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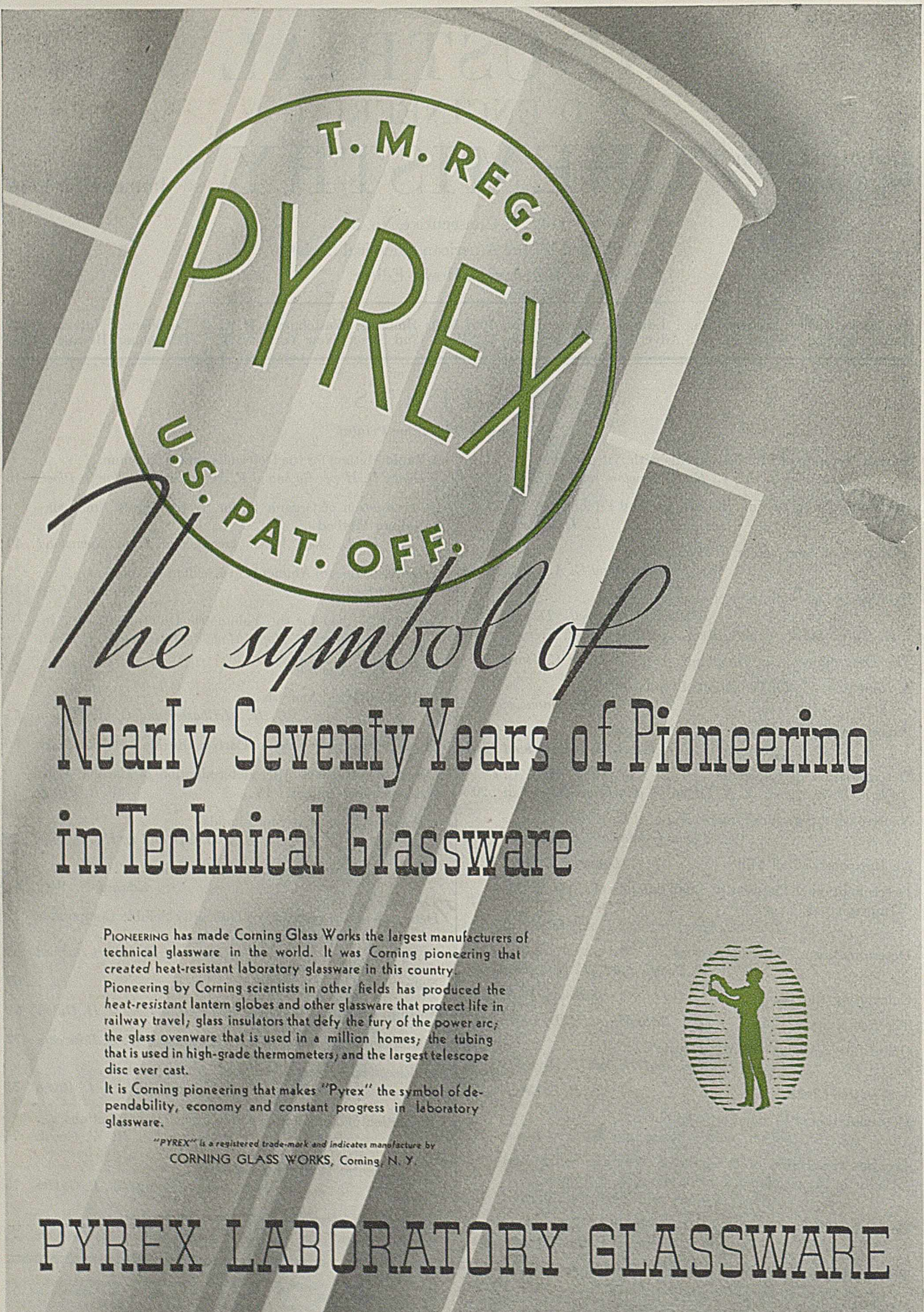


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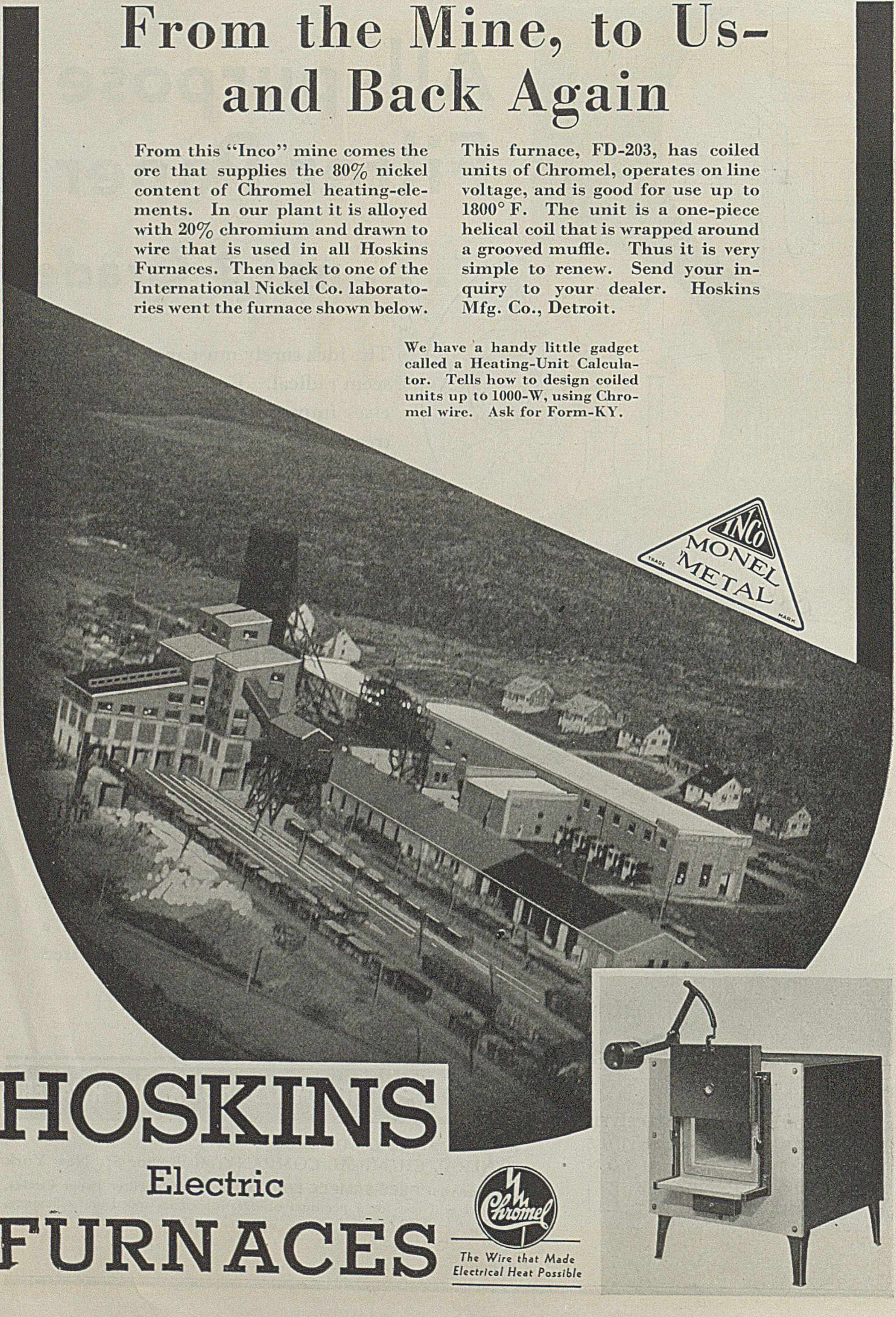
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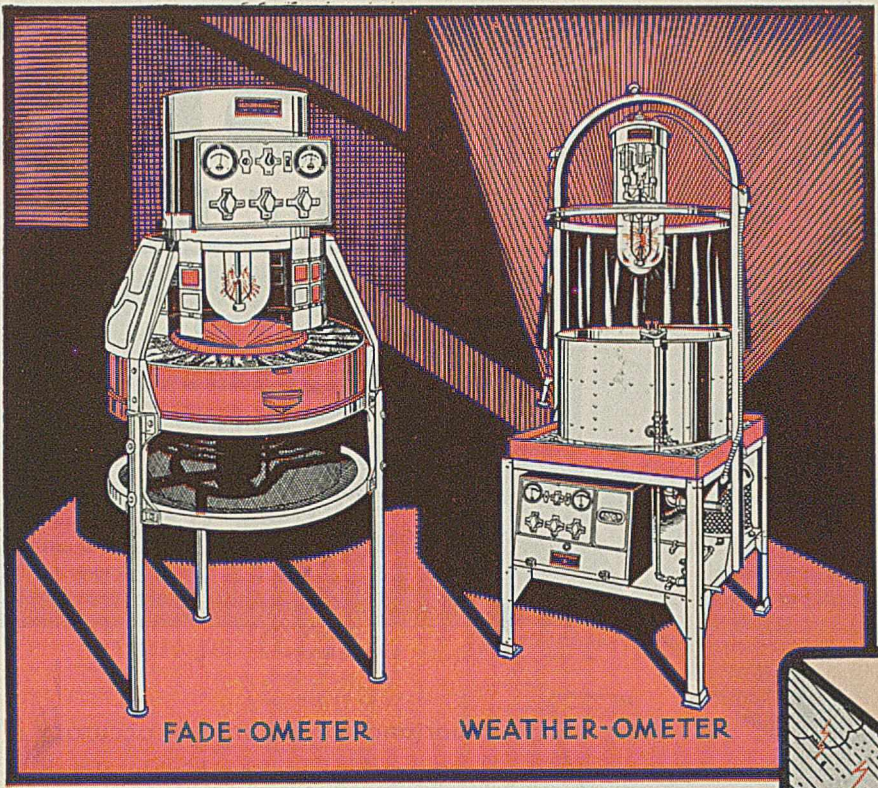
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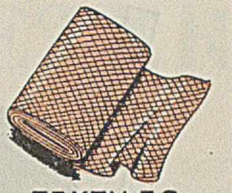


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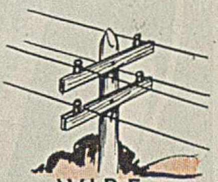


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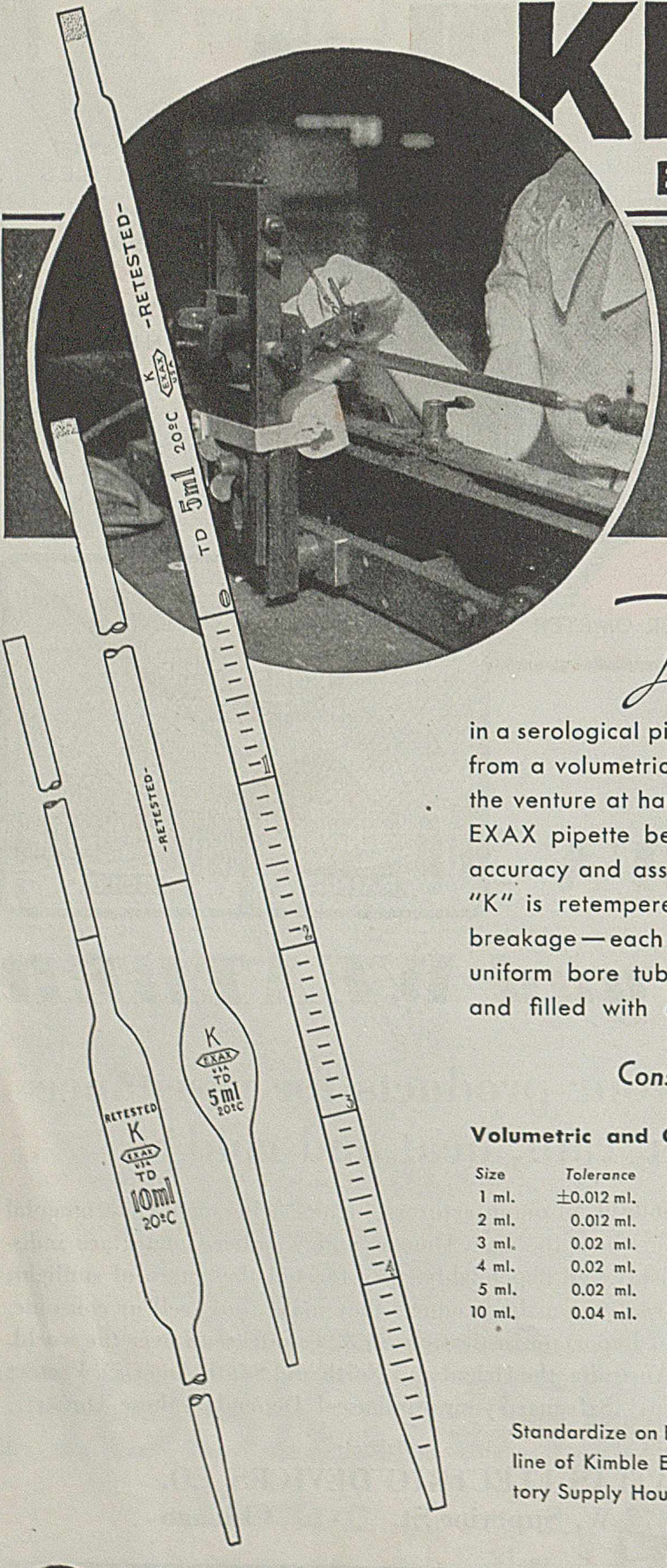

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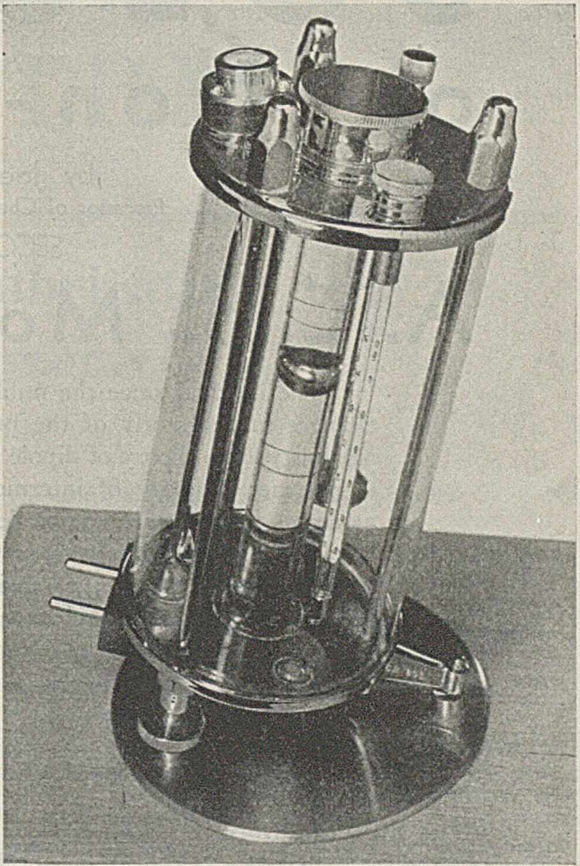

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A NEW EDITION

SOLUBILITY of Non-Electrolytes

by Joel H. Hildebrand, Ph.D
Professor of Chemistry in the University of California

SECOND EDITION—Revised

A. C. S. Monograph No. 17

The interval since the publication of the first edition (1924) has seen many changes in the study of the problems presented by the various phenomena of solubility; the theory of dipole moments has grown to maturity; the foundations of a general theory of intermolecular forces has been laid; several promising attempts have been made to deal quantitatively with the deviations of solutions from the ideal solution laws, particularly for that class of solutions that has come to be known as regular; extensive additions have been made to the body of data having theoretical significance. In consequence of these developments, this Monograph has been almost entirely rewritten.

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ANALYTICAL EDITION
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Solvent Refining of Lubricating Oils with Nitrobenzene

Analytical Methods

S. S. KURTZ, JR., C. E. HEADINGTON, AND B. ZIEBER, The Atlantic Refining Co., Philadelphia Pa.

The analytical methods presented can be used to determine the composition of the solvent-oil solution present in any part of the extraction system. Methods are also described for determining the concentration of low-boiling fractions in the charge oil and the concentration of nitrobenzene in water.

THIS paper describes the analytical methods which have been worked out during the period covering the development of the operation and equipment for the nitrobenzene process for solvent refining of lubricating oils as described in previous papers (*3*, *4*, *5*). These methods are also useful in the control of the commercial plants now using this process. The discussion is divided into five parts: source of samples, analysis of nitrobenzene-oil solutions of low nitrobenzene content, analysis of nitrobenzene-oil solutions of high nitrobenzene content, analysis of nitrobenzene-water solutions, and analysis of charge stocks. Methods for determining the purity of fresh nitrobenzene can usually be supplied by the producers of this material.

Source of Samples

Table I gives a summary of the plant samples on which analyses might be desirable, the point from which the samples are taken as shown on the flow diagram in Figure 1, frequency of sampling, probable concentration, method used for the analysis, and the approximate time required for the analysis.

The water samples, instead of being taken from the line at *L*, are actually taken from the bottoms of a small still inserted at this point and used to recover the small amount of nitrobenzene dissolved in the water from a water separator. These units also receive the condensed steam from the vacuum pumps.

Because of the widespread differences in the nitrobenzene content of samples taken at different points in the plant, it was necessary to develop several analytical methods giving the desired accuracy with a minimum expenditure of time. Accordingly, four groups of methods are presented: (1) methods for determining 0 to 5 weight–per cent of nitrobenzene in oil, (2) 5 to 100 weight–per cent of nitrobenzene in oil, (3) nitrobenzene in water, and (4) low-boiling fractions in charge stocks for the nitrobenzene plant.

Determination of 0 to 5 Per Cent of Nitrobenzene in Oil

Two materials in the plant contain nitrobenzene in concentrations of from 0 to 5 per cent: the extract and the raffinate. Two methods are presented for analyzing these materials. The first method involves the reduction of the nitrobenzene to aniline by titanous sulfate. It is accurate and reliable but requires 1 hour per determination and some

TABLE I. SUMMARY

Sample Taken	Where Taken (Figure 1)	Frequency of Sampling	Analysis Desired	Probable Concentration Range %	Analytical Method Used	Maximum Time for Analysis Min.
Raffinate	*A*	One sample per tank	Nitrobenzene	0 to 0.1	Titanous sulfate	60
	B	3 to 6 per day	Nitrobenzene	0 to 0.1	Pensky Martens flash	30
	C	For special purpose only	Nitrobenzene	0.1 to 1.0	Pensky Martens flash	30
	D	For special purpose only	Nitrobenzene	10 to 30	Specific gravity or distillation	60
	E	For special purpose only	Nitrobenzene	10 to 30	Specific gravity or distillation	60
Extract	*F*	For special purpose only	Nitrobenzene	50 to 90	Specific gravity or distillation	60
	G	For special purpose only	Nitrobenzene	50 to 90	Specific gravity or distillation	60
	H	For special purpose only	Nitrobenzene	0.1 to 1.0	Specific gravity or distillation	60
	I	One per day	Nitrobenzene	0 to 0.1	Pensky Martens flash	30
	J	One sample per tank	Nitrobenzene	0 to 0.1	Titanous sulfate	60
Recovered nitrobenzene	*K*	2 per month	Nitrobenzene	95 to 100	Distillation and freezing point	90
Water	*L*	3 to 6 per day	Nitrobenzene	0 to 0.2	Colorimetric	30
Charge stock	*M*	One sample per tank	Light oil	0 to 1.0	Flash difference or double distillation	90

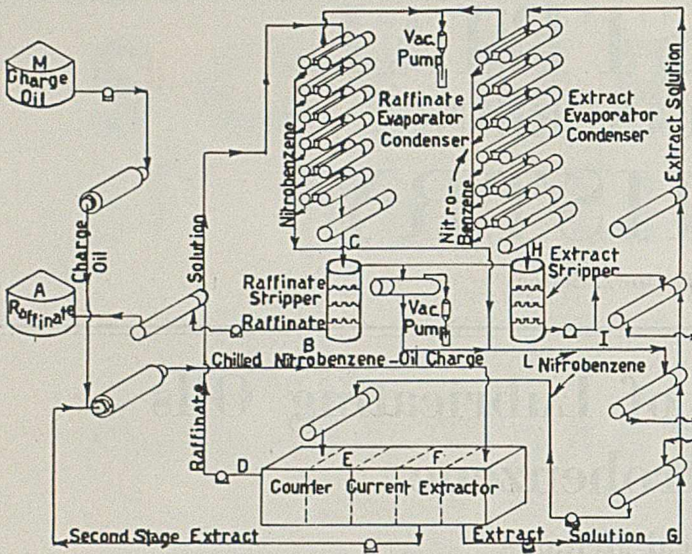

FIGURE 1

skill in manipulation; consequently it is used only to determine the nitrobenzene content of each tank of finished oil. The second method depends upon the fact that the presence of small amounts of nitrobenzene in a lubricating oil stock produces an appreciable lowering of the Pensky Martens closed-cup flash of the stock. This method is simple and rapid, and is used as a periodic check on plant operation.

TITANOUS SULFATE METHOD. In this method, described in a previous paper (*1*), a small sample of oil admixed with xylene, methyl alcohol, 40 per cent sulfuric acid, and standard titanous sulfate solution is boiled under an atmosphere of carbon dioxide. The nitrobenzene is reduced and the remaining titanous sulfate back-titrated with ferric alum, the titanous sulfate consumed in the reaction being the measure of the nitrobenzene present. Because titanous sulfate is oxidized in the presence of air it must be kept in an oxygen-free atmosphere at all times; hence the necessity for careful technic in this determination. When the proper technic is employed, the absolute error of the method varies from ±0.01 per cent on samples containing up to 0.1 per cent of nitrobenzene to 0.2 per cent on samples containing 5 per cent of nitrobenzene. All results are calculated to a weight-per cent basis.

PENSKY MARTENS FLASH METHOD. With the aid of Figure 2 the Pensky Martens closed-cup flash point (A. S. T. M. Designation D93-22) of an oil-nitrobenzene mixture may be compared with the flash point of the original stock and thereby used as a measure of the nitrobenzene content of the oil. Figure 2 is applicable for oils varying from 149 C. (300° F.) to 316° C. (600° F.) closed-cup flash, but is more accurate for oils having a flash point above 204° C. (400° F.). The series of curves shown were interpolated from many experimental data.

In using Figure 2, the curve corresponding to the flash point of the original stock, as indicated by the arrows, is selected. The point where this curve crosses the line representing the flash point of the mixture (read on the *y* axis) is read on the *x* axis as the weight-per cent of nitrobenzene in the mixture. The application of this method is limited to operation where the original charge oil has been properly stripped to eliminate light fractions, as evidenced by a small spread between the open- and closed-cup flashes, described in more detail below. If the closed-cup flash of the raffinate or extract differs from that of the charge, the closed-cup flash of the product in question should be used in evaluating its nitrobenzene content.

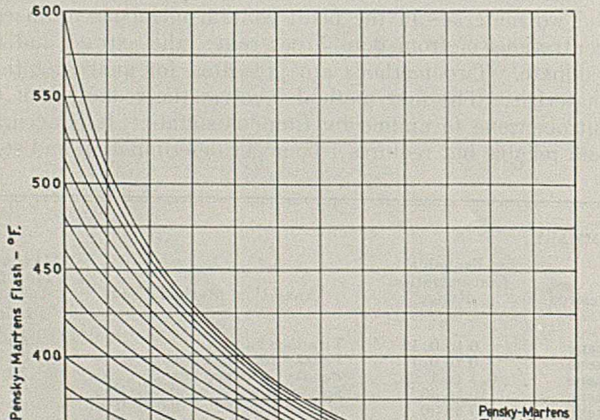

FIGURE 2

It will be observed from Figure 2 that this method will not indicate concentrations above 1.0 per cent. Its accuracy in the working range as based on test oil-nitrobenzene mixtures is given in Table II.

TABLE II. ACCURACY OF PENSKY MARTENS FLASH FOR DETERMINING NITROBENZENE

Nitrobenzene Present	Pensky Martens Flash of Original Stock	Pensky Martens Flash of Mixture	Nitrobenzene (Figure 2)	Deviation
%	° *F.*	° *F.*	%	%
0.01	495	485	0.02	+0.01
0.35	495	395	0.30	−0.05
0.05	440	430	0.03	−0.02
1.00	440	330	0.83	−0.19
0.05	400	390	0.05	0.00
0.50	400	350	0.40	−0.10
0.05	365	360	0.04	−0.01
1.00	365	310	1.00	0.00
0.01	305	305	0.00	−0.01
0.35	305	300	0.20	−0.15

Since this procedure is intended for rapid plant-control work, it has been found desirable to heat rapidly to about 149° C. (300° F.) in the case of high-flash oils and then adjust to the standard rate of heating prescribed in A. S. T. M. procedure D93-22.

Determination of 5 to 100 Per Cent of Nitrobenzene in Oil

While the methods given above are satisfactory for low concentrations of nitrobenzene in oil, their relative errors are high enough to preclude their use on samples coming from various points in the plant where the nitrobenzene content ranges from 5 to 100 per cent.

Two methods are presented for this concentration range. The first merely takes advantage of the wide difference between the specific gravity of oil and nitrobenzene. Because the specific gravity of the oil stock is usually known in plant operation, this method provides a simple and rapid control procedure. The second method may be used when the specific gravity of the oil is not known or when it is desired to isolate a sample of the oil from the nitrobenzene for physical property determinations. It consists of distilling the nitrobenzene from the oil under vacuum and measuring the weight of the residual oil. When a check on the oil boiling in the nitrobenzene range is desired, this method may be supplemented by a freezing point determination on the nitrobenzene distillate.

Specific Gravity Method. The additivity of the specific gravities of nitrobenzene and oil on a volume basis was checked experimentally for a variety of light and heavy oils. This offered a simple means of estimating nitrobenzene concentration when the oil gravity was known. Accordingly, a series of charts was prepared relating the specific gravity of the nitrobenzene-oil mixture to the volume and weight–per cent of nitrobenzene. A range of from 0.8 to 1.02 in the specific gravity was covered and in order to insure the homogeneity of the mixtures all specific gravities are taken at 60° C. (140° F.) or 100° C. (212° F.) depending on the viscosity of the mixtures. The specific gravity of plant nitrobenzene was found to be 1.167 at 60° C. and 1.127 at 100° C. Both values are referred to water at 15.5° C. (60° F.).

Vacuum Distillation and Freezing Point. This method for determining the nitrobenzene content of an oil-nitrobenzene mixture consists of a vacuum distillation of a weighed charge of the mixture to a specified liquid temperature, after which the oil is stripped free of nitrobenzene with an inert gas, the residual oil weighed, and any oil distilling over with the nitrobenzene may be estimated from the freezing point of the distillate and added to the residual oil.

In most cases this procedure may also be used when it is desired to isolate a sample of the oil from the mixture for physical property measurements. Experimental work has shown that using a properly stripped light stock (400° F. flash point) a maximum of 0.6 per cent of oil based on the mixture distills with the nitrobenzene. When using stocks of 260° to 316° C. (500° to 600° F.) flash point 0.1 per cent or less distills. Physical properties on the residual oil may then be used for plant control except where a light stock is present in the mixture in low concentrations.

The apparatus is illustrated in Figure 3. *A* is a 2-liter balloon flask fitted with a Claisen head, *B*. *B* is electrically heated by wrapping with 550 cm. of No. 30 nichrome wire, insulated with asbestos and heated by 110-volt alternating current. *C* is a capillary tube for admitting carbon dioxide and preventing bumping. *D* is 0° to 300° C. thermometer, *E* a water-cooled condenser, *F* an adapter provided with vacuum and manometer outlets, and *G* a 1-liter balloon flask. This size of apparatus permits the distillation of 1-liter samples, which is desirable when physical properties are to be determined on the residual oil.

When only the nitrobenzene content of the mixture is desired, flask *H* (upper left insert, Figure 3) is preferred. This is a 250-cc. distillation flask with the side arm bent as shown in order to decrease entrainment and is equipped with an additional side neck fitted with a capillary tube for admitting carbon dioxide gas.

The freezing point apparatus (right insert, Figure 3) is made of two test tubes, one placed inside the other to form an air-jacketed freezing point tube. A convenient size for these tubes is 15 and 25 mm. in diameter, respectively. A thermometer calibrated in 0.1° C. over the range 0° to 6° C. is placed through cork in the inside tube and stirring is effected by a wire loop stirrer.

A charge of approximately 1000 grams is weighed to 0.1 gram into the weighed distilling flask, *A*. The flask is connected to the Claisen head and the system is evacuated to a pressure of 30 mm. A small stream of carbon dioxide bubbles is admitted to the flask to prevent bumping, and the oil is distilled at 30 mm. pressure until the liquid temperature reaches 220° C. (428° F.). At this point, the carbon dioxide rate is increased somewhat and heating is continued until a temperature of 250° C. (482° F.) is reached in order to strip the residual oil of nitrobenzene. The temperature is held at this point for 3 minutes, after which the oil should be free of nitrobenzene. The flask and contents are then cooled and again weighed. The residual oil in the flask represents the heavy oil in the sample. The same procedure is used in the distillation of 100-gram samples, using flask *H* instead of *A* and Claisen head *B*.

In order to determine the oil in the nitrobenzene overhead, a portion of this material is poured through the condenser and adapter in order to dissolve any oil remaining from the stripping procedure, the total distillate is mixed, and the air-jacketed test tube filled half full of this mixture. Two drops of water are then added to the test tube and the tube is fitted with the thermometer and stirrer. The liquid is stirred vigorously for a few moments in order to saturate the sample with water, then placed in an ice-and-water bath, and the freezing point determined.

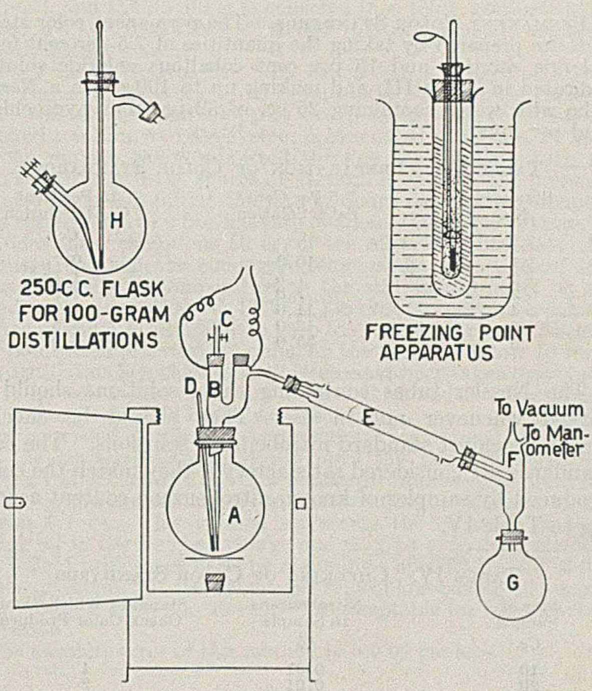

Figure 3

The weight–per cent of light oil distilling with the nitrobenzene is approximated from the freezing point by the following formula:

$$\text{Weight–per cent of oil} = \frac{(5.13 - \text{freezing point } ^\circ\text{ C.}) \times 165}{70} \times \text{weight–per cent of distillate.}$$

5.13° C. is taken as the freezing point of plant nitrobenzene, 165 is the experimentally determined molecular weight of oil distilling with nitrobenzene, and 70 is the freezing point constant (*6*) of nitrobenzene. The absolute error of the method is about ±0.5 per cent.

Determination of Nitrobenzene in Water

While the condensed steam from the vacuum pumps and the strippers of the nitrobenzene plant will retain less than 0.2 per cent of nitrobenzene, even this small amount can be economically recovered. This is accomplished by vaporizing about 10 per cent of the water, which on condensation throws out nitrobenzene while the water condensate saturated with nitrobenzene is reprocessed. Practically all the nitrobenzene will appear in this distillate and the remaining 90 per cent of the water can be discarded.

The nitrobenzene content of the stripped water bottoms is determined by a colorimetric method, based on the reduction of nitrobenzene to aniline which forms a colored product on reaction with sodium hypochlorite. The color intensity is a measure of the nitrobenzene content of the water examined. This method is a modification of Evolve's test for aniline (*2*).

Reagents and Apparatus: 1 to 1 hydrochloric acid; 32 per cent hydrochloric acid; 15 per cent potassium hydroxide; 15 per cent solution of cobaltous chloride crystals ($CoCl_2$, $2H_2O$) containing 25 cc. of 32 per cent hydrochloric acid per liter; 7.5 per cent solution of ferric chloride crystals ($FeCl_3$, $6H_2O$) containing 25 cc. of 32 per cent hydrochloric acid per liter; sodium hypochlorite solution containing 0.11 per cent of available chlorine; powdered zinc; solutions of nitrobenzene in water, 0.01, 0.03, 0.04, and 0.05 per cent by weight; one daylight lamp assembly; a test-tube condenser made of a test tube that will fit the neck of a 250-cc. Erlenmeyer flask and provided with a cork carrying water inlet and outlet tubes.

Permanent Color Standards. The permanent color standards are prepared by taking the quantities of 7.5 per cent ferric chloride solution and 15 per cent cobaltous chloride solution indicated in Table III, and making up to 100 cc. in a Nessler tube with water containing 25 cc. of 32 per cent hydrochloric acid per liter.

Table III. Preparation of Color Standards

Standard No.	7.5 Per Cent $FeCl_3$ Solution	15 Per Cent $CoCl_2$ Solution
	Cc.	*Cc.*
1	10.0	0.7
2	7.5	1.1
3	7.0	1.9
4	11.0	4.0
5	12.0	5.5
6	33.0	6.0

The Nessler tubes containing these solutions should be corked whenever not in use. They should be checked monthly against standard nitrobenzene solutions. The color standards are considered satisfactory if they match the colors produced by samples of known nitrobenzene content according to Table IV.

Table IV. Checking of Color Standards

Size of Sample	Nitrobenzene in Sample	Standard Which Should Check Color Produced
Cc.	%	
10	0.01	1
20	0.01	2
10	0.03	3
10	0.04	4
10	0.05	5
20	0.03	6

Procedure. If the sample contains sediment or oil, it should be filtered. The amount of sample taken will depend upon the concentration expected (Table V). The required amount is diluted to 25 cc. with distilled water in a 250-cc. Erlenmeyer flask which is provided with the test-tube water-cooled condenser extending into the flask about 11 cm., and 15 cc. of 1 to 1 hydrochloric acid are added. The solution is brought to a boil, approximately 0.3 gram of zinc dust added, and the condenser replaced as quickly as possible. The solution is allowed to stand for exactly 2 minutes and is then filtered, cooled in ice water, and 5 cc. of sodium hypochlorite (0.11 per cent of available chlorine) are added, followed by 50 cc. of 15 per cent potassium hydroxide solution. The solution is again cooled in ice water, filtered, and made up to 100 cc. in a Nessler tube which is placed in the tube rack. The color of this solution is compared, at the end of 30 minutes from the time when the sodium hypochlorite was added, with the permanent color standards by looking down through the full length of the tubes, a porcelain plate at the bottom of the rack being illuminated by a daylight lamp. Check determinations should be run.

Table V gives the weight–per cent of nitrobenzene for specified sizes of samples when the color developed corresponds to one of the color standards.

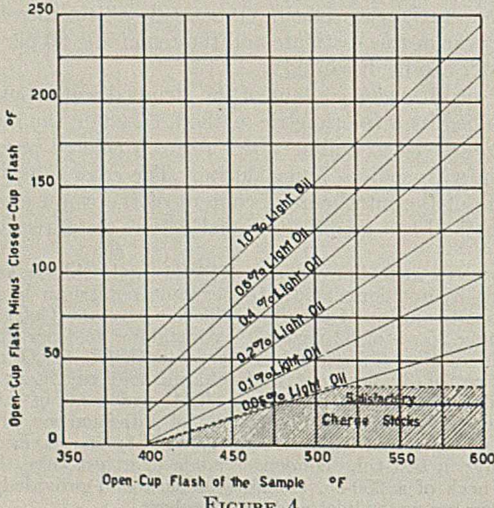

Figure 4

Table V. Weight–Per Cent of Nitrobenzene in Water

Volume of Sample Taken	Standard No.					
	1	2	3	4	5	6
Cc.	%	%	%	%	%	%
20	0.005	0.01	0.015	0.02	0.025	0.03
10	0.01	0.02	0.03	0.04	0.05	0.06
5	0.02	0.04	0.06	0.08	0.10	0.12
2.5	0.04	0.08	0.12	0.16	0.20	0.24

The accuracy of the method is indicated by the experimental data in Table VI.

Table VI. Accuracy of Colorimetric Method for Estimating Nitrobenzene in Water

Sample	Nitrobenzene Added	Nitrobenzene Estimated
	%	%
1	0.005	0.005
2	0.02	0.017
2	0.02	0.018
2	0.02	0.020
3	0.06	0.058
3	0.06	0.054
3	0.06	0.056
4	0.10	0.10
4	0.10	0.09

Charge Stock Analysis

In all solvent-refining processes it is necessary either to avoid contamination of the solvent with lighter fractions which may be brought into the system by the oil charge or else to resort to special methods of separating the oil and solvent.

If the oil charged to the plant contains fractions of the same volatility as nitrobenzene, in stripping solvent from oil some of the oil will be taken off with the solvent and so contaminate the latter with a nonselective diluent.

In the nitrobenzene process the introduction of contaminating oil fractions into the system is preferably and simply avoided by proper steam-stripping of the oil charge in the initial distillation of the crude. Experience has shown that less than 0.05 weight–per cent of light fractions in the oil charge gives negligible contamination of the solvent nitrobenzene. Consequently, oil charge stocks are examined for light oil content for which two test methods are available. The first method, for use on stocks having an open-cup flash point (A. S. T. M. Designation D92-33) above 232° C. (450° F.) depends upon the difference between the open- and closed-cup flash points of the sample, while the second method, for use on stocks having an open-cup flash of less than 232° C. (450° F.) consists of a double vacuum distillation and a direct measurement of the light oil present.

Flash Difference Method. Owing to the presence of air currents which carry away small amounts of vaporized oil, the open-cup flash point of a high-flash oil is only very slightly affected by the presence of oil boiling in the nitrobenzene range in concentrations up to 1.0 per cent. On the other hand, the Pensky Martens closed-cup flash point is very sensitive to small amounts of light oil. If no light oil is present the two flashes will be identical within the limits of experimental error (±5° F. for each flash).

This phenomenon has been utilized in the determination of low boiling oil in charge stocks to the nitrobenzene plant. It is very well suited for this purpose, because both the amount of oil that will distill with the nitrobenzene and the effect that it will have on the closed-cup flash point of the stock are roughly proportional to the volatility of the oil. Thus the only assumption necessary regarding the characteristics of the light oil is that its initial boiling point is not far below that of nitrobenzene, which has been the case in a variety of actual stocks examined. This assumption is necessary only because the lower boiling oil will tend to vaporize from the nitrobenzene in plant operation and be ejected from the system through the vacuum pumps, thus preventing its accumulation. Figure 4 correlates the per cent of low-boiling oil with the difference between the open- and closed-cup flashes for mixtures of varying open-cup flashes. Lines were drawn representing various percentages of light material. For a given concentration of light oil the difference between the open- and closed-cup flashes is much greater in the case of high open-cup flashes than for low ones, and for this reason the method is not satisfactory when the open-cup flash is below 232° C. (450° F.). Charge stocks which do not fall in the shaded area on Figure 4 are not acceptable for the nitrobenzene plant.

Because of the ±5° F. errors that cannot be avoided in the flash determinations, check values should be determined in order to obtain the best accuracy. Table VII is typical of the accuracy that can be obtained. The light oil used for the data in this table had a 50 per cent boiling point of 229° C. and an average molecular weight of 196.

TABLE VII. ACCURACY OF FLASH DIFFERENCE METHOD

Weight-Per Cent of Light Oil Added	Open-Cup Flash	Closed-Cup Flash	Open-Cup Minus Closed-Cup Flash	Weight-Per Cent of Light Oil Found	Deviation
	° F.	° F.			
0.005	555	555	0	0	−0.005
0.02	560	535	25	0.02	0.00
0.045	550	510	40	0.04	−0.005
0.045	560	500	60	0.07	+0.025
0.10	550	485	65	0.08	−0.02
0.20	550	435	115	0.25	+0.05
0.23	545	440	105	0.20	−0.03
0.25	560	440	120	0.24	−0.01
0.50	540	390	150	0.50	0.00
0.90	555	370	185	0.80	−0.10

DOUBLE DISTILLATION. For stocks having an open-cup flash of 232° C. (450° F.) or lower, the preferred procedure is the double-vacuum distillation which gives a direct measure of the light oil present. This method is more accurate but more time-consuming than the flash difference method.

The apparatus used for this method is very similar to that illustrated in Figure 3 for determining nitrobenzene in oil. The first distillation is carried out in the large-scale apparatus differing from Figure 3 only in that a 3-liter flask is used instead of a 2-liter flask, and the distillate is collected in a 100-cc. graduate instead of the 1-liter flask shown. The second distillation is carried out in a small apparatus using a 100-cc. Claisen flask, a small water-cooled condenser about 20 cm. long and inclined at an angle of 45°, and a small adapter similar to that shown in Figure 3, and the distillate is collected in a 10-cc. graduate calibrated in 0.1-cc. intervals. 0° to 300° C. thermometers are used in both distillations.

When the apparatus has been assembled, a charge of about 1300 grams of the stock to be examined is placed in the balloon flask, connections and stoppers are painted with collodion or celluloid solution, and the system is evacuated to 10 mm. or less. Carbon dioxide gas is admitted through the capillary tube at such a rate that if the source of vacuum is shut off the pressure in the system will fall at the rate of about 60 mm. per minute. This corresponds to a free gas rate of about 150 cc. per minute.

Under these conditions 50 cc. of the oil are distilled into the graduate, keeping the condenser temperature near that of the room. The liquid temperature in the still should never be allowed to rise above 300° C. (572° F.) in order to prevent cracking of the oil, and it is advisable to keep the temperature as far below this point as is practical by reducing the pressure below 10 mm. The distillation is continued until 50 cc. have been taken overhead, but in no case is a temperature of 300° C. exceeded. The distillate is then redistilled in the small set-up.

In the second distillation the pressure is maintained at 10 mm. and the material distilled slowly until the vapor temperature reaches 152° C. (305° F.). The condenser is allowed to drain for 5 minutes and the volume of distillate read in the graduate to the nearest 0.1 cc. This volume represents the quantity of low-boiling oil in the weighed charge and may be converted directly to a weight percentage basis by assuming a specific gravity of 0.8 for the distillate. If the weight-per cent of low-boiling oil is more than 0.05 per cent, the stock is not acceptable for nitrobenzene extraction.

The absolute error of this method is ±0.02 per cent.

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Determination of Radium in Carnotite and Pitchblende

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RADIUM is determined electroscopically by means of radon which is introduced into an electroscope chamber. Using a Lind electroscope the radium content of carnotite or pitchblende can be estimated accurately.

In the first method proposed the ore is fused with a mixture of sodium and potassium carbonates in a platinum boat (*3*), the fusion dissolved in nitric acid, and the radon collected in an electroscope chamber. The objection that the fusion sometimes does not dissolve, but remains hard and glassy in the boat, is met by chilling the fusion suddenly by partly submerging the boat immediately in cold water on removal from the flame or furnace. The fusion draws away from the boat and leaves the boat while in the boiling nitric acid. In every case all the radon is removed, and the results are not low. This method gives excellent results.

Barker proposed the bisulfate fusion method (*1*). Later he suggested the phosphoric acid method (*2*), stating that in the bisulfate method heating the fusion to drive out the radon breaks the test tubes by expanding the fusion. When the fusion is rolled on the side of the tube as the fusion cools, the Pyrex tubes are never broken.

All these methods give good results, and may be applied to any product from carnotite or pitchblende containing radium. Scott (*4*) gives methods for the analysis of radioactive solutions.

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A Method of Analysis for Fluoride

Application to Determination of Spray Residue on Food Products

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THE widespread use of fluorine compounds as insecticides and the establishment by the Federal Government of a tolerance, or upper limit to the amount of added fluorine which may be present on or in foodstuffs, have combined to stimulate interest in the quantitative determination of minute amounts of this element. Consequently, several dozen publications on various methods of analysis have recently appeared. Work on the subject was undertaken in this laboratory in connection with a study of the amounts of arsenic, lead, and fluorine which occur on fruit sprayed in various ways for the control of the codling moth in California.

Preliminary experiments with several suggested methods indicated the superiority of the reaction between fluoride and thorium ions in the presence of an indicator sensitive to excess thorium. Accordingly, an intensive investigation has been made of Armstrong's (*1*) modification of the Willard and Winter (*14*) method which involves the titration in 50 per cent alcohol of fluoride ion with standard thorium solution in the presence of sodium alizarin sulfonate. For comparison, the Sanchis (*9*) method adapted from that of Thompson and Taylor (*12*), which depends upon the bleaching effect of fluoride ion upon a zirconium-alizarin complex, has been used in certain cases.

Titration with Standard Thorium Solutions

Standard fluoride solutions were prepared from recrystallized c. p. sodium fluoride. Their accuracy was checked by the standard method of precipitation as CaF_2 (*10*). Stock solutions were made 0.05 *M* and dilutions to lower concentrations as needed. Very dilute solutions of sodium fluoride, such as 0.001 *M*, decrease in strength if kept in glass vessels, but if the containers are lined with paraffin the concentration remains constant for long periods. Thorium solutions, approximately 0.05 *M*, were made from c. p. thorium nitrate and were standardized by precipitating as thorium oxalate, heating, and weighing as the dioxide. The solutions were then diluted to 0.01 *M* or 0.001 *M* for use. These dilute solutions were made at intervals of 2 to 3 weeks, though they appear to be stable for longer periods. Comparison of the dilute standard solutions of fluoride and thorium by the method to be described gave excellent agreement.

The first experiments followed the procedure of Armstrong. It was soon found that three factors must be carefully controlled in order to obtain duplicable results: the volume of indicator added, the intensity of color in the blank and unknown, and the acidity. The first two are inseparably connected, for the more indicator used the smaller is the volume of thorium solution required to produce a given intensity of color in the blank. As judged by the eye, the pink color is most sensitive to changes in the amount of thorium added when its intensity is very low. It is not advisable to use large amounts of indicator in order to reduce the thorium needed in the blank, because the pink tint is masked by the yellow color of the indicator where much is used in acid solution. Summarizing a large number of experiments, it may be said that when a volume of 50 cc. is used for the blank, 0.040 cc. of a 0.05 per cent aqueous solution of sodium alizarin sulfonate—i. e., the concentration of the indicator in the solution is 4×10^{-5} per cent—plus 0.040 to 0.070 cc. of 0.001 *M* thorium solution gives a faint pink color which is very suitable for matching and is very sensitive to thorium ion. For other volumes in the blank, proportional amounts of the reagents should be used. It is advisable to run a fresh blank with each unknown, for the color slowly becomes more intense as the solutions are allowed to stand. This is undoubtedly due to slowness of one or more of the reactions which are involved in the equilibrium between Th^{++++}, F^-, and sodium alizarin sulfonate. In the somewhat analogous method used by Thompson and Taylor (*12*) and by Sanchis (*9*)—i. e., the bleaching of red zirconium alizarin sulfonate by fluoride—the solutions are brought to boiling to hasten the establishment of equilibrium, which is said to require 48 hours in the cold.

Effect of Acidity and Use of Buffer

Previous workers have paid scant attention to the acidity of the solution during titration. The usual directions have been to destroy the pink color with 1 to 50 hydrochloric acid solution (0.24 *N*) before adding the thorium solution. For precise work, however, the acidity is important. If the solution is decolorized, but no excess acid is added, extremely low values are obtained. The addition of one drop of acid in excess usually is satisfactory, but larger amounts of acid lead to the use of too much thorium solution (Table I). Vanselow (*13*) of the Citrus Experiment Station has found the same effect for excess acid. While it is possible to control the acidity by careful use of dilute hydrochloric acid, the use of a buffer offers advantages. Preliminary experiments, using the indicator bromophenol blue, indicated that the most desirable pH was approximately 3.5. In order to give this pH at half neutralization—i. e., at maximum buffering power—a buffer acid must have a paK of the same magnitude. The data of Jukes and Schmidt (*5*) show that paK for acetic acid is increased by about 0.7 in passing from water to 50 per cent alcohol. Hence, it seemed probable that the paK of the related acid, monochloroacetic, which is 2.8 in water, would be approximately 3.5 in a mixture containing equal parts of commercial 95 per cent alcohol and water—i. e., about 48 per cent alcohol.

The behavior of chloroacetic acid in 48 per cent alcohol was investigated by determining the pH of solutions containing 2.00 cc. of 1 *M* monochloroacetic acid solution and varying volumes of 1 *M* sodium hydroxide solution in a total volume of 100 cc. A hydrogen electrode was used and a glass electrode was standardized in the same solutions. The results are given in columns 1 and 2 of Table I.

TABLE I. pH OF CHLOROACETIC ACID–SODIUM HYDROXIDE BUFFERS (0.02 *M*) IN 48 PER CENT ALCOHOL

Molecular Ratio Acid:Base	pH	Relative Volumes of Th^{++++} Solution: Blank at constant buffer ratio 0.5	Blank and test solution at same buffer ratio, volume at 0.5 taken as unity
1:0.2	2.95	1.411	1.050
1:0.3		1.292	1.000
1:0.4	3.39	1.171	1.000
1:0.5		1.000	1.000
1:0.6	3.73	0.975	1.000
1:0.7		0.903	0.957
1:0.8	4.17	0.768	0.811

A plot of these results shows that at half neutralization the pH is 3.55, which is accordingly the paK value of chloroacetic acid in equal parts by volume of water and commercial ethyl alcohol. The corresponding dissociation constant, *Ka*, is 2.8×10^{-4}. It was necessary to prove that this buffer is able to maintain a constant pH during the titration with thorium solution. Typical titrations were made with varying amounts of fluoride ion present and the various buffer mixtures present at 0.02 *M* concentration. The hydrogen electrode did not function in the presence of the indicator, but the glass electrode gave very steady potentials exactly equal in all cases to those previously obtained in the buffer solutions alone. Since it may be necessary to analyze samples containing considerable acid or base, the most desirable procedure is to bring the solution to the approximate transition point of the indicator with dilute acid or base—e. g., 0.05 *N* hydrochloric acid or sodium hydroxide—before adding the buffer solutions.

The third column of Table I shows how greatly the volume of thorium solution required to obtain an end point is altered at various pH values of the test solution when the blank is held at a constant buffer ratio of 0.5. It is obviously not possible to obtain accurate results except over a very narrow pH range. In the last column it is shown that when the blank and test solutions have the same pH a much wider range is allowable. The buffer ratio 0.5, at which the pH is 3.55, is seen to be in the middle of the favorable range. The above results at once raise the question of how greatly the pH of a 48 per cent alcohol solution varies when treated with a dilute solution of hydrochloric acid as in the ordinary adjustment of acidity according to the directions of Willard and Winter (*14*) and of Armstrong (*1*). For the sake of greater delicacy, tests were made in which 0.05 *N* hydrochloric acid was used instead of the 0.24 *N* (1 to 50) recommended by the above workers, so that the changes in pH were smaller than with corresponding volumes of stronger acid solution. The results are given in Table II. A comparison of Tables I and II will show what very serious errors result from the inevitable inaccuracy involved in trying to add one drop of 0.24 *N* acid in excess to an unbuffered solution.

TABLE II. EFFECT OF pH UPON COLOR OF SODIUM ALIZARIN SULFONATE IN 50 PER CENT COMMERCIAL ALCOHOL

Volume of Acid	0.000	0.030	0.045	0.075	0.085	0.145
pH	8.8	7.2	6.3	5.2	4.8	4.1
Color	Pink	Pale pink	Very pale pink	Very pale yellow	Pale yellow	Yellow

In Table II is shown also the effect of pH upon the color of sodium alizarin sulfonate in 50 per cent commercial alcohol as determined by adding 0.05 *N* hydrochloric acid in small increments to 50 cc. of solution containing 0.04 cc. of 0.05 per cent solution of the indicator and made slightly basic at the start. The pH was determined with the glass electrode. Kolthoff and Furman (*6*) state that the color changes occur in water in the pH range 3.7 to 5.2.

It is obvious that the equilibrium between the acidic and salt forms of the indicator occurs in the alcoholic solution in a more alkaline range than in water, which is in agreement with the behavior of most weak acids.

Accuracy and Delicacy of the Titration

The procedure described above has been used many times in titrations of standard solutions of sodium fluoride. The range of concentration before addition of alcohol was from 0.00012 *M* to 0.0016 *M*—i. e., 2.3 to 30.4 p. p. m. as fluorine. The total fluoride in 25 cc. therefore varied from 57 to 760 γ. The maximum errors were +3.7 and −2.7 per cent, with an average error of −1.0 per cent. No distinct variation in percentage error occurred as the concentration of fluoride was varied over this range. This is a somewhat smaller average error than that of −1.7 per cent which may be calculated from the data of Willard and Winter (*14*) for the titration according to their procedure of standard fluoride solutions ranging in concentration from 0.0004 *M* to 0.004 *M*.

The limiting factor seems to be the slowness with which equilibrium is reached near the end point. As mentioned before, the color of the blank slowly becomes more intense. For larger amounts of fluorine the uncertainty thus introduced is negligible, but with small amounts the unavoidable difference in age of the blank and test solutions may cause an appreciable error. This may be eliminated to some extent by using a second blank which is matched against the sample. The average of the volumes of thorium solution used in the two blanks is used. Attempts to speed up the attainment of equilibrium by running the titrations at 60° C. were not successful, for the red thorium alizarin sulfonate was rapidly coagulated.

There is no *a priori* reason for using a volume as large as 50 cc. for titration, so a series of experiments was made in which the volume was made up to 5 cc. Small matched test tubes were used and it was found easy to obtain the same accuracy with 6 to 90 γ of fluoride as with the larger amounts in 50 cc.

For purposes of comparison with an entirely different method of analysis two series of solutions from fruits and vegetables treated with fluoride sprays were tested by the present method and by that of Sanchis (*9*). Over the range from 4 to 400 γ of fluorine in 25 cc. the latter method gave results which average 3.6 per cent higher than those obtained by titration. In many cases agreement was very close, but occasionally samples run by the Sanchis method were quite different in color from the standards.

Interfering Substances

When fluoride is present in solutions containing possible interfering ions or compounds, the recommendation is usually made that it be isolated by distillation from perchloric or sulfuric acid solution. Under such conditions, however, the halides, nitrate, sulfite, and other rarer contaminants are also distilled and the possibility always exists that nonvolatile substances will be carried into the distillate as spray. For these reasons a study has been made of the effects of a number of ions at various concentrations in order to determine, at least approximately, the maximum amounts which may be tolerated in the fluoride solution. This depends, of course, upon the amount of fluoride used and upon the accuracy desired. The tests were made with 1.00 cc. of 0.003 *M* sodium fluoride solution in a total volume of 50 cc. Varying amounts of the sodium salts of each ion were added and the pH was adjusted as described above. In Table III the concentrations are stated at which an appreciable increase in volume of thorium solution was required. The precise concentrations at which interference first develops is accordingly a little lower than the figures given. If a stronger pink color is taken as the end point of the titration, interference occurs at lower concentrations.

TABLE III. EFFECT OF VARIOUS IONS UPON TITRATION OF FLUORIDE WITH THORIUM

Ion	Concn. for Appreciable Effect	Ion	Concn. for Appreciable Effect
Halogens	0.1 *M*	AsO_3^{---}	1×10^{-4} *M*
NO_3^-	0.1 *M*	SO_4^{--}	1×10^{-6} *M*
ClO_4^-	0.1 *M*	AsO_4^{---}	1×10^{-6} *M*
SO_3^{--}	0.002 *M*	PO_4^{---}	$<1 \times 10^{-6}$ *M*

The only halogen ion which is likely to be encountered at concentrations high enough to interfere is chloride. It was found, however, that by adding an equal amount of it to the blank the effect is made equal in sample and blank and hence no error results. Similar observations concerning the effects of chloride and sulfate have been made by Sanchis (*9*) and of chloride and nitrate by Bowes (*3*). The tests with sulfite were complicated by the fact that all available so-called C. P. samples were contaminated with sulfate. When this was removed by adding excess barium, an error was introduced on account of the formation in the alcoholic solution of insoluble or slightly ionized barium fluoride. It is probable that this compound will yield its fluoride to thorium ion, but the equilibrium is established too slowly for practical purposes. But by precipitation of the sulfate with the minimum amount of barium a solution of pure sulfite was obtained and its effect determined.

Interference by sulfate at such low concentration is surprising, since thorium sulfate is soluble in water to the extent of approximately 1 per cent. However, the conductivity measurements of Barre (*2*) show that a 0.001 M solution in water is by no means completely dissociated, and it is to be expected that weakness of the salt will be greatly increased in the presence of alcohol. Phosphate appears to react quantitatively with thorium. Interference from this ion was noted previously by Reynolds (*7*).

It is possible to prepare a solution of fluoride free from the most harmful ions by distillation as hydrofluosilicic acid according to the procedure of Willard and Winter (*14*). Either perchloric or sulfuric acid may be used, but the serious effects produced by the slightest trace of sulfate carried over as spray, or volatilized if the temperature gets too high, provide an argument in favor of perchloric acid. Certain differences in the behavior of the two acids have been noted by Shuey (*11*) when organic matter is present. Some lots of C. P. sulfuric acid contain a volatile impurity which greatly increases the volume of thorium solution required to produce a light pink color with the indicator. Its nature has not been determined, but it can be removed completely by boiling the concentrated sulfuric acid vigorously for a few minutes. Only a small part of this effect is due to fluoride in the sulfuric acid. Data on this are given below.

Preparation of Samples for Analysis

This paper is not primarily concerned with the practical analysis of various materials which contain fluorine, since that phase of the investigation is to be reported elsewhere. However, certain data and observations are appropriate here. In agreement with other workers it has been found that organic matter is destroyed most satisfactorily by heating in a muffle furnace. Vegetable or fruit material should be divided very finely and mixed intimately with a known weight of high-grade calcium hydroxide powder in a porcelain dish. Sufficient reagent must be used to maintain a basic condition throughout the rest of the process. Two grams are sufficient for 50 to 100 grams of the numerous kinds of fruits and vegetables so far investigated.

After thorough drying, first on a water bath and then on a low-temperature sand bath until slight charring is noticeable, the sample is placed in a muffle furnace and ashed. The results of a study of the effects of different furnace temperatures will be discussed below. Forty cubic centimeters of a 50 per cent solution of the previously boiled and cooled sulfuric acid and 0.5 gram of fine silica are added to a 250-cc. distilling flask equipped with trap and condenser and the ash is quantitatively introduced. The porcelain dish sometimes retains a portion of the ash. To insure the removal of all fluorine the dish is treated for several minutes with a few cubic centimeters of sulfuric acid which is then added to the distilling flask. A few cubic centimeters of distilled water are placed in the receiving flask in order to cover the outlet of the condenser. The distilling flask is heated with a Bunsen burner and an auxiliary flask filled with distilled water is heated simultaneously and steam is passed from the latter vessel into the distilling flask. By regulation of the two burners it is easily possible to hold the temperature of distillation at any desired point.

The results of distillations at various temperatures may be summarized as follows: Below 110° C. very little fluoride is volatilized; from 110° to 130° volatilization is increasingly efficient but is not complete enough with reasonable volumes of distillate; above 130° up to the temperature at which phosphates and sulfates may be distilled, the hydrofluosilicic acid is rapidly volatilized; 140° C. was chosen as the most satisfactory temperature. When the above method of distillation was applied to a large number of ash samples from fruits and vegetables an average of 96.7 per cent of the total fluorine which could be volatilized was recovered from the first 150 cc. For practical purposes distillation of 200 cc. was found to reduce the loss to a negligible point. Similar results have been obtained by Vanselow (*13*) who has used an analogous method of distillation. Winter and Butler (*15*) found that only 50 to 75 cc. need be distilled from perchloric acid solution. The observation of Reynolds (*7*) that the siliceous coating which forms on the inside of the distilling flask holds back fluoride from solutions rich in that element and liberates it later to samples deficient in fluorine, was also noted in the present work; so the removal of such films with alkali at frequent intervals was adopted as a standard procedure.

A series of runs in which a known amount of sodium fluoride was added to 50-gram lots of crushed ripe apples was made in order to test the accuracy of the whole method and in particular the effect of burning at different temperatures. A solution of sodium fluoride containing 1785 γ of fluorine was added to each sample and the burning, distillation, and titration were carried out as described before. The results for four different temperatures of the muffle furnace and lengths of time in it are given in Table IV. All temperatures were determined with a calibrated chromel-alumel thermocouple and millivoltmeter.

TABLE IV. EFFECT OF TEMPERATURE AND TIME IN MUFFLE FURNACE

Temperature of Furnace ° *C.*	Time *Min.*	Appearance of Ash	Recovery of Fluorine %
520	120	Dark	86.1
620	60	Light	93.7
720	20	Dark	97.3
820	10	Dark	75.2

These recoveries of added fluorine agree closely with the results of similar experiments by Reynolds et al. (*8*) and Winter and Butler (*15*). The serious loss in only 10 minutes' heating at 820° C. is particularly striking. Since the lime used to "fix" the fluoride during drying and ashing of the sample contained some fluoride as an impurity, a series of runs was made with different amounts of calcium hydroxide carried through the entire process. From the consistent results obtained allowance could be made for the fluoride in any amount of lime plus the standard amount of sulfuric acid and silica. Various lots of supposedly C. P. calcium hydroxide were found to differ in fluoride content from approximately 30 parts per million to nearly 100. For most purposes it does not seem necessary to prepare fluorine-free lime as recommended by Dahle (*4*). Various lots of C. P. sulfuric acid differ considerably in fluoride content, four bottles varying from a minimum of 0.3 to a maximum of 19 parts per million. Previous workers have attributed the failure to secure complete recovery of fluoride added to organic matter to either loss during ashing or incomplete volatilization. The present work indicates that loss during ashing is much more likely to explain the discrepancy. However, it is possible that the reactions which form complex fluorides that are stable in hot acid solution occur only when ashing is done at a high temperature. For this reason and in the hope of overcoming all difficulties connected with the use of a muffle furnace, a method of ashing based upon combustion in oxygen is now being studied.

Summary

The estimation of fluoride by titration with standard thorium solution in the presence of sodium alizarin sulfonate as indicator has been studied. The most favorable procedure includes the use of the indicator at a concentration of 4 × 10^{-5} per cent, in a total volume of 50 cc., titration to match a blank in which the end point is taken at a very light pink shade, and careful regulation of the pH in both blank and sample, the most favorable pH being 3.5. This latter condition is readily met by the use of the buffer system of sodium hydroxide and chloroacetic acid at a ratio of 0.5 and total concentration of 0.02 *M*. The dissociation constant of chloroacetic acid in 50 per cent commercial alcohol has been found to be 2.8×10^{-4}. Sodium alizarin sulfonate in this alcoholic solution acts as an indicator for hydrogen ion over the pH range 4.8 to 7.2 instead of 3.7 to 5.2 as in water. In a volume of 50 cc. an average accuracy of 99 per cent has been secured with known amounts of fluoride ranging from 57 to 760 γ of fluorine. With 5-cc. volumes approximately the same accuracy is possible with 6 to 90 γ of fluorine.

