Technical Note

Iron(II) oxide determination in rocks and minerals

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Abstract

The determination of FeO of geologic materials by modern instrumental methods (such as atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray fluorescence (XRF), etc.) cannot distinguish between different oxidation states of elements. In many cases, the oxidation state of Fe has to be known in order to perform several chemical calculations (norms, etc.) and discuss the reactions that occur during weathering, hydrothermal alteration and other processes. A modified Wilson method is proposed, giving reproducible results in a much shorter time than the classical method. Back-titration with potassium dichromate and an Fe(II) and ammonia sulphate solution is used, after dissolution of the sample powder in a heated HF/H_3PO_4 mixture and an ammonium vanadate solution. This modified method, tested with several international reference materials, gives reliable results, equivalent to the ones cited in the literature for the reference materials. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Iron is one of the most important constituents of geologic materials, and its determination is routinely performed in analysis of rocks and minerals, usually by modern instrumental methods such as atomic absorption spectroscopy (AAS), X-ray fluorescence (XRF) or inductively coupled plasma atomic emission spectroscopy (ICP-AES). In this way, the iron content is assumed to be Fe_2O_3 or calculated as FeO. In many cases, however, the oxidation state of Fe has to be known, since FeO and Fe_2O_3 enter the composition of minerals in different ways. Most chemical calculations with rock compositions (e.g.,

norms, chemical indices, weathering profiles, etc.) or the distribution of Fe in the structural formula of iron-bearing minerals cannot be performed without knowledge of the Fe(II)/Fe(III) ratio.

Classical methods such as titration or colorimetry are still the only ones that can determine accurately the total amounts of Fe(II). Some advances have been made in the quantitative identification of oxidation states with Mössbauer spectroscopy, but the spectra of natural polyphase substances are exceedingly difficult to interpret.

The present study shows the results of Fe(II) determinations in several reference materials, both minerals and rocks, performed with a modified version of the Wilson (1955) method and a cold acid decomposition method (Maxwell, 1968), with a reduction in the dissolution time from 24 to 6 h for most rocks.

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1.1. Contamination and oxidation of natural samples during preparation of samples

The sample preparation procedures have to be scrutinized with care, since total Fe(II) can be changed by contamination and, in part, transformed into Fe(III) by faulty sample treatments. Rock samples are usually ground at the start of the procedure with jaw crushers, mostly equipped with cast iron or steel jaws, thus providing a first possibility of contamination with Fe particles. Further contamination can occur during the grinding stage, ideally to about 100 mesh or less, in planetary mills or ball grinders, since grinding surfaces are in some cases manufactured with steel. Today, jaw crushers or mills equipped with hard ceramic parts, tungsten carbide or agate are commercially available and should be preferred during the sample powder preparation, thus avoiding the addition of Fe to the sample.

On the other hand, the operation of grinding in air is itself a procedure that oxidizes the sample. Many authors (e.g., Fitton and Gill, 1970) have shown that only 4 min of fine grinding is sufficient to oxidize significantly the iron-bearing phases, more so, the hydrated minerals such as chlorites and biotites, than the anhydrous phases such as olivines and pyroxenes. The recommendation is to prepare the sample powders in iron-free mills and finely grind for not more than 30 s.

The procedures for the dissolution of the sample powder provide further possibilities of errors or contamination. The main causes are discussed in detail in an optimisation study by Whipple (1974) and further in Sulcek and Povondra (1989).

The oxidation of Fe(II) to Fe(III) is the most frequent change that occurs during or after dissolution of the sample powder. In the presence of fluorides, the redox potential of the system Fe(II)/Fe(III) decreases from 0.77 to about 0.1 V, thus enhancing the reaction into the oxidized state. A recommended procedure would be to perform the dissolution in an inert atmosphere (e.g., N_2 gas), but it is not easy to implement such a technique, which in any way may not be very effective in preventing oxidation.

A better way to monitor the oxidization effect is to trigger the oxidation reaction with the addition of a large known amount of an oxidizing agent, so that the ferrous ions passes immediately into the ferric state during the dissolution, thus avoiding secondary reactions such as oxidation by air.

The following procedure is a modification of the one introduced by Wilson (1955). This author proposed to dissolve the sample with a cold mixture of HF and an acid solution of ammonium metavanadate. The liberated Fe(II) is immediately oxidized into Fe(III), and the vanadate ions are reduced to vanadyl. Then, the excess of vanadate is determined by titrating with $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$. A solution containing only the reagents is also titrated. By difference, it is possible to quantify the amount of Fe^{2+} (or FeO) in the sample. Since this procedure takes over 24 h to be completed for most minerals and rocks, several secondary reactions can occur, such as the oxidation of vanadyl by a reverse reaction with Fe(III).

