as oxalate, solution in hydrochloric acid and titration with standard ceric sulfate.

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CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. II. DETERMINATION OF IRON

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The possibility of titrating ferrous iron with ceric sulfate has been investigated by the authors[2] and has been found to give quantitative results in either hydrochloric, sulfuric or perchloric acid solution. Furman[3] has also studied this reaction in sulfuric acid solution. It seemed important to study the application of this titration to the analysis of iron ores in which the iron was reduced in hydrochloric acid solution with stannous chloride, the excess of the latter being removed with mercuric chloride, because some of the present methods for titrating the iron after such a reduction have certain undesirable features. If permanganate is used as the oxidizing agent, the concentration of hydrochloric acid must be small because of its reducing action. Manganese sulfate is added[4] but even with this precaution the end-point obtained is fleeting, and some experience with the method is required for accurate results. This end-point has been determined electrometrically.[5] If the titration is made with dichromate, potassium ferricyanide may be used as an external indicator, an inconvenient process, or diphenylamine as an internal indicator,[6] the change in color being from a green to a deep blue shade. Many persons find it difficult to obtain a sharp color change in this latter case. The determination of the end-point electrometrically is very satisfactory.[7]

Experimental

A standard iron solution was made by dissolving electrolytic iron (99.97% Fe) in hydrochloric acid. The ferrous chloride was largely

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[1] From a dissertation submitted by Philena Young to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Willard and Young, THIS JOURNAL, **50**, 1322 (1928).

[3] Furman, *ibid.*, **50**, 755 (1928).

[4] Barnebey, *ibid.*, **36**, 1429 (1914).

[5] Erich Müller, "Elektrometrische Massanalyse," Th. Steinkopff, Dresden, **1926**, pp. 152–153; Müller and Möllering, *Z. anorg. allgem. Chem.*, **141**, 111 (1924).

[6] Knop, THIS JOURNAL, **46**, 263 (1924); Mehlig, *J. Chem. Education*, **3**, 824 (1926).

[7] Hildebrand, THIS JOURNAL, **35**, 847 (1913); Kolthoff, *Chem. Weekblad*, **16**, 450 (1919); Hostetter and Roberts, THIS JOURNAL, **41**, 1337 (1919); Eppley and Vosburgh, *ibid.*, **44**, 2148 (1922).

oxidized by the addition of potassium chlorate. To 20 cc. of this solution, containing 0.3032 g. of iron, 5 cc. of hydrochloric acid, sp. gr. 1.18, was added and the reduction carried out with stannous chloride in the usual way. The solution was cooled, diluted to 150 cc., 10 cc. of saturated mercuric chloride and the indicated volume of hydrochloric acid added, and the solution titrated with ceric sulfate which had been standardized against sodium oxalate.

TABLE I

RESULTS OBTAINED ELECTROMETRICALLY

HCl, sp. gr., 1.18, added before titration, cc.	Error, mg. Fe	Remarks
0	−0.1	Very slight HgCl ppt.
0	− .4	Heavy HgCl ppt.
15	− .2	Very slight HgCl ppt.
15	− .3	Heavy HgCl ppt.
30	− .2	Heavy HgCl ppt.
50	?	No permanent break in potential at end-point. Solvent action of HCl on HgCl and reducing action of latter probably responsible.

Experiments similar to those above, in which 35 mg. of arsenic as sodium arsenite, or 15 mg. of manganese as manganese sulfate or both, was added to the iron solution before reduction with stannous chloride, showed that neither of these elements caused any interference. Such would not be the case with arsenic in some other methods.

Since diphenylamine has been used as internal indicator in the ferrous iron titration with dichromate and the present authors have found that diphenylbenzidine gave similar results, it seemed probable that either of these indicators might be applicable in the ferrous iron-ceric sulfate titration. Such was found to be the case, and the color change at the end-point with this latter oxidizing agent was far superior in sharpness to that obtained in a dichromate titration. This might be expected because the ceric salt is a stronger oxidizing agent than dichromate and also because the change from a green chromic salt color to a deep purple is much more difficult to see than that from a colorless cerous solution to the same deep purple shade.

