

A SEMIMICROPROCEDURE FOR THE DETERMINATION OF FERROUS IRON IN NONREFRACTORY SILICATE MINERALS¹

ROBERT MEYROWITZ, *U. S. Geological Survey, Washington, D. C.*

ABSTRACT

The FeO content of 25–100 mg samples of nonrefractory silicate minerals is determined by a semimicrovolumetric method. The sample is decomposed by heating with hydrofluoric and sulfuric acids. The decomposition mixture is added to excess standard potassium dichromate and the excess dichromate titrated with standard ferrous ammonium sulfate in the presence of phosphoric acid using sodium diphenylaminesulfonate as indicator. Determinations of the FeO contents of various silicate minerals using this semimicroprocedure are in satisfactory agreement with those determined by standard macroprocedures.

INTRODUCTION

Many of the samples of silicate minerals received by the analytical laboratories of the U. S. Geological Survey are too small (100–1000 mg) for a complete chemical analysis by classical silicate methods or by "rapid methods." Semimicro- or micro-methods must therefore be used for their analysis.

Various methods for determining ferrous iron in small samples of silicate rocks and minerals have been published. Micro- and semimicro-versions of the normal macroprocedures for determining ferrous iron in silicate rocks and minerals have been described (Das-Gupta, 1941; Guthrie and Miller, 1933, p. 408; Hecht, 1937, p. 205–206; Shioiri and Mitui, 1938; and Vincent and Phillips, 1954, p. 9). In recent years new methods for determining ferrous iron in small samples of silicate materials have been proposed. In some the sample is decomposed in the presence of excess oxidant (Gekht and Putok, 1960; Jackson, 1957, p. 609–610; and Wilson, 1960) and in others the ferrous iron is determined spectrophotometrically (Riley and Williams, 1959, p. 520–521; Shapiro, 1960; and Wilson, 1960, p. 825–826). Clemency and Hagner (1961, p. 889–890) determine the ferric iron and calculate the ferrous iron by difference. The method of Hey (1941, p. 117–118) was developed for refractory silicate minerals which are decomposed by fusion with sodium metafluoroborate, $(\text{NaF})_2\text{B}_2\text{O}_3$.

The semimicroprocedure, proposed here, which is similar to those of Guthrie and Miller (1933, p. 408) and Vincent and Phillips (1954, p. 9), is an adaptation of the normal macroprocedure in which the sample is decomposed in the absence of an oxidant by heating with hydrofluoric and sulfuric acids. It differs in that the decomposition mixture is then added

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to excess potassium dichromate and the excess determined by titration with standard ferrous ammonium sulfate in the presence of phosphoric acid, using sodium diphenylaminesulfonate as indicator. This method of decomposition was chosen because of its simplicity. The addition of the decomposition mixture to an excess of oxidant was adopted to prevent air oxidation of the ferrous iron before titration. Potassium dichromate rather than potassium permanganate, ceric sulfate or vanadate was selected as the oxidant because it is a primary standard.

Before it was applied to the analysis of silicate minerals, this procedure was tested using standard rocks W-1 and G-1. The percentages of FeO in these two rocks, determined by the semimicroprocedure, when the sample used for the analysis contains the equivalent of 5 or more milligrams of FeO (Table II), are in satisfactory agreement with those determined by standard macroprocedures. The procedure is reliable when applied to the analysis of nonrefractory silicate minerals (Table III).

EXPERIMENTAL WORK

A complete study of the stoichiometry of the ferrous-dichromate reaction was not attempted. However, the author has observed that the visual titration of small amounts of standard potassium dichromate by ferrous ammonium sulfate in large volumes of solution is disproportionation. In a final volume of 300–350 ml of solution containing 25 ml 9*N* H₂SO₄, 15 ml 22*N* H₃PO₄, 2.5 ml concentrated HF, and 2 ml 0.01% sodium diphenylaminesulfonate (indicator), a standard 0.01*N* ferrous solution was found to have the following apparent normalities as the volume of standard 0.02000*N* K₂Cr₂O₇ titrated was changed:

| Volume of 0.02000 <i>N</i> K ₂ Cr ₂ O ₇ taken for titration (ml) | Normality of Fe ²⁺ Solution |
|---|--|
| 9.180 | 0.01003 |
| 8.085 | 0.01004 |
| 7.120 | 0.01004 |
| 6.140 | 0.01003 |
| 5.175 | 0.01010 |
| 4.145 | 0.01016 |
| 3.085 | 0.01019 |
| 2.120 | 0.01037 |
| 1.070 | 0.01087 |

