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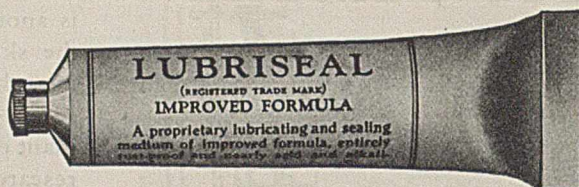




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# INDUSTRIAL and ENGINEERING CHEMISTRY

Harrison E. Howe, Editor

## Quantitative Determination of Aluminum by Precipitation with Urea

HOBART H. WILLARD AND NING KANG TANG, University of Michigan, Ann Arbor, Mich.

Aluminum can be accurately separated from large amounts of calcium, barium, magnesium, manganese, cobalt, nickel, zinc, iron, cadmium, and copper by precipitation as the dense basic succinate by boiling with urea the acid solution containing succinic acid. Hydrolysis of the urea forms ammonia gradually in a homogeneous solution, resulting in a pH of 4.2 to 4.6. Owing to the dense nature of the precipitate, it is easily filtered and washed and shows much less adsorption of other salts

**I**N PREVIOUS work (20) it was found that upon heating aluminum solutions containing sulfates to which urea had been added, the aluminum was precipitated as basic sulfate in a dense and easily filterable form. This was due to the slow, uniform increase in pH caused by the gradual hydrolysis of the urea. The advantages of this method of precipitation in the separation of aluminum from other metals were indicated: (1) The solution is homogeneous, since no reagents are added during precipitation. (2) The precipitate is much less bulky, thus reducing the error due to adsorption and facilitating filtration and washing. (3) The pH of the solution is easily controlled and can never be higher in any part of the solution than the final value obtained. It is not surprising, therefore, that the application of this process to the separation of aluminum should yield results surpassing in accuracy those obtained by the usual methods. This paper describes such separations in which the aluminum was precipitated as basic sulfate and basic succinate. There is little doubt that other anions, which form dense precipitates such as benzoate, would give similar results. The solubility of the basic sulfate was found to be about the same as that of aluminum hydroxide (20), equivalent to 0.2 mg. of aluminum oxide per liter in the pH range 6.5 to 7.5.

### Quantitative Determination of Aluminum by Precipitation as Basic Sulfate

**MATERIALS USED.** The aluminum metal was a special grade obtained from the Aluminum Company of America and contained 99.94 per cent of Al, 0.03 per cent of Si, 0.01 per cent of Ti, and 0.03 per cent of Fe. The latter two are, of course, always precipitated with the aluminum. The urea was a c. p. grade. Ammonium chloride was reagent quality material. Ammonium

than does the precipitate obtained by the usual methods. The basic sulfate precipitated in this way is also dense, but the pH must be 6.5 to 7.5 and separations in certain cases are less satisfactory. The accuracy of separations made by the urea method is far superior to that obtainable by the use of ammonia. This is attributed to a combination of four important factors—a dense precipitate, a slow, uniform increase in pH, a homogeneous solution, and a low final pH.

hydroxide was prepared by passing ammonia from a cylinder through a scrubbing bottle into redistilled water contained in a quartz flask.

**PROCEDURE.** Approximately 0.1 gram of the aluminum metal was weighed into 600-ml. beakers, tall-form, and dissolved in about 5 ml. of dilute hydrochloric acid, gently warming at the end to ensure complete solution. After diluting somewhat, dilute ammonium hydroxide was added until the solution became slightly turbid, then it was cleared with dilute hydrochloric acid, and one or two drops in excess were added. Four grams of urea, 20 grams of ammonium chloride, and 1 gram of ammonium sulfate were introduced and the volume was brought to 500 ml. The solution was then heated to boiling and kept gently boiling for 2 hours after the appearance of an opalescence, after which it was placed on an electric hot plate for 1 hour to allow the precipitate to settle. The precipitate was filtered off, and that adhering to the beaker removed as thoroughly as possible by means of pieces of filter paper.

To ensure complete removal of the last traces of the precipitate, it was dissolved in a little hydrochloric acid, reprecipitated by the procedure of Blum (2), and filtered through the paper containing the main portion of the precipitate. The combined precipitates were washed ten times with hot 1 per cent ammonium chloride solution, made alkaline to methyl red with ammonium hydroxide. After ignition to constant weight in a platinum crucible over a blast Meker at approximately 1200° C., it was weighed in a counterpoised weighing bottle. The pH of the filtrate and the amount of aluminum in the filtrate and washings, amounting to 0.078 to 0.1 mg., were determined colorimetrically (21).

Several workers (6, 10, 13, 14) have reported that sulfate which accompanies aluminum when it is precipitated as hydroxide from sulfate solutions, is very difficult to remove by ignition. An examination of the ignited oxide obtained above, by fusion with sodium carbonate and finally testing with barium chloride, showed that only a negligible amount of



TABLE I. QUANTITATIVE DETERMINATION OF ALUMINUM BY PRECIPITATION AS BASIC SULFATE

Final pH of Solution	Al <sub>2</sub> O <sub>3</sub> <sup>a</sup> Taken Gram	Al <sub>2</sub> O <sub>3</sub> Found Gram	Error Al <sub>2</sub> O <sub>3</sub> Mg.
7.08	0.1913	0.1916	+0.3
7.07	0.1954	0.1956	+0.2
7.03	0.1960	0.1957	-0.3
7.27	0.1950	0.1954	+0.4
6.77	0.1915	0.1912	-0.3
6.58	0.1909	0.1907	-0.2
7.09	0.1941	0.1940	-0.1
7.17	0.1920	0.1917	-0.3
6.94	0.1920	0.1921	+0.1
6.99	0.1914	0.1913	-0.1

<sup>a</sup> Corrected for impurities in the original metal.

TABLE II. SEPARATION OF ALUMINUM FROM OTHER ELEMENTS (Single precipitation)

Aluminum Taken Gram	Metal Added Gram	Amount Present in Precipitate Mg.
0.1	Ca <sup>a</sup> 1.0	Trace
0.1	Mg 1.0	None
0.1	Ni 0.125	0.7
0.1	Co 0.125	1.0
0.1	Zn 0.125	13.6
0.1	Mn 1.0	0.1
0.1	Cd 0.125	0.4
0.1	Cu 0.125	7.3

<sup>a</sup> 0.5 gram of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> used since 1 gram caused slight precipitation of CaSO<sub>4</sub>.

sulfate was retained. Since the earlier work (20) indicated that the precipitate was relatively rich in sulfate, this shows that sulfate can be completely removed by igniting to a sufficiently high temperature (1200° C.). The results obtained by the above procedure are given in Table I.

SEPARATION OF ALUMINUM FROM CALCIUM, MAGNESIUM, NICKEL, COBALT, ZINC, MANGANESE, CADMIUM, AND COPPER. According to Lundell and Knowles (12), aluminum can be separated from the alkalis, alkaline earths, magnesium, and moderate amounts of manganese and nickel by precipitating according to the procedure of Blum (2). The separation from copper, cobalt, and zinc is not satisfactory, from 4 to 20 mg. remaining after one precipitation, and from 1 to 10 mg. after two, using 100 mg. of aluminum and 50 mg. of the accompanying element (9). From the analytical qualities of the precipitate obtained by the present method, considerably better separations might be expected.

It was found that when separate solutions containing 0.5 gram of nickel, cobalt, zinc, manganese, cadmium, and copper as chlorides, together with 4 grams of urea and 1 gram of potassium sulfate were heated overnight on a hot plate, partial precipitation occurred. However, if the solutions contained 10 grams of ammonium chloride in addition to the above, no precipitate formed. The effectiveness of the separation of aluminum from these elements, and also from calcium and magnesium, was determined by precipitating the aluminum from individual solutions containing their chlorides, using the procedure described above. After filtering and washing, the precipitate was dissolved in hydrochloric acid, and the amount of accompanying element carried down was determined by an appropriate standard procedure. Table II gives the data obtained.

These results show that the separation of aluminum from calcium, magnesium, manganese, and cadmium, by a single precipitation with urea in the presence of sulfate, is satisfactory. Using this method only 0.1 mg. of manganese is carried down by 0.1 gram of aluminum in the presence of 1 gram of manganese, while with an ammonium hydroxide precipitation, 1.7 mg. of manganese accompanies the aluminum when these same amounts of the two elements are used. The separation from nickel, cobalt, zinc, and copper is not very good, although a single precipitation by this method is at least as effective

with the last three of these elements as a double one with ammonium hydroxide.

Since the final pH values of the solutions were 6.7 to 7.0, which is about the same as that of Blum's method, it is probable that the greater purity of the precipitate obtained by the present method is due to the reasons mentioned above. The gradual increase in the pH of the solution, which is uniform throughout, allows the major part of the aluminum to be precipitated before the pH rises to a point where there is danger of precipitating the more basic elements.

### Precipitation of Aluminum in the Presence of Succinate

PRELIMINARY INVESTIGATION. In the exploratory work on the influence of various anions on the quality of the precipitates obtained with urea, it was found that those formed in the presence of formate, oxalate, succinate, benzoate, and phthalate were dense, while that formed in the presence of acetate was flocculent (20). Several workers (1, 3, 15) have reported that the pH values at which hydroxides or basic salts begin to precipitate show some variation in the presence of different anions.

A series of determinations with different anions was made to determine the pH necessary for complete precipitation. Solutions of 500-ml. volume, containing approximately 0.1 gram of aluminum as chloride, 4 grams of urea, and 10 grams of ammonium chloride together with the amounts of the various salts shown in Table III, were heated in a boiling water bath until the appearance of a slight opalescence. The solutions were then rapidly cooled to room temperature and the pH was determined with a quinhydrone electrode. The solutions were then gently boiled for 2 hours, the precipitate was filtered off, the filtrate tested for complete precipitation, and the pH determined.

Further study of the basic acetate method employed by Mittasch (16), Funk (?), and Kling, Lassieur, and Lassieur (11) failed to establish any conditions which would give a dense precipitate when the neutralization was caused by the hydrolysis of urea. The basic formate method (5, 8) modified by heating with urea was unsuccessful, as shown by attempts to precipitate aluminum in the presence of nickel. If enough formate was present to give a dense precipitate, the aluminum was incompletely precipitated, and that portion which did precipitate showed the presence of nickel. With 4 grams of ammonium formate in the solution, only about 60 per cent of the aluminum precipitated, while with 15 grams present, about 33 per cent came down. With much smaller amounts of formate, the beneficial effect of the anion on the quality of the precipitate was not realized. Work with the succinate showed that conditions which would give a dense precipitate and quantitative precipitation could be attained easily if succinic acid was added instead of sodium succinate, since the latter causes an immediate precipitate.

CONDITIONS FOR COMPLETE PRECIPITATION OF ALUMINUM IN THE PRESENCE OF SUCCINATE. It was found that the amount of succinate present affected not only the character of the precipitate but also the completeness of the precipitation,

TABLE III. INFLUENCE OF CERTAIN ANIONS ON THE pH OF FIRST OPALESCENCE AND COMPLETE PRECIPITATION

Anion	Salt Used	Salt Grams	pH at First Opalescence <sup>a</sup>	pH after 2 Hours	Precipitation
Phosphate	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> <sup>b</sup>	3	2.3	6.1 <sup>c</sup>	Complete
Succinate	Acid	5	3.6	4.0	Complete
Phthalate	KHC <sub>8</sub> H <sub>4</sub> O <sub>4</sub>	3	3.8	4.9	Complete
Sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1	4.2	6.5-7.5	Complete
Formate	HCOONa <sup>b</sup>	3	4.8	6.0	Incomplete
Acetate	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>b</sup>	3	<sup>d</sup>	5.5	Complete

<sup>a</sup> pH measured at room temperature, opalescence noted at boiling point.

<sup>b</sup> Original solution contained sufficient hydrochloric acid to prevent formation of a precipitate while being brought to a boil.

<sup>c</sup> Precipitation probably complete in less than 2 hours.

<sup>d</sup> Precipitate flocculated too rapidly to allow determination of this value.



especially when other elements were present. Three grams of succinic acid and 10 grams of ammonium chloride in 500 ml. were sufficient to give a dense precipitate, and complete precipitation of aluminum when alone. However, if 0.15 gram of nickel or zinc was present, the precipitation of the aluminum was incomplete with 3 grams of succinic acid, but quantitative if 4 grams or 5 grams were used.

Since the pH of the solution and consequently the completeness of precipitation are dependent on the duration of boiling, this relationship was studied in a manner similar to the determination of the solubility of the basic aluminum sulfate precipitate. The solutions containing 0.1 gram of aluminum, 4 grams of urea, 5 grams of succinic acid, and 10 grams of ammonium chloride in 500 ml. were gently boiled, after the appearance of turbidity, for the lengths of time given in Table IV. The determinations were then completed as previously described (20).

This shows that for the complete precipitation of aluminum by heating with urea in the presence of succinate and ammonium chloride, it is necessary to boil gently for 1.5 to 2 hours after the appearance of turbidity, and that this procedure results in a pH of about 4.4.

### Quantitative Determination of Aluminum by the Succinate Method

**PROCEDURE.** The aluminum solution was prepared as described in the basic sulfate method. After diluting somewhat, 5 grams of succinic acid dissolved in about 100 ml. of water were added, followed by 10 grams of ammonium chloride and 4 grams of urea. The solution was diluted, heated to boiling, and gently boiled for 2 hours after it had become turbid (40 to 45 minutes after it had commenced to boil). The precipitate was allowed to subside for a few minutes, and after a little paper pulp was added, it was filtered and washed ten times with a 1 per cent succinic acid solution, made neutral to methyl red with ammonium hydroxide. The precipitate adhering to the beaker was removed as in the basic sulfate method, except that in this instance the small precipitate obtained with ammonium hydroxide was filtered on a separate paper. The combined precipitates were ignited to constant weight in a platinum crucible at 1200° C. The pH of the filtrate was determined with a quinhydrone electrode, and the amount of aluminum remaining in the filtrate (approximately 0.1 mg.) and in the wash waters (negligible) was ascertained colorimetrically as before.

**MODIFIED PROCEDURE.** When the entire neutralization is dependent on the decomposition of urea, considerable time is consumed before precipitation commences, especially when an acid reducing agent is added as in the determination of copper, discussed later. To avoid this, a partial preliminary neutralization with dilute ammonium hydroxide was tried. When this reagent was slowly added to a cold solution containing urea, ammonium chloride, and succinic acid until barely turbid, a flocculent precipitate was rapidly formed on heating to boiling. However, if it was added dropwise to the hot solution to the point of faintest opalescence, the precipitate obtained on further heating was entirely satisfactory. It was slightly more bulky than that obtained without preliminary neutralization, but was still compact enough to filter and wash rapidly. It had the distinct advantage of being more easily retained by the filter paper.

TABLE IV. EFFECT OF DURATION OF BOILING ON pH OF SOLUTION AND COMPLETENESS OF PRECIPITATION

Duration of Boiling <sup>a</sup> Hours	pH of Solution	Al <sub>2</sub> O <sub>3</sub> in Filtrate Mg./l.
0.25	3.30	
0.5	3.58	1.2
1	3.93	0.8
1.25	4.01	0.8
1.5	4.15	0.2
2	4.40	0.2

<sup>a</sup> After the appearance of turbidity.

<sup>b</sup> Sufficient aluminum left in the filtrate to give a precipitate with ammonium hydroxide.

TABLE V. QUANTITATIVE DETERMINATION OF ALUMINUM BY THE SUCCINATE METHOD

Volume Ml.	Duration of Boiling Hours <sup>a</sup>	pH of Solution <sup>b</sup>	Al <sub>2</sub> O <sub>3</sub> Taken Gram	Al <sub>2</sub> O <sub>3</sub> Found Gram	Error Al <sub>2</sub> O <sub>3</sub> Mg.
500	2	4.43	0.1912	0.1911	-0.1
500	2	4.57	0.1906	0.1903	-0.3
500	2	4.44	0.1906	0.1906	±0.0
500	2	4.32	0.1931	0.1927	-0.4
500	2	4.26	0.1899	0.1899	±0.0
500	2	4.26	0.1899	0.1895	-0.4
500	2	4.48	0.1899	0.1896	-0.3
250	2	4.36	0.1911	0.1911	±0.0
250	2	4.22	0.1903	0.1900	-0.3
250	2	4.44	0.0957	0.0956	-0.1
250	2	4.31	0.0960	0.0958	-0.2
250	2	4.53	0.0059	0.0059	±0.0
250	2	4.50	0.0057	0.0056	-0.1
250	2	4.62	0.0025	0.0015	-1.0
250	2	4.53	0.0017	0.0005	-1.2
250	3	4.77	0.0021	0.0021	±0.0
250	3	4.94	0.0023	0.0023	±0.0
Modified Method					
250	0.5	3.76	0.1894	0.1887	-0.7
250	1	3.96	0.1897	0.1898	+0.1
500	1	4.01	0.1897	0.1898	+0.1
500	1	3.98	0.1905	0.1908	+0.3
500 <sup>c</sup>	1	4.00	0.1903	0.1907	+0.4
500 <sup>c</sup>	1	3.86	0.1909	0.1906	-0.3
500 <sup>d</sup>	1	3.98	0.1901	0.1900	-0.1
500 <sup>d</sup>	1	4.03	0.1906	0.1906	±0.0

<sup>a</sup> After the appearance of turbidity.

<sup>b</sup> At room temperature.

<sup>c</sup> Bromophenol blue used as indicator.

<sup>d</sup> Methyl orange used as indicator.

Since turbidity appears at approximately the pH at which bromophenol blue or methyl orange changes color, it is sometimes convenient to employ one of these as indicators. It is, of course, not necessary to neutralize to the point of turbidity, but it is very important not to overstep it, since this will cause the formation of a somewhat flocculent precipitate on further heating. Table V shows the results obtained using both procedures. A correction was made for impurities in the metal.

Experiments on the ignition of the precipitate showed that heating for 1 hour at 1200° C. was sufficient to attain constant weight and to convert it into a nonhygroscopic (corundum) form which could be weighed directly in a covered crucible without the necessity of placing it in a covered weighing bottle. It was also found that Coors unglazed porcelain crucibles suffered no change in weight during such ignition and they were, therefore, used in place of platinum in most subsequent work.

It is evident that aluminum can be quantitatively precipitated by heating with urea in the presence of succinate and ammonium chloride for 1 to 2 hours after the appearance of turbidity if 5 mg. or more are present, and that the time can be shortened by partial preliminary neutralization. With smaller amounts, about an hour longer is required. The resulting low pH, combined with the granular quality of the precipitate, the slow rate of precipitation, and the homogeneity of the solution, should allow much more satisfactory separations from the more basic elements than precipitation by ammonium hydroxide or even as the basic sulfate.

### Separation of Aluminum from Other Metals

This method was applied to the separation of aluminum from a considerable number of other metals. In all cases the weight of aluminum taken was corrected for impurities. When a second precipitation was made, the basic succinate was dissolved from the filter into the same beaker by hot, dilute hydrochloric acid and the process repeated. The impurity in the oxide was determined by suitable methods.

**DETERMINATION OF ALUMINUM IN THE PRESENCE OF CALCIUM, BARIUM, MAGNESIUM, MANGANESE, AND CADMIUM.** These separations and determinations were made by a single precipitation from a volume of 250 ml. Table VI shows the results obtained, and indicates clearly that by this method a



TABLE VI. DETERMINATION OF ALUMINUM IN PRESENCE OF CALCIUM, BARIUM, MAGNESIUM, MANGANESE, AND CADMIUM BY PRECIPITATION AS BASIC SUCCINATE

Element Added	Al <sub>2</sub> O <sub>3</sub> Taken	Al <sub>2</sub> O <sub>3</sub> Found	Element with Al <sub>2</sub> O <sub>3</sub>	Error Al <sub>2</sub> O <sub>3</sub>
Gram	Gram	Gram	Mg.	Mg.
1.0 Ca	0.1897	0.1895	None	-0.2
1.0 Ca	0.1905	0.1903	None	-0.2
1.0 Ca	0.1905	0.1904	None	-0.1
1.0 Ca	0.1903	0.1904	None	+0.1
1.0 Ba	0.1909	0.1908	None	-0.1
1.0 Ba	0.1905	0.1905	None	±0.0
1.0 Mg	0.1906	0.1904	None	-0.2
1.0 Mg	0.1906	0.1907	None	+0.1
1.0 Mg	0.1892	0.1894	None	+0.2
1.0 Mg	0.1894	0.1890	None	-0.4
1.0 Mn	0.1904	0.1906	0.3	+0.2
1.0 Mn	0.1904	0.1906	0.3	+0.2
1.0 Mn	0.0949	0.0950	0.25	+0.1
1.0 Mn <sup>a</sup>	0.0949	0.0953	0.25	+0.4
1.0 Mn <sup>a</sup>	0.1903	0.1901	0.2	-0.2
1.0 Mn <sup>a</sup>	0.1906	0.1905	0.2	-0.1
0.5 Mn	0.1895	0.1897	0.2	+0.2
0.5 Mn	0.1890	0.1893	0.2	+0.3
1.0 Cd	0.1901	0.1901	<0.1	±0.0
1.0 Cd	0.1902	0.1900	<0.1	-0.2
1.0 Cd	0.1906	0.1907	<0.1	+0.1
1.0 Cd	0.1897	0.1897	<0.1	±0.0

<sup>a</sup> Precipitated from 500 ml.

TABLE VII. DETERMINATION OF ALUMINUM IN THE PRESENCE OF NICKEL AND COBALT BY PRECIPITATION AS BASIC SUCCINATE

Element Added	Number of Precipitations	Volume Ml.	Al <sub>2</sub> O <sub>3</sub> Taken	Al <sub>2</sub> O <sub>3</sub> Found	Ni or Co in Al <sub>2</sub> O <sub>3</sub>	Error Al <sub>2</sub> O <sub>3</sub>
Gram			Gram	Gram	Mg.	Mg.
1.0 Ni	1	250	0.1903	0.1921	1.8	+1.8
1.0 Ni	1	250	0.1901	0.1919	1.8	+1.8
1.0 Ni	1	500	0.1905	0.1922	1.3	+1.7
1.0 Ni	1	500	0.1901	0.1918	1.2	+1.7
1.0 Ni <sup>a</sup>	1	500	0.1897	0.1913	1.0	+1.6
1.0 Ni <sup>a</sup>	1	500	0.1893	0.1910	1.0	+1.7
1.0 Ni	1	500	0.0049	0.0050	Trace	+0.1
1.0 Ni	1	500	0.0056	0.0057	Trace	+0.1
0.5 Ni	1	250	0.1919	0.1935	1.3	+1.6
0.5 Ni	1	250	0.1905	0.1923	1.6	+1.8
0.1 Ni	1	250	0.1901	0.1904	0.3	+0.3
0.1 Ni	1	250	0.1901	0.1903	0.3	+0.2
1.0 Ni	2	250	0.1903	0.1903	0.2	±0.0
1.0 Ni	2	250	0.1901	0.1903	0.3	+0.2
1.0 Ni	2	500	0.1895	0.1893	0.1	-0.2
1.0 Ni	2	500	0.1901	0.1902	0.2	+0.1
1.0 Co	1	250	0.1894	0.1919	1.9	+2.5
1.0 Co	1	250	0.1897	0.1924	2.0	+2.7
1.0 Co	1	500	0.1913	0.1932	1.2	+1.9
1.0 Co	1	500	0.1906	0.1925	1.2	+1.9
1.0 Co <sup>a</sup>	1	500	0.1906	0.1921	1.2	+1.5
1.0 Co <sup>a</sup>	1	500	0.1899	0.1914	1.2	+1.5
1.0 Co	1	250	0.0058	0.0058	Trace	±0.0
1.0 Co	1	250	0.0040	0.0043	Trace	+0.3
0.5 Co	1	250	0.0964	0.0977	0.8	+1.3
0.5 Co	1	250	0.0954	0.0963	0.6	+0.9
0.1 Co	1	250	0.0954	0.0954	0.2	±0.0
0.1 Co	1	250	0.0968	0.0971	0.3	+0.3
1.0 Co	2	250	0.1895	0.1896	0.1	+0.1
1.0 Co	2	250	0.1902	0.1904	0.1	+0.2
1.0 Co	2	250	0.1899	0.1903	0.1	+0.4
1.0 Co	2	250	0.1904	0.1902	0.1	-0.2

<sup>a</sup> Modified procedure.

single precipitation from 250 ml. will satisfactorily separate approximately 0.1 gram of aluminum from 1 gram of the above elements.

**DETERMINATION OF ALUMINUM IN THE PRESENCE OF NICKEL AND COBALT.** Table VII shows the results obtained when this method is applied to the separation of aluminum from nickel and cobalt.

It is evident that one precipitation will effectively separate 0.1 gram of aluminum from an equal amount of cobalt or nickel or a few milligrams of aluminum from as much as 1 gram. A double precipitation gives a very satisfactory separation of 0.1 gram of aluminum from as much as 1 gram of these metals. This is a much better separation than that obtained by the use of ammonia, which, after one precipitation, leaves 0.6 mg. of nickel and 4.1 mg. of cobalt out of 50 mg. with the aluminum when one precipitation is made, and 1.2 mg. of cobalt after two precipitations (9).

**DETERMINATION OF ALUMINUM IN THE PRESENCE OF COPPER.** When this general procedure is applied to the deter-

mination of aluminum in the presence of copper, the separation is incomplete, owing to the relatively low solubility of cupric succinate. If, however, the copper is kept in the cuprous state, by the presence of a suitable reducing agent during the precipitation, the separation becomes entirely satisfactory, as the results given in Table VIII show.

When a reducing agent was used, 4 grams of hydroxylamine hydrochloride or 10 ml. of freshly prepared 2*N* ammonium bisulfite and 10 grams of ammonium chloride were added to the aluminum chloride solution. It was diluted to about 150 ml. and heated to boiling to reduce the copper to the cuprous state. When the solution had become colorless, 5 grams of succinic acid and 4 grams of urea were added, and the volume was brought to about 250 ml. Dilute ammonium hydroxide was added dropwise to the hot solution to incipient turbidity, and gentle boiling continued for 2 hours. The precipitate was filtered off while hot and washed with a hot solution containing per liter 10 grams of succinic acid and either 10 grams of hydroxylamine hydrochloride or 40 ml. of 2*N* ammonium bisulfite, the wash solution having been made neutral to methyl red with ammonium hydroxide. The determination was completed as described above.

The main points to be noted are that the copper must be completely reduced to the cuprous state, and the filtration and washing must be done hot.

These data show that aluminum can be very satisfactorily separated from large amounts of copper by a single precipitation, by heating with urea in the presence of succinate, ammonium chloride, and a suitable reducing agent. A double precipitation with ammonium hydroxide will usually leave as much as 8 mg. of copper out of 50 mg. with the aluminum, when precipitating 0.1 gram of the latter (9).

TABLE VIII. DETERMINATION OF ALUMINUM IN THE PRESENCE OF COPPER

No.	Cu Added	Reducing Agent	Al <sub>2</sub> O <sub>3</sub> Taken	Al <sub>2</sub> O <sub>3</sub> Found	Cu in Al <sub>2</sub> O <sub>3</sub>	Error Al <sub>2</sub> O <sub>3</sub>
	Gram		Gram	Gram	Mg.	Mg.
1	0.1	None	0.0947	0.0972	...	+2.5
2	0.1	None	0.0953	0.0976	...	+2.3
3	0.01	None	0.0945	0.0956	...	+1.1
4	0.01	None	0.0953	0.0960	...	+0.7
5	1.0	NH <sub>2</sub> OH·HCl	0.1897	0.1901	0.1	+0.4
6	1.0	NH <sub>2</sub> OH·HCl	0.1903	0.1901	0.1	-0.2
7	1.0	NH <sub>2</sub> OH·HCl	0.0951	0.0952	None	+0.1
8	1.0	NH <sub>2</sub> OH·HCl	0.0949	0.0952	None	+0.3
9	1.0	NH <sub>2</sub> OH·HCl	0.0953	0.0953	None	±0.0
10	1.0	NH <sub>2</sub> OH·HCl	0.0951	0.0950	None	-0.1
11	1.0	NH <sub>2</sub> HSO <sub>3</sub>	0.1891	0.1888	0.05	-0.3
12	1.0	NH <sub>2</sub> HSO <sub>3</sub>	0.1891	0.1891	0.05	±0.0

#### DETERMINATION OF ALUMINUM IN THE PRESENCE OF ZINC.

The general procedure applied to the determination of aluminum in the presence of zinc gave the results shown in Table IX, which indicate that, even with as little as 10 mg. of zinc present, an appreciable amount is to be found with the aluminum after a single precipitation. Only 0.1 to 0.2 mg., however, is found to be present after two precipitations, when as much as 1 gram was originally present. The superiority of this method over the use of ammonium hydroxide is obvious from the fact that in the latter case as much as 10 mg. out of 50 mg. of the zinc may accompany the aluminum after two precipitations (9).

Since zinc metal is readily volatilized at elevated temperatures, it should be possible to remove the small amount which accompanies the aluminum by ignition in a current of hydrogen or with carbon.

A single precipitation was made in the usual manner from 500 ml. of solution containing 1.0 gram of zinc and approximately 0.1 gram of aluminum. When the ignition was to be made in the presence of carbon, some paper pulp was added before filtration. The precipitate was ignited in a covered unglazed porcelain crucible over a Meker blast, occasionally lifting the cover to allow the zinc to escape. After ignition for an hour in this manner, the cover was removed, the remainder of the carbon burned off, and the ignition completed in an electrically heated muffle for 1 hour at 1200° C. In determinations 3 to 6 (Table X), this oxide, after weighing, was ignited for 1 hour at 1000° to 1100° C.



TABLE IX. DETERMINATION OF ALUMINUM IN THE PRESENCE OF ZINC

Zn Added Gram	Number of Precipitations	Volume Ml.	Al <sub>2</sub> O <sub>3</sub> Taken Gram	Al <sub>2</sub> O <sub>3</sub> Found Gram	Zn in Al <sub>2</sub> O <sub>3</sub> Mg.	Error Al <sub>2</sub> O <sub>3</sub> Mg.
1.0	1	500	0.1909	0.1929	1.0	+2.0
1.0	1	500	0.1906	0.1928	1.0	+2.2
1.0 <sup>a</sup>	1	500	0.1903	0.1917	1.2	+1.4
1.0 <sup>a</sup>	1	500	0.1908	0.1920	1.2	+1.4
0.5	1	500	0.1901	0.1915	b	+1.4
0.5	1	500	0.1909	0.1923	b	+1.4
0.1	1	500	0.1903	0.1911	0.3	+0.8
0.1	1	500	0.1906	0.1914	0.3	+0.8
0.01	1	500	0.1901	0.1904	0.3	+0.3
0.01	1	500	0.1914	0.1918	0.3	+0.4
1.0	2	250	0.0953	0.0957	0.2	+0.4
1.0	2	250	0.0951	0.0952	0.2	+0.1
1.0	2	250	0.0955	0.0956	0.2	+0.1
1.0	2	250	0.0953	0.0955	0.2	+0.2

<sup>a</sup> Modified procedure.<sup>b</sup> Not determined.

TABLE X. SEPARATION OF ALUMINUM FROM ZINC PRECIPITATE IGNITED WITH CARBON AND/OR IN A CURRENT OF HYDROGEN

(1 gram of zinc present. Single precipitation, volume 500 ml.)

No.	Al <sub>2</sub> O <sub>3</sub> Taken Gram	Al <sub>2</sub> O <sub>3</sub> Found after Igniting with Carbon Gram	Error Al <sub>2</sub> O <sub>3</sub> Mg.	Al <sub>2</sub> O <sub>3</sub> Found after Igniting in Hydrogen Gram	Zn in Al <sub>2</sub> O <sub>3</sub> Mg.	Error Al <sub>2</sub> O <sub>3</sub> Mg.
1	0.1892	0.1896	+0.4	....	...	...
2	0.1892	0.1894	+0.2	....	...	...
3	0.1905	0.1912	+0.7	0.1905	...	±0.0
4	0.1894	0.1895	+0.1	0.1893	...	-0.1
5	0.1899	0.1911	+1.2	0.1900	...	+0.1
6	0.1903	0.1917	+1.4	0.1903	...	±0.0
7	0.1903	....	...	0.1905	None	+0.2
8	0.1906	....	...	0.1906	None	±0.0
9	0.1909	....	...	0.1907	None	-0.2
10 <sup>a</sup>	0.1890	....	...	0.1889	None	-0.1

<sup>a</sup> Single precipitation from 250 ml.

over a Meker blast, in a current of hydrogen introduced through a silica Rose crucible cover and inlet tube. This treatment was followed by 1 hour at 1200° C. in the electric muffle. Determinations 7 to 10 were precipitated as described, but filtered without adding paper pulp. The filter paper was charred off and the oxide ignited in a stream of hydrogen, followed by 1 hour at 1200° C., as above.

The results, tabulated in Table X, show that the zinc carried down by the aluminum can be completely volatilized by heating the precipitate for 1 hour in a covered crucible in a current of hydrogen. This makes it possible to determine aluminum in the presence of large amounts of zinc by a single precipitation, following the given procedure.

The failure to remove the zinc by igniting with carbon may be due to the absence of any gas stream to sweep out the volatilized metal.

**DETERMINATION OF ALUMINUM IN ZINC-BASE DIE-CASTING ALLOYS.** These alloys contained about 2.8 per cent of copper and 92.5 per cent of zinc with very small amounts of lead, cadmium, magnesium, and iron.

A 1-gram sample of the alloy was dissolved in sufficient hydrochloric acid to be equivalent to about 10 grams of ammonium chloride, adding a few crystals of potassium chlorate at the end to obtain complete solution. Most of the free acid was neutralized with ammonium hydroxide, 0.1 to 0.2 gram of hydroxylamine hydrochloride was added, and the solution heated (see "Determination of Aluminum in the Presence of Copper"). Dilute ammonium hydroxide was added until the precipitate redissolved with difficulty, then 4 grams of urea and 5 grams of succinic acid were introduced and the volume was brought to about 250 ml.

When the solution had gently boiled for 2 hours after becoming turbid, the liquid was decanted through a filter paper containing a small amount of paper pulp. The precipitate was washed by decantation a few times with a solution containing 1 per cent succinic acid and 0.01 per cent hydroxylamine hydrochloride, and made neutral to methyl red with ammonium hydroxide. It was then dissolved in hydrochloric acid; 10 grams of ammonium chloride, 4 grams of urea, and 5 grams of succinic acid were added, and it was reprecipitated in a volume of 250 ml. The solution was filtered through the original paper, and the precipitate adhering to the beaker removed as before described. The precipitates were ignited together in an unglazed porcelain crucible, first at a low temperature to char off the paper and finally for 1 to 1.5 hours at 1200° C. in an electrically heated muffle. The first ten determinations in Table XI were made in the above manner.

Determinations 11 to 14 were made by the modified procedure. The samples were prepared and the reagents added as before. The solution was diluted to about 500 ml., and heated to boiling and dilute ammonium hydroxide was added dropwise to incipient turbidity. After gentle boiling for 1 hour, the precipitate was filtered off and washed, and the last traces were removed from the beaker as usual. The filter paper was charred off in an unglazed porcelain crucible, and the oxide was ignited for 1 hour in a current of hydrogen, then 1 hour at 1200° C. in air.

For the purpose of comparison, determinations 15 and 16 were made by the method of Craighead (4), in which zinc, copper, etc., are removed by electrodeposition at a mercury cathode. Num-

bers 17 and 18 were made using a combination of the mercury cathode method, followed by a double precipitation by the present method.

These results show that small percentages of aluminum can be accurately determined in a commercial alloy containing a large per cent of zinc by either of the two methods given.

TABLE XI. DETERMINATION OF ALUMINUM IN A ZINC-BASE DIE-CASTING ALLOY

No.	Sample	Number of Precipitations	Volume Ml.	Sample Taken Grams	Al <sub>2</sub> O <sub>3</sub> Found Gram	Al Found %	Al Present %
1	A	2	250	1.001	0.0738	3.91	3.92 <sup>a</sup>
2	A	2	250	1.002	0.0739	3.90	3.92
3	A	2	250	1.002	0.0739	3.90	3.92
4	A	2	250	1.000	0.0739	3.91	3.92
5	B	2	250	1.001	0.0739	3.91	3.92
6	B	2	250	1.002	0.0737	3.89	3.92
7	B	2	250	1.002	0.0744	3.93	3.92
8	B	2	250	1.002	0.0742	3.92	3.92
9	C	2	250	1.002	0.0747	3.94	3.94 <sup>b</sup>
10	C	2	250	1.002	0.0742	3.92	3.94
11	A	1	500	1.004	0.0739	3.90	3.92 <sup>a</sup>
12	A	1	500	1.002	0.0738	3.90	3.92
13 <sup>c</sup>	A	1	500	1.001	0.0739	3.90	3.92
14 <sup>c</sup>	A	1	500	1.001	0.0741	3.92	3.92
15	A	...	...	2.001	0.1470	3.89	3.92
16	A	...	...	2.000	0.1490	3.95	3.92
17	A	...	...	2.001	0.1470	3.89	3.92
18	A	...	...	2.002	0.1473	3.89	3.92

<sup>a</sup> Bureau of Standards analysis. Not a standard sample.<sup>b</sup> 3.94% Al by Gooch-Havens method using a 10-gram sample.<sup>c</sup> No. 13 ignited with carbon gave 3.90% Al, while No. 14 gave 3.95% Al.

**DETERMINATION OF ALUMINUM IN THE PRESENCE OF IRON.** Since ferric iron begins to precipitate at a pH of approximately 2, it is obvious that for any separation of aluminum as a basic salt the iron must be in the ferrous state, under which conditions it commences to precipitate at a pH of 5.5 (3). With the present method of precipitation, the final pH of the solution is seldom above 4.5, which should allow an excellent separation of aluminum from ferrous iron. This would require the presence of a reducing agent which is stable enough to withstand the rather extended time of heating and yet strong enough to keep the iron completely reduced. The reducing agents sodium thiosulfate, ammonium bisulfite, sodium hydrosulfite, phenylhydrazine, hydroxylamine hydrochloride plus a little copper as catalyst (19), hydroquinone, *p*-aminophenol, *o*-aminophenol, and *p*-anisidine were examined for this purpose.

