduce chlorates quantitatively in caustic soda at the boiling point was determined as follows:

To 7.5-gram portions of 50% sodium hydroxide were added 29.2-mg. portions of sodium chlorate. Sulfuric acid was added followed by 25 ml. of approximately 0.1 *N* (0.52-milliequivalent excess) ferrous sulfate. The solutions, which had a volume of about 100 ml. at this point, were boiled for 5 minutes, then cooled rapidly in a stream of water, and the excess ferrous sulfate was titrated. A minimum acid concentration of 1 *N* is required for quantitative recovery of chlorate under these conditions (Figure 1, curve 1).

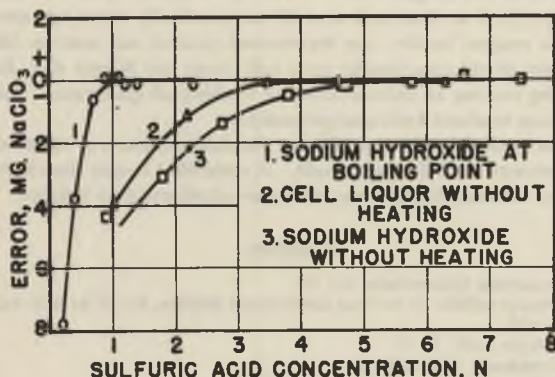


Figure 1. Effect of Sulfuric Acid Concentration on Recovery of Chlorate

Where a large number of samples must be analyzed time can be saved by carrying out the reduction at room temperature rather than at the boiling point. Consequently, the following experiments were performed to determine the minimum sulfuric acid concentration required to reduce chlorate without heating.

To 25-ml. portions of 100-gram-per-liter sodium hydroxide were added 6.2-mg. portions of sodium chlorate. Water was added to give a volume of 100 ml. after addition of the ferrous sulfate solution. Sulfuric acid was added followed by 2.2-milliequivalent excess of ferrous sulfate. The excess ferrous sulfate was titrated after 5 minutes. A minimum sulfuric acid concentration of 4.5 *N* was required for quantitative reduction (Figure 1, curve 3).

In practice it is desirable to carry out the reduction with the minimum excess of ferrous sulfate. The use of a minimum excess of ferrous sulfate increases the flexibility of the method as regards the range of sample sizes and chlorate concentrations that

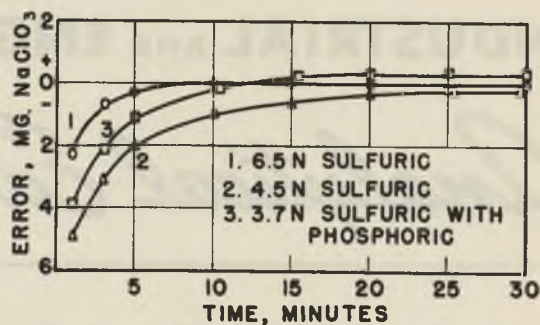


Figure 2. Time Required for Quantitative Recovery of Chlorate

can be analyzed. In the following tests only 0.5-milliequivalent excess of ferrous sulfate was used. In these tests the time required to effect quantitative recovery of chlorate at fixed acid concentrations was determined.

To 25 ml. of 100-gram-per-liter sodium hydroxide were added 5 ml. of a solution containing 6.2 mg. of sodium chlorate. There were then added 50 ml. of 12 *N* sulfuric acid followed by 8.5 ml. of 0.1 *N* ferrous sulfate (in 4 *N* sulfuric acid). The sulfuric acid concentration at this point was 6.5 *N*. The excess ferrous sulfate was titrated after a measured time with potassium dichromate. Reduction was complete after 10 minutes (Figure 2, curve 1).

This experiment was repeated using 50-ml. portions of the 100-gram-per-liter sodium hydroxide; the sulfuric acid concentration was 4.5 *N*. The maximum recovery was obtained after 25 minutes (Figure 2, curve 2).

In the above experiments, the phosphoric acid, which is required for the titration of ferrous ion with dichromate when using diphenylamine sulfonic acid as indicator, was added just before making the titration. It was thought that the addition of phosphoric acid prior to reduction might increase the rate of reaction. This possibility was tested by repeating the previous test, except that the sample was acidified with 25 ml. of 1 to 1 phosphoric acid, after which the ferrous sulfate and sulfuric acid were added in that order and in the same amounts as before. Since the total volume was 25 ml. greater than in the preceding test and the amount of excess sulfuric acid the same, the sulfuric acid concentration was only 3.7 *N*. Equilibrium was established after 20 minutes (Figure 2, curve 3).

From the above it is seen that chlorate is quantitatively reduced in 5 minutes in 4.5 *N* sulfuric acid by using 2.2-milliequivalent excess of ferrous sulfate. Reducing the excess ferrous sulfate to 0.5 milliequivalent increases to 25 minutes the time required to complete the reaction. The reaction can be completed at the lower excess of ferrous sulfate in 10 minutes by increasing the acid concentration to 6.5 *N*. Phosphoric acid increases the reaction rate slightly for given amounts of sulfuric acid and excess ferrous sulfate in spite of the dilution of the solution with the phosphoric acid.

From Figure 2 it is seen that there is a tendency to obtain somewhat higher recoveries when the sulfuric acid is added after the addition of ferrous sulfate. While the variations are only slightly outside the precision of the method as given in Table II, a similar tendency was observed in other experiments in which the time of reduction and sulfuric acid concentration were controlled to give quantitative recovery, and the amount of chlorate was varied. The difference may be due, at least in part, to the loss of some chlorate by decomposition when the sulfuric acid is added prior to the addition of ferrous sulfate.

Similar, although less detailed, studies were made on cell liquor. The minimum sulfuric acid concentration required to effect quantitative reduction of chlorate in cell liquor was determined in the same manner as for sodium hydroxide. A minimum

Table I. Range and Accuracy

Taken	Found Milligrams of NaClO_2	Error
0.00	0.00	0.00
1.25	1.30	+0.05
2.00	2.02	+0.02
2.50	2.52	+0.02
3.00	3.04	+0.04
3.75	3.79	+0.04
12.50	12.46	-0.04

Table II. Precision under Best Conditions

Test No.	NaClO_2 Found, %	Deviation, %
1	0.067	0.000
2	0.066	-0.001
3	0.066	-0.001
4	0.067	0.000
5	0.067	0.000
6	0.068	+0.001
7	0.066	-0.001
8	0.067	0.000
9	0.067	0.000
10	0.066	-0.001

Av.

0.067

Standard deviation of group
Standard deviation of infinite group
 LU_1 of method

± 0.00071
 ± 0.00076
 ± 0.0028

sulfuric acid concentration of 3.5 *N* was required for quantitative reduction in 5 minutes when using 2.2-milliequivalent excess of ferrous sulfate (Figure 1, curve 2). Thus, the presence of the chloride ion reduces somewhat the acid concentration required to give a fixed rate of reduction. It was found that 2.2-milliequivalent excess of ferrous sulfate gave quantitative reduction in less than 1 minute if the sulfuric acid concentration was increased to 6.3 *N*. Reduction required 5 minutes for completion at this higher acid concentration when the excess of ferrous sulfate was reduced to 0.7 milliequivalent.

In practice the phosphoric acid, ferrous sulfate, and sulfuric

acid are added in rapid succession in that order. This sample is allowed to stand while these reagents are added to all of a series of 20 to 30 samples before titrating the excess ferrous sulfate.

The range and accuracy of the method were determined as follows:

To 25-ml. portions of 100-gram-per-liter sodium hydroxide were added measured volumes of sodium chlorate solution. There were then added 25 ml. of 1 to 1 phosphoric acid, 25 ml. of 0.1 *N* ferrous sulfate, and 50 ml. of 12 *N* sulfuric acid in that order. The excess ferrous sulfate was titrated after 10 minutes or longer. The maximum error observed in the range up to 12.50 mg. of sodium chlorate is 0.05 mg. (Table I). When calculated on the basis of a 5-gram sample of 50% sodium hydroxide this is equivalent to a range of 0.25% and a maximum error of 0.001%. This error is well within the precision of the method as given in Table II and indicates that the method is free from constant errors.

The precision of the recommended method was determined by making replicate analyses of a sample of commercial 50% caustic soda according to the procedure outlined by Moran (2). The limit of uncertainty under the best conditions (LU_1) was $\pm 0.0023\%$ for a sample analyzing 0.067% (Table II). The limit of uncertainty under routine conditions was calculated from 24 analyses made by seven analysts over a 12-month period. The average value and precision under these conditions were $0.067 \pm 0.0046\%$.

ACKNOWLEDGMENT

The assistance of C. C. Meeker and G. F. Foy in performing most of the experimental work and of R. F. Moran and members of the Control Laboratory staff in supplying part of the precision data is gratefully acknowledged.

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- (2) Moran, R. F., *Ibid.*, 15, 361-4 (1943).

An Iodometric Method

DWIGHT WILLIAMS AND C. C. MEEKER

Commercial rayon-grade 50% caustic soda, which contains only a few parts per million of chlorate, is analyzed by boiling the acidified sample in the presence of the iodide ion, collecting the distilled iodine in a dilute solution of potassium iodide, and titrating with sodium thiosulfate solution. The error due to the oxidation of the iodide ion by air on boiling the acidified solution is reduced to a minimum by keeping the concentration of both the iodide ion and the hydrogen ion at a minimum. The interference of iron is stoichiometric, permitting a correction for this impurity. A constant correction is applied for manganese. The recommended method is subject to a constant error of -4% of the amount of chlorate present, necessitating the use of an empirical factor. The limit of uncertainty of the method under the best conditions (LU_1) is ± 0.46 p.p.m. of sodium chlorate for a sample analyzing 7.60 p.p.m.

A LOW concentration of sodium chlorate is desired in caustic soda which is to be used in the manufacture of rayon. Reduction with ferrous sulfate as described in the preceding paper (1) is not sufficiently sensitive for this application. After consideration of other methods it was decided to investigate an iodometric procedure. The reaction between hydrochloric acid and chloric acid was tested first but was found to be too slow. The reaction between hydrobromic acid and chloric acid was little better, but that between hydriodic acid and chloric acid at the boiling point proved to be sufficiently rapid.

The oxidation of hydriodic acid by the air proved to be a serious source of error, which was not eliminated by sweeping the air out with an inert gas. However, it was reduced to a minimum by reducing the concentrations of the hydrogen and iodide ions to a minimum. The conditions which were chosen for the analysis were those giving the best precision, but they resulted in a constant error of -4% of the amount of chlorate present. This constant error can be eliminated by increasing the concentration of the iodide ion but this also results in larger blanks and poorer precision.

Sodium hydroxide readily dissolves many compounds which reduce chlorate and prevent its quantitative recovery. Contact with rubber stoppers was found to be an especially serious source of error. Storage of samples in bottles closed with screw caps with which the sodium hydroxide does not react is recommended.

REAGENTS

Potassium iodide, 50 grams per liter. Dissolve 50 grams of of U.S.P. or c.p. potassium iodide in sufficient water to make 1 liter of solution. If a yellow color develops, add 0.01 *N* sodium thiosulfate solution dropwise until colorless.

Starch solution, 10 grams per liter. Store in sterile bottles or prepare fresh daily.

Hydrochloric acid, c.p., specific gravity 1.19.

Sodium thiosulfate, 0.01 *N*, containing 0.4 gram per liter of sodium carbonate.

Lubricant. All ground-glass joints and stopcocks are lubri-

cated with pure white Vaseline, Dow-Corning stopcock grease, or other lubricant which has been shown to cause no error in the analysis.

PROCEDURE

Samples of caustic soda which are to be used for this analysis must not be collected or stored in rubber-stoppered bottles. Harshaw Scientific, Cincinnati, Ohio, No-Sol-Vit screw-capped bottles are satisfactory for storage of samples.

Set up the apparatus shown in Figure 1. Weigh 25 ± 0.3 grams of 50% caustic soda into the reaction flask. Add 1 ml. of 50-gram-per-liter potassium iodide solution, 50 ml. of water, and one or two glass beads to prevent bumping. Connect the reaction flask to the dropping funnel. Introduce 50 ml. of 50-gram-per-liter potassium iodide solution and 5 ml. of starch solution into the receiver. Support the receiver on a wooden block so as to make a liquid seal at the outlet of the condenser. Introduce 32 ml. (5-ml. excess) of hydrochloric acid, specific gravity 1.19, into the separatory funnel. Open the stopcock to allow the acid to run into the reaction flask. Close the stopcock and light the burner. Adjust the flame so that the solution boils vigorously. Titrate the iodine as it is liberated with 0.01 *N* sodium thiosulfate solution. Continue boiling until no more iodine is liberated during a 2-minute interval. The total boiling time will be about 5 minutes if boiling is vigorous.

Prepare a reagent blank by introducing 100 ml. of water, 1 ml. of potassium iodide solution, and one or two glass beads into the reactor. Acidify with 5 ml. of hydrochloric acid and distill into a mixture of 50 ml. of potassium iodide solution and 5 ml. of starch solution. The iodine distills more slowly in this case and the distillation should be continued until half of the water distills over.

After each analysis rinse the reactor with water, wipe the ground-glass surfaces clean, and apply fresh lubricant.

$$\frac{(\text{Ml. of Na}_2\text{S}_2\text{O}_3 \text{ sample} - \text{ml. of Na}_2\text{S}_2\text{O}_3 \text{ blank}) N \text{ Na}_2\text{S}_2\text{O}_3 \times 17,700 \times 1.04}{\text{grams of sample}} = \text{apparent p.p.m. of NaClO}_2$$

Corrections must be applied for iron and manganese. A constant correction of 0.2 p.p.m. is applied for manganese. The iron content is determined colorimetrically by the *o*-phenanthroline method.

$$\text{Apparent p.p.m. of NaClO}_2 - (0.318 \times \text{p.p.m. of Fe} + 0.2) = \text{p.p.m. of NaClO}_2$$

Table I. Effect of Concentration of Potassium Iodide, Hydrochloric Acid, and Gas Sweep on Blank

Gas Sweep	KI Grams	HCl Milliequivalents	NaClO ₂ Found Micrograms
Yes	0.25	12	10
Yes	0.25	60	10
Yes	0.25	240	80
Yes	0.25	480	200
Yes	0.25	300	70
Yes	1.25	300	240
Yes	2.5	300	570
Yes	5.0	300	500
No	0.02	60	0
No	0.05	60	0
No	0.10	60	10
No	0.25	60	20
No	0.40	60	40

EXPERIMENTAL

In the initial experiments large excesses of hydrochloric acid and potassium iodide were used. High and erratic blanks were obtained under these conditions, owing to the reaction of the acidified iodide solution with the oxygen of the air. An attempt was made to exclude air by adding sodium carbonate to the sample prior to acidification. When sodium carbonate was added in sufficient quantities so that the resulting carbon dioxide swept all the air from the flask, recoveries of sodium chlorate were low, apparently because iodine was swept through the system by the carbon dioxide without coming in contact with the potassium iodide solution in the receiver.

Sweeping the reaction flask with natural gas prior to acidifying

with hydrochloric acid was tried unsuccessfully as a means of preventing oxidation by air. Consistently low blanks were finally obtained by reducing the excesses of potassium iodide and hydrochloric acid to minimum values, as was shown by the following experiments:

A measured volume of potassium iodide solution was introduced into the reaction flask and diluted to about 200 ml. Natural gas was then forced into the train through a tube which passed through a rubber stopper fitted to the top of the separatory funnel. The gas bubbled through the solution in the reactor and escaped by bubbling through the water seal in the receiver (Figure 1). Gas was passed through the system for 5 minutes at a rate of 300 ml. per minute. The total volume of gas was sufficient to displace all the air in the system ten to fifteen times. A measured volume of hydrochloric acid was then introduced through the separatory funnel and the analysis was completed as described above. In another series of tests the gas sweep was omitted.

The data in Table I show that high blanks are obtained regardless of the gas sweep if the concentration of the hydrogen or iodide ion is high. The blank may be reduced to a negligible value—the results are reported only to the nearest 10 micrograms—by keeping the concentrations of hydrogen and iodide ions low, even though the gas sweep is omitted. The use of 0.05 gram of potassium iodide (1 ml. of 50-gram-per-liter solution) and 60 milliequivalents of hydrochloric acid (5 ml., specific gravity 1.19) gave no detectable blank.

Any iron which is present in sodium hydroxide may be assumed to be present in the ferric state at the time of analysis, since ferrous iron is rapidly oxidized to ferric iron in this medium. The effect of ferric iron was determined as follows:

To 25-gram portions of 50% sodium hydroxide were added measured quantities of water solutions of c.p. sodium chlorate and c.p. ferric chloride. These mixtures were analyzed by the

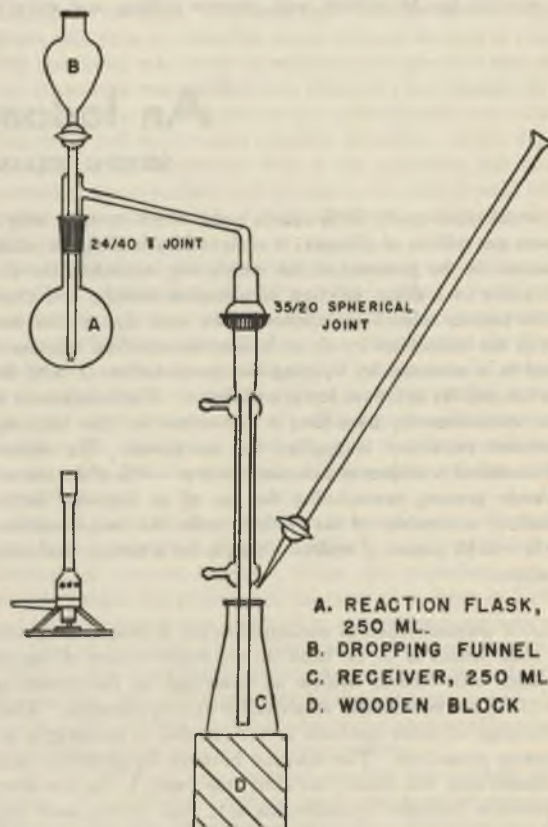


Figure 1. Diagram of Apparatus

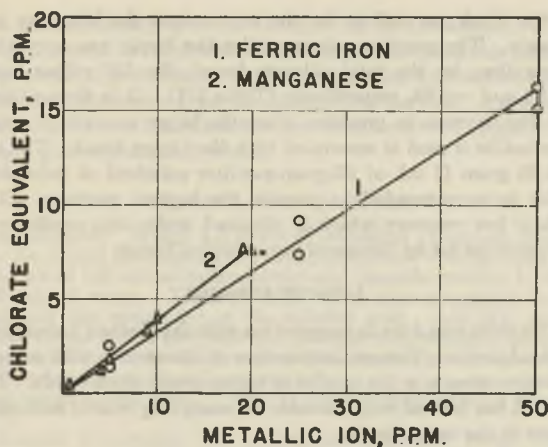


Figure 2. Effect of Manganese and Ferric Iron on Recovery of Chlorate

recommended procedure described previously. The apparent sodium chlorate content with no iron added was subtracted from that which was found when iron was added. The difference is the chlorate equivalent of the iron and was plotted against the amount of ferric iron added (Figure 2, curve 1). The slope of this curve is 0.328 p.p.m. of sodium chlorate per p.p.m. of iron. This agrees with the theoretical slope of 0.318 within the precision of the data.

The effect of manganese was determined in a similar manner. The observed slope is 0.390 while theory predicts a slope of 0.310 for a valence change from 3 to 2 (Figure 2, curve 2). Thus, the valence change for manganese appears to be slightly greater than from 3 to 2. Experience indicates that a constant correction of 0.2 p.p.m. of sodium chlorate can be applied for the manganese content of rayon-grade sodium hydroxide. Where the manganese content is unknown, it may be determined by the method of Williams and Andes (2).

Ammonia is known to react with free halogen under certain conditions. Because ammonia is likely to be present in caustic soda which has been purified by the liquid ammonia extraction process, the effect of this impurity was determined. No detectable error was observed in the recovery of chlorate when 0.04% of ammonia was present.

During the course of this work a number of observations indicated that some stopcock lubricants cause low recoveries of chlorates. To determine whether this apparent error was indeed real, the magnitude of the possible error was increased by adding a 2-gram portion of lubricant to the reaction mixture. Cello-grease, the laboratory lubricant in use at the time, caused negative errors of 10 to 20 p.p.m. Petrolatum, commonly sold under the trade-name Vaseline, caused no significant error. Another similar product, Parma, manufactured by Standard Oil Company of N. J., was found to cause no significant error. Dow-Corning stopcock grease is also without action. Another lubricant which was found to be without action was a paste made by mixing phosphorus pentoxide with phosphoric acid. Any of these lubricants is satisfactory.

It is common practice to take samples of commercial 50% caustic soda in rubber-stoppered bottles. Experimentation showed that added chlorate could not be recovered quantitatively from sodium hydroxide which had been stored in contact with rubber.

To determine the magnitude of this error, a new, size 4, gray rubber stopper was immersed in several successive 100-ml. portions of 50% sodium hydroxide at the boiling point for 1-minute intervals. The bloom was removed from the surface of the stopper by the first portion of sodium hydroxide. No chlorate was recovered from the first portion when 32 p.p.m. were added and errors of -5 and -6 p.p.m. were observed on the second and third portions, respectively. The same stopper was then immersed in a fourth portion of boiling sodium hydroxide for 5

minutes. The recovery of sodium chlorate was 23 p.p.m. low when 32 p.p.m. were added to this portion. Following this, the stopper was returned to the fourth portion of sodium hydroxide and allowed to stand for 16 hours at room temperature. No chlorate was recovered from this portion after this treatment. In another test a bottle of 50% sodium hydroxide was closed with a gray rubber stopper which had been treated with boiling 50% sodium hydroxide for 10 minutes, to remove the bloom. After shaking for 64 hours at room temperature to ensure contact between the sodium hydroxide and the stopper, the chlorate recovery was 6 p.p.m. low.

Red rubber stoppers and neoprene stoppers, neither of which are covered with bloom, were treated with boiling sodium hydroxide for 1-minute intervals. Recovery of chlorate added to these portions of sodium hydroxide was low by as much as 7 p.p.m. The polystyrene cap of a No-Sol-Vit bottle was treated with boiling sodium hydroxide for 5 minutes; the recovery of chlorate was 2 p.p.m. low. No error was observed in the recovery of chlorate from sodium hydroxide which had been agitated for 64 hours in a No-Sol-Vit bottle.

These data show that gray rubber stoppers must not come in contact with sodium hydroxide which is to be used for the determination of chlorates, even though the stoppers have been treated to remove bloom. Further, it appears desirable to avoid contact between the sodium hydroxide and any type of rubber stopper. The only part of a No-Sol-Vit bottle cap which comes in contact with the sodium hydroxide is the wax liner and the above data show that this liner has no significant reducing action under the conditions of this analysis.

The accuracy of the method was determined using 0.05 and 0.25 gram of potassium iodide. The recovery at each potassium iodide level was calculated by subtracting the apparent sodium chlorate content of the sodium hydroxide, with no sodium chlorate added, from the total sodium chlorate found. This sample blank was 2.8 p.p.m. for 0.05 gram of potassium iodide and 3.4 p.p.m. for 0.25 gram of potassium iodide. The recovery averaged 96% of the amount taken at the lower potassium iodide level. Accurate results may be obtained at this potassium iodide level by multiplying by the empirical factor, 1.04. Results at the higher potassium iodide level are within the precision of the method (Tables II and III).

Table II. Range and Accuracy of Method

KI Gram	NaClO ₂ Added P.p.m.	NaClO ₂ Recovered P.p.m.	NaClO ₂ Error P.p.m.	Recovery %
0.05	5.0	4.9	-0.1	98
0.05	10.0	9.6	-0.4	96
0.05	20.0	18.4	-1.6	92
0.05	40.0	38.4	-1.6	96
0.05	60.0	57.9	-2.1	97
0.25	1.0	1.0	0.0	100
0.25	2.0	2.3	+0.3	115
0.25	4.0	4.2	+0.2	105
0.25	8.0	7.7	-0.3	96
0.25	16.0	16.0	0.0	100
0.25	32.0	32.7	+0.7	102
0.25	64.0	63.8	-0.2	100

Table III. Precision of Method

No.	0.05 Gram of KI, Total found ^a	0.25 Gram of KI		
		Total found	Reagent blank	Net found
		Parts per Million		
1	7.5	9.0	0.9	8.1
2	7.8	9.4	1.6	7.8
3	7.8	9.3	2.1	7.2
4	8.0	9.2	1.6	7.6
5	8.0	9.0	2.0	7.0
6	8.1	9.5	1.8	7.7
7	8.0	9.5	1.3	8.2
8	7.8	9.5	0.9	8.6
9	7.9	8.7	1.3	7.4
10	8.0	8.7	1.7	7.0
Av.	7.90	9.18	1.52	7.66
Standard deviation of group	±0.14	±0.30	±0.40	±0.51
LU of method	±0.46	±0.98	±1.28	±1.64

^a Reagent blank 0.0 p.p.m.

The precision of the method was determined by making 10 analyses at each potassium iodide level. No correction was made for the iron on manganese contents of the sodium hydroxide which was used for the determination of the precision. Thus, the results represent the precision of the determination of the total oxidizing power of the sodium hydroxide, calculated as sodium chlorate. The reagent blank was equivalent to 0.0 p.p.m. of sodium chlorate at the lower potassium iodide level. Thus, the total chlorate found at this level is also the net chlorate found. The limit of uncertainty (*LU*) was ± 0.46 p.p.m. and the average analysis, after multiplying by the empirical factor 1.04, was 7.90 p.p.m. Since a substantial blank titration was expected at the higher potassium iodide level, a blank was run on the reagents after completing each analysis and the net chlorate was calculated by subtracting the corresponding blank from the sample titration. The limit of uncertainty obtained in this manner was ± 1.64 p.p.m. and the average analysis 7.66 p.p.m. This average analysis, while slightly lower than that which was obtained when using only 0.05 gram of potassium iodide, agrees with the latter within the precision of the method. The precision at this potassium iodide level was calculated for the total chlorate and

for the blank, as well as for the total minus the blank, or net chlorate. The precision observed for the blank was somewhat poorer than for the total chlorate found, the *LU* values being ± 1.28 and ± 0.98 , respectively (Table III). It is thus evident that the decrease in precision when the larger amount of potassium iodide is used is associated with the higher blank. The use of 0.05 gram (1 ml. of 50-gram-per-liter solution) of potassium iodide is recommended to provide the highest precision. The slightly low recovery which is obtained under this condition is compensated for by the use of the empirical factor.

ACKNOWLEDGMENT

This work was done in cooperation with the Control Laboratory of the American Viscose Corporation in connection with a study of improvements in the quality of rayon-grade caustic soda. The method has proved very valuable for analyzing caustic soda shipments to the rayon trade.

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A Colorimetric Method

DWIGHT WILLIAMS AND GEORGE S. HAINES

The use of *o*-tolidine, the conventional reagent for determining free chlorine, has been applied to the determination of small amounts of chlorates in caustic soda. A stable yellow color is formed in a strongly acid solution, permitting the colorimetric determination of as much as 300 micrograms of sodium chlorate in a 10-gram sample of 50% sodium hydroxide. A single determination requires about 15 minutes, but ten determinations can be made in 80 minutes or less. The limit of uncertainty under the best conditions (*LU*) was found to be ± 0.20 p.p.m. in a sample containing 5.00 p.p.m. of sodium chlorate. Iron and manganese cause positive errors proportional to their concentration, permitting corrections for these impurities.

THE iodometric determination of low concentrations of chlorate in high-purity, rayon-grade caustic soda as described in the preceding paper (16) is only one of a number of reactions which might be utilized for carrying out this analysis. The well-known advantages of colorimetric methods for determining small amounts of impurities indicated the desirability of investigating this type of procedure. One possible colorimetric method involves an adaptation of the ferrous sulfate reduction procedure which was described in the first paper of this series (14). Either the amount of ferric ion formed by reaction with chlorate, or the excess ferrous ion could be measured. The latter procedure was investigated briefly, using the *o*-phenanthroline method for estimation of the excess ferrous ion. Quantitative reduction of chlorates with an amount of iron which could be estimated colorimetrically was obtained at room temperature in 6 *N* hydrochloric acid. However, since this is a "by-difference" method and the solution must be buffered prior to development of the *o*-phenanthroline color, the procedure was abandoned in favor of a more direct procedure.

A brief survey of the literature indicated the paucity of colorimetric methods for the determination of small amounts of chlorate.

Snell (13) describes a method for chlorate based upon the yellow color produced by the action of chlorate on thiocyanate test papers, originally described by Offord (10). Although this method is indicated to be sensitive, the necessity of drying the test papers and the subjective nature of the measurements made it appear unpromising. Hunt (5, 6) reports that very small

amounts of chlorate may be detected by measuring the time required to decolorize a solution of indigo-carmin. The nature of the measurement in this test does not make it seem conducive to good precision. Mellor (9) describes colors obtained when chlorates react with brucine, resorcin (sic), and indigo.

Several colorimetric methods have been described which utilize the colors developed when chlorates react with amines. The colored compounds are oxidation products of amines and in general amines may be used as reagents for chlorates as well as for other oxidizing agents. Lesnicenko (7) reports that the reaction of chlorates with aniline may be made the basis of a sensitive method. The authors obtained a stable blue color with aniline in hydrochloric acid having a concentration of 4.5 *N* or greater. A spectrophotometric curve of the color showed absorption below 450 and above 650 millimicrons, but the method did not appear to be sufficiently sensitive for their application. Roy (11) utilized the color developed by the reaction of chlorates with pyridine in concentrated sulfuric acid. The necessity for developing the color in concentrated sulfuric acid made the method appear unpromising and experimentation showed that the color could not be developed in dilute sulfuric acid. Sa (12) reports that chlorate produces colors with phenyl- β -naphthylamine, di- β -naphthylamine, and phenyldihydrodibenzacridine which will distinguish it from nitrates and nitrites. While these reagents were not available in this laboratory at the time this work was done, they suggested that other amines be tried. Mellor (9) describes colors obtained when chlorates react with diphenylamine and a mixture of aniline and *o*-tolidine.

A solution of *m*-phenylenediamine in 6 *N* hydrochloric acid was found to give a faint pink color with 2 micrograms of sodium chlorate per milliliter. A similar solution of benzidine gave a faint yellow color with as little as 0.2 microgram of sodium chlorate per milliliter. It is possible that either of these reagents might be made the basis of a colorimetric method.

o-Tolidine, although widely used for the determination of free chlorine, has apparently never been applied to the quantitative determination of chlorate. Ellms and Hauser (1, 2) report that this reagent is sensitive to 0.005 p.p.m. of free chlorine, that it will react with oxidizing agents in general, and that chloride ion does not interfere. These observations made it appear very attractive for the authors' application, and experimentation indicated that it was probably the most sensitive of the reagents which were tested. The effect of the hydrochloric acid concentration on the rate of color development and on the stability of the color has been determined. Ellms and Hauser (1, 2) and Forsberg (3) report that iron interferes with the determination of oxidizing agents using *o*-tolidine. Hopkins (4) found that manganese interferes and Mellan (8) reported that copper reacts with *o*-tolidine. The interference of iron and manganese was found to be proportional to the amount present and copper did not interfere under the authors' conditions.

A limited amount of work was done on the development of the *o*-tolidine color in sulfuric acid solution and the use of this medium appears to offer a number of advantages over hydrochloric acid. However, the study of the development of the color in a sulfuric acid solution was abandoned before conditions were found which would give reproducible results.

REAGENTS AND APPARATUS

***o*-TOLIDINE.** Weigh 1.0 gram of *o*-tolidine (Eastman Kodak Co. No. P249) into a small mortar and triturate with portions of a solution of 100 ml. of hydrochloric acid (specific gravity 1.19) in 400 ml. of water. Transfer to a 1-liter glass-stoppered bottle and add the remainder of the diluted acid. Add 500 ml. of water to the bottle and heat the solution with swirling until the reagent is dissolved. This reagent is conveniently dispensed with an open-end 2-ml. short-form pipet.

HYDROCHLORIC ACID. Use c.p. concentrated (specific gravity 1.19).

SODIUM CHLORATE, 100 micrograms per ml. Weigh 0.100 gram of c.p. sodium chlorate into a 1-liter volumetric flask, add water to dissolve, dilute to mark, and mix well. Transfer to a glass-stoppered bottle.

SODIUM HYDROXIDE, 50%. To 750 ml. of water add 750 grams of c.p. sodium hydroxide pellets with stirring to dissolve. Allow the precipitate to settle and filter through a fine or medium porosity fritted-glass Büchner funnel. Store in an appropriate reagent bottle, avoiding contact of caustic with rubber stoppers or any other organic material.

PIPET, 6.5-ml. The 10-gram portions of 50% caustic soda can be measured conveniently by means of open-end 6.5-ml. pipets. These can be readily made by sealing a 16-cm. length of 6-mm. outside diameter Pyrex tubing to each end of a 5-cm. section of 12-mm. outside diameter tubing. Taper one end slightly to form the tip. Calibrate the pipet by clamping it vertically with its tip firmly against a rubber stopper. Introduce 6.5 ml. of water into the top of the pipet from a 10-ml. buret.

Make a temporary mark at the water level on the stem of the pipet and repeat to check the graduation. Make a permanent mark around the stem with a file. The pipet is now graduated to contain 6.5 ml. or about 10 grams of 50% sodium hydroxide.

PROCEDURE

The sample taken for chlorate analysis must be protected from contact with rubber stoppers and any other organic matter, unless it is known to have no deleterious effect upon the determination. The screw caps with wax liners used on No-Sol-Vit reagent bottles (No. H-5-925, Harshaw Scientific Cincinnati, Ohio) fulfill this specification.

Take a 6.5-ml. portion of the sample, equal to 10 grams, wipe off the outside of the pipet, adjust to mark, and transfer to a 250-ml. wide-mouthed flask. Blow out the tip of the pipet into the flask and rinse the pipet twice with water by filling approximately to the mark and draining into the flask.

To the diluted sample having a volume of about 20 ml., add 2 ml. of *o*-tolidine reagent. A white precipitate will form, but will dissolve upon neutralization. Swirl the sample to mix and place in a bath at 20° to 25° C. Neutralize by the dropwise addition of concentrated hydrochloric acid from a 50-ml. buret. The buret stopcock should be lubricated with petrolatum, which has been shown to have no reducing effect upon the chlorate. Considerable heat will be evolved during addition of the first 10 ml. of acid, which should be done with vigorous swirling over a period of 2 to 3 minutes with the flask immersed in the water bath maintained at 20° to 25° C. After dropwise addition of the first 10 ml. of acid, add more rapidly from the buret with swirling until a total of 40 ml. has been added. Allow the sample to stand from 8 to 10 minutes and then dilute to 100 ml. in a graduate, mixing well to dissolve any precipitated salt. Transfer the sample to an optical cell. Measure the yellow color within 10 minutes after dilution in a photoelectric colorimeter, using distilled water as the reference standard, and a Wratten C5-47 filter. Read the sodium chlorate to the nearest microgram from a calibration curve.

If the sample is known to contain more than 10 p.p.m. of sodium chlorate, dilute the 10-gram sample taken originally to 100 ml. and take for analysis a 10-ml. aliquot, equivalent to a 1-gram sample. To the aliquot add 2.0 ml. of *o*-tolidine and 20 ml. of water. Now add 30 ml. of hydrochloric acid rapidly with swirling in a bath at 20° to 25° C. Proceed as above, beginning with the 8- to 10-minute standing period.

If a large number of samples are to be analyzed, it is convenient to complete the analyses in groups of four or five. In this manner the samples can be acidified, allowed to stand, and diluted, and the color read without the last step interfering with the acidification of successive samples. For optimum speed in the analysis two burets should be available for acidification, as two samples can be conveniently acidified simultaneously.

To prepare the calibration curve, pipet 6.5 ml. of 50% c.p. sodium hydroxide into each of 8 flasks, rinsing the pipet by filling to the mark twice with water. To the flasks add 0, 5, 10, 25, 50, 75, 100, and 150 micrograms of sodium chlorate from the 100-microgram-per-ml. standard solution, using a 1.0-ml. Mohr pipet. Proceed as in the actual analysis, beginning with addition of *o*-tolidine. Plot micrograms of sodium chlorate against per cent transmittancy.

CALCULATION. The sodium chlorate concentration and correction for iron and manganese are calculated as follows:

$$\begin{aligned} &\text{Micrograms of NaClO}_3 \text{ from curve} \\ &\quad \text{grams of sample} \\ &(0.03 \times \text{p.p.m. of Fe} + \text{p.p.m. of Mn}) = \\ &\quad \text{p.p.m. of NaClO}_3 \end{aligned}$$

EXPERIMENTAL

The *o*-tolidine reagent was prepared according to Snell and Snell (13) to contain 1 gram of *o*-tolidine and 100 ml. of hydrochloric acid (specific gravity 1.19) in 1 liter of solution. Although the *o*-tolidine was triturated with some of the diluted acid, as recommended, it

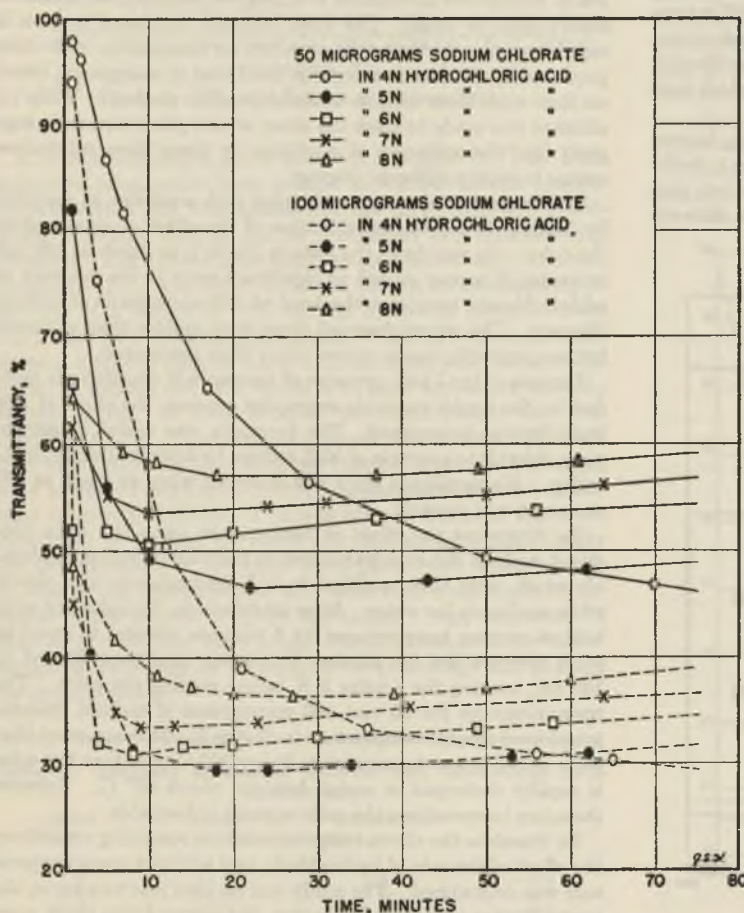


Figure 1. Development and Stability of Color

did not readily dissolve until the solution was heated with swirling. Preliminary experiments with this reagent indicated that a detectable color could be obtained with as little as 0.05 microgram per ml. of sodium chlorate in a strong hydrochloric acid solution. The yellow color produced indicated the use of a blue filter for photometric measurement of the color. Little difference was observed between Wratten filters H-45 and C5-47, but the latter was chosen because of the slightly greater absorption indicated. All colorimetric measurements were made on an Eimer & Amend colorimeter using 40-mm. square-type optical cells.

The effect of hydrochloric acid concentration upon the development and stability of the color produced with 50 and 100 micrograms of sodium chlorate was determined (Figure 1). Only a 1-gram sample of 50% sodium hydroxide was used in order to keep the resulting sodium chloride in solution at the high acid concentrations. As can be seen from Figure 1, both time and acidity were very critical. The color in 4 and 5 *N* hydrochloric acid shows the greatest development, but development of maximum color requires 20 minutes or longer. Color development was least with 8 *N* acid and was attained slowly. The color in 6 and 7 *N* acid developed rapidly and was intermediate between that developed in 5 and 8 *N*, respectively. For this reason the use of 6 *N* hydrochloric acid was adopted as providing a maximum, fairly stable color in 8 to 10 minutes. Because of the limited solubility of sodium chloride in concentrated hydrochloric acid, the 6 *N* solution is brought to a volume of 60 ml., allowed to stand for color development at this acidity, and then diluted to 100 ml. to dissolve the salt just before measuring the color. Because of the gradual decrease in color, as shown in Figure 1, the color should be measured promptly or at least after a fixed time lapse.

As in the case of the iodometric method described in the preceding paper (15), chlorate could not be recovered quantitatively from 50% sodium hydroxide which had been stored in rubber-stoppered bottles. No chlorate was recovered when 1500 micrograms of sodium chlorate were added to sodium hydroxide which had been boiled with a new gray rubber stopper. Quantitative recovery was obtained from 50% sodium hydroxide which had been stored in screw-capped No-Sol-Vit bottles.

The interference of iron was determined by adding known amounts of a standard iron solution, prepared from c.p. ferric chloride hexahydrate, to c.p. sodium hydroxide. The iron was observed to produce the same or a similar color as the chlorate

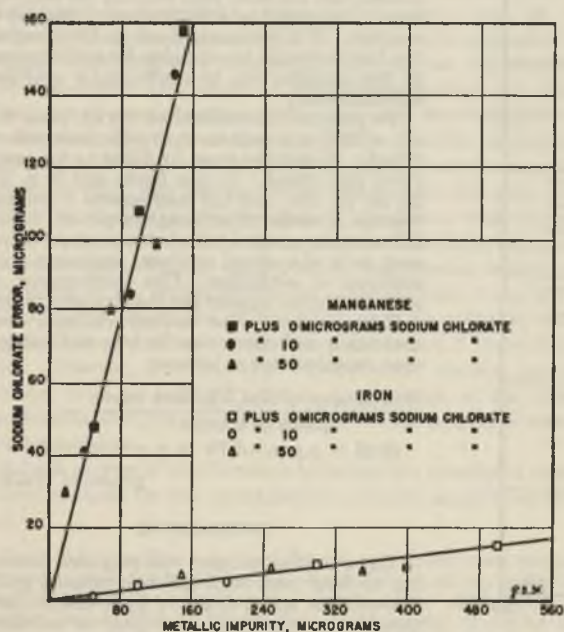


Figure 2. Interference of Iron and Manganese

Table I. Effect of Copper

Copper Added Micrograms	Sodium Chlorate		Error ^a
	Added	Found Micrograms	
0	0	2	..
10	0	1	-1
50	0	2	0
100	0	1	-1
0	10	10	..
10	10	12	+2
50	10	10	0
100	10	11	+1
0	100	105	..
10	100	108	+1
50	100	107	+2
100	100	110	+5

^a Error calculated as difference with and without copper present.

to the extent of about 0.030 microgram of sodium chlorate per microgram of iron (Figure 2).

Manganese of a valence greater than 2 is reported to interfere in the *o*-tolidine method for free chlorine by Hopkins (4), who found that manganous salts in acid solutions did not interfere. However, in alkaline solutions he found that the manganous hydroxide was converted to manganic by absorption of oxygen. Upon acidification, color was produced by reduction of the manganese by the *o*-tolidine. This was confirmed by adding known amounts of manganese to 50% sodium hydroxide before and after acidification and measuring the color produced with *o*-tolidine. No color was observed when manganese was added to the acidified solution. The addition of manganese to the caustic soda solution is shown in Figure 2 to cause an error equal to the manganese concentration. Although the interference of manganese appears erratic, errors in the correction for the 10 micrograms or less of manganese anticipated in a 10-gram sample of 50% caustic soda should be small. The color intensity produced by iron is only about one thirtieth that obtained for manganese, while that produced by chlorate is about one third that of manganese, based on their equivalent weights in the iodometric method. While no attempt was made to trace the cause of this phenomenon, it suggests that the oxidation of *o*-tolidine by these three substances occurs to widely different degrees.

The formation of a copper complex with *o*-tolidine as reported by Mellan (8) led to determination of the effect of copper upon the color. As seen from the data in Table I, as much as 100 micrograms of copper caused no significant error in the recovery of added chlorate except at the level of 100 micrograms of sodium chlorate. The errors observed there were greater than expected but are probably due to causes other than the copper.

Because of the likely presence of ammonia in caustic soda purified by the liquid ammonia extraction process, the effect of this impurity was determined. The ammonia was added as ammonium chloride to a sample of 50% sodium hydroxide after neutralization. No significant error was observed when as much as 1% ammonia was present.

To determine the effect of temperature upon the color produced, sodium chlorate was added to portions of sodium hydroxide which were then acidified to 6 *N* hydrochloric acid slowly while cooling in ice water. After acidification, the solutions were held at varying temperatures for 5 minutes, allowed to stand at room temperature for another 5 minutes, and then diluted to 100 ml., making the acidity 5 *N* before reading the color. The transmittancies for 50 and 100 micrograms of sodium chlorate are plotted against temperature in Figure 3. It is apparent that color development is incomplete below 20° C. and that the color is rapidly destroyed or never develops above 40° C. Between these two temperatures the color appears to be stable.

To translate the above temperatures into operating conditions, the effect of the rate of hydrochloric acid addition upon temperature was determined. The study was divided into two parts, the neutralization and the acidification, the former being much more exothermic than the latter. The 10 ml. of hydrochloric acid

(specific gravity 1.19) required for neutralizing a 10-gram sample of 50% caustic soda and the 30 ml. required to make the solution 6 N were added at varying rates while cooling by swirling the sample in a bath at 20° C. Temperature measurements indicated that the acid should be added slowly over a period of at least 2 minutes to maintain the temperature below 40° C. when starting with a sample at 20° C. The subsequent acidification of the solution may be made rapidly, as very little heat is developed if the solution is thoroughly swirled during the addition.

In Table II is shown the recovery of sodium chlorate added to a sample of commercial 50% caustic soda by the above procedure. The recovery appears to be very satisfactory.

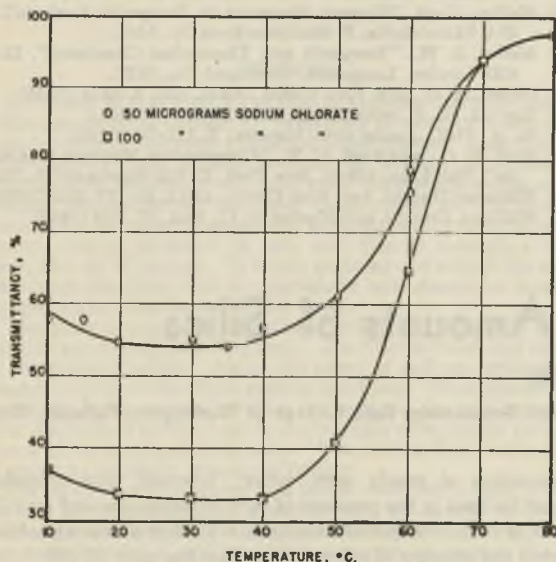


Figure 3. Effect of Temperature upon Color

A typical calibration curve is shown in Figure 4. Very little change in color results from changes in sodium chlorate concentration around 300 micrograms and not more than 200 micrograms of sodium chlorate can be determined with a satisfactory precision. The limit of uncertainty of the method under the best conditions (LU_1) was found to be ± 0.198 p.p.m. by analyzing 10 portions of a sample of 50% sodium hydroxide prepared from c.p. pellets and containing 5.00 p.p.m. of added sodium chlorate. As seen from the data in Table III, the mean analysis was 5.03 p.p.m. of sodium chlorate, which is in good agreement with the amount added. In these analyses the transmittancy was estimated to 0.01%. The sodium chlorate values were then read from a section of the curve shown in Figure 4 drawn to an enlarged scale to permit reading to 0.01% transmittancy and 0.1 microgram of sodium chlorate. This was done to minimize the errors introduced by reading the curve and thus measure more closely the true precision of the color development and measurement. In routine use, a compromise with these conditions might be desirable in the interest of speed and facility. Approximately 15 minutes are required for a single determination, but ten determinations were made in 70 minutes for an average of 7 minutes per determination.

Table II. Recovery of Sodium Chlorate from Commercial 50% Caustic Soda

Added	Found	Recovered	Error
		Parts per million	
0.0	1.2	0.7	-0.3
1.0	1.9	0.7	-0.3
5.0	6.2	5.0	0.0
10.0	11.1	9.9	-0.1

Table III. Precision of Method under Best Conditions, (LU_1)

Portion	Sodium Chlorate Found P.p.m.	Deviation P.p.m.
1	5.13	+0.10
2	4.99	-0.04
3	5.03	0.00
4	4.98	-0.05
5	5.09	+0.06
6	5.02	-0.01
7	4.98	-0.05
8	5.10	+0.07
9	5.03	0.00
10	4.92	-0.11
Av.		5.03
Standard deviation of group		± 0.081
Standard deviation of infinite group		± 0.066
LU_1 of method		± 0.198

The statement of Ellms and Hauser (2) that the interference of iron with the o-tolidine method for free chlorine was only one third or one fourth as great for the sulfate as for the chloride led to the investigation of sulfuric acid for neutralizing the caustic and developing the color. The effect of iron was found to be more erratic in sulfuric acid than in hydrochloric acid but it was only about one fifth as great, or about 0.006 microgram of sodium chlorate per microgram of iron. The interference of manganese was also less in sulfuric acid, averaging about 0.4 microgram of sodium chlorate per microgram of manganese. The stability of the color produced in sulfuric acid was determined by measuring the colors at intervals after standing in the laboratory light at room temperature. The color is stable for at least 24 hours and shows an appreciable fading only after 120 hours. The color intensity in sulfuric acid was about twice as great as in hydrochloric acid, permitting greater sensitivity of detection, but also limiting the maximum concentration which could be satisfactorily measured to about 1 microgram of sodium chlorate per ml. of solution. However, the sample size can be varied from 0 to at least 20 grams of 50% caustic soda without altering the recovery of the sodium chlorate. The greater solubility of sodium sulfate in sulfuric acid does not limit the sample size as does the use of hydrochloric acid.

Although the substitution of sulfuric for hydrochloric offers numerous advantages, it also involves several difficulties. At-

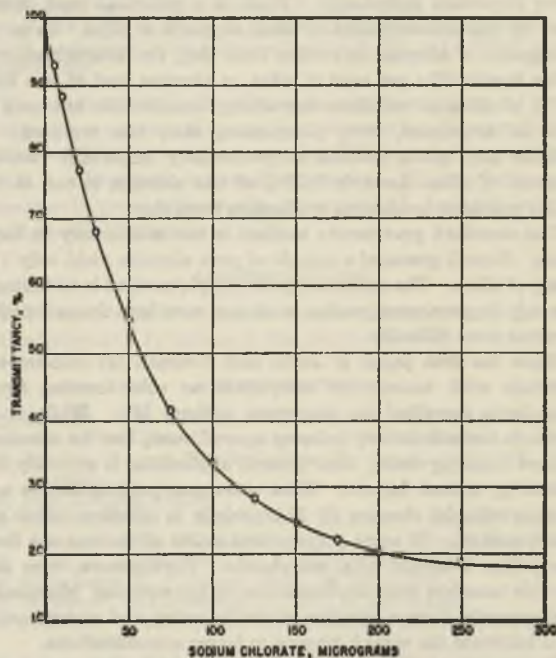


Figure 4. Typical Calibration Curve

tempts to develop the color in 6 *N* sulfuric acid, on the basis of experience with hydrochloric acid, were unsuccessful. Instead, it was found necessary to increase the concentration to 13 or 14 *N* to obtain maximum color. This high acid concentration necessitates the use of relatively concentrated sulfuric acid for the neutralization and acidification, resulting in the evolution of considerable heat. Limited data on the effect of temperature upon the color in sulfuric acid indicated that a temperature of about 75° C. was necessary to develop the color, and temperatures above 120° C. destroyed the color. The complete disappearance of the color in a hydrochloric acid solution at 75° C. indicates a much greater thermal stability of the color in sulfuric acid. The precision of the procedure using sulfuric acid was determined by analyzing 10 portions of a sample of commercial 50% caustic soda. No attempt was made to measure or control the temperature other than the approximate control of the rate of acidification. A limit of uncertainty of ± 1.05 p.p.m. in a sample analyzing 2.7 p.p.m. was found. This poor precision is probably associated with lack of temperature control. However, this factor was not investigated further and the use of sulfuric acid was abandoned in favor of hydrochloric acid, which had been studied more intensively.

ACKNOWLEDGMENT

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Determination of Small Amounts of Silica

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The need for a generally applicable colorimetric method for determining small amounts of silica is discussed. In a method which is to supplement the standard procedure all interfering substances should be removed and the silica brought into a reproducible molecular state. A method which satisfies these requirements is described. The yellow molybdisilicic complex is used.

SILICA is an important constituent and frequently a serious impurity in many materials which have become more and more important technically. There is a practical need, therefore, for the determination of small amounts of silica. In an investigation of alumina extraction from clay, the determination of a few hundredths per cent of silica in alumina and of less than 0.1% of silica in solutions containing considerable amounts of salts of aluminum, iron, phosphates, etc., was required. A reliable and quick method is particularly important because removal of silica down to 0.03% of the alumina is one of the major problems in alumina production from clay.

The standard gravimetric method is not satisfactory in these cases. Even 5 grams of a sample of pure alumina yield only 1 or 2 mg. of silica. The emission spectroscopic method is advantageous only in permanent routine work and even here the calibration presents some difficulty.

Since the first paper of Jolles and Neurath (5) colorimetric methods with ammonium molybdate as color-forming agent have been described by numerous authors (9). While these methods are satisfactory in many special cases, like the examination of drinking water, their general application is seriously impaired by several factors. Silica undergoes polymerization and various colloidal changes (6, 7) especially in solutions which are about neutral. In some polymerized states silica does not form the yellow complex with molybdate. Furthermore, iron and fluoride interfere with the formation of the complex, phosphates and arsenates form a complex of similar color, and many neutral salts influence the color if present in larger concentrations.