Data are given regarding the concentrations at which several interfering ions have an effect. The most serious of these are sulfate, arsenate, and phosphate, which fortunately are left behind when the fluoride is distilled as hydrofluosilicic acid. Sulfuric acid is entirely suitable for the distillation and a volume of 200 cc. distilled at 140° C. accounts for all but a trace of the fluoride. In the ashing of fruit samples containing fluoride for distillation it is very important not to allow the temperature to reach above 800° C., for loss is then excessive. Allowance must be made for the fluoride contained in the lime which is added to the sample before ashing. Recovery of fluoride added to apple pulp was 97.3 per cent under the most favorable conditions.

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Iodometric Determination of Copper

Adjustment of Hydrogen-Ion Concentration

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PARK (*3*) has recently described a method of determining copper in the presence of ferric iron and arsenic acid. By his method an iodometric titration is carried out in a solution containing ammonium bifluoride and potassium biphthalate. He states that the purpose of the bifluoride is to suppress the action of the ferric iron on potassium iodide, and that the biphthalate forms a buffer solution in which the pH is about 4.0, a value sufficiently high to cause no appreciable oxidation of iodide by the arsenic acid.

The problem of pH adjustment can be best understood if we consider the technic involved in the process. After decomposition of the ore with mineral acid, sufficient ammonium hydroxide is added to neutralize the excess mineral acid, arsenic acid, etc., precipitate the iron, convert the copper to the cupric ammonia complex, and produce a slight odor of ammonia. The bifluoride and biphthalate are then added. It is assumed that if the proper amount of biphthalate is added, the concentrations of phthalate and of biphthalate will be such as to produce an effective buffer solution at the pH desired. It is evident that an effective buffer action is necessary to allow for a reasonable variation in the amounts of excess ammonium hydroxide and of the other substances which react with the weak acid. In this process the possibility of the bifluoride's acting as a buffer evidently has been overlooked. Hudleston and his co-workers (*1*) have shown that hydrogen fluoride in its aqueous solutions undergoes the following equilibria:

$$\mathrm{H^+ + F^- \rightleftharpoons HF} \quad \mathrm{K_1} = \frac{[\mathrm{H^+}][\mathrm{F^-}]}{[\mathrm{HF}]} = 6.9 \times 10^{-4}\ (25^\circ\ \mathrm{C.}) \quad (1)$$

$$\mathrm{HF + F^- \rightleftharpoons HF_2^-} \quad \mathrm{K_2} = \frac{[\mathrm{HF_2^-}]}{[\mathrm{HF}][\mathrm{F^-}]} = 4.7\ (25^\circ\ \mathrm{C.}) \quad (2)$$

The ionization constant of biphthalate at 25° C. is 3.1×10^{-6}. To obtain a pH of 4.0, the ratio of concentrations of biphthalate to phthalate should be about 32 to 1, while the ratio of concentrations of hydrofluoric acid to fluoride should be about 1 to 7. At this pH the hydrofluoric acid should be a much more effective buffer than the biphthalate, and the pH at which it has maximum buffer efficiency is about 3.2. It seems reasonable to suppose, therefore, that it should be practicable to add such an amount of bifluoride that the concentrations of fluoride and of hydrofluoric acid formed would be sufficient not only to produce the ferric complex but also to yield simultaneously a buffer solution at a pH between 3 and 4.

It is the purpose of the present paper to show that under the conditions described by Park the pH at the end point is nearer 3.3 than 4.0, that this pH is high enough to insure no appreciable reaction between iodide and arsenic acid, that the biphthalate plays practically no part in the adjustment of the pH, and that it may be omitted without any material effect on the accuracy or precision of the method.

Reagents

The cupric sulfate solution was prepared from the salt which had been twice recrystallized from a solution of the C. P. pentahydrate, and was made 0.1152 *M* in copper sulfate. The concentration of this solution was determined electrolytically, and iodometrically by titration with thiosulfate solution which had been standardized against pure copper foil. Results by the two methods agreed within less than 0.2 per cent.

The sulfuric acid, ammonium hydroxide, potassium iodide, sodium thiosulfate, and potassium biphthalate consisted of C. P. reagents which conformed to the standards of Murray (*2*).

The iron and arsenic added as impurities were supplied from solutions of C. P. ferric nitrate and arsenic acid. These solutions contained approximately 0.1 gram each of iron and of arsenic in each cubic centimeter of reagent.

The ammonium bifluoride was Merck's Purified grade.

The starch solution was made from soluble starch prepared "according to Lintner."

Experimental Procedure and Results

Table I shows results of titrations of solutions of copper sulfate containing iron and arsenic as impurities. In series 1, 2, 4, 5, 7, 8, and 11 ammonium bifluoride, NH_4FH_2, alone was used, and in series 3, 6, 9, and 10 potassium biphthalate was also present. The procedure was as follows:

> To 25.00 cc. of copper sulfate solution containing 0.1831 gram of copper were added 5 cc. of a solution containing the impurities as designated in Table I and 5 cc. of concentrated sulfuric acid. This was followed by concentrated ammonium hydroxide until the blue copper complex began to appear. Then 6 *N* ammonium hydroxide was added dropwise until the solution smelled faintly of ammonia, and 2.0 grams of ammonium bifluoride and, in the runs indicated, 1.0 gram of potassium biphthalate were dissolved in the mixture. As soon as solution was complete, 10 cc. of 3 *M* potassium iodide were added and titration with thiosulfate was carried out. This procedure is essentially the same as that described by Park except in the cases in which the biphthalate was omitted. The amount of ammonium bifluoride added corresponded to 1 gram for each 0.1 gram of iron.

pH measurements were made by means of the quinhydrone electrode on separate solutions containing in 100 cc. (the approximate end-point volume) the same amounts of the same constituents that were present before the addition of the iodide. The iodide was omitted because it reduces the oxidized form of the quinhydrone and causes the pH determinations to be too high. Park in describing his procedure states that "the pH values of the solutions at the end point were determined by means of the quinhydrone electrode." If this means that potassium iodide was present, that condition alone might account for the fact that the authors' values are so much lower than his.

In the cases in which ammonium hydroxide was added until a faint odor was produced, the pH of the solution was approximately 3.3. In order to obtain a pH of 4.0 it was found necessary to add about 2 cc. of 6 *N* ammonium hydroxide more than that required to produce a faint odor of ammonia. This was introduced after the addition of the bifluoride. The quinhydrone potential was always read after the addition of the bifluoride. When the biphthalate was used, it was added after the bifluoride and its addition caused no recognizable change in the potential of the solution. In the cases in which the pH was 3.3, as well as those in which it was 4.0, the end points were sharp and after the titration was completed there was no further liberation of iodine for 15 minutes or more.

The values designated as "average per cent error" represent the percentage differences between the iodometric titration on the blank (performed as described in the first paragraph under "Reagents") and the average of the titrations in question. The value of the blank was 25.37 cc.

TABLE I. EFFECT OF IMPURITIES ON TITRATION OF COPPER IN BUFFER SOLUTIONS OF AMMONIUM BIFLUORIDE WITH AND WITHOUT POTASSIUM BIPHTHALATE

(Copper taken, 0.1831 gram. Volume of thiosulfate required, 25.37 cc.)

Series	Weight of Impurity Iron	Weight of Impurity Arsenic	NH_4HF_2	$KHC_8H_4O_4$	Thiosulfate	pH of Solution: NH_4OH added to faint odor	pH of Solution: 2 cc. of 6 *N* NH_4OH added in excess
	Gram	*Gram*	*Grams*	*Grams*	*Cc.*		
1	0.2	0.0	2.0	0.0	25.35	3.3	...
2	0.2	0.0	2.0	0.0	25.39	...	4.0
3	0.2	0.0	2.0	1.0	25.39	...	4.0
4	0.0	0.2	2.0	0.0	25.34	3.3	...
5	0.0	0.2	2.0	0.0	25.36	...	3.9
6	0.0	0.2	2.0	1.0	25.35	...	3.9
7	0.2	0.2	2.0	0.0	25.37	3.3	...
8	0.2	0.2	2.0	0.0	25.37	...	4.0
9	0.2	0.2	2.0	1.0	25.35	3.4	...
10	0.2	0.2	2.0	1.0	25.37	...	3.9
11	0.3	0.2	3.0	0.0	25.35	3.3	...

Average per cent error without biphthalate, −0.04; with biphthalate, −0.02. Average deviation of each result from mean without biphthalate, ±0.06 per cent; with biphthalate, ±0.06 per cent.

TABLE II. ANALYSIS OF A MIXTURE CONTAINING CUPRIC SULFIDE AND ARSENOPYRITE BY THE BIFLUORIDE METHOD

(Per cent of copper present, 14.72. Bifluoride added, 2.0 grams. Concentration of thiosulfate, 0.1022 *N*.)

Run	Weight of Sample	Volume of Thiosulfate	pH at End Point	Copper
	Grams	*Cc.*		%
1	1.097	24.86	3.3	14.73
2	1.241	28.15	3.3	14.74
3	0.9214	20.86	3.3	14.72
4	1.008	22.83	3.3	14.72
5	0.9210	20.88	3.3	14.73
6	1.051	23.77	3.3	14.70

Average percentage error, +0.01.
Average deviation of each result from mean, ±0.07 per cent.

Table II shows results of analyses of a mixture containing approximately 22 per cent of C. P. cupric sulfide and 10 per cent of copper-free arsenopyrite mixed with finely ground unglazed porcelain which gave no test for iron when treated with hydrochloric and nitric acids. The cupric sulfide was thoroughly mixed with the unglazed porcelain powder and a number of samples accurately weighed out. Some of the samples were analyzed for copper and the values thus obtained were used as a basis on which to determine the error of the method. To each of the other samples was added about 0.1 gram of arsenopyrite, the whole thoroughly mixed, and the copper determined by the bifluoride method.

The procedure used on the blanks was essentially the same as that employed in the standardization of the thiosulfate by copper foil. Runs were also made on the blank samples, using the procedure described below for the mixture after the addition of the arsenopyrite. The two sets of values agreed within 0.1 per cent.

The procedure used on the cupric sulfide arsenopyrite mixture was as follows:

> Fifteen cubic centimeters of concentrated nitric acid were added to the sample, evaporated to 5 cc., 10 cc. of concentrated hydrochloric acid and 10 cc. of 18 *N* sulfuric acid added, and the whole was evaporated to dense white fumes. In runs 1, 2, and 3, 10 cc. of concentrated nitric acid and 10 cc. of concentrated hydrochloric acid were then added, and the solution was again evaporated to dense white fumes and diluted with 20 cc. of water. In runs 4, 5, and 6 the fuming was followed by the addition of 20 cc. of water and 10 cc. of saturated bromine water, and the solution boiled until all bromine fumes were removed. These two types of procedure were found to be necessary to insure complete oxidation of the arsenic. After the addition of the water and boiling, the procedure was the same as in the titration

of the copper sulfate solutions previously described. In the present case it was not necessary to filter off the insoluble residue before making the copper titration.

Summary and Conclusions

In the Park method of determining copper in the presence of as much as 0.3 gram of iron and 0.2 gram of arsenic, the potassium biphthalate may be omitted without any appreciable effect on the accuracy or precision of the results.

The addition of biphthalate has no material effect on the pH of the solution.

The pH at the end point is nearer 3.3 than 4.0 and yet the end point is practically permanent.

To insure complete oxidation of an ore containing sulfide, iron, and arsenic, treatment with nitric acid alone is not sufficient. A double treatment with nitric and hydrochloric acids or a single treatment with the two acids followed by one with saturated bromine water is found necessary.

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The Determination of Rhenium

I. Qualitative

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Although a number of papers have appeared dealing wholly or in part with reactions of rhenium of value in the qualitative detection of the element, no mention has been made of its place in the conventional scheme. Data are presented which indicate that in the Prescott and Johnson system the element will concentrate with arsenic. Early work in the field has been critically examined and evaluated and several new tests are reported. New confirmatory tests are described.

SINCE the discovery of rhenium in 1925 (*28*) there have appeared a number of papers dealing wholly or in part with various qualitative tests for the identification of the element. Its place in the Noyes and Bray system was studied by Kao and Chang (*16*) who found that significant concentration was effected in the tellurium group. These authors reported that during the course of the analysis of the group, tellurium and rhodium could be precipitated in the presence of rhenium by reducing with hydrazine hydrochloride and sodium bisulfite in hydrochloric acid solution. Rhenium was subsequently precipitated as the sulfide from the filtrate.

The insolubility of rhenium heptasulfide was one of the characteristic properties early reported. Although this was a controversial subject for several years (*14*) it has been definitely established by several workers, notably Geilmann and Weibke (*9*), that the sulfide is quantitatively precipitated when a perrhenate solution containing as high as 33 per cent of hydrochloric acid by weight is treated with hydrogen sulfide. This separation is now used extensively in the analysis of rhenium. For reasons to be discussed below, the sulfide precipitation is not applicable to all rhenium-containing samples.

Table I. Rhenium Found by Prescott and Johnson System

(50 mg. of Re added)

	Sample 1		Sample 2		Sample 3		Sample 4	
	Mg.	%	*Mg.*	%	*Mg.*	%	*Mg.*	%
First analysis	1.5	3.0	4.3	8.6	4.7	9.4	3.5	7.0
Second analysis	1.4	2.8	6.4	12.8	11.9	23.8	16.1	32.2
Third analysis	44.7	89.4	29.9	59.8	29.1	58.2	28.8	57.6
Total	47.6	95.2	40.6	81.2	45.7	91.4	48.4	96.8

Prescott and Johnson System

Although rhenium heptasulfide is quantitatively precipitated from solutions containing a relatively high concentration of hydrochloric acid, the precipitation takes place slowly. In solutions containing less than 4 per cent of hydrochloric acid by weight it has been the author's experience as well as that of others (*9*) that precipitation is not quantitative. In light of this rather peculiar condition it was thought desirable to ascertain where in the conventional scheme of analysis the element would be concentrated and what precautions must be taken in order to insure a clean-cut separation.

A stock solution was prepared to which were added 5 mg. per 50 ml. of each of the following metals: Hg(ic), Pb, Cu, Cd, As(ous), As(ic), Sb, Sn(ic), Cr(ic), Fe(ic), Al, Ni, Co, Zn, Mn, Ca, Sr, Ba, Mg, K, and Na. Fifty-milliliter portions of this solution were carried through the qualitative scheme of Prescott and Johnson (*19*). Each group precipitate was washed thoroughly, digested with sodium hydroxide to expel all ammonia, oxidized with hydrogen peroxide, acidified with sulfuric acid, and treated with nitron acetate as described by Geilmann and Voigt (*7*).

In the case of solutions containing chromium and manganese it was necessary to add a few drops of alcohol to the acid solution prior to the nitron precipitation in order to reduce compounds of higher valence which yield precipitates with the reagent. Alcohol in low concentrations is without influence in the nitron precipitation (*31*). Certain normal constituents of complete group precipitates were excluded because it was found that they yielded insoluble nitron derivatives. For this reason tungstates, molybdates, palladium, gold, chloroplatinates, and germanium were not included in the stock solution.

A series of blank determinations using the stock solution was carried through the Prescott and Johnson separation and each group or subgroup analyzed according to the nitron method. No precipitate was obtained in any case. Fifty milligrams of rhenium as $KReO_4$ were then added to a 50-ml. portion of the stock solution and the separation and analysis repeated. Group 1 reagents yielded no precipitate. When hydrogen sulfide was passed into the 0.25 *N* hydrochloric acid solution for second group precipitation, some trouble was experienced in obtaining a flocculent precipitate. It filtered without difficulty, however, and was analyzed (*30*) for its rhenium content (first analysis, Table I).

The filtrate from the first precipitation with hydrogen sulfide was evaporated to a volume of 8 ml. for the arsenic precipitation. During the course of the concentration sulfur and rhenium sulfide separated from the solution. This was removed by filtration and analyzed for rhenium (second analysis, Table I). Samples 2, 3, and 4 were allowed to stand overnight before filtering.

The solutions were then acidified and saturated with hydrogen sulfide to precipitate the arsenic. The mixed sulfides were analyzed for rhenium (third analysis, Table I).

Analysis of group 3, precipitated in strict accord with the published procedure, yielded, in the case of the four samples, a barely perceptible precipitate of nitron perrhenate. Groups 4 and 5 likewise contained no rhenium. Colorimetric analysis of the sixth group indicated that the rhenium which had escaped precipitation in the second group had passed through with the alkali metals. Rhenium is normally precipitated completely with hydrogen sulfide from hydrochloric acid solutions of about the same concentration as those encountered in the precipitation of arsenic sulfide. The only apparent difference between the procedure followed in the Prescott and Johnson scheme and that followed in the routine quantitative analysis of rhenium products was that in the former case the solution was exposed to the action of hydrogen sulfide for but 5 minutes, whereas in the conventional Geilmann-Weibke precipitation the gas is passed through the solution for at least 1 hour.

Solutions were prepared containing 5 mg. per 50 ml. of the metals used in the previous separation and to these potassium perrhenate was added in varying amounts. The copper division sulfides were precipitated, quickly removed, and the filtrate was evaporated to 10 ml. The precipitate of sulfur and rhenium sulfide thrown out during concentration was not removed. Five milliliters of concentrated hydrochloric acid were added, the solution was warmed, and hydrogen sulfide passed in for 1 hour. The sulfide-sulfur precipitate was analyzed for rhenium.

Table II. Typical Results

Rhenium Added	Rhenium Found		Recovery
	Copper division	Arsenic division	
Mg.	*Mg.*	*Mg.*	%
7.0	0.0	6.9	99
11.0	0.1	11.0	101
16.0	0.1	16.0	101
25.0	0.4	24.7	100

Table II gives typical results obtained. It is apparent that heptavalent rhenium is concentrated in the arsenic group of the second division of the Prescott and Johnson system if a sufficient time is allowed for the precipitation of the sulfide. If the rhenium is present in the original sample in valence states lower than seven, the isolation not only will not be quantitative but in some cases most of the rhenium may pass into group 3. Chlororhenous acid and rhenium trichloride, for instance, are unusually stable in solutions containing hydrochloric acid. It has been previously shown (*4*) that only a very small amount of rhenium as $ReCl_6^{--}$ is precipitated by hydrogen sulfide. This, if present, would pass on into group 3 where it would be precipitated as hydrated ReO_2 when ammonia is added. Upon filtering and washing the group precipitate, oxidation takes place (*6*) and a portion of the rhenium passes on into group 4. The remainder will be oxidized to perrhenate when treated with sodium hydroxide and hydrogen peroxide, and passes through the aluminum, chromium, and iron separation without interfering with any of the confirmatory tests.

Any rhenium passing into group 4 as the result of oxidation during precipitation with ammonia or during the washing process will not be completely precipitated by hydrogen sulfide in ammoniacal solution. It is only by the long-continued passage of hydrogen sulfide into ammoniacal rhenium-containing solutions that appreciable amounts are precipitated (*21*).

Within the arsenic group large amounts of rhenium heptasulfide will not be dissolved when extraction is made with yellow ammonium sulfide. Rhenium if present in significant amounts may be detected in the residue by oxidizing a small portion with potassium hydroxide and hydrogen peroxide and observing the formation of characteristic rhombic bipyramides of potassium perrhenate. If desired, the sulfide may be brought into solution with sodium hydroxide and hydrogen peroxide and cesium chloride added to precipitate cesium perrhenate. The latter reaction is somewhat more sensitive than the potassium perrhenate precipitation. Both are microscopic reactions in common use for the rapid identification of perrhenates. If large amounts of molybdenum and small amounts of rhenium are present, as in most mineral or industrial concentrates, the rhenium may be lost during the yellow ammonium sulfide extraction. Whether this is due to actual solubility or to colloidal dispersion is not known. The direct separation with 8-oxyquinoline (*10*), while excellent for moderate amounts of the two elements, is not applicable to small amounts of rhenium in the presence of large amounts of molybdenum because of adsorption of perrhenic acid on the voluminous molybdenum-8-oxyquinoline complex. If, for instance, the molybdenum-rhenium ratio be much in excess of 100 to 1 serious losses are encountered. The direct separation of the bulk of the molybdenum from rhenium is probably best accomplished by the distillation method of Geilmann and Weibke (*8*).

The small amount of molybdenum which normally distills with the rhenium does not interfere with the microscopic detection of rhenium as $CsReO_4$ or $RbReO_4$. The large bulk of the distillate may be removed by slow evaporation without significant loss of rhenium. Although a great deal has been said about the volatility of perrhenic acid from hydrochloric acid solutions, the danger is not great if care is taken to have a small amount of fixed base present and if the evaporation is not carried out too rapidly or to dryness. This has been indicated by Kao and Chang (*16*) and has been the experience of several working in this laboratory. The following data are illustrative of this contention: Solutions containing 100 γ of rhenium as $KReO_4$ and 0.5 mg. of potassium chloride were diluted to 30 ml. with water and concentrated hydrochloric acid in the amounts indicated, and evaporated almost to dryness on a steam bath. Colorimetric analysis according to the method of Geilmann, Wrigge, and Weibke (*12*) was made upon the residual solution.

Table III. Colorimetric Analysis

Concentrated HCl	H_2O	Rhenium Found
Ml.	*Ml.*	γ
1.0	29.0	99
3.0	27.0	100
5.0	25.0	98
5.0	25.0	110
5.0	25.0	102
10.0	20.0	90
15.0	15.0	102
25.0	5.0	120
25.0	5.0	98

Evaporation of solutions of perrhenic acid with varying amounts of concentrated hydrochloric acid to a volume of about 0.5 ml. indicated upon analysis a loss of rhenium in some cases. One hundred gamma of rhenium was added in each case.

Table IV. Colorimetric Analysis

Concentrated HCl	Rhenium Found	Concentrated HCl	Rhenium Found
Ml.	γ	*Ml.*	γ
5	98	20	56
5	82	20	70
10	80	25	60
10	90	25	98
15	102	30	54
15	76	30	72

Noyes and Bray System

The place of rhenium in the Noyes and Bray (*29*) system has been studied by Kao and Chang (*16*), who found that the bulk of the rhenium recovered was with the tellurium-copper group and that concentration within the group was in the rhodium-iridium filtrate. The amount recovered was greatly increased by adding potassium chloride in the hydrochloric-nitric acid evaporation (procedure 72) and by adding the washings from the ether extraction to the aqueous layer (procedure 73). The new procedure recommended involves the precipitation of tellurium and rhodium with hydrazine hydrochloride and sodium bisulfite from a hot hydrochloric acid solution. Any rhenium present passes into the filtrate where it is detected in the conventional microscopic manner.

Although this modification appears to be satisfactory when significant amounts of rhenium are present and when the exact procedure recommended by the authors is followed, the reduction with hydrazine in hydrochloric acid solution should be done with care and caution. Briscoe and collaborators (*2*), Noddack (*24*), Kraus and Steinfeld (*17*), and others have observed that hydrazine in acid solutions reduces rhenium to the tetravalent stage. As has been mentioned (*4*) hydrogen sulfide will not precipitate tetravalent rhenium from hydrochloric acid solutions. That hydrazine and hydrochloric acid are effective in the reduction of heptavalent rhenium is shown by the following experiments, performed during the course of an investigation of analytical methods proposed for the quantitative determination of the element (*18*).

Five milliliters of saturated solution of hydrazine sulfate, 5 ml. of concentrated hydrochloric acid, 32.2 mg. of rhenium as $KReO_4$, and 50 ml. of water were evaporated on a sand bath until a volume of 15 ml. had been reached. The solution at first turned yellow and later hydrated rhenium dioxide settled out. The acidity was reduced to above pH 5 by the cautious addition of sodium hydroxide and the resulting precipitate dried in a hot vacuum desiccator containing phosphorus pentoxide. On the assumption that the precipitate was rhenium dioxide, recoveries of 30.8, 34.0, 31.1, 34.1, 31.8, and 16.4 mg. were obtained. Although it was later shown by Geilmann and Hurd (*5, 6*) that any method involving the handling of rhenium dioxide is unreliable because of oxidation and adsorption errors, the results are significant in light of the proposed qualitative separation. Another series of nine determinations using ammonia in place of sodium hydroxide to induce hydrolysis yielded results ranging from 7.9 to 20.0 mg. out of 32.2 mg. added. In this case a large amount of colloidal dioxide remained in the solution. In light of these data care should be taken to observe the exact concentrations of reagents and time and temperature specifications of Kao and Chang (*16*) when following their proposed scheme.

Direct Detection

The direct separation and detection of rhenium in the presence of large amounts of molybdenum, iron, manganese, and other metallic constituents of minerals has received much attention. The first method proposed was that of Noddack (*28*) who presumably used alternate reduction and oxidation to isolate rhenium from minerals and mineral concentrates. The method in brief was to reduce large samples of the material under investigation or sulfide concentrates therefrom with hydrogen at about 900° C. Following reduction, the sample was heated in oxygen until no further sublimate appeared. The process was repeated several times and the sublimate from the entire process examined röntgenographically. Incidentally, element 43, to which the authors assigned the name Masurium, was said to have been isolated in the same manner. Although chemical methods were also used by the same authors (*23, 26*), their report on the analysis of 1600 minerals (*26*) does not indicate which of the minerals were directly concentrated by the sublimation method and which were concentrated by other means. Inasmuch as our knowledge of the distribution of rhenium is based upon these determinations and in light of the experience in this laboratory, the distinction is of some importance.

To the author's knowledge all rhenium compounds when heated to 900° C. in an atmosphere of hydrogen are reduced to the metal. When reheated in oxygen, metallic rhenium is converted to the volatile heptoxide, Re_2O_7. In the presence of large amounts of basic oxides, however, the oxide immediately reacts with these to produce stable perrhenates. The vapor pressure of most of these is relatively low even at the temperatures used by the Noddacks. Inasmuch as the richest rhenium-containing mineral yet reported has a rhenium content of the order of 2×10^{-5}, the preponderance of basic material makes the escape of appreciable amounts of rhenium heptoxide somewhat difficult. In the case of essentially acidic minerals the chance of isolating rhenium is much better than in basic materials. That fixed bases are effective in preventing the loss of rhenium when ignited in air has been discussed previously (*14*).

In a forthcoming communication from this laboratory it will be shown that certain minerals which contain rhenium in appreciable quantities yield no rhenium-containing sublimate when analyzed in accord with the direct oxidation-reduction method. Therefore for the qualitative detection of the element in minerals and concentrates the sublimation procedure is to be avoided unless it has been demonstrated that with artificial mixtures good recovery may be realized.

If the mineral is insoluble in hydrochloric or nitric acid it should be fused with sodium carbonate or with carbonate-nitrate mixtures. Prolonged digestion with nitric acid or with sulfuric acid should be avoided because of the danger of volatilizing perrhenic acid. Oxidizing materials of the type of pyrolusite may apparently be dissolved directly in hydrochloric acid without danger of losing rhenium. Table V shows the results of an experiment in which varying amounts of potassium permanganate or rhenium-free manganese dioxide were added to rhenium-containing solutions, hydrochloric acid was added, and the solutions were digested until decomposition was complete. Rhenium was then determined according to the sulfide-nitron method of Geilmann and Weibke (*9*). The errors are of the same magnitude as those obtained in the usual routine determination of rhenium according to the sulfide-nitron method.

TABLE V. DETECTING OF RHENIUM IN PRESENCE OF MANGANESE

Rhenium Taken	$KMnO_4$ Added	Rhenium Found	Error
Mg.	*Grams*	*Mg.*	*Mg.*
28.8	1.0	28.3	−0.5
25.0	1.0	25.0	±0.0
28.8	2.0	28.7	−0.1
25.0	2.0	25.3	+0.3
30.2	3.0	29.3	−0.9
25.0	3.0	24.9	−0.1
28.8	4.0	28.4	−0.4
25.0	4.0	25.0	±0.0
25.0	5.0	24.9	−0.1
25.0	6.0	24.9	−0.1
25.0	7.0	24.8	−0.2
25.0	8.0	25.1	+0.1
	MnO_2 Added		
5.0	1.0	5.2	+0.2
5.0	2.0	4.9	−0.1
5.0	3.0	5.2	+0.2
5.8	4.0	5.9	+0.1
5.0	5.0	5.1	+0.1
6.5	6.0	6.7	+0.2
5.0	7.0	4.8	−0.2
4.5	8.0	4.1	−0.4

Either the hydrochloric acid solution of the carbonate-nitrate fusion or that resulting from direct acid decomposition of the ore may be adjusted for hydrochloric acid content (one-third by volume is recommended), heated to 90° C., and the rhenium precipitated with hydrogen sulfide. The sulfides may then be examined qualitatively for rhenium.

Spectroscopic Identification

According to Ida and Walter Noddack (*22*), if the rhenium content of a product is of the order of 10^{-6} the element may be detected by direct spectroscopic examination. As an illustration of this they cite the case of certain molybdenites having a rhenium content of from 10^{-5} to 10^{-6} in which they claim rhenium may be detected by direct resolution of the arc emission spectra.

The rhenium spectrum has been mapped by Meggers (*20*) who confirmed the early work of Noddack (*27*) regarding the wave length of the ultimate lines of the element. The three lines, known as the 3460 Å. triplet, have wave lengths of 3451.88 Å., 3460.47 Å., and 3463.72 Å. In addition there is a very strong line at 4889.15 Å. in the blue. Although more than 3000 spectral lines of the element are known, these four alone are of value to the analyst in the direct examination of rhenium-containing ores. The remainder drop out, under ordinary circumstances and with the usual equipment, when the amount of rhenium on the electrode is below 50 γ or 0.05 mg.

The spectrograph has been used extensively by the writer and his students in the direct examination of ores for the qualitative detection of rhenium. During the course of the work several instruments have been used—Hilger E_2 type Kruess single quartz prism with a low dispersion (10 Å. per mm. in the 3460 Å. region) but high intensity, a large Steinheil three-prism instrument of high dispersion in the 4889 Å. region and moderate intensity, a Bausch and Lomb constant-deviation spectrograph of low dispersion in the 4889 Å. region, but good intensity, and a large Bausch and Lomb instrument equipped with both quartz and glass optical systems. Both spark (20,000 volts) and arc (80 volts, direct current, 6 to 8 amperes) emission spectra have been studied. It is the conclusion of the writer that the direct spectrographic examination of minerals for rhenium is to be avoided and that a preliminary concentration should always be made. The reasons for this are several: In the first place no mineral is known which contains more than 2×10^{-5} rhenium. This in the author's experience automatically limits the lines available for study to the triplet and the 4889.15 Å. line in the visible region. All known rhenium-rich minerals have a very rich spectrum. Molybdenite, for instance, often contains appreciable amounts of iron in addition to the principal constituent, MoS_2. Columbite contains a wide variety of elements, many of which have a complex spectrum. Pyrolusite, a mineral which according to Noddack contains negligible amounts of element 75 but which according to Loring and Druce (*14*) contains considerable amounts, may contain from 1 to 5 per cent of iron with varying amounts of minor impurities in addition to manganese dioxide. When one considers that the rhenium content of no known mineral exceeds 2×10^{-5} it will be seen at once that a normal sample of ore placed on the end of an electrode represents at best but a few gamma of rhenium. This, coupled with the depressing effect which large amounts of other elements have upon the intensity of the rhenium spectrum, places it on the borderline of the sensitivity of our instruments. A further complication lies in the practical coincidence of lines of other elements with the four of rhenium. Iron, manganese, and molybdenum, for instance, have caused considerable trouble.

Whereas these elements would offer, for the most part, little interference in systems of high rhenium content, the exposures which the author has found necessary to bring out the rhenium lines in synthetic mixtures, when used on minerals, result in heavy broad lines which make positive identification of the rhenium spectrum somewhat doubtful.

Miscellaneous Qualitative Reactions

Perrhenic acid forms a large number of derivatives which have been proposed or used in qualitative identification. Of these, few are specific for rhenium. The microscopic precipitations of rubidium or cesium perrhenate as proposed by Geilmann and Brünger (*3*) are probably the most reliable and satisfactory. Care must be taken not to confuse the perrhenates with chlorostannates or chloroplatinates. The lower limit of sensitivity of the rubidium and cesium perrhenate reaction is given by the authors as 0.1 γ per 35 cu. mm. Tellurium, silver, and mercury perrhenate were found to have but limited application. Organic perrhenates investigated by the above authors and found to yield characteristic but not unique products were nitron, methylene blue, acriflavine, brucine, and strychnine. Nitron perrhenate precipitation has been utilized by Kronmann and Bibikowa (*24*) for the basis of a microchemical test. These authors allowed nitron acetate and sodium sulfide to react with a soluble perrhenate in a 10 per cent gelatin solution. When the mass had set, a drop of titanous chloride was added. Following the diffusion of this latter reagent into the gelatin a brownish yellow coloration around the nitron perrhenate crystals was to be seen. The reaction depends upon the relative speeds of the interaction of sodium sulfide, Re^7, and Re^4.

Although the reaction serves to distinguish between nitron nitrate and nitron perrhenate, it is not sensitive to much under 10 γ of rhenium and in such concentrations cesium or rubidium perrhenates are to be preferred. Heyne and Moers (*13*) prepared a veratrine derivative, the solubility of which indicated that it might serve as a micro reagent. During the course of a search for an organic reagent which would precipitate perrhenic acid but not chlororhenous acid (nitron yields an insoluble derivative with both), Scharf and Spiering (*32*) found that the following bases reacted with chlororhenous acid in concentrations of 5 γ per 25 cu. mm. but did not yield insoluble perrhenates in perrhenic acid solutions containing 30 γ per 25 cu. mm.: *m*-anisidine, *p*-anisidine, cinchonidine, tri-*n*-amyl amine, triisoamyl amine, dibenzyl amine, *o*-phenetidine, dimethyl-*o*-toluidine, methyl-*o*-toluidine, methyl-*m*-toluidine, dimethyl naphthyl amine, di-*n*-butyl aniline, di-*n*-amyl amine, diphenyl guanidine, 4-aminodiphenyl, and pararosaniline. Safranine and antipyrine form insoluble perrhenates and chlororhenates. *N*,*N'*-Tetramethyl-*o*-tolidine (Tetron) has been established as a reagent for the gravimetric determination of chlororhenous acid in the presence of perrhenic acid (*4*) and may be also used to identify the former in the presence of the latter. Tougarinoff (*33*) reported that if an acid solution of perrhenic acid be treated with stannous chloride and potassium ferrocyanide a red color is produced. With dimethylglyoxime a yellow-colored complex is formed. The sensitivity of these reactions under optimum conditions is about 10 γ.

Röstrohr, Flame, and Bead Tests

The röstrohr technic described by Geilmann and Wrigge (*11*) will serve to detect and identify rhenium in concentrations of about 5 γ per 10 mg. and up. The metal is heated in the bend of a röstrohr of the conventional type until the condensation of rhenium heptoxide is complete. A small amount of sulfur is then introduced into the lower end of the tube and heated until it burns. The sulfur dioxide passing up the tube serves to reduce rhenium heptoxide previously deposited with the production of a blue oxide or compound of unknown composition. In some cases where the rhenium heptoxide ring is too light to be seen, the blue reduction product will be clearly visible. If molybdenum is present the sensitivity is decreased to somewhere in the neighborhood of 50 γ per 10 mg.

Care should be taken in interpreting negative results obtained as a result of the execution of this test. Rhenium as $KReO_4$, or as any other perrhenate stable at the temperature used, will not respond with positive results. Although the perrhenates may be reduced prior to the heating, unless the alkali be removed but a minor portion of the rhenium will be volatilized. If substantial amounts of alkali are present the rhenium will not be volatilized under any circumstances.

The rhenium flame is blue-green. It is not an intense color and, as has been pointed out (*11*), it is easily masked by other elements. It is only in the oxidizing flame that the color is apparent.

Borax and phosphate bead tests yield with rhenium a gray color in a reducing flame. In the outer cone the color or turbidity, due to metallic rhenium, disappears as a result of oxidation.

Colorimetric Detection

The colorimetric determination of rhenium as developed by Geilmann, Wrigge, and Weibke (*12*) is by all odds the most convenient laboratory test available for the rapid detection of heptavalent rhenium. The Geilmann reaction is brought about by adding to a hydrochloric acid solution of a perrhenate, stannous chloride and ammonium or potassium thiocyanate. A yellow-brown thiocyanate is produced which is soluble in ether, butyl acetate, and cyclohexanol. The complex is insoluble in carbon bisulfide, carbon tetrachloride, methyl cyclohexane, and aniline. Commercial malonic ester, methyl salicylate, resorcinol, benzyl alcohol, furfural aldehyde, and acetoacetic ester extract the color but for various reasons are not satisfactory. Although the reaction is subject to numerous influences which must be controlled before it is satisfactory as a quantitative determination (*1*), it is of great value as a qualitative test. The same reaction is, however, characteristic of molybdenum and unless this element is known to be absent the reaction cannot be considered specific. Although a number of extractors have been investigated in this laboratory, no water-insoluble substance has been found which does not extract both the rhenium and the molybdenum complexes about equally well. During the course of a study on the determination of rhenium in ores, minerals, and industrial concentrates (*15*) it was found that, whereas ethyl xanthate reacted with molybdic acid to yield a violet-red chloroform soluble complex, rhenium did not.

TABLE VI. DETECTION OF RHENIUM IN PRESENCE OF MOLYBDENUM

Rhenium Taken	Molybdenum Added	Apparent Rhenium Recovery	Error
γ	γ	γ	%
150	50	143	− 4.7
200	50	216	+ 8.0
200	80	216	+ 8.0
250	100	242	− 3.2
300	100	255	−15.0
60	100	64.7	+ 7.8
150	200	143	− 4.5
200	200	214	+ 7.0
200	300	210	+ 5.0
300	300	308	+ 2.7
60	300	55.2	− 8.0
250	400	273	+ 9.2
100	500	108	+ 8.0
150	1000	164	+ 9.3
150	1000	139	− 7.3
60	1000	57.1	− 4.8
100	1000	110	+10.0

It was found that if solutions containing molybdenum and rhenium were first treated with ethyl xanthate and the molybdenum complex was removed with chloroform, rhenium could be determined with fair accuracy in the remaining solution. Neither stannous chloride, hydrochloric acid, ammonium thiocyanate, nor mixtures of the three produced a color with residual traces of the xanthate. Although the accuracy of the method is such that it is not satisfactory without refinement for quantitative work, it serves rather well for qualitative detection. Table VI gives data illustrative of results which were obtained. Analysis for rhenium was made as described by Geilmann, Wrigge, and Weibke (*12*) after molybdenum had been extracted as a xanthic acid complex with chloroform.

The data presented were obtained while working on solutions free from metals other than molybdenum and rhenium. Iron and copper are known to interfere. Oxidizing agents, excessive amounts of reducing agents, and high salt concentrations contribute to erratic results.

Phenyl hydrazine and thioglycolic acid both react with molybdenum but not with rhenium. Although like ethyl xanthate they are known to be unsatisfactory for the determination of molybdenum, an attempt was made to develop a satisfactory method which would allow the removal of the molybdenum so that rhenium could be determined in the residual solution. They were found to be unsatisfactory and inferior to ethyl xanthate.

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A Color Reaction for Detection of Cyclopentadiene

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SMALL quantities of cyclopentadiene can be detected as follows: One drop of the liquid to be tested is mixed with 1 cc. each of chloroform and glacial acetic acid and then treated cautiously with 2 or 3 drops of concentrated sulfuric acid. As little as 0.1 mg. of cyclopentadiene gives a distinct violet coloration.

Some higher boiling terpenes give a similar coloration but only with acetic anhydride, chloroform, and sulfuric acid.

RECEIVED November 30, 1935.

Potentiometric Determination of Mercaptans

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A new procedure is described for the quantitative determination of mercaptans based on precipitation with silver nitrate. The titration is performed in an alcoholic solution of sodium acetate, using enough alcohol to dissolve the hydrocarbon sample, and titrating with a solution of silver nitrate in isopropyl alcohol. The end point is determined potentiometrically using a silver electrode as an indicator, thus avoiding an excess of silver nitrate and eliminating the danger of simultaneously precipitating impurities.

The method is applicable to colored solutions, as the selection of the end point is not dependent on a color change of an indicator.

FROM the publications of various authors who have studied the methods of mercaptan determination, it may be concluded that a procedure based on the precipitation of silver mercaptides is the most reliable under conditions actually encountered in the analysis of petroleum products. The first such procedure, reported by Borgstrom and Reid (*2*), was a direct application of Volhard's determination of halides. In spite of some objectionable features which developed when applied to solutions of hydrocarbons, it has been considered by later workers the most reliable method in existence. Bond (*1*) used it with certain precautions to check the results of the copper oleate method. Malisoff and Marks (*7*) used the method in their work on thermal behavior of mercaptans. In the originally suggested form the procedure leads to the formation of emulsions, since aqueous silver nitrate is used for precipitation of mercaptans dissolved in hydrocarbons. The tendency of precipitated silver mercaptide to pass into the hydrocarbon phase, and to carry with it adsorbed silver nitrate, results in the necessity for a lengthy process of washing. An improvement of the method has been suggested recently by Malisoff and Anding (*6*), who found that the addition of methanol is beneficial, since the danger of formation of emulsions is minimized and the time of operation is shortened, there being no necessity for shaking and washing.

Outline of Proposed Method

The proposed procedure is based on precipitation of mercaptans with silver nitrate. By using enough alcohol to dissolve the sample and by titrating with an alcoholic solution of silver nitrate, the separation of phases, the formation of emulsions, and the resulting adsorption are completely eliminated. Furthermore, in order to avoid an excess of silver nitrate at the end of precipitation, the end point is determined potentiometrically with a silver electrode indicator. The method thus becomes applicable to colored solutions, as the selection of the end point is not dependent on a color change of the indicator. Finally, on account of the very low solubility of silver mercaptides, approximately equal to that of silver iodide, the method becomes applicable in the presence of substances which normally react with silver nitrate but form compounds more soluble than the silver mercaptides. The danger of the simultaneous precipitation of common impurities is thus minimized.

The influence of a number of substances likely to interfere with the suggested procedure was studied, especially those which occur naturally in petroleum products. Many were found to have no influence on the accuracy of the results, but hydrogen sulfide and elementary sulfur interfere with the procedure. Silver sulfide is considerably less soluble than the silver mercaptides and is therefore precipitated from a mixture of sulfide and mercaptans before the precipitation of silver mercaptides commences. Theoretically, therefore, it should be possible to perform the determination of both hydrogen sulfide and mercaptans in one solution by titration with silver nitrate in one operation. This actually can be done for a certain limited range of concentrations. The procedure is now being studied, but cannot be recommended at present because its limitations are not yet known; it is suggested therefore that hydrogen sulfide be removed by washing the sample with acidified cadmium sulfate (10 per cent cadmium sulfate, 2 per cent sulfuric acid, in water).

Elementary sulfur also interferes with the described procedure. Since the hydrocarbon sample to be titrated is added to a solution of sodium acetate in alcohol, and this solution is decidedly alkaline, a reaction between mercaptan and elementary sulfur takes place if both substances are present in the sample. Elementary sulfur should therefore be removed by shaking with mercury. This procedure does not alter the mercaptan content, as has been shown by Borgstrom and Reid (*2*).

A procedure which allows the estimation of elementary sulfur and mercaptans in one solution, based on the reaction between sulfur and mercaptans, will be described in a subsequent communication.

Apparatus and Experimental Procedure

A suitable simple arrangement for potentiometric titration of mercaptans is shown in Figure 1.

The cell consists of a silver half-cell sensitive to changes in silver-ion concentration and a mercury half-cell, *R*, used as the reference electrode. The silver half-cell consists of a silver electrode immersed in the beaker containing 50 cc. of 0.1 *N* sodium acetate in 96 per cent ethyl alcohol. The mercury half-cell and the bridge are filled with the same solution.

The silver electrode is a polished silver wire of about 2 mm. diameter, and the mercury electrode is a layer of mercury about 3 to 4 cm. in diameter. The cell is represented by the diagram

− Ag | 0.1 *N* sodium acetate in alcohol | 0.1 *N* sodium acetate in alcohol | Hg +

The e. m. f. of the cell is reasonably constant, about −0.070 volt, the minus sign signifying that the silver wire is the negative electrode. In the absence of any generally accepted standard reference electrode in alcoholic solutions, the mercury half-cell is used as the standard and the potential of the silver electrode is considered equal to the numerical value of the e. m. f. of the cell. Variations from this constant value may be caused by impurities on the silver wire. It is advisable to clean the electrode with a solution of potassium cyanide and then to wash it carefully with water.

On account of the somewhat high resistance of the cell, a reasonably sensitive potentiometer arrangement is required.

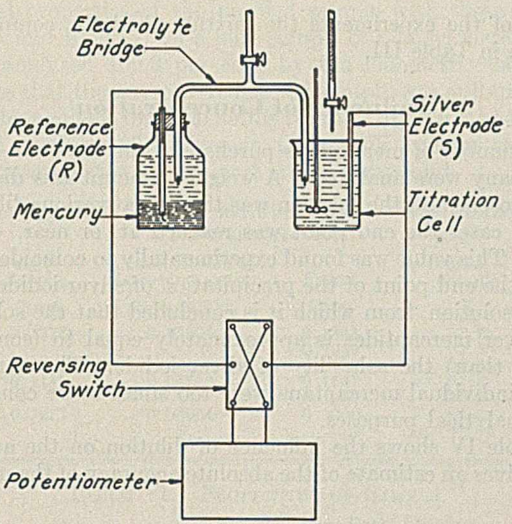

Figure 1. Apparatus

The sample is added to 50 cc. of the alcoholic sodium acetate solution in the silver half-cell. The size of the sample may vary according to the solubility in alcohol of the solution examined and the amount of mercaptan present and should be such that about 10 to 15 cc. of 0.01 N silver nitrate solution are consumed. From 5 to 10 cc. of a hydrocarbon sample are usually soluble in the cell liquid.

If the sample (free from hydrogen sulfide and elementary sulfur) contains mercaptan, the potential of the silver electrode will rise from -0.070 to about -0.380 volt.

Standard 0.01 N solution of silver nitrate in isopropyl alcohol is added in small portions to the beaker with occasional stirring and the values of the e. m. f. of the cell are recorded. A sudden drop of the potential of the silver electrode to less negative values occurs at the end point.

Selection of End Point. If titration curves are constructed from the data observed they appear to be symmetrical, as would be expected, since the reaction involves two monovalent ions (*5*). The end point of titration is therefore at the point of inflection of the curve. If the results are not plotted the values of $\frac{\Delta E}{\Delta c}$ are calculated and the end point is taken where this value is a maximum. A typical titration curve is shown in Figure 2.

Reagents

Sodium Acetate in Alcohol. Approximately 0.1 N solution of sodium acetate in 96 per cent ethyl alcohol is used as a medium for titration. Ethyl alcohol denatured with benzene or gasoline was found suitable.

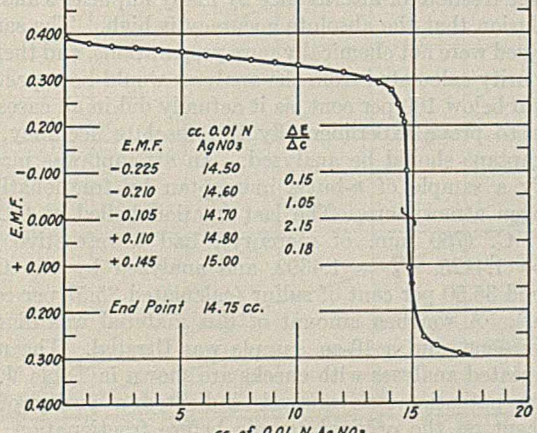

Figure 2. Titration of *n*-Butyl Mercaptan in Kerosene

5-cc. sample, 0.0295 M

Standard Solution of Silver Nitrate. Solution of silver nitrate of 0.01 N strength in isopropyl alcohol containing about 9 per cent of water is prepared by exact dilution of a 0.1 N stock solution. The stock solution is stable for months but should preferably be kept in darkness. The dilute 0.01 N solution should be prepared as needed, but has been found to remain stable for several weeks. Ethyl alcohol is unsuitable for preparation of these solutions because acetaldehyde is slowly formed and fine silver powder is precipitated.

Isopropyl Alcohol. This must be free of aldehydic impurities. Commercial alcohol is purified by dissolving 0.5 gram of silver nitrate in 1 liter of alcohol, and exposing in a clear glass bottle to direct sunlight for several hours. The alcohol is decanted from the precipitated silver, the excess silver nitrate is removed with sodium chloride, and the alcohol is redistilled. The azeotropic mixture containing 9 per cent of water can be used directly for preparation of solutions of silver nitrate, as this amount of water aids in the solution of silver nitrate.

Interfering Substances and Conditions

Influence of Solvent. The freedom of interference by the hydrocarbon solvent with the precipitation of silver mercaptides has been demonstrated by previous workers (*1*, *7*). No disturbing influence of the solvent could be detected experimentally when titrations were performed in kerosene, cracked gasoline, amylene, acetone, and various aliphatic alcohols.

Common Impurities. From a theoretical viewpoint substances reacting with silver nitrate and forming compounds substantially more soluble than silver mercaptides should not interfere with the procedure. Since the solubility of silver mercaptides is very low and nearly equal to the solubility of silver iodide, the chances of encountering an interfering substance are small.

The possible interference of a number of substances likely to be encountered in practice was studied experimentally. The procedure consisted in the titration of a solution of mercaptan of known strength, in the presence of a measured amount of substance examined for possible interference. Table I shows the results of analyses of *n*-butyl mercaptan solutions in kerosene containing varying amounts of diethyl disulfide.

Table I. Titration of *n*-Butyl Mercaptan in Presence of Diethyl Disulfide in Kerosene

Diethyl Disulfide Present	Mercaptan Present	Mercaptan Found
Mole/l.	*Mole/l.*	*Mole/l.*
None	0.0297	0.0297
0.030	0.0297	0.0297
0.030	0.0297	0.0297
0.090	0.00425	0.00428

Table II. Impurities Not Influencing Results

Sulfur Compounds			
	%		%
Ethyl sulfide	0.1	Ethyl sulfone	0.1
Ethyl disulfide	0.1–0.2	Butyl sulfone	0.1
Carbon disulfide	0.2	Sodium cymene sulfonate	0.1
Thiophene	0.1–0.6	β-Trithioacetaldehyde	0.7
Reducing Substances			
Formaldehyde	0.04–0.40	Acetaldehyde	0.04–0.40
Miscellaneous			
Nitrobenzene	2.0	Phenol	0.1
Fuchsin	0.004	Pyridine	10
Sodium oleate	0.1	Light nitrogen bases[a]	0.4
Sodium sulfate	1.4	Medium nitrogen bases[a]	0.4
Magnesium sulfate	0.5	Heavy nitrogen bases[a]	0.4
Aluminum sulfate	0.5	Purified naphthenic acids[a]	0.4
Sodium bicarbonate	0.1	Crude naphthenic acids[a]	0.4

[a] Separated from California crude oil.

By similar experiments it was found that certain substances had no influence on the results when present in the cell in the amounts shown in Table II.

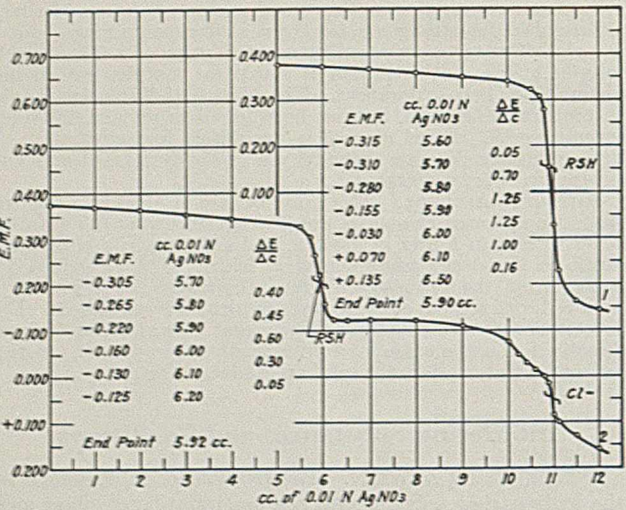

FIGURE 3. TITRATION OF *n*-BUTYL MERCAPTAN IN ALCOHOL

1. In absence of chloride 2. In presence of chloride

Determinations were not influenced by the presence of chloride ion. The end point of mercaptan titration is reached long before the precipitation of the chloride ion begins. Figure 3 shows a titration of a solution of *n*-butyl mercaptan, with and without chloride added.

OXIDIZING SUBSTANCES, PEROXIDES. The determination of mercaptans in the presence of peroxides is often required, although this fact is not generally appreciated in the literature concerned with the determination of mercaptans in petroleum products. Occurrence of peroxides in gasolines is common and the oxidation of mercaptans may proceed very slowly when both substances are present in concentration often found in gasolines (*8*). The present procedure gives reliable results in the presence of reasonable amounts of hydrogen peroxide, ethyl ether peroxide, and organic peroxides formed in cracked gasoline when exposed to ultraviolet light.

In order to show that the proposed method is applicable in the presence of peroxides and because of the lack of any method to check the results of titrations in the presence of peroxides, the rates of oxidation of mercaptans were measured. Upon mixing a solution of *n*-butyl mercaptan with solutions of various peroxides, so that the resulting mixture was 0.01 *M* with respect to both components, and titrating immediately, no decrease in the amount of mercaptan took place. A change could be noticed only after several hours.

TABLE III. COMPOSITION OF MIXTURES

Solution	Solvent	Nature of Peroxide	Active Oxygen[a]
			Mole/l.
1	Ethyl alcohol	Hydrogen peroxide	0.01
2	Mixture 95% Ethyl alcohol 5% Ethyl ether	Ethyl ether peroxide	0.01
3	Mixture 50% Ethyl alcohol 50% Ethyl ether	Ethyl ether peroxide	0.1
4	Cracked gasoline	......	0.01
5	Mixture 95% Hexane 5% Ethyl ether	Ethyl ether peroxide	0.01

[a] 0 = 16.

The results of several experiments in which the rates of oxidation were measured by potentiometric titration of mercaptans in presence of peroxides are shown in Figure 4. The regularity of the results suggests that the peroxides did not interfere with the determination of mercaptans. The curves represent the progress of oxidation of 0.01 *M* *n*-butyl mercaptan in various solvents by several peroxides. At the start of the experiments the mixtures had the composition shown in Table III.

Influence of Concentration

A number of mercaptans purchased from Eastman Kodak Company were analyzed. A weighed amount was dissolved in kerosene and the solution was titrated at various dilutions. In all cases the end point was reached at, or near, −0.100 volt. This value was found experimentally to coincide nearly with the end point of the precipitation of silver iodide in the same solution, from which it is concluded that the solubility of silver mercaptides is approximately equal to (somewhat lower than) the solubility of silver iodide. The variations with individual mercaptans were too small to be considered for analytical purposes.

Table IV shows the influence of dilution on the analyses and gives an estimate of the absolute accuracy of the method.

TABLE IV. INFLUENCE OF DILUTION

Mercaptan	Present	Found	Purity of Sample
	%	%	%
Ethyl	0.3229	0.2706	83.8
	0.3229	0.2761	85.5
	0.0807	0.0684	84.7
	0.0202	0.0176	87.2
Isopropyl	0.3816	0.3220	84.4
	0.3816	0.3180	83.3
	0.3816	0.3160	82.8
	0.0954	0.0789	82.7
	0.0239	0.0195	81.6
n-Butyl (1)	0.4109	0.3895	94.9
	0.1027	0.0968	94.3
	0.0257	0.0243	94.6
n-Butyl (2)	0.2877	0.2681	93.2
	0.2877	0.2681	93.2
	0.2877	0.2681	93.2
	0.2677	0.2674	92.9
n-Butyl (3)	0.1041	0.0971	93.3
	0.01041	0.0097	93.2
	0.001041	0.0010	96.1
Isobutyl	0.3860	0.3680	95.4
	0.3860	0.3690	95.6
	0.0965	0.0924	95.8
	0.0242	0.0231	95.5
n-Amyl	0.4036	0.3945	97.8
	0.1009	0.0984	97.5
	0.0252	0.0246	97.6
	0.0252	0.0250	99.2
n-Heptyl	0.4149	0.4110	99.1
	0.4149	0.4110	99.1
	0.1037	0.1023	98.7
	0.0259	0.0258	99.6
	0.0259	0.0258	99.6
Benzyl	0.4002	0.3898	97.4
o-Thiocresol	0.4013	0.3377	84.2
	0.1004	0.0846	84.3
	0.0250	0.0206	82.4

ACCURACY. The principles on which the method is based and the freedom of interference by many impurities allow the conclusion that the absolute accuracy is high. The samples analyzed were not chemically pure preparations, and therefore the purity calculated from the analyses would be expected to remain below 100 per cent, as it actually did in all cases. In order to prove experimentally the absolute accuracy, pure mercaptans should be analyzed. An attempt was made to purify a sample of *n*-butyl mercaptan by fractionation in nitrogen atmosphere. The last fraction boiled at 98.0° to 98.3° C. (760 mm. of mercury), had a refractive index $n^{20}_{D} = 1.4425$, $n^{25}_{D} = 1.4392$, and analyzed by the Carius method 35.50 per cent of sulfur (calculated 35.57 per cent of sulfur). A weighed amount of this material was dissolved in kerosene, and a 10-cc. sample was titrated. The results of repeated analyses with checks are shown in Table V.

The potentiometric analysis indicated a purity of 93.3 per cent on the original sample before fractionation. The purified sample analyzed 97.6 per cent (average) by the potentiometric method, and 97.1 per cent by the iodometric method of Kimball, Kramer, and Reid (*4*). A comparison of the physical properties of the purified sample with those given by Ellis and Reid (*3*) for a pure sample of *n*-butyl mercaptan which analyzed 100.3 per cent by the iodometric method, suggests that the authors' redistilled sample was still impure. Since the analysis for total sulfur by the Carius method indicated a purity of 99.8 per cent, the sample appears to have been contaminated by an inert sulfur compound.

TABLE V. ANALYSIS OF *n*-BUTYL MERCAPTAN PURIFIED BY FRACTIONATION

Weight of Sample	Concentration of Kerosene Solution	Found	Purity of Sample
Gram	*Gram/100 cc.*	*Gram*	*%*
0.1376	0.05504	0.1344	97.7
		0.1339	97.3
		0.1339	97.3
0.1183	0.04732	0.1157	97.8
		0.1152	97.7
0.1271	0.05084	0.1240	97.6
			Av. 97.57

TABLE VI. PROPERTIES OF SAMPLE

	n-Butyl Mercaptan	
	Ellis and Reid	Sample purified by fractionation
Boiling point, ° C.	98.6–99.0 (768 mm. Hg)	98.0–98.3 (760 mm. Hg)
n_D^{25}	1.4401	1.4392
Purity, %		
Iodometric method	100.3	97.1
Potentiometric method		97.6

PRECISION. The relative accuracy of individual determinations is governed by two factors—the solubility of the sample in alcohol and the amount of silver nitrate consumed per sample. The end point of titrations can be established with an accuracy of ±0.02 cc. This amount indicates 2×10^{-7} mole of mercaptan in the sample, which should be the error in the absolute amount of mercaptan found in the titration. Consequently, the precision shown in Table VII can be expected, if 10 cc. of sample are added to the cell.

TABLE VII. PRECISION

Molality of Sample	Mercaptan in Sample[a]	Calculated Error
	%	%
0.1	1.0	±0.02
0.01	0.1	±0.2
0.001	0.01	±2.0

[a] Molecular weight = 100.

The experimental results of Tables IV to VI agree reasonably well within the calculated limits, considering that the extreme precision indicated by the calculations for the titration of more concentrated solutions could be verified only by observing special precautions. The somewhat erratic results obtained with ethyl mercaptan were probably due to its volatility.

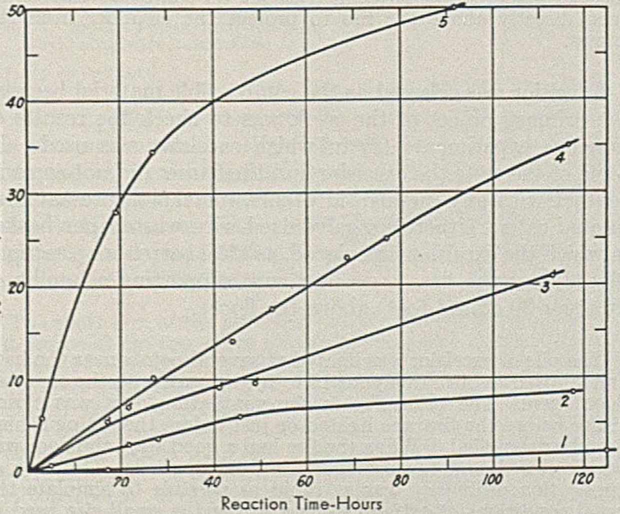

FIGURE 4. OXIDATION OF 0.01 *M* *n*-BUTYL MERCAPTAN BY PEROXIDES IN VARIOUS SOLVENTS

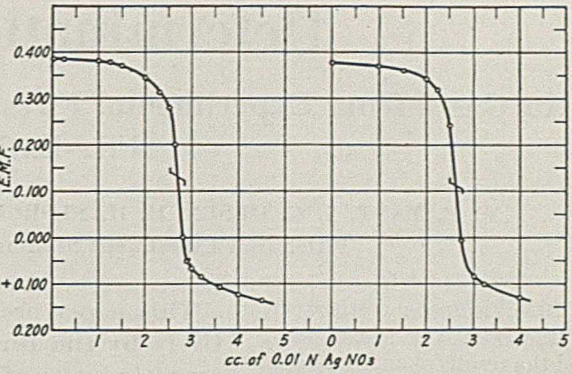

FIGURE 5. TITRATION OF MERCAPTANS IN A SAMPLE OF CRACKED GASOLINE FROM CALIFORNIA PETROLEUM

Table VIII shows the reproducibility of mercaptan determinations in a sample of cracked gasoline from California crude; Figure 5 shows the reproducibility of the titration curves. Since solution was approximately 0.0025 *M* with respect to mercaptan, the expected error was ±0.2 × 4 = ±0.8 per cent. The maximum discrepancy found experimentally was about 2.0 per cent, an error of ±1.0 per cent, which is in reasonable agreement with the calculated value.

TABLE VIII. DETERMINATION OF MERCAPTANS IN CRACKED GASOLINE FROM CALIFORNIA CRUDE

Size of Sample	0.01 *N* $AgNO_3$ Required	Mercaptan	Mercaptan Sulfur
Cc.	*Cc.*	*Mole/l.*	*%*
10.0	2.70	0.00270	0.0115
10.0	2.70	0.00270	0.0115
10.0	2.70	0.00270	0.0115
10.0	2.65	0.00265	0.0113

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IRON GALLATE INKS—LIQUID AND POWDER. A general study of iron gallate writing ink was undertaken at the National Bureau of Standards in an attempt to improve the keeping quality of ink without increasing the acid content. All inks of this type contain iron, and since the standard ink contains 3 grams of iron per liter, this figure was used as the starting point in devising the ink formulas. Experimental inks, using different materials in varying concentrations, were prepared and tested according to the Federal Specification. The use of gallic acid without tannic acid produced an ink with greater stability, and consequently the acid content could be decreased. This, in turn, decreased the corrosion of steel pens. The resulting ink had remarkably good stability. This modified formula could be adapted to the preparation of an ink powder without changing the characteristics of the ink.

Determination of Phosgene

In Gases from Experimental Fires Extinguished with Carbon Tetrachloride Fire-Extinguisher Liquid

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This paper presents work done coöperatively by the Bureau of Mines and representative manufacturers of carbon tetrachloride–type fire extinguishers to check the values for phosgene reported by the Bureau of Mines in 1920 (2), which had been criticized (6) on the basis that the analytical method used gave results which were too high owing to hydrolysis of carbon tetrachloride in the alkaline reagent and subsequent titration as phosgene. This possibility of error was excluded in the present work by using the aniline method. The results obtained for phosgene are of essentially the same order and check the former work.