The procedure was similar to that employed in the determination of aluminum in the presence of copper. The amount of electrolytic iron shown in the tables was dissolved in hydrochloric acid and added to the aluminum chloride solution. After reducing the iron as completely as possible by adding fresh ammonium bisulfite to the hot solution, the ammonium chloride, urea, succinic acid, and reducing agent were introduced. The solution was diluted to 500 ml., heated to boiling, and neutralized to incipient turbidity with ammonium hydroxide, and the determina-



TABLE XII. EFFECTIVENESS OF REDUCING AGENTS ON THE SEPARATION OF ALUMINUM FROM IRON BY PRECIPITATION AS BASIC SUCCINATE

No.	Fe Taken Grams	No. of Ppts.	Reducing Agent <sup>a</sup>	Al <sub>2</sub> O <sub>3</sub> Taken Gram	Al <sub>2</sub> O <sub>3</sub> Found, Corrected for Fe <sub>2</sub> O <sub>3</sub> Gram	Fe <sub>2</sub> O <sub>3</sub> in Pptn. Mg.	Error Al <sub>2</sub> O <sub>3</sub> Mg.
1	1.0	1	5 grams Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	0.1910	0.1912	3.0	+0.2
2	1.0	2	5 grams Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	0.1904	0.1902	0.2	-0.2
3	1.0	2	5 grams Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	0.1918	0.1922	0.4	+0.4
4	1.0	2	5 grams Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	0.1918	0.1918	0.5	+0.0
5	1.0	2	5 grams Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	0.1897	0.1898	0.4	+0.1
6	1.0	1	5 grams Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	0.1893	0.1893	2.2	+0.0
7	1.0	1	0.5 ml. phenylhydrazine	0.1889	0.1920	1.3	+2.1
8	1.0	1	1.5 grams sodium hydrosulfite	0.1894	0.1941	1.8	+4.7
9	1.0	2	1.5 grams sodium hydrosulfite	0.1903	0.1897	..	-0.6
10	1.0	2	4 grams NH <sub>2</sub> OH·HCl, 25 mg. Cu	0.1913	0.1915	0.4	+0.2
11	1.0	2	3 grams NH <sub>2</sub> NH <sub>2</sub> ·2HCl, 25 mg. Cu	0.1903	0.1901	0.4	-0.2
12	1.0	2	3 grams NH <sub>2</sub> NH <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub>	0.1901	0.1907	0.5	+0.6
13	1.0	2	3 grams NH <sub>2</sub> NH <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub>	0.1903	0.1911	0.5	+0.8
14 <sup>b</sup>	0.05	1	2 grams NH <sub>2</sub> NH <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub>	0.1892	0.1890	0.5	-0.2
15 <sup>b</sup>	0.05	1	2 grams NH <sub>2</sub> NH <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub>	0.1892	0.1888	0.4	-0.4
16	1.0	2	3 grams NH <sub>2</sub> NH <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub>	0.1943	0.1944	0.8	+0.1
17	1.0	2	3 grams NH <sub>2</sub> NH <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub>	0.1898	0.1897	0.6	-0.1
18	1.0	1	3 grams NH <sub>2</sub> NH <sub>2</sub> ·H <sub>2</sub> SO <sub>4</sub>	0.1900	0.1896	1.9	-0.4
19	1.0	2	0.5 ml. phenylhydrazine	0.1895	0.1882	0.3	-1.3
20	1.0	2	3 grams <i>p</i> -aminophenol	0.1934	0.1915	0.3	-1.9
21	1.0	2	3 grams <i>p</i> -aminophenol	0.1908	0.1898	0.4	-0.9
22	1.0	2	3 grams <i>o</i> -aminophenol hydrochloride	0.1891	0.1888	0.4	-0.3
23	1.0	2	3 grams <i>o</i> -aminophenol hydrochloride	0.1910	0.1904	0.2	-0.6
24	1.0	2	3 grams <i>o</i> -aminophenol hydrochloride	0.1899	0.1852	0.2	-4.7
25	0.02	1	3 grams hydroquinone	0.1912	0.1913	0.5	+0.1
26	1.0	2	2 grams hydroquinone	0.1889	0.1890	0.2	+0.1
27	1.0	2	3 grams hydroquinone	0.1894	0.1893	0.3	-0.1
28	1.0	2	2 grams hydroquinone	0.1898	0.1901	0.4	+0.3
29	1.0	2	3 grams hydroquinone	0.1905	0.1903	0.25	-0.2
30	1.0	2	3 grams hydroquinone	0.1920	0.1923	0.3	+0.3
31	1.0	2	3 grams hydroquinone	0.1912	0.1914	0.3	+0.2
32	1.0	2	3 grams hydroquinone	0.1905	0.1907	0.3	+0.2
33	2.0	2	3 grams hydroquinone	0.0433	0.0433	0.35	+0.0

<sup>a</sup> Same reducing agent used in second precipitation.

<sup>b</sup> Precipitation and filtration made in an atmosphere of carbon dioxide.

tion was completed as usual, washing the precipitate with a solution of 1 per cent succinic acid and a little of the reducing agent, made neutral to methyl red with ammonium hydroxide. Whenever a double precipitation was made, the first precipitate was dissolved in hydrochloric acid and the process repeated. The iron accompanying the aluminum was determined colorimetrically with thiocyanate after fusion of the ignited oxide with potassium pyrosulfate.

TABLE XIII. DETERMINATION OF ALUMINUM IN THE PRESENCE OF IRON

(2 ml. of phenylhydrazine added as reducing agent in each precipitation)

Fe Taken Grams	No. of Ppts.	Al <sub>2</sub> O <sub>3</sub> Taken Gram	Al <sub>2</sub> O <sub>3</sub> Found, Corrected for Fe <sub>2</sub> O <sub>3</sub> Gram	Fe <sub>2</sub> O <sub>3</sub> in Pptn. Mg.	Error Al <sub>2</sub> O <sub>3</sub> Mg.
0.01	1	0.19325	0.19350	0.13	+0.25
0.02	1	0.19035	0.19030	0.13	-0.05
0.035	1	0.18980	0.18980	0.26	+0.00
0.05	1	0.18975	0.19020	0.30	+0.45
0.05	1	0.19125	0.19110	0.30	-0.15
0.135	1	0.18965	0.18955	0.60	-0.10
1.0	1	0.19060	0.19085	1.15	+0.25
1.0	2	0.19060	0.19050	0.09	-0.10
1.0	2	0.19835	0.19850	0.15	+0.15
2.0	2	0.03985	0.03970	0.07	-0.15
2.0	2	0.05735	0.05755	0.13	+0.20
2.0	2	0.02360	0.02355	0.10	-0.05

Several methods were attempted to remove the iron from the ignited oxide, but no particular success was attained. Ignition of the impure oxide for 1 hour in a current of hydrogen, followed by extraction with hot concentrated hydrochloric acid, failed to remove all the iron and at the same time dissolved from 0.1 to 0.2 mg. of aluminum. Repeated heating of the ignited oxide in an air bath with a mixture of ammonium chloride and ammonium bromide (17, 18) showed that the process was inefficient and of doubtful analytical value for the present purpose. Representative results of this preliminary work are given in Table XII, while Table XIII shows the results obtained using phenylhydrazine as reducing agent.

Tables XII and XIII show that phenylhydrazine is the best suited of any of the above-mentioned reducing agents for keeping the iron reduced, and preventing it from being precipitated with aluminum by urea from a solution contain-

ing succinate and ammonium chloride. This is probably due to its tendency to volatilize with steam, thus maintaining a reducing atmosphere above the liquid. In all cases where 1 gram of iron was present, a rust-colored rim of precipitate formed on the wall of the beaker at the surface of the liquid during the first precipitation. This was much less pronounced with phenylhydrazine than with any of the others. If the solution has a volume of approximately 500 ml., the presence of 2 ml. of phenylhydrazine will give a satisfactory separation of 0.1 gram of aluminum from 0.2 gram of iron in a single precipitation. If more iron is present, reprecipitation is necessary. A double precipitation will separate 0.1 gram of aluminum from 1 gram of iron, or 0.03 gram from 2 grams of iron.

Hydroquinone was not quite as effective, 0.2 to 0.4 mg. of ferric oxide usually remaining after two precipitations. Hydroxylamine appeared to keep the iron reduced while the solution was appreciably acid, but as the pH value became high enough for the complete precipitation of aluminum, the iron readily oxidized. This would seem to confirm the views of Solaja (19) that ferric iron is easily reduced by this reagent in acid solution, while in alkaline solution ferrous iron is readily oxidized by it.

Sodium thiosulfate, sodium hydrosulfite, and hydrazine sulfate and hydrochloride did not prove at all satisfactory, since they failed to keep the iron reduced or prevent its oxidation at the surface of the liquid. Both *o*- and *p*-aminophenol gave consistently low results for aluminum and at the same time were not particularly good for preventing the precipitation of iron. *p*-Anisidine and ammonium bisulfite proved to be so valueless that no final determinations were made with them.

The above procedure was applied to the determination of aluminum in Bureau of Standards iron ore No. 26, containing 1.01 per cent of Al<sub>2</sub>O<sub>3</sub>, 0.07 per cent of TiO<sub>2</sub>, and 0.09 per cent of P<sub>2</sub>O<sub>5</sub>. The ore was dissolved with hydrochloric acid, the silica was removed and volatilized in the usual way, and the residual oxides were added to the main solution. The iron was reduced, phenylhydrazine added, and the aluminum precipitated twice according to the above procedure. After weighing the aluminum oxide it was fused with potassium pyrosulfate, the iron and titanium were precipitated by cupferron, and the iron was determined colorimetrically. The phosphorus in the filtrate was determined. The weight of the precipitate was corrected for these impurities. The results are shown in Table XIV.

In Nos. 5 and 6 ammonium sulfate was added instead of succinate, in the hope of obtaining more complete precipitation of phosphorus and aluminum. It is obvious that the method tends to give results which are slightly low. It is possible that some phosphorus was lost in the fusion with pyrosulfate, but it is certain that in the succinate method not all is retained by the precipitate. This was also true when 0.1 gram of aluminum was added to the ore, the recovery in this case being about 60 per cent of the total, whereas by the sulfate method the precipitation of phosphorus was complete.

Attempts were made to precipitate aluminum as phosphate by the use of urea. Although the precipitate filtered exceptionally well, the results were erratic and always too high by 1 to 15 mg., regardless of whether sulfate, succinate, or neither



TABLE XIV. DETERMINATION OF ALUMINUM IN IRON ORE

No.	Wt. of Sample Grams	Al <sub>2</sub> O <sub>3</sub> Present %	Al <sub>2</sub> O <sub>3</sub> Found %	Error %	Phosphorus Present %	Phosphorus in Ppt. %
1	3.0370	1.01	0.73	0.28	0.09	0.037
2	4.8573	1.01	0.95	0.06	0.09	0.031
3	3.4992	1.01	0.98	0.03	0.09	0.028
4	3.6156	1.01	0.98	0.03	0.09	0.031
5	3.2485	1.01	0.95	0.06	0.09	0.087
6	2.8595	1.01	1.00	0.01	0.09	0.081

was present. It is probable that some of the aluminum, precipitated while the solution is still rather acid, forms an acid phosphate.

A preliminary study of the effect of various anions on the precipitation of other weak bases showed that while sulfate invariably caused the formation of a dense precipitate, there was no uniformity in the action of other anions.

The method has already yielded good results in the case of gallium. If titanium is present it is quantitatively precipitated with the aluminum. By a suitable modification of this method to be described in a later paper it has been found possible to separate titanium from aluminum. The quantitative precipitation of other bases is being investigated.

### Summary

It has been found that aluminum can be quantitatively precipitated at a pH of 6.5 to 7.5 by gently boiling for 1 or 2 hours after the appearance of turbidity, its solution containing 4 grams of urea, 10 or 20 grams of ammonium chloride, and 1 gram of ammonium sulfate. A single precipitation gives a very good separation of 0.1 gram of aluminum from 1 gram of calcium, magnesium, and manganese, while the separation from nickel, cobalt, zinc, and copper is much superior to that obtained by the use of ammonia.

The substitution of succinate for sulfate makes the precipitation of aluminum quantitative at a pH of 4.2 to 4.6, from a solution otherwise of similar composition. If the hot solution is first neutralized to incipient turbidity with dilute ammonia, the time required may be considerably shortened without much change in the character of the precipitate.

By this method a single precipitation will effectively separate 0.1 gram of aluminum from an equal amount of nickel or cobalt, or from 1 gram of calcium, barium, magnesium, manganese, and cadmium, or a few milligrams of aluminum from 1 gram of cobalt or nickel. If the final oxide is ignited in a current of hydrogen to volatilize zinc, one precipitation will also serve to separate 0.1 gram of aluminum from 1 gram of zinc. A double precipitation will give an excellent separation of the same quantity of aluminum from 1 gram of nickel, cobalt, or zinc.

The separation from copper in one precipitation is successful if a suitable reducing agent is present to keep the copper in the cuprous state. Iron must also be kept in the ferrous form and phenylhydrazine was found to be the best for this purpose. Two precipitations give a good separation of 0.1 gram of aluminum from 1 gram of iron or of 0.03 gram of aluminum from 2 grams of the latter, but any phosphate present is only partially precipitated. Aluminum can be accurately determined in a zinc-base die-casting alloy containing large amounts of zinc and some copper.

Aluminum phosphate precipitated by this method contains excess of phosphate. The success of this method depends on the slow increase in pH caused by the decomposition of the urea, resulting in a dense precipitate, a homogeneous solution, and a low final pH.

### Acknowledgment

The authors are greatly indebted to H. C. Fogg for a large part of the work on the separation of aluminum and iron.

### Literature Cited

- (1) Anderegg and Daubenspeck, *Proc. Indiana Acad. Sci.*, **35**, 141 (1925).
- (2) Blum, W., *J. Am. Chem. Soc.*, **38**, 1282 (1916).
- (3) Britton, H. T. S., *J. Chem. Soc.*, **127**, 2110 (1925).
- (4) Craighead, C. M., *IND. ENG. CHEM., Anal. Ed.*, **2**, 188 (1930).
- (5) Doebereiner, J., *J. prakt. Chem.*, **1**, 371 (1833).
- (6) Fresenius, "System of Instruction in Quantitative Analysis," p. 169, London, Churchill and Sons, 1865.
- (7) Funk, W., *Z. anal. Chem.*, **45**, 181 (1906).
- (8) *Ibid.*, **45**, 489 (1906).
- (9) Hillebrand, W. F., and Lundell, G. E. F., "Applied Inorganic Analysis," p. 391, New York, John Wiley & Sons, 1929.
- (10) Jander, G., and Weber, B., *Z. anorg. allgem. Chem.*, **131**, 266 (1923).
- (11) Kling, A., Lassieur, A., and Lassieur, Mme. A., *Compt. rend.*, **178**, 1551 (1924).
- (12) Lundell, G. E. F., and Knowles, H. B., *J. Am. Chem. Soc.*, **45**, 676 (1923).
- (13) Lunge, G., *Z. angew. Chem.*, **1889**, 635.
- (14) Miller, L. B., *U. S. Pub. Health Repts.*, **38**, 1995 (1923).
- (15) *Ibid.*, **40**, 351 (1923).
- (16) Mittasch, A., *Z. anal. Chem.*, **42**, 492 (1903).
- (17) Moser, L., *Monatsh.*, **53**, 39 (1929).
- (18) Moser, L., and Marian, S., *Ber.*, **59B**, 1335 (1926).
- (19) Solaja, B., *Z. anal. Chem.*, **80**, 334 (1930).
- (20) Willard, H. H., and Tang, N. K., *J. Am. Chem. Soc.*, **59**, 1190 (1937).
- (21) Winter, O. B., Thrun, W. E., and Bird, O. D., *Ibid.*, **51**, 2721 (1929).

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## Simple and Inexpensive Electric Heating Apparatus

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AN APPARATUS which is peculiarly adapted to the heating of volatile solvents for reflux or distillation consists of an ordinary flowerpot with an upper diameter of about 15 cm. and a base of about 9 cm. The hole in the bottom is enlarged (with a rat-tailed file) to accommodate a carbon-filament electric bulb. A set of rings from the ordinary copper water bath is placed on the pot. The whole apparatus is used in a ring stand or tripod support.

The device reduces the danger of solvent inflammability, is free from water vapors which may injure a sensitive reaction, and so illuminates the flask contents as to make observation easy. It successfully refluxes quantities of ether up to 400 to 500 cc.; with higher boiling solvents (benzene, ethyl alcohol) volumes of about 100 cc. can be distilled off, if a towel or asbestos paper is wrapped around the flask for insulation.

The heat output can be varied by substituting a low-wattage tungsten-filament bulb or a heating unit with standard lamp socket thread, such as is used in electric heaters of the reflector type.

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# Determination of Small Quantities of Oxygen in Gases and Liquids

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Oxygen in gaseous mixtures and dissolved in liquids can be accurately determined in small quantity by absorption on copper wetted with an ammoniacal solution of ammonium chloride, the resulting oxide being dissolved in the same solution, and the copper derived being estimated by titration of a blank to the same depth of blue color. The arrangement of apparatus described is capable of measuring oxygen with an accuracy of 3 per cent in amounts from 0.02 to 2 ml. No interference is caused by gases usually encountered, and determinations are made at a rate of four in an hour.

IN THE control of furnace atmospheres, in hydrogenation processes, and in catalytic syntheses, there has developed a need for a simple and rapid method of determining oxygen in gaseous mixtures in concentrations much lower than those that are accurately measured by analysis apparatus of the Orsat type. The method described here has been found capable of measuring oxygen with good accuracy at any concentration down to 20 parts per million, and permits of three or four determinations in an hour. The apparatus is simple and lends itself readily to series of many determinations as in control work. The method is offered also as an alternative to the manganous hydroxide method of determining oxygen dissolved in water, with the advantages of requiring less time and smaller samples, with no less accuracy.

## Principle of the Method

Hempel (3) described a reagent for the quantitative absorption of oxygen that consisted of an ammoniacal solution of ammonium carbonate in contact with metallic copper. Haehnel and Mugdan (2) preferred an ammoniacal solution of ammonium chloride on account of its lower ammonia vapor pressure. The absorptive powers of reduced copper solutions were investigated by Badger (1), who recommended a solution consisting of equal parts of concentrated ammonia and of water, the mixture saturated with ammonium chloride, and who remarked that oxygen was not completely removed unless some metallic copper were left uncovered by the solution. The procedure that has been developed in this laboratory is based on the use of copper for removing traces of oxygen from commercial nitrogen, made by Van Brunt (4), and avoids the difficulties inherent in exact measurements of volume as required by the usual methods of gas analysis.

Oxygen is absorbed on a surface of copper wetted with a solution of ammonium chloride and ammonia, the resulting oxide is washed off with the same solution, and the copper in the washings is determined by a colorimetric titration. The amount of oxygen is calculated by the use of a conversion factor which is independent of concentration.

## Apparatus

The principle of the method may be incorporated in different designs of apparatus suited to particular purposes. The

arrangement illustrated (Figure 1) and described here was used in the investigation of the possibilities of the method and for determinations of oxygen in the atmosphere of an industrial heat-treating furnace.

The analysis cell, 1, of about 25-ml. volume, is filled with short lengths of 22-gage copper wire supported by a constriction at 2. All-glass capillary (1-mm. bore) connections lead to the 250-ml. gas-sampling tube, 3, through the 3-way stopcock, 4, to the atmosphere through stopcocks 5 and 6, to the wash-solution reservoir, 7, through stopcock 8, and at position 9 through stopcock 10, and finally to a source of oxygen-free nitrogen at position 9. The wash-solution reservoir, 7, is filled with a solution made by mixing equal volumes of a saturated solution of ammonium chloride and concentrated aqua ammonia, and is provided with a water-sealed outlet. The gas-sampling tube, 3, may be filled with mercury through stopcock 11 by raising the leveling bulb. A second 3-way stopcock, 12, allows the sampling tube to be filled with the gas or liquid to be analyzed, or to be exhausted to the atmosphere. For the sake of convenience a by-pass has been inserted with stopcocks 13 and 14 by which mercury may be run into the sampling tube at any desired rate. This rate is controlled by adjustment of stopcock 14, which once set is left alone, and the mercury is turned off or on by stopcock 13. Stopcock 15 leads to a constricted jet at 16, by which means a small amount of mercury may be withdrawn and weighed when it is desired to draw into the sampling tube a known volume of air for calibration purposes.

Oxygen-free nitrogen is obtained by passing the commercial article through the copper turnings in the bulb, 17, which are kept wetted with ammoniacal ammonium chloride solution by the operation of the lift pump, 18, to which the flow of solution is regulated by the screw clamp, 19. During use, nitrogen is drawn from the cylinder at the rate of 3 to 4 liters per hour, and the flow is cut down almost to zero during other times.

## Method of Operation

When not in use the apparatus is left under a pressure of nitrogen, with the analysis cell and sampling tube empty of liquid, stopcock 10 open, all others closed, and 4 open between the cell and the sampling tube. Nitrogen then passes out through 9 and bubbles through the solution in 7, keeping it oxygen-free. In a small room a strong smell of ammonia may be avoided by acidifying the water in the outlet seal.

Before a series of determinations, the absence of oxygen in the system is tested by a blank determination with nitrogen in exactly the same way described below for the analysis of a gaseous sample. The nitrogen in 3 is expelled through 4 and 12 by opening 11 and raising the leveling bulb until the mercury reaches stopcock 12. The sample, containing less than 2 ml. of oxygen, is drawn in through 12 by lowering the mercury and 4 is opened to the cell. Stopcock 11 is closed and the mercury reservoir is raised to the height of stopcock 4 and converted to a Mariotte bottle by inserting a stopper in its neck with a glass tube reaching nearly to the bottom of the bulb. With 14 adjusted to pass mercury at a rate of 25 ml. per minute, 13 is opened, 5 is opened, and 10 is closed. The sample of gas then passes through the cell and is vented at 5.

When the sample has been driven past 4, that stopcock is closed and 10 is opened, and the cell is swept with nitrogen for 2 minutes. Stopcock 5 is then closed, 8 is opened, and 100 ml. of wash solution are drawn off through 6 into a 100-ml. Nessler tube. A second Nessler tube is nearly filled from 5 by closing 6 and opening first 5 and then 8, after which these are closed and the apparatus is ready for the introduction of the next sample. Care should be exercised that mercury is not carried over from the sampling tube to the analysis cell. Should this occur, the use of the cell need not be discontinued at once, as the copper is not immediately affected, but amalgamation will so lower the activity of the copper within a few days that the replacement of the copper turnings will be necessary.

If the sample contained oxygen, the contents of the first Nessler tube, taken from 6, will be colored blue in comparison with the liquid in the second, owing to copper derived from the



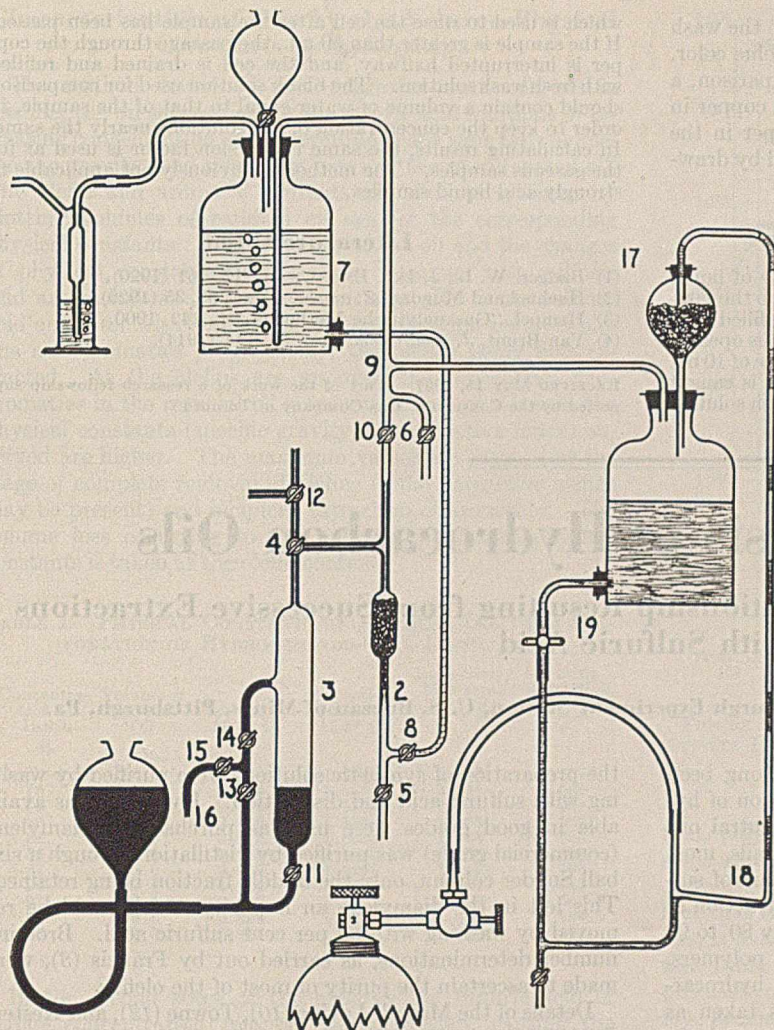


FIGURE 1. DIAGRAM OF APPARATUS

cell. The amount of this copper is proportional to the oxygen that was passed through the cell, and provides the means of measuring it. To the second Nessler tube, a standard solution of copper is added from a buret until the depth of blue color is the same in the two tubes, and the amount of oxygen in the sample is calculated from the volume of copper solution added. A blank determination on the oxygen-free nitrogen should yield a result of less than 0.002 per cent of oxygen.

### Estimation of Copper

A method based on the blue color of the cupric ion in ammoniacal solution was chosen as the most convenient method of analysis of the wash solution after the examination of several other methods, and yields results of sufficient accuracy with only a few simple precautions. The color does not develop completely until the solution is exposed to air and cuprous ions are oxidized; consequently the solution is thoroughly stirred before comparison is made. The concentration of ammonia and ammonium chloride must be nearly the same in the tubes being matched; otherwise there will be a difference in color which will make judgment of intensity difficult.

The tubes are viewed lengthwise from above, and illuminated nearly equally from below. An inclined mirror receiving light through a frosted-glass screen from a 60-watt light is used in this laboratory. Most people judge a color to be deeper on one side than the other, so that the tubes should be switched about, right to left, several times in making a com-

parison. Matching is easiest when the solutions contain about 2 mg. of copper. If this be exceeded, an aliquot should be taken and diluted with wash solution to the original volume. It is convenient to use a standard copper solution containing between 0.1 and 0.2 mg. of copper per ml. in a 25-ml. buret. Matching may easily be carried out to a precision of 0.2 ml. of such a solution, corresponding to 0.002 to 0.004 ml. of oxygen.

### Constancy of Copper-Oxygen Ratio

In developing the method the authors aimed at securing a ratio between the amount of copper determined in the wash solution and the amount of oxygen taken in the sample that would correspond to the formula  $\text{Cu}_2\text{O}$ ; that is, 11.36 mg. of copper per ml. of oxygen ( $0^\circ\text{C}$ ., 760 mm.). The ratio found was affected by the rate of passage of the gas sample over the copper, by the manner of washing the cell afterwards, and by the concentration of the wash solution. The procedure, described above, yielded a ratio of 10.45 mg. of copper per ml. of oxygen, which ratio was found to be independent of the concentration of oxygen in the sample for amounts of oxygen ranging from 0.02 to 2 ml. A calibration curve was therefore unnecessary, the ratio 10.45 being used as a straight conversion factor. The degree of precision with which this factor was reproduced in test determinations may be seen in Table I.

Tests 11 to 18 were carried out by an operator who had no previous experience with either the apparatus or the method.

### Interference from Other Gases

The method is very specific for oxygen, so that in nearly all cases no preliminary treatment of the raw sample is necessary. The reaction between copper and oxygen is quantitative in the presence of any concentrations of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, benzene, and their homologs. Sulfur dioxide interferes only in concentrations greater than 10 per cent of a 250-ml. sample. Small amounts of hydrogen sulfide and carbon bisulfide are admissible, but in

TABLE I. DETERMINATIONS OF COPPER-OXYGEN RATIO

(Total volume of each sample, 270 ml. Standard copper solution, 0.138 mg. per ml.)

Test No.	Oxygen Taken <sup>a</sup> Ml.	Copper Found Mg./ml.	Copper-Oxygen Ratio Mg./ml.	Oxygen Found $R = 10.45$
1	0.0598	0.629	10.52	0.0602
2	0.0733	0.758	10.34	0.0725
3	0.109	1.14	10.46	0.109
4	0.178	1.91	10.73	0.183
5	0.266	2.77	10.41	0.265
6	0.353	3.69	10.45	0.353
7	0.781	8.07	10.33	0.773
8	1.62	16.9	10.43	1.62
9	2.41	24.8	10.28	2.37
10	4.73	48.2	10.19	4.62
		Av. (1 to 8)	10.46	
11	0.145	1.48	10.21	0.142
12	0.235	2.51	10.67	0.240
13	0.325	3.42	10.52	0.328
14	0.531	5.50	10.36	0.526
15	0.626	6.52	10.41	0.624
16	0.694	7.28	10.49	0.697
17	1.22	12.7	10.44	1.22
18	1.41	14.8	10.46	1.41
		Av.	10.44	

<sup>a</sup>  $0^\circ\text{C}$ ., 760 mm.



large quantities these gases impart a yellow color to the wash solution which interferes with the matching of the blue color. This interference may be avoided by using, for comparison, a yellow blank obtained by passing the gas over the copper in the cell after the removal of oxygen. If the copper in the cell becomes blackened by sulfide, it may be cleaned by drawing into the cell a dilute solution of nitric acid.

### Determination of Dissolved Oxygen

For the determination of dissolved oxygen a sample of liquid containing about 0.1 ml. of oxygen is drawn directly into the sampling tube on top of the mercury. The analysis cell is filled with wash solution up to stopcock 10, which is then closed, 5 is opened, and the sample is passed through the flooded cell at a rate of 10 ml. per minute. The mixture of water and wash solution is caught in a Nessler tube at 5, and made up to 100 ml. with wash solution

which is used to rinse the cell after the sample has been passed. If the sample is greater than 50 ml., the passage through the copper is interrupted halfway, and the cell is drained and refilled with fresh wash solution. The blank solution used for comparison should contain a volume of water equal to that of the sample, in order to keep the concentration of the solutions nearly the same. In calculating results, the same conversion factor is used as for the gaseous samples. The method is obviously not applicable to strongly acid liquid samples.

### Literature Cited

- (1) Badger, W. L., *J. IND. ENG. CHEM.*, **12**, 161 (1920).
- (2) Haehnel and Mugdan, *Z. angew. Chem.*, **33**, 35 (1920).
- (3) Hempel, "Gasanalytische Methoden," p. 142, 1900.
- (4) Van Brunt, *J. Am. Chem. Soc.*, **36**, 144 (1914).

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# Graphic Analysis of Hydrocarbon Oils

## Volume-Physical Constants Relationship Resulting from Successive Extractions with Sulfuric Acid

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SULFURIC acid of various concentrations has long been used as a reagent in determining the composition of hydrocarbon oils, such as gasoline, kerosene, and neutral oils from coal-tar distillates. Although differing in details, most of these procedures (4, 9) employ two concentrations of sulfuric acid and follow the outline given below. Extraction of the oil with the acid of lower concentration (usually 80 to 92 per cent), followed by distillation to remove olefin polymers, is recommended for the estimation of unsaturated hydrocarbons. The distillate obtained in this manner is taken as olefin-free oil and used in the second stage of the analysis. Aromatic hydrocarbons usually are determined in the olefin-free oil by sulfuric acid of higher concentration (96 to 100 per cent and fuming acid are recommended), the oil not removed as water-soluble sulfonic acids being considered as saturated hydrocarbons. Although this procedure for analyzing hydrocarbon oils has been studied and used extensively, it is generally agreed that methods of this kind are not very satisfactory.

Since attempts to devise improved modifications of the analytical procedure described above have been disappointing, it appeared that a study directed to methods of another type might be profitable. The graphic method of characterizing hydrocarbon oils described in the present paper, developed during a recent investigation (2) of sulfuric acid extraction methods of determining olefins and aromatics, is a departure from the usual type of sulfuric acid method and has several interesting advantages. The new method is based on the changes in physical constants that accompany the stepwise removal of olefins and aromatics, as effected by successive extractions with several sulfuric acid solutions. As is shown below, a hydrogenated-coal distillate and two synthetic solutions were analyzed more accurately and characterized more completely by this method than by several methods of the older type.

### Materials and Procedure

In most cases the concentrated sulfuric acid solutions were analyzed by titration, the more dilute acid solutions by the specific gravity method. Some of the hydrocarbons used in

the preparation of synthetic solutions were purified by washing with sulfuric acid and distillation. Hydrocarbons available in good grades were used as purchased. Diamylene (commercial grade) was purified by distillation through a six-ball Snyder column, only the middle fraction being retained. This left in the diamylene an impurity which could be removed by washing with 80 per cent sulfuric acid. Bromine number determinations, as carried out by Francis (3), were made to ascertain the purity of most of the olefins.

Details of the Morrell-Levine (10), Towne (12), and Kester-Pohle (6) methods used to analyze the synthetic solutions of Table II may be obtained from the original articles. Procedures not previously reported are described in appropriate places in the text.

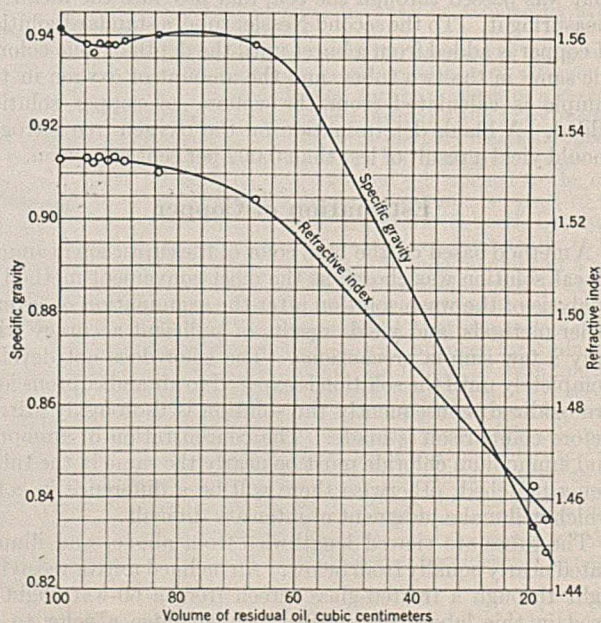


FIGURE 1. PHYSICAL CONSTANTS AND VOLUME OF RESIDUAL OIL (HYDROGENATED COAL DISTILLATE)



## Characterization of Oils by the Volume-Physical Constants Relationship

The method developed in the present work consists in washing the oil successively with sulfuric acid solutions of increasing concentration and determining each time the volume, specific gravity, and refractive index of the unsulfonated oil. The olefin and aromatic contents are then ascertained by plotting volumes of residual oil against the corresponding physical constants. The behavior of the oil and the changes in physical constants during these washings with sulfuric acid are as follows: Treatment initially with dilute sulfuric acid and later with acid of higher concentration removes olefins and aromatics progressively, the olefins being first extracted. As the olefins are removed the concentration of aromatics in the residual oil is increased and, as a result, the physical constants (specific gravity and refractive index) observed are higher. The maximum values are reached at the stage of complete removal of olefins (some unreactive olefins may be present) and incipient extraction of aromatics. The volume loss occurring to the point of maximum physical constants is taken as the olefin content.

TABLE I. PHYSICAL CONSTANTS OF RESIDUAL OIL FROM SULFONATION OF HYDROGENATED-COAL DISTILLATE

Concentration of H <sub>2</sub> SO <sub>4</sub> %	Volume of Residual Oil Cc.	Sp. Gr. at 15.5° C.	Refractive Index at 15.5° C.	Refractivity Intercept, $n - \frac{d}{2}$	Specific Refraction, $\frac{n-1}{d}$
(Original oil)	100	0.941	1.5335	1.063	0.567
75	95.5	0.938	1.5340	1.065	0.569
77	94.5	0.936	1.5325	1.065	0.569
80	93.5	0.938	1.5340	1.065	0.569
82	92.0	0.938	1.5330	1.064	0.569
84.5	91.0	0.938	1.5340	1.065	0.569
87	89.0	0.939	1.5333	1.064	0.568
90	83.5	0.940	1.5309	1.061	0.565
93	67.0	0.937	1.5248	1.056	0.560
96	19.0	0.834	1.4624	1.045	0.554
98	17.0	0.827	1.4555	1.042	0.551

In the second stage of the analysis the sulfuric acid of higher concentration removes the aromatics, causing the physical constants to fall until the removal of aromatics is complete, when the constants observed are those of the residual naphthenes and paraffins. Treatment with strong sulfuric acid beyond this point has not been studied extensively, but it is known that the volume of oil and physical constants are little changed by further treatment unless the reagent is fuming sulfuric acid. The aromatic content of the original oil is represented by the volume loss occurring between the point of maximum values for physical constants, observed at the beginning of the extraction of aromatics, and the point at which the physical constants become approximately constant because of the complete removal of aromatics. This procedure and its application to neutral oil analysis are clarified by an examination of the curves obtained in the present work (Figures 2, 3, and 4).

This method of examining hydrocarbon oils may overcome some of the difficulties attending the use of previous methods, such as the interaction of olefins and aromatics, extraction of aromatics before olefin removal is complete, etc. It has been shown (5) that dilute sulfuric acid dissolves olefins, moderately concentrated acid polymerizes olefins, and more concentrated acid causes olefins to condense with aromatic hydrocarbons. The concentrations of acid required to bring about these reactions vary according to the olefins present. It follows, therefore, that repeated washing with acid solutions of increasing concentration should give all olefins an opportunity to dissolve, since each olefin, regardless of its reactivity, is at some time in contact with acid of favorable concentration. In the older type of analysis the one concentration of acid used as olefin reagent simultaneously causes dissolu-

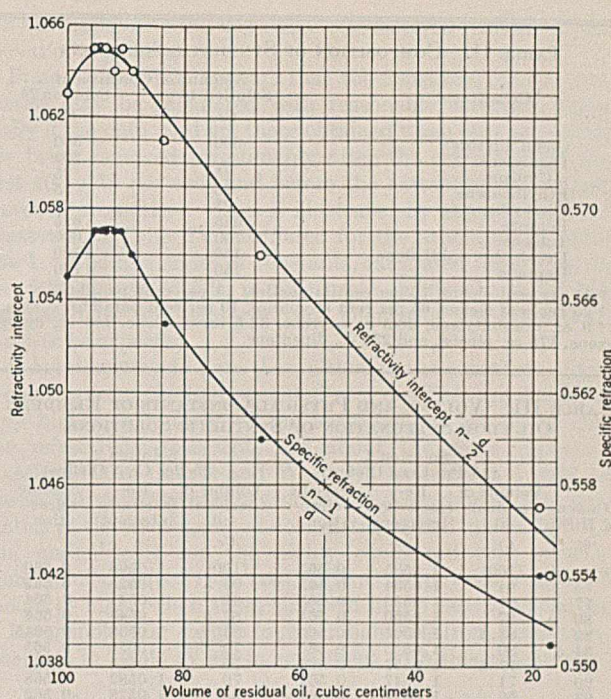


FIGURE 2. VOLUME, SPECIFIC REFRACTION, AND REFRACTIVITY INTERCEPT OF RESIDUAL OIL (HYDROGENATED COAL DISTILLATE)

tion, polymerization, condensation with aromatics and, for some unreactive olefins, no attack at all.

Another advantage of the graphic analysis method is the fact that the nature of the constituents, as well as the quantities, is indicated. An inspection of the curves or calculations (see Table IV) makes it possible to draw conclusions as to the physical constants, and hence the characteristics, of the olefins, aromatics, and saturated hydrocarbons in the oil. For example, the curves may be quite different in shape and position although the maximum and minimum physical constants occur at corresponding volumes of residual oils. This makes possible a further characterization of hydrocarbon oils of the same olefin and aromatic contents that would appear to be identical by the usual sulfuric acid analysis.

The volume losses and changes in physical constants caused by washing a neutral hydrogenated-coal distillate (initial volume, 100 cc.) successively with various sulfuric acid solutions are shown in Table I. The acid solutions ranged in concentration from 75 to 98 per cent by weight. The same procedure, agitation for 5 minutes in a separatory funnel with three volumes of acid, was employed in each washing. From the data obtained in the present work and in a previous investigation (11) (see Figure 4) it appears that about ten treatments with sulfuric acid afford data sufficient to characterize both coal-tar and petroleum oils. The relationship between the volume and physical constants of the unsulfonated oil is shown by Figure 1. The specific refractions (Gladstone-Dale) and refractivity intercepts, calculated by the formula of Kurtz and Ward (7), were also plotted against the volumes (Figure 2).

An inspection of Figures 1 and 2 shows that the refractive index, specific refraction, and refractivity intercept reached their highest values when the volume of the residual oil was about 93 to 94 cc. The olefin content thus indicated is 6 to 7 per cent, a value in good agreement with the analyses described in Table VI. As the washings with sulfuric acid were not continued beyond the extraction of aromatics (and the incipient removal of saturates), it was not demonstrated that



TABLE II. COMPOSITION OF SYNTHETIC SOLUTIONS

Constituent	Amount of Constituent	
	Solution 1 <sup>a</sup>	Solution 2 <sup>b</sup>
	Cc.	Cc.
Olefin mixture <sup>c</sup>	300	300
Diamylene	200	200
p-Cymene	25	25
Ethylbenzene	25	25
Diethylbenzene	25	25
Benzene	625	625
Toluene	700	600
Decahydronaphthalene	150	100
Heptane	150	100

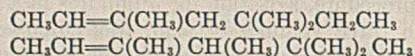
<sup>a</sup> 15 per cent olefins, 70 per cent aromatics, 15 per cent paraffins.  
<sup>b</sup> 25 per cent olefins, 65 per cent aromatics, 10 per cent paraffins.  
<sup>c</sup> 9 cc. diisobutylene, 26.5 cc. styrene, 33.5 cc. octylene, 156 cc. cyclohexene, 178 cc. pinene, and 238 cc. dipentene.