The method of Dienert and Wandenbulcke (8) apparently eliminates the influence of the previous history of the silica in the

examination of nearly pure water; however, this procedure cannot be used in the presence of salts of aluminum and iron (9). It would require a special examination for any accessory solutes, as even the presence of chlorides modifies the color (8, 10).

It was thought that a treatment in acidic or alkaline solution might produce a definite molecular state of the silica. Numerous tests were carried out in sulfuric acid solutions of various concentrations and in alkaline solutions. Boiling with acids of moderate concentrations or alkali has an appreciable depolymerization effect, but the results were not so well reproducible that a reliable method could be based on a treatment of silica in solution.

A radical deviation from previous methods appeared still more desirable because iron and phosphates interfere with the colorimetric determination even if any polymerization error is avoided. The numerous methods suggested in the literature would require special investigations for every kind of sample substance; hardly any could be relied upon in the presence of large amounts of aluminum and iron.

It was concluded that a generally applicable method has to eliminate completely all accessory constituents without loss of silica, and erase the influence of the previous colloidal history.

The first step can be achieved only in acidic solution, because otherwise losses of silica cannot be safely prevented. Evaporation with perchloric acid is the most convenient way of separation. It can be carried out quickly because only small samples are required in the colorimetric method. The use of perchloric acid, however, has been found objectionable if large amounts of salts are present in the dehydration of small amounts of silica. In these cases losses of silica due to solubility in perchloric acid are not negligible and the dehydration, therefore, is to be carried out with sulfuric acid.

Fusion of the dehydrated silica with sodium carbonate presents the simplest method not only for dissolution, but also for ensuring a definite and suitable molecular state of the silica.

While this method was developed with special regard to alumina and alumina-containing solutions, its applicability extends to numerous other cases—e.g., the analysis of magnesium alloys.

Table I. Test Analyses

Sample	Silica, Gravimetric G./l.	Silica, Colorimetric G./l.
A	1.054	1.07
B	1.054	1.02
C	1.054	1.03
	%	%
D	1.25	1.25
E	1.25	1.26
F	—	0.029
G	—	0.032
H	—	0.031
I	—	0.033
K	—	0.033
L	—	0.034

PROCEDURE

Perchloric acid is used if the sample contains not more than 10 milliequivalents of cations per milligram of silica or if the whole sample contains not more than 5 milliequivalents. A sample containing about 1 mg. of silica is dissolved, digested in a platinum crucible with perchloric acid (not more than 100% excess of the amount equivalent to the basic constituents of the sample), evaporated to fumes of perchloric acid, digested 5 more minutes, cooled, diluted to about 10 ml., and filtered through a 5-cm. filter, No. 40 Whatman. It is not necessary to collect the entire residue on the filter, but the perchloric acid should be removed completely by washing with cold water.

The filter is put back into the crucible and the walls of the crucible are wiped with the paper. The filter is dried and ignited in the tilted crucible. About 0.5 gram of sodium carbonate is placed directly on the slight residue and fused. Then the crucible is brought into a vertical position in the flame, the melt spreading over the bottom of the crucible and slightly creeping up the wall. The crucible is quenched in water. The melt is dissolved in 5 ml. of water by carefully heating to boiling.

The solution is transferred to a 50-ml. volumetric flask, a small amount of phenolphthalein is added, and the sample is titrated with approximately 10 N sulfuric acid from a microburet. About the same amount of acid is added once more to replace the carbonic acid of the bicarbonate. In addition, 0.5 ml. of the acid is added to make up for a final concentration of 0.1 equivalent per liter. After addition of 2 ml. of ammonium molybdate solution (10%), the sample solution is made up to 50 ml. Colorimetric readings are taken after 5 minutes. The color is constant for more than one hour.

Colorimetric comparison or calibration with a buffered solution of potassium chromate according to Swank and Mellon (10) has been found reliable and convenient. In the present method, however, the colorimetric sample solution is 0.1 N in acid—i.e., between the two concentrations 0.02 N and 0.4 N used in the procedures described by Swank and Mellon. The selection of an intermediate acid concentration is advisable because the higher concentration is close to the limit of a satisfactory color development, and because in the present method the acid concentration cannot be conveniently adjusted to the lower concentration with sufficient precision. It was to be expected that a concentration of potassium chromate between the two values 0.58 and 0.63 gram per liter of Swank and Mellon is to be used. The required concentration, 0.602 gram of potassium chromate per liter, was established by eight determinations on samples containing 0.2 to 1.1 mg. of silica. The maximum deviation from the average corresponded to 7 micrograms of silica. The standard silica solution was prepared from pure silica gel and standardized gravimetrically.

Following Swank and Mellon, the stock solution is diluted to the desired concentration, which should not exceed the equivalent of 40 mg. of silica per liter, and is conveniently kept between 5 and 20 mg. of silica per liter. The solution used for comparison should contain 0.5% $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

For samples containing less than 1 mg. of silica the volume of the sample solution prepared for colorimetric comparison can be reduced to 25 or 10 ml. without appreciable inconvenience. The amounts of sulfuric acid and molybdate are to be reduced in proportion.

A blank determination is required for the correction of the amounts of silica introduced in the procedure. If the tap water, as in this laboratory, contains considerable amounts of silica variable amounts may appear in the ordinary distilled water. The use of redistilled water is, therefore, advisable. In this case silica is introduced practically only by the filter paper.

The whole procedure requires about 0.5 hour for a single determination, and somewhat less for determinations in a series.

If the cation content appreciably exceeds 5 milliequivalents per sample and 10 milliequivalents per milligram of silica, perchloric acid should be replaced by sulfuric acid. Evaporation is continued almost to dryness, and the soluble salts are taken up in a 4% ammonium chloride solution (4). This procedure is not advisable in the presence of substances such as nickel and chromium which form difficultly soluble sulfates. In a case like this the size of the sample should be chosen so that not more than 5 milliequivalents of cations are present even though the precision of the determination is reduced. The evaporation should be carried out with perchloric acid.

Too high results were obtained on dehydration with perchloric acid in the presence of both titania and phosphate. The separation of titanium phosphate from silica tends to be incomplete. Phosphate in the final solution interferes seriously because it gives the same color as silica with molybdate. Good results were obtained in this case with a mixture of perchloric and sulfuric acids.

Caution is advised if lead is present and sulfuric acid is used. Lead sulfate should be filtered off before evaporation, since it otherwise stays with the silica. In the soda fusion it is reduced by the filter paper and ruins the platinum crucible. Even if this were prevented by means of an oxidant, the presence of lead sulfate in the colorimeter solution would interfere with color comparison. For the latter reason barium sulfate should also be removed.

Calcined alumina was fused with soda and boric oxide (1) and treated with sulfuric acid.

Aluminum metal is conveniently dissolved by sodium hydroxide in presence of hydrogen peroxide. As the A.C.S. specifications for sodium hydroxide allow as high as 0.01% silica, the reagent must be tested and an appropriate correction must be made. If the sample contains appreciable amounts of fluorine, the standard procedure (4) for elimination of fluorine as used in the gravimetric method is to be followed.

TESTS

A few of the test analyses are recorded in Table I.

The influence of substances likely to interfere was tested in samples A, B, and C, which contained 25 mg. of alumina, 2.5 mg. of ferric oxide, 5 mg. of phosphorus pentoxide, 0.5 mg. of titanium oxide, and 0.525 mg. of silica.

Samples D and E were basic aluminum sulfate.

Samples F, G, H, and I, K, L were taken from calcined alumina which, according to the label, contained 0.032 and 0.039% silica, respectively.

The results on the calibration of the potassium chromate in the section on procedure indicate that the method is reproducible within $\pm 1\%$ for a sample containing 0.5 mg. of silica or within about 5 micrograms for smaller samples. If interfering substances or large amounts of salts are present, the limits of error are about double this amount.

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Determination of Hydrogen, Carbon, and Nitrogen in Magnesium Alloys

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The analysis of magnesium alloys for extractible, gaseous, non-metallic impurities has been investigated by three methods—extraction with an inert gas, vacuum extraction, and electrical degassing by ion bombardment. The chemical methods of microcombustion for carbon and hydrogen, and micro-Kjeldahl for nitrogen were adapted to magnesium alloys in order to check the reliability of the extraction methods. The gases ordinarily extracted from magnesium alloys are hydrogen, the oxides of carbon, and trace quantities of nitrogen. The results from all methods are consistent in the analyses for these gases. The extraction methods are of greater precision for the determination of hydrogen; however, none of the extraction methods compares favorably in precision with the combustion method for carbon or with the Kjeldahl method for nitrogen.

RESEARCH on the metallurgical significance of gases in magnesium alloys has focused considerable attention on the determination of the gas-forming nonmetallic impurities in these metals. Some studies of this question have been reported for pure magnesium (2, 8, 16, 19), and the literature cites results that are at wide variance where reasonable consistency should be expected.

The purpose of this investigation was to study the various possibilities for the determination of gases in magnesium alloys in order to resolve some of the discrepancies reported in the literature, and also to evaluate the possible analytical procedures from the standpoint of their convenient utilization for certain types of experimental investigations.

The earlier literature concerning this problem is very deficient in experimental details; hence, it is difficult to compare this work with that of other investigators. These earlier studies were concerned primarily with the vacuum methods of "hot extraction" and "ion bombardment". These procedures were reinvestigated in this laboratory. To the extent that it is possible to compare the authors' results with the literature, it can be concluded that the apparent inconsistencies of the earlier data by these two methods were the results of remediable constant errors of experimental technique.

Besides establishing the agreement of the results of the older methods, the two other experimental techniques of combustion and helium extraction have been developed as a check on the possible constant errors of the vacuum methods.

The purpose of this investigation was to clarify the general status of the analytical problem rather than to exploit either method to its greatest advantage. It is the opinion of the authors that this objective has been achieved, although it is conceivable that considerable development is possible yet in improving the precision of either method. However, these methods, as they are here described, are of an accuracy and precision that compare favorably with the methods used for other metals, and even without further refinement they should find considerable application for metallurgical research and control.

Method I. Extraction with an Inert Gas

This method was based on the observation that reversibly soluble gases can be extracted from molten metals by bubbling through the melt some inert and insoluble gas (1). Either nitrogen or any inert gas of the helium group should be useful as an extracting gas. Helium was the only one used in these experi-

ments. The procedure required a careful purification of the helium at the source, and an analysis for the gases in the helium after it had been passed through the molten metal. The method of analysis was specific for hydrogen, water vapor, and the oxides of carbon. No attempt was made to account for nitrogen or other possible trace constituents of the gaseous extract.

APPARATUS

The melting furnace used in this investigation is illustrated in Figure 1.

The graphite crucible within the silica furnace tube was heated by induction. The power was provided to a 7.5×10 cm. water-cooled coil by an Ajax-Northrup 3-kw. converter operated on a 220-volt, 60-cycle supply line. A porcelain shield tube was inserted into the furnace in order to protect the silica in the event that some metal should splash from the crucible. The porcelain and silica furnace parts were baked in a muffle at 800°C . before assembling. The graphite crucible was given a vacuum bake-out at 2500°C . and stored over phosphorus pentoxide until it was used in the furnace assembly.

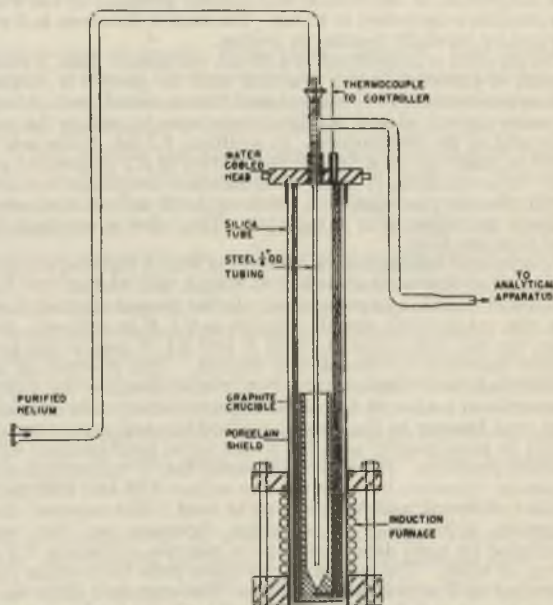


Figure 1. Furnace for Helium Extraction of Gases from Molten Magnesium Alloys

The hollow, water-cooled, steel furnace head was fastened in place by sliding the collar over a ring of hot De Khotinsky cement that was spread around the outer edge of the silica tube. The furnace head was provided with two openings, at one of which the thermocouple leads were cemented into place. The thermocouple leads were passed between the walls of the graphite crucible and porcelain shield, and the thermocouple junction was inserted into a 3-mm. hole, drilled so as to place the junction horizontally about 3 mm. below the molten charge in the crucible. The thermocouple, together with a Bristol mechanical temperature controller, was used to actuate a circuit-breaker relay that interrupted the power supply to the converter when a desired holding temperature was exceeded. This arrangement made possible holding the temperature constant to $\pm 15^\circ\text{C}$. A side-arm T-tube was cemented into the larger opening of the furnace head. A 3-mm. steel tube was fastened into place by a plug of cement that

was placed between the side-arm outlet and the 12/5 standard Pyrex spherical joint of the T-tube. (A steel tube can be used without trouble when the furnace charge is pure magnesium; however, the magnesium-aluminum alloys attack low-carbon steel, and ultimately the tube becomes plugged with the iron-aluminum reaction products. For prolonged immersion in the alloys, graphite tubes are preferred to steel.) A convenient length of Pyrex tubing connected the helium input end of the steel tube to the helium purification train.

The helium purification train contained in series a Pyrex-Vycor copper oxide furnace (at 700° C.) and absorption tubes filled, respectively, with Ascarite and magnesium perchlorate. The tank helium source was connected to the purification train in parallel with a mercury manometer. The helium flow rate was controlled by direct adjustment of the valve on the tank. The flow rate and pressure on the manometer could be maintained constant, and at a pressure of 5 to 10 cm. of mercury, the desired flow rate of 25 to 35 cc. per minute would prevail even when the furnace was charged with molten metal. Any rise in the pressure, at a constant setting of the valve, served as an indication that an obstruction was developing in the flow line, and probably in the crucible. Usually, a temporary speed-up of the flow rate would remove such an obstruction.

The helium flowing from the furnace through the side arm of the T-tube was passed through an analytical train containing in series two microabsorption tubes filled, respectively, with magnesium perchlorate and Ascarite, then a copper oxide furnace (at 500° C.), and two more absorption tubes like the first pair. The rate of gas flow was measured by the displacement of water from a Mariotte bottle connected in series with the last absorption tube of the analytical train, through a U-tube filled with magnesium perchlorate. This arrangement of the copper oxide furnace and absorption tubes made possible the analysis of the helium for water, carbon dioxide, hydrogen, and carbon monoxide. The magnesium perchlorate protection tube was used only to protect the absorption train in the event that the gas flow through the system should be interrupted.

PROCEDURE

The assembled apparatus was tested for leaks by plugging the end of the last absorption tube in the analytical train, and evacuating the apparatus with a pump that was connected in parallel with the manometer on the helium input side of the system. If a vacuum of better than 5 mm. of mercury could be held for several minutes after the pump was shut down, the system was considered leakproof, and helium was admitted to a pressure of one atmosphere. The system was then opened and the flow of helium was adjusted to 25 to 35 cc. per minute. The absorption tubes were removed for weighing, and, during this weighing period, the furnace was given a preliminary bake-out by holding the graphite crucible at 850° C. The absorption tubes were then replaced in the analytical train, and the bake-out was continued at 650° to 750° C. The absorption tubes were weighed after each 3 liters of helium had flowed through the system. When the carbon and hydrogen determination was low and constant for two or more weighings, the heating was discontinued, and the furnace was cooled.

For the purpose of determining the probable blank correction, the dry furnace was opened to the atmosphere for the duration of time that is usually required to load a sample. After assembling the apparatus again, the bake-out to a low and constant helium blank was repeated. This correction represented the total of the carbon and hydrogen that remained in the purified helium plus the carbon and hydrogen picked up by atmospheric contamination of the baked furnace parts.

A duplicate set of absorption tubes was made available, in order that the helium flow need not be interrupted while a weight determination was in progress.

After the blank had been determined, the furnace was opened and charged with the metal to be analyzed. About 30 grams of metal, in the form of 6-mm. rods, were set into the crucible concentrically around the steel, helium-input tube. The apparatus was then assembled, tested for leaks, and baked-out to a low "helium blank" at a temperature 75° C. below the melting point of the metal.

When the carbon and hydrogen evolution from the furnace was low and constant, the metal was melted by raising the crucible temperature to 800° C. for 2 to 5 minutes. The flow rate of helium was readjusted to compensate for the greater flow resistance, and the temperature control was set at 100° C. above the melting point of the metal. The extraction with helium was continued until the carbon and hydrogen pickup in the absorption tubes corresponded to that observed in the last premelting bake-out period.

DISCUSSION OF METHOD

For the experimental conditions described for this method, the rate of extraction of hydrogen can be represented by the equation,

$$L = 1/k \log a/a - x$$

where a is the total number of millimoles of hydrogen per 100 grams of metal that are extracted from the melt, x is the number of millimoles of hydrogen per 100 grams of metal that are extracted after passing through the melt L liters of helium, and k is the rate constant.

The rate constant, k , for each alloy is nearly independent of the helium flow rate over the range of 25 to 45 ml. per minute, and is insensitive to temperature fluctuations as great as $\pm 50^\circ$ C. Depending on the alloy composition, k has numerical values of 0.5 to 0.1, with pure magnesium having the greater extraction rate.

The extraction data are described by a linear rate function only when the blank is under good control—that is, the extent of the helium purification is constant and no extraneous gas evolution is taking place as a result of the reaction of magnesium vapor with adsorbed water on the furnace walls. This latter difficulty usually manifests itself by causing deviations from linearity of the rate function in the earlier stages of the extraction process. Variations in the purity of the helium effect smaller but yet apparent deviations from linearity at almost any stage of the degassing interval. Where neither of these troubles occurs, the values of k are constant to $\pm 2\%$ over the entire range of the extraction period.

The kinetic consideration of the extraction data provides an excellent measure of the extent of the analytical control of the experiment. It has been observed that in all instances where the extraction of hydrogen progressed in the theoretically expected manner, the results of duplicate determinations of hydrogen and carbon monoxide agreed, respectively, to ± 1 and $\pm 10\%$. The extraction of water vapor or carbon dioxide indicated a contamination of the sample surface or of the furnace parts. When these gases occurred in the helium extract, the inconsistency of duplicate determinations could be assumed without any further analysis of the data.

Method II. Vacuum Extraction

The extraction of dissolved gases by diffusion from the molten metal in vacuo has served as the basis of a technique for the gas analysis of several metals (4, 6, 13, 15, 18). Varying claims have been made for the validity of such a technique, and the general consensus of opinion favors the reliability of this procedure.

Winterhager (19) has claimed that gases can be extracted from magnesium and zinc during sublimation of these metals. This study has confirmed the results of Winterhager for pure magnesium, and has extended the application of the vacuum extraction method to the analysis of magnesium alloys.

APPARATUS

FURNACES. The two types of furnaces used in this investigation are illustrated in Figures 2 and 3.

Figure 2 represents a modification of the type used by Winterhager (19). The design was such that an appropriate change in the stopcocks could effect a reversal of the pumping direction for the gases being removed from the furnace. An induction coil was used to heat the metal, which was held in a porcelain or alumina boat. Usually, the greater part of the magnesium vapor would condense in a ring on the porcelain shield 2 to 5 cm. beyond the end of the coil. This condensed metal was resublimed by induction heating of this originally cold furnace zone. The pumping direction could be reversed when the heating zone approached either end of the furnace, and hence, the metal could be sublimed, condensed, and again resublimed as often as desired.

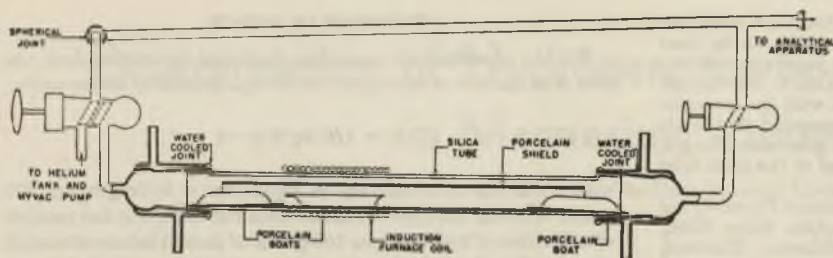


Figure 2. Winterhager Type of Sublimation Furnace for Degassing Magnesium

Winterhager (19) contended that this resublimation principle was essential to degassing magnesium completely. However, early experience with the furnace of Figure 2 demonstrated that one resublimation was sufficient for extracting at least 90% of the hydrogen from pure magnesium. This observation does not necessarily contradict Winterhager's, since different techniques were practiced. In this work, the more rapid induction heating and a faster pumping rate were used, as compared to the slower resistance furnace heating and slower pumping rates prevailing in Winterhager's experiments.

When the requirement of several resublimations had been eliminated, the use of this Winterhager type of furnace was abandoned in favor of the type shown in Figure 3. Most of the work was done with this second twin combination of furnaces. No differences of results were observed when duplicate samples were analyzed using both types of furnaces.

The vertical type of furnace, with the graphite crucible, was better suited for handling the alloy samples that melted after partial sublimation of the magnesium had occurred. The one required resublimation could be made easily by moving the induction coil around the initial condensation zone above the lip of the crucible. Moreover, the arrangement that permitted the loading of duplicate samples at the same time in the twin furnace tubes was effective in saving half the time required for duplicate determinations with the old type of furnace.

ANALYTICAL APPARATUS. The analytical apparatus used for the collection and analyses of the gases extracted from the metal was designed according to the principles recommended by Chipman and Fontana (4). The two-stage mercury pump of the apparatus unit was of the type described by Naughton and Uhlig (11). The accuracy and precision of analysis of gases with this system were the same as described by the former authors for a similar type of apparatus. The minor modifications in design of this unit are apparent if Figure 4 is compared with the illustrations given in the paper of Chipman and Fontana (4).

PROCEDURE

With the mercury pump discharging into the fore pump, the analytical system and vacuum furnace were evacuated to a McLeod gage pressure of 10^{-4} mm. of mercury, or less. During the pumping operation, the copper oxide furnace was heated at 475°C . If the analytical equipment had been opened recently to the atmosphere, a mild flaming of the glass with a hand torch speeded the attainment of good vacuum. Considerable time was saved in this pumping operation if the silica and porcelain furnace parts were baked at 800°C . for several hours and the graphite crucibles were given a vacuum bake-out at 2500°C . before the furnace was assembled and connected to the analytical system. The spherical joints through which the furnaces were connected to the analytical system were backed with picein wax whenever it became apparent during the pumping operation that the vacuum grease was not providing an effective seal against leakage.

When the apparatus had been tested for vacuum tightness, the graphite crucible in the furnace was heated with the induction coil until the mercury pump could maintain a pressure of less than 10^{-4} mm. on the furnace side of the apparatus when the crucible was held at orange heat (about 750° to 850°C .). (This procedure describes only the use of the vertical type of furnace that contained the graphite crucibles. When the Winterhager type of furnace was used, a high-temperature bake-out of the furnace parts before assembly was sufficient to control a low blank.)

When the furnace had been vacuum-conditioned, the stopcocks of the analytical system were adjusted so that the mercury pump would transfer gases from the furnace into the storage volume of the apparatus. A blank determination was then made, wherein the crucible was given the same heating schedule that would prevail in the degassing of a metal sample. The usual blank correction had the magnitude of 0.005 to 0.01 millimole of gas of the approximate composition of 80% CO , 15% N_2 , 3% H_2 , and 2% CO_2 .

Experiments were made wherein the blank determination was repeated after the furnace was filled with dry air and opened to the atmosphere for the duration of time required to load a sample. On all except very humid days, this second blank determination differed less than 20% from the first. In many instances, no blank correction was recorded for hydrogen, but invariably, a correction was necessary for carbon monoxide and nitrogen.

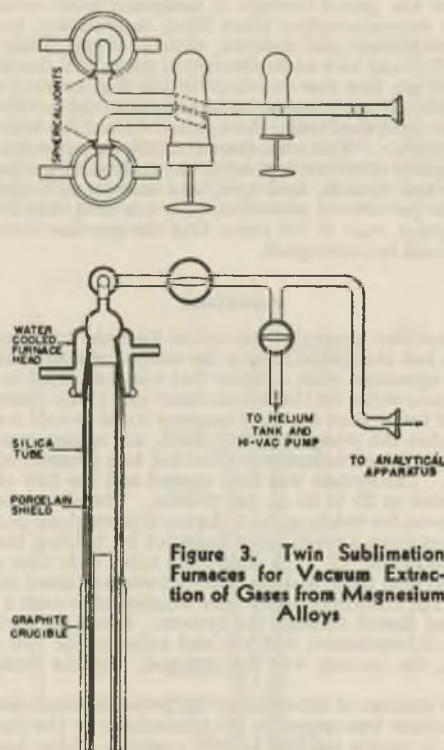


Figure 3. Twin Sublimation Furnaces for Vacuum Extraction of Gases from Magnesium Alloys

The samples were handled in the most convenient form of cast or machined rods of 0.5- to 1.0-cm. diameter. The samples were degreased with benzene, dried in a blast of warm air, and polished to brightness with aluminum oxide cloth. During the polishing operation, and in subsequent manipulations, the sample was handled with metal tongs or with a piece of dry paper. The cleaned samples could be stored indefinitely over Ascarite or magnesium perchlorate without changing the analysis; however, an atmospheric exposure of only a few minutes could cause higher results for hydrogen. Consequently, after the sample had been polished, it was loaded immediately into the furnace or transferred, while still warm from the polishing, to a sealed desiccator.

With the metal charge in the furnace, the crucible was heated by induction to a dull red glow (650° to 750°C .), and the gases evolved from the metal were pumped into the storage system of the analytical apparatus. The heating was continued until gas evolution ceased. This required 2 to 3 minutes of heating time for pure magnesium and up to 10 minutes for the magnesium-aluminum alloys. The progress of the degassing was followed by measuring the pressure on the storage system. When no increase of pressure followed after continued heating of the crucible, the induction coil was raised to surround the furnace cold

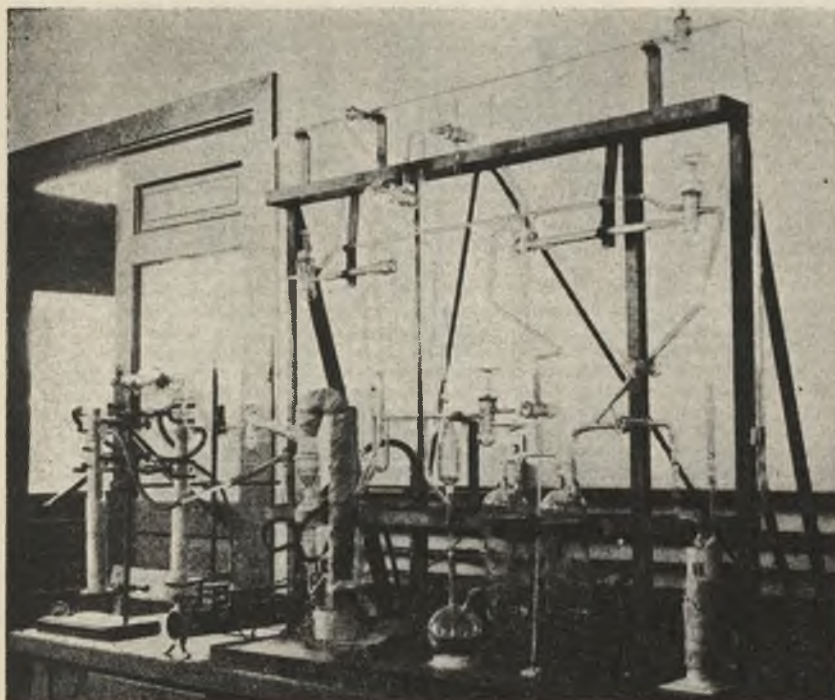


Figure 4. Apparatus for Vacuum Extraction and Analysis of Gases in Magnesium Alloys

zone above the crucible, and the heating was continued at that point until no more gas evolution could be detected. The coil was moved further up the furnace tube, and the same procedure of heating the magnesium condensate was repeated. Finally, the coil was returned to the original position around the crucible, and the alloy residue was heated again in order to test the completeness of the degassing. When the gas extraction was complete, the stopcock, separating the furnace from the analytical system, was closed, and an analysis was made of the gases contained in the storage volume.

The procedure of analysis used in these experiments is described adequately by other authors (4, 18).

DISCUSSION OF METHOD II

From the viewpoint of speed and precision, the vacuum extraction method is the most desirable for routine measurements. This procedure has the advantage that samples as large as 10 grams can be handled conveniently. The use of large samples minimizes the errors that are the result of imperfect cleaning of the sample or of inhomogeneity of the sample material.

The extraction of gases from pure magnesium is rapid—that is, about 2 to 3 minutes of heating at 600° C. are sufficient for the complete degassing of the metal. On the other hand, the difficulty of extraction of gases from the alloys increases with increasing aluminum content, and about 10 to 15 minutes of heating at 650° to 750° C. are required for the complete degassing of alloys such as Dowmetal O alloy (8.5% Al, 0.5% Zn, 0.3% Mn) and the magnesium-aluminum compound ($Mg_{17}Al_{12}$). The removal of the last quantities of gas from the alloys is so slow that it can be confused with the blank degassing of the furnace if the blank is not known with a high degree of accuracy. Consequently, when working with the alloys, it is important that the blank should be low and should be known with a higher degree of accuracy than is necessary for the analysis of pure magnesium. The longer heating period required for degassing the high aluminum alloys tends to aggravate the difficulties of the blank evaluation, and, hence, a very thorough vacuum conditioning of the furnace is required before charging the metal into the crucible. Many

earlier analyses of the alloys were invalidated because these factors were not recognized at that time.

Method III. Electrical Degassing

In recent years, a few investigators have claimed considerable success for an electrical degassing procedure as the basis of an analytical method for gases in metals. The method has been tried for magnesium (2), aluminum (9, 17), iron (9), tantalum (14), and palladium (14). Most of these results are in serious disagreement with those obtained by the conventional vacuum extraction methods. Some of these investigators have assumed that the electrical degassing techniques yielded more correct results than the extraction methods. This assumption has been questioned on theoretical grounds (5), but no experimental work has been reported either to prove or disprove the claims of the greater validity of the results of the electrical degassing method. The work of this laboratory makes it possible to clarify the status of this

method, at least in so far as it is applied to magnesium.

The principal technique of the method involves the degassing of a metal sample by making it the cathode in a vacuum discharge tube. The theoretical reasons for the effectiveness of this procedure are not clear. Chaudron (5) has advanced the explanation that bombardment of the cathode with mercury ions induces an ionization of the gas atoms within the surface layers of the metal, and that the ionized gases are then drawn from the metal by the high potential field between the electrodes. The discharge tube is evacuated continuously during the "ion bom-

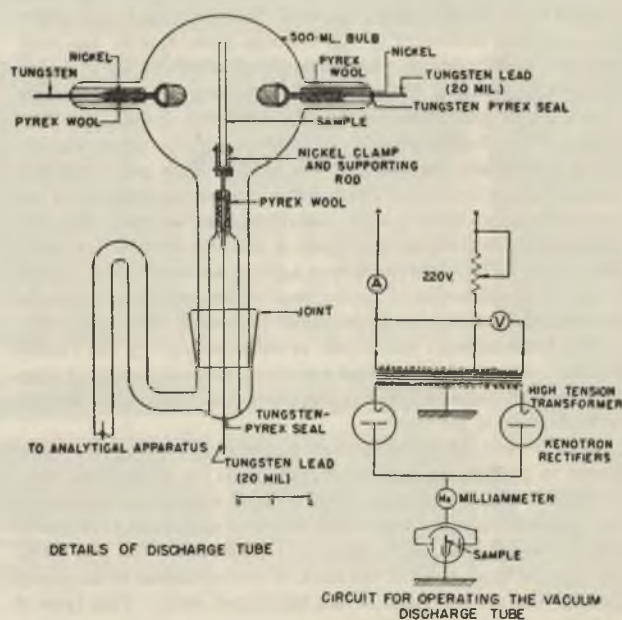


Figure 5. Discharge Tube for Electrical Extraction of Gases from Magnesium Alloys

bombardment" process, and the gases are collected for analysis in a suitable apparatus.

APPARATUS

DISCHARGE TUBE. The structural details of the discharge tube, together with its circuit diagram, are given in Figure 5.

The anodes were constructed by drawing conical buttons of 8-mm. maximum diameter and 10-mm. depth from 2.5-mm. nickel sheet, and welding these buttons to support rods that were machined from the same sheet stock. The cathode, sample-holding clip consisted of two parallel 1.5-cm. square plates of 2.5-mm. nickel sheet, held together by adjustable Monel screws at each corner of the clip. One of the plates was welded to a nickel support rod. A 1.2-cm. hole was drilled through the center of the plates in order to allow for maximum exposure of the sample that could be fastened within the clip. The Pyrex-metal seals at the electrodes were made over tungsten lead wires that were welded to the electrode support rods.

The large ground-glass joint in the neck of the tube was very convenient for loading the sample, and it has been used in all apparatus units of this type that are described in the literature (9, 17). However, this convenience can be the cause of serious errors that result from the uncontrolled bombardment of the vacuum grease in the joint by stray ions or electrons. The quantity of gas evolved from decomposition of the lubricant can exceed the quantity derived from the metal. This extraneous gas evolution was found to increase during the discharge period as the pressure in the tube dropped and the applied voltage was increased. Minimum interference from this source was prevalent in the early stages of the bombardment when the gas evolution from the sample was greatest. It is probable that the extremely high results obtained by the French workers (2, 9) for magnesium and aluminum were caused by this interference. Studies of chemical reactions in a quiet electrical discharge (7) support the predictions that most of the gas evolved from bombardment of the lubricant should be hydrogen; consequently, the fact that mostly hydrogen is evolved during the discharge process presents no strong argument that the gas is derived from the metal.

The results of Schmid and Schweinitz (17) for aluminum seemed more reliable than those of Chaudron and co-workers (9, 14). The technique of the German investigators was such that the bombardment was discontinued after the early period of rapid degassing of the metal had been completed. The errors of extraneous gas evolution are at a minimum during these first stages of the bombardment; however, such a practice fails to effect a complete degassing of the metal. This point was not made clear by the data of Schmid and Schweinitz, principally because the quantity of gas in aluminum was so small that the probable incompleteness of degassing was obscured by the blank correction. The same technique applied to magnesium caused errors in the direction of giving results that obviously could be attributed to incomplete degassing of the metal. The more drastic ion bombardment conditions, as recommended by the French workers, were essential to effect a near-complete degassing of magnesium, and these conditions introduced the maximum trouble in the control of the blank.

In this work, the problem was minimized by using a metallic shield to protect the lubricated joint from ion or electron bombardment. This was found to be a more convenient solution to the problem than the other alternative of eliminating the use of the lubricated joint in the apparatus. Aluminum foil was coiled around the inner walls of the neck of the tube so as to fit closely around the greased edge of the lubricated joint. This type of shielding reduced the blank to more reasonable proportions. Without the shielding, the blank correction could be 50 to 70% of

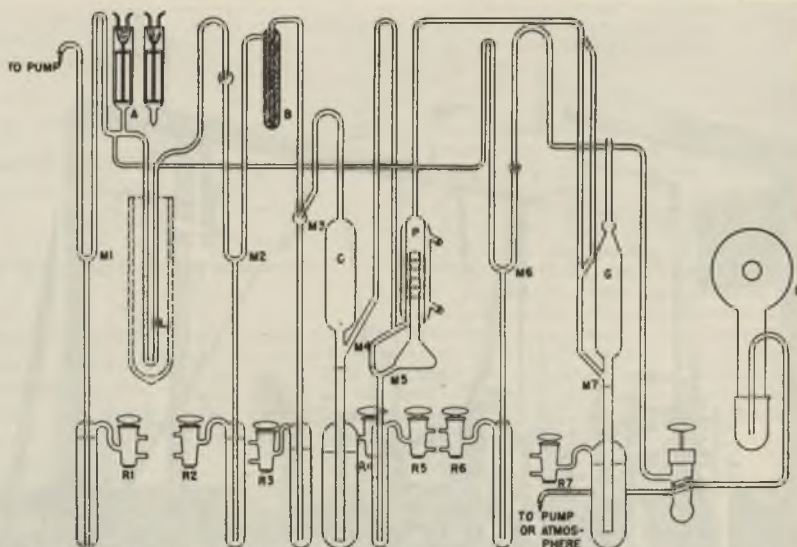


Figure 6. Details of Apparatus for Electrical Extraction and Analysis of Gases in Magnesium Alloys

the total gases evolved during the discharge process, whereas with shielding, the blank correction seldom exceeded 10 to 20% of the total gas quantity.

ANALYTICAL APPARATUS. The analytical apparatus, with the attached discharge tube, is shown in Figures 6 and 7.

When all the mercury cutoffs had been opened, the whole analytical system could be evacuated through the glass tubing ahead of cutoff M1. The pump system used for this purpose consisted of a Distillation Products, Inc., two-stage, oil condensation pump in series with a Cenco Megavac mechanical pump. The two-way stopcock, in front of the discharge tube, made it possible to make or break the vacuum on the tube without disturbing the vacuum conditions of the analytical system. The mercury in the cutoffs was controlled by opening the stopcocks on the mercury reservoirs either to a rough vacuum or to the atmosphere.

The mercury reservoir, R5, on the small mercury pump was desirable in that the mercury could be removed from the pump boiler during the period when the apparatus was heated in order to speed its vacuum conditioning. With the pumps in operation, this heating was accomplished with the soft flame of a hand torch. The drastic bake-out technique recommended by other workers (13) was not followed, since it was discovered that such a technique did more harm than good by conditioning the glass as a good adsorbent for gases. The more desirable technique of vacuum conditioning involves milder heating and a longer period of pumping.

The procedure of operating the apparatus was as follows:

When a vacuum of better than 10^{-6} mm. of mercury (as measured by the McLeod gage, G) had been attained by vacuum-conditioning the system, cutoffs M1, M2, and M3 were closed and the small, two-stage mercury pump, P, was put into operation by heating the boiler with a microburner. The mercury pump transferred gases from the discharge tube, D, to the storage bulb of the Toepler pump, C. When the Pirani gage, A, indicated a rising pressure on the low-pressure side of pump P, the Toepler pump was operated to decrease the fore pressure by transferring the gases into the closed volume between cutoffs M2 and M3. The cold copper oxide furnace, B, was a part of this storage volume. [Experiments with known gas mixtures demonstrated that no serious adsorption errors were caused by the use of the copper oxide furnace to store the gases before analysis. When the prior bake-out of the copper oxide was severe (at temperatures above $475^{\circ}\text{C}.$), a small tendency for adsorption of the oxides of carbon was demonstrated.]

The use of the Toepler pump and mercury pump was continued until the Pirani gage, A, indicated that a limiting vacuum had been attained on the low-pressure side of the mercury pump. Cutoff M6 was then closed, the mercury pump was cooled, the collected gases were expanded through the known volume of the analytical apparatus between cutoffs M1 and M6, and the pressure on the system was measured with the McLeod gage. The gas temperature was assumed to be equal to the room temperature

and the volume of the apparatus, calibrated in the manner described by Norton and Marshall (13), was known to be 1350 ± 15 cc. With these data, the number of millimoles of gases in the system could be calculated from the gas laws.

For the purpose of analysis, the mercury pump was used to circulate the gases through the liquid air-cooled trap both when the copper oxide furnace was cold and when it was heated to 350°C . The first circulation, with the copper oxide cold, removed the liquid air-condensable fraction of the gas, which consisted mostly of carbon dioxide. The second circulation removed the hydrogen and carbon monoxide, and left a residue of non-condensable gas which was assumed to be nitrogen. After each circulation process, the pressure of the residual gases was measured under the conditions described above.

When the two circulation processes had been completed, the liquid air bottle was replaced by another bottle containing a mixture of solid carbon dioxide and acetone. After allowing a few minutes for temperature equilibrium to establish itself in the cold trap, *L*, the pressure on the analytical system was measured. It was assumed that the increase of pressure was the result of the complete vaporization of carbon dioxide from the cold trap, and that this pressure was equal to the initial sum of the partial pressures of carbon monoxide and carbon dioxide. The data were then sufficient to compute the composition of the gases in carbon dioxide, nitrogen, carbon monoxide, and hydrogen. These data were sufficient for the calculation because no water was found in any of the gas mixtures that were analyzed. If water had been present initially, this variable could have been accounted for by one more measurement—namely, warming the cold trap to room temperature and measuring the increase of pressure resulting from total water vaporization by means of the calibrated Pirani gage. This operation was performed a sufficient number of times to establish that no water was evolved during the ion bombardment process.

PROCEDURE

SAMPLE PREPARATION. The samples were cut from 1- to 4-mm. sheets to the approximate rectangular dimensions of 20×50 mm. Where sheet stock was unavailable, the samples were either machined or etched to these approximate dimensions. A suitable etchant was provided by a 3-molar solution of hydrochloric acid. The samples either were abraded to brightness with aluminum oxide cloth or were baked at 350° to 400°C . for several hours before they were loaded into the discharge tube. Samples treated by the latter procedure usually gave higher results for the oxides of carbon, but the results for hydrogen were the same in both instances for samples that otherwise had received identical treatments.

DEGASSING THE SAMPLE. The tube was given a preliminary degassing by maintaining the discharge between the anodes and the empty sample clip, while the gases were evacuated continuously through the oil condensation pump and fore pump. The first glow discharge was started easily at a potential of 10 kv. and a current of 8 to 10 ma. This discharge could be maintained at this amperage for 20 to 30 minutes if the applied potential was raised gradually to 20 kv. When gas evolution from the electrodes had ceased, sparking began to occur and a steady glow discharge could not be maintained without increasing the power input to the point where the overheating of the anodes endangered the glass-metal seals at the electrodes. When this condition prevailed, the discharge was stopped and the tube was allowed to cool. For the next several hours a glow discharge could not be started in the cold tube even by applying a potential up to 100 kv. However, after a rest period of 24 to 48 hours, the glow discharge could be started again by raising the potential to 60 to 80 kv. Once started, the discharge glow could be maintained at 8 to 12 ma. by an applied potential of 20 kv.

Sometimes it was necessary to heat the anodes to redness by prolonged sparking at high potentials before the quiet discharge could be started. The gas evolution from the tube was negligi-

ble during this period of sparking, and it increased to a maximum during the first 5 minutes of the quiet discharge. After a time the gas evolution again decreased to a minimum value, which coincided with the condition where the glow discharge could not be maintained at a reasonable power input. The procedure of repeating the glow discharge treatment and successive rest periods was continued until a limiting condition was realized wherein the discharge could not be started at potentials up to 100 kv. even after 72 hours had elapsed since the last operating period. In this series of treatments, each successive glow discharge period was of shorter duration until the final limiting state was reached where the proper type of operation could not be maintained at all under high vacuum conditions.

When this limiting state had been attained, the discharge tube was flushed with dry air, opened, and the sample was fixed into the cathode clip. The procedure for degassing the sample was the same as that which was used for conditioning the discharge tube, except that the evolved gases were collected in the analytical apparatus instead of being discharged through the pumps. An analysis was made of the gas recovered in each ion bombardment period.

The number of ion bombardment periods required to degas a sample depended on the sample thickness. About two bombardments with an intervening 24-hour rest period were sufficient for samples of 1.0- to 1.5-mm. thickness, while samples of 3- to 4-mm. thickness required four or five treatments at 24-hour intervals. Each successive discharge could be started more easily if sufficient nitrogen was flushed back into the discharge tube to raise the pressure to 0.001 to 0.01 mm. of mercury. When the discharge had started, the evacuation of the tube was begun, and the discharge would be steady as long as gas was evolved from the sample. When the sample had been degassed to near completion by prior ion bombardment treatments, the glow discharge could not be sustained when the original quantity of gas that had been flushed into the tube was removed. This behavior provided a practical test for the completeness of the degassing of the metal sample. Of course, this observation applied only to the tubes wherein the organic lubricant of the ground joint was shielded. In the other instance, the glow discharge could be sustained by continuous gas evolution from the grease even after the sample had been degassed.

BLANK DETERMINATION. The discharge tube containing the degassed sample was opened to the atmosphere for the length of time that is usually required to load a new sample. After the tube had been reassembled and evacuated, it usually was possible to start and maintain the discharge glow for several minutes. This one ion bombardment period was all that could be sustained before the limiting degassed state of the tube was restored. The

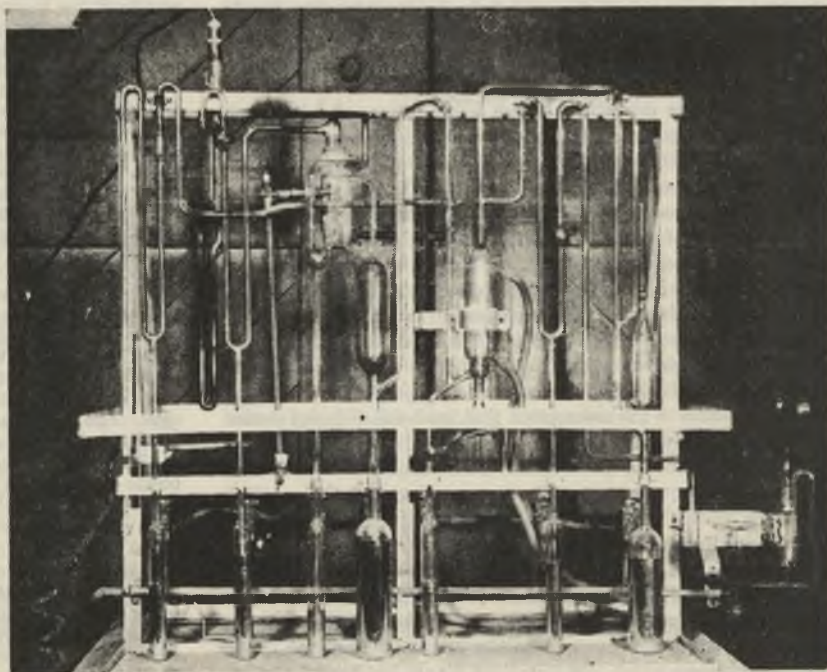


Figure 7. Apparatus for Electrical Extraction and Analysis of Gases in Magnesium Alloys

magnitude of the blank corrections was 0.003 to 0.005 millimole of hydrogen, 0.0005 to 0.001 millimole of nitrogen, and 0.001 to 0.005 millimole of the oxides of carbon.

The blank for each component was also determined indirectly by a graphical method wherein the sample weight was plotted as a function of the quantity of the gas that was evolved from the discharge process. The blank was estimated by extrapolating the curve for each component of the gas mixture to zero sample weight.

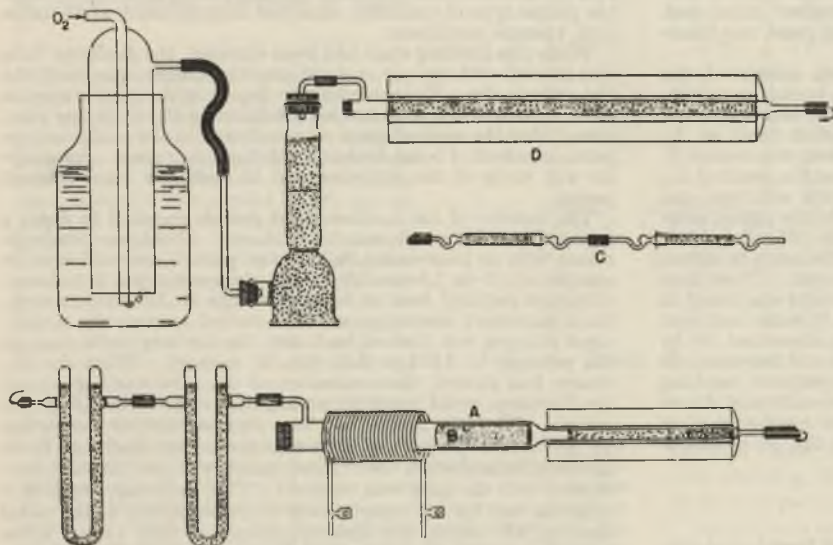


Figure 8. Combustion Train for Determination of Carbon and Hydrogen in Magnesium Alloys

The calculated and experimentally observed blank corrections differed by 20 to 50%. This uncertainty of the blank correction is the principal fault of the method.

DISCUSSION OF METHOD III

The study of the ion bombardment method was discontinued when it became apparent that this procedure could not be developed into a convenient analytical technique. There is a possibility that research concerned with the electrical characteristics of discharge tubes could suggest modifications that would make the method more desirable. These modifications should make possible the complete degassing of the sample in one short discharge period. The question of bringing the blank under better control presents another serious problem. The method, as it is now developed, provides an excellent degassing technique that is nondestructive of the sample; however, it cannot be recommended as a good analytical method for the gases contained in the metal. From the viewpoints of convenience and accuracy, it compares unfavorably with the vacuum extraction method.

The requirement of repeated ion bombardments with intervening rest periods, as claimed by the French workers (3, 9), appears to be justified. Such a requirement would have a reasonable explanation in the assumption that ion bombardment cleans up the surface layers of the metal, and that these surface layers must be replenished by gas diffusion from within the metal before further degassing can occur. The observed fact that the speed of degassing varies inversely with the sample thickness seems to make the diffusion assumption reasonable.

In general, this work has shown that the techniques of neither the French (2, 3) nor the German (17) investigators could be applied to the analysis of magnesium. The former were in error because of their failure to control the blank, whereas the latter used a technique which minimized the blank, but resulted in incomplete gas extraction.

Method IV. Combustion

In this procedure, the metal was burned in pure oxygen, and the water and carbon dioxide liberated were absorbed by magnesium perchlorate and Ascarite, respectively. The principle of the method is simple, and it has been tried with varying success on several of the heavier metals (10, 18). The technique, however, presented numerous difficulties, and required a high degree of refinement in its manipulation.

The application of this method to the analysis of magnesium is described nowhere in the literature.

APPARATUS

A diagram of the apparatus is illustrated in Figure 8. The following specifications have been developed for the units of the apparatus:

A. The combustion tube for burning the metal was made of Pyrex-Vycor tubing as follows: A 320-mm. length of 25-mm. inside diameter tubing was sealed to a 300-mm. length of carbon and hydrogen microtubing. The latter was 10 mm. in inside diameter and had a 30-mm. length of 3-mm. outside diameter tubing on the exit end. About 25 mm. from the open end of the large tube, there was placed a side arm of 3- to 5-mm. outside diameter tubing for admitting oxygen. The large end of the combustion tube was closed with an aluminum foil-covered rubber stopper.

The combustion tube, beginning at the small end, was filled with 10 mm. of silver wool, 3 mm. of asbestos plug, 70 mm. of silver wool, 2 mm. of asbestos plug, 150 mm. of copper oxide, and finally another plug of asbestos to hold the copper oxide in place. This filling was different from the usual micro carbon and hydrogen filling, in that the lead dioxide was replaced with silver wool. The copper oxide was heated to 650° C. in a microfurnace. The 20- to 30-mm. portion of silver wool that is next to the copper oxide was heated in the same furnace to a probable temperature of 500° to 600° C. The remainder of the silver wool was heated to 177° C. by a constant-temperature mortar that was placed between the microfurnace and the end of the combustion tube.

B. About 12-cm. lengths of magnesia tubes (obtained by special order from the Massillon Refractory Company, Massillon, Ohio) of 2.5-cm. outside diameter and 1.5-cm. inside diameter were used as containers for holding the metal. Alundum or nickel boats that were coated with magnesium oxide were used for the same purpose in a few experiments; however, the magnesia tubes gave smaller blanks and afforded greater protection to the combustion tube during the burning of the metal. Consequently, use of magnesia tubes was preferable even though they were costly and very fragile.

C. The standard types of carbon and hydrogen absorption microtubes were used for collecting water and carbon dioxide. These tubes were filled with magnesium perchlorate and Ascarite.

D. The oxygen was purified by passing the gas through a train containing in series a copper oxide furnace (at 700° C.) and U-tubes filled, respectively, with Ascarite and magnesium perchlorate. The last U-tube was connected to the side arm of the combustion tube with a short length of rubber tubing. The rate of gas flow was measured by displacement of water from a Mariotte bottle connected to the end of the analytical train.

PROCEDURE

A 10-cm. length of rolled platinum gauze was inserted into the magnesia tube that was to be used for holding the metal, and small pieces of magnesia were inserted loosely into each open end of the tube to serve as baffles. With the platinum-loaded magnesia tube in the center of the combustion furnace, the platinum was heated by induction to a temperature of 700° to 800° C. while pure oxygen was passed through the system. (The induction

coil is not essential to the use of this procedure, since an equivalent amount of heating can be performed directly with the oxygen torch. Induction heating has value because it saves considerable time in heating of the combustion tube and ignition of the sample.)

After several minutes of this type of heating, the induction coil was moved to the cold end of the combustion tube, and the Vycor tube in the hot-zone area was heated to 800° to 900° C. with an oxygen torch. When the furnace had cooled to 300° C., the platinum gauze was replaced by a 2 to 3-gram sample of the magnesium alloy, most conveniently handled in the form of rods 0.5 to 0.8 cm. in diameter. Each sample was polished with aluminum oxide cloth before loading into the furnace.