It is not the intention of this bureau to discourage the use of carbon tetrachloride–type fire extinguishers, which are excellent for stopping incipient fires, but rather to determine the decomposition products which may result from their use and which should be recognized and properly evaluated.

IN 1920, Fieldner and others (2) of the Bureau of Mines published the results of an investigation of the gases formed when excelsior fires are extinguished with carbon tetrachloride fire extinguisher liquid in a closed room. In 1931, Olsen (6) published a report which described the results obtained in a series of tests using the acetone method, the caustic soda method, and the aniline method for the determination of phosgene. In reporting the results obtained by the caustic soda method it was stated "as this method was used by Fieldner and his associates this source of error must have given high results in their experiments." The error referred to was the hydrolysis of carbon tetrachloride in the alkaline reagent and its subsequent titration as phosgene. Following publication of this article Matuszak (4, 5) called attention to the possibility of errors in Olsen's work which could equally explain the discrepancies found.

During 1933–34 the manufacturers of carbon tetrachloride–type fire extinguishers collaborated with the Bureau of Mines to check the results reported by Fieldner and others (2). This work was done by utilizing the same test chamber as that employed in 1920 and duplicating the test fires, conditions of burning, and test procedure as nearly as possible, except that the aniline method (1, 3), which is more specific for phosgene, was used. The results of this investigation are in substantial agreement with those reported by Fieldner and others (2).

Two sets of coöperative experiments were performed, the first at the bureau's Pittsburgh Experiment Station in the same chamber originally used in the 1920 tests, and the second in a gas laboratory previously used by Olsen and located at one of the manufacturer's plants at Newark, N. J. The representatives of the Bureau of Mines and of the manufacturers made separate determinations of phosgene during each series.

It must not be concluded that these tests with free-burning excelsior fires and heated iron in a small closed chamber show the quantities of phosgene which will be formed whenever and under whatever conditions carbon tetrachloride–type extinguishers are employed in extinguishing fires. The gases from fires are influenced by many factors, such as the kind and amount of burning materials, the condition of combustion, the moisture present, the absorption by materials with which they come in contact, and the size of the confining compartment or the lack of confinement. Attention is directed to these factors because it is undesirable to have erroneous conclusions drawn as to the usefulness and efficiency of fire extinguishers of this type, which enjoy a long, well-established record of effective service.

Experiments at Pittsburgh

EQUIPMENT AND PROCEDURE. The chamber employed at the Pittsburgh Experiment Station of the U. S. Bureau of Mines is the one used in the previous investigation (2).

The dimensions are 3.8 × 3.05 × 2.4 meters. An air lock, 1 × 1 × 2.4 meters, permits entering or leaving the chamber without much dilution of the chamber atmosphere. The total volume is approximately 28 cubic meters and exclusive of the air lock is 26 cubic meters. An opening in the ceiling is connected through a mercury-sealed bell-type valve to a suction fan which provides ventilation or removal of the chamber atmosphere when desired. A large circulating fan is located at one end and near the floor of the chamber. The ceiling is galvanized sheet metal, the walls are approximately half glass and half sheet metal, and the floor sheet metal is covered with linoleum. The metal surfaces have had many coats of paint and varnish in the course of their varied use. The exposed coating when the experiments discussed in this report were made was ordinary inside white paint. The fires were built on sheets of heavy transite board, supported in the center of the chamber 6.3 cm. above the floor by firebrick. A sheet of asbestos was suspended about 30 cm. below the ceiling area, directly above the fire to protect the chamber from the flames.

Excelsior was selected as the combustible material because the primary object of the work was to check the results of previous experiments (2) in which excelsior was used. In some of the tests the excelsior and the flames did not come in contact with any metals; in others, metal was present to a limited extent either as a galvanized-wire wastepaper basket in which the excelsior was placed, as steel barrel-hoop sections placed over the fire, or as iron wire supporting a bundle of excelsior 30 cm. (1 foot) above the floor.

The pile of excelsior was lighted at several points near the base and allowed to burn freely for 15 to 160 seconds with the chamber door open. The bell-valve in the ventilating duct was closed either before the fire was lighted or just before the extinguishing liquid was applied. When the fire had a good start the door was partly closed and the extinguisher fluid applied. The rate of application ordinarily was as rapid as possible to simulate the usual conditions of extinguishing a fire of the small size used in the experiments; in a few instances the application was slow, to prolong the duration of the small fires and thereby simulate conditions of extinguishing fires larger than were permitted without damage to the test chamber. In certain cases the operator of the extinguisher was a representative of the Bureau of Mines and in others a representative of the manufacturers. Where the rate of extinguishing the fire was purposely delayed, it was manifestly necessary to protect the operator with a gas mask. In no instance did the representative of the manufacturers wear a mask. The extinguisher fluid was the preparation marketed by the manufacturers of carbon tetrachloride-type fire extinguishers and not ordinary commercial or c. p. carbon tetrachloride. It was applied to the fire with a standard 0.95-liter (1-quart) size hand-operated extinguisher. When the fire was extinguished the operator left the chamber and closed the doors, which made it gastight except for a 5-cm. (2-inch) hole in one side, left open to accommodate pressure differences created by cooling of the air, which otherwise would have collapsed the walls.

Tables I and II list the experimental conditions. In seven of the thirteen experiments the stirring fan was operated after the fire appeared to be extinguished. In experiments 2, 5, 9, and 10 (two with and two without the stirring fan in operation) the fire reignited, and it was necessary to enter the chamber three or four times and use the extinguisher.

TABLE I. EXPERIMENTAL CONDITIONS

(Application of carbon tetrachloride fire extinguisher fluid to excelsior fires and heated iron. Experiments at Pittsburgh.)

Experiment	Material Used for Experiment	Rate of Extinguishing	Stirring Fan Used	Loss in Weight of Excelsior
				Grams
1	1135 grams of excelsior placed on transite board on floor in center of chamber	Rapid	Yes	227
2	1135 grams of excelsior in wire basket on same board. Weight of basket, 500 grams	Slow	Yes	[a]
3	1135 grams of excelsior in wire basket on same board. Weight of basket, 500 grams	Rapid	Yes	[a]
4	1135 grams of excelsior in wire basket on same board. Weight of basket, 500 grams	Slow	Yes	[a]
5	1135 grams of excelsior in wire basket on same board. Weight of basket, 500 grams	Rapid	Yes	136
6	1135 grams of excelsior placed on board	Rapid	Yes	[a]
7	1135 grams of excelsior placed on board	Rapid	No	427
8	227 grams placed directly on board; control experiment, no extinguishing liquid used	None used	No	227
9	1135 grams in wire basket placed on board	Slow	No	[a]
10	1135 grams of excelsior on board and 8 semicircular sections of sheet-iron barrel hoops placed over excelsior	Rapid	No	454
11	1135 grams of excelsior on board and 8 semicircular sections of sheet-iron barrel hoops placed over excelsior	Rapid	No	454
12	One end of 15-cm. I-beam weighing 8.7 kg. heated to red heat	Fluid applied slowly with dropping funnel	Yes	None used
13	1135 grams of excelsior suspended 1 meter above floor by baling wire from ceiling	Rapid	No	[a]

[a] Not determined.

METHOD OF SAMPLING AND ANALYSIS. The sampling of the atmosphere in the chamber was begun 3 to 5 minutes after the extinguishing fluid was applied to the fire. Two samples were taken simultaneously, each through a purifying tube—a 5-cm. glass U-tube with arms 22 and 30 cm. long. Figure 1 shows a purifying tube inside the chamber and a sampling train outside the chamber.

The short arm of the purifying tube contained 6 cm. of absorbent cotton at the top where the gas entered, and below the cotton 12 cm. of 10- to 12-mesh calcium chloride, previously neutralized with hydrogen chloride gas. The calcium chloride was not included until experiment 7. A small amount of cotton was placed in the connection between the two arms of the U. The long section of the purifying tube contained 10 cm. of amalgamated mossy tin at the bottom, then 3 cm. of mossy tin, and at the top 15 cm. of closely packed mossy zinc. Both purifying units were 1 meter above the floor and 10 cm. from the wall; unit 1 was at the midpoint of a long wall, and unit 2 was in the far corner of the adjacent wall.

Each sample was led through two simple absorption tubes of the petticoat bubbler type in series, each of which contained 25 cc. of the phosgene absorbent. The purifying train and connections to the absorption tubes were purged with the test atmosphere before the samples were taken.

Of the two samples taken simultaneously that taken through unit 1 was split into two parts, A and B in Table II. Each part was drawn through the purifying tube by means of a 20-liter aspirating bottle at a rate of 1 liter per minute. Sample C, taken through purifying unit 2, was started at the same time as samples A and B and was measured by a calibrated flowmeter. The sampling rate for sample C was 3.371 liters per minute for experiments 1 to 6, inclusive, and 3.268 liters per minute for experiments 7 to 13, inclusive.

The samples taken simultaneously in each of the first seven tests did not check, and it was thought that the discrepancies were due to variations in the chamber atmosphere at the two rather widely separated sampling points, particularly because each was near a wall where a minimum of mixing would be expected. Following experiment 7, the inlets to both purifying units were connected by 12-mm. glass tubing to a common sampling point 160 cm. above the floor at the center of the chamber. This sampling arrangement was used for the remainder of the experiments. The reaction of aniline in aqueous solution with phosgene (*1*, *3*) to form *s*-diphenylurea, $COCl_2 + 4C_6H_5NH_2 = CO(NHC_6H_5)_2 + 2C_6H_5NH_2.HCl$, has been found (*6*) to give quantitative results for small amounts of phosgene in air.

In preparing the absorption solution an excess of aniline is kept in a bottle of distilled water for a week with occasional shaking, then phosgene is passed through the solution until a permanent precipitate of diphenylurea is formed and the mixture is kept ready for use. When a determination is to be made some of the solution is filtered several times through a Gooch crucible, and 25-cc. portions are placed in each of the bubblers. After the measured volume of sample is passed through the bubblers they are allowed to stand 2 hours, and the aniline reagent is then filtered through a weighed Gooch. Any precipitate which adheres to the sides of the bubblers is dissolved in warm alcohol and evaporated almost to dryness in a small beaker on a steam bath; several cubic centimeters of water are added and the evaporation is continued until there is no longer an odor of alcohol. This additional precipitate is then washed (with thorough policing) into the Gooch crucible and the entire precipitate is washed thoroughly with a solution of 1 *N* hydrochloric acid saturated with pure diphenylurea; the precipitate is then aërated several minutes and finally dried at 70° to 80° C. to constant weight.

The diphenylurea is extracted from the Gooch by washing with several portions of boiling ethyl alcohol, and the crucible is again dried at 70° to 80° C. to constant weight. The alcoholic extracts were dried in tared weighing bottles, first to dryness at room temperature, and then to constant weight at 70° to 80° C. These final weights were used in calculating the phosgene content of the gas.

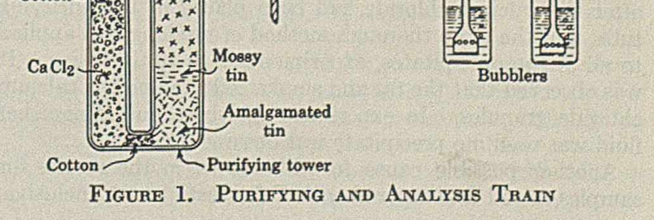

FIGURE 1. PURIFYING AND ANALYSIS TRAIN

Table II. Determinations of Phosgene

(In atmospheres created by application of carbon tetrachloride fire extinguisher fluid to excelsior fires and heated iron in 28-cubic meter chamber. Experiments at Pittsburgh)

Experiment number	1	2	3	4	5	6	7	8	9	10	11	12	13
Extinguisher fluid, grams	510	1880	540	940	900	630	625	None	1755	1545	980	790	1305
Number of times fire reignited	0	3	0	0	2	0	0	0	3	2	0	[a]	0
Number of applications of extinguisher fluid	1	3	1	1	3	1	1	0	3	3	1	1	1
Preliminary burning before application of extinguisher fluid, seconds	15	67	51	71	75	22	23	85	160	114	52	0	35
Total time of application of extinguisher fluid, seconds	20	168	15	81	22	8	14	0	198	54	33	420	70
Volume of sample, liters													
Sample A	18	18	18	18	18	18	18	18	18	18	18	18	18
Sample B	18	18	18	18	18	18	18	18	18	18	18	18	18
Sample C	62.4	60.7	60.7	60.7	57.3	60.7	58.8	58.8	58.8	58.8	58.8	32.7	58.8
Weight of diphenylurea found, mg.													
Sample A	0	31.6	25.1	15.0	10.7	10.8	2.7	0	11.9	5.8	5.1	21.0	2.8
Sample B	0	24.9	[b]	[b]	[b]	14.5	3.5	0	12.0	6.0	3.7	21.5	3.4
Sample C	2.1	47.3	4.8	9.5	5.0	9.6	6.8	0	32.1	14.9	8.8	33.3	6.6
Phosgene found, p. p. m. by volume													
Sample A	0	206	82	49	35	70	18	0	78	38	33	137	18
Sample B	0	162	[b]	[b]	[b]	95	23	0	78	39	24	140	22
Sample C	4	92	9	18	10	19	14	0	64	30	18	119	13

[a] Hot iron beam, no fire. [b] A and B combined for filtering and weighing.

At a room temperature of 23° C. and the usual barometric pressure at this location of 740 mm. of mercury, 1 mg. of diphenylurea is equivalent to 0.1175 cc. of phosgene. This value may be calculated in parts of phosgene per million parts of air by volume as follows:

$$1 \text{ mg. of diphenylurea} = \frac{0.1175 \times 1000}{\text{volume of sample in liters}} \text{ p. p. m.}$$

Results of Investigation. Table II gives the results obtained from the experiments at the Bureau of Mines. Three determinations (A, B, and C) were made during each experiment. In experiments 3, 4, and 5 figures appear for only samples A and C, sample B having been combined with A after precipitation of the diphenylurea.

In experiments 1 to 6, inclusive, the values for A and B do not check with sample C, which was of much greater volume. This discrepancy may be accounted for by the different method of treatment used on the precipitates from A and B compared with that used for sample C in these experiments.

The former were first treated with 0.5 to 1.0 cc. of concentrated hydrochloric acid, then after filtration the precipitates were washed with the filtrate containing aniline and undoubtedly some aniline hydrochloride and flushed with air to remove the aniline by vaporization. Sample C was washed thoroughly four or five times with 10 to 20 cc. of a 1 *N* solution of hydrochloric acid saturated with pure diphenylurea and filtered before use. The treatment used for sample C was also used for all samples from tests 7 to 13, inclusive. Its suitability had been checked previously by determination of known concentrations of pure phosgene in air and by washing known weights of pure diphenylurea in the same manner and drying again to constant weight.

It is possible that the treatment used for samples A and B in experiments 1 to 6 allowed varying amounts of aniline and aniline hydrochloride to be retained with the precipitate and calculated as phosgene, which accounts for the unusually high results found where it was used. The treatment used for sample C permitted more thorough washing of the precipitate without appreciable loss. The precipitates from experiments 1 to 6 were yellow-brown, probably owing to the presence of small amounts of tar or to oxidation during drying of the aniline or aniline hydrochloride retained in samples A and B, but in all cases sample C had definite crystals of diphenylurea which were easily recognized under the microscope. Virtually white precipitates were obtained after the calcium chloride had been placed in the purifying tube, and the more thorough method of washing was applied to all of the precipitates, experiments 7 to 13, inclusive. It was observed that the tar and smoke collected on the calcium chloride granules. In experiment 8, where no extinguisher fluid was used, no precipitate was obtained.

Another possible cause for differences in the results for samples A and B compared with C for tests 1 to 6, inclusive, and also test 7, was variation in the composition of the chamber air at the two widely separated inlets to the sampling tubes; samples A and B were taken from one side of the chamber and sample C from a far corner. Figure 1 shows the connection to the common sampling tube to the center of the chamber that was used in tests 8 to 13, inclusive.

Purity of Diphenylurea Precipitates and Control Experiments on Procedure. Melting point determinations were made on the precipitates obtained in several of the C samples, Table II. The results obtained were: Sample 2-C, 228° to 230° C.; sample 4-C, 228° to 231.5° C.; sample 10-C, 214° to 222° C.; sample 11-C, 228° to 230° C.; and sample 13-C, 233° C.

These melting points were obtained without any purification or recrystallization of the precipitate. A Thiele melting point tube and a Bureau of Standards calibrated thermometer were used.

The melting points of samples A were also determined, as follows: Sample 2-A, 183° to 190° C.; sample 3-A, soft at ordinary temperatures; sample 4-A, 181° C.; sample 5-A, 160° C.; sample 6-A, 164° C.; sample 9-A, 220° C.; sample 10-A, 210° C.; sample 11-A, 215° C.; and sample 12-A, 240° C. This indicates that the latter samples up to 6-A contained a much greater amount of impurity, which may therefore account for the high results found for these samples in Table II.

To obtain a sample of pure diphenylurea for a melting point determination the precipitates remaining from experiments 9-C, 10-C, 11-C, and 13-C, 47.3 mg. in all were taken up in 10 cc. of hot ethyl alcohol, evaporated to about half, then 10 cc. of water and 1 cc. of hydrochloric acid were added. Diphenylurea is fairly soluble in this mixture and sparingly soluble in water, but as the objective was only a purer specimen and not a quantitative yield, the mixture was filtered through a Whatman No. 42 paper and the precipitate washed thoroughly with water. It was then extracted with 20 cc. of hot absolute alcohol and evaporated slowly to dryness in a weighing dish and dried to constant weight at 60° C. A total of 19.6 mg. of crystals was obtained, which melted at 235.6°, 236.5°, and 236.5° C. in three determinations. The melting point given for diphenylurea in the International Critical Tables is 235° C.

For a control experiment 535 p. p. m. of hydrogen chloride and 356 p. p. m. of chlorine were put in the chamber and 110 liters were sampled at 11 liters per minute through two bubblers, each of which contained 25 cc. of aniline water. The gases were passed through the same purifying system that had been used for the samples of gases from the fires. No precipitate was formed. This indicated that these gases, which may be present in the gases from fires extinguished with carbon tetrachloride extinguishing liquid, did not interfere with the determination of phosgene by the method used.

When 23.2 p. p. m. of phosgene were added to this mixture of hydrogen chloride and chlorine in air and a 275.5-liter sample was taken at a rate of 11.02 liters per minute for 25 minutes, 19 mg. of diphenylurea, equivalent to 8.1 p. p. m. of phosgene, were found.

The chamber was ventilated, and 20.5 p. p. m. of phosgene were added from the cylinder, which had been thoroughly flushed out by allowing the gas in the cylinder to escape and be replaced by vaporization of the liquid. A sample taken for 25 minutes at a rate of 11.02 liters per minute yielded 47.2 mg. of diphenylurea, equivalent to 20.1 p. p. m. of phosgene.

Experiment 8 (Tables I and II) was duplicated, using 1135 grams of excelsior, which was ignited and allowed to burn for 30 seconds with no ventilation, then smothered with a large metal can. The heavy smoke was stirred and a 188.8-liter sample taken in 20 minutes through five parallel sets of two bubblers with 25 cc. of the aniline reagent in each. The samples were combined and filtered and treated the same as a regular phosgene determination. A small amount of black precipitate was obtained, which weighed 1.5 mg., but when calculated as phosgene on the assumption that the precipitate was diphenylurea it would be equivalent to only 0.93 p. p. m.

When 10 p. p. m. of phosgene were added to this same atmosphere, stirred for 5 minutes, and sampled and analyzed by the same procedure used in the previous experiment, 6.4 mg. of precipitate, equivalent to 4 p. p. m. of phosgene or 40 per cent of that added, were obtained.

A concentration of approximately 4000 p. p. m. of carbon tetrachloride vapor was made in a small chamber by evaporating a dish of the liquid on a hot-plate. Thirty-six liters of this gas were sampled through two bubblers in series containing 25 cc. of the aniline reagent in each at 2 liters per minute. No precipitate was observed in the reagent after standing for 2 hours. It was observed in other work that approximately 0.5 mg. of diphenylurea precipitate was readily visible in the solution.

A fire made by lighting 1135 grams of excelsior was allowed to burn 18 seconds with the chamber exhaust valve closed, and then was extinguished in 78 seconds with 973 grams of extinguisher liquid. A sample was started immediately and taken for 20 minutes at a rate of 9.44 liters per minute, total 188.8 liters, with the stirring fan on continuously. The final alcoholic extract of the diphenylurea was allowed to evaporate slowly and before it became dry 14.6 mg. of large crystals, needles 2 to 3 cm. long, were lifted out on a spatula. These had a melting point of 231.6° C. and represented 9.0 p. p. m. of phosgene. The remainder, upon drying, weighed 18.2 mg. and represented 11.3 p. p. m. of phosgene or a total of 20.3 p. p. m.

Experiments at Newark

A chamber was constructed early in 1934 in the plant of one of the manufacturers in Newark, N. J., to continue combustion researches previously carried out in a temporary structure. This chamber is similar in many respects to that at the Pittsburgh Experiment Station of the Bureau of Mines.

The dimensions are approximately 3 × 5 × 2 meters. The volume, including window bays and door frame, is approximately 32 cubic meters. The walls and floor are concrete, and the ceiling is transite asbestos board. It has five steel casement windows, 70 × 100 cm. (four opening to the outside and one to the laboratory) and a door in the end of the laboratory wall. The inside of the chamber had been given two heavy coats of sodium silicate and then brushed with dilute hydrochloric acid previous to its use for experiments with fires.

Experiments similar to those at the Bureau of Mines were conducted in this chamber, but no phosgene had been found when 18- to 36-liter samples were taken over a 36-minute sampling period. A very small amount of phosgene was found when iron sheets were suspended over the fire.

Since these results did not check those obtained at the Bureau of Mines the bureau agreed to send representatives to Newark for coöperative work to ascertain the cause of the apparent discrepancy.

METHOD OF SAMPLING AND ANALYSIS. The same analytical methods were used as in the Pittsburgh work, except for a few minor changes.

The purifying unit was slightly smaller, being one straight glass tube, 5.7 × 38 cm., with the inlet at the top. The sample passed through a 2.5-cm. layer of absorbent cotton, 7 cm. of "dessichlora," 10 cm. of 20-mesh zinc, 10 cm. of mercuric sulfide on 8- to 10-mesh pumice, and 5 cm. of 20-mesh zinc. For separating the precipitates of diphenylurea from the aniline reagent, Gooch crucibles with medium-fine sintered-glass disks were used instead of the asbestos-mat type. These crucibles with the precipitates came to constant weight after drying at 70° C. for 2 hours. Large bubblers with 50 cc. of aniline water were used in sets of two in series for each sample. Eighteen- to 51-liter samples were taken through the phosgene absorbent with aspirator bottles, and larger 113- to 229-liter samples were taken by means of a suction pump and measured with a drymeter. The drymeter was checked against the aspirator bottles and found to agree within 2 per cent on a 36-liter sample. Corrections were applied to compensate for reduced pressure in the sampling system due to resistance of the purifying tower and bubblers. This did not exceed 40 cm. of water or a volume correction of about 4 per cent.

EXPERIMENTS WITH PURE PHOSGENE. Table III gives the results of experiments in which pure phosgene was admitted to the chamber for the purpose of checking the possibility of losing phosgene by reaction with the siliceous coating on the walls. The first section of Table III includes results of experiments made with the chamber in the condition in which it had been used previously for experiments with fires in which no phosgene was found. An old, very small purifying train, which had been used for experiments with fires, was included in the first two of these experiments; the second two sets of samples were taken directly from the chamber to the bubblers. The results for experiments 1, 3, 5, and 7 show no phosgene when 18-liter samples (the size used for experiments with fires in this chamber) were examined, although 5.67 to 22.9 p. p. m. of phosgene had been put into the chamber. With much larger samples (113 liters) the recovery was only from a trace to 11 per cent of the amount introduced. When 22.9 p. p. m. of phosgene were put into the chamber in the fourth of these experiments, not enough remained after a half hour to detect by odor, which indicates the amount present was less than 5.6 p. p. m. (Chemical Warfare Service, American University Experiment Station, Washington, D. C.)

TABLE III. EXPERIMENTS WITH PURE PHOSGENE INTRODUCED INTO CHAMBER AT NEWARK

Experiment	$COCl_2$ Put into Chamber		Air Added with Gas	Sample Taken	Time of Sampling	Diphenylurea	$COCl_2$ Found	Recovery
	Cc.	P. p. m.	Liters	Liters	Min.	Mg.	P. p. m.	%
1[a]	250	5.67	[b]	18	36	0	0	0
				113	33	Trace	Trace	...
3[a]	750	22.5	[b]	18	36	0	0	0
				113	30	1.6	1.6	7
5	750	22.9	19.8	18	36	0	0	0
				113	30	1.8	1.8	8
7	750	22.9	16.1	18	36	0	0	0
				113	36	2.4	2.5	11
		Chamber Sprayed with Bakelite Lacquer						
8	750	22.9	31.0	18	36	2.7	17.3	75.5
				113	29	8.6	8.8	38.0
9	3000	91.6	[b]	113	31	0	0	0[c]
10	290	8.8	5.7	113	29	2.4	2.5	28.0
11	580	17.6	17.0	18	26	0	0	0[d]
				113	27	3.9	3.9	22.0[d]
12	580	17.6	17.0	18	31	2.6	16.7	94[d]
	(+ gases from test 11)			113	29	11.4	11.6	65[d]
14	580	17.6	18.4	18	40	1.1	7.0	39[e]
				113	40	10.0	10.2	58
15	580	17.6	22.6	36	21.5	0	0	0[f]
				113	22	0	0	0
16	580	17.6	50.9	36	18	3.7	11.9	68
				113	18	7.3	7.5	43
17	580	17.6	31.9	51	32	4.9	11.1	63
				113	32	6.3	6.4	36

[a] Analysis of phosgene used in experiments 1 and 3 gave a purity of 74.4 and 98.4 per cent. For the other experiments analysis showed a purity of 100 per cent. These values were used in calculating p. p. m.

[b] Not determined.

[c] The phosgene was allowed to remain in the chamber 2.5 hours to saturate the walls, after which the room was ventilated and a test was run which showed that no phosgene was present in the atmosphere.

[d] With fire gases from smothered excelsior fire.

[e] Stirring fan on only before sampling.

[f] With fire gases and a freshly prepared purifying tower.

These experiments show that the chamber absorbed phosgene rapidly and provide an acceptable explanation for the failure to find phosgene in previous experiments with fires in this chamber. The rapid absorption very probably was due to adsorption by the silica gel formed on the walls by first coating them with sodium silicate and then treating with dilute hydrochloric acid. Reaction with moisture on this kind of a surface would hasten removal of the phosgene. The cold concrete walls were continually wet from condensation of moisture from the atmosphere.

TABLE IV. DETERMINATION OF PURITY OF PHOSGENE USED IN NEWARK EXPERIMENTS

Experiment	Phosgene Used	Air Added for Dilution	Temperature	Diphenylurea	Purity
	Cc.	*Liters*	*° C.*	*Mg.*	*%*
2	5.05	1	30	32.0	74.4
4	12.50	2	22	107.7	98.4
22	12.10	28	24	109.1	103.7

TABLE V. EXPERIMENTAL CONDITIONS FOR APPLICATION OF CARBON TETRACHLORIDE FIRE EXTINGUISHER FLUID TO EXCELSIOR FIRES

(Experiments at Newark. Material used, 1135 grams of excelsior placed on transite board on floor in center of chamber.)

Experiment	Rate of Extinguishing	Stirring Fan Used	Loss in Weight of Excelsior
			Grams
13	Rapid	No	[a]
18	Rapid	No	303
19	Rapid	No	624
20	Slow	No	737
21	Slow	No	595

[a] Not determined.

Following experiment 7 the chamber was cleaned and sprayed with two coats of a Bakelite-type varnish. After the varnish had dried overnight, further experiments were made on the reaction of phosgene with the chamber walls. In 6 experiments where 8.8 to 22.9 p. p. m. of phosgene were added, with and without fire gases present, the recovery was 22.0 to 94.0 per cent. However, in another experiment (No. 15) when a freshly prepared purifying tower was used and fire gases were present the recovery was zero after the addition of 17.6 p. p. m. The fire gases present in tests 11, 12, and 15 were produced by igniting 1135 grams of excelsior in the chamber and smothering with a large metal can.

Table IV gives the results of three experiments performed to determine the purity of the phosgene used in these tests. The phosgene was taken directly from the cylinder of compressed (liquefied) gas into a gas buret, using mercury as the confining liquid. The measured volume was then diluted with air and passed through aniline water, the analytical method used being the same as that described previously. The result found in experiment 2 (74.4 per cent) was low; therefore the valve was first opened to allow the gas above the liquid to escape and be displaced by freshly vaporized phosgene. When this precaution was taken the gas from the cylinder was found to be over 98 per cent pure phosgene. These results were used as a basis for calculating the amounts of phosgene added to the chamber.

RESULTS OF EXPERIMENTS WITH FIRES. When it was ascertained that after varnishing the surfaces about 50 per cent of the phosgene which was put into the chamber could be recovered in a 36-minute sampling period, five experiments with fires were made igniting 1135 grams of excelsior and extinguishing the fire with carbon tetrachloride fire extinguisher liquid, the experimental procedure being similar to that employed at Pittsburgh. Table V gives the conditions and Table VI the results of these experiments.

All the fires were made with the excelsior placed on a transite board platform 180 × 122 cm., placed near the center of the chamber and supported 7 cm. above the floor by tiles. A transite board shield of the same size was suspended 25 cm. below the ceiling to protect it and the ventilating valve. The excelsior was placed loosely on the transite boards and ignited around the edges, except in experiment 20, in which it was hollowed out and lighted under the pile.

The amount of phosgene found in these experiments ranged from 3.5 to 34.8 p. p. m. The precipitate from experiment 13, which showed 34.8 p. p. m., was not subjected to melting point or refractive-index tests. In this experiment the fire reignited and was allowed to burn during sampling until all the excelsior was consumed.

Large and small samples were taken in the Newark experiments, as in those conducted at Pittsburgh. One 56.6-liter sample was taken in experiment 13, but in each of the other four experiments with fires a small 36-liter sample and a large 176- to 229-liter sample were taken. This same arrangement was carried out in the experiments with pure phosgene in the chamber at Newark. The results from the larger samples are considered more reliable because the errors in weighing and from contamination of the precipitate with the aniline reagent or losses from solubility of the precipitate are smaller in proportion to the weight of the precipitate.

All precipitates from the 5 fire experiments reviewed in Table V were practically white; very little tar was observed, probably because the larger amount of fine material in the purifying tower was more effective in removing it. The melting points of the precipitates examined were much closer to the accepted value, 235° C., than those found in the Pittsburgh tests; in fact, several agreed closely with the melting points, 239° to 239.5° C., found for a specimen of Eastman Kodak Company's pure diphenylurea when determined under the same conditions with the same thermometer. A microscopic examination of the crystals for shape and refractive index also showed close agreement with crystals of the diphenylurea obtained from the Eastman Kodak Company.

TABLE VI. DETERMINATIONS OF PHOSGENE

(In atmospheres created by application of carbon tetrachloride fire extinguisher fluid to excelsior fires in a 32-cubic meter chamber. Experiments at Newark.)

Experiment number	13	18	19	20	21
Extinguisher fluid, grams	1308	991	936	960	1227
Number of times fire reignited	1[a]	0	0	0	0
Number of applications of extinguisher fluid	1	1	1	1	1
Preliminary burning before application of extinguisher fluid, seconds	30	47	32	25	25
Total time of application of extinguisher fluid, seconds	30	11	28	73	60
Volume of sample, liters					
Sample A	56.5	36	36	36	36
Sample B	...	229	199	205	176
Weight of diphenylurea found, mg.					
Sample A	17.0	1.9	3.9	7.0	6.0
Sample B	...	6.8	15.6	35.4	30.5
Phosgene found, p. p. m. by volume					
Sample A	34.8	6.1	12.5	22.5	19.3
Sample B	...	3.4	9.0	19.9	20.0

[a] This fire reignited 4 minutes after it was extinguished and burned for 2 minutes during the sampling.

TABLE VII. MELTING-POINT DETERMINATIONS AND MICROSCOPIC EXAMINATIONS OF DIPHENYLUREA PRECIPITATES

(From experiments with fires extinguished with carbon tetrachloride fire extinguisher fluid at Newark.)

Sample	Melting Point[a]	Approximate Purity from Microscopic Examination	Beta Index
	° C.	*%*	
13	[b]	[b]	[b]
18 A	221.5	80 to 90	1.62
B	235.5	75	1.62
19 A	232.5	80	1.62
B	235.5 to 237.5	80 to 90	1.62
20 A	229.5 to 235.5	90 to 100	1.62
B	238.5 to 239.5	95 to 100	1.62
21 A	229.5 to 234.5	90	1.62
B	235.5 to 238.5	90 to 100	1.62
Eastman Kodak Company's diphenylurea	239 to 239.5	100	1.62
Eastman Kodak Company's diphenylurea recrystallized from ethyl alcohol, dried at 70° C.	238.5 to 239.5	100	1.62

[a] The thermometer used was compared with a Bureau of Standards calibrated thermometer, and the necessary corrections were made.
[b] Not determined.

In all cases the beta index was 1.62. Table VII gives the melting points found for these precipitates and an estimate of the approximate purity of each precipitate as judged from its appearance under the microscope.

Absorption and Reaction of Phosgene

Attention is called to the importance of using materials for test chambers which absorb minimum amounts of phosgene, as this gas is highly reactive. Many contradictory results as to the formation and nonformation of phosgene, reported by different investigators engaged in work similar to that described in this paper, may be due to overlooking this important detail.

Summary

An article of comparatively recent publication (*6*) criticized the results previously reported by the Bureau of Mines in measuring phosgene in the gases from excelsior fires which were extinguished by carbon tetrachloride on the basis that the analytical method gave erroneously high values. This bureau, with the coöperation of the manufacturers of the carbon tetrachloride–type fire extinguisher, has repeated the investigation under a reproduction of the former conditions, except that a different analytical method was used. The phosgene found in these sixteen experiments in which excelsior fires were extinguished in a small sealed chamber ranged from 4 to 92 p. p. m. by volume, with an average of 23.6 p. p. m. When carbon tetrachloride was dropped on an I-beam previously heated to red heat and without fire present, the amount of phosgene found was 119 p. p. m. These results are in substantial agreement with those formerly reported by the Bureau of Mines. The report gives a detailed description of the experimental procedures and methods and a tabulation of the results obtained. The rapid reaction of the phosgene formed with other products of fire gases and with walls of the rooms in which the tests were made is pointed out and briefly discussed.

Acknowledgment

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Analyses and Softening Temperatures of Coal Ash

From Coals in the Northern Anthracite Field

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A REVIEW of the technical literature discloses very little information on the chemical composition of coal ash and its relation to fusibility and clinker formation from Pennsylvania anthracites, particularly for coals from the northern anthracite field. This paper has been written to supply data of this nature, to give a description of a method of minimizing clinkering troubles by means of draft control or the maintenance of oxidizing conditions in the fuel bed, and to illustrate a very simple method of estimating the ash-softening temperature from the chemical composition.

Table I contains analyses and softening temperatures of six samples of prepared anthracites, as marketed, selected from various localities in the northern anthracite field, and of two composite samples, made up by mixing a number of individual samples taken from different veins throughout the northern anthracite field. The ash-forming constituents of these coals consist mainly of high-fusing silica and alumina, with lesser amounts of the oxides of iron, calcium, magnesium, and the alkalies. The latter, with the exception of the oxides of iron, do not materially affect the softening temperature on account of their small quantities.

The copper shown in the analyses of two of these samples has been included because of its rarity in the ash of an anthracite and because of its possible effects as a catalyst in certain processes of coal treatment. The mineralogical constituents of coal ash as given by Marson and Cobb (*4*) are shown in Table II.

Draft Control to Minimize Clinker Formation

During the past 3 years the writers have carried out a number of experiments, both in the laboratory and on full-size combustion equipment, using anthracites from Pennsylvania, Wales, Scotland, Russia, and the Chinese Republic, and also coke and bituminous coal, for the purpose of obtaining further data on the causes of clinker formation and possible means of controlling it. The results of these investigations indicate that the ash-softening temperature of Pennsylvania's northern field anthracites, over the softening temperature

Table I. Chemical Analyses and Softening Temperatures of Coal Ashes

(From various localities in northern anthracite field of Pennsylvania)

Constituent	A	B	C	D	E	F	G	H
SiO_2	55.00	55.70	56.62	55.10	56.08	55.04	55.4	56.5
Al_2O_3	38.12	36.75	30.78	36.03	34.92	31.80	31.1	36.0
Fe_2O_3	2.06	3.05	7.62	4.24	4.05	8.12	10.1	3.8
TiO_2	1.82	1.32	1.10	1.52	0.96	1.22	1.8	1.2
CuO	...	...	0.09	0.04	...	...	...	...
MnO	0.03	0.08	0.10	0.05	0.10	0.12	...	...
CaO	1.20	1.40	1.10	0.91	1.40	1.30	0.3	0.8
MgO	0.60	0.62	0.72	0.68	0.84	0.76	0.0	0.3
$Na_2O + K_2O$	0.44	0.48	0.96	0.73	0.95	0.72	1.2	1.3
P_2O_5	0.13	0.10	0.11	0.08	0.08	0.14	...	...
SO_3	0.60	0.50	0.80	0.62	0.62	0.78	0.0	...
Softening temperature, ° F.	3000	3000	2925	2975	3000	2925	2660	2980

Samples A to F, inclusive, were analyzed in the laboratory of The Hudson Coal Company, and the ash-softening temperatures determined in the same laboratory by the A. S. T. M. method.

Samples G and H were analyzed at the laboratory of the Anthracite Institute and the softening temperatures determined by E. P. Barrett at the Pennsylvania State College.

range ordinarily met with in commercial practice, is primarily dependent upon the content of iron compounds and to a lesser extent upon the content of the basis, lime, magnesia, and the alkalies.

Table II. Mineralogical Constituents of Coal Ash

Element	Form
Silicon	Silicates and sand
Aluminum	Alumina in combination with silica
Iron	Small quantities of pyrite and marcasite, ferrous oxide, ferrous carbonate, ferrous sulfate, ferric oxide, ferric sulfate, "organic" iron, and iron silicates
Calcium	Carbonates, sulfates, silicates
Magnesium	Carbonates and silicates
Sodium and potassium	Silicates, carbonates, chlorides
Manganese	Carbonates and silicates
Sulfur (inorganic)	Small quantities of pyrite and marcasite, ferrous sulfate, and ferric sulfate
Phosphorus	Phosphates

Silica and alumina make up approximately 90 per cent of the ash from the northern field coals (Table I). Figure 1 (*1*) shows the melting points for the system silica-alumina. The silica-alumina ratios of the northern field anthracites fall on the small segment *A*, and it can be seen at once that such changes in the silica-alumina ratio as may ordinarily be expected in these coals will not greatly affect the softening temperature of the ash. Lowering of the ash-softening temperature below the range indicated at *A* is then necessarily due to the presence of the approximately 10 per cent of minor constituents, of which the compounds of iron form the major portion.

Fieldner, Hall, and Feild (*2*) have shown that coal ashes containing iron in the ferrous state soften at a lower temperature than when the iron is in the ferric state. For example, when pyrite, one of the important iron-bearing minerals found in the mineral matter of coal, burned under highly oxidizing conditions, the iron is oxidized to the basic oxide (Fe_2O_3) and when this combines with silica it forms high-melting compounds. If the atmosphere is partially reducing, the iron is oxidized to ferrous oxide (FeO) which forms low-melting compounds with silica. A still further reducing atmosphere will reduce the iron to the metallic state and thus has the effect of increasing the melting point toward that of the corresponding point on the silica-alumina curve by eliminating the oxides of iron and therefore their slagging effect. Proper regulation of draft and thickness of fuel bed will assist materially in overcoming or minimizing clinkering tendencies. Four practical rules for the accomplishment of this result in practice are given by Haslam and Russell (*3*).

1. Use thin fires and keep fuel bed level by placing fresh coal on thin spots. Disturb the fuel bed as little as possible.
2. Fire the coal in small charges to minimize crust formation.
3. Do not allow burning coal in the ash pit. It is a good plan to keep water in the pit or, if it is not water-tight, to blow waste steam through the grate if the coal clinkers badly.

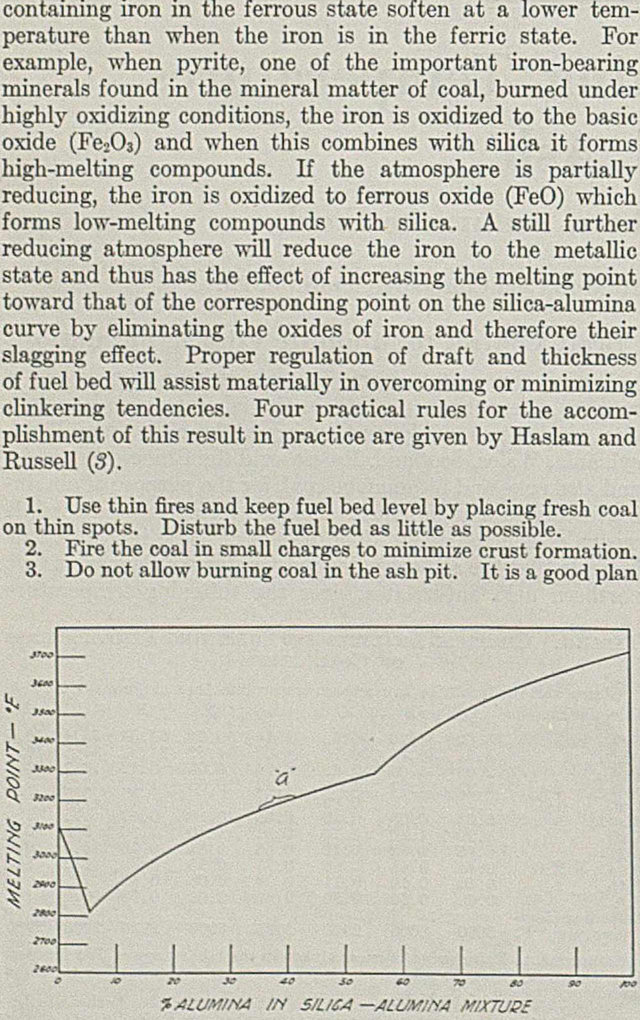

Figure 1

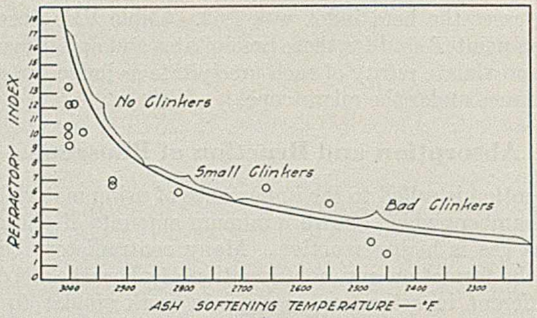

Figure 2

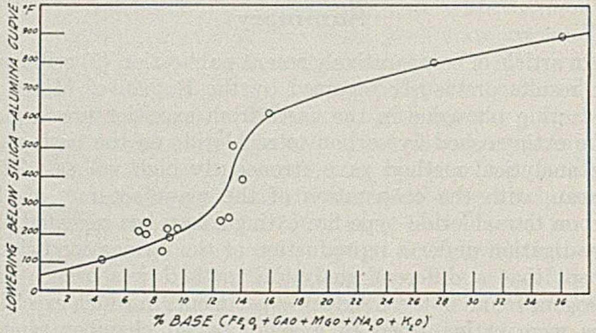

Figure 3

4. Keep the ash-pit door open and regulate the draft by means of the damper.

Prepared anthracite is practically free from extraneous pyrite, which is one reason for its high ash-softening temperature.

Table III. Chemical Analyses, Softening Temperatures, and Clinkering Characteristics of Anthracite Coal Ashes

	I	J	K	L	M	N	O
Duration of test, days	9.47	10.70	10.60	10.71	5.07	4.64	4.83
Draft, inches of water	0.029	0.028	0.029	0.030	0.029	0.027	0.028
Coal burned per hour, pounds	15.1	15.3	15.0	15.3	13.0	13.6	12.9
Rating developed, per cent	80.1	81.5	80.7	81.5	83.2	82.0	81.7
Clinkering	None	None	None	Small	Bad	Bad	Bad
Refractory index	21.0	9.4	10.7	6.1	2.7	5.3	1.8
Ash-softening temperature, ° F.	3000	3000	3000	2810	2475	2550	2450
Chemical analysis of ash:							
SiO_2	69.0	51.0	62.4	52.4	35.4	54.4	26.9
Al_2O_3	26.5	39.4	29.1	33.5	38.2	29.7	36.9
Fe_2O_3	3.2	9.6	5.7	10.9	19.3	9.9	28.9
CaO	0.4	..	0.3	2.0	5.8	6.0	4.4
MgO	0.2	..	0.3	0.6	1.5	..	1.3
$Na_2O + K_2O$	0.7	..	2.2	0.6	0.7	..	1.5

I, J, K, and L are Pennsylvania anthracites. M, N, and O are Welsh, Scotch, and Russian anthracites, respectively. Chestnut-size coals.

Refractory Index for Estimating Probability of Clinkering

Nicholls, Selvig, and Ricketts (*5*) show a fair relationship between the ratio

$$\frac{SiO_2 + Al_2O_3}{Fe_2O_3 + CaO + MgO + N_2O + K_2O}$$

and the softening temperatures of coal ashes. The results obtained by the writers are in agreement with this, as shown by Table III, which contains seven examples drawn from fifty or more tests yielding similar data. Figure 2 shows a plot of the data given in this paper.

Estimation of Ash-Softening Temperature from Chemical Composition

A rapid but approximate estimation of the softening temperature of a coal ash or a mixture of coal ashes (as in blending) may be made from the chemical analysis of the ash as follows:

1. Determine the percentage of alumina on a basis of silica plus alumina equals 100.
2. From Figure 1 find the melting point of a silica-alumina mixture corresponding to the percentage of alumina found under 1 above.
3. Determine the percentage of basis (oxides of iron, calcium, magnesium, and the alkalies).
4. From Figure 3 determine the softening temperature lowering due to these bases.
5. From the figure found under item 2, subtract the lowering due to basis found under item 4 and obtain the softening temperature to be expected.

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An Inexpensive Ball Mill

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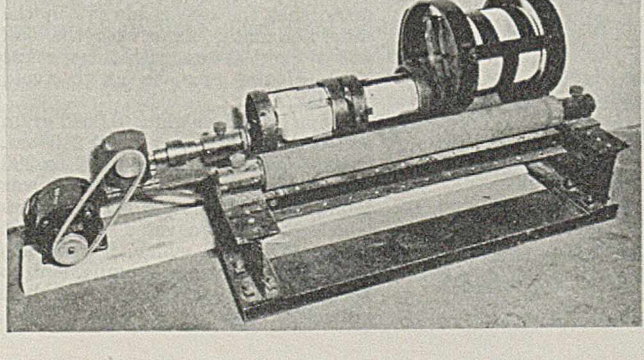
IN SOME chemical laboratories a ball mill is a very useful and much needed piece of apparatus, although it may not be used as continuously as in a ceramics or other laboratory where large quantities of powdered materials are required. The most satisfactory ball mill in such laboratories should not occupy too much floor space, should be adaptable for use with ball mill jars or other containers of various sizes, and should be fairly inexpensive, simple, efficient, compact, and, if necessary, portable. The ball mill shown in the figure was designed and constructed to meet these requirements. A ball mill involving the same principle has been described by Furnstal (*1*).

The principle of the device is simple, there being two rollers on which cylindrical objects may be placed. The rollers are made from 90-cm. (3-foot) lengths of 7.5-cm. (3-inch) pipe, the ends of which are plugged. (Longer rolls can be used.) A piece of steel rod is inserted in the center of each plug to serve as the bearing axle. Ordinary brass bearing supports for holding the Babbitt metal, having a grease cup on top for lubrication, are used. The rear roller is connected through a speed reducer (20 to 1 ratio) and an ordinary V-belt to a motor, and is thus the "power" roller, while the front roller is free to rotate as it will. To increase the traction between the rollers and the racks for the jars and to quiet the operation of the mill, a piece of automobile inner tube is slipped over each roller. There is ordinarily sufficient traction between the objects and the rolls so that it is not necessary to connect the rollers by a belt. However, when small bottles about 5 cm. (2 inches) in diameter are used for preparing mixtures, traction is secured by placing a short length of pipe of about the same diameter on the rollers.



In the figure, the support for the rollers is shown as pieces of I-beam, about 40 cm. (2 feet) long. If I-beam is not available, pieces of timber, railroad rail, or other material may be used. A series of holes is drilled in the upper surface of each I-beam. Each of the two bearings for the "idler" has two pins projecting from its lower surfaces. It is therefore possible to regulate the distance between the rollers by placing the pins in the proper set of holes, and to use containers of various sizes on the same machine. The rolls are close together when small jars are used; for larger jars, the distance between the rollers is increased.

The racks for holding the ball jars also can be made from inexpensive and easily obtainable materials. The rings for the racks are made from pipe of suitable diameter. For the small jars shown, 15-cm. (6-inch) pipe is used, and for the large ones, 30-cm. (12-inch) pipe. (The small jars hold about 1 liter, the large ones, 6.5 liters.) The rings for the large jars are attached to each other by two pieces of T-iron which also act as supports for the metal straps holding the jar in the rack. The rings for the small jars are held in place by strips of 1.3-cm. (0.5-inch) strap iron. One end of the small rack is partially closed by a cross of the strap iron. The jars are held in these small racks by a screw passing through a small bar of steel, which also holds the cover of the jar in place. When the bar is placed crosswise against one of the rings, the screw may be turned down against the cover of the jar, and the jar against the cross closing the other end of the rack, thus holding both the jar and the cover in their proper places.

Since for different sized containers there is an optimum speed for obtaining the best grinding results, this particular mill is driven by a direct current motor, the speed of which can be varied by a rheostat.

This particular set-up can also be used for producing uniform mixtures such as those used in ceramics, paints, etc. The materials can be put in a bottle or other suitable container and subjected to the rolling process in exactly the same manner as the ball mill jars are used.

The ball jars used for this mill were purchased from the Ceramics Department, University of Illinois. The actual construction of the machine was done by Arthur E. Wood, mechanician for the Chemistry Department, who also deserves credit for his many valuable suggestions. The cost of materials, which included three small and two large jars, was about forty-five dollars.

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Determination of Viscosity of Small Samples of Oil from Oil-Impregnated Paper

Method and Apparatus

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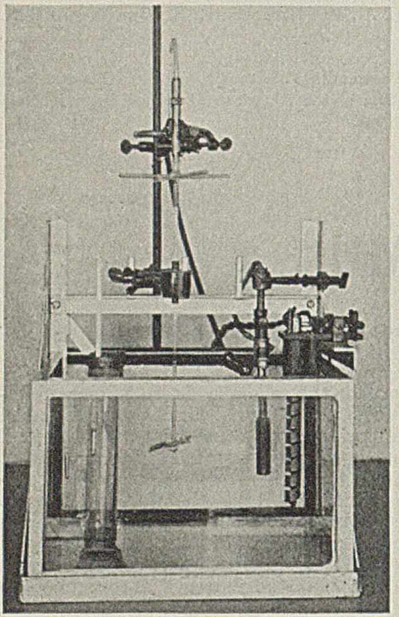

FIGURE 1. PHOTOGRAPH OF APPARATUS

IT HAS been observed in the examination of the insulation of paper- and oil-insulated high-voltage cables taken from service that the viscosity of the oil in the insulation varies markedly from the center to the outside of the cable. This condition was also observed in cables subjected to laboratory treatments simulating service conditions. In order to interpret these changes, it was necessary to evaluate them numerically. This was difficult because only 0.5 to 2 ml. of the oil were available for test.

In the course of the investigations, several methods for determining the viscosity of small amounts of oil were tried. The first was the Ostwald method, which had to be abandoned because of the time involved in making the determination and the difficulty encountered in introducing the viscous oil into the apparatus. The second, which involved the use of a calibrated pipet, also proved unsatisfactory because of the difficulty of making suitable orifices adaptable over the wide range of the various cable oils tested.

A method using the ball and inclined tube type of viscometer has been found to eliminate these difficulties. Although the apparatus and method described herein may have numerous shortcomings, they have been used successfully. They are applicable to viscosity determinations on small samples, are fairly rapid, and lend themselves to ease of manipulation.

Description of Apparatus

The essential parts of the apparatus which is shown in Figures 1 and 2 consist of a capillary tube of approximately 2-ml. capacity for holding the oil to be tested and a small steel ball, the diameter of which is approximately one-half that of the capillary. During the development of the apparatus, it was found that when the capillary tube was placed directly in the thermostatically controlled water bath good checks could not be obtained. This was attributed to the fact that the bimetallic temperature-control mechanism which was readily available at that time was not sufficiently sensitive to control the temperature more closely than 0.28° C. (0.5° F.). The tube is held in position in a concentric glass water jacket by means of rubber stoppers in such a manner that the capillary tube protrudes slightly through each end of the water jacket. By placing the concentric or "static" jacket around the capillary and then placing the jacketed tube in the water bath, a more nearly constant temperature could be obtained. The jacket also served to keep the tube nearer the desired temperature during the introduction of the oil into the tube. The temperature of the water surrounding the capillary tube is obtained by means of an A. S. T. M. viscometer thermometer (0.11° C., 0.2° F. graduations) inserted in the upper rubber stopper. During the determinations this part of the apparatus is immersed in a thermostatically controlled water bath.

The capillary tube is scaled each 4 cm., so that the viscosity may be measured by the time necessary for the ball to pass between any two or more divisions, depending on the viscosity of the oil and the amount of oil available.

Manipulation of Apparatus

The manner of determining viscosity values is as follows:

With the capillary tube, *B*, open at both ends, the oil to be tested is poured slowly into it, care being taken to entrap no air. Because of the high viscosity of the oil it will not flow quickly into and through the tube, so that the lower stopper can be removed. When the tube is completely filled or when all the oil available has been added, a small cork is inserted into the lower end of the tube. The jacketed capillary tube assembly is then placed in a transparent walled water bath, maintained at a desired temperature (37.8° C., 100° F., in the case of the determinations mentioned herein), in such a manner that the capillary tube is held at an angle of 60° from horizontal.

The ball, which has been brought to the temperature of the oil, is quickly introduced through the top end of the capillary tube. The measure of the viscosity is determined from the length of time in seconds required for the ball to travel between selected graduations on the tube. Viscosity values are converted to the terms of a standard viscosity scale by means of factors obtained during the calibration of the instrument using oils of known viscosity. In observing the position of the ball care should be taken that the eye is always in the same horizontal plane with the ball and at right angles with the vertical plane of the tube, so as to avoid parallax.

Using a ball weighing 0.0548 gram and with a diameter of 0.237 cm. (0.0935 inch) and times of 8 to 300 seconds for a travel of 90 mm., it was found that the range of viscosities which could be covered was about 0.70 to 25 poise, which, for the oils under consideration, is equivalent to about 300 to 10,000 seconds, Saybolt Universal.

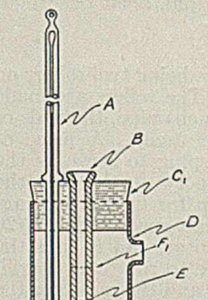

FIGURE 2. DIAGRAM OF ROLLING-BALL VISCOMETER

A. Thermometer, A. S. T. M.
B. Capillary tube
C_1, C_2. Rubber stoppers
D. Water jacket
E. Steel ball
F_1, F_2, F_3, F_4. Scale marks
G. Cork

Calibration of Apparatus

As it has been observed that oils extracted from aged cable sometimes exhibit viscosity values which vary over a wide range, it has been found necessary to calibrate the apparatus using several oils of known viscosity over a comparable range. The calibration consisted of a series of runs with the ball and inclined tube viscometer using oils of known viscosities. The conversion factors obtained from these data are used in the calculation of the viscosity of the test samples.

This work forms a part of a general research program on the deterioration of high-tension underground cable being undertaken by The Detroit Edison Company.

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Determination of Water in Glycerol

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IF WATER is the only impurity in glycerol, it can be determined by specific gravity and reference to the tables of Bosart and Snoddy (*2*). However, all commercial glycerol contains other impurities which affect the specific gravity, so that an accurate value for water cannot be obtained in this way. A knowledge of the true water content is often required—for example, in the explosives industry to compare nitroglycerin yields on the basis of dry glycerol. Also, a direct determination is necessary in the complete analysis of crude glycerol. The international committee which adopted standard methods of glycerol analysis in 1910 (*7*) did not specify a method for the determination of water, indicating the unsatisfactory status of the methods available at that time.

Various methods depending on the measurement of physical properties have been described. Schmidt and Jones (*10*) and Kameyama and Semba (*6*) measured conductivity of electrolytes dissolved in glycerol. Grün and Wirth (*3*) used the determination of boiling point as an indication of water content. Hoyt (*4*) gave data on refractive index of glycerol containing various percentages of water. It is obvious that all these methods have the common defect of being accurate only for solutions of pure glycerol and water.

Berth (*1*) used boiling tetrachloroethane to remove water from glycerol, condensing the vapors and collecting the water in a graduated tube. Hoyt and Clark (*5*) used toluene for the same purpose. Lawrie (*8*) mentioned the use of calcium carbide to liberate acetylene equivalent to the water present. He also gave in detail the method of Rojahn (*9*) as modified by this laboratory.

The original Rojahn method consisted of distributing about 1 gram of the sample of glycerol on ignited asbestos in a special weighing bottle and exposing it to phosphorus pentoxide in a desiccator evacuated to 10 to 15 mm. After 12 hours under these conditions, the loss in weight was calculated as per cent moisture. The modifications developed here consisted of an improvement in design of the weighing bottle, substitution of fine glass wool for asbestos, and extension of the time of desiccation to 24 hours.

The modified Rojahn method has been used for a number of years as a standard procedure, but has not been entirely satisfactory. Duplicate determinations under the same conditions usually showed good agreement, but often did not agree with determinations by other laboratories on portions of the same sample. In some cases, an experienced analyst was unable to check his previous determination at a later date. Therefore, a further investigation was made with the object of learning the cause of these variations.

Preparation of Pure Glycerol

Dynamite glycerol was refluxed with a large volume of toluene for 16 hours, collecting the water in a Bidwell-Sterling type of moisture-receiving tube. A considerable amount of the water was removed in this way. The toluene was separated from the glycerol in a separatory funnel, and the glycerol placed in a 3-liter distillation flask having a 25-cm. (10-inch) unpacked fractionating neck. It was then distilled slowly at about 5 mm. pressure and collected in a receiver which permitted fractionation without interrupting the distillation. The first 25 per cent of the distillate and a residue of about 15 per cent were discarded. Only the middle cut was retained. This distillation was repeated twice and a final middle cut was collected, without exposure to the air, in stoppered sample bottles, which were sealed with paraffin until used.

The determination of the specific gravity offers a convenient and reliable method for establishing the water content of pure glycerol (*2*). This method is recognized by the Committee on Glycerol Analysis and therefore has official status. Using it, the glycerol prepared as described above contained from 0.01 to 0.13 per cent of water. Considering the rapidity with which anhydrous glycerol absorbs moisture from the atmosphere and the necessary exposure in making a specific gravity determination, the purity and substantial freedom from water of the stock glycerol are well established.

In order to avoid absorption of moisture from the atmosphere, it was important that a technic for handling this essentially anhydrous glycerol should be developed. The following method was used:

The specific gravity was first determined in the usual manner in a Walker-type pycnometer. Upon completion, a one-hole rubber stopper was slipped around the outside of the neck of the pycnometer in an inverted position—that is, the large diameter of the stopper faced down. The capillary tube was now removed and the pycnometer quickly inverted over the mouth of a dry, tared Erlenmeyer flask, in which the inverted stopper fitted. As soon as the glycerol had been transferred, the pycnometer was removed and the flask carefully stoppered. Water and other impurities could now be added and their proportion determined by weight. The water found by the specific gravity determination on the purified glycerol was always included in the "calculated" water content of the sample. In order to remove samples for analysis, a Lunge pipet or a shortened 5-ml. pipet was used. In either case the pipet was introduced into the flask containing the glycerol through a rubber stopper, and filled by compressing a rubber suction bulb. In this way the glycerol was exposed to the atmosphere for a minimum of time, and no difficulty was experienced from this source.

Modified Rojahn Method

Portions of the specially purified glycerol, the water content of which had been established by specific gravity determinations, were made up to contain various percentages of water, such as are normally found in dynamite glycerol and crude glycerol. These were analyzed by the modified Rojahn method, as shown in Table I, which also includes similar determinations made in the presence of trimethylene glycol, a common impurity which is more volatile than glycerol.

The trimethylene glycol was prepared by distilling Eastman's practical grade at atmospheric pressure and collecting the fraction boiling at 212.6° to 214.5° C. This portion was redistilled once. It then contained 0.29 per cent of water (de-

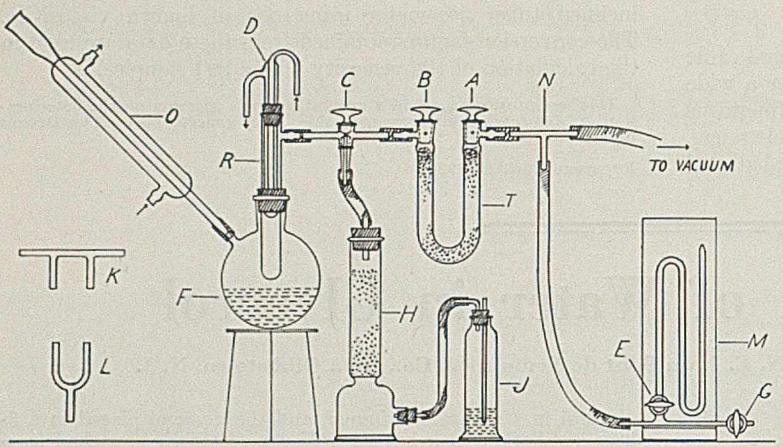

FIGURE 1. DIAGRAM OF ASSEMBLED APPARATUS

A, B. Stopcocks of U-tube
C. Three-way stopcock, Arthur H. Thomas Co., catalog No. 9294
D. Dephlegmator (details Figure 2)
E. Stopcock closing manometer
F. Flask (details Figure 2)
G. Stopcock opening to atmosphere
H. Drying cylinder, height 260 mm., charged with potassium hydroxide pellets to exclude atmospheric moisture when vacuum is released
J. Bubble counter, half-filled with light oil (Nujol) to control rate of release of vacuum
K. Manifold for double apparatus
L. Y-tube for double apparatus
M. Mercury manometer
N. T-tube
O. Liebig condenser, 250-mm. size
R. Sample tube (details Figure 2)
T. U-tube, 150-mm. size with glass stopcocks

termined by the vacuum distillation method, described below). The water added in this form was insignificant, but was nevertheless included in calculating theoretical per cent.

