

IMPROVEMENTS TO THE QUANTITATIVE ASSAY OF NONREFRACTORY MINERALS FOR Fe(II) AND TOTAL Fe USING 1,10-PHENANTHROLINE

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Abstract—A method using 1,10-phenanthroline (phen) to quantify Fe(II) and total Fe in nonrefractory minerals was modified to improve the accuracy and precision and to eliminate the inconvenience of performing much of the analysis under darkroom conditions. Reagents were combined to minimize solution-handling errors, volumes of the reagent additions were determined gravimetrically and the acid-matrix solution was preheated to near-boiling before sample contact. The darkness requirement, which stems from the photoreduction of Fe(III) to Fe(II) in the presence of phen, was eliminated by the use of opaque amber-colored high-density-polyethylene bottles during the digestion step and for storage of the digestate and subsequent dilutions before Fe(II) analysis. Reduction of Fe(III) for total-Fe analysis was accomplished either by exposure to light from a Hg-vapor lamp or by reaction with hydroxylamine, NH₂OH. Although the minimum periods required for adequate reduction ranged from 1.5 to 4 h, the optimum reduction periods were between 6 and 10 h. When standard samples containing Fe(II) and MnCl₂ were digested and analyzed for total-Fe using the light treatment (with incidental heating to 35–45 °C), significant decreases and in some instances, oscillations, in absorptivity were obtained. Similar experiments with NH₂OH, or with CrCl₃ showed no effect. The absorptivity of most digestates stored in opaque bottles was stable for at least 2 weeks, although digestates with Mn concentrations above 3 µg mL⁻¹ showed proportional decreases in absorptivity. Analysis of 8 geochemical reference materials by the modified method (using NH₂OH) yielded excellent agreement with published values and a mean relative standard deviation of 0.6%. Total-Fe results obtained using the light treatment, however, were generally lower (~2% relative) than the NH₂OH values, although this difference decreased with longer irradiation periods. Use of NH₂OH was deemed preferable because it was simpler, faster, minimized interferences from Mn and eliminated the need for specialized apparatus. Lastly, MICA Fe was shown to be unreliable as a primary reference material for Fe(II) determinations.

Key Words—1,10-Phenanthroline, Belousov–Zhabotinsky Reaction, Fe, Fe(II), Ferrous Iron, Hydroxylamine, Oscillatory Reaction, Photoreduction, Total Iron.

INTRODUCTION

Iron (Fe) is the dominant redox-sensitive element in most minerals and, consequently, quantification of the amounts of Fe present in the ferrous [Fe(II)] and ferric [Fe(III)] oxidation states has always been an essential step in the characterization of mineral specimens. Because no direct spectroscopic technique exists that is both rapid and inexpensive, wet-chemical techniques based on decomposition and solubilization of the mineral and subsequent measurement of the amounts of Fe(II) and/or Fe(III) have been the most common approach taken. This approach, however, poses a significant analytical challenge, which drives a continual need for improvements in wet-chemical techniques for Fe oxidation states, particularly in the areas of accuracy, precision and convenience.

As summarized by Schafer (1966), and more recently by Amonette et al. (1994), the analytical methods for Fe redox states can be distinguished on the basis of how the Fe is brought into solution, and then, how it is quantified. Dissolution by HF (usually in combination with H₂SO₄) is used almost universally to decompose the nonrefractory minerals, a group that includes the layer silicates. Quantification of the Fe(II)

and Fe(III) in the HF-H₂SO₄ digestates can be either by titrimetric or colorimetric means. Titrimetric methods rely on the reaction of redox-sensitive constituents with a known amount of oxidant or reductant and thus are not element-specific. Although they tend to be very precise (Van Loon 1965; Banerjee 1974; Amonette and Scott 1991) they also measure everything that can be oxidized or reduced by the titrant [organic matter and other transition metals such as Ti(III) and V(III)] and are thus best suited to measurements of overall reductive or oxidative capacity at specific formal reduction potentials. Colorimetric methods for Fe involve the specific complexation of Fe(II) or Fe(III) by a chromophore and the subsequent determination of concentration by spectrophotometry. Competition for the chromophore by protons and by other metals, competition for the Fe by other ligands (such as fluoride or phosphate), photochemical reactions leading to reduction or even destruction of the Fe-chromophore complex, and the presence of other species that absorb light in the analytical spectral region are the main factors causing error with the colorimetric approach. Because of their elemental specificity, the colorimetric methods can be adapted to measure both oxidation

states of Fe, for example by first measuring the initial Fe(II) concentration, converting all the Fe(III) to Fe(II) by chemical or photochemical means, and then making a second measurement of the total-Fe concentration [with the Fe(III) concentration determined by difference]. However, because they are sensitive to concentration rather than to the absolute amount present, dilution errors tend to make the colorimetric methods less precise than the titrimetric methods. Regardless of whether colorimetry or titrimetry is used to quantify the Fe, the largest source of error in Fe redox-state determinations stems from the oxidation of Fe(II) during the sample decomposition step and before quantification. This error is minimized in the best titrimetric and colorimetric approaches by the presence of the active reagent (that is, an acid-stable oxidant, reductant or chromophore) during the decomposition of the sample in the HF-H₂SO₄ acid matrix. Ideally, this reagent reacts with Fe immediately upon its release from the sample and preserves the information about its redox status until the quantification step.

1,10-phenanthroline Procedures

Because it forms very strong tris complexes with Fe(II) ($\log \beta_3 = 21.4$; Schilt 1969) with high absorptivity in the visible region ($\epsilon_{510\text{ nm}} = 11,100\text{ M}^{-1}\text{ cm}^{-1}$, Schilt 1969) and is relatively inexpensive (ca \$0.50 mmol⁻¹), 1,10-phenanthroline (phen) has become the reagent of choice for colorimetric determinations of Fe in strong-acid digestates of minerals. However, following its synthesis and the discovery of its ability to complex with Fe(II) by Blau (1898), a generation passed before chemists realized that it could be used for analytical purposes. Walden et al. (1931) noted that it was an ideal indicator for oxidimetric titrations. Soon thereafter, analytical chemists began to use phen for determinations of total Fe in fruit juice and wine (Saywell and Cunningham 1937). Fortune and Mellon (1938) and Bandemer and Schaible (1944) identified the critical factors affecting accurate use of phen for total-Fe determinations. Included in these factors were the optimal pH range for color development (2–9), suitable pH buffers (for example, citrate), suitable reductants (for example, hydroxylamine), order of reagent addition (phen and reductant, then buffer), equilibration time after buffer addition and before analysis (30 min) and interferences from other metals and ligands such as phosphate.

Yet another generation passed before it was realized that phen could be used for analysis of Fe(II) and total Fe in geological samples. Shapiro (1960), who was influenced by Wilson's paper (1955) describing the advantages of having the redox reagent (in this instance, vanadate) present during the sample decomposition step, devised a new method for Fe(II) in which phen powder was added to the sample before contact with the HF-H₂SO₄ matrix. After addition of H₃BO₃ and

citrate buffer, the absorbance of the tris-phen-Fe(II) complex was determined at 555 nm. Roth et al. (1968) improved on this method by adding the phen as a 10% solution in 95% ethanol, measuring the absorbance at 510 nm and incorporating the capability for measuring total Fe on a second aliquot of the digestate that had been reduced with hydroxylamine and allowed to react for 24 h. Stucki and Anderson (1981) identified several sources of error in the Shapiro–Roth method, notably the tendency to obtain falsely high Fe(II) values due to photoreduction of Fe(III) to Fe(II) in the presence of phen by ordinary fluorescent lighting. Stucki (1981) corrected this problem in the Fe(II) analysis by conducting the digestion and dilution steps under red lighting (typical of darkroom conditions). He then turned the photoreductive process into an advantage by using a fluorescent light to reduce the Fe(III) for total-Fe determinations, thereby eliminating the need for a chemical reductant. With this method of reduction, Fe(II) and total Fe could be determined on the same dilution to avoid an additional source of error. Stucki and Anderson (1981) also reported a loss in precision associated with the use of chemical reductants and slightly higher absorptivities when hydroxylamine was added to a digestate containing (nominally) only Fe(II) than when only NaCl was added. This latter result could have stemmed from Fe(III) impurities in the Fe(II) standard being reduced by the hydroxylamine rather than from any effect of the reductant, as even primary-standard-grade Fe(II) has been shown to contain Fe(III) impurities (Amonette and Scott 1991). Komadel and Stucki (1988) further refined the phen method by using a Hg-vapor lamp to reduce the Fe(III) in a matter of 90 min, which was a significant improvement over the 36 h required when the fluorescent lamp was used.