When the sample had been loaded into the furnace, the weighed absorption tubes were connected into the analytical train. While the furnace was heated to 300° to 400° C., with a hand torch, about 300 ml. of oxygen were passed through the system at a rate of about 15 ml. per minute. The heating was then discontinued, and 700 ml. more of oxygen were swept through the furnace in order to clean the furnace of the water and carbon dioxide that were evolved during the heating period. The absorption tubes were removed, wiped, and weighed as in the usual technique for carbon and hydrogen microdeterminations. The heating and sweeping treatments were repeated until the weight gains of the absorption tubes were less than 0.08 and 0.03 mg., respectively, for water and carbon dioxide.

When this low blank had been attained, the end of the combustion tube was plugged, and the analytical train was made ready for immediate connection to the combustion tube. The hot zone of the combustion furnace was warmed to 400° to 500° C. with a hand torch, and then the induction coil was moved into position and the metal sample was heated until ignition occurred. The oxygen consumption was rapid during the brief combustion period and 3 grams of metal required about 3000 ml. of oxygen. With the help of the reservoir, shown in Figure 8, an adequate rate of oxygen feeding could be maintained by temporary readjustments of the valve at the tank source.

When the pressure regulator at the oxygen source indicated that the combustion had been completed, the analytical train was connected to the furnace tube, and the system was swept with 250 ml. of oxygen at a flow rate of about 15 ml. per minute. During this period, the glass of the furnace in the vicinity of the combustion zone was heated to 700° to 1000° C. with an oxygen torch. As the furnace was allowed to cool, another 1000 ml. of oxygen were passed through the combustion tube and analytical train. The weight gain of the absorption tubes was again determined in the usual manner.

With platinum substituted for the magnesium metal, a blank determination was made wherein all the manipulations described above were reproduced. The one important, nonreproducible variable was the rapid oxygen consumption during combustion of the sample. Where the purification of the oxygen is insufficiently thorough, this variable can be the occasion of serious random errors in this method. Any improvements of this technique would probably bring the oxygen purification under better control.

DISCUSSION OF METHOD IV

The combustion technique did not provide a rapid and convenient analytical method. The procedure was time-consuming and even minor deviations from the correct technique could introduce as much as 100% variations in the results for duplicate samples. However, when the recommended manipulations were adhered to carefully, consistent duplicate results were derived from several determinations. Where such internal consistency of the combustion data prevailed, the results invariably were in fair agreement with other methods. Most of the errors of the combustion technique were such as to give high results for carbon and hydrogen. Consequently, even under nonoptimum operating conditions, these results provide a maximum limit for the carbon and hydrogen that should be determined by other methods. The knowledge of such limits makes untenable some of the literature claims for the very high gas content of magnesium (2, 20), and also increases confidence in the results of some of the other more precise analytical methods.

Consistent combustion data are seldom in error to such an extent that they fail to define the correct order of magnitude of the measured quantities. This fact makes the method very desirable as a check on the results of the extraction techniques. For example, the combustion method made possible the early detection

of certain subtle constant errors in the vacuum extraction procedure. The differences in the earlier results by the two methods for the aluminum-containing alloys prompted the discovery of the fact that such alloys are degassed in a vacuum with far greater difficulty than is pure magnesium. When this fact was recognized, the subsequent results of the two methods were brought into better agreement.

The method should find considerable utility for investigations of the role of carbon as a nonmetallic impurity in magnesium alloys. For homogeneous samples, the precision of the determination is greater for carbon than for hydrogen. No other reliable method is known for the precise determination of carbon in magnesium-base alloys.

Method V. Kjeldahl Determination of Nitrogen

In this procedure, the metal was dissolved in acid. After making the resulting salt solution alkaline, the ammonia, that had been produced by decomposition of magnesium nitride, was transferred by a microdistillation into an excess of standard acid, and the residual acid was determined iodometrically.

PROCEDURE

A 1.0- to 1.5-gram polished sample was dissolved in a slight excess (15 to 22 ml.) of 6 *N* sulfuric acid, and the cooled salt solution was diluted to the calibrated volume in a 50-ml. volumetric flask. A 10-ml. aliquot of this solution was transferred to a microdistillation apparatus (12), and made alkaline with 5 ml. of 50% potassium hydroxide. With the condenser tip of the apparatus immersed in 3 ml. of 0.01 *N* hydrochloric acid, the alkaline salt solution was distilled for 4 minutes. The distillation was continued for another minute after the standard acid solution (in a 25-ml. Erlenmeyer flask) had been lowered below the condenser outlet, and the outside of the condenser tip was rinsed into the acid solution with a fine stream of ammonia-free water.

One milliliter each of 5% potassium iodide and 4% potassium iodate solutions was added successively to the acid solution in the condensate receiving flask. After 3 minutes, the free iodine was titrated with 0.01 *N* sodium thiosulfate solution, using a few drops of 1% starch solution as an indicator near the end point of the titration. The thiosulfate solution was standardized in equivalence to the 0.01 *N* acid at the completion of each series of determinations.

For each series of analyses, a blank determination was made for ammonia in the reagents. The blank correction usually accounted for 0.05 to 0.1 ml. of the 0.01 *N* acid. One milliliter of 0.01 *N* acid is equivalent to 0.14 mg. of nitrogen.

DISCUSSION OF METHOD V

Other than the usual precautions required to protect the reagents from ammonia contamination, this determination presents no special problems of technique. The occurrence of a wide inconsistency in the results of supposedly duplicate determinations was most often explained by the nonhomogeneity of the sample material. When the quantity of nitrogen determined was low (less than 0.003%), the alloy samples usually were homogeneous in nitrogen, and the individual results, determined on random samples taken from the bulk material, deviated from the mean value by less than $\pm 0.0003\%$ nitrogen. In the instances where a pronounced segregation of the nitrides has occurred in a large bulk of metal, the sampling becomes more involved, and the sampling procedure is determined by the extent of the nonhomogeneity of the sample and the purpose for which the determinations are being made.

Data and Conclusions

This investigation was handicapped by the yet unsolved difficulty of preparing synthetic standards for the purpose of estimating the accuracy of the analyses. The only criterion of accuracy that exists is to be found in the consistency of the results of the hydrogen determination by the different procedures that should

Table I. Determination of Hydrogen in Magnesium Alloys by Extraction and Combustion Methods

Sample No.	Alloy Type	Alloying Metals, %	% Hydrogen			
			Vacuum extraction	Helium extraction	Electrical extraction	Combustion
1	Magnesium	...	0.0023	0.0022	0.0020	0.0024
2	Dowmetal M	2 Mn	0.0017	0.0016
3	Dowmetal M	2 Mn	0.0030	0.0030
4	Dowmetal M	2 Mn	0.0023	...	0.0030	0.0030
5	Dowmetal FS-1	3 Al, 1 Zn, 0.4 Mn, 0.2 Ca	0.0019	0.0025	...	0.0026
6	Dowmetal R	8.5 Al, 0.5 Zn, 0.2 Mn	0.0024	0.0027
7	Dowmetal O-1	8.5 Al, 0.5 Zn, 0.2 Mn	0.0011	0.0010
8	Dowmetal H	6 Al, 3 Zn, 0.3 Mn	0.0010	0.0013
9	Dowmetal C	9 Al, 2 Zn, 0.2 Mn	<0.0002	0.0003
10	Mg-Al compound	45 Al (Mg ₉₅ Al ₅)	...	0.0047	...	0.0056
11	Mg-Al compound	45 Al (Mg ₉₅ Al ₅)	<0.0002	<0.0003	...	0.0004
12	Mg-Al compound	45 Al (Mg ₉₅ Al ₅)	0.0010	0.0013
13	Mg-Al binary	42 Al	0.0011	0.0014
14	Mg-Al binary	6 Al	<0.0002	0.0005

not be subject to the same types of constant error. The results of the hydrogen determination by the different methods are in excellent agreement. The data for carbon and nitrogen are less easily compared because of the more complex aspects of the chemistry involved in the occurrence of these impurities in metals; however, even in these instances, a comparison of the results of the different methods provides significant information concerning the analytical problem. Most of the emphasis of this investigation has been placed on the hydrogen determination. The problems of carbon and nitrogen have received a less thorough study than may be within the scope of possibility with these methods.

The data for hydrogen, as determined by two or more methods for duplicate samples, are given in Table I. The result cited for hydrogen by each method represents the mean of at least two, and usually four to six determinations. The measurements with each method were repeated until a mean value was obtained such that the average of the deviations from this mean value was equal to or less than $\pm 0.0002\%$ hydrogen for the vacuum extraction and helium extraction methods, and $\pm 0.0005\%$ hydrogen for the combustion and electrical extraction methods. Considering the difference in precision of the four methods, it can be concluded that the results of the hydrogen determination for each alloy are in substantial agreement. The constant errors of either method are probably less than the magnitude of the average deviations of the less precise methods.

The results for the determination of carbon are not compared readily because of the considerable difference in the precision of the extraction and combustion methods. The oxides of carbon ordinarily extracted from the metals represent only about 10% of the gases obtained for analysis, and the blank correction, resulting from the degassing of the furnace parts, is frequently as great as the total quantity of the carbon oxides that originate from the metals. Moreover, elemental carbon can occur as inclusions in the metal, particularly if the alloy has been melted or cast in graphite containers. This free carbon escapes detection in the three extraction methods, but it is determined in the combustion method. The possibility of a magnesium reduction of the carbon oxides to carbon should be recognized as a potential source of interference in the hot extraction methods.

Considering all the possible sources of error, it is surprising that the agreement of the results of the combustion and extraction methods is as good as has been observed in many instances. These comparisons of the results from different methods are given in Table II. None of the metals listed in Table II were melted or cast in graphite, and the general agreement in the order of magnitude of the results by the extraction and combustion methods suggests that most of the carbonaceous impurities in

these alloys were extractable as gaseous oxides. For metals that have been melted in graphite crucibles, the results for carbon by the combustion method will usually be higher than the extraction results by a factor of at least ten. Such differences in the results for the carbon content of the metal can be ascribed obviously to contamination of the metal with free carbon; in fact, electron microscopy can detect crystalline graphite inclusions in the

metal. However, where the differences between the results of the two methods are smaller, it is not yet possible to determine whether the lack of agreement is the result of interferences with the quantitative extraction of the oxides or whether it represents a degree of contamination with free carbon that is below the range of sensitivity of metallographic detection.

Table II. Determination of Carbon in Magnesium Alloys by Extraction and Combustion Methods

Sample No.	Alloy Type	% Carbon and Average Deviation			
		Vacuum extraction	Helium extraction	Electrical extraction	Combustion
1	Magnesium	0.0010 \pm 0.0005	0.002 \pm 0.001	0.002 \pm 0.001	0.0016 \pm 0.0001
2	Dowmetal M	0.0006 \pm 0.0003	0.0005 \pm 0.0002
3	Dowmetal M	0.002 \pm 0.001	0.0022 \pm 0.0002
4	Dowmetal M	0.0010 \pm 0.0005	...	0.003 \pm 0.001	0.0027 \pm 0.0003
5	Dowmetal FS-1	0.0006 \pm 0.0002	0.0010 \pm 0.0005	...	0.0026 \pm 0.0001
6	Mg ₉₅ Al ₅	0.004 \pm 0.002	0.004 \pm 0.001
7	Dowmetal R	0.0018 \pm 0.0001	0.003 \pm 0.001
8	Dowmetal O	0.0006 \pm 0.0001	0.0006 \pm 0.0001
9	Dowmetal H	0.0005 \pm 0.0001	0.0009 \pm 0.0002

The combustion method has been applied to measure the extent of the degassing of metals in the extraction techniques. It was demonstrated that the quantity of hydrogen remaining in the metal residues after vacuum or helium extraction was so low as to be obscured by the blank correction of the combustion method—that is to say, the extraction of hydrogen was at least 90% complete. A similar type of estimate for the carbon extraction was impossible, since the vacuum-extracted or helium-extracted residues had been melted in graphite. However, it was possible to use the combustion technique to determine the efficacy of electrical extraction in removing from the metal both carbon and hydrogen (Table III). Apparently, this electrical degassing technique extracts the carbon oxides quantitatively, but leaves a measurable residue of hydrogen. In considering these results, it should be noted that the combustion method tends to give consistently higher results than either extraction method. If these usual trends toward higher results for hydrogen represent an underestimate of the blank correction, then the extent of the electrical degassing of hydrogen may be greater than the combustion data indicate.

The quantity of nitrogen recovered from the metal by vacuum extraction was usually 2 to 5% of the total gases evolved. In many instances, the magnitude of the blank correction for nitrogen was greater than the net quantity of nitrogen determined. Unless the vacuum conditioning of the apparatus was far more thorough than was required for a good hydrogen determination, the results for nitrogen were completely obscured by the uncertainty of the blank correction. However, a few determinations were made wherein special precautions were taken to control a low and constant blank for nitrogen, and the results of these measurements are compared in Table IV with the Kjeldahl results

Table III. Determination of Carbon and Hydrogen in Magnesium Alloys

(By electrical degassing and combustion methods)				
	Pure Mg Sample 1	Sample 2	Dowmetal M Sample 3	Sample 4
H (extraction)	0.0020	0.0020	0.0027	0.0023
H (combustion)	0.0024	0.0024	0.0030	0.0030
H (combustion) after extraction	0.0004	0.0007	0.0006	0.0008
of total hydrogen extracted	80	70	80	75
C (extraction)	0.0020	0.0020	0.0040	0.0025
C (combustion)	0.0017	0.0017	0.0022	0.0022
C (combustion) after extraction	<0.001	<0.0002	<0.0002	<0.0002
of total carbon extracted	>50	>90	>90	>90

Table IV. Determination of Nitrogen in Magnesium Alloys

(Dowmetal alloy Type M)						
	1	2	3	4	5	6
Nitrogen, %						
Kjeldahl	0.0020	0.0065	0.0040	0.0053	0.0035	0.0023
Average deviation	±0.0003	±0.0003	±0.0005	±0.0006	±0.0004	±0.0004
Vacuum extraction	0.0010	0.006	0.001	0.004	0.002	0.002
Average deviation	±0.0007	±0.001	±0.000	±0.001	±0.001	±0.001

on duplicate samples. The fact that the quantity of nitrogen measured is small is confirmed by both methods; however, the agreement of the two methods for a specific sample cannot be predicted to a consistently high degree of precision.

It is unknown whether the greater deviations among the extraction results are the result of an uncertain blank correction or whether the reaction of nitrogen with magnesium vapor inhibits complete extraction. A Kjeldahl determination on the less volatile metal residues showed less than 0.0001% nitrogen; however, there was no convenient way in which the condensed magnesium on the furnace walls could be collected for a chemical determination of nitrogen. Even if it were demonstrated that the extraction of nitrogen was nearly complete, the technique of vacuum extraction would have to be modified greatly to make it a convenient procedure for determining the usual small quantities of this gas in the metal. The volatility of magnesium sets practical limitations to the maximum size of the sample that can be handled in any simplified design of furnace.

Some investigators have claimed that electrical degassing extracts nitride nitrogen from metals (2, 3, 14). These workers formed this conclusion by establishing a favorable comparison between the results for nitrogen by their extraction and Kjeldahl methods. Unfortunately, they report no Kjeldahl analyses for supposedly degassed samples; hence, their claims are open to some doubt. Similar comparisons of Kjeldahl with extraction data have been made for some magnesium alloys. These results, given in Table V, illustrate that a superficial comparison of the extraction and Kjeldahl results can be misleading if a chemical analysis of the electrically degassed metal is omitted. An agreement of extraction and chemical results can be accidental, possibly because the uncertainty of the blank correction in the extraction technique is often as great as is the small quantity of nitride nitrogen found in the metal. Considering the results of the Kjeldahl determination before and after electrically degassing duplicate samples of metal, it becomes difficult to conclude whether the ion bombardment treatment has effected a removal of even a small part of the nitride nitrogen. There is no way of determining whether the trace quantities of nitrogen recovered in the extraction method are explainable entirely as the blank correction or whether they represent the evolution of free nitrogen that was entrapped mechanically within the sample. This latter hypothesis does not seem too probable, since the metal samples used in these experiments were rated as nonporous when examined by both microscopic and radiographic methods.

In general, it can be concluded that the extraction methods are most applicable to the determination of hydrogen, which is the

major gaseous impurity in magnesium alloys, whereas the chemical methods are superior for the determination of carbon and nitrogen, which occur in lesser molar quantities. This preference is deduced from considerations of the precision of the respective methods. The approximate agreement of the extraction and chemical methods indicates the improbable occurrence of constant errors of such a magnitude as would invalidate the results of the more precise system of measurements for each component. This conclusion cannot be deduced readily from a study of the earlier literature concerning this problem (2, 3, 19, 20).

This investigation has concerned itself with the analysis of clean metal—that is, nonporous metal which has been polished and handled carefully so as to prevent contamination of the oxide surface film with moisture or carbon dioxide. However, these methods should be applicable also to the determination of these same gaseous impurities in surface films. In this respect, the electrical extraction procedure should be particularly useful, since it effects a thorough degassing of films before any appreciable quantities of gas are removed from the interior of the metal. For example, a combination of the electrical or vacuum extraction methods with the combustion method can provide data that will differentiate between free carbon inclusions and extractable carbon oxides in the metal. It is conceivable that other situations can be proposed wherein the combined use of the chemical and extraction procedures will provide information defining not only the content of the metal in carbon, hydrogen, and nitrogen, but also the manner of occurrence of these impurities.

Table V. Determination of Nitrogen in Dowmetal Alloys

Sample No.	Alloy	% Nitrogen		
		Electrical degassing	Kjeldahl Method Before electrical degassing	After electrical degassing
1	Dowmetal M	0.0007	0.0021	0.0021
2	Dowmetal M	0.0013	0.0040	0.0033
3	Dowmetal M	0.0019	0.0020	...
4	Dowmetal M	0.0009	0.0043	...
5	Dowmetal M	...	0.0036	0.0035
6	Dowmetal J	...	0.0031	0.0035

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Determination of Sodium and Potassium in Silicates

An Improved Method

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The use of hydrofluoric and perchloric acids as a decomposition mixture was investigated. It was shown that, by the use of this mixture, the major difficulties of both the Berzelius and the J. Lawrence Smith methods of decomposition could be avoided and most of their advantages retained. A procedure was devised whereby the solution obtained from the acid decomposition could be purified preparatory to an alkali analysis. Data were obtained on synthetic and National Bureau of Standards samples.

THE problem of an alkali analysis by the J. Lawrence Smith method may be divided into two parts. The first part concerns the preparation of a solution containing the alkalis along with some or all of the other metallic elements found in the sample. This is followed by an appropriate purification by which a mixture of the alkalis is separated from all the other metallic elements. The second part concerns a separation of the alkalis (usually only sodium and potassium) one from the other. This paper deals directly with the first problem. The work was conducted and the proposed method devised on the basis that the G. F. Smith (13) method would be employed for the separation of the individual alkalis, the second of the above two problems.

Sodium may be determined directly by the triple acetate method in the presence of many of the metals. The method of Barber and Kolthoff (1) employs the zinc salt, while Caley (4) did most of the work on the magnesium salt. These methods are well adapted to the determination of small amounts of sodium but are not desirable for large amounts. Potassium may be determined directly by the perchlorate method without the removal of aluminum, calcium, magnesium, sodium, and other metals according to the method of Willard, Liggett, and Diehl (18) in which the distillation of hydrofluosilicic acid is employed. (An excellent review of the methods for the determination of the alkali metals is given by Willard and Diehl, 17.)

The use of ammonium fluoride as a flux for the decomposition of refractory silicates, according to the method of Shead and Smith (12), was not attempted in this investigation, since it seemed to offer no particular advantage over a direct attack by means of perchloric and hydrofluoric acids.

At present two procedures are in general use for decomposition of a mineral structure preparatory to an alkali analysis.

The older procedure, published in 1824 by Berzelius (2), involves the use of the acid decomposition mixture hydrofluoric-sulfuric acids. The second and by far the more popular procedure, the J. Lawrence Smith method (14), breaks down the silicate structure by sintering the ground material with a calcium carbonate-ammonium chloride mixture.

The Berzelius method depends upon sulfuric-hydrofluoric acid mixture to open up the silicate structure, followed by heating to volatilize and eliminate the silica as silicon tetrafluoride, and subsequent fuming of the sulfuric acid to eliminate all fluorides. The inherent disadvantage of this method is the introduction of sulfate into the analysis, which must be removed before sodium and potassium can be successfully separated. The removal of sulfate can be accomplished but requires the use of barium ion in excess, which in turn must be removed by carbonate ion. The entire procedure is long and involved, and is used very little at the present time.

With the advent of the J. Lawrence Smith method of silicate decomposition the disadvantage of the Berzelius procedure was

avoided, and at the same time there was provided a solution of the alkalis requiring but little purification. The main difficulty encountered in the J. Lawrence Smith procedure is the necessity of grinding an already weighed sample, a procedure rather difficult to maintain quantitative. At least one attempt has been made at correcting this disadvantage by grinding the sample with the calcium carbonate-ammonium chloride mixture under ethanol (16). In addition, a number of other modifications of the original method have been published (3, 5, 6, 7, 9, 10, 11, 15). However, the recommended changes have not improved upon the fundamental basis of the method and consequently have retained its main disadvantage.

This research was undertaken to attempt to combine the desirable features of both the Berzelius and the J. Lawrence Smith methods of decomposition. It was found that mixed hydrofluoric-perchloric acid could be substituted for mixed hydrofluoric-sulfuric acid as an acid decomposition mixture, and that iron, aluminum, and magnesium (as in the J. Lawrence Smith method) could be removed simultaneously by a suitable procedure.

When mixed hydrofluoric-perchloric acid is used for the decomposition of a silicate, the solution obtained, after the removal of excess hydrofluoric acid by fuming, contains the perchlorates of the metals present in the mineral with possibly some fluoaluminates. Evaporation yields, in the case of a typical mineral, a solid mixture of the perchlorates of sodium, potassium, magnesium, calcium, iron, and aluminum. The thermal decomposition of the perchlorates in this mixture provides a means for the separation of sodium, potassium, and calcium from magnesium, iron, and aluminum in one step.

A qualitative test on the aqueous extract from the thermal decomposition of the perchlorates gave no test for fluorides, indicating that complex fluoaluminates are decomposed by such treatment. Tests further indicate that less than 1 mg. of fluoride remains after the decomposition.

Thermal decomposition studies on sodium, potassium, lithium, calcium, magnesium, iron, and aluminum perchlorates were made by Marvin and Woolaver (8) in order to determine the temperature at which decomposition occurs and the products of such a decomposition. The thermal decomposition of the perchlorates of sodium, potassium, and calcium gives the corresponding chlorides and the evolution of oxygen. On the other hand, the perchlorates of magnesium, iron, and aluminum are hydrolyzed by the water of hydration contained in the molecule to yield perchloric acid, water, and the corresponding oxide. Sodium, potassium, and calcium are separated from magnesium, iron, and aluminum by making use of the difference in solubility existing between the chlorides and oxides formed. By leaching the decomposed perchlorates with hot water made slightly alkaline with ammonium hydroxide (to repress the solubility of magnesium oxide), a solution is obtained containing essentially only sodium, potassium, and calcium chlorides. Thus, at this point, the solution is exactly similar to one obtained by the J. Lawrence Smith method of decomposition. Only the removal of calcium and ammonium salts from this solution is required to obtain a solution to which the G. F. Smith method of alkali analysis can be applied.

The use of mixed hydrofluoric-perchloric acid retains the ease of manipulation of an acid decomposition procedure as compared to a sintering method, and introduces no interfering ions. At the same time it is possible to remove from the solution by one

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operation a number of interfering metals. These facts greatly simplify the purification of a sample in preparation for an alkali analysis.

PROCEDURE FOR SYNTHETIC SAMPLES

Nine synthetic samples were prepared by mixing one 25-ml. portion of each of six stock solutions. A stock solution was prepared for each metallic element (sodium, potassium, calcium, magnesium, iron, and aluminum as chlorides) desired in the sample. The concentration of four of these solutions—calcium, magnesium, iron, and aluminum—was 50 ± 10 mg. per 25 ml. The concentration of sodium and potassium was accurately determined by precipitating the chloride with silver and weighing the residue; their approximate concentrations were 100 mg. per 25 ml. Suitable aliquots were taken to obtain smaller quantities. The total sodium chloride plus potassium chloride in the samples was calculated from the chloride analyses (Table I). In addition to the six primary elements listed above, sample 1 contained 10 ± 2 mg. each of titanium, manganese, lead, and barium; sample 2 contained 10 ± 2 mg. of phosphorus; and sample 3 contained 10 ± 2 mg. of arsenic.

Table I. Analyses on Synthetic Samples^a

Sample No.	NaCl and KCl Added	NaCl and KCl Found
	Gram	Gram
1	0.1912	0.1920
	0.1912	0.1918
2	0.1912	0.1846
	0.1912	0.1851
3	0.1912	0.1914
	0.1912	0.1913
4	0.2162	0.2167
	0.2162	0.2171
5	0.0432	0.0432
	0.0432	0.0439
6	0.0108	0.0102
	0.0108	0.0105
7	0.0021	0.0029
	0.0021	0.0022
8	0.1015	0.1019
	0.1015	0.1017
9	0.0992	0.0993
	0.0992	0.0993

^a Results were obtained by procedure outlined with due care to observe usual precautions for securing a residue free of impurities.

The samples were placed in 250-ml. tall-form beakers, 5 ml. of 60 to 70% perchloric acid added, and the solutions slowly evaporated to dryness. The dry residues were baked for a short time on a gas hot plate. After being covered with watch glasses, the beakers were placed in a muffle furnace regulated at 550°C . for 30 minutes. This temperature was high enough to ensure the complete decomposition of all the perchlorates present. The decomposition proceeded very smoothly with no tendency to spatter. After cooling, the residue was carefully crushed and leached with two successive 50-ml. portions of hot water each containing 5 ml. of ammonium hydroxide solution (sp. gr. 0.90), followed by two 10-ml. portions. This step must be carefully followed to ensure complete extraction of all sodium and potassium salts. The washings were filtered, the filtrates heated to just below boiling, and 10 ml. of 0.5 *N* ammonium oxalate solution added. The solutions were allowed to stand for one hour and then filtered. The filtrates were reheated to about 60°C . (no higher) and 5 drops of a 5% 8-hydroxyquinoline solution in dilute acetic acid (1 to 10) added.

After standing for one hour at room temperature, the solutions were filtered, and the filtrate was acidified with hydrochloric acid and evaporated to dryness. (It is possible these two precipitations might be incorporated and performed together, but this was not tried.) The residues were treated with 25 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid, covered with watch glasses, and vigorously boiled. After the initial reaction had subsided, and 25 ml. of hydrochloric acid had been added, the solutions were again boiled and finally evaporated to dryness. The beakers were cautiously heated over a free flame to drive off any remaining ammonium salts or organic matter. The soluble material was dissolved in distilled water and

filtered into weighed 100-ml. tall-form beakers. A few milliliters of concentrated hydrochloric acid were added and the solutions evaporated to dryness. The residues were cautiously heated to drive off any moisture, cooled, and weighed. The results are tabulated in Table I.

PROCEDURE FOR BUREAU OF STANDARDS SAMPLES

From the long list of samples available, the following set of six was chosen as best representing the field of alkali silicate analysis:

B. of S. Sample No.	Material
70	Feldspar, potash
89	Glass, lead-barium
91	Glass, opal
93	Glass, high-boron
80	Glass, soda-lime
99	Feldspar, soda

One-gram amounts of each sample were weighed into flat-bottomed platinum dishes (Payne form), and 15 ml. of 60 to 70% perchloric acid and 10 ml. of 47% hydrofluoric acid were added. The mixtures were very cautiously heated on an electric hot plate until the volume of each was substantially reduced. The dishes were placed under a heating unit suspended over an electric hot plate and the heating was continued to copious fumes of perchloric acid. When the solutions had almost reached dryness they were removed and 5 ml. of perchloric acid added. The dishes were returned to the overhead evaporator and the heating was continued until the solutions were again almost dry. The solutions and any precipitate were washed into individual 250-ml. tall-form beakers and slowly evaporated to dryness on an electric hot plate. After being covered with watch glasses, the beakers were placed in a muffle furnace regulated at 550°C . for 30 minutes. This temperature was high enough to ensure the complete decomposition of all perchlorates present. The decomposition proceeded very smoothly with no tendency to spatter.

After cooling, the residue was carefully crushed and leached with two successive 50-ml. portions of hot water each containing 5 ml. of ammonium hydroxide solution (sp. gr. 0.90), followed by two more 10-ml. portions. This step must be carefully followed to ensure complete extraction of all sodium and potassium salts. The washings were filtered, the filtrates heated to just below boiling, and 10 ml. of 0.5 *N* ammonium oxalate solution added. The solutions were allowed to stand for one hour and then filtered. The filtrates were reheated to about 60°C . (no higher) and five drops of a 5% 8-hydroxyquinoline solution in dilute acetic acid (1 to 10) added. After standing for one hour at room temperature, the solutions were filtered, and the filtrate was acidified with hydrochloric acid and evaporated to dryness. (These two precipitations might be performed together, but this was not tried.)

The residues were treated with 25 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid, covered with watch glasses, and vigorously boiled. After the initial reaction had subsided, and 25 ml. of hydrochloric acid were added, the solutions were again boiled and finally evaporated to dryness.

Table II. Analyses of Bureau of Standards Samples^a

Sample No.	Weight of Chlorides Theoretical	Weight of Chlorides Found
	Gram	Gram
70	0.2439	0.2439
	0.2439	0.2442
89	0.2406	0.2412
	0.2406	0.2408
91	0.2112	0.2009
	0.2112	0.2116
93	0.0810	0.0810
	0.0810	0.0798
80	0.3145	0.3147
	0.3145	0.3147
99	0.2088	0.2042
	0.2088	0.2088

^a As a test of applicability in the hands of an expert analyst the above procedure was used by E. B. Read for analysis of Bureau of Standards Sample 70 and 0.2353, 0.2354, and 0.2363 gram of chloride obtained. This degree of agreement between the theoretical value of the chlorides and the values obtained is considered to be within the limits of manipulative error for an analyst using this method for the first time.

The beakers were cautiously heated over a free flame to drive off any remaining ammonium salts or organic matter. The soluble material was dissolved in distilled water and filtered into weighed 100-ml. tall-form beakers. A few milliliters of concentrated hydrochloric acid were added and the solutions evaporated to dryness. The residues were cautiously heated to drive off any moisture, cooled, and weighed. The results obtained (total weight of sodium chloride plus potassium chloride) are tabulated in Table II.

DISCUSSION

Perhaps the most attractive feature of the J. Lawrence Smith method of silicate decomposition is the simultaneous removal of most of the nonalkali basic constituents. The hydrofluoric-perchloric acid decomposition, as used above, accomplishes the same purpose. The perchlorates of magnesium, iron, and aluminum all form oxides upon thermal decomposition, thus rendering them insoluble. The sodium, potassium, and calcium salts, however, form soluble chlorides which can readily be dissolved away from the insoluble oxides. Inasmuch as the special equipment required for the hydrofluoric-perchloric acid decomposition is a platinum dish, and the operation of grinding an already weighed sample may be avoided, this method has certain advantages over the J. Lawrence Smith method.

Examination of Tables I and II shows that satisfactory results are obtained in all cases except where phosphorus is present in the solution, and one value for Bureau of Standards Sample 91. The presence of phosphorus apparently ties up the alkalis in a form which cannot be extracted out of the solid mass of perchlo-

rate decomposition products. No attempt was made to investigate this matter further. Sulfates are incompatible with the principle involved in this method. They would interfere seriously and if present in the original material this method is not applicable in the present form.

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Agar-Streak Method for Assaying Antibiotic Substances

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The agar-streak method for assaying antibiotic substances is rapid, does not require a sterile sample, permits testing unknown substances against several bacteria or fungi at one time, and can be used to test substances in nonaqueous solutions. Although it is less precise and less rapid than some other methods, it has marked advantages, especially in screening tests with a large number of organisms and in isolation procedures of the antibiotic substances.

IT HAS long been recognized that the results of assaying bacteriostatic and bactericidal substances depend largely upon the methods employed. Such results may vary considerably, and are influenced by the species of test organism used, the composition and reaction of the medium, and the time and temperature of incubation. Although standard conditions can be established for accurate evaluation of a single substance or of a crude preparation containing a single antibiotic agent, the results may not be very reliable when several antibiotic substances are compared, since substances may vary greatly not only in their selective action upon different bacteria, but also in their mode of attack upon the same organisms; this is especially true of crude products which may contain either a mixture of widely different types of antibiotic substances or a group of closely related modifications of the same general type of substance.

In selecting a method for measuring quantitatively the activity or potency of an antibiotic substance, it is essential to recognize several pertinent facts, which bear upon the nature and antibacterial properties of antibiotic substances in general.

Antibiotic substances are primarily bacteriostatic in their action; they are bactericidal to only a limited degree, although some substances may possess marked bactericidal properties.

Antibiotic substances are selective in their action; they are able in very low concentrations to prevent the growth of some bacteria, whereas much larger amounts are required to prevent the growth of other bacteria; some bacteria may not be inhibited at all by a particular substance even in very high concentrations.

The conditions for the bacteriostatic activity of different antibiotic substances vary greatly; some are not active at all or their activity is greatly reduced in certain media, because of the antagonistic action of some of the constituents of the media upon the antibiotic substance; others require for their activity the presence of certain specific chemical compounds in order to become effective.

The mechanism of action of antibiotic agents varies; some interfere with bacterial cell division, some affect bacterial respiration, still others interfere with the utilization of essential metabolites by the bacteria, either by replacing or combining with a substance necessary for the nutrition of the organisms.

Many antagonistic organisms produce more than one antibiotic substance; the culture filtrate of the organism may differ, therefore, in the nature of its activity from that of the active fractions obtained from it.

These facts have an important bearing upon the methods used for measuring the activity of or assaying an antibiotic substance. Methods already developed include:

1. The serial dilution or titration method (2, 7)
2. The agar diffusion or cup (cylinder plate) method and its modifications (1, 4, 7, 8)
3. The agar-streak method (10, 14)
4. The turbidimetric method (3)
5. A variety of other methods (9)

Considerable precision may be obtained with the serial dilution and cup methods. For special purposes, as for measuring the concentration of the antibiotic in body fluids, special methods may have to be devised.

The agar-streak method described herein has been in use in this and other laboratories since 1940, but has been described only briefly (14, 15) in the literature. It is rapid, it does not require a sterile sample, it permits the testing of unknown substances against several bacteria or fungi at one time, and it can be utilized for testing substances in nonaqueous solutions. It is less precise than the agar diffusion or cup method, the serial dilution method in liquid media, and the turbidimetric method, all of which require separate assays with each bacterium; it is also less rapid than some of these methods. The cup method, moreover, is limited to water-soluble diffusible substances, and a standard preparation of the substance must be maintained for reference. The serial dilution method in liquid medium and turbidimetric methods requires sterile samples. Sterilization by heat destroys many antibiotic substances, and sterilization by filters of the Seitz or Berkefeld types may lead to large losses by absorption.

The agar-streak method thus makes possible an immediate insight into the nature of the "bacteriostatic spectrum" (9) of a given antibiotic substance long before it has been isolated and chemically identified. This information is of particular importance in the study of new antibiotic substances, or even of known agents when produced by new organisms or under different conditions of culture. Much of the confusion brought about by the use of new names attached to the same substance when isolated from other organisms might have been avoided had the agar-streak method been employed in testing the new agents, because each agent has its own characteristic bacteriostatic spectrum and different substances can be differentiated on the basis of such spectra (12, 14). Thus, if a newly isolated substance is tested simultaneously against several organisms, its possible relationship to an agent already known may become evident.

Table I. Bacteriostatic Potency of Three Antibiotic Substances Produced by *A. fumigatus* (11)

Test Organism	Fumigatin	Fumigacin	Gliotoxin
	Dilution units by agar-streak method		
<i>E. coli</i>	1,200	1,200	6,000
<i>S. aureus</i>	200,000	2,000,000	1,500,000
<i>B. subtilis</i>	40,000	100,000	750,000
<i>S. lutea</i>	100,000	1,000,000	2,000,000

Usually the following four organisms are employed, the American Type Culture Collection numbers being given in parenthesis: (1) *Escherichia coli* (ATCC 9637), to represent the gram-negative group of bacteria; this organism is now used as a standard test culture in streptothricin and streptomycin assays. (2) *Bacillus subtilis* (ATCC 6633), to represent the gram-positive rod-shaped bacteria; this organism is used in penicillin and in streptomycin assays, and is highly sensitive to these substances. (3) *Staphylococcus aureus* (ATCC 6538), to represent the coccus group of organisms; it is used as the standard in penicillin assays. (4) *Bacillus mycoides* (ATCC 6462) is included because of its resistance to certain antibiotic substances, especially penicillin and streptothricin; it can thus be used for differentiation purposes. Different strains of the same organism may show great variation in sensitivity to the same antibiotic substance (13); hence, only known strains must be employed in order to have the results comparable.

Certain other bacteria may occasionally be added to this list—for example, *Sarcina lutea*, a saprophytic gram-positive coccus, *Serratia marcescens*, a gram-negative rod-shaped, pigment-producing culture, certain hemolytic streptococci, and others.

PROCEDURE FOR AGAR-STREAK METHOD

MEDIUM. The medium most commonly used consists of 0.5% Difco peptone, 0.5% sodium chloride, 0.3% Difco meat extract, and 1.5% agar in tap water. This medium is distributed in 10-ml. portions in test tubes and autoclaved at 7-kg. (15-lb.) pressure for 20 minutes. The pH of the medium is 7.0.

TEST ORGANISMS. *E. coli*, *B. subtilis*, *B. mycoides*, *S. aureus*, and *S. lutea*, obtainable from the American Type Culture Collection, as well as certain other organisms, may be used. The bacterial growth from agar-slant cultures, 20 to 24 hours old, is suspended uniformly in 5 to 10 ml. of sterile tap water by scraping the bacterial growth from the agar with a sterile wire loop. Some bacteria, such as *B. mycoides*, will not produce heavy, uniform suspensions. In such cases, the growth is scraped from the agar and broken up as much as possible; the larger particles are allowed to settle out, and the supernatant is used for subsequent streaking.

Table II. Yield of Chaetomin in Extracts of Culture of *C. cochliodes* (5)

	<i>S. aureus</i>	<i>B. mycoides</i>	<i>B. subtilis</i>	<i>S. lutea</i>
	Dilution units per gram of preparation			
Acetone extract of mycelium	80,000	30,000	80,000	100,000
Crude chaetomin	100,000,000	50,000,000	100,000,000	200,000,000
Purified chaetomin	500,000,000	100,000,000	500,000,000	1,000,000,000
Culture filtrate	300	200	300	300
Crude chaetomin from filtrate	50,000,000	20,000,000	50,000,000	100,000,000

DETAILS OF METHOD. The following procedure is used with typical samples of culture filtrates. Each of a series of six sterile 10-cm. (4-inch) Petri dishes is marked off into four or five sectors, and to each of five dishes is added a portion of the solution to be tested, usually 1.0, 0.3, 0.1, 0.03, and 0.01 ml., respectively. None of the sample is added to the sixth, or control, dish. The agar medium is melted, cooled to 45° C., added in 10-ml. quantities to each dish, and mixed thoroughly with the sample by rocking the dish in the hands. After about 20 minutes, when the agar has solidified, the test organisms are streaked on the plate, each within a marked sector. Three discrete streaks of each organism are made by means of a bent wire needle that will produce a streak approximately 1 cm. wide. The wire is sterilized in a flame and dipped into a uniform suspension of the test organism, and the three streaks are made on the agar without recharging the inoculating needle. The needle is flamed and recharged between plates.

The inoculum streaked on the plate cannot be strictly controlled, since the volume of liquid applied by the wire needle varies with the viscosity and surface tension of the bacterial suspension. It has also been found more difficult to produce a uniform streak with a new, smooth wire than with one which has been in use for some time and has become slightly roughened. The actual number of bacterial cells in the suspension will vary somewhat from day to day with the abundance of growth on the agar slant. Although these factors may limit the precision of the method, they do not appreciably affect its usefulness.

The plates are incubated at a temperature of 28° C. for 18 to 20 hours, and the results recorded. The growth of the bacterial cultures on each plate is compared with their corresponding growth on the control plate. The end point is taken as the highest dilution at which growth is completely or almost completely inhibited. The result is expressed in "dilution units", that amount of material which, added to 1 ml. of the test medium, will just inhibit the growth of the test organism.

Unitage is calculated by dividing the volume of agar in the plate by the amount of the antibiotic substance added to that plate which showed the end point. For example, if out of a series of plates the one containing 0.1 ml. of the antibiotic preparation shows no growth of *E. coli*, whereas the plate containing 0.03 ml. of the preparation shows normal growth of *E. coli*, the end point is said to have been reached in the first plate. The concentration of the active substance is thus 10/0.1, or 100 units per ml. of the preparation. Sometimes the end point lies between successive plates of the series. For example, the plate containing 0.3 ml. of the active substance may show complete inhibition; the plate containing 0.1 ml. may show normal growth on two streaks and no growth of the test organism on the third streak; the plate containing 0.03 ml. may show normal growth on all three streaks. In this case, an interpolation is made, and the preparation is said to contain 50 or 60 dilution units per ml. of the active substance.

Alcoholic solutions of an antibiotic agent may be assayed in the same way, but the volume of 95% ethyl alcohol added to 10 ml. of agar must not exceed 0.3 ml.; higher concentrations of alcohol are bacteriostatic. The same is true of methyl alcohol, ethyl acetate, and acetone. The maximum is 0.1 ml. per 10 ml. of agar with dioxane, and even less with pyridine.

Pure antibiotic substances, crude concentrates, and experi-

Table III. Antibacterial and Antifungal Action of Antibiotic Substances (6)

Antibiotic substance	Antibacterial activity		Fungistatic Activity			
	<i>E. coli</i>	<i>B. subtilis</i>	<i>Fusarium</i> sp.	<i>Aspergillus clavatus</i> 14a	<i>Trichophyton mentagrophytes</i> 598	<i>Cryptococcus neoformans</i>
			Dilution units per gram			
Actinomycin	15,000	>20,000,000	<500,000	<500,000	5,000,000	1,500,000
Chaetomin	<1,000	750,000,000	<4,000	<4,000	<4,000	<4,000
Clavacin	100,000	200,000	25,000	3,000	35,000	10,000
Fumigacin	7,200	600,000	22,000	3,000	14,800	30,000
Glutoxin	15,000	2,000,000	600,000	200,000	6,000,000	>20,000,000
Streptomycin	125,000	625,000	<45	<45	<45	<45
Streptothricin	100,000	500,000	9,000	<60	4,500	12,000

mental fractions may be tested in the same way. Preliminary dilution may be required.

In addition to bacteria, fungi can be employed as test organisms. Cultures of fungi usually require a longer incubation period, such as 2 days, for development. Details of the application of the agar-streak method to the testing of antifungal properties of antibiotic substances are given elsewhere (6).

EXPERIMENTAL DATA

This method has proved very useful in determining both the bacteriostatic and the fungistatic activities of various antibiotic agents (Tables I to IV). The antibacterial activity of several chemical compounds produced by the same fungus is given in Table I. The use of the method for isolating a substance from the crude medium is given in Table II. A comparison of the antibacterial activity of different substances is presented in Table III. In order to illustrate the fact that the results are readily reproducible, even at different periods and under different conditions, duplicate assays were run using the same sample of a certain antibiotic on two consecutive days. The results indicated that the need for daily standards is eliminated by the use of this method. However, when standards are available, it is desirable occasionally to check the results obtained with unknown preparations of a given antibiotic substance against such standards, in order to bring out possible variations in the method, as influenced by composition of medium and test organisms (Table IV).

The agar-streak method of testing antibiotic substances has also proved its value in extraction and fractionation procedures, in the purification of antibiotic substances (5, 11), and for inactivation studies. In such cases both the inactivating agent and the antibiotic substance may be incorporated in the agar medium. When several different test organisms are used, certain finer, qualitative differences can be brought out between different, sometimes closely related, antibiotic substances.

1. A difference in the ratio of the units of activity of a given substance against *S. aureus* and *B. subtilis* definitely indicates certain important differences in the physiological response of the organisms and biological behavior of the substance. Occasionally, different chemical configurations of the same substance may be produced by different strains of the same organism or by the same strain under different cultural conditions. These dif-

ferences can be frequently brought out by the agar-streak method, whereas they may be missed when other methods with a single test organism are employed.

2. Two closely related substances, streptothricin and streptomycin, can be differentiated readily by the fact that the second substance has an activity against *B. mycoides* similar to that against *B. subtilis*, whereas the first substance has very little activity against *B. mycoides*.

3. In a study of the inactivation of antibiotic substances by cysteine, it was found that the test organism is of great importance; certain organisms are sensitive to cysteine, whereas others are

resistant (Table V); the selection of the right organism may influence greatly the significance of the results obtained.

Table V. Effect of Cysteine upon Antibacterial Activity of Streptomycin

Cysteine, Mg. per 10 ml. of Agar	(As shown by the plate method) Growth of Organism in Presence of Streptomycin ^a			
	0 unit	25 units	100 units	
	<i>E. coli</i>			
0.0	+++	0	0	
0.1	+++	0	0	
1	+++	0	0	
10	+++	+++	0	
100	+++	+++	++	
	<i>B. subtilis</i>			
	0 unit	1 unit	3 units	10 units
0.0	+++	+++	++	0
0.1	+++	+++	+	0
1	0	0	0	0
10	0	0	0	0
100	0	0	0	0

^a Units per 10 ml. of agar.

SUMMARY

The agar-streak method for testing antibiotic substances offers sufficiently marked advantages over other methods to justify its wider use, especially in screening tests with a large number of organisms and in isolation procedures of the antibiotic substances.

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Table IV. Bacteriostatic Activity of a Purified Preparation of Streptomycin Tested on Two Consecutive Days

Organism	Activity in dilution units per gram	
	A Test	B Test
<i>E. coli</i> 9637	30,000	30,000
<i>E. coli</i> ATCC 6880	7,500	10,000
<i>E. coli</i> ATCC 8677	100,000	100,000
<i>Proteus vulgaris</i> ATCC 6898	100,000	75,000
<i>Proteus vulgaris</i> ATCC 8427	20,000	10,000
<i>B. subtilis</i> NRS 972	30,000	30,000
<i>B. subtilis</i> ATCC 6633	300,000	200,000
<i>B. subtilis</i> W9	250,000	250,000

Determination of Vitamin A

Correlation of Improved Spectrophotometric and Colorimetric Methods with Multiple-Level Bioassays

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On the basis of spectrophotometric and multiple-level bioassays it has been demonstrated that a fish liver oil is more likely to pass the biological assay when its extinction ratio, $E_{300/328}$, is less than 0.72. An oil with an $E_{300/328}$ value equal to or above 0.72 has about an even chance of passing the animal test. On the other hand, the vitamin A estimates obtained by the authors' adaptation of the antimony trichloride method agree well with the biological estimates and are independent of the $E_{300/328}$ value. The simplicity and reliability of the colorimetric procedure make it the method of choice in assaying pharmaceutical and vitamin A-fortified foods, whose unsaponifiable fractions may contain relatively large amounts of materials absorbing nonspecifically at 328 m μ .

USEFUL though they may be for purposes of research and control, the physical and chemical methods for the estimation of vitamin A do not eliminate the need for accurate biological assays. The latter measure vitamin A potency or activity which may be due to various forms of preformed and provitamin A. Biological assays make it possible to distinguish between the content of vitamins and their physiological availability. They also permit the critical evaluation of new chemical and physical assay procedures. The use of so-called conversion factors in the nonbiological methods is predicated upon reliable biological assays and the fact should not be overlooked that the accuracy of an estimate calculated by means of a conversion factor is no greater than that of the biological assays upon which the factor is based.

In this paper are presented the results of studies correlating the improved spectrophotometric (6) and colorimetric (7) methods for vitamin A with multiple-level bioassays. The tests were conducted on a total of 110 samples of fish liver oils, pharmaceutical products, and vitamin A-fortified foods; only illustrative data are given in this report.

ASSAY METHODS

In a previous report (6) dealing with the spectrophotometric determination of vitamin A the desirability of plotting absorption curves in terms of extinction ratios rather than extinction coefficients was emphasized. For this purpose the extinction coefficient at 328 millimicrons (E_{328}) is regarded as unity and extinction coefficients at other wave lengths are expressed as ratios to E_{328} . This method of presenting the data permits the distinction between an oxidized or otherwise atypical vitamin A curve and that of true vitamin A, independently of dilution. It has since proved convenient merely to state the extinction ratios at 300 and 350 millimicrons ($E_{300/328}$ or $E_{350/328}$) in justifying the acceptability of the spectrophotometric estimate of vitamin A content based upon the reading taken at 328 millimicrons. Evidence was also presented (6) in support of basing the spectrophotometric measurements on the unsaponifiable extracts.

The spectrophotometric data reported in this study were obtained with the Beckman quartz spectrophotometer using the tungsten light source and Corex cells, with slit widths of 1.0, 0.4, 0.2, and 0.1 mm. for readings taken at 300, 310, 328, and 350 millimicrons, respectively. Corrections for absorption of the Corex cells, while insignificant at 328 millimicrons, may be appreciable at the shorter wave lengths. Pure isopropanol, which does not

absorb in the critical vitamin A region, was employed as the solvent for the test materials. Spectrophotometric estimations of potency were based on the commercial standard conversion factor of 2000.

The colorimetric method employed in this study (7) is based on the use of an internal standard, the reaction being carried out directly in the photoelectric colorimeter with appropriate corrections for color or turbidity.

A few remarks concerning this technique may be in order. Inasmuch as the colorimetric method is based upon a fleeting reaction and the use of an internal standard, it is essential that the apparatus employed for the photometric recordings be capable of precise and rapid readings. A direct-reading photoelectric colorimeter, and not a null-point instrument, should be employed. The galvanometer must be critically damped and have a short period. The time required to swing from 0 to 100 and become stable should not be more than 3 seconds. Once the instrument is set for 0 and 100% transmission, it should remain constant with infrequent adjustments. Only interchangeable test tubes should be employed. The Evelyn photoelectric colorimeter, manufactured by the Rubicon Company, Philadelphia, Pa., and accompanying "selected" test tubes have proved very satisfactory. It is desirable to add the internal standard to the test solution in the small volume of 0.1 ml. in order to avoid volume distortions. By use of a micropipet, where 11-cm. length is equivalent to 0.1 ml., the vitamin A increment may be added to the test solutions with the same degree of precision expected from macrotechniques. The fact that chloroform is the solvent in the standard vitamin A solution favors quantitative manipulations, since no doubts exist about complete drainage from the micropipet. The potency of the standard distilled esters preparation is taken as $E_{328} \times 2000$, the validity of this factor having been established by numerous biological assays; the ultraviolet absorption curve of the distillate duplicates that of pure vitamin A and the values obtained for vitamin A in the distilled esters and the unsaponifiable extract thereof, agree when determined by both spectrophotometric and colorimetric methods (7). When turbidity is encountered on the addition of the antimony trichloride reagent because of residual moisture in the test solutions, it can be corrected for by the reading taken with the 720-millimicron filter (7) or by the direct procedure of adding 2 or 3 drops of acetic anhydride to the test solutions prior to addition of the antimony trichloride reagent.

The U.S.P. procedure (9) was employed for the biological assay of vitamin A. The method as published is a minimal potency assay—i.e., the response of a single assay group is compared with that of a single reference group. Interpretation is therefore limited to the statement that the test material contains less than or not less than the amount of vitamin A assumed to be present in establishing its dose level. For the purpose of the present study, however, it was necessary to obtain more quantitative evaluations by conducting multiple-level assays—i.e., assays in which the biological response to graded doses of vitamins is determined. Thus, the bioassay technique in this study was the unmodified U.S.P. procedure, but experimentally designed to ascertain by analysis of variance (1) (a) whether the animals responded sensitively enough to yield a statistically valid response gradient, (b) whether the slopes of the curve of response to equal vitamin increments were substantially the same in both the assay and reference groups, (c) whether departures from linearity of the dose-response relationship was sufficiently great to vitiate the assay, and (d) the limits within which the estimate of potency may be regarded as reliable. The mean standard error of estimate in 110 such bioassays was 11%.

In each test two equal-sized groups of rats (all males and at least eight in each group) received the unknown material, and two the standard. Distribution of litter-mates among these groups was balanced to the best possible extent. The intervals between dosage levels of both assay material and reference oil were the same, the animals receiving either 1.5 or 2.5 U.S.P. units of the U.S.P. reference cod liver oil No. 2 daily or the same relative doses (expected unitages) of the assay material. Assays in which the slope of response was not significant, or in which the

slope of response of the assay group differed significantly from that of the reference group, or in which the error of the estimate was inordinately high, were not considered; however, such instances were rare.

RESULTS

In Table I is presented a comparison of biological, spectrophotometric, and colorimetric assays of 12 fish liver oils or concentrates in terms of the per cent deviation of the nonbiological estimates from bioassay values. In these preliminary tests the ultraviolet absorption curves were not obtained. The estimates based on the spectrophotometric tests of the whole oils averaged 16% greater than the bioassay values and except for a few cases were consistently on the high side. Similarly, the spectrophotometric estimates based on the unsaponifiable extracts of these oils were about 13% above that of the bioassay. This may be taken to indicate that in two thirds of these cases the factor 2000, employed for converting the $E_{1\text{ cm}}^{1\%}$ 328 $m\mu$ reading to vitamin A unitage, was too high. The colorimetric procedure applied to the whole oil also gave high estimates in the majority of instances. However, the average estimate of vitamin A content based on the colorimetric test of the unsaponifiable fraction was close to the bioassay values, the distribution of the deviation being fairly well balanced.