TABLE III. VOLUME AND PHYSICAL CONSTANTS OF RESIDUAL OIL FROM SULFONATION OF SYNTHETIC SOLUTIONS

Concn. of H <sub>2</sub> SO <sub>4</sub> %	Solution 1 (15 Per Cent Olefins)			Solution 2 (25 Per Cent Olefins)		
	Volume of residual oil Cc.	Refractivity intercept	Specific refraction	Volume of residual oil Cc.	Refractivity intercept	Specific refraction
(Orig. oil) (100)	100	1.0535	0.563	100	1.0508	0.560
75	94	1.0554	0.565	93.5	1.0525	0.562
77	91	1.0553	0.565	91	1.0541	0.564
80	87	1.0550	0.564	87.5	1.0548	0.564
82	83.5	1.0565	0.566	83	1.0538	0.5645
84.5	80	1.0555	0.565	79	1.0550	0.565
87	77.5	1.0557	0.565	75	1.0586	0.569
90	71	1.0547	0.564	70	1.0582	0.568
93	50	1.0527	0.562	53	1.0528	0.562
96	30	1.0534	0.5635	35.5	1.0518	0.561

the physical constants had attained constant values. However, the removal of aromatics, almost complete after the treatment with 96 per cent acid, must have been thorough after the final washing with 98 per cent acid (2). Therefore, the oil remaining consisted of saturated hydrocarbons, and its volume may be taken as the paraffin and naphthene content of the original oil. The value (17 per cent) thus obtained for the saturated hydrocarbons and the aromatic content calculated by difference (76.5 per cent) agree well with analyses made by another method (Table VI).

A better test of the accuracy of the graphic method was afforded by the analysis of two synthetic solutions of known composition. In order that the synthetic solutions might resemble the complex neutral oils obtained from coal, the aromatic contents were made high, and several different representatives of each hydrocarbon group were included. Relatively reactive olefins were employed in solution 1, while solution 2 (Table II) contained a considerable quantity of an unreactive olefin (diamylene) as well as unsaturated hydrocarbons more easily attacked by sulfuric acid. Diamylene recently has been demonstrated (1) to consist of the two olefins:



In spite of the high aromatic contents and the presence of an unreactive olefin in solution 2, very satisfactory results were obtained by the graphic method. Although the observed values for specific gravity (hydrometer) and refractive index were not corrected for temperature, these data (Table III) were sufficient to indicate the olefin contents (15 and 25 per cent) of the synthetic solutions with considerable accuracy. The relationships among volume of unsulfonated oil, refractivity intercept, and specific refraction (Gladstone-Dale) are shown in Figure 3. The sulfuric acid treatments were not continued long enough to remove all the aromatics; this is indicated by the physical constants of the oil remaining after the last washing.

It may be observed from the data in Table III that the volumes of oil removed from the synthetic solutions by any one concentration of acid are almost identical. If, as in most sul-

furic acid methods, the physical constants were not considered, it might be concluded that both solutions have similar olefin and aromatic contents (see also the analyses in Table V). Since the maximum values for physical constants occur at distinctly different points (75 and 85 cc. of unsulfonated oil), the olefin contents must be considerably different and the graphic method is therefore to be preferred to the older methods for these solutions.

Data obtained previously by Ormandy and Craven (11) with two gasolines may be plotted as previously (Figures 1 to 3) to ascertain the concentration of olefins and aromatics. These data are interesting because the oils studied, being derived from petroleum, are different in composition from the highly aromatic oils considered above.

The English investigators employed an extraction procedure very similar to that used with the hydrogenated-coal distillate (Table I) and synthetic solutions 1 and 2 (Table II). The oil (50 cc.) was shaken mechanically for 0.5 hour with 150 cc. of acid (79 to 100.5 per cent) and allowed to stand for 20 hours. The residual oil was separated from the acid layer and weighed. The fact that this procedure differs slightly from that used in the present work is unimportant, since such differences should have little or no effect on the volume-physical constants relationship.

Comparison of the curves (Figures 4 and 5) showing the relationships between the volumes and physical constants indicates that these petroleum oils are different from oils derived from coal. Consideration of the volumes corresponding to the maximum and minimum physical constants (especially the refractivity intercept which reaches a minimum when aromatics are completely removed) warrants the conclusion that the olefin and aromatic contents are 1.5 and 6.5 per cent and 5 and 14 per cent, respectively, for gasolines 1 and 2.

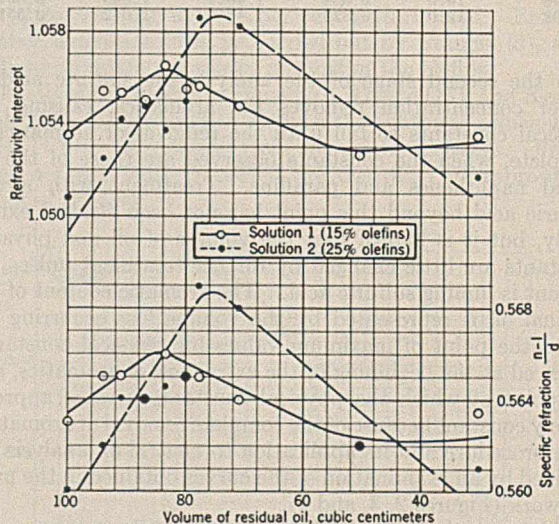


FIGURE 3. VOLUME, SPECIFIC REFRACTION, AND REFRACTIVITY INTERCEPT OF RESIDUAL OIL (SYNTHETIC SOLUTIONS)

The stage corresponding to complete olefin removal for gasoline 2 is not sharply defined by the volume-refractivity intercept curve (Figure 5). Hence the olefin content of gasoline 2 probably is shown better by the volume-density and volume-refractive index curves (Figure 4), which have sharp peaks in the region of maximum olefin removal. Conversely, the olefin content of the hydrogenated-coal distillate is best indicated by the volume-refractivity intercept and volume-specific refraction curves (Figure 2).

To obtain the data for gasoline 2 (Figures 4 and 5) Ormandy and Craven (11) used sulfuric acid of the following concentra-



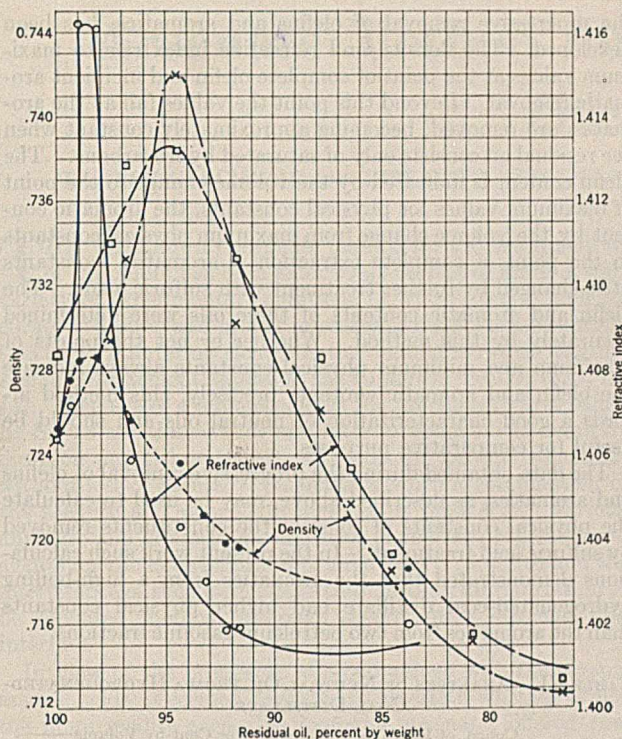


FIGURE 4. VOLUME AND PHYSICAL CONSTANTS OF RESIDUAL OIL FROM SULFONATION OF TWO GASOLINES (ORMANDY AND CRAVEN)

tions (per cent by weight): 79.1, 84.2, 89.5, 91.9, 94.5, 96.2, 97.7, 99.7, and 100.5. In a similar experiment the same gasoline was washed twice (instead of once as in previous cases) with each of the following sulfuric acid solutions (per cent by weight): 80.2, 84.9, 90.1, 91.9, 93.7, 95.8, 97.8, 99.6, and 100.2. Volume-physical constant curves drawn from the data thus obtained were found to be almost identical with the corresponding curves for gasoline 2 in Figures 4 and 5. This indicates that slight differences in procedure and acid concentration are unimportant.

The data obtained by extracting olefins and aromatics progressively in the manner described above may be used to calculate the physical constants of the constituents thus removed. The calculations are made on the experimentally supported (8) assumption that the physical constants are additive on a percentage basis.

TABLE IV. PHYSICAL CONSTANTS OF OLEFINS AND AROMATICS REMOVED WITH SULFURIC ACID

Oil Treated	Constituent Removed	Sulfuric Acid Treatment			Physical Constants of Oil Removed (Calculated)		
		Oil used %	Residual Oil %	Oil removed %	Sp. gr.	Refractive index	Refractivity intercept
Hydrogenated coal	Olefins	100	95.5	4.5	1.005	1.523	1.021
	Olefins	95.5	94.5	1.0	1.127	1.676	1.113
	Aromatics	67.0	19.0	48.0	0.9778	1.5495	1.0606
Gasoline 1	Olefins	100	99.0	1.0	0.500	0.4362	0.186
	Aromatics	98.1	92.2	5.9	0.8644	1.6395	1.2073
	Aromatics	96.6	92.2	4.4	0.8472	1.4896	1.0660
Gasoline 2	Olefins	100	96.9	3.1	0.461	1.27	1.04
	Aromatics	94.5	84.6	9.9	0.8684	1.4944	1.0602
	Aromatics	91.8	84.6	7.2	0.8677	1.4917	1.0579

The calculated constants for the olefins and aromatics removed with sulfuric acid from a neutral hydrogenated-coal distillate (graphic analysis in Figure 2) and two petroleum light oils (Figures 4 and 5) are given in Table IV. Some of the constants calculated for the olefins obviously are incorrect. This is due partly to the fact that the changes in volumes and constants were small and hence not as satisfactory

for calculations as the large changes observed during the removal of aromatics.

From Table IV it appears that the constants for the aromatics may be calculated with reasonable accuracy, especially if the data used are those obtained when only aromatics are being removed (presumably after the extraction of the first 10 to 15 per cent and before the extraction of the last traces of aromatics). This is illustrated by the two series of constants in Table IV calculated for the aromatics in gasoline 1. The first series of constants, calculated for a weight-per cent change of 5.9, is inaccurate, while the constants calculated for a weight-per cent change of 4.4 agree with those to be expected.

It is interesting to note that, although the constants of the aromatics from the hydrogenated-coal distillate are considerably higher than those of the lower-boiling petroleum oils, the refractivity intercepts are about the same (approximately 1.060). Kurtz and Ward (?) have given 1.0627 as the refractivity intercept of aromatic hydrocarbons. The aromatics in the hydrogenated-coal distillate boil up to 350° C. and undoubtedly are the highly condensed type usually found in oils derived from coal. Hence its physical constants should be higher than those observed in the case of aromatics of lower molecular weight found in light oils from petroleum. The data in Table IV are in agreement with this expectation.

#### Analyses with Other Sulfuric Acid Methods

The two synthetic mixtures described in Table II were analyzed by several sulfuric acid methods of the conventional type to compare these methods with each other and with the graphic method considered above.

TABLE V. ANALYSES OF SYNTHETIC SOLUTIONS

Method of Analysis	(Volume per cent)					
	Solution 1			Solution 2		
	Olefins 15%	Aromatics 70%	Paraffins 15%	Olefins 25%	Aromatics 65%	Paraffins 10%
Morrell and Levine	23.4	66.6	10	36.8	56.2	7.0
	24.3	65.2	10.5	38.0	56.5	7.5
Towne	30	55	15	30	59.5	10.5
	29	57	14	31	59	10
Kester and Pohle	16	69.3	14.7	18	68.8	13.2
	17	68.6	14.4	18	70.4	11.6

All the methods thus studied include distillation to remove olefin polymers but are unlike in several minor points. No one method was found to be completely satisfactory for both synthetic solutions. The Kester and Pohle method (6) was accurate only for solution 1, which contained reactive olefins. The other methods gave high values for olefins and low values for aromatics.

The high olefin values obtained by the Morrell and Levine method (olefins determined with 91 per cent acid and distillation) indicate that the distillation residue was too great for substitution in their empirical formulas (10). The large distillation residue probably was due to the formation of high-boiling alkylated aromatics. Petroleum distillates containing small amounts of aromatics might yield only negligible amounts of such condensation products when treated with 91 per cent acid, but the formation of considerable amounts of alkylated aromatics is to be expected in aromatic-rich synthetic solutions and coal-tar oils.

Towne (12) extracted olefins with 93 per cent acid which had been cooled previously to 1.67° C. (35° F.). Another sample of oil was then treated with 98 per cent acid and distilled to the original end point. From the data obtained the olefin and aromatic contents were calculated. The data in Table V indicate that aromatics were removed along with the olefins in the treatment with 93 per cent sulfuric acid. This is not astonishing in view of the high aromatic contents of the synthetic solutions and the tendency of 93 per cent acid to sulfonate aromatic hydrocarbons (2).



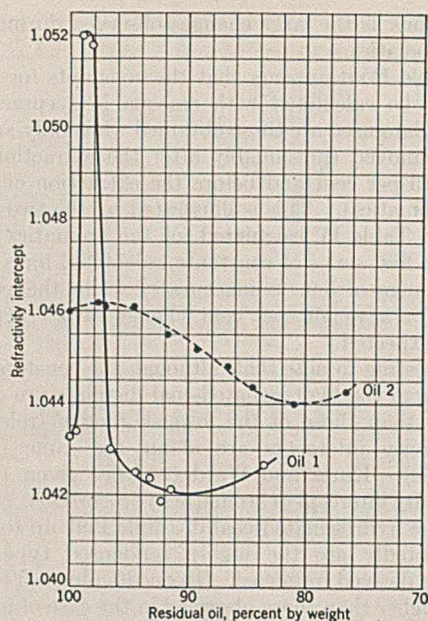


FIGURE 5. VOLUME AND REFRACTIVITY INTERCEPT OF RESIDUAL OIL FROM SULFONATION OF TWO GASOLINES (ORMANDY AND CRAVEN)

The results obtained with the Kester and Pohle method (6) indicate that their olefin reagent (80 per cent sulfuric acid) is satisfactory for neutral oils of the type obtained from coal if only small quantities of unreactive olefins are present. With solutions containing appreciable amounts of unreactive olefins, it is probable that low olefin and high aromatic values would result. Since there is no evidence for the presence of large quantities of unreactive olefins in coal-tar oils (known to have high aromatic contents), the Kester and Pohle analysis is to be preferred to the other methods of this type that employ concentrations of sulfuric acid much over 80 per cent as olefin reagents.

The hydrogenated-coal distillate characterized by the graphic method (Figure 2) was analyzed also by the Kester and Pohle procedure (6). Since there is some question as to the optimum concentration of acid for determining olefins by this type of method, several determinations, differing only in the concentration of olefin reagent, were made. The procedure used was as follows:

Fifty cubic centimeters of oil were shaken for 5 minutes with three volumes of the olefin reagent (80, 82, 84.5, or 87 per cent sulfuric acid). The oil not dissolved by this treatment was distilled to a temperature 5° above the original end point through a Vigreux column, all volume measurements being made in a cylinder graduated to 50 cc. in 0.5-cc. subdivisions. The olefin-free oil thus obtained was shaken for 5 minutes with three volumes (60 cc.) of 98 per cent sulfuric acid to extract the aromatics. In three of the olefin analyses (3, 4, and 5, Table VI) the oil was washed twice with two different sulfuric acid solutions before being distilled.

The data (Table VI) show that similar olefin values were obtained with all the olefin reagents except 87 per cent acid. Since 87 per cent acid may sulfonate appreciable quantities of aromatics (2), the olefin values obtained with this reagent probably are high. The other analytical data in Table VI agree very well with the analysis carried out by the graphic method (Figure 2).

### Summary and Conclusions

A graphic method of characterizing hydrocarbon oils, based on changes in volume and physical constants caused by

the progressive removal of olefins and aromatics, has been developed. The density and refractive index rise to maximum values at the point of complete olefin and incipient aromatic removal. Beyond this point the values fall as the aromatics are removed, becoming approximately constant when the residual oil consists only of saturated hydrocarbons. The olefin content is indicated by the volume change to the point of maximum values for physical constants, the aromatic content by the volume change from maximum physical constants to the point of complete extraction of aromatics (constants little changed by further treatment with sulfuric acid). The olefin and aromatic contents of three oils were determined accurately by this method. Whether or not the points of maximum and minimum physical constants always indicate the olefin and aromatic contents precisely, this method affords a good characterization of neutral oils and should be useful for comparative purposes.

The data obtained during the progressive removal of olefins and aromatics, as described above, may be used to calculate the physical constants of some of the constituents removed by sulfuric acid treatment. In the present work such calculations demonstrated that the aromatics from a high-boiling hydrogenated-coal distillate had higher physical constants than the aromatics from two petroleum gasoline fractions.

TABLE VI. ANALYSES OF NEUTRAL OIL FROM A HYDROGENATED-COAL DISTILLATE

No.	Concn. of H <sub>2</sub> SO <sub>4</sub> in Olefin Determination	Per Cent by Volume		
		Olefins	Aromatics	Paraffins
1	80	5.5	74.8	19.7
2	82	6	77	17
3	80 then 82	6	75	19
4	80 then 84.5	7	75	18
5	80 then 87	9	74.2	16.8
6	84.5	7	76.4	16.6
7	87	8	75.9	16.1

Using two synthetic solutions which had been analyzed accurately by the graphic method, several previously described sulfuric acid methods for determining olefins and aromatics were compared. Although no one method was completely satisfactory, the Kester and Pohle procedure (olefins determined with 80 per cent sulfuric acid) gave the most accurate results.

### Acknowledgment

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### Literature Cited

- (1) Drake, N. L., Kline, G. M., and Rose, W. G., *J. Am. Chem. Soc.*, **56**, 2076-9 (1934).
- (2) Fisher, C. H., and Eisner, Abner, "Sulfuric Acid Extraction Methods for Determining Olefins and Aromatics in Hydrocarbon Oils: Optimum Conditions and Concentrations of Acid," in press.
- (3) Francis, A. W., *IND. ENG. CHEM.*, **18**, 821-2 (1926).
- (4) Howes, D. A., *J. Inst. Petroleum Tech.*, **16**, 54-88 (1930).
- (5) Ipatieff, V. N., Carson, B. B., and Pines, H., *J. Am. Chem. Soc.*, **58**, 919-22 (1936).
- (6) Kester, E. B., and Pohle, W. D., *IND. ENG. CHEM., Anal. Ed.*, **3**, 294-7 (1931).
- (7) Kurtz, S. S., Jr., and Ward, A. L., *J. Franklin Inst.*, **222**, 563-92 (1936).
- (8) MacFarlane, W., and Wright, R., *J. Chem. Soc.*, **1933**, 114-18.
- (9) Morrell, J. C., and Egloff, G., *Nat. Petroleum News*, **28**, No. 12, 33 (1936).
- (10) Morrell, J. C., and Levine, I. M., *IND. ENG. CHEM., Anal. Ed.*, **4**, 321-2 (1932).
- (11) Ormandy, W. R., and Craven, E. C., *J. Inst. Petroleum Tech.*, **12**, 68-76 (1926).
- (12) Towne, C. C., *Ibid.*, **17**, 134-41 (1931).



# Arsenate Method for the Determination of Zirconium

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THE well-known phosphate method for the determination of zirconium has been extensively employed under a wide variety of experimental conditions (4, 7, 15), but if high accuracy is desired and proper provision is made for the elimination of all interfering elements, the method is rather lengthy. A similar statement applies to the cupferron method (2, 3, 11, 14). The use of selenious acid as the precipitant, first tested by Smith and James (13) and later investigated in detail by Simpson and Schumb (12), shortens the process somewhat without loss of accuracy, particularly when a combination of the selenite and phosphate methods is used (12). Various aliphatic and aromatic arsonic acids have been proposed as reagents for the determination of zirconium (1, 5, 6, 10) and the interference of such elements as titanium and thorium is said to be obviated thereby, although several other elements still interfere.

In view of the promising results obtained with the organic arsonic acids, it seemed desirable to ascertain whether or not the more readily accessible inorganic arsenates offered possibilities as reagents for the determination of zirconium. Paykull (9) observed in 1873 that zirconium was completely precipitated from hydrochloric acid solution by disodium arsenate, and ascertained that the composition of the precipitate corresponded to that of the normal arsenate,  $Zr_2(AsO_4)_4 \cdot 5H_2O$ . Moser and Lessnig (8) fifty years later applied this method of precipitation to the determination of zirconium in the presence of titanium, ceric cerium, and thorium. In this method, in order to convert the zirconium into the dioxide—a form suitable for weighing—the arsenic was eliminated from the arsenate precipitate by volatilization as the trichloride, hydrazine sulfate being employed as a reducing agent. Zirconium was precipitated from the residual solution by ammonium hydroxide, and finally weighed as  $ZrO_2$ .

**PLAN OF INVESTIGATION.** In the present work c. p. ammonium arsenate was chosen as the precipitating agent rather than the sodium salt because of the greater ease of elimination of adsorbed reagent from the precipitated zirconium arsenate. The objectives of the investigation were: to determine the most favorable conditions for the quantitative precipitation of zirconium by ammonium arsenate; to determine what elements are adsorbed by or co-precipitated with zirconium under these most favorable conditions; to devise methods of eliminating interference by such adsorbed or co-precipitated elements; to devise a suitable method of analysis for zirconium in complex materials using ammonium arsenate; and to apply the proposed method of analysis to a variety of natural or industrial materials containing zirconium.

## Experimental Work

**MATERIALS USED.** The zirconyl chloride employed was the purest obtainable grade of  $ZrOCl_2 \cdot 8H_2O$  and was found to be free from significant quantities of other elements (with the exception of the customary hafnium content). A solution of this substance was made up of such concentration that each 25 cc. furnished 0.1200 gram of  $ZrO_2$ . The solution was standardized both by the cupferron and selenious acid methods, which gave perfect agreement.

Solutions containing 1 gram and 10 grams, respectively, of c. p. ammonium arsenate per 100 ml. of solution were employed as precipitants.

**METHOD OF PRECIPITATION.** The zirconium contained in a 25-ml. portion of the zirconyl chloride solution, diluted to 360 ml., and 2.75 *N* in hydrochloric acid or 3.75 *N* in nitric acid, was quantitatively precipitated by dropwise addition of 50 ml. of the 1 per cent ammonium arsenate reagent at room temperature with stirring. The solution was then brought to boiling and 15 ml. of the 10 per cent reagent were added from a graduate, the boiling being continued for 20 minutes. The flocculent, highly hydrated precipitate corresponds to the normal arsenate containing adsorbed ammonium arsenate, and the above provisions were adopted after a series of experiments had shown that the extent of adsorption was reduced thereby to a minimum. After boiling for 20 minutes the solution may be filtered at once and may be ignited directly to  $ZrO_2$ , maintaining forced reducing conditions, as described below, to bring about complete volatilization of the arsenic.

**METHOD OF IGNITION AND ELIMINATION OF ARSENIC.** Of the various methods of removal of arsenic from the precipitated zirconium arsenate, direct ignition under oxidizing conditions was found to lead inevitably to slightly high results even when the full heat of an electric muffle furnace was applied for 6 hours, owing to the tendency shown by arsenic pentoxide to assume a vitreous, difficultly volatile form when strongly heated. Ignition in hydrogen led to more satisfactory results, but a simpler and adequate expedient proved to be the volatilization of the arsenic after reduction by means of the carbon resulting from the ashing of filter paper. A double paper was used during filtration of the precipitate to ensure the presence of sufficient carbon during ignition. Precipitate and paper were dried at 105° C. With the crucible supported in an upright position, the paper was ashed by the full flame of a Bunsen burner. To facilitate the removal of the last bits of carbon, the crucible was tilted. It was then returned to an upright position, covered with a porcelain cover, with the exception of a small slit, and the ignition was continued for 1 hour with the full heat of the Meker burner.

Strict adherence to this method was found to be essential for accuracy in the results.

## Effect of Acids and Quantity of Reagent upon Precipitation

The effect of hydrochloric, nitric, and sulfuric acids in varying concentration upon the completeness of precipitation of zirconium arsenate was investigated systematically.

In the case of hydrochloric acid the maximum concentration of acid at which precipitation of zirconium was complete was found to be 2.5 *N*, with nitric acid 3.75 *N*, while with sulfuric acid, precipitation is slightly incomplete even in less than 0.5 *N* acid solution. The precipitate from hydrochloric acid solutions is bulky and easily filtered if a sufficient excess of reagent is used, but finely divided if a smaller amount is employed. From 3.75 *N* nitric acid the precipitate is flocculent and easily filtered if handled at once, but tends to assume a colloidal nature on standing.

For the complete precipitation of the zirconium contained in 25 ml. of the zirconyl chloride solution 20 ml. of the 10 per cent arsenate reagent, or its equivalent, were found to be adequate. It was determined by trial that the period of boiling of the solution containing the precipitate should not be less than 20 minutes. Standing of the precipitate following the boiling was shown to have no effect upon the results.

## Other Metals Precipitated by Ammonium Arsenate

Results of a series of tests with solutions of over fifty cations and anions proved that while in nearly neutral solution many elements are precipitated by ammonium arsenate, from 2.5 *N*

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TABLE I. RESULTS OF ARSENATE METHOD APPLIED TO ZIRCONIUM SOLUTIONS

Milligrams of Element															ZrO <sub>2</sub>		Error Gram		
Fe <sup>+++</sup>	Co <sup>++</sup>	Ni <sup>++</sup>	Cr <sup>+++</sup>	Al <sup>+++</sup>	Mn <sup>++</sup>	Zn <sup>++</sup>	MoO <sub>4</sub> <sup>--</sup>	WO <sub>4</sub> <sup>--</sup>	Cu <sup>++</sup>	Sn <sup>+++</sup>	VO <sup>+++</sup>	Nd <sup>+++</sup>	UO <sub>2</sub> <sup>++</sup>	Ce <sup>+++</sup>	Ti <sup>+++</sup>	Th <sup>+++</sup>		Present Gram	Found Gram
50	50	50	50	..	..	..	50	..	..	..	50	..	..	..	..	..	0.1149	0.1152	+0.0003
50	50	50	50	..	50	..	..	..	..	..	..	..	..	..	..	..	0.1052	0.1048	-0.0004
50	50	50	50	..	50	..	..	..	..	..	..	..	..	..	..	..	0.1052	0.1049	-0.0003
50	50	50	50	50	50	50	50	..	50	50	..	..	..	..	..	..	0.1052	0.1050	-0.0002
50	50	50	50	50	50	50	50	..	50	50	..	..	..	..	..	..	0.1052	0.1051	-0.0001
50	50	50	50	50	50	50	50	..	50	50	50	50	50	..	..	..	0.1052	0.1054	+0.0002
50	50	50	50	50	50	50	50	..	50	50	50	50	50	..	..	..	0.1052	0.1054	+0.0002
20	..	..	..	20	..	..	..	..	..	..	..	..	..	..	..	..	0.1056	0.1059	+0.0003
20	..	..	20	20	..	..	20	..	..	..	..	..	..	..	..	..	0.1056	0.1058	+0.0002
20	20	20	20	20	..	..	..	..	..	20	..	..	..	..	..	..	0.1056	0.1055	-0.0001
50	..	..	..	..	..	..	..	..	..	50	..	..	..	..	..	..	0.1056	0.1057	+0.0001
50	..	50	..	..	..	..	..	..	..	..	..	..	..	..	..	..	0.1056	0.1053	-0.0003
..	..	..	..	..	..	..	..	..	..	..	50	..	..	..	..	..	0.1056	0.1058	+0.0002
10	..	20	20	20	20	..	..	..	55	20	..	..	..	..	..	..	0.1094	0.1090	-0.0004
10	20	20	20	20	20	..	..	..	55	20	..	..	..	..	..	..	0.1094	0.1094	+0.0000
10	20	20	20	20	20	..	..	..	55	20	..	..	..	..	..	..	0.1094	0.1093	-0.0001

hydrochloric or 3.75 *N* nitric acid solutions very few are brought down; zirconium and hafnium are precipitated practically at once, while titanium, tantalum, and columbium come out only on long standing. Thus zirconium and hafnium apparently have the least soluble arsenates of all the elements. In the presence of zirconium, however, ceric cerium, thorium, and tungsten are partially brought down by co-precipitation. Thus the interfering elements are hafnium, thorium, titanium, ceric cerium, tungsten, tantalum, and columbium. Hafnium accompanies zirconium, in general, to the extent of about 1 per cent and no attempt is made to separate it from zirconium in any of the usual procedures. The effect of ceric cerium, titanium, and thorium may be eliminated by double precipitation from either hydrochloric or nitric acid solution, but the interference of tungsten persists to a serious degree. If both titanium and thorium are present, titanium then interferes, and is best provided for by a colorimetric determination on the ignited zirconium dioxide residue. The use of hydrogen peroxide to prevent precipitation is not recommended, especially in nitric acid solutions, as even small amounts of hydrogen peroxide then cause incomplete precipitation of zirconium, due to formation of a soluble perzirconate.

The most serious difficulty is caused by the presence of tungsten. A complex, soluble in hydrochloric acid, is formed by zirconium in the presence of a tungstate, and none of the ordinary precipitants of tungsten is then effective. Evaporation to dryness of the acid solution fails to separate the tungstic acid unless sulfuric acid is present, in which case repeated evaporation with concentrated hydrochloric acid, followed by one evaporation with a mixture of hydrochloric and nitric acid and baking to 105° C., succeeded in eliminating about 95 per cent of the tungsten as yellow tungstic acid, but the remaining tungsten caused interference. The best provision for tungsten was found to be a preliminary fusion with sodium carbonate.

### Proposed Procedure for Determining Zirconium

Bring the sample, containing not more than 0.1 gram of zirconium, into solution as the chloride, and adjust the solution to a volume of 360 ml., 2.75 *N* in hydrochloric acid. Add 50 ml. of 1 per cent ammonium arsenate reagent slowly with stirring at room temperature. Bring the solution to boiling, add 15 ml. of 10 per cent ammonium arsenate reagent from a graduate, and boil for 20 minutes. After the precipitate has settled, filter at once, rinse the beaker several times with 1 *N* hydrochloric acid, and wash the precipitate with hot water. Pierce the tip of the paper, thoroughly flush the precipitate back into the same beaker with hot water, and evaporate on the water bath until a paste results (but do not take to dryness). Over the paper and upon this paste pour 82 ml. of hydrochloric acid (sp. gr. 1.19) and follow with 100 ml. of water, collected separately in a small beaker. Cover and boil gently for exactly 5 minutes to dissolve the precipitate, add the reserved wash water and dilute the solution to 360 ml. Let stand until cool and reprecipitate as described, except that 10 and not 15 ml. of reagent should be added after bringing the

solution to boiling. Filter this time through a double paper. Wash the precipitate first with 1 *N* hydrochloric acid, then hot water. Transfer the paper and precipitate to a tared porcelain crucible, dry at 110° C., ash and ignite in the special manner described above, cool in a desiccator, and weigh as ZrO<sub>2</sub>.

If titanium and thorium were present together in the original material, titanium may contaminate the ZrO<sub>2</sub> residue. In this case fuse the residue in platinum with a little potassium pyrosulfate, leach with hot water, and bring to a volume of 100 or 200 ml. Add 3 ml. of 3 per cent hydrogen peroxide and match the yellow color of a sample of the solution in a test tube with the color of a standard. (The standards consisted of solutions of titanium sulfate ranging in concentration from 1 to 0.1 mg. of TiO<sub>2</sub> per 100 ml. and colored by the presence of 3 ml. of 3 per cent hydrogen peroxide. They were preserved in tightly stoppered test tubes.) The titanium content of the ZrO<sub>2</sub> residue may thus be determined easily to within 0.1 mg. of TiO<sub>2</sub> and a correction applied.

If tungsten was present in the original material, the first precipitation is carried out with strong, fresh ammonium hydroxide instead of ammonium arsenate. Boil gently for 10 to 15 minutes, wash down any precipitate above the solution, and keep hot on the water bath for an hour. Filter and wash with hot water. Discard the filtrate. Dry the precipitate and paper in a platinum crucible, fuse with 10 grams of sodium carbonate, and leach the cooled melt in hot water. Filter with the aid of paper pulp, wash sparingly with hot water, transfer the precipitate and paper back to the crucible, dry, and ash. Add potassium pyrosulfate until the crucible is one-third full, cover, and heat with a gradually increasing flame until a quiet, clear melt is obtained at red heat. Leach the cooled melt in hot water, filter off any insoluble material, dilute the filtrate to 400 ml., and precipitate again with ammonium hydroxide. (If silica may be present, add 20 ml. of 18 *N* sulfuric acid and evaporate to fumes, dilute, and filter off any silica before making ammoniacal.) Filter and wash the precipitate; then flush it back into the same beaker with hot water. Wash down the paper with 82 ml. of hydrochloric acid (sp. gr. 1.19), following with 100 ml. of water. Bring the solution to a volume of 360 ml. and proceed with a double precipitation by ammonium arsenate as already described.

The effectiveness of the arsenate method for the determination of zirconium in the presence of various other ions may be clearly seen in Table I, in which the quantities of elements present in solutions containing zirconyl ion are expressed in

TABLE II. ANALYSIS OF ZIRCONIUM ORES  
(Weights in grams)

Sample No.	1 <sup>a</sup>	2	3	4	5
ZrO <sub>2</sub>	0.1003	0.1024	0.1055	0.1084	0.1010
Slate	0.30	0.30	0.20	0.20	0.15
Phosphate rock	0.10	0.10	0.10	0.050	0.050
Cb <sub>2</sub> O <sub>4</sub>	0.0500	..	..	..	0.0250
ThO <sub>2</sub>	..	0.0500	0.0500	..	0.0500
TiO <sub>2</sub>	0.0500	0.0500	..	0.0500	0.0500
CeO <sub>2</sub>	..	..	..	0.0500	0.0500
Fe <sub>2</sub> O <sub>3</sub>	0.0500	..	0.0500	..	..
Total weight of sample	0.6503	0.6024	0.5055	0.4584	0.4760
ZrO <sub>2</sub> found	0.0993	0.1040	0.1050	0.1076	0.1020
TiO <sub>2</sub> found	0.0001	0.0010	..	..	0.0005
ZrO <sub>2</sub> corrected	0.0992	0.1030	0.1050	0.1076	0.1015
Zr present, %	11.42	12.58	15.45	17.51	15.71
Zr found, %	11.29	12.66	15.38	17.38	15.79

<sup>a</sup> Fused twice with K<sub>2</sub>CO<sub>3</sub>.



milligrams of the element concerned. The last three columns indicate that the method compares well in accuracy (as it does in rapidity) with any of the other methods in customary use. The average error is  $\pm 0.0002$  gram.

### Analysis for Zirconium in Ores

The proposed method of analysis was applied to the determination of zirconium in mixtures of the dioxide with oxides of various other metals, together with slate and phosphate rock, so as to simulate the conditions in a complex ore. (Preliminary experiments upon steels of various compositions have indicated that the arsenate method is also applicable to the determination of zirconium in these materials, and that the customary preliminary extraction of iron with ether may be omitted without affecting the accuracy of the method.)

Of the various fusion processes which have been employed in the preliminary treatment of natural zirconium materials, the sodium carbonate fusion followed by potassium pyrosulfate was selected in this work. Tungsten and phosphorus are eliminated thereby; if potassium carbonate is used, tantalum and columbium as well. A second fusion may be required if large percentages of these elements are found present. Details of the fusion process are given in the recommended procedure.

Table II shows the results of typical analyses carried out on mixtures according to this method.

### Summary

Zirconium forms a difficultly soluble precipitate with ammonium arsenate. The precipitate is bulky, flocculent, and easily filtered if an excess of arsenate is used; its composition corresponds to that of the normal arsenate,  $Zr_3(AsO_4)_4$ , highly hydrated and containing some adsorbed ammonium arsenate. The precipitate may be ignited directly to  $ZrO_2$  by the use of forced reducing conditions in ashing and igniting; without this precaution arsenic is retained to a variable extent.

Precipitation is best made from boiling hydrochloric acid solution not exceeding 2.5 *N*, or from nitric acid not exceeding 3.75 *N*. Sulfuric acid even in small concentrations prevents complete precipitation. The precipitate is soluble in hot or cold concentrated hydrochloric or nitric acids, or in 6 *N* sulfuric acid. If dehydrated it becomes very slightly soluble even in hot, concentrated sulfuric acid. A second precipitation is best carried out in hydrochloric acid not more concentrated than 2.2 *N* (or 3.0 *N* nitric acid). Hydrogen peroxide in the presence of nitric acid leads to incomplete precipitation of zirconium, probably because of perzirconate formation. In hydrochloric acid solution this difficulty is not met.

Of elements other than zirconium (or hafnium), in 2.5 *N* hydrochloric acid (or 3.75 *N* nitric acid) only titanium, tantalum, and columbium precipitate, and titanium may be held in solution by hydrogen peroxide. In the presence of zirconium (hafnium) only ceric cerium, titanium, thorium, tungsten, tantalum, and columbium are co-precipitated by ammonium arsenate under the most favorable conditions in hydrochloric acid. In nitric acid slight adsorption effects are noted with many elements.

The interference of ceric cerium is eliminated by double precipitation; that of thorium is also entirely eliminated if the precipitations are carried out in the cold, with dropwise addition of 1 per cent arsenate reagent, followed by boiling to complete precipitation of zirconium. Titanium is best corrected for by a colorimetric estimation on the ignited  $ZrO_2$  residue.

Most of the reagents which normally give precipitates with alkali tungstates fail to do so when a moderate amount of zirconium is present, because of complex formation between the zirconium and tungstate. Although as much as 95 per

cent of the tungsten may be precipitated by evaporation with sulfuric acid and baking, tungsten is best eliminated by a preliminary sodium carbonate fusion. If potassium carbonate instead of sodium carbonate is used, tantalum and columbium are also eliminated in this way.

For the decomposition of zirconium ores in general, sodium carbonate fusion, followed by potassium pyrosulfate fusion is recommended. A proposed method of analysis for zirconium in solutions and ores is given, which is applicable with slight modification to steels.

### Literature Cited

- (1) Arnold and Chandlee, *J. Am. Chem. Soc.*, **57**, 8 (1935).
- (2) Baudisch and King, *J. IND. ENG. CHEM.*, **3**, 629 (1911).
- (3) Brown, *J. Am. Chem. Soc.*, **39**, 2358 (1917).
- (4) Ferguson, *Eng. Mining J.*, **106**, 356, 793 (1918).
- (5) Klinger and Schliessman, *Arch. Eisenhüttenw.*, **7**, 113 (1933).
- (6) Knapper, Craig, and Chandlee, *J. Am. Chem. Soc.*, **55**, 3945 (1933).
- (7) Lundell and Knowles, *Ibid.*, **41**, 1801 (1919); **42**, 1429 (1920).
- (8) Moser and Lessnig, *Monatsh.*, **45**, 323 (1924).
- (9) Paykull, *Oefvers. Sv. Akad. Förh.*, **621** (1873).
- (10) Rice, Fogg, and James, *J. Am. Chem. Soc.*, **48**, 895 (1926).
- (11) Schroeder, *Z. anorg. Chem.*, **72**, 88 (1911).
- (12) Simpson and Schumb, *J. Am. Chem. Soc.*, **53**, 921 (1931); *IND. ENG. CHEM., Anal. Ed.*, **5**, 40, 211 (1933); **7**, 36 (1935).
- (13) Smith and James, *J. Am. Chem. Soc.*, **42**, 1764 (1920).
- (14) Thornton and Hayden, *Am. J. Sci.*, **38**, 137 (1914).
- (15) Wunder and Jeanneret, *J. Soc. Chem. Ind.*, **30**, 1412 (1911).

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## Separation of Gold from Tellurium and Selenium

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THE use of hydroquinone and related aminophenols as precipitants of gold in the presence of base metals has been discussed by Beamish, Russell, and Seath (1). It was decided to determine whether hydroquinone could be used for the separation of gold from tellurium and from selenium, and whether the use of hydroquinone would interfere with the subsequent precipitation of selenium and tellurium. During the progress of the investigation it became evident that the sulfur dioxide method of selenium determination was unnecessarily slow and that there were certain errors incident to the sulfur dioxide tellurium analysis which could easily be avoided. The results recorded in this report were all obtained by means of a microbalance and the essential technique is that described by Beamish, Russell, and Seath (1).

### Solutions Used

A gold solution was made by dissolving 1.0012 grams of spectrographically pure gold in aqua regia, subsequently taking it down with hydrochloric acid in the presence of sodium chloride, and finally diluting it to 1 liter; 25.00-cc. samples of this solution on analysis by means of hydroquinone yielded 25.01 mg. of gold.