TABLE I. DETERMINATION OF WATER IN KNOWN SAMPLES BY DESICCATION OVER P_2O_5

Sample Contains Water	Sample Contains Trimethylene glycol	Water Found 24 Hours	Water Found 48 Hours	Water Found 72 Hours	Water Found 96 Hours
%	%	%	%	%	%
0.09	None	0.10	0.26	0.33	0.41
0.63	None	0.78	0.68	0.69	..
0.70	None	0.79	0.83	1.01	1.03
1.49	None	1.53	1.76	1.88	..
1.14	1.01	1.25	1.64	1.81	..
4.93	None	{4.71 {4.76	4.97 4.92	4.97 4.92	.. ..
4.85	4.66	5.33	5.79	6.14	..

TABLE II. WATER FOUND BY DESICCATION OVER P_2O_5

Water in Samples	Temperature Min.		Temperature Max.		Time Exposed 24 Hours	Time Exposed 48 Hours	Time Exposed 72 Hours
%	° C.	° F.	° C.	° F.	%	%	%
1.49	27.22	81	32.78	91	1.89	2.01	2.11
1.49	12.78	55	23.33	74	1.17	1.27	1.45

The samples containing trimethylene glycol show a relative error of +10 per cent at 24 hours. For the same period the other analyses in some cases check the known value closely, though all the errors are plus except one. Additional 24-hour periods of drying cause further losses, greater when trimethylene glycol is present. The loss in weight in 24 hours cannot be depended upon to give the true water content of glycerol and, when a longer period is used, the volatilization of glycerol introduces serious errors. It is reasonable to suppose that glycerol is volatilized in the first 24 hours also. Hence, where results check the theoretical per cent of water, it is probably accidental, due to a balance between glycerol volatilized and water not removed.

The Rojahn method has several additional undesirable features, relating especially to technic. Because of the small weight of sample taken for analysis, an error of 0.1 mg. in weighing causes an error of approximately 0.01 per cent in terms of water content. Furthermore, the presumably bone-dry glycerol must be exposed momentarily, while the covers are placed on the individual weighing bottles. A definite difference in per cent of water has been noted following directly the order in which the lids are placed on the bottles. The 24-hour period required before results are available may often be a decided disadvantage in routine work. While time and pressure are controlled within well-defined limits in the method, no temperature control is provided. That temperature variation is a definite factor, perhaps the greatest cause of error in the Rojahn method, is indicated by the data in Table II.

Other Methods

Objections to methods depending on determination of physical properties have already been stated. Those in which water is removed by boiling with an organic solvent and collecting the water in a graduated tube have the disadvantage that some glycerol distills over and is measured in the water layer. In the method of Hoyt and Clark (*5*), it is recommended that a correction for glycerol be made by an acetin determination on the water layer. This introduces a tedious and cumbersome procedure, making the method impracticable.

Acetylene evolution methods were thoroughly investigated. It was found that the reaction between calcium carbide and water could not be carried to completion without causing decomposition of the glycerol. No consistent results could be obtained on known samples.

Vacuum Distillation Method

Experience with other methods investigated indicated that the rapid and complete separation of water from glycerol requires elevated temperatures and diminished pressure, besides a provision for counteracting the vapor pressure of glycerol and other normal impurities under these conditions. Duplication of results demands control of these conditions within well-defined limits. The vacuum distillation method was developed on these principles.

The water is distilled from a sample of glycerol at 100° C. and 2- to 3-mm. pressure and absorbed in a weighed U-tube charged with anhydrous magnesium perchlorate (Dehydrite). A water-cooled dephlegmator, interposed between the sample and U-tube, condenses vapors of glycerol and lower boiling impurities. After weighing the U-tube, it is replaced in the apparatus and the distillation continued for two additional short periods to determine the gain in weight of the U-tube caused by leakage. This blank must be deducted.

APPARATUS. The assembled apparatus is shown in Figure 1. It is connected to a "Hyvac" pump, not shown. Provision may be made for making two simultaneous determinations in which case the manifold, *K*, replaces *N*, and a Y-tube, *L*, is used in the top of the drying cylinder, *H*, instead of the straight glass tube. The flask, *F*, serves as a bath for maintaining the sample at approximately 100° C. It is filled with water, to a point about 1 cm. below the end of the tube, so that only the vapors heat the tube. The condenser, *O*, is used to maintain this level without refilling. A few glass beads in the flask reduce the tendency to superheating. While the flask, sample tube, and dephlegmator are simple, they are not listed in catalogs and, therefore, are shown in detail in Figure 2.

Special attention should be given to the preparation of the U-tube, *T*. It should always be filled before the ground-glass surfaces are lubricated and these surfaces should be protected from particles of glass wool and dust from the desiccant with a cylinder of paper. The tube should be filled quickly with anhydrous magnesium perchlorate, after which a small wad of fine glass wool should be placed in each arm of the tube (cotton must not be substituted here). The ground-glass surfaces are best lubricated with "lubriseal." A piece of wire is used to suspend the tube on the balance. Before the U-tube is weighed, it is always wiped with a dry, clean cloth.

In preparing the sample tube, *R*, it is first fitted with a No. 8 rubber stopper, which has been drilled so that it can be placed around the outside of the tube in a position about midway of its length. A twist of copper wire, placed around the tube between this stopper and the side arm, serves as a convenient support for suspending the tube on the analytical balance. A wad of fine glass wool, about 40 to 50 mm. in depth, is packed in the bottom. The tube thus prepared is dried in an oven, preferably overnight, at 95° to 100° C. If a tube is needed on short notice, it may be dried in position in the apparatus at 100° C. and 2- to 3-mm. pressure for 15 minutes. When dry, the open end is closed with a rubber stopper and the side arm with a short piece of rubber tubing, plugged with a piece of glass rod. After being cooled to room temperature, the stopper should be raised momentarily in order to bring the pressure within the tube to normal. The tube thus prepared is weighed to the nearest milligram.

In taking a portion of a sample for analysis, it has been found useful to employ an ordinary 5-ml. pipet which has had both ends cut off at a point about 75 mm. from the bulb. The pipet is fitted with a one-hole rubber stopper of the size used for closing the end of the sample tube, *R*. This is placed against the lower side of the bulb of the pipet. The upper end of the pipet is closed with a 2-ml. medicine-dropper bulb, while to the lower end is attached a piece of glass tubing by means of a short piece of rubber tubing. The length of the glass tube may be varied according to the size of the bottle containing the sample. The sample is drawn into the pipet using a rubber suction bulb, after which the top is closed with the medicine-dropper bulb. The glass tube is then removed from the lower end of the pipet, which is carefully placed in the sample tube, *R*. It is then discharged by slowly compressing the medicine-dropper bulb several times, thus introducing a sample of 3 to 5 grams into the sample tube, prepared as above. Care must be taken not to deposit any glycerol on the side of the tube.

METHOD OF OPERATION. At the end of a determination, the apparatus is left completely assembled until the next analysis is made.

Assuming this to be the starting point and referring to Figure 1, stopcock *G* is closed, cocks *E*, *A*, and *B* are opened, and cock *C* is turned so as to connect tube *R* with U-tube *T*. The vacuum pump is then started and run 5 to 10 minutes. This serves to dry out the system after standing and to bring the U-tube, *T*, to the proper condition for weighing. This time may be employed in weighing the sample. To release the vacuum, close cocks *E* and *A*, stop vacuum pump, and open cock *G;* then turn cock *C* to allow air to enter the U-tube slowly through *H* and *J;* close cock *B*.

Place the dephlegmator, *D*, which has been dried in an oven, in the sample tube, *R*. Connect *R* to the weighed U-tube *T*, through the three-way stopcock, *C*, and put in place in the flask, *F*. Make water connections to dephlegmator *D*, and apply heat to flask *F*. Close stopcock *G*, open *E*, *A*, and *B*, and turn *C* to connect *R* with *T*. Start the vacuum pump, and continue the dehydration for 45 minutes, accurately timed. Release the vacuum as described above. After turning *C* so that *R* is closed off, remove *T* and weigh to 0.1 mg. The drying cylinder, *H*, must be inspected occasionally to see that it is not clogged. If it is, the vacuum may not be completely released in the U-tube and weighings will be erratic.

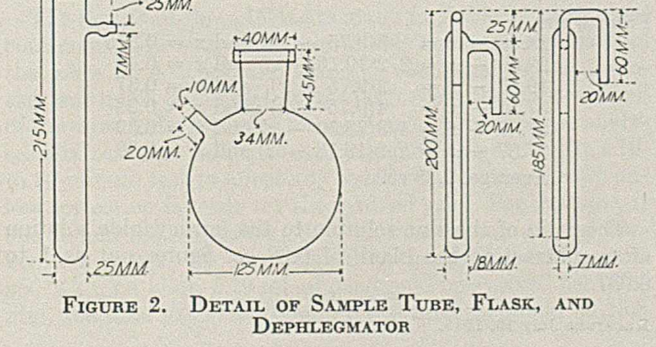

FIGURE 2. DETAIL OF SAMPLE TUBE, FLASK, AND DEPHLEGMATOR

Now restore the U-tube to the apparatus, close cock *G* and open *A*. Start the vacuum pump, turn *C* to connect sample tube *R* to U-tube *T*, then open cocks *B* and *E*. Continue the dehydration for 15 minutes, when the U-tube is again removed and weighed as before. At least two periods, 15 minutes in length, should be used to determine the completion of the dehydration and to estimate the gain due to leakage of the apparatus. The leakage gain should be constant within a few tenths of a milligram and be less than 1.5 mg. Constant leakage gains larger than this denote a need for renewal of the rubber somewhere in the system. Results are calculated as follows:

$$\frac{\left(W - \frac{TC}{15}\right) 100}{\text{Weight of sample}} = \text{Per cent moisture}$$

in which W = total weight gained by U-tube
T = total time elapsed in minutes
C = average correction due to leakage for a 15-minute period

The course of the dehydration is rapid for the first 30 to 45 minutes, at which time there is a sharp change in the rate of dehydration and from here on the gain is small but constant. That this is due to leakage and not to slow volatilization has been demonstrated by runs made with the sample tube empty. It is logical, therefore, that a leakage correction be made. It must, however, be determined for each run, as it varies slightly, depending on the tightness of the apparatus and atmospheric conditions.

TABLE III. ANALYSIS OF KNOWN SAMPLES BY VACUUM DISTILLATION METHOD

Water Present, %	Trimethylene Glycol Present, %	Per Cent of Water Found 1	2	3	4	Mean	Deviation From mean	From theory
0.02	..	0.02	0.04	..	..	0.03	0.01	+0.01
0.06	..	0.03	0.05	0.04	..	0.04	0.01	−0.02
0.05	..	0.03	0.05	..	..	0.04	0.01	−0.01
0.68	..	0.72	0.68	0.69	..	0.70	0.02	+0.02
1.10	..	1.06	1.11	1.10	..	1.09	0.03	−0.01
1.49	..	1.51	1.46	1.51	1.47	1.49	0.03	0
4.93	..	4.83	4.90	4.83	..	4.85	0.05	−0.08
0.06	1.19	0.04	0.05	0.04	..	0.04	0.01	−0.02
1.19	1.18	1.23	..	..	..	1.23	..	+0.04
1.10	1.15	1.14	1.14	1.10	1.14	1.13	0.03	+0.03
1.14	0.97	1.08	1.15	1.11	..	1.11	0.04	−0.03
4.85	4.65	4.90	4.84	4.94	4.86	4.89	0.05	+0.04

While the first determination is in progress, the sample for the next may be prepared or other work carried on. When the determination is complete, the water is turned off the dephlegmator and the water inlet tube removed first. This allows the water to siphon out of the dephlegmator, and prevents flooding of the apparatus.

The above procedure is given in considerable detail, but with a little experience it will be found simple and convenient. A determination may be completed in 2 hours or less. The attention of the analyst is required during only a part of this time so that other work can be carried on simultaneously.

DATA. The same glycerol was used to prepare known samples as in the study of the modified Rojahn method. Trimethylene glycol, also prepared as above, was added to several samples to demonstrate that it does not interfere. The results obtained are shown in Table III.

The data on known samples show that the vacuum distillation method is precise and accurate for determination of water in pure glycerol and in glycerol containing trimethylene glycol. The relative error is not greater than 3 per cent in samples containing normal amounts of water. With ordinary care there is no difficulty in getting the agreement on duplicates shown in Table III. A limited number of check analyses by other laboratories have shown excellent agreement, which is gratifying in view of the fact that they had no previous experience with the method.

In Table IV are shown typical results obtained on analysis of commercial crude and dynamite grades of glycerol in comparison with similar analyses by the modified Rojahn method.

TABLE IV. DETERMINATION OF WATER IN COMMERCIAL GLYCEROL

(Comparison of the new method with the Rojahn method)

	Per Cent of Water Found					
	Vacuum distillation			Desiccation over P_2O_5 for:		
Sample	1	2	Av.	24 hours	48 hours	72 hours
Dynamite No. 1	0.44	0.45	0.45	0.75	0.81	0.90
Dynamite No. 2	0.73	0.74	0.74	0.82	0.93	1.04
Crude No. 1	5.79	5.77	5.78	5.57	5.92	5.92
Crude No. 2	4.41	4.43	4.42	3.89	4.52	4.77

This is further evidence that the desiccation over P_2O_5 is unreliable. One of the dynamite glycerols showed fairly good agreement with the new method in 24 hours, while the other gave a result almost 70 per cent too high. In the crudes both were somewhat low at 24 hours and gave more nearly correct values at 48 hours. The longer time required appears to be caused by the formation of a layer of phosphoric acid over the surface of the phosphoric anhydride, thus reducing its efficiency as a desiccant. Over activated alumina, a desiccant which is granular and porous but admittedly of lower efficiency than P_2O_5, a value of 4.50 per cent of water was obtained on crude No. 2 in 24 hours.

Precaution

Anhydrous magnesium perchlorate should be classed as a potentially dangerous chemical, just as are sulfuric acid, metallic sodium, etc. Accidents have resulted from the accidental admixture of sulfuric acid with this compound to form perchloric acid, which, in turn, exploded in contact with organic matter. In view of this, the following precautions must be followed:

1. Never use sulfuric acid to replace potassium hydroxide in drying tower *H*.
2. The chemical should be kept free from organic material as far as possible. Never use a cotton plug to replace glass wool in the U-tube.
3. The chemical should be handled and the spent material disposed of only by the chemist, and never should be left to a janitor or clean-up boy.
4. The spent chemical should not be thrown into waste jars or sinks. It should be dissolved in water and disposed of in a drain, ditch, or other safe place outside the laboratory.

Where these precautions are observed, there should be no trouble resulting from the use of anhydrous magnesium perchlorate as a desiccant.

Summary

A critical study has been made of the modified Rojahn method, showing that it only approximates the true water content. It gives varying results due to inadequate control of the following factors: (1) the temperature of the room as it affects the volatility of glycerol at the reduced pressure; (2) the presence of varying amounts of volatile impurities other than water; and (3) the loss of efficiency of the desiccant when comparatively large quantities of water are present, as in crude glycerol.

A new method, designated the vacuum distillation method, is described. It is based on the removal of water from glycerol at 100° C. and 2- to 3-mm. pressure. The volatility of the glycerol and low-boiling impurities in glycerol is controlled by a reflux condenser, which separates these ingredients from the water vapor. The water vapor is absorbed in a desiccant and weighed.

The vacuum distillation method is shown to give the true water content of glycerol with a relative error of not over 3 per cent on samples containing 0.5 to 5 per cent of water. Results are readily duplicated and are available in a maximum time of 2 hours. The attention of the chemist is required during only a fraction of this time. The method is applicable to crude and refined glycerol.

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Calculating the Blank

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MANY volumetric determinations require an excess of the reacting solution to produce a visible end point. For accurate work this excess must be subtracted from the total amount added in order to obtain the correct titer. The magnitude of this excess may be determined directly by titrating a blank, on which the end point is apt to be uncertain, or it may be calculated in the following manner.

If two or more samples of different weights are run under exactly the same conditions, the amount of excess reagent should be the same in each case and simple equations may be used to calculate it.

Example

A zinc solution was titrated with ferrocyanide, using uranium nitrate as outside indicator and a volume of 200 cc. at the end point with the following results:

10 cc. of zinc = 9.75 cc. of ferrocyanide
20 cc. of zinc = 19.13 cc. of ferrocyanide
30 cc. of zinc = 28.50 cc. of ferrocyanide
40 cc. of zinc = 37.87 cc. of ferrocyanide

From which

$$\begin{aligned}
28.50 - x &= 3(9.75 - x) \text{ and } x = 0.375\\
28.50 - x &= 3/2(19.13 - x) \text{ and } x = 0.40\\
19.13 - x &= 2(9.75 - x) \text{ and } x = 0.37\\
37.87 - x &= 4(9.75 - x) \text{ and } x = 0.38\\
37.87 - x &= 4/3(28.50 - x) \text{ and } x = 0.39\\
37.87 - x &= 2(19.13 - x) \text{ and } x = 0.39
\end{aligned}$$

Average, 0.38 cc.

The ratio of the zinc solution to the ferrocyanide solution after subtracting the blank of 0.38 cc. figures out as 1 to 0.937.

RECEIVED July 15, 1935.

The Reactivity of Coke

An Improved Method for Determining the Reactivity of Coke in Carbon Dioxide

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IN THE investigation of the gas-, coke-, and by-product-making properties of American coals, thirty coals have been tested by the Bureau of Mines–American Gas Association method (*4*) at carbonizing temperatures of 500°, 600°, 700°, 800°, 900°, 1000°, and 1100° C. The charges are large enough so that the structure of the coke is similar to that produced industrially. Certain physical and chemical properties of the carbonization products have been reported (*4*); this investigation of the reactivity of the cokes is a continuation of such studies.

Development of the Method

A wide variety of methods for determining the reactivity of coke is available, most of them using carbon dioxide or air as reactants and a few using steam. The Bureau of Mines used all three media in a previous study (*3*) but prefers carbon dioxide because it does not have the disadvantage of large dilution with an inert gas. Steam is particularly applicable where it is desired to test the coke as water-gas fuel. Carbon dioxide was adopted for the present study.

The temperature at which reactivity usually is measured is 900° to 950° C., which is approximately that at which high-temperature cokes are made. Heating to a higher temperature than that used in manufacture may change the structure and chemical composition of the coke, which will influence the determination of initial reactivity. In comparing the reactivities of cokes made at temperatures from 500° to 1100° C. it was necessary to obtain initial reactivity as nearly as possible, since low-temperature cokes change structurally and chemically on reheating, as will be shown. Also, the reaction temperature chosen must be high enough to distinguish between the insensitive high-temperature cokes and yet not approach the upper theoretical limit for low-temperature cokes. Time of heating is also a factor.

CHANGES IN LOW-TEMPERATURE COKES CAUSED BY REHEATING TO HIGH TEMPERATURES. The first method considered involved bringing a 10.5-ml. sample sized to pass 10-mesh and remain on 20-mesh to 950° C. in nitrogen, which required about 1 hour, flushing out the nitrogen with carbon dioxide, and then passing exactly 100 ml. of carbon dioxide in 20 minutes. The gas from this final 100 ml. of carbon dioxide was collected in a buret over potassium hydroxide, which absorbed the excess. The residual gas, presumably pure carbon monoxide, was measured and its amount reported as per cent reactivity. Residual gases from several low-temperature cokes tested in this manner contained appreciable amounts of hydrogen and methane.

Devolatilization tests at 950° C. were then made on three cokes from Sewell bed coal, which were heated in nitrogen from room temperature to 950° C. in 70 minutes. The gases evolved were collected over dilute sulfuric acid and analyzed.

The results of these tests are given in Table I. The gases continued to be evolved in appreciable amounts from each of the cokes for 4 hours, and although the initial rate of evolution was much the lowest for the 900° coke, the rates were all of the same order after the second hour. From the gas analyses it is clear that sufficient carbon monoxide is evolved in a 10- to 20-minute test to affect any reactivity result seriously unless correction is made for the evolved gas. For example, if one should make a test at 950° C. on 10.5 ml. of coke carbonized at 900° C. devolatilized by heating in nitrogen at 950° C. for 1 hour, 0.79 ml. of gas would be evolved per minute; the total gas in a 20-minute test interval would be 15.8 ml. The volume of carbon monoxide would be 2.55 ml. Obviously it will be impractical to determine reactivity of coke accurately by any method involving the direct use of carbon monoxide content of the gases from the test as a measure thereof.

TABLE I. GASES EVOLVED FROM COKES ON REHEATING AT 950° C.

(Coal No. 27)

Time Heated at 950° C., Hours	Average Rate of Gas Evolution during 1-Hour Periods, Cc./Min./10.5 Cc. of Coke 500° coke	 700° coke	 900° coke
1	Gas not collected		
2	1.52	1.45	0.79
3	0.57	0.55	0.48
4	0.45	0.31	0.40
Gas evolved	Analysis of gas[a]		
	%	%	%
CO_2	0.2	0.5	0.4
H	75.3	75.6	76.9
CO	15.6	15.8	16.2
CH_4	2.4	2.1	1.5
N	6.3	6.0	5.0
Total gas collected, cc.	152	139	100

[a] Gas from 500° and 700° cokes during 3rd and 4th hours, from 900° coke during 2nd, 3rd, and 4th hours.

Additional data on the gases evolved on reheating were afforded by a carbonization test in which a 70-pound charge of coke made from Freeport coal at 600° was cooled in the retort and then recarbonized at 1000° C. The time required for recarbonization was 2 hours and 53 minutes, and the yields of volatile products were: 3.9 per cent gas, 0.7 per cent tar, 0.05 per cent light oil, no liquor, and 0.04 per cent ammonia. The yield of gas on the volume basis was 5100 cubic feet per ton of coal originally charged, and most of this gas was hydrogen (Table II).

TABLE II. GAS OBTAINED ON RECARBONIZING A CHARGE OF 600° COKE AT 1000° C.

Gas	%
CO_2	0.7
Illuminants	0.6
O_2	0.9
H_2	83.3
CO	3.8
CH_4	7.1
C_2H_6	0.0
N_2	3.6
Total	100.0

The shrinkage of the charge as a whole due to recarbonization was approximately 5 per cent, but the shrinkage of actual coke substance probably was minimized by development of radial fissures in the monolithic charge which would cause apparent expansion.

SHRINKAGE OF COKE SUBSTANCE ON REHEATING. Under the reactivity test conditions first selected—that is, heating to 950° C. in nitrogen in 1 hour—shrinkage was observed for several cokes from coals of different ranks, illustrated by the results for Illinois No. 6 coal given in Table III.

TABLE III. SHRINKAGE OF COKES FROM ILLINOIS COAL ON REHEATING TO 950° C. IN REACTIVITY TEST

Carbonizing Temperature ° C.	Shrinkage %
500	21
600	21
700	10
900	3
1100	nil

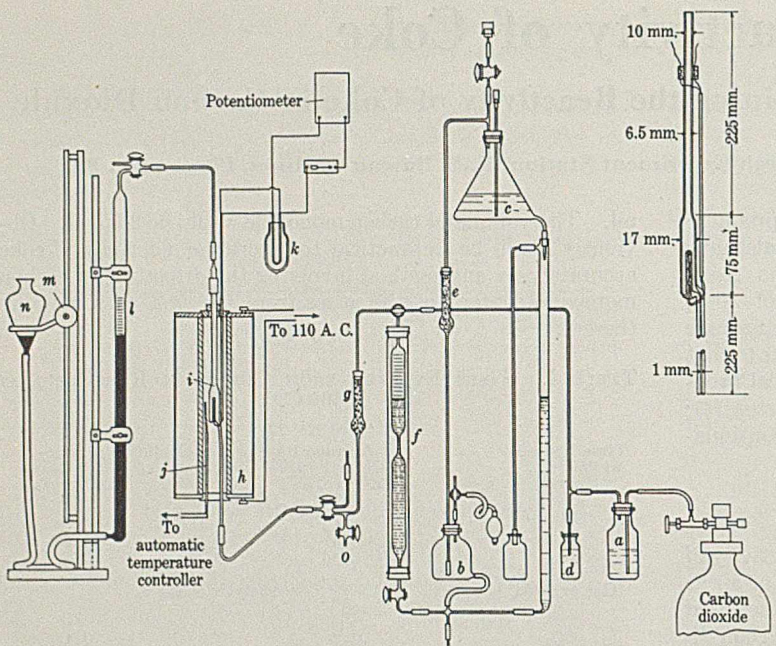

FIGURE 1. DIAGRAM OF APPARATUS

Since no fissures developed in the particles of coke and no new particles finer than 20 mesh were produced, the shrinkage obtained represented actual shrinkage of the coke particle. Furthermore, it appeared on comparison of the heated and unheated cokes under the microscope that the size of exposed cells had diminished. On reheating cokes from Summerlee coal shrinkage began at approximately 700°, was most rapid between 700° and 760°, and was practically uniform between 760° and 900° C.

Obviously, reheating low-temperature cokes tends to cause both chemical and structural changes which may affect the reactivity result obtained. Therefore, when data on initial reactivity are wanted it is desirable to have the test temperature as low as practical, to reduce the heating time as much as possible, and to reduce the "dead space" in the reaction tube to a minimum, so that the time for sweeping out the nitrogen may be decreased.

SIZE OF COKE AND RATE OF PASSAGE OF CARBON DIOXIDE. Previous experience had shown that reactivity could be determined satisfactorily with 10 to 15 ml. of 10- to 20-mesh (U. S. standard sieve) coke, passing 5 ml. of carbon dioxide per minute. This rate, which was continued throughout this investigation, is equivalent to a flow of 0.5 ml. of gas per ml. of coke per minute and is approximately the same as that used by Jones, King, and Sinnatt (*5*) in their standard method for determining reactivity of coke in carbon dioxide. With slight modification the writers have adopted the method used by these investigators for measuring and passing the carbon dioxide into the reaction tube.

DESIGN OF REACTION TUBE. A fused silica tube was designed so that the dead space to be swept out in starting a test would be small as possible, and was made with a bulb of size just sufficient to contain the sample of coke. A capillary tube was sealed to one end of the bulb for introducing the gas, and a tube of larger bore was sealed to the other end for charging the sample. A thermocouple well was fused into the bulb or coke chamber, extending half-way to its center. This permitted charging the coke, already contained in an inert atmosphere, into the preheated furnace, with the thermocouple in place, thus exposing the coke to the test temperature for a minimum time before the test was begun. Those methods in which the coke is charged into a cold furnace and the whole system heated gradually to the test temperature may be criticized if used for testing low-temperature cokes, because of changes brought about in the coke by prolonged heating.

CHOICE OF REACTION TEMPERATURE. As a basis for choice of the reaction temperature tests of cokes from several coals were made at 800°, 850°, 900°, and 950° C. At 800° most high-temperature cokes are so slightly reactive that no differences are apparent. At 900° and 950°C. the low-temperature cokes are generally so highly reactive that all approach the upper limit of reactivity for a practical rate of gas flow. The results at 850° C. for both high- and low-temperature cokes are well distributed over the theoretically possible range, and therefore this was the test temperature adopted. Reactivities are expressed as the per cent of carbon dioxide converted to carbon monoxide.

Apparatus and Procedure

The apparatus finally adopted is shown in Figure 1. The water-jacketed buret, *f*, is constricted at the middle so that the volume of each half is 100 ml., and is connected to a vertical tube of uniform bore into which a saturated solution of magnesium chloride may flow from the reservoir, *c*. This reservoir is fitted with a capillary drain and an adjustable air inlet tube by which the flow of liquid into the buret may be regulated. The lower bottle, *b*, to which the aspirator bulb is connected, serves as a receiver for the solution in the buret as it is displaced by carbon dioxide. The solution may be forced from this bottle by air pressure upward through the glass wool filter, *e*, and into the reservoir, *c*. Capillary glass tubing connects the buret to the calcium chloride drier, *g*, and thence to the inlet of the silica reaction tube, *i*.

The reaction tube assembly is shown in detail in Figure 1. The inlet is capillary silica and the outlet of small-diameter silica with a bore large enough to permit charging and discharging the granular coke. The volume of the coke chamber is 10.5 ml., and the total volume of the silica assembly, including inlet and outlet tubes, is 18.5 ml. A small, thin-walled silica tube with closed end is sealed into the lower end of the coke chamber, projecting to its center, to serve as a thermocouple sheath.

The furnace is heated electrically and is provided with an automatic temperature controller. That portion of the furnace containing the coke chamber was tested under conditions of automatic control and found to be heated uniformly.

The silica tube outlet, which also serves for charging and dis-

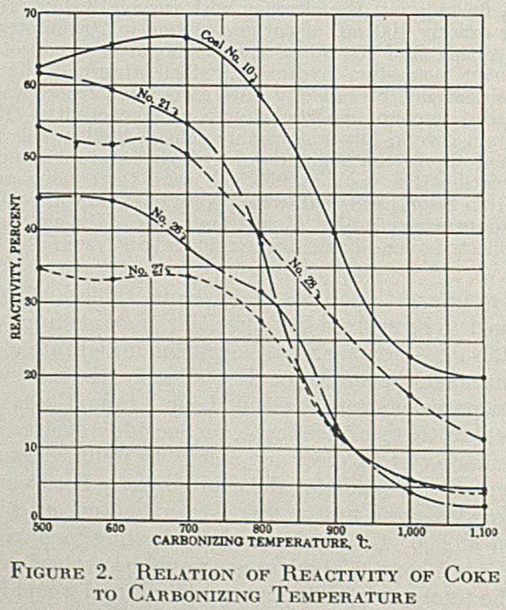

FIGURE 2. RELATION OF REACTIVITY OF COKE TO CARBONIZING TEMPERATURE

Table IV. Analysis and Plastic Properties of Coals

(In order of decreasing fixed carbon in coal)

Coal No.	Bed	State	County	Dry Mineral-Matter-Free Fixed Carbon	Proximate Analysis (as Carbonized Basis)				Modified Layng-Hathorne	
					Moisture	Volatile matter	Fixed carbon	Ash	Plastic range	Maximum pressure, mm. of water
				%	%	%	%	%	° C.	
26	Sewell	W. Va.	Raleigh	78.6	1.3	20.8	75.8	2.1	119	600
27	Sewell	W. Va.	Fayette	72.5	1.9	26.5	69.2	2.4	133	910
28	Pittsburgh	Pa.	Fayette	62.6	1.8	35.1	57.7	5.4	61	340
10	Illinois No. 6	Ill.	Franklin	60.6	7.9	32.1	47.7	12.3	45	26
21	Green River	Ky.	Muhlenberg	57.0	10.1	36.2	47.0	6.7	49	55

charging, is connected as shown to a glass capillary leading to a mercury-filled buret of 200-ml. capacity, which serves to collect the gaseous products of the reaction. A leveling bottle mounted on a suspension arranged to travel over a gear rack permits adjusting the level of the mercury in the buret uniformly and slowly.

A 10.5-ml. sample of coke was used for each test. It was poured through the silica charging tube into the reaction chamber and settled with slight tapping to the junction of the chamber and the tube. As the furnace was vertical the charged coke particles were not free to move, and the fuel bed was uniform at the beginning of all tests. The coke did not enter the capillary gas-inlet tube. After charging, nitrogen was passed through the coke to displace the air.

With the furnace previously heated to 850° C., a cap was placed on the charging or outlet tube, and after the rubber tubing connecting the capillary to the nitrogen cylinder was removed the charge was placed in the furnace. The connection to the capillary inlet was made, the cap removed from the outlet, and connection made to the mercury-filled buret. The 3-way cock of the latter buret was left open to permit the escape of gases while the coke chamber was coming up to temperature.

The magnesium chloride solution was forced up into the reservoir, *c*, and the air inlet of this reservoir was set at a point (predetermined) which insured the required drip of solution to expel the carbon dioxide from the buret at the test rate of 5 ml. per minute. The volume of the carbon dioxide in the lower half of the buret was reduced to exactly 60 ml., and the test was started exactly 5 minutes after charging, this period being sufficient to bring the temperature of the coke up to 850° C. With the liquid in the tube at the same level as that in the buret, thus insuring atmospheric pressure therein, the gas flow through the coke was started, the effluent gases being vented at the 3-way cock. During the 12-minute period in which the gas from the lower half of the supply buret was displaced, the temperature and the rate of gas flow were checked. As the last of the gas was expelled the 3-way cock was turned so that the effluent gases collected in the buret, and during the remainder of the test atmospheric pressure was maintained inside the system by slowly lowering the mercury reservoir.

With the carbon dioxide flowing at the rate of 5 ml. per minute the time required for a determination was 20 minutes. After a little experience it was not difficult to obtain good adjustment of the rate, and the test periods, which were all timed, were close to that required. After passage of exactly 100 ml. of carbon dioxide the collected gases were measured and analyzed for carbon dioxide, that found being the residue not reacting with the coke. The difference between this volume and 100 is equal to the per cent of carbon dioxide reacting and is the reactivity sought. Each result reported is the average of two determinations agreeing to within 1.0 per cent. In a few cases it was necessary to make more than two tests because of wider variations.

Cokes Tested

The cokes selected for study were made from samples representing five ranks of coking coals according to the proposed classification of the American Society for Testing Materials (*1*). The proximate analyses of these coals and their plastic properties as determined by the Layng-Hathorne method are shown in Table IV. The coals were carbonized by the Bureau of Mines–American Gas Association method. Chemical analyses and certain physical properties of the cokes have been published (*4*), but since no relationship was noted between these properties and the results of the reactivity tests they are not included here.

Results of Tests

Table V and Figure 2 show the results obtained by this method. Cokes made at 500° have reactivities of 34.6 to 62.8 per cent. The 600° cokes are of nearly the same order of reactivity as those made at 500°, four being slightly less reactive and one (No. 10) slightly more reactive. Of the 700° cokes, three decrease in reactivity from that obtained at 600°; No. 10 increases, whereas the reactivity of 700° coke from coal No. 27 remains approximately the same as the 500° and 600° cokes from this coal. The reactivities of all the cokes decrease as the temperature of carbonization is raised to 800°, 900°, and 1000°. The 1100° cokes generally are less reactive than those made at 1000°, but this difference is marked only in the case of the reactive No. 28 and No. 10 cokes. Summarizing these results, it may be concluded that reactivity of coke from a given coal decreases with increase in the carbonizing temperature and that this decrease is most marked between carbonizing temperatures 700° and 900°.

There is no direct relation between the fixed-carbon content of the coal (Table IV) and the reactivity of the corresponding coke. While it may be true that the rank of a coal affects the reactivity of the coke made from it, other factors are apparently of sufficient influence to change entirely the order in which reactivities of cokes align themselves in relation to this property in the coals.

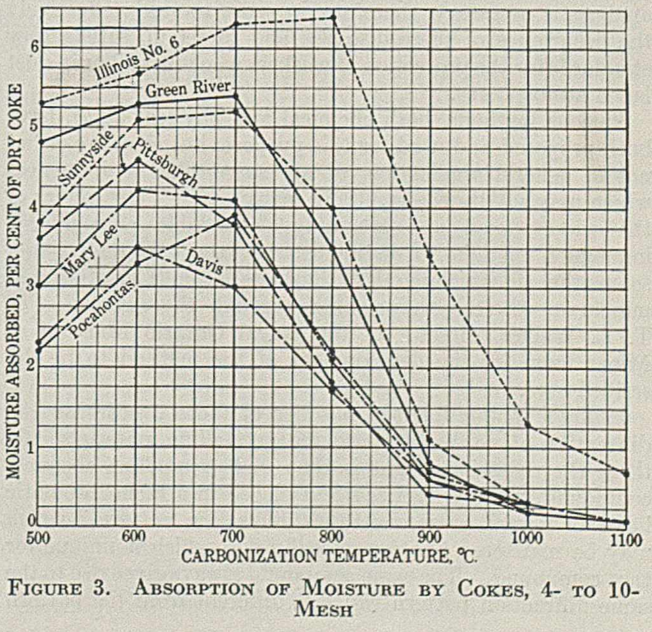

Figure 3. Absorption of Moisture by Cokes, 4- to 10-Mesh

Table V. Reactivity of Cokes in Carbon Dioxide at 850° C.

Coal No.	Carbonization Temperature, ° C. 500	600	700	800	900	1000	1100
10	62.8	65.8	66.9	58.7	39.9	22.9	20.1
21	61.9	59.4	54.7	38.4	12.7	6.4	4.9
28	54.1	51.8	50.7	39.3	27.9	17.7	11.5
26	44.1	44.0	37.5	31.7	13.2	4.3	5.0
27	34.6	33.3	33.9	27.9	12.1	6.6	4.4

These cokes were among those used by Davis and Auvil (*2*) in their study of electrical conductivity. They found that the electrical conductivity of the 800° cokes increases and the plastic range decreases in the order No. 10, 21, 28, 26, and 27, which is also the order (Figure 2) of reactivity in which the 500°, 600°, and 700° cokes align themselves. It is not true that cokes made from coals of different rank invariably will have reactivities aligning with rank.

Relation of Reactivity to Hygroscopicity of Coke. Reynolds recently published results (*6*) of an investigation of the hygroscopicity of cokes made at different carbonizing temperatures by the Bureau of Mines–American Gas Association method. Two of the series of cokes used (coal No. 10 from Illinois No. 6 bed and coal No. 21 from Green River bed) were the same samples used for the reactivity tests given in this paper. The curves showing change of hygroscopicity with carbonizing temperature (Figure 3) and reactivity (Figure 2) exhibit similar trends. The main difference relates to the 500° cokes, which are invariably of lower hygroscopicity than those made at 600°, whereas this drop in reactivity occurs in only one case. The curves for Illinois coal are conspicuously high in both cases.

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Quantitative Analysis of Mine Dusts

An X-Ray Diffraction Method

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In order to study occupational diseases—silicosis, silicatosis, etc.—in relation to the constituents of mine or factory dusts, it is necessary to have exact quantitative knowledge concerning the chemical composition of the materials entering the lungs of workers. It has been pointed out repeatedly that the mineralogical composition, or state of chemical combination, of the factory or mine dust is of considerable importance in relation to the occurrence of these diseases, while the elementary composition—the chemical elements present—is of relatively little importance. An absolute, dependable method of quantitative mineralogical analysis is necessary, therefore, in order to study effectively the occurrence of these diseases, and to set up satisfactory standards for the protection of workers who must labor in dust laden atmospheres.

Various methods, both chemical and physical (*4, 5*), have been proposed and used for this purpose, but they are either not of general application, or are susceptible to influences which may vitiate the results in many cases. The failure of the widely used and generally dependable petrographic immersion method to distinguish between free quartz and some other silicate minerals in the dusts of some Canadian gold mines was directly responsible, through the suggestion of T. L. Walker, director of the Royal Ontario Museum of Mineralogy, for the development of the method to be described here.

Hull (*3*) pointed out a number of facts concerning the diffraction of x-rays by powdered crystalline materials. Of these the most important is that each crystalline chemical compound, when pulverized and placed in a monochromatic beam of x-rays, gives rise to a "diffraction pattern," which may be registered photographically and which is unique for that compound. The same compound always gives rise to the same diffraction pattern which is different from the pattern obtainable from any other compound or from an allotropic modification of the same compound. For a mixture of crystalline materials, each substance present gives its own pattern, regardless of the presence of the other constituents, and the resultant pattern is the sum of the patterns of all the constituent compounds. By proper resolution of such a complex pattern into its constituent parts it is found that x-ray diffraction is a most powerful method of qualitative analysis, in that it shows not only the elements present but also their true state of chemical combination.

It was suggested at the time that the method should be capable of development as a quantitative analysis by the use of diffraction patterns of known mixtures for comparison with the pattern of the unknown. Since that time (*1*), relative line densities have been used for a rough estimation of the amounts of the various compounds present in a mixture, but up to now no one has seen fit to apply the highly developed technic of quantitative analysis by ultraviolet spectroscopy to x-ray powder diffraction.

The method as developed here, for which the preliminary work has been previously reported (*2*), is an adaptation of the "internal standard" method (*6*) of ultraviolet spectroscopy to the Hull method of x-ray diffraction by a crystalline powder. A pure crystalline powder, known not to be present in the mixture being examined, is added to the unknown in a definite ratio, and the x-ray diffraction pattern registered by a suitable apparatus. The ratio of the density of a line of the substance sought to that of a nearby line of the added standard is determined photometrically. The ratio thus obtained is proportional to the line intensity of the substance sought, which in turn is proportional to the amount of substance in the mixture. By reference to a curve which is prepared empirically using mixtures of known composition, the percentage of the constituent sought is obtainable at once.

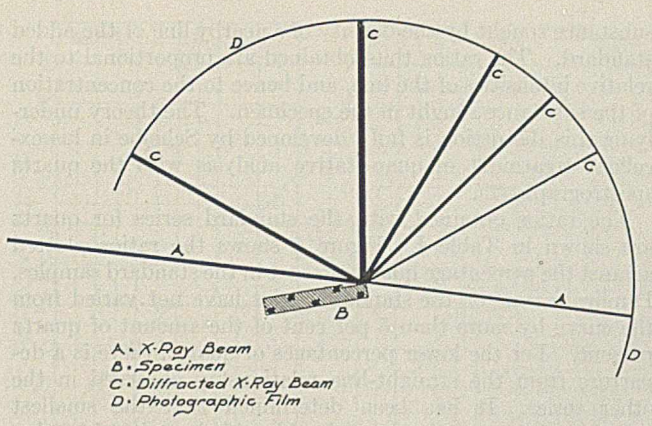


FIGURE 1. DIAGRAM OF X-RAY DIFFRACTION CAMERA

Apparatus and Diffraction Technic

For the registration of the diffraction pattern a circular reflection-type camera, shown diagrammatically in Figure 1, was used.

The specimen being examined was pressed into the shape of a wedge and mounted so that the tip of the wedge fell at the center of the camera. The tip of the wedge was bathed by the lower half of the main x-ray beam, which was defined by a series of lead pinholes 0.075 cm. (0.030 inch) in diameter. The resulting diffraction pattern was registered on a photographic film which was held tightly against the outside of a machined circle of which the tip of the wedge was the geometric center. It is observed that in certain directions from the wedge there is a focusing effect which causes a narrowing of the diffraction lines in these directions. By taking advantage of this, a high degree of resolution can be obtained in any desired portion of the pattern, together with a rather uniform background blackening in the region particularly to be investigated.

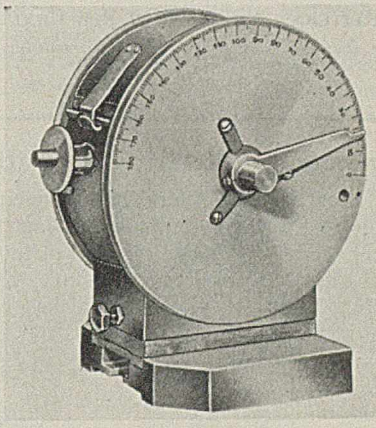
Figure 2 shows a camera of the type used in this work, arranged so that the wedge-shaped specimen may be revolved about its tip. This allows the side of the wedge next to the x-ray tube to be inclined at any angle to the incident beam of x-rays, so that the maximum effect of the focusing may be realized. Results may be duplicated exactly because the shape of the specimen is always the same, it can be set at the same angle to the beam every time, and all parts of the camera are permanently fixed with respect to each other and may be locked into position on the instrument table, so that conditions surrounding the registration of the diffraction pattern may be maintained at maximum constancy.

The specimen was irradiated with a Philips Metalix fine-structure-research x-ray tube with copper anode, mounted in a Hayes x-ray spectrograph, operating at 30 kvp. and 25 milliamperes. The exposure time varied from 1 to 6 hours, depending upon the concentration range of the specimen being examined, those specimens having the lowest percentages of the substance sought requiring the longer exposures.

Preparation of Samples

The natural ores and mine dusts submitted for analysis had been pulverized to pass a 200-mesh screen. Patterns for two of the dust samples as received, one high and one low in free quartz content, are shown in Figure 3, compared with patterns of pure rock crystal powder. The spotted lines showed that the average particle size was too large to give smooth diffraction lines. It was necessary to resort to some method of reducing the average particle size, for, unless smooth diffraction lines were obtained, photometer curves of the patterns would be meaningless. Furthermore, when it is considered that the amount of sample actually bathed by the x-ray beam is somewhat less than 1 mg., it is important to have an absolutely homogeneous specimen, with the added standard thoroughly incorporated with the sample. Both these ends were accomplished by developing a steel ball mill, using ball bearings in a cylindrical steel case, of such size that samples 1 gram in size could be handled without appreciable loss. Twenty-four hours' grind was found to be necessary to reduce quartz, which had already passed 200-mesh, to a powder of the required fineness.

The standard series of samples were prepared from powdered quartz and calcite, with the quartz content varying from 0 to 100 per cent. To cover the entire range, it was found necessary to divide it into three sections, the first extending from 0 to 10, the second from 10 to 60, and the third from 60 to 100 per cent. To 2 grams of the sample prepared as above, 0.5 gram of fluorite was added for the first two sections, and 1 gram for the third, as the internal reference standard, and the resulting mixture ground in the ball mill for 24 hours, using a high-boiling petroleum ether as a dispersion liquid to prevent caking of the powder. After grinding, the samples were freed of the petroleum ether, mounted in the diffraction camera, and the diffraction pattern was registered as described. A series of patterns for the 10 to 60 per cent range is shown in Figure 4.



Courtesy, J. B. Hayes, Inc.

FIGURE 2. X-RAY DIFFRACTION CAMERA

In the examination of the samples submitted for analysis, it was necessary to make preliminary patterns, to make certain that there were no lines present which would interfere with the desired line of the added standard and to determine by inspection the range in which the sample fell according to quartz content. The same relative amount of fluorite was added to the unknown as was used in the same range class for the standard series, and the resulting mixtures treated in the same manner as were the standard series.

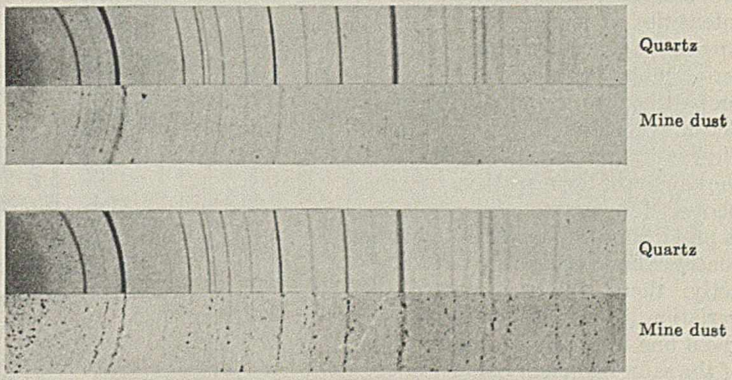


FIGURE 3. PATTERNS FOR TWO DUST SAMPLES

Upper, mine dust No. 21 as received. Very low in quartz
Lower, mine dust No. 23 as received. High in quartz

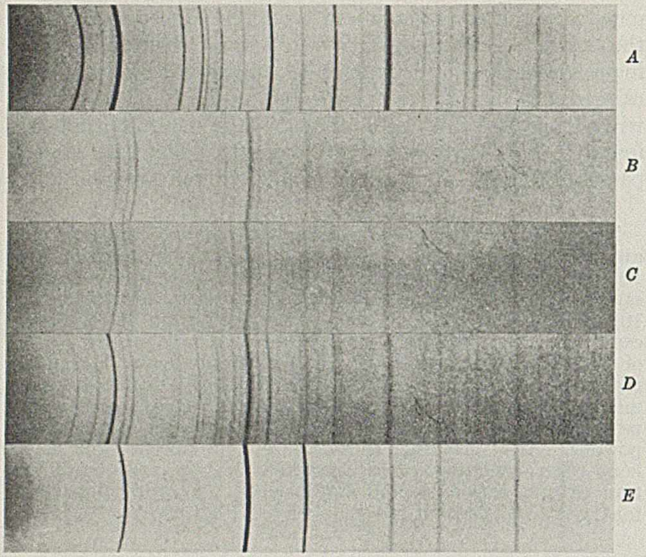


Figure 4. Patterns for 10 to 60 Per Cent Range

A, pure quartz
B, 10 per cent quartz
C, 30 per cent quartz
D, 50 per cent quartz
E, fluorite

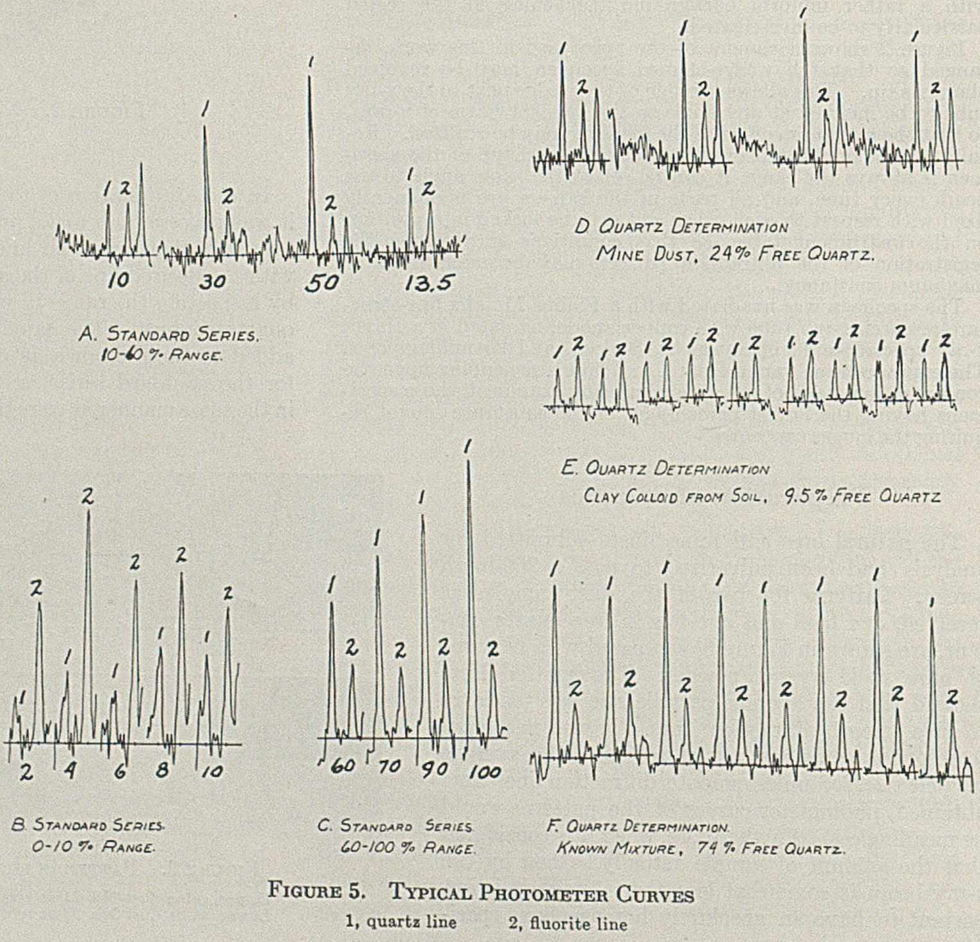
Measurement of Relative Intensities

The portion of each film containing the principal lines of quartz and fluorite was photometered using the Hayes microphotometer. The microphotometer is of the Moll type with a bismuth-silver vacuum thermocouple, and records photographically. From six to ten curves were made for each pattern at various points along the lines in order to get fair and dependable average measurements. A series of typical photometer curves is shown in Figure 5.

The density of a photographically recorded diffraction line may be considered as proportional to the height of its photometer curve above the general background of the pattern. If, for a series of samples, it is considered that all conditions surrounding the registration of the patterns are constant, the relative intensities of a given line appearing in all the patterns may be considered proportional to the relative densities of the line, and therefore proportional to the heights of the respective photometer curves. As it is practically impossible to control the conditions exactly, there will be some variation in density of a given line from film to film of the same sample. Small variations are satisfactorily taken care of by dividing the density of the line of the substance sought by the density of a nearby line of the added standard. The ratios thus obtained are proportional to the relative intensities of the line, and hence to the concentration of the substance sought in the specimen. The theory underlying this discussion is fully developed by Scheibe in his excellent treatment of quantitative analysis with the quartz spectrograph (7).

The ratios obtained with the standard series for quartz are shown in Table I. Figure 6 shows the ratios plotted against the percentage quartz present in the standard samples. Duplicate runs on the standard series have not varied from the curve by more than 5 per cent of the amount of quartz present. For the lower percentages of quartz, there is a departure from the straight-line relationship observed in the other series. It has been determined that the smallest amount of quartz that can be identified positively using the technic described here is about 1 per cent, and it appears that the least amount that can be measured accurately is about 4 per cent. The method is certainly not to be recommended for traces. The reason for this is found in the multiplicity of lines of the other substances present in large amounts, which causes difficulty in the accurate placing of the base lines on the photometer curves.

In order to determine the influence of minerals other than calcite on the ratios, samples were prepared using picked crystals of zircon, titanite, and microcline in the place of calcite. These substances were chosen because, in addition to being silicate minerals, they give strong diffraction lines very close to those of quartz and fluorite, and contain elements of higher atomic number, with correspondingly higher absorption coefficients for x-rays, than calcite. The patterns of these minerals, together with those for their mixtures with quartz and fluorite, are shown in Figure 7. For zircon the



A. Standard Series. 10-60 % Range.

B. Standard Series. 0-10 % Range.

C. Standard Series 60-100 % Range.

D. Quartz Determination Mine Dust, 24% Free Quartz.

E. Quartz Determination Clay Colloid from Soil, 9.5 % Free Quartz

F. Quartz Determination. Known Mixture, 74 % Free Quartz.

Figure 5. Typical Photometer Curves

1, quartz line 2, fluorite line

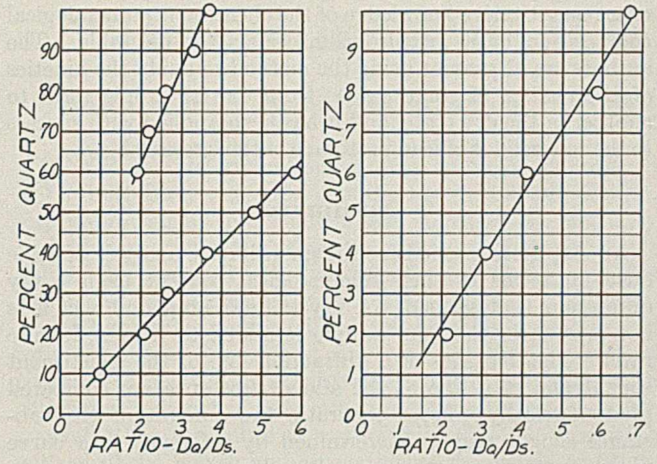


FIGURE 6. RATIOS

Dq, density of quartz line *Ds*, density of standard line

strong quartz line and a strong zircon line almost coincide. The photometer curves for these patterns barely show resolution of the quartz line as an inflection point on the side of the curve for the zircon line. In the case of titanite and microcline, there are no coincident lines, but the lines are so numerous in the neighborhood of the quartz and fluorite lines used that some difficulty was experienced in fixing the base lines on the photometer curves.

TABLE I. STANDARD SERIES

Sample	Composition Quartz *Grams*	Calcite *Grams*	Fluorite *Gram*	Quartz %	Ratio *Dq/Ds*
		A. 0 to 10 per cent			
KC 1	0.04	1.96	0.50	2	0.21
KC 2	0.08	1.92	0.50	4	0.31
KC 3	0.12	1.88	0.50	6	0.41
KC 4	0.16	1.84	0.50	8	0.59
KC 5	0.20	1.80	0.50	10	0.67
		B. 10 to 60 per cent			
KS 4	0.20	1.80	0.50	10	1.0
KS 5	0.40	1.60	0.50	20	2.1
KS 6	0.60	1.40	0.50	30	2.7
KS 7	0.80	1.20	0.50	40	3.6
KS 8	1.00	1.00	0.50	50	4.8
KS 9	1.20	0.80	0.50	60	5.8
		C. 60 to 100 per cent			
KD 1	1.20	0.80	1.00	60	1.9
KD 2	1.40	0.60	1.00	70	2.2
KD 3	1.60	0.40	1.00	80	2.6
KD 4	1.80	0.20	1.00	90	3.3
KD 5	2.00	0.00	1.00	100	3.7

TABLE II. INFLUENCE OF OTHER MINERALS PRESENT

	20 Per Cent Quartz		40 Per Cent Quartz	
Diluent	Ratio	Apparent per cent	Ratio	Apparent per cent
Calcite	1.7	20.0	3.0	40.0
Zircon	1.6	19.0	3.1	41.0
Microcline	1.8	21.0	3.0	40.0
Titanite	1.6	19.0	2.9	39.0

The results of these tests are shown in Table II. The indicated percentage of quartz is in no case more than 5 per cent from the true value, and the agreement is better for the higher percentages. This is undoubtedly due to the fewer number of lines from the foreign substances present, with less interference in fixing the base lines on the photometer curves. In general, the variation of 5 per cent may be taken as a measure of the precision of the method, and, since the method is almost entirely empirical, 5 per cent may be taken as its accuracy. This corresponds to the best work done with the quartz spectrograph as used for quantitative analysis.

Results of Analysis and Discussion

Some of the results of analyses of submitted samples are shown in Table III. This method cannot be considered to estimate "free silica," but only that part of the free silica which is present as "free quartz." If a sample contains silica in any other crystal form or as a glass, this silica will not be estimated as quartz by this method. This may explain in part the discrepancies between the results by the x-ray method and the petrographic immersion method upon samples K7, K8, and K9. An extended comparison between the two methods is now under way, and will be reported at a later date.

A rather conclusive test of the accuracy of the method was made by Walker. Without the authors' knowledge, he submitted two samples of mine dust, along with a series of unknowns, which had previously been analyzed by the x-ray method, and to which he had added a known amount of rock crystal powder. The results of this test are shown in Table IV, which is taken from Walker's report (*8*). The results fall well within the 5 per cent limit determined above.

Although the data presented here have to do only with the estimation of quartz, there is no theoretical reason why any other mineral in a mixture could not be determined quantitatively, since the method is limited only by the necessity of having pure minerals available for the preparation of the series of standard samples.

Care must be exercised in the choice of a reference standard. The line of the standard to be used for comparison must be

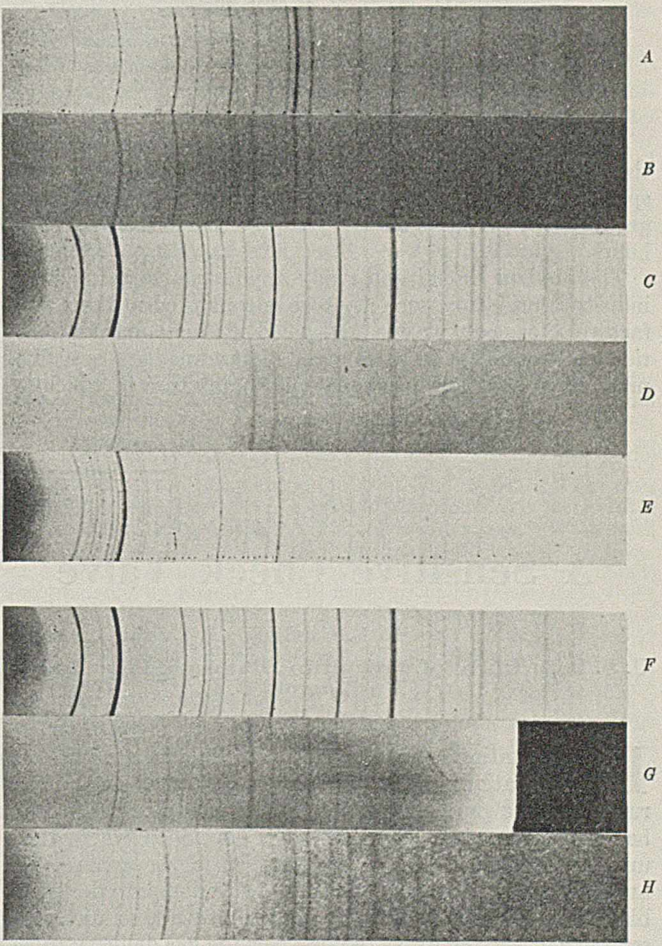


FIGURE 7. X-RAY PATTERNS

A, pure zircon
B, 60 per cent zircon, 40 per cent quartz, with fluorite
C, pure quartz
D, 60 per cent microcline, 40 per cent quartz, with fluorite
E, pure microcline
F, pure quartz
G, 60 per cent titanite, 40 per cent quartz, with fluorite
H, pure titanite

distinctly separated from lines produced by other minerals present in the sample to be analyzed, and it should be as near as possible to the line of the substance sought, so that the two will undergo the same absorption effects and will have nearly the same general background fogging. Using the technic described here, a separation of 0.3 mm. is satisfactory for good resolution. Since each crystalline substance present in the sample gives several diffraction lines, a suitable line may be found in almost every case for the satisfactory application of the method.

Table III. Results of Analyses

Sample	Material	Quartz	
		X-ray method	Microscopic method
		%	%
K 1	Mine dust	24.5	..
K 2	Mine ore	31.5	..
K 7[a]	Feldspar	26.0	33.8
K 8[a]	Corundum	Less than 1	0.8
K 9[a]	Abrasive wheels	Less than 1	8.3
K 21	Mine dust	3.5	..
K 22	Mine dust	13.2	..
K 23	Mine dust	54.6	..
K 24	Mine dust	16.7	..
K 25	Mine dust	13.4	..

[a] These samples were obtained from the Research Laboratories of the Aetna Life Insurance Company, Hartford, Conn., and were examined there for quartz by the petrographic immersion method.

Table IV. Test of X-Ray Method (*8*)

Sample	Quartz Found	Quartz Calculated
No. 2 with added quartz	37.0	35.5
No. 22 with added quartz	54.6	56.6

The apparatus used is necessarily expensive, but no more so than that required for dependable analysis with the quartz spectrograph. Aside from the time required for the long grinding operation, an analysis may be completed in about 4 hours.

The method should find ready application to many other industrial problems, such as those encountered in the manufacture of cement, plaster, and allied products, in identification and quantitative estimation of intermediate and final products in industrial processes, and in any case in which an exact quantitative knowledge of the chemical or mineralogical composition of a mixture is necessary or desirable. The authors are at present using the method to study the kinetics of the change of some oxides from one allotropic form to another in the dry state, and it has been applied with success to the compounds of lead in storage battery research.

Summary

An empirical method for the quantitative analysis of mine dusts in terms of their mineralogical content using x-ray diffraction is described. A crystalline compound which is not present in the dust sample is added to it in a definite ratio. The densities of a diffraction line of the constituent sought and of a line of the added substance are compared photometrically. From the ratio the amount of the substance sought may be determined by reference to a curve in which similar ratios are plotted against per cent substance sought, the curve being prepared using synthetic standard samples of known composition. Duplicability of results is within 5 per cent of the amount of the substance sought in the case of quartz. The method has been applied only to quartz-silicate ore mixtures, ranging between 0 and 100 per cent, but should prove applicable to many other minerals.

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A Sensitive Check Valve

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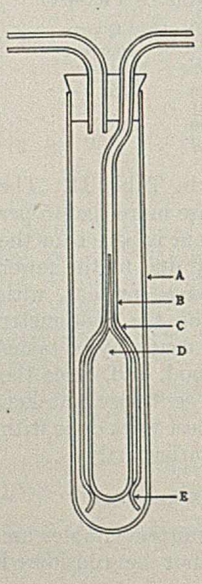
In precipitating copper by hydrogen sulfide, a number of determinations were lost because of accidental interruption of the gas stream before all the solutions in the train had been saturated. Partial vacua developed where these unsaturated solutions took up the gas in the connections, and finally the solutions in the flasks backed up into the scrubbing devices. To prevent any such movement, an unusually sensitive check valve was required for the gas delivery tubes. The device illustrated has served this purpose.