On the basis of these preliminary tests, it was concluded that there was no advantage in conducting colorimetric assays of whole oils. Since it was clearly demonstrated that the unsaponifiable extract could be prepared without loss of vitamin A (δ), the data strongly suggested that the colorimetric procedure applied to the unsaponifiable extract furnished a more accurate (specific) measure of true vitamin A content. In order to determine why good agreement was obtained between bioassay and spectrophotometric estimates in some samples and not in others, it was decided to supplement all readings of E_{328} with the critical extinction ratios. Experiments in this laboratory and elsewhere have demonstrated that almost without exception the extinction ratio $E_{310}/328$ of oils and concentrates approximates that of pure vitamin

Table I. Per Cent Deviation of Nonbiological Estimates of Vitamin A Content from Bioassay Values

Sample	Bioassay Value U.S.P. units/g.	Whole Oil		Unsaponifiable Fraction	
		Spectrophotometric ^a %	Colorimetric ^b %	Spectrophotometric ^a %	Colorimetric ^b %
5	225,400	- 4.3	- 4.3	- 5.7	- 5.9
19	68,860	- 5.7	- 1.7	- 5.4	-13.5
23	207,800	- 6.6	-17.2	- 7.2	-21.1
26	144,000	30.0	26.4	33.3	15.2
31	960,000	26.2	26.0	20.8	1.9
36	104,000	39.7	31.5	34.2	16.1
37	270,000	32.6	33.0	26.7	14.1
40	158,800	19.8	15.6	16.9	7.7
47	1,170,000	12.5	13.0	5.5	- 0.9
64	197,000	- 2.1	- 7.2	- 6.1	-13.9
83	301,400	31.7	27.7	24.1	18.1
93	335,000	17.7	4.4	17.3	1.1
Av.		15.96	12.27	12.87	1.58
Standard deviation		16.88	17.10	15.91	13.17

^a $E_{328} \times 2000$.

^b Standard = distilled esters (sample 5) ($E_{328} \times 2000 = 215,600$).

A, falling between 0.45 and 0.65. The most significant region of the ultraviolet absorption curve of vitamin A has been shown (δ) to lie below 328 millimicrons. For this reason major emphasis in this paper has been placed upon the extinction ratio $E_{300}/328$. As may be expected from the upward swing of the left leg of the curve upon oxidation of vitamin A (δ), the deviation of the extinction ratio from that of the pure vitamin is of considerably greater magnitude at 300 $m\mu$ than, for example, at 310 $m\mu$. This is not compensated by the slightly greater precision of the readings at E_{310} when the Beckman spectrophotometer is employed with the tungsten lamp. Thus, although the data are available, $E_{310}/328$ values are not reported in this paper.

No study has yet been published on the correlation between the biological assay values and the deviations in the extinction ratio curve from that of pure vitamin A. One of the purposes of the present paper is to present such data, in order to ascertain whether or not a value may be established for the extinction ratio $E_{300}/328$ above which spectrophotometric estimates of vitamin A content, based upon the 328 $m\mu$ readings, may be considered to be questionable.

Figures 1 to 3 are spot diagrams, presenting the results obtained in testing fish liver oils and concentrates by multiple-level bioassays with values yielded by spectrophotometric and colorimetric tests, the latter conducted on the unsaponifiable fractions. In Figure 1 the percentage deviations from the bioassay estimates of the spectrophotometric results based on analyses of the whole oils or concentrates are plotted against the values for $E_{300}/328$. Statistical studies in these laboratories and elsewhere have shown that the standard error of the U.S.P. minimal potency (single-level) bioassay as ordinarily conducted approximates 25 to 30%. This is considerably greater than the standard error of the series of multiple-level assays here reported. For the purpose of this presentation the permissible deviation of the spectrophotometric estimate from the bioassay is taken to be 20%, and is indicated by the ordinate drawn at that point. By inspection, an abscissa can be drawn which differentiates those samples showing fair agreement between the spectrophotometric and biological assay estimates from those in which the incidence of deviation is high. It is then seen that somewhat more than half of the oils whose extinction ratios at 300 $m\mu$ fell in the higher range yield spectrophotometric estimates which deviated from their biological potencies by more than 20% and in many cases by more than 30%. On the other hand, of the 22 samples with the lower extinction ratios, only 4 samples deviated from the bioassay figures by more than 20% and in only one case by more than 30%. That this relation of the extinction ratio of the whole oil to the deviation from the biological assay is real and not due to chance has been confirmed by the chi square test. These data furnish experimental justifi-

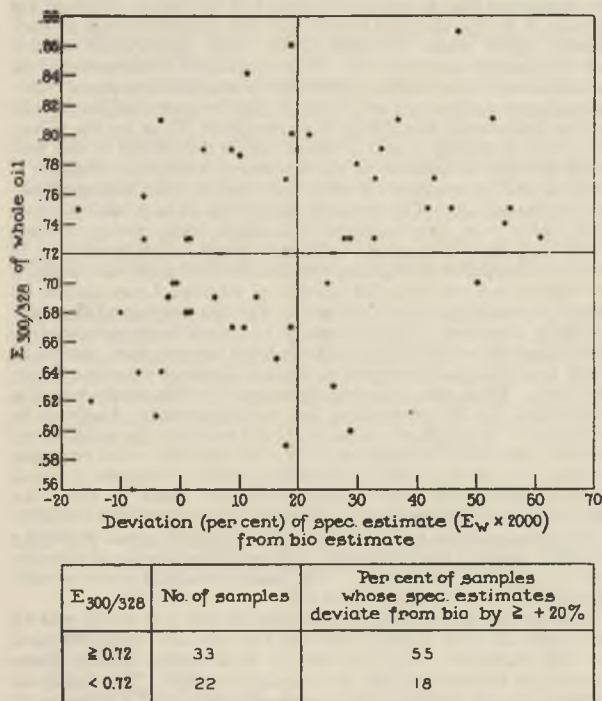


Figure 1. Relation of Extinction Ratio to Deviation from Bioassay of Spectrophotometric Estimate

Based on analysis of whole oil

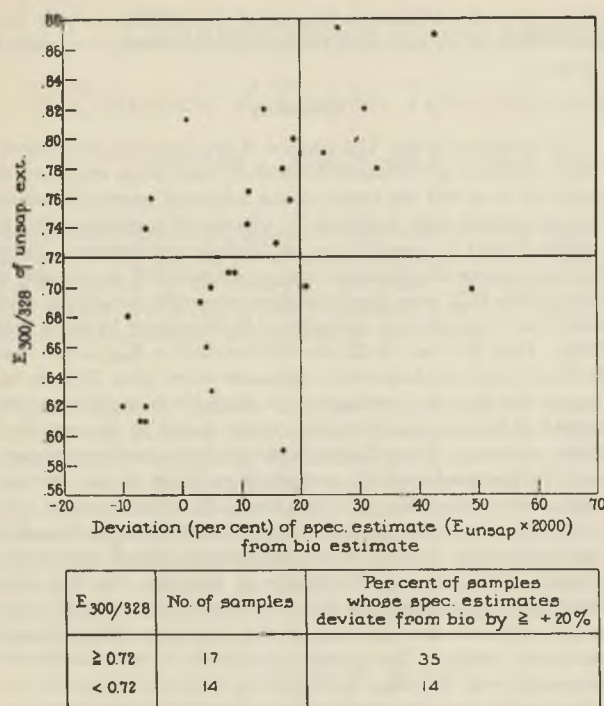


Figure 2. Relation of Extinction Ratio to Deviation from Bioassay of the Spectrophotometric Estimate

Based on analysis of unsaponifiable extract

cation for the more or less arbitrary adoption of 0.73 as the critical ratio in specifications of the War Food Administration for vitamin A-bearing oils.

A similar diagram has been constructed (Figure 2) relating the extinction ratios to the deviations from the bioassays of the spectrophotometric estimates when the tests were based on unsaponifiable extracts. While this is a somewhat smaller series, it is obvious that samples with extinction ratios equal to or above 0.72 showed a greater incidence of significant deviation from the biological estimates than samples whose extinction ratios are below 0.72. In fact, if the ordinate for maximal permissible deviation is constructed at the 10% point the distinction between samples with ratios above or below 0.72 is even more marked; in that case the chi square test indicates a probability of less than 1% that this distribution is due to chance.

In Figure 3 the extinction ratios of a series of 37 oils or concentrates are plotted against the deviations from bioassays of the colorimetric estimates (all tests on unsaponifiable extracts). It will be seen that in only four cases was this deviation greater than 16% and that the agreement between the colorimetric and biological estimates was independent of the extinction ratios.

U.S.P. reference standard No. 2 was employed in the bioassays here reported. It has since been replaced by No. 3, a fresh bottling of the same oil, which the authors have found by bioassay as well as by the nonbiological tests to be of higher vitamin A potency. Had the reference standard No. 3 been used in these bioassays the spectrophotometric and colorimetric estimates might have deviated even more from the bioassay values.

Most analysts will agree that spectrophotometric estimates of vitamin A content are maximal values, since other materials may be present which also absorb light at 328 millimicrons. However, many are of the opinion that, despite the inherent tendency on the part of the spectrophotometric method to overestimate potencies, this procedure can be used to obtain a valid relative picture of the fate of vitamin A during processing, storage, etc. This is possible only as long as the ultraviolet absorption curves for the test extracts continue to be characteristic of the vitamin A

curve. In order to illustrate this point the results of a study are presented involving periodic determinations of vitamin A in a pharmaceutical emulsion during storage.

The data, presented in Figure 4, indicate that the absorption curve of the unsaponifiable fraction obtained from the freshly prepared emulsion deviated somewhat, but not markedly, from that of pure vitamin A alcohol. $E_{300/328}$ was about 0.69. After storage at room temperature for about one month, a significant upward swing in the left leg of the curve was noticed, which increased progressively, until at 6 months' storage practically all semblance to the vitamin A curve had disappeared. However, there was no corresponding downward trend in the extinction coefficients at 328 millimicrons, despite the fact that the tests were based on the unsaponifiable extracts.

The correlation of the above spectrophotometric data with the colorimetric values and those obtained by multiple-level biological assays is shown in Table II. The vitamin A estimates obtained spectrophotometrically showed no marked change even after 6 months' storage of the emulsion at room temperature; the colorimetric values, however, decreased progressively. Furthermore, the colorimetric estimate was significantly lower than the spectrophotometric in the case of the freshly prepared emulsion, and in better agreement with the theoretical value based upon the vitamin A content of the fortifying oil. All colorimetric estimates were in excellent agreement with the vitamin A potency as determined biologically. Obviously, therefore, in the freshly prepared emulsion, substances were present which absorbed light at 328 m μ and these increased in concentration during the period of storage to a degree more than sufficient to offset the loss of true vitamin A. This illustrative case demonstrates that caution must be exercised when the spectrophotometric method is employed, even when the test is applied to a single product undergoing change upon storage.

It is also held by some that the spectrophotometric method may be used for the analysis of a food mixture known to contain no preformed vitamin A, and fortified with a good quality of oil or concentrate characterized by an ultraviolet absorption curve in

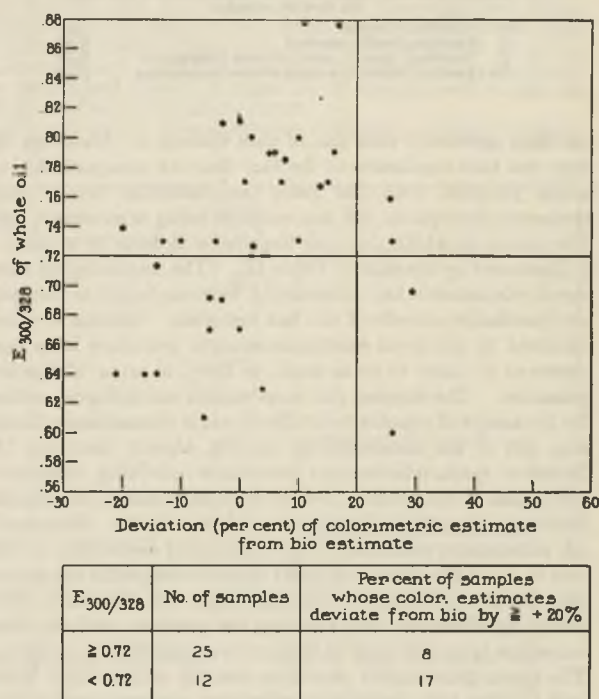


Figure 3. Relation of Extinction Ratio to Deviation from Bioassay of the Colorimetric Estimate

Based on analysis of unsaponifiable extract

Table II. Estimation of Vitamin A Potency of Pharmaceutical Emulsion Based upon Various Test Procedures

Sample	Vitamin A Estimate ^a			Standard Error of Bioassay %
	Spectrophotometric	Colorimetric	Bioassay	
	U.S.P. units per gram			
Freshly prepared	980	610	596	8
Stored 1 month at room temperature	780	425	439	8
Stored 6 months at room temperature	980	320	345	6

^a Spectrophotometric and colorimetric tests were conducted on aliquots of same unsaponifiable extracts. Theoretical value for freshly prepared emulsion was 615 U.S.P. units per gram.

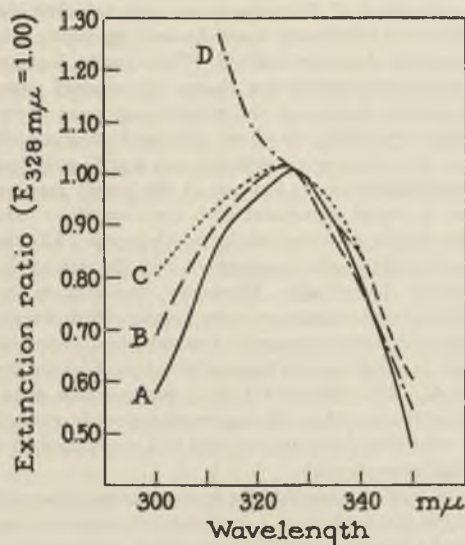


Figure 4. Spectrophotometric Data

Obtained in tests conducted on a freshly prepared and stored fish liver oil emulsion

A.	Vitamin A alcohol	E_{328}
B.	Emulsion, freshly prepared	0.49
C.	Emulsion, stored 1 month at room temperature	0.39
D.	Emulsion, stored 6 months at room temperature	0.49

excellent agreement with that of pure vitamin A. However, this does not take cognizance of the fact that the unsaponifiable extracts prepared from the basic test materials usually show irrelevant absorption, 328 $m\mu$ readings being erroneously high. The extent to which this may interfere with tests for vitamin A is illustrated by the data in Table III. The nonbiological tests, spectrophotometric and colorimetric, were conducted on the same unsaponifiable extracts of the test materials. Vitamin A values obtained by the direct spectrophotometric procedure have been observed at times to be as much as 250% in excess of the true potencies. The simplest and most reliable nonbiological method for the assays of vitamin A-fortified foods is the antimony trichloride test of the unsaponifiable extract, already described (7). Modified spectrophotometric procedures involving destructive irradiation of the vitamin (2-5, 8) to obtain a blank correction for irrelevant absorption likewise are open to criticism. Such methods necessitate preliminary proof of complete destruction of vitamin A and of the absence of newly created nonspecific absorption; they involve additional analytical steps, the vitamin is determined by difference, thus reducing the precision, and the blank correction is usually large in relation to actual vitamin A content. The spectrophotometric procedure recently published by Wilkie and DeWitt (10), involving preliminary chromatographic fractionation of the unsaponifiable extract, has interesting possibilities, but according to the authors it requires elaborate precautions for avoiding difficulties and yields extracts with atypical

absorption curves (necessitating use of the 340 $m\mu$ reading—i.e., on the slope of the curve—as the basis for converting to vitamin A unitage).

SUMMARY

In the present study 110 samples of fish liver oils, pharmaceutical products, and vitamin A-fortified foods were employed to ascertain how well the results of the improved spectrophotometric and colorimetric methods for vitamin A correlate with the values yielded by quantitative, multiple-level bioassays. Fifty-five per cent of oils whose extinction ratios at 300 $m\mu$ equaled or were above 0.72 gave spectrophotometric estimates which deviated from the biological estimates of their potency by more than 20%. Only four out of 22 oils with values for $E_{300/328}$ less than 0.72 gave spectrophotometric estimates more than 20% in excess of the biological estimates. A similar relationship was observed in the spectrophotometric values based on the unsaponifiable extracts. These findings indicate that a spectrophotometric estimate based upon E_{328} is much more likely to pass the biological assay when $E_{300/328}$ is less than 0.72, whereas an oil with a ratio equal to or above 0.72 has only an even chance of passing the animal test; in other words, the validity of such spectrophotometric estimates may justifiably be doubted. On the other hand, good agreement was noted between biological and colorimetric estimates and this was for the most part independent of extinction ratios. The greater specificity of the colorimetric procedure over the other nonbiological methods was noted only when the determination was based on the unsaponifiable fraction. The simplicity and reliability of the colorimetric procedure make it the preferred method for assaying pharmaceutical and vitamin A-fortified food products, whose unsaponifiable extracts show nonspecific absorption at 328 $m\mu$.

Table III. Comparison of Values for Vitamin A Content of Fortified Foods^a Obtained by Spectrophotometric, Colorimetric, and Biological Assays

No.	Sample	Vitamin A Estimate ^b			Standard Error of Bioassay %
		Spectrophotometric	Colorimetric	Bioassay	
		U.S.P. units per lb.			
1	Margarine	32,200 (2.90) ^c	14,400	16,700	24
2		---	8,800	10,200	17
8		---	13,400	18,300	10
15		---	13,500	16,000	13
16	Poultry feed supplement	54,500 (1.20) ^c	33,000	33,000	8
70		182,000 (1.17) ^c	88,500	91,000	..

^a Products, initially containing no preformed vitamin A or carotene, enriched with vitamin A oils or concentrates of good quality as ascertained by spectrophotometric, colorimetric, and biological assay data.

^b Spectrophotometric and colorimetric tests conducted on aliquots of same unsaponifiable extracts.

^c Values are extinction ratios, $E_{340/328}$, of test solutions; they indicate marked departure from typical vitamin A absorption curve. Thus, spectrophotometric estimates are in themselves unreliable.

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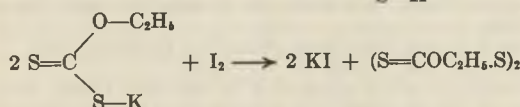
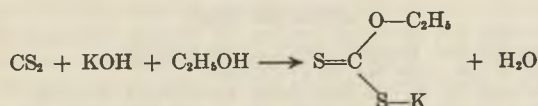
PRESENTED before the Division of Agricultural and Food Chemistry at the 108th Meeting of the AMERICAN CHEMICAL SOCIETY, New York, N. Y.

Quantitative Determination of Carbon Disulfide In Presence of Carbon Tetrachloride by Use of the Dead-Stop End Point

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The iodometric titration of xanthate has been adapted to the determination of 1 to 200 p.p.m. of carbon disulfide in carbon tetrachloride, by use of the dead-stop end point. The method is rapid, precise, and accurate, and is especially suited for routine analysis of many samples concurrently by one analyst.

OF SEVERAL methods for the determination of small amounts of carbon disulfide (1-4, 6), none was found fully satisfactory for determining this substance in carbon tetrachloride. A satisfactory method, however, was developed by the adaptation of the iodometric method of Matuszak (3), who has reviewed the pertinent literature. This method involves the formation of a xanthate by the reaction between carbon disulfide and alcoholic potassium hydroxide. The xanthate formed is quantitatively determined by direct titration with 0.001 *N* iodine using the dead-stop end point.



1 mole of $\text{CS}_2 \approx 1$ mole of $\text{S}:\text{COC}_2\text{H}_5.\text{SK} \approx \frac{1}{2}$ mole of I_2

The original method of Matuszak (3) was tried with little success because it was impossible to obtain a good end point with starch indicator in the presence of a large amount of carbon tetrachloride.

APPARATUS

The apparatus for adding the iodine and stirring the solutions was exactly like that used by Wernimont and Hopkinson (8), except that an ordinary 50-ml. buret was substituted for the automatic buret. The dead-stop apparatus employed was very similar to that described by Wernimont and Hopkinson (7), with the potential between the electrodes set at 100 millivolts. Some trouble was encountered when mercury was used as a contact medium between the short platinum tips and the copper lead wires in the glass tubing of the electrodes. This was eliminated by using a 15-cm. (6-inch) length of platinum wire, so that a solid contact could be made between the platinum and the copper leads.

The Serfass electron-ray titrimeter (5) was tried in place of the dead-stop apparatus, but was not sensitive enough to produce a sharp end point when used with 0.001 *N* reagents.

REAGENTS

SODIUM THIOSULFATE SOLUTION. A standard 0.1 *N* solution was made by dissolving 25.0 grams of reagent grade sodium thiosulfate pentahydrate in freshly boiled and cooled distilled water to make 1 liter of solution. This solution was standardized against N.B.S. potassium dichromate and then stored in a glass-stoppered bottle. When prepared and stored in this manner the solution did not show a change in strength over a period of several weeks.

Standard 0.001 *N* sodium thiosulfate solution for standardizing the iodine was made up fresh when needed by diluting the proper amount of 0.1 *N* solution to 1 liter with freshly boiled and cooled distilled water.

IODINE SOLUTION. A 0.1 *N* iodine solution was prepared by dissolving 12.7 grams of reagent grade iodine and 20 grams of reagent grade potassium iodide in distilled water to make 1 liter of solution. This stock solution was stored in a dark brown glass-stoppered bottle.

Standard 0.001 *N* iodine solution was made up fresh daily by diluting 10 ml. of the stock 0.1 *N* iodine solution to 1 liter with distilled water. The 0.001 *N* iodine was then standardized against a measured amount of 0.001 *N* sodium thiosulfate solution, using the dead-stop end point at 100 millivolts electrode potential. No attempt was made to obtain a 0.001 *N* iodine solution from a carefully measured amount of standard 0.1 *N* iodine because a slight error develops from the loss of iodine in high dilution.

ALCOHOLIC POTASSIUM HYDROXIDE. Six grams of reagent grade potassium hydroxide were dissolved in 100 ml. of absolute alcohol. This solution should be prepared fresh each week and stored in a refrigerator in a reagent bottle with a paraffined glass stopper.

ACETIC ACID. Sixty grams of reagent grade glacial acetic acid were diluted to 1 liter with distilled water.

Ethyl alcohol, 3A specially denatured. Carbon tetrachloride, Eastman Reagent No. 444 (carbon disulfide-free). Carbon disulfide, reagent grade. Starch indicator. Phenolphthalein indicator.

GENERAL PROCEDURE

The procedure resulting from the experimental work outlined in this paper and found most satisfactory for routine purposes is as follows:

Measure a 25-ml. sample of the material to be tested in a graduated cylinder, and pour it into a 250-ml. glass-stoppered Erlenmeyer flask. (In cases where a preliminary run shows more than 50 p.p.m. of carbon disulfide to be present, it is best to take a smaller sample.) Add 2 ml. of alcoholic potassium hydroxide to the sample and allow it to stand for 30 minutes with occasional agitation while the xanthate forms.

Add one drop of phenolphthalein indicator and make the solu-

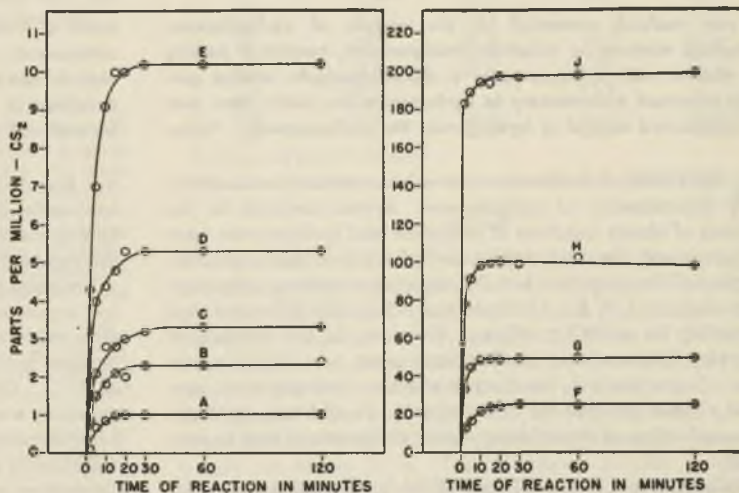


Figure 1. Time of Reaction to Form a Xanthate for Knowns of Carbon Disulfide in Carbon Tetrachloride

CS_2 present, p.p.m.: A, 1. B, 2. C, 3. D, 5. E, 10. F, 25. G, 50. H, 100. J, 200

Table I. Analysis of Knowns

Sample No.	Amount of Sample Ml.	0.001 N Iodine Solution, Net Ml.	Carbon Disulfide		
			Present P.p.m.	Found P.p.m.	Difference P.p.m.
1	25	0.58	1.0	1.1	+0.1
2	25	1.16	2.0	2.2	+0.2
3	25	1.68	3.0	3.2	+0.2
4	25	2.78	5.0	5.3	+0.3
5	25	5.29	10.0	10.1	+0.1
6	25	12.89	25.0	24.6	-0.4
7	10	10.27	50.0	49.0	-1.0
8	10	20.63	100.0	98.4	-1.6
9	5	20.55	200.0	196.0	-4.0

Specific gravity of samples at 20°/4° C. = 1.5937

tion slightly acid by the addition of dilute acetic acid from a buret until 3 or 4 drops in excess are indicated. Immediately add 50 ml. of ethyl alcohol (3A specially denatured), connect the flask to the titration apparatus, and titrate to a dead-stop end point with 0.001 N iodine solution. Similarly treat a blank containing all the reagents and omitting the sample. At the start of the titration the galvanometer will show no reading. As the end point is approached the galvanometer will show a temporary deflection of about 3 scale divisions as each drop of iodine reagent is added. At the true end point one drop of reagent causes a permanent galvanometer deflection of 3 to 5 scale divisions. However, greater speed in the titration may be obtained without loss in accuracy by choosing a point at 10 or 15 on the galvanometer scale as the final end point and titrating to this same point with the blank and all the samples.

CALCULATION. 1 ml. of 0.001 N iodine = 76 micrograms of carbon disulfide.

EXPERIMENTAL RESULTS

The first series of experiments was made to find the time required to complete the reaction of the carbon disulfide with the alcoholic potassium hydroxide, and to determine the stability of the xanthate formed. Knowns of from 1 to 200 p.p.m. of carbon disulfide were used for this experiment. Figure 1 shows that any length of time from 30 minutes to 2 hours may be allowed for this

reaction. However, the 30-minute point was chosen for a routine procedure to speed up the analysis.

A second series of experiments was carried out to determine the precision and accuracy of the method when applied to carbon tetrachloride containing various amounts of carbon disulfide (Table I).

The samples were prepared by carefully weighing known quantities of carbon disulfide in a weighed 100-ml. glass-stoppered volumetric flask containing about 25 ml. of carbon disulfide-free carbon tetrachloride. The mixture was then diluted to the mark at 20° C. Aliquots of this first 100-ml. mixture were measured from a jacketed buret at 20° C. and further diluted with carbon tetrachloride to obtain the desired knowns.

SUMMARY

The method described in this paper was found to be very practical and rapid, giving a relatively high degree of precision and accuracy. It was especially useful in routine work where a large number of samples, with approximately the same amount of carbon disulfide impurity, had to be analyzed in a short time.

ACKNOWLEDGMENT

The authors are indebted to F. J. Hopkinson of the Industrial Laboratory for many helpful suggestions and for the equipment used in this work.

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Analysis of Cyclopropane-Propylene Mixtures by Selective Hydrogenation

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A new method, presented for the analysis of cyclopropane-propylene mixtures by selective hydrogenation, consists in passing the mixture with hydrogen over a nickel-kieselguhr catalyst partially poisoned with mercury to hydrogenate the olefin, then over a nonpoisoned catalyst to hydrogenate the cyclopropane. Accu-

A SEARCH of the literature reveals no method for the direct determination of cyclopropane. Several methods for the analysis of binary mixtures of propylene and cyclopropane have been proposed, the most widely used of which is based upon absorption of the propylene in a 3% aqueous potassium permanganate solution (1, 2, 4). Cyclopropane is found by difference after correcting for solubility effects. However, in the presence of saturated hydrocarbons or other inert gases, no analysis is possible. A new method, based upon selective hydrogenation, provides a direct analysis for cyclopropane. In addition, small gas volumes (~1 cc. at normal temperature and pressure) may be analyzed.

Willstätter and Bruce (5) studied the hydrogenation of cyclopropane over a nickel catalyst and found that appreciable reac-

racies of ± 0.5 numerical % are obtained. The presence of inert components such as gaseous paraffins does not interfere with the analysis and hence a real advantage is realized over other methods described in the literature. Small samples (~1 cc. N.T.P.) may be analyzed with good accuracy.

tion occurred only at temperatures above 80° C. while propylene was easily hydrogenated at room temperatures. Accordingly, hydrogenation studies were undertaken in an attempt to apply this reported differential effect to a scheme of analysis.

Preliminary experiments were carried out using a nickel catalyst supported on kieselguhr. Results showed that this catalyst after reduction in hydrogen completely reduced cyclopropane to propane in a few passes over the catalyst at temperatures as low as 0° C. Consequently, a reduction of the activity by partial poisoning was attempted. It was found that the introduction of a few drops of mercury sufficiently deactivated the catalyst so that reduction of propylene was complete after a few passes while cyclopropane was unchanged at temperatures up to 200° C. The poisoning technique is described below. A nonpoisoned catalyst was used for the hydrogenation of cyclopropane.

Presumably the differences in activity of the Willstätter and Bruce catalyst and the one employed by the authors are attribut-

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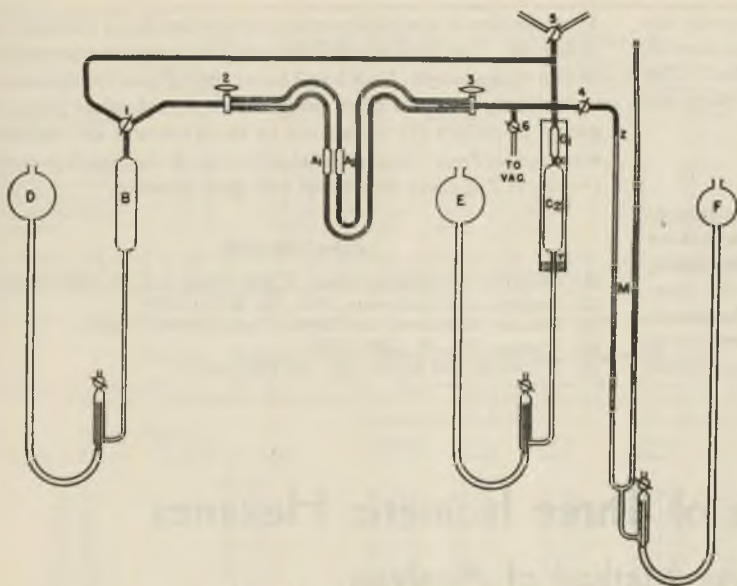


Figure 1. Diagram of Apparatus

able to differences in composition and method of preparation. The catalyst used in the authors' experiments is described by Trenner, Morikawa, and Taylor (3) as follows: "The nickel catalyst was a very active nickel-kieselguhr preparation, made by precipitation of the carbonate on kieselguhr, ignition, and reduction in hydrogen at progressively increasing temperature to 450°. It contained 15% nickel." Willstätter and Bruce (5) describe their catalyst as a mixture of equal parts of nickel oxide and pumice, reduced to the metal at 280° C.

A second difficulty encountered was adsorption on the catalyst surface. Saturation with hydrogen or with a hydrogen-hydrocarbon mixture before analysis proved unsatisfactory because of unequal adsorption of the constituents of the mixture. These effects were eliminated by evacuating the catalyst chambers with a Toepler pump after each hydrogenation and returning the recovered gases to the sample. As a further precaution, small volumes of catalyst were employed. The expected volumes were recovered within experimental error in all cases.

Since the usual stopcock greases absorb hydrocarbons readily, it was necessary to employ a lubricant made up of glycerol, dextrin, and mannitol, in which hydrocarbons are nearly insoluble.

APPARATUS AND PROCEDURE

A diagram of the apparatus is shown in Figure 1. Bulbs A_1 and A_2 each contained 2 or 3 cc. of catalyst (actually one bulb was placed behind the other). An electrically heated furnace with rheostat control was placed around these bulbs. C_1 , used for the analysis of small samples, had a capacity of approximately 4 cc., while C_2 had a volume of 100 cc. These were enclosed in a water jacket. B , which served for passing the gaseous mixture over the catalysts, was also used as the Toepler pump for evacuating the catalyst bulbs. The manometer, M , completed the apparatus. Capillary tubing throughout minimized the dead space.

REDUCTION OF CATALYSTS AND POISONING TECHNIQUE. The catalysts were reduced in a slow stream of hydrogen, starting at 250° and slowly increasing to 400°. Tank hydrogen was purified by passing first over platinized asbestos and then through a liquid air trap to remove water.

After reduction was complete, the temperature was reduced to 150°, the hydrogenation temperature, and one of the catalysts was partially poisoned. A few drops of mercury from bulb B were introduced into the capillary between stopcocks 1 and 2 and then pushed over into the catalyst chamber with hydrogen by lifting bulb D after filling B with hydrogen. The catalyst then possessed the desired activity. Fifteen or twenty analyses could be made before regeneration of the catalysts became necessary. This was carried out by again passing hydrogen over the catalysts

at approximately 300°. Mercury was driven off the poisoned catalyst, after which the activity returned to normal as measured by its ability to reduce cyclopropane readily. The catalyst was again poisoned by the technique described.

ANALYTICAL PROCEDURE. Before analysis the catalyst bulbs (maintained at 150°) were evacuated with the Toepler pump with stopcock 3 closed; three pumpings of each catalyst were sufficient. With the Toepler pump filled with mercury and stopcock 1 closed, the hydrogen pressure was adjusted at 400 to 500 mm. and the manometer read with the mercury levels at marks b and c . The hydrocarbon sample was then introduced and the manometer read with the mercury levels at marks b and c as before. To determine the olefin content, the mixture was passed several times over the poisoned catalyst and the pressure recorded after evacuating the catalyst. To check completeness of hydrogenation, the process was repeated. The cyclopropane was then determined over the active catalyst. Saturates, if present, were obtained by difference. The capillary tubing must be swept out during the analysis to ensure contact of all the sample with the catalysts.

For small samples, pressures were read with the mercury level adjusted to mark a . Before the mixture was passed over the catalysts, the volume was expanded by lowering E and reductions were carried out at low pressures. No noticeable difference was detected in the rates of hydrogenation at these reduced pressures. By this procedure very small samples (~1 cc. N.T.P.) could be analyzed.

A buret may be substituted for bulbs C_1 and C_2 for analyses at constant pressure. For small samples it would be necessary to attach a bulb below a microburet for expansion to facilitate hydrogenation.

The details of procedure outlined above apply to the highly active catalyst employed. Although the authors have no data on the behavior of less active catalysts, with appropriate modification in operating temperature and the like, such differential hydrogenation based on partial poisoning with mercury should be successful with any reasonably active supported catalyst.

Table I. Analysis of Cyclopropane-Propylene Mixtures

Volume of Sample + H_2 Cc.	Composition of Synthetic		Found by Analysis	
	Cyclopropane	Propylene	Cyclopropane	Propylene
	Vol. %	Vol. %	Vol. %	Vol. %
100	21.6	78.4	21.4	78.6
100	24.6	75.4	24.2	76.0
100	33.6	66.4	33.4	66.8
100	40.0	60.0	40.0	59.7
100	48.5	51.5	48.1	51.8
100	73.2	26.8	72.7	27.2
100	73.8	26.2	74.3	25.9
100	80.2	19.8	80.4	20.0
4	100.0	—	99.5	—
100	100.0	—	100.2	—
100 ^a	27.3	26.1	27.0	26.2
100 ^a	30.1	42.3	30.3	42.0

^a Balance of sample *n*-butane.

RESULTS

Various mixtures of known composition have been analyzed and the results are tabulated in Table I. On a numerical percentage basis, accuracies of $\pm 0.5\%$ are obtained. An examination of the data reveals little or no difference in precision for the large or small samples—perhaps because of the few data presented. Errors arising from such factors as adjusting mercury levels would be magnified when analyzing small samples. However, it was found that reproducibility in adjusting these levels for one small sample was within 0.5%. The importance of using a stopcock lubricant in which hydrocarbons are nearly insoluble cannot be overemphasized.

Van der Waals corrections for perfect gas deviations were within experimental error and hence no corrections have been applied.

An apparatus similar to the one described, but using only one catalyst, may be employed for determining the olefin content in gaseous mixtures containing only olefins and paraffins. The method possesses definite advantages, since adsorption effects are minimized and very small samples may be handled.

CONCLUSIONS

A method developed for the analysis of cyclopropane-propylene mixtures by selective catalytic hydrogenation with accuracies of $\pm 0.5\%$ provides for the direct determination of cyclopropane, and hence the presence of saturated hydrocarbons does not interfere. No data are available as to possible interference by substituted acetylenes. Other methods described in the literature do not analyze for cyclopropane directly. Propylene is determined

by absorption in a suitable reagent and cyclopropane obtained by difference. The time required for analysis probably represents a saving—for example, from 1 to 2 hours are required for the analysis of binary mixtures when using the dilute potassium permanganate procedure (1) while from 15 to 30 minutes are required with this method. An additional advantage is that small samples (~ 1 cc. N.T.P.) may be handled with good accuracy.

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Ternary Mixtures of Three Isomeric Hexanes Quantitative Method of Analysis

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Solution temperature measurements were made using all the isomeric hexanes with both nitrobenzene and diethyl phthalate. Data are given which make it possible for a hexane ternary mixture composed of 2,2-dimethylbutane, 2,3-dimethylbutane, and 2-methylpentane to be analyzed with an accuracy of 0.5% in approximately one hour.

IN CONNECTION with research at the General Motors Research Laboratory it was necessary to analyze hexane mixtures that contained much smaller quantities of the doubly-branched than of the singly-branched hexanes.

The automatic stills available at this laboratory are able to separate the isomeric hexanes (6) and, when the distillation curve is supplemented with a refractive index curve, a good analysis of a hexane mixture can be obtained as long as there is a sufficient quantity of each isomer in the mixture to obtain a flat portion in both the refractive index and boiling point curves. Table I shows that as the boiling point of the hexanes increases the refractive index alternates up and down.

In the distillation of the mixtures under investigation there was not enough 2,3-dimethylbutane present to give a flat on the refractive index curve. In the distillation break between 2,2- and 2,3-dimethylbutane the refractive index would rise but before it reached the value for pure 2,3-dimethylbutane it would turn downward again, showing that some 2-methylpentane was in the distillate. This particular part of the distillate was a ternary mixture composed of 2,2- and 2,3-dimethylbutane with 2-methylpentane, the composition of which could not be determined accurately.

A previous paper (5) described a method for quantitative analysis of ternary mixtures of three isomeric hept-

anes based on their solution temperature in nitrobenzene and diethyl phthalate. This paper covers the extension of this method of analysis to the above-mentioned hexane ternary mixture. This work makes it possible to analyze a ternary mixture composed of 2,2-dimethylbutane, 2,3-dimethylbutane, and 2-methylpentane with an accuracy of 0.5% in approximately one hour.

In the previous paper (5), the author stated that no mention had been found in the literature of any attempt to use critical solution temperature measurements for the quantitative deter-

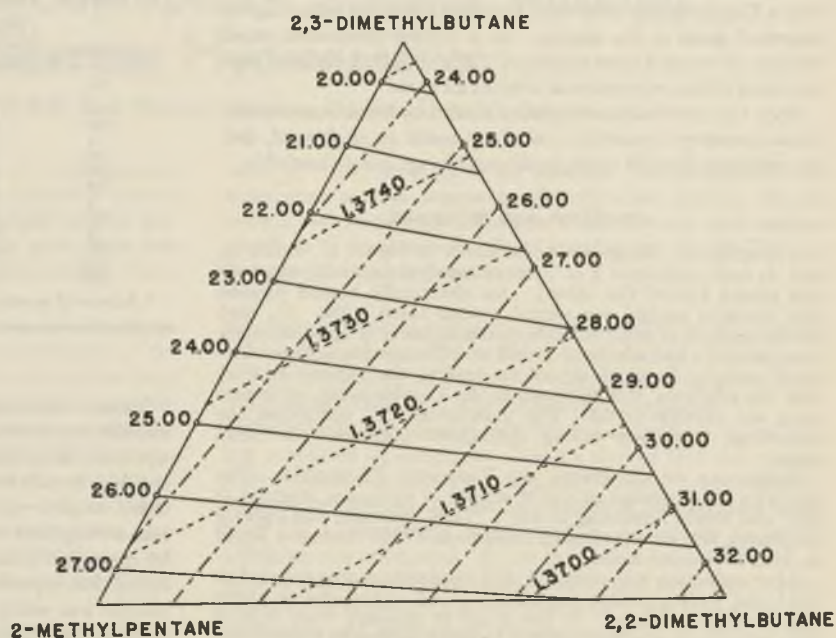


Figure 1. Bath Temperature from Refractive Index

————— Diethyl phthalate point data
 - - - - - Nitrobenzene point data
 Refractive index data

Table I. Physical Properties of Isomeric Hexanes

Hydrocarbon	Boiling Point, Wibaut (7) ° C.	n_D^{20} Wibaut (7)	This work	Solution Temperature				
				Aniline		Nitrobenzene		Diethyl phthalate ^a ° C.
				Wibaut ° C.	Maman (4) ° C.	Maman (4) ° C.	This work ^a ° C.	
2,2-Dimethylbutane	49.70	1.3689	1.3689	81.2	(76.1)	(27.9)	32.60	26.73
2,3-Dimethylbutane	58.05	1.3751	1.3752	71.9	71.8	24.1	23.38	19.37
2-Methylpentane	60.30	1.3716	1.3717	73.9	73.9	25.7	25.19	27.42
3-Methylpentane	63.30	1.3766	1.3768	69.3	69.0	21.4	20.69	20.59
n-Hexane	68.75	1.3750	1.3751	69.1	69.2	21.3	20.29	24.85

^a Values obtained at hydrocarbon concentration of 66.7% (by volume), hydrocarbon saturated with water at 70° F., and nitrobenzene and diethyl phthalate had n-heptane calibration values of 19.27° and 28.26°, respectively (n-heptane saturated with water at 70° F.).

Table II. Solution Temperature Data of Hexane Binary Mixtures

(3.00 ml. of hydrocarbon + 1.50 ml. of solvent. Hydrocarbon saturated with H₂O at 70° F. Solvent calibrations: nitrobenzene-N-heptane, 19.27° C.; diethyl phthalate-N-heptane 28.26° C.)

% by Weight of		Diethyl Phthalate Point, ° C.			Nitrobenzene Point, ° C.		
2,2-Me ₂ Butane	2,3-Me ₂ Butane	Calculated ^a	Observed	Difference	Calculated ^a	Observed	Difference
100.00	100.00	19.37°	19.37°	---	23.38°	23.38°	---
9.60	90.40	20.077	20.02	-0.06	24.265	24.21	-0.055
19.67	80.33	20.818	20.72	-0.10	25.194	25.11	-0.084
39.58	60.42	22.283	22.12	-0.16	27.030	26.90	-0.13
49.52	50.48	23.015	22.86	-0.155	27.946	27.82	-0.126
59.46	40.54	23.746	23.59	-0.16	28.862	28.74	-0.12
79.79	20.21	25.243	25.14	-0.10	30.737	30.63	-0.107
90.08	9.92	26.000	25.93	-0.07	31.686	31.62	-0.066
100.00	---	---	26.73	---	---	32.60	---
2-Me Pentane	2,3-Me ₂ Butane	---	19.37°	---	---	23.38°	---
9.70	90.30	20.151	20.22	+0.07	23.556	23.56	+0.004
19.80	80.20	20.964	21.12	+0.16	23.738	23.75	+0.012
39.79	60.21	22.573	22.79	+0.22	24.100	24.12	+0.02
49.71	50.29	23.372	23.59	+0.22	24.280	24.31	+0.03
59.64	40.36	24.171	24.37	+0.20	24.460	24.48	+0.02
79.84	20.16	25.797	25.93	+0.13	24.825	24.83	+0.005
90.13	9.87	26.625	26.74	+0.115	25.011	25.01	---
100.00	---	---	27.42	---	---	25.19	---
2,2-Me ₂ Butane	2-Methylpentane	---	27.42°	---	---	25.19	---
9.68	90.32	27.353	27.38	+0.03	25.907	25.85	-0.06
19.82	80.18	27.283	27.35	+0.07	26.659	26.57	-0.09
39.91	60.09	27.145	27.28	+0.13	28.147	28.04	-0.11
59.73	40.27	27.008	27.14	+0.13	29.616	29.53	-0.09
79.97	20.03	26.868	26.97	+0.10	31.116	31.03	-0.09
90.23	9.77	26.797	26.86	+0.06	31.876	31.82	-0.06
100.00	---	---	26.73	---	---	32.60	---

^a Calculated values based on assumption that data would be straight-line function. Differences show how observed data vary from such straight-line function.

mination of individual paraffin compounds which are present in a mixture. He deeply regrets the fact that Francis' previously published paper (3) on the analysis of butane-isobutane mixtures was overlooked. For this he offers his apology to Francis, who has made an extensive study of the critical solution temperature of various types of hydrocarbons in a wide variety of solvents (2).

EXPERIMENTAL

The apparatus and techniques used were the same as those previously described (5).

SOURCE OF HYDROCARBONS. Four of the five isomeric hexanes were obtained by carefully fractionating commercial mixed hexanes in automatic 100-plate columns (6). The fifth hexane, 2,2-dimethylbutane, was a synthetic product. The refractive index of each of these hydrocarbons compares favorably with that given in the literature (see Table I).

The critical solution temperatures obtained with aniline (Table I) by Wibaut and co-workers (7) and Maman (4) agree well enough (except for 2,2-dimethylbutane) to show that their methods were comparable. The data obtained with nitrobenzene by Maman (4) and the author are of the same order of magnitude except with 2,2-dimethylbutane. The refractive index obtained by Wibaut and the author for this hydrocarbon agree, while that of Maman (1.3705) is 0.0016 high. The densities given by Egloff (1) and Wibaut (0.6492) for this hydrocarbon agree, while that of Maman is 0.0026 high. These data indicate that the 2,2-dimethylbutane prepared by Maman contained some impurity which raised its refractive index and density and lowered its solution temperature in both aniline and nitrobenzene. The C.S.T. of 2,2-dimethylbutane in nitrobenzene which is reported by Maman, in addition to being considerably lower than that reported in the present work, is also lower than that reported by Woodburn and co-workers (8), whose C.S.T. values

with nitrobenzene in general are somewhat higher than those obtained here.

The data of Wibaut, Maman, and Woodburn are actual critical solution temperature data, while the author's data were obtained at a hydrocarbon concentration of 66.7% (by volume) with water-saturated hydrocarbons.

HYDROCARBON CONCENTRATION. In the earlier work, critical solution temperature curves for 2,2,3-trimethylbutane, 2,2-, and 2,4-dimethylpentane with nitrobenzene showed that a hydrocarbon concentration of 66.7% (by volume) was the best point at which to work with these heptanes.

The critical solution temperature curve for 2-methylpentane with nitrobenzene was determined through a limited range of concentration and the results obtained were very similar to those obtained with the heptanes and nitrobenzene. Thus, the proper concentration to use with the hexanes as well as with the heptanes is 3.00 ml. of hydrocarbon plus 1.50 ml. of nitrobenzene.

PREPARATION OF CALIBRATION CHARTS. Binary mixtures of freshly distilled 2,2- plus 2,3-dimethylbutane, 2-methylpentane plus 2,3-dimethylbutane, and 2-methylpentane plus 2,2-dimethylbutane were prepared by weight, the refractive index of each sample was determined at 20° C., and the samples were then saturated with water at 70° F. The solution temperature of each sample was determined with nitrobenzene and diethyl phthalate and the data obtained (Table II) were plotted on the same large scale that was used for the heptanes. These values fall within 0.01° of a smooth curve and again in all cases the observed values do not

fall on a straight line. There seems to be no consistency in either the direction or magnitude of this divergence from a straight-line function. The refractive index observations on these mixtures were within 0.0002 of those calculated from a linear relation.

Table III. Bath Temperature from Refractive Index

Solution Temperature, ° C.	% 2,3- in 2,2-	% 2,3- in 2-Me	% 2,2- in 2-Me
Diethyl phthalate point data			
27.00	---	6.2	76.7
26.00	9.1	19.4	---
25.00	22.1	32.3	---
24.00	35.2	45.1	---
23.00	48.6	57.6	---
22.00	62.2	69.7	---
21.00	76.4	81.6	---
20.00	90.7	92.9	---
Nitrobenzene point data			
32.00	6.0	---	92.6
31.00	16.3	---	79.5
30.00	26.9	---	66.1
29.00	37.7	---	52.7
28.00	48.4	---	39.4
27.00	59.3	---	25.7
26.00	70.3	---	11.8
25.00	81.5	10.5	---
24.00	92.8	66.6	---
Refractive index data, n_D^{20}			
1.3690	1.4	---	97.5
1.3700	15.7	---	68.2
1.3710	31.1	---	29.3
1.3720	47.0	8.2	---
1.3730	63.1	35.5	---
1.3740	79.5	63.3	---
1.3750	96.5	93.5	---

Table IV. Analysis of Hexane Ternary Mixtures

Sample No.	Solution Temperature		% 2,2-Dimethylbutane		Difference	% 2,3-Dimethylbutane		Difference	% 2-Methylpentane		Difference
	Diethyl phthalate	Nitrobenzene	Present	Found		Present	Found		Present	Found	
76	26.64	25.68	9.79	10.0	+0.21	9.93	10.2	+0.27	80.28	79.8	-0.48
77	23.47	24.98	9.69	10.1	+0.41	50.40	50.0	-0.40	39.91	39.9	-0.01
78	24.04	26.56	29.63	29.9	+0.27	40.53	40.0	-0.53	29.84	30.1	+0.26
79	20.89	24.42	9.68	10.1	+0.42	80.59	80.6	+0.01	9.73	9.3	-0.43
80	26.07	30.86	80.22	80.2	-0.02	9.95	9.6	-0.35	9.83	10.2	+0.37
81	23.75	28.02	49.68	49.8	+0.12	40.56	40.4	-0.16	9.76	9.8	+0.04

fractive index is concerned, a ternary mixture of 2,2- and 2,4-dimethylpentane with 2,2,3-trimethylbutane is essentially a heptane binary mixture.

ACCURACY OF METHOD. After all the calibration charts had been constructed from these experimental data from the binary mixtures,

six ternary mixtures of these pure hydrocarbons, in widely varying proportions by weight, were prepared and saturated with water at 70° F. The nitrobenzene and diethyl phthalate points of each sample were determined and from these data the percentage composition of each sample was determined graphically by the method described in the previous paper (5). When the percentage of each of the three components found was compared with that of each actually present, it was seen that the maximum deviation was 0.5% (Table IV). Points A, B and C, D (Figures 2 and 3) form the ends of the iso-nitrobenzene point and iso-diethyl phthalate point lines, respectively, for the graphical determination of the composition of the hexane ternary mixture sample 81 (Table IV).

This analysis is made possible by the fact that the iso-nitrobenzene point line again has a negative slope with respect to the iso-diethyl phthalate point line (see Figure 1). This results from a different order of increasing solution temperature for the three hydrocarbons with these two solvents:

	Diethyl Phthalate Point ° C.	Nitrobenzene Point ° C.
2,3-Dimethylbutane	19.37	23.38
2,2-Dimethylbutane	26.73	32.60
2-Methylpentane	27.42	25.19

The greater degree of accuracy with this hexane ternary mixture than with the heptane ternary mixture is due to the sharper angle of intersection of the iso-solution temperature lines obtained from the hexane solution temperature data. This is caused by the fact that the diethyl phthalate point of 2,3-dimethylbutane is comparatively widely separated from that of the other two hydrocarbons, while with nitrobenzene, in addition to reversal of the order of increasing solution temperature of 2,2-dimethylbutane and 2-methylpentane, the solution temperature of 2,2-dimethylbutane is comparatively widely divergent from that of the other two (see Figure 2):

ACKNOWLEDGMENT

The author wishes to thank C. R. Begeman for suggesting this problem and for distilling the hydrocarbons used in this investigation.

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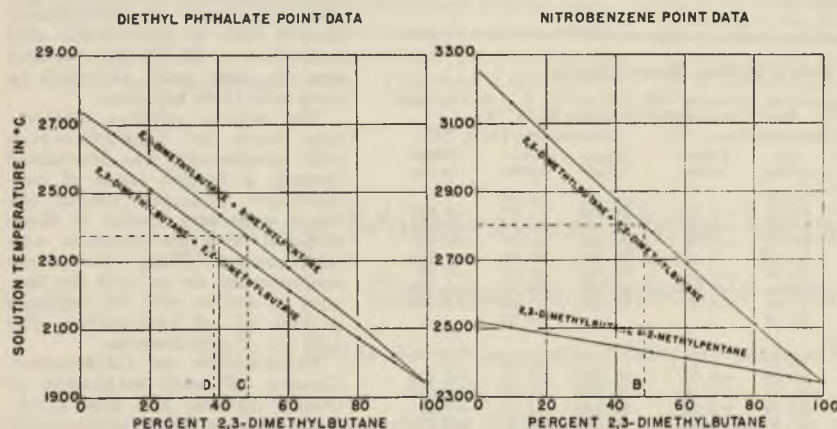


Figure 2. Diethyl Phthalate and Nitrobenzene Point Data

APPROXIMATE BATH TEMPERATURE OBTAINED FROM REFRACTIVE INDEX. The time required to make a solution temperature determination on an unknown sample can be considerably shortened if the approximate temperature at which to set the bath is known. This desired bath temperature setting can be obtained from a small-scale triangular plot of the iso-refractive index and iso-solution temperature lines (for an explanation of these terms see 5). The refractive index of the unknown sample is located on this chart and the approximate bath temperature can be read directly from the chart (see Figure 1 and Table III).