The standard iron solution was reduced as described above. To the 150 cc. of solution were added 15 cc. of phosphoric acid, sp. gr. 1.37 (prepared by diluting acid of sp. gr. 1.75 with an equal volume of water), the stated volumes of hydrochloric acid and 0.1% diphenylamine (d.p.a.) or diphenylbenzidine (d.p.b.), after which it was titrated with ceric sulfate which had been standardized against sodium oxalate.

In the last two experiments the volume of the solution was 400 cc. at the beginning of the titration. The data in Table II show that no blank cor-

Table II

Results Obtained with a Visual End-Point

HCl, sp. gr. 1.18, cc.	Indicator, 0.1%	Error, mg. Fe	Character of color change
0	0.8 cc. d.p.b.	−0.3	Very sharp
15	0.8 cc. d.p.b.	− .3	Satisfactory
30	0.8 cc. d.p.b.	− .3	Satisfactory
0	0.8 cc. d.p.a.	− .2	Very sharp
15	0.8 cc. d.p.a.	− .3	Satisfactory
30	0.8 cc. d.p.a.	− .3	Satisfactory
5	1.6 cc. d.p.b.	− .4	Satisfactory
5	3.2 cc. d.p.b.	− .4	Not so sharp as preceding one
5	1.6 cc. d.p.a.	± .0	Sharp
5	3.2 cc. d.p.a.	+ .8	Not so sharp
0	0.8 cc. d.p.a.	± .0	Development of color much slower
0	0.8 cc. d.p.b.	− .3	Development of color much slower

rection is required for 0.8 cc. of either indicator, the amount used to obtain a sharp end-point, but that a correction is necessary with larger amounts of diphenylamine. If the end-point in a titration is overstepped it is possible to add a slight excess of standard ferrous sulfate solution, and after a few moments titrate to the end-point with ceric sulfate. The change in color of the indicator in the reverse titration is much slower in the strong acid solution than is the development of the color with the first drop excess of ceric salt—too slow to use it in the determination of cerium.

The consistent error of 0.2–0.3 mg. iron for 0.3 g. present, or approximately one part in a thousand, appearing in Tables I and II, might easily be caused by oxidation by the air. The addition of 1 g. of cerous sulfate to the ferrous solution caused no increase in this error, so that its catalytic action, if any, is very slight. This error was found to disappear when the titrations were made in an atmosphere of carbon dioxide. A weight buret was used here. Because of the constancy of this error, it is possible in the analysis of iron ores either to standardize the ceric sulfate solution against oxalate and multiply by 1.001 or to standardize the solution against an iron ore of known value or electrolytic iron, using the same experimental technique as employed in the unknown ore analyses.

Three Bureau of Standards iron ores were analyzed and a summary of the results obtained is given in Table III. Four-tenths to six-tenths g. samples were treated with 5 cc. of water and 25 cc. of concd. hydrochloric acid, and the material kept just below the boiling boint until all of the ore was decomposed. The insoluble residue was filtered off, decomposed with hydrofluoric and sulfuric acids, and the salts remaining were taken up with dilute hydrochloric acid and returned to the main filtrate. Ore No. 29 contained so much silica that after treatment with hydrofluoric and a drop of sulfuric acids, the material was evaporated to dryness, a small amount of sodium carbonate added and the mixture fused for 3–4 minutes. The fusion was dissolved in dilute hydrochloric acid and added to the main solution. After evaporation to 10–15 cc., the solutions were heated to boiling, reduced with a slight excess of stannous chloride, cooled, diluted to 150 cc., 10 cc. of saturated mercuric chloride solution was added and the titration with ceric sulfate made electrometrically. For the indicator method, 15 cc. of phosphoric acid (sp. gr. 1.37) and 0.8 cc. of indicator were added before the titration. In these analyses as well as in the standardization of the ceric sulfate against electrolytic iron (99.97% Fe) no carbon dioxide was used.

