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# A single-dissolution technique for determining FeO and $Fe_2O_3$ in rock and mineral samples

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## Abstract

A single-dissolution technique has been devised to measure % FeO and $\Sigma$Fe as % $Fe_2O_3$ on small (< 10 mg) samples. Colorimetric determination of FeO is patterned after Shapiro's (1960) method with time-saving modifications due to gravimetric dilutions. After the colorimetric measurements, the solutions are analyzed for $\Sigma$Fe as % $Fe_2O_3$ by atomic absorption spectrophotometry. The results for both analyses give values that are in reasonable agreement with other wet chemical methods and with Mössbauer spectral techniques.

Because FeO and total iron are both measured in a solution produced by a single digestion, weighing errors of the dry sample do not affect the ferric–ferrous ratio obtained in the analyses. This ratio should thus be determinable on vanishingly small sizes, provided that the resulting solutions lie within the detection limits of the analytical instruments.

## Introduction

The iron content of silicates can be determined by several different analytical techniques. Electron microprobe spectroscopy measures a sample's total iron—usually expressed as % FeO. Mössbauer spectroscopy is capable of directly measuring the $Fe^{3+}$–$Fe^{2+}$ ratio, as well as determining site occupancy of iron within the crystal structure of a mineral; however it does not yield quantitative measurements of a sample's iron content. Ironically, it is the less glamorous wet chemical methods that provide analytical versatility that can be used to obtain analyses of both FeO and $Fe_2O_3$. From these values, the $Fe^{3+}$–$Fe^{2+}$ ratio is easily calculated.

Most wet chemical measurements of $Fe^{2+}$–$Fe^{3+}$ contents of rocks and minerals involve a 2-step dissolution process in which a sample is first analyzed for total iron expressed as $Fe_2O_3$. This is normally followed by a separate dissolution to directly determine the sample's FeO content.

The manner in which a sample is dissolved dictates the valence of iron in the final solution used for total iron analysis. The two most common techniques employed in the dissolution of silicates for whole rock analyses are the $LiBO_2$ fusion procedure (Medlin et al., 1969) and the $H_3BO_3$/HF attack described by Bernas (1968). Both techniques oxidize the iron so that only $\Sigma$Fe as $Fe_2O_3$ can be analyzed–typically by atomic absorbtion spectrophotometry. Alternatively, a sample can be treated with a strong reducing agent. In this case, the iron in the final solution is ferrous so that $\Sigma$Fe as FeO is determined colorimetrically (Shapiro and Brannock, 1962).

The next step in the wet chemical analysis of iron usually necessitates a second dissolution of the powdered sample for direct determination of FeO. This FeO determination can be performed by titration or colorimetry.

Several different titration techniques have been described in the literature. In the technique of Schaefer (1966), the dissolution and titration procedures are carried out in a nitrogen atmosphere to prevent oxidation by atmospheric oxygen during digestion and analysis procedures. The disadvantage of this technique is the tedious requirement of working in an oxygen-free environment. Inattentiveness to this requirement may lead to a low value for a sample's % FeO (Fritz, 1976). The techniques described by Reichen and Fahey (1962) and by Wilson (1955) as modified by Whipple (1974) do not require an oxygen-free atmosphere; the sample is dissolved and oxidized in the presence of a known amount of oxidizing agent. The excess oxidizing agent is then titrated with a ferrous-bearing solution, and the $Fe^{2+}$ content of the sample calculated. Aside from the disadvantage of relatively long dissolution times (overnight), titration techniques generally require more elaborate procedures and well-honed analytical proficiency.

In the colorimetric determination of FeO, a sample is dissolved by a mixture of HF and $H_2SO_4$ in the presence of o-phenanthroline. This organic reagent serves two purposes: (1) it prevents oxidation of the sample's ferrous iron during dissolution by selectively complexing with the released ferrous iron during acid attack; and (2) it forms an orange-colored complex with $Fe^{2+}$ whose intensity is directly proportional to the ferrous content of the digested sample. This procedure, outlined by Shapiro (1960), is relatively tolerant of atmospheric oxygen and thus obviates the need for dissolution under oxygen-free conditions. Moreover, the 10 mg sample size prescribed by Shapiro (1960) lends this technique to being modified to accommodate dissolution of samples even smaller than 10 mg.

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Apart from the tedium of dissolving two dry aliquots of the same sample, the disadvantage of the standard two-stage dissolution process to determine $Fe^{2+}$ and $Fe^{3+}$ is that inhomogeneity of the powdered sample may result in selection of a non-representative dry aliquot for anlayses of FeO and ΣFe as $Fe_2O_3$. This problem is minimized if both iron analyses are performed on a solution obtained from a single dissolution of one dry aliquot.