Improvements

Although the method of Komadel and Stucki (1988) has many worthwhile features, our experience in the use and development of Fe redox methods suggested that several improvements could still be made in the areas of accuracy, precision and convenience. Accuracy and precision could both be improved by ensuring complete decomposition of the sample and minimal interaction with atmospheric oxygen. To accomplish these goals, we note [after the observations of French and Adams (1972) and Begheijn (1979)] that addition of a hot-acid mixture to the sample in a plastic bottle achieves rapid and complete sample decomposition and also produces a dense vapor that isolates the digestate from atmospheric oxygen. Precision could also be improved by minimizing the number of solutions added, using gravimetry to determine the actual volumes of the solutions added, determining the final digestate volume by summing the individual solution volumes and determining the digestate density by cal-

culating a weighted average of the individual solution densities. It was also clear to us from the outset that the requirement for performing a large part of the analysis under darkroom conditions was a major inconvenience. To circumvent this problem, we substituted 125-mL opaque amber-colored high-density-polyethylene (HDPE) bottles for the 100-mL centrifuge tubes used in the sample decomposition step and similar 30-mL bottles for dilution of digestates for Fe(II) analysis.

Lastly, our own experience as well as published data of Stucki (1981) suggested that, for some reason, values for total Fe obtained when light was the reductant tended to be slightly lower than those obtained by other techniques. One possible explanation for this would be interferences from the other metals present in the minerals. A second possibility could be the incomplete reduction of all the Fe(III) by the photoreduction step. To investigate these possibilities, we conducted a series of experiments looking at the effects of Mn(II) and Cr(III) (among the most abundant metals to be found with Fe in minerals) on the Fe(II) and total-Fe values obtained. A series of experiments that compared hydroxylamine with light as the reductant for the total-Fe analysis was also conducted.

In what follows, we present a detailed description of our improvements to the phen method for Fe(II) and total Fe in nonrefractory minerals, the results of our analysis of a series of geochemical reference materials using the improved method and, last, the results of our investigations into the effects of trace metals and type of reduction method on the Fe data.

MATERIALS AND METHODS

Reagents

Primary-standard-grade ferrous ethylenediammonium sulfate (FES, Spectrum Chemical Co., Lot# GD305) was used as the standard for Fe(II) and total Fe [standard additions revealed that 3% of the Fe in FES was Fe(III)]. Reagent-grade 1,10-phenanthroline monohydrate (Aldrich Chemical, Lot #02103PF), 95% ethanol, H_3BO_3 , H_2SO_4 , HNO_3 , HF (48%), $MnCl_2 \cdot 4H_2O$, $CrCl_3 \cdot 6H_2O$, $(NH_2OH)_2 \cdot H_2SO_4$ and Na_3 -citrate $\cdot 2H_2O$ were used without further purification. All aqueous solutions were prepared using deionized water. All reagent and reaction containers were rinsed in 1% HNO_3 , then in deionized water.

The following stock solutions were used: 10% phen in 95% ethanol (freshly prepared and stored in the dark); 10% H_2SO_4 ; 5% H_3BO_3 ; 1% Na_3 -citrate; 1% $(NH_2OH)_2 \cdot H_2SO_4$ in 1% Na_3 -citrate (freshly prepared, reagent slowly oxidizes over time). Preparation of the acid-matrix solution, which was a 1:2:12 volumetric mixture of 48% HF, 10% phen and 10% H_2SO_4 , is described in the procedure. The density of each of these solutions at room temperature was determined

by exactly weighing 100 mL in a volumetric flask that had been calibrated with water.

Mineral Samples

A total of 8 powdered samples from 4 micas, a granite, a basalt and a syenite were analyzed. Two of the micas were samples from the collection of A. D. Scott (Department of Agronomy, Iowa State University [ISU], Ames, Iowa) prepared by dry-grinding sheets of each mineral in a Waring Blendor® and separating the different size-fractions by sedimentation in H_2O . These samples were a biotite from Bancroft, Ontario, Canada (Biot 1A, <50 μm , R₁₇₆), and a ferroan biotite originally described as a "lepidomelane" from Faraday Township, Ontario, Canada (Lane 3B, 10–20 μm , W₁₅₅). The remaining samples were geochemical reference specimens. These include a specimen of MICA Mg (specimen #2-7268) and 2 specimens of MICA Fe obtained on separate occasions from the Centre de Recherches Petrographiques et Geochimiques (CRPG) reference collection (Dr. K. Govindaraju, Geostandards, CRPG, B.P. 20, 54501 Vandoeuvre Cedex, France). The first of the MICA-Fe specimens [MICA Fe (ISU)] was obtained in 1984 while the senior author was at ISU and was identified by the supplier as specimen #3-3200. The second sample [MICA Fe (PNNL)] was obtained in 1993 at the senior author's current location and was identified as specimen #19094. Also analyzed were 3 specimens from the U.S. Geological Survey (USGS) reference collection obtained from Dr. Stephen Wilson, USGS Reference Materials Program, USGS, Box 25046, MS 973, Denver Federal Center, Denver, Colorado. These included a Rhode Island granite (G-2, split 100, position 7), an Icelandic basalt (BIR-1, #0396) and an Oregon nepheline syenite (STM-1, split 15, position 31).

Apparatus

Narrow-mouth amber-colored opaque HDPE bottles were used for the sample decomposition (125-mL) and Fe(II) dilution (30-mL) steps. Clear glass scintillation vials (20-mL) were used for the total-Fe dilution and reduction steps. Sample decomposition was performed by partly immersing the amber bottles in a boiling water bath having an acrylic cover with holes that matched the diameter of the bottles to keep them upright. Reagent solutions and digestates were transferred using automatic programmable pipets (Rainin Instruments) and volumes determined gravimetrically using a top-loading electronic balance with 1-mg resolution. A plastic syringe (20-mL or larger) with a 10-cm section of 3.18-mm ID Tygon® tubing attached to the end was used to measure and transfer the hot (near-boiling) acid-matrix solution to the amber bottles containing the samples. Absorbance data were obtained

with a Hewlett Packard HP8452A diode-array ultraviolet/visible spectrophotometer.

The photochemical reduction step was carried out using a 175-W mercury-vapor lamp (Philips Lifeguard H39KB-175) in an Electripak Security Lite fixture (R-175M), which was positioned over a 36-cm-diameter, 23-cm-deep galvanized bucket. Samples were placed in the bottom of the bucket about 30 cm below the source.