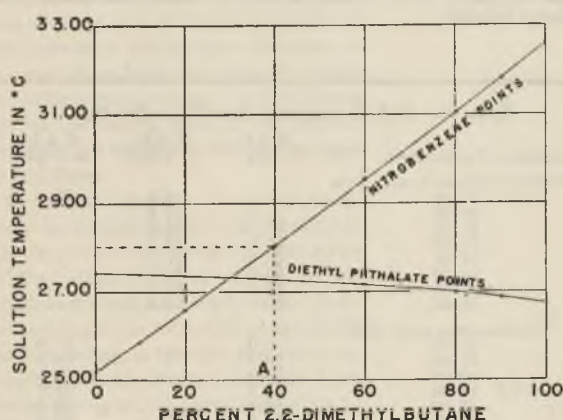


Figure 3. Solution Temperature of 2,2-Dimethylbutane plus 2-Methylpentane

This triangular graph does not give so accurate an approximation of the bath temperature setting as was obtained with the heptane ternary mixture; 2,4- and 2,2-dimethylpentane have practically the same refractive index, so that, as far as the re-

Identification of Sulfonated Azo-2-naphthol Dyes

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A rapid and simple method has been developed for the identification of sulfonated azo-2-naphthol dyes by catalytic reduction of the azo bond, and the separation of the scission products with ethanol. Equivalent weight determination of the aminosulfonic acid and its conversion to the *S*-benzyl isothiouraea derivative enable the analyst to differentiate between isomeric compounds. The method is not applicable to mixtures.

THE identification of the reduction products from sulfonated azo dyes usually presents many difficulties to the dyestuff chemist that are not encountered in the analysis of the analogous unsulfonated compounds. As shown in a previous paper (8), the differential solubility of the amines, diamines, and amino-2-naphthol in immiscible solvents can be used to effect their separation. The same procedure, however, is not applicable to the reduction products of the sulfonated azo-2-naphthol colors because it necessitates the introduction of a buffer salt which interferes with the isolation of the pure sulfonic acid.

Many analytical methods have been proposed for the characterization of aromatic sulfonated amines, and the literature on this subject has been thoroughly and excellently reviewed by Chambers and Watt (2) and Chen and Cross (3). The latter authors pointed out the complications involved in this type of analysis, and suggested the formation of the stable arylamine salts of the sulfonic acids as a means of identifying these compounds. The method involves the protective acetylation of the amino group, as a necessary preliminary to the formation of the

arylamine salt, and it does not include certain naphthylamine disulfonic acids which are of importance to the color chemist because of their use in the manufacture of certain commercial dyes.

Of the proposed procedures, only one, the formation of the *S*-benzylthiuronium salts of the sulfonated amines, showed evidence of being rapid in execution and simple in application (1, 2, 5, 6, 9). These derivatives are crystalline and have melting points which enable the analyst, in most cases, to differentiate between isomeric aminosulfonic acids. Where the melting points of the isomeric compounds are close to each other, the determination of the equivalent weight is a deciding factor, because of the presence of molecularly combined water (see footnotes to Table I). In all analyses the equivalent weight was found to be identical with the molecular weight.

The aminosulfonic acid, isolated from the reduction reaction, is purified by crystallization from water, and the establishment of the equivalent weight by titration with 0.1 *N* sodium hydroxide provides both an indication as to the identity of the acid and a convenient source for the formation of the desired derivative.

As in previous work (8), the hydrogenation apparatus of Cheronis and Koeck (4) was utilized for the reduction. The scission products of the sulfonated azo-2-naphthol dyes were separated from each other by means of the differential solubility of the aromatic aminosulfonic acid and the amino-2-naphthol in ethanol, the former being relatively insoluble.

Technical grades of aromatic aminosulfonic acids were used to synthesize the dyes, and the purification of the colors was not found to be necessary.

Table I. Identification of Sulfonated Azo-2-naphthol Dyes

Diazotized Aryl Aminosulfonic Acid	Molecular Weight		Yield of Crystallized Sulfonic Acid Gram	M.P. of Benzyl Isothiouraea Derivative		Sulfur Content of Benzyl Isothiouraea Derivative	
	Calcd.	Found		Observed (Uncorr.) ° C.	Literature ° C.	Calcd. %	Found %
1. Sulfanilic acid	173.1	170.5	0.242	184-5	187-8	18.68	18.78
2. Metanilic acid	173.1	173.3	0.134	147-8	----	18.68	18.67
3. 2-Aminotoluene-5-sulfonic acid	187.1	190.5	0.064	190-1	----	18.12	18.44
4. 4-Aminotoluene-2-sulfonic acid	187.1	188.0	0.260	153-4	----	18.12	18.28
5. 4-Aminotoluene-3-sulfonic acid	187.1	188.2	0.261	168-9	----	18.12	18.28
6. 4-Amino- <i>m</i> -xylene-6-sulfonic acid	201.2	201.0	0.174	152-3	----	17.44	17.23
7. 3-Chloro-4-aminobenzene sulfonic acid	207.5	209.3	0.081	191-2	----	9.49 ^a	9.69 ^a
8. 2-Amino-4-chlorobenzene sulfonic acid	207.5	211.0	0.100	195-6	----	9.49 ^a	9.39 ^a
9. 2-Amino-5-chlorobenzene sulfonic acid	207.5	211.5	0.100	180-1	----	9.49 ^a	9.98 ^a
10. 3-Amino-6-chlorotoluene-4-sulfonic acid (Red Lake C base)	221.5	217.3	0.245	171-2	----	16.51	16.80
11. 2-Chloro-4-aminotoluene-5-sulfonic acid (2 B acid)	221.5	217.5	0.120	163-4	----	9.15 ^a	9.10 ^a
12. 1-Aminonaphthalene-6-sulfonic acid (Cleve's acid 1-6)	223.1	223.4	0.132	190-1	----	16.44	16.55
13. 1-Aminonaphthalene-7-sulfonic acid (Cleve's acid 1-7)	223.1	224.2	0.194	163-4	----	16.44	16.49
14. 2-Aminonaphthalene-1-sulfonic acid (Tobias acid)	223.1	223.3	0.178	138-9	----	16.44	16.68
15. 1-Aminonaphthalene-4-sulfonic acid (naphthionic acid)	223.1	224.0	0.356	96-7	195.1 ^b , 103-4 ^c	16.44	15.96
16. 1-Aminonaphthalene-5-sulfonic acid (Laurent's acid)	223.1	223.5	0.247	182-3	179.4	16.44	16.52
17. 2-Aminonaphthalene-6-sulfonic acid (Broenner's acid)	223.1	233.2 ^d	0.278	182-3	----	16.44	16.53
18. 1-Aminonaphthalene-8-sulfonic acid ^e (Peri acid)	223.1	237.5 ^d	0.048	150-2	300 (dec.) ^b	16.44	16.45
19. 4-Amino-2,5-dichloroaniline-4-sulfonic acid	242.0	246.5	0.090	181-2	----	17.37 ^a	17.64 ^a
20. 2-Aminobenzene-1,4-disulfonic acid	253.1	337.5 ^f	0.272	176-7	----	21.87 ^g	22.06 ^g
21. 1-Aminonaphthalene-4,8-disulfonic acid (disulfonic acid S)	303.2	312.2 ^h	0.130	213-4	----	20.14 ^g	20.40 ^g
22. 2-Aminonaphthalene-3,6-disulfonic acid (Amino R acid)	303.2	393.0 ⁱ	0.314	202-3	----	20.14 ^g	20.06 ^g
23. 2-Aminonaphthalene-4,8-disulfonic acid	303.2	388.5 ^j	0.396	226-7	209-11 (dec.) ^j	20.14 ^g	20.42 ^g
24. 2-Aminonaphthalene-6,8-disulfonic acid (amino G acid) ^k	303.2	368.5 ^k	0.201	oil	276 (dec.) ^j	20.14 ^g	----

^a Halogen content.

^b Chambers and Watt (2) report presence of 20 moles of water.

^c Hennion and Schmidle (7).

^d Purified sample showed presence of 1 mole of water, on titrating with 0.1 *N* sodium hydroxide.

^e Benzyl derivative of amino-2-naphthol not isolated.

^f Isolated as acid barium salt, with 1 mole of water.

^g Calculated as double benzyl isothiouraea derivative.

^h If barium salt of dye is used, acid barium salt will be isolated.

ⁱ Excessive decomposition of amino-2-naphthol occurred, and no benzoyl derivative isolated.

^j Chambers and Watt (2) report presence of 1 mole of water.

^k Isolated as acid barium salt.

^l Chambers and Watt (2) report presence of 8 moles of water.

GENERAL PROCEDURE

PREPARATION OF REDUCTION PRODUCTS. Freshly ground Adams-Voorhees platinum oxide (0.05 gram) is placed in the Cheronis hydrogenating unit, and the catalyst is suspended in 20 ml. of distilled water. Hydrogen gas at atmospheric pressure, preferably from a tank, is bubbled through the suspension for 2 to 5 minutes, in order to convert the platinum oxide to colloidal platinum black.

Then 1 gram of dye, 10 ml. of concentrated hydrochloric acid, and 30 ml. of isopropyl alcohol are added to the platinum black suspension, the hydrogenating unit is heated by immersion in hot water to 80° to 90° C., and hydrogen gas is passed through the mixture at such a rate that continuous agitation is maintained. The end of the reduction is indicated by decolorization of the dye solution.

SEPARATION OF REDUCTION PRODUCTS. The isopropyl alcohol-water mixture of the scission products is transferred to an evaporating dish, 0.25 ml. of a stannous chloride solution containing 100 grams of stannous chloride in concentrated hydrochloric acid per 100 ml. of solution is added to prevent excessive decomposition of the amino-2-naphthol, and the mixture is evaporated to dryness on the steam bath. The dried residue is triturated with 25 ml. of 95% ethanol for about 1 minute, filtered, and washed with 10 ml. more of the solvent.

Then 0.25 ml. of the stannous chloride solution is added to the filtrate containing the amino-2-naphthol, the ethanol is removed by evaporation, and 5 ml. of benzoyl chloride and 200 ml. of a 5% sodium hydroxide solution are added to convert the amino derivative of the coupling component to the dibenzoyl compound. Crystallization from 95% ethanol gives a product that has a melting point of 232-3° C.

The alcohol-insoluble aminosulfonic acid is crystallized from water that has been acidified with 5 ml. of 6 *N* hydrochloric acid, and to which has been added a small quantity of Norite. After filtration, the solution is concentrated to a very small volume and chilled in the refrigerator, usually overnight. The precipitate is collected, washed with a few milliliters of 95% ethanol, and dried at 110° C.

A weighed quantity of the acid is dissolved in 100 to 200 ml. of water, heated if necessary to effect solution, and titrated with

0.1 *N* sodium hydroxide to determine its equivalent weight, using phenolphthalein as the indicator. (Acids that do not dissolve in water titrate with no detectable decrease in accuracy.) The sodium salt of the sulfonic acid is concentrated to 4 to 10 ml., depending upon the original quantity of acid, and is cooled and added to 1.5 times its weight of *S*-benzyl isothiurea hydrochloride, dissolved in 2 to 5 ml. of water. The derivative usually precipitates out immediately or, if not, does so on stirring. If an oil results, standing overnight causes solidification of all but one of the acids studied. One crystallization from a minimum quantity of water, using decolorizing Norite, usually yields the correct melting point of the aminosulfonic acid derivative.

Occasionally, the presence of excessive inorganic adulterant in the original dye will result in an exceptionally small crop of the purified aminosulfonic acid. When such is the case, the analyst can start with a larger color sample or, when an additional sample is not available, the mother liquor containing residual aminosulfonic acid can be evaporated to dryness. Sulfonic acid can be converted to the *S*-benzyl isothiurea derivative by titrating to a phenolphthalein end point and adding the concentrated solution of the sodium salt to 0.2 gram of the addition component.

ACKNOWLEDGMENT

The authors wish to express their appreciation to their director, W. C. Bainbridge, for his kind encouragement in this work.

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Quantitative Determination of Bases by Means of Calomel Application to Lime in Commercial Calcium Arsenate

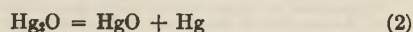
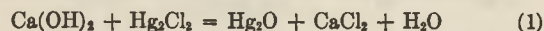
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A NEW method for the determination of bases depends upon the reaction between the base and calomel (mercurous chloride). Of special interest is the determination of free (uncombined) lime in commercial calcium arsenate, which contains calcium hydroxide in variable amounts up to about 12%. The following exposition, therefore, relates chiefly to the reaction between lime and calomel. Although known for a long time (it is the basis of the preparation of *Lotio nigra*, N.F.), its application to the determination of basic compounds appears to be new.

THEORY

When calcium oxide or hydroxide, calomel, and water are brought together, immediate blackening occurs. The liquid portion of the mixture gives a positive test for chloride ion, and for mercury (with either sodium sulfide or stannous chloride), but a negative test for mercurous ion (with hydrochloric acid). The dissolved mercury is therefore present as mercuric ion. The reaction is probably complicated but may be represented as follows:



The significant feature of the reaction is the formation of soluble chloride, which, with excess of calomel, forms in quantity stoichiometrically equivalent to the hydroxide.

Formation of mercuric oxide is visually confirmed by a glimpse of yellow precipitate. This precipitate quickly disappears, however, probably because of the incompatibility of mercuric oxide with soluble chloride, leading to solubility of the oxide as a loose, water-soluble complex. This view is in agreement with the known increased solubility of mercuric oxide in the presence of chloride (1). The formation of mercuric ion requires the breakdown of the mercurous oxide (Equation 2), with consequent formation of elemental mercury, to which the blackening is due.

Since the quantity of soluble chloride formed is chemically equivalent to the hydroxide originally present, determination of the latter follows simply by determining the chloride. Excess of calomel does not interfere, since it is insoluble. The chloride determination is conveniently made by direct titration with silver nitrate or, where this procedure is inapplicable, by the Volhard method. In either case the dissolved mercury must first be removed. As a practical means of removing mercury ion the solution is treated with a more electropositive metal, zinc being suitable for the purpose.

EXPERIMENTAL

TESTS WITH LIME. Experiments were first made on pure Iceland spar to establish validity of the method. A known weight

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Table I. Analysis of Iceland Spar

[1 ml. of 0.1 N AgNO ₃ = 3.705 mg. of Ca(OH) ₂ or 5.005 mg. of CaCO ₃]			
Spar Taken Mg.	Ca(OH) ₂ Mg.	CaCO ₃ Mg.	Recovery %
58.8	43.5	58.8	100
52.2	38.2	51.6	99
62.5	46.7	63.1	101
58.3	43.5	58.8	101

of ground spar was ignited to constant weight. The resulting calcium oxide was mixed with 2 to 3 times the equivalent of calomel (1 gram of CaO = 8.4 grams of Hg₂Cl₂), water added, the mixture stirred well a few minutes, and the black deposit filtered off and washed free of soluble chloride. The filtrate was stirred well with zinc dust and the residue filtered off and washed free of chloride. The second filtrate was then titrated with silver nitrate solution, with potassium chromate or dichlorofluorescein as indicator.

In a series of experiments, each involving about 60 mg. of spar, the recovery ranged from 99 to 101% (Table I). The reaction was, therefore, shown to be quantitative.

TESTS WITH CALCIUM ARSENATE. The foregoing procedure must be modified for analysis of a material such as commercial calcium arsenate, which hydrolyzes to produce alkali in addition to the free lime. The modification consists in conducting the reaction at a fixed volume, thereby standardizing to that degree the conditions of hydrolysis. Tests conducted at volumes ranging from 100 to 500 ml. gave a slight increase in result with increased dilution, amounting to about 3.5% for the range stated. There was no measurable difference between volumes of 100 and 200 ml., and the latter volume was selected as a matter of convenience. It was found necessary to agitate the mixture for at least 0.5 hour to attain complete reaction—that is, to reach the maximum value. The appreciable time required for calcium arsenate in contrast to the short time for a simple material like calcium hydroxide suggests a close union or interlocking of free lime and the arsenate. The following procedure was adopted:

A 1-gram sample of calcium arsenate in a 250-ml. glass-stoppered Erlenmeyer flask was mixed well with about 3 grams of calomel. Exactly 200 ml. of freshly boiled and cooled distilled water were added, followed by mechanical agitation (end over end) for 0.5 hour. The solution was filtered twice through a dry paper. About 3 grams of zinc dust were added to the filtrate, with thorough stirring. After another filtration a 150-ml. aliquant was taken for the titration, conducted by the Volhard method. (Titration methods requiring neutral solution are not applicable, owing to precipitation of silver arsenate.)

Three samples of commercial calcium arsenate were analyzed by this (calomel) method, and also by the acidimetric method of Smith and Hendricks (3), which has been heretofore generally used for this purpose. The results calculated to Ca(OH)₂ are shown in Table II, which includes results obtained by the calomel method on the same samples to which known amounts of calcium hydroxide were added.

The calomel method shows satisfactory agreement with the acidimetric method. The recovery of added calcium hydroxide is also satisfactory. The three samples analyzed represent types of high, medium, and low water-soluble arsenic content, containing 10.8, 6.9, and 1.3% of As₂O₃, respectively, as determined by the Geneva method (2). The new procedure is evidently suitable for any commercial calcium arsenate.

The calomel method possesses two advantages over the older method: The argentometric end point is sharper than the acidimetric end point; and the presence of dyes, which occur in some calcium arsenates, makes determination by the older method difficult but does not interfere in the calomel method.

Since commercial calcium arsenate usually contains other substances that might react with calomel—viz., calcium carbonate, normally present to the extent of several per cent, and magnesium hydroxide, seldom present to more than 1%—these were also investigated. Calcium carbonate in the form of Iceland spar, gave an apparent calcium hydroxide content of 0.4%, independent of the quantity taken, whether 1 or 10 grams. The error caused

in a sample containing 5% of calcium carbonate would therefore be only 0.02%. Actually, the result obtained on a mixture of 1 gram of calcium carbonate and 1 gram of calcium arsenate was not measurably different from that on the calcium arsenate alone.

Magnesium hydroxide responds to the calomel method in the same way as calcium hydroxide; a sample of magnesium oxide showing 79.2% MgO content by acid titration gave 78.0% by the calomel treatment. The calomel method, therefore, like that of Smith and Hendricks (3), when applied to calcium arsenate gives a measure of both calcium and magnesium hydroxides—i.e., total basicity, which is ordinarily referred to as "free lime" because of the almost negligible content of magnesium hydroxide. Although magnesium hydroxide causes a poor end point in the acidimetric titration, the argentometric end point is unaffected.

OTHER APPLICATIONS. As the foregoing equations suggest, the reaction is a general one for bases and is therefore applicable in other cases. For example, the normality of a solution of sodium hydroxide was determined as 0.0728 by the calomel method, which agrees well with 0.0730 found by acid titration. Ammonium hydroxide, of course, cannot be so determined because of the formation of mercuric aminochloride or similar complex. Another application of the reaction is in the determination of calomel, for which excess of base is taken; preliminary experiments have given satisfactory results.

Table II. Analysis of Samples of Commercial Calcium Arsenate

Ca(OH) ₂ Found		Ca(OH) ₂ Added Mg.	Added Ca(OH) ₂ Recovered	
Calomel method %	Acidimetric method %		Mg.	%
3.3	3.4	178.6	174.8	97.9
5.8	5.6	178.6	177.8	99.6
4.1	4.0	178.6	178.3	99.8

CONCLUSION

The calomel method as outlined affords a reliable, convenient means of determining bases. For the determination of free lime in commercial calcium arsenate it possesses certain advantages over the acidimetric method of Smith and Hendricks, giving a sharp end point even in the presence of magnesium hydroxide, and being unaffected by dyes. The reaction may also be adapted to the determination of calomel.

SUMMARY

The reaction between bases, except ammonium hydroxide, and excess calomel, evidenced by immediate blackening, proceeds quantitatively with the formation of soluble chloride in amount stoichiometrically equivalent to the quantity of base present. After removal of dissolved mercury by means of zinc, the soluble chloride is determined by argentometric titration.

1 ml. of 0.1 N AgNO₃ = 3.705 mg. of Ca(OH)₂

Results obtained by this method in the determination of free lime in calcium arsenate agree well with those by the acidimetric method of Smith and Hendricks. The calomel method possesses the following advantages over the acidimetric method: The end point is sharp even in the presence of magnesium hydroxide, and the method is applicable in the presence of dyes. By employing a base in excess, calomel may be determined.

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Metallo-Organic Complexes in Organic Analysis

Colorimetric Determination of Alcohols

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A colorimetric method for alcohols based upon the reaction with ammonium hexanitratocerate makes possible determination of relatively small amounts of alcohol in mixtures with approximately 5% accuracy. The disadvantages of the method are the low stability of the color and the interference of certain common reducing agents.

THE red coordination complex produced upon the addition of an alcohol to ammonium hexanitratocerate solution has been used qualitatively to identify the alcoholic hydroxyl group (1). Primary and secondary alcohols slowly reduce the cerium to the trivalent state with resultant dissipation of color (1). It was found, however, that with concentrations of alcohols in the colorimetric range, the extinction decay with time is a straight-line function for 15 minutes or more, allowing extrapolation to zero time. Although the sensitivity of the method is lowered, the cerate solution is prepared without acidification to increase the color stability.

REAGENTS AND APPARATUS

AMMONIUM HEXANITRATOCERATE SOLUTION. The commercial product was dissolved in the minimum amount of water, and diluted so that 1 liter contained 667 grams of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. Filtration through sintered glass or fine glass cotton is necessary if the solution is cloudy.

ALCOHOL SOLUTIONS. Alcohols of the best commercial grade were diluted with water to 5% alcohol by volume.

A CENCO-SHEARD SPECTROPHOTOMETER was used throughout the investigation. The entering and exit slit widths were held constant at 1 mm. and 10 μ , respectively.

Table I. Color Stability at Room Temperature

Alcohol	Decrease in Extinction % per min.	Alcohol	Decrease in Extinction % per min.
Methanol	1.1	Isobutanol	0.95
Ethanol	1.0	Isopropanol	0.37
n-Propanol	1.1	sec-Butanol	0.36
n-Butanol	1.0	tert-Butanol	Stable

EXPERIMENTAL

OPTIMUM CERATE CONCENTRATION. To 25-ml. volumetric flasks were added in duplicate 1.0, 1.5, 2.0, 2.5, 3.0, and 5.0 ml. of the stock cerate solution. The duplicate in each case was diluted to the mark with water, and to the other flask were added 0.5 ml. of 5% ethanol and water to the mark. Using the corresponding aqueous cerate as a blank, the transmission of each ethanol solution was measured at 475 μ . The decrease in transmission with increasing cerate concentration was very marked to between 2.5 and 3.0 ml. of cerate per 25 ml., but was small between 3.0 and 5.0 ml. of cerate per 25 ml. Therefore, 2.5 ml. of stock solution per 25 ml. were selected as providing the optimum cerate concentration.

TRANSMISSION MINIMUM. *tert*-Butanol which produces a stable color was selected for the measurements of the transmission over the range of wave lengths 400 μ to 700 μ . Five milliliters of the 5% alcohol solution were added to 2.5 ml. of the cerate solution, and the mixture was diluted to 25 ml. The reference was an identical solution of cerate without the alcohol. A transmission minimum was found in the range 460 to 475 μ ; this minimum was duplicated using ethanol in place of *tert*-butanol. Because the transmission of the reference increased sharply from 460 to 475 μ , the latter wave length was selected for the determinations. The butanol curves are shown in Figure 1.

COLOR STABILITY. Employing the wave length and concentrations selected as described, the decay of the extinction with time was measured for three different concentrations of each of the eight lower aliphatic alcohols, methanol through the butanols.

The percentage rate of decay was found to be substantially independent of concentration and a straight-line function for at least 15 minutes for the higher concentrations (Table I).

EXTINCTION vs. CONCENTRATION CURVES. Working curves were prepared for the alcohols methanol through the butanols. The time of mixing and the time of reading in each case were recorded and the extinctions were corrected to zero time, using the formula

$$E_x = \frac{100 E_m}{100 - A_t}$$

where E_x is the extinction at zero time, E_m the measured extinction, A the percentage decay per minute (from Table I), and t the time in minutes. The plots of molar concentration vs. extinction at zero time appear in Figure 2.

PROCEDURE. To 2.5 ml. of the stock cerate solution in a 25-ml. volumetric flask is added the unknown alcoholic solution. After dilution to the mark and thorough mixing, the extinction is read

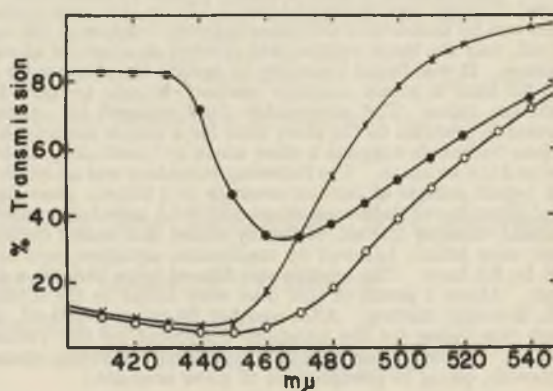


Figure 1. Butanol Curves

x. Cerate vs. water
o. Cerate plus alcohol vs. water
●. Cerate plus alcohol vs. cerate

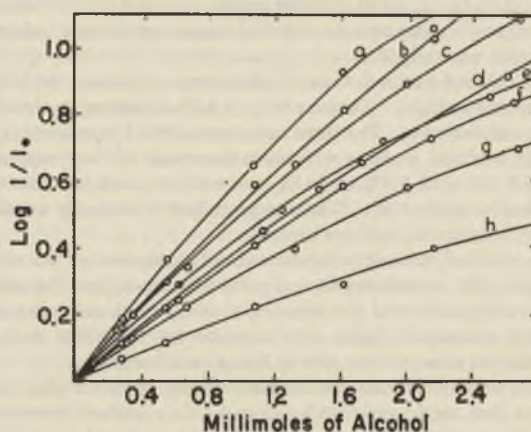


Figure 2. Extinction vs. Concentration Curves

a. Isobutanol
b. n-Butanol
c. n-Propanol
d. Ethanol
e. Methanol
f. sec-Butanol
g. Isopropanol
h. tert-Butanol

Table II. Analysis of Pure Aqueous Alcohols

Alcohol	Taken Mg.	Found Mg.	Error %
Methanol	60	58	-3.3
Ethanol	80	79	-1.2
n-Propanol	40	41	+2.5
Isopropanol	40	42	+5.0
n-Butanol	120	123	+2.5
Isobutanol	40	38	-5.0
sec-Butanol	80	83	+3.8

Table III. Analysis of Aqueous Ethanol, Other Substances Present

Solvent Present Ml.	Ethanol Taken Mg.	Ethanol Found Mg.	Error %
Acetone, 10	80	72	-10
Acetone, 2.5	40	39	-2.5
Dioxane, 10	40	39	-2.5
Ethyl acetate ^a	80	81	+1.2
Ether ^a	40	40	0
Acetaldehyde, 2.5	40	45	+12.5
Butyraldehyde ^a	80	81	+1.2
Acetic acid, 0.2	80	73	-9
Acetic acid, 2	40	4.3	-90

^a 20 ml. of saturated aqueous solution present.

at 475 m μ , the reference being an identical solution minus the unknown. The time of mixing and the time of reading are recorded, and one or two additional readings are taken at 2 to 3 minute intervals. The extinction extrapolated to zero time is compared with the working curve to find the amount of alcohol present. If pure aqueous alcohol is being determined, the method of extrapolation used in the above paragraph may be employed. The reference solution should be replaced each half hour, because in dilute solutions the cerate has a tendency to change color due to a hydrolytic reaction which finally results in the precipitation of basic ceric nitrate.

INTERFERENCES. Phenols, enols, and aromatic amines interfere by producing anomalous colors. 1,2-Oxygen-containing

compounds are good reducing agents for tetravalent cerium (3) and therefore should be absent. Ethylene glycol is the only member of this series which yields a stable enough color for determination. Formaldehyde, acetaldehyde, and propionaldehyde interfere, the former by reducing the cerium, and the others by producing varying amounts of color. For example, pure acetaldehyde which has stood at 20° C. appears to have the extinction of about 1% aqueous ethanol, while that kept at 0° C. yields the color of a 5 to 10% alcoholic solution, and propionaldehyde behaves similarly to a lesser extent; the polymeric forms of these aldehydes probably contain hydroxyl groups. No common inorganic reducing agents, bases, or highly colored compounds may be present. The alcohol should be separated from all common anions by distillation of the neutral solution, because all common anions compete with the alcohol in complex formation. Very high concentrations of noninterfering organic compounds cause deviation of the time extrapolation from a straight line. The method is not useful on mixtures immiscible with the reagent, although water extracts methanol and ethanol quantitatively from most mixtures of this type (2).

APPLICATION OF PROCEDURE. Pure aqueous alcohol solutions were analyzed (Table II).

Solutions of ethanol containing large amounts of common nonalcoholic solvents were analyzed with the results listed in Table III.

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Colorimetric Determination of Molybdenum in Iron and Steel

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A photometric method for determining molybdenum in ferrous metals employs water-soluble solvents of low volatility which produce a very stable molybdenum-thiocyanate complex color without the necessity for extraction. Interferences and their elimination, as well as the precision and accuracy of the method, are discussed.

WITH recent progress in the manufacture of precision electric photometric apparatus, colorimetric methods for routine analyses have greatly simplified many determinations. One of these is the determination of molybdenum by measuring the intensity of the color of the molybdenum-thiocyanate complex. This molybdenum complex is customarily extracted from solution, after reduction by stannous chloride, using ether (5, 6), butyl acetate (4), or cyclohexanol (3) as extractants. The limitations of these solvents (2) and of the extraction method became apparent when an attempt was made to standardize a routine method for use with a Fisher A.C. Model photometer using 23-ml. absorption cells.

In an attempt to overcome these limitations and to develop a method characterized by the ease and simplicity of a direct determination the possibility of using water-soluble, less volatile solvents, the glycol ethers was studied. Those available for immediate considerations were Cellosolve, diethyl Cellosolve, butyl Cellosolve, Carbitol, methyl Carbitol, and butyl Carbitol obtained from the Carbide and Carbon Chemicals Corp.

EXPERIMENTAL

Preliminary investigation showed that the molybdenum-thiocyanate complex color was strongly developed in solution,

without the necessity of extraction. The method developed for carbon and alloy steels and cast irons consists of dissolving the sample in perchloric acid, adding the appropriate solvent, and developing the color subsequently with potassium thiocyanate and stannous chloride.

In high-chromium and stainless steels it was necessary to remove most of the chromium in order to get the required accuracy; the procedure outlined by Smith (8) for volatilizing the chromium as chromyl chloride was found effective.

As perchloric acid is unsatisfactory for dissolving tungsten steels, the methods of Cunningham (1), Smith (9), and Poole (7) were investigated. The perchloric-phosphoric acid mixtures (7, 9) were further studied, since they conformed more to the procedures adopted for the other steels. Subsequent work revealed that the acid ratio of Smith (9) provided the optimum solvent for the sample weight taken and it was therefore chosen for more complete study.

The transmittance characteristics of the color developed using butyl Cellosolve and butyl Carbitol were checked with a universal spectrophotometer and it was found that maximum absorption occurred at a wave length of approximately 470 m μ . Accordingly a Corning filter No. 430 having a maximum transmittance of light of this wave length was used for all subsequent work.

The least amount of solvent that could be added conveniently and still ensure maximum color development was determined to be 15 ml. Less than this led to a rapid fading of the color, while more produced no increase in intensity.

Figure 1 shows the results obtained, using the six solvents mentioned above, on National Bureau of Standards steel 72b containing 0.223% molybdenum. Obviously, on the basis of color

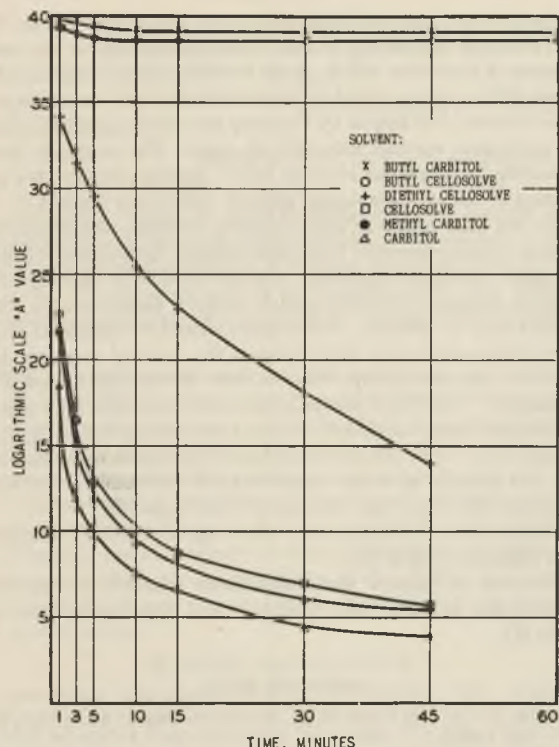


Figure 1. Time Studies of Color Stability of Molybdenum Thiocyanate Complex in Various Solvents

stability, butyl Cellosolve and butyl Carbitol are superior to the others.

These two solvents were chosen for time studies of the color stability of the molybdenum-thiocyanate complex at various concentrations. As can be seen from Figure 2, this color attains maximum stability 10 minutes after its development and remains stable for at least 90 minutes. The molybdenum concentrations in the Bureau of Standards steels used are listed in Table I. From these concentrations and the logarithmic scale values obtained, the standard curves shown in Figure 3 were developed.

REAGENTS

POTASSIUM THIOCYANATE SOLUTION. Dissolve 50 grams of c.p. potassium thiocyanate in distilled water and dilute to 1 liter.

STANNOUS CHLORIDE SOLUTION. Dissolve 350 grams of stannous chloride dihydrate in 250 ml. of concentrated hydrochloric acid, using a temperature of 50° C. or less to effect solution. Cool, add 250 ml. of water, transfer to a 1-liter volumetric flask, and dilute to the mark with 1 to 1 hydrochloric acid. If clear, add 3 to 5 grams of c.p. metallic tin and let stand 24 hours. If not clear, let stand 24 hours, filter, and add 3 to 5 grams of c.p. metallic tin.

PHOSPHORIC-PERCHLORIC ACID MIXTURE. To 500 ml. of water, add 333 ml. of phosphoric acid (85%) and 167 ml. of perchloric acid (70 to 72%). Thoroughly mix and cool.

SOLVENT. Butyl Cellosolve (ethylene glycol monobutyl ether) or butyl Carbitol (diethylene glycol monobutyl ether) made by Carbide and Carbon Chemicals Corp.

ANALYTICAL PROCEDURE

CARBON AND LOW-ALLOY STEELS. Dissolve 1.0 gram of the sample in 5 ml. of 1 to 1 hydrochloric acid and 15 ml. of perchloric acid (70 to 72%) using a covered 300-ml. tall-form lipped beaker. [For steels containing over 0.5% carbon or 0.05% sulfur, dissolve first in 20 ml. of 1 to 1 hydrochloric acid. Add concentrated nitric acid dropwise to complete oxidation, cool slightly, then add 15 ml. of perchloric acid (70 to 72%).] Heat gently to dense fumes and continue fuming for 5 to 7 minutes. Cool slightly, then submerge in cold running water. Add 20

Table I. National Bureau of Standards Steels Used in Establishing Figure 3

	Steel No.	Certificate Value, % Mo		Steel No.	Certificate Value, % Mo
1	72b	0.223	5	33c	0.032
2	106a	0.203	6	65b	0.006
3	72	0.149		11e	0.007
4	32c	0.063			

Nos. 1 to 6 refer to position in Figure 2.

ml. of water to dissolve salts and boil 3 to 5 minutes. Cool, transfer quantitatively to a 200-ml. volumetric flask, dilute to the mark with distilled water, and mix thoroughly.

Pipet exactly 25 ml. of the above into a 100-ml. volumetric flask, and add from a buret and in the following order, with swirling, 15 ml. of solvent, 5 ml. of potassium thiocyanate, and 5 ml. of stannous chloride. Dilute to the mark, immediately after adding the stannous chloride, with distilled water and mix thoroughly. Let stand 10 minutes and measure the color photometrically.

HIGH-CHROMIUM AND STAINLESS STEELS. Dissolve 1.0 gram of the steel in 5 ml. of 1 to 1 hydrochloric acid and 20 ml. of perchloric acid (70 to 72%) using a 500-ml. Erlenmeyer flask or a covered 300-ml. tall-form lipped beaker. Heat gently to dense fumes and continue fuming 5 to 7 minutes. Cool slightly and add 1 to 2 ml. of concentrated hydrochloric acid while swirling the vessel. Heat again until dense fumes are evolved. Repeat addition of hydrochloric acid and subsequent heating until yellowish-orange fumes of chromyl chloride cease to be evolved. During volatilization, it may be necessary to add perchloric acid to prevent crystallization. When the chromium content has been reduced as much as possible, cool the solution, add 20 ml. of water, and proceed as for carbon and low-alloy steels.

If the high-alloy steel sample dissolves with difficulty in the above acid mixture, it may be dissolved first in 20 ml. of 1 to 1 hydrochloric acid, followed by dropwise oxidation with concen-

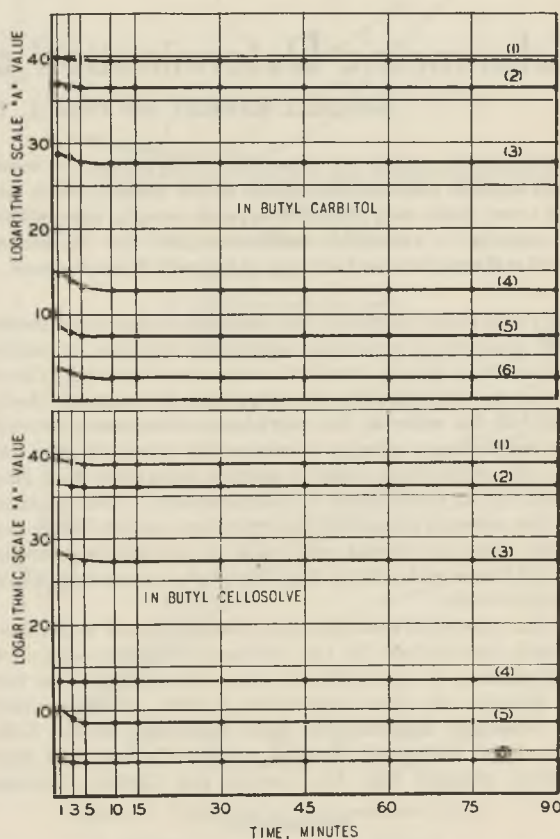


Figure 2. Time Studies of Color Stability at Various Concentrations of Molybdenum Thiocyanate Complex

Table II. Analysis of National Bureau of Standards Samples

Sample No.	Type	Additions	Certificate Value	Proposed Method	Deviation
			% Mo	% Mo	% Mo
10e	Bessemer		0.010	0.011	+0.001
30b	Cr, V (SAE 6135)		0.014	0.014	0.000
19d	A.O.H.		0.017	0.016	-0.001
33e	Ni (SAE 2335)		0.032	0.032	0.000
30d	Cr, V (SAE 6135)		0.034	0.035	+0.001
		20% W	0.034	0.036	+0.002
20d	A.O.H.		0.062	0.063	+0.001
32c	Cr, Ni (SAE 3140)		0.063	0.065	+0.002
		20% W	0.063	0.062	-0.001
72	Cr, Mo (SAE X4130)		0.149	0.152	+0.003
		20% W	0.149	0.152	+0.003
			0.149	0.150	+0.001
106a	Cr, Mo, Al (Nitalloy G)		0.203	0.203	0.000
		20% W	0.203	0.202	-0.001
			0.203	0.203	0.000
111a	Ni, Mo (SAE 4620)		0.203	0.205	+0.002
		20% W	0.222	0.224	+0.002
			0.222	0.222	0.000
			0.222	0.224	+0.002
130	Lead-bearing		0.222	0.223	+0.001
8f	Bessemer	0.225% Mo	0.003	0.224	-0.004
135	5 Cr, 0.5 Mo	0.225% Mo	0.001	0.225	-0.001
			0.575	0.570	-0.005
			0.575	0.574	-0.001
			0.575	0.566	-0.009
133	14 Cr, 0.6 Mo		0.559	0.564	+0.005
			0.559	0.558	-0.001
			0.559	0.551	-0.008
73a	14 Cr		0.069	0.069	0.000
36	2 Cr, 1 Mo		1.01	0.996	-0.014
			1.01	1.008	-0.002
			1.01	1.004	-0.006
101a	18 Cr, 9 Ni (SAE 30-905)	0.225% Mo	0.010	0.240	+0.005
121a	18 Cr, 10 Ni (Ti-bearing)	0.225% Mo	0.020	0.249	+0.004
21c	A.O.H.	18% W, 4% Cr, 1% V, 0.225% Mo	0.005	0.239	+0.009
50	18 W, 4 Cr, 1 V	0.225% Mo	0.01	0.250*	+0.015
6e	Cast iron	0.225% Mo	0.016	0.243	+0.002
	Cast iron	0.225% Mo	0.016	0.245	+0.004

* Average of 12 determinations, 0.5-gram sample used.

trated nitric acid, and subsequent addition of and fuming with perchloric acid.

For volatilization of the chromium as chromyl chloride, 1 to 2 grams of sodium chloride salt may be used rather than concentrated hydrochloric acid. This, however, produces a high salt concentration which may lead to troublesome crystallization before elimination of enough chromium.

TUNGSTEN STEEL. Dissolve a 0.5-gram sample with 20 ml. of phosphoric-perchloric acid mixture in a covered 300-ml. tall-form beaker. (For larger samples use a proportionately greater volume of acid.) Apply heat slowly until sample is completely dissolved and begins to fume gently (approximately 175° to 190° C.). When solution is complete, as indicated by its clear green or brown color, cool slightly and add 10 ml. of perchloric acid (70 to 72%). Reheat this solution until dense fumes of acid are evolved. Reduce the chromium content, volatilizing it as chromyl chloride, by adding dropwise successive 2- to 3-ml. portions of concentrated hydrochloric acid; the solution will assume a green color with formation of reduced chromium. Heat again until dense fumes are evolved.

Repeat the addition of hydrochloric acid and subsequent heating until the yellowish-orange chromyl chloride ceases to be evolved. During this volatilization it is necessary to replace the lost perchloric acid by cooling and adding 5-ml. portions. When the chromium concentration has been reduced as much as possible, cool the solution and add 5 ml. of perchloric acid (70 to 72%). Heat to fuming and continue fuming for 3 to 4 minutes to remove the last traces of hydrochloric acid. Cool, dilute to approximately 100 ml. with water, mix thoroughly, and boil 2 to 4 minutes. Again cool, transfer to a 200-ml. volumetric flask, dilute to the mark, and mix. From this, pipet exactly a 25-ml. aliquot into a 100-ml. volumetric flask, and add 10 ml. of sulfuric acid (1 to 1). Cool under water and add successively, and while swirling the flask, 15 ml. of solvent, 5 ml. of potassium thiocyanate, and 5 ml. of stannous chloride. Dilute to the mark with water, immediately after adding the stannous chloride. Let stand 20 minutes before measuring the developed color on the photometer, using a 470-A filter.

Certain precautions must be followed to prevent precipitation of tungsten. The addition of more perchloric acid than that recommended, following solution of steel or during volatilization of chromium, is likely to cause precipitation. An excessive loss of phosphoric acid during fuming may lead to formation of a turbidity in the final solution; this may be prevented by adding 10 ml. of 20% ammonium tartrate or citrate (1, 5) following addition of the sulfuric acid. Addition of more than 10 ml. of sulfuric acid (1 to 1) at this point will also prevent precipitation of tungsten. If desired, 5 ml. of a sulfuric-perchloric acid mixture (1 to 1) may be substituted for the final 5 ml. of perchloric acid before fuming. By thus raising the temperature of the solution to 203° to 205° C. complete oxidation is assured.

CAST IRON. Dissolve 1.0 gram of the sample in 25 ml. of 1 to 1 hydrochloric acid using a covered 300-ml. tall-form beaker. When solution is complete, add concentrated nitric acid dropwise. Add 10 ml. more of concentrated nitric acid and heat 3 to 5 minutes to ensure complete oxidation. Cool the solution and filter the precipitate, using a Whatman No. 41 filter paper, or equivalent. Wash the precipitate alternately with hot 1 to 1 hydrochloric acid and hot water, 6 times or more if necessary. Wash finally with hot water until the filtrate is clear. Reduce the volume of the filtrate to about 15 ml. by boiling, cool, and add 15 ml. of perchloric acid (70 to 72%). Mix thoroughly and boil

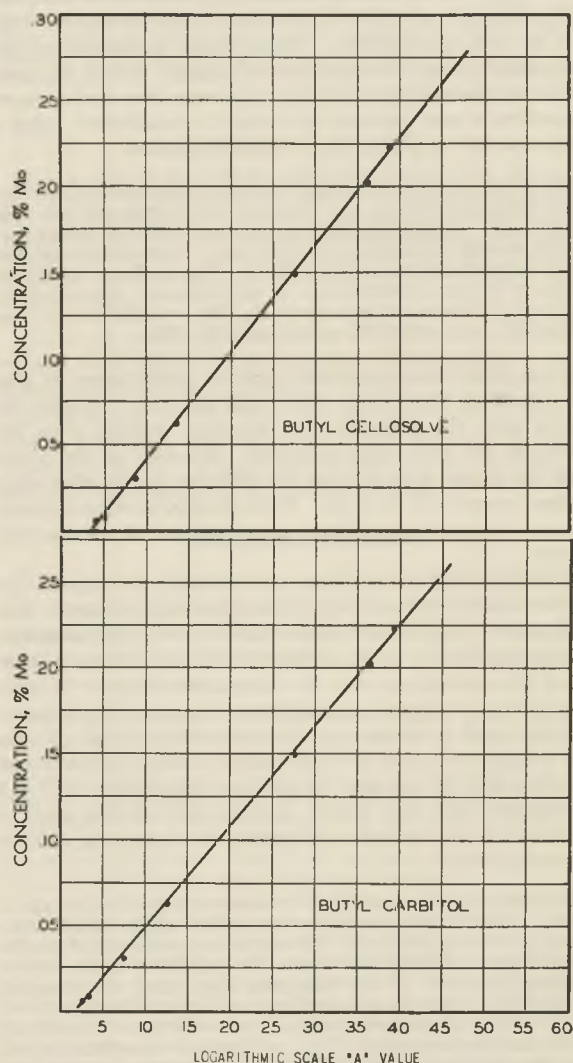


Figure 3. Relationship between Molybdenum Concentration and Amount of Absorption

Table III. Deviations Due to Interfering Elements

N.B.S. Steel No.	Type	Additions	N.B.S. Certificate Value % Mo	Proposed Method % Mo	Maximum Deviation % Mo
72b	Cr-Mo (SAE X4130)	0-20% W	0.223	0.221-0.225	+0.002
		0-3.0% V	0.223	0.223-0.231	+0.008
		0-3.0% Al	0.223	0.223-0.220	-0.003
		0-0.3% Cu	0.223	0.223	0.000
		0.3-1.5% Cu	0.223	0.225-0.235	+0.012
		Gum arabic			
111a	Ni-Mo (SAE 4620)	0-3.0% Ti	0.222	0.222-0.219	-0.003
		0-12% Ni	0.222	0.222-0.225	+0.003
		0-10% Cr	0.222	0.222-0.282	+0.060
		0-15% Co	0.222	0.222-0.233	+0.011

until dense fumes are evolved. Continue fuming for 5 to 7 minutes. Cool, dilute, and develop the molybdenum-thiocyanate complex as outlined for carbon and low-alloy steels.

DISCUSSION AND NOTES

The 1.0-gram sample weight specified was chosen so that other elements, such as nickel, chromium, and manganese, could be conveniently determined from the single sample. The size of the aliquot taken for molybdenum and the final volume used in the procedures as outlined were chosen to give a working range of 0 to 0.3% molybdenum. When higher concentrations are encountered, proportionately smaller samples should be used, making up the difference with a molybdenum-free steel. As an alternative, a new standard curve may be established, using a smaller sample or greater final volume of solution.

Of interest to those who might prefer a smaller sample, so that direct dilution to 100 ml. may be made, 0.125-gram samples were weighed out. The proposed procedure was followed except that the acid solvent consisted of 5 ml. of 1 to 1 hydrochloric acid and 10 ml. of perchloric acid (70 to 72%). The resultant maximum deviation in the determination of molybdenum was -0.002% in the case of Bureau of Standards No. 72; -0.003% in the case of No. 106a; and -0.003% in the case of No. 72b.

It was found that the solvent could be added before or after the potassium thiocyanate with equal accuracy. Adding the solvent after the reduction with stannous chloride gives low results, as the color fades somewhat. If added in the proper order the elapsed time between the additions has no effect upon the final intensity of the color. Final dilution to volume should, however, be made immediately after addition of the stannous chloride.

In determining the optimum concentration of reagents, the addition of small and convenient quantities was the basis for their preparation. Experiment showed that 5 ml. of a 5% potassium thiocyanate solution were sufficient to ensure complete conversion of the molybdenum into the thiocyanate complex. A minimum of 5 ml. of stannous chloride was chosen as the volume of reducing agent to be used, in the concentration noted. To ensure complete solution of the stannous chloride and its subsequent stability on standing, an optimum concentration of 1 to 1 hydrochloric acid was found. Letting this solution stand a minimum of 24 hours after its preparation ensures its stability and workability.

Alloying elements most likely to be encountered in the type of ferrous metals under consideration, which might cause interference in the molybdenum determination, were added to National Bureau of Standards steels 72b and 111A in the form of standard solutions of the salts, made up using c.p. reagents (Table III). The solutions used were nickel chloride (1 ml. = 5 mg. of nickel), chromium trioxide (1 ml. = 5 mg. of chromium), ammonium metavanadate (1 ml. = 1 mg. of vanadium), aluminum chloride (1 ml. = 1 mg. of aluminum), copper sulfate (1 ml. = 1 mg. of copper), c.p. cobalt nitrate (1 ml. = 5 mg. of cobalt), and molybdenum-free sodium tungstate (1 ml. = 2 mg. of tungsten). The standard titanium solution (1 ml. = 1 mg. of ti-

tanium) was prepared by fusing c.p. titanium dioxide with sodium carbonate and dissolving the melt in hydrochloric acid (1 to 1).

The presence of aluminum, vanadium, titanium, and nickel in varying concentrations, as high as might be encountered in the usual ferrous analyses, caused deviations well within permissible limits.

Interference of chromium becomes greater with increased concentration. At 10% chromium the error in the determination of molybdenum is 0.06% molybdenum. It was subsequently found that if the chromium content was reduced as much as possible by volatilization as chromyl chloride as outlined in the procedure for stainless steels, the deviation was likewise reduced—e.g., less than 0.002% molybdenum at 0.25% chromium. Non-stainless types of steels containing less than 1% chromium can be run without volatilization of the chromium, since the maximum interference at this concentration was 0.002%.

Copper was added in the range from 0 to 1.5%. Up to 0.3% no interference was encountered. Above this amount turbidity caused by precipitation of cuprous thiocyanate made accurate photometric readings impossible. This turbidity can be prevented by adding gum arabic in a 10% aqueous solution. If the gum solution was added in the ratio of 0.1 gram of gum per 0.1% copper to the 25-ml. aliquot before addition of further reagents, molybdenum could be determined satisfactorily. At 1.5% copper the deviation was only 0.012% molybdenum. The photometric readings were most accurate if made from 5 to 15 minutes after the color development.

Cobalt was studied in the range from 0 to 15%. Up to 5.0% cobalt, no interference was encountered. The interference at 6.0% cobalt was +0.001% molybdenum, reaching a maximum deviation of +0.011% molybdenum at 15% cobalt.

Tungsten is found in tool steels up to 20%. Standard molybdenum-free sodium tungstate solution was added to alloy steels 72b, 30d, 32c, 72, 106a, and 21c to give concentrations up to 20% tungsten. In no case did the deviation from the accepted values exceed 0.009%. In order to accomplish this accuracy it was necessary to dissolve the sample in phosphoric-perchloric acid mixture and to follow all the precautions outlined in the procedure for tungsten steels to prevent precipitation of tungstic acid. The chromium was necessarily removed by volatilization.

In Table II are listed Bureau of Standards ferrous metals analyzed in accordance with the proposed procedures. It is from the accuracy and reproducibility obtained that the conclusions regarding interferences were drawn.

The method as outlined gives results well within the limits of accuracy and reproducibility required. It eliminates the necessity of extracting the molybdenum thiocyanate complex color before its intensity can be measured and gives a color which experience has shown will remain stable for 24 hours.

ACKNOWLEDGMENT

The authors wish to thank Floyd A. Charley for his assistance and to thank those who contributed by helpful suggestions and criticisms.

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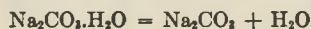
Anhydrous Sodium Carbonate as a Standard of Reference in Acidimetry

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During the transformation of sodium bicarbonate to sodium carbonate, moisture to the extent of approximately 0.1% is occluded within the product. This moisture is lost very slowly at temperatures even as high as 300° C. No detectable amounts of sodium hydroxide were found in samples of sodium carbonate that had been transformed at temperatures below 300° C. Samples of five leading brands of reagent grade sodium carbonate were found to have purity factors satisfactory for a standard of reference in acidimetry.

SINCE the beginning of the century sodium carbonate has been widely used as a standard of reference in acidimetry. Lunge (7) showed that sodium carbonate was stable when heated for a long period at temperatures as high as 300° C. At the present time there is uncertainty concerning not only the temperature and conditions under which sodium bicarbonate may be completely transformed into the normal carbonate, but also the purity of the product.