Roth et al. (1968) devised a scheme by which FeO and $Fe_2O_3$ could be obtained from a single dissolution. They dissolved their samples according to Shapiro's (1960) method to obtain % FeO. Thereafter, they added $NH_2OH \cdot Cl$ (hydroxylamine hydrochloride) to reduce all the soluble iron to the ferrous state. After a 24 hour wait, these solutions were analyzed for ΣFe as FeO by colorimetry.

This study describes a simpler and quicker wet chemical procedure for analysis of FeO and $Fe_2O_3$ in silicate samples by a single dissolution technique. Shapiro's (1960) dissolution procedure is adopted with time-saving modifications brought about by gravimetric dilutions using a top-loading balance. Following the colorimetric determination of FeO, the solutions are analyzed by atomic absorption spectrophotometry for determination of ΣFe as $Fe_2O_3$. The technique requires relatively few steps requiring quantitative measurements, and is carried out on instruments available in most modestly equipped laboratories.

To gauge the accuracy of this technique, 10 rock standards and 10 previously-analyzed amphiboles were treated as unknowns, and the observed values are compared to the published data. Moreover, the $Fe^{3+}$–$Fe^{2+}$ ratios obtained for the amphiboles by this wet chemical method are compared to ratios obtained from published Mössbauer analyses.

## Analytical procedure

The list of equipment and reagents needed to perform the FeO and $Fe_2O_3$ analyses is given in the appendix.

### *Weighing procedure*

Special care must be exercised in precision weighing of extremely small samples. One source of error that results from transferral of sample from weighing paper to the digestion vessel can be circumvented if the sample is weighed directly into the vessel, in this case a pre-labelled, 4 ounce polypropylene bottle. The most troublesome weighing difficulty is weight gain or loss of the sample during the weighing procedure. To insure the samples are free of absorbed water prior to weighing, the rock standards and unknowns should be dried at 110°C for at least 12 hours, removed and allowed to cool in a desicator.

The uncapped digestion bottle and its cap are placed on the pan of an analytical balance and weighed to the nearest 0.01 mg. This requires patience because a newly opened, clean polypropylene bottle sorbs water such that three minutes sometimes elapse before the bottle's weight has stabilized. With the balance still in full pan position, the balance window is opened and a small amount of sample is dropped into the bottle. The balance window is quickly closed and the weight is recorded to the nearest 0.01 mg. Because the accuracy of this weighing step is crucial to the accuracy of both the FeO and $Fe_2O_3$ analyses, the sample weight should be measured in a minimal amount of time in order to minimize adsorption of water by the powdered sample. With practice, this weighing step can be performed in less than 20 seconds. All standards and unknowns should be accurately weighed with the same dispatch so that exposure of all samples to the laboratory's humidity is of the same time interval.

Next, a small amount of crystalline o-phenanthroline is placed into the bottle containing the weighed sampled. The exact amount of this reagent is not critical. The only requirement is that enough o-phenanthroline be present to complex all of the FeO in the sample. One mole of o-phenanthroline (180 grams) can complex 2 moles of $Fe^{2+}$. Thus, the addition of 20 mg of o-phenanthroline will complex the ferrous iron content of 16 mg of pure FeO. Because excess o-phenanthroline is not deleterious to the colorimetric technique, any small amount over 20 mg will suffice. Weighing of the standards and unknowns can be done days in advance of the actual digestions and spectrophotometric measurements.

Shapiro (1960) recommends weighing 10.0 mg of rock powder for the FeO determination. To achieve this exact weight necessitates exposing the rock powder to the humidity of the laboratory for times greatly exceeding 20 seconds. A single dropping of the powdered sample directly into the 4 oz. polypropylene bottle minimizes the error caused by undue sorption of water by the sample. Moreover, the variation of sample size resulting from this rapid weighing method does not affect the overall analytical results.

Figure 1 is a plot of absorbance of the ferrous-phenanthroline complex versus milligrams of sample dissolved for two rock standards. Sample sizes range from 4 to 20 mg. The figure demonstrates that for the different rock standards, absorbance is strictly a function of the absolute amounts of FeO in the dissolved sample and is thus independent of the varying solution matrix caused by dissolution of different weights of the same sample. The extreme similarity of the Δ% FeO/Δ abs. relations of the two lines of Figure 1 means that if absorbance were plotted versus absolute % FeO, all 9 samples of these two rock standards would plot on a line having a slope of about 29.18% FeO/1.000 absorbance unit, and an intercept of 0.01% FeO. Thus, it is possible that only one rock standard can be used for the FeO calibration curve, provided that a wide range of weights of that *accurate* rock standard is employed. This would be advantageous for those analysts whose stock of rock standards is extremely limited.