Kinetic color-development studies were carried out with individual samples using a closed-loop continuous-flow system designed to maintain constant temperature and controlled lighting conditions at every point in the loop. The sample was placed in a 20-mL vial in the bottom of the bucket, closed with a special cap pierced by 2 sections of microbore tubing for effluent and influent sample streams. The tubing was routed through a peristaltic pump, a 1-cm path-length flow-through quartz cell in the cell compartment of the spectrophotometer and then back to the vial. The entire liquid volume of the tubing and quartz cell was about 5 mL, and the solution was pumped at a rate of about 1.5 mL min⁻¹. Between the sample vial and the spectrophotometer, the microbore tubing was in close contact with 9.5-mm OD Tygon® tubing connected to a circulating water bath and the entire length of tubing was enclosed with foam insulation and aluminum foil to isolate it from the room and the lighting. Temperature and lighting could also be controlled for the sample in the bucket. Samples could be run in complete darkness at 25 °C if water were placed in the bottom of the bucket (maintained by coil of 6.3-mm OD Cu tubing connected to the circulating water bath at the end of the sample cooling loop) and the bucket covered with foil. Photoreduction experiments were conducted with the Hg-lamp positioned on top of the bucket and with the sample maintained at 25 °C by the water bath or with no water in the bucket. In the latter instance, the sample temperature typically increased to about 35–45 °C within 1 h of the start of the experiment. Sample temperature was monitored indirectly to within 0.1 °C by a thermocouple temperature probe (Cole-Parmer Model 8502-20) inserted into a separate scintillation vial containing a phen dilution that was placed next to the actual samples in the bucket.

Analytical Procedure

The analytical procedure (Figure 1) is modified from that of Komadel and Stucki (1988) and includes 2 methods for determination of total Fe. The recommended method (NH₂OH reduction) is indicated by solid arrows.

SAMPLE DECOMPOSITION. Quantitatively transfer a mineral sample weighing between 25 and 50 mg (± 0.01 mg) and containing less than 10 mg of total Fe into a tared 125-mL amber bottle. Immediately before starting the analysis prepare the acid-matrix solution in a 500-mL HDPE bottle by mixing 12 mL of stock 10%

H₂SO₄ solution, 2 mL of stock 10% phen solution and 1 mL of 48% HF for each sample to be analyzed (prepare an additional 15–20 mL of this mixture to ensure easy transfer for the last sample). Place the loosely capped bottle containing the acid-matrix solution in a 2-L beaker containing boiling water and sitting on a hot plate until the solution is near the boiling point. Working next to the boiling water bath (preferably located in a fume hood), quickly transfer 15 mL of the acid-matrix solution into each sample bottle, swirl to cause fumes to fill the bottle, cap tightly and shake to ensure complete wetting of the sample, then loosen the cap to relieve pressure and place the bottle into a position in the boiling-water bath so that it is partly immersed. After 30 min, remove the bottle from the water bath and allow it to cool to room temperature (keep the cap loosened to equalize the pressure inside and outside the bottle). After ensuring that the bottle is completely dry on the outside, weigh it on a top-loading electronic balance (± 1 mg), add 10 mL of stock 5% H₃BO₃, reweigh, cap tightly and mix thoroughly. Reweigh the bottle (some gain may have occurred due to absorption of air), add about 90 mL of H₂O using a graduated cylinder, weigh again, cap tightly and mix. The bottle now contains the digestate, which is stable in most circumstances for at least 2 weeks.

Fe(II) DETERMINATION. Tare a 30-mL amber bottle on the top-loading balance, add 10 mL of the stock 1% Na₃-citrate solution and reweigh (this step can be done before starting the run or during the sample decomposition). Add 1 mL of sample digestate and reweigh. Cap tightly and mix thoroughly. Measure the absorbance of the sample at 510 nm in a 1-cm path-length quartz cell. If determination of total Fe after photoreduction is desired, retain about 5–6 mL of the sample.

TOTAL FE DETERMINATION AFTER PHOTOREDUCTION. Transfer the remainder of the Fe(II) dilution from the 30-mL amber bottle to a 20-mL clear-glass scintillation vial. Expose the vial to the Hg-lamp for at least 90 min (each setup needs to be calibrated), preferably for several hours. Measure absorbance at 510 nm as in the Fe(II) determination.

TOTAL FE DETERMINATION AFTER REDUCTION WITH HYDROXYLAMINE. Tare a 30-mL amber bottle on the top-loading balance, add 10 mL of the stock 1% Na₃-citrate + 1% (NH₂OH)₂-H₂SO₄ solution and reweigh (this step can be done before starting the run or during the sample decomposition). Add 1 mL of sample digestate and reweigh. Cap tightly, mix thoroughly and let stand for at least 90 min, preferably several hours. Measure the absorbance of the sample at 510 nm as in the Fe(II) determination.

CALIBRATION. Prepare amber bottles to contain between 0 and 70 mg of FES. Carry these standard samples through the same procedure [sample decomposition,

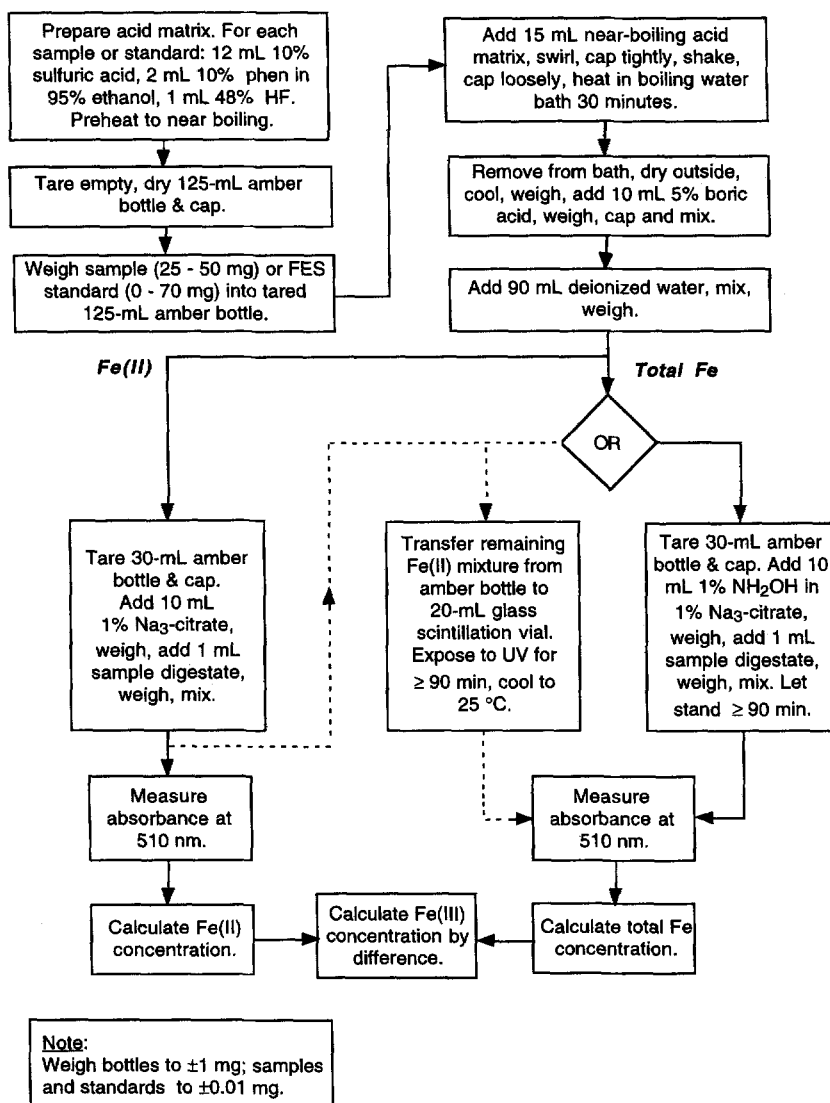


Figure 1. Flow chart of modified phen method for Fe(II) and total Fe in nonrefractory minerals. The recommended method (NH_2OH reduction for total Fe) is indicated by solid arrows.