In the procedure described in this paper, the sample is dissolved with a mixture of HF/H_3PO_4 and an acid solution of ammonium metavanadate at 60 ± 5°C. The ferrous iron is oxidized to ferric iron and then stabilized in complexes (in this case, with phosphate), thereby inhibiting the possibility of secondary reactions during or after dissolution. Phosphoric acid acts also as a solubilizing agent of various resistant minerals, such as Fe-chlorites, lepidolites, biotites and muscovites, as well as tourmalines, garnets of various compositions, sillimanite and other phases (Sulcek and Povondra, 1989).

Subsequently, the vanadate is completely reduced with a $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ solution. The Fe(II) of the sample is then determined by a back-titration with potassium dichromate. $K_2Cr_2O_7$ is very stable in solution and its concentration can be easily determined. With this modified method, the total dissolution time is reduced to about 6 h.

2. Methodology

2.1. Reactants and glassware

In the proposed modified Wilson procedure, the rock or mineral samples should not contain more than about 0.5% MnO, Co^{2+}, sulfides and organic matter in total, in order to prevent faulty measurements. The following reactants and equipments are used: 48% (w/w) hydrofluoric acid, analytical grade;

85% (w/w) phosphoric acid, analytical grade; solution of 1% (w/v) ammonium metavanadate in H_2SO_4 0.9 M; acid solution of $H_3PO_4/H_2SO_4/H_2O$ in the volume proportions 1:2:2; saturated H_3BO_3 solution; 2% w/v $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ solution in H_2SO_4 1M; 0.2% (w/v) solution of barium diphenylamine sulphonate; standard $K_2Cr_2O_7$ solution 0.05 N. In addition, 10-ml volumetric pipettes, 100-ml polyethylene flasks with a screw cap, 500-ml erlenmeyer glassware and a 10-ml burette were used.

2.2. Procedure

About 0.2 g of powder (grain size at least less than 100 mesh) is weighted, to the fourth or fifth decimal point, in a polyethylene flask. To the sample, 5 ml of the 1% ammonium metavanadate solution is added with a volumetric pipette. Next, 40 ml of the 85% (w/w) phosphoric acid is introduced. The flask is gently shaken, and 5 ml of the 48% (w/w) hydrofluoric acid is added. Four blank samples are also prepared, following the same procedure without sample.

The flasks are closed with the screw cap, and left in a water bath at 60°C for approximately 5 h, or till the samples are completely dissolved, as determined by a visual inspection.

The flasks are then taken out of the water bath and 10 ml of the acid solution is added, and gently agitated till the solution has a uniform look. The solution is then transferred into a 500-ml erlenmeyer already containing 100 ml of the saturated solution of boric acid. The flask is rinsed twice with 50 ml of boric acid, each time; this solution is added to the sample solution, and then homogenized.

Ten milliliters of the 2% $(NH_4)_2SO_4 \cdot 6H_2O$ solution is added to the sample solution with the volumetric pipette. Again, the solution is homogenized and 1 ml of the barium diphenylamine sulphonate is added. Next, the sample solution is titrated with 0.05-N solution of potassium dichromate.

The formula that gives the total amount of FeO is as follows:

$$\%FeO = [N_{K_2Cr_2O_7} \times (V_{sample} - V_{blank}) \times 7.185] / m_{sample},$$

where $N_{K_2Cr_2O_7}$ is the normality of the potassium dichromate, V_{sample} and V_{blank} are, respectively, the sample and blank volumes of the titrant that were spent in milliliters, and m_{sample} is the initial sample weight in grams. The factor 7.185 is the transformation of the dichromate in Fe(II) equivalents (5.5847) and the mass of Fe(II) into FeO (FeO/Fe(II) = 1.2865).