Because the absorbance of all unknowns must be bracketed by absorbance of rock standards, the concentration of FeO in an unknown solution must be less than that of the highest rock standard used in calibration. In this study, the rock standard, "Fe–Mica", a high-iron biotite

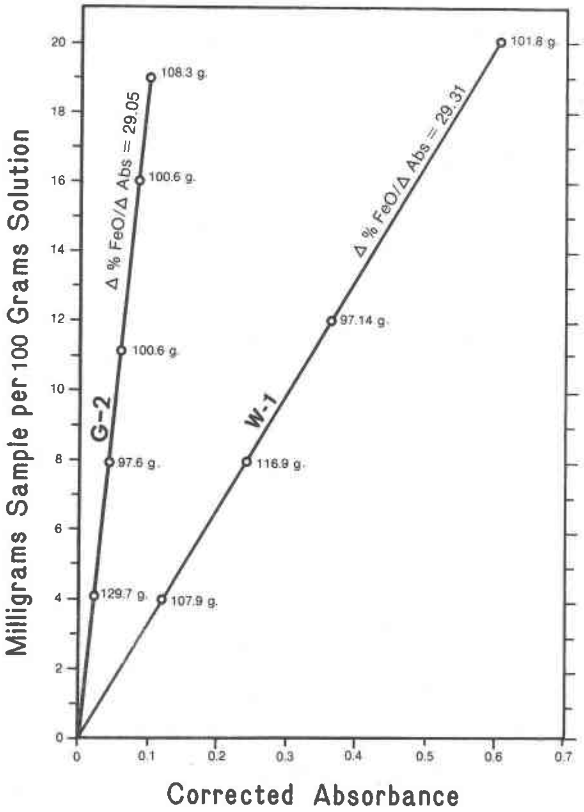

Fig. 1. Variation of absorbance with sample size of two rock standards, G-2 and W-1. Reported % FeO for G-2 and W-1 are 1.44% and 8.73%, respectively (Abbey, 1980). Because the absorbance of different weights of samples of the same standard fall on a line, the linearity of the absorbance–% FeO relationship is not affected by matrix effects caused by dissolving different amounts of the same sample. The number adjacent to each datum point represents the total grams of solution to which the digested sample was diluted with deionized water.

(FeO = 18.99%, total Fe as $Fe_2O_3 = 25.76\%$ (Abbey, 1980)), serves to anchor the highest position of the calibration curve for both FeO as well as for $\Sigma$Fe analyses. As long as a weighed unknown has an absolute FeO content less than that of Fe-Mica, the absorbance of that unknown will be bracketed by rock standards. Unknowns having very high ferrous contents would, of course, have to be weighed in amounts substantially less than that of the most FeO-rich standard.

### *Dissolution procedure*

Standards and unknowns are routinely dissolved in batches of seven because seven 4 oz. polypropylene bottles form a tightly-packed hexagon that fits neatly into the 4 liter glass beaker containing boiling water. The use of automatic pipets in volumetric dispensing greatly reduces the time required for analyses. Three ml of 10% $H_2SO_4$ are dispensed into each of the bottles containing the weighed sample and the o-phenanthroline. This is followed by an input of 0.5 ml of 48% HF delivered from a syringe inert to HF. The cap is replaced and tightened until resistance is first felt. Back off one quarter turn and tape the cap to the bottle's side with electrical tape. This small opening prevents gas build-up during digestion. The secured cap also insures no contamination of the digesting sample by splashing from the water bath.

The 7 bottles are arranged in a tightly-packed hexagon to obtain a circular pattern. The bottles are bound together with two rubber bands and this assembly is placed into a 4 liter glass beaker which is about half filled with boiling water. Samples are digested for exactly 30 minutes and removed. Into each bottle are successively added 20 ml of 10% Na-Citrate and 5 ml of 5% boric acid solution. The order in which these two solutions are delivered to the samples should be the same as that in which the $H_2SO_4$ and HF were dispensed prior to thermal digestion. The orange-color denoting the presence of the ferrous-phenanthroline complex usually appears after the addition of the Na-Citrate. However, for highly ferrous samples, the orange color may have already been developed during the digestion.

After the addition of the boric acid, the solutions are immediately diluted with deionized water. Shapiro (1960) recommended diluting each solution with deionized water in a 100 ml volumetric flask. This step is done faster and more accurately by directly adding deionized water to the solution in the digestion bottle, which is placed on the pan of a top-loading balance. Deionized water is added until the total weight of the solution + bottle + cap is about 100 gm greater than the original weight of the dry bottle and cap. The total solution weight should be recorded to the nearest 0.01 gm. The total solution weight need not be exactly 100.00 gm. The only critical consideration in diluting the orange-colored solution is that the pH of the final solution to be measured colorimetrically falls within the range of 2.8 to 3.5 (Roth et al., 1968).