Fe(II) determination, total Fe determination]. About 8.7 mg of FES corresponds to $1 \mu\text{g Fe mL}^{-1}$ measured in the spectrometer.

CALCULATIONS. The final volume of the digestate (V_{dig} , mL) is determined from the densities (ρ , g mL^{-1}) and net weights (W , g) of the individual added solutions by:

$$V_{\text{dig}} = \frac{GW_{\text{acid}} - (TW + W_{\text{samp}})}{\rho_{\text{acid}}} + \frac{W_{\text{H}_3\text{BO}_3}}{\rho_{\text{H}_3\text{BO}_3}} + \frac{W_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} \quad [1]$$

where GW_{acid} is the gross weight of the bottle after addition of the sample and acid-matrix, TW is the original bottle tare weight, W_{samp} , $W_{\text{H}_3\text{BO}_3}$ and $W_{\text{H}_2\text{O}}$ are the weights of the mineral sample, 5% H_3BO_3 solution and water,

respectively, and ρ_{acid} , $\rho_{\text{H}_3\text{BO}_3}$ and $\rho_{\text{H}_2\text{O}}$ are the densities of the acid matrix, 5% H_3BO_3 solution and water, respectively. The density of the digestate (ρ_{dig}) is calculated from the net weight and volume of the digestate.

The sample dilution factors (F_{citr} , $F_{\text{NH}_2\text{OH}}$) for Fe(II) and total-Fe determinations are calculated from the measured net weights and densities of the digestate, and of the solutions of 1% citrate or 1% $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ + citrate that were used to prepare each dilution.

The nominal concentrations of Fe(II) and total Fe in the FES calibration-standard final dilutions ($C_{\text{STD}_{\text{dil}}}$ in units of $\mu\text{g Fe mL}^{-1}$) are calculated by an equation of the general form:

$$C_{\text{STDdil}} = (10^6 \times W_{\text{STDsamp}} \times AW_{\text{Fe}}) / (EW_{\text{FES}} \times F \times V_{\text{dig}}) \quad [2]$$

where AW_{Fe} is the atomic weight of Fe (55.847 g mol⁻¹), EW_{FES} is the equivalent weight of the FES standard (393.78 g mol⁻¹ for Fe(II) in this study, 382.16 g mol⁻¹ for total Fe) and F is the appropriate dilution factor (that is, F_{citr} or $F_{\text{NH}_2\text{OH}}$). These nominal concentrations (C_{STDdil}) are then regressed against the corresponding observed absorbance values for the calibration standards (A_{STD}) to obtain paired values for the slope (m) and intercept (b) for each type of analysis [Fe(II), total Fe by photoreduction and total Fe by NH₂OH reduction].

The concentrations of Fe(II) or total Fe in the final mineral-sample dilutions (C_{sampdil}) are calculated from the corresponding observed absorbance values for these samples (A_{samp}) using an equation of the form:

$$C_{\text{sampdil}} = mA_{\text{samp}} + b \quad [3]$$

in which the appropriate regression-determined values of m and b for the type of analysis are used. Lastly, the concentration of Fe(II) or total Fe in the original sample (C_{samp} , in units of wt% Fe) is calculated from the C_{sampdil} values (in units of μg Fe mL⁻¹) by:

$$C_{\text{samp}} = (C_{\text{sampdil}} \times F \times V_{\text{dig}}) / (10^4 \times W_{\text{samp}}) \quad [4]$$

using the appropriate sample dilution factor (F_{citr} or $F_{\text{NH}_2\text{OH}}$) and digestate volume individually calculated for each sample. These calculations are best implemented in a spreadsheet program.

In many instances, this degree of precision may not be needed and theoretical values may be substituted for the calculation of individual digestate volumes and dilution factors. The theoretical values of F and V_{dig} are 11 and 115 mL, respectively. The theoretical value for m is 5.0313 μg mL⁻¹, assuming C_{samp} in units of wt% Fe, a molar absorptivity of 11,100 L mol⁻¹ cm⁻¹ in dilute solution (Schilt 1969), a 1-cm pathlength and an intercept, b , of 0. Typical molar absorptivities closer to 10,850 are seen, which correspond to an m value of 5.15. Thus, for quick estimates of the Fe(II) or total-Fe concentrations (wt% Fe) in a sample, a simpler form of Equation [4]:

$$C_{\text{samp}} = 0.651 \times A_{\text{samp}} / W_{\text{samp}} \quad [5]$$

may be used in which the constant is calculated with an m value of 5.15 and W_{samp} is given in g.

Kinetic Studies

A series of experiments was conducted using the closed-loop continuous-flow apparatus in order to assess the stability of the absorbance value at 510 nm under a variety of conditions. Typically, the experiments involved simultaneous preparation of 2 dilutions from a digestate (usually FES). For example, one of the dilutions was in the 1% citrate solution and was

exposed to the Hg-vapor lamp. The other was either a second citrate dilution or a dilution in the 1% NH₂OH in 1% citrate solution. The second dilution vial was wrapped in Al foil to exclude light and placed next to the first dilution vial in the bucket so that temperatures in the 2 vials were similar. The initial absorbances of both dilutions were measured and then the absorbance of the first dilution was monitored for 18 h by continuous circulation through the spectrophotometer cell. At the end of the experiment, usually 24 h after the start, the final absorbance values of the 2 vials were measured. Among the factors measured in these studies were temperature (25 °C and 35–45 °C), reductant (light, NH₂OH, neither or both) and the effect of other transition metals (Mn and Cr).

Metal Interference Studies

The effects of Mn and Cr on the Fe(II) and total-Fe values obtained by the phen method were assessed both through the ordinary application of the method (on FES samples spiked with various amounts of the metal-chloride salt) and through the use of the continuous-flow apparatus to monitor the time-dependent changes associated with photoreduction and reduction by NH₂OH. The ordinary measurements were performed with about 0.11 mM Fe in the digestate and Mn or Cr present at a 0.1:1, 1:1, 10:1 or 100:1 metal:Fe mole ratio. Measurements of Fe(II) and of total Fe (after reduction by either light or NH₂OH) were taken under routine conditions. The continuous-flow experiments were performed with the same Fe concentration in the digestate, and either a 1:1 or a 7:1 metal:Fe mole ratio. In these experiments, the changes in the absorbance at 510 nm were monitored continuously during the first 18 h of the photoreduction process. Absorbance values for the Fe(II) and NH₂OH-treated dilutions were determined at the start and end of the run. Extreme care was taken to ensure that identical dilutions were made to isolate differences in absorbance among the treatments from random error in the dilutions.

