NOTES

QUANTITATIVE ASSAY OF MINERALS FOR Fe^{2+} AND Fe^{3+} USING 1,10-PHENANTHROLINE: III. A RAPID PHOTOCHEMICAL METHOD

Reliable, quantitative analysis of aluminosilicate minerals for Fe^{2+} and Fe^{3+} is fundamental to the proper characterization of many soil and mineral processes. Mössbauer spectroscopy is a common and powerful method for measuring many properties of these two oxidation states of Fe, but it is only semi-quantitative with respect to determining the absolute quantity or ratio of the two states. Numerous quantitative methods have been developed (e.g., Clemency and Hagner, 1961; review by Loveland, 1988), including the use of the reagent 1,10-phenanthroline (phen). This reagent has proven to be a reliable colorimetric indicator for Fe^{2+} (Schilt, 1967) and has been used by many clay and soil scientists to determine Fe^{2+} and Fe^{3+} (by difference after complete reduction) quantitatively in mineral samples.

Stucki and Anderson (1981) reported that methods using the phen reagent for Fe^{2+} analysis of minerals are photosensitive if Fe^{3+} is present. This interference occurs because the addition of phen to a solution containing both Fe^{2+} and Fe^{3+} forms two complexes: tris(1,10-phenanthroline)iron(II), which is the red-orange complex measured at 510 nm, and the uncolored tetrakis(1,10-phenanthroline)-μ-oxodiiron(III) complex (Wehry and Ward, 1971; David *et al.,* 1972). The latter is readily reduced photochemically to the former by ultraviolet-visible radiation, with λ <500 nm. By protecting analyte solutions from all except red visible light, Stucki (1981) demonstrated that the method becomes highly reliable for Fe^{2+} even in the presence of Fe^{3+}.

For total Fe analysis, on the other hand, the photosensitivity of the Fe^{3+} complex is an asset, because light may be used instead of chemical reducing agents to reduce the Fe^{3+}, thereby simplifying the procedure and avoiding minor ancillary interferences (Stucki and Anderson, 1981). Stucki (1981) described such a method using fluorescent light, but that method had two inherent weaknesses: (1) the time required for complete photoreduction (36 hr or more) was too long and, thus, offered little advantage over chemical reducing agents; and (2) the effectiveness of commonly available fluorescent bulbs has deteriorated considerably since the method was introduced, presumably because of efforts

by manufacturers to decrease emissions of ultraviolet radiation. In the present study, an alternative light source was identified and tested with regard to reliability and time for complete photochemical reduction. Following are the results of those tests and a recommended method for the rapid determination of Fe^{2+} and Fe^{3+} in aluminosilicate minerals using the phen reagent.

MATERIALS AND METHODS

Materials

The aluminosilicates used in this study (Table 1) represent a wide range of Fe^{2+} and total Fe contents. The vermiculite (VM1) and U.S. Geological Survey standard (PCC-1) samples were exactly the same as discussed in Part II of this series (Stucki, 1981). The same raw material was used for the Garfield nontronite (GAN), but the particular sample was prepared at a different time from the sample used in Part II. Montmorillonites and nontronites were fractionated to <2 μm, saturated with Na^+, dialyzed, and freeze-dried. The maghemite fraction was removed from sample NG-1 by passing a hand magnet through the initial suspension (Lear *et al.,* 1988). The smectite from Hroznětín, Czechoslovakia, was fractionated to <2 μm, saturated with Ca^{2+}, dialyzed, dried at 105°C, and ground to <200 μm. The biotite was fractionated to 5–20 μm after wet grinding, then air-dried. All other samples were used as supplied with no further processing.

The light source used for photochemical reduction of the Fe^{3+} complex was a 175 W mercury vapor lamp (Philips Lifeguard H39KB-175) mounted into a Mercury Luminaire fixture (R-175M).

High grade 1,10-phenanthroline monohydrate reagent from Sigma Chemical was used. The quality of this reagent is critical, and experience suggests that a melting point of 90° to 100°C and a hydrated H_2O content of 7–10% are appropriate indicators of high quality. Results using phen with a melting point of >100°C have been unsatisfactory.

Methods

Samples were digested and analyzed for Fe^{2+} as described by Stucki (1981), except three aliquots (0.803 ml each) instead of one from the calibrated dilutor were transferred from the digestion tube to a 50-ml Erlenmeyer flask containing three aliquots of 10% sodium citrate solution. This solution was then diluted with three portions (7.22 ml each) of water from the dilutor, giving a final volume of 26.48 ml in the flask.