In Figure 1, the number adjacent to each datum point represents the total grams of solution to which the digested sample was diluted with deionized water. The wide range of total solution weights in Figure 1 (97.6 to 129.7 gm) indicates a moderate toleration of dilution with respect to maintaining the solution's pH within the range where color intensity is simply a function of the concentration of the ferrous-phenanthroline complex. This toleration of dilution can be beneficial in the absorbance measurements of highly ferrous unknowns that must be diluted in order to be bracketed by the most FeO-rich standard. Occasionally, the intensity of the orange-colored solution of an unknown after the additions of the citrate and boric acid solutions is visually observed to be darker than that of the highest rock standard. This arises when too much powder of the highly ferrous unknown was weighted into the 4 oz. polypropylene bottle. To insure that the absorbance of this unknown is less than that of the highest rock standard, the highly ferrous unknown can be diluted with as much deionized water allowable by the volume of the 4 oz. bottle. The rock standard having the highest ferrous content can then be diluted with substantially less water such that its dissolved ferrous concentration becomes greater than that of the highly-diluted unknown.

### *Spectrophotometric measurements*

In the colorimetric determination of FeO, the color intensity of the ferrous phenanthroline complex is time-dependent (Shapiro, 1960; Roth et al., 1968). As such, the absorbance of the colored solutions must be performed in chronological order at precise intervals measured from the time of digestion. A two-person operation facilitates this requirement as well as expediting the runs. One person's responsibilities are to handle the addition of the reagents to the samples as well as to manage the digestion procedure. The other analyst's chore is to dilute the colored solutions with deionized water and to record the colorimetric measurements.

Absorbance readings are also performed in batches of seven, commencing when the seventh sample in that batch has been diluted with deionized water. Absorbance of the diluted orange-colored solution was performed on a dual beam spectrophotometer, (a Bausch and Lomb Spectronic 2000), using matched glass cuvets with a path length of 10 mm. The reference solution was a blank, against which the absorbance of all standards and unknowns was compared. The blank consisted of rock crystal quartz digested in the same fashion as all the other samples. Absorbance of all samples was measured at 555 nm, with background readings taken at 640 nm. The absorbance reading at 640 nm corrects for turbidity of the solution arising from possible incomplete digestion of the sample (Shapiro, 1960).

Figure 2 is a typical calibration curve of standards for a set of FeO analyses. The linearity of the concentration-absorbance relationship testifies to the obediance of Beer's Law up to highly ferrous rock standards such as Fe-Mica. The high value for the linear correlation coefficient for this calibration curve was typical of all FeO runs. The different positioning of the same rock standards along the line is due to differing initial weights of their dry powders, as well as to their varying total solution weights.

Because both the dry sample weight and final solution weight vary from sample to sample, all blank- and background-corrected absorbance data must be normalized against some arbitrary reference values in order to obtain absolute FeO contents of the unknowns. In the analyses reported here, the reference values were selected to be 10.0 mg dry sample weight, and 100.0 gm of solution. The "normalized % FeO" values plotted on the ordinate of Figure 2 have been corrected in this manner. Thus, the "normalized % FeO" of a rock standard is equal to its reported % FeO multiplied by Dilution Fraction One ($F_1$), where

$$F_1 = \frac{\text{(sample weight in mg)}}{10\text{ mg}} \cdot \frac{\text{(100 grams)}}{\text{weight of solution in gm}} \qquad (1)$$

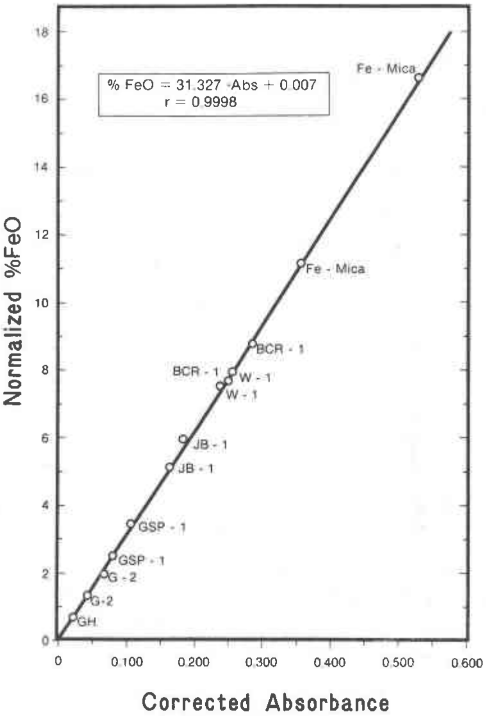

Fig. 2. Typical FeO calibration curve showing normalized % FeO of rock standards vs. their corrected absorbance readings. These rock standards were used in this study for FeO and ΣFe analyses for the amphiboles. Normalized % FeO is equal to the reported % FeO of a rock standard multiplied by Dilution Factor One (see text).