The tellurium solution was prepared by dissolving 1.0123 grams of tellurium metal in aqua regia, evaporating to dryness making three careful evaporations in the presence of hydrochloric acid, and diluting to 1 liter.

The selenium solution was made by dissolving about 1 gram of selenium in aqua regia, evaporating in the presence of hydrochloric acid, and diluting to 1 liter.



TABLE I. GOLD AND TELLURIUM DETERMINATIONS

Added		Extracted	
Gold Mg.	Tellurium Mg.	Gold Mg.	Tellurium Mg.
25.01	25.31	24.99	25.32
25.01	25.31	25.02	25.33
25.01	25.31	24.99	25.29
25.01	25.31	25.01	25.24
25.01	25.31	24.99	25.29
25.01	25.31	24.99	25.24

TABLE II. DETERMINATION OF GOLD IN PRESENCE OF SELENIUM

Added		Extracted	
Selenium Mg.	Gold Mg.	Selenium Mg.	Gold Mg.
16.96	25.01	16.05	24.98
16.96	25.01	16.47	24.99
16.96	25.01	...	24.99

### Determination of Tellurium

Exactly 25.00 cc. of tellurium solution were acidified to 4 *N* hydrochloric acid strength and the tellurium was precipitated by aqueous sulfur dioxide solution and hydrazine hydrochloride according to the procedure outlined by Hillebrand and Lundell (2). The mixture was filtered through a porcelain-bottomed filtering crucible, A2 grade, washed with water until free of chloride and then with alcohol, and dried for 45 minutes at 105° C. The calculated weight of tellurium in a 25.00-cc. sample was 25.31 mg. The weights obtained in two analyses were 25.49 and 25.59 mg.

The above procedure was followed, except that the precipitated tellurium was dried over P<sub>2</sub>O<sub>5</sub> in a vacuum at room temperature for 2 days; sample 1 weighed 25.47 mg. and sample 2 weighed 25.71 mg. Sample 1 was then dried in an air oven at 105° for 0.5 hour and weighed 25.45 mg. Sample 2 was dried at 105° for 6 hours and weighed 25.71 mg.

When this procedure was followed, except that the tellurium precipitates were dried in an oven at 105° for 0.75 hour in an atmosphere of carbon dioxide delivered by a Rose inlet tube, fitted into the air oven, and in series with a flowmeter, the results obtained were 25.30 and 25.26 mg., respectively. A third 25.00-cc. portion of tellurium, treated in exactly the same manner, was found to weigh 25.32 mg. This was dried immediately afterwards in an air oven at 140° C. for 2 hours and its weight was then found to be 25.67 mg.

When 25.00-cc. portions of tellurium solution were treated with sulfur dioxide, and dried in a carbon dioxide atmosphere as described, but alcohol was not employed as a final washing, the results were 25.37 and 25.32 mg.

It has generally been accepted that the standard sulfur dioxide-tellurium procedure yields results which are slightly high and the above experiments confirm this. It appears that drying with carbon dioxide is productive of accurate results and avoids the use of alcohol which in isolated laboratories is sometimes difficult to obtain.

### Separation of Gold and Tellurium

Two 50-ml. samples were prepared, each containing 84.60 mg. of gold and 30 mg. of tellurium. The gold was precipitated from the usual 1.2 *N* hydrochloric acid solution by 30 mg. of hydroquinone. The weights of gold obtained were 84.56 and 84.54 mg.

Samples of 25.00 cc. of tellurium solution were mixed with 25.00 cc. of the gold solution and the acidity was adjusted to 1.2 *N* with hydrochloric acid. The solution was brought to incipient boiling and 5 cc. of 0.5 per cent hydroquinone solution were added very slowly at first. Boiling was continued for 5 minutes to ensure coagulation and then the gold was filtered out by means of a 3-cc., A2 grade, porous-bottomed filtering crucible and washed with about 75 cc. of water. The filtrate was adjusted to 4 *N* with hydrochloric acid and the tellurium was precipitated by means of sulfur dioxide and hydrazine hydrochloride. In each case the precipitate was dried in a carbon dioxide atmosphere. The results obtained are given in Table I.

### Determination of Selenium

A 25-cc. portion of the selenium solution was adjusted to 9 *N* with hydrochloric acid and the selenium was precipitated by means of hydrochloric acid saturated with sulfur dioxide, ac-

ording to the procedure outlined by Hillebrand and Lundell (2). The metal was dried in an air oven for 3 hours at 30° to 40° C. and then for 2 hours at 140° C. The weight of precipitate was 16.90 mg. The procedure was repeated, except that the precipitate was not washed with alcohol and ether but transferred, after hydrochloric acid and water washing, to the air oven and dried in the carbon dioxide atmosphere for 45 minutes. The results were 16.93 and 16.95 mg. By this method the results obtained were as accurate as those from the standard procedure and the time of analysis was greatly shortened.

### Determination of Gold in Presence of Selenium

A 25.00-cc. portion of the gold solution was mixed with 25.00 cc. of the selenium solution and the gold precipitated as in the case of gold and tellurium. The filtrate was adjusted to an acidity of 9 *N* with hydrochloric acid and then treated as described above for selenium. The results obtained are recorded in Table II.

Two 25-cc. portions of selenium solution were adjusted to 1.2 *N* acidity by hydrochloric acid and treated with hydroquinone exactly as described for gold. The slight red precipitate was dried in carbon dioxide as outlined for selenium.

The results obtained were 0.66 and 0.48 mg. for samples 1 and 2, respectively. The selenium in the filtrates of these samples was precipitated with sulfur dioxide from 9 *N* solutions and the weights were: sample 1, 16.27 mg.; sample 2, 16.42 mg.; total weight of selenium, 16.93 and 16.90 mg., respectively.

While the use of hydroquinone does not interfere in the reduction to selenium by means of sulfur dioxide, it cannot be used when selenium and gold are to be determined from a single sample. The small amount of selenium carried with the gold apparently burns off when the gold is annealed.

### Determination of Gold, Tellurium, and Silver

The following is a résumé of the procedure used by the authors to determine silver, tellurium, and gold present together in the precipitate obtained by treatment of mill cyanide solutions with zinc. The filtrates from the silver, gold, and tellurium precipitations can be used for the complete determination of the associated base elements.

The dried gray precipitate is treated with nitric acid and is evaporated to complete dryness several times with hydrochloric acid to aid in coagulation of the silica which has a tendency to pass through the filter paper. The dried residue is again treated with aqua regia to redissolve gold which has baked out, then evaporated carefully, and finally moistened three times with hydrochloric acid in the presence of sodium chloride to remove the nitric acid. The solution is then diluted with about 40 cc. of water, boiled for 5 minutes, and cooled. The silver and silica are filtered off by means of a Whatman 7-cm. No. 42 filter paper and washed with water. The gold and tellurium are precipitated from the filtrate as described above. The silver chloride-silica residue and filter paper are treated with sulfuric acid and fuming nitric to dissolve the silver chloride, and the silica is filtered off. Then the silver sulfate solution is treated with hydrochloric acid, and silver determined as the chloride. Results obtained on approximately 150-mg. samples of one such precipitate will serve to illustrate the percentage difference usually obtained on duplicate determinations: gold, 36.12, 36.17; silver, 5.20, 5.23; tellurium 5.33, 5.32. This sample treated by fire assay yielded 36.17 per cent of gold.

### Summary

Hydroquinone precipitates gold quantitatively in the presence of tellurium and selenium.

Tellurium can be determined directly from the filtrate by means of sulfur dioxide and hydrazine hydrochloride after adjusting to the usual acid concentration. Tellurium and selenium precipitated by means of sulfur dioxide can be efficiently dried in an atmosphere of carbon dioxide.

### Literature Cited

- Beamish, F. E., Russell, J. J., and Seath, J., *IND. ENG. CHEM., Anal. Ed.*, 9, 174 (1937).
- Hillebrand and Lundell, "Applied Inorganic Analysis," pp. 258-67, New York, John Wiley & Sons, 1929.



# The Peroxide Method for Vanadium

## A Spectrophotometric Study

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A WELL-KNOWN colorimetric method for vanadium (4) is based upon the formation of a reddish brown color by a reaction between quivalent vanadium and hydrogen peroxide in acid solution. The color is supposedly due to peroxyvanadic acid,  $HVO_4$  (1). The method was first proposed by Slawik (3) and was extended by McCabe (2) among others (4).

The authors (5) outlined the advantages of the spectrophotometer for studying the general nature of colorimetric reactions and the significant factors affecting the color. The object of the present paper was to make such a study of the peroxide method for vanadium.

little peroxide is necessary for development of maximum color, while an excess causes a diminution in the color intensity. The optimum concentration appears to lie between 0.2 and 3 ml. of 3 per cent hydrogen peroxide solution, over which range practically no variation in color is observed.

### Effect of Diverse Ions

In addition to the ions listed in Table III, the following substances were found to have no effect at stated concentrations (total volume 100 ml.): 10 grams of  $NaNO_3$ ; 500 mg. of  $Bi^{+++}$ ,  $Zn^{++}$ ,  $Cd^{++}$ , As (as  $H_3AsO_4$ ),  $Th^{++++}$ ,  $Hg^{++}$ ,  $Ca^{++}$ ,  $Mg^{++}$ ,  $Sr^{++}$ ,  $Ba^{++}$ ,  $Pb^{++}$ ,  $Al^{+++}$ ,  $C_2H_2O_2^-$ ,  $C_4H_4O_6^-$ ,  $ClO_3^-$ ,  $P_2O_5$  [as  $(NH_4)_2HPO_4$ ]; 250 mg. of  $Li^+$ ,  $Be^{++}$ ,  $B_2O_3$  (as  $Na_2B_4O_7$ ); 100 mg. of  $Sb^{+++}$ ,  $Zr^{++++}$ ; 50 mg. of  $SiO_2$  (as  $Na_2SiO_3$ ); and 100 mg. of  $Ag^+$ .

The main type of interference is furnished by the elements molybdenum, titanium, and tungsten, which form colored solutions with the reagents. Titanium is the worst source of interference, 0.05 mg. being sufficient to cause a maximum deviation of about 2 per cent from the standard curve. Molybdenum and tungsten both interfere by the formation of a yellow color with the reagents, but are not so sensitive in this respect as titanium. In the case of molybdenum a yellow heteropoly complex compound between the vanadium and tungsten is the probable source of interference.

TABLE I. EFFECT OF ACID

No.	Acidity Ml./100 ml.	Transmittancy Differences	
		Unknown-Standard Max.	Average
1 <sup>a</sup>	None	+68	33
2	10, 6 N $H_2SO_4$	+ 2.5	1.2
3	25, 6 N $H_2SO_4$	0	0
4	50, 6 N $H_2SO_4$	- 0.5	0.1
5	85, 6 N $H_2SO_4$	+ 1.0	0.5
6	25, 36 N $H_2SO_4$	+ 5.0	2.2
7	10, 6 N $H_2SO_4$	+ 3.5	2.0
8	25, 6 N $H_2SO_4$	+ 1.0	0.3
9	50, 6 N $H_2SO_4$	0	0
10	25, 6 N $HNO_3$	+ 3.0	1.0
11	25, 6 N $HCl$	+ 3.0	1.0

<sup>a</sup> All solutions contain 2.0 mg. of vanadium per 100 ml.; solutions 1 to 5 contain 1 ml. and 6 to 11 contain 5 ml. of 3 per cent hydrogen peroxide; transmittancy differences cover the range 400 to 700  $\mu$ .

TABLE II. EFFECT OF PEROXIDE CONCENTRATION

No.	3 Per Cent Hydrogen Peroxide Ml.	Transmittancy Differences	
		Unknown-Standard Max.	Average
1 <sup>a</sup>	0.1	+3.0	1.5
2	0.2	0	0
3	0.5	0	0
4	3.0	0	0
5	10.0	+3.5	2.5

<sup>a</sup> All solutions contain 2.0 mg. of vanadium and 25 ml. of 6 N  $H_2SO_4$  per 100 ml. total in 4.983-cm. cells; transmittancy differences cover the range 400 to 700  $\mu$ .

Mallinckrodt U. S. P. 3 per cent hydrogen peroxide solution was used. A description of other reagents, apparatus, and experimental methods may be found in an earlier paper (5).

Typical spectrophotometric curves covering the most useful range of concentrations are shown in Figure 1 for a cell length of 5.00 cm.

### Effect of Acid Concentration

As shown in Table I, the maximum color intensity is not developed until the solution has an acid concentration of about 0.6 N. As the acid concentration is increased further up to 6 N, little change takes place, while at 9 N the color begins to fade. If a higher concentration of peroxide is employed, the solution must be at least 1.5 N in acid concentration for development of maximum color. The type of acid used appears to affect the hue somewhat, although not enough to be detected visually.

### Concentration of Peroxide

Table II shows the variation in color with change in peroxide concentration. These data show that comparatively

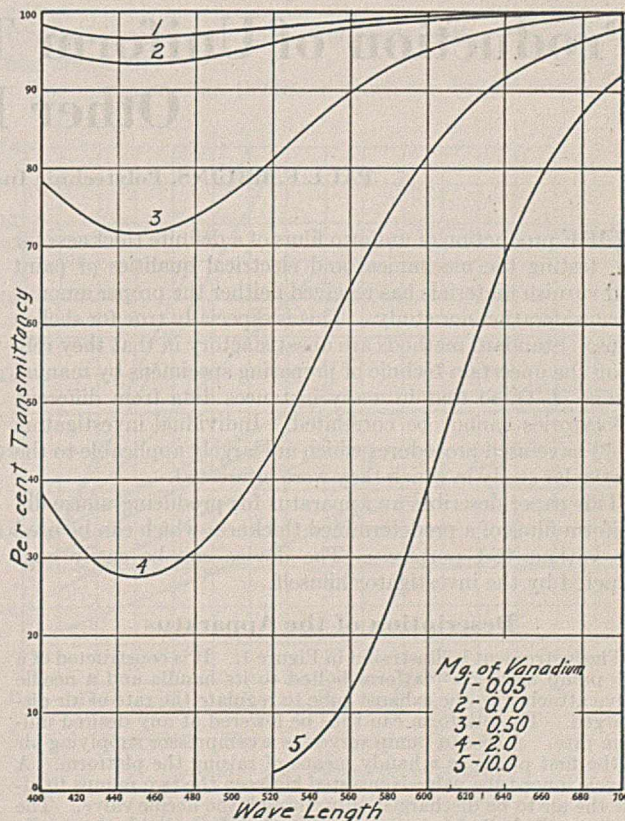


FIGURE 1. TYPICAL CURVES

<sup>1</sup> Present address, Dow Chemical Company, Midland, Mich.



TABLE III. EFFECT OF DIVERSE IONS

No.	Substance	Limiting Concn. per 100 ml.	Transmittancy Differences Unknown-Standard	
			Max.	Av.
1 <sup>a</sup>	Co(NO <sub>3</sub> ) <sub>2</sub>	10 mg. Co	- 2.0	1.5
2	Cu(NO <sub>3</sub> ) <sub>2</sub>	10 mg. Cu	-10.0	1.5
3	Fe(NO <sub>3</sub> ) <sub>3</sub>	10 grams Fe	-14.0	1.0
4	KCl	10 grams KCl	- 1.0	0.5
5	KCNS	10 mg. CNS	+ 1.5	2.0
6	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	1.0 mg. Cr	- 4.0	2.5
7	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	10 mg. C <sub>2</sub> O <sub>4</sub>	- 4.0	2.5
8	KI	2.0 mg. I	-10.0	5.0
9	NaBr	500 mg. Br	-12.0	1.0
10	Na <sub>2</sub> SO <sub>4</sub>	10 grams Na <sub>2</sub> SO <sub>4</sub>	- 4.5	1.0
11	Na <sub>2</sub> WO <sub>4</sub>	100 mg. W	-16.0	1.5
12	NH <sub>4</sub> Cl	10 grams NH <sub>4</sub> Cl	- 2.0	0.5
13	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	5 mg. Mo	-15.0	2.0
14	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	10 grams (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	+ 3.0	2.5
15	Ni(NO <sub>3</sub> ) <sub>2</sub>	20 mg. Ni	- 6.0	2.0
16	SnCl <sub>4</sub>	400 mg. Sn	- 2.0	1.5
17	TiOSO <sub>4</sub>	0.05 mg. Ti	- 2.0	1.0
18	UO <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	50 mg. U	- 5.5	1.0

<sup>a</sup> All solutions contain 2.0 mg. of vanadium, 25 ml. of 6 N H<sub>2</sub>SO<sub>4</sub>, and 1.0 ml. of 3 per cent hydrogen peroxide per 100 ml. total; cell length 4.983 cm.; transmittancy differences cover the range 400 to 700 m $\mu$ .

TABLE IV. STABILITY

No.	Age	Transmittancy Differences Unknown-Standard	
		Max.	Av.
1 <sup>a</sup>	15 min.	0	0
2	7 days	+ 0.5	0.1
3	15 min.	0	0
4	47 hours	0	0
5	4 days	+13.5	9.0

<sup>a</sup> All solutions contain 2.0 mg. of vanadium and 25 ml. of 6 N H<sub>2</sub>SO<sub>4</sub> per 100 ml.; solutions 1 and 2 contain 5 ml. and 3 to 5 contain 1 ml. of 3 per cent hydrogen peroxide; transmittancy differences cover the range 400 to 700 m $\mu$ .

### Stability

Table IV shows the stability of the peroxyvanadate solutions. The solutions have the compositions stated in Table

IV and were kept in glass-stoppered bottles when not in use. The conclusions which may be drawn from these data are that the solutions are stable for 2 days with small amounts of hydrogen peroxide and a week or more if a slight excess (5 ml. total) of hydrogen peroxide solution is added. The more acid solutions fade most rapidly.

### Summary

Typical transmittancy curves are given in Figure 1.

The solutions should have an acid concentration between 0.6 and 6 N in sulfuric, nitric, or hydrochloric acids.

The solutions should contain 0.5 to 3 ml. of 3 per cent hydrogen peroxide solution per 100 ml. An excess of hydrogen peroxide decreases the color, but consistent use of more hydrogen peroxide (up to 10 ml.) is permissible.

Titanium is the worst interfering element. Table III gives maximum allowable concentrations of diverse ions.

Under recommended conditions, the solutions are stable for at least 2 days. An excess of hydrogen peroxide promotes stability.

### Literature Cited

- (1) Latimer, W. M., and Hildebrand, J. H., "Reference Book of Inorganic Chemistry," p. 270, New York, Macmillan Co., 1933.
- (2) McCabe, C. R., *Chem. Eng.*, 13, 243-7 (1911); *J. IND. ENG. CHEM.*, 5, 736-7 (1913).
- (3) Slawik, P., *Chem.-Ztg.*, 34, 648 (1910).
- (4) Snell, F. D., and Snell, C. T., "Colorimetric Methods of Analysis," p. 367, New York, D. Van Nostrand Co., 1936.
- (5) Wright, E. R., with Mellon, M. G., *IND. ENG. CHEM., Anal. Ed.*, 9, 251 (1937).

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# Production of Uniform Test Films of Shellac and Other Finishes

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THE production of uniform films of a definite thickness for testing the mechanical and electrical qualities of paint and varnish materials has received neither the proper amount of consideration nor study. This is especially true for shellac films. Standard methods are unsatisfactory in that they rely upon the uncertain technic of preparing specimens by manual means (1-4), so that in many instances data from different laboratories cannot be correlated. Individual investigators (5-7) have used procedures which are largely applicable to the particular study in which they were interested.

This paper describes an apparatus for producing unusually uniform films of a predetermined thickness which can be used for various test purposes. The device can be easily constructed by the investigator himself.

### Description of the Apparatus

The instrument is illustrated in Figure 1. It is constructed of a tire pump having a platform bolted to its handle and a needle valve attached to the exhaust tube to regulate the rate of air discharged. The platform can thus be lowered at any desired uniform rate. A second pump serves as a compressor supplying air to the first pump as a handy means of raising the platform. A bicycle inner-tube valve is inserted between the two pumps to allow the air to be discharged only through the needle valve. The apparatus is bolted to a ring stand and a clamp holds the needle valve in such a position that its setting can be accurately adjusted

by means of an attached pointer placed in front of a suitable scale, as shown.

### Procedure for Forming Films

The device operates upon the principle that films of a uniform thickness are formed when they are withdrawn from the coating material at a uniform rate which is lower than that of the rate of drainage of the varnish or paint. Suitable films for test purposes are obtained when the following directions are followed:

Surfaces to be coated must be clean and uniform in character. The object is suspended by means of the clamp shown in Figure 1, above the container which is filled with the coating material. The varnish or paint should be well mixed, free from foreign particles and air bubbles, and at a standard temperature. The object is immersed by raising the platform, keeping the needle valve in a closed position, and is allowed to stand until the surface is thoroughly wet with the varnish and all air bubbles are freed from it. Withdrawal is effected by setting the needle valve at the proper position, depending upon the characteristics of the coating material which have been determined beforehand. After dipping, the piece can be removed and allowed to dry under controlled conditions in a vertical position.

The thickness of the films obtained with this device is in direct proportion to the rate at which an object is withdrawn from the varnish, until a point is reached where the rate of



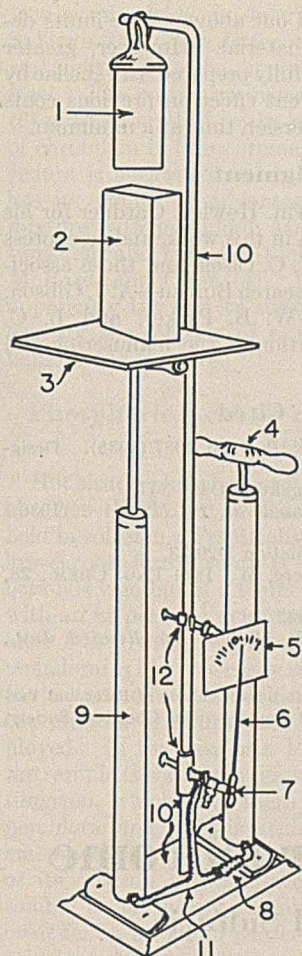


FIGURE 1. DIPPING DEVICE

1. Test plate
2. Varnish container
3. Platform
4. Air pump
5. Scale
6. Pointer
7. Needle valve
8. Check valve
9. Elevating pump
10. Ring stand
11. Rubber hose
12. Clamp

tion. All measurements of thickness should be made after the film is completely dry.

### Controlled Dipping Method

**PRECISION.** Measurements of film thickness in this investigation were made with a Brown and Sharpe micrometer having a deep throat, so that measurements could be made up to 3 inches from the edge of the film. Agreements on measurements by three observers were obtained with this instrument to within 0.0001 inch. Film thickness was determined by measuring the combined thickness of the dry film and its support and obtaining the film thickness by the difference between that measurement and the thickness of the supporting medium.

Measurements of film thickness along a diagonal line extending across the film showed a deviation from the average thickness for any film of  $\pm 0.0001$  inch. Typical measurements are shown in Table I. This uniformity of thickness was obtained over the entire film with the exception of the extreme bottom edge, which, being the last to emerge from the coating material, carried a bead of greater thickness. This bead can be trimmed off or disregarded in any subsequent tests.

dipping approaches that of the drainage of the varnish from the coated object. Above this value, the thickness of the films is less than what would be expected from a straight-line relationship. The amount of increase in film thickness which occurs with increase in rate of withdrawal and the maximum uniform thickness which can be obtained vary according to the coating material and to the character of the surface coated. This is illustrated in Figure 2.

Although the film-forming characteristics of one sample of a varnish cannot be taken as a precise indication of the results which will be obtained with another sample of the same body or cut, there is a definite relation between the viscosity of a product and the film thickness which can be obtained. It is possible to obtain films of a predetermined thickness by selecting the proper withdrawal rate, by preparing calibration curves such as those shown in Figure 3, for 3- and 5-pound shellac varnishes. The proper setting of the needle valve for varnishes of a viscosity intermediate between those used for the calibration can be readily estimated from the curves by interpolation.

TABLE I. FILM THICKNESS OF A CLEAR LACQUER ON BRASS

Withdrawal Rate Inches/min.	Position of Measurement	Thickness				
		Plate and 2 films Inch	Plate and 1 film Inch	Plate bare Inch	1st film Inch	2nd film Inch
1	1 (top)	0.0262	0.0259	0.0256	0.0003	0.0003
	2	0.0262	0.0259	0.0256	0.0003	0.0003
	3	0.0260	0.0257	0.0254	0.0003	0.0003
	4	0.0258	0.0256	0.0253	0.0002	0.0003
	5	0.0253	0.0251	0.0249	0.0002	0.0002
	6	0.0249	0.0246	0.0243	0.0003	0.0002
	7 (bead)	0.0253	0.0250	0.0247	0.0003	0.0003
2	1 (top)	0.0253	0.0250	0.0247	0.0003	0.0003
	2	0.0257	0.0252	0.0247	0.0005	0.0005
	3	0.0259	0.0255	0.0251	0.0004	0.0004
	4	0.0261	0.0257	0.0254	0.0004	0.0003
	5	0.0262	0.0258	0.0253	0.0004	0.0005
	6	0.0261	0.0257	0.0253	0.0004	0.0004
	7 (bead)	0.0264	0.0259	0.0255	0.0005	0.0005
4	1 (top)	0.0264	0.0260	0.0256	0.0004	0.0004
	2	0.0265	0.0261	0.0256	0.0004	0.0005
	3	0.0265	0.0260	0.0255	0.0005	0.0005
	4	0.0263	0.0258	0.0254	0.0005	0.0004
	5	0.0260	0.0255	0.0250	0.0005	0.0005
	6	0.0255	0.0249	0.0244	0.0006	0.0005
	7 (bead)	0.0258	0.0251	0.0244	0.0007	0.0007
8	1 (top)	0.0266	0.0260	0.0253	0.0006	0.0007
	2	0.0269	0.0262	0.0256	0.0007	0.0007
	3	0.0266	0.0260	0.0254	0.0006	0.0006
	4	0.0265	0.0259	0.0254	0.0006	0.0005
	5	0.0263	0.0256	0.0250	0.0007	0.0006
	6	0.0250	0.0263	0.0246	0.0007	0.0007
	7 (bead)	0.0276	0.0260	0.0245	0.0016	0.0015

**APPLICABILITY.** Although the method was developed primarily for the purpose of overcoming the difficulties involved in producing uniform shellac films of about one mil in thickness, it appears to have a wider range of utility, and to be equally applicable to many other coating materials as a simple and more rapid means of preparing test films.

This controlled dipping method as described is limited in application to the coating of rigid nonporous surfaces, but might be adapted to other materials. It cannot be satisfactorily applied to extremely viscous dopes or plastic paints, except possibly as a means for measuring the "after flow" of these compositions by noting the angle of the wedge-shaped film obtained.

The maximum film thickness which can be obtained in one

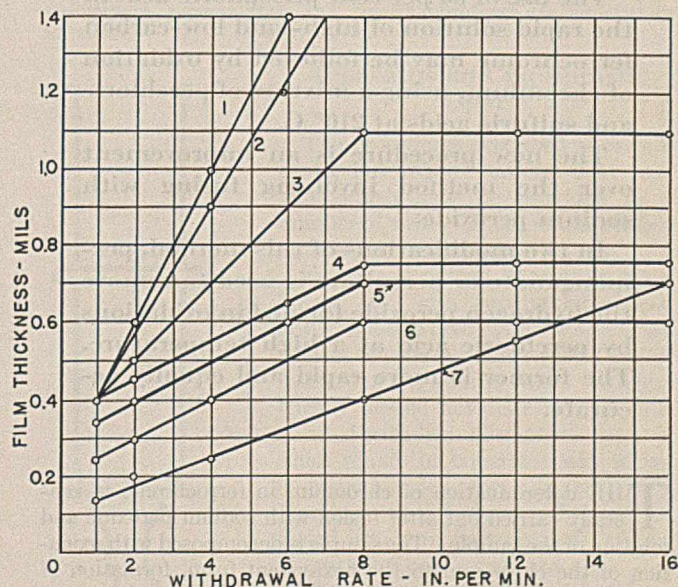


FIGURE 2. EFFECT OF SURFACE COATED

1. Bleached shellac, 5-pound cut on glass
2. Orange shellac, 4-pound cut on glass
3. White lacquer, brass or glass
4. Oil varnish on brass
5. Clear lacquer on brass
6. Oil varnish on glass
7. Clear lacquer on glass



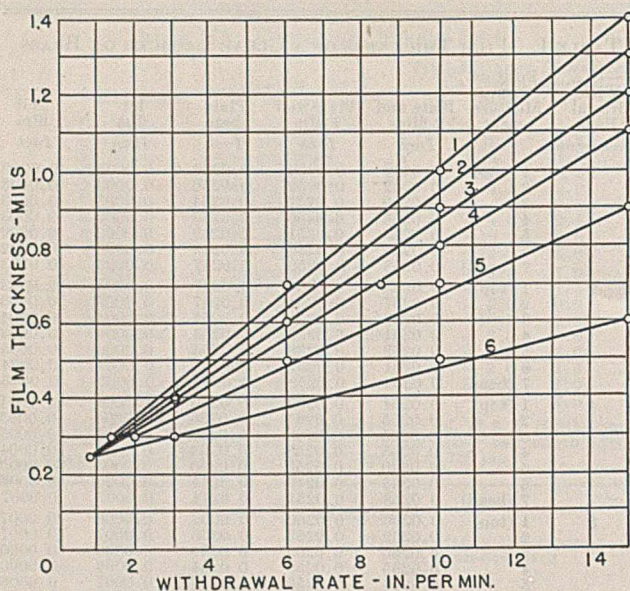


FIGURE 3. CALIBRATION CURVES FOR DEWAXED BLEACHED SHELLAC ON GLASS SURFACE

1. 5 pounds per gallon, 720 seconds Saybolt, 25° C.
2. 5 pounds per gallon, 500 seconds Saybolt
3. 5 pounds per gallon, 250 seconds Saybolt
4. 3 pounds per gallon, 500 seconds Saybolt
5. 3 pounds per gallon, 250 seconds Saybolt
6. 3 pounds per gallon, 60 seconds Saybolt

application is limited, as pointed out above. The limits depend upon the nature of the material. However, greater film thicknesses have been successfully prepared with shellac by applying successive coats. Solvent effect on previous coats was avoided by keeping the immersion time at a minimum.

#### Acknowledgment

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#### Literature Cited

- (1) Am. Soc. Testing Materials, *Proc.*, Pt. I, 35, 1087 (1935). Designation D115-35T.
- (2) *Ibid.*, Pt. I, 35, 876 (1935). Designation D406-35T.
- (3) Am. Soc. Testing Materials, *Standards*, Pt. II, 781-3 (1936). Designation D154-28.
- (4) *Ibid.*, Pt. II, 760 (1936). Designation D29-33.
- (5) Gardner, W. H., and Kappenberg, W., *IND. ENG. CHEM.*, 28, 437-9 (1936).
- (6) Paisley, J. W., *Ibid.*, 24, 163 (1932).
- (7) Rangaswami, M., and Aldis, R., *Indian Lac Research Inst.*, *Research Note*, No. 4 (1933).

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## Determination of Chromium in Ferrochrome

### Phosphoric Acid as Solvent with Mixed Perchloric and Sulfuric Acids as Oxidant

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The use of 85 per cent phosphoric acid in the rapid solution of high- and low-carbon ferrochrome may be followed by oxidation of chromium, using a mixture of perchloric and sulfuric acids at 210° C.

The new procedure is an improvement over the method involving fusing with sodium peroxide.

In two modifications of this method, permanganate or persulfate is used to remove the hydrogen peroxide formed in oxidations by perchloric acid at a high temperature. The former is more rapid and equally accurate.

THE determination of chromium in ferrochrome is generally carried out after fusion with sodium peroxide and solution of the sample. The sample is decomposed with oxidation of the chromium to the hexavalent form, formation of ferric oxide and sodium silicate, and oxidation of carbon. The fusion is leached with water, filtered, and washed, the filtrate is acidified, and the hexavalent chromium is determined by titration with standard ferrous sulfate. The required fusion with sodium peroxide, the troublesome filtration and washing, and subsequent acidification before titra-

tion of the oxidized chromium make this procedure far from satisfactory. It gives excellent results, but is not rapid.

Both the high- and low-carbon types of ferrochrome are easily and completely soluble in sirupy phosphoric acid in 8 to 10 minutes at temperatures between 180° and 250° C. A portion of the silicon is left as flocculent silicic acid and a small amount of carbon may remain. The iron and chromic phosphates are readily soluble in hot concentrated phosphoric acid. If the oxidation of chromium in the presence of phosphoric acid can be conveniently provided for, this method of solution can be used to improve greatly the speed and convenience of determining chromium in ferrochrome. The present paper describes new procedures which are probably the most rapid known and leave little to be desired in economy, accuracy, and convenience.

#### Previous Work

The theoretical considerations involved in the use of a mixture of perchloric and sulfuric acids as a powerful oxidizing mixture have been discussed by Smith (1). The formation of appreciable amounts of hydrogen peroxide from the interaction of these two acids at a temperature in the region of 200° C. (1) necessitates corrective procedures to counteract the reducing action of the hydrogen peroxide. The complicating influence of hydrogen peroxide formation is more pronounced when a mixture of phosphoric, perchloric, and sulfuric acids is used in an analytical application, since the greatest oxidizing action takes place at 205° to 210° C. The former condition is illustrated in the analysis of chromium



in chromic oxide as described by Smith, McVickers, and Sullivan (4). The latter condition is described by Smith and Smith (5) in the determination of chromium in stainless steel. The corrective measures used by Smith and Smith (5) must be applied to the present work in the determination of chromium in ferrochrome. In addition, an alternative procedure is suggested which, although more time-consuming, has its points of advantage. The use of phosphoric acid mixture with perchloric acid as solvent for tungsten, ferro-tungsten, and tungsten tool steels was described by Smith, McHard, and Olsen (3). Willard and Thompson (6) were apparently the first to suggest the use of sirupy phosphoric acid for the solution of refractory materials, applying it to bauxite and iron ore.

### Phosphoric Acid as Solvent for Metallurgical Materials

Hot sirupy phosphoric acid is an excellent solvent for ferrochrome. Hydrogen is liberated and most of the silicon is held in solution. Practically all the carbon in both high- and low-carbon ferrochrome is evolved as hydrocarbons. The action is vigorous at a temperature of 160° to 170° C. starting with an 85 per cent acid, and is complete at 220° to 250° C., after 8 to 10 minutes gradual increase in temperature. Ferrovanadium is likewise easily soluble under the same conditions; the solvent effect is much more convenient than solution in the mixture of hydrofluoric and nitric acids ordinarily employed. In the case of a high-speed tungsten tool steel, all the sample is soluble in hot sirupy phosphoric acid except the tungsten, which may then be dissolved by the addition of perchloric and sulfuric acids. Many types of chromite ore are practically insoluble in hot concentrated perchloric acid or its mixture with sulfuric acid. Such samples are easily soluble in hot sirupy phosphoric acid, in which case solution must follow a sodium peroxide fusion if the use of phosphoric acid is excluded. All these applications of phosphoric acid are at present being investigated as a starting point in the development of improved methods of analysis in the determination of chromium, vanadium, tungsten, iron, and sulfur in metallurgical materials.

### Alternative Procedures for Determining Chromium in Ferrochrome

**PERMANGANATE PROCEDURE.** A 100-mg. sample of high- or low-carbon ferrochrome is weighed accurately from a small weighing bottle into a 500-ml. Erlenmeyer flask, and a 5-ml. portion of 85 per cent phosphoric acid is added. A 200° to 250° C. Anschütz thermometer, 130 to 140 mm. in length and suspended from the neck of the flask by a small platinum wire, is adjusted inside the flask. A refluxing still head is placed in the neck of the flask. The heating is then begun, using a modified Rodgers ring burner, and applying sufficient heat to bring the flask contents to a temperature of 250° C. The first application of heat volatilizes water from the sirupy phosphoric acid and a vigorous evolution of hydrogen and hydrocarbons begins at 160° C. By the time the flask and contents have attained the full heat (8 to 10 minutes), all the sample will be dissolved and the clear green solution will contain only small amounts of silica and precipitated carbon. Any fine particles not completely dissolved will be made evident by a rapid local evolution of bubbles of gas. When all gas evolution has stopped, a 15-ml. portion of mixed perchloric and sulfuric acid (equal volumes of 72 per cent perchloric acid and 80 per cent by volume sulfuric acid) is added. The temperature of the reacting mixture falls to approximately 160° C. With adjustment of the burner to heat the flask contents to 210° C., the sample begins to oxidize rapidly at 200° C. The flask and contents are heated 5 minutes at 210° C. and then allowed to cool to 205° C.

The refluxing still head is then raised and 35 to 40 mg. of finely divided potassium permanganate are added. The flask is swirled and immediately plunged into cold water, continuing the swirling motion. In 10 seconds the contents can be diluted (cautiously at first) with 100 ml. of water. The thermometer is then removed and rinsed and a small boiling chip of Filter-Cel and 10 ml. of

1 to 4 hydrochloric acid are added. The solution is boiled 5 minutes and cooled under running tap water, 20 ml. of 1 to 1 sulfuric acid are added and the solution is titrated with 0.05 *N* ferrous sulfate from a 100-ml. buret. When the solution is 90 per cent titrated, as indicated by the color change from bright yellow to a yellowish green, 3 drops of 0.025 *M* *o*-phenanthroline ferrous ion (ferroin) are added. The remaining hexavalent chromium oxidizes the indicator to its almost colorless form.

The titration is then completed with dilution to 400 ml., if desired, to sharpen the end point, which is marked by the production of a decided pink cast with one drop excess of ferrous sulfate solution. No indicator correction is required, since the indicator was added in the ferrous form and remains at the end of the titration in the same form. In calculating results, the standard factor is obtained by titration of the ferrous sulfate solution with standard ceric sulfate, which has in turn been standardized using U. S. Bureau of Standards sodium oxalate. One milliliter of 0.05 *N* ferrous sulfate is equivalent to 8.6666 mg. of chromium. The ferrous sulfate solution may be standardized, using a sample of ferrochrome of known chromium content, by the procedure described above.

The permanganate procedure demands a rapid cooling and dilution of the sample after the addition of the potassium permanganate, and if this portion of the operation requires more than 10 seconds, low results may be expected (5). To avoid breakage of the retaining flask, this procedure must be mastered by repeated trials.

**PERSULFATE PROCEDURE.** The slight reversal of the oxidation of chromium by the small amount of hydrogen peroxide formed by decomposition of perchloric acid at 205° C. can be corrected for and danger of breakage avoided by using ammonium persulfate after a more leisurely dilution of the hot mixed acid solution of the sample.

The persulfate procedure is exactly the same as the permanganate procedure up to the point at which the hot oxidized solution is cooled and diluted. In the persulfate method the cooling and dilution can be made less rapidly. The solution is diluted, after cooling 15 to 20 seconds with the flask immersed in cold water, by the addition of 100 ml. of water, and heated to boiling for 1 minute to drive off most of the chlorine. One milliliter of 0.1 *N* silver nitrate and 2.5 grams of ammonium persulfate are added. The solution is diluted to 300 ml. with hot water and, after adding a Filter-Cel boiling chip, boiled for 10 minutes to decompose excess persulfate. Ten milliliters of 1 to 4 hydrochloric acid are added, the solution is boiled 5 minutes, cooled under running tap water, and 20 ml. of 1 to 1 sulfuric acid are added. It is then titrated, using 0.05 *N* ferrous sulfate from a 100-ml. buret until approximately 90 per cent of the hexavalent chromium is reduced. Three drops of 0.025 *M* ferroin indicator are added and the solution is titrated to a decided pink cast. The persulfate procedure requires 10 to 15 minutes longer for completion than the permanganate process, but the results obtained are practically identical.

### Apparatus and Equipment Used

The procedures described above are rapid, but require uniform heat control, which may be provided in a number of ways. Those recommended as most convenient are as follows:

Using a modified Rodgers ring burner (2), with two variable heat adjustments, a predictable temperature control can be obtained with 1° or at most 2° of the desired value. An electrically heated hot plate can be substituted with less efficient results. A small square of Nichrome wire gauze is recommended for use with the Rodgers ring burner; asbestos-protected iron wire gauze is just a source of irritation as a substitute.