TABLE III

SUMMARY OF ANALYSES OF IRON ORES

		Indicator	
Ore	Electrometric	d.p.a.	d.p.b.
B. of S. No. 27	69.21	...	69.25
69.26% Fe	69.27	...	69.26
	69.28	...	...
	69.23	...	...
B. of S. No. 26	58.57	58.54	...
58.62% Fe	58.54	58.57	...
B. of S. No. 29	55.75	55.73	...
55.75% Fe	55.80	55.70	...

Diphenylamine was found to be a much more satisfactory indicator than diphenylbenzidine. When ceric sulfate was added to an iron ore solution containing the latter indicator, a rather heavy, white precipitate formed which dissolved slowly. This difficulty was not encountered with diphenylamine.

Analyses were made of B. of S. ore No. 27, following the directions for the stannous chloride method through the fuming of the siliceous residue with hydrofluoric and sulfuric acids and the returning of this material to the main filtrate. Four cc. of concd. sulfuric acid was added to the solution and it was evaporated to fumes of SO_3 to remove all hydrochloric acid. Twenty-five cc. of water was added to the moist residue and the liquid heated a few moments until a clear solution was obtained. Pieces of pure aluminum were added and the solution was boiled for ten minutes after it had become colorless. The aluminum was removed, the solution diluted to 150 cc. and the titration with ceric sulfate made electrometrically. For the indicator method, 15 cc. of phosphoric acid (sp. gr. 1.37) and 0.8 cc. of 0.1% diphenylamine were added before the titration. With the electrometric end-point the percentage of iron found was 69.20% and with the indicator 69.24%, both of which agree very well with the B. of S. value of 69.26%.

Summary

1. Standard ceric sulfate may be used to titrate the iron in iron ores after a stannous chloride reduction in hydrochloric acid or a reduction with aluminum or zinc in sulfuric acid solution.

2. Arsenious acid does not interfere in the method.
3. The end-point in the titration may be determined electrometrically or with diphenylamine as internal indicator.
4. Analyses of three Bureau of Standards ores show that this method of titrating the ferrous iron is a very accurate one.
5. Because of the constancy of the slight error due to oxidation of the ferrous iron by air during a titration, the ceric sulfate solution may be standardized against sodium oxalate and a very small correction factor applied, or against a standard iron ore or electrolytic iron of known purity, using the same experimental technique as employed in the analyses.

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THE ACTIVITY COEFFICIENTS OF IONS IN AQUEOUS SOLUTIONS OF NON-ELECTROLYTES

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1. Introductory

The interionic attraction theory of Debye and Hückel[2] and of Debye[3] provides a means of evaluating the electrical potential and therefore the deviations from the ideal state of the ions in a dilute solution. These deviations may be calculated in terms of the osmotic coefficient of the solvent, φ, in terms of the activity coefficient, f_i of an ion of the i^{th} sort, or in terms of the activity coefficient, f_s, of the salt itself. The results of the calculations are,

$$1 - \varphi = w \frac{\epsilon^2}{6DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} n\Sigma\nu_i} \qquad (1)$$

$$-\ln f_i = z_i^2 \frac{\epsilon^2}{2DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} \Sigma n_i z_i^2} \qquad (2)$$

$$-\ln f_s = \frac{\Sigma\nu_i z_i^2}{\Sigma\nu_i} \cdot \frac{\epsilon^2}{2DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} \Sigma n_i z_i^2} \qquad (3)$$

These three equations have been reduced to simpler terms, as follows, by Brönsted and LaMer[4] in one of the previous papers of this series water being used as the solvent:

$$1 - \varphi = \alpha z_1 z_2 \sqrt{\mu} = 0.38\, z_1 z_2 \sqrt{\mu} \qquad (1a)$$

$$-\log f_i = \frac{3}{2.3} \alpha z_i^2 \sqrt{\mu} = 0.50\, z_i^2 \sqrt{\mu} \qquad (2a)$$

$$-\log f_s = \frac{3}{2.3} \alpha z_1 z_2 \sqrt{\mu} = 0.50\, z_1 z_2 \sqrt{\mu} \qquad (3a)$$

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[1] National Research Council Fellow in Chemistry.

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[3] Debye, *ibid.*, **24**, 334 (1923); **25**, 97 (1924).

[4] Brönsted and LaMer, THIS JOURNAL, **46**, 555 (1924).