The corrected (blank and background) absorbance of an unknown measured against the "normalized % FeO" standard curve translates to a "raw" % FeO. This FeO value must be corrected for the unknown's sample weight and the total weight of the diluted solution by dividing the unknown sample's raw % FeO by its $F_1$. An example of this calculation is provided below.

For a single analysis of grunerite CK-1, 3.21 mg of amphibole were dissolved and diluted to a final solution weight of 158.88 gm. This gives an $F_1$ for this sample of 0.2020. A background- and blank-corrected absorbance of 0.290 was measured against the absorbance of the rock standards shown in Figure 2. Thus, the raw % FeO (9.09%) of this unknown is obtained by substituting 0.290 absorbance into the equation given in Figure 2. The absolute % FeO (45.01%) is obtained by dividing the raw % FeO by $F_1$.

Total iron expressed as % $Fe_2O_3$ was determined on the orange-colored solution of the FeO analyses by atomic absorption spectrophotometry, using a dual beam unit (Perkin-Elmer Model 603). Absorbance was measured at 248.3 nm and the instrument was zeroed with the quartz blank. Absorbance is measured against normalized % $Fe_2O_3$ of the rock standard where the normalized value for each rock standard is obtained by multiplying that standard's $F_1$ by its reported value for $\Sigma Fe$ as % $Fe_2O_3$.

Figure 3 shows a typical calibration curve for total iron analysis. The reported linear working range for iron on the P-E 603 unit is 5 ppm. This translates to a total iron content of 7.14% $Fe_2O_3$ of the dry sample if the sample's $F_1$ were unity. For this reason, the calibration curve begins to depart from linearity at higher concentrations. Despite the non-linearity of the absorbance-$\Sigma Fe$ relationship, there is a high degree of confidence in fitting the data points to a parabolic curve (Fig. 3).

The total iron of the unknowns can be measured with or without further dilution. If an unknown solution is directly aspirated into the atomic absorption unit, its computed raw $\Sigma Fe$ value is then divided by its $F_1$ to obtain the absolute value of $\Sigma Fe$ expressed as % $Fe_2O_3$. The disadvantage of this method lies in noisy signals for high absorbance values that translate to large relative errors due to a decreased sensitivity on the non-linear segment of the analytical curve. The analyzed amphiboles discussed below were all iron-rich such that noisy signals were especially troublesome during absorbance readings of these samples.

Since the stability of absorbance readings is greater for samples containing lower iron concentrations, the unknowns were diluted with the quartz blank to yield absorbances for these samples that lay within the linear working range of the instrument. Quartz blank is used as a dilutant rather than deionized water to minimize matrix effects. This dilution is performed gravimetrically on a top-loading balance. A small amount of the orange-colored solution is placed in a tared, 4 oz. polypropylene bottle and the solution weight is recorded. Quartz blank is added to an amount necessary to achieve the desired dilution, normally about two to three times that of the unknown solution. The total solution weight is recorded. This dilution gives rise to Dilution Factor Two ($F_2$) which is:

$$F_2 = \frac{\text{(gm unknown)}}{\text{(grams unknown + gm quartz blank)}} \qquad (2)$$

Before this method is adopted, the analyst must be convinced that the absorbance of the lower-iron rock standards defines a straight line passing through the origin. The dashed line of Figure 3 shows that such a trend exists. Having established which standards plot on a line passing through the origin, the analyst is free to choose any one of these rock standards as the basis by which to compare the absorbance of the unknowns to that of the standard for purpose of calculating the raw $\Sigma Fe$ as % $Fe_2O_3$ of the unknowns. Alternatively, all rock standards falling on the linear segment of the calibration curve could be used to define the slope. In either case, the absolute $\Sigma Fe$ as % $Fe_2O_3$ of an unknown is equal to its raw $\Sigma Fe$ value divided by both $F_1$ and $F_2$.