Thermometers with external calibration markings are not satisfactory, as their etched markings are generally darkened by use of chromic oxide which is soon dissolved off the instrument, introducing error and leaving the

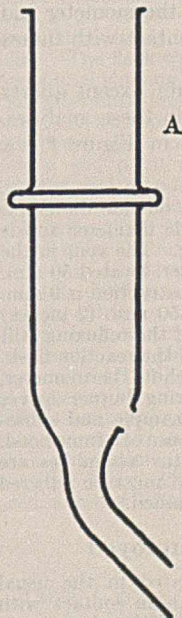


FIGURE 1



TABLE I. ANALYSIS OF HIGH- AND LOW-CARBON FERROCHROME

(Comparison of results by two different methods with U. S. Bureau of Standards sample 64)

Sample	Analysis No.	Weight Gram	Method Used				Deviation	Deviation	
				FeSO <sub>4</sub> N	FeSO <sub>4</sub> Ml.	Chromium %	from Mean %	from Known Value %	
Sample 204-2	1	0.1579	KMnO <sub>4</sub>	0.05112	127.00	71.29	+0.18	.....	
	2	0.1228	KMnO <sub>4</sub>	0.05112	98.30	70.95	-0.16	.....	
	3	0.1013	KMnO <sub>4</sub>	0.05112	81.30	71.13	+0.02	.....	
	4	0.1298	KMnO <sub>4</sub>	0.05112	103.80	70.88	-0.23	.....	
	5	0.1379	KMnO <sub>4</sub>	0.05112	110.60	71.08	-0.03	.....	
	6	0.1303	KMnO <sub>4</sub>	0.05112	104.30	70.95	-0.16	.....	
	7	0.1112	KMnO <sub>4</sub>	0.05112	89.50	71.33	+0.22	.....	
	8	0.0864	KMnO <sub>4</sub>	0.05093	69.54	71.06	-0.05	.....	
	9	0.1127	KMnO <sub>4</sub>	0.05093	77.30	71.36	+0.25	.....	
				Av. 71.11		Av. 0.14			
Sample 64	10	0.1049	KMnO <sub>4</sub>	0.05112	80.50	68.01	+0.04	+0.11	
	11	0.0870	KMnO <sub>4</sub>	0.05112	66.70	67.94	-0.03	+0.04	
	12	0.1183	KMnO <sub>4</sub>	0.05112	90.70	67.94	-0.03	+0.04	
	13	0.0805	KMnO <sub>4</sub>	0.05112	61.70	67.92	-0.05	+0.02	
	14	0.1242	KMnO <sub>4</sub>	0.05093	95.75	68.05	+0.08	+0.15	
				Av. 67.97		Av. 0.05 Av. +0.07			
Sample 203-2	15	0.24315	KMnO <sub>4</sub>	0.05055	191.65	69.08	-0.05	.....	
	16	0.22030	KMnO <sub>4</sub>	0.05055	173.80	69.15	+0.02	.....	
	17	0.08790	KMnO <sub>4</sub>	0.05055	69.34	69.14	+0.01	.....	
	18	0.10800	KMnO <sub>4</sub>	0.05055	85.17	69.12	-0.01	.....	
	19	0.12855	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	101.40	69.14	+0.01	.....	
	20	0.11700	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	92.26	69.11	-0.02	.....	
	21	0.11330	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	89.46	69.20	+0.07	.....	
					Av. 69.13		Av. 0.03		
	Sample 204-2	22	0.1456	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	118.20	71.15	-0.09	.....
		23	0.1069	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	87.20	71.50	+0.26	.....
24		0.1035	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	84.02	71.15	-0.09	.....	
25		0.0787	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	63.60	70.83	-0.41	.....	
26		0.0970	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	68.90	71.29	+0.05	.....	
27		0.1116	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	90.00	71.01	-0.23	.....	
28		0.0960	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	78.10	71.30	+0.06	.....	
29		0.1168	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	95.15	71.40	+0.16	.....	
30		0.1212	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	98.85	71.49	+0.25	.....	
					Av. 71.23		Av. 0.18		
Sample 204-2, reground	31	0.08840	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	71.60	70.99	-0.11	.....	
	32	0.12975	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	105.25	71.10	±0.00	.....	
	33	0.12130	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	98.45	71.14	+0.04	.....	
	34	0.12765	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05055	103.76	71.24	+0.14	.....	
	35	0.14065	KMnO <sub>4</sub>	0.05055	113.97	71.02	-0.08	.....	
	36	0.08890	KMnO <sub>4</sub>	0.05055	72.10	71.08	-0.01	.....	
	37	0.12985	KMnO <sub>4</sub>	0.05055	106.10	70.94	-0.16	.....	
	38	0.11475	KMnO <sub>4</sub>	0.05055	93.34	71.29	+0.19	.....	
					Av. 71.10		Av. 0.09		
Sample 64	39	0.09660	KMnO <sub>4</sub>	0.05055	.....	67.81	-0.09	-0.09	

thermometer difficult to read. Only an Anschütz type of thermometer should be used. A convenient size of thermometer is 135 mm. (5.25 inches) long, calibrated over the range 180° to 250° C. in single degree intervals. No trouble has been encountered in the use of this type of thermometer and the markings can be easily read, even in contact with fumes from perchloric acid and sulfuric acid.

The authors know of no suitable substitute, except quartz flasks for 500-ml. Pyrex Erlenmeyer flasks in these analyses. A refluxing still head of the design shown in Figure 1 is a necessity.

The Pyrex tube, A, is 25 mm. (1 inch) in outside diameter. The flange is 35 mm. (1.375 inches) in outside diameter and is made 50 mm. (2 inches) from the top opening. The vent in the side of the tube is 6 mm. (0.25 inch) in diameter, located 50 mm. (2 inches) below the flange. The bottom construction is 9 mm. (0.375 inch) in outside diameter and extends 50 mm. (2 inches) below the wide portion of tube A. The end of the refluxing still head should make contact with the side wall of the reaction flask. The assembly of 500-ml. Erlenmeyer flask, Anschütz thermometer, refluxing still head, and modified Rodgers ring burner leaves nothing to be desired. The solution of the sample and subsequent oxidation can be carried out without the use of a fume hood. If substitute equipment and modified apparatus assemblies are used, the experimental conditions as described must be adhered to closely or unsatisfactory results will be obtained.

### Reagents and Chemicals Employed

Standard ferrous sulfate solution is prepared in the usual manner and is best stored in an 18-liter bottle in contact with hydrogen, following the use of the Zintl and Rienacker standard storage bottle and buret (7).

Standard ceric sulfate solution is prepared from ceric ammonium sulfate, Ce(SO<sub>4</sub>)<sub>2</sub>·2(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O, by solution in 0.5 to 1.0 N sulfuric acid, and is standardized using pure sodium oxalate in hot dilute perchloric acid solution. The determination of the ratio between ferrous and ceric sulfates completes the standardization.

Ferrous indicator in 0.025 M concentration can be purchased already prepared.

Phosphoric acid, 85 per cent sirupy phosphoric acid, U. S. P. grade.

Perchloric acid, 72 per cent free from chromium, either c. p. or technical grade.

Sulfuric acid, 95 per cent chromium-free is diluted with water to make 80 per cent strength (by volume).

Mixed perchloric and sulfuric acids (ferrochrome oxidant). Equal parts by volume of 72 per cent perchloric and 80 per cent sulfuric acids.

Ammonium persulfate. Any high-grade crystalline form is applicable.

Standard Ferrochrome. U. S. Bureau of Standards sample 64 (high carbon). British Chemical Standards high- and low-carbon ferrochrome samples 204-2 and 203-2. The certificate values for these latter samples had not been issued at the time of the present work.

### Development of the Method

A study of the proper proportion of phosphoric acid as solvent and of mixed perchloric and sulfuric acids as oxidant was first made. Five milliliters of 85 per cent phosphoric acid are suitable for dissolving a 100- to 125-mg. sample and 15 ml. were finally chosen as the most desirable proportion of ferrochrome oxidant.

A study was then made of the proper temperature and time of heating of the dissolved sample with the mixed acids for complete oxidation. An oxidation temperature of 205° C. for 3 minutes was found adequate for low-carbon ferrochrome, but 5 minutes at 210° C. were required in the case of high-carbon ferrochrome. The conditions finally chosen were the same for both high- and low-carbon samples: 10 minutes for solution of sample, 5 minutes for oxidation at 210° C., followed by dropping the temperature to 205° C. before adding permanganate, and rapid or leisurely cooling followed by persulfate treatment. One-half hour per sample is required for the permanganate process and 45 minutes for the persulfate method. By analyzing a number of samples concurrently, the average time per sample is materially reduced.

### Final Test Analyses

A long series of analyses of the new British Bureau of Standards ferrochromes 203-2 and 204-2 was carried out by the authors in the capacity of referee analysts, using as control U. S. Bureau of Standards ferrochrome 64, having a certificate value of 67.9 per cent chromium. Analyses of each sample by each method were carried out concurrently. The unknown sample series constituted the major portion of the work. A study was made of the degree of nonuniformity of the unknown high-carbon ferrochrome 204-2 by making a comparison between a series of analyses on the reground and mixed sample and the sample as received. The results are shown in Table I.

Table I shows a close agreement in the analysis of low-carbon ferrochrome (sample 203-2) by the two procedures.



TABLE II. SUMMARY OF RESULTS OF ALL ANALYSES

Sample	Method of Analysis	Average Chromium Content %	Mean Deviation from Average %	Number of Determinations
204-2	KMnO <sub>4</sub>	71.11	0.14	9
64	KMnO <sub>4</sub>	67.97	0.05	5
203-2	KMnO <sub>4</sub>	69.12	0.03	4
203-2	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	69.15	0.03	3
204-2	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	71.29	0.18	9
204-2 reground	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	71.12	0.07	4
204-2 reground	KMnO <sub>4</sub>	71.00	0.12	4

The agreement in the analyses of high-carbon ferrochrome (sample 204-2) is not so close, the persulfate method giving the higher results (71.20 as compared to 71.11 per cent). The mean deviation of values from the average shows a greater degree of uniformity in samples 203-2 and 64 than in sample 204-2. This is shown by the results obtained with reground 204-2. With Bureau of Standards sample 64 the two pro-

cedures gave practically the same close agreement with the certificate value, 67.9 per cent chromium but the persulfate values are omitted from Table I in the interests of brevity. The results in Table I are in all series consecutive determinations with no omissions, but a number of series of results were omitted because of obviously unsatisfactory individual analyses.

### Literature Cited

- (1) Smith, *IND. ENG. CHEM., Anal. Ed.*, 3, 88 (1931).
- (2) Smith, *Ibid.*, 8, 484 (1936).
- (3) Smith, McHard, and Olsen, *Ibid.*, 8, 350 (1936).
- (4) Smith, McVickers, and Sullivan, *J. Soc. Chem. Ind.*, 54, 369T (1935).
- (5) Smith and Smith, *Ibid.*, 54, 185T (1935).
- (6) Willard and Thompson, *IND. ENG. CHEM., Anal. Ed.*, 3, 399 (1931).
- (7) Zintl and Rienäcker, *Z. anorg. allgem. Chem.*, 155, 84 (1926).

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## Titration of Aromatic Amines with Nitrous Acid

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A STUDY of the literature reveals that although the titration of the monoamines with nitrous acid has been investigated to some extent, very little work has been done on the diamines, and no work has been done on the quantitative titration of monocyclic triamines. Of the monoamines, aniline has been most carefully studied (6, 9, 13). The titration of sulfanilic acid is well known and indeed this reaction has been applied as a means of standardizing sodium nitrite solutions (11, 14). Among the other monoamines quantitatively titrated are: *o*-(1), *p*-(1, 11), and *m*-aminobenzenesulfonic acids (1, 8); dehydrothio-*p*-toluidine sulfonic (10); 3-amino-4-hydroxytoluene (3); *o*- and *p*-toluidine (9, 15); *o*- and *p*-anisidine (15); *p*-phenetidine (15); 5-aminosalicylic acid (15); *p*-nitroaniline (9, 10); *o*-(5) and *p*-(15) aminophenol; and *m*-xylydine (9). Of the diamines, 2,4-diaminophenol (2) and 3,5-diamino-*o*-cresol (4) have been titrated.

Although there is no reference in the literature to the complete diazotization of monocyclic triamines, in a previous paper (12) the authors found it necessary to determine the yields of triamine formed. Two methods were tried. The first method—adding sodium nitrite solution slowly to the amine solution until a faint permanent end point appeared on starch-potassium iodide paper—gave low results. The second method—using excess of sodium nitrite solution and back-titrating with standard aniline hydrochloride or sulfanilic acid solution—gave fairly quantitative results, and was therefore used. Methods for back-titrating have been described (7, 10), but a more direct method was desired.

### Purification of Amines

In general the triamines were purified in the following manner:

A sample of the triamine was dissolved in a little warm water, treated with boneblack, and filtered under an atmosphere of natural gas. The filtrate was chilled and saturated with hydrogen chloride gas. The resultant precipitate was filtered, washed with several portions of alcohol-ether and ether, and then dried in a vacuum desiccator over potassium hydroxide and calcium chloride for 48 hours. The purity of some of the triamines

was then checked by elementary analysis (12). The mono- and diamines were purified by distillation and crystallization.

### Standardization of Sodium Nitrite Solution

Approximately 0.1 *N* sodium nitrite solution was standardized with aniline hydrochloride, sulfanilic acid, and potassium permanganate solutions, yielding 0.1099 *N*, 0.1093 *N*, and 0.1132 *N*, respectively.

### General Procedure

A known weight of the purified amine or amine hydrochloride given in Table I was dissolved in 100 cc. of aqueous solution containing 10 cc. of concentrated hydrochloric acid in a glass-stoppered Erlenmeyer flask. The sodium nitrite was added, dropwise, at 20° to 23° C. (not more than 2 cc. per minute) until a test drop immediately turned starch-potassium iodide paper strongly blue. The flask was then stoppered and allowed to stand (with occasional shaking) for 15 minutes. If a test drop of the solution after this time gave only a faint end point or no end point, then 2 cc. more of the sodium nitrite solution were added and the procedure was repeated. If, however, a test drop still gave a strong end point after 15 minutes, the solution was back-titrated with standard aniline hydrochloride (0.100 *N*) or sulfanilic acid (0.100 *N*) solution till only a faint end point persisted.

Because there was usually about 2 cc. excess of sodium nitrite solution for 15 minutes before back-titration, and because nitrous acid is relatively unstable, especially at room temperature, a blank determination was made to determine the amount of sodium nitrite solution lost. The sodium nitrite solution lost in this way was not utilized in the reaction and was therefore subtracted from the total amount of sodium nitrite used. When 2 cc. of (0.110 *N*) sodium nitrite solution were added to 100 cc. of aqueous solution containing 10 cc. of concentrated hydrochloric acid, allowed to stand (with occasional shaking) for 15 minutes, and then back-titrated with standard aniline hydrochloride solution, a loss of 0.20 cc. of sodium nitrite solution occurred. When 25 cc. of concentrated hydrochloric acid were used, a loss of 0.23 cc. of sodium nitrite solution occurred.

### Results

Table I gives the results obtained by titrating varying amounts of the amines. It was found that 2,4,6-triaminobenzene (*D*) could not be completely titrated in aqueous



TABLE I. RESULTS OF TITRATIONS

(Temperature, 20°-23° C.)

A = 2,4,6-triaminobenzoic acid-3HCl  
 B = 2,4,6-triaminotoluene-3HCl·H<sub>2</sub>O  
 C = 1,3,5-triaminobenzene-3HCl  
 D = 2,4,6-triaminochlorobenzene-3HCl  
 E = metanilic acid  
 F = *m*-phenylenediamine  
 G = *m*-toluylenediamine-HCl  
 H = 2,4,6-triaminophenol-3HCl  
 I = 1,2,4-triaminobenzene-3HCl  
 J = *o*-phenylenediamine  
 K = *p*-phenylenediamine-2HCl

Com- pound	Weight Grams	100 Cc. of Solution Contain- ing:	NaNO <sub>2</sub> Used		Back-Titration Aniline- Sulf- HCl, nilic acid,		Titra- tion %
			0.110 N	0.117 N	0.100 N	0.100 N	
A	0.0515	d	10.6	..	..	0.3	99.7
	0.1020	d	21.5	..	..	1.4	99.5
	0.1505	d	..	29.0	..	1.3	99.2
	0.2020	d	..	38.2	..	0.8	99.6
	0.2500	d	..	48.0	..	2.0	99.4
	0.0605	d	13.0	..	0.7	..	101.9
	0.1000	d	21.0	..	1.3	..	99.5
	0.1490	d	30.0	..	0.7	..	99.2
	0.2100	d	43.0	..	1.8	..	99.4
	0.1480 <sup>a</sup>	d	27.0	..	0.0	..	92.4
B	0.0550	d	12.5	..	1.2	..	98.8
	0.1060	d	22.3	..	0.5	..	99.0
	0.1520	d	33.0	..	1.6	..	100.0
	0.1702	d	36.0	..	0.5	..	100.7
	0.2080	d	44.0	..	1.2	..	99.5
	0.1500	d	32.0	..	1.4	..	99.7
	0.1109 <sup>b</sup>	d	20.0	..	1.0	..	82.6
	0.0620	d	16.0	..	1.4	..	99.7
C	0.1163	d	28.5	..	1.0	..	100.3
	0.1570	d	38.0	..	1.2	..	99.6
	0.2080	d	51.0	..	2.0	..	100.3
	0.2150	d	51.5	..	1.2	..	99.5
	0.1500	d	36.5	..	1.3	..	99.7
	0.0650	d, f	15.5	..	1.0	..	96.8
D	0.1120	d, f	26.0	..	1.3	..	99.3
	0.1600	d, f	36.0	..	1.9	..	99.5
	0.2005	d, f	44.0	..	2.1	..	98.5
	0.0540	d	..	6.1	..	0.6	100.6
E	0.1200	d	..	13.2	..	1.2	100.9
	0.2090	d	..	21.2	..	0.5	99.4
	0.2500	d	..	25.6	..	1.0	99.4
	0.3045	d	..	31.1	..	1.1	99.6
	0.0648	d	..	22.3	..	2.0	99.4
F	0.1106	d	..	36.5	..	1.8	99.0
	0.1530	d	..	49.5	..	1.8	98.6
	0.2004	d	..	65.0	..	2.2	99.2
	0.0604	d	..	14.5	..	1.5	99.8
G	0.1125	d	..	26.2	..	2.0	100.1
	0.1510	d	..	34.0	..	1.6	99.6
	0.2003	d	..	45.1	..	2.0	100.0
	0.0540 <sup>c</sup>	d	8.5	..	0.6	..	65.4
H	0.1010 <sup>c</sup>	d	16.0	..	1.0	..	67.2
	0.1340 <sup>c</sup>	d	21.0	..	1.1	..	67.3
	0.1750 <sup>c</sup>	d	27.0	..	0.8	..	67.9
	0.2200 <sup>c</sup>	d	33.0	..	0.5	..	67.0
	0.2748 <sup>e</sup>	d, f	55.0	..	3.0	..	83.7
	0.1785 <sup>e</sup>	d	31.0	..	2.5	..	72.8
	0.1505 <sup>e</sup>	d	24.0	..	1.1	..	68.9
	0.0562	d	7.2	..	0.6	..	48.9
	0.1062	d	14.0	..	1.3	..	50.6
	0.1555	d	20.0	..	1.4	..	50.8
I	0.2300	d	27.5	..	0.5	..	49.7
	0.1528 <sup>a</sup>	d	21.5	..	0.5	..	58.1
	0.2000 <sup>c</sup>	d, f	30.0	..	1.0	..	58.8
	0.0560	d	..	10.5	..	1.6	50.5
	0.1013	d	..	17.5	..	1.4	50.3
J	0.1573	d	..	26.0	..	1.3	49.6
	0.2075	d	..	34.5	..	1.4	50.4
	0.0540	d	..	6.5	..	1.5	48.6
K	0.1160	d	..	12.0	..	1.0	49.8
	0.1606	d	..	17.0	..	1.9	50.0
	0.2010	d	..	20.0	..	1.2	49.4
	0.2760	d	..	27.5	..	1.5	49.8

<sup>a</sup> Without back-titration the result is low.<sup>b</sup> Temperature was kept at 0-5° C.<sup>c</sup> Temperature was kept at 5-10° C.<sup>d</sup> Concentrated hydrochloric acid, 10 cc.<sup>e</sup> Temperature was kept at 20-23° C.<sup>f</sup> Ethyl alcohol, 20 cc.<sup>g</sup> Concentrated hydrochloric acid, 25 cc.<sup>h</sup> Use of 25 cc. of concentrated HCl gives higher results.<sup>i</sup> Use of alcohol gives higher results.

and 20 cc. of ethyl alcohol. It was found that 1.5 cc. of sodium nitrite (0.110 N) had to be added before a faint end point could be obtained on starch-potassium iodide paper; hence this amount plus 0.23 cc. was subtracted when the amine was titrated.

Metanilic acid (*E*) was investigated because the literature contains no reference to its rapid quantitative titration. The method of Doolittle (8) requires 12 to 15 hours for quantitative results.

The accuracy of the titration of *m*-phenylenediamine (*F*) was limited somewhat by the appearance of a false end point which appeared before the true end point (at about 85 per cent complete titration) and which turned starch-potassium iodide paper bluish black. However, this color did not form instantaneously on the potassium iodide paper, and could therefore be differentiated from the true end point.

Titration of 2,4,6-triaminophenol (*H*), using 100 cc. of solution containing 10 cc. of concentrated hydrochloric acid at 10° C. (maximum temperature), gave only two-thirds complete titration. The use of higher temperatures and more acid gave higher and variable results. Thus for consistent results the temperature and concentration of hydrochloric acid must be kept within fairly close limits.

1,2,4-Triaminobenzene (*I*), *o*-phenylenediamine (*J*), and *p*-phenylenediamine (*K*) were approximately 50 per cent titrated.

## Summary

Since most aromatic amines cannot be quantitatively titrated with nitrous acid in a short time by the usual direct manner, a method was devised by which excess sodium nitrate is used, and the excess back-titrated with standard aniline hydrochloride or sulfanilic acid solutions (both of which react rapidly with sodium nitrite). The amines titrated were: 2,4,6-triaminobenzoic acid, 2,4,6-triaminotoluene, 1,3,5-triaminobenzene, 2,4,6-triaminochlorobenzene, metanilic acid, *m*-phenylenediamine, *m*-toluylenediamine, 2,4,6-triaminophenol, 1,2,4-triaminobenzene, *o*-phenylenediamine, and *p*-phenylenediamine.

## Literature Cited

- (1) Amantiov and Titkov, *Anilinokrasochnaya Prom.*, 2, No. 8-9, 24-6 (1932).
- (2) Bradt and Brown, *Trans. Electrochem. Soc.*, 56, 429 (1929).
- (3) Bradt and Hart, *Ibid.*, 60, 205 (1931).
- (4) Bradt and Linford, *Ibid.*, 69, 353 (1936).
- (5) Brown and Warner, *Trans. Am. Electrochem. Soc.*, 41, 225 (1922).
- (6) Bucherer, in Lunge-Berl., "Chemisch-technische Untersuchungsmethoden," 7 Aufl., Vol. IV, p. 897, Berlin, Julius Springer, 1924.
- (7) Chervinskaya, Russian Patent 39,774 (Nov. 30, 1934).
- (8) Doolittle, *Trans. Am. Electrochem. Soc.*, 45, 57 (1924).
- (9) Jones and Lee, *IND. ENG. CHEM.*, 16, 948 (1924).
- (10) Lee and Jones, *Ibid.*, 16, 930 (1924).
- (11) Lunge, *Chem.-Ztg.*, 28, 501 (1904).
- (12) Phillips and Lowy, *Trans. Electrochem. Soc.*, 71 (preprint) (1937).
- (13) Sabalitschka and Schrader, *Z. angew. Chem.*, 34, Aufsatzteil 45 (1921).
- (14) Schultz and Vaubel, *Z. Farben-Ind.*, 1, 37, 149, 339 (1902).
- (15) Ueno, Shigezo, and Sekiguchi, Haruo, *J. Soc. Chem. Ind., Japan*, 37, Suppl. Binding, 235-7 (1934).

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solution, even if 25 cc. of concentrated hydrochloric acid were used; however, the addition of ethyl alcohol (20 cc.) gave almost quantitative results. As a preliminary check, a blank determination was made using a solution containing, 55 cc. of water, 25 cc. of concentrated hydrochloric acid,





# Extraction of Minute Amounts of Morphine

## Use of Pyrogallol for Preventing Losses Due to Oxidation

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THE literature (1-4) contains many references to the ease with which morphine is oxidized, especially in alkaline solutions where the oxidation may be accomplished by atmospheric oxygen. In customary quantitative procedures, dealing with sensible quantities of the alkaloid, the extent of oxidation may be of slight importance, and the author has been unable to find any reference describing other than usual precautions to prevent oxidative changes.

In the qualitative analysis of horse saliva for the detection of drugs which may have been administered to the animal, such drugs, of which morphine is one, are present in very minute quantities in most instances. The loss of an otherwise insignificant amount of the drug therefore becomes, in this work, of paramount importance.

The routine method used in this laboratory for the analysis of saliva is a modification of the classic Stas-Otto (1, 2, 3) procedure for the isolation of alkaloids and related drugs. After preliminary purification procedures, any alkaloid present is contained in a small amount of acidified water. This solution is extracted (A) with successive, equal portions of ether, made alkaline with sodium hydroxide, and again extracted (B) with ether, then neutralized with hydrochloric acid, made alkaline with ammonium hydroxide, and, after addition of a little alcohol, extracted (C) with a hot chloroform-alcohol mixture (9 plus 1). Morphine, if present in minute amount, is contained only in the C extract, and will have been subjected to oxidation by atmospheric oxygen during both the B and C extractions.

In a series of analyses designed to determine the limit of sensitivity of the method, it was found that the final extraction residues from saliva samples to which had been added 250, 100, and 25 gamma of morphine gave evidence, by the formation of precipitates with general alkaloidal reagents, of the presence of an alkaloidal substance in each in graduated amounts. However, characteristic color tests and formation of typical microcrystals were obtained only in the case of samples to which the largest amount of morphine (250 gamma) had been added, and these identifying tests were weak in view of the comparatively large amount of morphine which had been used. It was therefore concluded that when amounts of morphine less than 250 gamma were used, atmospheric oxygen was converting the alkaloid to pseudomorphine or similar oxidation products which were capable of giving amorphous precipitates with general alkaloidal reagents, but which, of course, would not give tests characteristic of morphine. It was accordingly felt that if a method could be devised for the prevention of oxidation, its use would tend to prove these suppositions and at the same time render the general method more sensitive for the detection of morphine.

As the oxygen-absorbing qualities of alkaline pyrogallol solutions are well known, it was thought that the introduction of pyrogallol into the alkaline solutions containing morphine might inhibit the oxidation of the alkaloid.

### Experimental

To three 10-cc. portions of water were added, respectively, 250 gamma of morphine (as sulfate), 250 gamma of morphine (as sulfate) and 0.1 gram of pyrogallol, and 0.1 gram of pyrogallol. Each solution was analyzed as follows:

Sufficient dilute sodium hydroxide was added to make the solution distinctly alkaline to litmus. It was then extracted three

times with equal volumes of ether, and the ether extracts were combined and washed three times with 2-cc. portions of water containing 10 drops of 20 per cent sodium hydroxide solution in each 100 cc. The ether was then dried with anhydrous sodium sulfate and evaporated. The residue from evaporation was dissolved in a small amount of slightly acidified water and drops of the solution were tested with various alkaloidal precipitants and color reagents with negative results. The alkaline aqueous solution remaining after the extraction with ether was neutralized with dilute hydrochloric acid, made alkaline with ammonium hydroxide, and, after addition of 1 cc. of alcohol, extracted three times with equal volumes of hot chloroform-alcohol mixture (9 plus 1). The extracts were combined and washed three times with 2-cc. portions of ammoniacal water-alcohol mixture (75 cc. of water, 25 cc. of alcohol, 10 drops of ammonium hydroxide). The extract was then dried with anhydrous sodium sulfate and evaporated.

The residue from evaporation was dissolved in a small amount of slightly acidified water and tested for morphine with alkaloidal precipitants and color reagents. Strongly positive tests were obtained with the residue from the morphine-pyrogallol solution, weakly positive tests with the residue from the morphine solution without pyrogallol, and negative tests with the residue from the solution containing only pyrogallol.

NOTES. The B residues (those from the ether extractions of the solutions alkaline with sodium hydroxide) were tested because it was desired to make certain that no impurities would be introduced through the use of pyrogallol which would interfere with the detection of alkaloids that might be present in these residues in routine use of the method.

Both the ether and the chloroform-alcohol extracts were slightly colored, presumably because of extraction of oxidation products of pyrogallol. This has since been found not to be an invariable condition, the extracts frequently being colorless even when made under seemingly identical conditions. In any event the washings with alkaline water or water-alcohol mixture readily remove the color from the solvents.

To three samples of horse saliva measuring about 150 cc. were added 250 gamma, 100 gamma, and 25 gamma, respectively, of morphine (as sulfate). These samples were analyzed by the routine procedure except that the extractions with immiscible solvents were made in the manner just described, adding 0.1 gram of pyrogallol to the acid aqueous solutions following the A extractions. In each case morphine was recovered and identified both by the formation of characteristic microcrystals and by color tests with appropriate reagents. In the case of the sample to which 25 gamma of the alkaloid had been added, the color test was stronger and the microcrystals better formed than in the case of the 250-gamma sample run without using pyrogallol. This tended to prove that atmospheric oxidation had been responsible for considerable loss of morphine, that pyrogallol used as described greatly minimized loss by oxidation, and that the use of pyrogallol increased the sensitivity of the method toward morphine by more than ten times.

Occasionally slight amorphous or crystalline precipitates are obtained when Kraut's reagent is added to the solutions of the B and C residues. Experiments indicate that this is due to some pyrogallol oxidation product which is not removed by the washings. It does not, however, interfere with alkaloid detection, nor are such precipitates formed with any other reagent than Kraut's.

To ascertain whether use of pyrogallol would affect results with other alkaloids, duplicate samples were prepared containing graduated amounts of strychnine, heroin, cocaine, and caffeine. One set of samples was analyzed with and the other without pyrogallol. With the exception of those containing caffeine, all samples gave as good or better results



with pyrogallol than without. The results with heroin, which during the process of analysis is in large part hydrolyzed to morphine, were improved in about the same degree as those with morphine itself. Otherwise better results were probably due to more thorough elimination of traces of impurities by reason of washing solvents after extraction. The sensitivity of the method toward caffeine was somewhat decreased, probably because of loss in washing the solvents. As this alkaloid is recovered in the *A* extract, which is not washed, as well as in the *C* extract, the slight loss is not serious.

### Summary

The use of pyrogallol will prevent serious loss of morphine due to oxidation in alkaline solution during extraction with immiscible solvents.

A method for its use and comparative results without its use are described.

The use of pyrogallol in the manner described does not interfere with the detection of other alkaloids (cocaine, strychnine, and caffeine).

### Literature Cited

- (1) "Allen's Commercial Organic Analysis," 5th ed., Vol. VII, "The Vegetable Alkaloids," Philadelphia, P. Blakiston's Son & Co., 1929.
- (2) Autenrieth, W., "Laboratory Manual for the Detection of Poisons and Powerful Drugs," tr. by W. H. Warren, 6th American ed., Philadelphia, P. Blakiston's Son & Co., 1928.
- (3) Peterson, Haines, and Webster, "Legal Medicine and Toxicology," 2nd ed., Vol. II, W. B. Saunders Co., 1923.
- (4) Small, L. F., and Lutz, R. E., "Chemistry of the Opium Alkaloids," *Suppl. Pub. Health Repts.* 103 (1932).

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# Determination of Primary Calcium Phosphate In Mixtures of the Calcium Orthophosphates

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THE unsatisfactory state of the methods for analyzing mixtures of the calcium phosphates (1, 6-9, 12, 13) is well recognized and is due primarily to the fact that the methods are largely empirical. It is the purpose of this paper to present a new method, which is free from empiricism, for the determination of primary calcium phosphate in mixtures of the calcium orthophosphates. The method involves the titration of the primary calcium phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , with 0.2 *N* sodium hydroxide solution to a definite pH to determine the amount of this phosphate in the sample.

### Preparation of Materials and Methods of Analysis

Primary calcium phosphate was prepared by adding to a suspension of commercial secondary calcium phosphate (c. p. ana-

lyzed quality), the theoretical amount of phosphoric acid, as calculated from the solubility curve of Cameron and Seidell (2) where the primary salt is the solid phase. The solution was filtered and evaporated until crystals started to form which were then allowed to separate out slowly. The crystals were filtered on a Büchner funnel, washed with 95 per cent alcohol and finally with anhydrous ether, dried for 15 minutes at 100° C., and kept in a desiccator over calcium chloride. Analyses of the product showed it to be the pure monohydrate of primary calcium phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , with a  $\text{P}_2\text{O}_5/\text{CaO}$  ratio of 2.53 in perfect agreement with the theoretical value.

To prepare secondary calcium phosphate, the primary calcium phosphate was dissolved in water and a little phosphoric acid. Carbon dioxide-free sodium hydroxide was then added slowly until the solution had a pH of 3.8, using bromophenol blue as an indicator. The crystals of secondary calcium phosphate that separated out at this hydrogen-ion concentration were filtered off, washed first with alcohol and then with ether, and air-dried. Upon analysis this proved to be the dihydrate of secondary calcium phosphate,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , having the theoretical  $\text{P}_2\text{O}_5/\text{CaO}$  ratio of 1.27.

Tertiary calcium phosphate was prepared by dissolving 12 grams of secondary calcium phosphate in a little nitric acid with subsequent dilution with distilled water to a volume of nearly 4 liters. A moderate excess of carbonate-free ammonium hydroxide was then added rapidly with continual stirring. Because of the gelatinous nature of the precipitate it was washed eight times by decantation, using 4 liters of distilled water each time. It was then filtered on a Büchner funnel, washed with alcohol, then with ether, and air-dried. The  $\text{P}_2\text{O}_5/\text{CaO}$  ratio of this material was found to be 0.829, slightly below the theoretical 0.845 for pure tricalcium phosphate.

Carbonate-free ammonia was prepared by allowing ammonium hydroxide to stand overnight in contact with an excess of calcium hydroxide, and then distilling into carbon dioxide-free distilled water.

Calcium was determined by the sulfate method as outlined by Gooch (5), and phosphorus by the customary molybdate method with the final precipitation as magnesium ammonium phosphate.

The hydrogen-ion concentration was determined both colorimetrically and electrometrically. For the first method a series of buffer solutions with pH values ranging from 3.0 to 7.0, with intervals of 0.2 pH, was prepared as described by Clark and Lubs (3). The indicator solutions used were those recommended by Clark and Lubs (3) for this range, and 5 drops were used for each 10 cc. of solution to be tested.

For the electrometric method a cell was used, consisting of a normal calomel electrode, a saturated potassium chloride bridge, a lightly platinized platinum electrode, and hydrogen which was bubbled through pyrogallol solution and two vessels with water. The electromotive force was read by means of a Leeds & Northrup potentiometer, and the pH was calculated from the equation

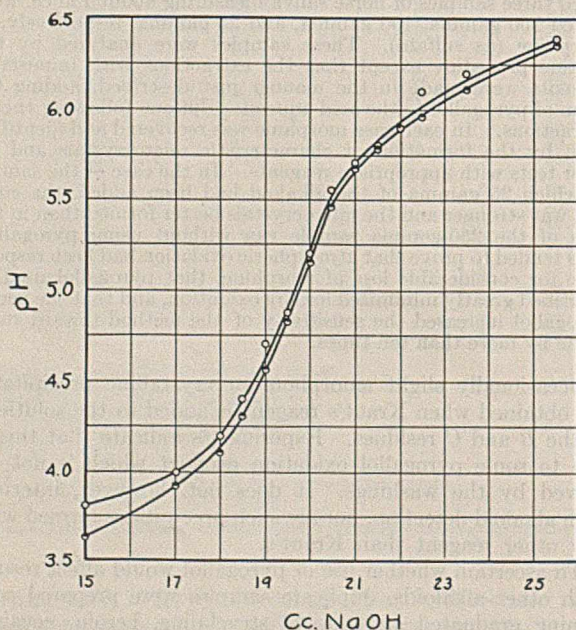


FIGURE 1. TITRATION OF PRIMARY CALCIUM PHOSPHATE WITH SODIUM HYDROXIDE

○, colorimetric pH  
◻, electrometric pH



$$pH = \frac{e. m. f. - 0.2805}{0.00019844 T}$$

Using this setup, it was possible to obtain duplicate values for the  $pH = 0.01$ .

### Titration of Primary Calcium Phosphate

To determine the amount of primary calcium phosphate in the sample, the material was titrated with 0.2 N sodium hydroxide to a definite hydrogen-ion concentration and the amount of titrating solution was compared with that necessary to reach the same pH in a sample that was pure primary calcium phosphate.

TABLE I. TITRATION OF PRIMARY CALCIUM PHOSPHATE WITH SODIUM HYDROXIDE

Indicator	0.2 N NaOH Cc.	pH, Colori- metric	pH, Electro- metric	Ca Remaining in Solution as Mg. of Ca- (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O
Bromophenol blue	15.0	3.8	3.63	202.24
	17.0	4.0	3.92	116.45
	18.0	4.2	4.11	70.11
	18.5	4.4	4.30	46.01
Methyl red	18.5	4.4		
	19.0	4.7	4.56	32.33
	19.5	4.9	4.83	16.79
	20.0	5.2	5.15	8.23
	20.5	5.5	5.46	...
Bromocresol purple	20.5	5.6		
	21.0	5.7	5.68	4.78
	21.5	5.8	5.79	...
	22.0	5.9	5.91	...
	22.5	6.1	5.97	1.44
	23.5	6.2	6.11	...
	25.5	6.4	6.37	...

The results are given in Table I. The second column gives the number of cubic centimeters of sodium hydroxide used, the third and fourth the pH determined by the two methods, and the last the total calcium in the solution calculated as milligrams of primary calcium phosphate. The titration curve obtained by the two methods is shown in Figure 1. There is a constant difference (average deviation 0.07 pH) between the pH determined by the two methods. This is probably due to the "salt effect" upon the indicators, giving pH values from the colorimetric method consistently higher than those obtained electrometrically. The residual calcium in the solution is shown in Figure 2, where the values

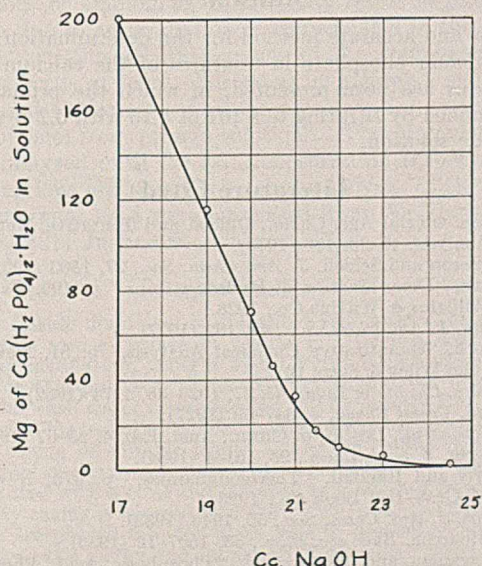


FIGURE 2. RESIDUAL CALCIUM IN SOLUTION DURING TITRATION OF PRIMARY CALCIUM PHOSPHATE

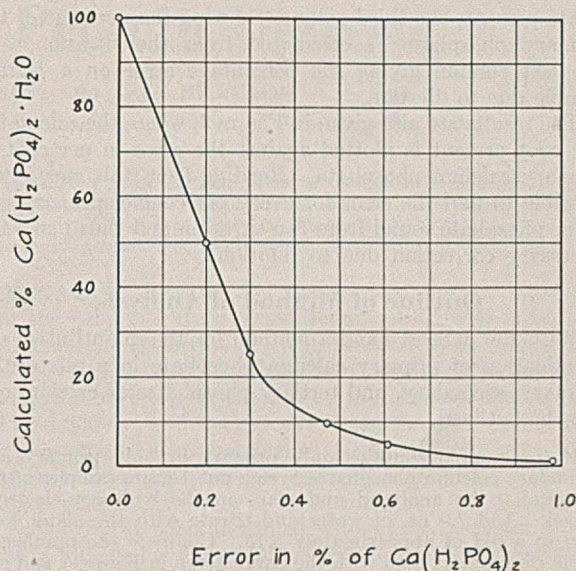


FIGURE 3. ERROR IN PER CENT OF PRIMARY CALCIUM PHOSPHATE

in the last column of Table I are plotted against the cubic centimeters of sodium hydroxide.