This disproportionality is not as pronounced when the volume is $\frac{1}{4}$ – $\frac{1}{3}$ the original volume. In a final volume of 95–115 ml of solution containing 6.25 ml 9*N* H₂SO₄, 3.75 ml 22*N* H₃PO₄, 1 ml concentrated HF, and 0.5 ml 0.01% sodium diphenylaminesulfonate, a standard ferrous solution was

found to have the following apparent normalities as the volume of standard 0.02000*N* $K_2Cr_2O_7$ titrated was changed:

| Volume of 0.02000 <i>N</i> $K_2Cr_2O_7$ taken for titration (ml) | Normality of Fe^{2+} Solution |
|---|---------------------------------|
| 9.155 | 0.00989 |
| 8.165 | 0.00989 |
| 7.165 | 0.00990 |
| 6.205 | 0.00990 |
| 5.165 | 0.00991 |
| 4.140 | 0.00993 |
| 3.090 | 0.00995 |
| 2.145 | 0.00996 |
| 1.100 | 0.01010 |

The apparent normalities of the same ferrous iron solution standardized in the large and small volumes using approximately 9 ml of standard 0.02000*N* $K_2Cr_2O_7$ differ. For the large volume it was 0.01003*N* Fe^{2+} and for the smaller volume it was 0.00993*N* Fe^{2+} .

The 0.01*N* ferrous ammonium sulfate solution is relatively stable (Table I).

The disproportionality described above resembles the disproportionality observed in the volumetric determination of small amounts of uranium using a visual titration by $K_2Cr_2O_7$ with sodium diphenylaminesulfonate as the indicator (Rodden, 1958, p. 25; DeSesa, 1958, p. 58-59; Toni, 1962). In this determination the U^{4+} reacts with excess Fe^{3+} and the Fe^{2+} formed is titrated with $K_2Cr_2O_7$.

TABLE I. STABILITY OF 0.01*N* FERROUS AMMONIUM SULFATE (1*N* H_2SO_4) DURING USE

| Normality of Fe^{2+} | Days |
|-------------------------------|------|
| 0.00993, 0.00993 ¹ | 0 |
| 0.00991, 0.00991 | 1 |
| 0.00989, 0.00990 | 2 |
| 0.00992, 0.00992 | 5 |
| 0.00993, 0.00995 | 7 |
| 0.00992, 0.00993 | 12 |
| 0.00992, 0.00992 | 13 |
| 0.00994, 0.00992 | 14 |
| 0.00989, 0.00990 | 16 |
| 0.00989, 0.00989 | 19 |
| 0.00989 | 20 |
| 0.00988 | 22 |

¹ Duplicate determinations were made the same day.

TABLE II. FeO CONTENT OF STANDARD ROCKS W-1 AND G-1

| Rock | Sample Size (mg) | % FeO Found | % FeO Reported by Conventional Procedures ¹ |
|------|------------------|-------------|--|
| W-1 | 105.5 | 8.72 | Arithmetic Mean=8.63; Median=8.75; Adopted limits of acceptability=8.22-9.04; ¹ Stevens and others, 1960, p. 32 |
| | 104.4 | 8.73 | |
| | 84.8 | 8.70 | |
| | 83.5 | 8.62 | |
| | 81.6 | 8.73 | |
| | 61.4 | 8.54 | |
| | 50.51 | 8.59 | |
| | 49.7 | 8.73 | |
| | 37.62 | 8.65 | |
| | 25.56 | 8.46 | |
| | 13.74 | 8.21 | |
| | Mean | 8.61 | |
| G-1 | 90.6 | 0.90 | Arithmetic Mean=0.99; Median=0.98; Adopted limits of acceptability=0.89-1.10; ¹ Stevens and others, 1960, p. 31 |
| | 104.2 | 0.86 | |

For optimum results the sample size (between 25 and 100 mg) should contain the equivalent of 5-7 mg FeO and, if possible, closer to 7 mg FeO, and the volume of 0.02000*N* K₂Cr₂O₇ used in each determination should be approximately 9 ml. The large amount of FeO taken (7 mg FeO) would minimize the error in the determination due to the uncertainties in the standardization of the ferrous ammonium sulfate. The use of a large volume of potassium dichromate would avoid the error due to the disproportionality described above. The "indicator error" is reduced by

- (a) adding the indicator after most of the dichromate has been reduced, and by
- (b) adopting as the end-point of the titration the disappearance of the purple or violet color of the indicator, at which point the indicator is in the same state (reduced form) in which it was added.