Grunerite CK-1 is again used as an example of the calculation procedure. Into a clean 4 oz. polypropylene bottle was poured 7.73 grams of the orange-colored solution left over from the FeO analysis. Quartz blank was added to bring the total solution weight to 15.35 grams. Thus, $F_2$ for the sample is 0.5036. The absorbance of this solution, 0.069, was measured against the zero absorbance value of the quartz blank and those rock standards defining a straight line passing through the origin for which the slope is 73.48% $Fe_2O_3$/1.000 absorbance unit (Fig. 3). The raw (i.e., uncorrected) % $Fe_2O_3$ is equal to:

$$\frac{73.48\%\ Fe_2O_3 \times 0.069 \text{ abs. unit}}{1.00 \text{ abs. unit}} = 5.07\%\ Fe_2O_3.$$

If this value is divided by $F_1$(0.2020) and $F_2$(0.5036), the result, 49.86%, is the absolute $\Sigma Fe$ of the sample, expressed as % $Fe_2O_3$.

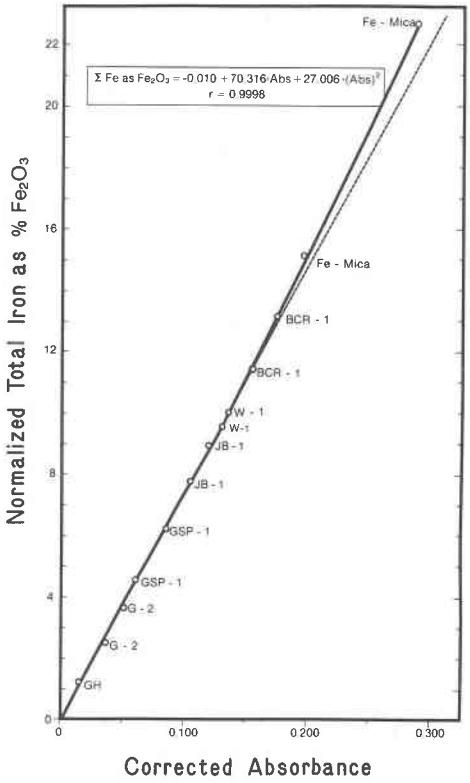

Fig. 3. Typical $\Sigma Fe$ as % $Fe_2O_3$ calibration curve showing normalized % $Fe_2O_3$ of rock standards vs. their blank-corrected absorbance readings. The dashed line shows the extension of the linear segment of the calibration curve whose slope is 73.48. For analyses of high iron unknowns, samples were diluted with a quartz blank such that their absorbances usually ranged from 0.50 to 0.100 absorbance units.

The main source of error in the atomic absorption determination of $\Sigma Fe$ resides in fluctuation of absorbance readings about the observed value. Although these fluctuations are generally on the order of only 0.001–0.002 absorbance units, this uncertainty is divided by $F_1$ and $F_2$ to yield potentially large errors about the observed value for $\Sigma Fe$. Several steps can be taken to minimize this uncertainty. Since the percent relative error is inversely proportional to

Table 1. Observed versus reported values of FeO and $\Sigma$Fe as $Fe_2O_3$ of 10 common rock standards. Reported values obtained from Abbey (1980).

| Rock Standard | Analyzed wt.% FeO | Reported wt.% FeO | Analyzed total Fe as %$Fe_2O_3$ | Reported total Fe as %$Fe_2O_3$ |
|---|---|---|---|---|
| DT-N | 0.12 (0.06) | 0.10 | 0.20 (0.30) | 0.66 |
| GH | 0.69 (0.02) | 0.84 | 1.29 (0.08) | 1.34 |
| JG-1 | 1.48 (0.05) | 1.62 | 2.22 (0.10) | 2.17 |
| GA | 1.29 (0.06) | 1.32 | 2.73 (0.18) | 2.83 |
| GS-N | 1.54 (0.13) | 1.66 | 3.43 (0.39) | 3.77 |
| AGV-1 | 2.21 (0.02) | 2.03 | 6.84 (0.28) | 6.82 |
| DR-N | 5.12 (0.13) | 5.32 | 9.13 (0.38) | 9.69 |
| NIM-N | 7.48 (0.33) | 7.30 | 8.91 (0.22) | 8.91 |
| W-1 | 8.76 (0.05) | 8.73 | 11.53 (0.70) | 11.10 |
| NIM-D | 14.59 (0.30) | 14.63 | 16.77 (0.48) | 16.97 |

the magnitude of the true absorbance reading, it is advisable to base the calibration on the highest iron-bearing standards that still lie on the linear segment of the calibration curve. Furthermore, the unknown's dilution with the quartz blank should be enough to render an absorbance reading below that of the standard; yet, this dilution should not be so large as to render a very low absorbance of this mixture. Third, all $\Sigma$Fe analyses should be performed in triplicate for each diluted mixture.