Total Fe analysis was accomplished by placing the flask with the remaining solution (covered with parafilm) on a 3.1-mm-thick sheet of Pyrex glass located 40 cm above the horizontally mounted mercury vapor lamp. The 40-cm distance above the lamp was selected to avoid temperature changes in

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Table 1. Sample descriptions and sources.

Sample	Type	Source
JP	Montmorillonite	Jelšový Potok, Czechoslovakia,
UPM	Montmorillonite	API 25, Upton, Wyoming (Ward's Natural Science Establishment, Rochester, New York)
PCC-1[1]	Peridotite	U.S. Geological Survey Standard, Split 75 Position 14
VM[1]	Vermiculite	Unknown
HCZ	Smectite	Hroznětín, Czechoslovakia
B1	Biotite	Bancroft, Ontario (Ward's Natural Science Establishment, Rochester, New York)
SWa-1	Nontronite	Grant County, Washington (Source Clay Repository of The Clay Minerals Society)
NG-1	Nontronite	Hohen Hagen, Federal Republic of Germany (Source Clay Repository of The Clay Minerals Society)
GAN	Nontronite	API 33-a, Garfield, Washington (Ward's Natural Science Establishment, Rochester, New York)

[1] Samples described in Stucki, 1981.

the sample solution during exposure and to minimize intensity differences due to radial dispersion from the source. After light exposure for the desired time, the solution absorbance at 510 nm was determined. Analysis for Fe^{2+} or total iron required about 8 ml of solution.

Calibration curves for Fe^{2+} and photochemical determination of total iron were prepared by substituting $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (ferrous ammonium sulfate hexahydrate) crystals for the sample in the digestion tube. Otherwise, the standard samples were treated identically to the unknown samples.

For comparison, total Fe was also determined by atomic absorption spectroscopy (AA) at 248.3 nm. Citrate is a known source of interference in iron determination by AA, so to test the importance of this interference, H_2O was substituted for citrate in the dilution of one set of samples. Standard solutions were prepared from $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and subjected to the same treatments as the samples.

To ascertain the optimum exposure time, the absorbance of the sample solution was continuously monitored at 510 nm by circulating the solution at 0.05 ml/s from the irradiated flask through a flow cell in the spectrophotometer using a peristaltic pump. Data were recorded digitally at 1-s intervals.

RESULTS AND DISCUSSION

The calibration curve for Fe^{2+} linearly followed the Beer-Lambert Law from 0 to 8 μg Fe/ml, giving an

Table 2. Assay of selected mineral samples for Fe^{2+} and total Fe.

Sample[1]	Fe^{2+}		Total iron			
	1988[2]	1981[2]	1988[2]	1981[2]	CAA[3]	WAA[4]
JP	0.01	n.d.	2.20	n.d.	1.90	2.24
UPM	0.19	n.d.	2.66	n.d.	2.30	2.70
PCC-1	4.15	4.12	5.33	5.22	5.30	n.d.
VM1	1.23	1.29	6.60	6.57	6.60	n.d.
HCZ	3.33	n.d.	8.40	n.d.	8.38	8.49
B1	12.63	n.d.	13.72	n.d.	13.62	n.d.
SWa-1	0.07	n.d.	17.58	n.d.	17.22	17.34
NG-1	0.12	n.d.	20.03	n.d.	19.49	19.73
GAN	0.08	0.05	21.76	24.04	21.20	21.33

[1] See Table 1 for sample descriptions.
[2] 1981 = photochemical method of Stucki (1981); 1988 = photochemical method this study; n.d. = not determined.
[3] CAA = atomic absorption method with citrate in samples.
[4] WAA = atomic absorption method with water instead of citrate in samples.

absorptivity (ϵ) of 0.1899 ± 0.0015 cm²/μg. This value gradually decreased with increasing age of the phen solution; with an 8-week-old solution the value was 0.1850 ± 0.0018 cm²/μg. The absorptivity also may decrease with time between dilution of the digest solution and preparation of the final solution. Using fresh phen solution, immediate dilution into the final flask resulted in the value reported above (0.1899 cm²/μg), whereas storing the digest solution for 24 hr in darkness yielded a value of 0.1888 ± 0.0012 cm²/μg. After five days, a visible precipitate was found in the solutions having high (>6 μg/ml) Fe concentrations, and ϵ consequently decreased by 14 to 35%; hence, a reliable analysis was impossible. These absorptivity values are similar to the value of 0.1852 ± 0.0017 cm²/μg reported by Stucki (1981). The difference may be due to the age of the phen solution, which was not monitored in the previous study.

