

5.0, and, likewise, by corresponding acidification of monochloro-amine solutions. It was identified through its behavior with immiscible solvents and by its chlorine-nitrogen ratio.

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THE DETERMINATION OF FERROUS IRON IN SILICATE ROCKS.

II. ELECTROMETRIC

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In a previous article¹ it was shown that the ferrous iron content of silicate rocks can be determined by decomposing the sample with hydrofluoric acid in a pyrex glass flask, diluting with a solution of boric acid and titrating with standardized potassium permanganate. The method has two advantages over that commonly used: (a) the course of decomposition can be watched, and (b) solution and titration are conducted in the same vessel. The most significant disadvantage is that a correction must be applied for the permanganate reduced by dissolved glass constituents.

A consideration of the composition of pyrex glass² suggested that arsenic might be the only disturbing element. It was therefore decided to try ceric sulfate as the oxidizing agent, Willard and Young³ having reported that the titration is not affected by a moderate amount of arsenious acid. The results obtained were satisfactory and led to the development of the method herein advocated.

Materials

Apparatus.—The decomposition flasks were of two sorts: (1) ordinary 250-cc. pyrex glass suction flasks, each having an especially made, well fitting, glass stopper provided with an outlet tube 1 cm. in diameter and bent sharply at the lower end to almost touch the side of the flask; (2) 250-cc. transparent, fused quartz, Erlenmeyer flasks with similar stoppers.

Titration was conducted with the aid of a bimetallic electrode system similar to that suggested by Furman and Wilson.⁴ The resistance used was 240,000 ohms. The electrodes were prepared from pieces of No. 27 B. and S. gage platinum wire and silver wire⁵ annealed at 100–105°, then sealed into the ends of glass tubes as usual. About 3 cm. of the platinum and 6 cm. of the silver wire projected. When not in use the anode was kept in a solution of ceric sulfate and the cathode in dilute ammonia water.

¹ Soule, *THIS JOURNAL*, 50, 1691 (1928).

² U. S. Bureau of Standards Tech. Paper 107, p. 8.

³ Willard and Young, *THIS JOURNAL*, 50, 1335 (1928).

⁴ Furman and Wilson, *ibid.*, 50, 277 (1928).

⁵ This work was nearing completion when the article by Brann and Clapp, *ibid.*, 51, 39 (1929), appeared.

Reagents

The ceric sulfate solution was prepared from U. S. P. quality cerium oxalate by a method similar to that of Willard and Young.⁶

The electrolytic iron, especially prepared and carefully preserved under hydrogen in the form of cubes weighing approximately 0.1 g., had been analyzed by several workers and found to contain impurities totaling not over 0.03%.

Carbon dioxide was obtained from a commercial cylinder and passed through chromous chloride to remove any oxygen.⁷ The purified gas was tested and found satisfactory.

Water for standard solutions was redistilled first from alkaline permanganate then from sulfuric acid. Just before use all water was boiled and cooled.

All other reagents were carefully tested in order to prove that they would introduce no error.

Weighings.—Standard solutions were weighed directly. All other weighings were by substitution.

Experimental

Standardization of Ceric Sulfate.—A single cube of electrolytic iron was placed in a glass flask filled with carbon dioxide; 10 cc. of sulfuric acid (1:6) was added and the flask gently warmed. After fifteen to twenty minutes, when the iron had dissolved, the rate of flow of carbon dioxide was increased. Then 100 cc. of water containing 5 g. of boric acid and 5 cc. of hydrofluoric acid (48%) was added, with care that no air should be drawn in during the operation. After the addition of a few drops of concentrated hydrochloric acid the mixture was titrated electrometrically with ceric sulfate.

Four consecutive determinations gave an average iron equivalence of 0.0034685 g. of iron per gram of solution, that is, a normality of 0.04828.

Determination of Ferrous Iron in Magnetite.^{8,9}—A 0.3–0.4 g. sample of magnetite¹⁰ was placed in a glass flask filled with carbon dioxide. Next

⁶ Willard and Young, *THIS JOURNAL*, 50, 1322 (1928); 51, 149 (1929).

⁷ Moser, *Z. anorg. Chem.*, 110, 126 (1920).

⁸ U. S. Bureau of Standards, Sample No. 29, even though it contains but 12.02% of SiO₂, was selected to illustrate the method proposed because of its status. The FeO content is 24.78% according to the certificate, dated Dec. 1, 1910. This value, apparently contrary to the present practice of the Bureau, is the work of but one analyst, which point together with the early date should be taken into consideration when comparing the figure with averages here reported.