RESULTS AND DISCUSSION

Color Development

Fe(II) DETERMINATION. Measurements of the absorbance of dilutions made in amber bottles confirmed the observations of Stucki and Anderson (1981) that full color development is achieved immediately upon dilution in 1% citrate. Essentially no change (that is, <0.2%) in absorbance values for FES [which contained 0.03 mol Fe(III) per mol total Fe] or MICA-Fe samples was seen over an 18-h period if the digestate and dilution were stored in the amber bottles. In short, the 30-min color development period recommended in earlier methods (Shapiro 1960; Roth et al. 1968) is unnecessary for Fe(II) determination. These results also

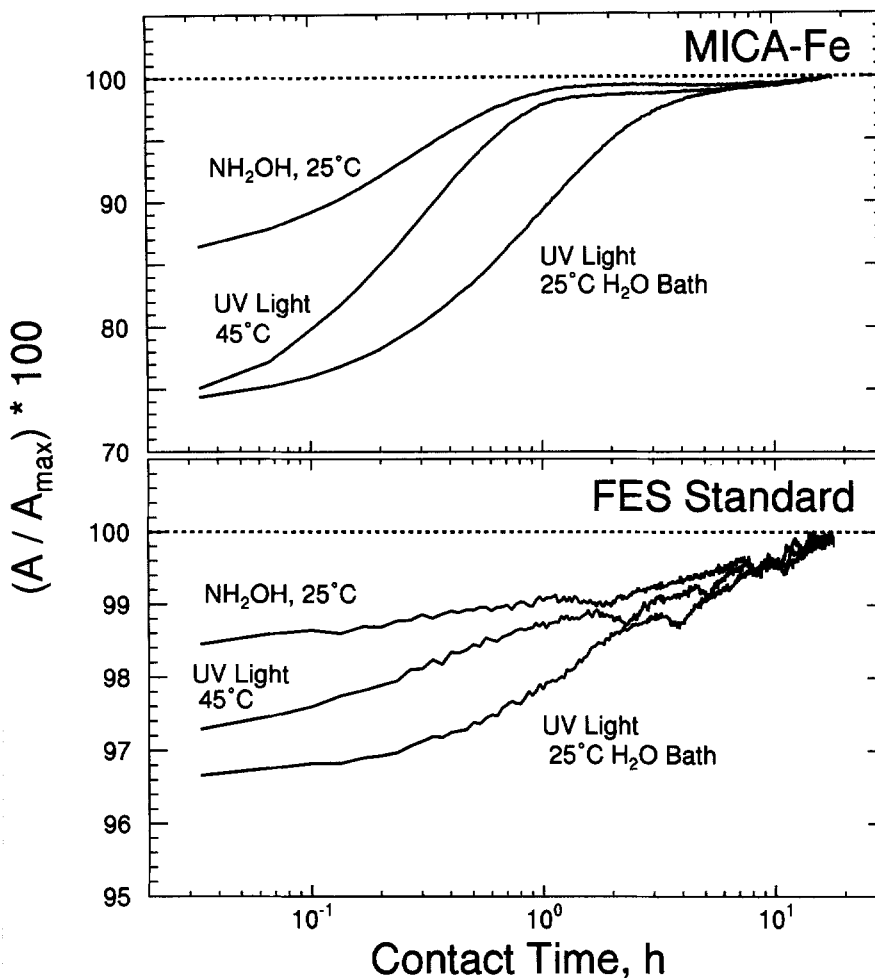


Figure 2. The approach to maximum absorbance for total-Fe determinations using NH_2OH , UV light at 25 °C or UV light at 45 °C for a MICA Fe sample (top) and an FES standard sample (bottom).

clearly demonstrate that the use of the amber bottles obviates the need to work in a darkened laboratory.

TOTAL Fe DETERMINATION. Reduction of Fe(III) in the dilutions is not immediate and, consequently, a series of kinetic experiments was performed with FES and MICA-Fe samples to identify the minimum and optimum periods required for full color development. Three ways of reducing the Fe(III) were investigated: 1) reduction by NH_2OH at 25 °C; 2) photoreduction without temperature control (incidental heating of sample to about 45 °C occurred); and 3) photoreduction at 25 °C using the water bath to moderate sample temperature. The NH_2OH treatment reduced about 50% of the Fe(III) immediately and 99% of the maximum absorbance was attained within 90 min of preparing the dilution (Figure 2). Little change occurred in the absorbance of the MICA-Fe sample during the next 8–10 h, with most of the remaining increase oc-

curing during the last 8 h of the experiment. Similar results were obtained when NH_2OH reduction of an FES dilution was performed under UV light at 25 °C (data not shown). The photoreduction treatments proceeded more slowly than the NH_2OH treatment during the first hour of the experiment. As with the NH_2OH treatment, a plateau was reached near 98% of maximum absorbance after about 90 min for the 45 °C treatment with the MICA-Fe sample. The 25 °C treatment, however, required at least 5–6 h before reaching the same plateau. Because absorption of light by the water bathing the sample vial also decreased the intensity of light reaching the sample, it is unclear to what extent the difference in these 2 photoreduction treatments is due to temperature. In contrast to the MICA-Fe sample, the FES sample showed little sign of reaching a plateau in absorbance regardless of the reduction method used. Rather, a pseudo-first-order

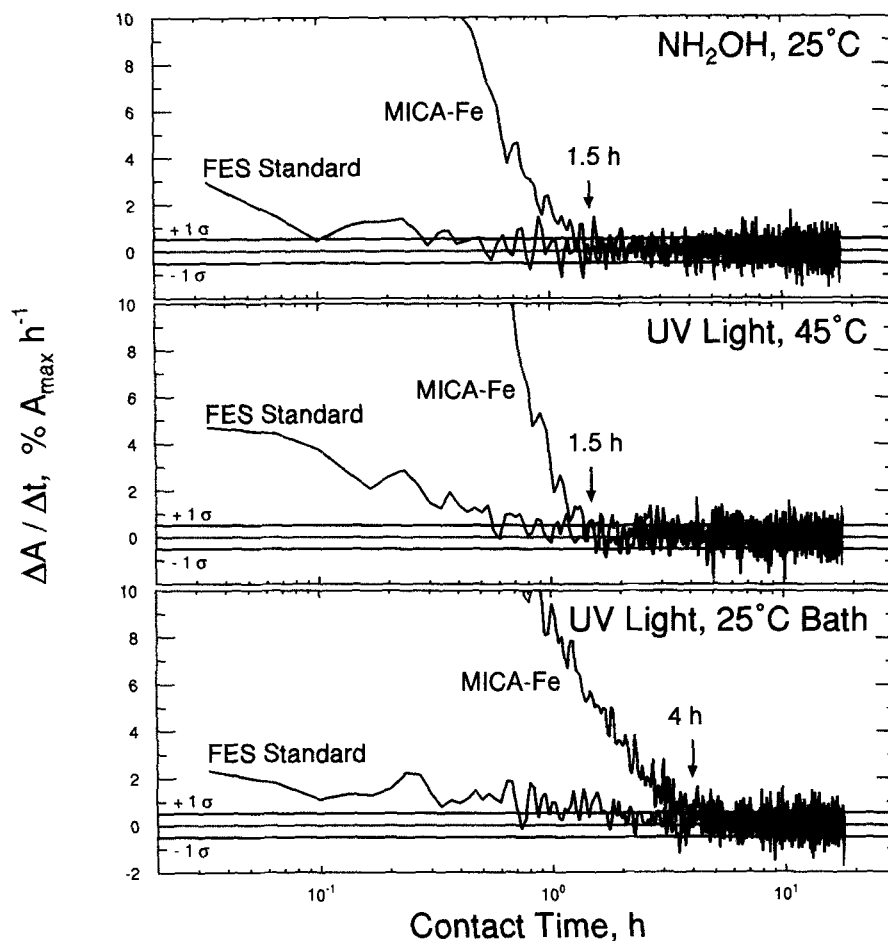


Figure 3. The rates of approach to maximum absorbance for total-Fe determinations for a MICA-Fe sample and an FES standard sample using NH_2OH (top), UV light at 45°C (middle) or UV light at 25°C in a water bath (bottom).

decay in the rate of approach to the maximum absorbance value was observed.

Although it is difficult to identify the period required to reach an absolute maximum absorbance value, one relevant measure could be the period required for the relative rates of the standard- and sample-absorbance increases to coincide. First-derivative plots of the data in Figure 2 clearly show the minimum period required for the standard and sample absorbances to reach equivalent rates of increase (Figure 3). Based on these plots, a minimum of 90 min is required for both the NH_2OH and 45°C photoreduction treatments (using this apparatus), whereas about 4 h is needed for the 25°C photoreduction treatment. For a few hours after this minimum color-development period, the noise level in the absorbance data seems to be at a minimum and then increases again towards the end of the experiment. This observation, coupled with the close agreement among the 3 reduction methods after about 5–6 h (Figure 2), suggests that the optimum col-

or-development periods for total-Fe determinations after photoreduction are on the order of 6 to 10 h.