## Results

In order to test the accuracy and precision of the technique, well documented rock standards were employed. A series of ten rock standards were analyzed as unknowns, using seven other rock standards to obtain the calibration curves for both FeO and total iron as $Fe_2O_3$. The results of three replicate analyses are given in Table 1; the numbers in parentheses represent 1-standard-error values. In general, the agreement between the observed and reported values is reasonable. Even though the relative error for total iron is large for several of the Fe-poor samples (e.g., DT-N), the absolute differences between the observed and reported values is never more than 0.2 wt.% when the 1-standard-error values are considered. The relatively large absolute errors for total iron analyses may result from the fluctuations of the absorbance readings as discussed above, or from possible inhomogeneity of the small sample sizes of the rock powders.

The technique was tested further for ten natural amphibole mineral separates obtained from a number of different sources. The results are shown in Table 2. The one-standard-error values given in parentheses were obtained from three replicate analyses of all samples except CK-1, CA and SC, for which the number of replicate analyses were six, four and two, respectively. As might be expected, the agreement between the observed and reported values is poorer than for the well-calibrated rock standards. Compared to the reported wet chemical analyses, four of the amphiboles (TP-1, SLO-5, C-4980, and Y42-BX) show differences that are considered to be excessive. However, for three of those samples (TP-1, SLO-5, and C-4980) the observed molar $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ values show better agreement with the values reported from Mössbauer spectral analyses than do the values obtained from the reported wet chemical analyses. Mössbauer analyses are not available for sample Y42-BX. Overall, the observed ferric–ferrous ratios are in reasonable agreement with those ob-

Table 2. Observed versus reported values of FeO, $\Sigma$Fe as $Fe_2O_3$, and molar ferric–ferrous ratio of 10 natural amphiboles.

| | | | | | | | Molar $Fe^{3+}/(Fe^{3} + Fe^{2+})$ | | |
|---|---|---|---|---|---|---|---|---|---|
| Amphibole | Average Sample Weight in mg | Number of Samples Analyzed | Observed % FeO ($\pm 1\sigma$) | Reported % FeO | Observed $\Sigma$ Fe as $Fe_2O_3$ ($\pm 1\sigma$) | Reported $\Sigma$ Fe as $Fe_2O_3$ | Observed ($\pm 1\sigma$) | Reported Wet Chemical | Reported Mossbauer |
| TP-1 (glaucophane)[a] | 5.02 | 3 | 5.63(0.06) | 6.12 | 8.10(0.05) | 9.69 | 0.228(0.012) | 0.298 | 0.230, 0.217[e] |
| SC (magnesioriebeckite)[a] | 6.22 | 2 | 7.11(0.08) | 7.07 | 17.62(0.26) | 17.74 | 0.555(0.007) | 0.557 | 0.542, 0.526[e] |
| SLO-5 (glaucophane)[a] | 6.35 | 3 | 12.64(0.24) | 12.11 | 16.22(0.06) | 15.02 | 0.135(0.015) | 0.104 | 0.166 |
| 175-A (glaucophane)[a] | 6.94 | 3 | 9.21(0.20) | 9.21 | 14.67(0.73) | 14.87 | 0.302(0.022) | 0.312 | 0.293 |
| 409 (crossite)[a] | 7.45 | 3 | 10.79(0.04) | 10.31 | 18.82(0.18) | 19.40 | 0.363(0.008) | 0.409 | 0.397 |
| 423 (glaucophane)[a] | 7.48 | 3 | 12.25(0.26) | 12.02 | 17.93(0.37) | 17.71 | 0.241(0.007) | 0.246 | 0.273 |
| C-4980 (magnesioriebeckite)[a] | 4.43 | 3 | 6.63(0.46) | 5.23 | 23.49(0.06) | 22.58 | 0.687(0.016) | 0.743 | 0.684 |
| CK-1 (grunerite)[b] | 3.48 | 6 | 44.36(1.13) | 44.99 | 49.08(1.05) | 50.00 | -0.004(0.008) | 0.000 | |
| CA-(riebeckite)[c] | 3.94 | 4 | 20.80(0.31) | 20.67 | 34.73(0.11) | 34.60 | 0.334(0.011) | 0.336 | |
| Y42-BX (cummingtonite)[d] | 4.19 | 3 | 21.86(0.48) | 23.12 | 24.77(0.48) | 26.81 | 0.019(0.006) | 0.042 | |

a. Sample obtained from W.G. Ernst. Wet chemical analyses performed by several different analysts as reported by Ernst and Wai (1970). Mossbauer analysis also from Ernst and Wai (1970).
b. Sample obtained from C. Klein. Analysis reported in Klein (1964).
c. Sample obtained from M.C. Gilbert. FeO analyzed by Whipple using technique of Whipple (1974). Total Fe from electron microprobe analysis by M.C. Gilbert.
d. Sample obtained from P. Robinson. Analysis reported in Robinson and Jaffee (1969).
e. Second mossbauer value from Bancraft and Burns (1969), as reported by Ernst and Wai (1970).