Kunz-Krause and Richter (4) reported that decomposition of sodium bicarbonate was only 99% complete when heated to constant weight at 250° C. but was complete when the material was stirred several times at that temperature. Smith and Hardy (9) found that 2 hours were required for complete decomposition of the acid salt at 305° C. at atmospheric pressure because of the slowness of the reaction



Lunge (6) reported that bicarbonate is completely converted into the carbonate upon being heated for a few minutes at 260° to 270° C., and is free of bicarbonate, water, and sodium oxide after being heated for 0.5 hour at not over 300° C. More recently Lidner and Figala (5) reported that the reaction is complete after several hours at 130° to 140° C., and Waldbauer, McCann, and Tuleen (10) concluded that any sample of sodium bicarbonate heated above 150° C. is completely converted, regardless of the time of heating, and since their product was found to have a factor of purity greater than unity, that sodium hydroxide is produced during the reaction. Hou (3) also obtained a product (by conversion in a rotary furnace at temperatures ranging from 160° to 220° C.), the factor of purity of which was over unity.

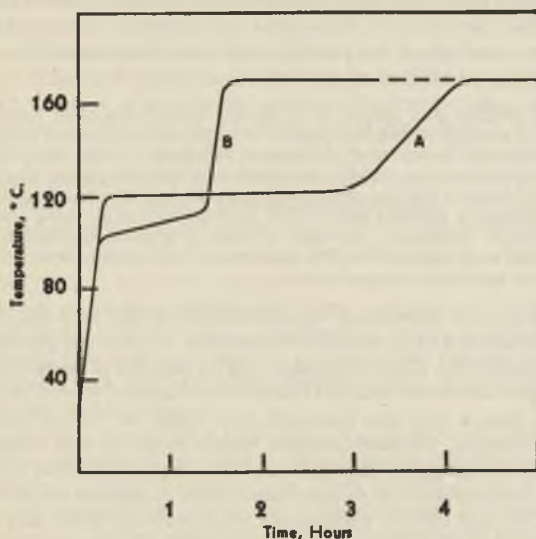


Figure 1

Many past investigations were not sufficiently precise for establishing the conditions in the preparation of a reagent to be used as a standard of reference in analysis. Whether a reaction may be considered complete may depend upon the precision used in the experimental work. In the present work precision requirements were kept in mind, with a view to clearing up the uncertainty concerning the methods of preparation and the purity of sodium carbonate.

MATERIALS AND REAGENTS

All materials and reagents were reagent grade. Three different samples of sodium bicarbonate were used: the first supplied by a well-known firm, the second prepared from this by recrystallization from hot aqueous solution, and the third prepared by saturating a solution of the normal salt with carbon dioxide. Standard hydrochloric acid solutions were made from constant-boiling acid prepared according to Foulk and Hollingsworth (2). Two standard acid stock solutions were prepared from independently prepared constant-boiling hydrochloric acid. A sample of sodium carbonate analyzed by one standard solution showed a factor of purity of 99.99%, and by the second solution 100.00%. The alcohol was thoroughly tested and found free from significant amounts of acid- or base-neutralizing components.

METHODS OF ANALYSIS

The purity of the sodium carbonate product was determined by titration against standard hydrochloric acid approximately 0.5 N. Methyl yellow modified with methylene blue (1) was used. All methods were designed to correspond to a precision of 1 part in 10,000. Relatively large samples were analyzed, weighing burets were used, and weights were adjusted to the vacuum basis.

Factors of purity were determined on 19 different samples involving more than 50 determinations. The average of the 19 average deviations was 1.4 parts per 10,000. The work was carried out during months when the relative humidity inside the heated laboratory was very low. When ordinary precautions were exercised the hygroscopic properties of the product were found not to interfere to any significant extent.

TIME-TEMPERATURE STUDIES

The fact that the reactions involved are endothermic suggests that the course of the reactions can be studied by following the temperature at the center of a comparatively large mass of the substance over the transformation period. Experimental conditions were as follows:

An ordinary 30-ml. (1-ounce) wide-mouthed bottle was filled with the samples, which weighed approximately 30 grams. The bottle was closed with a cork stopper through which the thermometer was inserted, so that the bulb was in the center of the sample. The cork had a small groove to allow the decomposition products to escape. The bottle was suspended horizontally in an oven, the temperature of which was thermostatically regulated. Temperature readings were taken until the temperature at the center of the sample became equal to that of the oven.

Runs were made at oven temperatures of 290°, 200°, 170°, and 130° C. The results in each case were similar. After a short rapid rise to approximately 120° C. the temperature at the center of the reaction mass remained practically constant at this temperature for periods ranging from 0.5 hour at the highest oven temperature to 8 hours at the lowest temperature, then rose rapidly to oven temperature. In each case only one constant-temperature period was found. The upper part (above 160°) of each curve for runs made at the higher temperatures was practically identical with the curve of the corresponding blank run. When samples of the product obtained from the runs at 170° and 200° were ignited in a furnace for 3 hours at 290° C., losses in weight

Table I. Time-Temperature Runs
(30-gram sample in 1-ounce bottle)

Sample	Oven Temperature ° C.	Constant Temperature ° C.	Period of Constant Temperature Hours
NaHCO ₃	290	125	0.8
	200	122	2.0
	170	121	3.5
	130	118	8.0
Na ₂ CO ₃ · H ₂ O	170	112	1.5

Table II. Time for Completion of Reaction
(5-gram sample of NaHCO₃ in crucible)

Temperature, ° C.	140	160	200	290
Time, hours	3.0	1.5	0.5	0.4

were 0.02 and 0.01%, respectively. In the same way time-temperature runs were made on samples of sodium carbonate monohydrate, which gave a practically constant-temperature period at 112°.

Details of the time-temperature runs (Table I) and characteristic curves (Figure 1) demonstrate that the decomposition proper of sodium bicarbonate takes place at relatively low temperatures and that carbon dioxide and water are lost simultaneously. The rate of decomposition increases rapidly with increase in the temperature, so that the reaction is practically complete by the time the entire sample has reached 160° C.

OPTIMUM CONDITIONS FOR PREPARING PURE SODIUM CARBONATE

In determining the optimum methods for producing pure sodium carbonate, easily reproducible experimental conditions were selected.

An approximately 5-gram sample of bicarbonate was placed in a 20-ml. crucible. For temperatures up to 220° C. an oven was used; above that an ordinary ignition furnace. The crucible was placed in the oven without cover and out of direct contact with the heating element or its radiations. Preliminary runs were made to determine the time of heating necessary for completion of the reaction at several temperatures ranging from 140° to 300°. The completeness of the reaction was determined by ascertaining the loss in weight upon further ignition for 3 hours at 300°. Later results indicated that ignition at 300° C. does not necessarily result in a completely dehydrated product, but for the purposes of this investigation this test was adequate.

In every case decomposition came to practical completion from 140° to 280° C. with some dispatch; following this was a period in which the samples lost weight slowly. Practically identical results were obtained in more than 50 ignitions on three different samples of sodium bicarbonate. The time necessary for consummation of the fast reaction for several temperatures is given in Table II. The amount of the "slowly lost" weight approximated 6 parts per 10,000. The work of Richards and Hoover (8) indicates that this slowly lost weight consists of moisture occluded in the crystals of the products.

To test the validity of this, several samples of sodium carbonate previously ignited at 300° C. were moistened with water, dried at 140°, and reweighed. During the process the samples became caked and gained an average of 0.02% in weight. This responded to ignition in much the same way as the slowly lost portion of the decomposition product of the bicarbonate.

Up to this point identical results had been obtained for each of the three samples studied. For the remainder of the work one sample only was used, that supplied by a well-known firm.

As the amount of slowly lost weight is roughly independent of the method used for preparing the acid salt, one may conclude that it consists of moisture occluded in the crystals of the product. Since it resists complete elimination at temperatures as high as 300° C., a study was made of effective ordinary means for eliminat-

ing most of the occluded moisture. It was found that pulverization of the product was helpful, and that after being thoroughly ground in an agate mortar the product became substantially constant in weight after 1 hour ignition at 140° C. and above. All the moisture is not eliminated at these temperatures, however, since upon further ignition at 270° C. the pulverized product dried for 1 hour at 140° lost an additional 0.02%, while that dried at 200° lost an additional 0.01%. These later ignitions were all carried out in weighing bottles with well-fitted glass stoppers since the desired precision could not be obtained when an ordinary covered porcelain crucible was employed.

The factor of purity of the product obtained from the first sample mentioned above at each of several transformation temperatures was determined by titration against standard hydrochloric acid. The results of nine analyses involving 18 determinations are given in Table III. The largest average deviation of the series was 0.02% and the author believes that the uncertainty in any case is no greater than this amount. These results verify the fact that transformations at temperatures below 300° C. produce a product containing less than 0.1% of moisture and that this moisture may be partially eliminated by pulverization of the sample and re-ignition.

Table III. Purity of Sodium Bicarbonate Transformation Product

Sample No.	Transformation Temperature ° C.	Time Hours	Product Ground	Reheating Temperature ° C.	Na ₂ CO ₃ %
1	180	2	No	---	99.92
2	220	2	No	---	99.92
3	220	12	No	---	99.95
4	270	1	No	---	99.91
5	270	4	No	---	99.94
6	220	12	Yes	220	99.99
7	200	1	Yes	160	99.95
8	200	1	Yes	200	99.96
9	200	1	Yes	270	99.97

Table IV. Extraction with Alcohol

Conversion Temperature ° C.	Sodium Carbonate Before extraction %	After extraction %
165	99.93	99.93
200	99.93	99.94

DETERMINATION OF SODIUM HYDROXIDE CONTENT

These results included nothing that would suggest the presence of sodium hydroxide in the product transformed at temperatures below 300° C. A complete investigation, made to determine whether there were significant traces of sodium hydroxide in the product produced at the several temperatures, comprised two parts: analysis of the product before and after extraction with alcohol, and analysis of the alcoholic extract.

A sample was placed in a 50-ml. narrow-mouthed flask, 20 ml. of alcohol were added, and the mixture was allowed to stand for several hours with infrequent shaking. The clear liquid was carefully but rapidly decanted into another 50-ml. flask, 20 ml. of carbon dioxide-free water were added, and the liquid was immediately titrated with 0.05 *N* hydrochloric acid, using phenolphthalein indicator. In case a trace of sodium carbonate was carried over during the first decantation, a second served to ensure a perfectly clear solution.

Numerous extractions were carried out on the products of decomposition at the several temperatures, on products previously extracted with alcohol (blanks), and on samples of reagent grade sodium carbonate obtained from five producers of pure chemicals. The titer in each case was small, and within the limit of error of the titration, the same for every sample extracted and independent of the weight of the sample. Two samples of sodium carbonate transformed from sodium bicarbonate by ignition for 24 hours at 200° and 165° C., respectively, were analyzed before and after extraction with alcohol. Results in Table IV demonstrate that

sodium carbonate transformed from the acid salt at temperatures below 300° C. contains no measurable amounts of sodium hydroxide extractable with alcohol.

Finally, to determine the purity of reagent grade sodium carbonate obtainable on the market, samples of five leading brands were dried in the oven at 140° for 1 hour and analyzed by titration against standard hydrochloric acid, with the following results: 99.99, 99.98, 100.00, 99.99, and 99.98%. This demonstrates that reagent grade sodium carbonate ordinarily obtainable is pure enough to meet even the most exacting requirements as a standard in acidimetry.

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Laboratory Distillation at Atmospheric Pressure of Normally Liquid Hydrocarbons

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The factors involved in the laboratory distillation of normally liquid hydrocarbons when it is desired to separate near-boiling components are discussed and suitable fractionating columns are described. In a generally useful column the fractionating section is packed with single-turn wire helices, the column being insulated with an especially designed electrical heater which makes it possible to maintain the fractionating section in an adiabatic condition. This column is equipped with a special head provided with electrical means for automatically maintaining the desired reflux ratio. Columns of this design containing up to about 100 equivalent theoretical trays have been found to operate satisfactorily.

DURING the past decade much work has been done on the design of laboratory fractionating columns, particularly with respect to the development of efficient packing materials. Highly efficient column packings have been developed and incorporated in the fractionating columns described by Baker (1), Bruun (2, 3), Fenske (6-9), Podbielniak (17), Selker (20), and Stedman (21).

The factors involved in the selection of a column packing have been discussed by Ward (24). In general, a good packing should present a large area to effect efficient contacting of liquid and vapor, and should have a high percentage of free space, since this permits high vapor velocities with resulting high throughput. In addition, it should pack uniformly into the distilling tube to minimize channeling and flooding difficulties. From the latter standpoint symmetrically shaped packings are to be preferred over irregular shapes.

In addition to an efficient packing, the fractionating section must be suitably insulated against gain or loss of heat. The loss of heat to the surroundings results in internal reflux which reduces the capacity of the column and may also decrease column efficiency if the amount of such reflux is large. The heat capacity of the insulating jacket should be as low as possible in order to decrease the time required for the column to come to equilibrium. Low heat capacity also tends to reduce flooding troubles sometimes encountered when a component having a considerably higher boiling point begins to move up the column. Suitable heat insulation may be obtained with vacuum jackets equipped with metal reflecting shields, or with suitable lagging and electrical heating.

The type of distilling head used has much to do with the stable operation of the column. The total condensation type is preferred to partial condensation types because of the critical control required by the latter. The somewhat increased efficiency which may sometimes be obtained with partial condensation types is usually more than offset by their irregular opera-

tion, which tends to keep the column from reaching equilibrium. In addition, the still-head design should embody means for maintaining steady volumes of reflux and product.

The operation and degree of control required of a fractionating column naturally vary with the kind of sample being analyzed and the separation desired. For very close cutting it is essential that column operation be smooth and that once the column has reached equilibrium nothing be done to disturb this equilibrium. This involves close control of the heat input to the kettle, accurate control of reflux ratio and product take-off rate, and maintenance of adiabatic conditions over the fractionating zone of the column. In addition, it is essential to keep the kettle liquid actively boiling. If this is not done the lighter components may become exhausted from the surface while considerable amounts still remain in the lower parts of the kettle liquid, thus producing false "breaks".

The behavior of fractionating columns may be shown visually by fractionating mixtures of propane, butane, and diazomethane, a yellow compound boiling at -23° C., in glass columns. Such studies illustrate vividly the difficulty with which the last traces of light material are removed from the kettle, and the time required to re-establish equilibrium after momentary upsets caused by irregular operation.

DESCRIPTION OF FRACTIONATING COLUMN

In Figure 1 are shown details of the construction of a column which has been found to be stable in operation, and to require but little attention. It is capable of giving very good fractionation with a wide variety of samples.

Both metal and glass columns have been constructed. The type most generally used is a glass column with a packed section from 60 to 180 cm. long with an inside diameter of from 1.2 to 3.1 cm.

The packing material used is generally 1/16- or 3/32-inch single-turn helices made of Nos. 36 and 30 wire, respectively, of the type described by Fenske (8). This packing is available in a wide variety of metals and alloys. Usually rings made of 18 chromium-8 nickel are preferred, since the metal has good corrosion resistance and can be readily cleaned with strong acids. According to Whitmore *et al.* (25) the HETP of this type of packing varies with the diameter, height, and throughput or boil-up rate. For 2.5 cm. and smaller columns the HETP is in the range of 1.5 to 3 cm. The maximum throughput or boil-up rate for a 2.0 cm. inside diameter column packed with 3/32-inch helices made of No. 30 wire is in the range of 1200 to 1300 cc. per hour, which corresponds to a vapor velocity of about 24.0 cm. per second. Proper installation of the packing is essential for highest throughputs. The tamping method described by Fenske has been found satisfactory. If the column is improperly packed, so that there are zones of close packing and zones of loose packing, flooding is likely to occur in the column at relatively low

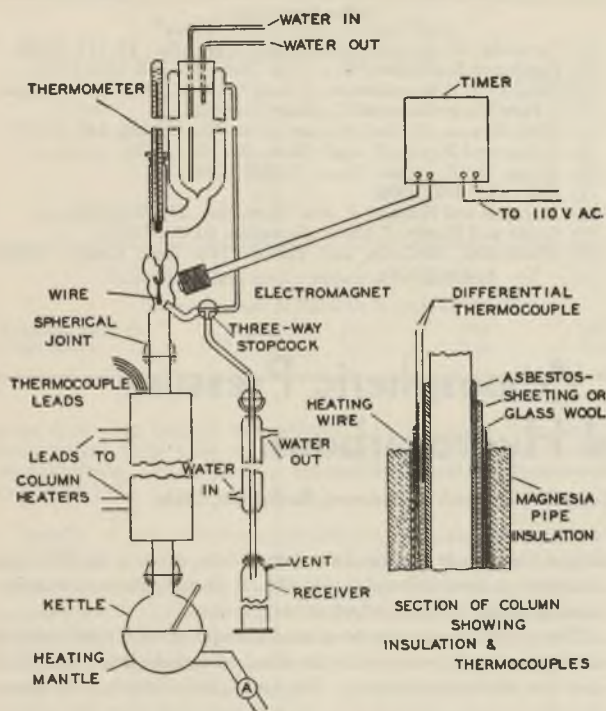


Figure 1. High-Temperature Fractionating Column

throughputs. Flooding can be avoided at the bottom of the column by supporting the packing either on an inverted cone as described by Fenske, or on a graded bed of larger rings which in turn rest upon a screen. This screen should not be perfectly horizontal but tilted somewhat. Flooding at the top may be prevented by expanding the distilling tube at this point to increase the area.

The method of insulating the fractionating section shown in Figure 1 has proved very satisfactory in use, requiring but little attention except when a higher boiling product begins to move up the column. The column proper is covered with about 0.3 cm. of an insulating material such as asbestos sheet or rope, or glass wool. The hot junction of a thermocouple is soldered or brazed to a thin sheet of copper 6 to 12 sq. cm. in area and is fastened to the outside of this insulation. A second layer of lagging, about 0.6 cm. thick, is then applied. The cold junction of the thermocouple is attached to this layer of insulation in the same manner as the hot junction and directly over the hot junction. A third layer of insulation from 1.2 to 1.8 cm. thick is then installed, and an evenly spaced heating winding placed on this layer. A fourth layer of insulation is then placed over the heater winding.

With this type of insulation the heating current is adjusted to null reading of the differential thermocouple galvanometer. At this point there is no temperature difference across the layer of insulation between the two junctions of the thermocouple, and an adiabatic condition has been established. The direction of swing of the galvanometer needle shows whether the heating current needs to be increased or de-

creased. By use of a suitable controller, jacket temperatures may be maintained automatically.

The placement of the hot junction in the insulation rather than next to the distilling tube is preferred, as the control is less sensitive and less apt to be upset by short-term irregularities in column operation. To some degree the column temperature is free to "float" with the arrangement described.

One differential couple is used per heating section. The number of sections employed depends upon the length of the column. In practice, three heating sections of 200 to 300 watts have been found satisfactory for 150-cm. columns.

Thermocouples may be placed on the column proper in order to measure its temperature if desired. Such readings show the position of the next higher-boiling constituent in the column. The differential couples give a similar indication since as the higher boiling component rises in the column, a greater heat input is necessary for that part of the column to balance the differential thermocouple.

The distilling head is of the total condensation type, and is a modification of the head described by Carter and Johnson (4). The condenser is so designed that either water or dry ice may be used as coolant. It is convenient to use dry ice to separate butane from the sample. The condensate is collected and caused to flow over a twisted iron wire suspended from a hook. This consists of 2 or 3 strands of No. 18 iron wire twisted together. At intervals as determined by the timer setting, an electromagnet is energized, pulling the end of the wire into a small cup. The condensate flows down the wire into the cup and passes through a small liquid seal and condenser into the product receiver. When the current ceases to flow through the electromagnet the wire swings away from the cup and the condensate is returned to the column as reflux. The reflux ratio is thus equal to the ratio of the duration of the two intervals, and is determined by the timer setting. In many instances it is preferable to make the interval of withdrawal short to prevent any disturbance of the column equilibrium. At a given reflux ratio the rate of product withdrawal is determined by the heat input to the kettle (boil-up rate).

The distilling temperature is measured by either a thermometer or thermocouple which is placed in the full stream of hydrocarbon vapors passing to the condenser. For very accurate temperature measurement in the higher temperature ranges, it is desirable to use a radiation shield around the thermometer bulb.

In use the entire still head, except the condenser, is insulated. For temperatures up to about 150° C. glass wool is satisfactory.

Spherical joints are used on the kettle and head. These joints reduce breakage due to strains caused by slight misalignment, and hold well if the temperature is not too high. For kettle temperatures much above 150° C. it has been found preferable to seal the kettle directly onto the column.

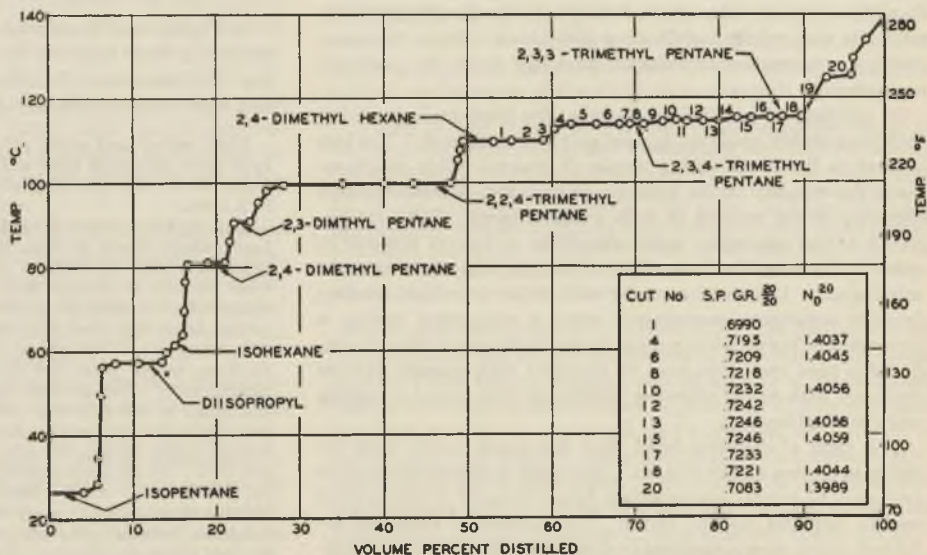


Figure 2. Fractionation of a Paraffinic Alkylate

OPERATION

In operation the column is stable and requires but little attention from the operator. In locations where the voltage varies over a considerable range, operation is improved by the use of a constant-voltage regulator. The kettle is usually of such size that it is about $\frac{3}{4}$ filled by the sample. The sample size itself should be selected with reference to the working column holdup and the degree of separation required of the component present in the smallest amount. The working holdup has been reported by Whitmore *et al.* (25) for columns up to 5 cm. in diameter. The holdup varies with both column diameter and throughput, but may be estimated for a given column from the data given. A manometer for measuring the kettle pressure is useful not only for indicating flooding, but also for estimating throughput and holdup. For a 2.5-cm. column packed with $\frac{3}{32}$ rings the working holdup varies regularly with throughput from about 1.2 to about 3.4 cc. per theoretical plate as throughput is increased from 0.1 to 0.6 liter per sq. cm. per hour. Usually the column is operated at throughputs of 60 to 90% of the flooding value.

The number of equivalent theoretical plates required to effect a given separation may be estimated by the methods of Rose and Welshans (18) or Fenske (6).

The usual starting procedure is to weigh the sample into the kettle, attach the kettle to the column, and insulate it with glass wool. The kettle and jacket heaters are turned on and the column is allowed to flood as recommended by Fenske (6). At this time the kettle heater and jacket voltages are reduced to approximately the required values as determined from experience, and the kettle insulation is removed to pull the liquid down from the column. If the liquid does not come down promptly, the top of the kettle may be cooled by placing a wet cloth against it. As soon as the flood has been reduced, but before the packing begins to dry out, the kettle insulation is replaced and the column allowed to operate at total reflux until it has reached equilibrium. This point may usually be determined as the point where the overhead temperature becomes constant. However, in some cases, as where very close-boiling components are being separated, it may be desirable to withdraw a small portion of the overhead product for analysis to determine the degree of separation being obtained. Usually from 1 to 3 hours are sufficient, but in some cases longer times are required. During the fractionation the kettle is kept actively boiling. In some cases, as when the sample is substantially a pure hydrocarbon, boiling may be irregular unless boiling stones or the equivalent are used.

Usually, the distillation is run throughout at a constant reflux ratio. However, on some samples, particularly when a single component is present in large amount, the distillation time may be decreased by employing a lower ratio on the front end of the plateau.

EXAMPLES

In Figures 2 and 3 are shown distillation curves obtained on columns of the type described.

The column employed for the analysis shown in Figure 2 had an internal diameter of 1.2 cm. and a packed section of 150 cm.

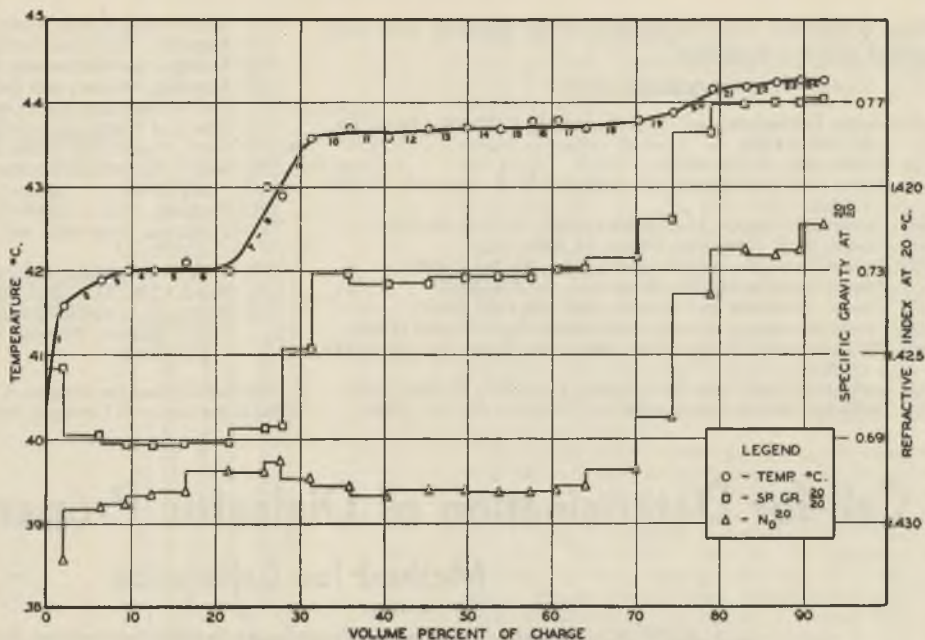


Figure 3. Fractionation of a Mixture of Piperylene and Cyclopentene

It was packed with $\frac{1}{16}$ -inch helices. The column was equipped with a 1-liter kettle. The sample volume was 850 cc., 780 cc. of which were distilled overhead at a reflux ratio of 80 to 1. Working holdup was approximately 40 cc. The individual paraffins designated in Figure 2 are assigned merely on a basis of boiling point without confirmatory identification.

In Figure 3 is shown the fractionation curve obtained when a narrow-boiling mixture of piperylene and cyclopentene was distilled. The column employed was 1.4 cm. in diameter, and contained 188 cm. of $\frac{1}{16}$ -inch helices. It was insulated by an air jacket containing a polished metal radiation shield, the air jacket being covered with magnesia steam pipe insulation. Overhead temperature was measured with a calibrated 5-junction thermocouple. The average throughput was approximately 300 cc. per hour and working holdup approximately 55 cc. It was estimated that the minimum number of equivalent theoretical plates was 60. It was operated at a reflux ratio of 75 to 1, the product withdrawal rate being 4 cc. per hour.

It will be noted that fractions 3, 4, 5, and 6 distilled on a definite plateau at 41.9° to 42.1° C. The densities and refractive indices were nearly constant, but the densities were a little high and the refractive indices a little low for the low-boiling stereoisomer of piperylene. Later work has shown that about 9% of cyclopentene was present in these fractions, and that they were probably composed of a constant-boiling mixture of cyclopentene and low-boiling piperylene. Similarly fractions 10 to 19, which distilled on a plateau at 43.6° to 43.9° C., were probably a constant-boiling mixture of cyclopentene and high-boiling piperylene, containing about 50% of each hydrocarbon.

SHORT CUTS

Frequently, in the analysis of liquid hydrocarbons it is possible to use special methods or short-cut procedures to reduce the time necessary for analysis, particularly where the samples are of a routine or recurrent nature. Thus samples may be distilled through short columns at low reflux ratios using definite procedures which have been rigidly standardized against known mixtures.

Close-cut samples containing only two or three components are particularly adapted to short-cut analysis. One such method is that described by Hachmuth and Tooke (10) for the analysis of commercial isopentane. The method consists essentially of a simple distillation under rigidly controlled conditions, the results

being interpreted from calibration curves obtained with mixtures of known composition.

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Cell for Determination of Dielectric Properties of Liquids Method for Calibration

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A SIMPLE and reliable cell for measuring the dielectric properties of liquids consists principally of two glass tubes and two electrodes in the form of concentric nickel or Monel cylinders. Its dimensions are not critical and, using glass, nickel or Monel, tungsten, and copper, it can be constructed by any laboratory equipped with glass-blowing facilities. The cell has been found very satisfactory for measuring the dielectric constant, dissipation factor, and resistivity of liquids. Since only small quantities of specimens are available in the investigation of many synthetic liquids, it is significant that this cell requires only 10 to 15 cc. of liquid. Moreover, it is applicable over a wide frequency range, both above and below room temperature, as well as over a wide frequency range extending to 500 kc.

Many of the cells now in use require the use of organic insulation under the liquid level. Organic materials may be either slightly soluble or absorb some of the liquid being measured, which usually causes contamination of subsequent samples. Porosity of the metals used in some cells has caused similar difficulties. Such cells are usually very difficult to clean properly. Copper and brass have long been known to be undesirable metals for use as electrodes because of their catalytic and other effects on many liquids. Plating copper or brass with such metals as rhodium, nickel, chromium, and gold has not always proved satisfactory. Such platings rarely remain continuous over long periods of time. Plating produces particularly poor results in cases where the various parts of the cell are either screwed or soldered together.

A higher voltage power factor cell made from solid nickel or Monel, which overcomes the objections cited, was described in 1936 by the writer (2). This three-terminal cell (Leeds & Northrup Co., Philadelphia, Pa.) is rather expensive, but where high-voltage power factors of high accuracy are desired, has been found well worth its high cost. Another three-terminal cell suitable for high-precision measurements was described by Balbaugh and Howell (1). This cell, whose electrodes consist of platinum cylinders, is well constructed and will be found very useful where facilities for handling three-terminal cells are available. Other cells of merit are described in the literature.

Three-terminal cells require the use of rather specialized bridges equipped with a guard circuit in order to hold the third electrode, usually called the "guard electrode", at the proper potential. The guard electrode performs two functions: it eliminates the effects of a fringing field at the edges of the measuring electrode and it provides a means for by-passing any leakage

currents which may flow over the solid insulation used to maintain the spacing between electrodes. The calibration of a three-terminal cell, however, is somewhat simpler than for a two-terminal cell. The added complications encountered in the use of a three-terminal cell are justified in the highest precision work, especially at low frequencies. However, for measurements on liquid dielectrics, the errors resulting from the omission of the guard electrode are negligible, provided a properly constructed and calibrated two-terminal cell is used. A two-terminal cell is particularly useful for measurements above the audio-frequency range, because the difficulties of having to use a bridge equipped



Figure 1. Two Principal Parts of Cell

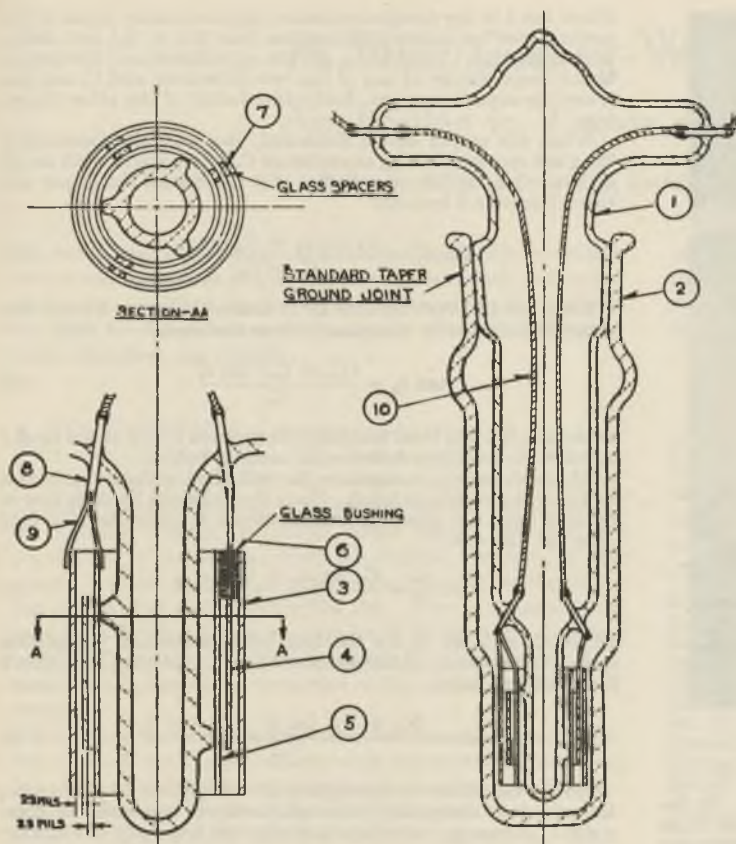


Figure 2. Diagram of Cell

with a guard circuit operable at such frequencies are avoided. In any case, bridges suitable for use with two-terminal cells are more generally available.

The simple two-terminal cell described in this paper has proved very satisfactory for dielectric constant and power factor measurements on a wide variety of liquids. It is particularly useful for studying synthetic liquids where in many cases only small amounts are available. Measurements can be made on as little as a 10-cc. sample. The cell has been used over the temperature range of -60° to 150° C. and the frequency range from 50 cycles to 500 kc. Dissipation factor measurements were made with commercially available alternating current bridges in which the voltage on the cell varied from a fraction of a volt to 100 volts. The cell is connected to bridge by means of a low-loss polyethylene coaxial cable. The cable capacitance can be accounted for by the use of well-known substitution methods in making the measurements. In the case of resistivity measurements, voltages as high as 500 volts have been applied to the cell. Commercially available electronic resistance bridges were used.

DESCRIPTION OF CELL

Figure 1 shows a photograph of the two principal parts of the cell which are assembled by means of a ground-glass joint. Figure 2 gives the details of construction.

The electrodes consist of three concentric cylinders machined from solid nickel or Monel bar stock. This ensures perfectly cylindrical and rigid cylinders which cannot be obtained by rolling cylinders from sheet material. The inner and outer cylinders are connected by means of a nickel ribbon, which is spot-welded to the cylinders on one end, and to one of the tungsten rods sealed through the glass at the other end. The middle cylinder, which is connected to the other tungsten rod, constitutes one electrode while the other two cylinders form the second elec-

trode. The spacing between cylinders is about 0.023 inch. The capacitance of the empty cell is about 35 mmf. The latter can be increased somewhat if desired by increasing the length of the middle cylinder.

The glass enclosure as well as the spacers between cylinders is made of low-loss Corning No. 707 glass. Pyrex is unsuitable because of its relatively high dielectric losses, particularly at temperatures over 50° C. The first cells were made with quartz spacers which were very difficult to form. The substitution of Corning No. 707 glass spacers has proved entirely satisfactory. A list of the materials used for the numbered items of Figure 2 is given in Table I.

The dimensions of the cell are a matter of choice. As the cells are now being built, the over-all length is 8 inches, the diameter of the outer glass tube is 1.5 inches, and the diameter of the inner glass tube is 1 inch. The dimensions of the cylinders used are given in Table I.

Figure 3 shows a number of cells in a shielded air oven which is used for measurements at room temperature and above. The ungrounded leads pass through the side of the oven in quartz tubes and then to plug receptacles mounted on the outside of the oven. The various cells can be connected to the bridge in turn through the use of a coaxial cable. Measurements below room temperature are made by mounting the cell in a Dewar flask in which a carbon dioxide-alcohol mixture is used as the coolant. Besides the normal measurements on liquids, the cell has also been used in following changes in electrical properties of reactants in a vessel during the course of the reaction.

CALIBRATION OF CELL

The cell can be used for dielectric constant, resistivity, and dissipation factor measurements. For dielectric constant measurements, the effective air capacitance between cylinders must be found. This can be done conveniently by making a measurement on the empty cell and a second measurement with the cell filled with a liquid of known dielectric constant.

The measured capacitance of the empty cell may be expressed as follows:

$$C_1 = C_a + C_s \quad (1)$$

where C_1 is the measured capacitance of the empty cell, C_a is the desired air capacitance, and C_s includes the capacitance of the glass spacers and the leads. The measured capacitance of the cell filled with the liquid of known dielectric constant may be expressed by:

$$C_2 = \epsilon' C_a + C_s \quad (2)$$

where C_2 is the capacitance of the cell filled with the liquid of known dielectric constant, ϵ' is the known dielectric constant of the liquid, and C_a and C_s are the same as before. The values of C_a and C_s can easily be determined from Equations 1 and 2. c.p. benzene was used as the calibrating liquid because of the abundance of data on its dielectric constant in the literature.

Table I. Materials Used in Cell

Item No. ^a	Material
1	Corning 707 glass
2	Corning 707 glass
3	$\frac{1}{4}$ inch O.D. \times $\frac{1}{4}$ inch I.D. \times $\frac{1}{16}$ inches long nickel or Monel
4	$\frac{1}{4}$ inch O.D. \times $\frac{1}{4}$ inch I.D. \times $\frac{1}{4}$ inch long nickel or Monel
5	$\frac{1}{4}$ inch O.D. \times $\frac{1}{4}$ inch I.D. \times $\frac{1}{16}$ inches long nickel or Monel
6	Corning 707 glass
7	Corning 707 glass
8	Tungsten
9	Nickel
10	Copper

^a For identification of items, refer to Figure 2.

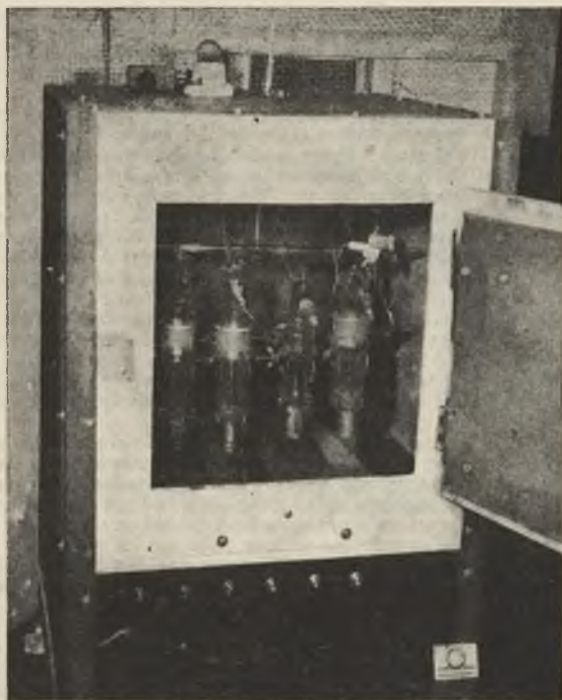


Figure 3. Four Cells in an Air Oven

Pure benzene has a dielectric constant of 2.27 at 25° C. In determining the dielectric constant of an unknown liquid, let C_t be the measured capacitance of the cell containing the unknown liquid. The dielectric constant of this liquid, ϵ'_x , is then computed from the following simple relation:

$$\epsilon'_x = \frac{C_t - C_g}{C_a} \quad (3)$$

where the symbols are the same as before, except that C_g includes not only the capacitance of the glass spacers and leads of the cell proper, but also the capacitance of any other leads or cables entering into the measurement.

In measuring resistivity or conductivity it is necessary to know the ratio of the effective electrode area to interelectrode distance. This is called the cell constant and can be determined very simply from a measurement of the air capacitance, C_a , of the cell.

It can be shown by the use of the well-known formula for the capacitance of a cylindrical capacitor (as well as for any other capacitor of simple shape) that the cell constant and the air capacitance are related through the following simple expression:

$$\text{Cell constant} = C_a / 0.08854 = 11.29 C_a \quad (4)$$

where C_a is in micromicrofarads and the cell constant in centimeters. The resistivity then is expressed by:

$$\rho = 11.29 C_a R \text{ ohm-cm.} \quad (5)$$

where ρ is the resistivity in ohm-cm. and R the measured resistance of the liquid in the cell. The leakage through the glass, which is usually found to be small compared with that through the liquid, is neglected in Equation 5.

In general, no correction for the dissipation factor of the empty cell is necessary for temperatures of 100° C. and below unless liquids of extremely low dissipation factors are to be measured. The empty cell usually has a dissipation factor of the order of 0.0005 at 100° C. and less at lower temperatures. This influences the results to a negligibly small extent in most practical work. However, should it be desirable to make this correction, it can be done through the use of the following expression for the dissipation factor of two dielectrics in parallel:

$$\tan \delta = \frac{C_1 \tan \delta_1 + C_2 \tan \delta_2}{C_1 + C_2} \quad (6)$$

where $\tan \delta$ is the dissipation factor (approximately equal to the power factor for values of either less than 0.1) of the two dielectrics in parallel, C_1 and $\tan \delta_1$ are the capacitance and dissipation factor, respectively, of one of the two dielectrics, and C_2 and $\tan \delta_2$ are the capacitance and dissipation factor of the other dielectric.

When the empty cell is measured, the dielectric (essentially the glass spacers) having capacitance C_g is in parallel with an air dielectric having capacitance C_a . For the case of the empty cell then, Equation 6 becomes

$$\tan \delta_1 = \frac{C_g \tan \delta_g + C_a \tan \delta_a}{C_g + C_a} \quad (7)$$

Since $\tan \delta_a$ is zero because air is assumed to have no loss, the dissipation factor for the glass spacers becomes

$$\tan \delta_g = \frac{(C_g + C_a) \tan \delta_1}{C_g} \quad (8)$$

where $\tan \delta_1$ is the total measured dissipation factor of the empty cell and the other symbols are the same as before.

The next step is to measure the cell filled with the unknown liquid, which results in $\tan \delta_2$. Since the unknown liquid is now in parallel with the glass spacers, Equation 6 takes the following form for this case:

$$\tan \delta_2 = \frac{C_x \tan \delta_x + C_g \tan \delta_g}{C_x + C_g} \quad (9)$$

where C_x and $\tan \delta_x$ are the true capacitance and dissipation factor, respectively, of the unknown liquid. Solving Equation 9 for $\tan \delta_x$, we have

$$\tan \delta_x = \frac{(C_x + C_g) \tan \delta_2 - C_g \tan \delta_g}{C_x} \quad (10)$$

All the quantities on the right side of Equation 10 are known; thus the true dissipation factor of the liquid can easily be computed. However, correction is rarely ever necessary in ordinary work.

CLEANING THE CELL

It is very important to clean the cell properly, for imperfect cleaning can lead to very erroneous results, especially as to dissipation factor. New cells and those used with very badly deteriorated oils or other liquids should be given a wash with 25% nitric acid solution. Care must be taken not to leave this solution in the cell long after the first bubbles appear; otherwise the electrodes and leads will become badly etched. This should be followed by several washes of distilled water, after which the cell should be soaked for a few hours in 10% ammonium hydroxide solution, again followed by several successive washings with distilled water.

Once the new cell has been cleaned as suggested, a less drastic cleaning procedure will suffice during normal use. The following procedure has been found adequate, provided no badly contaminated or deteriorated liquids are placed in the cell.

1. Fill cell with toluene or like solvent while hot and let it soak for 15 minutes.
2. Remove toluene and rinse electrodes with fresh toluene, using a wash bottle.
3. Repeat 1 and 2 in order given.
4. Repeat 1 and 2, using acetone instead of toluene.
5. Place cell in 100° C. oven until all traces of solvent are removed.

ACKNOWLEDGMENT

The design of this cell has evolved over a period of years and various members of the Insulation Department of the Westinghouse Research Laboratories have contributed to it.

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A New Cutting-Wire Plastometer

Application to Viscous and Plastic Materials

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The construction and operation of a cutting-wire plastometer suitable for use with substances of high viscosity are described, and typical results with asphalt and aqueous solid soaps are presented. Methods are given for the evaluation of the data in terms of yield values, elastic aftereffect, and viscosity.

MEASUREMENTS of the rheological properties of a high-consistency material that has a complex thixotropic structure can be divided into two classes: dynamic and static. Dynamic measurements are obtained by an instrument such as the rotating cylinder viscometer, which usually measures the consistency of a material after the original structure of the sample has been partially or completely destroyed by the shearing process that occurs during the test. Very few instruments have been developed that are capable of giving static measurements. This paper describes a cutting-wire plastometer that measures the rheological properties of the original, undisturbed material.

Wire plastometers have been used for rheological studies before (1, 7, 9), but the instruments were not capable of obtaining force-flow data nor has any attempt been made to relate the data so obtained to those available from conventional instruments. The plastometer here described is so designed that differ-

ent shearing forces may be applied, thus giving force-flow data from which a consistency curve may be plotted. The yield value of plastic solids and the extent of any elastic aftereffect can also be measured with this instrument.

INSTRUMENT

The principle of this plastometer is the measurement, for a given driving force, of the velocity of a wire moving perpendicular to its longitudinal axis as it cuts through the material. The instrument itself is simple in design, adapting a torsion balance to provide a steady vertical motion of a wire as it cuts through a sample.

The plastometer (Figures 1 to 4) has an arrangement whereby the cutting wire is rigidly attached to one arm of the balance. A number of stainless steel wires were used, the diameters being determined with a micrometer. The driving force necessary to produce motion is provided by adding weights to one of the balance pans. The wire then cuts a sample, 2.72 cm. in width, contained in a stainless steel cutting box, *B*, which has slits of 0.3 cm. (0.125 inch) wide cut into its sides, enabling the wire to travel downward through the sample. The vertical movement of the cutting wire is observed by watching a spot of light that is reflected from a small mirror, *A*, which is attached by a thin rod to the fulcrum point of the balance. The magnification is such that when the spot of light travels 5 cm. (2 inches) on a wall scale, the wire has cut 0.09 cm. of the sample. In this manner, velocities of cutting as low as 10^{-4} cm. per second may be measured.

A two-way ratchet is incorporated into the inverted U-bar, across which is stretched the cutting wire, so that the wire can always be stretched to the same tension. The total length of the cutting wire is 8 cm., and in order that the wire may have the same tension in all experiments a rod 1.25 cm. (0.5 inch) in diameter is placed in the position usually occupied by the cutting box. The wire is considered tight enough to use if a deflection of less than one division (5 cm., 2 inches, on the wall scale) is obtained for a load of 500 grams when the wire is pushing against this rod. The cutting box can be moved horizontally on the traveling table, *C*, enabling the wire to cut the sample in any of the seven slits. The distance between neighboring slits is 1.25 cm. (0.5 inch). The U-bar, cutting box, and traveling support are all inside a double-wall air oven, *D*, in which the temperature and humidity are held constant. The temperature of the oven is controlled by a mercury regulator; and the humidity, measured by a simple wet-dry bulb thermometer arrangement, is kept constant by regulating the amount of steam entering the oven from a small steamer. A 0.02-h.p. motor with a 15-cm. (6-inch) fan blade circulates the air in the oven. The temperature of the sample is measured to 0.1° C. by thermometer *E*, pushed through a small hole in one end of the cutting box.

The distance of each division of the wall scale in terms of the movement of the cutting wire was determined by the use of a micrometer, mounted on a solid support in such a manner that the cutting wire rested on its movable jaw. Thus the cutting wire could be moved a definite distance corresponding to a movement of one division on the wall scale.

EXPERIMENTAL TECHNIQUE

FLOW CURVES. To determine the velocity for a given load, the time required for the spot of light to move across a given number of divisions is measured by means of a stop watch. The data for a flow curve are obtained by varying the driving force, *F*, and measuring the corresponding velocity, *U*. A complete flow curve over a wide range of driving forces can be obtained in 15 minutes by this technique.

YIELD VALUES. The "practical" yield value is defined (*δ*) as the force at which flow becomes observable under the usual conditions of the test. With this instrument the yield value, *f*, is

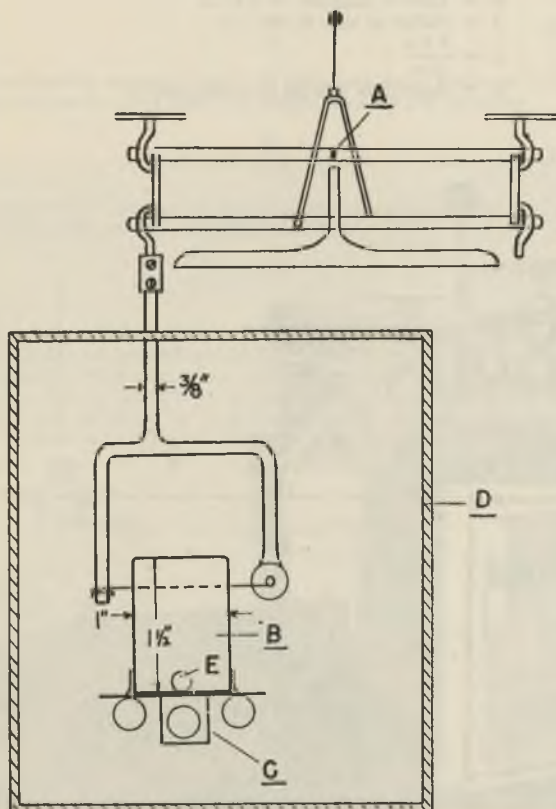


Figure 1. Side View of Cutting-Wire Plastometer

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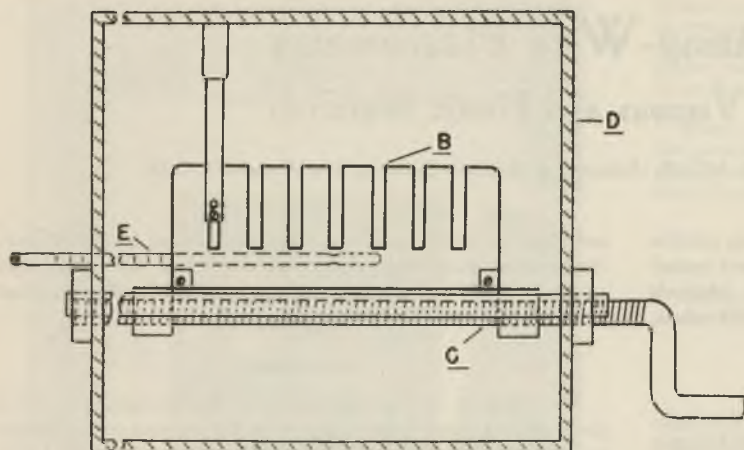


Figure 2. Front View of Cutting-Wire Plastometer

determined under the following conditions. The wire is pushed 2 to 3 mm. into the sample, then weights are added until the spot of light on the wall scale begins to move, corresponding to a velocity of the wire of about 10^{-4} cm. per second. The load is decreased until this motion stops and then if a small increase in the load imparts a barely detectable motion to the wire, this load is taken as the yield value. If the sample is rheologically homogeneous this value may be reproduced to within 3 to 5%.

PREPARATION OF ASPHALT SAMPLES. Since most asphalts harden rapidly with time (11, 13) it is essential that studies of such materials be made at the same age if values are to be compared. Normally, a determination on an asphalt is started one hour after pouring. Preliminary experiments showed that this was sufficient to allow the asphalt to reach the desired temperature. The procedure followed in preparation of asphalt samples was as follows:

First the cutting box was removed from the traveling table and wrapped tightly with wrapping paper to prevent the asphalt from flowing out through the slits. The box was then placed in a wooden mold and the space between box and mold filled with a 0.94-cm. (0.375-inch) thickness of plaster of paris. After the plaster of paris had set, the cast enclosing the cutting box was removed from the mold and put into an air oven at 115°C . At the same time a beaker containing the asphalt was placed in the oven. After one hour, the cutting box was removed from the oven, and the asphalt poured into it. The asphalt was allowed to cool in air for 15 minutes and then was put into a 25°C . water bath; 45 minutes later the cutting box was removed from the bath, the plaster of paris cast removed, excess asphalt trimmed from the box, and the cutting box clamped on the traveling table.

The data for flow curves were obtained as follows:

The wire was lowered until it rested on the surface of the asphalt, then weights were added to one of the balance pans and the time for each scale division of penetration was measured by a stop watch. Each division corresponds to roughly 0.09 cm. and in general the wire traveled 15 to 20 divisions in each slit. The wire was then removed from the asphalt, cleaned with a cloth soaked in carbon tetrachloride, and moved to the next slit. This process was repeated using different driving forces.

PREPARATION OF SOAP SAMPLES. The procedure for obtaining a flow curve was as follows:

The soap was trimmed with a knife until it could be forced into the cutting box. The box

was put into the constant temperature-humidity oven and the temperature raised to 60°C . After the soap had reached temperature equilibrium for 0.5 hour, the initial yield value was determined and data for a flow curve were taken. The control of humidity was sufficiently good to prevent the soap from drying out at this temperature; the water content of a bar of soap left in the oven for 24 hours at 60°C . changed only 1% on the surface, while the composition of the soap in the middle of the bar changed only 0.5% (analysis by drying to constant weight at 105°C .).

CALCULATIONS

Rheological properties are best classified in terms of plots of shearing stress against rate of shear, typical examples of different cases being shown by Houwink (4). Such curves permit easy differentiation of purely viscous, quasi-viscous, purely plastic, and quasi-plastic flow. Unfortunately it is not possible to obtain absolute values of rate of shear and shearing stress from the present data. Even so, however, it is

possible to use the formal resemblance of the curves of U vs. F (velocity of the wire vs. driving force) to those of D vs. τ (rate of shear vs. shearing stress) to derive a yield value, a measure of consistency related to the apparent viscosity, and information as to whether the flow is viscous, plastic, quasi-plastic, etc.