Almost any point on the curve in Figure 1 could be used as a so-called end point for the titration. The theoretical number of cubic centimeters, if the reaction took place in accordance with the following equation,



would be 19.83 cc. Some value near this point should be chosen as an end point, because the almost complete neutralization of the primary salt gives an unbuffered solution which shows a greater change in pH for a small addition of sodium hydroxide. At this point there is but a small amount of the primary calcium phosphate still in the solution (9.78 mg.).

In all further work the point on the curve represented by 20 cc. for a solution having a pH of 5.15 electrometrically and 5.2 colorimetrically was taken as the end point of titration.

In running a titration on an actual sample of less than 100 per cent of primary calcium phosphate, an error is introduced, due to the fact that 7.0 cc. of water are added to each sample. This increases the dilution of the primary calcium phosphate, so that the pH of the end point of titration will be reached before the equivalent amount of sodium hydroxide has been added. To determine the error introduced, different amounts of primary calcium phosphate were weighed out and dissolved in 7.0 cc. of water. These were then titrated with the sodium hydroxide, using the hydrogen-electrode titrating vessel, to a pH of 5.15.

TABLE II. ERROR IN TITRATION OF 1-GRAM SAMPLE OF PHOSPHATE

Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O Titrated Gram	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O Present %	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O Caled. from Titration %	Error for 1-Gram Sample %
1.0000	100	100.00	0.00
0.5000	50	49.80	0.20
0.2500	25	24.70	0.30
0.1000	10	9.53	0.47
0.0500	5	4.39	0.61
0.0200	2	1.01	0.99

The results are given in Table II, the first column giving the number of grams of primary calcium phosphate titrated, the second giving the actual per cent of primary calcium phos-



phate present, the third column showing the per cent of the primary phosphate as calculated from the titration, and the last column giving the percentage error on a 1-gram sample due to dilution.

The results are also given in Figure 3, where the calculated per cent present is plotted against the error in per cent of primary calcium phosphate. Reading from this curve it is possible to find the error for every per cent of primary calcium phosphate found from the titration and thus make the necessary correction due to dilution.

### Outline of Method of Analysis

With the data at hand a method for the quantitative determination of primary calcium phosphate in a mixture of primary, secondary, and tertiary phosphates of calcium can now be outlined.

If the sample contains only primary or only primary and secondary calcium phosphates, weigh out 1-gram samples of the material to be analyzed and place in the hydrogen-electrode vessel. Add 7.0 cc. of water and titrate with the alkali solution to a pH of approximately 5.15. Compare the number of cubic centimeters used with the curve given in Figure 1 and calculate the per cent of primary calcium phosphate present. To make the necessary correction for dilution, read from the curve in Figure 3 the amount to be added to the per cent calculated.

If, however, the sample is a mixture also containing tertiary calcium phosphate, the following method should be used:

Grind the sample to a very fine powder. The importance of thorough grinding cannot be too strongly emphasized, if accurate results are desired. Weigh out carefully two 1-gram portions of the sample, place one in the titrating vessel, add 7 cc. of distilled water, and then slowly 0.2 N sodium hydroxide until the solution has a pH of about 5.15. Note the volume of alkali used. Wash and dry the titrating vessel, add 7 cc. of water and the same amount of alkali as was used in the titration just completed, and in addition about 0.5 cc. more. To this alkali solution add the other 1-gram portion and stir thoroughly for a few minutes; this procedure is followed to prevent the primary salt from reacting with the tertiary. Determine the pH of the solution, remembering to stir it at intervals until the potentiometer reading remains constant after two consecutive stirrings.

The per cent of primary calcium phosphate present can be calculated as before.

As an alternative procedure, the pH may be determined colorimetrically, but because of inherent inaccuracies, the percentages of primary calcium phosphate are only reliable to  $\pm 0.20$  per cent.

To compare this work with other research along similar lines, the following calculations were made: The mass law equation for the second ionization constant of phosphoric acid may be written

$$\frac{(a_{H^+})(m_{(HPO_4^{--})}) \gamma_2}{(m_{H_2PO_4^-}) \gamma_1} = K_2 \quad (1)$$

and also in the following logarithmic form:

$$pH + \log \frac{m_{H_2PO_4^-}}{m_{HPO_4^{--}}} = pK - \log \frac{\gamma_1}{\gamma_2} \quad (2)$$

where  $pK$  is the negative logarithm of  $K_2$ .

To make use of Equation 2, first the total number of moles of phosphate ion and of calcium ion left in solution at the end point chosen were calculated, and were found to be (3.998) ( $10^{-3}$ ) and (3.263) ( $10^{-3}$ ), respectively. To find how the phosphate was distributed between the primary and secondary ions, Equation 2 was applied. The value of pH was taken from Table I, and  $pK$  was found from Nims' (11) value for the second ionization constant of phosphoric acid (6.226) ( $10^{-8}$ ). The ratio of the activity coefficients was calculated from the relationship given by Cohn (4)

$$\log \frac{\gamma_1}{\gamma_2} = \frac{1.5 \sqrt{\mu}}{1 + 1.65 \sqrt{\mu}}$$

where  $\mu$  is the ionic strength (10) of the solution. Since  $\mu$  is a function of the concentrations of the phosphate ions, a method of successive approximations was used to find the ratio desired. Starting with the assumption that  $\gamma_1 = \gamma_2$ , the second solution of Equation 2 gave the consistent values:

$$\frac{m_{H_2PO_4^-}}{m_{HPO_4^{--}}} = 50$$

$$\log \frac{\gamma_1}{\gamma_2} = 0.36$$

$$\mu = 0.1549$$

Using this ratio of molarities, there were found to be (3.92) ( $10^{-3}$ ) mole of primary phosphate ion and (7.84) ( $10^{-5}$ ) mole of the secondary. Based upon these figures and the assumption that only the four ionic species,  $Ca^{++}$ ,  $Na^+$ ,  $H_2PO_4^-$ , and  $HPO_4^{--}$  were present in significant quantities, it was found that (4.01) ( $10^{-3}$ ) mole of sodium ion was needed for electroneutrality. This compares well with the (4) ( $10^{-3}$ ) mole added.

### Analyses of Samples

Samples of known mixtures of the primary with the secondary and with the tertiary calcium phosphate were analyzed for the primary phosphate with the results given in Table III. The data show that with the electrometric method the results are accurate.

TABLE III. ANALYSES OF SAMPLES

Analyst	Ratio of Primary, Secondary, and Tertiary Calcium Phosphate	Ca( $H_2PO_4$ ) $_2$ ·H $_2$ O Present	Found
		%	%
C	8-2-0	80.00	79.98
K	8-2-0	80.00	79.93
K	7-3-0	70.00	69.93
K	6-4-0	60.00	59.92
C	6-4-0	60.00	59.96
C	4-6-0	40.00	39.94
K	8-0-2	80.00	80.06
K	7-0-3	70.00	69.97
K	6-0-4	60.00	60.06
K	6-2-2	60.00	60.13

### Summary

A new and accurate method for the determination of primary calcium phosphate in mixtures of the calcium orthophosphates has been presented, in which the primary salt is determined by titrating to a pH of 5.15 with 0.2 N sodium hydroxide solution.

### Literature Cited

- (1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 19-23, 186 (1933).
- (2) Cameron and Seidell, *J. Am. Chem. Soc.*, 27, 1503 (1905).
- (3) Clark, "Determination of Hydrogen Ions," p. 199, Baltimore, Williams & Wilkins Co., 1928.
- (4) Cohn, *J. Am. Chem. Soc.*, 49, 182 (1927).
- (5) Gooch, "Quantitative Chemical Analysis," p. 81, New York, John Wiley & Sons, 1912.
- (6) Graire, *Chimie & Industrie*, 27, 1023-36, 1274 (1932).
- (7) Herd, *Cereal Chem.*, 4, 347-69 (1927).
- (8) Jacob, et al., *IND. ENG. CHEM., Anal. Ed.*, 4, 25-37 (1932).
- (9) Lepper, *Z. anal. Chem.*, 98, 161-4 (1934).
- (10) Lewis and Randall, "Thermodynamics," p. 373, New York, McGraw-Hill Book Co., 1923.
- (11) Nims, *J. Am. Chem. Soc.*, 55, 1946 (1933).
- (12) Sanfourche, *Bull. soc. chim.*, 53, 1507-12 (1933).
- (13) Waggaman and Easterwood, "Phosphoric Acid, Phosphates, and Phosphatic Fertilizers," pp. 261-2, New York, Chemical Catalog Co., 1927.



# A Rapid Method for Protein Dialysis

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THE usual methods for removing inorganic ions from proteins in the final stage of purification are time-consuming and troublesome. If simple dialysis is employed, the time necessary for removal of the salt is extremely long. Collodion or Cellophane membranes suspended in large volumes of dialyzing solution may break, causing loss of the sample. According to Gortner (1), simple dialysis does not always remove the last traces of salts from colloids.

casing through the funnel. Protein solution is then placed inside the casing and distillation is begun. The wash solution returning to the still is tested at intervals for inorganic ions, and when only a faint test is obtained, distillation is stopped.

DISCUSSION. Because the casing need not be removed from the tube to empty its contents, mechanical injury to the membrane is obviated. The greatest hydrostatic pressure to which it is subjected is 20 cm. of water, the distance from the funnel top to the top of the casing. The casing will hold 600 cc., and the space between the filled casing and the glass tube has a volume of 50 to 100 cc. At a distillation rate of 1200 cc. per hour, the dialyzing water is changed completely every 3 to 5 minutes. The casing, if left in the Pyrex tube and filled with water to which a few drops of toluene have been added will keep in good condition for at least 2 months. In case the membrane is broken, the volume of the protein solution is increased only 50 to 100 cc.

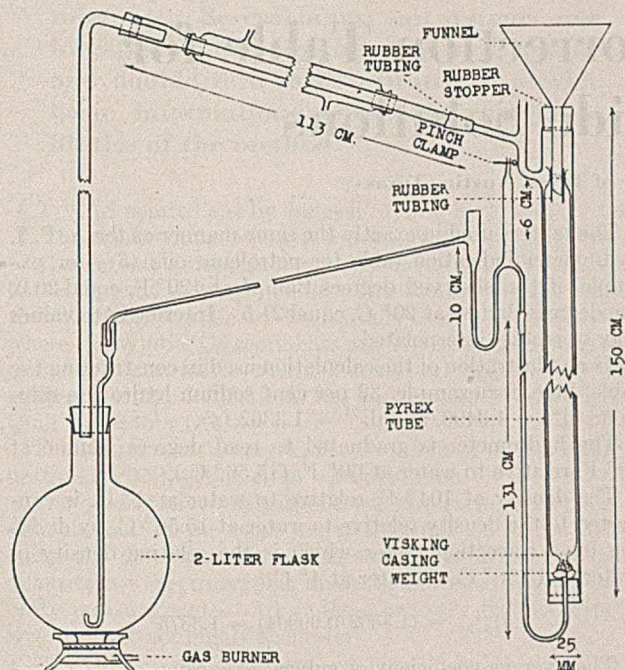


FIGURE 1. SIMPLE DIALYZER

Electrodialysis of protein solutions containing high concentrations of ammonium sulfate may result in acid denaturation due to accumulation of sulfuric acid in the protein solution. In this laboratory, use of the equipment made from materials at hand, illustrated in Figures 1 and 2, has been found to decrease the time necessary for complete removal of salts from protein solutions. The protein solution is first dialyzed until the salt concentration is low and the remaining ions are removed by electrodialysis. (The dialyzing membranes used were purchased from the Visking Corporation, 4311 Justine St., Chicago, Ill.)

## Simple Dialyzer

A 2.5 (inside diameter)  $\times$  150 cm. Pyrex glass tube is fitted with a side arm as shown in Figure 1. Distilled water is obtained by distillation, using a 2-liter Pyrex flask and glass condenser for this purpose. After passing around the protein solution, the wash water returns to the still by gravity flow. After being tested for leaks, a "1-inch" (actual diameter about 2.2 cm.) Visking casing of suitable length is tied by rubber bands to a funnel stem covered with rubber tubing. The lower end of the casing is tied with a cord and fastened to a 50-gram weight, and the empty casing is lowered into the Pyrex tube. About 100 cc. of water are poured into the glass tube to prevent strain on the membrane; the casing and funnel are filled with distilled water. The apparatus is connected to the still and distillation is started for the purpose of testing the operation of the apparatus and detecting possible leaks in the dialyzing membrane. By raising the lower end of the glass tube, the water is emptied from the

## Electrodialyzer

Platinum foil ( $8 \times 0.1 \times 130$  mm.) is inserted through two two-hole stoppers, size four, glass tubing is fitted as illustrated, and the stoppers are inserted into the round wooden cover. A cooling coil is bent from 6-mm. glass tubing. A jar of convenient size may be made from a gallon bottle. Two 2.2-cm.

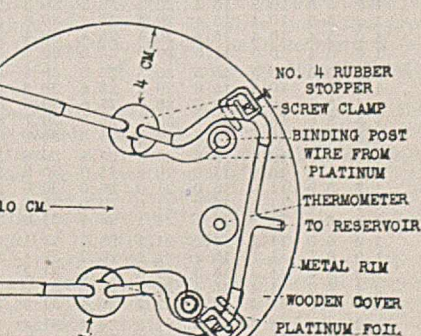
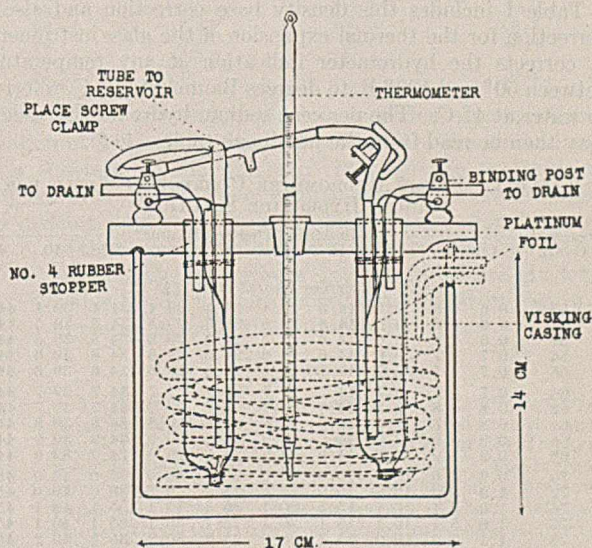


FIGURE 2. ELECTRODIALYZER



(1-inch) casings are tied separately, with cord, to each stopper to prevent leakage. The protein solution is placed in the jar and covered with toluene. A 110-volt potential drop is applied across the electrodes. Distilled water is circulated around each electrode at a rate of about 400 cc. an hour, and tap water is circulated through the cooling coil. Electrolysis is continued until tests for ions are negative.

As an additional check for the absence of ions, an ammeter and voltmeter are placed in the circuit. Conductivity of distilled water placed in the jar at the same level as the protein solution is tested, and the value obtained is compared with the conductivity of the protein solution.

### Experimental

An egg albumin solution (350 cc., containing 9 grams of ammonium sulfate and 35 grams of egg albumin) was dia-

lyzed for 14 hours in the simple dialysis apparatus described. The test for sulfate ion at the end of this time was faint. The volume of protein solution had increased to 600 cc. This solution, after 48 hours of continuous electro dialysis, had the same conductivity as the distilled water circulated through the apparatus. The final volume of the solution was 640 cc.

### Literature Cited

- (1) Gortner, R. A., "Outlines of Biochemistry," p. 75, New York, John Wiley & Sons, 1929.

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# Baumé Hydrometer Correction Table for Sodium Hydroxide Solutions

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THE table is a convenience in determining the concentration of sodium hydroxide solutions by means of the Baumé hydrometer for heavy liquids. The readily available hydrometer tables for sodium hydroxide solutions give the concentrations versus degrees Baumé at 20° C. referred to water at 4° C. (1, 2). However, the common Baumé hydrometers are graduated at 60° F. relative to water at 60° F.

Table I includes this density base correction and also a correction for the thermal expansion of the glass instrument. It corrects the hydrometer indication at any temperature between 50° and 130° F. to degrees Baumé at 20° C. referred to water at 4° C. The per cent sodium hydroxide by weight may then be read from the handbook tables (1, 2).

TABLE I. BAUMÉ HYDROMETER CORRECTION TABLE FOR SODIUM HYDROXIDE SOLUTIONS

Observed Temp. ° F.	Indicated Degrees Baumé <sup>a</sup>									
	1	5	10	15	20	25	30	35	40	45
	Degrees Baumé at 20°/4° C.									
50	0.6	4.5	9.5	14.5	19.4	24.4	29.4	34.4	39.4	44.4
52	0.6	4.6	9.6	14.5	19.5	24.5	29.5	34.5	39.5	44.5
54	0.6	4.6	9.6	14.6	19.5	24.5	29.5	34.5	39.5	44.5
56	0.7	4.7	9.6	14.6	19.6	24.6	29.6	34.6	39.6	44.6
58	0.7	4.7	9.7	14.7	19.6	24.6	29.6	34.6	39.6	44.6
60	0.7	4.7	9.7	14.7	19.7	24.7	29.7	34.7	39.7	44.7
62	0.8	4.8	9.8	14.8	19.7	24.7	29.7	34.7	39.7	44.7
64	0.8	4.8	9.8	14.8	19.8	24.8	29.8	34.8	39.8	44.8
66	0.9	4.9	9.9	14.9	19.9	24.9	29.9	34.9	39.9	44.9
68	0.9	4.9	9.9	14.9	19.9	24.9	29.9	34.9	39.9	44.9
70	0.9	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0
72	1.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0
74	1.0	5.1	10.1	15.1	20.1	25.1	30.1	35.1	40.1	45.1
76	1.0	5.1	10.1	15.1	20.1	25.1	30.1	35.1	40.1	45.1
78	1.1	5.2	10.2	15.2	20.2	25.2	30.2	35.2	40.2	45.2
80	1.1	5.2	10.3	15.3	20.2	25.2	30.2	35.2	40.2	45.2
82	1.2	5.3	10.3	15.3	20.3	25.3	30.3	35.3	40.3	45.3
84	1.2	5.3	10.4	15.4	20.4	25.4	30.3	35.3	40.3	45.3
86	1.2	5.4	10.4	15.4	20.4	25.4	30.4	35.4	40.4	45.4
88	1.3	5.4	10.5	15.5	20.5	25.5	30.4	35.4	40.4	45.4
90	1.3	5.5	10.5	15.5	20.5	25.5	30.5	35.5	40.5	45.5
92	1.4	5.5	10.6	15.6	20.6	25.6	30.5	35.5	40.5	45.5
94	1.4	5.6	10.7	15.7	20.7	25.6	30.6	35.6	40.6	45.6
96	1.5	5.6	10.7	15.7	20.7	25.7	30.7	35.6	40.6	45.6
98	1.5	5.7	10.8	15.8	20.8	25.8	30.7	35.7	40.7	45.7
100	1.6	5.7	10.8	15.8	20.8	25.8	30.8	35.7	40.7	45.7
102	1.6	5.8	10.9	15.9	20.9	25.9	30.8	35.8	40.8	45.8
104	1.7	5.9	11.0	16.0	21.0	26.0	30.9	35.8	40.8	45.8
106	1.7	5.9	11.0	16.0	21.0	26.0	31.0	35.9	40.9	45.9
108	1.8	6.0	11.1	16.1	21.1	26.1	31.0	36.0	41.0	45.9
110	1.9	6.0	11.2	16.2	21.2	26.1	31.1	36.0	41.0	46.0
112	1.9	6.1	11.2	16.2	21.2	26.2	31.1	36.1	41.1	46.0
114	2.0	6.2	11.3	16.3	21.3	26.2	31.2	36.1	41.1	46.1
116	2.1	6.2	11.4	16.4	21.3	26.3	31.2	36.2	41.2	46.1
118	2.1	6.3	11.4	16.4	21.4	26.4	31.3	36.3	41.2	46.2
120	2.2	6.4	11.5	16.5	21.5	26.4	31.4	36.3	41.3	46.2
122	2.3	6.4	11.6	16.6	21.5	26.5	31.4	36.4	41.3	46.3
124	2.3	6.5	11.6	16.7	21.6	26.5	31.5	36.4	41.4	46.3
126	2.4	6.6	11.7	16.7	21.7	26.6	31.5	36.5	41.4	46.4
128	2.5	6.7	11.8	16.8	21.7	26.7	31.6	36.5	41.5	46.4
130	2.5	6.7	11.9	16.9	21.8	26.7	31.7	36.6	41.5	46.5

<sup>a</sup> Using hydrometer correct at 60°/60° F.

The table is used in exactly the same manner as the A. P. I. hydrometer indication table for petroleum oils (3)—for example, if the observed degrees Baumé at 120° F. equal 20.0, the degrees Baumé at 20° C. equal 21.5. Intermediate values may be readily interpolated.

As an illustration of the calculation used in constructing the table, take, for example, 32 per cent sodium hydroxide solution:  $d_4^{20} = 1.3490$ , and  $d_{15.56}^{104} = 1.3362$  (4).

The hydrometer is graduated to read degrees Baumé at 60° F. relative to water at 60° F. (15.56° C.).

The density at 104° F. relative to water at 4° C. is converted to the density relative to water at 15.56° C. by dividing by a correction factor which is the relative density of water at 15.56° C. to water at 4° C.

$$d_{15.56}^{104} = (1.3362/0.99904) = 1.3375$$

The average coefficient of cubical expansion of glass used for volumetric instruments is  $25 \times 10^{-6}$  per ° C. or  $(25/1.8) \times 10^{-6}$  per ° F.

The volume of the hydrometer at 104° F. relative to its volume at 60° F. is

$$1 + (25/1.8) (10^{-6}) (104 - 60) = 1.000611$$

The "apparent" or indicated density of the solution at 104° F. is then  $(1.3375) (1.000611) = 1.3384$ , or 36.66° Baumé according to the conversion formula.

The density in degrees Baumé of the 32 per cent solution at 20° C. referred to water at 4° C. taken from the handbook is 37.5. Referring to the table, it is found that a hydrometer indication of 35.0° at 104° F. is 35.8° corrected. Adding the 1.7° which were dropped in order to use the closest column of the table, 36.7° Baumé indicated at 104° F. are 37.5° Baumé at 20° C., referred to water at 4° C.

### Literature Cited

- (1) Hodgman, C. D., "Handbook of Chemistry and Physics," 21st ed., p. 1120, Cleveland, Ohio, Chemical Rubber Publishing Co., 1936.
- (2) Lange, N. A., "Handbook of Chemistry," p. 870, Sandusky, Ohio, Handbook Publishers, Inc., 1934.
- (3) Nat. Bur. Standards, *Circ. C-410*, 6 (1936).
- (4) Perry, J. H., "Chemical Engineers' Handbook," 1st ed., p. 370, New York, McGraw-Hill Book Co., 1934.

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# The Rare Earth Metals and Their Compounds

## Thermal Analysis of Rare Earth Nitrate Mixtures

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A method of analysis is proposed which utilizes the characteristic melting points of the hydrated salts and the liquidus curves of the binary salt mixtures for the estimation of the composition of rare earth mixtures. Several binary salt systems were investigated, employing very pure simple and double rare earth nitrates to provide basic information concerning the possibilities of the method.

IT WAS pointed out by Jantsch (3) and by Friend (2) that the double magnesium nitrates and the simple nitrates of the cerium group rare earth elements exhibit relatively low congruent melting points. The double nitrates correspond in composition to the formula  $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$ , where the symbol Ce represents any one of the cerium group elements. Conclusive thermal analytical evidence for the existence of the double salts has been presented recently by Quill and Robey (4).

The simple nitrates crystallize in the form of the hexahydrate,  $Ce(NO_3)_3 \cdot 6H_2O$ , from water solution.

The quantitative analysis of most rare earth mixtures is a difficult matter, the most important methods in use today being the determination of the average equivalent weight, quantitative spectrographic analysis, and magnetic susceptibility measurements. All of these are very tedious, expensive, and yet not highly accurate.

sible because (1) a true solid solution results upon the mixing of corresponding rare earth salts and (2) knowledge of the behavior of solid solutions in general permits the conclusion that the melting temperatures of these mixtures are related in a simple fashion to their compositions.

The determination of the position of the liquidus curve of a binary rare earth salt system would yield the melting temperatures of all possible binary mixtures. Conversely, if the melting temperature of a mixture were determined, reference to the liquidus curve would yield the composition of the mixture. A thermal analytical method employing simple apparatus might be used in a very direct fashion to analyze rare earth mixtures and to follow the progress of separation of the rare earth elements in a fractional crystallization series.

TABLE I. CRYSTALLIZATION TEMPERATURES OF THE RARE EARTH AND BISMUTH MAGNESIUM DOUBLE NITRATES

Atomic Number	Element	Temperature	
		Jantsch (3) ° C.	This investigation ° C. (4)
57	La	113.5	113.5
58	Ce	111.5	112.0
59	Pr	111.2	
60	Nd	109.0	108.8
62	Sm	96.2	92.0
64	Gd	77.5	
83	Bi	...	70.8

In a method of analysis which is dependent upon an interpolation of a liquidus curve, the precision of the method will be a function of the difference between the crystallizing temperatures of the pure component salts. Accordingly, the melting points of the pure double magnesium nitrates of the cerium group elements as determined by Jantsch (3) and by the authors' investigations are given in Table I. The values have been plotted in Figure 1 against the respective atomic numbers.

### Experimental

**MATERIALS.** The samarium and neodymium materials employed in this investigation were prepared from the pure oxides kindly lent by B. Smith Hopkins of the Department of Chemistry, University of Illinois. The lanthanum nitrate was prepared as described in a previous paper (4). The arc emission spectra of these materials showed them to be free from foreign rare earth elements.

The cerium material was derived from the G. F. Smith Chemical Company's pure analytical ceric sulfate reagent. The cerium was purified by three successive precipitations by the well-known basic bromate method (a process described in all textbooks on the rare earth elements).

Ultimately the cerium was precipitated as the oxalate, the oxalate digested with concentrated nitric acid on the steam bath, the solution evaporated to a sirup and taken up in water containing a little hydrogen peroxide. The absorption and the arc emission spectra showed that no rare earth elements other than cerium composed the resulting material.

Baker's magnesium oxide of best purity with an unusually low calcium content was used in the preparation of the double magnesium salts. The magnesium and rare earth materials were dissolved in Grasselli's "chemically pure" nitric acid in the ratio of three to two gram-atomic weights, respectively, and the double nitrate was made to crystallize from the solution. A chemically pure grade of Baker's bismuth nitrate pentahydrate was employed for the preparation of the bismuth double salt.

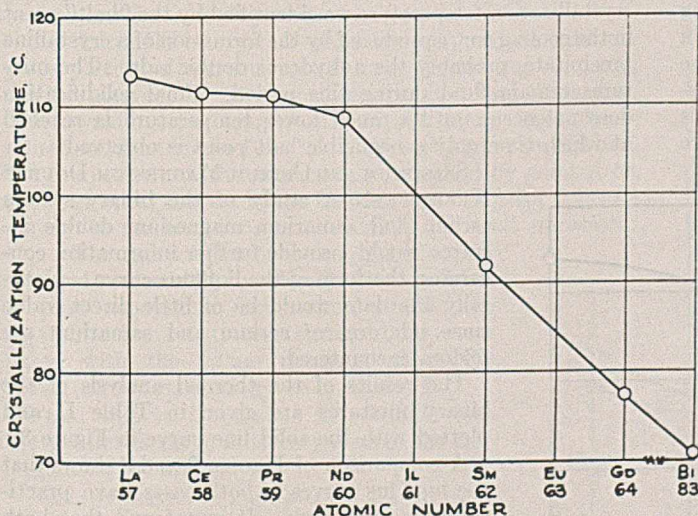


FIGURE 1. VARIATION OF CRYSTALLIZATION TEMPERATURES (MELTING POINTS) OF CERIUM GROUP MAGNESIUM DOUBLE NITRATES WITH ATOMIC NUMBER

Since the melting points are so characteristic for the various rare earth simple and double nitrates, it seems likely that the determination of the melting temperatures of rare earth nitrate mixtures might be a means to the quantitative estimation of the composition of the mixtures. This is pos-



The rare earth simple nitrates were crystallized from the nitric acid solution of the oxide, except cerium, in which case the oxalate dissolved. The resulting nitrate crystals were dissolved in water and recrystallized from water solution two or three times. All of the prepared salts were dried over 55 per cent sulfuric acid solution in a desiccator before use.

**PROCEDURE.** Simple apparatus suffices for the thermal analysis of the low melting salts and their mixtures. The experimental method was that used by other investigators (1) with low melting salts. Briefly, it consisted of heating the prepared mixtures in Pyrex glass test tubes inserted in a well-stirred oil bath to a temperature somewhat above their melting temperatures. The constantly stirred mixtures were then permitted to cool, the rate of cooling being determined by means of a thermometer. The thermometer was comparatively calibrated with a Bureau of Standards certified instrument. The temperature difference between the mixtures and bath was always kept as small as possible.

### Binary System

**SAMARIUM AND BISMUTH MAGNESIUM DOUBLE NITRATES.** Bismuth magnesium double nitrate is isomorphous in the crystalline state with the cerium group rare earth magnesium double nitrates. The double magnesium nitrates are salts which are employed largely in the separations of the cerium group elements by means of systematic fractional crystallization.

Urbain's modification of the usual methods of fractional crystallization consists in adding to the series a bismuth salt corresponding to the salt in crystallization. Since the salt possesses an intermediate solubility, it greatly aids the separation of the binary mixtures of samarium and europium which otherwise separate only slowly. Bismuth thus acts as a separating element. It is also a good separating element because it can be easily removed after use.

In adding bismuth magnesium nitrate to a series containing samarium magnesium double nitrate it is evident that certain fractions after repeated fractional crystallization will become binary solid solutions of the bismuth salt in samarium magnesium double nitrate. The results of the thermal analysis of a series of these binary mixtures of known composition are

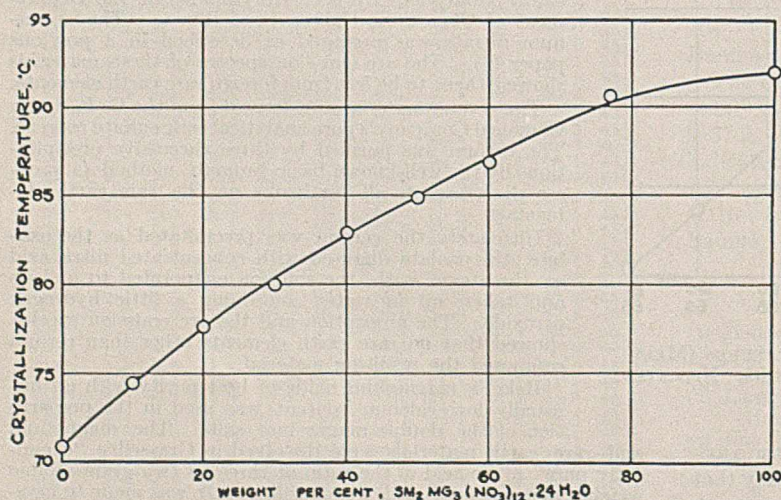


FIGURE 2. LIQUIDUS CURVE OF SYSTEM BISMUTH AND SAMARIUM MAGNESIUM DOUBLE NITRATES

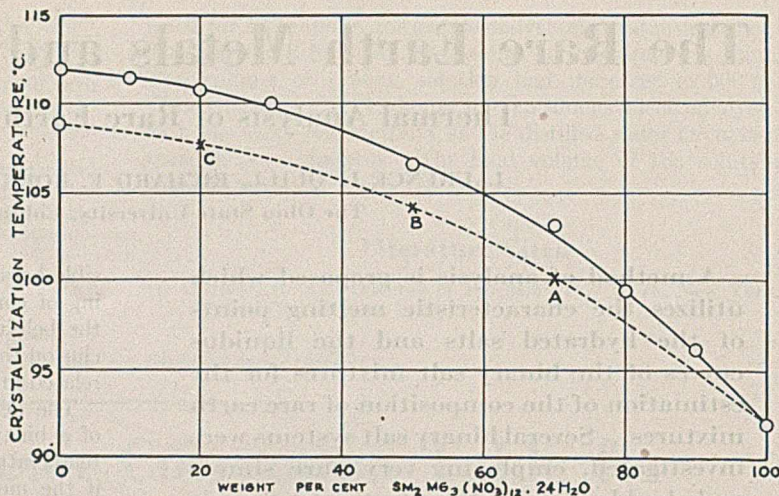


FIGURE 3. LIQUIDUS CURVES  
Solid line, cerous and samarium magnesium double nitrates. Broken line, neodymium and samarium magnesium double nitrates

given in Table II, which has been derived from time-differential temperature cooling curves of the various mixtures, and are plotted in Figure 2.

TABLE II. CRYSTALLIZATION TEMPERATURES OF BINARY SYSTEMS

Bismuth and Samarium Magnesium Double Nitrates		Cerous and Samarium Magnesium Double Nitrates	
Samarium double salt Weight per cent	Temperature ° C.	Samarium double salt Weight per cent	Temperature ° C.
100.0	92.0	100.0	92.0
78.8	90.9	90.0	96.1
60.0	87.0	80.0	99.5
50.0	85.0	70.0	103.2
40.0	83.0	50.0	106.2
30.0	80.0	30.0	110.0
20.0	77.7	20.0	110.8
10.0	74.5	10.0	111.5
0.0	70.8	0.0	112.0

Slight losses of water were noted, especially among the higher melting mixtures on repeated determination. The crystallization temperature was identified by the "halt" point in the cooling curve produced by the formation of a crystalline precipitate, probably the anhydrous double salt. The mixtures remain fluid during this period. Final solidification does not occur until a much lower temperature is reached at which time only a negligible halt point is observed.

**SAMARIUM AND CERIUM MAGNESIUM DOUBLE NITRATES.** A study of the binary system cerium and samarium magnesium double nitrates would provide further information concerning the form of the liquidus curve. Naturally the data would be of little direct value since mixtures of cerium and samarium are seldom encountered.

The results of the thermal analysis of the binary mixtures are given in Table II and plotted with the solid line curve in Figure 3.

A comparison of Figures 2 and 3 shows that the liquidus curves in both cases have practically the same form. It was found that both curves can be expressed approximately by the same mathematical equation. The composition of a mixture is related to the crystallizing temperature of the mixture by the equation

$$P = 50 [(f^2 - 4F)^{1/2} - f]$$

where  $P$  is the weight per cent composition of the mixture



$$f = \left[ \frac{d^3 - 32d^2 - 63d - 16}{16} \right]$$

$$F = D^2 + \left[ \frac{63 + 16d - d^2}{16} \right] D$$

$d$  = the difference in degrees between the crystallizing temperatures of the two pure components, and  
 $D$  = the difference in degrees between the crystallizing temperature of the mixture and that of the lower melting component

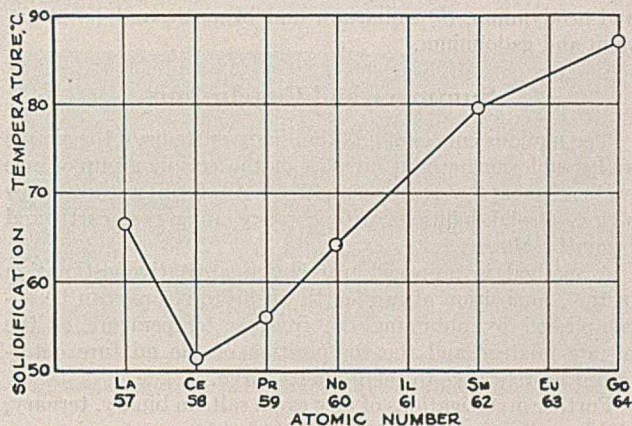


FIGURE 4. VARIATION OF SOLIDIFICATION TEMPERATURES (MELTING POINTS) OF HEXAHYDRATED CERIUM GROUP NITRATES WITH ATOMIC NUMBER

It is not unreasonable to assume that this empirical equation would be valid also for the liquidus curves of the other closely related rare earth double nitrate systems which possess a similar value of  $d$ ; and that curves derived from this empirical equation might be used for the analysis of binary mixtures.

To test the validity of this method of analysis the composition of an "unknown" mixture was determined as follows:

1. The derived liquidus curve of the binary system neodymium and samarium magnesium double nitrates was plotted according to the above equation. It is given as the broken line curve in Figure 3.

2. A sample of crystals was removed from an intermediate portion of a fractionation series containing the mixed double magnesium nitrates of neodymium and samarium. The crystallization temperature of the sample was determined and found to be 100.0°. If the curve is the correct one, the composition of the mixture is represented by point A on the theoretical curve and the fraction is composed of approximately 30 per cent neodymium and 70 per cent samarium.

3. The composition of the sample was then changed successively by adding known weights of pure neodymium magnesium nitrate, the crystallization points redetermined and compared with the values predicted from the curve. The results are given in Table III.

From this it is possible to conclude that the predicted curve falls very near to the true liquidus of the system.

HEXAHYDRATED CERIOUS AND LANTHANUM NITRATES AND HEXAHYDRATED CERIOUS AND NEODYMIUM NITRATES. The simple nitrates also are amenable to study in binary systems with the view to employing the data for analyzing mixtures. The easily separable element, cerium, has been chosen as one constituent for the mixtures.

The melting points of the pure simple hexahydrated nitrates as determined recently by

TABLE III. CRYSTALLIZATION TEMPERATURES

Point	Composition	Crystallization Temperature Predicted ° C.	Crystallization Temperature Observed ° C.
A	30 per cent Sm salt Changed to	...	100.0
B	50.0 per cent Sm salt Changed to	104.2	104.0
C	20.0 per cent Sm salt	107.4	107.2

TABLE IV. SOLIDIFICATION TEMPERATURES OF THE CERIUM GROUP SIMPLE HEXAHYDRATED NITRATES

Atomic Number	Element	Friend (2) ° C.	Temperature This investigation ° C.
57	La	65.4	66.5
58	Ce	...	51.4
59	Pr	56.0	...
60	Nd	67.5	64.1
62	Sm	...	79.5
64	Gd (98%)	...	87.0

TABLE V. SOLIDIFICATION TEMPERATURES OF BINARY SYSTEMS

Hexahydrated Lanthanum and Cerous Nitrates		Hexahydrated Neodymium and Cerous Nitrates	
Hexahydrated lanthanum nitrate Weight per cent	Temperature ° C.	Hexahydrated neodymium nitrate Weight per cent	Temperature ° C.
100.0	66.5	100.0	64.1
90.0	63.5	90.0	62.8
80.0	63.0	80.0	62.0
70.0	61.9	70.0	60.0
60.0	60.0	60.0	58.0
50.0	58.4	50.0	56.0
40.0	57.5	40.0	53.8
30.0	56.4	30.0	53.5
20.0	55.0	20.0	53.0
10.0	53.7	10.0	51.8
0.0	51.4	0.0	51.4

Friend (2) and by the authors are given in Table IV. These values have been plotted against the respective atomic numbers in Figure 4.

The value of the solidification temperature of the gadolinium nitrate should be taken only as indicative of trend, since the perfectly white salt was labeled 98 per cent pure as purchased from the A. D. Mackay Company.

In observing the cooling curves of the molten hexahydrated nitrates, a slight halt is noted when a slight cloudiness makes its appearance. It is probably due to a lower hydrate. The major halt point, unlike the double magnesium nitrates, is found at the point of apparently complete solidification.