tained from Mössbauer analysis: the largest difference between these two sets of measurements is 3.4 absolute % for sample 409. It should be noted, however, that for sample 409 the ferric–ferrous ratio from the reported wet chemical analysis agrees well with the Mössbauer value. For sample 423, the observed and reported ratio are in good agreement, but differ from the Mössbauer value by approximately 3 absoute %. Considering the possible sources of inhomogeneity and impurities in micro-sized samples of natural mineral separates, the results are encouraging.

The most iron-rich sample, grunerite CK-1, requires additional discussion. Because of its high iron content, a small average sample size, 3.48 mg (Table 2), was necessary in order to bracket the solution by the most iron-rich rock standard. Shown in Table 3 are the six individual analyses obtained for the sample. For three of the analyses (replicates #1, 5, and 6) both FeO and total iron are significantly lower than the reported values. These differences are interpreted to result from weighing errors, possibly from sorbtion of water onto the sample or digestion bottle during weighing. Despite the differences in absolute FeO and total iron, the ferric–ferrous ratio of all six analyses agrees well with the reported value.

Because FeO and total iron are both measured in a solution produced by a single digestion, weighing errors of the dry sample do not affect the ferric–ferrous ratio. If a weighing error of, say, 10% exists, the absolute amounts of FeO and total iron will be in error by 10%, but this error will cancel when the ratio is calculated. Thus, determination of a ferric-ferrous ratio can, in point of fact, be carried out independent of any knowledge of the dry sample weight. If only the ratio and not absolute amounts are desired, the analyses could be carried out on unweighed samples, provided, of course, that the dilutions are carried out accurately, as discussed above. Even though weighing errors for samples smaller than ~2 mg may preclude the determination of accurate absolute FeO and total iron values, the lower limit for sample size on which the ferric–ferrous ratio can be determined should be limited only by the detection limits of the analytical instruments.

## Conclusions

1. The method described here can be used to determine absolute amounts of FeO and total iron as $Fe_2O_3$ on small sample sizes (< 10 mg).

2. The technique gives results that, in general, are in reasonable agreement with other wet chemical techniques and with Mössbauer spectral techniques.

3. The more cumbersome procedures of volumetric dilution are replaced by faster and inherently more accurate gravimetric dilution techniques. Those steps that do require volumetric measurements require only the precision of automatic pipets or of syringes.

4. The method is quite versatile in terms of dry sample weights and dilutions. High accuracy in dilution is required, but precise duplication of weights between samples is not required.

Table 3. Replicate analyses of grunerite (CK-1). Each replicate represents a separate dissolution and the observed FeO and $\Sigma$Fe values are an average of triplicate analyses. Reported values are from Klein (1964).

| | Observed | | | | | | Reported |
|---|---|---|---|---|---|---|---|
| Analysis # | 1 | 2 | 3 | 4 | 5 | 6 | |
| % FeO | 44.02 | 45.30 | 45.66 | 44.92 | 42.71 | 43.54 | 44.99 |
| $\Sigma$ Fe as % $Fe_2O_3$ | 48.47 | 50.06 | 49.92 | 49.81 | 47.38 | 48.82 | 50.00 |
| $\frac{Fe^{3+}}{Fe^{3+} + Fe^{2+}}$ | -0.009 | -0.006 | -0.017 | -0.002 | -0.002 | +0.009 | 0.000 |

5. The procedure is relatively rapid. After the dry samples have been weighed into the digestion bottles, a two-person analysis team can typically analyze 40 samples for both FeO and total iron, using a 7 standard calibration curve, in an 8 hour day.

6. The ferric–ferrous ratio should be able to be determined on vanishingly small sizes, provided that the resulting solutions lie within the detection limits of the analytical instruments.

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## Appendix

*Equipment*

- double beam atomic absorption spectrophotometer
- double beam colorimetric spectrophotometer and matched cuvets having a 10 mm path length.
- analytical balance with readability of 0.01 mg
- top loading balance with readability of 0.01 grams
- 4 oz. polypropylene bottles
- $\frac{1}{2}$ ml plastic syringe
- 3 automatic pipet dispensers
- a 4-liter glass beaker
- ring stand and bunsen burner

*Reagents*

- at least 6 well-characterized rock standards
- 10% (v/v) $H_2SO_4$ solution
- 5% (w/w) $H_3BO_3$ solution
- 10% (w/w) Na Citrate solution
- crystalline o-phenanthroline
- 48% HF