TABLE II.   EFFECT OF OTHER IONS

(Ferrisul Solution III)

Added Salt		$Fe_2(SO_4)_3$ Found
	%	%
		8.83
$FeSO_4.7H_2O$	25	8.86
$CuSO_4.5H_2O$	25	8.81
$MnSO_4.2H_2O$	62	8.78
$ZnSO_4.7H_2O$	100	8.87
$NiSO_4.6H_2O$	42.5	8.87
$Cr_2(SO_4)_3$	3	8.81
NaCl	25	13.1

do not affect the method outside of experimental error. Chloride, as would be expected, caused interference.

Discussion

Aside from the simplicity of a copper reduction method, it has the all-important advantage here of being applicable directly to brass pickling baths containing large amounts of cupric ions, which would not be the case with a zinc or stannous chloride reduction. The fact that chloride is not required as in a mercury (2, 6) or silver (11) reduction makes it possible to use a simple permanganate titration. The absence of special apparatus, such as a reductor tube or colorimetric standards, makes the method particularly suited to millwork where such equipment could be subjected to careless handling and breakage. The simple equipment used in this method is easily replaced without the attention of a trained chemist.

The method requires no special skill and the accuracy and precision of the results show that interference by cuprous compounds and air oxidation is negligible. The use of precipitated copper powder so accelerates the reduction that the method becomes one of the fastest and simplest of analytical methods, which should recommend its use in other applications. The precision of the results is consistent with the technique used and no results were obtained which would indicate that the method could not be made even more precise than 3 parts per thousand, if desired, by introducing refinements.

Acknowledgment

Literature Cited

(1) Birch, *Chem. News*, 99, 273 (1909).
(2) Campbell and Hook, *Soc. Chem. Ind. Victoria Proc.*, 31, 544 (1931).
(3) Carnegie, *J. Chem. Soc.*, 53, 471 (1888).
(4) Fontes and Thivolle, *Bull. soc. chim.*, 33, 844 (1923).
(5) Hendel, IND. ENG. CHEM., 16, 951 (1924).
(6) McCay and Anderson, *J. Am. Chem. Soc.*, 43, 2372 (1921).
(7) Pickles, *Chem. News*, 124, 93 (1922).
(8) Scagliarini and Pratesi, *Ann. chim. applicata*, 19, 85 (1929).
(9) Storch, *Ber. Österr. Ges. Förder. chem. Ind.*, 15, 9 (1893).
(10) Swift, E. H., "System of Chemical Analysis", p. 303, New York, Prentice-Hall, 1939.
(11) Walden, Hammett, and Edmonds, *J. Am. Chem. Soc.*, 56, 350 (1934).

Volumetric Determination of Iron and Aluminum in Cement with 8-Hydroxyquinoline

LEO KAMPF, Division of Analyzing and Testing, President of the Borough of Queens, Long Island City, N. Y.

IN THE usual procedure (2–10, 11, 14) for the determination of iron and aluminum with 8-hydroxyquinoline, the acidity is generally set with acetic acid and ammonium acetate at a pH close to 7, and an acetic acid solution of the 8-hydroxyquinoline is added to precipitate the metals.

Results obtained by this procedure are erratic. While the gravimetric results are satisfactory, the volumetric results are consistently low; although the metals are completely precipitated, they do not come down completely as the oxine. This is due to the fact that the pH for precipitation as the oxine is the same as for precipitation of these elements as the basic acetates. Moyer and Remington (12) have shown that iron is precipitated completely with oxine at a pH of 3.45 to 4.00 and aluminum at a pH of 5.0. At both these points the basic acetate precipitates. When the metals are ignited to the oxides the results are satisfactory, but when the oxine precipitate is weighed, the results are a little low because the basic acetates are lighter than the oxines. In the volumetric determination the metal which comes down as the basic acetate is not determined. The amount of error which this procedure can cause will depend on the dilution, the temperature, and the time of heating, all of which favor the formation of the basic acetate.

To precipitate both iron and aluminum, the pH must be above 5.0. The addition of tartaric acid prevents the formation of the basic acetate at this pH, and the metals can then be precipitated completely as the oxine.

Since divalent iron reacts with only 2 instead of 3 moles of

the oxine, it is necessary to boil the solution with bromine water before adding the oxine.