Table III presents a comparison for various silicate minerals of the FeO content obtained by the semimicroprocedure described below and that obtained by a standard macroprocedure in which the mineral sample had been decomposed by heating with hydrofluoric and sulfuric acids. All the minerals used as test samples had been analyzed completely by the U. S. Geological Survey laboratories in Denver or in Washington, D. C. The results for FeO obtained by the semimicroprocedure are in satisfactory agreement with those determined by standard macroprocedures. The relatively large difference in the garnet samples No. 157726 and No. 157713 is probably due to the variability in the completeness of the de-

TABLE III. FeO CONTENT OF VARIOUS SILICATE MINERALS—A COMPARISON OF RESULTS OBTAINED BY SEMIMICROPROCEDURE AND MACROPROCEDURES

| Lab. Number | Field Number | Mineral | Semimicroprocedure ¹ | | Macroprocedure | | %FeO Semi-microprocedure less %FeO Macroprocedure |
|-------------|--------------|---------------|---------------------------------|--------------|--------------------|------------------|---|
| | | | Sample Size (mg) | % FeO | % FeO | Sample Size (mg) | |
| H-3399 | 50-CZ-60F | Epidote | 97.0, 125.1 | 0.55, 0.57 | 0.64 ¹ | 500 | -0.09, -0.07 |
| H-3394 | 50-CZ-60A | Pumpellyite | 74.2, 75.6 | 3.10, 3.13 | 3.16 ¹ | 500 | -0.06, -0.03 |
| H-3618 | KJM-72 | Augite | 72.8, 72.4 | 5.77, 5.76 | 6.08 ¹ | 500 | -0.31, -0.32 |
| H-3617 | P-1 | Augite | 80.5, 75.9 | 5.82, 5.88 | 6.16 ¹ | 500 | -0.34, -0.34 |
| 158421 | P919-Bio | Biotite | 83.2, 103.8 | 8.56, 8.58 | 8.7 ² | 500 | -0.1, -0.1 |
| 158414 | P918A-Px | Augite | 74.0, 85.2 | 9.49, 9.53 | 9.6 ² | 500 | -0.1, -0.1 |
| H-3396 | 50-CZ-60C | Glaucophane | 71.3, 79.5 | 11.53, 11.51 | 11.62 ¹ | 500 | -0.09, -0.10 |
| 158412 | P904-Px | Titano-augite | 63.2, 70.9 | 12.36, 12.36 | 12.6 ² | 500 | -0.2, -0.2 |
| 158422 | P918A-Bio | Biotite | 51.0, 45.2 | 16.07, 16.05 | 16.2 ² | 500 | -0.1, -0.1 |
| 157730 | 113-RGC-58 | Garnet | 30.85, 37.67 | 22.96, 22.90 | 22.8 ² | 500 | +0.2, +0.1 |
| H-3398 | 50-CZ-60E | Chlorite | 35.95, 30.20 | 24.12, 24.03 | 24.36 ¹ | 500 | -0.22, -0.32 |
| 157726 | 50-CZ-60 | Garnet | 29.03, 31.26 | 25.37, 25.08 | 25.7 ² | 500 | -0.3, -0.6 |
| 137729 | 100-RGC-58 | Garnet | 30.49, 32.47 | 26.04, 25.92 | 25.8 ² | 500 | +0.2, +0.1 |
| 157713 | 201-RGC-59B | Garnet | 31.50, 29.43 | 27.05, 26.90 | 26.1 ² | 500 | +1.0, +0.8 |

¹ Analyzed in U. S. Geological Survey, Denver, Colorado.

² Analyzed in U. S. Geological Survey, Washington, D. C.

³ Duplicate Samples.

composition of these relatively more refractory minerals. The precision of the duplicate samples (other than the garnets) analyzed by the semimicroprocedure is good. Three procedural blanks were equivalent to 0.03, 0.00, and 0.00 mg FeO. These blanks are within the experimental error of the standardization of the 0.01*N* Fe²⁺ by 0.02000*N* K₂Cr₂O₇.