Table 1
Means (%) and standard deviations obtained in this work and the ones presented in the literature for the analyzed reference materials

Materials	1[a]	2[a]	3[a]	4[a]	5[a]	6[a]	7[a]	Mean[a]	s^a	%RSD[a]	Mean (n)[b]	s^b	References
Mica-Fe	18.54	18.24	18.79	19.12	18.45	18.36	18.53	18.58	0.29	1.59	18.91 (18)	0.45	(1)
Fer-2	15.24	14.84	15.24	15.07	15.13	15.22	15.34	15.15	0.16	1.08	15.27 (16)	0.32	(2)
BR	6.49	6.57	6.71	6.60	6.41	6.62		6.57	0.10	1.60	6.57 (25)	0.26	(1)
JB-1a	5.62	5.34	5.61	5.87				5.61	0.22	3.86	5.78 (21)	0.24	(3)
OU-1	5.05	5.13	5.26	5.19	4.93	4.93		5.08	0.14	2.68	4.995 (12)	0.078	(4)
DR-N	5.34	5.42	5.39	5.42				5.39	0.04	0.70	5.40 (26)	0.25	(1)
UB-N	3.10	3.05	3.10	2.76	3.00	2.83	3.02	2.98	0.13	4.47	2.68 (22)	0.60	(1)
MA-N	0.36	0.26	0.59	0.56				0.44	0.16	35.9	0.31 (60)	0.09	(1)
BX-N	0.53	0.54	0.57	0.49				0.53	0.03	6.20	0.26 (11)	0.21	(1)
Nim-N	7.02	6.93	6.91	7.16				7.01	0.11	1.63	7.47	×	(5)
Nim-D	14.40	14.60	13.80	13.60	13.89	13.91		14.03	0.38	2.73	14.63	×	(6)
Nim-G	1.30	1.21	1.37	1.19				1.27	0.08	6.58	1.30	×	(7)

Literature references: (1) Govindaraju (1995); (2) Abbey et al. (1983); (3) Terashima et al. (1994); (4) Thompson et al. (1998); (5) South African Bureau of Standards (1984a); (6) South African Bureau of Standards (1984b); (7) South African Bureau of Standards (1984c).
[a] This paper.
[b] Literature mean and standard deviations; n = number of determinations.
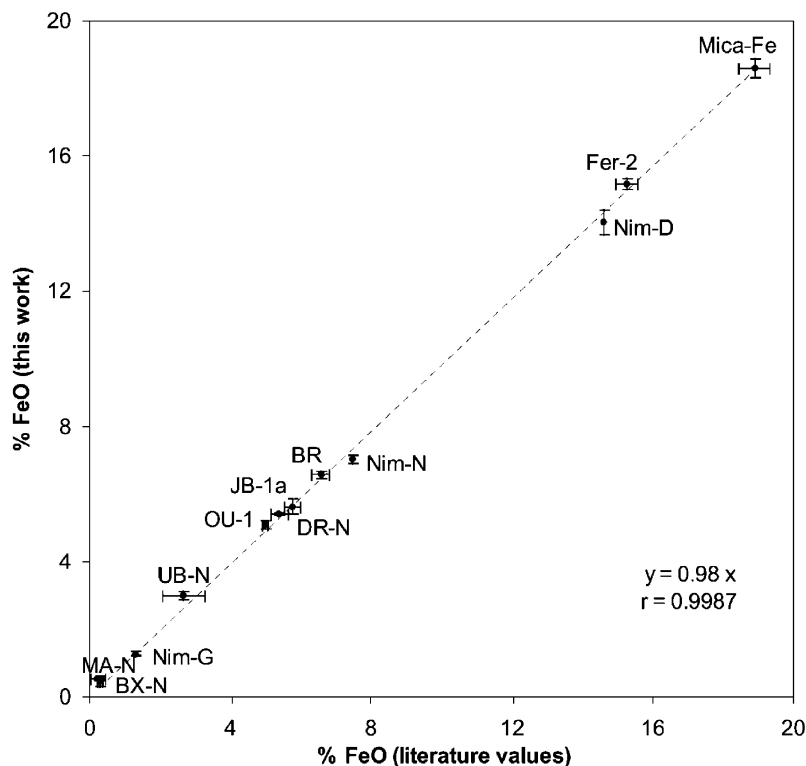
Fig. 1. Representation of FeO% values obtained in this paper, and recommended values cited in the literature (cf. text and Table 1); bars identify one standard deviation.

The sample powder weight needed for samples with over 10% FeO is reduced to 0.1 g (weighted to the fourth or fifth decimal point).

3. Results

The above analytical method was applied to several geologic reference materials, and the obtained results as well means and standard deviations obtained in this work, and the means and standard deviations cited in the literature are presented in Table 1.

The reference material AQ-1 is a Brazilian basalt from Araraquara, São Paulo (Jurassic Serra Geral Formation), used as an in-house reference material for FeO determination in our laboratory. It was analyzed repeatedly during almost 4 years and shows a mean FeO value of $10.05 \pm 0.32\%$ (24 determinations), with an RSD of 3.18%, comparable to those

presented by several reference materials in the literature.