Lamb (6) has derived a hydrodynamic equation for the free motion of an infinite cylinder in a direction normal to its length through an infinite viscous liquid:

$$F = \frac{4\pi\eta U}{0.5 - \gamma - \ln \frac{1}{2}\kappa r} \quad (1)$$

where F = driving force in dynes per cm. of wire
 U = velocity of wire in cm. per second
 η = coefficient of viscosity in poises
 γ = Euler's constant = 0.5772
 r = radius of wire in cm.
 $\kappa = \frac{2U\rho}{4\eta}$
 ρ = density of sample in grams per cc.

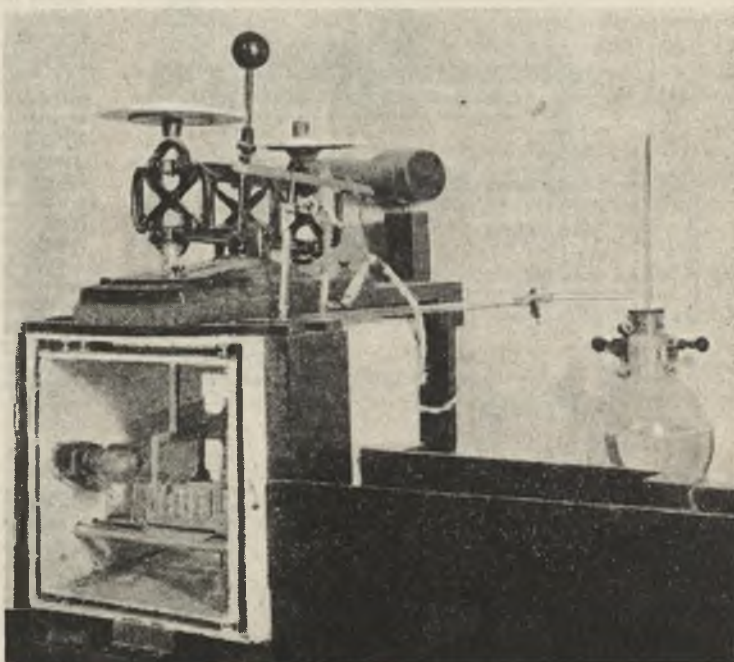


Figure 3. Cutting-Wire Plastometer

For purposes of calculation we propose to treat the wire in this plastometer as though it were such a cylinder.

For calculation by this equation plots are first made of the velocity, U , against the driving force, F , from which values of U and F may be determined at any point. These values are then used in Burger's approximate equation (2).

$$F = \frac{4 \pi \eta U}{0.5 - \ln r} \quad (2)$$

to obtain a rough value of η which is used to assist in the solution of Equation 1 by the method of successive approximations.

In applying these equations to the present experimental results it cannot be assumed that the calculated values of the constants will be quantitatively correct. The equation given by Lamb requires for attainment of constant velocity by the wire either that the viscous liquid be confined between two parallel plates of infinite extension or that inertial effects be important and considered, neither of which conditions is satisfied in the present apparatus. In addition, the area over which the driving force is effective may not be the same as the total area of the wire. Finally, and probably most important, basic Equation 1 was deduced for a purely viscous medium in which the fluid "closes in" completely around the falling cylinder, whereas with many materials cutting occurs without the material flowing together again behind the wire, even though plastic flow occurs immediately below the wire.

Despite these reservations it seems worth while to calculate results according to Equation 1, since the values of η so obtained afford a convenient means of comparing the relative consistency of the various samples. It is also of interest to compare these values with absolute values of η obtained by other methods and reported in the literature, as an indication of what degree of practical success may be achieved by the admittedly illegitimate use of this equation.

For a purely viscous material the rate of shear, D , by definition is

$$D = \frac{\tau}{\eta} \quad (3)$$

The shearing stress, τ , which by definition is the force per unit area, may be obtained from the present data by the equation

$$\tau = \frac{F}{2 \pi r} \quad (4)$$

if it is assumed that the force is applied uniformly over the whole area of the wire, while, from Equation 1,

$$D = \frac{2U}{r(0.5 - \gamma - \ln \frac{1}{2} \pi r)} \quad (5)$$

It is evident from Equation 1 that U is directly proportional to F except for its appearance in the logarithmic term in the denominator. Moreover, τ is directly proportional to F and D to U except for the term $\ln \frac{1}{2} \pi r$ (in the denominator). Since in practice the value of $\ln \frac{1}{2} \pi r$ changes only slightly even with large changes in U , a plot of U against F will show features similar

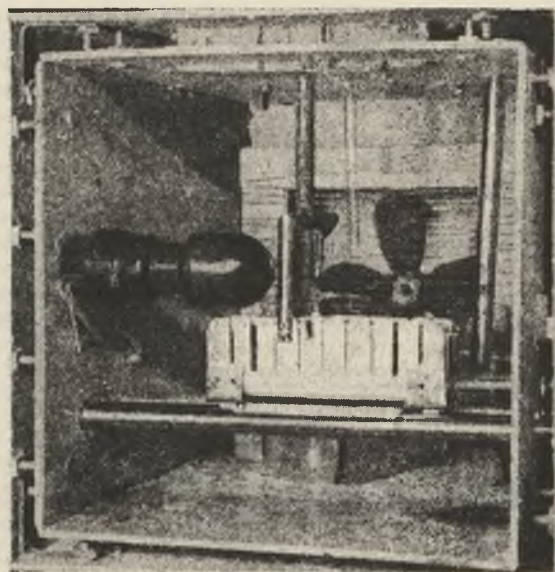


Figure 4. Detail View of Interior of Cutting-Wire Plastometer

to those of a $D - \tau$ plot with respect to classification of the rheological behavior of materials. Thus it may be assumed that for a truly viscous system the $U-F$ diagram will be very nearly a straight line through the origin.

For plastic substances the $U-F$ curve will no longer be so simple. In such cases the $U-F$ relationship is often represented satisfactorily by the Bingham equation,

$$U = \frac{1}{\eta} (F - f_B) \quad (6)$$

where f_B is the extrapolated Bingham yield value. In this case viscosities may be calculated as before except that $(F - f_B)$ is used instead of F in Equations 1 and 2.

RESULTS WITH ASPHALT

This material was chosen to test the possibilities of the instrument, since it is a high-viscosity substance which has already been extensively studied. (The authors wish to thank R. N. Traxler and W. E. Kuhn of the Texas Company for furnishing asphalt samples of known consistency.) Characterizing data on the asphalt samples, together with the various values obtained for the "viscosity", are presented in Table I.

The many curves determined on the original asphalt samples were similar and only the one representative flow curve is shown in Figure 5. This curve shows that the asphalt exhibits viscous behavior in that under the rates of shear investigated the velocity is directly proportional to the force at all values and falls to zero at zero load. These samples have a high degree of elasticity since, as shown by the points under the curve, the velocity of the wire decreased progressively under constant load with increasing penetration of the asphalt, this effect being greater the higher the velocity. Apparently part of the external driving force is used to overcome the elastic resistance of the stretched asphalt behind the wire. That such elastic elements are actually present was proved by the observation that on release of the load after penetration of the asphalt the wire moved upward through the sample almost to its original position. Similar observations were made by Ford and Arabian (3) on a blown asphalt using a conical cylindrical viscometer.

A value for the apparent viscosity was calculated from these data by Equation 1, using values of U and F from the straight line drawn through the points representing initial penetration of the asphalt, this being selected to minimize the effect of elasticity. The values so obtained (Table I) are all higher by about a factor

Table I. Data on Asphalt Samples^a

Characteristics	Sample A	Sample B	Sample C
Softening point, ° C.	43	44	46
Penetration at 0° C.	30	26	16
Penetration at 25° C.	122	92	76
Density, grams per cc.	1.013	1.013	1.017
Rotary viscometer data, 25° C.			
Rate of shear of 0.00981 sec. ⁻¹ , viscosity, megapoises	0.44	0.87	1.48
Rate of shear of 0.0981 sec. ⁻¹ , viscosity, megapoises	0.42	..	1.50
Cutting-wire plastometer data on original samples ^b			
Viscosity, megapoises (apparent)	4.16	7.56	15.0

^a All rotary viscometer data and characteristics except density furnished through courtesy of the Texas Company.

^b Wire radius 0.015 cm. except 0.036 cm. for sample C.

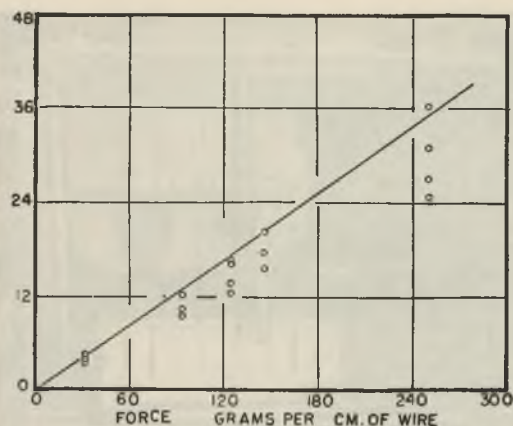


Figure 5. Flow Curve on Fresh Asphalt

Points below the line show progressive decrease in velocity with increasing penetration of sample due to its elastic properties.
Velocity, cm. per second $\times 10^4$

of 10 than those obtained with the rotary viscometer. This might be due to failure of the system to conform with the requirements of the equation used to calculate the results. However, it has been shown (12) that the consistency of asphalt changes with time, owing to its colloidal structure. The values by the rotary viscometer method in Table I are for a steady state where an equilibrium has been reached between any tendency toward spontaneous formation of structure within the asphalt and the disaggregating effect due to the constant shearing action of the instrument. It would be expected that such a value of η would be lower than that measured by the cutting-wire plastometer, since in the latter case there is probably little breakdown of structure, the wire continually passing through a new portion of the sample.

ELASTIC AFTER EFFECT. The applicability of the cutting-wire plastometer to study of the elasticity of asphalt was investigated following the method of Pendleton (10). The elastic aftereffect was studied quantitatively at two different loads with the results shown in Figures 6 and 7, data for one of these runs being given in Table II. The initial period, *AB*, is the time required for penetration under constant driving force. At *B* the driving force is removed and the wire moves back toward its original position, the elastic recovery of the asphalt being measured by *BC*.

To obtain the amount of viscous flow from these data the recovery curve was inverted and subtracted from the initial deformation curve, this being done by subtracting from the observed deformation (curve *AB*) the amount due to elastic stretch. The elastic deformation was obtained from the recovery curve, *BC*, by plotting observed recovery as a positive deformation starting with zero time at the moment recovery begins. Subtraction of

the inverted recovery curve, *B'C'*, from the original deformation curve gives the displacement resulting from purely viscous flow, *AB-B'C'*.

Curves obtained in this manner for viscous flow are entirely similar to those obtained by Pendleton (10) using a Pochettino (14) moving cylinder method. With both the cutting-wire plastometer and the telescoping coaxial cylinders, the deformation due to elastic stretch was found to be far greater than that due to viscous flow. Contrariwise, in experiments on the same asphalt by a penetrometer method (10) elastic deformation amounts to less than 1% of the total. These differences are due to no fault of the different plastometers, but rather are typical of the difficulties inherent in measuring rheological properties of complicated systems which are sensitive to previous heat treatment.

AGED SAMPLES. The same samples of asphalt were tested again after standing 8 months at room temperature, and it was found that in all cases the elasticity had disappeared. Flow curves characteristic of typically viscous materials were obtained—i.e., straight lines passing through the origin—with no elastic recovery and no variations greater than 0.3 to 0.4 second in the time required for the wire to cut through successive equal depths in the sample. This behavior is clearly shown by the typical data in Table III.

Table III. Reproducibility of Flow Data on Aged Samples

(Asphalt sample A, wire radius 0.015 cm.)

Divisions	Load, Grams per Cm.					
	7.35	11.02	14.70	18.40	22.05	25.55
	Time, Seconds per Division					
0-1	18.3	12.6	9.3	7.4	6.5	5.9
1-2	18.6	12.4	9.3	7.5	6.7	6.0
2-3	18.8	12.4	9.5	7.3	6.7	6.0
3-4	18.6	12.6	9.5	7.4	6.7	6.1
4-5	18.8	12.4	9.5	7.5	6.7	6.0
5-6	18.0	12.4	9.6	7.3	6.7	6.0

These data constitute the most favorable case for application of Equation 1, since the asphalt here appears to undergo true viscous flow. Flow curves were obtained on sample A asphalt using several wires of different diameter to determine whether the calculated viscosity is constant as it should be if the equation holds. The data are summarized in Table IV, which also shows the values of the calculated viscosities.

Since the apparent value of η increases roughly linearly with the radius of the cutting wire it is evident that the equation does not hold exactly. However, the values obtained with the different wires are all of the same order of magnitude. The increase with increasing wire size may be due to (a) failure of the system

Table II. Elastic Aftereffect of Asphalt

(Sample C, wire radius = 0.036 cm.)

F, grams per cm. of wire	Recovery, 0.0 gram									
	47 grams									
Divisions cut	0-2	2-3	3-4	4-5	11-10	10-9	9-8	8-7	7-6	6-5
	5-6	6-11			5-4	4-3	3-2			
Total time, seconds	20	33	49	69	94	302	315	334	356	389
			295			496	623	806		432
Data for Inverted Curve B'C'										
Divisions cut	11-10	10-9	9-8	8-7	7-6	6-5	5-4	4-3		
Inverted division*	0-1	0-2	0-3	0-4	0-5	0-6	0-7	0-8		
Time from point B	7.5	21	39	61	94	137	201	328		
Data for Curve AB-B'C'										
Divisions	0.5	1.0	1.6	2.1	2.7	3.2				
Time, seconds	50	100	150	200	250	295				

* A terms used to describe amount of recovery assuming point B as 0.

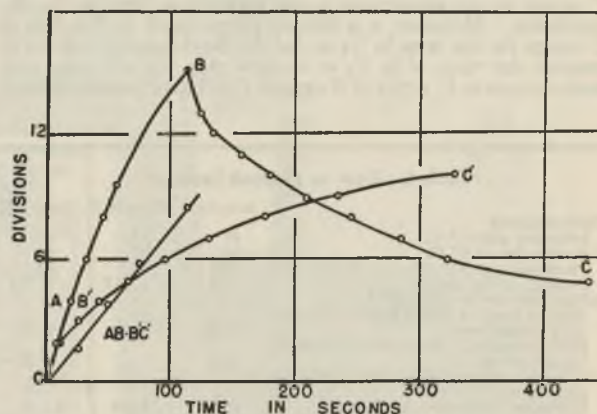


Figure 6. Elastic Aftereffect at a 47-Gram Load

AB is total deformation, *BC* elastic recovery, *B'C'* inverted recovery curve, and *AB-B'C'* deformation due to viscous flow

Table IV. Flow Data on Asphalt Sample A with Wires of Different Radii

Load, Grams per Cm.	Radius, Cm.				
	0.0150	0.0206	0.0255	0.0360	0.0497
5.51	...	3.58	...	3.06	...
7.35	4.38	...	3.88
11.02	7.01	6.6	6.05	5.70	4.97
14.70	9.28	...	7.98	7.50	...
18.40	11.9	10.1	...	8.68	8.35
22.05	13.1	9.75
25.55	14.6	14.9	13.2	13.5	11.0
33.10	17.2	...
Viscosity, megapoises	3.22	3.26	3.63	3.74	4.18

to conform to the model postulated in the derivation of the equation, (b) departure from purely viscous flow in the immediate vicinity of the wire, (c) adherence of a thin layer of asphalt to the wire, thus effectively increasing the radius, or (d) longer periods of heating at 115° C. in the later than the earlier runs. Since the same asphalt was used in all these determinations, it had been heated one hour longer at 115° in each successive run, the runs with the larger diameter wires being made last. However, it is generally assumed that heating at 115° or lower, unless long continued, does not cause any fundamental change in the colloidal nature of asphalt.

It is of interest to compare the different values of apparent viscosity obtained for asphalt in the various experiments. With a 0.015-cm. radius wire the approximate value for a fresh sample of asphalt A is 4.16×10^6 poises, while aged sample A is only 3.22×10^6 poises. The direction of the difference is as would be expected from the loss of elasticity on aging. Fresh samples of asphalt C, using a wire of 0.036-cm. radius, have an apparent viscosity of 1.50×10^7 poises as calculated from initial flow curves (as in Figure 5). With this same sample the value for viscous flow from which the effect due to elastic deformation has been subtracted (as in Figures 6 and 7) is 1.28×10^6 poises.

RESULTS WITH SOAP

Soap was chosen for investigation as a representative of substances exhibiting plastic flow. The aerated converter soap used in these experiments was purchased from a local market, while the framed soap was supplied through the courtesy of the Lever Brothers Company. Neither contained any potash. The characteristics of these soaps (15) are given in Table V.

Since these substances have yield values, there is no flow of the soap in behind the wire as it travels downward through the

sample, and hence the limiting conditions of Equation 1 are not fulfilled. However, the wire does not pass through the cake by a crumbling or cleaving effect, close observation at the edge of the sample showing conclusively that the soap was flowing around the bottom of the wire.

It soon became apparent with framed soap Q at room temperature that the velocity of flow for a given load was not constant. As a result of numerous experiments it was shown that the velocity of flow depended in a rather complicated manner on the depth of penetration of the sample, passing through several successive maxima and minima as the depth of penetration increased. These maxima and minima occurred at roughly the same depth of penetration of the bar in all of several different cross-sectional cuts through the same bar.

Three possible explanations for this behavior are:

1. A "layer structure" in the soap, due to orientation of flow or other causes, which gives rise to alternately hard and soft portions within the sample.
2. Elasticity of the soap, similar to that observed with asphalt. As the wire travels downward at constant load the velocity would decrease because of increasing elastic stretch until the elastic limit was reached, at which point the velocity would rise rapidly and then decrease again.
3. Abnormal flow about the wire, the soap piling up in front of the wire and decreasing the velocity until it sloughs off, followed by repetition of the process.

Table V. Characteristics of Soaps Used

	% H ₂ O	% Cl	Equivalent Weight of Fatty Acids	Iodine Value of Fatty Acids	Free Acid as % HCl	Free Base as % Na ₂ O
Framed soap Q	33.5	1.89	263.1	43.1	0.13	...
Converter soap C	21.2	0.92	260.8	40.9	...	0.02

Similarly, in the case of the converter soaps, the velocity of flow for a given load is not constant at temperatures lower than 50° C. Consequently flow curves on these samples were run at 60° C., at which temperature there is some soap boilers' neat soap present with the more solid phases, judging from the visual appearance of the samples. Determination of the yield value of such samples with this plastometer has been discussed elsewhere (15).

The flow curves obtained on converter soap C with two different wires are shown in Figure 8 and typical data are given in Table VI. Except at the highest velocities, where the time interval being measured was too short, constant speed was obtained for successive increments of distance cut through the bar. At low velocities, AB, the velocity is not directly proportional to the load. At higher velocities the flow curve shows a linear relation between velocity and load. This is the behavior typical of a quasi-plastic (4) material.

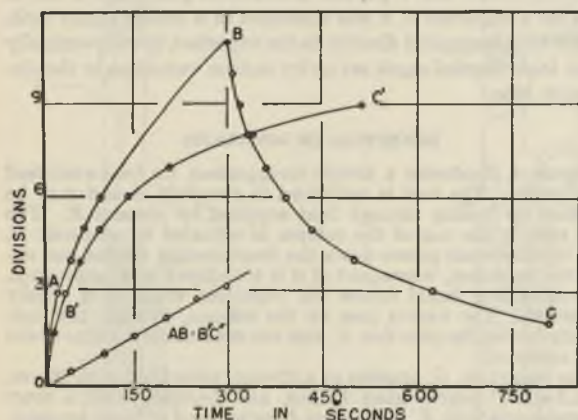


Figure 7. Elastic Aftereffect at a 156-Gram Load

AB is total deformation, BC elastic recovery, B'C' inverted recovery curve, and AB-B'C' deformation due to viscous flow

Table VI. Flow Data for Aerated Converter Soap C at 60° C.

r = 0.0206 Cm.		r = 0.0150 Cm.	
Velocity Cm./sec. $\times 10^{-3}$	Load G./cm.	Velocity Cm./sec. $\times 10^{-3}$	Load G./cm.
0.69	16.53	3.70	16.55
1.53	18.40	6.58	18.40
4.94	22.05	9.50	20.23
6.13	23.90	16.50	22.20
12.80	26.75	21.60	23.90
20.70	28.20	23.70	23.90
21.50	28.20		
Yield Value		Yield Value	
(f)	14.70	(f)	11.04
(f _B)	22.10	(f _B)	17.60

Although the flow conditions here do not conform to those behind the basic equation, it is possible to carry out formally a calculation of the absolute viscosity of the soap by means of Equations 1 and 2, using $F - f_B$ instead of F . Assuming the density to be 0.8 and taking values of F and U from the linear portions of the curves of Figure 8, the apparent viscosity of converter soap C is 4.95×10^4 poises

with a wire of 0.0150-cm. radius. With a 0.0206-cm. wire η also calculates to be 4.95×10^4 poises. Despite this agreement the significance of the figures is questionable, since the complex nature of the flow has not been taken fully into account in any of the equations. Interestingly, McBain and Watts (8) using an extrusion plastometer found values between 2.9×10^5 and 2.7×10^4 poises, depending on the driving force, for the apparent viscosity at room temperature of a partly crystallized aqueous system containing 63% potassium laurate.

SUMMARY

The construction and operation of a new cutting-wire plastometer are described, suitable for use with substances of high viscosity which must be maintained at constant relative humidity as well as at constant temperature. Yield values, rate

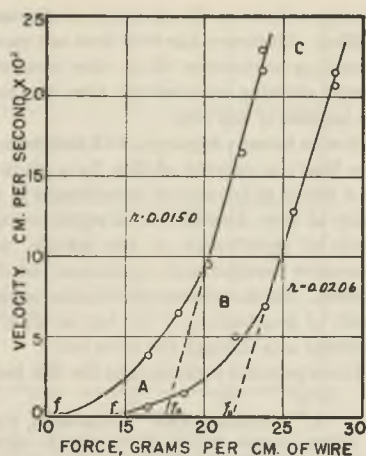


Figure 8. Flow Curves on Aerated Soap at 60° C.

f and f_B are, respectively, initial and Bingham yield values

of flow at different velocities, and extent of elastic recovery can be studied with this instrument, thus permitting construction of curves which depict the complete rheological behavior of the material being studied.

Experiments were carried out on asphalt and soap. The particular asphalt samples studied were found to be truly viscous substances after aging, but initially showed a high degree of elastic recovery. The calculated value of apparent viscosity was around 3.5×10^6 poises. The soaps studied exhibited the behavior of a quasi-plastic material, with an apparent viscosity of about 5×10^4 poises.

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Backward-Feed Distillation Column

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A BACKWARD-FEED or stripping column, in contrast to the usual batch-distillation column, has the feed introduced at the top. The higher boiling fractions are removed as product at the bottom. While the same result can be obtained whether backward-feed or the usual forward-feed batch distillation is used, the apparatus described here has several advantages in operation over the customary methods. Control of the distillation rate is effected by adjustment of a stopcock. The method of vaporization employed does not require close control of heat input and has practically no fire hazard. It is better suited for heat-sensitive liquids and liquids which bump or froth, but cannot be used for liquids containing an appreciable amount of solids or nonvolatile liquids.

This type of column has received little attention because of the difficulty in constructing a vaporizer for the liquid leaving the bottom of the column which automatically vaporizes any liquid entering with very low holdup. Bosschart (1) has described a backward-feed column for analyzing low-boiling liquids. Vaporization of the liquid stream was obtained by means of the usual still flask. Its main disadvantage, besides large liquid holdup, was that it required adjustment of the heat input. Fenske *et al.* (2) have constructed an all-metal, backward-feed column with a film-type vaporizer having automatic operation

and low holdup. However, this column is unsuitable for general laboratory use where glass construction is required.

It was found that a packed or indented glass tube could be used for a vaporizer if it was immersed in a heated liquid bath. Where heat is supplied directly to the vaporizer, it will eventually crack from thermal shock set up by sudden variations in the distillation rate.

DESCRIPTION OF APPARATUS

Figure 1 illustrates a simple arrangement for backward-feed distillation. The feed is contained in reservoir A and may be agitated by boiling through heat supplied by element B. The feed rate to the top of the column is adjusted by stopcock D. The liquid stream passes down the fractionating section and enters the vaporizer, where part of it is withdrawn at F as product. The remaining liquid enters the vaporizer where it is totally vaporized. The vapors pass up the column, through the electrically heated by-pass line, C, and the condensate returns to the feed reservoir.

The vaporizer, G, consists of a 25-mm. tube filled with 30 cm. of 0.3-cm. (1/8-inch) glass helices, and provided with a short thermocouple well, E, and section F for removal of liquid product. The liquid bath of mineral oil is contained in the 60-mm. tube, H. The bath is heated either by an external heating element wound directly on tube H or by an internal element wound directly on vaporizer G. The external element is held in place by Alundum

cement. The internal element is wound in a double pitch spiral and the coils are spaced by small knobs on tube *G*. The ends of the element are fastened to glass binding posts located below the oil level to prevent fire hazard and cracking of the oil at surface.

A more flexible arrangement, illustrated in Figure 2, allows ordinary flasks of the desired size to be used for the feed reservoir. It also allows the feed to be introduced at the bottom so that it can be operated as a forward-feed column. For the latter case, one arrangement is illustrated where sufficient air pressure is supplied at *G* to reservoir *H* to compensate for the pressure at the base of the column. The construction of sections *A* and *B* and the method of attaching the flasks have been described in a previous paper (3).

The operation of this arrangement is the same as that of Figure 1. The vapors, however, leave from the bottom of the vaporizer through line *F*, thus avoiding the appreciable superheating which occurs at the stagnant bottom end of the vaporizer in Figure 1. A short section of packing is provided at *D*, if desired, to ensure that the correct boiling point is measured. At slow distillation rates the vapors may be superheated several degrees. The vaporizer tube is constructed of a 30-mm. tube with an indented

Table I. Fractionation of an Equivolume Mixture of *m*-Xylene, Toluene, and Benzene

% Distilled	Temperature, °C.	% Distilled	Temperature, °C.
0-25	138	59	105
26	136	60	100
28	132	63	96
30	126	64	92
33	118	66	88
35	116	68	85
36	117	70	84
38	117	72	84
41-55	113-111	75	82
55	110	77-81	81
57	109		

section 30 cm. long. Heating is supplied by an external heating element wrapped around the tube holding the oil bath. The indentations are made by means of a graphite rod, 1 cm. square, ground to give the form illustrated. Tube *E* leaving the bottom of the vaporizer may be used to remove non-volatile liquid residues from the column.

The above apparatus has been used over the past year for batch distilling, at atmospheric pressure, a variety of liquids boiling up to 150° C. The results are the same as with forward-feed operations except that the heavy ends are removed first.

As an illustration a distillation of an equivolume mixture of *m*-xylene, toluene, and benzene is given in Table I. A charge of 900 cc. was fractionated in a perforated plate column (15 plates, plate efficiency 70%, holdup 2.5 cc. per plate). The column was run at total reflux using the arrangement shown in Figure 1 with a 20-cc. holdup receiver (4) inserted between the fractionating section and the vaporizer.

VAPORIZER OPERATION AND CONSTRUCTION

The tests with the vaporizers were run with benzene using a mineral oil bath heated to 200° C. The heat was supplied by the external heating element. The 25-mm. tube, *G*, Figure 1, packed with 0.3-cm. (1/8-inch) glass helices was found to have a vaporizing capacity of 3.5 liters per hour, which is considerably higher than the flooding point for a fractionating section of the same size and packing. Coarser packing materials, such as 0.25-inch berl saddles and 6-mesh Carborundum, had a capacity of less than 1 liter per hour. The indented vaporizer (Figure 2) was found to have a capacity of 2.5 liters per hour. This indented vaporizer could not be run without a bottom take-off line, owing to its flooding characteristics. The packed tube (Figure 1) was also tested with a bottom take-off line similar to that of the indented vaporizer. Using 1/8-inch helices as packing its capacity was 1.5 liters per hour.

The heating method illustrated here has one minor disadvantage. In case the distillation stops and the column is unattended, there is danger that the heating bath may undergo decomposition. This may be avoided by using a stable, high-boiling liquid for the heating bath. This liquid is contained in a jacket sealed to the vaporizer and vented at the top through an external condenser. Any excess heat is removed by the liquid refluxing in the condenser.

ADVANTAGES. The distillation rate is adjusted rapidly and closely by means of a stop-cock. Exact control can be obtained by using a calibrated orifice in series with the feed reservoir.

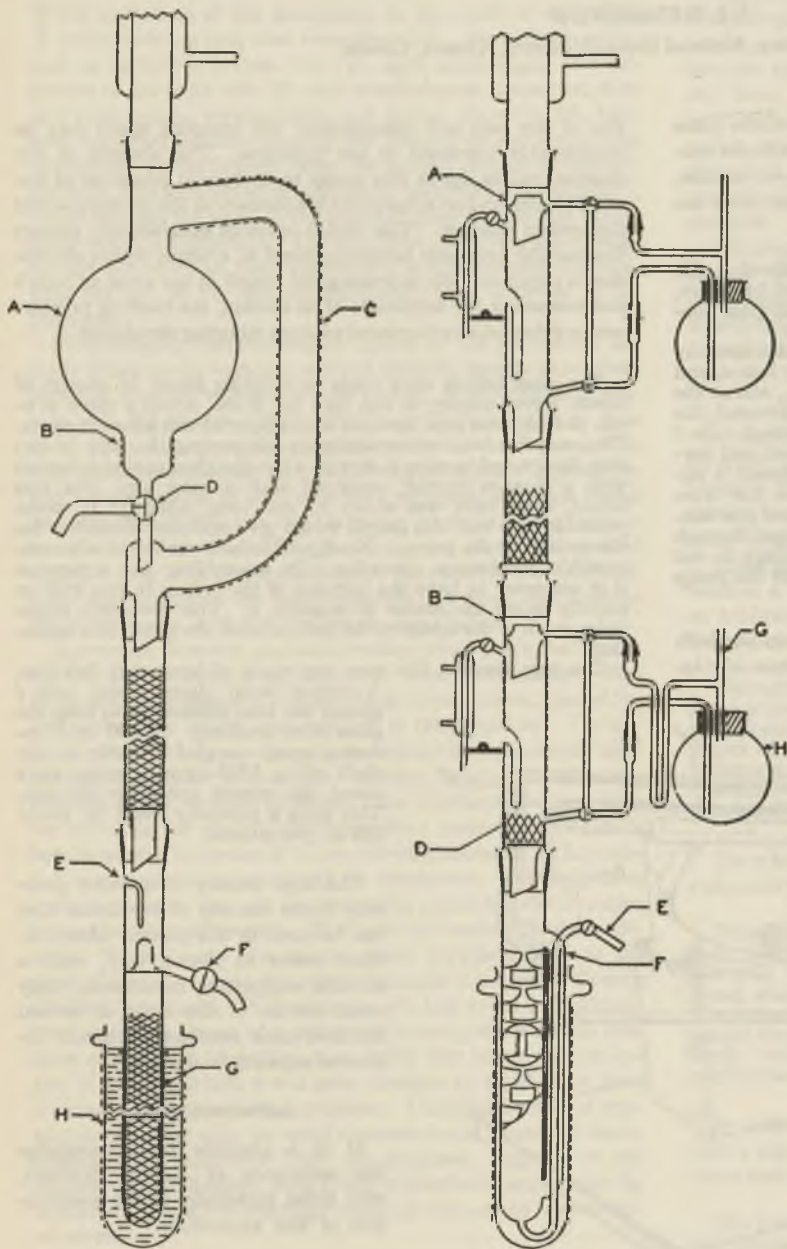


Figure 1

Figure 2

There is no loss of liquid if the column floods when unattended.

There is less fire hazard than with the usual type of column. In case of breakage there is little liquid in the vaporizer and column proper and the distillation can be stopped immediately. The jacket bath can be enclosed and insulated, so that inflammable liquids will not be ignited.

Thermal decomposition of heat-sensitive materials can be decreased by keeping the feed liquid cold. The removal of the heavy ends first should also decrease thermal decomposition.

There is no tendency for liquids to bump or froth with the type of vaporization employed.

Where there is lack of head space, several columns can be oper-

ated in series, using a vaporizer as an automatic pump for taking liquid from the bottom of one column to the top of the next.

DISADVANTAGES. Large amounts of solids or nonvolatile viscous liquids will plug up the vaporizer.

The vaporizer has more liquid holdup than the condenser used in the reverse type of operation.

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- (4) Oldershaw, C. F., *Ibid.*, **13**, 267 (Figure 5) (1941).

A Constant-Volume Pump for Circulating Gases

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AN APPARATUS that has been devised to circulate gases in a system where it is necessary to keep the volume constant consists of two Toepler pumps of about 100-cc. volume, connected as shown in the figure, so that the exhaust from one becomes the intake of the other.

The assembly moves freely in a vertical plane about *e*, the amount and timing of this movement being controlled by a cam, *g*. Free movement about *e* is accomplished, with all-glass construction, by means of two helices, attached as shown.

The operation of the pump is simple. As bulb *b* is raised by the cam, the mercury contained in it flows by gravity into *a*, and completely fills it. This forces any gas in *a* through *c*, and at the same time allows *b* to fill with gas through *d*. As *b* is lowered, the mercury in *a* flows into *b* and forces the gas in *b* through tube *f* into *a*. The cam is shaped to maintain *b* in the raised and lowered position for an equal period of time, and its speed is adjusted to give just sufficient time for the mercury to flow from one bulb to the other when *b* is in the raised or lowered position. With each rotation of the cam 100 cc. of gas are forced through the pump. In practice, *f* was made of 2-mm. capillary to cut down the dead space and to give added strength where the pump is supported by the cam.

Since the time required for the mercury to flow from one bulb to the other is less at low than at high pressures, the rate of rota-

tion of the cam and consequently the pumping speed may be considerably increased at low pressures. The absence of mechanical valves allows this pump to operate at pressures as low as 0.001 mm. and no adjustment is necessary as the pressure within the system changes. This device operates satisfactorily against the backing pressures normally found in systems where circulation is required. By increasing the length of the arms on bulb *b* and increasing the amplitude of its motion, the backing pressure can be substantially increased without stopping circulation.

The glass helices were made by winding about 1.5 meters of 6-mm. Pyrex tubing, at one turn per 2 cm., about a piece of 5-cm. (2-inch) iron pipe, covered with a layer of wet asbestos paper. This may be done conveniently by supporting the pipe in two ring clamps and turning it slowly, while the glass tubing is heated with a Bunsen burner, equipped with a wing top. For this model, each helix was about 15 cm. long, although it seems probable that half this length would give sufficient flexibility for the motion of the pump. No sign of failure was found after one month's continuous operation. In assembling the apparatus it is necessary to have the bottoms of the helices in line with or slightly below the center of rotation, *e*. This procedure eliminates much of the strain on the helices when the pump is in operation.

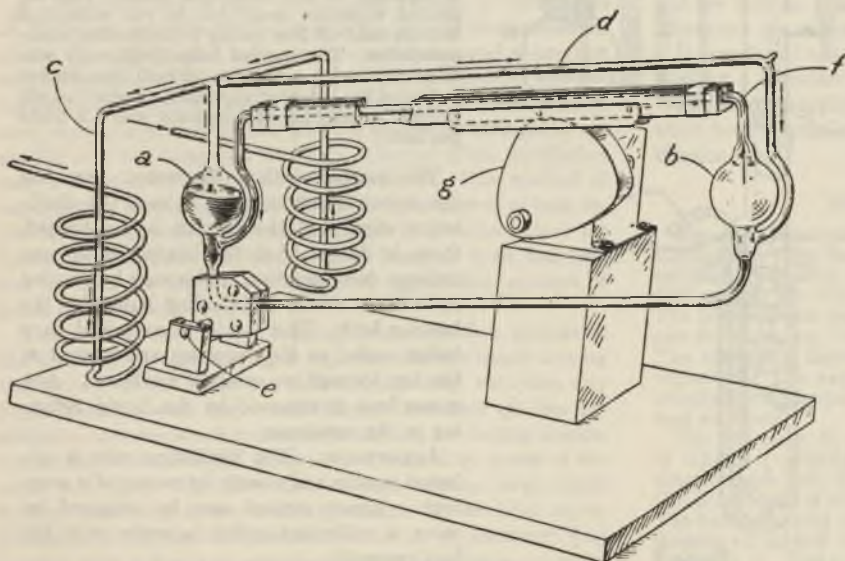
The cam used in this case was made of laminated Bakelite.

A strip of wood placed under tube *f* spread the load sufficiently to keep the glass from cracking. A 600 to 1 reducing gear, coupled directly to the shaft of a 1725-r.p.m. motor, gave about the correct speed for the cam. This gave a pumping speed of about 300 cc. per minute.

The high density of mercury probably limits the size of the bulbs that can be used in this pump. However, there seems no reason why, with a suitable supporting mechanism, they could not be of the order of several hundred cubic centimeters, should increased capacity be desired.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the assistance of George Richard, who aided materially in the construction of this apparatus.



MICROSCOPE GONIOMETRY

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Crystal identification by microscopical examination has been hampered by the difficulty of correlating published goniometric data with the angular measurements made on the various views of the crystal, as seen in the microscope. Known graphical methods of crystal drawing and properties of the stereographic projection are here applied quantitatively to interpret microscopical views in terms of published data. Conversely, the axial elements of a crystalline substance can be derived from microscopical measurements of angles between edges or projected edges.

THE usefulness of the microscope in the study of crystalline compounds has long been recognized (10). Optical properties, such as refractive indices (11, 14), optic axial angle, and dispersion of the optic axes (9), and morphological properties, such as crystal system, crystal habit, and outline angles (6, 13), have been employed in characterizing new compounds and identifying unknowns. In the present paper the authors propose to describe methods, here grouped under the name "microscope goniometry", which enhance the value of the morphological studies that can be made with the microscope. The principles underlying these methods are not new, but their application to microscopical observations has not, to the authors' knowledge, been discussed in the literature.

Morphological observations by means of the microscope are made either on dry crystals, selected from the sample as received provided they are sufficiently well formed, or on crystals in contact with the mother liquor, after recrystallization on a glass slide. In either event, the immediate objective of the examination is the determination of the following properties: crystal system, Miller indices of the faces, and apparent interedge angles seen on different "views"—that is to say, on crystals lying on various faces. With these data, the compound may be recognized again, as long as it is recrystallized in the same manner and contains approximately the same impurities as when the observations were made, so that it exhibits the same habit.

In practice, however, such observations often prove inadequate for the identification of an unknown. The chief reason is that published descriptions of microscopical crystal views, needed for comparison, are scanty and scattered in the literature. The microscopist must rely on other morphological data, universally used in crystallographic publications—namely, interfacial angles, coordinate angles, or axial elements. The interfacial angles, which are available for some 12,000 crystalline compounds (?), have been measured by means of the one-circle goniometer. They cannot, in general, be measured with the microscope. [Methods have been proposed in the past for measuring actual interfacial angles by means of the microscope. They have not received wide acceptance. When a zone axis can be placed perpendicularly to the stage of the microscope, the interfacial angle is measured directly (Mallard's method). The inclination of a face to the vertical may be obtained by means of a calibrated focusing screw and an eyepiece micrometer (9).] The same holds true for coordinate angles of faces (azimuth ϕ and polar distance ρ), which have been obtained on the two-circle goniometer. Condensed tables of crystal constants list only the axial elements (axial ratios and interaxial angles), calculated from the measured angles. For the purpose of identification, axial ratios or interfacial angles must be translated in terms of interedge angles as seen on the microscopical views.

The angle between two edges that are parallel to the plane of the microscope stage is seen in true value. In general, the true

interedge angle cannot be measured on the rotating stage whenever one of the edges, or both, are oblique to the plane of the stage. The projection of the true angle onto the stage is called the apparent angle. This is the angle actually measured.

When the goal of the examination is the characterization of a new compound, it is desirable to know, in addition to the apparent interedge angles actually observed, the approximate axial elements or the Barker determinative angles (2) of the crystal. These constants are not, in general, readily apparent from the microscopical observations.

Two problems, therefore, need to be considered: (1) Given the morphological constants of a crystal (axial elements, interfacial angles, or coordinate angles), to determine the apparent angle between any two edges that will be seen when the crystal lies on any face. (2) Given the apparent interedge angles measured from microscopical views (one, two, three, or five independent angles, depending on the crystal system), to determine the morphological constants (axial elements or interfacial angle between any two faces). These problems will be solved by graphical methods.

The proposed methods are intended for use by chemical microscopists. For the benefit of those who may not be familiar with crystal projections and terminology, a short section on definitions is included. The reader is referred to standard texts on crystallography for a fuller discussion.

DEFINITIONS

A zone is the assemblage of all the faces parallel to a common direction, called the zone axis. Faces in a zone are said to be tautozonal. Tautozonal faces, produced if necessary, intersect along parallel edges; the direction of these edges is that of the zone axis. A face parallel to a given face is called its counterface.

There are two methods of representing the directions of crystal faces on a sphere, drawn around any point inside the crystal with an arbitrary radius. The first method, which may be called the direct method of spherical representation, is as follows:

Through the center of the sphere passes a plane parallel to every face (or to every pair of parallel faces). This face plane intersects the sphere along a great circle, called the face circle. The face planes of tautozonal faces intersect in a diameter, which therefore punctures the sphere in a pair of diametrically opposite points. The latter are called the zone points; they give the direction of the zone axis.

The second method, which may be called the polar method (or reciprocal method), is as follows:

From the center of the sphere drop a perpendicular on every face. This face normal punctures the sphere in a point, called the face pole. The face normals of tautozonal faces lie in a diametral plane, which therefore intersects the sphere along a great circle. The latter is called a zone circle. The zone axis is given by a line passed through the center perpendicularly to the plane of the zone circle; such a line punctures the sphere in two diametrically opposite points, called the poles of the zone circle.

In order to project the spherical representation of the crystal onto a plane, use is made of the stereographic projection, which dates back to Ptolemy.

The South Pole of the sphere is taken as the projection point and the plane of the equator as the projection plane (Geographical parlance is chosen for convenience.) In this system of projection, circles on the sphere are projected as circles (or straight

lines), a property whose first complete proof probably is that given by Clavius in 1593. The projection, moreover, is angle-true, as was shown by Halley in 1695. It is easily seen that all the points in the Northern Hemisphere are projected inside the equator (primitive circle) and that points on the equator are themselves their own stereographic projections. Points in the Southern Hemisphere, with the above convention, would be projected outside the primitive circle. In order to make their projections fall within the primitive circle, such points are projected to the North Pole instead of the South Pole. They are represented by circlets in stereographic projection, whereas the projections of points in the Northern Hemisphere or on the equator are marked by points (or by crosses).

In the established though unfelicitous crystallographic usage, the term stereographic projection is construed to mean the stereographic projection of the face poles (polar method), while the stereographic projection of the face circles (direct method) is called cyclographic projection. In the following, these terms are used in the crystallographic sense.

The dihedral angle between two faces is given by its supplement (called the interfacial angle). The plane angle between two edges,

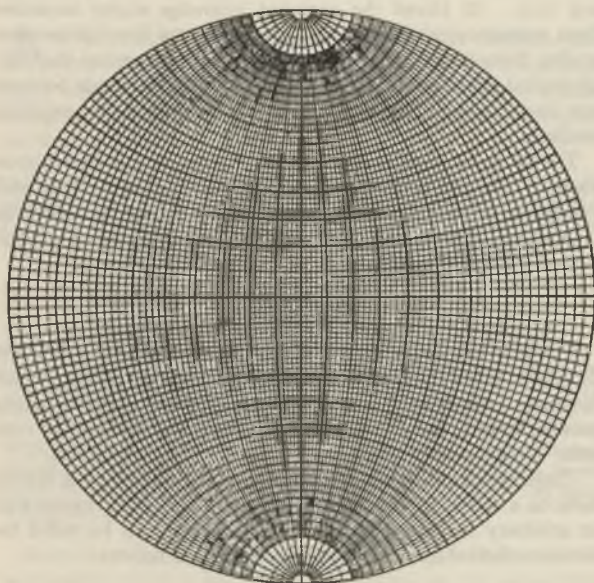


Figure 1. Stereographic Net

the interedge angle, is likewise given by its supplement (called the interzonal angle). In stereographic projection an interfacial angle appears as the arc of great circle between two face poles, an interzonal angle as the angle between two zone circles. In cyclographic projection an interzonal angle appears as the arc of great circle between two zone points, an interfacial angle as the angle between two face circles. The projection of an interedge angle on any plane is, of course, the supplement of the projection of the interzonal angle on the same plane.

The rotating stereographic net (so-called Wulff net) is used for graphic constructions (1). It consists (Figure 1) of a circle, usually of 10-cm. radius, on which two families of circles have been projected: great circles, 2° apart, intersecting in a diameter of the equator, and small circles, likewise 2° apart, perpendicular to the same diameter. The net is pasted on heavy cardboard and a thumbtack is pushed through its center from the back. [Such nets, prepared by M. A. Peacock, may be purchased from the University of Toronto Press, Toronto, Ontario, Canada (50 cents a dozen).] All constructions are made on a sheet of tracing paper which is rotated around the thumbtack. The center of the sheet is reinforced by means of Scotch tape.

Plotting the stereographic projection of a crystal from given interfacial angles is carried out in general as follows:

Two face poles are arbitrarily located on the primitive circle, at the given angular distance apart. Any other face, whose interfacial angles with the first two faces are known, may be located at the intersection of the loci of the points which are at the required angular distances from these two faces. The locus of the points which are equally distant from any given point on the primitive circle is given by one of the small circles of the Wulff net. Every pair of face poles thus located determines a zone circle, a great circle on the net, whose intersections with other zone circles in turn determine the poles of other faces, either observed faces or possible faces. The cyclographic projection is constructed from interzonal angles in an analogous manner.

PRINCIPLES OF THE GRAPHICAL SOLUTIONS

PROBLEM I. *Given the Crystallographic Constants of a Crystal (Axial Elements or Angles), to Find the Apparent Angle between Two Edges Seen on Any Microscopical Crystal View.*

The solution of this problem is based on known methods of crystal drawing (1, 5, 12). The first step is to plot the stereographic projection of the crystal by means of the Wulff net. Let us first assume that there is a face pole, c , in the center of the projection and that the crystal lies on the counterface of c (Figure 2). How can we find the direction of the edge, $[ab]$, between two given faces a and b , as it will be seen on such a view—that is to say, projected onto the plane of c , which is the plane of the microscope stage? Edge $[ab]$, by definition, is parallel to the axis of

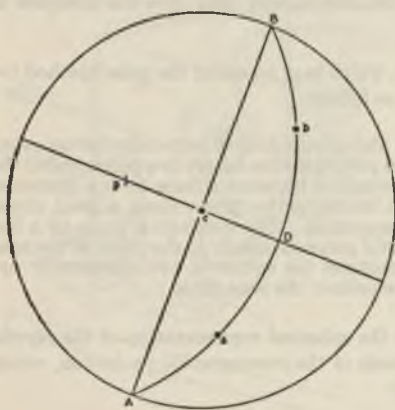


Figure 2. Edge between Two Faces Projected on the Plane of the Stereographic Projection

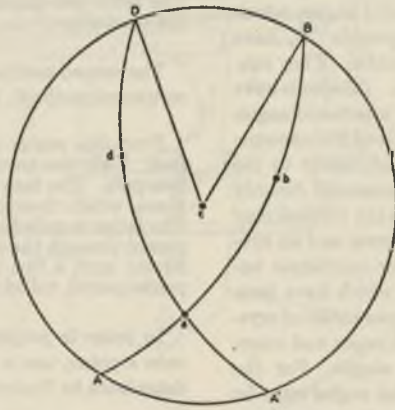


Figure 3. Apparent Angle between Two Edges Projected on the Plane of the Stereographic Projection

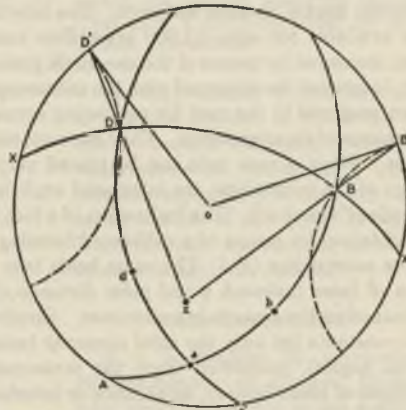


Figure 4. Case of a Crystal Lying on a Plane Different from the Plane of the Stereographic Projection

zone ab . Pass the zone circle $AabB$, intersecting the primitive circle along the diameter AB . The pole, p , of the zone circle is located on the diameter, Dc , perpendicular to AB , at a stereographic distance, Dp , of 90° . Call O the center of the sphere. The zone axis, Op , is projected in cp . Hence the direction of the projected edge $[ab]$ is perpendicular to the diameter, AB , determined by the zone circle ab .

Retaining the assumption that the crystal lies on the counterface of c , whose pole is the center of the stereographic projection, it is easy to determine the apparent angle between two edges, in this particular case. Consider (Figure 3) the stereographic projection of four faces, a , b , c , d , of the crystal. The edges, $[ab]$ and $[ad]$, between the pairs of faces a , b and a , d , respectively, are oblique to the plane of c . The true interzonal angle, supplementary to the angle between these two edges, is the angle, bad , seen on the stereographic projection. The apparent interzonal angle, or the supplement of the angle between the two edges projected onto c , is given by the angle, BcD , between the diameters AB and $A'D$, since the angle between the projected edges is given by the perpendiculars to these diameters. Note that the desired angle is given by the arc, BD , which the zone circles ab and ad intercept on the primitive circle. Also note that the primitive circle is the cyclographic projection of the face c .

Removing our previous assumption, we can now consider the general case in which the crystal is lying on a plane different from the plane of the stereographic projection. Let x (Figure 4) be the stereographic projection of the face on the counterface of which the crystal is lying. The great circle, $XBDX$, whose pole is x , is the cyclographic projection of the face x . The apparent interzonal angle of the edges $[ab]$ and $[ad]$ (projected onto x) is measured by the arc, BD , intercepted by the sides of the angle bad on the cyclographic projection of x . On Figure 4 this arc is projected stereographically, but its value can be read off in degrees by means of the Wulff net. (By a known theorem, the true value of BD is also given by the arc $B'D'$, where B' and D' are the intersections of the straight lines xB and xD with the primitive circle.) If it is desired to draw a view of the crystal orthographically projected on the x plane, which is the view that will be seen under the microscope, it is known that the direction of the edge $[ab]$, in such a projection, will be given by the perpendicular to the radius OB' . The point B' can also be located at the point where the primitive circle is intersected by the small circle BB' , the locus of all the points whose spherical distance from X is equal to XB .

PROBLEM II. *Given the Values of Interzonal Angles, or Apparent Interzonal Angles, Measured on the Rotating Stage of the Microscope, to Find the Axial Elements.*

If the axial elements are to be calculated by spherical trigonometry, it is sufficient to sketch an approximate stereographic projection of the crystal, merely to show the general distribution of faces and zones. For graphical solutions, however, it is imperative to plot the stereographic projection, by means of the Wulff net, as accurately as possible. This task is peculiarly awkward when the data are interzonal angles, because the latter appear as angles in the spherical triangles, in contradistinction to interfacial angles, which appear as sides. It is much easier to construct a spherical triangle on the net when its sides are known than when its angles are known. For this reason, it is advisable either to use the cyclographic projection throughout or at least to plot it as a preliminary step and to derive the stereographic projection from it. An interzonal angle (or its supplement, the interedge angle) can thus be used without difficulty, because it becomes a side in a spherical triangle.

APPLICATIONS OF THE GRAPHICAL METHODS

The following examples illustrate the application of these methods to problems confronting the microscopist.

EXAMPLE I. Confirmation of the Identity of a Compound.

An impurity in an organic sample consisted of prismatic crystals. These were suspected to be terpin hydrate, and a con-

fimation was desired. One of the crystals was isolated (Figure 5) and the following angles were measured on the rotating stage: $\angle 1 = 126.5^\circ$; $\angle 2 = 41^\circ$; $\angle 3 = 106^\circ$. Translated in terms of interzonal angles, the measurements become $o_4m_1m_4 = 53.5^\circ$; $o_4o_1m_1$, projected on $m_1 = 139^\circ$; $o_2o_1o_4$, projected on $m_1 = 74^\circ$. The interference figure showed the optic plane to be parallel to the elongation, with the acute bisectrix inclined about 40° to the left, as shown.

The suspected compound, *cis*-terpin monohydrate, is described by Groth (8), the following data being especially noted (Figure 6)

$$m_1:m_4 = (110):(1\bar{1}0) = 77^\circ 49'$$

$$q_1:q_2 = (011):(0\bar{1}1) = 50^\circ 57'$$

$$o_1:m_1 = (111):(110) = 52^\circ 49'$$

Orthorhombic bipyramidal, biaxial positive, plane of optic axes parallel to (010), acute bisectrix = a axis.

From the habit and optical properties it is evident that if the unknown crystal actually is terpin hydrate, it consists of the four m faces, terminated by o faces, and elongated along the c axis. The b and q faces, illustrated by Groth, are missing. The optical properties are in qualitative accord with the data for terpin hydrate, but without a comparison of Groth's goniometric data with the microscopically measured angles, a quantitative check is lacking. (To be sure, the refractive index n_x also given by Groth, could be measured on the crystal to provide an additional check on the identity of the compound.)

The stereographic projection of terpin hydrate (Figure 7) is constructed with the aid of the Wulff net from the goniometric data. The positions of the three pinacoids are first located, with $a(100)$ at the center of the net, and, since the compound is orthorhombic, with $b(010)$ and $c(001)$ 90° apart on the primitive circle. Since the poles of faces m_1 and m_4 are $77^\circ 49'$ apart, each is placed at half this value from a on zone $b'ab$. The pole of o_1 will lie on zone circle cm_1c' , $52^\circ 49'$ from m_1 , the angular distance being counted off along the zone circle on the Wulff net. Since the crystal system is orthorhombic, two independent measurements suffice to locate all faces, and the projection may be completed without additional angular data, the $q_1:q_2$ angle (or any other) serving as a check on the accuracy of the construction. It remains to determine from the projection the angles to be expected for a crystal, of the habit observed, lying on face m_1 .