The outer shell, *A*, is an ordinary 25-mm. (1-inch) test tube cut to a suitable length. *B* is made by sealing a piece of 4-mm. tubing to a piece of 15- to 18-mm. test tube of the indicated length. At point *C* the neck of part *D* is ground into *B* to an airtight seat. To avoid sticking, this joint should have a blunt rather than a long taper. Part *D* is made from a 10-mm. test tube. A tail is drawn on the upper end to guide it into its seat. A tail on the lower end serves as a handle during the grinding and is then sealed off. When *D* is finished it must float less than half submerged in water. With *D* in place, the lower end of *B* is softened and three indentations are pressed into it to retain *D*.



In use, as small a quantity of water as will serve is placed in *A*. A current of gas entering through *B* displaces the water from it into *A* and *D* falls away from its seat. As soon as the current of gas tends to reverse, the water rises inside *B* and floats *D* into its seat. A reverse pressure too slight to close one of these valves but still capable of backing gas through it is impossible.

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Determination of Free Sulfur in Rubber

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SINCE the determination of free sulfur in vulcanized rubber is an analytical operation of utmost importance, any improvement in technic which increases the accuracy and also shortens the time required is of considerable value. In practically all the methods used in the past, the sulfur has been extracted with hot acetone and then determined by various means: direct weighing (*2*), oxidation and estimation as barium sulfate, conversion into thiocyanate and titration with silver nitrate (*3*), reaction of copper gauze with sulfur and iodometric determination of the hydrogen sulfide evolved when the gauze is treated with acid (*4*), treatment with alcoholic potash and estimation of the sulfide and thiosulfate formed (*5*). These methods usually require 8 hours or more for the extraction of the sulfur, and its estimation in the extract is a lengthy process.

Although much time is required for oxidation, precipitation, filtration, and weighing, the oxidation and gravimetric methods have proved best for routine work. Volumetric methods have not been satisfactory because of lack of satisfactory end points, side reactions, incomplete reactions, and tedious manipulations. The volumetric method to be discussed, however, makes it possible to shorten the time required for a free sulfur analysis to less than 3 hours per set of duplicate determinations.

In 1933 Bolotnokov and Gurova (*1*) introduced a volumetric method based on the fact that free sulfur is transformed into sodium thiosulfate when a rubber sample is heated in an aqueous solution of sodium sulfite. The authors have checked this method and have found the extraction and conversion into sodium thiosulfate to be complete and quantitative (as shown in Table I) in 2 hours when checked gravimetrically, using the Kratz, Flower, and Coolidge oxidation method on stocks containing non-sulfur-bearing accelerators.

TABLE I. CHECK DETERMINATIONS

Type of Stock	Free Sulfur	
	Gravimetric	Volumetric
	%	%
Tube	0.36	0.36
Tube	0.94	0.95
Tire tread	0.22	0.22
Mechanical	1.21	1.24
Uncured rubber-sulfur mix	32.20	32.40
	32.40	32.50
	32.40	32.60

When the method of extraction of the sulfur and its conversion into sodium thiosulfate were found to be quantitative, the authors set out to simplify the procedure and to make it a rapid and practical one for routine testing of rubber stocks containing sulfur-bearing as well as non-sulfur-bearing accelerators.

Improved Volumetric Method

The presence of mercaptobenzothiazole causes the thiosulfate method to give high results (due to oxidation of mercaptobenzothiazole to benzothiazyl disulfide) when compared with corrected results from the Kratz, Flower, and Coolidge method, obtained by subtracting the sulfur content of the mercaptobenzothiazole present from the results obtained by their gravimetric procedure. The mercaptobenzothiazole content was determined for this correction by extracting the rubber sample with acetone, treating the extract with a benzene solution of cupric oleate, and estimating the precipitated cuprous salt of mercaptobenzothiazole gravimetrically (*6*).

Since the correction cannot be conveniently made in the volumetric method, it was decided to separate mercaptobenzothiazole from the sodium sulfite solution by precipitation. Although the various metals noted below form precipitates which may be filtered out, only the cadmium salt was found to be satisfactory in this case. Silver reacts with the thiosulfate to form silver sulfide. Lead thiosulfate is only sparingly soluble. Cuprous copper will react quantitatively with mercaptobenzothiazole, but any cupric copper will oxidize thiosulfate. Cadmium alone of all the metals tried precipitated mercaptobenzothiazole without reaction with thiosulfate.

The addition of 5 mg. of sodium stearate (which serves as a wetting agent in the extraction) and 0.5 gram of paraffin (which prevents frothing) were found to be beneficial. Air condensers are unnecessary, since cover glasses work satisfactorily when paraffin is used.

The fatty acids present in rubber stocks are extracted during the heating with sodium sulfite. These are precipitated along with the fatty acid from the soap by a solution of strontium chloride. The excess strontium forms insoluble strontium sulfite which helps to break up the other flocculent precipitates, thus keeping the filters from clogging.

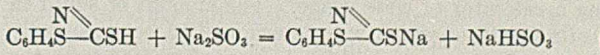
Since the final titration is a thiosulfate-iodine reaction, it is necessary to eliminate or render inert the excess sodium sulfite. The addition of formaldehyde accomplishes this by forming a formaldehyde–sodium sulfite addition product.

The end point is improved by using a large volume (approximately 600 cc.) of solution acidified with acetic acid, and cooled below 15° C. with crushed ice. A very distinct end point is obtained which will last 2 to 3 minutes.

Procedure

Place 2 grams of thinly sheeted sample 0.05 to 0.075 cm. (0.02 to 0.03 inch) in a 400-cc. Underwriters' flask. Add 100 cc. of 5 per cent sodium sulfite solution, 5 cc. of a 0.1 per cent sodium stearate suspension in water, and approximately 1 gram of paraffin. Cover the flask with a small watch glass and heat so as to boil gently for 2 hours. Remove the flask and add 100 cc. of 0.5 per cent strontium chloride solution and 10 cc. of 3 per cent cadmium acetate solution. Separate the rubber and precipitates by filtration, using a Büchner funnel with suction. Wash with two 75- to 100-cc. portions of a wash solution containing 40 cc. of 3 per cent cadmium acetate solution per liter. (The funnels are prepared by forming a thin asbestos pad over a single sheet of qualitative filter paper. Filters thus prepared can be used numerous times.) To the filtrate, add with stirring 5 cc. of 40 per cent formalin solution, 10 cc. of glacial acetic acid, and 5 cc. of 1 per cent starch solution. Add enough crushed ice to bring the temperature of the solution below 15° C., and titrate with a standard solution of iodine to a blue end point. A blank determination is run on the reagents and this figure, usually 0.2 to 0.3 cc., is subtracted from the titrations on the samples.

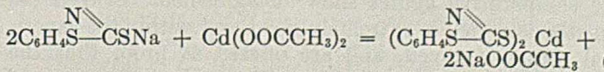
$$S + Na_2SO_3 = Na_2S_2O_3 \qquad (1)$$



$$C_6H_4S\text{—}CSH + Na_2SO_3 = C_6H_4S\text{—}CSNa + NaHSO_3 \qquad (2)$$

$$2NaOOC(CH_2)_{16}CH_3 + SrCl_2 = Sr[OOC(CH_2)_{16}CH_3]_2 + 2NaCl \qquad (3)$$

$$Na_2SO_3 + SrCl_2 = SrSO_3 + 2NaCl \qquad (4)$$



$$2C_6H_4S\text{—}CSNa + Cd(OOCCH_3)_2 = (C_6H_4S\text{—}CS)_2\,Cd + 2NaOOCCH_3 \qquad (5)$$

$$Na_2SO_3 + Cd\,(OOCCH_3)_2 = CdSO_3 + 2NaOOCCH_3 \qquad (6)$$

$$HCHO + Na_2SO_3 + H_2O = H_2C(OH)SO_3Na + NaOH \qquad (7)$$

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI \qquad (8)$$

Table II. Comparative Determinations

(Stocks containing non-sulfur-bearing accelerators)

Sample	Free Sulfur	
	Gravimetric	Thiosulfate
	%	%
Tread	0.53	0.49
	0.49	0.44
	0.21	0.19
	0.36	0.35
	0.22	0.23
	0.07	0.07
	1.05	1.02
Cushion	1.00	0.99
	0.79	0.75
	0.75	0.71
Carcass	0.53	0.50
	0.25	0.22
	0.37	0.36
	0.20	0.18
Tube	1.00	0.98
	0.52	0.52
	1.02	0.98
	0.52	0.52
Valve bases	0.15	0.13
	0.52	0.51
	0.87	0.84
	0.88	0.87
	0.18	0.16
	0.04	0.05

Table III. Comparative Determinations

(Stocks containing mercaptobenzothiazole)

Sample	Free Sulfur	
	Corrected gravimetric	Thiosulfate
	%	%
Tread	0.15	0.16
	0.46	0.47
	0.11	0.15
	0.23	0.21
	0.54	0.52
	0.43	0.43
Carcass	0.20	0.22
	0.42	0.39
	0.82	0.78
	0.25	0.29
	0.26	0.24
Tube	0.36	0.36
	0.23	0.19
	0.11	0.07
	0.05	0.04
	0.01	0.01
	0.07	0.08
Juvenile tires	0.75	0.78
	0.43	0.46

From Equations 1 and 8 it is evident that one equivalent of iodine is required for each equivalent of sulfur; hence 1 cc. of a 0.1 *N* solution would be equal to 0.003206 gram of sulfur. It has been found convenient to use 0.0624 *N* iodine solution, so that 1 cc. is equivalent to 0.00200 gram of sulfur or 0.10 per cent free sulfur on a 2-gram sample.

Discussion of Results

A comparison of results obtained by both the Kratz, Flower, and Coolidge and the thiosulfate methods (Table II), on stocks containing non-sulfur-bearing accelerators, shows that the volumetric method usually gives results very slightly lower than the gravimetric, the maximum being 0.05 per cent on the compound.

A similar comparison (Table III) was made on stocks containing mercaptobenzothiazole as a representative sulfur-bearing accelerator of wide usage. The amount of sulfur in the acetone extract which was determined to be organically combined as mercaptobenzothiazole was subtracted from the gravimetric value to give the corrected gravimetric free sulfur value.

The comparative figures show an agreement between the two methods which is extremely good and within the experimental errors involved, and are offered as proof that the thiosulfate method obtains free sulfur values that are of practical worth in a minimum of time.

In addition to all common fillers, softeners, etc., the following compounds have no effect upon the accuracy of the method: thiocarbanilide, guanidines, aldehyde amines, tetramethylthiuram monosulfide, mercaptobenzothiazole, benzothiazyl disulfide, *p*-aminophenol, naphthylamines, xanthates, carbamates, and vulcone.

Table IV. Determinations on Mercaptobenzothiazole Tread Stocks

Gravimetric Free Sulfur	Correction	Gravimetric Free Sulfur Corrected	Thiosulfate
%	%	%	%
0.67	0.09	0.58	0.61
0.38	0.14	0.24	0.24
0.36	0.02	0.34	0.35
0.72	0.27	0.45	0.43
0.78	0.27	0.51	0.51
0.85	0.28	0.57	0.57
0.54	0.16	0.38	0.40

Table V. Comparison of Methods

Stock	Free Sulfur			
	Katz, Flower and Coolidge			
		Corrected	Bromine	Thiosulfate
	%	%	%	%
Guanidine	0.35	....	0.34	0.34
	0.72	....	0.70	0.69
	0.71	....	0.72	0.71
	0.79	....	0.74	0.74
Mercaptobenzothiazole	0.85	0.57	0.68	0.57
	0.72	0.45	0.56	0.43
	0.50	0.37	0.36	0.34
	0.26	0.10	0.18	0.13
	0.48	0.32	0.39	0.35

Accelerators such as tetramethylthiuram disulfide, which also function as vulcanizing agents, liberate the available sulfur during the heating with sodium sulfite and the thiosulfate thus formed influences the accuracy of the free sulfur determination on such stock. This is perhaps no serious handicap because gravimetric results on such stocks are of no particular value because of the high percentage of organically combined sulfur in the acetone extract.

Conclusions

Values obtained by the volumetric method herein described compare favorably with those obtained by gravimetric methods when corrections are applied to the latter for the sulfur in the organic compounds in the acetone extract.

The precision of the method is excellent, as duplicates in each set usually check within 0.01 per cent of free sulfur on the compound.

This method is much faster than previous methods.

The cost of the reagents is low when compared with most other methods.

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Rustproofing Paints. A number of experiments concluded in Germany tend to prove that the old method of red lead priming followed by two coats of good varnish constitute the most reliable rust protection for exposed iron and steel objects. German railroad specialists state that experience of many years has brought out nothing to improve on red lead as a rust preventive. Sand blast cleaning has been found to produce the best results.

Accurate Separation of Precipitated Mercuric Sulfide and Sulfur in the Gravimetric Determination of Mercury

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THE common method for the determination of mercury as the sulfide suffers from the disadvantage that the precipitate is often contaminated with sulfur. The usual practice is to attempt to remove the free sulfur from the precipitate by various methods before weighing. Hot extraction with carbon disulfide is considered one of the best methods (*3*). Another is the successive washing of the precipitate with hydrogen sulfide water, hot water, alcohol, carbon disulfide, alcohol, and ether (*1*). All such procedures involve an element of uncertainty because of the difficulty of knowing when the removal of sulfur is complete, particularly since some forms of sulfur are but slightly soluble in certain of these solvents. The method of final treatment presented here avoids this possible source of error. It consists, in brief, of drying and weighing the precipitate without attempting to remove the free sulfur, treating it with cold concentrated hydriodic acid to dissolve out the mercuric sulfide without affecting the sulfur, and weighing this residual sulfur. The difference between these two weights gives the weight of pure mercuric sulfide present.

That hydriodic acid dissolves mercuric sulfide even in the cold was first observed by Kekule (*2*). With acid as concentrated as the constant-boiling mixture, hydrogen sulfide is vigorously evolved, and only a comparatively small volume is required to dissolve a given amount of the sulfide, the mercury going into solution in the form of a very soluble complex. The reaction can be expressed by the equation

$$HgS + 4HI \rightarrow H_2HgI_4 + H_2S$$

Though this reaction proceeds even more vigorously with hot concentrated acid, the latter cannot be applied in this method because free sulfur reacts to a slight extent with it forming hydrogen sulfide and iodine. The cold acid apparently does not react with sulfur, at least during the short period of contact required in the practical procedure.

For this purpose hydriodic acid stabilized with hypophosphorous acid is the most convenient to use, since the rapid formation of troublesome free iodine from air oxidation is thus avoided. The hypophosphorous acid content in no way interferes with the separation. Merck's ordinary grade of specific gravity 1.70 was used in all the experiments recorded in this paper. The mercuric sulfide was prepared by precipitation of a solution of recrystallized mercuric chloride with hydrogen sulfide under conditions that led to the formation of no free sulfur. Samples treated with hydriodic acid gave no weighable residues. The specimen of pure finely divided sulfur was found to have no appreciable solubility in cold concentrated hydriodic acid. In testing this point the weighed samples of sulfur were placed in weighed glass crucibles, treated with about 5 ml. of the acid for several minutes with stirring, then washed with water and dried for 2 hours in a vacuum desiccator. In a typical run a 0.4225-gram sample left a 0.4222-gram residue after treatment, a difference of 0.0003 gram, which was probably in large part a weighing error.

Collect the precipitated mercuric sulfide in a weighed glass or porcelain filtering crucible, wash with cold water, dry thoroughly at 110° C., and weigh. Replace the crucible in the holder without turning on the suction pump, and add cold stabilized constant-boiling hydriodic acid in the proportion of about 5 ml. for each gram of precipitate. Stir the mixture with a glass rod until all black particles of mercuric sulfide have disappeared, then turn on a gentle suction and draw the solution from the crucible. Wash the residual sulfur first with three or four successive 5-ml. portions of dilute (5 to 10 per cent) hydriodic acid and then with cold water. Water must not be used for the initial washings because of the danger of decomposing the soluble mercury complex, thus precipitating mercuric iodide in the pores of the filtering disk. Dry the crucible and its contents for about 2 hours in a vacuum desiccator and reweigh. The difference in the two weighings gives the amount of pure mercuric sulfide present.

Results from experiments on the quantitative separation of synthetic mixtures of mercuric sulfide and sulfur by this method are shown in Table I. The sharpness of the separation is evident.

TABLE I. SEPARATIONS OF MERCURIC SULFIDE FROM SULFUR

Mercuric Sulfide Taken	Sulfur Taken	Sulfur Found	Error
Gram	*Gram*	*Gram*	*Gram*
0.0865	0.4220	0.4221	+0.0001
0.1717	0.0822	0.0821	−0.0001
0.2099	0.0802	0.0801	−0.0001
0.3895	0.0052	0.0055	+0.0003

Apparently this method can be applied also to the rapid estimation of the mercuric sulfide content of technical grades of this sulfide prepared in the dry way, since, when genuine, these are mixtures of mercuric sulfide with more or less free sulfur. Results of test analyses of actual specimens are shown in Table II.

TABLE II. ANALYSES OF COMMERCIAL MERCURIC SULFIDES

Variety	Sample Taken	Residue Found	Mercuric Sulfide
	Grams	*Gram*	%
Black	0.5860	0.0275	95.31
	1.1210	0.0531	95.26
	0.3855	0.0182	95.28
	0.6103	0.0289	95.26
	0.4807	0.0226	95.30
Red	0.3748	0.0087	97.68
	0.7638	0.0178	97.67
	0.5385	0.0124	97.70
	0.4529	0.0104	97.70
	0.4768	0.0110	97.69

In these determinations the samples were weighed directly into weighed glass crucibles and treated by the above procedure. The very satisfactory agreement of duplicate trials on the same sample is evident. Since mercuric sulfide should be the only component in unadulterated commercial sulfides that is soluble in hydriodic acid, this method should also be highly accurate. Certainly it has the advantages of being much more rapid and much simpler than the usual procedures for the estimation of the mercuric sulfide content of such products.

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Determination of Formic Acid in Pyroligneous Liquors

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DETAILED study of the products and yields from the destructive distillation of agricultural wastes has necessitated repeated determination of the formic acid content of the pyroligneous liquors produced under different operating conditions. Methods of formic acid determination now in use are undependable or very time-consuming, when applied to such liquors, which usually contain comparatively small quantities of formic acid together with large quantities of other chemical compounds. These may interfere with or give positive reactions with the usual formic acid tests, and recommended prepurification procedures (*3*) have certain difficulties of application. There exists, therefore, a need for a convenient and accurate method for the determination of small quantities of formic acid in pyroligneous liquor.

Present methods of determining formic acid are, in general, based on steam-distilling the volatile components from the nonvolatile and then treating the solution with mercuric chloride and weighing the calomel precipitated (*1*); titrating the hydrochloric acid formed (*5*); estimating total acids before and after removal of the formic acid by oxidation with mercuric oxide (*2*); or estimating the carbon dioxide evolved by oxidation of the formic acid with mercuric oxide or other oxidants, using various methods of carbon dioxide absorption (*2*, *8*). These methods are open to certain objections. Various impurities, especially aldehydes or unsaturated bodies that may act as reducing agents, will affect the calomel precipitation.[1] Gravimetric methods are likely to show relatively large percentage errors when the quantity of formic acid is small. Oxidation methods usually require the removal of dissolved carbon dioxide from the sample before subjection to the action of oxidizing agents, involving special apparatus or procedure. The use of an insoluble oxidizing agent is attended by difficulties in preventing the admission of carbon dioxide from the air during addition, securing an even rate of oxidation, avoiding possible oxidation of impurities due to the excess oxidant present, avoiding loss of carbon dioxide due to failure of absorption systems of small capacity to take care of uneven liberation of gas, etc.

In the present experimentation, since an oxidation–carbon dioxide absorption scheme seemed to offer the greatest flexibility, various modifications of the methods now in use were studied in a effort to overcome known limitations. Various substances normally present in pyroligneous liquors were studied individually to ascertain the extent of error from such presence, and to learn how much preliminary purification is required for the accurate determination of formic acid under the conditions. After a trial the use of Truog towers (*11*) for absorbing carbon dioxide was abandoned because of difficulties resulting from absorption of carbon dioxide from the air during the washing of alkali from the tower, and in controlling the flow of carbon dioxide–free air at a uniform rate. A number of soluble and insoluble oxidizing agents were tried, and mercuric acetate solution, the addition of which can be easily controlled, was finally adopted as most suitable. Barium hydroxide solution was used for absorbing the carbon dioxide, which was estimated volumetrically. As a result of these experiments a closed circulatory absorbing system was evolved which is believed to minimize the disadvantages of other systems. It is cheap, easily constructed, easily regulated, and almost automatic in action, and, when it is once assembled, formic acid determinations may be performed rapidly, in sequence, about 30 minutes being required for an accurate determination on a pure or purified sample. Rates of oxidation, circulation, and absorption can be controlled at will without danger of admission of carbon dioxide from the air. Circulation may be maintained for any desired period, insuring complete absorption. Titration can be accomplished without air contamination, and various oxidants may be used as desired.

Various methods for removal of interfering impurities have been studied by other investigators, that of Fincke (*3*) appearing most adaptable for the present purpose. The method of formic acid determination here presented is a combination of the desirable features of several methods, especially those of Fincke (*3*) and Osburn (*8*), used in conjunction with an absorption apparatus evolved from one used by Partridge and Schroeder (*9*) for carbon dioxide absorption. It is believed that the proposed apparatus, with slight modification, may be applied to other organic determinations depending on measurement of evolved carbon dioxide.

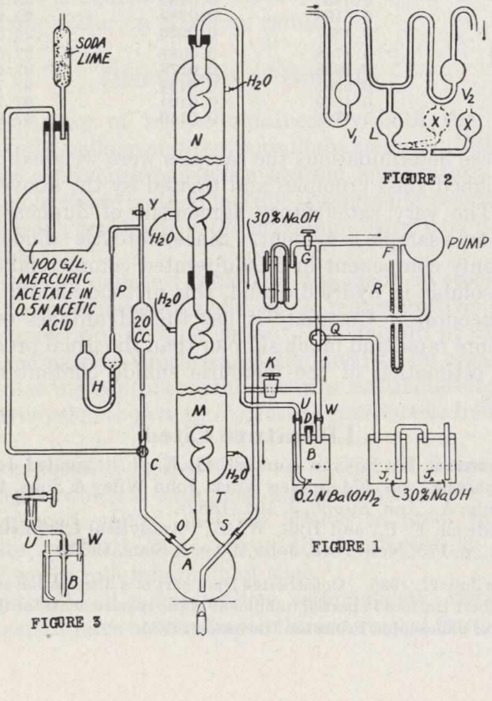

FIGURE 2

FIGURE 1

FIGURE 3

Description of Absorption Apparatus

The proposed apparatus (Figure 1) consists of a 200-cc. Pyrex reaction flask, *A*, with one center and two side outlets. Above the center outlet, *T*, are mounted two spiral condensers, *M* and *N*, placed vertically, in series, and connected to the flask by a ground-glass joint. Through side outlet *S* is inserted an air-intake tube reaching nearly to the bottom of the flask, and joined to a pump system (Figure 2) as shown. The remaining outlet, *O*, is connected by means of a rubber tube to a three-way stopcock, *C*, permitting the addition of measurable amounts of the oxidizing solution through a 20-cc. pipet, which is connected

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[1] The use of potassium acetate and hydroxylamine has been recommended as increasing the accuracy of the calomel method by J. C. Carlin of the Tennessee Products Corporation, Nashville, Tenn., but prepurification is required (private communication).

as shown for measuring and adding the oxidizing solution. To a side arm on the upper end of the pipet is attached a capillary tube, *P*, which retards to about 10 minutes the time necessary for emptying the pipet. To the other end of the capillary tube is attached a U-tube, *H*, containing sodium hydroxide solution. This tube serves the double purpose of removing all carbon dioxide from the air drawn through and of preventing the last few cubic centimeters of the solution from flowing into reaction flask *A*, thereby forming a liquid seal which prevents any carbon dioxide formed in the reaction from rising into the pipet. A cock at *Y* is opened to permit rapid filling of the pipet.

Evolved carbon dioxide passes through condensers *M* and *N* and is absorbed in titration bottle *B* (Figure 3). This is tightly closed by means of a three-hole rubber stopper, through which tube *U* brings the carbon dioxide air stream to the bottom, where it bubbles through the alkaline absorbing solution. Tube *D* allows addition of both the barium hydroxide and hydrochloric acid titrating solutions, while *W* is the exit through which the gas returns to the pump. A by-pass, *K*, is connected across *U* and *W* to allow pressure equalization.

J_1 and J_2 are two air-scrubbing bottles containing 30 per cent sodium hydroxide solution. During the preliminary period required for removing carbon dioxide from the system, carbon dioxide–free air in any required amount can be introduced through this scrubber and forced through the system by means of the pump, the air exit being at the upper end of tube *U*, where *B* is disconnected.

At *G* additional means is provided for releasing pressure or for admitting small amounts of air from which carbon dioxide has been removed by a scrubbing system containing sodium hydroxide. A mercury manometer U-tube, *R*, of rather small bore and registering pressure changes up to 100 mm., is attached at *F*.

Constant circulation of the enclosed air system is accomplished by a pump (Figure 2) consisting of an ordinary automobile windshield-wiper mechanism having a radial arm motion and bearing at the end of the arm a mercury reservoir, *X*, which is connected by glass and rubber tubing to a bulb, *L*. Vertical oscillation of reservoir *X* causes a fluctuating mercury level in *L*, forcing the enclosed gas in the system to circulate through two glass valves, V_1 and V_2, containing sufficient mercury for proper valve operation. This pump valve device is similar to one described by Maass (*6*).

Determination

Steam-distill 25 cc. of crude pyroligneous acid and 5 cc. of sirupy phosphoric acid in a 500-cc. Claisen flask heated at 140° to 150° C. in a glycerol bath. (A somewhat more accurate procedure is to treat the original crude liquor with 20 per cent excess of *N* sodium hydroxide solution in a stoppered flask at room temperature for 24 hours, then acidify with phosphoric acid—5 cc. in excess—and distill as directed.) During the 2.5 hours (approximate) allowed for collecting the 1 liter of distillate, maintain the volume of liquor in the flask at about 10 cc. For formic acid determinations, neutralize 300 cc. of distillate (or a suitable aliquot containing from 0.05 to 0.1 gram of formic acid) to phenolphthalein with barium hydroxide solution and evaporate to dryness on the steam bath. (The remainder of this distillate is available for determination of methanol, acetic acid, acetone, and other constituents of the crude liquor.) Dissolve the residue in 50 cc. of warm water and transfer to reaction flask *A* (Figure 1). Add a small piece of paraffin (to reduce foaming) and 5 cc. of *N* acetic acid, and dilute the contents of the flask to about 100 cc.

Set stopcock *Q* so scrubbers J_1 and J_2 connect directly with intake valve V_1 of pump, and boil contents of flask for 10 minutes while passing carbon dioxide–free air through the solution and system to remove dissolved carbon dioxide. Connect titration bottle *B*, which contains a known quantity of standardized barium hydroxide (approximately 50 cc.), and continue boiling solution in the reaction flask. (Martin and Green, *7*, add barium chloride to increase absorbing efficiency.)

Open three-way stopcock *C* and allow 20 cc. of the mercuric acetate oxidizing solution (Dissolve 100 grams of mercuric acetate in 1 liter of 0.5 *N* acetic acid and boil 1 hour to remove carbon dioxide. Keep tightly stoppered.) to flow slowly into flask, continuing circulation for 20 minutes. Stop pump and titrate contents of bottle *B* with standard 0.2 *N* hydrochloric acid (free from carbon dioxide) using phenolphthalein (Schollenberger, *10*, recommends thymolphthalein.). Near the end point gently evacuate at *W* a few times, to draw solution from immersed tubing. Differences of pressure may be equalized at *K*, which should be open when pump is not operating and when bottle *B* is being connected or disconnected, to avoid drawing absorbing solution up into apparatus.

Calculation of Results

One cubic centimeter of 0.2 *N* barium hydroxide is equivalent to 0.0046 gram of formic acid.

$$2(CH_3COO)_2Hg + HCOOH = CO_2 + 2CH_3COOH + 2CH_3COOHg$$

Formic, acetic, or other volatile acids will carry over in the apparatus to a small extent causing absorption of alkali. The total correction for such volatilized acids under the conditions set forth was 0.04 cc. of 0.2 *N* alkali, which is so small that it may usually be disregarded. A blank determination will correct for this and for impurity of reagents.

Time Factor

During the development of the method it was found necessary to ascertain the time required to absorb all carbon dioxide evolved in the closed system during a determination.

After the apparatus had been freed from carbon dioxide, a solution containing 0.263 gram of dried anhydrous sodium carbonate dissolved in 25 cc. of carbon dioxide–free water was added to 75 cc. of carbon dioxide–free distilled water in flask *A* (Figure 1). Bottle *B* was then connected, and an excess of dilute sulfuric acid (free from carbon dioxide) was added to flask *A* through the pipet at *O*. At intervals of 5 minutes the pump was stopped, titration bottle *B* was changed, and its contents were titrated. Absorption occurred as follows:

	Cc. 0.2018 *N* Alkali Consumed
First 5 minutes	17.52
Second 5 minutes	7.04
Third 5 minutes	0.02
Total	24.58 (equivalent to 0.263 gram of sodium carbonate)

A 15-minute circulation is therefore ample for complete absorption of the carbon dioxide in the system, unless progress of the oxidation is retarded.

Effect of Certain Impurities

Crude pyroligneous acid consists of a mixture of water, tar, oil, formic, acetic, and higher acids, acetone, methanol, esters, ketones, aldehydes (especially formaldehyde, acetaldehyde, and furfural), acetals, phenols, pyridine, allyl alcohol, etc. Homologs and condensation and interaction products of these compounds are probably present, the percentages varying with the temperature of the destructive distillation. The acetic content is usually in excess of the formic. In the various existing formic acid methods which depend on oxidation many of these compounds may react, affecting the results in several ways: they may oxidize, yielding carbon dioxide; they may be carried over into the alkali and combine with it; or their presence may inhibit the liberation and oxidation of the formic acid.

Experiments were individually conducted with a number of these compounds to determine their behavior under the oxidation conditions of the method described herein. The results, shown in Table I, indicate that acetone, methanol, ethanol, glycerol, and lactic acid yield no carbon dioxide under the conditions of the method, while pyridine, allyl alcohol, acetaldehyde, "soluble" tar, "high-boiling" acid, unsaponifiable "chemical wood oil," oxalic acid, and various tar oil fractions and their phenols yield varying small amounts of carbon dioxide. Substances such as furfural and formaldehyde apparently oxidize slowly and yield carbon dioxide, the degree of oxidation depending on the time and concentration conditions. A previous saponification seems to be essential before the determination of the combined formic acid in formic esters, as in the case of the lower boiling compounds direct determination is often affected by unhydrolyzed ester passing out of the reaction flask.

Table I. Oxidation Behavior of Individual Substances, under Limits of Proposed Method

Substance	Amount of Sample		Length of Run	Oxidizing Agent (Mercuric Acetate)	Carbon Dioxide Present		
					Theoretical	Found	Per cent of theoretical found
	Grams	*Cc.*	*Min.*	*Grams*	*Grams*	*Grams*	%
Acetone, c. p.	0.1	..	20	2	0.228	Trace	
	0.8	..	20	2	1.820	0.00045	0.02
Glycerol	1.25	..	20	2	.....	None	....
Ethanol	....	50.0	20	2	.....	None	....
Methanol, c. p.	0.08	..	20	2	0.11	Trace	
	0.80	..	20	2	1.1	0.00090	0.08
Oxalic acid, c. p. (anhydrous)	0.0833	..	20	2	0.0813	0.000976	1.20
	0.2	..	20	2	0.1956	0.00045	0.23
Lactic acid (analytical)	....	0.25	20	2	.....	Trace	....
Pyridine (analytical)	4.95	..	10	2	13.77	0.00106	0.01
Furfural (technical redistilled)	1.16	..	20	2	2.66	0.01355	0.51
Acetaldehyde (redistilled)	0.80	..	20	2	1.60	0.000452	0.03 (affects alkali)
"Soluble" tar (from pecan shells)	0.1455	..	20	2	.....	0.00227	....
"High-boiling acid" (Suida process)	....	0.5	15	2	.....	0.0034 (essentially a mixture of propionic, butyric, and acetic acids and lactones)	
"Wood chemical oil"	....	5.0	20	2	.....	0.0216	....
Same (washed with sodium hydroxide)	....	10.0	20	2	.....	0.0146	....
Corncob "chemical oil" (redistilled) fraction up to 136° C.	....	5.0	20	2	.....	0.0213	....
Same, fraction 136° to 225° C.	....	5.0	20	.	.....	0.00354	....
Peanut-shell tar oil (caustic-soluble portion, phenols)	....	5.0	20	.	.....	0.00632	....
Formaldehyde (technical formalin)	0.1		30	5	0.1465	0.00286	1.95
			+ 30[a]			0.00183	
			+ 30[a]			0.00241	
			+ 30[a]			0.00263	
			+ 30[a]			0.00263	
Total			150			0.01236	8.44
Sample 2	0.06		30	2	0.088	0.00071	0.80
			+ 30[a]			0.00217	
Total			60			0.00288	3.27
Sample 3	1.0		20	2	1.465	0.01845	1.26
Allyl alcohol (Eastman Kodak Co.)	4.27		90	2	9.71	0.013	0.13
			+ 20[a]			0.00195	
Total			110			0.01495	0.15
Sample 2	4.27		10	2	9.71	0.001855	0.19
			+ 15[a]			0.0063	
			+ 15[a]			0.0042	
			+ 15[a]			0.00177	
Total			55			0.014125	1.46
Sample 3	0.854		20	2	1.943	0.0108	0.56
Ethyl formate (basis 100% ester)	0.1306		30	2	0.0777[b]	0.0772	99.4
	0.1306		30	2	0.0777[b]	0.0777	100.0
	0.1306		30	2	0.0777[b]	0.0780	100.4

[a] Additional time periods on same experiment. [b] Equivalent to carboxyl present. Saponified before determination.

The removal of soluble and insoluble tar from the crude liquor by a preliminary distillation before estimation of formic acid, etc., seems to be necessary (as shown in Table I), since the presence of tar also seems to affect the analytical procedure. Tests were therefore made to determine the quantity of distillate needed to effect total recovery of all the acids present in the crude, using the described procedure but analyzing successive 250-cc. portions of distillate. The average distribution of formic and total acid in the distillate was found to be as follows:

	Total Acid	Formic Acid
	%	%
1st 250 cc. of distillate	92.87	95.87
2nd 250 cc. of distillate	4.44	3.29
3rd 250 cc. of distillate	1.87	0.84
4th 250 cc. of distillate	0.82	Not analyzed
	100.00	100.00

Because the results given in Table I indicated the necessity of removing certain interfering volatile constituents from this distillate before determining formic acid, experiments were undertaken to devise a convenient and efficient means for such removal (prepurification) without affecting the formic acid present. It was found that all the volatile interfering substances could be removed by neutralizing the acid mixture with barium hydroxide and evaporating to dryness on a steam bath. Since the barium salt of formic acid is stable at temperatures well above 100° C. (*4*), none is lost in this procedure, but more than a slight excess of barium hydroxide must be avoided. Results of tests with this prepurification treatment are given in Table II.

Discussion of Results

Table II shows the accuracy of the proposed method, as applied to pure formic acid solutions and to formic acid solutions containing interfering impurities, when determined with and without preliminary steam distillation and barium hydroxide pretreatment. For pure formic acid solutions, the direct determination gave an average experimental error of −0.24 per cent, the barium hydroxide treatment, when used, apparently not affecting these results. A combination of steam distillation and subsequent barium hydroxide treatment showed a +0.99 per cent error. The results secured on pure formic acid by substituting mercuric oxide for mercuric acetate were of similar accuracy. The results on sodium formate when determined alone showed a slightly greater error than when sodium acetate was added.

Experimentation with a test solution (solution A) containing known quantities of formic acid, acetic acid, formaldehyde, acetaldehyde, furfural, and allyl alcohol, the mixture representing a concentration of volatile interfering components normally present in the distillate from a crude pyroligneous acid, gave results 3.17 per cent too high on direct determination of formic acid without steam distillation or pretreatment. When this mixture was subjected to the preliminary barium hydroxide treatment to remove volatile interfering substances, this excess value was reduced to +0.79 per cent. Experiments to show the extent of removal of interfering substances by steam distillation and by barium hydroxide treatment (combined or separate), when applied to a sample of crude pyroligneous acid (solutions B and C), indicated that with no pretreatment the results were 26 per cent higher than the actual formic acid percentage shown after the combined purification treatments. Barium hydroxide treatment alone, when applied to the same liquor, reduced the high value slightly, while subsequent steam distillation reduced this further to 13.1 per cent. Barium hydroxide pretreatment when applied subsequent to a steam distillation gave a value which is assumed to be the actual percentage of formic acid present.

Since the exact amount of formic acid actually present in a crude pyroligneous acid cannot be definitely established directly, the removal of formic acid from such crudes was studied by the expedient of adding formic acid to a crude liquor of low known formic content in known amounts and determining the recovery of this added acid, the amount not recovered being determined by difference. As shown in Table II, the percentage of formic acid not recovered by this procedure (per cent error) was less (2.3 per cent) when a saponification procedure was used than with the regular steam distillation only (3.4 per cent). Saponification of the crude liquor increased the amount of determined formic acid by about 20 per cent, indicating the presence of a significant quantity of formic esters.

Fincke (*3*) found that the recovery of formic acid by steam distillation, from mixtures other than pyroligneous acid, was not over 95 per cent even with prolonged distillation. Quantitative recovery of formic acid by the steam distillation of pure formic acid solutions is shown in Table II. It is probable that the recovery of formic acid from various complex mixtures will vary according to the physical and chemical properties of each mixture.

REMOVAL OF FORMALDEHYDE. Special attention was also given to the behavior of formaldehyde under the conditions of the proposed method. Since part of the formaldehyde vaporizes, and since the nonvaporized portion apparently oxidizes slowly to formic acid and subsequently to carbon dioxide under distillation, there are only two alternatives, either to oxidize it completely to carbon dioxide in the original liquid, or to destroy or remove it before making the determination, the recommended prepurification methods (distillation from tar and evaporation with barium hydroxide) apparently being satisfactory. A preliminary oxidation of the formaldehyde, by Fehling's solution, was tried. This reagent oxidized the formaldehyde to formic acid, but apparently did not oxidize the formic acid further to carbon dioxide. However, on subsequent oxidation with mercuric acetate, a portion of the excess Fehling's solution was oxidized to carbon dioxide, giving yields in excess of the theoretical. During the oxidation of the formaldehyde by the Fehling's solution no carbon dioxide was formed, although appreciable amounts of cuprous oxide were deposited. It may therefore be possible to determine the percentages of formaldehyde and formic acid in a mixture by selective oxidation.

Summary

A method is presented for the convenient determination of formic acid in pyroligneous acid, based upon the removal of certain volatile and nonvolatile interfering substances, followed by the oxidation of the formic acid to carbon dioxide in a closed system using mercuric acetate as oxidizing agent. The evolved carbon dioxide is absorbed by circulation of the enclosed air stream through standard barium hydroxide in a special apparatus, and the amount of formic acid (equivalent to the carbon dioxide absorbed) is calculated from titration data. This method determines small amounts of formic acid in pyroligneous liquors with an accuracy of about 97.0 per cent. Greater accuracy (over 99.5 per cent) is attained on pure formic acid solutions.

TABLE II. RESULTS OF PREPURIFICATION TREATMENT

Material Analyzed	Formic Acid Present *Gram*	Formic Acid Found [a] *Gram*	Error %	Barium Hydroxide Purification Treatment
Formic acid (pure)	0.0617	0.0616	− 0.16	No
	0.0617	0.0615	− 0.32	No
	0.0755	0.0756	+ 0.13	Yes
	0.0755	0.0751	− 0.53	Yes
	0.0814(b)	0.0821	+ 0.99	Yes
	0.0814(b)	0.0821	+ 0.99	Yes
Formic acid (c) (mercuric oxide substituted for mercuric acetate)	0.0656	0.0653	− 0.46	No
	0.0656	0.0656	0.0	No
Sodium formate, 0.1375 gram, equivalent to	0.0930	0.0940	+ 1.07	No
Sodium formate, 0.1375 gram plus 6 grams of sodium acetate, equivalent to:	0.0930	0.0930	0.0	No
25 cc. of solution A(d)	0.0378	0.0390	+ 3.17	No
	0.0378	0.0381	+ 0.79	Yes
	0.0378	0.0374	− 1.06	Yes
Solution B(e)		0.5280	26.0 (f)	No
		0.5200	24.1 (f)	Yes
Solution C(g)		0.4740	13.1 (f)	No
Solution C(g)		0.4190	0.0	Yes
Solution D(h)		0.0833		Yes
Solution D(h) (0.4968 gram of formic acid added)		0.0855		Yes
		0.570	− 3.4	Yes
		0.553	(average)	Yes
Solution D (h) (saponified)		0.0997		Yes
		0.1025		Yes
Solution D (h) (saponified and 0.4968 gram of formic acid added)		0.5822		Yes
		0.5858	− 2.3 (average)	Yes

(a) Calculated from carbon dioxide produced.
(b) Steam-distilled.
(c) Five grams of mercuric oxide used as oxidizing agent. The mercuric oxide was first added, carbon dioxide removed from the system, and the sample of formic acid, dissolved in carbon dioxide-free water, then added.
(d) Solution A consists of formic acid, 0.756 gram; acetic acid, 0.74; allyl alcohol, 0.18; furfural, 0.19; formaldehyde, 0.18; acetaldehyde, 0.18 in 500 cc.
(e) Solution B consists of a 100-cc. sample of original crude pyroligneous acid (undistilled).
(f) These values are calculated on the assumption that 0.4190 is the correct formic acid content.
(g) Solution C consists of distilled pyroligneous acid (total distillate from 100 cc. of same crude liquor as solution B).
(h) Solution D represents the formic acid found in the first 750 cc. of steam distillate from 25 cc. of crude pyroligneous acid (crude liquor from sample B). Saponification and addition of formic acid, where indicated, preceded steam distillation.

Mercuric acetate has been found to possess certain advantages over mercuric oxide as an oxidizing agent, especially in the presence of dissolved carbon dioxide, because of its solubility in water.

The effect of interfering impurities on the method is shown. Impurities may for the most part be easily removed from distilled pyroligneous acid by neutralizing with barium hydroxide solution, followed by evaporation of the sample to dryness on a steam bath.

Preliminary saponification of crude pyroligneous liquors increased the formic acid percentages found, when formic esters were present.

A distillation procedure is described for removing volatile acids from crude pyroligneous acid.

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A Rapid Method for the Determination of Titanium

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BECAUSE of the increased use of titanium pigments, a rapid and accurate method for its quantitative estimation has become of considerable industrial importance. Gravimetric separations involving titanium are generally long and tedious because of the interference of many other common metals.

The general commercial method now in use involves the reduction of the titanium by means of a Jones reductor and subsequent titration with an oxidizing agent. However, because of the extreme susceptibility of the titanous ion to oxidation, the complete reduction and protection of the reduced titanium by this method requires over-large apparatus, a long period of time for the reduction, and a device for the protection of the reduced solution with carbon dioxide.

The method herein described gives quantitative results within 30 minutes and requires apparatus easily constructed from available laboratory glassware. Its use results in a saving of at least one-half of the normal time necessary for titanium determination by any of the standard methods now in use. It has been tested against samples of wide range of titanium content.

Discussion

Nakazono (*1*) developed an apparatus for the reduction of various ions using liquid zinc amalgam as a reducing agent. The use of a liquid amalgam has the advantage of exposing a greater area of zinc than could be obtained by a Jones reductor and therefore gave complete reduction in a much shorter time. The disadvantage of the Japanese method, however, was in the use of special apparatus which was not readily available. The authors have modified their apparatus so that it may be easily constructed from common laboratory glassware (illustrated).

The apparatus consisted of a 250-cc. globular separatory funnel, closed with a rubber stopper, *C*, carrying a piece of 0.63-cm. (0.25-inch) glass tubing, *B*, 5 cm. (2 inches) long which was stoppered by a small cork, *A*. The outlet tube of the funnel was connected to a 20- to 30-cc. glass tube, *D*, by means of a length of rubber tubing, *E*, which was closed by means of a pinchcock, *F*. Tube *D* was an old 25-cc. volumetric flask, but any small bulb may be used in its place.

After a number of experiments using both potassium permanganate and ferric ammonium sulfate as oxidizing agents for the titanous ion, it was found that ferric ammonium sulfate gave much superior results, probably because of the elimination of any iron interference. In general the method consisted of the reduction of the titanium to the trivalent state by use of liquid zinc amalgam and its titration with ferric ammonium sulfate using potassium thiocyanate as an indicator. The end point was the appearance of the usual wine-colored ferric thiocyanate complex.

Reagents

0.1 *N* potassium permanganate.

Cooled, freshly boiled, distilled water containing 1 per cent of sulfuric acid.

Ferric ammonium sulfate solution (approximately 0.7 *N*).

Liquid zinc amalgam.

Tablets of sodium bicarbonate (approximately 5-grain) purchased at any drug store.

Potassium thiocyanate (saturated solution).

Procedure

The ferric ammonium sulfate reagent is prepared by dissolving 30 grams of the salt in 300 cc. of distilled water acidified with 10 cc. of sulfuric acid. Potassium permanganate solution is added drop by drop, as long as the pink color disappears, and the solution is then diluted to 1 liter. This solution is standardized, after reduction with zinc amalgam in the special reductor, by titration with standard potassium permanganate.

The zinc amalgam (*1*) is prepared as follows:

Fifteen grams of fine-mesh zinc well washed with dilute sulfuric acid are heated for 1 hour on a water bath with 300 grams of mercury plus 5 cc. of dilute sulfuric acid (1 to 4). After cooling, the amalgam is washed several times with dilute sulfuric acid. The liquid portion is separated from the solid by means of a separatory funnel. The solid is discarded. The liquid amalgam is preserved under dilute sulfuric acid.

For the determination of titanium a sample equivalent to approximately 0.1 to 0.2 gram of titanium dioxide is digested with 20 cc. of concentrated sulfuric acid and 15 grams of powdered ammonium sulfate until it is entirely dissolved. Bulb *D* and the rubber tubing up through the stopcock are filled with the boiled water and both stopcocks are closed. Fifteen cubic centimeters of the zinc amalgam are added and the cooled sample is transferred to the funnel, using about 75 cc. of the distilled water. Two tablets of the sodium bicarbonate are now added and stopper *C* is inserted with cork *A* removed. When effervescence has ceased, two more tablets, broken into small pieces, are dropped through tube *B*. When the gas evolution is completed, cork *A* is immediately replaced and the entire apparatus vigorously shaken for 5 minutes.

The two stopcocks are now opened and the amalgam is allowed to flow into *D*. This displacement is best accomplished by alternately squeezing and releasing tube *E* with the fingers. As soon as the last particle of amalgam has dropped from the funnel, both stopcocks are closed and bulb *D* is removed for convenience while titrating. Stopper *A* is removed and 5 cc. of the potassium thiocyanate solution are added by means of a pipet through *B*. Stopper *C* is removed and both tube and stopper are washed into the funnel with distilled water. The solution is titrated in the funnel with the ferric ammonium sulfate. It is important that the ferric ammonium sulfate be added very rapidly until the first appearance of a wine-red color. The upper stopcock is now opened and tube *E* squeezed several times to force its liquid into the funnel. This will cause the wine color to disappear. The titration is completed by adding the ferric ammonium sulfate drop by drop to the end point.

Calcium sulfate, which is present in some commercial titanium pigments, does not interfere with the reduction because its precipitation is prevented by the high concentration of sulfuric acid. Barium sulfate should be removed by filtration before the reduction of the titanium.

Results

The pure titanium dioxide used in samples 1 and 2 was prepared in the laboratory of the Titanium Pigment Co., Inc.,

Table I. Results of Analyses

Sample	Weight of Sample	Titanium[a] Dioxide Present	Titanium Dioxide Found	Error
	Gram	*Gram*	*Gram*	*Gram*
1	0.2000	0.2000	0.2006	+0.0006
2	0.2000	0.2000	0.2000	0.0000
3	0.2500	0.2470	0.2463	−0.0007
4	0.2500	0.2470	0.2470	0.0000
5	0.5000	0.1468	0.1459	−0.0009
6	0.5000	0.1468	0.1470	+0.0002
7	0.5000	0.1459	0.1448	−0.0011
8	0.5000	0.1459	0.1452	−0.0007
9	0.5000	0.1459	0.1458	−0.0001

[a] Analyses by the Titanium Pigment Co., Inc.

by the method of Plechner and Jarmus (*2*). Samples 3 and 4 were Titanox A, a technical titanium dioxide pigment. Samples 5 to 9, inclusive, were Titanox C, which contains a large percentage of calcium sulfate. All the commercial samples were analyzed in the aforementioned laboratories and the results were forwarded to the authors.

Acknowledgment

The authors wish to thank Joseph L. Turner, director of research of the Titanium Pigment Co., Inc., for the numerous analyzed samples contributed and for the private analytical methods of this corporation (*3*).

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Determination of Organic Sulfur by the Liquid Ammonia–Sodium Method

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CHABLAY (*1*) and later Vaughn and Nieuwland (*3*) showed that halogens were quantitatively removed as sodium halide from all types of organic compounds by the action of sodium in liquid ammonia. This reaction proved to be the basis of an excellent method for the quantitative determination of organic halogen.

The observation that certain organic sulfur compounds were decomposed by the action of sodium in liquid ammonia, led to the belief that sulfur in organic compounds might be reduced to sodium sulfide or sulfite by this method of treatment. If so, the resulting inorganic sulfur could be oxidized to sodium sulfate with the subsequent determination of sulfur by precipitation as barium sulfate. Such proved to be the case.

Kraus and White (*2*) studied the action of sodium in liquid ammonia on phenyl mustard oil, sodium benzene sulfonate, thiophenol, and diphenyl sulfide, and reported positive qualitative tests for sodium sulfite as a decomposition product of sodium benzene sulfonate. They also reported the formation of sodium sulfide in the decomposition of phenyl mustard oil and diphenyl sulfide. Williams and Gebauer-Fulnegg (*4*), however, have since shown that no sodium sulfide is formed in the case of organic sulfides, disulfides, and mercaptans.

Inasmuch as the success of this method depends upon the formation of sodium sulfide or sulfite, it is apparent that not all types of sulfur compounds can be analyzed by this method. Diphenyl sulfide and related compounds might, however, be analyzed by this method if they are first oxidized to sulfones, sulfoxides, etc.

Procedure

One-tenth gram of the material to be analyzed is placed in a 250-ml. beaker and approximately 175 ml. of liquid ammonia are added. If solution does not take place upon stirring, ether, monobutylamine, or other organic solvent inert towards sodium in liquid ammonia is slowly added until the sample is dissolved. Small pieces of freshly cut sodium are now added until a persistent blue solution of uniform depth is obtained. When the reaction is complete, the covered beaker is placed in a water bath at room temperature and the solution allowed to evaporate to approximately 25 ml. At this point 3 to 5 grams of ammonium chloride dissolved in a few milliliters of liquid ammonia are added to destroy the excess sodium not utilized in the reaction. Evaporation is then continued to dryness.

The solids are dissolved in 75 ml. of hot water and 2 grams of sodium peroxide are added with stirring. The solution is heated to boiling, acidified with dilute hydrochloric acid, and heated vigorously for a few minutes to expel all traces of carbon dioxide and oxygen. A 5 per cent solution of barium chloride is then slowly added dropwise with constant stirring until the sulfate is completely precipitated. The precipitate is digested on a steam bath, filtered, washed, ignited, and weighed in the conventional manner.

The beaker containing the sample should be cooled by placing in a shallow dish containing about 0.5 cm. of liquid ammonia before the solvent ammonia is added. This avoids the violent spattering caused by the rapid vaporization of the ammonia on contact with the bottom of the beaker.

It has been found convenient at times to use a concentrated solution of sodium in liquid ammonia rather than finely cut pieces of metal. This modification is particularly useful when a large number of decompositions are being carried on at a single operation.

The use of organic solvents reduces the time of reaction and minimizes the possibility of error through incomplete decomposition.

Low results in analyses of compounds only slightly soluble in liquid ammonia or other solvents are partially remedied by the use of small samples and an excess of solvent. For example, by doubling the amount of solvent and reducing the size of the sample by one-half, the percentage of error in the determination of sulfur in thiourea was reduced from 1.3 to 0.26.

Results of analyses of sulfur compounds are given in Table I. All percentages are the average of at least two determinations.

Table I. Analyses of Sulfur Compounds

Compound	Sulfur Calculated	Sulfur Found	Difference
	%	%	
Thiourea	42.12	42.01	0.11
Benzoyl sulfimide	17.48	17.35	0.13
Acetone diethyl sulfone	28.09	27.89	0.20
Dinitrophenylthiocyanate	14.24	13.49	0.75
Diphenyl sulfone	14.68	14.13	0.55
Benzenesulfonamide	20.41	20.51	0.10
Benzenesulfonyl chloride	18.16	18.07	0.09
n-Propyl-*p*-toluenesulfonate	14.97	14.83	0.14
p-Toluenesulfonic acid	16.86	16.45	0.41
2-Naphthylamine-5,7-disulfonic acid	16.81	16.27	0.54

Table II. Agreement of Analyses

Compound	Sample I	Sample II
Thiourea	41.96	42.05
Acetone diethyl sulfone	26.84	27.35
Dinitrophenylthiocyanate	13.48	13.50
Benzoyl sulfimide	17.31	17.39
Benzenesulfonamide	20.45	20.56
n-Propyl-*p*-toluenesulfonate	14.87	14.79

The agreement between duplicate analyses of the same sample of various sulfur compounds is shown in Table II.

Summary

A method has been outlined by which a large number of organic sulfur determinations can be carried on simultaneously and without the aid of special apparatus.

In those compounds which are soluble in liquid ammonia and do not form intermediate products which cannot be reduced to inorganic compounds, sulfur can be determined more quickly and just as accurately by this method as by the present lengthy bomb or fusion method.

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A Source of Loss of Ammonia in Kjeldahl Distillations

Method of Eliminating This Loss

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IN THE Kjeldahl distillation process, the first portions of ammonia liberated are so diluted with air as to escape complete absorption in the standard acid. This loss, generally overlooked, is appreciable and may easily be reduced by the use of a proper delivery tube. The purpose of this paper is to show the magnitude of the error and how to reduce it.

Moose (*1*) obviated the loss in the determination of ammonia in ammonium salts by suspending the salt in a small vial in the neck of a Kjeldahl flask and releasing the salt into the alkaline solution, after the solution started to boil. Though the accuracy of his results was one part per thousand, this procedure is not applicable to the usual Kjeldahl process.

The usual method of distillation is to make the sulfuric acid solution alkaline with a cold saturated solution of sodium hydroxide, pouring it carefully down the side of the flask so that it does not mix immediately with the acid solution, adding a few pieces of granulated zinc, pumice stone, or glass beads to prevent bumping. The distilling flask is then connected to a Hopkins distilling head which is in turn joined to a condenser, to which is attached a delivery tube dipping into standard sulfuric acid. The distillation is carried out slowly at first, the total time being about 1 hour.

In order to determine the loss of ammonia resulting from the usual method of distillation, a known solution of ammonium chloride was used.

Twenty-five cubic centimeters of an ammonium chloride solution equal to 42.55 mg. of ammonia (35.00 mg. of nitrogen) were pipetted into an 800-cc. Kjeldahl flask to which had been added some glass beads to prevent bumping upon subsequent distillation. Two hundred cubic centimeters of distilled water were added. Five cubic centimeters of a cold 41 per cent sodium hydroxide solution were carefully poured down the side of the flask, after which the flask was immediately attached to a Hopkins distilling head which by means of rubber tubing had been connected to a block-tin condenser. There was joined to the outlet of the condenser a delivery tube (a calcium chloride–type tube) which dipped under the surface of 50 cc. of standard sulfuric acid, contained in a 400-cc. beaker, into which the ammonia was distilled.

The distillation was carried out very slowly for the first 30 minutes, during which time about 15 cc. of distillate were obtained. The total time of distillation was 1.25 hours, at the end of which 175 cc. of solution had distilled over. The results obtained from forty-seven 25-cc. samples of the ammonium chloride solution are given in Table I, and show a loss of 1.26 per cent of the total nitrogen, with a deviation from the experimental average of ±1.24 per cent.

Table I. Nitrogen Loss in Usual Method

Theoretical Nitrogen *Mg.*	Nitrogen Found *Mg.*	No. of Determinations	Deviation from Average *Mg.*
35.00	34.35	11	±0.26
	34.58	11	±0.27
	34.83	3	±0.10
	34.37	11	±0.62
	34.85	11	±0.18
	Av. 34.56 ± 0.43		

In order to show that this loss of nitrogen is due to the incomplete absorption of ammonia, at the beginning of the distillation, the 5 cc. of sodium hydroxide were suspended in the neck of the Kjeldahl flask by means of a small glass vial hung to a bent glass rod which led through the stopper of the Kjeldahl flask to the outside. After the ammonium chloride solution had been boiled to expulsion of the air, the vial of sodium hydroxide was released into the ammonium chloride solution. The distillation from this point onward was identical to that described for the determinations given in Table I. The average amount of nitrogen obtained from nine determinations was found to be 35.01 ± 0.01 mg. The average of these nine determinations is 0.03 per cent higher than the theoretical; the average deviation is ±0.03 per cent, which may be considered as negligible.

Obviously this method of distilling off the ammonia cannot be applied to the sulfuric acid Kjeldahl solutions. As an alternative, it was thought that if the air bubbles were broken up by passing them through very minute openings, the ammonia which they contained would be absorbed by the standard sulfuric acid into which it is distilled. In order to ascertain whether or not the air bubbles could be broken up to such an extent as to prevent the loss of nitrogen from this source, the delivery end of the calcium chloride–type tube was closed and flattened. Ten holes, each 0.08 mm. in diameter, were made in the bottom of the tube. Eight distillations were carried out, except for this modification, identical with those described for the results obtained in Table I. The experimental average of these eight determinations is 34.99 ± 0.02

mg. This average is 0.03 per cent less than the theoretical; the average deviation from the mean average is ±0.06 per cent.

In order to make this last procedure comparable to a regular Kjeldahl distillation, 20 cc. of concentrated sulfuric acid were added to the ammonium chloride solution plus 180 cc. of distilled water. Fifty-seven cubic centimeters of 41 per cent sodium hydroxide solution were carefully poured down the side of the flask and the distillation carried out as outlined in the previous procedure. The experimental average from eight determinations is 34.98 ± 0.04 mg. of nitrogen. This average is 0.06 per cent lower than the theoretical; the deviation from the mean average is ±0.12 per cent.

Summary

Loss of ammonia by the usual Kjeldahl distillation procedure has been ascribed to the fact that some ammonia during the first few minutes of distillation is diluted with air to such an extent that part of it escapes absorption by the standard sulfuric acid through which it passes.

The average loss of nitrogen resulting from forty-seven determinations with ammonium chloride solution has been shown to be 1.26 per cent, the average deviation being ±1.24 per cent.

The usual Kjeldahl procedure has been improved by the use of a delivery tube containing holes, each 0.08 mm. in diameter, which cause the air bubbles resulting during the first few minutes of distillation to be broken up to such an extent that the average loss of nitrogen resulting from eight determinations is 0.06 per cent, with an average deviation of ±0.12 per cent.

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A Rapid Method for the Volumetric Determination of Indium

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THE recent commercial availability of indium has revealed the need for rapid analytical methods for its determination. The method usually employed in commercial laboratories at the present time consists of precipitation of the indium as the hydroxide and ignition to the oxide (*4*). This procedure is unsatisfactory because of the unavoidable interference of iron, and because of the excessive time required for routine determinations.

A potentiometric method has been devised (*1*) using potassium ferrocyanide and the usual potentiometric equipment. This equipment is not always available in commercial laboratories.

The method to be described involves the titration of an indium acetate solution with potassium ferrocyanide in the presence of diphenylbenzidine as an internal oxidation-reduction indicator.

Reagents

Diphenylbenzidine, 2 grams in 100 cc. of concentrated sulfuric acid (sp. gr. 1.84).

Potassium fluoride, 10 grams of salt in 100 cc. of water.

Potassium ferrocyanide, 2.5 grams of trihydrate in a liter of water plus 0.2 gram of potassium ferricyanide.

The sulfuric acid used to make up the indicator solution should be free from nitrates and nitrites. Heating the acid until fumes of sulfur trioxide are evolved will eliminate these radicals.

Procedure

Weigh out a sample containing approximately 10 to 15 mg. of indium and dissolve in a suitable acid such as nitric acid or aqua regia. Remove the metals of Groups I and II with hydrogen sulfide. Make alkaline with ammonia in slight excess and digest on a steam bath or boil gently on a hot plate until faintly ammoniacal. Filter through a tight filter paper and wash sparingly with water.

Dissolve the precipitate in about 15 cc. of concentrated warm acetic acid (glacial) by repeatedly pouring the acid through the filter. Wash the filter with 10 additional cc. of the acetic acid and then with three 5-cc. portions of hot water, uniting both acid and washings. The resulting solution will contain both the indium and whatever iron is present as acetates.

If iron is present, as indicated by the tawny color of the hydroxides, add 0.5 gram of potassium fluoride dissolved in water as described above. The resulting solution should be about 60 per cent by volume of glacial acetic acid.

Cool the indium solution if necessary and add 2 drops of indicator. Titrate with standard ferrocyanide solution in a small cone flask, rotating the flask steadily until the end point is reached. The color change at the end point depends on the presence or absence of iron. If iron is absent and no fluoride has been added, the color change is sharp from slate blue to pea green which persists for 10 seconds with shaking. If iron is present and fluoride has been added, the end point is a sharp change from dull green to bright blue, the blue to persist for at least 10 seconds.

Discussion

One of the major applications of indium at the present is in dental gold alloys, which usually contain (in addition to indium) gold, silver, platinum metals, copper, and zinc. The indium can be separated from the other metals in such an alloy by means of a sulfide precipitation.

Dissolve the sample in aqua regia, add 5 to 10 cc. of sulfuric acid, take to fumes of sulfur trioxide, add enough hydrochloric acid to make about 1 *N* in total acidity (to prevent precipitation of indium sulfide), heat to boiling, and pass in a rapid stream of hydrogen sulfide for 30 minutes on a hot-plate. Filter off the sulfides without delay, boil the filtrate to expel hydrogen sulfide, and make slightly alkaline with ammonia. Digest, filter off the precipitated indium hydroxide, and treat as previously described. Acetic acid must be used to dissolve the precipitated hydroxide. For small percentages of indium no reprecipitation of the sulfides is necessary.

The potassium ferrocyanide solution is most conveniently standardized by titration against a solution of known indium content, best prepared by dissolving the pure metal in dilute nitric acid and proceeding as with an unknown sample. Should the supposedly pure indium contain tin, its presence will be indicated by a white residue insoluble in nitric acid.

The freshly precipitated indium hydroxide is very gelatinous and difficult to filter (*5*). Aging or digestion remedies this condition (*2*).

The sulfuric acid used to make the indicator solution should be fumed to sulfur trioxide to insure its being nitrite-free, as the presence of this ion causes a permanent blue in the indicator.

The titrating solution must be cooled to room temperature before the addition of the indicator (*2*).