A slightly different apparatus is used for photoreduction at Whitman College. In this implementation, the source is the same, but is placed under the samples in an Al-foil lined box. The samples are placed in a test-tube rack suspended 20 cm above the lamp and incidental heating of samples to about 40°C is seen. With this arrangement, minimum photoreduction times on the order of 30 to 60 min are attained because the bottle caps do not block the light from reaching the dilutions. A similar bottom-irradiation apparatus was described by Komadel and Stucki (1988) except that a sheet of glass is used to support the samples 40 cm above the source mainly to minimize temperature changes and light intensity differences. Minimum photoreduction times of 90 min are needed with this apparatus. The wide range in color-development periods for photoreduction treatment (0.5 to 4 h) clearly demonstrates the need to calibrate each individual apparatus.

Table 1. Results of analyses of geochemical reference materials for Fe(II) and Total Fe by the improved phen method.

Reference material	Fe(II)†		Total Fe†		
	Measured‡	Reference§	Measured (light)‡	Measured (NH ₂ OH)‡	Reference§
	----- %Fe -----				
G-2	1.18 (0.01)	1.13 (<0.06)	1.70 (0.02)	1.77 (0.02)¶	1.87 (<0.09)
STM-1	1.59 (0.01)	1.62 (<0.08)	3.34 (0.06)	3.37 (0.03)	3.65 (<0.18)
BIR-1	6.73 (0.02)	6.51 (<0.33)	7.92 (0.05)	8.03 (0.03)	7.88 (<0.39)
MICA Mg	5.24 (0.05)	5.23 (<0.26)	6.39 (0.07)	6.56 (0.03)	6.62 (<0.33)
MICA Fe (ISU)	14.43 (0.04)¶	14.70 (<0.73)	17.30 (0.11)¶	17.92 (0.05)¶	17.94 (<0.90)
MICA Fe (PNNL)	15.15 (0.06)	14.70 (<0.73)	17.99 (0.06)	18.05 (0.06)	17.94 (<0.90)
L'ane 3B	14.41 (0.04)	14.50 (0.02)#	16.62 (0.05)	16.82 (0.04)	17.17 (0.07)††
Biot 1A	12.47 (0.07)	13.18 (0.03)#	14.18 (0.06)	14.33 (0.05)	14.24 (0.11)††
	----- % -----				
Mean relative error	2.6 (1.8)	—	3.6 (3.5)	2.4 (2.7)	—
Mean relative standard deviation	0.6 (0.3)	—	0.8 (0.6)	0.5 (0.4)	—

† Mean (standard deviation).

‡ $n = 5$.

§ Potts et al. (1992), p 42, 44, 50.

¶ $n = 4$.

Titrimetric method, Amonette and Scott (1991).

†† Atomic absorption spectrometry, F. A. Khan (unpublished data).

Geochemical Reference Materials

To test the accuracy and precision of the improved phen method, a set of 8 geochemical reference materials was analyzed for Fe(II), total Fe (after photoreduction) and total Fe (after reduction by NH₂OH). The analyses were performed in 2 successive batches in a 12-h period using identical stock solutions. Total-Fe dilutions were allowed to equilibrate for 1.7 h before analysis in the first batch and for 6 h in the second batch. Five replicates were analyzed for each reference material.

ACCURACY. The results (Table 1) show very good agreement with the reference values. The relative standard deviation associated with the CRPG and USGS reference material values is estimated at 5% (Potts et al. 1992). Fifteen out of 18 of the measured values for the 6 reference materials fall within 5% of the reference values. An overall assessment of the accuracy of the method is given by the mean relative error (MRE), which is calculated using the absolute value of the difference between the measured and reference value for each sample. An MRE of about 2.5% was obtained for the Fe(II) and total-Fe (NH₂OH) data, whereas the MRE of the total-Fe (photoreduced) data is 3.6%. If only the USGS and CRPG data are considered, MREs of 2.5% for Fe(II), 4.3% for total Fe (photoreduction) and 2.8% for total Fe (NH₂OH) are obtained. Similar calculations on the USGS reference-material data of Stucki (1981) yield MREs of 6.0% for Fe(II) and 8.5% for total-Fe (photoreduction). Other data for USGS and CRPG reference materials (F. A. Khan, unpublished data) using the method of Komadel and Stucki (1988) yields MREs of 3.9% for Fe(II) and 4.1% for total-Fe (photoreduction). Although differences among

laboratories and analysts make absolute comparisons difficult, the accuracy of the data in Table 1 is clearly equal to or better than any that has been reported with the phen method.

PRECISION. The precision of the improved method is also quite good (Table 1). Mean relative standard deviations (MRSD) between 0.5% and 0.8% were obtained, which are considerably lower than the range in MRSDs (1.6% to 3.3%) calculated for other phen datasets (Stucki 1981; F. A. Khan, unpublished data) and approach the MRSD of 0.4% obtained for a precise titrimetric method (Amonette and Scott 1991). Substitution of fixed values for the digestate volume and dilution factors using the mean values obtained for all the samples in the analysis had essentially no impact on the accuracy of the method but lowered the precision by about 50%.

MICA FE. Two separate samples of MICA Fe were analyzed because preliminary runs showed the PNNL samples to yield significantly higher results for Fe(II) than expected from the reference value and previous work. To verify that the PNNL sample was indeed different, we obtained some of the MICA-Fe sample from ISU that had been used in our earlier work (Amonette and Scott 1991; F. A. Khan, unpublished data). The ISU sample results for Fe(II) proved closer to the reference value, but on the low side (Table 1).

A recent highly accurate Mössbauer analysis of a third MICA-Fe sample by researchers at the University of Ottawa (A. E. Lalonde and D. G. Rancourt, personal communication, 1997) yielded an Fe(II) value of 14.16%, which is outside the range for the 2 samples we analyzed. These investigators also noted significantly higher levels of Fe(III) in the powdered form

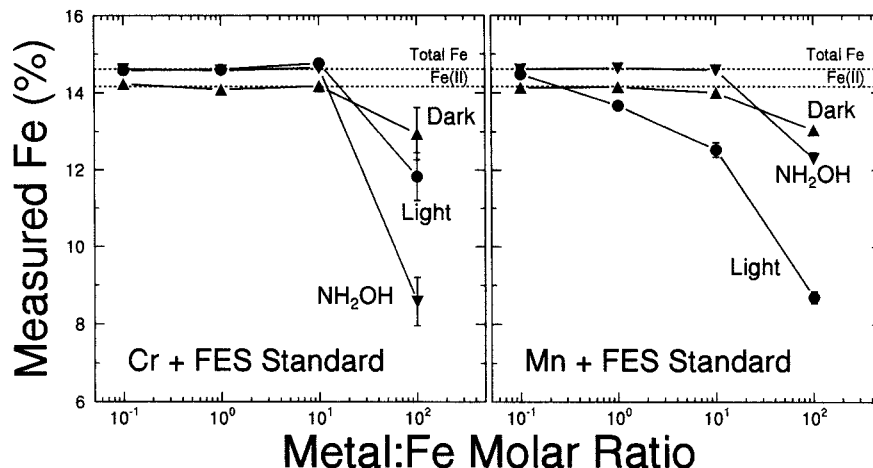


Figure 4. The amounts of Fe(II) and total Fe measured in samples containing FES and different amounts of Cr(III) (left) or Mn(II) (right). Expected values of Fe(II) and total Fe are shown by dashed line.

of MICA Fe than in the granulate form, although the 2 forms are nominally of the same composition (Lalonde et al. 1997). In contrast, Mössbauer analysis of a separate powdered MICA-Mg sample by the Ottawa group yielded an Fe(II) value of 5.21%, in excellent agreement with the measured and reference values in Table 1. Of the 3 reference materials for which we have analyzed separate samples (i.e., MICA Fe, MICA Mg and G-2, data not shown for the latter two), only MICA Fe has yielded gross discrepancies in Fe(II) values among separate samples. We conclude, therefore, that MICA Fe cannot be relied upon as a primary reference material for Fe(II) determinations.