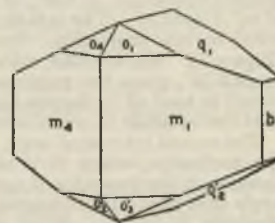


Figure 6. Crystal of Terpin Hydrate

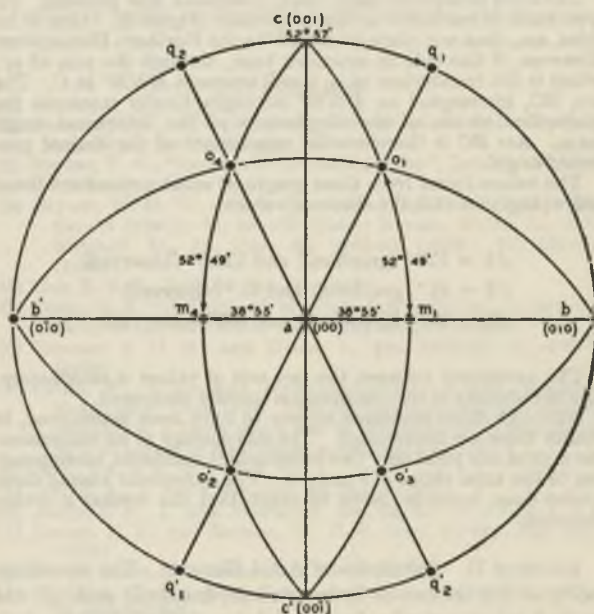


Figure 7. Stereographic Projection of Terpin Hydrate

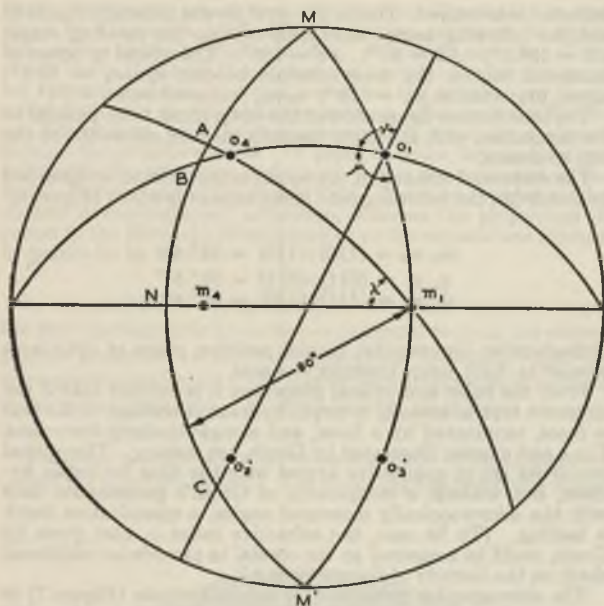


Figure 8. Determination of Microscopically Measured Angles for Terpin Hydrate

The method outlined in Problem I is followed. First the cyclographic projection, MNM' , of face m_1 is drawn, 90° from the pole of m_1 (Figure 8). The interzonal angle $o_4m_1m_4$ is immediately located on the projection. Its vertex is at m_1 ; it is marked λ (Figure 8). The arc, NA , which its sides m_1o_4 and m_1m_4 intercept on MNM' , gives the measure of λ in stereographic projection. It will be read off in degrees along the great circle of the Wulff net that can be made to coincide with MNM' .

The second interzonal angle, $o_4o_1m_1$, is likewise easily located on the projection, where it is marked μ (Figure 8). This angle, however, is the true value of $o_4o_1m_1$ —that is, the supplement of the angle that would be measured if the crystal were viewed perpendicularly to face o_1 . What is wanted is the projection of angle $o_4o_1m_1$ on plane m_1 . As seen above (Problem I), the projected angle is measured, in stereographic projection, by arc BM' which angle μ intercepts on the cyclographic projection, MNM' , of face m_1 .

The third interzonal angle, $o_2o_1o_4$, presents a new problem. Its true value is marked ν on the projection (Figure 8). One of its sides, o_1o_2 , does not intersect MNM' in the Northern Hemisphere. However, if this side be extended back, through the pole of o_2' , which is the counterface of o_2 , it will intersect MNM' at C . The arc, BC , intercepted on MNM' stereographically measures the projection on m_1 of the supplement of the interzonal angle $o_2o_1o_4$. Arc BC is therefore the supplement of the desired projected angle.

The values found from these graphical constructions are listed below, together with the observed values:

- $\angle 1 = 127^\circ$ (graphical) and 126.5° (observed)
- $\angle 2 = 42^\circ$ (graphical) and 41° (observed)
- $\angle 3 = 107^\circ$ (graphical) and 106° (observed)

The agreement between the two sets of values is satisfactory, and the identity of the compound is thereby confirmed.

Although three constants appear to have been determined, in reality these are interrelated. The morphology of an orthorhombic crystal can yield only two independent constants, corresponding to the axial ratios $a:b$ and $c:b$. The agreement among three angles does, however, serve to check that the crystal is orthorhombic.

EXAMPLE II. Calculation of Axial Elements. The crystallography of the lactone of hydroxytetrahydroabietic acid (4) was studied microscopically first, and later checked by two-circle goniometry.

Recrystallization from alcohol on a microscope slide gave the views shown in Figure 9. These were recognized as monoclinic, Class 2 in the Mauguin notation, on morphological and optical evidence, and the faces were assigned the following compatible Miller indices: $c(001)$, $m_1(110)$, $\omega_1(\bar{1}\bar{1}1)$, $\omega_2(\bar{1}\bar{1}\bar{1})$. The following angles were measured on the rotating stage: $\angle 1 = 76.3^\circ$, $\angle 2 = 68.0^\circ$, $\angle 3 = 116.0^\circ$, $\angle 4 = 162.0^\circ$. Translated in terms of interzonal angles, the measurements become: $m_1cm_4 = 103.7^\circ$; $m_3m_4c = 112.0^\circ$; $m_3m_4\omega_1 = 64.0^\circ$; m_4m_1c , projected on $m_4 = 18.0^\circ$.

When it is known the crystal is monoclinic, the stereographic projection may be constructed as follows (Figure 10): Let the c face be the plane of projection. Zone m_1cm_3 may be drawn, and zone m_4cm_2 is constructed so that the interzonal angle, m_1cm_4 , marked λ on the figure, is equal to 103.7° . The pole of the possible face $b(010)$ lies on the primitive circle. The zone circle $bc'b'$, here a diameter, bisects angle m_1cm_2 . The zone circle aca' , also a diameter, bisects angle m_1cm_4 ; the location of zone circle ω_1m_4b' is found by a cyclographic determination of its pole. The cyclographic projection of c is the primitive circle. The pole of zone m_4c or edge $[m_4c]$ is A ; the pole of zone m_1c or edge $[m_1c]$ is B . Draw the locus of the points whose spherical distance from A is equal to $\mu = 68^\circ$ and the locus of the points 68° from B . The intersection, D , of the two loci is the cyclographic projection of the edge $[m_1m_4]$. But this is the stereographic projection of the pole of the zone circle m_1m_4 , which may now be drawn. The zone circle $m_4\omega_1$ is then located on the Wulff net, by utilizing the interzonal angle, $m_3m_4\omega_1$, marked ν on the figure, which is the supplement of $m_3m_4\omega_1$ and is equal to 64° . The pole ω_1 is located at the intersection of this zone with zone m_1c , and the stereographic projection may readily be completed by passing zone circles through the appropriate faces.

From the stereographic projection, the views observed with the microscope can be accurately constructed, by known methods of

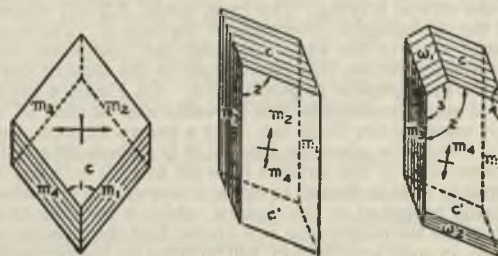


Figure 9. Observed Forms of the Lactone of Hydroxytetrahydroabietic Acid

Visible faces oblique to the plane of the stage are hachured

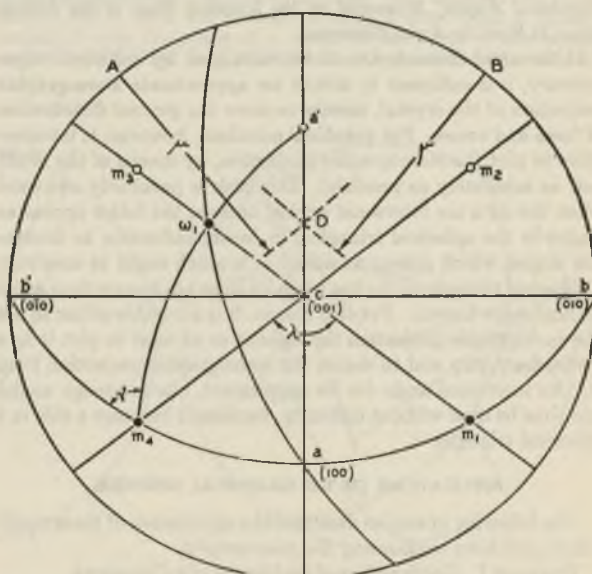


Figure 10. Lactone of Hydroxytetrahydroabietic Acid Stereographically Projected on the c Face

crystal drawing (1, 5, 12), and compared with the corresponding notebook sketches.

The axial elements are given (5) by the formulas:

$$\begin{aligned}\beta &= 180^\circ - ca \\ a:b &= \tan m_1ca \\ c:b &= \tan \omega_1ac\end{aligned}$$

Angle m_1ca is equal to half the measured angle m_1cm_4 —that is, 51.85° . The other two angles, ca and ω_1ac , are read from the stereographic projection, 61.0° and 34.0° , respectively.

The axial elements found graphically are:

$$a:b:c = 1.27:1:0.67, \beta = 119.0^\circ$$

For comparison, the axial elements calculated from the microscopical data by spherical trigonometry are:

$$a:b:c = 1.272:1:0.670, \beta = 118^\circ 27'$$

The axial elements calculated from two-circle optical goniometry data are:

$$a:b:c = 1.2875:1:0.6635, \beta = 117^\circ 17'$$

The accuracy of the results obtained by microscope goniometry may thus be estimated. It is of the order of 1% (0.5% in favorable cases, 2% in unfavorable cases). The values obtained by Weissenberg x-ray goniometry are:

$$a_0:b_0:c_0 = 1.285:1:0.670, \beta = 117.3^\circ$$

It is interesting to note that, after the crystal system has been determined as monoclinic, one view alone (Figure 9, c) is sufficient to calculate the axial elements. Including the apparent angle between edges $[m_1m_4]$ and $[m_1c]$, which was not used in the foregoing construction, the view presents three independent angles and is therefore sufficient for the calculation. The stereographic projection (Figure 11) may be constructed graphically, as follows: The plane of projection is perpendicular to the c axis. The zone $m_1m_2m_3m_4$ is projected on the primitive circle. The face pole m_4 is arbitrarily located; the zone circle m_4cm_2 makes an angle, m_4m_2c , of 112° with the primitive circle. The cyclographic projection AB of m_4 is drawn. On AB the interzonal angle m_4m_1c intercepts an arc, BD , equal to 18° (Problem I). Point D may so be located. The projection is pivoted on the Wulff net until D comes on the great circle which makes an angle of 112° with the primitive circle. This great circle is the zone circle m_1cm_2 . It determines the pole c , at its intersection with the zone circle m_4cm_2 . The face pole ω_1 is located by drawing the zone circle $m_4\omega_1$, so that the interzonal angle $m_4m_1\omega_1$ equals 64° , and determining its intersection with the zone circle m_1cm_2 . The rest of the projection may then be readily completed.

The axial elements read from this graphical construction are:

$$a:b:c = 1.27:1:0.67, \beta = 118^\circ$$

in satisfactory agreement with the elements given above.

In the monoclinic system, the Barker angles (2), used for identification purposes, are: $cr(001):(101)$, $ra(101):(100)$, $am(100):(110)$, $bq(010):(011)$. These form letters and Miller indices refer to an arbitrary setting, known as the Barker setting, different from the one used above. The values calculated from two-circle goniometry and those obtained graphically from microscope goniometry are compared below:

	cr	ra	am	bq
Calculated (2-circle goniometry)	$29^\circ 9'$	$57^\circ 4'$	$48^\circ 51'$	$56^\circ 2'$
Graphical (microscope goniometry)	29°	59°	49°	57°

Graphically determined Barker angles will be serviceable, if allowance is made for a possible error of 2° .

FINAL REMARKS

It may not be superfluous, in conclusion, to concede that the rotating stage of a microscope will never supersede the optical reflection goniometer as an instrument for measuring crystal angles. The goniometer measures the angles between face normals (interfacial angles in single-circle goniometry, coordinate angles in two-circle goniometry) with an accuracy that depends more on the perfection of the faces than on the precision of the instrument. This accuracy is usually a matter of 5 to 10 minutes; in exceptional cases, it may be 1 or even 0.5 minute. Al-

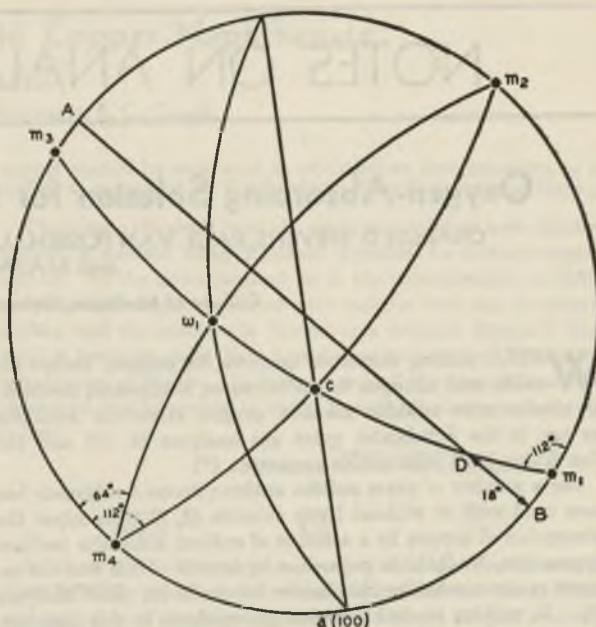


Figure 11. Lactone of Hydroxytetrahydroabietic Acid Stereographically Projected on a Plane Normal to the c Axis

though the rotating stage of the microscope is commonly equipped with a vernier that permits reading to 0.1° , the usual error of an angular measurement is 0.5° ; the accuracy may be increased somewhat by averaging a large number of readings. The accuracy of microscope goniometry is satisfactory for many purposes, especially in order to exploit the possibility of measuring interzonal angles.

Although the microscope is less accurate than the goniometer, the problem of determining axial elements from the measured angles is essentially the same in both cases. The microscope, in a sense, is the equivalent of a single-circle goniometer. There are differences, however: Angles between coplanar edges, instead of angles between tautozonal faces, are measured for each setting of the crystal or, in other words, for each view; and the projections of interzonal angles on the plane of the stage can also be measured.

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NOTES ON ANALYTICAL PROCEDURES

Oxygen-Absorbing Solution for the Scholander Quick Gas Analyzer

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WHILE making numerous analyses for oxygen, carbon dioxide, and nitrogen in gas mixtures, it appeared desirable to obtain more suitable alkaline oxygen absorbent solutions for use in the Scholander quick gas analyzer (8, 10) and the Van Slyke-Neill manometric apparatus (7).

For a number of years sodium anthraquinone- β -sulfonate has been used with or without ferric chloride (3, 7) to catalyze the absorption of oxygen by a solution of sodium dithionite (sodium hyposulfite, $\text{Na}_2\text{S}_2\text{O}_4$) in potassium hydroxide. This was the reagent recommended by Scholander for use in his quick analyzer (8). In making several thousand gas analyses in this analyzer, the anthraquinone reagent was found unsatisfactory because (1) its dark color made accurate reading of the meniscus almost impossible; (2) it did not indicate when absorption of the oxygen was complete, or when the reagent neared exhaustion; and (3) it formed a crusty foam which interfered with absorption (5, 8). If ferric chloride was also present, a black precipitate floating on the surface made the meniscus even more obscure.

Alkaline pyrogallol, another solution commonly used for oxygen absorption, also has several disadvantages, not least among which is the production of carbon monoxide when it is placed in contact with gas mixtures containing oxygen, particularly if the oxygen constitutes a high proportion of the mixture. This carbon monoxide production is apparently not a consistent finding, but observations regarding it are numerous (4, 6, 9); it may be minimized by allowing the reagent to age before use, according to Haldane (6).

In the present work, these reagents and others were tested in several ways, and a useful oxygen-absorbing solution for the Scholander quick analyzer is here suggested. No reagents more suitable than those in present use were developed for the Van Slyke-Neill apparatus.

METHODS

Most of the materials investigated were tested for their ability to increase the rate of oxygen absorption by a 28% solution of sodium hyposulfite in 10% potassium hydroxide, using a method somewhat like that employed by Fieser (2). For testing, 0.2 gram of the material was added to 25 ml. of solution in a 25-ml. flask, stoppered, and shaken. Two milliliters were removed in a syringe and injected into a 50-ml. Erlenmeyer flask containing 1 ml. of mercury. The flask was promptly connected to a mercury manometer. Eight of these 50-ml. flasks were mounted on a shaker in a 23° C. water bath, each equipped with a manometer leading to a mercury-filled trough. Each mixture was thus tested in quadruplicate against a solution of 0.4 gram of the anthraquinone and 7 grams of sodium hyposulfite in 25 ml. of 10% potassium hydroxide.

Oxygen absorbents which gave promise of being useful were further tested in the Scholander quick analyzer and in the Van Slyke-Neill apparatus.

RESULTS

The results of these tests led to the conclusion that a useful oxygen solution for the quick analyzer consists of 15 grams of a 10 to 1 mixture of sodium hyposulfite and indigo carmine plus 100 ml. of 10% potassium hydroxide. This solution had the following advantages:

1. Its light color facilitated reading of the meniscus.

2. It formed little foam in comparison with the reagent containing anthraquinone.

3. On standing a few seconds in the presence of oxygen in the unabsorbed gases the meniscus turned blue; or, if only a trace of oxygen was present, the meniscus was a dark reddish brown, particularly if the reagent was fresh.

4. As it approached exhaustion, the solution darkened and gave a deep blue foam (blue precipitate) when shaken after the gas injection.

5. It was nearly as rapid and gave the same analytical results as the anthraquinone.

The oxygen-absorbing solution containing pyrogallol with sodium hyposulfite, whether freshly made or allowed to stand several months was rapid in its action, but always in both Van Slyke and Scholander apparatus evolved about 0.1% of the original volume of oxygen as a gas absorbable by Winkler's reagent for carbon monoxide. This gas, presumably carbon monoxide, was not evolved by the solution containing indigo carmine or anthraquinone with sodium hyposulfite. The carbon monoxide was determined by use of the syringe-capillary technique of Scholander and Roughton (9).

Other materials investigated were: safranines O and Y (1); kindly supplied by the Cincinnati Chemical Works, Inc., alizarin light blue SE, xylene milling blue GL and BL, alizarin light blue B, phenyl rosinduline acid B, pyridine pure blue, hydron blue G, Ciba brown; also methylene blue, methylene violet, aurin tri-carboxylic acid ammonium salt, alizarin, pyronine, thymol blue, aniline blue, thionine, and orange G. Some of these materials were excellent oxygen indicators but not more effective than the anthraquinone as a catalyst. In several instances, this was because of their low solubility in the alkaline sodium hyposulfite solution.

SUMMARY

Solutions of sodium hyposulfite in 10% potassium hydroxide with various added materials were tested for oxygen absorption rate in a small manometric apparatus and those showing promise were further tested in the Scholander quick analyzer and the Van Slyke-Neill manometric apparatus. Indigo carmine was found more advantageous than sodium anthraquinone- β -sulfonate as an indicating catalyst in the oxygen-absorbing solution employed in the quick analyzer.

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Determination of Copper in Copper Naphthenate

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IN 1944, Weatherburn, Weatherburn, and Bayley (2) published a method of determining copper in copper naphthenate. This method has been used in these laboratories since June, 1943, for analyzing mixtures which, in addition to copper naphthenate and solvent, contained gums. The ash method had been used previously with extreme care as dryness was approached. However, Cuprinol Limited, London, England, complained that it gave low results and stated that their chemist used the extraction method. The latter method, having been tested and found accurate as well as easier than other methods, was adopted.

In the analyses, 10 N sulfuric acid was used. The mixture of copper naphthenate concentrate and acid was warmed to 60° C. and cooled, and the sulfuric acid layer having been run off, the naphthenate layer was washed free of copper with dilute sulfuric acid. Weatherburn, Weatherburn, and Bayley suggested that the mixture be heated to boiling and boiled for 2 or 3 minutes. This requires care to avoid the losses by entrainment, frothing, and spattering, which are so likely in mixtures of this type. Accurate results have been obtained by warming the mixture to 60° C.; consequently it is unnecessary to risk these losses. The extract of copper naphthenate concentrate contains a small amount of organic material in colloidal suspension. Because of this, in the first analyses, the copper was precipitated as oxide (1), then redissolved in nitric acid before it was determined. Later it was realized that this was unnecessary, for the concentrate always contains traces of iron and possibly other elements that form insoluble hydroxides. These may be precipitated by an excess of ammonium hydroxide and since the precipitate is so small, provided it is thoroughly washed with hot 1% ammonium nitrate containing 2 drops of concentrated ammonium hydroxide per 100 ml., the amount of copper adsorbed is negligible—i.e., for industrial analyses reprecipitation is unnecessary. This precipitate adsorbs the trace of organic matter, and consequently filtration cleans the solution, permitting the copper to be determined in the filtrate without further treatment. If an organic solvent miscible with water is used in the preservative mixture, the

copper should be separated as oxide before determination, or as sulfide as suggested by Weatherburn, Weatherburn, and Bayley.

The results obtained from the extraction method were checked against a method using Kjeldahl digestion to destroy organic matter. In the latter method, as in the determination of nitrogen, the concentrate is mixed with sulfuric acid and potassium sulfate and the mixture is heated in a covered Kjeldahl flask until it becomes clear, then transferred to a beaker for the determination of copper. In this manner all the organic matter is destroyed and no copper is lost. Two check analyses are given below:

	Copper Content	
	Extraction method	Kjeldahl method
	%	%
Sample 1	8.65	8.66
Sample 2	8.22	8.26

All three methods were found to give accurate results if sufficient care was used, but the extraction method was the quickest and easiest, and therefore was the most likely to give accurate results consistently.

ACKNOWLEDGMENT

The author wishes to thank J. S. Tait & Company, Limited, 940 Richards St., Vancouver, B. C., for granting permission to use the results of the analyses of their material and the method of analysis; and the others who have helped with suggestions in the preparation of this note.

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Lundegårdh Air-Acetylene Burner

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IN 1938 Lundegårdh (6) published an article showing a diagram of a new type of air-acetylene burner and stating: "A burner of a new type with a flat top was used (see Figure 1, 4). The dimensions of the opening in the mouthpiece are 1 × 20 mm. An advantage of this burner is the fact that it works without platinum nets. The gas mixture is sufficiently cooled by the flat mouthpiece, and explosions are entirely eliminated."

In Lundegårdh's own laboratory in 1938, only the new type of burner was in use. This diagram of the new burner was reproduced with Lundegårdh's permission in an article from Wellesley College (4) in 1941. Ells (2, 3) has also published work done at the University of Missouri in which the new type of burner was used. Both burners were constructed under Lundegårdh's supervision. McClelland and Whalley (7) in 1941 and Cholak and Hubbard (1) in 1944 have published diagrams of burners which are essentially the discarded Lundegårdh (5) type. The former state that this apparatus "does not correspond with Lundegårdh's latest design" but they felt justified in giving the account of it because of its efficiency. The latter say mistakenly, "In details of construction this equipment follows Lundegårdh's latest design as described by McClelland and Whalley."

It seems important to point out this discrepancy, so that American chemists and spectrographers may understand that

it is not necessary to construct burners of the more complicated type which Lundegårdh himself discarded several years ago. Moreover, the Jarrell-Ash Company of Boston, which plans to put the new type Lundegårdh burner on the market, and which has studied the design of both burners, has advised us that the construction of this new type is "considerably less expensive" than that of the older type. Emission in the air-acetylene flame has the great advantages of simplicity of procedure, accuracy, and reproducibility of results, for certain elements.

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Addition of Solids to Reaction Mixtures

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THE selection of a suitable method for adding solids to reaction mixtures is a problem which often confronts the chemist, particularly when the solid must be added gradually throughout the course of a reaction or it is necessary to use a sealed system, so as to exclude moisture. Types of apparatus designed to handle this problem in the research laboratory include the one suggested by Fieser (2) in which the solid is placed in an Erlenmeyer flask connected to the reaction vessel by a large rubber tube, and that of Webster and Dennis (4) which consists of a hopper with a ground-in valve at the bottom. Dennis and Anderson (1) have also described a hopper and valve arrangement for the addition of solids. Stock and Guttman (3) have utilized a vertical screw to feed powdered material from a hopper into a reaction chamber, making use of a mercury seal.

In the course of research work in this laboratory a new device (Figure 1) was constructed for the intermittent controlled addition of solids to reaction mixtures.

The device can be filled with a solid and attached to the reaction vessel by the ground joint at the bottom. By raising the plunger to the appropriate height, any desired amount of the solid may be made to flow into the reaction vessel, and the flow can be completely sealed off by merely twisting down

the plunger until the rubber ring stops the opening. The seal is tight enough to keep anhydrous aluminum chloride for several hours without any perceptible reaction with moisture. The extension of the plunger to the tip of the joint prevents caking in the constriction. Caking in the hopper may be overcome by cutting the rubber gasket with a saw-like upper edge which may be twisted to loosen the cake. The hopper may be refilled during a reaction without breaking the seal by lifting the stopper while holding down the pipet.

This apparatus may be constructed readily from glassware often discarded—chipped flasks and pipets with broken tips. The dimensions given on the drawing are for a model used in this laboratory. Another was made from a 250-ml. Erlenmeyer flask and a 25-ml. pipet, and larger sizes could be constructed. If solvents which attack rubber are used, a neoprene gasket may be substituted for the rubber one. The gasket is cut from a piece of rubber tubing of such a diameter as to fit the pipet snugly. The rubber tubing at the top is lubricated with castor oil to make an airtight joint which will allow free movement of the plunger. The authors have found this apparatus to work very satisfactorily for sodium carbonate, anhydrous aluminum chloride, phosphorus pentoxide, red lead, phosphorus pen-

tachloride, sodium amide, and solid carbon dioxide. When solid carbon dioxide was used, a groove was cut in the rubber gasket in order to prevent pressure increase in the hopper.

Where it is desirable to add the material continuously, the apparatus shown in Figure 2 operates well. This is designed to add solids to sealed reaction mixtures at a steady rate over an extended period of time, and once started, will do this automatically. The system can be kept sealed at all times, if an airtight hopper is used to feed the apparatus. Since it is constructed entirely of glass, corrosion is avoided. Construction is not difficult for anyone with moderate skill in glassblowing.

The solid material is moved forward in a glass tube at a constant rate by means of a close-fitting rotating glass spiral. The material drops from a hopper onto the spiral and is carried forward to drop from the other end into the reaction flask at a rate which can be controlled by varying the speed of the motor turning the spiral.

The dimensions of the apparatus in Figure 2 are those used on a successful model in this laboratory, but the size can be varied readily; it is well to retain the thick center axle which is necessary for strength.

To make the spiral, a piece of 10-mm. Pyrex rod is held in the right hand and about 40 cm. of 5.7-mm. rod in the left hand. The two are sealed together at the end, and the joint is annealed in an air flame. The spiral is then made by heating the smaller rod close to the point of contact with the larger, holding them so that the angle between the axes of the two rods is about 60°, and rotating the larger rod as the small rod softens until about five turns have been made. The distance between turns will be about 3.3 cm. The smaller rod is then pulled away and the end sealed to the larger rod and annealed. If any difficulty is encountered in making the turns an equal distance apart, a spiral made with the spaces between successive turns slightly less will work equally well.

At this point, the spiral is too large to enter the tube, and must be ground down slightly to a snug fit. This is readily done on a power fine-grained grinding wheel, holding the spiral lightly against the wheel with the thumbs in back of it, and rotating it slowly in order to move it evenly across the wheel. High places in the spiral can be readily felt and smoothed down and the whole gradually decreased in diameter until it will almost slide into the tube. It is then ground into a smooth fit with Carborundum, using another tube of the same size. It takes about 3 hours to make the ground spiral and the holder.

In attaching the joint to the tube in which the spiral fits, care must be taken not to let it sink in at any point. The ground joints shown are not essential and some flexibility might be gained by joining the apparatus to the reaction system with snug rubber tubing instead. In place of the upper joint a hopper could be sealed on or a hopper like that shown in Figure 1 used. The seal at the back end of the apparatus is made airtight by lubricating

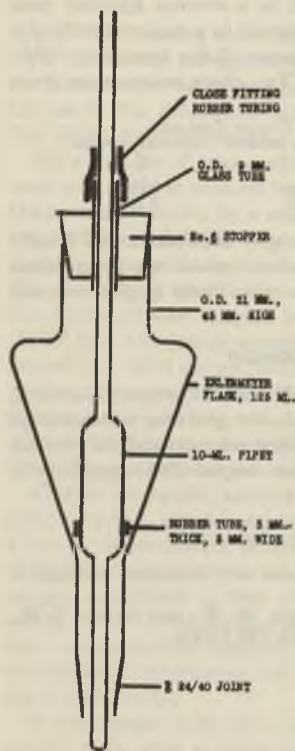


Figure 1

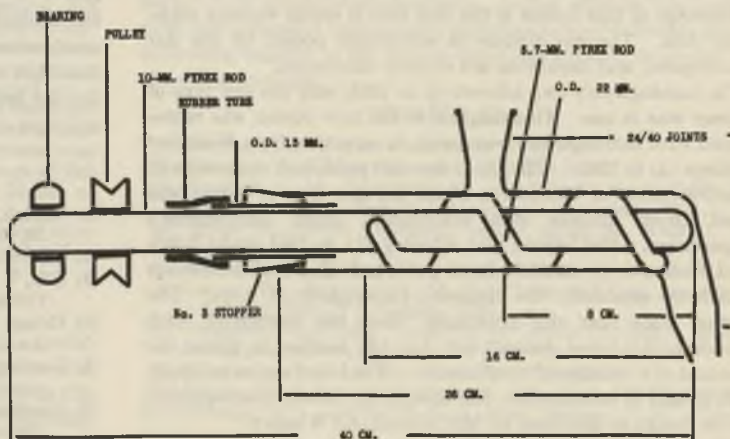


Figure 2

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the rubber tubing with castor oil. The (8-cm. wooden) pulley may be made to fit tightly by boring the hole through it slightly too large (1.6 cm., 0.625 inch) and then working it over a short piece of rubber tubing which has been split along its axis and placed on the rod.

The authors' model was driven by a 0.125-h.p. motor, operating at 1525 r.p.m., connected with a 40 to 1 reducing gear. The pulley on the reducing gear was placed below the pulley on the shaft of the apparatus, and the connecting belt kept taut by allowing part of the weight of the motor and gear to hang from the belt. The bearing at the end of the Pyrex rod which consists of sheet asbestos lubricated with graphite, supports most of this weight. When anhydrous aluminum chloride, phosphorus pentachloride, and sodium carbonate were used this system always operated smoothly with no tendency to stick.

All-Glass Stirrer

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IN A recent article (1) an all-glass stirrer was pictured which is compact, inexpensive, easy to construct, and eliminates the danger of contamination of the solution by corrosion products from an electric motor.

The device is not suitable for agitation of large volumes, nor of heavy viscous liquids, but is extremely useful for agitation of volumes such as are constantly used in analytical work. In electrometric titrations the electrodes may be attached to the stirrer, thus eliminating the cluttered condition normally encountered in electrometric operations. A method of attaching electrodes is shown in Figure 1.

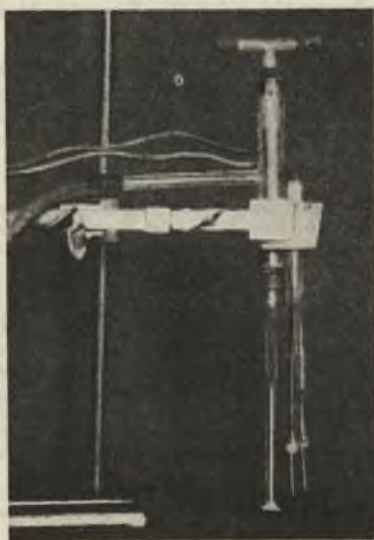


Figure 1. All-Glass Stirrer

Stirrers of the type described are available commercially but cannot be disassembled for cleaning or lubricating. Foreign particles, particularly rust scale, may come through air lines and lodge between bearings and shafts, seriously affecting the efficiency of operation. Occasionally broken parts cannot be replaced on commercial stirrers.

The stirrer is an air-driven type operating on low pressure (not over 10 pounds) on the pinwheel or rocket principle (Figure 2). The stator is a T-tube fitted with rubber stoppers which are bored to accommodate glass bearings. The rotor is in two parts.

In tests with this model when the spiral was turning at the rate of about 12 revolutions per minute, it delivered 14 ml. of anhydrous sodium carbonate, and about the same amount of aluminum chloride per minute.

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The small T, which furnishes the power to drive the shaft, is connected to it with a short length of rubber tubing, which serves as universal joint, to absorb stresses due to approximate shaft alignment, makes disassembly possible, and admits air to jets through the hole in the center.

Tight or binding bearings will not operate, but slight high spots may be quickly ground to fit. Too great clearance results in air leakage with poor performance.

Bearings should be lubricated with a drop of medium oil before assembly and occasionally thereafter. Oil of S.A.E. 30-40 is satisfactory.

When the unit is assembled, stoppers should be adjusted by rotating until minimum bind and friction are obtained and the shaft turns freely. A properly aligned stirrer should turn when blown by mouth.

The danger of the rotor's disintegrating while in operation is extremely remote. Dozens of these stirrers have been made and used in this laboratory under all kinds of conditions. The only breakage encountered has been in electrometric titrations, where the rotor has been shattered by contact with the buret. To prevent this, small pieces of rubber tubing extending slightly beyond the ends of the rotor, and with holes corresponding to hole locations in the rotor, may be installed.

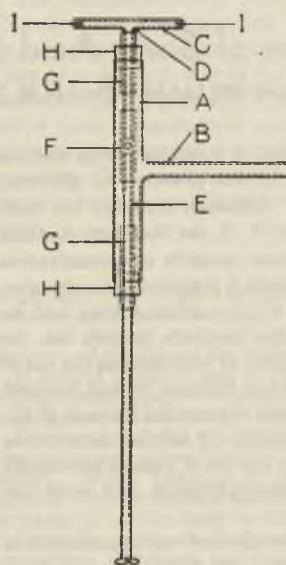


Figure 2. Diagram

- Stator. A. 14-mm. tubing, 11 cm. long. B. 8-mm. tubing, 7 to 8 cm. long.
- Rotor. C. 6-mm. tubing, 6 cm. long, 1-mm. hole on each end, opposite sides. D. 6-mm. tubing, 6 cm. long, serves as shaft.
- Stirrer Shaft. E. 6-mm. tubing, 18 cm. long, with propeller or other agitating device formed on end about 1.5 cm. wide.
- Universal Joint. F. Snug fitting rubber tubing 4 to 5 cm. long with hole in center 3 to 5 mm. in diameter.
- Bearings. G. Cut from standard Pyrex tubing, with an inside diameter providing a fairly close fit to shafts. Bearings should be 3 to 4 cm. in length.
- H. Rubber stoppers bored to accommodate bearings.
- I. Holes in rotor serving as jets. All glass tubing should be standard wall thickness Pyrex. Diameter measurements are outside.

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Electrically Operated Buret

FREDERICK C. NACHOD

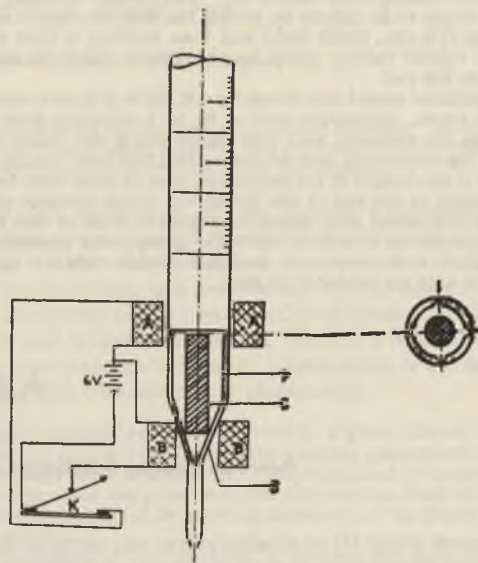
The Atlantic Refining Company, Philadelphia, Pa.

IN A series of experiments which were carried out several years ago, the problem of avoiding contamination of the titration liquid by stopcock grease was encountered. The solutions mainly consisted of bromine dissolved in light and "heavy" methanol (CH_3OH and CH_3OD), and were used in the determination of keto-enol equilibria (1).

The apparatus employed, shown in the diagram, consists of a conical seal, *S*, which must be ground with great care; the male part of the seal is formed into a plunger, *P*, which contains an iron core, *C*, suitably made of about 6 iron nails. This core is about 1.5 cm. long and 0.5 cm. in diameter. A top view of the upper cross section of the plunger is shown at the right. The four protrusions maintain the plunger in its vertical position during motion.

Two solenoids, *A* and *B*, made from bell wire, and consisting of about 20 windings each, are connected over a 6-volt battery by means of a Morse key, *K*. If the key is released, solenoid *B* is actuated and provides magnetic "suction" for the seal; if the key is pressed down or tapped, the plunger rises and the solution is permitted to flow out of the buret.

In preparing the assembly, it is recommended to start with the conical seal, to connect the seal to a calibrated buret, and then to slide in the plunger. The apparatus described was made for a 10-ml. buret but can be adapted to larger burets.



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Titration of Boric Acid in the Presence of Mannitol

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IT IS well known that the titration of boric acid with sodium hydroxide is satisfactory only in the presence of glycerol, mannitol, or some similar polyol. Although mannitol has been found most suitable for this purpose (5, 8), the literature contains no satisfactory report on the optimum quantity or concentration of mannitol. Schäfer (6) recommends a mannitol concentration at least 0.2 *M*, but the accuracy of his conclusion may well be questioned because he used a buret accurate to 0.01 ml. for titrations of less than 0.9 ml. Mellon (4) recommends the use of 1 gram of mannitol, while Kolthoff and Furman (2) and Kolthoff and Sandell (3) call for 0.5 to 0.7 gram of mannitol for each 10 ml. of solution, and Hillebrand and Lundell (1) ask for the addition of 1 to 2 grams. Scott (7) calls for the use of 1-gram increments of mannitol until a permanent phenolphthalein end point has been reached.

This paper presents a study of the effect of varying amounts of mannitol on the titration of boric acid with sodium hydroxide to the phenolphthalein end point.

EXPERIMENTAL

REAGENTS. Boric acid, approximately 0.057 *M*, was prepared by dissolving the Merck reagent in freshly boiled distilled water. Carbonate-free sodium hydroxide, approximately 0.045 *N*, was standardized with potassium acid phthalate. Mannitol, Eastman No. 155, was found to be neutral and used without further purification.

PROCEDURE. Twenty-five milliliters of the standard boric acid solution were diluted to a given volume and 2 drops of 0.03 *M* phenolphthalein per 100 ml. of solution (volume at equivalence point) were added. A known amount of mannitol was added, and the solution was titrated potentiometrically at room temperature with a Beckman pH meter, laboratory model. In the vicinity of the equivalence point, the incre-

ments of sodium hydroxide were 0.10 ml. The buret readings at the phenolphthalein end point (pH of 8.30) and at the steepest point of the titration graph (equivalence point) were observed. The difference in these readings is given in Table I under the heading of "Titration Error".

The results obtained from the titration graphs are given in Table I.

DISCUSSION

From Table I, it is obvious that with an initial volume of 100 ml., the proper quantity of mannitol is about 7 grams, corresponding to a ratio of 27 moles of mannitol per mole of boric acid. When the initial volume is 25 ml., 3.9 grams of mannitol, corresponding to a molar ratio of 15, will give satisfactory results. These conclusions show very clearly that the molar ratio of

Table I. Titration of 25 Ml. of Standard Boric Acid with Sodium Hydroxide

Volume before Titration Ml.	Weight of Mannitol Grams	Moles of Mannitol Moles of Boric Acid	pH of Acid	pH at Equivalence Point	Slope at Equivalence Point	Titration Error Ml.
100	0.00	0.0	6.01	10.29	0.12	...
100	0.26	1.0	5.03	9.91	0.22	-14.47
100	0.52	2.0	4.72	9.70	0.38	-7.27
100	1.04	4.0	4.25	9.45	0.82	-2.13
100	2.08	8.0	3.93	8.82	1.48	-6.56
100	4.16	16.0	3.62	8.48	2.70	-0.05
100	8.32	32.0	3.43	8.18	4.50	+0.03
100	16.64	64.0	3.18	7.65	5.50	+0.12
100	33.3 ^a	...	3.01	7.36	6.70	+0.19
25	0.49	1.9	3.80	10.01	1.04	-5.46
25	1.97	7.6	3.02	8.57	3.5	-0.06
25	3.93	15.2	2.88	8.50	8.4	-0.01

^a This quantity did not dissolve entirely.

mannitol to boric acid is not the deciding factor in determining the amount of mannitol necessary for a good titration. The concentrations of mannitol at the equivalence point are 0.30 and 0.38 *M* with initial volumes of 100 and 25 ml., respectively.

SHARPNESS OF END POINT. The sharpness of the end point is determined by the slope of the graph at the equivalence point. If the phenolphthalein end point is to be satisfactory, the slope should be at least 3.0 pH units per ml. Table I shows that the slope at the equivalence point exceeds 3.0 in both cases if the recommended quantities of mannitol are used.

CONCLUSION

If the mannitol is present in a large excess over the boric acid, a concentration of about 0.35 mole of mannitol per liter of solution at the equivalence point will yield both a small titration error and a sharp end point. This observation agrees very well with the recommendations of Kolthoff and Furman (2) and Kolthoff and Sandell (3).

ACKNOWLEDGMENT

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Recommended Practice for Microscopical Reports on Crystalline Materials, in A.C.S. Publications

IN 1942 a committee of the Division of Analytical and Micro Chemistry was appointed to present a recommended procedure for reporting microscopical crystallographic data. The members were: W. M. D. Bryant, Experiment Station, E. I. du Pont de Nemours & Company; Mary L. Willard, Pennsylvania State College; E. F. Williams, Research Laboratory, American Cyanamid Company, and C. W. Mason, Cornell University, Chairman.

After considerable discussion, and correspondence with other microscopists and with the American Mineralogical Society, the recommendations given below were formulated and presented to the Division at the Cleveland meeting, April 4, 1944, where an

informal ballot was taken, to submit them for the approval of the Executive Committee of the Division.

The recommendations were also discussed with the A.C.S. Committee on Nomenclature, which voiced no objections, and became an official action of the Division of Analytical and Micro Chemistry by authority of its Executive Committee. They are published for the guidance of authors, upon whose willingness to follow them depends their success in bringing more clarity and accuracy of expression to a field where ambiguity has been all too prevalent. They will also serve as an established reference for the use of reviewers and editors when dealing with papers in microscopical work.

C. W. MASON

WITH the increasing use of microscopical crystal studies in research and technology, and the wider knowledge of the underlying experimental techniques, such information should be more frequently and extensively published for the benefit of those chemists who have come to depend on it as a primary or supplementary means of identification.

Authors should be encouraged to give detailed crystallographic descriptions (geometrical and optical) of crystals, in all papers where crystallinity is reported; the editors should consider such data as deserving of space as is conventional chemical information, and where necessary for clarity should allow the publication of drawings or photomicrographs.

When feasible, crystal descriptions may well be reviewed separately. The author may be advised to extend his report, or on the other hand to clarify it for the benefit of those not well versed in the condensed style of formal crystallographic terminology.

The term **amorphous** should not be used as synonymous with "very fine grained" or "unresolvable", unless qualified—for example, "apparently amorphous", "microscopically amorphous within the limits of visual (or ultraviolet, or electron) microscopy", etc.

The term **crystal** may be applied to any solid possessing a single continuous lattice structure throughout its extent, whether the crystal exhibits faces (euhedral) or is irregularly bounded (anhedral) or is a cleavage fragment. Twinned crystals properly are only those in which the differently oriented portions bear a specific geometrical relationship to each other; accidentally adhering or intergrown crystals are not considered twins.

Crystal habit or mode of development should be stated in conjunction with the conditions of formation. The particular habit of a given substance can vary markedly with the method of crystallization, solvent, temperature, rate, associated impurities, etc., which should be reported. For crystals grown on a micro-

scope slide from solution or fusion, the common view or preferred orientation should be given. Drawings or photomicrographs may well be used to describe the habit, particularly if it is consistent and significant for descriptions.

If several different sets of similar faces ("forms" in crystallographic terminology) are exhibited, their relative sizes should be indicated; it is customary to list the dominant ones first.

Cleavage, skeletal or dendritic habit, and any other readily observable and characteristic features should be included in the report. Where cleavage is reported, it is desirable that the number of directions and their mutual angular relationship (true, or traces on a given face) be stated.

Crystallographic studies are based primarily upon *directional* properties: directions and orientations must be unambiguously designated if the description is to have meaning.

If **crystallographic axes** and **Miller indices of faces** are used the assumed setting of the axes should first be stated, with reference to some conspicuous geometrical or optical features, and in accordance with conventional crystallographic practice. Descriptive terms such as "prisms" or "rhomboheda", which connote a specific crystal form (a group of faces having the same relationship to the crystallographic axes) should be avoided or used in quotation marks unless the faces of these particular forms are present.

If axial ratios are given, the method of measuring the essential angles should be stated. Axial ratios calculated from microscopical measurements have little value.

Angles should be measured wherever possible, but care should be taken that the particular angle involved is clearly and unambiguously designated, preferably on a drawing. Distinction should be made between silhouette ("profile") angles and true interfacial angles, and between microscopical and goniometric data. In order to avoid confusion with the symbols for refractive indices, the angles of inclination between the inclined crystal-

lographic axes in monoclinic and triclinic should be designated as "angle α ", "angle β ", "angle γ ".

Crystal system, and if possible symmetry class, should be reported. A mere statement of crystal system, without the supporting geometrical or optical evidence, is not acceptable.

The geometrical description should be separated from the description of optical properties. Drawings are almost essential for geometrical descriptions, and may further be used to represent the orientation of optical properties. Clinographic projection (perspective) is appropriate for geometrical purposes, but for records of optical properties and microscopical appearances orthographic projections (plans and elevations) are preferable.

Optical properties should be reported as fully as the specimen, the available apparatus, and the author's ability permit. Even brief and simple descriptions are better than none, provided they are accurate as far as they go. Optical data are particularly important in those cases where crystal faces are not well developed. It is essential that reported optical properties be clearly related to crystallographic features or to the geometrical appearance of the material as seen under the microscope.

In the order of importance and ease of observation, the following optical properties are desirable:

1. Isotropic or anisotropic character; may differ from different views.

2. Location of vibration directions (axes of elasticity) with reference to prominent edges, faces, or planes of symmetry. Parallel (symmetrical) extinction versus oblique extinction. The extinction angle should be clearly designated with respect to the face, edge, or crystal axis of reference, preferably by a drawing. Phrases such as "extinction angle 20° to the long edge, measured in the acute (or obtuse) angle β " may well be used. Different extinctions, as obtained on different views of a crystal, should be clearly indicated.

3. Refractive indices exhibited by crystals in readily available orientations such as lying on prominent faces.

The view examined should be stated, and the refractive indices corresponding respectively to the vibration directions for that view should be clearly designated, preferably on a drawing. Refractive indices should be reported for the different principal views of the crystals, if possible.

If refractive indices are not determined numerically, nevertheless some statement should be made regarding their relative magnitude and difference, for different principal views. The direction of vibration of the slower component (axis of less elasticity, or higher refractive index) should be observed by means of a compensator (first order red plate or quartz wedge). If crossed arrows are used to indicate on a drawing the axes of elasticity, the shorter arrow should correspond to the higher refractive index less "optical elasticity". The strength of double refraction (difference in refractive indices) for each view may be roughly estimated from the "order" of the polarization colors, thickness being considered. Mere statement of the polarization colors exhibited is of little significance, unless the thickness is specified or is consistent for the method of crystallization.

The numerical values given for refractive indices should indicate the probable accuracy of the method as actually carried out; this may differ in different ranges and for different materials. Solubility in immersion liquids may well be reported.

If monochromatic illumination is used, as will be necessary if marked dispersion exists, it is advisable that determinations be made with sodium light (in addition to any other wave lengths employed) to aid in comparison with the approximate refractive indices obtainable with white light.

Refractive indices should be designated by Greek letters or other symbols only if it is known that they are the principal values, corresponding to the axes of the index ellipsoid.

For crystals known to be uniaxial (in the tetragonal or hexagonal systems) ϵ and ω should be employed to designate the principal indices; ϵ' may be used to designate an intermediate value. For crystals known to be biaxial (orthorhombic, monoclinic, triclinic), α , β , and γ should be employed to designate the principal indices; "primes" may be used to designate intermediate values, as α' , β' , etc.

When the refractive indices as measured are not readily related to the principal values, they may be designated as n_1 , n_2 , n_3 , and their relationship to the observed crystal habit should be clearly indicated by a drawing or otherwise.

N_p , N_m , N_g should not be used instead of the Greek letters, to designate principal refractive indices.

Principal vibration directions (axes of elasticity) should be designated by the Greek letters as used for the respective refractive indices. O and E , corresponding to ω and ϵ , and X , Y , Z , corresponding to α , β , γ , may also be used.

The views which best exhibit principal values of refractive index should be indicated, for ease in checking values by other observers.

4. Color and pleochroism. These should be observed on thick crystals; unless very marked, the former may sometimes be more apparent with dark-field illumination.

Pleochroism should be sought in all colored anisotropic crystals, and should be described with reference to the vibration directions for each observed. A mere statement that "a red-yellow pleochroism is observed" is not adequate; the respective orientation for each color should be given.

Surface color and reflection pleochroism may be observable on highly colored materials.

5. Interference figures, indicating uniaxial or biaxial and positive or negative character.

These should be obtained if at all possible, even when refractive indices are not observed, or as a check on the latter. The quality of the interference figure obtained, and the orientation that best exhibits it, should be stated.

The axial plane, acute bisectrix, and optic axial angle should be reported, often best by means of one or more drawings. The value given for the optic axial angle should be consistent with the accuracy of the determination; $2V$ is preferable, provided β is known approximately; $2E$ and $2H$ may also be given. In any case, the method of determination (calculation from n 's, estimation, or measurement by a universal stage) should be stated.

Dispersion of refractive indices, of birefringence, or of optic axes or axial plane should be reported if possible, particularly when marked enough to be readily observable with ordinary apparatus or specimens.

Tabulation of optical properties is desirable where several substances are studied and compared, but usually the necessary condensation and use of symbols will involve a sacrifice of clarity and ease of interpretation by semiskilled observers. Additional separate descriptive paragraphs on each substance are therefore highly desirable.

Phase changes involving crystals (polymorphism, desolvation, etc.) should be reported whenever noticed. Observations and conclusions drawn from them should be clearly differentiated.

If enantiotropic (reversible) polymorphism exists, the approximate transition temperature should be determined, together with the method of observing it. The properties of the high- and low-temperature phases, and the ease and manner of the transformation from one to the other should be given.

If monotropic (irreversible) polymorphism exists, the properties of the stable and metastable phases should be given, and also the method by which the metastable phase may be consistently obtained.

Unless the system is fully established, the use of Greek letters (α for the lowest temperature phase, etc.) is not advisable; Roman numerals are preferable designations.

NBS Spectrographic Steel Standards

Nickel-Molybdenum Steel (SAE 4620) is now being issued in two sizes—standard No. 419, $7/16$ -inch rod, and standard No. 819, $1/2$ -inch rod—with the following percentage composition: Mn 0.72, Cu 0.080, Si 0.27, Ni 1.71, Cr 0.24, Mo 0.22, and Sn 0.009. Price per sample is \$3.00.

Open Hearth Ingot Iron is now being issued in two sizes—standard No. 420, $7/16$ -inch rod, and standard No. 820, $1/2$ -inch rod—with the following percentage composition: Mn 0.020, Cu 0.050, Ni 0.020, Cr 0.006, Co 0.007, Mo 0.002, Al 0.002, and Sn 0.005. Price per sample is \$3.00.

Certification of Values for Low Concentrations of Aluminum and Tin in Samples Previously Issued

Caution. For determination of small amounts of aluminum, use of aluminum-base abrasives in cleaning and shaping rods must be avoided and outer cylindrical surface of $7/16$ -inch standards must be removed to a depth of 0.002 inch.

Standard	Aluminum %	Standard	Tin %
403, 803	0.005	412, 812 ^a	0.026
406, 806	0.023	414, . . .	0.014
407, 807	0.055	417, 817	0.020
414, . . .	0.020	419, 819	0.009
416, 816	1.06	420, 820	0.005
417, 817	0.013		
420, 820	0.002		

^a Sample 812 now out of stock but certified tin value will apply to samples previously issued.

A general certificate of analysis of steel standards revised to include the new standards, other than boron steels, is furnished with shipments of standards.

Of the standards originally issued, Nos. 810, 811, and 812 are out of stock and cannot be supplied.