Table I. Results

Weight of Sample *Grams*	Indium Present *Gram*	Indium Found *Gram*	Error *Gram*
0.0226	0.0226	0.0224	−0.0002
0.0226	0.0226	0.0228	+0.0002
0.0452	0.0452	0.0449	−0.0003
0.0192	0.0192	0.0192	0.0000
0.0113	0.0113	0.0114	+0.0001
0.0141	0.0141	0.0142	+0.0001
0.0168	0.0168	0.0169	+0.0001
1.5047[a]	0.0089	0.0089	0.0000
1.5970[a]	0.0094	0.0091	−0.0003
1.5493[a]	0.0090	0.0087	−0.0003

[a] Dental gold alloys, C. A. Wamser, analyst, J. F. Jelenko & Co.

The end point cannot be obtained in the presence of chlorides.

If no fluorides have been added, the titrating solution should be made up to contain about 40 per cent by volume of glacial acetic acid. If fluoride is used, the final concentration should be about 60 per cent acid. The fluoride reduces the ferric-ion concentration by the formation of the complex $[FeF_6]^{-3}$ thereby preventing the formation of Prussian blue on the addition of potassium ferrocyanide. In this way the laborious separation of iron by 1-nitroso-2-naphthol (*3*) is entirely avoided.

The end point is not permanent, as in the case of the permanganate titration of iron in the presence of chloride ion, and it is therefore necessary to standardize the ferrocyanide under exactly the same conditions as prevail in the routine analysis.

This volumetric method requires considerably less time than the usual gravimetric analysis.

Acknowledgment

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Lignin in Douglas Fir

Composition of the Middle Lamella

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THE middle lamella has been subjected to extensive research, yet our knowledge of its structure and composition is far from complete. The exact relationship of this membrane to the various physical properties of wood is still a matter of conjecture. The nature of the so-called matrix surrounding each cell in wood is also an extremely important consideration in the impregnation of wood with preservatives. Furthermore, dissolution of the middle lamella is a goal of chemical pulping, yet even its approximate composition is unknown.

Previous Work

Initial investigations of the middle lamella were made by botanists who, on the basis of anabolic processes, stains, and solvents, concurred in the main in the belief that pectin or a derivative of it comprised most, if not all, of the middle lamella. This botanical concept was supported by the work of Fremy, Treub, Strasburger, Mangin, Timberlake, Allen, and others (*1*) who relied largely on supposedly specific pectic stains and solvents. It was demonstrated that in certain tissues the middle lamella could be stained with ruthenium red or completely dissolved by pectic solvents; in nearly all tissue this staining effect was observed prior but not subsequent to treatment with a pectic solvent; hence, the conclusion that the middle lamella of most tissue was pectic. Botanists, however, studied tissues exceedingly diverse in kind, function, and age, and some recognized differences in the middle lamella which they attributed to differences in physical structure or chemical composition. While chemists, on the other hand, have disagreed almost unanimously with the botanical concept of the composition of the middle lamella, the two schools of thought were not always controverting the same thing, since studies by chemists were confined chiefly to mature xylem. As neither proponent completely or conclusively disproved the other, it appears probable that both are partially correct. At any rate, each has made valuable contributions, while the controversy has stimulated progress. In view of the present knowledge of the combination and adsorption of stains, it seems probable that the early botanical investigators overestimated the significance of parallelism in staining effects, since Ritter, Harlow, Scarth, et al., demonstrated the unreliability of specific stains and solvents (*10*). These and other investigators found the lamella of mature xylem to be largely soluble in lignin solvents and insoluble in cellulosic solvents, to exhibit staining effects with supposedly specific lignin stains, and to possess optical properties attributive to lignin (*2*). Although the evidence in favor of chemists' conception of the composition of the lamella preponderates, there are no data indicative of the complete absence of pectic compounds or of an integral lignin content.

Experimental Procedure

In view of the fact that investigation of the middle lamella by the usual technic, *in situ*, did not make quantitative results possible, a method was developed to isolate mechanically a quantity sufficient for analysis.

With the aid of a micromanipulator of the Janse and Péterfi type (Figure 1), it was found possible to remove the lamella[1] in virtually a pure state. After experimenting with various types of glass microinstruments, a satisfactory tool was devised by grinding high-grade sewing needles to a chisel-like point on a silicon carbide stone, maintaining a constant grinding angle by mounting the needle in a small block of wood much as a blade is mounted in a carpenter's plane, and rotating the needle through

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[1] Ritter's definition of the middle lamella (*2*), "the isotropic peripheral layer of cell wall, including the irregular masses of isotropic material commonly formed when three or more cells adjoin," describes the isolated material rather accurately.

180° when necessary to obtain equal grinding on each side, thus insuring the approximate equality of the length of the chisel edge and the diameter of the needle, as well as centration of the edge itself. The chisel was sharpened by the usual method of sharpening microtome knives, using the same block to maintain a constant sharpening angle. After mounting in a small wooden adapter which was then attached to the needle-holder of the micromanipulator, the needle could be actuated through the mechanism and made to perform exact and uniform movements in the three dimensions of space in its application to microscopic objects in the field of view of the microscope.

Various methods were tested, but it was found expedient to fasten sections to a slide by spreading a thin layer of an imbedding medium—of unusually desirable properties for this purpose, described elsewhere (*3*)—on the glass, allowing a tough film to form on the surface, and then pressing the section onto the layer of the imbedding agent. By mounting the slide on the mechanical stage of the microscope and simultaneously actuating the stage with one hand and the microtool with the other, it was possible to cut off fragments of the tissue, the size of which was limited only by the magnification, which, in turn, was limited by the working distance of the objective. By proper manipulation—i. e., moving the section of wood against the cutting tool by means of the mechanical stage, much as a log on a carriage is moved against a saw, with the section oriented so that only the tip of the knife could slide along the edge of a radial row of cells—it was possible to split off the outer radial row of cells, owing to a lack of cohesion in the middle lamella. The lamella itself was found to fracture approximately in the center, irregularly, or to tear loose from the adjacent secondary lamella; in the latter case the entire lamella adhered to one of the radial rows of cells.

This protruding material could be resected from the secondary wall (Figure 2) by moving the row of cells toward the vertical knife-edge and moving the knife nearer to or farther from the row of cells. The particles removed adhered to the knife, presumably because of static electrical charges, since the metallic knife was insulated by the wooden adapter. This permitted lifting the particles clear of the slide and inserting them, still on the knife, into the open end of a capillary tube mounted on the opposite standard of the micromanipulator. By discharging the knife or tapping it gently, the particles were dislodged and fell to the retaining capillary tube; the knife was removed—all the above operations being observed through the microscope—and the particles of lamella transferred to a microweighing bottle. The above disposition of instruments and use of the mechanisms of the mechanical stage and micromovements of the two standards had numerous advantages, foremost of which was the constant approximate centration of the knife in the field of view without additional adjustment.

To prevent inclusion of material other than the lamella, each particle was scrutinized for homogeneity. The middle lamella was found to be easily distinguishable from other lamellae by its dark finely granular appearance as contrasted with the almost colorless, crystal-like character of the remainder of the cell wall. Through the use of this technic on unstained and unextracted transverse sections of Douglas fir (*Pseudotsuga taxifolia*) heartwood, 200 microns thick, enough material consisting solely of the middle lamella was isolated from the summerwood to permit analysis. All resection was carried out under a magnification of approximately 100 diameters and grosser operations at a lower magnification. Material consisting of wood rays, summerwood, and springwood—the latter two containing the constituent ray tissue—was also isolated.

Samples of these tissues were analyzed for lignin by a micromethod developed by the author for the purpose (*4*).

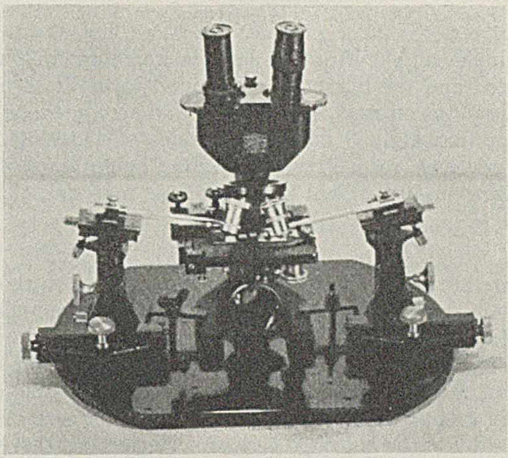

Figure 1. Front View of Micromanipulator and Binocular Microscope Used in Isolation

Standard on right carries the needle-holder and microchisel; the other carries the glass capillary.

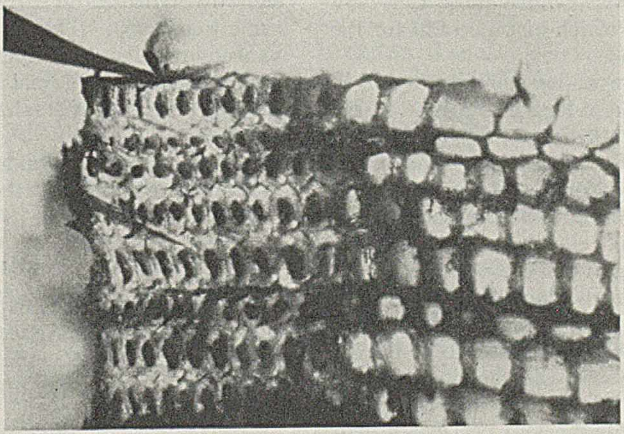

Figure 2. View of a Section on a Slide

A radial row of cells has been split off, leaving most of the lamella adhering to the secondary wall of the exposed radial row of cells. The knife has resected part of the lamella. Section 200 μ thick; photographed in air without a cover glass. × 135

The sample of wood ray tissue was washed with hot alcohol-benzene solution prior to hydrolysis to remove resin; the other material was not extracted. In all the tissue analyzed, except the middle lamella, samples of approximately 3 mg. were used which was the size the author recommended for the microprocedure; only 0.5 mg. of middle lamella was available for analysis. The results of twenty-seven previous analyses (*4*) showed an extreme difference between highest and lowest values of 0.79 per cent with an average difference of 0.58 per cent, using samples of approximately 3 mg. This degree of precision probably obtains for the values obtained in the analysis of the wood rays, summerwood, and springwood, as the size of samples and analytical conditions were identical. In the case of the middle lamella, however, only 0.5 mg. of material was available for analysis. Since work of other investigators seemed to indicate that at least half of the middle lamella might be lignin, this quantity of material would yield 0.25 mg. of lignin, corresponding to a sample of wood of approximately 0.75 mg., or only one-fourth the size of sample which should have been used in microprocedure. As it was impractical to adapt the microprocedure to a smaller sample, preliminary analyses were carried out using samples of approximately 0.75 mg. to determine the error introduced by the use of the smaller sample. Four analyses showed an extreme difference between highest and lowest values of 1.56 per cent with an average difference of 1.21 per cent. The average lignin content obtained was 33.18 per cent, as compared with the earlier average of 33.41 per cent obtained on samples of approximately 3 mg. (*4*). This loss of precision was probably due to the approach to the sensitive limit of the balance (a Kuhlmann microbalance permitting weighing with a precision of ±0.001 mg. with a maximum load of 20 grams on each pan) and to the solubility of the lignin, since the average yield of lignin is lower with the smaller samples.

Results

A single sample of middle lamella weighing 0.521 mg. was analyzed and the lignin content found to be 71.38 per cent. Samples of wood rays, springwood, and summerwood, weighing approximately 3 mg., gave values of 41.09, 35.24, and 31.56 per cent, respectively, all values being based upon the original oven-dry weight of the isolated material.

Discussion

There are no comparative quantitative data on the middle lamella. As the lignin content was found to be higher than the minimum assumed above, the precision is probably greater than was found to be the case with the 0.75-mg. sample. The amount of lignin isolated corresponded to a sample of wood slightly greater than 1 mg., or one-third the size of sample proposed for the microprocedure. Neglecting the effect of other variables, such as the effect of the dissolved carbohydrates, it would seem that the value of 71.38 per cent is susceptible to a maximum error of half of 1.39 per cent, which is the extreme difference between highest and lowest values which would be expected (assuming a direct relation between size of error and size of sample) with a sample of wood of approximately 1 mg. In other words, it seems probable that the lignin content of 71.38 per cent in the middle lamella isolated is not in error by more than 0.70 per cent of the true lignin content as measured by the microprocedure which was used in the analysis. In view of the fact that these experimental data must contain not only indeterminate errors—since there is no absolutely weight-constant receptacle, no absolutely insoluble compound, no absolutely pure precipitate or residue, and no absolutely accurate physical measurement—but also determinate errors, it seems valueless to apply statistical method in an attempt to determine deviation and error which, in this case, could have no significance. There was no evidence to indicate that the proportionately larger errors in balance reading, solubility and adsorption, etc., were not compensated sufficiently to permit the accuracy noted above.

Concerning the 28 per cent of the composition of the middle lamella left unaccounted for, part is probably due to the fact that, in spite of all precautions, the lamella isolated contained extraneous material. Each particle was examined minutely before it was accepted for analysis. In the author's opinion, the presence of 5 per cent of foreign material would probably be somewhat too high an estimate; in any case it is believed that it could not exceed 10 per cent. This would still leave some material unidentified. There is some evidence to indicate that the middle lamella contains hemicellulose as several investigators have suggested (*7*), which may account for the remainder of the lamellar substance.

Many botanists observed more or less definite layers in the middle lamella itself (discussed at length in Allen's paper, *1*) and suggested (1) a splitting of the immature lamella with subsequent infiltration or excretion of other substance, (2) that the first thin layer of lamella decomposed during maturation of the entire lamella, or (3) in agreement with the later work of Harlow and Anderson that chemical metamorphosis of the lamella occurred, beginning at the secondary wall and proceeding toward the center of the lamella. Incomplete metamorphosis would then cause a layering effect. Anderson and Harlow considered this metamorphosis to be from a pectic compound to lignin. However, the pectin content of mature wood is very low. Pectin contains the radicals of araban and galactan derivatives, lignin and pectin are high in carbon and methyl content—recent findings indicate a high methyl content in hemicellulose (*14*)—pectin and lignin are associated with hemicellulose in plant tissue, and hemicellulose has been split from lignin (*9*) and from pectin. Consequently, the suggestion that the central layer of the lamella may consist of hemicellulose which may be an intermediate product between pectin and lignin is perhaps worthy of more than casual consideration.

After removal of all lignin from wood chips by sulfite digestion, Klason noted that the dried chips were almost as stiff as the original wood, which effect he ascribed to residual hemicellulose (*12*). Klason's results were confirmed by the author (*5*) and similar effects noted earlier by delignification of wood by Ritter and Kurth, who also suggested hemicellulose in the middle lamella as the cause (*14*).

Carpenter and Lewis observed that the first effect of chemical digestion was a splitting of the middle lamella which left the fibers encased in the remains of the lamella, consisting largely of a spirally wound layer insoluble in cuprammonium solution and sulfuric acid (*7*), in rather striking agreement with the botanical conception of the double nature of the middle lamella. One hypothesis that might account for the initial splitting action of digestion is that the central layer of the middle lamella consists largely, if not completely, of hemicellulose which is hydrolyzed sooner or more easily than the lignin.

During the mechanical isolation of the lamella the author noted a definite tendency of the lamella to "cleave" either approximately in the center or at the union of the secondary wall, indicating a definite lack of cohesion in these points. When central cleavage occurred, it was frequently irregularly repand, serrate, or crenelated, the depths of the lacunae, however, being limited to a definite central zone. It was also frequently possible when the lamella was torn from the secondary wall to see very minute straplike elements on the edge of the lamella which had adjoined the secondary wall. These were probably fragments of the lamellar sheath of Carpenter and Lewis (*7*). Minute examination of the straplike elements showed them to have the same general appearance as the remainder of the lamella. Owing to the manner of isolation it was not possible to determine whether or not these elements had a spiral arrangement on the secondary wall. No confirmatory evidence was found regarding Lüdtke's claim that the middle lamella is many-layered (*13*).

Contrary to Forsaith (*8*), but in agreement with Harlow and Wise (*11*), the lignin content of wood rays was found to be considerably greater than in the total wood. This is supported further by the fact that wood rays have been shown to be sufficiently lignified to resist chemical digestion and beating and to appear intact in the finished sheet of paper (*6*).

The analyses of spring- and summerwood show about the same differences as do Ritter and Fleck's original values on the same wood (*15*). The most obvious explanation is that advanced by Allen and many others: that the lamella is of approximately the same absolute thickness in spring- and summerwood, but of smaller relative thickness in the summerwood.

Additional work is under way at the present time in an attempt to establish further the chemical composition of the middle lamella.

Acknowledgment

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Methods of Wine Analysis

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SAMPLING is more of a problem than one might suspect in an apparently homogeneous liquid such as wine. Air coming in contact with dry wine under certain conditions causes the formation of volatile organic acids. As this may occur at the top of a tank, the difference between the volatile acid content of the top and the bottom of a tank may amount to as much as 0.020 per cent. One tank was found to contain at the bottom, 0.108 per cent; middle, 0.125 per cent; and top, 0.148 per cent of volatile acid.

To secure a truly accurate sample, the entire tank should be thoroughly agitated; satisfactory results can usually be obtained by mixing samples from the top, middle, and bottom of the tank. For routine tests, a sample from the center of the tank will suffice.

Alcohol. Alcohol is usually determined in California wineries with the ebullioscope, but with the increasing number of chemists entering the wineries, the use of hydrometers and pycnometers is increasing. Some laboratories are increasing the accuracy of their ebullioscopes by determining the boiling point of wine distillates, but most plants still test the wine without this precaution. In the case of sweet wines, a dilution is sometimes made to reduce the effect of sugar on the boiling temperature. A limit of accuracy of 0.1 per cent is considered desirable.

Accurate alcohol spindles are now available at a reasonable figure and can be used in as little as 100 cc. A convenient method used in some plants is to distill 100 cc. of wine plus 50 to 75 cc. of water into a 100-cc. volumetric flask, and determine the alcohol on the distillate with a spindle. The residue in the boiling flask can be washed into a 100-cc. volumetric flask and the solids or "dry extract" roughly determined with a Balling hydrometer. This dealcoholized residue may be saved for the subsequent determination of reducing sugar and tannin.

Volatile Acids. This term is used to describe those substances removable from wine by steam distillation and possessing an acid reaction to phenolphthalein. In the United States volatile acids are calculated as acetic acid. With the recent introduction of new limits on volatile acids, this test becomes vitally important and greater accuracy in its determination is desired than previously, a limit of 0.005 per cent being frequently requested.

Slight variations of the official method (*1*) are in general use; usually a 10-cc. sample is steam-distilled until 50 to 100 cc. of distillate are collected, titrated, and calculated as acetic acids.

At present the various regulatory agencies, following the official method of the Association of Official Agricultural Chemists, do not make allowance for the fact that any sulfur dioxide in the wine is distilled and measured as a volatile acid. Certain types of wines (Haut Sauterne and Château Yquem) need up to 0.035 per cent of sulfur dioxide to prevent fermentation in the bottle. When titrated as a volatile acid, 0.035 per cent of sulfur dioxide is equivalent to 0.066 per cent of acetic acid. The limit on a white wine is 0.110 per cent of volatile acid as acetic; $0.110 - 0.066 = 0.044$ per cent of normal volatile acid, which might be taken as the limit for these types of wines. Such a limit excludes with certainty any wines over a year old.

Total Acids. This is the term used to describe the total titratable acidity in wine. It includes both volatile and fixed acids and is calculated as tartaric acid. The determination of total acidity in white wine presents little difficulty when phenolphthalein is used as an inside indicator (*1*), but the intense red color of red wine makes the use of phenolphthalein as an inside indicator difficult unless diluted with 50 to 150 volumes of boiling distilled water.

Some chemists use a mixture of 1 per cent phenolphthalein powder in powdered potassium sulfate as an outside indicator. For rough work many chemists use the change in color of the natural anthocyanin pigment of the grape as an indicator. Absolute accuracy is not as important in this determination as some others.

Reducing Sugars. Reducing sugars are frequently determined by the Lane and Eynon method (*3*), which measures the amount of unused cupric ion after the wine has been boiled with a known amount of Fehling's solution. The official or Munson and Walker (*5*) method is not very popular among the wineries, because it is slow and requires an analytical balance. The Shaffer and Hartmann (*8*) method, a volumetric iodometric method, is being used in many plants where a high degree of accuracy is desired, and is popular in the various fruit industries in California. An accuracy of 0.010 or 0.020 per cent is desirable in the reducing sugar test.

METALS. Iron and other metals are to be avoided in wine because they form a recurring cloud and render the wine difficult to stabilize. The limits for iron and tin, the two worst metals in wine (*7*), are about 2 to 5 p. p. m. The method of Leavell and Ellis (*4*) is being used for the determination of iron with apparent satisfaction by several plants.

SULFUR DIOXIDE. Sulfur dioxide in wine is best determined by the bicarbonate-hydrochloric acid (*6*) method such as is in general use in the dried fruit industry. Satisfactory results may be obtained using a 32- or 50-cc. sample, distilling into iodine, and titrating with thiosulfate. The federal limit on sulfur dioxide in wines is 0.035 per cent and an accuracy of 0.005 per cent may be expected of the analyses.

TANNIN. Tannin in wines is usually considered of insufficient importance to warrant analysis. However, where desired, the official method (*2*), using indigo-carmine as an indicator and titrating with standard permanganate, is followed.

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Micro-Dumas Generation of Carbon Dioxide

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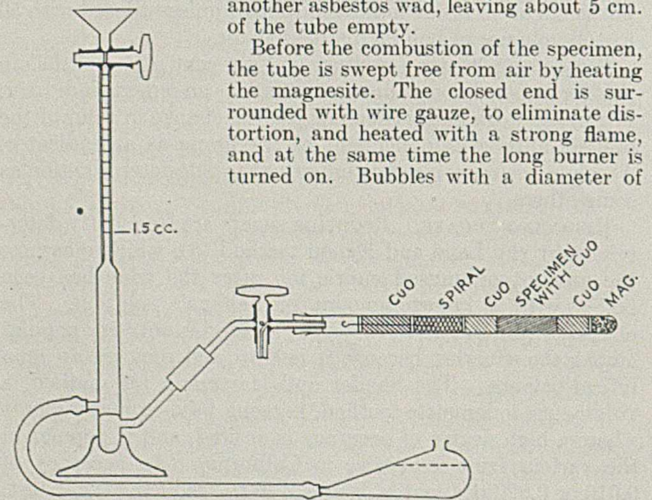
WHILE the use of the Kipp generator as a source of carbon dioxide is satisfactory, this is true only when two generators are coupled in series.

A much simpler method is to generate the carbon dioxide from magnesite, contained in the closed end of the combustion tube. This method utilizes very little space, an item of consideration in most laboratories, and the cost of equipment is greatly reduced, the combustion tube and the microazotometer being all that is necessary in addition to the balance. Berl and Burkhardt (*1*) have described a semi-micromethod for the determination of nitrogen, using magnesite as the source of carbon dioxide and an average specimen of 30 to 40 mg. of substance. They use an azotometer with a graduated volume of 10 cc. (*2*).

In the present method an ordinary microcombustion tube is used, one end being sealed off and rounded, making a tube approximately 40 cm. long. Magnesite is introduced into the closed end of the tube to a depth of about 3 cm. It is necessary to use Kahlbaum magnesite (*für anal.*), the pea size being broken into smaller pieces. Following the magnesite in successive order are an asbestos wad of about 3 mm., 4 cm. of copper oxide, the specimen (3 to 4 mg.) mixed with copper oxide, copper oxide for about 5 cm., an asbestos wad, reduced copper spiral followed by asbestos, 5 cm. of copper oxide, and finally another asbestos wad, leaving about 5 cm. of the tube empty.

Before the combustion of the specimen, the tube is swept free from air by heating the magnesite. The closed end is surrounded with wire gauze, to eliminate distortion, and heated with a strong flame, and at the same time the long burner is turned on. Bubbles with a diameter of one-tenth division appear in from 4 to 5 minutes, and true microbubbles are obtained if heating is continued for another minute. When bubbles of one-tenth division appear in the azotometer the flame under the magnesite is turned down until the barely luminous flame just touches the gauze, so that the generation of carbon dioxide is nearly stopped.



The combustion is carried out in the usual manner. The rate of decomposition of the compound can be controlled very accurately, as there is very little free space behind the specimen, and any change in the rate of decomposition is indicated immediately in the azotometer. When the specimen is completely decomposed and the burner under the specimen has reached the long burner, the flame under the magnesite is increased slowly until the nitrogen has been removed and the microbubbles appear in the azotometer. The writer uses two combustion tubes, one being filled while the other is in use.

The decomposition of the specimen and sweeping of the gases take from 25 to 30 minutes, depending on the amount of nitrogen in the compound. The azotometer is read after 10 to 12 minutes. The total time from the beginning of sweeping until the final reading of the nitrogen volume should not exceed 50 minutes. From the volume of nitrogen collected, 2.2 per cent is deducted to give the net volume to be reduced to normal conditions. This value is determined by analyzing a known compound—for example, Kahlbaum hippuric acid—at the beginning and end of each series of analyses. This value has remained constant, and obviously represents a blanket correction, apart from temperature and pressure corrections. All the nitrogen values in the publications from this laboratory during the past three years have been determined by this procedure.

The method was investigated at the suggestion of J. S. Buck of this laboratory.

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Direct Simultaneous Microdetermination of Carbon, Hydrogen, and Oxygen

IV. Analysis of Bituminous Coals and Derived Products

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This paper describes the application of a method for direct determination of oxygen, developed on pure compounds (*10, 11, 12*), to the complicated substances, coal and products derived from it. The previously described work on this general method of analysis showed that knowledge of the types of nitrogen linkage in the compound to be analyzed is necessary for exact computation of the oxygen content from the combustion data. When this knowledge is not available, as in the case of coal, the use of the present analytical method permits one to reverse the argument and draw conclusions regarding the type of nitrogen linkage predominantly present in the substance analyzed. In this respect the paper describes a method of analysis which may be used to determine not only elementary composition, but also, in part, chemical constitution. The fact that the application of this method to coal permits conclusions to be drawn regarding the type of the nitrogen linkage present emphasizes that the method has indirect as well as direct value.

THE oxygen content of coal is generally calculated by difference—that is, the sum of the percentages of all directly determined elements is subtracted from one hundred and the difference is considered to be oxygen. In such a method, all the errors, cumulative or compensative, made in the individual determinations are included in the value assigned to oxygen. The importance of a direct method for the determination of oxygen in coal and its products has been stressed repeatedly (*22*). The purpose of this paper is to report the results obtained in the direct determination of carbon, hydrogen, and oxygen in various fuels using the gasometric microcombustion method which was developed in this laboratory on pure organic compounds (*10, 11, 12*).

Two methods have been suggested for the direct determination of oxygen in fuels. The hydrogenation method of ter Meulen and Heslinga (*16*) has been applied to the analysis of coal and its products by a number of investigators (*1, 3, 15, 19*). In a critical study of this method as applied to the analysis of coal, Schuster (*19*) pointed out that although it yields excellent results for oxygen in pure compounds, it is not faultless when applied to coal. This is due to the simultaneous hydrogenation of the mineral matter present in the coal sample. Besides Schuster's criticism, this method also possesses the disadvantage that in analyzing complex substances, such as fuels, the determination of the oxygen content of the sample becomes less simple, less direct, and hence less accurate the greater the number of elements present besides carbon, hydrogen, and oxygen. Also because of the deposition of carbon and poisoning by sulfur and halogens, the catalyst rapidly loses its activity and must be frequently renewed. An advantage of the method is that oxygen can be determined independently without the necessity of also determining other elements.

The gasometric combustion method has also been used for the direct determination of oxygen in various fuels (*4, 5*). Previous investigators using this method have assumed that the nitrogen present in the sample escaped completely in the elementary state and the sulfur was oxidized completely to sulfur dioxide or trioxide. A critical analysis of the results obtained with this method has revealed that they contain rather large compensative errors and that certain of the assumptions made are incapable of experimental confirmation. For this method to be successful when applied to fuels, much greater accuracy must be attained in the carbon-hydrogen determination than has so far been reported because errors in the determination of these elements are multiplied by large factors in terms of oxygen. Likewise, the accuracy of the gasometric determination of "oxygen consumed" is capable of considerable improvement. Also, the fate of the nitrogen and sulfur must be determined so as to be able to correct the volume of oxygen consumed as well as to permit accurate calculation of the oxygen content of all of the combustion products. These details have been worked out in this laboratory using pure organic compounds, and the results have already been published (*10, 11, 12*).

Schuster (*18*) has also criticized this method from a theoretical standpoint. He asserts that "ash reactions" will likewise be involved, the most important being the splitting out of hydrate-water from silicates, evolution of carbon dioxide from inorganic carbonates, and the formation of sulfates, especially calcium sulfate. These reactions compensate to some extent, the first two tending to make the oxygen values high while the last tends to make them low. The net result, in the case of fuels in which sulfate formation is low, such as bituminous coals, would be to yield high results, while fuels in which sulfate formation is high, owing to a high content of calcium salts, as in brown coals, would tend to yield low results.

The particular advantage of this method is that carbon, hydrogen, and oxygen are determined simultaneously, and these, as well as moisture and ash, can be determined on a single weighed sample. Another advantage is that the presence of sulfur, halogens, and nitrogen has no harmful influence on the combustion tube filling and numerous series analyses can be made without changing the filling. A disadvantage is that in order to determine the oxygen content of a sample it is necessary to know the percentage of other elements (except halogens) present in the sample. For the purposes of this laboratory this is not a serious disadvantage since, in general, the complete composition of the sample is desired in order to make up elementary balances. The direct oxygen determination then serves as a control on all the other analyses made on the sample. The final advantage of this method when applied to microsamples is that it is essentially a modification of the Pregl carbon-hydrogen determination and Pregl's classical development of this method serves as the basis for the procedure. In case of the hydrogenation method, much fundamental work must undoubtedly be done in order to convert it into a micromethod.

Experimental

The apparatus and procedure used in the analyses on coal and its products are identical to those used in the studies on pure organic compounds (*10, 11, 12*).

In the determination of the oxygen content of the fuel samples the hypotheses derived from the work on pure compounds were used. The nitrogen and sulfur in the fuels, determined by independent analyses, are considered, as a result of thermal decomposition, to be present in simple fragments which are then oxidized, under the conditions existing in the combustion tube, yielding only elementary nitrogen, nitrogen peroxide, and sulfur trioxide. As has been demonstrated (*12*) the ratio of nitrogen peroxide to nitrogen is a function of the type of nitrogen linkage present in the compound. In order to determine the oxygen content of the fuel samples, the type of nitrogen linkage present must be known.

Very little is known regarding the manner in which nitrogen is linked in coal and its derived products (*17*). Most authorities seem to agree that protein materials are the source of nitrogen in coal. According to Shacklock and Drakeley (*20*), the amount of nitrogen which can be extracted from fuels with 33 per cent sulfuric acid varies inversely with the rank of the fuel. Coalification appears to convert basic nitrogen compounds into substances of a neutral nature.

Terres (*21*) has pointed out that when bituminous coal is subjected to dry distillation the greatest part of the nitrogen (40 to 65 per cent) remains in the coke in a very thermostable form, 10 to 14 per cent evolves as ammonia, and the residue (21 to 50 per cent) is evolved as elementary nitrogen, cyanogen, or hydrogen cyanide or is present in the tar. Since some ammonia is obtained on dry distillation Terres concluded that probably all the nitrogen in the coal first appears as ammonia, the other nitrogen-containing substances being formed as a result of secondary reactions of the ammonia. Terres dry-distilled a variety of pure compounds at a temperature of 700° to 900° C., in an atmosphere of carbon dioxide, and found that only compounds containing amino or substituted amino groups were capable of yielding ammonia under these conditions and concluded that these groups must be present in coal.

However, it seems rather unlikely that any considerable number of such chemically active groups as amino or imino groups can be present in bituminous coal after having been subjected to as rigorous a reaction as coalification. The amino group is generally more reactive than the hydroxyl group, toward the same reagents, and bituminous coal is known to contain very few free hydroxyl groups even though the percentage of oxygen is much higher than the percentage of nitrogen. The hydroxyl number of coals also decreases regularly as the rank of the coal increases (*7*). It would seem more reasonable to believe that the nitrogen in coal is bound in a heterocyclic linkage as a result of condensation of amino or substituted amino groups with other reactive groups.

It is well known that on subjecting bituminous coal to low-temperature coking, high-temperature coking, and gasification processes, the amount of nitrogen in the residue decreases in the order named. The ammonia content of the gases from low-temperature coking is low, is high from high-temperature coking, and again low from gasification. The fact that any ammonia is obtained on gasification is due to the protection of the ammonia against further reaction by the presence of other gases and water vapor. Muhlert (*17*) states that in the absence of steam during gasification, the nitrogen compounds of coal, just as in combustion, yield no ammonia but are completely decomposed into elementary nitrogen. In a combustion analysis the coal is, in reality, subjected successively to all three of the above-named reactions. It is conceivable that during the first stages of the combustion some ammonia would be evolved according to Terres' idea, but here the ammonia is mixed with a huge excess of oxygen and is not protected from thermal decomposition and so would undergo this reaction as well as a high-temperature catalytic oxidation. In the final stage of the combustion the residual coke is gasified and in this stage only elementary nitrogen would be expected.

On the basis of the hypotheses advanced in connection with the study of pure nitrogen-containing compounds (*12*), if little or no hydrogen is attached to the nitrogen in the coal—that is, postulating that the nitrogen of the coal is predominantly present in a heterocyclic linkage—very little ammonia but rather cyanogen and perhaps hydrogen cyanide would be expected as a result of thermal decomposition and these, on oxidation, would yield nitrogen peroxide and nitrogen. The formation of ammonia could be explained, without assuming its direct evolution from the coal, by the reaction between the cyanogen and hydrogen cyanide with water vapor which is formed simultaneously. It is this type of reaction which is considered to occur when coke is treated with steam in order to improve the yield of ammonia, the coke nitrogen being practically quantitatively converted into ammonia (*2, 21*), and is the basis of the Mond process.

Although the heterocyclic linkage of nitrogen in coal is preferred, and since the type of linkage is not definitely known, it was decided to calculate the percentage of oxygen present on the assumption that (1) the nitrogen is present as heterocyclic nitrogen (method 1 in the tables), and (2) the nitrogen is present in amino or amido groups (method 2 in the tables). From the work on pure nitrogen-containing compounds (*12*), it was found that the first-mentioned type gave satisfactory results for oxygen when it was postulated that 59 per cent of the nitrogen was converted to nitrogen peroxide and 41 per cent to nitrogen. The second types gave satisfactory results for oxygen when it was postulated that 26 per cent of the nitrogen was converted to nitrogen peroxide and 74 per cent to nitrogen.

Table I gives the results obtained on a bituminous coal A, Table II on Edenborn coal, which is being intensively studied in this laboratory, and Table III on the residue remaining after Edenborn coal had been subjected to the action of 5 *N* sodium hydroxide solution for 24 hours at 300° C. Unless otherwise noted, the analyses were performed in the Coal Research Laboratory on microsamples. In accordance with the results obtained on pure sulfur-containing compounds (*11*), all the calculations include the complete oxidation of the sulfur present in the sample to sulfur trioxide, followed by absorption as silver sulfate, one atom of oxygen being consumed in the last reaction for each atom of sulfur present.

In Tables I, II, and III on the basis of the first assumption, the directly determined oxygen is, with two exceptions, higher than oxygen calculated by difference and the sum of all directly determined constituents approximates, but averages slightly greater than 100 per cent. On the basis of the second assumption, the directly determined oxygen is, in every case, lower than oxygen calculated by difference and the sum of all directly determined constituents falls considerably short of 100 per cent. The data in Table II also indicate the slow oxidation which the Edenborn coal has been undergoing during storage. Both the oxygen determined directly and that calculated by difference show that the sample stored in glass in 1931 had oxidized to a smaller extent than a sample which had been stored in a large steel drum.

These data on coals appear to confirm the theoretical deductions of Schuster (*18*) regarding the absolute magnitude

Table I. Coal Sample A

Weight of Sample	Moisture-Free					Moisture- and Ash-Free		Oxygen by Difference Moisture-Free	Direct Oxygen		Sum of Directly Determined Constituents	
	C	H	N	S	Ash	C	H		Method 1	Method 2	Method 1	Method 2
Mg.	%	%	%	%	%	%	%	%	%	%	%	%
6.554[a]	82.18	4.62	1.24	0.57	6.42	87.83	4.94	4.97	5.14	3.74	100.17	98.77
7.496[a]	82.03	4.68	1.24	0.57	6.78	87.99	5.01	4.70	4.67	3.27	99.97	98.57
6.986[a]	82.92	4.64	1.24	0.57	5.67	87.90	4.92	4.96	4.40	2.99	99.44	98.03
6.792[a]	82.79	4.68	1.24	0.57	5.73	87.82	4.96	4.99	5.52	4.11	100.53	99.12
7.300[a]	82.22	4.68	1.24	0.57	6.21	87.65	4.99	5.08	5.60	4.21	100.52	99.13
Mean	82.43	4.66	1.24	0.57	6.16	87.84	4.96	4.94	5.07	3.66	....	...
[b]	83.09	4.70	1.28	0.57	5.91	88.31	5.00	4.45	..	..	....	...
[c]	83.39	4.79	1.21	0.57	5.59	88.33	5.07	4.45	..	..	....	...

[a] Analyzed November, 1934.
[b] Analyzed October, 1933, by Laboratory A.
[c] Analyzed May, 1934; mean of two determinations.

Table II. Apparent Atmospheric Oxidation of Edenborn Coal Samples in Storage

Weight of Sample	Moisture-Free					Moisture- and Ash-Free		Oxygen by Difference Moisture-Free	Direct Oxygen		Sum of Directly Determined Constituents	
	C	H	N	S	Ash	C	H		Method 1	Method 2	Method 1	Method 2
Mg.	%	%	%	%	%	%	%	%	%	%	%	%
[a]	79.0	5.1	1.6	1.0	7.6	85.5	5.5	5.7	..	..	....	...
[b]	78.27	5.26	1.62	0.98	8.39	85.44	5.74	5.48	..	..	....	...
[c]	78.07	5.21	1.66	0.95	7.98	84.84	5.66	6.13	..	..	....	...
[d]	77.92	5.15	1.66	0.96	7.90	84.60	5.59	6.41	..	..	....	...
6.906[e]	77.54	5.27	1.52	1.00	7.96	84.26	5.72	6.71	7.50	5.78	100.79	99.07
7.614[e]	77.41	5.14	1.52	1.00	7.96	84.10	5.58	6.97	7.33	5.62	100.36	98.65
7.389[e]	77.79	5.15	1.52	1.00	7.96	84.52	5.60	6.58	7.27	5.58	100.69	99.00
7.597[f]	78.32	5.09	1.65	1.00	8.00	85.13	5.53	5.94	7.02	5.15	101.08	99.21
7.376[f]	78.27	5.06	1.65	1.00	8.07	85.14	5.51	5.95	6.77	4.89	100.82	98.94

[a] Analyzed September, 1931 [*Bur. Mines Tech. Paper* 525 (1932)].
[b] Analyzed February, 1933.
[c] Analyzed May, 1934, by Laboratory A.
[d] Analyzed July, 1934, by Laboratory A.
[e] Analyzed December, 1934.
[f] Analyzed February, 1935. Sample ground and sealed (with paraffin) in glass bottles in June, 1931. Air displaced by natural gas.

Table III. Alkali-Treated Edenborn Coal Residue

Weight of Sample	Moisture-Free					Moisture- and Ash-Free		Oxygen by Difference Moisture-Free	Direct Oxygen		Sum of Directly Determined Constituents	
	C	H	N	S	Ash	C	H		Method 1	Method 2	Method 1	Method 2
Mg.	%	%	%	%	%	%	%	%	%	%	%	%
6.636[a]	84.77	5.28	1.62	0.33	2.19	86.66	5.40	5.81	6.36	4.52	100.55	98.71
7.728[a]	84.86	5.28	1.62	0.33	2.23	86.79	5.40	5.68	6.39	4.56	100.71	98.88
Mean	84.82	5.28	1.62	0.33	2.21	86.73	5.40	5.75	6.38	4.54	....	...
[b]	85.30	5.41	1.62	0.33	2.12	87.15	5.53	5.22	..	..	....	...

[a] Analyzed December, 1934.
[b] Analyzed October, 1934.

of the values for oxygen as obtained by these methods. However, work on pure compounds has shown that the carbon-hydrogen determination is rarely perfect, the general tendency in this direct method being to yield slightly high values, especially for hydrogen. Since any error in hydrogen is multiplied by a rather large factor, the values obtained for oxygen tend to be high by about +0.3 per cent. In fact, direct determinations for carbon, hydrogen, and oxygen were made on samples of benzoic acid for the purpose of control, one just before the series of coal analyses and one just after. The direct oxygen values obtained in these determinations were high by +0.32 and +0.34 per cent, respectively. On this basis, using the sum of all directly determined constituents as a criterion, the value for oxygen which yields a sum slightly greater than 100 per cent would be preferred. Such values were obtained only when using the ratio of 59 per cent nitrogen peroxide to 41 per cent nitrogen. This is considered to offer strong support to the idea that by far the greatest part of the nitrogen in coal is present in some form other than amino or amido groups and it is suggested that the most likely form would be that of a heterocyclic linkage. In connection with the analyses made on the residue from alkali-treated Edenborn coal (Table III) it should be pointed out that any amide linkages, if present, would very likely be hydrolyzed under such drastic hydrolytic conditions. However, the nitrogen content of this residue is practically the same as that of the original coal and only a faint odor of ammonia was noticed on opening the bomb after completion of the reaction. This evidence would also indicate the absence of amido groups in the coal and justify the use of the ratio of 59 per cent nitrogen peroxide to 41 per cent nitrogen in the calculations.

In order to determine the magnitude of the error introduced by the so-called "ash reactions" mentioned by Schuster, a calculation was made using the combustion data obtained in the first December, 1934, analysis on Edenborn coal. The composition of the ash from this coal is available (*6*) and was used in calculating the mineral matter present in the sample (*9*). The oxygen content of the "hydrate-water" liberated from the various hypothetical hydrates as well as the oxygen content of the carbon dioxide liberated from hypothetical carbonates, is deducted from the previously used value for the oxygen present in the combustion products. The amount of "oxygen consumed" in oxidizing hypothetical lower oxides and sulfides to ferric oxide is also calculated and subtracted from the previously determined value for oxygen consumed. The formation of sulfates is not considered since, in this coal, the percentage of volatile sulfur is practically identical to the total sulfur. If the correction which results from these calculations is used, the value for the oxygen present in the sample is lowered by 0.53 per cent, so that, on the basis of 26 per cent

Table IV. Standard Nitro Humic Acid

Weight of Sample	Moisture-Free					Moisture- and Ash-Free		Oxygen by Difference Moisture-Free	Direct Oxygen		Sum of Directly Determined Constituents	
	C	H	N	S	Ash	C	H		Method 1	Method 2	Method 1	Method 2
Mg.	%	%	%	%	%	%	%	%	%	%	%	%
8.792[a]	64.35	2.76	4.28	0.66	1.00	65.00	2.79	26.95	32.38	27.54	105.43	100.59
8.708[a]	64.44	2.70	4.28	0.66	1.11	65.17	2.74	26.81	31.95	27.09	105.14	100.28
Mean	64.40	2.73	4.28	0.66	1.06	65.09	2.77	26.87	32.17	27.32	....	....
[b]	64.52	2.73	4.21	0.67	1.19	65.30	2.76	26.68	...	...	....	....

[a] Analyzed December, 1934.
[b] Analyzed October, 1934.

Table V. Coke Sample A

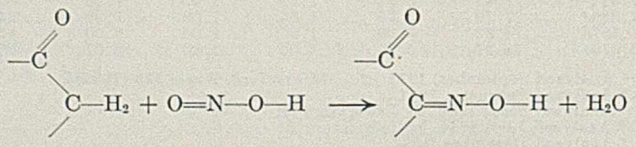
Weight of Sample	Moisture-Free					Moisture- and Ash-Free		Oxygen by Difference Moisture-Free	Direct Oxygen			Sum of Directly Determined Constituents		
	C	H	N	S	Ash	C	H		Method 1	Method 2	Method 3	Method 1	Method 2	Method 3
Mg.	%	%	%	%	%	%	%	%	%	%	%	%	%	%
6.318[a]	89.96	0.54	0.86	0.50	7.72	97.50	0.59	0.42	1.61	0.65	−0.11	101.19	100.23	99.47
7.257[a]	89.59	0.59	0.86	0.50	8.01	97.39	0.64	0.45	2.16	1.17	+0.41	101.71	100.72	99.96
Mean	89.78	0.57	0.86	0.50	7.87	97.45	0.62	0.44	1.89	0.91	+0.15	....	....	...
[b]	90.27	0.54	0.89	0.57	7.43	97.52	0.58	0.30	..	..	....	....	....	...
[c]	89.68	0.65	0.86	0.50	7.57	97.03	0.70	0.74	..	..	....	....	....	...

[a] Analyzed December, 1934.
[b] Analyzed October, 1933, by Laboratory A.
[c] Analyzed May, 1934; mean of two determinations.

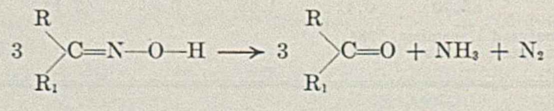
nitrogen peroxide to 74 per cent nitrogen it becomes 5.24 per cent and on the basis of 59 per cent nitrogen peroxide to 41 per cent nitrogen, 6.97 per cent. The latter, preferred value now agrees fairly satisfactorily with the oxygen calculated by difference but is still slightly higher. The sum of all directly determined constituents becomes 98.53 and 100.26 per cent, respectively. This indicates even more clearly the likelihood of the nitrogen in the coal being present as a heterocyclic or similar linkage. The deviation of the sum of the constituents from 100 per cent in the last case cited is practically identical to the deviations of the control analyses in which benzoic acid was used.

Two analyses were made of a "nitro" humic acid prepared by boiling Edenborn coal with *N* nitric acid for one week. This treatment increased the nitrogen content from 1.52 to 4.28 per cent. Such a reaction involves fairly drastic hydrolysis and it is doubtful if any amide groups could survive. Calculating the results on the basis of 59 per cent nitrogen peroxide formation (method 1) gave, in this case, the unreasonable total of 105.43 and 105.14 per cent for the sum of directly determined constituents. When calculated on the basis of 26 per cent nitrogen peroxide formation (method 2), the sum of directly determined constituents was 100.59 and 100.28 per cent. Since the oxygen values for the original coal were satisfactory when calculated by method 1 and unsatisfactory when calculated by method 2, it was anticipated that method 1 would also yield satisfactory results for the nitro humic acid. However, as indicated above, the reverse is true. As observed from a comparison of the elementary analyses of the original coal and the nitro humic acid, the nitric acid treatment reduced the carbon content from 78 to 64 per cent, the hydrogen from 5.2 to 2.7 per cent, and the ash from 8 to 1 per cent, and increased the nitrogen from 1.5 to 4.3 per cent. Aside from these changes, one would hardly expect such a deep seated change in the "nucleus" of the original coal as to invalidate the method of calculation which yielded satisfactory oxygen values for the original coal, nor would one expect any extensive change in type of the nitrogen linkage of the nitrogen present in the original coal, such as conversion from heterocyclic to amino or amido linkages.

How can this apparent anomaly be explained? According to Fuchs (*8*), when coal is heated with nitric acid the coal is oxidized and the nitric acid is reduced to nitrous acid. The latter reacts with active methylene groups in the coal forming isonitroso ketones:



On combustion, the fate of the nitrogen in an isonitroso ketone will depend, according to the hypotheses previously mentioned, upon what happens on pyrolysis and subsequent oxidation of the pyrolytic products. In a study of the action of heat on ketoximes, which are closely related, structurally, to isonitroso ketones, Kötz and Wunstorf (*13*) found that certain of these substances, in an atmosphere of carbon dioxide and at temperatures as low as 170° C., react practically quantitatively:



$$3\ \begin{matrix} R \\ \rangle C{=}N{-}O{-}H \\ R_1 \end{matrix} \longrightarrow 3\ \begin{matrix} R \\ \rangle C{=}O \\ R_1 \end{matrix} + NH_3 + N_2$$

If it is assumed that the original nitrogen present in the coal is not affected by the nitric acid treatment, then 35.5 per cent of the total nitrogen in the nitro humic acids, on thermal decomposition and oxidation would be transformed into nitrogen peroxide and nitrogen in the ratio 59 to 41. The balance of the nitrogen, according to the above equation, would be converted into ammonia and nitrogen in the ratio 33.3 to 66.7. This ammonia would then be oxidized to nitrogen peroxide and nitrogen in the ratio 26 to 74. The net result of this series of reactions would yield, by calculation, 26.5 per cent of the nitrogen as nitrogen peroxide and 73.5 per cent as elementary nitrogen, which is approximately the ratio which was found to yield satisfactory results for oxygen in this sample. This agreement would appear to explain the anomaly mentioned above and also justify the use of the ratio of 26 per cent nitrogen peroxide to 74 per cent nitrogen for this particular substance and also confirm Fuchs's idea that the nitrogen, added to coal on treatment with nitric acid, is present in the form of an isonitroso ketone linkage. The data are summarized in Table IV.

Finally, two analyses were made on a sample of coke. The results are given in Table V. When calculated on the basis of 59 per cent nitrogen peroxide to 41 per cent nitrogen, the sum of all directly determined constituents is 101.19 and 101.71 per cent, whereas, when calculated on the basis of 26 per cent nitrogen peroxide to 74 per cent nitrogen, the sum is 100.23

and 100.72 per cent, which, as in the case of the original coal, appears to be a more reasonable figure.

According to Muhlert (*17*), gasification of coke in the absence of steam yields no ammonia, the nitrogen present being evolved, as in combustion, exclusively as elementary nitrogen. In the present work the combustion was conducted in an atmosphere of dry oxygen, and since coke contains a very low percentage of hydrogen there is little opportunity for steam formation. Muhlert also points out that the hydrogen in coke does not take part in the formation of ammonia during gasification. Van der Ley and Wibaut (*14*) likewise state that thermal decomposition of the carbon-nitrogen complex in coke prepared from coal begins at about 800° C. and is still slow at 1000° C., the nitrogen being split out solely in the elementary form.

On the basis of this information calculations were made assuming that all of the nitrogen of the coke was evolved as elementary nitrogen (method 3, Table V). The direct oxygen values obtained were -0.11 and $+0.41$ per cent, the sum of all directly determined constituents being, respectively, 99.47 and 99.96 per cent. While, in general, summations of over 100 per cent are preferred, because of the tendency of this method to yield high results, it is possible in this case that they are low because of the fact that the nitrogen values for the coke, determined by the micro-Kjeldahl method, are probably low. The oxygen values, calculated on the assumption that the nitrogen of the coke is all evolved as elementary nitrogen, are lower than those calculated on the other bases and also lower than those calculated by difference, which is, perhaps, the direction which many fuel chemists feel the oxygen values in coke should tend.

Summary

The gasometric microcombustion method for the direct determination of carbon, hydrogen, and oxygen has been applied to the analysis of two samples of bituminous coal as well as to an alkali-treated coal residue, a nitro humic acid, and a coke all derived from a bituminous coal.

With the knowledge available from the work on pure nitrogen-containing compounds (*12*), this method not only directly determines the oxygen content of fuels, but also enables certain deductions to be drawn as to the probable type of nitrogen linkage present in the various fuels analyzed. From the results obtained it is indicated that the nitrogen present in bituminous coal exists in some linkage other than that of an amino or amido group, a heterocyclic linkage being preferred. In the case of the nitro humic acid, evidence is given which confirms the idea that treatment of a bituminous coal with nitric acid introduces nitrogen in the form of an isonitroso ketone linkage. In the case of coke the best results for oxygen are obtained on the assumption that all the nitrogen is evolved, during combustion, in the elementary state.

The preferred, directly determined oxygen values are, with the exception of those obtained in the coke analyses, higher than the values obtained for oxygen when calculated by difference. In the case of coke, the preferred direct results for oxygen are lower than those calculated by difference.

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A Precision Pycnometer for Liquids

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DURING some work on the concentration and reactions of heavy water, it was necessary to follow changes in composition by density measurements. Since numerous determinations were to be made and very slight changes in density detected, the method had to be both simple and accurate. Several common types of laboratory pycnometers were tried, but the results were not very satisfactory. The chief faults found were difficulty of thermostating both the liquid and container, evaporation losses at ground-glass joints, loss of liquid during filling (very important in handling expensive liquids), and difficulty of determining the density at some definite temperature.

After preliminary work, the pycnometer shown in Figure 1 was evolved, and is believed to eliminate the faults enumerated above. It is 16.25 cm. (6.5 inches) long with capillary tubing having an outside diameter of 4 mm. and an inside diameter of 0.75 mm. The size of the bulb is limited by the size of the sample available or the accuracy desired. Sizes from 0.1 to 25 cc. have been used.

The liquid reservoir should be a test tube long enough to allow the pycnometer with cap removed to touch the bottom and with just enough clearance at the top to allow the stopcock to turn. The diameter of this tube should be such that no partial vacuum is created when the filled pycnometer is removed. Too close a fit will cause some of the contents to be removed. A thin rubber stopper which has been slit from the

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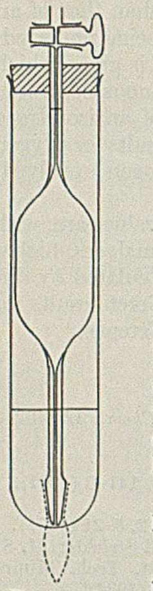

FIGURE 1

periphery to the center will serve very well as a stopper for the ensemble. It should contain a tiny hole to admit air during the filling.

After thorough cleansing with acid dichromate, the stopcock should be greased on the inner part only. Since the pycnometer is wiped after handling, any weight lost due to the removal of stopcock lubricant would introduce an error.

The test-tube reservoir should contain slightly more liquid than is necessary to fill the pycnometer. If more than this is used, the pycnometer contents will be under a slight hydrostatic back pressure which when removed will cause the liquid level to fall below the mark. It is therefore well to have a mark on the test tube to indicate the proper liquid level.

In determining the density of a liquid, the procedure was as follows:

With the liquid up to the mark in the test-tube reservoir, the pycnometer without its cap was carefully inserted and the rubber stopper set in place. This ensemble was clamped into a glass-walled thermostat with the lip of the test tube only a short distance from the surface of the thermostat water, and allowed to come to thermal equilibrium (about an hour).

A rubber tube was connected to the stopcock, which in turn was connected to a three-way stopcock, a 100-cc. reservoir (to prevent any water from the leveling bulb from draining into the pycnometer), and a leveling bulb filled with water. The pycnometer stopcock was opened and the three-way stopcock adjusted so that water could be drawn up into the bulb. When the water was almost up to the upper capillary, the three-way stopcock was turned to allow the leveling bulb to make the careful final adjustment. Great care must be used in bringing the liquid up to the mark, as capillary action tends to draw it up. A screw arrangement on the leveling bulb will help this. The greatest accuracy is attained if the meniscus is brought up to the mark and the pycnometer stopcock closed, instead of going past the mark and then bringing it back.

With the pycnometer filled to the mark, it was removed from the test tube, the stopper removed, quickly wiped with a downward sweep of a towel, and the ground-glass cap placed on it. The rest of the pycnometer was then wiped. It was suspended in the balance in a vertical position by means of a small stirrup which hooked around the stopcock. After remaining in the balance for a standardized period of time, the weight was taken.

Under carefully controlled conditions and using a good analytical balance, it was possible to check weights to 0.1 mg.

The pycnometer has the disadvantage that, in working with a liquid having a high vapor pressure at room temperature, the interval between filling and weighing must be short, as the vapor pressure of the liquid tends to force it slowly out of the pycnometer. This might be overcome by placing the small opening in the cap nearer the ground-glass joint and allowing the liquid to drip into the cap during a weighing.

RECEIVED October 28, 1935.

ZINC PIGMENTS IN PAPER AFFECT ALPHA CELLULOSE, COPPER NUMBER, AND ACIDITY TESTS. Consideration of fiber purity in terms of alpha cellulose content and copper number has been recommended by the National Bureau of Standards in choosing record papers that are required to have a long life. It has been found, however, that when papers contain zinc pigments, the test values obtained by the present methods are affected. P. F. Wehmer, chairman of the TAPPI Subcommittee on Chemical Methods for Paper Testing has reported that amounts of zinc sulfide commonly used in papers appreciably increase the test values for both alpha cellulose and copper number. Furthermore, that the total acidity value, obtained by titration of an aqueous extract of the paper, is reduced. Until modified testing procedures can be developed to avoid the errors caused by the zinc pigments, the probable stability of papers containing them must be judged in some other way. Another criterion recommended is the amount of folding endurance retained by paper on heating it.

An Apparatus for Sugar and Other Titrations

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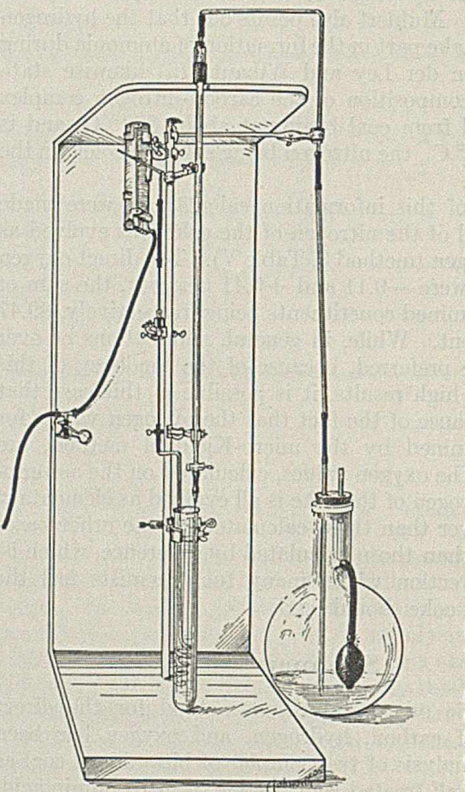

FOR a number of years the writer has been using a titration apparatus in sugar determinations which has made the work a great deal easier and also improved the accuracy. Because of the interest shown in the apparatus by workers who have seen and used it, an illustration and brief description of it is given.

As shown in the figure, a vacuum windshield motor (which may be of any good type) is connected by a side arm (6.25 cm., 2.5 inches long) to a vertical metal shaft (0.47 × 26.25 cm., 0.1875 × 10.5 inches) by means of a small coil spring. The shaft runs through a short glass-tube bearing. The lower end of the shaft is attached to the glass stirring rod by a short piece of pure gum tubing. The 25-cc. buret (preferably graduated in 0.05-cc. intervals) is fitted with a 20-gage stainless-steel hypodermic needle (cut to 2.5 cm., 1 inch, length) by means of a piece of pure gum tubing. The writer cuts the tip of the buret to fit snugly into the hub of the needle. The buret is fitted with a siphon automatic leveling device by fastening a glass tube, with vent hole, over the top through which passes a tube into the buret. The tip of the tube should be constricted and preferably ground. It is placed so that when the titrating solution is pumped into the buret above the zero mark and the pressure released in the flask, the solution is siphoned to the zero mark on the buret. The leveling device should be well supported.

The glass stirring rod should extend almost to the bottom of the sugar tube on the down stroke. Either a loop or spiral rod is satisfactory, the spiral type being somewhat preferable. The buret, stirring rod, and sugar tube are placed so that the tube can be easily slipped into or out of the clamp when the stirring rod is raised.

The vacuum motor may be driven by a good water pump or other suitable source of vacuum and the speed of stirring controlled by inserting a T-tube and screw clamp in the vacuum line.

The 20-gage needle tip delivers about 0.008 cc. of aqueous solution per drop and insures good buret drainage and accurate end points.

The apparatus obviously may be used for many different kinds of titrations, though acid solutions should not be passed through the needle tip. A glass tip with fine point may be substituted for the metal tip when acid solutions are used.

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Detection and Separation of Difficultly Soluble Compounds by Concentrated Hydriodic Acid

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Concentrated hydriodic acid is a valuable general reagent for the detection and separation of compounds that are insoluble in hydrochloric acid, nitric acid, or aqua regia. It not only reacts in a distinctive manner with most of the individual compounds, but mixtures can be analyzed qualitatively by its use, and certain pairs or groups of insolubles can be separated quantitatively. Analytical procedures based upon the use of this acid are frequently much more rapid and convenient than the fusion processes usually employed. The relatively high cost of this reagent is not such a serious objection as it may seem, for the methods usually require small volumes of hydriodic acid and the time saved by its use often more than offsets the expense of the acid.

A BRIEF note published by the senior author (*2*) indicated that concentrated hydriodic acid should be a general reagent of considerable value for the analytical treatment of compounds of low solubility. It is especially useful for the examination of compounds unattacked by hydrochloric acid, nitric acid, or aqua regia, for their detection or separation may be more conveniently accomplished in many cases by the use of hydriodic acid than by the fusion processes and special methods usually employed. Since most of these new methods require but small quantities of hydriodic acid, and since much time can often be saved by its use, its comparatively high cost is not a serious objection. In this paper are reported the results of systematic analytical experiments with the following difficultly soluble compounds of common elements: stannic oxide, aluminum oxide, chromic oxide, silicon dioxide, barium sulfate, strontium sulfate, calcium sulfate, lead sulfate, chromic dihydroheptasulfate, silver iodide, silver bromide, silver chloride, calcium fluoride, and anhydrous chromic chloride.

Preparation of Materials

In the majority of the experiments Merck's ordinary grade of hydriodic acid of specific gravity 1.70 was used. This not only gives the same general results as the pure acid, but, as it is stabilized by the addition of 1 to 2 per cent by volume of 50 per cent hypophosphorous acid, is actually superior to the pure acid for certain qualitative tests, because the reactions are not obscured by the liberation of free iodine. For certain experiments, however, a highly pure acid of similar concentration was used, this being prepared either by passing hydrogen sulfide into a water suspension of iodine or synthetically by using a modification of the contact process of Bodenstein (*1*).

The various difficultly soluble compounds were especially prepared for the experiments by methods that yielded highly pure products.

General Qualitative Technic

Samples carefully weighed on an assay balance were employed in the test, particular attention being paid to the lower limit of observable reaction in order to determine the practical sensitivity for each substance. Small Pyrex test tubes were used for holding samples, since 2 to 3 ml. of acid were ample for exhibiting the characteristic reactions. In the case of compounds unattacked in the cold, the tubes were partially immersed in a beaker containing colorless mineral oil, so that the reaction mixtures could be heated to definite temperatures. In the experiments with the sulfates, lead acetate paper or paper dipped into an ammoniacal solution of sodium nitroprusside was used in testing for the evolution of hydrogen sulfide. After decomposition of the samples by acid treatment, appropriate tests were made for the ions present in the resulting solutions.

Qualitative Behavior of Individual Compounds

As stated previously (*3*), stannic oxide is not noticeably attacked by concentrated hydriodic acid in the cold, but at temperatures of 90° to 95° C. and above the compound is rapidly converted superficially into the red iodide according to the equation

$$SnO_2 + 4HI \rightleftharpoons SnI_4 + 2H_2O$$

This distinctive reaction could be plainly observed on a sample weighing only 0.1 mg. With samples weighing 0.3 mg. or more, continued heating causes the stannic iodide to appear as a yellow to orange sublimate on the sides of the test tube above the liquid, any iodide remaining on the bottom of the tube also changing to this lighter colored form. It was further noticed that if a sample of stannic oxide is heated with the acid for a short time and then allowed to cool, a salmon-pink to red color develops in the solution above the oxide, depending upon the amount of oxide taken. This is an additional characteristic reaction for confirming the presence of stannic oxide when testing for it in this manner. Samples of the oxide weighing but 0.1 mg. were found sufficient to give this color reaction. Extraction tests with organic solvents demonstrated that this color was not due to liberated iodine. It seems likely that it results from the presence of a complex formed between dissolved stannic iodide and hydriodic acid, probably iodostannic acid. No mention of this phenomenon could be located in the literature. There is a possibility that it might be made the basis of a general analytical reaction for tin.