REAGENTS AND EQUIPMENT

Sulfuric acid, 9*N*: 500 ml of solution contains 125 ml concentrated H₂SO₄, ACS Reagent.
Phosphoric acid, 22*N*: 500 ml of solution contains 250 ml of concentrated H₃PO₄, ACS Reagent.

Concentrated HF, ACS Reagent.

Sodium diphenylaminesulfonate—0.01%: 100 ml of solution contains 10 mg sodium diphenylaminesulfonate.

Potassium dichromate—0.02000*N*: one liter contains 980.7 mg U. S. National Bureau of Standards Standard Sample No. 136, K₂Cr₂O₇.

Ferrous ammonium sulfate—0.01*N* (1*N* H₂SO₄): one liter contains 3.922 g Fe (NH₄)₂(SO₄)₂·6H₂O, ACS Reagent, and 28 ml concentrated H₂SO₄, ACS Reagent.

Stirring bar, magnetic, plastic-coated, $\frac{7}{8}$ in. × $\frac{3}{8}$ in.

Stirring bar, magnetic, plastic-coated, $\frac{3}{8}$ in. × $\frac{1}{8}$ in.

Beaker, Berzelius, tall-form, borosilicate glass, 100 ml.

Burette, Precision Bore, Class A, 25 ml, graduated in 0.01 ml intervals.

Burettes, (2), Precision Bore, Class A, 10 ml graduated at either 0.05 ml or 0.02 ml intervals.

Magnetic stirrers (at least 2) approximately 4 in. wide.

Hot plate, semimicro, approximately 70 watts; diameter, approximately 3 in.; overall height, 2 in. (The overall height of the hot plate should be such that there is good magnetic coupling between the magnet of the stirrer and the stirring bar.)

Autotransformer, variable, to regulate temperature of hot plate.

Crucible and cover, platinum, 10 ml (the bottom of the crucible flattened to insure maximum contact area with the hot plate and the handle portion of cover bent slightly upward).

Platinum stirring rod, heavy gauge wire, 0.064 in. diameter, with one chisel-pointed end.

Tweezers, with long platinum tips whose ends have been bent at right angles.

Tongs, crucible, Blair type, with platinum tips shaped to fit the 10 ml platinum crucible.

PROCEDURE FOR THE STANDARDIZATION OF 0.01*N* FERROUS AMMONIUM SULFATE

Transfer 6.25 ml 9*N* H₂SO₄ to a 100 ml Berzelius beaker containing a $\frac{7}{8}$ in. \times $\frac{3}{8}$ in. magnetic stirring bar. Add 3.75 ml 22*N* H₃PO₄ and 25 ml of water. Add from a 10 ml buret 9.1 to 9.2 ml 0.02000*N* K₂Cr₂O₇. Rinse tip of buret with water. Add 1 ml concentrated HF using a plastic pipet. Rinse down inside of beaker with water and dilute to 75–85 ml. Place on magnetic stirrer and mix well. Titrate with 0.01*N* ferrous ammonium sulfate (using the 25 ml buret) until the yellow color of the solution appears to disappear. Use a piece of white paper under and behind the beaker as a background. Add 0.5 ml of 0.01% sodium diphenylaminesulfonate. Add the ferrous solution dropwise until the violet or purple color just disappears. Rinse tip of buret with water. Add 0.02000*N* K₂Cr₂O₇ dropwise with constant stirring until the purple or violet color reappears. Rinse tip of buret with water. Add the ferrous solution, "cracking" the drops added, until the purple or violet color just disappears. The tip of the buret is rinsed with water after the addition of each "cracked" drop.

Calculations

$$N \text{ Fe}^{2+} = \frac{\text{ml of K}_2\text{Cr}_2\text{O}_7 \times \text{Normality of K}_2\text{Cr}_2\text{O}_7}{\text{ml of ferrous solution}}$$

The ferrous solution is standardized in duplicate each day it is used.