⁹ Compare Adam, *J. S. African Chem. Inst.*, 8, 7 (1925). A copy of this article was obtained after the work here reported had been finished. In agreement with Adam it should be emphasized that HCl + HF + water as a solvent was found far more satisfactory than H₂SO₄ + HF + water, especially, for magnetites. Ores that were dissolved only after long and repeated boiling in the latter mixture were completely decomposed by the former in less than five minutes at a temperature approximating 50°. Combinations of sulfuric acid and hydrochloric acid in various ratios were distinctly less efficient than hydrochloric acid alone.

¹⁰ See U. S. Bureau of Standards Circular No. 26, p. 4, for procedure when drying sample.

10 cc. of hydrochloric acid (35%) and 3 cc. of hydrofluoric acid (48%) were added and the flask gently warmed (40–50°) until no black residue was discernible. This required three to five minutes. Then the rate of flow of carbon dioxide was increased and 100 cc. of water containing 5 g. of boric acid and 5 cc. of sulfuric acid (1:6) was added. The mixture was titrated immediately. Results obtained on three consecutive days are given in Table I.

TABLE I

DETERMINATION OF FeO IN BUREAU OF STANDARDS MAGNETITE (IRON ORE No. 29)
1 g. of $Ce(SO_4)_2$ soln. \approx 0.0034685 g. FeO. Certificate value of FeO in Fe_2O_3 = 24.78%

	Fe_2O_3 , g.	$Ce(SO_4)_2$ soln., g.	FeO, %	
1	0.2776	19.635	24.53	} Average, 24.57
	.2806	19.900	24.58	
	.3012	21.355	24.59	
2	.3793	26.832	24.54	} Average, 24.56
	.4019	28.445	24.55	
	.3192	22.649	24.60	
	.3852	27.229	24.52	
	.4206	29.824	24.60	
3	.4609	32.613	24.54	} Average, 24.54
	.4077	28.859	24.55	
	.3683	26.038	24.52	

Restandardization of Ceric Sulfate.—On the same day that the third set of magnetite samples was analyzed the ceric sulfate was again standardized against electrolytic iron using essentially the method originally employed. The average of results obtained was 0.04827 *N* by weight. The solution was then compared with a different primary standard, retaining, in so far as possible, a final reaction essentially similar to that originally used. The three steps following were completed in one day.

First, 0.1 *N* potassium permanganate was standardized against Bureau of Standards sodium oxalate.¹¹ Next, portions of a sample of ferrous sulfate, selected and tested for uniformity of composition, were transferred to 500-cc. Erlenmeyer flasks filled with carbon dioxide; 200 cc. of water and 10 cc. of sulfuric acid (1:1) were added and the solution was titrated at once with the permanganate just standardized. Determining the equivalence point visually the average of three consecutive results, expressed in ferrous iron content, was 26.63% of FeO. Finally, the ferrous sulfate was titrated with ceric sulfate, using the same reagents as for analysis of magnetite but modifying the procedure to the extent that the reagents were all added at once and the titration was carried out immediately. The average of three consecutive determinations showed an iron content of 26.60% of FeO. Later, the ferrous sulfate was

¹¹ For details of procedure see the certificate or McBride, *THIS JOURNAL*, 34, 393 (1912).

again analyzed using exactly the same procedure as for magnetite. The results averaged 26.66% of FeO.

In order to detect any effect due to the decomposition flask, samples of magnetite were analyzed by the usual procedure in flasks of transparent fused quartz. The average of three consecutive results was 24.58% of FeO.

As a final variation a silver chloride electrode¹² was substituted for the silver wire. Three more analyses of magnetite gave an average of 24.55% of FeO.

Discussion

Among the sources of error encountered in the determination of ferrous iron those leading to low results are considered to be the more common. In the work under consideration thorough preliminary tests and the experiments with ferrous sulfate would indicate that the reagents were satisfactory and the measures for protecting against atmospheric oxidation adequate. The question of low results due to the current generated during titration by the method of Furman and Wilson can be dismissed after a brief calculation. Assuming a titration period double that required and the maximum instead of the average galvanometer deflection only 1.5×10^{-6} g. of FeO would be oxidized.

Another source of error mentioned especially by Adam⁹ is "whether the HCl decomposition takes place without oxidation of a part of the ferrous iron." In the preliminary work experiments were conducted involving variations in amount of hydrochloric acid up to 25 cc. and time of digestion up to 160 minutes. No effect attributable to such variations was found.

Summary

Ferrous iron can be determined quickly and accurately in magnetites and materials of higher silicate content by electrometric titration with ceric sulfate after decomposition in a pyrex glass flask by a mixture of hydrochloric and hydrofluoric acids. Reducing agents derived from the glass have no effect.

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¹² Willard and Fenwick, *THIS JOURNAL*, 44, 2508 (1922).