In general, the other insoluble oxides exhibit no characteristic reactions with concentrated hydriodic acid. When highly ignited they are all unattacked by the acid.

It has been shown (*4*) that the alkaline earth sulfates, though not decomposed by cold concentrated hydriodic acid, are attacked at higher temperatures, the decomposition being in accordance with the general equation

$$MSO_4 + 10HI \longrightarrow MI_2 + 4I_2 + 4H_2O + H_2S$$

In the application of this reaction for qualitative purposes the best results are obtained at a temperature just below the boiling point of the constant-boiling acid. The use of boiling acid is not advisable, because of danger from bumping and the evolution of fumes that tend to interfere with tests for

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hydrogen sulfide. On the other hand, a temperature as low as 100° C. is unsuitable, since barium sulfate then reacts too slowly. By observing the best conditions it was found that definite indications of the evolution of hydrogen sulfide were given by 0.1-mg. samples of all three alkaline earth sulfates, especially when nitroprusside paper was used. Lead acetate paper is slightly less reliable under the conditions of the test, because lead iodide formed by hydrogen iodide fumes and small amounts of condensed free iodine tend to obscure any lead sulfide that may be formed. Diluted acid is not suitable for testing for the presence of these insoluble sulfates in this way.

Even very small samples of barium sulfate cannot be completely decomposed by hot concentrated hydriodic acid in a reasonable time, but a sufficient concentration of barium ion can be obtained in solution in a few minutes to respond to the usual tests. Before adding any reagent it was found best to dilute the reaction mixture to about twice its original volume and then filter. This serves in the case of barium sulfate to remove any undecomposed sample, and with large samples of strontium or calcium sulfate it removes any sulfur that may have formed from the interaction of iodine and hydrogen sulfide above the reaction mixture. The iodine remaining in solution does not seriously obscure the usual precipitation reactions for the cations if time is allowed for precipitates to settle. Definite reactions for barium by sulfuric acid precipitation and by the flame test could be obtained on a solution resulting from the treatment of a 0.1-mg. sample. Barium sulfate, unlike the other two sulfates, is apparently not attacked by 3 *N* or 1 *N* acid. In testing a solution resulting from the decomposition of strontium sulfate, addition of ethyl alcohol up to 50 per cent by volume is necessary before testing with sulfuric acid. By this technic the lower limit was found to be about 0.3 mg. The lessened sensitivity in this case apparently results not only from the greater intrinsic solubility of this sulfate as compared with that of barium, but also from the adverse effect of a high hydriodic acid concentration, since after decomposition of samples as small as 0.1 mg. with either 3 *N* or 1 *N* acid strontium ion could be detected in the resulting solution by the above method.

After decomposition of calcium sulfate samples, calcium ion was tested for in the resulting solutions after neutralization by the addition of ammonium oxalate reagent. A complication enters here when using hydriodic acid stabilized with hypophosphorous acid, since the latter apparently contains calcium as a usual impurity. Employing the pure constant-boiling acid, the solution from a 1.0-mg. sample of this sulfate gave an almost immediate precipitate of calcium oxalate. Samples smaller than this gave a precipitate only on standing for periods up to an hour, 0.3 mg. being about the lower limit for definite reaction. The lessened sensitivity of the oxalate test for calcium under these conditions evidently results from the effect of high iodide-ion concentration on the solubility of calcium oxalate, for when acid as dilute as 1 *N* was used a definite reaction for calcium could be obtained in the solution from a 0.1-mg. sample of the sulfate.

It will be noted that the difference in behavior with acid of moderate concentration can serve to differentiate barium sulfate from the other two sulfates. Hydriodic acid appears to be of greater practical value for determining whether or not a given difficultly soluble unknown contains sulfate than for obtaining a solution to be used for the usual wet tests, particularly when mixtures of alkaline earth sulfates are encountered, since then the metals present can be more readily detected by flame or spectroscopic tests.

Lead sulfate, like the alkaline earth sulfates, is decomposed by hot concentrated hydriodic acid, the reaction being in accordance with the following equation:

$$PbSO_4 + 11HI \longrightarrow HPbI_3 + 4I_2 + 4H_2O + H_2S$$

Here again a 0.1-mg. sample was found sufficient to give a distinct test for hydrogen sulfide with nitroprusside paper. Lead sulfate also dissolves in cold concentrated hydriodic acid owing to complex formation, the resulting solution having a faint yellow to deep golden yellow color, depending upon the lead concentration. The reaction in this case can be represented by the equation

$$PbSO_4 + 3HI \longrightarrow HPbI_3 + H_2SO_4$$

On dilution of a solution obtained in this manner there precipitates out, by reason of the decomposition of the iodoplumbous acid, characteristic golden yellow lead iodide in a very finely divided form. This behavior can be used as the basis of an identification reaction for lead sulfate. Unfortunately, the test is not very sensitive owing to the solubility of lead iodide, but samples down to 2.0 mg. gave very satisfactory reactions. For smaller samples a better procedure is to evaporate the hydriodic acid solution of the sample to dryness on the steam bath to effect the decomposition of the complex. Any characteristic crystals of lead iodide then remaining behind are easily recognized. It was found that 0.1 mg. of the sulfate was sufficient to give a definite test, regardless of whether the samples were decomposed originally with cold or with hot concentrated hydriodic acid.

The resistance of chromic dihydroheptasulfate to decomposition by hot concentrated hydriodic acid is approximately of the same order as that of barium sulfate, since complete solution of even very small samples is obtained only after long heating. No difficulty, however, was experienced in obtaining a test for hydrogen sulfide from a sample weighing but 0.1 mg. In order to obtain good tests for chromic ion in a solution prepared by treating samples of this sulfate with hydriodic acid, it was necessary to remove the excess acid by evaporation on the steam bath. The residue was then taken up in a little distilled water, and the perchromate test for chromium was performed in the usual manner on this solution. With a sample weighing 0.5 mg. the blue color in the ether layer was definite, but smaller samples gave uncertain or negative results.

The silver halides dissolve copiously in cold concentrated hydriodic acid, owing to complex formation. In the case of the iodide the reaction can be expressed by the equation

$$3AgI + HI \longrightarrow HAg_3I_4$$

With the chloride or the bromide the reaction follows the course

$$3AgX + 4HI \longrightarrow HAg_3I_4 + 3HX$$

When large enough samples are used the hydrogen halide is expelled from solution with effervescence, but with very small samples evolution of the gas is not evident, since it remains dissolved in the solution. These reactions are noticeably hastened by increase in temperature and by agitation. In all three cases dilution of a solution obtained in this manner results in the precipitation of finely divided silver iodide by reason of the decomposition of the iodoargentous acid.

With the volume of acid generally used in these experiments, samples as small as 0.4 to 0. 5 mg. responded to the test. In order to obtain the characteristic precipitation of silver iodide on dilution when smaller samples were taken, it was necessary either to expel most of the excess acid by evaporation or to employ initially not more than a few drops. When this was done no difficulty was experienced in obtaining a reaction from a halide sample weighing but 0.1 mg. With small samples attempts to differentiate between the chloride and bromide by collecting the evolved gas in a small volume of water and making the appropriate tests on the resulting solution were not successful, owing largely to the difficulty of preventing traces of hydriodic acid from being carried over.

It does not seem to have been previously observed that calcium fluoride is attacked by hot concentrated hydriodic acid according to the equation

$$CaF_2 + 2HI \longrightarrow CaI_2 + H_2F_2$$

This reaction, though slow even in the boiling acid, takes place rapidly enough for qualitative purposes. On small samples the decomposition appears to work about as well as when sulfuric acid is used. When the reaction was carried out in soft glass test tubes just below the boiling point of the constant-boiling acid, distinct etching of the walls of the vessels took place with samples as small as 3.0 mg. By using a more sensitive apparatus consisting of a small platinum dish covered with a piece of perforated platinum foil upon which a microscope cover glass was placed, definite etching patterns were obtained from samples weighing 0.4 mg. on heating with the usual volume of acid at 120° C. for 20 minutes. By using a smaller volume of acid, a definite test could be obtained with 0.2 mg. of calcium fluoride. Parallel experiments on a ground sample of pure fluorite gave identical results.

Though dissolved but slowly by cold concentrated hydriodic acid, anhydrous chromic chloride is rapidly dissolved by the hot acid. It was concluded as the result of experiments that the solution of the compound by this reagent follows a different course than when reducing agents like stannous chloride are used to promote its hydration. That the effect is noncatalytic with hydriodic acid is indicated by the fact that no oxidation-reduction changes are involved, and that acid of low concentration is ineffective. It appears that a definite displacement reaction is involved, which can be represented by the equation

$$CrCl_3 \text{ (anhydrous)} + 3HI \longrightarrow CrI_3 \text{ (hydrated)} + 3HCl$$

Actual evolution of hydrogen chloride is observable when sufficiently large samples are taken. The hot solution exhibits a characteristic dark brown to nearly black color, but when cooled this changes to dark green, a rapidly reversible effect that can be repeated indefinitely. This change is apparently connected with a change in the structure of the hydrated chromic iodide in solution. With very small samples, however, the solution appears green at all temperatures. Though scarcely necessary because of the characteristic color of the compound itself and the color changes observable on dissolving it, a confirmatory test for chromium can be made on the solution in the same manner as described under the sulfate. Here again the lower limit for a positive reaction by the perchromate test was reached with a 0.5-mg. sample.

Qualitative Experiments on Mixtures

Complete investigation of the manner and extent to which the sensitivities of the foregoing tests are affected by the presence of varying quantities of one or more other difficultly soluble compounds would obviously require a vast number of experiments. However, results in certain representative cases will serve to indicate the applicability of this general method for the examination of unknown mixtures of insolubles. In these experiments the sensitivity of the test for a given compound in the presence of either 100 or 1000 mg. of some other compound was determined. In a few cases the tests were tried in the presence of two other difficultly soluble compounds.

STANNIC OXIDE IN MIXTURES. It was found possible to detect as little as 0.1 mg. of stannic oxide in the presence of 100 mg. of relatively inert compounds like silica, chromic oxide, barium sulfate, or calcium fluoride when the salmon-pink to red coloration which develops in the acid was used as the basis of the test. In the presence of 1000 mg. of admixed compound 0.3 mg. of tin oxide could be detected. With the exception of those containing chromic oxide, red particles of stannic oxide were also observable in these mixtures. In the case of chromic oxide mixtures it was necessary, in order to obtain a reaction for the stated amounts, to filter the acid solution through a fine-grained, sintered-glass filtering crucible before making observations, so as to remove suspended fine particles which tend slightly to obscure the color reaction. The definite formation of a sublimate of stannic iodide in all the above cases occurred when the quantity of tin oxide present reached 0.5 mg.

Though they react with hydriodic acid, silver halides do not interfere with the color test. Experiments on mixtures of silver chloride and stannic oxide showed that the sensitivity is about the same as in the cases just discussed. The sublimation test is, however, slightly less sensitive with these particular mixtures, about 0.7 mg. of oxide being required to give a noticeable sublimate of the iodide.

In the presence of compounds that react with hydriodic acid to liberate iodine, direct observation of the stannic oxide reactions is not possible. Thus with calcium or strontium sulfate mixtures it was necessary to decompose the sulfate completely, decant, wash the residual particles of stannic oxide and iodide with water, and finally add fresh acid, the test then being made in the usual way. As this manipulation entails slight losses, the test under these conditions is not as sensitive. Lead sulfate behaves similarly, though it is preferable to remove the lead salt from the mixture with cold concentrated acid, followed by washing the residual stannic oxide first with acetone and then with water before performing the test. In this manner it was possible to detect 0.2 mg. of stannic oxide in admixture with 100 mg. of lead sulfate or 0.4 mg. of oxide in 1000 mg. of sulfate. Since in the presence of anhydrous chromic chloride the intense color of the solution resulting from the treatment of the sample also prevents observation of the reactions, it was necessary in this case likewise to decant and add a fresh portion of acid. The sensitivity experiments gave the same results as those on lead sulfate just cited.

Experiments on the detection of stannic oxide in the presence of two difficultly soluble compounds gave about the same results as those with single compounds and it therefore seems probable that similar small amounts of the oxide can be detected by this test in nearly any combination of insolubles likely to be met with in practice.

SULFATES IN MIXTURES. For most of these experiments strontium sulfate, taken as representative of the group of difficultly soluble sulfates, was mixed with stannic oxide, chromic oxide, silver bromide, calcium fluoride, or anhydrous chromic chloride. Since nearly identical results were obtained with the various binary mixtures, experiments with the individual pairs need not be discussed separately. With nitroprusside paper evolution of hydrogen sulfide could be detected when 0.3 mg. of the sulfate was admixed with 100 mg. each of these substances; with 1000 mg. of added insoluble, 0.5 mg. of strontium sulfate gave a positive reaction in each case. In general the experiments indicated that no difficulty should be experienced in detecting the presence of like small amounts of any of the insoluble sulfates in admixture with any combination of the other difficultly soluble compounds.

SILVER HALIDES IN MIXTURES. Silver iodide was taken as representative of the group. The presence of the silver compound was detected in each case by the reprecipitation of silver iodide on diluting the solution obtained by treatment of the solid mixture with cold concentrated hydriodic acid. Inasmuch as certain of the difficultly soluble compounds not attacked by the cold acid tend to remain in suspension, it was necessary to filter the solution before dilution. In each case the mixture was treated with 2 ml. of acid and then filtered through a fine-grained sintered-glass filtering crucible. By adding the clear solution to about 200 ml. of water, definite reactions were obtained with samples that contained down to 1.0 mg. of silver iodide mixed with either 100 or 1000 mg. of stannic oxide, aluminum oxide, chromic oxide, barium sulfate, calcium fluoride, or anhydrous chromic chloride. Better results could be obtained if time was first taken to evaporate the filtrate to a volume of about 2 drops before diluting, 25 ml. of water being used here. In this way 0.1 mg. of the silver halide could be detected in admixture with the stated quantities of the above substances. Lead sulfate is apparently the only difficultly soluble compound that interferes with the direct detection of silver halides in mixtures by this method, since lead iodide precipitated on dilution can effectively mask a silver iodide precipitate. In such a case a convenient procedure is to filter off the mixed iodides of lead and silver, and place them in a warm concentrated ammonium acetate solution which, by dissolving the lead iodide, leaves the silver iodide in suspension so that it can be readily recognized.

General Qualitative Procedure

From the results of the foregoing experiments it is evident that the following scheme can be used for the systematic examination of an unknown insoluble or mixture of insolubles:

Add to the dry powdered sample stabilized hydriodic acid of specific gravity 1.70 in the proportion of about 5 ml. of acid for each gram of solid. After digesting with occasional stirring for about 5 minutes, filter, preferably through a sintered-glass funnel or crucible, and wash the residue with several successive 1-ml. portions of the concentrated acid. The filtrate and washings should be caught in a test tube. Transfer about half the residue to a small test tube, add 2 ml. of the acid, heat nearly to boiling, and examine for sulfates by testing for the evolution of hydrogen sulfide. Allow the solution to cool in order to observe the formation of a pink to red coloration or a yellow to orange sublimate indicative of the presence of stannic oxide. If the solution is deeply colored from dissolved iodine, decant, and add fresh acid before making the tests for tin oxide.

Use the other half of the residue for an etching test in order to detect the presence of calcium fluoride. Tests by conventional methods for the presence of silica, silicates, alumina, and other resistant substances should then be made on any residual material that fails to react with the hydriodic acid. Heat the filtrate from the above separation and test for the evolution of hydrogen sulfide in order to detect dissolved sulfate. Then transfer the solution to a small dish and evaporate nearly to dryness on a water bath in order to observe the formation of lead iodide from dissolved lead sulfate. Take up the concentrated solution or residue with about 25 ml. of water to bring about the precipitation of silver as iodide. If the presence of lead iodide interferes with the silver test, the ammonium acetate separation described in the preceding paragraph should be applied. This general system of examination should be supplemented by the more usual special tests on the original material when additional or confirmatory information is required.

Quantitative Separations

It was also found possible to make accurate separations of difficultly soluble compounds dissolved by hydriodic acid from those inert to the action of this acid. In quantitative experiments, for example, silica in the form of quartz, chromic oxide, crystallized alumina in the form of Alundum, or that prepared by ignition at 1000° C. for a number of hours, suffered no detectable loss on being heated with constant-boiling acid at temperatures between that of a water bath and the boiling point of the acid for various periods ranging from 0.5 to 7 hours. Such separations can be divided into two types, those that require the use of hot concentrated acid, and those that can be made with the unheated acid.

Of the first type are separations of alkaline earth sulfates from such inert substances. Some results obtained on mixtures of strontium sulfate and silica are shown in Table I.

TABLE I. SEPARATIONS OF STRONTIUM SULFATE FROM SILICA

Digestion Time	$SrSO_4$ Taken	SiO_2 Taken	SiO_2 Found	Difference Error
Min.	*Gram*	*Gram*	*Gram*	*Gram*
80	0.4119	0.1005	0.1008	+0.0003
60	0.4120	0.0518	0.0520	+0.0002
40	0.4005	0.1032	0.1042	+0.0010
40	0.2071	0.0450	0.0451	+0.0001
30	0.2055	0.0525	0.0525	±0.0000
15	0.1541	0.1147	0.1148	+0.0001
10	0.1090	0.4070	0.4072	+0.0002
10	0.0228	0.1228	0.1227	−0.0001
5	0.0225	0.0875	0.0877	+0.0002
10	0.0010	0.0959	0.0959	±0.0000

In these experiments the carefully weighed mixtures of sulfate and finely divided quartz were placed in small flasks and treated with 10 to 15 ml. of the stabilized acid, at or just below the boiling point. When decomposition of the sulfate appeared to be complete, as shown by the times given in Table I, the solutions were diluted with water and filtered through weighed glass crucibles. After washing with hot water the crucibles and their contents were dried at 110° C. and weighed.

The separation is good, and is fairly rapid unless too much strontium sulfate is present. The third result shows the danger of allowing insufficient time for the decomposition when handling larger amounts. In order to secure complete decomposition in such cases it was necessary to boil the acid, with constant stirring to prevent loss from bumping. In addition, high results may be due to the separation of some free sulfur. For these reasons the method is best applied in practice to mixtures that contain not more than about 0.2 gram of strontium sulfate.

A similar series of experiments was made using calcium sulfate. In these the time required for complete decomposition was found to be 20 minutes or less even for quantities of calcium sulfate that weighed around 0.5 gram. The method is, therefore, rapid in this case and sharp separations were obtained in all the trials. The quantitative separation of inert substances from barium sulfate by this process is possible, but is not feasible from a practical analytical viewpoint, mainly because of the long time required for the decomposition of even small samples of this sulfate.

That an accurate separation of anhydrous chromic chloride from silica can be made with hydriodic acid is indicated by Table II.

TABLE II. SEPARATIONS OF ANHYDROUS CHROMIC CHLORIDE FROM SILICA

$CrCl_3$ Taken	SiO_2 Taken	SiO_2 Found	Difference Error
Grams	*Grams*	*Grams*	*Gram*
1.0318	1.0125	1.0126	+0.0001
0.6170	0.0331	0.0331	±0.0000
0.2269	0.1120	0.1119	−0.0001
0.1488	1.5854	1.5852	−0.0002

In these trials 10-ml. portions of acid were used, and only 10-minute treatments at the boiling point were required, the silica being collected and weighed in glass crucibles as before.

In Table III are shown the results of separations made by means of the cold concentrated acid.

TABLE III. SEPARATIONS OF DIFFICULTLY SOLUBLE COMPOUNDS FROM SILICA

(By treatment of mixtures with cold concentrated hydriodic acid)

Salt	Salt Taken	SiO_2 Taken	SiO_2 Found	Difference Error
	Grams	*Grams*	*Grams*	*Gram*
$PbSO_4$	0.4306	0.0656	0.0659	+0.0003
	0.3820	0.0420	0.0424	+0.0004
	0.1193	0.1080	0.1081	+0.0001
	0.1184	0.1218	0.1217	−0.0001
	0.0144	0.1150	0.1148	−0.0002
	0.0011	0.1299	0.1297	−0.0002
	0.0009	0.1027	0.1025	−0.0002
AgI	1.4292	1.0121	1.0121	±0.0000
	0.4826	0.0354	0.0357	+0.0003
	0.1157	0.0322	0.0320	−0.0002

In these experiments the carefully weighed and mixed samples were placed in glass crucibles and treated with the acid, three successive 5-ml. portions being used with the larger amounts of lead sulfate and single 10-ml. portions for the other runs. After apparently complete solution of the salt in each case, which took but a few minutes, the resulting solutions were drawn through the crucibles by suction. Since water decomposes the soluble complex compounds with the consequent precipitation of the iodides in the case of both these salts, it could not be used for the initial washing. Experiments with other solvents having shown that acetone was highly suitable, the remaining solution was washed through the crucibles with successive portions of this liquid. The final washings were then made with water, and the residual silica was dried and weighed in the usual way. Separations of this sort are not only rapid and very easy to carry out, but accurate results are obtainable.

Concentrated hydriodic acid has been found to be an excellent agent for the removal of certain precipitates, particularly silver halides, from glass or porcelain filtering crucibles without causing vessels to lose weight appreciably.

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RECEIVED July 27, 1935. Constructed from part of a dissertation submitted by M. Gilbert Burford in partial fulfillment of the requirements for the degree of doctor of philosophy, Princeton University, 1935.

Note to Authors

IN THE preparation of manuscripts authors should address themselves to specialists in their particular fields, rather than to the general reader. If the article describes a new method, the author should endeavor to tell the complete story, so that the reader will not have to wait for succeeding contributions or duplicate the unpublished tests in order to find out whether he can apply the method in his own work.

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

1. Preliminary statement or introduction, in which the need for the method should be stated, brief reference to other methods or literature given, etc.
2. Experimental
    - Outline of proposed method
    - Description of apparatus and reagents
    - Procedure
    - Data
        - Interfering substances or conditions
        - Concentration range through which the method is applicable
        - Accuracy of the method
        - Precision of the method
3. Discussion and summary

The author should state at the outset what the original features of the paper are. If it deals with a method of analysis, he should give some comparison with established methods in point of speed, applicability, accuracy, and cost. Extensive reviews of the literature should not be given and such references as are cited should be carefully checked. Incorrect references are inexcusable and cast doubts on the author's reliability. The theoretical considerations on which the method is based should be clearly set forth.

In the experimental part, previously published or well-known procedures which have been followed should only be designated or references given to them. If, however, the method is new, the data upon which it is based should be presented but in no greater detail than is necessary to prove its soundness. New procedures should be clearly described, that readers can easily duplicate the work. Loose directions should be avoided, unless the author knows that no possible harm can result from the most liberal interpretation that can be made of such expressions as "to the faintly acid solution," "wash the precipitate," "ignite," etc. If new or uncommon reagents are needed, the author should state their probable cost, where they can be purchased if rare, or how they can be prepared, if not on the market.

The author should distinguish carefully between precision and accuracy. Briefly but somewhat roughly stated, accuracy is a measure of degree of correctness; precision is a measure of reproducibility. The precision of a result does not necessarily have anything to do with its accuracy; it serves merely as a measure of the duplicability of the procedure in the hands of a given operator. No claim for accuracy should be made unless the author believes that he has satisfactorily established the correct result.

The author should be frank and define the limitations of the method. Tests dealing with the effects of foreign compounds should be made on mixtures in which the ratios of the compounds sought to the foreign compounds are varied and simulate conditions that are likely to be encountered in practice. If the author has made no such tests, he should state that he has no knowledge of the effects of foreign substances. It is desirable that possible applications of methods should be stated.

A summary or prefatory abstract should acquaint the reader with the main points of the article. This should give concisely where possible the substances determined, nature of material to which determination is applicable, interfering substances, range of concentration to which method is applicable, whether or not a sensible constant error is involved—that is, the accuracy of the method—and its precision. Either the summary or the prefatory abstract is so often used by abstractors that the author may well spend considerable time in their preparation, in order to be certain that proper emphasis is given to the main features of the contribution.

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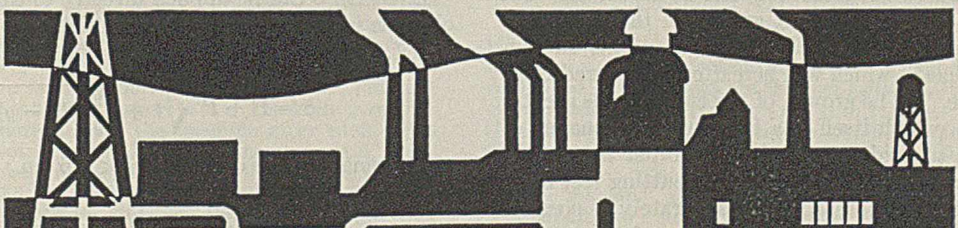

An Impact Cutting Test for Tire Tread Stocks

J. H. DILLON, The Firestone Tire & Rubber Co., Akron, Ohio

The problem of tire tread cutting is discussed in relation to the various measurable characteristics of rubber stocks such as tear resistance, cracking resistance, and hardness. Theoretical reasons are given for selecting a high-speed, high-load, knife-impact test for the laboratory evaluation of the cutting resistance of tread stocks. The impact cutting device used in this work is described in detail and results obtained with it are discussed in their relations to the physical variables involved, compounding trends, and road tests.

THE importance of the problem of pneumatic tire tread cracking is generally recognized by rubber technologists. The closely allied problem of tread cutting, however, has received comparatively little attention in the literature (*2–5, 7*). This fact is surprising in view of the possible causal nature of cutting with respect to cracking. The published work on cutting of rubber stocks, referred to above, all deals with what may be termed static tests—that is, the cutting tools employed were applied to the rubber test pieces with velocities much lower than those with which a tread button impinges on an obstacle in normal service. Some of these tests (*3, 4, 5*) were designed for evaluating cutting resistance of rubber-insulated electric conductors. The methods described in these papers are satisfactory for evaluating the cutting resistance of rubber insulating materials, but fail in some cases to evaluate correctly the cutting resistance of tire tread stocks. In the most recent of these papers, which deals specifically with the cutting of tire treads, Clarke (*1*) using a slow-moving cutting tool (15 cm., 6 inches, per minute) drew conclusions concerning the relative values of various compounding ingredients in increasing or decreasing cutting resistance. None of Clarke's conclusions was radically different from those found in the impact tests described in this paper. (The unpublished preliminary work on impact cutting tests at this laboratory, carried out by J. H. Howey and B. A. Jones with a small pendulum device, led to the considerations underlying the test to be described.)

Theoretical Aspects of Tread Cutting

It should be borne in mind that the cutting resistance of a rubber stock is a very complex function of several interrelated factors, some of which are themselves complex. The most important of these factors are hardness, tear resistance, elastic modulus, tensile strength, aging resistance, and temperature. At first thought, it might seem desirable to determine the functional relationship between cutting resistance and these factors and thus evaluate cutting resistance in terms of simpler quantities. This procedure has not proved practicable in the experiments performed in this laboratory, for it was not found possible to express this relationship as a simple, single-valued function. For example, it was found that, in general, cutting resistance increased with increasing hardness but, in certain cases, a stock with a greater hardness than another stock was worse from the standpoint of cutting. Hence, it was concluded that cutting resistance should be evaluated by a special cutting test.

A distinction should be made between initiation of a cut in a tire tread and the consequent growth of the cut into a cracking or chipping failure. The initiation of the cut depends on that property which will hereafter be referred to as "cutting resistance." The growth of the cut depends greatly on tear resistance, which itself is a function of frequency of flexing, resistance to oxidation, and many other factors.

In developing an empirical test, which a cutting test must be, it is desirable to incorporate in it as accurately as possible the factors existing in service. In the case of the cutting test it was possible to use the same order of impact velocities and forces with which a tread button impinges on a sharp obstacle in the road. The exact form of the cutting object could not be reproduced. Thus, it was necessary to use an arbitrarily designed wedge. A 20° steel wedge was selected mainly because it gave reproducible cuts of reasonable depths using the velocities and impact forces with which a tread button strikes an obstacle.

The impact velocity of a tread button on an obstacle of height y was calculated on the assumption that the tire is a rigid hoop of outer diameter $2a$ rolling on a horizontal plane with angular velocity ω. The expression for the impact velocity V thus deduced from the equations of a cycloid is:

$$V = \omega\sqrt{y}\,\sqrt{2a - y} \tag{1}$$

This expression is only approximate for a deformable pneumatic tire for, sidewise bulging neglected, only the extreme shoulder portions of the tread have pure cycloidal motion. However, Equation 1 gives at least the order of magnitude of the impact velocity in the central portion of the tread.

The impact force S was calculated as follows: Consider a body of weight P striking a relatively immovable body with velocity V and causing an instantaneous deformation d. The energy stored in the immovable body is $Sd/2$ and is equal to the sum of the kinetic energy of the moving body at impact ($PV^2/2g$) and the work, Pd, done by the movable body in traversing the distance d. Hence,

$$\frac{Sd}{2} = \frac{PV^2}{2g} + Pd \tag{2}$$

If e is the static deformation for a load P, by Hooke's law

$$\frac{S}{P} = \frac{d}{e} \tag{3}$$

Eliminating d from Equations 2 and 3 gives

$$eS^2 - 2ePS - \frac{P^2V^2}{g} = O \tag{4}$$

The solution of Equation 4 is

$$S = P + P\sqrt{1 + \frac{V^2}{eg}} \tag{5}$$

which relates the momentary maximum force or impact force S and the static load P. (This equation is not original with the author but is derived here for the convenience of the reader. For a similar expression see *6*.)

Equation 5 can be applied directly to the case of a cutting obstacle impinging on a tire with velocity V given by Equation 1. Thus by Equations 1 and 5,

$$S = P + P\sqrt{1 + \frac{\omega^2 y}{eg}(2a - y)} \tag{6}$$

or, for small values of y ($o < y < 2.5$ cm.) where $e \cong y$,

$$S = P + P\sqrt{1 + \frac{2a\omega^2}{g}} \tag{7}$$

In Equation 7, ω and a are known. The factor P is simply a function of y or the static load applied to a cutting edge to cause a deflection y without actually cutting the rubber.

In order to determine P for various static deflections e, a device was employed by means of which a 20° steel wedge was pressed against the contact area of the tread of a normally inflated and loaded tire. In this manner, a load-deflection curve was determined from which the values of P corresponding to various values of $e = y$ were directly obtained. Inserting these values of P into Equation 4, the impact force S was calculated. Values of impact velocity and impact force, calculated from Equations 1 and 7, respectively, are given in Table I.

TABLE I. IMPACT VELOCITY AND IMPACT FORCE

(Heavy-duty tire 81 × 15.2 cm.; rolling radius, 38.9 cm.)

	Obstacle Height 0.25 Cm.		Obstacle Height 0.62 Cm.		Obstacle Height 2.5 Cm.	
Car Speed	Velocity	Force	Velocity	Force	Velocity	Force
Km./hr.	*Cm./sec.*	*Kg./cm.*	*Cm./sec.*	*Kg./cm.*	*Cm./sec.*	*Kg./cm.*
16.1	52	62	79	163	158	775
32.2	104	124	158	326	316	1550
64.4	208	248	316	652	632	3100
96.6	312	372	474	978	948	4650

The simplest type of apparatus which could be used with these values of impact velocity and force appeared to be a steel knife falling freely under gravity. For such a device, the impact velocity would be determined by the height of free fall and the impact force by the load attached to the falling knife. The relation between the load, L, on the knife and the impact force is obtained directly from Equation 2 by replacing $\frac{V^2}{2g}$ by h and takes the form

$$S = 2L\left(1 + \frac{h}{d}\right) \tag{8}$$

where h is the height of fall and d is the depth of penetration of the knife before cutting occurs.

In the impact cutting device, described in detail below, the impact velocities ranged from 300 to 600 cm. per second, and the impact forces varied from 360 to 1200 kg. per cm. of knife edge. Comparing these actual values of velocity and force used on the apparatus with the calculated values of Table I, it is seen that the impact cutting device could be operated under conditions approximating those found in road service.

It is true that the tread rubber on a tire is mounted on a pneumatic base, whereas the test piece of the impact cutting test was a rubber block, 12.7 cm. (5 inches) in length, 1.9 cm. (0.75 inch) in width, and 3.8 cm. (1.5 inches) in height, mounted on a heavy steel platen. However, it was thought that the use of a pneumatic backing for the test block of the impact cutting device would introduce into the test a variable very difficult to control. Thus, the pneumatic backing of a tire was simulated qualitatively by using a rather tall (3.8 cm.), and therefore highly deformable, test block.

Apparatus and Analysis of Results

The impact cutting device illustrated in Figure 1 consists, mainly, of an accurate vertical slide which guides a loaded knife in approximately free fall. The slide is rigidly suspended from the top end. The knife, which is a 20° wedge of altitude 3.8 cm. (1.5 inches) and has an edge of 7.6 cm. (3 inches), impinges on a rubber test block and produces a cut which can be measured with an ordinary steel scale. The sliding Dowmetal carriage which bears the knife is constructed so as to permit different combinations of weights to be attached to it. The knife is readily detachable and is removed from the machine after each series of tests, oiled, and kept in a closed box until needed again.

The machine is also equipped with a vertically movable electromagnet with which the knife and carriage can be raised to the desired height and released by reversing the current in the coils of the magnet. The magnet is raised and lowered by means of a windlass. The slide is equipped with a number of stops (not shown in Figure 1) set at known heights, which can be used by the operator to ascertain when the carriage has been raised to the correct height. Two rubber bumpers at the bottom of the slide cushion the blow of the carriage and make it impossible for the knife edge to hit the platen face. Blocks of certain stocks deform to such an extent that the carriage hits the bumpers before completion of the cut. A trip device (not shown) mounted at the base of the slide, lights a small lamp when the carriage strikes the bumpers. In cases where the light is thus turned on, the test results are discarded.

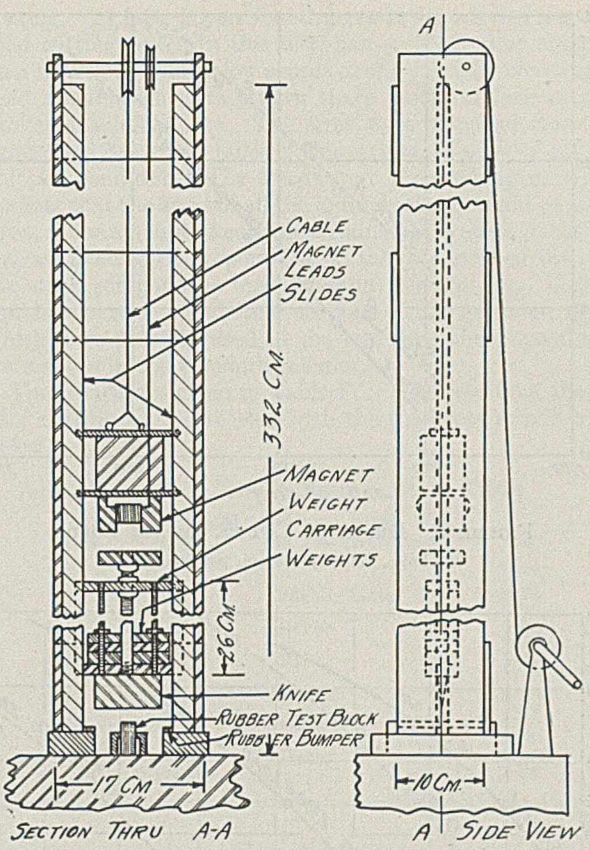

FIGURE 1. IMPACT CUTTING APPARATUS

The rubber test block, 12.7 × 1.9 × 3.8 cm. (5 × 0.75 × 1.5 inches), is placed in a holder at the bottom of the slide and rests on the large face of a steel platen 51 × 51 × 10 cm. (20 × 20 × 4 inches). The block rests on its 12.7 × 1.9 cm. (5 × 0.75 inch) face with its long axis perpendicular to the knife edge. Two cuts are made in each block at positions 3.2 cm. (1.25 inches) from the ends of the block. The deeper cuts are usually uniform in depth across the width of the block and can thus be measured with a steel scale after slitting through the rubber remaining at the bottom of the cut. The shallow cuts are, in general, less regular in depth than the deep cuts. However, with a little practice, the operator can estimate the average depth of the shallow cuts without much difficulty.

The cutting knife is of hardened steel and is carefully ground in the form of a 20° wedge. The feather edge is removed from the knife with a fine abrasive cloth. The sharpness of the knife changed with use but, by always running a control stock simultaneously with an experimental stock, it was found that the relative cutting results were essentially uniform over a period of 2 years. In this study of the aging of the knife edge, the effect of the aging of the rubber was avoided by using new samples.

In the method of testing adopted as standard, at least six test blocks of each stock or cure to be tested are cured in a 12-cavity mold in a press, the temperature of which is very carefully controlled. The blocks are then set aside for 1 week to allow the cutting resistance to come to a stable state. The hardness is then measured with a Firestone 1.36-kg. (3-pound) penetrometer (*8*) at various points on the 12.7 × 1.9 cm. face of the blocks. Two cuts are then made in each block with the impact cutting machine, as described above. Thus, using six blocks, it is possible to obtain twelve cuts in each stock or cure. These cuts are usually made at 2 or more loads chosen to give a depth of cut *vs.* load (D vs. L) curve. The cutting velocity is usually

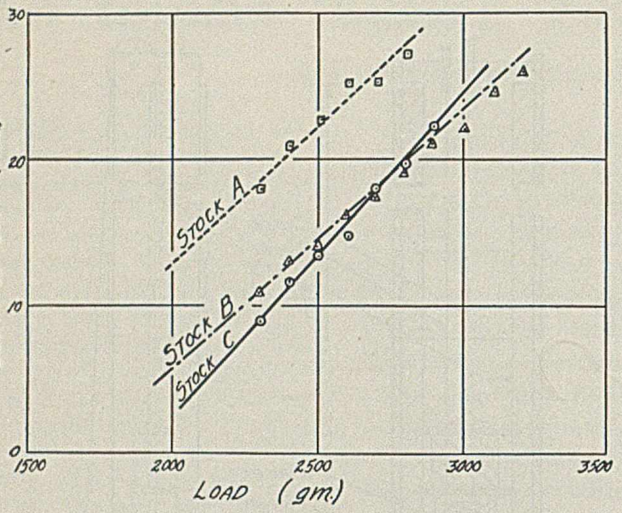

Figure 2. Depth of Cut *vs.* Impact Load

20° knife, velocity 488 cm. per second

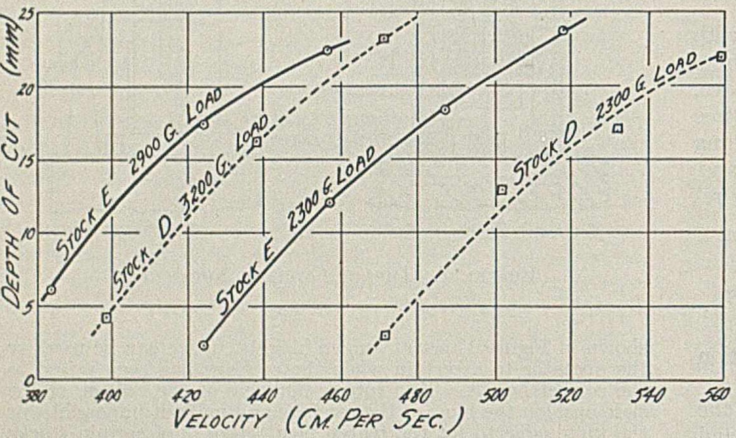

Figure 3. Depth of Cut *vs.* Impact Velocity

20° knife

set at 424 cm. per second (13.9 feet per second). In practically every case the D vs. L curve is linear (Figure 2).

To be very exact, there are two physically independent indexes of cutting resistance—i. e., the slope of the D vs. L curve and the extrapolated load intercept. However, it is difficult to interpret data on the basis of two indexes. Hence, the load necessary to give a 25-mm. cut, L_{25}, has been selected as a single cutting index. This index, L_{25}, has been found very satisfactory, in that results arrived at through its use agree with road test results and with results evaluated by means of the slopes and load intercepts of the D vs. L curves.

Functional Relationships

As mentioned above, the relationship between depth of cut and load is linear. That both the slope and load intercept vary for different stocks is clearly demonstrated in Figure 2. The relationship between depth of cut and velocity at constant load is not linear, however (Figure 3). In general, the D vs. V curves are convex upward, though occasionally a curve which is concave upward is found. Unlike the D vs. L curves, the D vs. V curves do not cross in the range of velocities investigated. The practice of running tests at a single velocity is therefore justified.

The curves of Figure 4 show that L_{25}, a measure of the cutting resistance, decreases rapidly with increasing temperature. In making these tests, the test blocks were kept in an ice box or oven until the center of the blocks had reached the desired temperature, as measured by a mercury-in-glass thermometer inserted in a hole in the block. The tests were then run immediately to minimize temperature changes occurring after removal from the oven or ice box. This dependence on temperature indicates the necessity of recording the room temperature for all tests.

Table II. Cutting Resistance *vs.* Resistance to Tear

Stock	L_{25} *Grams*	Hand Tear Estimate
A	4300	Best
B	4040	Very good
C	4180	Very good
D	4230	Very good
E	4350	Good
F	4390	Fair
G	4360	Fair

The index of cutting resistance, L_{25}, generally increases with hardness [Firestone 1.36-kg. (3-pound) penetrometer] as is shown in Figure 5. However, in several cases, distinct reversals occurred—for example, stock IX *vs.* stock X and stock VII *vs.* stock VIII.

Cutting resistance does not always correlate with tear resistance. This fact is clearly shown in Table II, where two stocks which appear to be best from the cutting standpoint show up as distinctly inferior to the others from the tear standpoint.

The accuracy of the results of the impact cutting test depends upon the number of tests averaged. For example, where six blocks of a given stock were tested, the mean deviation was 4 per cent; where twelve blocks were tested, the mean deviation was 3 per cent. In individual cases the accuracy is much greater and can be determined in each case—for example, the mean deviations for the tests of Table IV were much less than 3 per cent.

Compounding Trends in Resistance to Cutting

The cutting resistance generally increased with the carbon black loading, as is shown in Figure 6. To obtain these data, the carbon black content in a commercial mercaptobenzothiazole tread stock was varied so as to give loadings varying from 38 to 76 parts by weight per 100 parts of rubber. It may be seen that the cutting resistance increased with increasing carbon black loading up to a loading of 67 per cent and then began to decrease. The existence of this maximum in cutting resistance with respect to carbon black loading has very little practical significance, since 67 per cent black is considerably above present practical compounding limits for

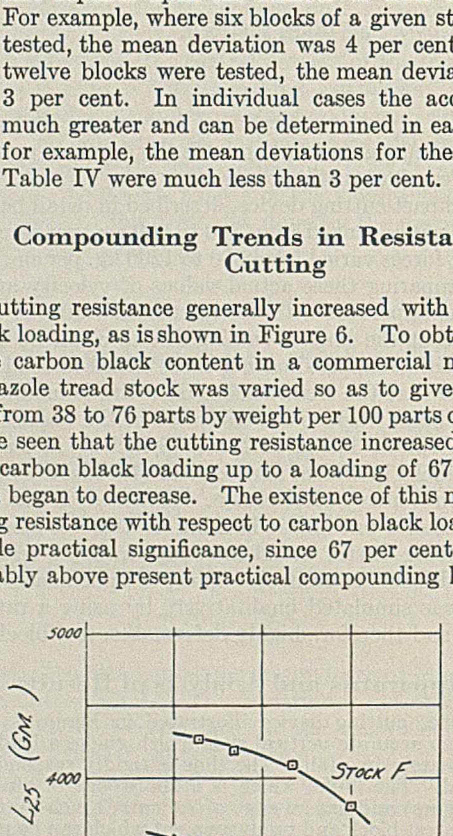

Figure 4. Cutting Resistance *vs.* Temperature

20° knife, velocity 424 cm. per second

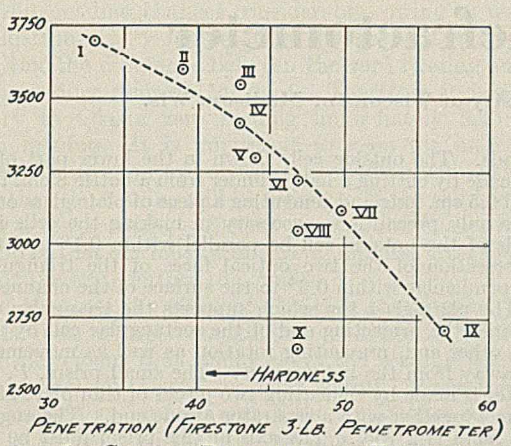

FIGURE 5. CUTTING RESISTANCE *vs.* HARDNESS

Ten stocks; each point average of 12 tests; 20° knife: velocity 424 cm. per second

treads. However, the fact that the cutting resistance increases to that point indicates that, for special types of service where cutting resistance is the major consideration, the loading of carbon black should be increased above the limits considered satisfactory for other types of service.

The effect upon the cutting resistance of varying the amount of carbon black in a mercaptobenzothiazole tread stock where glue is used is shown in Table III. The addition of 5 per cent glue had no appreciable effect on the cutting resistance; furthermore, the cutting resistance increased with increasing black loading to a maximum at approximately 57 parts by weight per 100 parts of rubber.

TABLE III. CUTTING RESISTANCE AS A FUNCTION OF CARBON BLACK LOADING WITH GLUE USED AS A SOFTENER

Per cent by Weight on Rubber Glue	 Carbon black	L_{25}
0	49.4	4600
5	49.4	4650
5	53.7	4760
5	57.0	5000
5	60.0	4990

Comparison of Impact Cutting with Road Tests

Great care must be exercised in comparing the results of a laboratory cutting test with road test results, for most so-called cutting tests on the road involve cracking as well as cutting. In fact, it was found necessary to devise a special road cutting test. In this test, half-and-half tires mounted on a truck were run at low speeds over a specially constructed road upon which were strewn sharp pieces of furnace slag, broken insulators, etc. The tires were removed from the rims, after 200 to 500 miles of this service, in a badly cut and chipped condition. The treads were then cut up in such a manner that the areas of all the individual cuts could be measured. The amount of cutting sustained by a stock in the test was assumed to be proportional to the total area of the cuts. Six stock comparisons were made in this manner. Cutting test blocks were cured from sections of the extruded treads which were actually used in the test tires and impact tests were made in the standard manner.

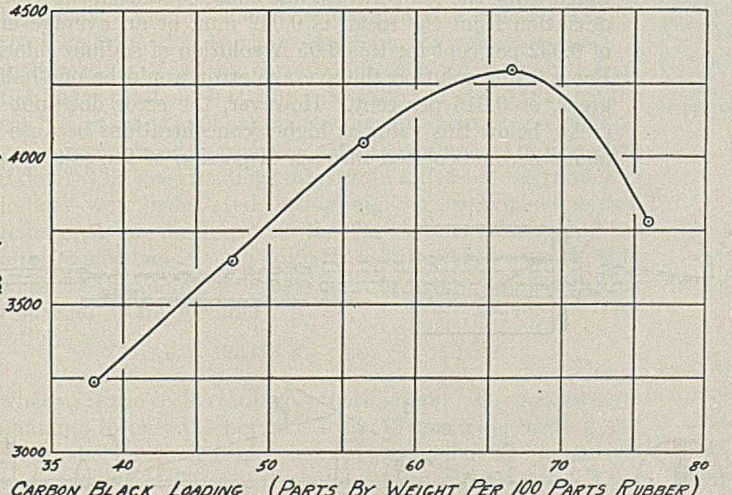

FIGURE 6. CUTTING RESISTANCE *vs.* CARBON BLACK LOADING

20° knife, velocity 424 cm. per second

The results are given in Table IV. The results of the impact cutting test correlated with the road test results in all cases.

TABLE IV. IMPACT TESTS *vs.* ROAD TESTS

(81 × 15.2 cm. tires)

Tire	Stock	Road Test Evaluation	L_{25} *Grams*
I	A	Slightly better	3270
	B		3270
II	C	Better	3700
	D		3270
III	E	Better	3240
	F		3150
IV	G	Worse	3180
	H		3270
V	I	Better	3600
	J		3260
VI	K	Worse	3310
	L		3590

Conclusion

The impact cutting device described in this paper is recommended for testing the cutting resistance of tread stocks because of its simplicity and the accuracy with which its results agree with road test results. The fact that the device was designed on semi-quantitative theoretical grounds gives some additional confidence in its results. It is possible that other cutting devices, designed with no regard to theory whatsoever, might operate as well as the impact device. However, it is felt that, since most laboratory tests on rubber stocks are necessarily largely empirical, it is well to attempt to design a testing machine which will operate in the ranges of the variables found in service.

Acknowledgment

The author desires to acknowledge the work of B. A. Jones, who designed the impact cutting device and performed the preliminary tests, and to thank N. Johnston and R. J. Bonstein for their helpful suggestions, and N. A. Shepard under whose direction the work was done.

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A Differential Refractometer

D. RAU AND W. E. ROSEVEARE, University of Wisconsin, Madison, Wis.

THIS refractometer was designed to be a rapid and reliable instrument for determining concentrations of solutions too dilute to permit the use of the Pulfrich or immersion refractometers. It makes use of the bending of a ray of light when passed through a rectangular cell containing a triangular compartment, the former being filled with pure solvent and the latter with solution. This part of the instrument is similar in principle to the Ketteler (*2*) and Haber-Löwe (*1*) refractometers, but is much more practical because of the new method of observing and measuring the deflection and of determining the zero reading.

The complete instrument is shown in Figure 1. The upper diagram in Figure 2 shows the essential parts of the refractometer, while the lower diagram shows the path of the light ray.

The achromatic lens, *L*, projects through the cell an enlarged image of the slit, S_2, at point *F*, 110 cm. from the lens. This image is broken up into three bright interference bands by the double slits, S_3, which are 0.31 cm. (0.125 inch) wide and 0.31 cm. (0.125 inch) apart. The appearance of the interference bands and cross hairs is shown in the circle. These interference bands are observed by the microscope, *M*, having cross hairs in the eye piece. Readings are taken by means of the position of a small-angle water prism, *P*, in a glass cell which slides on a 60-cm. steel metric scale. This prism is moved along the scale until the interference bands are brought back to the zero position. It does not displace the interference bands at all when at the focal point of the microscope, but when moved toward the cell it displaces the image nearly in proportion to the distance moved from the zero point, *F*. The mounting for this prism has guides that slide along the sides of the steel scale and prevent it from rotating more than 0.02°. Larger rotations would affect the readings. It is made as thin as possible. The collimator of a spectroscope serves very well for the lens, *L*, and slit, S_2, if the edges of the slit are ground smooth on an oil stone. The lens has a focal length of 20 cm. The light source, *J*, is a 100-watt opal-glass electric light bulb. The larger slit, S_1, protects the end of the collimator tube from the heat of the lamp. The collimator tube supporting S_2 is surrounded by a larger tube to protect it from drafts which would make the readings erratic. A Gaertner M101 microscope is suitable to observe the interference bands. All parts of the refractometer are mounted on a piece of 10-cm. (4-inch) channel iron 125 cm. long.

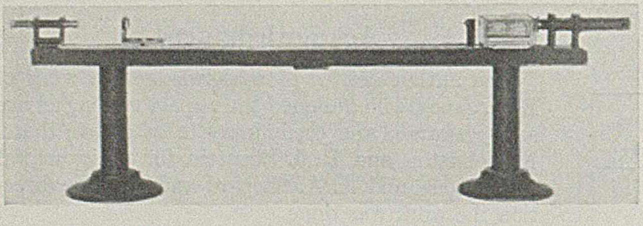

FIGURE 1. COMPLETE INSTRUMENT

The triangular cell, shown in the upper part of Figure 3, is built on the under side of a piece of plate glass, having a 2-cm. round hole in the middle. The optical faces are pieces of ordinary commercial plate glass and extend 1 cm. below the bottom of the triangular cell, which is 1.2 cm. deep and has an inside length of 8.5 cm. The angle between the faces is 137°. One piece of heavy platinum foil is used for the bottom and back of the cell because of its higher heat conductivity. A narrow slot 1.5 mm. deep is cut in the plate glass so that the platinum foil is mortised into the glass. This prevents the cement from covering much of the optical surface and gives it much greater strength. This cell requires 5 cc. of liquid in order to transmit bright interference bands. The outside cell, shown in the lower part of Figure 3, is made by cutting a half cylinder from a bottle 8 cm. in diameter and 9.5 cm. long and cementing a piece of plate glass on each end. The only precautions necessary in making the cells is that the ends of the outside cell be parallel within 0.1° and the line of intersection of the two optical faces of the triangular cell be perpendicular within 0.3° to the surface of the channel iron.

The plate-glass top which supports the triangular cell is held against the projecting end of the rectangular cell by a spring at the other end, preventing rotation as well as movement toward or away from the light source. The small prism, *P*, containing water is made by cementing two pieces of thin plate glass (1.5 × 3 cm.) together with a separator at one end. The angle between the faces is 2° 55′. The axis of this prism must be parallel to that of the cell prism within 0.3°. A shutter placed at *O* can be turned up or down to cut out the light from either the upper or lower parts of the triangular cell. Both light paths are left open except when the solution is so very dilute that the two sets of bands overlap. With pure water in both compartments, the readings through the upper and lower compartments should be identical. If these readings are different, it is due to a strain in the triangular cell.

The first step in adjusting the instrument is to fill the rectangular cell with distilled water, leaving the triangular cell out for preliminary adjustments.

Open slit S_2 wide and move it toward or away from the lens until an image of it is projected at point *F* on a piece of white paper. Close the slit slowly, observing the image of the slit through the microscope. When the slit can just barely be seen, refocus the microscope on this image. Interference bands should then appear. The quality of the bands can be improved by slight changes in the width of the slit and position of the microscope. When sharp interference bands are obtained, replace the triangular cell and fill it with water. Look at the slit from point *O*. If the light coming from both double slits does not appear the same, move the triangular cell until it lets both beams of light pass through it equally well and make a final readjustment of the microscope to give the best interference bands.

Table I shows readings taken every minute for 14 minutes, after filling the triangular cell with a solution of 0.05 *N* sodium chloride. The last reading was taken after leaving the solution in the cell until the next day. The readings became constant in 5 minutes after filling the cell. The reading at 10 minutes is an accidental error of observation due to eye fatigue, from looking continuously at the interference bands. Eliminating this value and the first four taken while the temperature was being equalized, the average deviation from the mean is 0.042 mm. or an average error of 0.032 per cent for this 0.05 *N* solution of sodium chloride. For a 0.1 *N* solution the average error would be one-half as great, or 0.016 per cent. However, the error does not decrease below this value at higher concentrations because the bands become colored through dispersion of the salt.

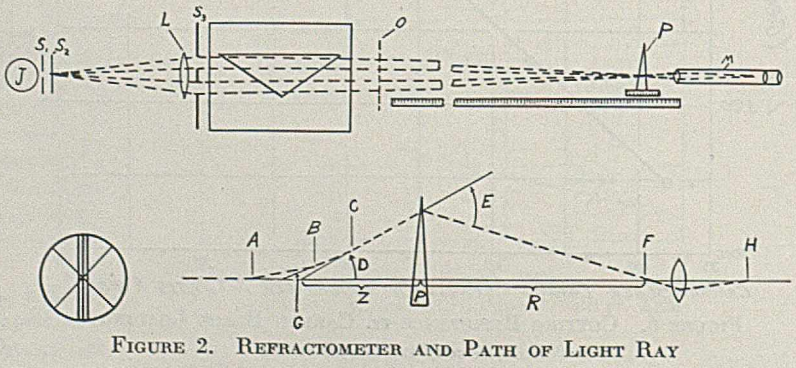

FIGURE 2. REFRACTOMETER AND PATH OF LIGHT RAY

The zero reading changes considerably, owing to warping of the instrument by temperature changes and relieving of strains, but the difference between the zero reading and the solution reading remains constant. Therefore it is always necessary to take a zero reading immediately before the solution reading. It is important to keep the instrument out of drafts when in use or the zero reading will change so rapidly that the reading will be erratic. If the cell is opened for only a few seconds, sufficient evaporation occurs to cool the liquid so that one must wait several minutes after covering again for the temperature to equalize.

Table II shows the effect of changing the position of the triangular cell in the rectangular compartment. The only small displacement that would affect the reading is moving the triangular cell toward the light source. Since the glass plate is pressed against one end of the rectangular cell, it can always be replaced so that the reading will be affected less than 0.03 mm., a negligible error.

TABLE I. READINGS

Time	Zero Reading	Solution Reading	Difference
Min.			*Cm.*
1	0.08	13.30	13.22
2	0.04	13.28	13.24
3	0.04	13.28	13.24
4	0.06	13.29	13.23
5	0.07	13.28	13.21
6	0.07	13.28	13.21
7	0.09	13.30	13.21
8	0.12	13.33	13.21
9	0.10	13.32	13.22
10	0.10	13.36	13.26[a]
11	0.11	13.32	13.21
12	0.12	13.33	13.21
13	0.13	13.35	13.22
14	0.14	13.35	13.21
Next day	0.25	13.47	13.22

[a] Accidental error.

TABLE II. EFFECT OF CHANGING POSITION OF CELL

Prism Position	Zero Reading	Solution Reading	Difference
Normal position	1.77	14.98	13.21
0.5° to right	2.27	15.48	13.21
0.5° to left	0.86	14.07	13.21
2 mm. to side	1.67	14.88	13.21
6 mm. toward light	1.76	15.16	13.40
Original position	1.51	14.72	13.21

The sensitivity of the instrument increases rapidly as the angle of the triangular cell is increased, but angles larger than 137° are not recommended since the bands become weaker and more diffuse as the angle is increased. The water prism, *P*, gives the instrument more than twice the range that it would have with a prism of ordinary glass. The higher dispersion of the water compensates considerably for the dispersion due to the solution in the refractometer. A scale reading of 60 cm. corresponds to a difference in refractive index of about 0.002 or a deviation of about 0.5° by the cell. For such small angles, the displacement of the movable prism is practically proportional to the difference in refractive index. The scale readings for certain differences in refractive indices were calculated, using eight-place trigonometrical functions, for the mean of the two beams which give the interference bands. The difference in refractive index, with water as the reference liquid, is given within one part in ten thousand by the formula

$$\Delta n = (33355\ S - 2.83\ S^2) \times 10^{-9}$$

where S is the scale reading in centimeters. The second term amounts to only 0.1 per cent for a 13-cm. scale reading and for smaller readings it may be neglected. For the maximum scale reading of 60 cm., the second term amounts to 0.5 per cent. Since the difference in refractive index in general is not exactly proportional to the concentration, it is more convenient for analytical purposes to calibrate the instrument directly in terms of concentration of the solution to be analyzed. If the solution has a refractive index below that of the reference liquid, the prism, *P*, is reversed on the scale. If absolute differences of refractive indices are desired, it is easier to calibrate the instrument with two solutions of known refractivity than to measure the angles of the prisms. This refractometer has been used for transference number determinations. For the small concentration changes involved, the concentration was proportional to the scale reading, within 0.1 per cent. Using this 137° cell, $\Delta n = 0.002003$ for a 60-cm. or maximum scale reading. This would be the reading given by a 0.23 *N* sodium chloride solution. If more concentrated solutions are to be analyzed, they may be diluted or a prism with a smaller angle may be used.

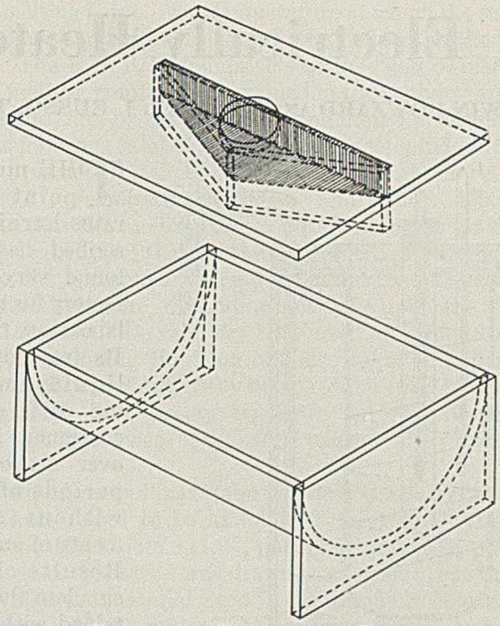

FIGURE 3. DIAGRAM OF CELLS

Summary

A differential refractometer has been developed that uses white light and has a sensitivity of 5 × 10^{-7}. It has been used to determine the concentrations of aqueous solutions with refractive indices from 0.0004 to 0.002 greater than pure water with an accuracy of 0.1 per cent. This corresponds approximately to 0.04 to 0.2 *N* sodium chloride solutions. The scale readings are nearly a linear function of the difference in refractive indices. Readings can be taken much more easily and rapidly than with the liquid interference refractometer.

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(1) Haber and Löwe, *Z. Elektrochem.*, 13, 460 (1907); 16, 37 (1910).
(2) "Handbuch der Physik," Vol. XVIII, p. 675, Berlin, Julius Springer, 1927.

RECEIVED May 29, 1935.

CORRECTION. In the paper on "A Modified Persulfate-Arsenite Method for Manganese" by E. B. Sandell, I. M. Kolthoff, and J. J. Lingane [IND. ENG. CHEM., Anal. Ed., 7, 256 (1935)] the 15th line from the bottom in the first column of page 258 should read "Dissolve 1.2 to 1.3 grams of pure arsenic trioxide—," instead of "Dissolve 2.5 grams of pure arsenic trioxide—."

I. M. KOLTHOFF

An Electrically Heated Melting Point Apparatus

EDWIN DOWZARD AND MICHAEL J. RUSSO, The New York Quinine & Chemical Works, Inc., Brooklyn, N. Y.

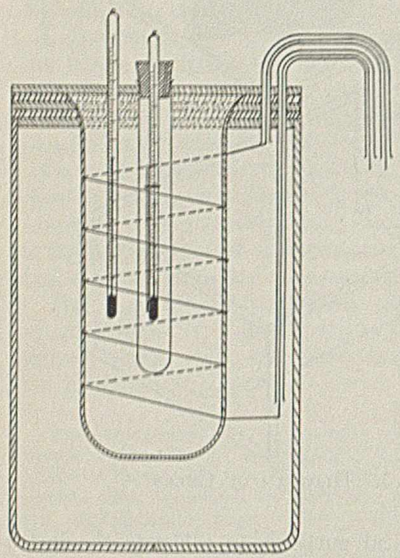

FIGURE 1. MELTING POINT APPARATUS

THE melting point apparatus herein described has been found very satisfactory for routine laboratory testing. Its freedom from liquids and moving parts assures continuous service over extended periods of time without adjustments of any sort. Results closely simulate those obtained with large, mechanically stirred, liquid baths. It is suitable for the determination of melting points up to about 310° C., with a reproducibility of within 0.5° C.