The same standard solutions were used for the calibration curve for total iron, except after Fe^{2+} determination the solutions were exposed for 90 min to the mercury vapor light along with the analyte solutions. Resulting values of ϵ for total iron were 0.2025 ± 0.0008 cm²/μg for solutions diluted immediately and 0.2002 ± 0.0007 cm²/μg for solutions diluted 24 hr later. Although the difference between these values is small, it slightly exceeds the sum of the standard deviations of the respective means. This fact, combined with the similar trend observed in the Fe^{2+} calibration curve, advises against waiting between digestion and final dilution.

The Fe^{2+} content (Table 2) of samples PCC-1, VM1, and GAN compare well with previous analyses. These results confirm that the method continues to be stable for Fe^{2+}. Similar excellent agreement was observed for total iron in these samples, except the value for GAN was greater in the previous study. This discrepancy is probably due to natural variability within the clay, inasmuch as the two samples were taken from different batches of particle size separation and cation saturation.
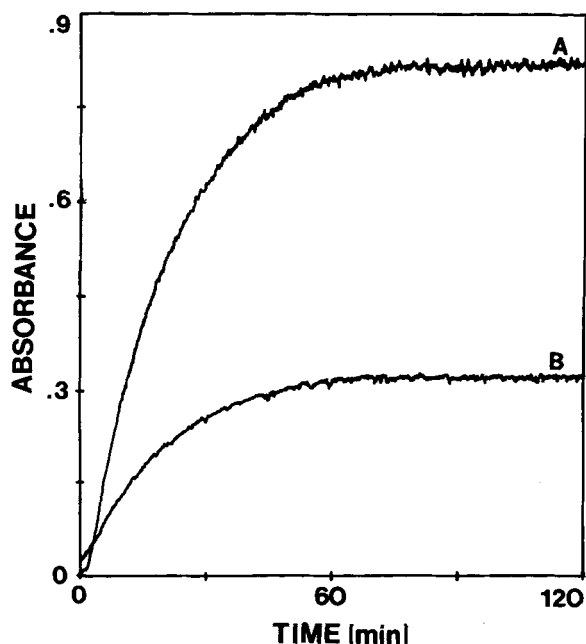
Total iron analyses by the new photochemical meth-

Figure 1.   Absorbance at 510 nm of analyte solutions from HF-H₂SO₄-1,10-phenanthroline digestates of (A) Hohen Hagen nontronite (NG-1) and (B) Upton, Wyoming, montmorillonite (UPM) samples as affected by time exposure to mercury vapor light.

od also agree extremely well with results obtained by AA, particularly if the interference of citrate on AA is taken into account. Comparison of results with values obtained from samples prepared using H_2O (denoted WAA Table 2) instead of citrate (denoted CAA) is preferred, not because of the more favorable comparison, but because of the known interference of citrate with iron determination by AA. This interference is confirmed by lower total iron values reported from the CAA (diluted with citrate) treatment than from the WAA (diluted without citrate) treatment. Because the standard solutions were treated identically to the samples, this interference is beyond normal correction by the standard curves.

The time required for complete photochemical reduction was about 60–75 min (Figure 1) regardless of the total iron content or Fe^{2+}:Fe^{3+} ratio. An exposure time of 90 min is recommended. This interval is sufficiently great to ensure complete reduction, but small enough to expedite the procedure.

CONCLUSIONS

The recommended method for Fe^{2+} and total iron is exactly as described by Stucki (1981), except: (1) the volume of each component in the final dilution is increased three-fold, (2) only one final solution is required, and (3) for total iron, a 90-min exposure to a mercury vapor lamp replaces the 36-hr exposure to a fluorescent lamp.

Mercury vapor light photochemically reduces the tetrakis(1,10-phenanthroline)-μ-oxodiiron(III) complex formed in the HF-H₂SO₄-phen digestates of clay minerals. Results for total iron determined by this photochemical reduction agree favorably with atomic absorption spectroscopic data and provide an efficient, rapid method for measuring both Fe^{2+} and total iron in the same sample. The reliability of the method described by Stucki (1981) for Fe^{2+} is confirmed. Dilution of a second set of flasks for total iron is eliminated, inasmuch as both Fe^{2+} and total iron are determined in the same solution.

Department of Agronomy   PETER KOMADEL[1]
University of Illinois   JOSEPH W. STUCKI
Urbana, Illinois 61801

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[1] Present address: Institute of Inorganic Chemistry, Center of Chemical Research, Slovak Academy of Sciences, 84236 Bratislava, Czechoslovakia.