PROCEDURE FOR THE DETERMINATION OF FeO

Weigh by difference 25–100 mg of silicate mineral (containing approximately 7 mg FeO) in a 10 ml platinum crucible. Use a semimicrobalance (± 0.01 mg) for samples 25–40 mg and a macrobalance (± 0.1 mg) for samples 40–100 mg. Place in the crucible a plastic-coated $\frac{3}{8}$ in. \times $\frac{1}{8}$ in. stirring bar. Using a fast-flowing 2 ml pipet add 2 ml 9*N* H₂SO₄ to the platinum crucible, rinsing down the inside surface of the crucible. The crucible is rotated during the addition of the acid. Add 1 ml concentrated HF (using a plastic pipet) dropwise to the crucible. Cover with crucible cover. Place crucible on the hot-plate whose surface temperature is $350^\circ \pm 10^\circ$ F. (calibrated using a bimetallic spiral surface thermometer). The hot-plate sits on a magnetic stirrer. Heat for three minutes. Start the magnetic stirrer and continue heating for another seven minutes.

While the sample is being decomposed, add to the 100 ml Berzelius

beaker a plastic-coated $\frac{7}{8}$ in. \times $\frac{3}{8}$ in. magnetic stirring bar, 4.25 ml 9*N* H₂SO₄, and 3.75 ml 22*N* H₃PO₄. Rinse down inside surface of beaker with water. Add 9.1–9.2 ml 0.02000*N* K₂Cr₂O₇ from a 10 ml buret. Rinse tip of buret with water. Dilute with water to such a height in the beaker that the 10 ml crucible, when lying on its side in the beaker, will be completely submerged. Mix the solution well using the magnetic stirrer. Using the heavy platinum wire and the Blair platinum crucible tongs quickly transfer the crucible and its cover to the beaker containing the K₂Cr₂O₇, plunging it beneath the solution so that it is completely covered. Using the heavy platinum wire, the crucible is twirled a few times keeping it completely submerged during the mixing of the crucible contents and the K₂Cr₂O₇ solution. The crucible is set upright and the solution in the crucible stirred using the platinum wire. The crucible is again set on its side and the crucible again twirled in the beaker a few times.

Using a plastic wash bottle with a fine nozzle the platinum tips of the tongs are rinsed with water into the beaker. The tongs are held in such a position that when the water is added dropwise at the upper portion of the platinum tips, it will roll down to the end of the tips. Each of the pair of tips is rinsed at least five times. The crucible cover is removed from the solution and rinsed at least three times on both sides with water. This operation is performed in the following manner. The "handle" portion of the crucible cover has been bent slightly upward in order to facilitate its removal from the beaker. The platinum wire is used to lift it on its edge and then it is taken out of the solution by using the pair of platinum-tipped tweezers. Set the crucible upright in the beaker, using the platinum wire. Rinse the platinum wire into the beaker with water. The platinum tweezers with bent tips are used to lift the crucible out of solution and the contents carefully poured out into the beaker. Rinse the inner and outer surfaces at least three times with water using a plastic wash bottle with a fine nozzle. This operation is performed in the following manner. First, the platinum tips of the tweezers are rinsed down using drops of water. Second, the inner surface of the crucible is rinsed from the top of the crucible down until the crucible is about one-half full. It is then inclined slightly and the outside surface rinsed from the top downward. The crucible is emptied carefully with the rim of the crucible touching the inner surface of the beaker so that the contents of the crucible are drained as completely as is possible. The portion of the inside of the beaker down which the contents of the crucible flowed is rinsed down dropwise with a small amount of water. This complete cycle of rinsing is repeated at least two times. Minimum amounts of water are used for the rinsings so that a maximum number of rinsings can be made. After the rinsings have been completed, the inside surface of the beaker is rinsed down. The volume of the solution in the beaker should be approximately 75–85 ml.

Titrate with 0.01*N* ferrous ammonium sulfate using the 25 ml buret if more than 10 ml of 0.01*N* Fe²⁺ is needed for the back titration. If less than 10 ml of 0.01 Fe²⁺ is required, use the 10 ml buret. Complete the titration as it is described for the standardization of the 0.01*N* ferrous ammonium sulfate.

Calculations

$$\% \text{FeO} = \frac{[(\text{ml of K}_2\text{Cr}_2\text{O}_7 \text{ used} \times \text{normality of K}_2\text{Cr}_2\text{O}_7) - (\text{ml Fe}^{2+} \text{ used} \times \text{normality of Fe}^{2+})] \times 71.84 \times 100}{\text{Weight of sample in milligrams}}$$

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