Apparatus

A round battery jar (Figure 1), about 150 × 230 mm., is fitted with a cover composed of four disks of asbestos board, each 5 mm. thick and 150 mm. in diameter, cemented together by means of water glass. The diameter of the bottom disk is reduced so that it fits snugly into the jar. Two small holes, about 25 mm. apart, are drilled 12 mm. from the outer circumference of the cover to take two Pyrex tubes 3 mm. in inside diameter. In addition to these holes, a tapering hole is cut in the center of the cover to hold an 80 × 180 mm. Pyrex tube, closed at one end, firmly centered in the jar. This tube has two 3-mm. holes, 12 mm. apart, drilled 25 mm. from the top, and two similar holes just at the start of the curve at the bottom.

The tube is set into the hole in the cover and then wound with five equally spaced turns of Nichrome ribbon 0.15 × 0.0125 cm. (0.06 × 0.005 inch), the ribbon being anchored by means of the small holes at the ends of the tube and then brought up through the glass tubes in the cover to serve as lead-in wires. The individual turns of ribbon about the tube are securely fastened in place by spotting each turn with a drop of paste made of short asbestos fiber and water glass. The holes in the 80 × 180 mm. tube and the ends of the lead-in tubes are also sealed with this paste.

A fifth disk of asbestos board, similar to those already described, is drilled to take the two small lead-in tubes, a hole to support a Pyrex test tube, 18 × 150 mm. (to hold the melting point thermometer and capillary), centered in the 80 × 180 mm. tube, and a fourth hole to insert a 0° to 250° C. thermometer midway between the tubes. This board is put in place, the lead-in tubes are inserted, and it is then "tacked" down to the main portion of the cover in several spots with water glass.

Number 14 gage rubber-covered wire is used throughout the electrical circuit, connection being made to the Nichrome ribbon by means of brass wire connectors. The electrical input to the heating coil is controlled by means of a 5-ampere Allen Bradley radiostat and measured by an ammeter having a range of 0 to 5 amperes in 0.2 ampere divisions. For safety and convenience, a toggle switch and a 10-ampere fuse are inserted in the circuit.

In order to make the apparatus a complete unit, capable of being moved about the laboratory quickly and easily, a base 40 × 27.8 × 18.75 cm. (16.375 × 11.125 × 7.5 inches) was constructed with 1.25-cm. (0.5-inch) angle iron. This base served to support not only the jar but all the other electrical equipment as well. As neither the size nor shape of this base affects the operation of the apparatus, it may be varied to suit the individual's requirements. However, a very definite idea of its construction may be obtained from Figure 2.

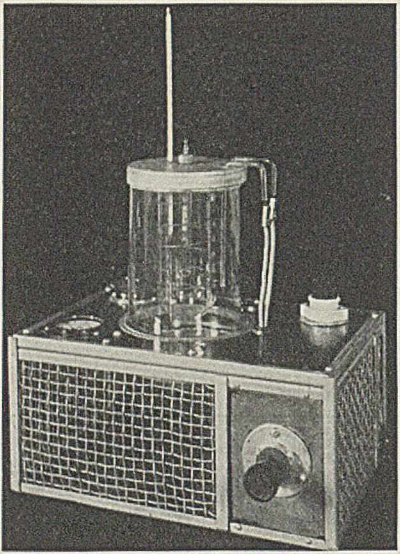

FIGURE 2. PHOTOGRAPH OF MELTING POINT APPARATUS

Operation

The manipulation of the apparatus should not entail any difficulty after a few trial runs are made to familiarize the operator with its behavior.

The capillary, containing the sample, is attached to an Anschutz thermometer of appropriate range and set into the inner test tube, the thermometer being held in place by means of a cork stopper with a very small slit up the side to allow for air expansion within the tube. The current is then turned on and the input regulated so as to attain a rapid increase in temperature until a point approximately 25° below the supposed melting point of the substance is indicated on the auxiliary thermometer.

The input is then reduced until a steady rise of about 3° per minute is attained in the inner tube. As the melting point

TABLE I. TEMPERATURE FOR GIVEN INPUT

Elapsed Time	1—Ampere Input		2—Ampere Input		3—Ampere Input		4—Ampere Input		5—Ampere Input	
	Temp.	Temp. rise	Temp.	Temp. rise	Temp.	Temp. rise	Temp.	Temp. rise	Temp.	Temp. rise
Min.	*° C.*	*° C./min.*	*° C.*	*° C./min.*	*° C.*	*° C./min.*	*° C.*	*° C./min.*	*° C.*	*° C./min.*
0	26.0	..	26.0	..	24.5	..	28.5	...	26.5	...
5	..	..	..	..	41.5	3.4	63.0	6.9	87.0	12.1
10	..	..	48.0	..	79.0	7.5	131.5	13.7	202.5	23.1
15	..	..	62.4	2.88	108.0	5.8	173.0	8.3	244.0	8.3
20	..	..	72.8	2.08	127.0	3.8	191.6	3.7	262.5	3.7
25	..	..	79.4	1.32	139.1	2.4	203.0	2.3	271.0	1.7
30	41.0	..	84.2	0.96	146.5	1.5	211.0	1.6	280.2	1.8
35	42.4	0.28	87.6	0.68	151.5	1.0	217.2	1.24	284.4	0.84
40	43.6	0.24	90.5	0.58	155.0	0.7	221.5	0.86	285.6	0.24
45	44.8	0.24	92.6	0.42	157.0	0.4	224.2	0.54	287.6	0.40
50	45.2	0.08	94.5	0.38	157.2	0.04	224.5	0.06	288.6	0.20
55	45.7	0.10	95.5	0.20	157.4	0.04	...	...	289.7	0.22
60	45.8	0.02	96.2	0.14	...	..	...	...	...	...
65	46.0	0.04	..	..	...	..	...	...	...	...
70	46.2	0.04	..	..	...	..	...	...	...	...

is approached the input is further gradually reduced until, at a point about 3° below the supposed melting point of the substance, a temperature rise not exceeding 0.75° per minute is obtained.

Table I, listing temperature for a given input at various elapsed times, should be considered as being only approximate. The given temperatures are those indicated on an Anschutz thermometer placed in the inner test tube. No account was taken of the lag of the apparatus at any particular point. During the preliminary rapid rise of temperature, up to about 200° C., this lag is a noticeable and variable factor, depending mainly upon the rate of temperature rise and must be taken into account for accurate temperature control. A close approximation of its magnitude may be obtained by placing a long-range thermometer midway between the tubes, as is illustrated in Figure 1.

As indicated in Table I, temperatures up to about 284° C., with the correct rate of temperature rise at that point, may be obtained by using 5 amperes. However, the time required to reach this point may be considerably shortened and the useful range of the apparatus increased to approximately 310° C., at the expense of a slight overload, by using 5.33 amperes.

Experimental

It having been stated (*1*) that melting point apparatus employing an air bath yields results that are consistently higher than those obtained in a liquid bath, it was deemed advisable to check the authors' apparatus against one employing a bath of phosphoric acid, previously heated as directed by Snell (*2*) to determine the magnitude of this variation under present conditions. The bath, having a volume of 1.5 liters, was electrically heated and mechanically stirred during each determination. The rate of temperature rise, in all cases, was between 0.5° and 0.75° C. per minute at the melting point. The temperature at which the substance became a clear fluid throughout was defined as the melting point. The U. S. P. X defines this as the "end of melting."

The melting points as determined in the authors' apparatus (first figure) and by the modified Snell method (second figure) were as follows: salol 42.6° and 42.4°, acetanilide 115.0° and 114.5°, phenobarbital 176.0° and 176.0°, saccharin 225.0° and 224.5°, phenolphthalein 261.0° and 260.8°. The results indicate that the melting points obtained in the air bath are slightly higher than these obtained in the liquid bath. However, as the apparent melting point of a substance is a somewhat variable figure, depending not only upon the diameter and thickness of the capillary tube used and upon the slight variations in filling the tube but also upon the operator, a second series was obtained by means of the authors' apparatus to determine how closely triplicate determinations would check. All figures were obtained by one operator on successive days.

The minimum and maximum values of the observed melting points were found to be as follows: salol 42.5° and 42.6°, antipyrine 110.5° and 111.0°, phenobarbital (The phenobarbital used in this series was drawn from a lot other than that from which the material used in the previous determination was taken.) 174.8° and 175.1°, caffeine 235.0° and 235.4°, phenolphthalein 260.7° and 261.0°. The maximum difference obtained was 0.5°. If this figure is taken as the maximum experimental error, the differences in results obtained with the described apparatus and the phosphoric bath are insignificant.

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(1) Markley, K. S., Ind. Eng. Chem., Anal. Ed., 6, 475 (1934).
(2) Snell, F. D., *Ibid.*, 2, 287 (1930).

Received October 19, 1935.

Prevention of Foaming in Crude-Fiber Determinations

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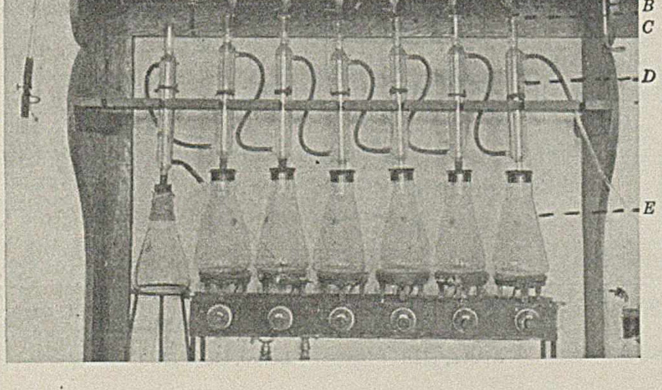
THE mechanics of crude-fiber determinations is made tedious by a tendency of many materials to foam during digestion. The custom of breaking the foam by blowing through an auxiliary tube or through the condenser requires the constant attention of the analyst.

The author has found that a fine jet of air projected on the center of the boiling liquid is as effective in dispersing the foam as a larger current of air. Furthermore, if proper precautions are taken, a fine jet of air may be projected on the surface of the digesting material throughout the digestion period without increasing evaporation. The diagram illustrates a convenient arrangement of apparatus for routine crude-fiber determinations, in which compressed air is let into the digestion flasks by means of capillary tubes through the condensers.



Tube *A* is a compressed air supply from a laboratory pump to the apparatus connected with a capillary tube, *C*, through stopcock *B*. Tube *C* may be of any suitable diameter, but is drawn out at the tip to a diameter of about 1 mm. To prevent possible breakage, tube *C* is made just long enough to reach the bottom of condenser *D*. A stream of air is thus projected onto the surface of the digest in flask *E*.

The author has used this apparatus for more than a hundred determinations consisting of mixed feeds and packing-house residues. Analyses were made by the official method (*1*). There was a great saving of time on the part of the analyst, and good results were obtained.

Literature Cited

(1) Assoc. Official Agr. Chem., Official and Tentative Methods, 3rd ed. (1930).

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An Automatic Recording Balance

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An automatic, electrically operated, continuous recording balance fitted with oil damping and counterbalanced for an initial load of 100 grams is described. Losses in weight up to 17 grams, with an accuracy in the order of 0.01 gram, are recorded without manual attention by means of an automatic device which places weights, in the form of steel bearing balls, upon the pan. Recording is performed, through the use of a timed spark, upon a paper chart carried on the drum of a variable-speed kymograph which has a range of from 12 hours to 6 days.

STUDIES of the rate and magnitude of the moisture losses occurring during the drying of macaroni products involve a series of determinations at relatively frequent intervals extending over a period of several days. In this type of work it is necessary either to remove samples for the determination of residual moisture or to weigh directly a sample suspended within the drying cabinet. The removal of material at frequent intervals disturbs the drying schedule, introduces sampling errors, and is subject to the possibility of changes in moisture content during the operations involved. In view of these difficulties, direct weighing of a sample suspended from a balance external to the cabinet is preferable. Since the actual drying is carried out in a stream of conditioned air, as described by Binnington and Geddes (*2*), a certain amount of motion is imparted to the sample which renders it essential to use a type of balance insensitive to this condition. In order to overcome the inconvenience of frequent weighings at regular intervals over extended periods and to secure a continuous record of the weight loss, the automatic recording balance described in this paper was developed.

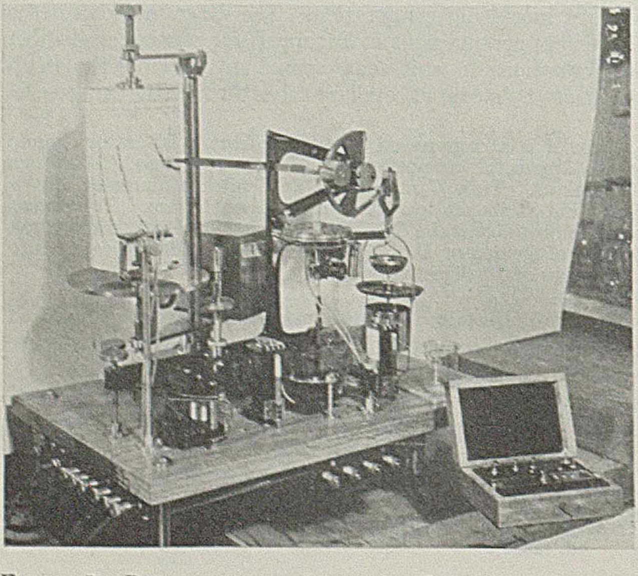

FIGURE 1. PHOTOGRAPH OF AUTOMATIC RECORDING BALANCE

The literature on recording balances is rather meager. The simplest form appears to consist of a mirror attached to the beam of a standard balance, registering by means of a light beam upon sensitized paper; such devices have been described by Abderhalden (*1*), Tryhorn and Wyatt (*7*), and Köhler (*5*). The weight range covered by this type of balance is rather limited and the recording system somewhat cumbersome. A method based on the automatic addition of uniform increments of weight has been described by Oden (*6*). This was later improved by the addition of an electromagnetic balancing system and a suitable recording device. The perfected instrument is described by Coutts et al. (*3*) and is known as the Oden-Keen automatic recording balance. The balance proper is essentially a standard analytical model which is not suited to weighing material subject to a certain amount of motion. It accordingly became necessary to design a balance based on somewhat different principles from those hitherto described.

The instrument was built up around an old type of unequal-arm balance (ratio approximately 5 to 1) and is designed

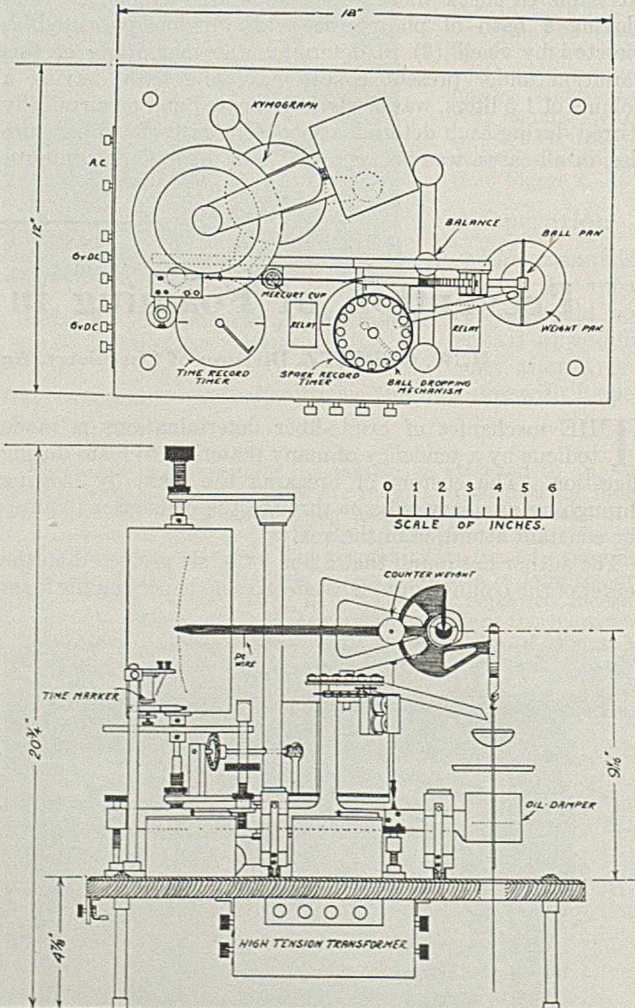

FIGURE 2. DETAILS OF COMPLETE ASSEMBLY

Above, plan Below, elevation

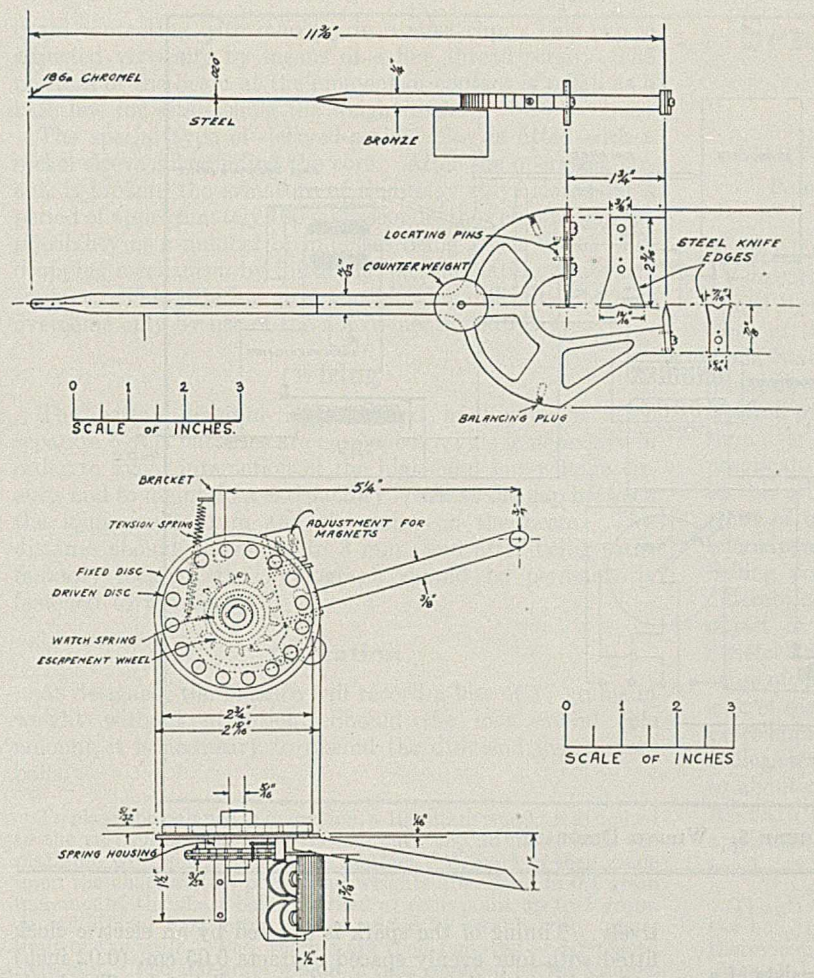

Figure 3. Details of Balance Beam (Above) and Ball-Dropping Mechanism (Below)

primarily for recording loss of weight, although it may be used without alteration for weight increases of not more than 1.5 grams. The entire assembly is illustrated in Figures 1 and 2.

The balance is adjusted to carry a 100-gram load, and its oscillation is reduced to a minimum by a simple oil damping device. The actual record is produced on a paper chart carried upon the drum of a variable-speed kymograph by means of a high-tension spark. This spark is produced between a nichrome point on the end of the balance beam and the metal of the recorder drum, thus burning a small hole through the chart; the duration is about 0.2 second and the frequency interval may be varied from 15 to 60 seconds. A time record is also produced upon the chart by a suitable device. When the beam reaches the lower end of its travel, which corresponds to a weight loss of 1.04 grams, a platinum wire contacts with mercury and actuates a device which places a 1.04-gram steel bearing ball upon the balance pan, thus restoring the beam to its starting position. The record thus obtained consists of a series of descending curves, from which the total loss in weight, the hourly loss, and the rate of loss over any time interval, may be calculated. The entire assembly is mounted as a unit upon a heavy oak base standing on tall brass pillars. In use, it is placed on top of the drying cabinet, the sample being hung over a stirrup attached to the balance pan by means of a fine nichrome wire which passes through a small hole drilled in the top of the cabinet.

Balance

The balance is of very simple design, the remodeled beam details being shown in Figure 3.

It was remodeled from an old type "ash" balance (sold by A. Gallenkamp & Co., Ltd., London, England, *4*) designed to carry a load of 30 grams and indicating weight directly to 0.01 gram. The scale and part of the frame were removed, a counterweight was fitted, and the position of the smaller knife edge altered to obtain stable equilibrium. The spring-type pan arrest was also removed and a simple oil damper fitted. The pan suspension was extended to enable the attachment of a sample carrier which was suspended within the cabinet. A small additional pan for receiving the ball weights was also installed and a nichrome wire point, 0.46 cm. (0.19 inch) long, 18 gage, attached to the end of the beam. All these alterations and additions were made prior to counterbalancing for a 100-gram load. The balance was fixed upon the base by means of brass cups into which the leveling screws fitted; these cups were screwed onto the base after final location of the instrument.

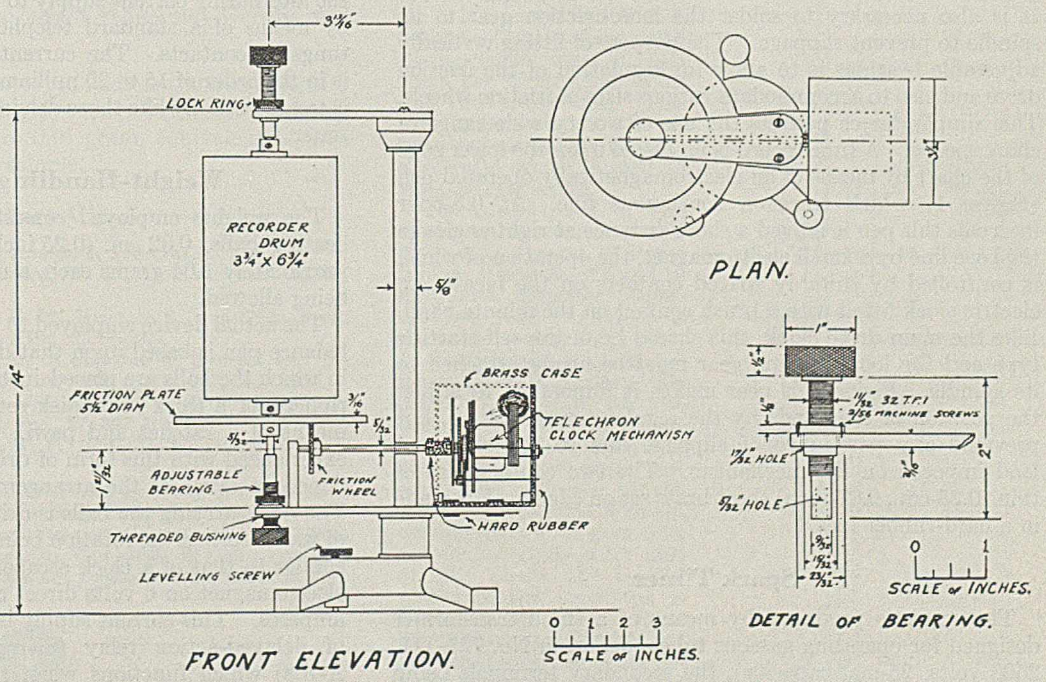

Figure 4. Details of Kymograph

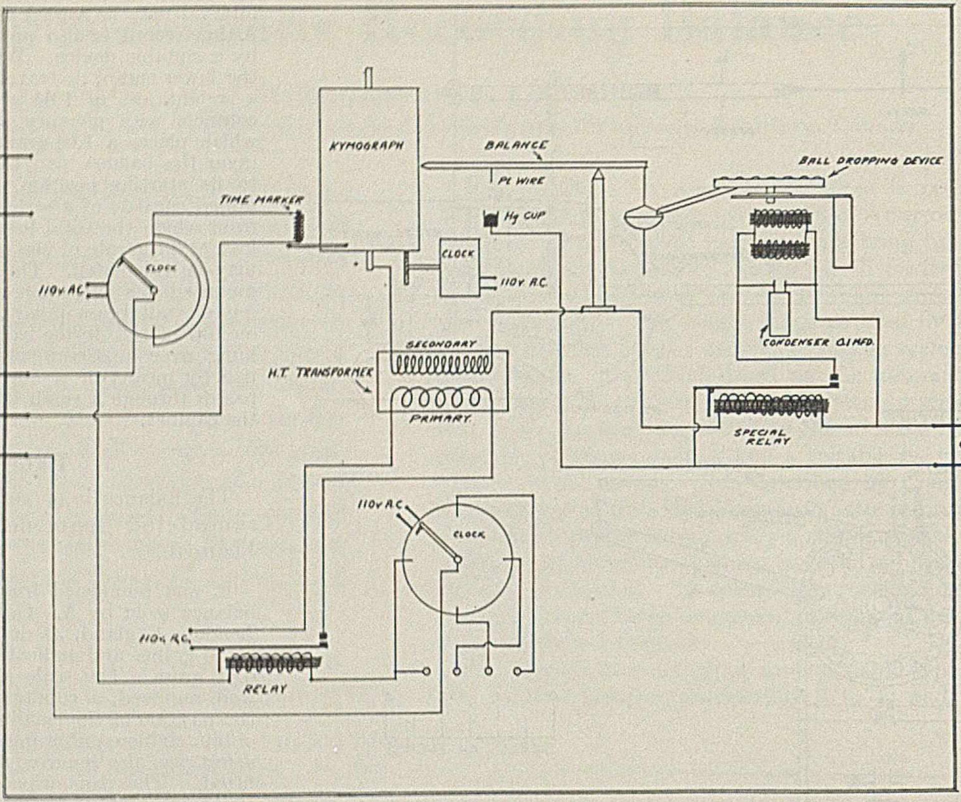

Figure 5. Wiring Diagram

Kymograph

The kymograph is illustrated in Figure 4 and consists of a brass drum 93.75 × 16.875 cm. (3.75 × 6.75 inches) mounted in vertically adjustable bearings and driven through the medium of a friction wheel and plate from the hour spindle of an electric clock. It is essential to employ a clock mechanism of the self-starting (telechron) type and it must be completely insulated from the metallic support of the kymograph. It is also necessary to solder the loose-friction gear to its spindle to prevent slippage. The purpose of fitting vertically adjustable bearings is to allow for regulation of the friction drive and also to accommodate various sizes of friction wheels. This simple device permits the use of a very wide range of chart speeds. A time record is produced upon the lower edge of the chart by means of an electromagnetically operated pen (Figure 1) which traces a continuous line. At 0.5-hour intervals this pen is moved a short distance at right angles to the base line by a small electromagnet, the operation of which is controlled by suitably spaced contacts on the face of an electric clock fitted with a brush contact on the minute hand. Like the main drive clock, this should be of the self-starting type and the loose friction gear must be firmly attached to its spindle. Fixing this gear makes it impossible to adjust the position of the hands by the regular time-set knob, but prevents any possibility of slippage due to the abnormal load imposed on the mechanism. The two contacts are of thin (0.25-cm., 0.01-inch) sheet brass set on edge in slots made in a hard-rubber face.

Spark Timer

The spark is produced by means of a small transformer designed for operating gaseous tubes (Jefferson No. 721–171, 2500 volts, 25-ma. capacity), the secondary terminals being connected to the kymograph and balance supports, respectively. Timing of the spark is effected by an electric clock fitted with four evenly spaced contacts 0.05 cm. (0.02 inch) wide, and a brush contact on the second hand. The leads from the four contacts are carried to terminals placed at the front of the base and arranged so that connecting the first two gives a spark every 30 seconds, connecting all a spark every 15 seconds, and with no connections, a spark every 60 seconds. In order to minimize oxidation of the clock contacts, the alternating current supply to the transformer is controlled by means of a standard telephone relay fitted with heavy tungsten contacts. The current flowing through this relay is in the order of 15 to 20 milliamperes. The clock employed is treated exactly like those driving the kymograph and record timer.

Weight-Handling Mechanism

The weights employed consist of selected standard steel bearing balls, 0.32 cm. (0.25 inch) in diameter, weighing approximately 1.04 grams each, a maximum variation of 3 mg. being allowed.

The actual device employed to place these weights upon the balance pan is based upon that described by Coutts et al. (*3*) in which the balls are placed in holes located around the periphery of a thick brass disk rotated electromagnetically by means of a ratchet and pawl. Considerable difficulty was experienced with this form of drive and it was finally abandoned in favor of the arrangement illustrated in Figure 3. The disk carrying the balls is driven by means of a few turns of watch spring, the rotation being controlled by a mechanism similar to that of a clock escapement. It is operated by an electromagnet on 6 volts direct current and drawing about 7 amperes. This current supply is controlled by a special type of delayed-action relay (Siemens Bros. of Canada, No. A-108) which functions when the beam reaches the lower end of its travel by means of a platinum wire attached to the beam contacting with mercury in a steel cup. This cup is adjusted vertically by means of a fine thread screw. The position of the beam at the moment of contact is taken as a base line for establishing the weight scale.

The special type of delayed-action relay is fitted with a nickel sleeve surrounding the core. After the operating circuit is broken, the armature of this relay stays closed for a period of approximately 100 milliseconds, thus eliminating the possibility of a number of impulses being given to the ball-dropping mechanism by "jittering" at the platinum-mercury contact. This jittering gave considerable difficulty and was overcome only by use of the above-mentioned relay.

Wiring

The wiring diagram is illustrated in Figure 5. Two separate 6-volt batteries are employed. This is necessary in order to avoid interaction of the high- and low-voltage circuits and to maintain a satisfactory spark at the gap between the kymograph drum and the point on the beam. This distance should be from 1 to 3 mm., and after being satisfactorily located, the kymograph should be permanently fastened to the base.

Operation

As designed, the balance will record a loss of 17 grams in weight without attention. Should the loss exceed this amount, it is necessary to rewind the disk and insert more balls.

To place the balance in operation, a 100-gram weight is attached to the suspension wire, and the mercury cup adjusted until the platinum wire just fails to make contact. A mark is then made upon the chart at this point, and weights are added in 0.1 gram increments, the chart being marked at each point up to 1 gram. An additional 0.04 gram is then added to establish the upper limit of the scale. The weights are then removed and replaced by a ball. The 100-gram weight is then replaced by the sample, exactly 100 grams being secured by balancing to the upper point on the weight scale. If exact adjustment in this way is not feasible, approximately 100 grams may be taken, the exact amount being ascertained by the addition of balance weights to the pan, which remain during the duration of the test. Upon completion of the record, the chart is removed, weight lines are drawn on at 0.1-gram intervals, and time lines inserted with a guide cut to the curvature of the arc traveled by the recording points. Total or intermediate weight values may then be read directly from the chart.

The apparatus has been employed in drying and equilibrium studies for some time with highly successful results, it being possible to read the record to 0.01 gram, equivalent to 0.01 per cent, using a 100-gram sample.

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Semi-Micro-Cottrell Boiling Point Apparatus

MARY L. WILLARD AND DELCENA E. CRABTREE
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VARIOUS types of boiling point apparatus constructed according to the Cottrell principle (*1*) have been designed by previous workers—Davis (*2*), Swietoslawski (*5*, *6*), those at the Petroleum Refining Laboratory of the Pennsylvania State College (*4*), and others—for the accurate determination of boiling points on a macro scale. Although the Cottrell principle of bubbling the liquid and vapor in equilibrium over the thermocouple or thermometer seems logical and practical, it is believed that no method has been developed on this principle for the accurate determination of the boiling point of a small volume of liquid. The construction of a microapparatus not only suitable for the determination of boiling points accurate to 0.1° C., but also adaptable to differential use, presents an interesting problem, and is the object of this research. The apparatus of Davis and of Swietoslawski (*2*, *5*, *6*) were said to be very accurate, but because of the greater probability of accurate results and greater ease of manufacture with reduction in size, the design of the Petroleum Refining Laboratory of the Pennsylvania State College was used, decreased to about one-tenth the size. A scale drawing of the apparatus is shown in Figure 1.

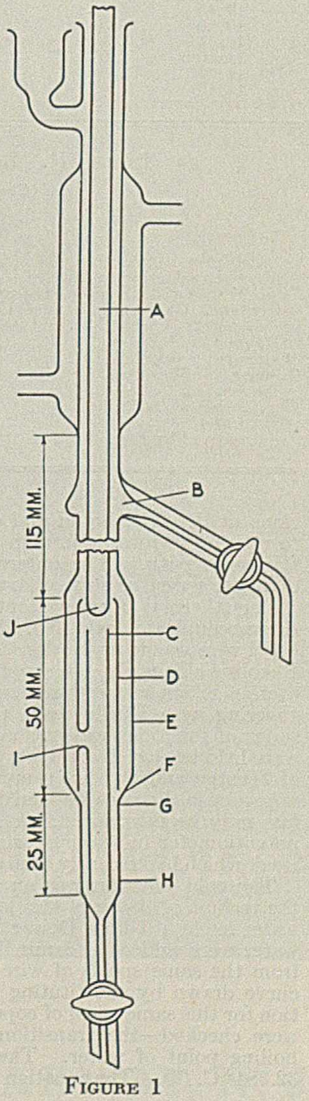

FIGURE 1

The glass tube, *A*, contains the hot junctions of the thermocouples, cemented in place at *J*. *B* is provided to determine the boiling point spread, and also, in the present case, for convenience in determining the minimum quantity of liquid upon which a boiling point can be determined. Heat is applied to the apparatus by winding it between *G* and *H* with 0.9 meter (3 feet) of enameled thermocouple wire of 14.3 ohms per meter (4.35 ohms per foot) resistance. This wire is connected to the alternating current line through a rheostat which is used to vary the heat input.

The inner part of the apparatus is a separate unit made of two pieces of Pyrex tubing, *C* and *D*, of 5 and 10 mm. outer diameter, respectively, held together as shown by a very short tube, *I*, which forms a canal between them. Several file marks are made on the bottom end of *D* to permit free circulation, since this unit rests on the outer unit at a level indicated by the point *F*. The tube of smallest diameter, *C*, is then free, not touching the outer unit at all. Thus, the liquid placed in the apparatus is heated by the external heating unit between *G* and *H* and boils up through the space between *C* and *D*, to be bubbled out on the thermocouple junc-

Table I. Boiling Point Data

(Charge, 5 cc. of carbon tetrachloride; barometer, 727.1 mm.; n_D^{20}, 1.4600.)

Time	Left	Millivolts per Couple	Boiling Point Found	Calculated Vapor Pressure
	Cc.		*° C.*	*Mm.*
Thermocouple position as shown in Figure 1				
3:49	5.0	3.426	75.07	727.3
3:51	5.0	3.426	75.07	727.3
3:54	4.5	3.426	75.07	727.3
3:58	4.0	3.426	75.07	727.3
4:10	3.5	3.426	75.07	727.3
4:13	3.0	3.426	75.07	727.3
4:16	2.5	3.426	75.07	727.3
4:19	2.5	3.426	75.07	727.3
4:21	2.3	3.426	75.07	727.3
4:22	2.0	3.426	75.07	727.3
4:28	1.5	3.427	75.09	...
4:30	1.2	3.424	74.96	...
Thermocouple 1 cm. above position indicated in Figure 1				
4:40	5.0	3.426	75.07	727.3
4:48	4.5	3.426	75.07	727.3
4:52	4.0	3.426	75.07	727.3

Table II. Boiling Point Data

(Charge, 6 cc. of distilled water; barometer, 730.7 mm.; thermocouple position as shown in Figure 1.)

Time	Left	Millivolts per Couple	Boiling Point Found	Calculated Vapor Pressure
	Cc.		*° C.*	*Mm.*
10:10	6.0	4.619	98.90	730.5
10:15	6.0	4.619	98.90	730.5
10:20	6.0	4.619	98.90	730.5
10:25	5.5	4.619	98.90	730.5
10:30	5.0	4.619	98.90	730.5
10:35	4.5	4.619	98.90	730.5
10:40	4.0	4.619	98.90	730.5
10:45	3.5	4.619	98.90	730.5
10:50	3.0	4.619	98.90	730.5
10:55	2.5	4.619	98.90	730.5
11:00	2.0	4.619	98.90	730.5
11:06	1.5	4.621	98.94	...
11:10	1.0	4.620	98.92	...

Table III. Boiling Point Data

(Charge, 5 cc.)

Liquid	n_D^{20}	Boiling Point Expt.	Boiling Point Calcd.	Barometer
		° C.	*° C.*	*Mm.*
Carbon tetrachloride (redistilled)	1.4600	75.07	75.06	727.1
Benzene (redistilled) thiophene-free	1.4997	78.53	78.55	725.6
n-Heptane,[a] California Chemical Co.	1.3878	97.20	97.24	731.4
Isoöctane[a] 2,4,4-trimethyl pentane, Röhm and Haas	1.3918	97.74	97.75	727.8
Water (triple distilled)	....	98.90	98.90	730.5
Toluene (to be used for nitration), Barrett Co.	1.4933	109.02	109.04	727.8
Chlorobenzene (redistilled)	1.5238	130.07	130.04	728.6

[a] Approved by the Bureau of Standards for knock-rating purposes.

tions at *J*. The liquid and condensed vapor are then allowed to return downward through *C*, whence they may again follow the same path. The outermost tube, *E*, of 17 mm. outside diameter served as an auxiliary jacket.

For thermal measurements multiple-junction copper-copel thermocouples of gage No. 28 enameled wire were used. The copel wire was from Hoskins, and the copper wire from John R. Roebling's Sons Co. There were ten hot and ten cold junctions, each of which was soft-soldered together and then insulated by covering with Durite resin, using acetone as a solvent. Each series of junctions was enclosed in a glass tube. The junctions were held in placed at the very tip of the tube by a small amount of litharge and glycerol cement. If the cement extends to any appreciable distance beyond the junctions, an appreciable heat loss may be introduced. A Leeds and Northrup double-range potentiometer indicator, portable precision type, No. 8662, was used, which had recently been checked at the factory.

The cold junction was an ice bath constructed according to the technic of Aston of this laboratory. Finely shaven distilled water ice in a 1-liter Dewar was used, and 50 cc. of distilled water were added to insure intimate contact. Thermocouples from the same spools of wire had been found to conform to the curve drawn by substituting in the Bureau of Standards equation for this same spool of copel wire. Two points on the curve were checked—the transition point of $Na_2SO_4 \cdot 10H_2O$ and the boiling point of water. The transition point of $Na_2SO_4 \cdot H_2O$ is 32.384° C. (*3*). The equation is as follows:

$$E = 42.074\ T - 0.04986\ T^2 - 0.0000310\ T^3$$

E is expressed in microvolts and *T* in degrees Centigrade.

Experimentation

The data given in Tables I to III were obtained using the apparatus illustrated. A determination of the boiling point range of a liquid can be made in 15 minutes or less.

Discussion

From these and other data of a similar nature it was found that the mean deviation of experimental from calculated boiling point was 0.02° C. The calculations were made from existing vapor pressure–temperature data. As may be seen by reference to Table III, all were accurate to 0.1° C. It was also found that the use of a jacket around the apparatus was expedient; that, starting with 5 cc., a 60 per cent take-off could be made without causing any variations in the millivolt readings—i. e., boiling point measurements accurate to 0.1° can be made on as little as 2 cc. of liquid—that the method of wiring by winding with thermocouple wire between *G* and *H* (Figure 1) was most satisfactory; that the variation of heat input by as much as 100 per cent did not affect the millivolt readings; and that bumping was negligible.

A 2-cc. apparatus of the same sort was designed and constructed. The boiling points obtained with it were consistently lower than those obtained with the 5-cc. apparatus under the same conditions. For this reason the take-off was removed from the smaller apparatus and replaced by a side return for the condensed vapors. Results obtained with this apparatus were also low in spite of the use of a jacket. A possible explanation of the lowness of the results lies in the fact that with decrease in size the ratio of surface exposed to volume of liquid increases. This would introduce a greater heat loss and well might be the cause of the low results.

Experiments have been conducted on a 1-cc. apparatus of similar design, but the same difficulties are encountered as with the 2-cc. apparatus. None of the various adaptions in structure have completely removed the sources of error. The readings are consistently lower than calculated. The specific causes for this are not known, but are being investigated.

Summary

With an apparatus of 5-cc. capacity boiling points were found which were accurate to 0.1° C. The mean deviation for the liquids tried was 0.02° C.

Starting with 5 cc. of pure material, a take-off of 60 per cent may be made without causing any variation in the millivolt reading obtained.

Work has been done on a smaller apparatus of the same Cottrell type, but the results were not satisfactory.

Acknowledgment

Acknowledgment is due to Frank C. Whitmore and to Dorothy Quiggle for their valuable suggestions throughout the course of this research.

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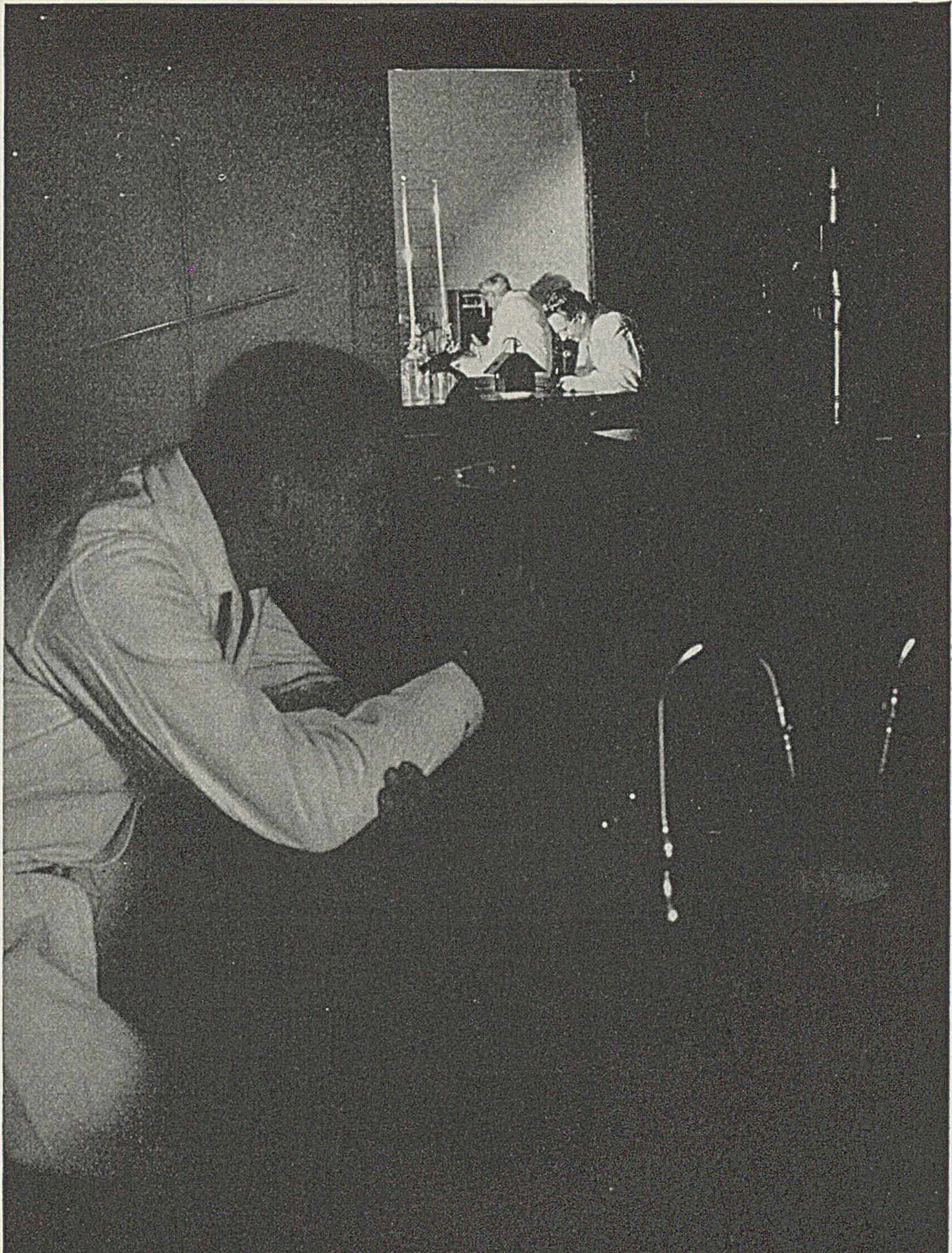

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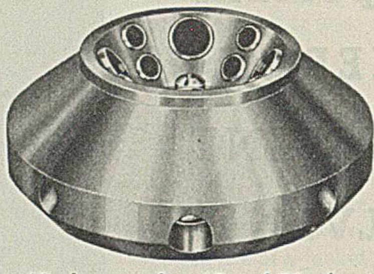

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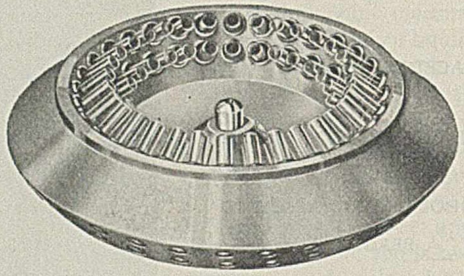

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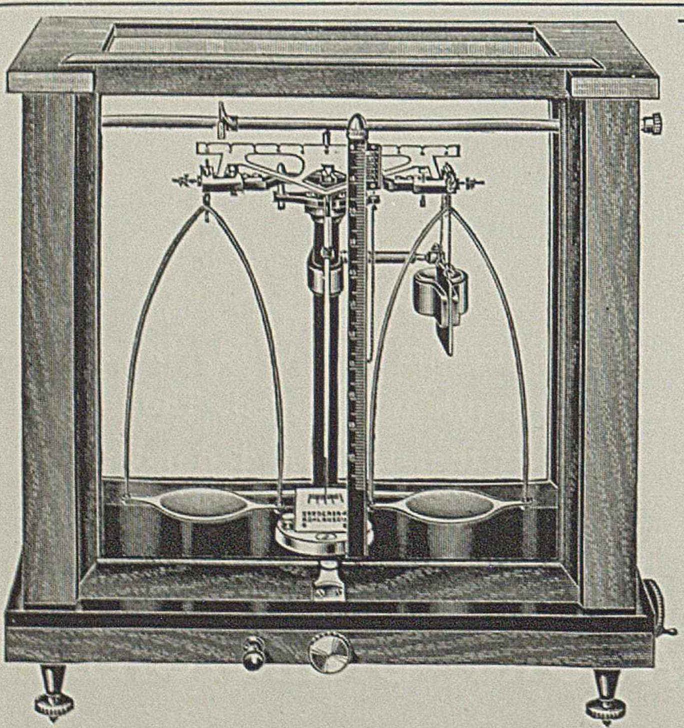

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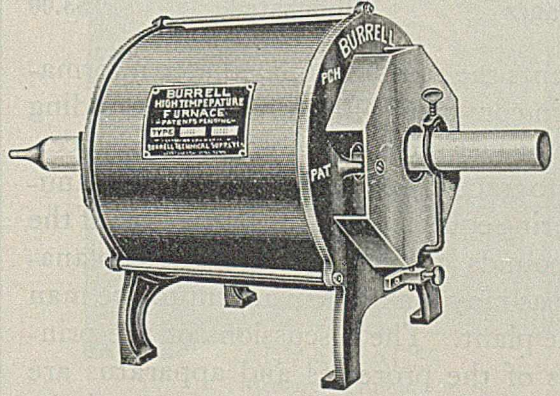

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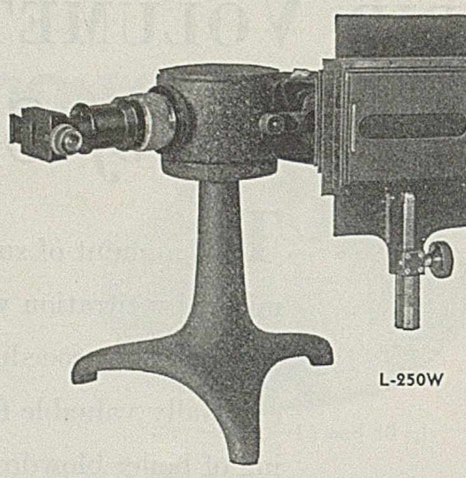
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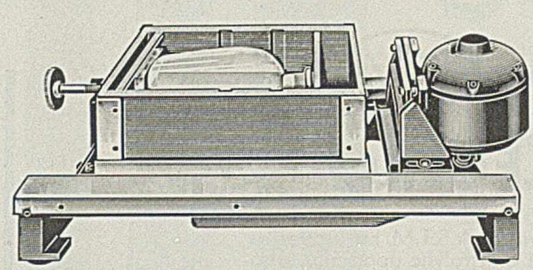

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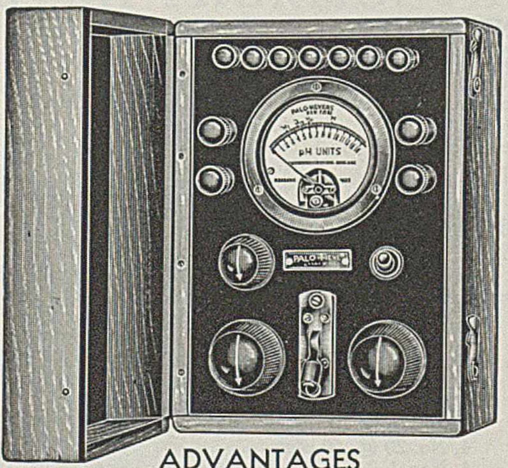

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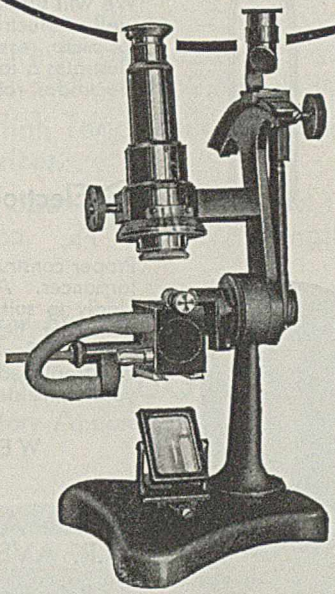

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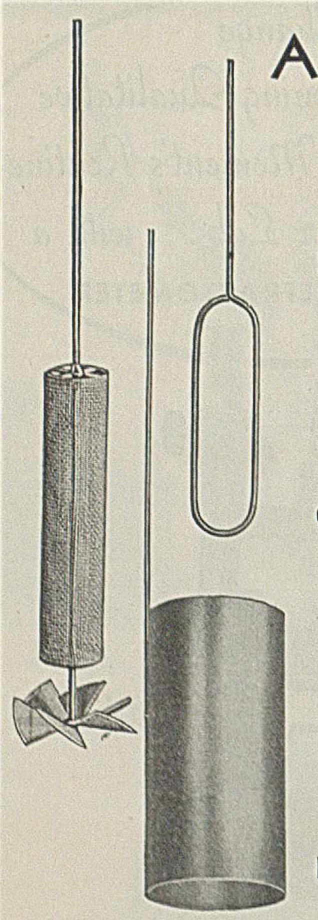

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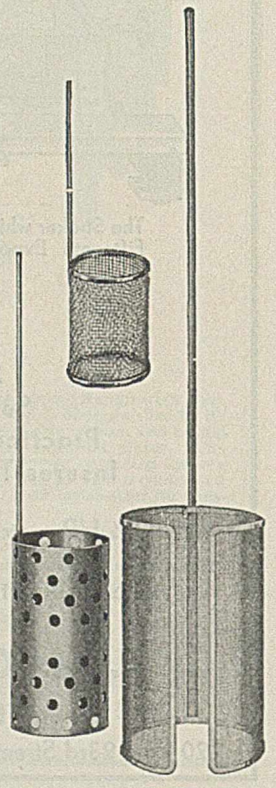

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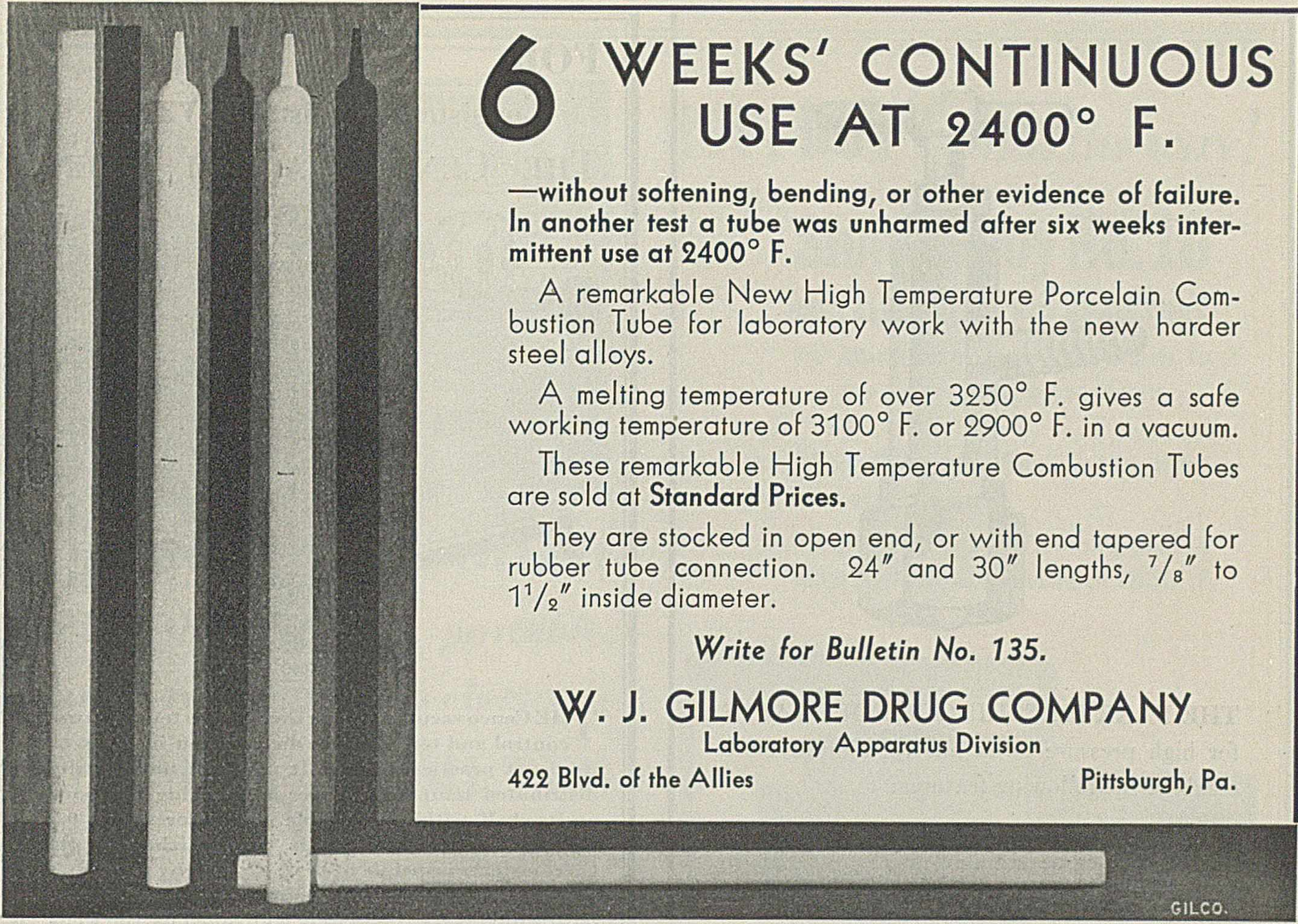
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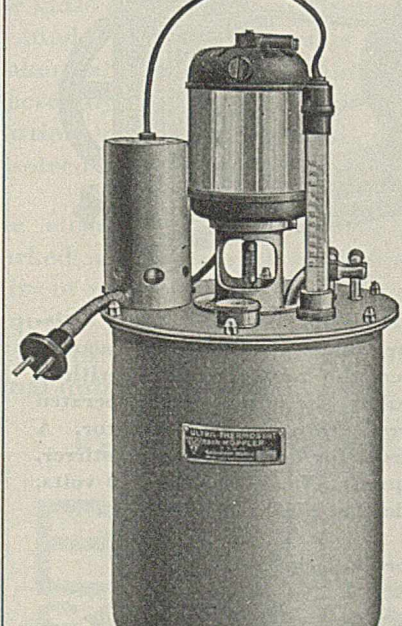

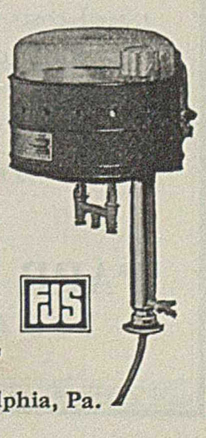

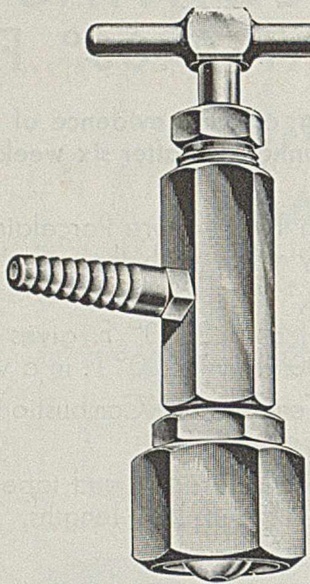

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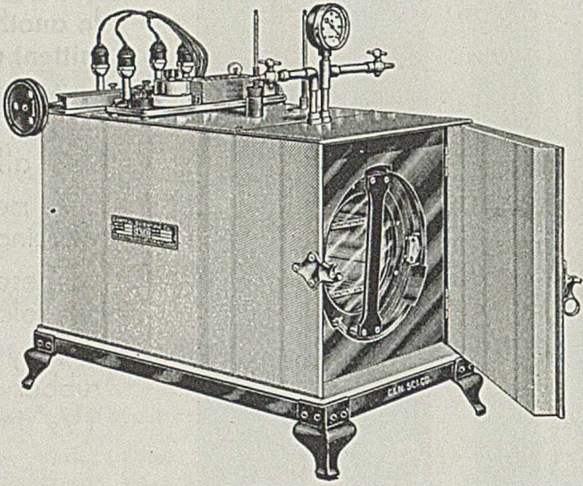

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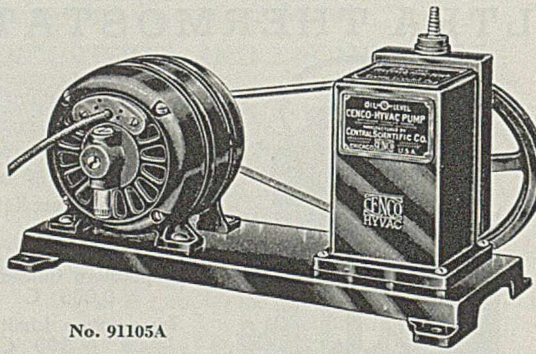

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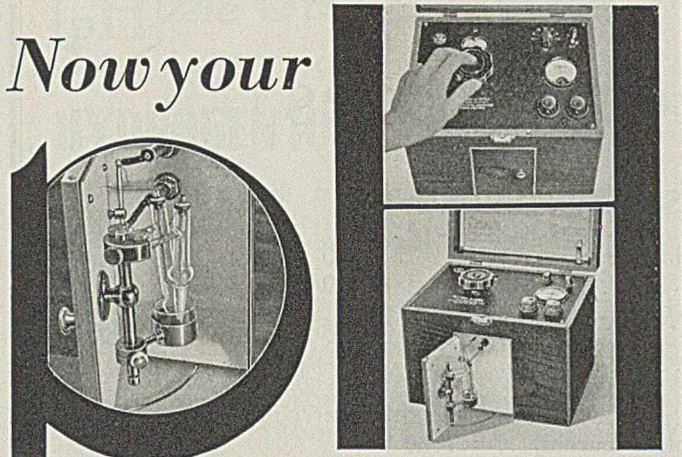

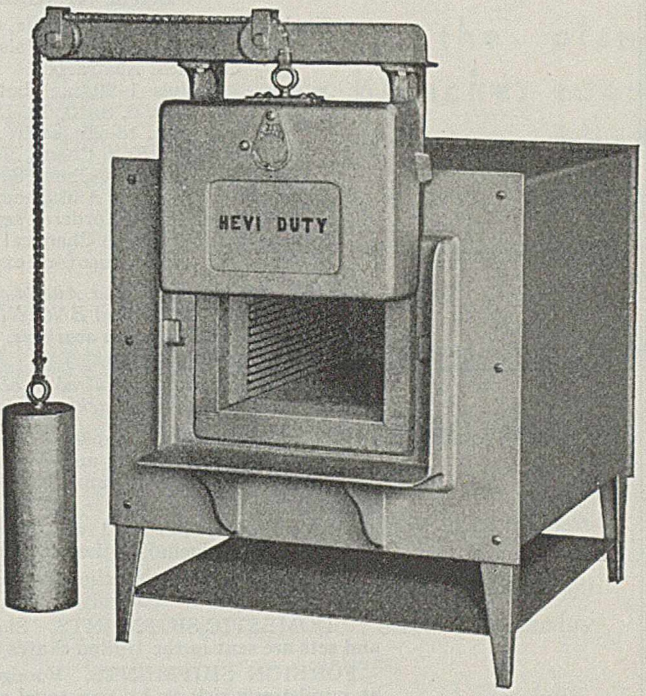
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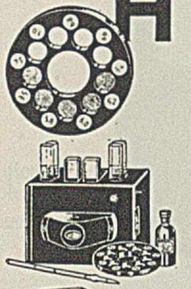

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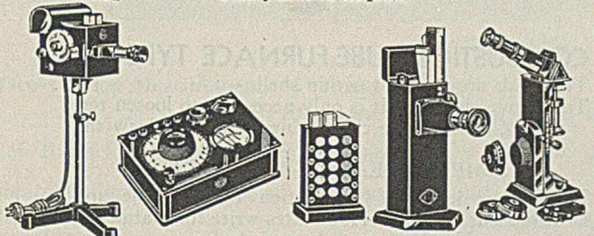

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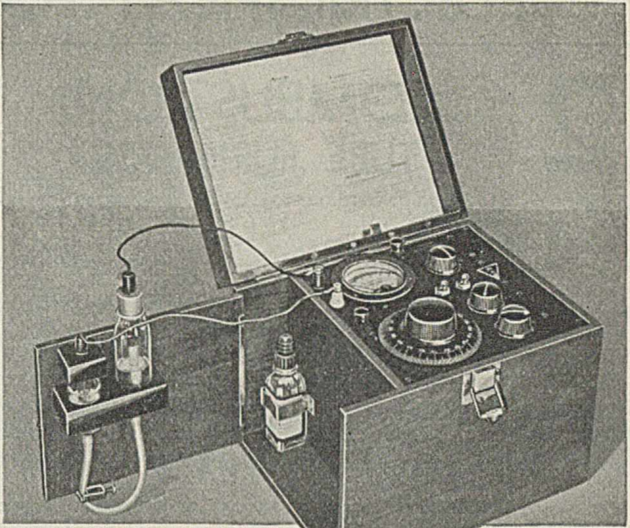

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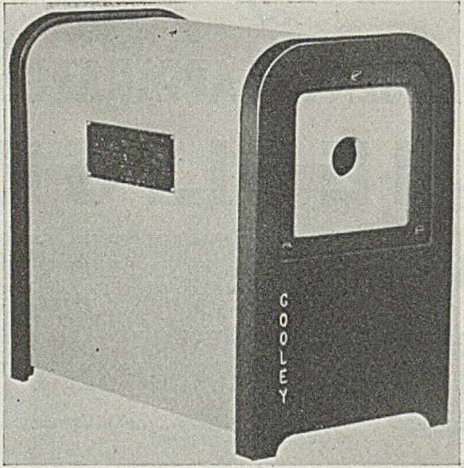
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