REDUCTION METHOD FOR TOTAL FE. Comparison of the total-Fe results obtained after photoreduction with those obtained after reduction with NH_2OH (Table 1) show the photoreduction results to be slightly less accurate, less precise and about 2% lower on average than the NH_2OH data. The reasons for the discrepancy are not clear, especially since separate dilutions of the same FES-standard digestates were prepared and used to calibrate the data for each method. One possible reason, however, may be that much longer color-development times are needed for the photoreduction step than the data in Figures 2 and 3 would suggest. To test this hypothesis, the photoreduction periods were varied between the 2 runs used to produce the data in Table 1. The first run used essentially the minimum time suggested (about 100 min), whereas the samples in the second run were irradiated for 6 h. Although different samples were analyzed in the 2 runs [G-2, BIR-1, MICA Mg and MICA (ISU) were analyzed in the first run], comparison of the MREs obtained for the 2 sets of total-Fe data should give a good estimate of the degree to which irradiation period affects the total-Fe value. With Fe(II) data where no difference between runs would be expected, the 2 runs

had MREs of 2.5% and 2.7% (using deviations from the reference values). For the total-Fe data, the 100-min run had an MRE of 2.9%, whereas the 6-h run had an MRE of only 0.8%. It seems likely, therefore, that the slow kinetics of the photoreduction process are at least partly responsible for the discrepancy between results of the total-Fe methods.

Metal Interference

Another factor possibly contributing to the discrepancy in total-Fe data obtained by different reduction methods could be interference from other transition metals in the digestates. To assess this possibility, we selected Mn(II) (on the basis of its abundance in minerals and its photoreactivity) and Cr(III) for testing with FES as a source of Fe. The results of Fe(II) and total-Fe analyses, in which duplicate samples representing a range in metal:Fe mole ratios of 0.1 to 100 were carried through the digestion, dilution and reduction (3-h) procedures, show that Cr(III) had no effect on Fe values until mole ratios above 10 were encountered (Figure 4). Even at $60 \mu\text{g Cr(III) mL}^{-1}$ (that is, a 10:1 Cr:Fe mole ratio) Fe values were accurate regardless of treatment. In contrast, the presence of Mn(II) in the digestate caused a decrease in the Fe(II) values at Mn:Fe mole ratios of 10 and higher, and substantial decreases in total-Fe values, even at the 0.1 Mn:Fe mole ratio, when light was used to reduce the Fe(III) (Figure 4). As with the Cr(III) additions, the use of NH_2OH as the reductant showed no effect of Mn(II) on total-Fe values at Mn:Fe mole ratios of 10 and below. These results suggest that the effect of Mn is catalyzed by light and minimized (at Mn:Fe mole ratios less than 10) when NH_2OH is the reductant. Very high levels of Cr and Mn (that is, metal:Fe mole ratios ≥ 10) can be expected to cause significant de-

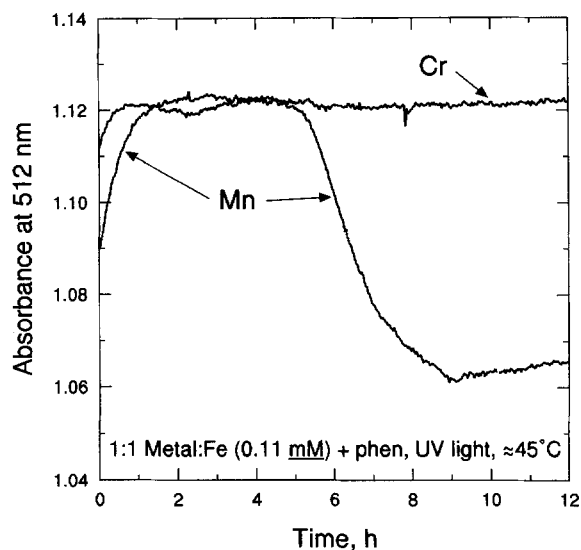


Figure 5. Changes in the absorbance of diluted digestates containing 0.11 mM Fe from FES and equivalent amounts of Cr(III) and Mn(II) during photoreduction treatment for total Fe.

creases in Fe(II) values and in total-Fe values regardless of reduction treatment.

Kinetic studies of metal interferences during photoreduction (Figure 5) again showed no effect of Cr and, in some instances, an induction period before the decrease associated with Mn was observed. The length of the induction period varied. No effect with Mn could be seen between 1.5 and 5 h for the run in Figure 5, in contrast to the significant effects shown in Figure 4 after a 3-h photoreduction treatment and in Figure 6 after just 1 h. It was not evident what controlled the length of the induction period, although the light intensity and sample temperature during the reduction were expected to be major factors.

In most silicate rocks and minerals, Mn concentrations are typically low enough ($<3000 \mu\text{g Mn g}^{-1}$ yielding $<0.12 \mu\text{g Mn mL}^{-1}$ in the final dilution) that the interference from Mn would seem to be of little importance. Indeed, as already noted, the use of longer photoreduction periods (6–10 h) seems to eliminate a large part of the difference in total-Fe values between the NH_2OH - and photo-reduced samples. The slight decrease in Fe(II) values at Mn:Fe mole ratios of 10 and higher suggests that the Mn effect occurs at a significant rate even in the absence of light. To assess this possibility with mineral digestates, the Fe(II) concentrations in a single digestate for each mineral analyzed in Table 1 were determined after 2 weeks of storage in the amber bottles. For 8 of the mineral digestates, no change in absorbance [that is, $<0.01\%$ Fe(II)] was seen. The 2 samples having the highest Mn concentrations (0.92% Mn in Biot 1A and 0.72% Mn in L'ane 3B), however, yielded "decreases" in Fe(II) content of 0.13% and 0.08%, respectively. The highest Mn

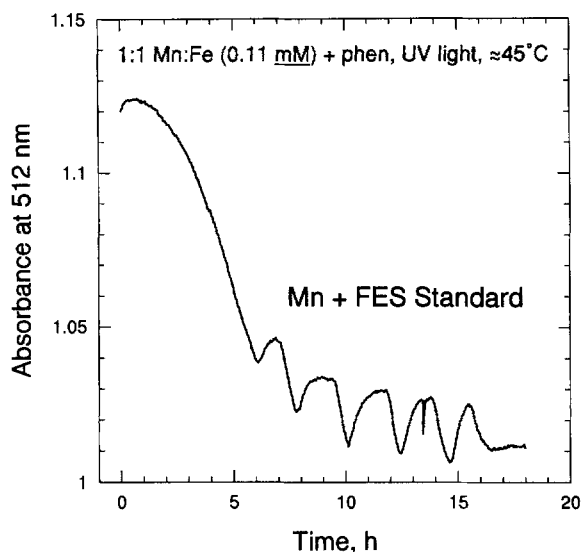


Figure 6. Oscillatory changes in the absorbance of a diluted digestate containing 0.11 mM Fe from FES and an equivalent amount of Mn(II) during photoreduction treatment for total Fe.

content for which no change in Fe(II) concentration was observed was 0.27% in the MICA Fe samples. Extrapolation of these results suggests that the long-term stability of Fe(II) values for digestates containing more than about $3 \mu\text{g Mn mL}^{-1}$ is questionable.