Fig. 1 presents the results obtained in our laboratory, compared with the figures cited in the literature, with an overall correlation coefficient of 0.9987.

4. Discussion and conclusions

The analytical results presented in Table 1 are compatible with the precision obtained by the laboratories that provided the original data. It is also shown that the precision was maintained during the 3 years in which the tests were run in our laboratory, both in standard deviations and RSD.

The application of the Student's t-test for the reference materials Mica-Fe, OU-1, Fer-2, Br, UB-N, JB-1a, DR-N, indicates that there are no significant differences between our results and the ones cited in the reference literature (at a significance level of

95%, $\alpha = 0.05$). There are discrepancies for the samples BX-N and MA-N, which have low levels of FeO, close to the detection limit obtained in our work (0.28% FeO, equivalent to 3σ of the standard deviation obtained in the blank samples). Our result for the bauxite BX-N is 0.53% FeO, twice the figure of 0.26% cited in the literature, but still acceptable by Student's *t*-test (at a significance level of 99%, $\alpha = 0.01$), on account of the high standard deviation of the published value. The published value for the MA-N granite is 0.31 (± 0.09, for 60 determinations), probably close to the quantification limit of the various methods that were used; our four determinations of this sample yield a mean of 0.44 (± 0.16), and also a high RSD of 36%, not acceptable in Student's *t*-test.

The present data show a good correlation with the ones cited in the literature, with a slight negative deviation of about 2%, as pointed out by the slope coefficient of 0.98 in the regression line (Fig. 1).

A precise and reproducible determination of the FeO content of rocks and minerals can therefore be performed with this modified Wilson method, as shown above, with a significant decrease in the dissolution time (reduced from 24 to 6 h), for FeO contents that fall roughly between $\sim 1\%$ and $\sim 20\%$. This method is also safer than the modification proposed by Goldich (1984) to the Pratt method, where the analyst is subjected to dangerous levels of SO_3 and HF emanations, because the sample is solubilized with a boiling mixture of H_2SO_4/HF.

Acknowledgements

References

Abbey, S., McLeod, C.R., Liang-Guo, W., 1983. FeR-1, FeR-2, FeR-3 and FeR-4: four Canadian iron-formation samples prepared for use as reference materials. Geol. Surv. of Can., Pap. 83 (19), 1–51.

Fitton, J.G., Gill, R.C.O., 1970. The oxidation of ferrous iron in rocks during mechanical grinding. Geochim. Cosmochim. Acta 34, 518–524.

Goldich, S.S., 1984. Determination of ferrous iron in silicate rocks. Chem. Geol. 42, 343–347.

Govindaraju, K., 1995. 1995 Working values with confidence limits for twenty-six CRPG, ANRT and IWG–GIT geostandards. Geostand. Newsl. 19 (1), 1–32.

Maxwell, J.A., 1968. Rock and mineral analysis. In: Elving, P.J., Kolthoff, I.M. (Eds.), Chemical Analysis. Wiley-Interscience, New York, pp. 419–421.

South African Bureau of Standards, 1984a. Certificate of Analysis of NIM-N, "Norite," unpublished, 5 pp.

South African Bureau of Standards, 1984b. Certificate of Analysis of NIM-D, "Dunite," unpublished, 5 pp.

South African Bureau of Standards, 1984c. Certificate of Analysis of NIM-G, "Granite," unpublished, 5 pp.

Sulcek, Z., Povondra, P., 1989. Methods of Decomposition in Inorganic Analysis. CRC Press, FL, 325 pp.

Terashima, S., Imai, N., Itoh, S., Ando, A., Mita, N., 1994. 1993 Compilation of analytical data for major elements in seventeen GSJ geochemical reference samples, igneous rock series. Bull. Geol. Surv. Jpn. 45 (6), 305–381.

Thompson, M., Potts, P.J., Kane, J.S., Webb, P.C., Watson, J.S., 1998. GeoPT2: international proficiency test for analytical geochemistry laboratories. Geostand. Newsl. 22 (1), 127–156.

Whipple, K.R., 1974. A study of Wilson's determination of ferrous iron in silicates. Chem. Geol. 14, 223–238.

Wilson, A.D., 1955. A new method for the determination of ferrous iron in rocks and minerals. Bull. Geol. Surv. G. B. 9, 56–58.