Two methods for the titration of the oxine precipitate are used. The first—to titrate the oxine directly with a bromate solution before using neocarmine, methyl red, or other dye as the indicator—is not generally used because the color of the dye fades gradually and the end point is not sharp (7, 13). The second method—to add an excess of the bromate and back-titrate with potassium iodide and thiosulfate—cannot be used in the titration of the iron oxine because the potassium iodide also reacts with the ferric ion.

The poor end point with the first method was therefore studied. It was found that the color produced in this titration was not reversible. A very small amount of the bromate solution is able to decolorize a large amount of the indicator. Thus, during the titration, the indicator is being used up by the bromate. To eliminate this it is only necessary to add more indicator when the solution starts to become decolorized. Another reason for the poor end point is that when methyl red, for example, is used in a weak acid solution, the color change is from red to orange to green to yellow. The final transition from green to yellow is very indistinct and it is easy to overrun the end point by as much as 1 cc. If, however, the acid concentration is above 15 per cent, the green color is eliminated and a sharp transition from orange to yellow will be observed, the red changing to orange just before the end point is reached. A satisfactory end point can then be obtained by direct titration with the bromate solution.

Results obtained with these modifications as shown in Table I are typical of many similar determinations.

To determine the iron and aluminum volumetrically the two metals can be precipitated together as the oxine and titrated as indicated above. The iron can then be determined volumetrically on a separate portion in the usual way, or determined on the same portion oxidimetrically.

To determine iron and aluminum in the same solution, both were precipitated with oxine and titrated with the bromate solution; then the iron was titrated oxidimetrically in the same solution. The first titration gave satisfactory reproducible results, but the second did not. When the iron was titrated with potassium permanganate by the Zimmerman-Reinhardt method, the very high results were due, apparently, to an oxidation of the oxine. An oxidizing agent with lower potential (potassium dichromate) gave better results but still high. The iodometric method, which has a much lower potential, was then tried and, after modification, gave satisfactory results as shown in Table I.

TABLE I. DETERMINATION OF IRON AND ALUMINUM

Sample	Metal Present		Bromate Titration	Thiosulfate Titration	Error
		Gram			Mg.
1	Al_2O_3	0.0107	0.0108	....	+0.1
2	Al_2O_3	0.0270	0.0267	....	−0.3
3	Al_2O_3	0.0480	0.0480	....	0.0
4	Fe_2O_3	0.0080	0.0081	....	+0.1
5	Fe_2O_3	0.0186	0.0185	....	−0.1
				0.0187	+0.1
6	Fe_2O_3	0.0362	0.0363	....	+0.1
				0.0361	−0.1
7	Al_2O_3	0.0261	0.0267	....	+0.6
	Fe_2O_3	0.0196	....	0.0195	−0.1
8	Al_2O_3	0.0262	0.0259	....	−0.3
	Fe_2O_3	0.0170	....	0.0173	+0.3
9	Al_2O_3	0.0346	0.0341	....	−0.5
	Fe_2O_3	0.0116	....	0.0114	−0.2

Procedure

Dissolve 0.5 gram of cement in perchloric or hydrochloric acid, depending on whether the silica is determined by the perchloric acid or the ammonium chloride method. After removal of the silica, add an excess of 10 ml. of hydrochloric acid, 2 drops of methyl red, and 5 ml. of 20 per cent tartaric acid. Make just alkaline with concentrated ammonium hydroxide and add 1 to 10 hydrochloric acid till a slight red color appears. Add 20 ml. of a 25 per cent solution of ammonium acetate and bring the solution to a boil. This procedure sets the pH at 5.8; however, it drops to 5.0 after precipitation, because of the release of hydrogen ions in the formation of the oxine complex and because the reagent contains acetic acid.

Cool slightly and add an excess of the 8-hydroxyquinoline reagent (shown by the yellow color of the supernatant liquid). Prepare the reagent by dissolving 12.5 grams of oxine in 30 ml. of glacial acetic acid and diluting with water to 1 liter. Let the precipitate stand 15 to 30 minutes, filter through a coarse filter paper, such as Whatman 41H, keeping the precipitate at least 1.25 cm. (0.5 inch) from the top of the paper because the iron oxine creeps excessively. Wash with warm water. Wash the precipitate back into the original beaker with a stream of hot water and pour 50 ml. of hot 1 to 2 hydrochloric acid over the filter paper to dissolve the remaining precipitate into the original beaker. Heat carefully till the precipitates just dissolve. Cool, add 2 drops of methyl red, and titrate with 0.2 N bromide-bromate solution. When nearing the apparent end point, add another 2 drops of methyl red, allowing 15 seconds before continuing the titration. Continue adding 2 drops of the indicator and titrating until the color changes to an orange and then a yellow within 15 seconds after adding the indicator. For greater accuracy, correct for the amount of bromate used up by the indicator by counting the number of drops of indicator added and determining on a blank the bromate equivalent. Fifteen drops of 0.5 per cent methyl red are decolorized by 0.10 ml. of bromate solution and 10 to 15 drops of indicator are generally used up in a titration.