In some instances when Mn was present, oscillatory behavior similar to that of a Bray or Belousov–Zhabotinsky reaction (Bray 1921; Zhabotinsky 1964a, 1964b; Degn 1972; Nicolis and Portnow 1973; Noyes and Field 1974; Wood and Ross 1985) was observed (Figure 6). The Bray reaction involves the alternate oxidation and reduction of the iodine/iodate couple by hydrogen peroxide in dilute sulfuric acid, whereas the Belousov–Zhabotinsky reactions generally occur in sulfuric acid solutions containing citric or malonic acid, a metal catalyst (Ce, Mn or Fe-phen) and an oxidized halide species (such as bromate, iodate or chlorite). Although the pH of the diluted digestate (ca 4) is higher than expected, many of the reagents for an oscillatory reaction are present or could be generated by irradiation of the sample (for example, the oxidized halide species could possibly be supplied by the oxidation of Cl^{-1} ions by photoinduced H_2O_2). The reaction was not observed consistently (compare Figures 5 and 6), but such chaotic (randomly induced) behavior has been suggested as one of the features of oscillatory reactions (Epstein et al. 1983). At this juncture, we can only say that we have possibly identified an oscillatory reaction—further study is needed to define the reaction and the parameters that control its behavior.

CONCLUSIONS

The changes to the phen method for Fe(II) and total Fe in nonrefractory minerals, which include 1) the use

of opaque HDPE bottles for digestion and Fe(II) dilutions, 2) the use of gravimetry for quantification of all reagent additions, 3) the addition of a near-boiling acid-matrix solution, 4) the minimization of numbers of solutions added and 5) optimum reduction periods for total Fe of 6–10 h, yield a substantial improvement in the accuracy, precision and convenience of the procedure. Slightly lower values for total Fe obtained with photoreduction relative to chemical reduction by NH_2OH are largely offset by longer reduction periods, but may also represent an effect of Mn in some samples. Sample digestates stored in opaque HDPE bottles are stable for at least 2 weeks unless they contain more than $3 \mu\text{g Mn mL}^{-1}$, in which case low values for Fe(II) will be obtained in addition to the low values for total Fe. The presence of Cr in the digestates has no effect at levels typically encountered, but clearly the use of this method for analysis of Fe in high-Mn samples is fraught with the potential for error. In general, reduction by NH_2OH is preferable to that by ultraviolet light, because the method is simpler, faster, minimizes the effects of Mn and eliminates the need for a separate apparatus specifically calibrated for this purpose.

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REFERENCES

- Amonette JE, Khan FA, Scott AD, Gan H, Stucki JW. 1994. Quantitative oxidation-state analysis of soils. In: Amonette JE, Zelazny LW, editors. Quantitative methods in soil mineralogy, SSSA Miscellaneous Publication. Madison, WI: Soil Sci Soc Am. p 83–113.
- Amonette JE, Scott AD. 1991. Determination of ferrous iron in non-refractory silicate minerals—I. An improved semi-micro method. *Chem Geol* 92:329–338.
- Bandemer SL, Schaible PJ. 1944. Determination of iron. A study of the o-phenanthroline method. *Ind Eng Chem Anal Ed* 16:317–319.
- Banerjee S. 1974. Direct determination of ferrous iron in silicate rocks and minerals by iodine monochloride. *Anal Chem* 46:782–786.
- Begheijn LTh. 1979. Determination of iron(II) in rock, soil, and clay. *Analyst* 104:1055–1061.
- Blau F. 1898. Über neue organische Metallverbindungen. Ein Beitrag zur Kenntniss der Metallake—I. Mittheilung. *Monatsh Chem* 19:647–683.
- Bray, WC. 1921. Periodic reaction in homogeneous solution and its relation to catalysis. *J Am Chem Soc* 43:1262–1267.
- Degn H. 1972. Oscillating chemical reactions in homogeneous phase. *J Chem Ed* 49:303–307.
- Epstein IR, Kustin K, De Kepper P, Orban M. 1983. Oscillating chemical reactions. *Sci Am* 248:112–123.
- Fortune WB, Mellon MG. 1938. Determination of iron with o-phenanthroline. A spectrophotometric study. *Ind Eng Chem Anal Ed* 10:60–64.
- French WJ, Adams SJ. 1972. A rapid method for the extraction and determination of iron(II) in silicate rocks and minerals. *Analyst* 97:828–831.
- Komadel P, Stucki JW. 1988. Quantitative assay of minerals for Fe^{+2} and Fe^{+3} using 1,10-phenanthroline: III. A rapid photochemical method. *Clays Clay Miner* 36:379–381.
- Lalonde AE, Rancourt DG, Ping JY. 1997. Accuracy of ferric/ferrous determinations in phyllosilicates: A comparison of Mössbauer and wet-chemical methods. Program with Abstracts; 11th Int Clay Conf; 15–21 June 1997; Ottawa, Canada. p A45.
- Nicolis G, Portnow J. 1973. Chemical oscillations. *Chem Rev* 73:365–384.
- Noyes RM, Field RJ. 1974. Oscillatory chemical reactions. *Ann Rev Phys Chem* 25:95–119.
- Potts PJ, Tindle AG, Webb PC. 1992. Geochemical reference material compositions. Boca Raton, FL: CRC Pr. 313 p.
- Roth CB, Jackson ML, Lotse EG, Syers JK. 1968. Ferrous-ferric ratio and CEC changes on deferration of weathered micaceous vermiculite. *Israel J Chem* 6:261–273.
- Saywell LG, Cunningham BB. 1937. Determination of iron. Colorimetric o-phenanthroline method. *Ind Eng Chem Anal Ed* 9:67–69.
- Schafer HNS. 1966. The determination of iron(II) oxide in silicate and refractory minerals—I. A review. *Analyst* 91:755–762.
- Schilt AA. 1969. Analytical applications of 1,10-phenanthroline and related compounds. Oxford, UK: Pergamon Pr. 193 p.
- Shapiro L. 1960. A spectrophotometric method for the determination of FeO in rocks. *Prof Pap US Geol Surv* 1960: B496–B497.
- Stucki JW. 1981. The quantitative assay of minerals for Fe^{+2} and Fe^{+3} using 1,10-phenanthroline: II. A photochemical method. *Soil Sci Soc Am J* 45:638–641.
- Stucki JW, Anderson WL. 1981. The quantitative assay of minerals for Fe^{+2} and Fe^{+3} using 1,10-phenanthroline: I. Sources of variability. *Soil Sci Soc Am J* 45:633–637.
- Van Loon JC. 1965. Titrimetric determination of the iron(II) oxide content of silicates using potassium iodate. *Talanta* 12:599–603.
- Walden GH, Hammett LP, Chapman RP. 1931. A reversible oxidation indicator of high potential especially adapted to oxidimetric titrations. *J Am Chem Soc* 53:3908.
- Wilson AD. 1955. A new method for the determination of ferrous iron in rocks and minerals. *Bull Geol Surv Eng* 1955:56–58.
- Wood PM, Ross J. 1985. A quantitative study of chemical waves in the Belousov–Zhabotinsky reaction. *J Chem Phys* 82:1924–1936.
- Zhabotinsky AM. 1964a. Periodic process of the oxidation of malonic acid in solution (study of kinetics of Belousov's reaction). *Biofizika* 9:306–311.
- Zhabotinsky AM. 1964b. Periodic liquid phase oxidation reactions. *Dokl Akad Nauk SSSR* 157:392–395.

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