The solidification temperatures for the binary systems hexahydrated lanthanum and cerous nitrates and hexahydrated neodymium and cerous nitrates are given in Table V. The liquidus curves have been plotted in Figure 5. Both liquidus curves are very roughly linear between the points

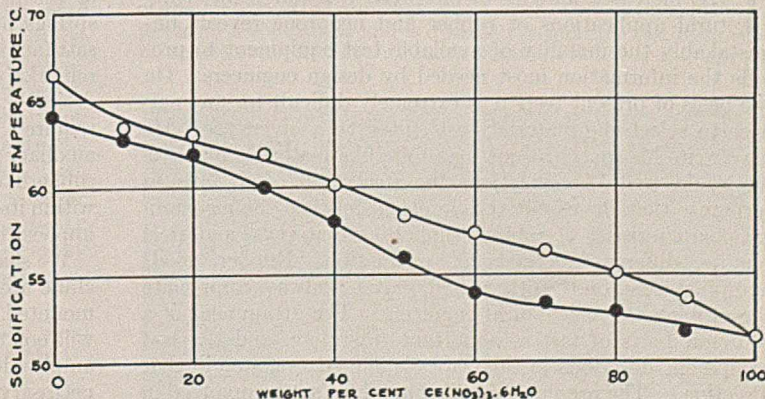


FIGURE 5. LIQUIDUS CURVES

○, hexahydrated lanthanum and cerous nitrates. ●, hexahydrated neodymium and cerous nitrates



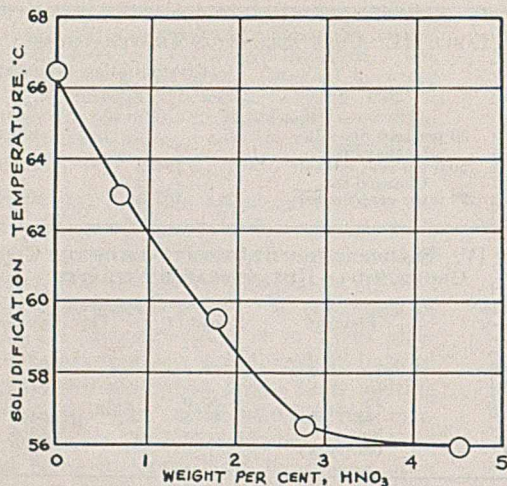


FIGURE 6. EFFECT OF NITRIC ACID ON SOLIDIFICATION TEMPERATURE OF HEXAHYDRATED LANTHANUM NITRATE

representing the pure components. The irregular features of the curves are probably due to the effect of the formation of ceric cerium by autoxidation of the cerous nitrate at the elevated temperature. The colorless cerous salt and colorless mixtures containing the salt retained a slightly yellowish cast after heating. Titration of the ceric cerium thus formed by standard ferrous solution, using orthophenanthroline ferrous complex indicator in dilute sulfuric acid solution, showed that the ceric concentration never exceeded 1 per cent.

The necessity of obtaining the crystallized hexahydrated nitrates free from small amounts of residual impurities, such as nitric acid, is emphasized by the data plotted in Figure 6. Less than 1 per cent of the acid lowers the solidification point several degrees.

An inspection of Figures 2 and 4 reveals that the following frequently associated pairs of simple nitrates and double magnesium nitrates possess crystallization temperatures sufficiently far apart to be useful in analysis through their binary liquidus curves: mixtures of the hexahydrated nitrates of (a) lanthanum and cerium, (b) lanthanum and praseodymium, (c) praseodymium and neodymium, (d) cerium and neodymium, and (e) neodymium and samarium, and mixtures of the double magnesium nitrates of (a) samarium and neodymium, (b) samarium and bismuth, and (c) samarium and gadolinium.

### Summary and Conclusions

The liquidus curves of certain binary systems of the simple and double magnesium nitrates of the cerium group of rare earth elements were investigated. All form a continuous series of solid solutions with corresponding rare earth and bismuth salts.

A method is proposed whereby quantitative estimation of the composition of rare earth nitrate mixtures can be accomplished by obtaining the freezing temperature of the nitrate mixture and the composition of the mixture determined by reference to the liquidus curve.

Further investigations of rare earth salts in binary, ternary, and even quaternary systems are obviously necessary in order to realize the full value of the method.

### Literature Cited

- (1) Ewing, W. W., Brandner, J. D., Slichter, C. B., and Griesinger, W. K., *J. Am. Chem. Soc.*, **55**, 4822 (1933).
- (2) Friend, J. N., *J. Chem. Soc.*, **1935**, 824, 1430.
- (3) Jantsch, G., *Z. anorg. Chem.*, **76**, 303 (1912).
- (4) Quill, L. L., and Robey, R. F., *J. Am. Chem. Soc.*, **59**, 1071 (1937).

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## The Evaluation of Rubber and Rubberlike Compositions as Vibration Absorbers

### Apparatus for Automatic Recording

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THE increased amount of information required for structural applications of rubber and neoprene reveals unmistakably the inability of available test equipment to provide the information most needed by design engineers. On the basis of present tests it is extremely difficult for an engineer to select the material best suited to a given use. He may write his specifications for rubberlike materials such as he would write specifications for steel, and often fails to recognize that the essential differences between the mechanical characteristics of rubber, rubberlike materials, and steel require different methods of evaluation. Rubber goods manufacturers, on the other hand, may not always appreciate the problems of mechanical engineers. The attainment of a common basis of test is important, therefore, and the test equipment described in this paper is offered as a step in that direction. The present paper is limited to factors involved in the evaluation of rubber and rubberlike compositions as vibration absorbers.

It is necessary at the outset to have a clear understanding

of the field of application for rubber mountings. Metallic springs have been used for mountings for many years and satisfactorily meet many needs. They possess resilience to a remarkable extent, which under certain conditions is highly desirable, but where oscillation must be absorbed they usually require a shock absorber of one of the conventional types as auxiliary apparatus. The peculiar virtue of rubber or a rubberlike composition as a mounting material is that it has within itself the ability to damp out vibration. This damping implies the conversion of mechanical energy into heat.

We shall assume that the characteristics of a vibrating machine are thoroughly known and that this machine is to be mounted on a framework in such a way that excessive shocks will not be transmitted to the frame, and oscillations of high amplitude will be prevented. To meet the first condition it is necessary to provide a composition of the proper modulus, which will extend the time element in shock sufficiently to reduce considerably the force transmitted.

To meet the second condition it is necessary to consider the



critical speeds of the complete assembly. We will assume that by selecting material with a sufficiently low modulus the critical speeds will be kept low. This simplifies the problem by reducing the required energy absorption to oscillations at low frequencies, a condition naturally favorable to the durability of the vibration-damping composition. At critical frequencies every impulse serves to increase the amplitude of oscillation of the machine; hence, it is at critical frequencies that the vibration damper must absorb the maximum amount of energy.

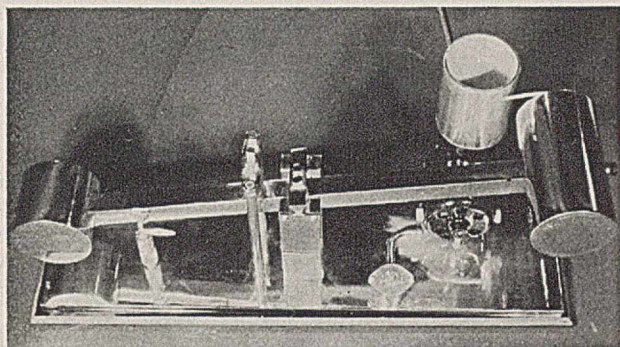


FIGURE 1

No composition for mechanical mountings will be satisfactory unless throughout its life it maintains its original elastic characteristics and form to a reasonable degree. For example, it is desirable that the characteristics of a vibration damper remain reasonably fixed over a wide range of temperatures. However, the art of compounding does not yet appear to have reached the goal where no changes in modulus and damping characteristics occur with changes in temperature. Since complete elimination of temperature dependence is not possible, a suitable tolerance must be allowed in the original plans.

Tolerance must also be allowed for change in form. Obviously a thermoplastic material is not suitable; yet all rubber and rubberlike materials will show a certain amount of permanent deformation under the influence of the dead load. Thus, some slight drift must be expected and in almost all instances can be allowed for in design.

Other factors affecting permanence are principally resistance to oxidation, fatigue, excessive heat build-up, and deterioration in oils or active chemicals. In considering mechanical fatigue it is obvious that a stock cannot be used beyond a certain allowable stress. This limits not only the original applied load but also involves the extent of motion in vibration. The intensity of the load is related to the question of permanent set, structural disintegration upon repeated working, and extent of heat build-up. The temperature rise during the use of a vibration damper must not be excessive. The limitations of temperature rise are dictated by the resistance of the stock to progressive cure and to deterioration when exposed to air, ozone, and solvents. Oil resistance can be eliminated as a factor by special features of design, which shield the stock from contact with lubricants, but the necessity of shielding from the lubricants may so restrict the design as to limit its suitability. For that reason, there are many instances requiring a stock which is itself inherently oil-resistant.

Mechanical tests must reveal several characteristics. It is necessary to know the static stress-compression characteristics of a proposed vibration absorber. This characteristic determines the allowable load per unit area and is a primary factor in the appearance of drift under a dead load over long periods of time. The test should also reveal the dynamic

modulus of the stock as a quality definitely distinguished from static modulus. It is true that the static and dynamic moduli will be very nearly the same if the stock is highly resilient, but high hysteresis causes a difference to appear between the two. Since the dynamic modulus should be considered in properly relating the design of a motor mounting to the frequency characteristics of the motor, the necessity of properly evaluating it should not be overlooked.

The rate of absorption of energy is important. This is the damping feature of the mounting, and since it is a significant factor in choosing rubber, for example, in preference to steel springs, a ready means for its evaluation is extremely important.

Another factor very important in design is the knowledge of the deflections which will result from the application of a given shock load. Although it is possible to calculate the permissible dead load from the static characteristics and to limit the drift by keeping this below certain limits, the question of allowable deformation must be dealt with as a dynamic consideration. Here again hysteresis characteristics and static modulus determine the dynamic hardness. The term "dynamic hardness" is used in this paper to represent the dynamic relationship between impact load and deflection. Thus, a stock with high hysteresis and a given static modulus shows a greater dynamic hardness than a stock with the same static modulus and low hysteresis.

The rapid measure of drift occurring in the first minute of loading may be an indication of the drift to be expected over a more extended period of time, but this does not necessarily follow. However, drift over one period of time is of interest and such data can at times be an indication of trends which are undesirable. It is necessary to distinguish clearly between the sluggish action which characterizes a high hysteresis stock and the definite plastic flow which is characteristic of undercured rubber or rubberlike materials and thermoplastic materials.

## Apparatus

The apparatus which is described in this paper combines measurements hitherto not accessible from simple apparatus, and is a means of evaluating rubber and rubberlike compositions both statically and dynamically. Figures 1 and 2 illustrate the construction.

The machine consists of an unbalanced lever with a 20-pound weight on one end and a 10-pound weight on the other, pivoted on a knife edge at the midpoint of its length. The test piece is a small rubber cylinder 0.75 inch in diameter and 0.5 inch high. During the test this is compressed between a stationary horizontal surface and the upper surface of the unbalanced lever in such a position that the compression of the test specimen resists the tendency of the 20-pound weight to fall. Thus, if the heavy end of the lever is lifted and then released, the test specimen is subjected to a shock load and is distorted beyond the static equilibrium position. In this way an oscillating system is established

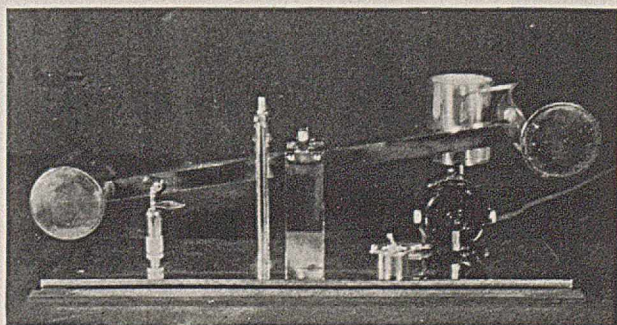


FIGURE 2



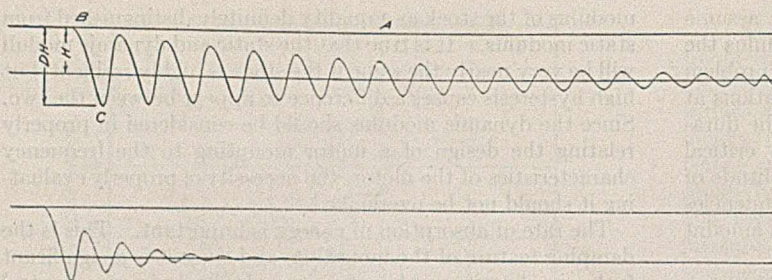


FIGURE 3. ACTUAL TEST RESULTS

and the 20-pound weight rises and falls while the test specimen goes through various degrees of compression. Each oscillation is smaller than the previous one, owing to the internal friction or mechanical hysteresis of the test piece, and eventually the lever comes to rest. A hook shown in the left foreground of Figures 1 and 2 secures the weight initially in a definite position and is adjustable in height. By releasing the hook, the weight falls from a predetermined height, and the energy input is determined by multiplying the height through which the 20-pound weight falls by the number of pounds of unbalanced weight.

A pen mounted on the heavy end of the lever traces a record on a revolving drum which is driven by a synchronous motor. Thus, the amplitude and frequency of the oscillations can be permanently preserved for analysis.

Figure 3 (upper) is an actual test result obtained from a fairly resilient composition. Line A is the zero reference made by lowering the pen to the surface of the drum and allowing the drum to rotate through one revolution with the pen in a stationary position. On the second revolution the heavy end of the lever is released at point B. Point C represents maximum compression of the pellet, and the distance from C to the line A is a measure of dynamic hardness. The line BC is a graphic indication of the response of the test specimen to an impact load. Subsequent oscillations indicate the rate at which the impact is absorbed. If successive amplitudes rapidly diminish, the composition is one which will not

readily support vibration at critical frequencies. The rapidity with which the oscillation record crosses the time axis is an indication of frequency and is related to the value of the dynamic modulus under the given test conditions.

Figure 3 (lower) is an actual test result obtained from a composition with much lower resilience.

If a stock has a tendency to drift under a dead load, this can readily be detected by allowing the drum to rotate through two or three revolutions when the lever is resting in its static equilibrium position. Qualitative information of this sort may often be useful.

### Applicability

To illustrate the applicability of the test to the evaluations of a variety of compounds, static and dynamic characteristics of six rubber and neoprene compositions (Table I) are given. Shore durometer hardness is also given to provide a rough basis of comparison with present test methods (Table II).

Dynamic hardness, static hardness, and the amplitude of the sixth rebound are given in arbitrary units of hundredths of an inch as measured on the autographic record. The ratio of the amplitude of the sixth rebound to the original elevation of the 20-pound weight is arbitrarily taken as the figure for the resilience of the stock.

There is no reliable correlation between shore durometer hardness and dynamic hardness as evaluated by this test. The durometer makes a surface test, whereas the apparatus described herein makes a volume test, which is obviously in closer agreement with the loading to which a motor mounting is subjected.

Compounds 3 and 4 have approximately the same static hardness. Compound 4, however, shows noticeably greater hysteresis since the resilience is lower. This factor contributes to the lower measured dynamic hardness of 128 as compared with 138 for compound 3. Compounds 1 and 2 are rubber stocks having high hysteresis and are presented to show the differences in hardness revealed by this test both dynamically and statically. Compounds 5 and 6 are neoprene stocks.

The machine can be designed for use either in an oven or a refrigerator by mounting the recording mechanism outside of the box and by providing a remote control of the weight-release mechanism. By such an arrangement tests of a given test piece can be made over a wide range of temperatures. If a stock is reasonably oil-resistant, its characteristics before and after an immersion test can be compared. The machine can also be used as a valuable auxiliary to one of the existing fatigue machines, to evaluate a test piece periodically throughout the duration of a life test.

### Summary

The equipment is simple and foolproof. It provides an autographic record in a few seconds, from which can be evaluated dynamic hardness, dynamic modulus, internal friction, static hardness, and drift.

It can be used to test rubber and rubberlike compositions over a very wide range of temperatures—for example, from  $-40^{\circ}$  to  $150^{\circ}$  C.—for testing compositions which have been exposed to solvents or gases, and in conjunction with a fatigue machine for evaluation at various stages in a life flexing test.

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TABLE I. COMPOUNDS TESTED

	No. 1	No. 2	No. 3
Smoked sheets	100.	100.	100.
Zinc oxide	5.	5.	5.
Channel black	40.	40.	...
Soft carbon black <sup>a</sup>	...	20.	...
Stearic acid	1.5	1.5	1.5
Pine tar	6.	6.	6.
"D" Phenyl- $\beta$ -naphthylamine	1.	1.	1.
Zenite B <sup>b</sup>	0.8	0.8	0.8
Sulfur	3.	3.	3.
	No. 4	No. 5	No. 6
Neoprene type E	100.	100.	100.
Extra light calcined magnesia	10.	10.	10.
Channel black	...	25.	50.
FF rosin	5.	5.	5.
"D" Phenyl- $\beta$ -naphthylamine	2.	2.	2.
Sulfur	1.	1.	1.
Zinc oxide	5.	5.	5.

Press cure:

Compounds 1 and 2, 40 minutes at 40 pounds' steam pressure ( $141.5^{\circ}$  C.)

Compound 3, 25 minutes at 40 pounds' steam pressure ( $141.5^{\circ}$  C.)

Compounds 4 to 6, 40 minutes at 60 pounds' steam pressure ( $153^{\circ}$  C.)

<sup>a</sup> P. 33 used.

<sup>b</sup> 90 per cent zinc salt of mercaptobenzothiazole-10 per cent diorthotolylguanidine.

TABLE II. RESULTS OF TESTS

Compound	Dynamic Hardness	Static Hardness	Amplitude of Sixth Rebound	Resilience, %	Shore Durometer Hardness
3	138	87	49	56	38
4	128	86	11	13	41
1	119	84	2	2	52
2	108	77	2	2	57
5	98	69	3	5	56
6	71	53	1	2	74



# Differentiation of Oils by Enzymic Hydrolysis

## Agar Plate Method and Its Application to the Detection of Adulteration of Butterfat (Ghee)

K. VENKATA GIRI AND P. N. BHARGAVA, Department of Biochemistry, Indian Institute of Science, Bangalore, India

THE use of enzymes as reagents is now being increasingly adopted in analytical practice. Because they are more selective in their action, enzymes are replacing other chemical methods for the determination and detection of complex substances of biological importance. It is possible to use certain enzymes as reagents for the differentiation of complex substances like starches, fats, and proteins, and in such cases their use promises to be of considerable value. The most striking examples of such usefulness are to be found with amylase and lipase. In previous communications (1, 3, 4) from this laboratory the use of amylase for the differentiation of starches and cereal flours and their detection in mixtures have been indicated.

In the present investigation the copper-soap test described by Carnot and Mauban (2) for the detection of lipases has been modified and extended to the differentiation of fats and oils. The method to be described takes advantage of the difference in the fatty acids of oils hydrolyzed by lipase, which form soaps with copper sulfate. The copper soaps obtained from the fatty acids of butterfat are sharply distinguished from those obtained from other oils, in that they produce different colors when treated with iodine solution. A method for the detection of other oils in butterfat based on this fact is also described in the present paper.

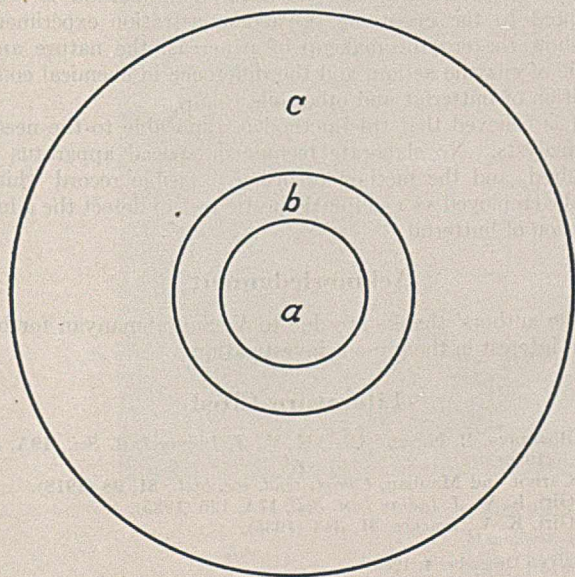
### Reagents and Apparatus

A saturated solution of copper sulfate, a 0.01 *N* solution of iodine in potassium iodide, and 3 per cent agar media, containing 0.2 gram of soluble starch in 100 cc. A known amount of agar and soluble starch were weighed, added to water, and sterilized in an autoclave for about 15 minutes. The melted agar was then made up to the required strength.

Acetic acid-acetate buffer, 0.2 *M* (pH 6.0).

Pancreas extract. Pig's pancreas was treated with acetone and ether and 10 grams of the dry powder were extracted with 60 cc. of 85 per cent glycerol for about 2 to 3 hours at laboratory temperature and centrifuged. One cubic centimeter of the glycerol extract was diluted to 3 cc. with water.

Petri dishes, 7.5 cm. (3 inches) in diameter.



### Experimental Procedure

PREPARATION OF SAMPLES. In India clarified butter is known as ghee. Pure ghee is made exclusively from butter, from which the water has been evaporated by heat and which contains no admixture of any substance not derived from the milk of the cow, buffalo, goat, or sheep. The samples of pure ghee employed in the present study were kindly supplied by the Imperial Dairy Expert, from a herd at the Imperial Dairy Institute, Bangalore. Other samples of pure ghee from the milk of buffalo, cow, and goat were prepared in the laboratory by collecting the thick layer of "skin" which formed when boiled milk was left at a moderately warm temperature and by churning in a household butter churn. The buttermilk or whey was separated from the fat, which was gently heated, strained, and stored.

TABLE I. TESTS OF PURE OILS

Group	Oil or Fat	Color of Central Zone
1	Pure ghee (cow, buffalo, goat)	Dirty yellow with faint green tint
2	Coconut oil	Green
3	Sesame, groundnut, mahua, safflower, lard, castor	Bluish green

The oils were prepared in the laboratory by crushing the seed and subjecting it to hydraulic pressure in the cold. The expressed oils were neutralized with alkali and clarified by washing, heating, and finally filtering after treatment with fuller's earth.

PROCEDURE. Three cubic centimeters of the melted agar while still warm were transferred to a test tube, and 1 gram of the oil under examination and 1 cc. of acetic acid-acetate buffer were added. The mixture was shaken vigorously for a minute and then poured at once into a petri dish. On solidification, one drop of the pancreas extract was placed on the center of the agar plate with a pipet, and the enzyme was allowed to diffuse through the agar gel for about 20 hours at room temperature (26° C.). At the end of this period the plate was flooded with 10 cc. of a saturated solution of copper sulfate for 5 minutes and poured out. The surface was rinsed with water, again flooded with 10 cc. of 0.01 *N* iodine solution for 2 minutes, and finally rinsed with water.

After this treatment, two distinct zones surrounded by a violet background, *c*, could be clearly seen at the center of the plate. The form of the zones is given in the Figure. The outer zone, *b*, was entirely colorless, while the central zone, *a*, was colored either dirty yellow, green, or bluish green, depending on the nature of the oil. The formation of the colorless outer zone, *b*, is due to the hydrolysis of starch by the action of amylase present in pancreas extract, and the central zone, *a*, is formed by the hydrolytic action of the lipase on the oil. The fatty acids thus liberated form soaps with copper sulfate, which produce zones of different colors with iodine, depending on the nature of the fatty acids liberated.

Several pure samples of butterfat and other oils were tested by the method just outlined and the results of the tests are reported in Table I.

It is clear that butterfat can be easily differentiated from other oils by its characteristic color zone. The color of the central zone produced by different oils depends on the glycerides of which they are composed. Butterfat differs es-



essentially in composition from all other oils and fats except coconut and palm-kernel oils in having a large percentage of steam-volatile and water-soluble fatty acids. Moreover, butyric glyceride, which is so prominently present in butterfat, is not present in coconut and palm-kernel oils, and it is this important and least variable constituent which differentiates butterfat from almost all other known fats.

The special influence of butyric glyceride and other soluble volatile fatty acids contained in butterfat on the color of the central zone is clearly seen by comparing the colors obtained when the fatty acids are impregnated in agar medium and flooded with the reagents. Table II gives the results obtained with different fatty acids when they are impregnated in agar medium and flooded with the reagents. In some cases, particularly in fatty acids having higher melting points, the methyl or ethyl esters of the acids were used. The esters were impregnated in the agar medium and flooded with the reagents after hydrolysis with the pancreas extract.

TABLE II. TESTS OF FATTY ACIDS

Fatty Acids	Colors Obtained after Flooding with Reagents		
	Copper sulfate	Iodine	Copper sulfate and iodine
Butyric	Colorless	Yellow	Yellow
Caproic	Light blue	Yellow	Greenish yellow
Caprylic	Light blue	Yellow	Greenish yellow
Capric	Light blue	Light yellow	Blue
Lauric	Blue	Traces of yellow	Blue
Myristic	Blue	Traces of yellow	Blue
Palmitic	Blue	Traces of yellow	Blue
Stearic	Blue	Traces of yellow	Blue
Oleic	Blue	Light yellow	Bluish green

It follows that the formation of the yellow color is mainly due to the presence of butyric, caproic, caprylic, and capric acids in some of the fats. The predominance of yellow in the color zone produced by butterfat is due to the presence of the above acids and of butyric glyceride, which reacts only with iodine and not with copper sulfate to produce the yellow color. Butterfat and coconut oil produce yellow-colored central zones, when treated with iodine after hydrolysis with the pancreas extract, the intensity of the color being less in the case of coconut oil. Only butterfat and coconut oil contain notable amounts of these acids which materially contribute to the yellow color of the central zone. These acids are more or less soluble in water and volatile with steam. It is on this principle that the Reichert-Meissl values which are usually employed for the determination of the purity of butterfat are based. The relationship of this test to the Reichert-Meissl value is very important and may give useful information.

This test has been applied to butterfats from different sources and the results obtained are of interest in establishing the relationship between the Reichert-Meissl value and the color test. Thus, fats from ass' and human milk give bluish green color zones, while the butterfats obtained from buffalo's, cow's, and goat's milk produce a yellow color. These observations are in conformity with the Reichert-Meissl values of these butterfats, since the Reichert-Meissl values of ass' and human milk fats have been found to be too low (ass = 13.1; human = 15.8) while those of buffalo, cow, and goat lie between 20 and 36.

### Detection of Adulteration of Butterfat

The purity of butterfat is generally ascertained by determining the analytical constants in the sample. But the various constants of pure butterfat are subjected to wide variations depending upon the nature of the animal, the season, and the type of food and no single method has been satisfactory for the determination.

Ghee is a very important article of diet in India, and since adulteration is being extensively practiced here, a simple and convenient method for the detection of adulteration is needed. The method outlined is very well suited for this purpose. The test was therefore extended to known samples of pure ghee, adulterating them with known oils in various proportions. It was found that the color of the adulterated sample, on comparison with the color of the central zone produced by pure ghee, was changed from dirty yellow to bluish green, the intensity depending on the concentration of the adulterant. The addition of any of the oils belonging to groups 2 and 3 (Table I) always had the effect of increasing the bluish green tint, thereby altering the color of the central zone characteristic of pure ghee. The admixture of 20 per cent and more of sesame groundnut, coconut, lard, and other oils with a sample of pure butterfat could readily be detected by this method.

The depth of bluish green color of the central zone is to a certain extent proportional to the amount of the other oil present in butterfat, and by making comparative tests with mixtures of butterfat and the oil in various proportions some idea as to the amount of the adulterant can be obtained.

Samples of pure ghee stored in bottles and tested after about a year produced zones having the same color as that of a pure fresh sample. The entire surface of the agar plate was colored light green when flooded with copper sulfate, however, probably because of the presence of fatty acids formed in the sample after storage. It is hoped that with the help of a tintometer the test can be standardized in terms of the color units, and that a standard color unit for pure butterfat can be established.

### Other Applications

In addition to effecting the differentiation of oils and the detection of adulteration of butterfat, the test gives a comparative idea of the relative micellar weights of the two enzymes, amylase and lipase. It can be seen from Figure 1 that the amylase diffuses through the gel more rapidly than the lipase, probably because the amylase is associated with colloids of relatively small molecular size and lipase with colloids of large molecular size. Based on this difference in properties it should be possible to separate the enzymes from one another by physical methods.

The method is capable of wide application in the detection of lipases. It can also be usefully employed in following the changes in the activity of the two enzymes which always occur together in pancreas. The method is well adapted to the classroom, as a demonstration experiment to show the enzyme makeup of pancreas, the nature and mode of enzyme action, and the difference in chemical composition of butterfat and other oils.

It is believed that this method is applicable to the needs of analysts. No elaborate technic or special apparatus is required, and the method furnishes a visible record which can be employed as a simple domestic test, to detect the adulteration of butterfat.

### Acknowledgment

The authors' thanks are due to V. Subrahmanyam for his keen interest in the present investigation.

### Literature Cited

- (1) Bhargava, P. N., and Giri, K. V., *J. Indian Inst. Sci.*, **19A**, 53 (1936).
- (2) Carnot and Mauban, *Compt. rend. soc. biol.*, **81**, 98 (1918).
- (3) Giri, K. V., *J. Indian Inst. Sci.*, **17A**, 126 (1935).
- (4) Giri, K. V., *Science*, **81**, 343 (1935).



# Surface Effects of the Platinum Metals on Silver Assay Beads

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**B**ECAUSE the wet analysis for the platinum metals in a silver assay bead is a long and tedious process, various attempts have been made to devise simple and rapid methods for their determination.

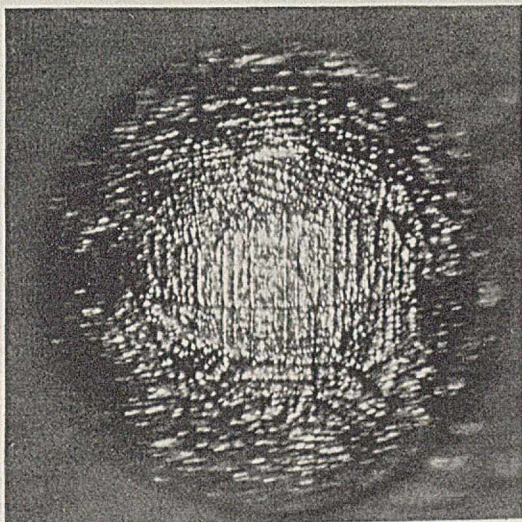


FIGURE 1. PLATINUM-SILVER, 1 TO 12  
Magnification,  $\times 40$ . Weight, 30 mg.

Several authors have suggested that by classification of the surface effects of the platinum metals on the silver assay bead, a surface examination might yield not only qualitative but also approximately quantitative data.

Bannister and Patchin (1) investigated the binary systems, platinum metals-gold and platinum metals-silver, and not only dealt with the qualitative effects but also attempted to

determine the minimum percentages of each of the platinum metals which would yield specific surface phenomena.

Byers (2) described surface effects on the binary systems, platinum metals-silver, stating that characteristic effects are visible in silver beads containing as low as 0.1 per cent of platinum. The authors have made some 1000 platinum metals-silver cupellations with subsequent examination for surface phenomena and have not been able to confirm this conclusion. Byers (2) described the effects of osmium on silver beads, but did not state how the composition of the beads was determined; it is probable that the proportions of osmium and silver stated to be present were those added to make the bead. Experimental data to show that the cupellation of silver-osmium beads may result in complete loss of the osmium will be published later by the authors.

Byers (2) discussed also the surface effects of the binary systems, platinum metals-gold, and stated that the various members of the platinum group are more often associated with gold than with silver.

According to Langer and Johnston (3), the Sudbury precious metal residue contained about 372 parts of silver and 13 parts of gold to 100 parts of platinum metals. Native platinum derived from most of the world sources also contains comparatively little gold. Placer deposits, however, very often carry gold in predominant proportions mechanically mixed with native platinum, and in cases such as these the data given by Byers (2) may be of considerable value because, unlike silver, the surface of a pure gold bead is normally smooth with a characteristic color.

In the fire assay for platinum metals, silver is usually added to the charge in the proportion of about 15 to 20 parts to 1 of total platinum metals, in order to facilitate parting by means of sulfuric or nitric acids. Therefore the present report is confined to the discussion of the surface phenomena of the silver-platinum metals bead.

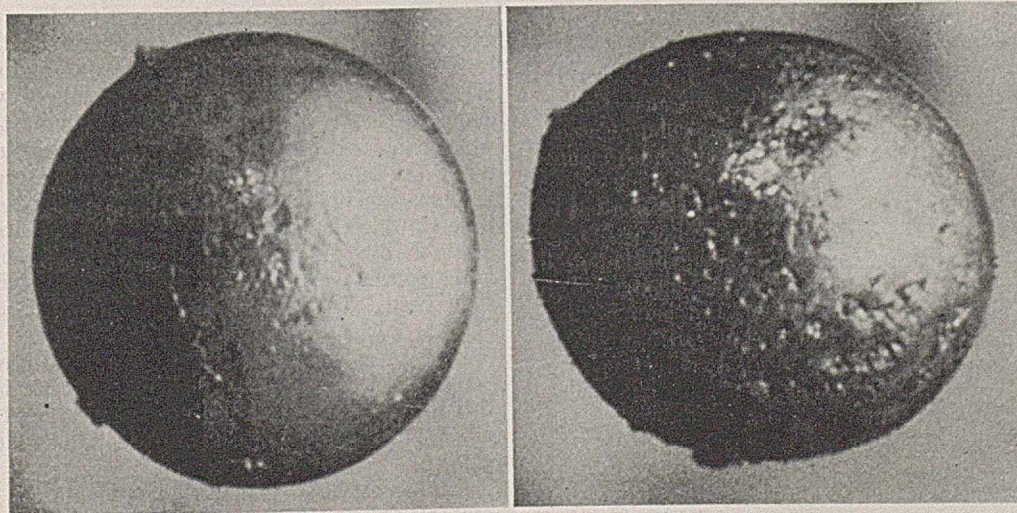


FIGURE 2. PLATINUM-SILVER  
Magnification,  $\times 30$ . Weight, 40 mg.  
Left, 1 to 50  
Right, 1 to 60



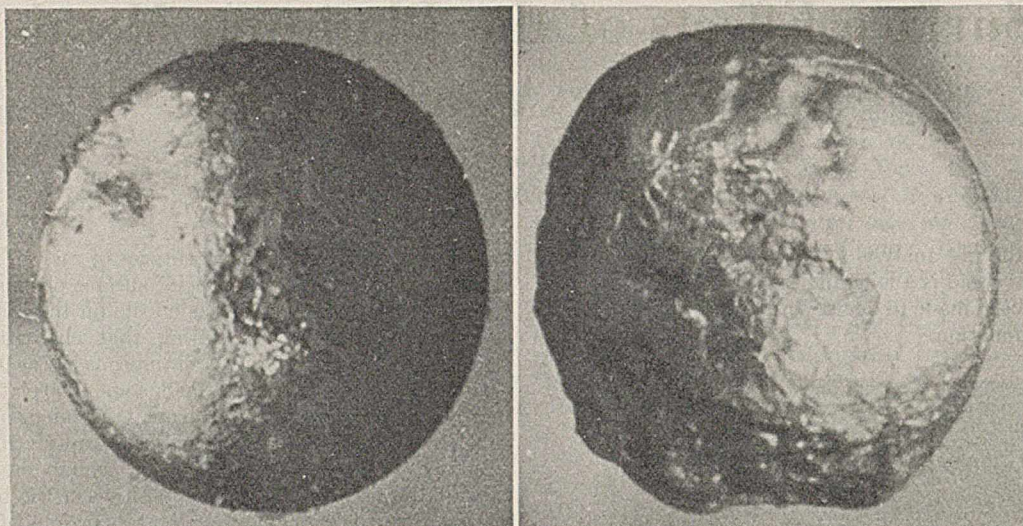


FIGURE 3. SILVER  
Magnification,  $\times 30$ . Weight, 40 mg.

### Preparation of Beads

Three procedures were followed in preparing the lead regulus:

1. Half-assay ton samples of synthetic ore and the necessary flux were salted with the platinum metals and the fusion was maintained at about  $1200^{\circ}\text{C}$ . for 0.75 hour. The buttons used weighed about 30 grams.

2. Clean lead shot was placed in a cylinder, and the platinum metals and silver were added and covered with sufficient shot to make a button weighing 30 grams. A piston was fitted into the mold and the samples were submitted to pressure of about 1500 pounds per square inch, producing a smooth compact button.

3. Solutions of the pure platinum metals and silver were made and the required volumes added to a 30-gram sheet-lead dish and carefully evaporated over steam. The lead was rolled to include the platinum metals and silver in the center of the button.

The proportion of platinum metals was determined by analysis of the bead. The reported compositions can be considered accurate to about 0.5 part per hundred.

The cupellation temperature recorded is that of the walls of the bone-ash cupel and was determined by means of an

optical pyrometer. No attempt was made to determine the actual temperature of the cupeling bead. In each case, unless otherwise recorded, the cupellation temperature was  $950^{\circ} \pm 25^{\circ}\text{C}$ . After completion of the cupellation process the beads were removed slowly in order to avoid spitting.

These salted beads were arranged in sets, associated with a number of pure silver beads prepared under identical conditions, and were examined by three operators experienced in this work, who had no previous knowledge of the bead composition. The beads were brightly illuminated and examined by means of a microscope with a  $\times 40$  magnification.

### Binary Systems

**PLATINUM-SILVER.** In the case of high percentages of platinum (Figure 1) the surface phenomenon is a somewhat regular pattern of pits characterized by a continuously smooth surface. As the percentage of platinum is decreased, these pits become less frequent.

Figure 2 (left), containing one part of platinum to 50 parts of silver, shows very slight platinum effects, while in Figure 2 (right) the platinum effects are more marked, in spite of the fact that this bead contains 1 part of platinum to 60 parts of silver. This indicates that the intensity of specific platinum effects under the condition above specified could be only very roughly proportional to the percentage of platinum present. When the proportion of platinum to silver was less than about 1 part of platinum to 90 of silver, the operators were unable to distinguish such beads from silver beads made up to the same size and subjected to identical conditions. A comparison of Figure 3 (left), a pure silver bead, and Figure 2 (left), which is near the border area of sensitivity, will indicate the difficulty in identifying beads which contain a much lower percentage of platinum. Figure 3 (right) is also a silver bead. The lower extremely rough portion of the bead is the area which was attached to the cupel.

**PALLADIUM-SILVER.** When palladium is present in high percentages (Figure 4) the beads resemble platinum-silver in that the surface is covered with smooth-surfaced pits. These pits are much smaller than with platinum and less regular in pattern.

**IRIDIUM-SILVER.** When iridium is present in high percentages (Figure 5), the bead forms an irregular, often elongated black mass spread over a considerable surface of the cupel. Very often numerous small particles of the bead can be found separated from the main body. As the proportion

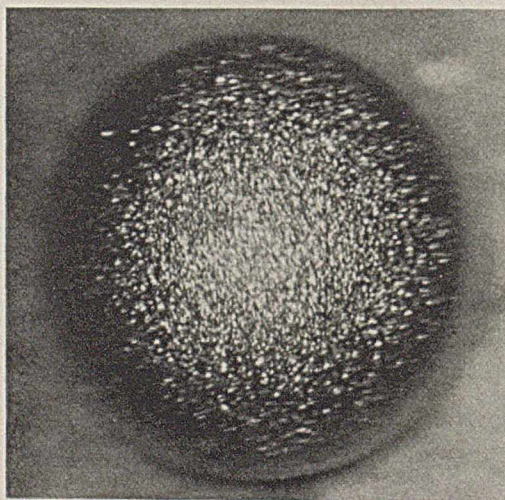


FIGURE 4. PALLADIUM-SILVER, 1 TO 10  
Magnification,  $\times 40$ . Weight, 30 mg.





FIGURE 5. IRIDIUM-SILVER, 1 TO 7  
Magnification,  $\times 20$ . Weight, 30 mg.

of the iridium is decreased, the bead assumes a spherical shape and projections of blue-black crystalline clumps appear scattered over the surface. The bead finally assumes a form similar to low percentage platinum beads.

**RHODIUM-SILVER.** With large percentages of rhodium (Figure 6), the bead assumes an irregular shape and is coke-black in color with an extremely rough surface.