Add a few drops of the oxine and cool to 15° to 20° C. Add about 6 grams of sodium carbonate and then 20 ml. of 15 per

TABLE II. INTERFERENCE

Sample	Al_2O_3 Present	P_2O_5 Present	Al_2O_3 Found
	Gram	Mg.	Gram
10	0.0267	5	0.0264
11	0.0267	10	0.0261
12	0.0267	15	0.0257
13	0.0267	20	0.0255
14	0.0267	25	0.0257

cent potassium iodide. After 5 minutes add 10 cc. of concentrated hydrochloric acid and titrate with 0.02 N thiosulfate, adding starch when the solution becomes a light yellow. Any color that develops after this titration should be ignored (this is due to the decomposition of the potassium iodide which occurs at the high acidity necessary to keep the iron oxine in solution). The iodometric titration must be run immediately after the bromometric titration because the iron is reduced on standing.

The bromate solution can be standardized with potassium iodide and thiosulfate. The thiosulfate can be standardized against potassium dichromate, or both solutions can be standardized by using the above procedure with Bureau of Standards' Sibley iron ore 27b or standard iron wire.

The interfering elements are large amounts of silica (which causes slightly lower results), copper (4), cadmium, cobalt, nickel, zinc, titanium, and zirconium. Less than 5 mg. of phosphate do not interfere. Table II shows the interference when more than 5 mg. are present. Magnesium and calcium do not interfere. The only interfering elements in this list, besides silica, that are likely to occur in cements are titanium and zirconium.

This method has the following advantages for routine laboratory analysis over the ammonium hydroxide method. It is free from most of the errors indicated by Hillebrand and Lundell (7): phosphate ion interference, traces of silica in the sample and in the reagents (especially ammonia), improper ignition (aluminum oxide requires 1200° C.), absorption of moisture by the ignited oxides, etc.

After the iron and aluminum are determined as above, the calcium can be precipitated at the same pH by the addition of ammonium oxalate and also determined volumetrically. Magnesium can then be precipitated by heating to 70° C., adding more oxine, then 30 ml. of concentrated ammonium hydroxide, stirring for 15 minutes, and letting settle 10 minutes. It is determined volumetrically in the same manner as the iron and aluminum. Cements contain up to 1 per cent of P_2O_5. This amount does not interfere with the oxine method but is carried down in the ammonium hydroxide method. Consequently, this method, in the presence of this ion, will give lower results than the A. S. T. M. method (1). Samples 7, 8, and 9 are cements with only a trace of P_2O_5.

Literature Cited

(1) Am. Soc. Testing Materials, p. 10, Part II, 1939.
(2) Berg, R., J. prakt. Chem., 115, 178 (1927).
(3) Berg, R., "Separation and Determination of Metals with 8-Hydroxyquinoline", Stuttgart, F. Enke, 1938.
(4) Berg, R., Z. anal. Chem., 71, 369 (1927).
(5) Bright, H. A., and Fowler, R. M., Bur. Standards J. Research, 10, 327 (1933).
(6) Hillebrand and Lundell, "Applied Inorganic Analysis", p. 116, New York, John Wiley & Sons, 1929.
(7) Ibid., p. 395.
(8) Hopkins and Williams, Ltd., London, "Organic Reagents for Metals", p. 65, 1938.
(9) Kolthoff, I. M., and Sandell, E. B., J. Am. Chem. Soc., 50, 1900 (1928).
(10) Lundell, G. E., and Knowles, H. B., Bur. Standards J. Research, 3, 91 (1929).
(11) Mitchell, A. D., and Ward, A. M., "Modern Methods in Quantitative Chemical Analysis", London, Longmans, Green and Co., 1932.
(12) Moyer, H. V., and Remington, W. J., IND. ENG. CHEM., Anal. Ed., 10, 212 (1938).
(13) Smith, G. S., Analyst, 64, 577–81 (1939).
(14) Zan'ko, A. M., and Butenko, G. A., Zavodskaya Lab., 5, 415 (1936).