The authors conclude that under conditions above described the presence of platinum and palladium can be detected with certainty only in proportions of 1 or more of platinum or palladium to about 70 of silver. Additional tests made on beads of about 500 and 10 mg. indicate that the

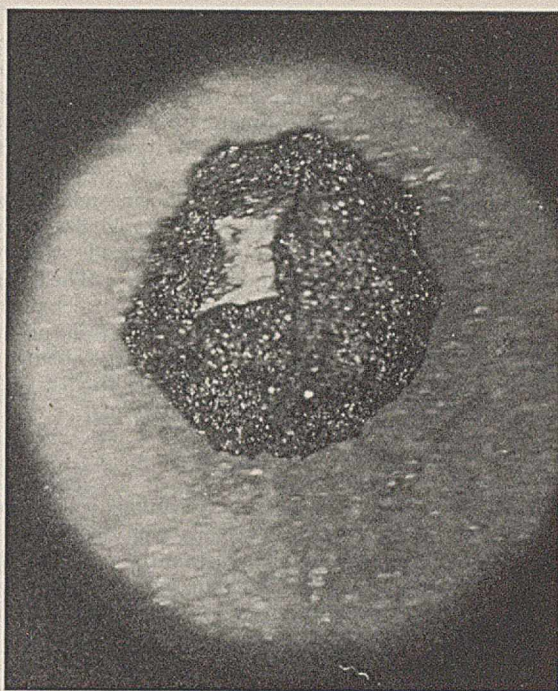


FIGURE 6. RHODIUM-SILVER, 1 TO 10  
Magnification,  $\times 17$ . Weight, 30 mg.

limit of sensitivity with respect to platinum is also 1 of platinum to about 70 of silver.

#### Polycomponent Systems

Buttons were made containing approximately the relative proportion of each of the platinum metals often found in norite deposits—i. e., 8.3 parts of platinum, 9.4 parts of palladium, 0.6 parts of rhodium, 0.6 part of iridium, and 3.0 parts of gold. These buttons were cupeled and the beads examined exactly as described for the binary systems.

Figure 7 (left) illustrates the surface phenomenon, which is different from that of platinum-silver. Examination indicated that under the conditions described above it was possible to detect the platinum metals when the proportion

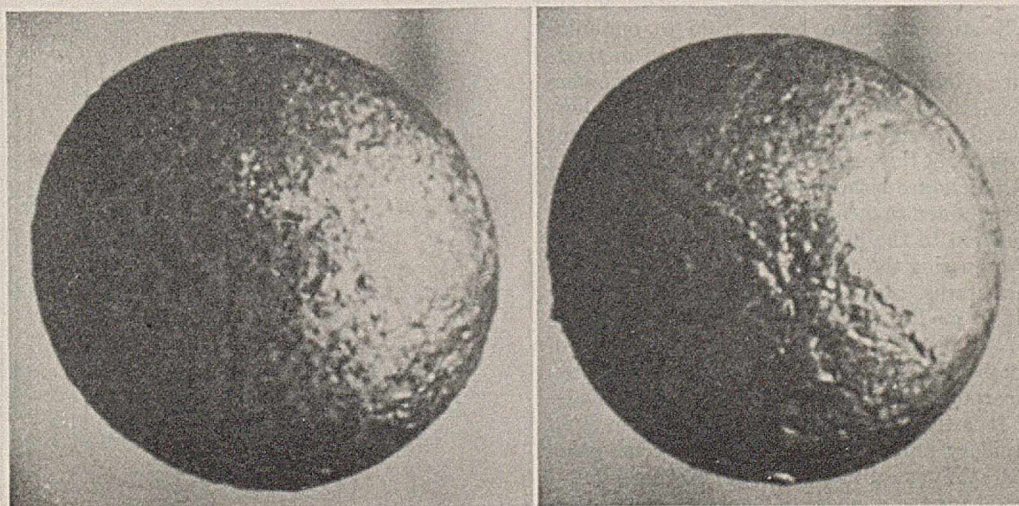


FIGURE 7. PLATINUM METALS-SILVER  
Magnification,  $\times 30$ . Weight, 40 mg.  
Left, 1 to 30  
Right, 1 to 140



present was about 1 or more of total platinum metals to 150 of silver. Figure 7 (right) indicates the decrease in intensity of surface effects upon reduction of platinum metals content.

Beads containing the same percentage of silver and platinum metals but weighing approximately 8 mg. were prepared as described above; the limit of sensitivity was about the same as with those weighing 40 mg.

Buttons were made containing the following relative proportions of platinum metals; 23.1 per cent gold, 3.2 per cent iridium, and 73.7 per cent platinum. The beads were prepared and treated exactly as described above. The surface phenomena characteristic of platinum could be detected when the percentage of platinum metals was high, but disappeared when the ratio of platinum metals to silver was about 1 to 80; the operators were then no longer able to distinguish beads containing platinum from pure silver beads.

### Conclusions

Because so very little information is recorded about properties of the polycomponent systems, platinum metals-silver, the authors feel that more emphasis than is reasonable has been placed upon the value of the surface effects on assay beads for the detection and rough estimation of platinum metals content. The present report is submitted as an attempt to convince the inexperienced assayer that definite conclusions concerning the effect of the platinum metals on a silver assay bead must be avoided.

A number of platinum-silver beads cupeled with a finishing temperature of about 1300° C. gave surface effects of an entirely different character than beads of similar composition cupeled at 950° C.

The rate of cooling also seems to exert a marked effect on the character of surface phenomena.

The authors' experience on at least two occasions has borne out Stanley's (4) statement that sometimes one bead will be free from surface effect while others from the same sample show signs.

By reducing the percentage of silver in the bead, an experienced operator can sometimes determine that the ore under examination is of commercial value with respect to total platinum metals, but the absence of specific surface phenomena does not necessarily mean absence of commercial values of platinum metals.

Only an analyst thoroughly familiar with the appearance of platinum metals-silver beads, as well as pure silver beads, can make even approximately accurate guesses concerning the qualitative composition of the platinum metals assay bead.

### Acknowledgment

The authors are indebted to H. Mills of Toronto for the photographs of some of the beads, and to H. Collins of Toronto who assisted with the examination of beads.

### Literature Cited

- (1) Bannister, C. O., and Patchin, G., *J. Chem. Met. Mining Soc. S. Africa*, 14, 478 (1914).
- (2) Byers, J. L., *Am. Inst. Mining Met. Eng.*, preprint (1932).
- (3) Langer and Johnston ("Platinum and Allied Deposits of Canada," by J. J. O'Neill and H. C. Gunning), *Can. Dept. Mines, Geol. Survey, Rept. 2346, Ec. Geol. Ser. No. 13*, 67 (1934).
- (4) Stanley, D. H., *J. Chem. Met. Mining Soc. S. Africa*, 14, 482 (1914).

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# Modified Capillary Combustion Unit

## For a Gas Analysis Apparatus

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NUMEROUS attempts have been made to minimize the danger of explosions in slow-combustion methods when carried out by inexperienced operators. Some workers have tried to achieve this purpose by modifying the slow-combustion pipet (3, 5), while others have developed different methods for carrying out this analysis (1, 7).

The modified pipets are either mechanically unstable, or cannot be readily adapted to technical gas analysis apparatus. The serious objection to the catalytic oxidation methods is the difficulty of preparing the catalyst and the complexity of the resulting apparatus. In most investigations attempts have been made to modify the position or character of the platinum spiral. While the literature contains a number of references to combustion capillaries (2, 4, 6), no attempt has been made to incorporate this device into a standard gas analysis apparatus. It is the purpose of this paper to show that the modified capillary unit can replace the slow-combustion pipet and eliminate the hazard of explosions. It offers a more convenient method for the analysis of combustible gases.

### Description of Apparatus

The Levy platinum-silica capillary pipet appeared to offer a solution to these problems, but because of the difficulty of

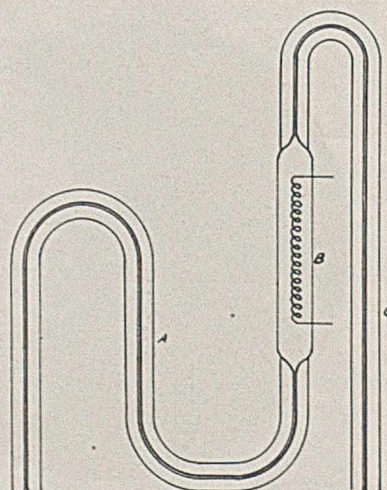


FIGURE 1. DIAGRAM OF APPARATUS

- A. Intake capillary
- B. 8 × 50 mm. combustion unit
- C. Outlet capillary



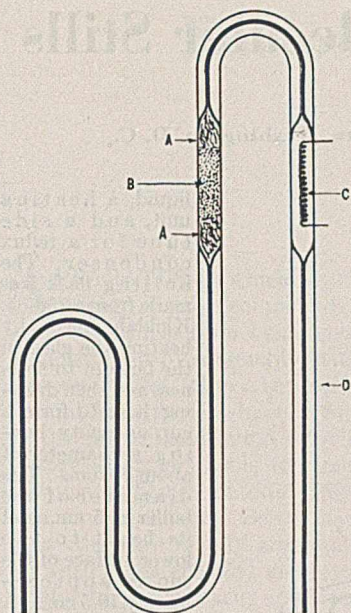


FIGURE 2. DIAGRAM OF CAPILLARY

- A. Glass wool  
B. 80-mesh sand  
C. Heating element  
D. Capillary tube

trodes and the tubes resealed.)

Initial experiments were made with methane-oxygen mixtures. In order to prevent explosions from carrying on through to the buret, a safety valve was incorporated in the intake capillary of the combustion unit. The first safety device employed consisted of a bulb, in the capillary of which was placed a mercury bead. Because of the difficulty of maintaining the mercury in the bulb, this method was abandoned.

Further investigation revealed the interesting fact that no auxiliary safety device was required for methane-oxygen mixtures when the intake capillary was less than 0.5 mm. in diameter. However, this method was not applicable to the oxidation of other gases. Experiments with other combustible gases [notably acetylene, hydrogen, and butane (Flamo)] indicated that their flames were readily propagated through even smaller capillaries. To prevent backfire in these cases, a number of devices were tried (mercury traps, valves, fritted-glass plates) but they were either found to be impractical or did not stop the flame.

The simplest possible scheme—namely, a sand trap—then suggested itself. Working with acetylene-oxygen mixtures, which gave the most vicious explosions, it was shown that 10 cm. of 80-mesh sand were required to prevent backfire. On the basis of this information a plug consisting of 2 cm. of 80-mesh sand in a 6-mm. tube was found to stop the flames of such combustible gases as mixtures of oxygen with ethylene, hydrogen, carbon monoxide, and butane. Since the determination of acetylene by combustion methods appears to be impractical, it was not deemed necessary to employ a greater depth of sand.

The capillary that was finally adopted is shown in Figure 2. The intake capillary tubing used in this apparatus was 0.5 mm. in diameter. The sand plug was placed in such a position that the moisture formed during the combustion would not wet the sand.

### Experimental

In order to check the range and limitations of the coil, test runs were made with varying concentrations of methane in oxygen at different space velocities. Results indicated that

making the unit and of replacing the coil, this device was not adopted.

Another capillary was designed which eliminated both the use of silica and the water cooling. This unit (Figure 1) was made of Pyrex glass, with tungsten leads (made of 20-gage wire) sealed through the glass. The platinum spiral was made of 36-gage wire. The current necessary to cause the wire to glow did not heat the tungsten leads appreciably. The temperature of the spiral was maintained by placing a variable resistance (rheostat, 94 ohms, 2.2 amperes) in series, using a 110-volt alternating current.

(In order to replace the platinum spiral, the pipet may be cut at the seal between the capillary tube and the combustion chamber. The coil can then be readily attached to the elec-

it was safe to pass methane-oxygen mixtures even in theoretical proportions over the heated spiral. (This was also found to apply to all combustible gases investigated, except acetylene.)

The rate at which the gas could be introduced depended on the concentration. When the methane content was low, the gas was noiselessly burned regardless of the rate. At the higher concentrations (1 part of methane to 2.5 parts of oxygen) as the space velocities were increased, the reaction in the combustion tube became audible. The rate of oxidation was adjusted so that the sound was just perceptible.

The procedure for carrying out an analysis differed from the conventional methods in the following manner: The sample of gas was introduced into the buret and measured, and then sufficient oxygen was added to ensure a slight excess. The total volume was measured before combustion and then passed into the gas reservoir to ensure mixing. This mixture was passed three times over the bright red coil and by-passed back to the buret; thus the gases were always introduced to the combustion chamber from the same direction. The conventional slow-combustion pipet was used as a gas reservoir.

The results of a number of typical analyses are given in the Table.

TABLE I. DETERMINATION OF METHANE

Capillary Pipet %	Slow- Combustion Pipet %
91.8	91.9
82.2	82.1
40.9	41.1
12.5	12.3

In addition, oxygen mixtures of carbon monoxide, butane (Flamo), and ethylene were shown to be completely oxidized under similar conditions.

To adapt this method to a standard gas analysis apparatus two modifications are offered, both of which were found to be satisfactory.

1. For combustible gases, one may employ a mounting similar to the usual cupric oxide tube with intake (three-way stopcock) placed between gas buret and potassium hydroxide pipet, and the exit placed between the first and second pipets of the gas train.

2. For methane residues, one may incorporate the combustion unit in one arm of the cupric oxide tube (Figure 3). This permits the use of a simpler manifold.

### Summary

The modified capillary combustion pipet offers a safe, precise, and convenient method for the analysis of combustible gases (except acetylene). The unit can be easily incorporated into the standard gas analysis apparatus.

A simple method is given for preventing the propagation of flames through capillary tubing.

### Literature Cited

- (1) Dennis, L. M., "Gas Analysis," 2nd ed., p. 198, New York, Macmillan Co., 1929.
- (2) Evans and Davenport, *IND. ENG. CHEM., Anal. Ed.*, 7, 174 (1935).
- (3) Kobe, *Ibid.*, 3, 159 (1931).
- (4) Lunge and Ambler, "Technical Gas Analysis," p. 133, London, Gurney and Jackson, 1934.
- (5) Steacie, *J. Am. Chem. Soc.*, 52, 2811 (1930).
- (6) Walker and Christensen, *IND. ENG. CHEM., Anal. Ed.*, 7, 9 (1935).
- (7) Weaver and Ledig, *J. IND. ENG. CHEM.*, 12, 363 (1920).

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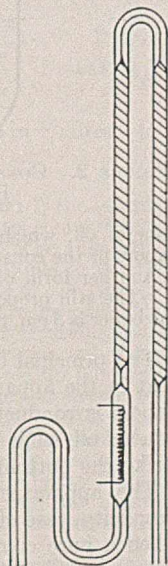


FIGURE 3



# Constant-Temperature Bath for Molecular Stills

O. A. NELSON AND H. L. HALLER

Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture, Washington, D. C.

THE desirability of maintaining accurate control of temperature during distillation processes has been known for a long time. It is particularly important in processes involving fractional separation of two or more components from a mixture, regardless of whether the distillation is carried out at atmospheric pressure, under slightly reduced pressure, or at high vacuum. While it is true that if a perfect vacuum could be obtained a liquid would give off vapor at any temperature, nevertheless for liquids of comparatively high boiling points the rate of distillation at room temperature would be so low that no appreciable quantities could be obtained in experimental time. At elevated temperatures the rate of distillation is increased, but the rate may vary for different substances, and it is just this difference in rate of distillation that permits of separation of phlegmatic liquids from one another by the process of fractional distillation (1).

Various methods have been proposed for the control of temperature during distillation in the molecular still. In most cases such devices are complicated, require considerable attention, or cannot be depended upon to give satisfactory control.

An apparatus that provides a constant temperature with a minimum amount of attention is shown in Figure 1. It consists essentially of a boiler, B, containing a constant-boiling

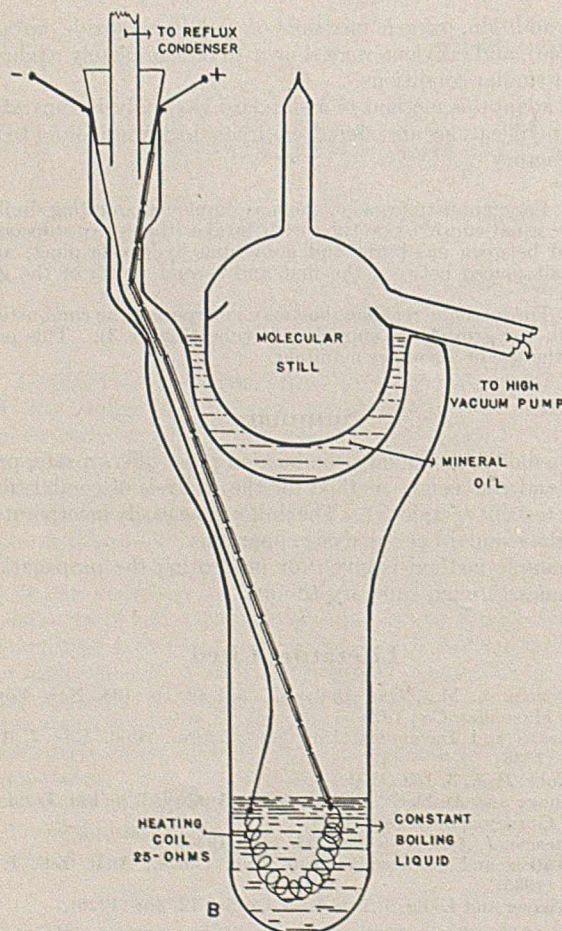


FIGURE 1. CONSTANT-TEMPERATURE BATH

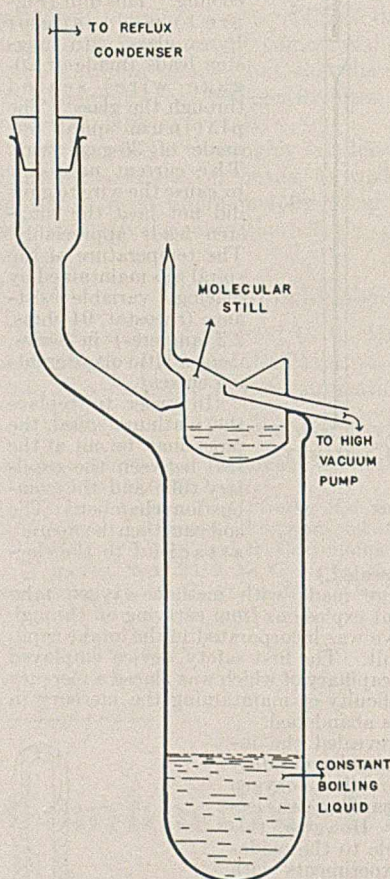


FIGURE 2. CONSTANT-TEMPERATURE BATH

liquid, which functions as a heat conductor between the vapors of the constant-boiling liquid and the material in the still.

Another form of the same apparatus is illustrated in Figure 2. The still proper (Hickman type) is 3.8 cm. in diameter and the boiler is 5 cm. in diameter and about 16.5 cm. long.

The principal difference between the two modifications is that in the apparatus shown in Figure 1 the heat from the vapors is conducted to the still by means of a high-boiling mineral oil, while in the one shown in Figure 2 the hot vapors strike the bottom of the still directly.

The apparatus herein described has the advantages of simplicity, ease of construction, and reliability. In addition, when a pure compound is used as a constant-boiling bath, the necessity of determining the temperature of the material in the still is eliminated.

By so controlling the rate of refluxing that no apparent condensation takes place on the bottom of the cup or still, constant temperature can be maintained for any desired length of time. Both constant-temperature baths and stills have been used in this laboratory over long periods of time with satisfactory results.

## Literature Cited

- (1) Hickman, K., *J. Franklin Inst.*, 213, 119 (1932).
- (2) Mair, B. J., Schicktanz, S. T., and Rose, F. W., *J. Research Natl. Bur. Standards*, 15, 557 (1935).

RECEIVED May 27, 1937.



# Enclosed Apparatus for Laboratory Crystallizations

JOHN D. PIPER AND N. A. KERSTEIN  
The Detroit Edison Company, Detroit, Mich.

APPARATUS in which crystallization of low-melting or highly reactive compounds is to be effected should prevent the sample from being contaminated by condensation of moisture or by interaction with the components of the atmosphere. Several such devices have been built by the authors and found to be satisfactory laboratory tools for fractionally crystallizing material from its own mother liquor. Being made of glass, they are readily adaptable for use with other enclosed glass systems employing partial vacua or inert gases.

The general principle upon which each device operates is the same. The liquid to be purified is partially crystallized in one compartment at a chosen temperature, after which the remaining liquid is drained from the crystals and transferred to a second compartment. The crystallized material is then melted and the process is repeated as many times as is desirable, preferably at temperatures progressively closer to the freezing point of the pure liquid. The purified portion is then isolated from the rejected portions by separating the two compartments. Differences in the structure and operation of the devices are illustrated in Figures 1 to 4.

## Design of Apparatus

In the case of the apparatus shown in Figure 1, the sample is introduced through a large-bore capillary into compartment *a* and the capillary is sealed off at *b* as shown. The apparatus is then tilted in such manner as to allow the sample to flow into compartment *c* through either capillary tube *d* or *e*. The apparatus in the position shown is then immersed in a suitable bath at the temperature desired for the first crystallization. Baths of carbon dioxide and acetone mixtures in wide-mouthed thermos bottles have usually been used for temperatures below about 1° C. Seeding may be accomplished by undercooling a small part of compartment *c*. After crystallization has progressed to the desired extent, the apparatus is removed from the bath, inverted, and quickly restored to the bath in the inverted position. The mother liquor is thus allowed to drain from the crystals through capillary *d* into compartment *a*, capillary *e* serving to equalize the pressure of the system, thus allowing free flow.

When drainage is completed, the apparatus is removed from the bath and restored to its original position by rotating it in the direction shown by the arrow. The rejected liquor is thus trapped in one end of compartment *a*. In repeating the process after subsequent crystallizations, the apparatus is inverted by rotating it in the opposite direction to that shown by the arrow in order to prevent return of the rejected liquor to compartment *c*. After the last crystallization, *d* and *e* are sealed off. Connection of compartment *c* to the apparatus in which its contents are to be used is made at *f*, after the protecting cap, shown at that point, has been removed. Communication between the compartment and the new system is established by breaking window *g* with a suitable hammer enclosed in the system when the connection is made.

Where a number of sample tubes are to be filled with the purified material, the apparatus shown in longitudinal sec-

tion in Figure 2 is convenient. This apparatus may be operated only under greatly reduced pressures. Similar lettering is used to identify similar parts of the various pieces of apparatus shown in Figures 1 to 4.

In addition to *a* and *c*, the apparatus illustrated in Figure 2 has a compartment *h*, which is filled with sample tubes, *i*, having open capillary ends extending to the open end of *h* as shown. Chiefly because the arrangement gives better mechanical strength, tube *e*, instead of being connected directly to *c*, communicates with it through *h* and *e'*. The shapes of the compartments and the positions of the connecting tubes are designed to prevent trapping of condensed vapors during the drying process.

With the apparatus in the position indicated the liquid is dried over an appropriate desiccant in flask *k* and distilled into flask *l* through capillary *m*, which is then sealed off. Additional drying, if necessary, may be accomplished by interposing similar flasks between *k* and *l*. The liquid in flask *l* is then refluxed over the desiccant and finally distilled into the crystallization apparatus. During the distilling process compartments *a*, *c*, and *h* are placed parallel to the line marked "filling angle."

After fractional crystallization has been completed in essentially the same way as was described in connection with Figure 1 and the purified liquid has been isolated by sealing off capillary tubes *d* and *e*, the liquid from *c* is transferred to *h* by alternately warming and cooling the two compartments, if necessary. Tube *e'* is then sealed off and, with the tips pointing downward, the sample tubes are filled by slowly admitting dry nitrogen through capillary *j*, the end of which is broken within a rubber tube supplying the nitrogen. The sample tubes thus filled are then removed from *h*, which is cracked open, and the capillary ends of the tubes are sealed.

In cases where the mother liquor does not readily drain from the crystallized material, apparatus employing centrifugalization has been used. One of these devices is shown in inverted position in Figure 3.

Except that compartment *a* is almost in line with compartment *c* and that tube *e*, being unnecessary, is omitted, the glass part of this apparatus is similar to that shown in Figure 1. Op-

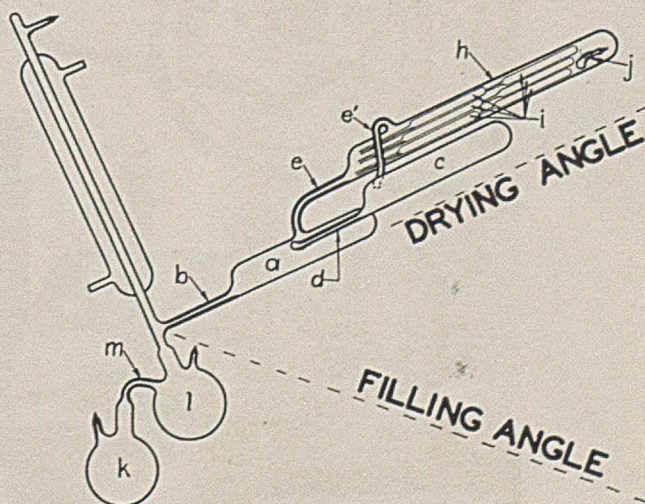


FIGURE 2



eration is also similar, except that during the draining periods the apparatus is suspended in a bath in a centrifuge cup, *n*, by means of a suitable split clamp, *o*, containing a split rubber cushion, *p*, and the entire assembly is rotated at low speeds in the usual manner.

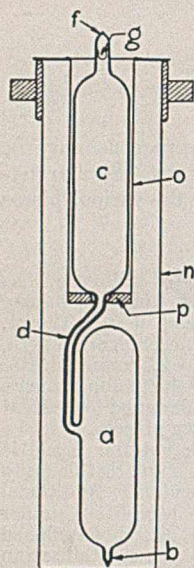


FIGURE 3

Operation is similar to that of the apparatus shown in Figure 1, except that, after the sample contained in the lower half of compartment *c* is partially crystallized, the enclosed system is rotated about its *y-y* axis by means of a stirring motor attached at *f*. The mother liquor is thus discharged by centrifugal force through capillary tubes *d* and *d'* into compartment *a*, which has a larger diameter than *c*. The top of thermos bottle *n* is closed with a tight-fitting stopper, *q*, through which extends thermometer *r* and brass upper bearing *s* which may be made from a cork borer of suitable size. The lower bearing, *t*, is simply a strip of metal through which a hole has been punched large enough to accommodate *b*. The ends of the strip are fastened, as shown, to a split circular collar which is held against the inside of the thermos bottle by friction. The buoyancy of the enclosed system in a carbon dioxide and acetone bath is such that the end thrust is upward and is taken up by the bearings of the stirring motor. Unless the center of gravity of that system is too far from the *y-y* axis, vibrations due to small imperfections in construction of the glass parts seem to do no harm, provided the thermos bottle is mounted in some soft material, such as cotton, which permits the bottle to move slightly. Sufficient bath is used to fill the bottle up to the stopper, and keep compartment *c* in contact with the bath during centrifuging.

Because centrifuge cups that can be used with an ordinary laboratory centrifuge are of limited size and are difficult to insulate, the use of this apparatus is limited to small samples of materials whose melting points are not too different from the temperature attained in the centrifuge during operation.

For use with materials of low melting point, the apparatus shown in Figure 4 is satisfactory.

The several devices are easily made by anyone who can do simple glass blowing, and though the parts are isolated during the crystallizations, they may be reassembled repeatedly. Types of apparatus shown in Figures 1 and 2 have been used rather extensively for crystallizing some organic acids for investigations concerning dielectrics (1, 2). The acids crystallized are listed by Piper et al. (1, 2), with comment concerning their purity.

Apparatus shown in Figures 3 and 4 represent more recent modifications, which up to the present time have been used to crystallize two hydrocarbons, indene and dimethyl fulvene, whose melting points in sealed tubes at approximately their own vapor pressures were  $-1.8$  and  $3.4$ , respectively. No melting point determinations were made at atmospheric pressure in these cases. Other modifications more suitable for a particular purpose may be suggested by these descriptions.

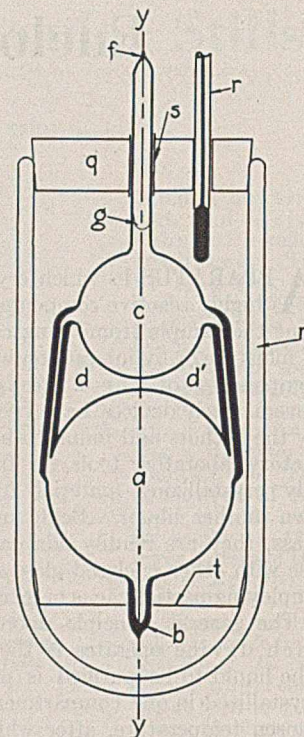
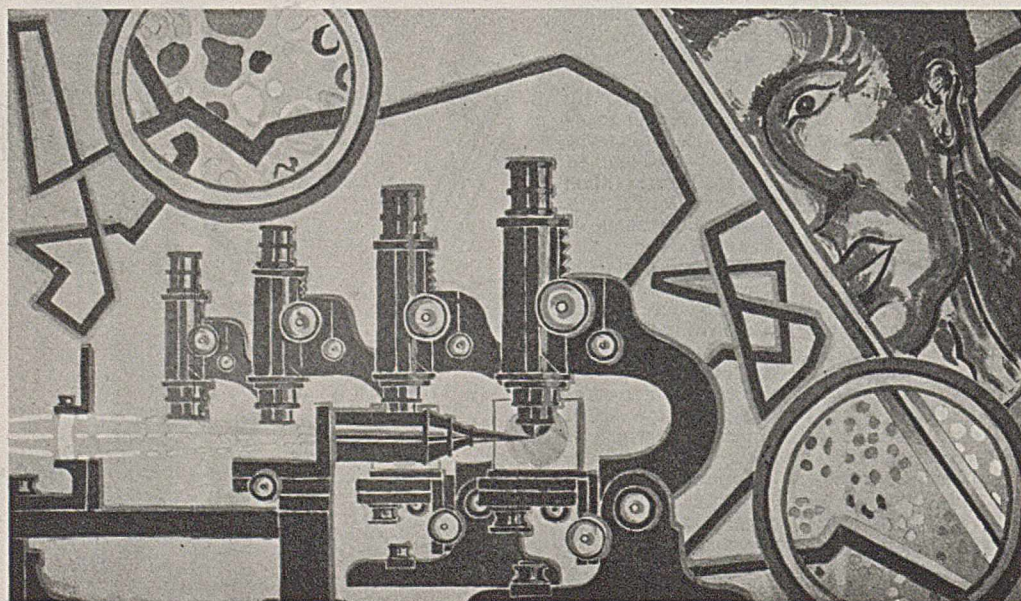


FIGURE 4

#### Literature Cited

- (1) Piper, J. D., Kerstein, N. A., and Fleiger, A. G., *IND. ENG. CHEM.* (to be published).
- (2) Piper, J. D., Thomas, D. E. F., and Smith, C. C., *Ibid.*, **28**, 843 (1936).

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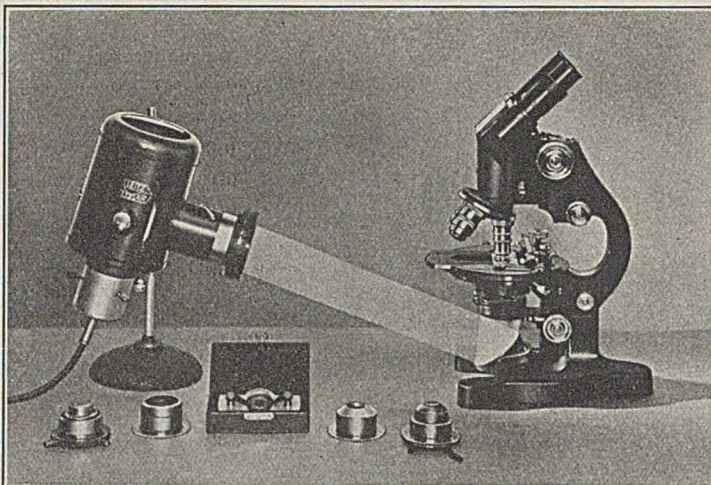
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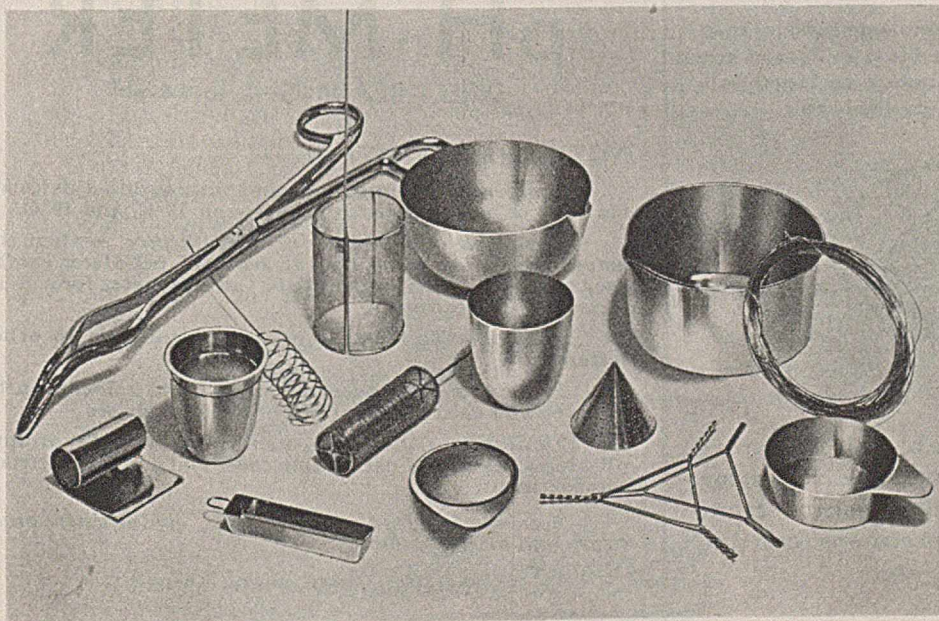
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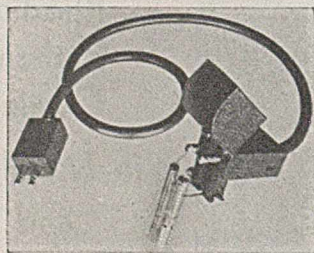
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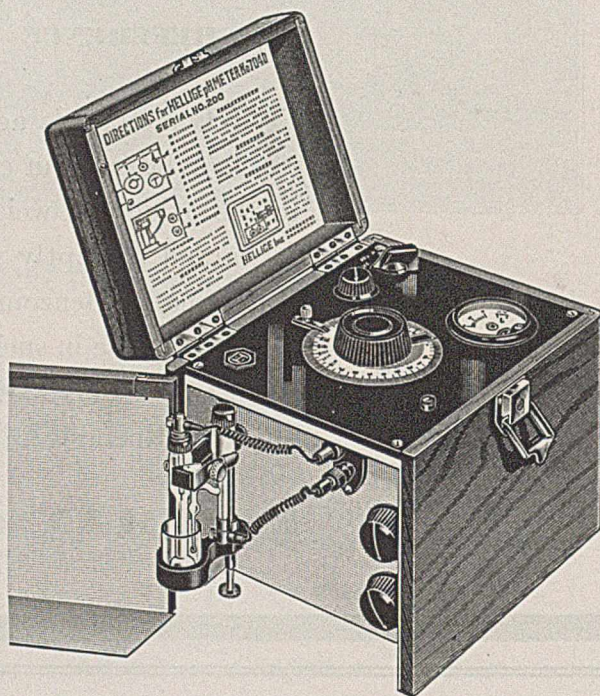


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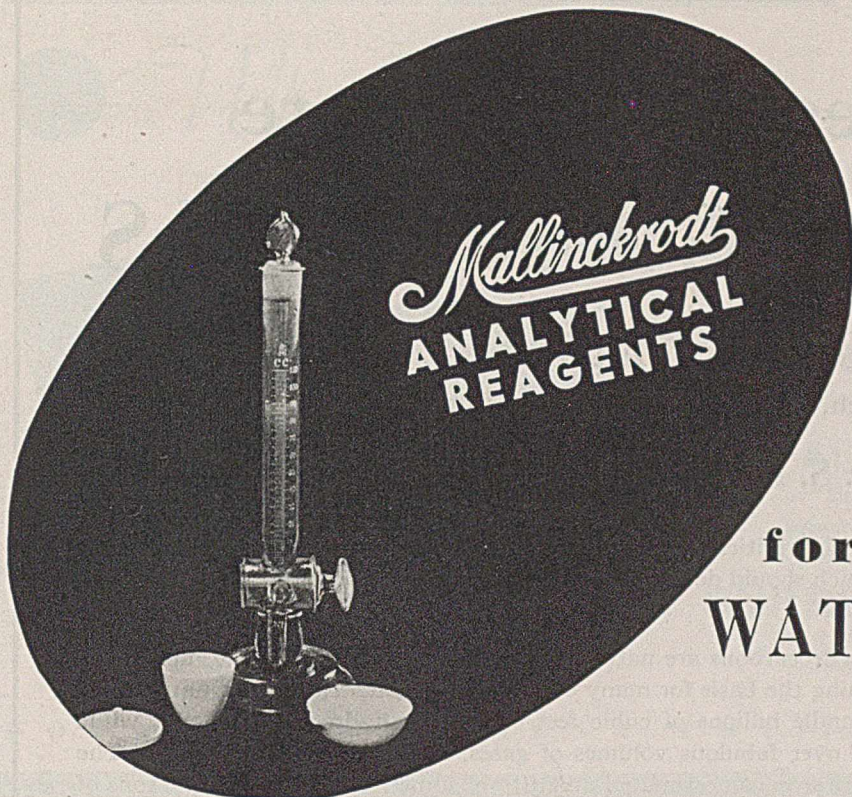
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Almost unbelievable quantities of hydrocarbons are naturally available all over the world, appearing as gases, liquids and solids and forming the basis for many of the largest industries. The natural gas and manufactured gas industries handle billions of cubic feet of gaseous hydrocarbons daily, while the petroleum industry is guardian over fabulous volumes of gases, oils, waxes and asphalts. The coal industry in its turn has within its scope an estimated quantity of some 7,000 billion metric tons of coal and lignite, starting material containing valuable hydrocarbons of which all manner of use may be made. Moreover, hydrocarbon oil to the estimated amount of 300 billion barrels is potentially present in oil shale deposits.

There are seven distinct hydrocarbon groups outlined for the purposes of this book:—paraffins, olefins, acetylenes, aromatics, cycloparaffins and cycloolefins, and terpenes. Each group is individual in its properties, its reactions toward various agencies, thermal, electrical and catalytic; and its reactivity with other hydrocarbons or with unrelated substances. Despite these characteristics, however, each group is capable of being produced from most of the other hydrocarbon groups, and is equally capable of producing its fellow hydrocarbon groups under varying and, to a high degree, controllable conditions. Natural gas in the United States which is available at the rate of billions of cubic feet per day is made up of methane, ethane, propane, and butanes.

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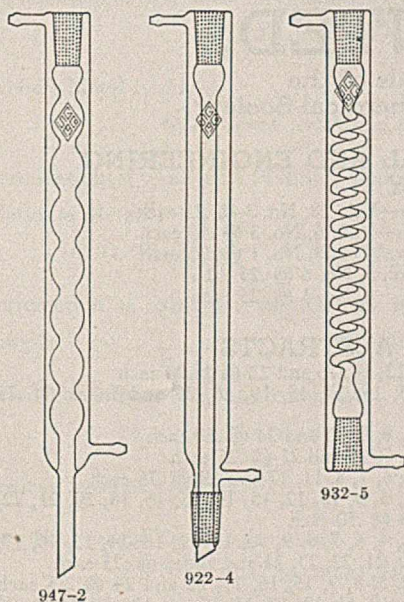
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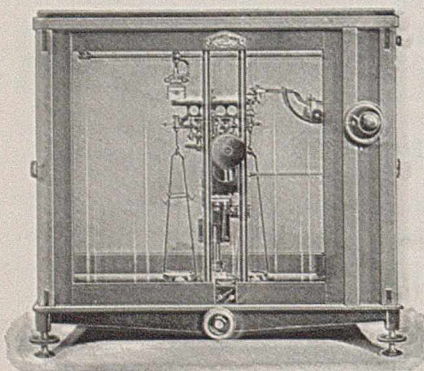
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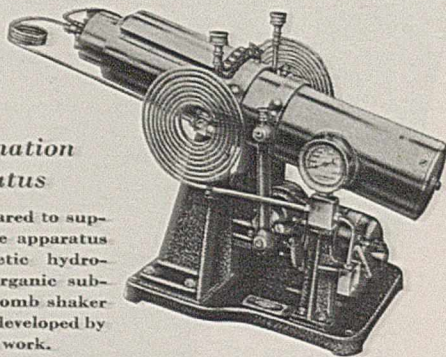
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