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Determination of ferrous and total iron in refractory spinels

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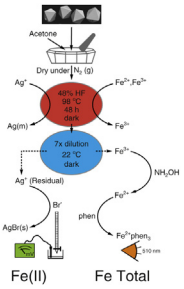
HIGHLIGHTS

- Refractory samples, such as spinels, are the most difficult for Fe redox analysis.
- Oxidimetric(Ag^+)/colorimetric (phen) method allows analysis of a single sample.
- Fe^{2+} measured by Ag^+ potentiometry, total Fe by Fe-$phen_3$ absorbance at 510 nm.
- Excellent accuracy, relative differences of 0.4% for Fe^{2+} and 1.2% for total Fe.
- Modest precision, relative standard deviations of 3.7% for Fe^{2+} 3.3% for total Fe.

GRAPHICAL ABSTRACT



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ABSTRACT

Accurate and precise determination of the redox state of iron (Fe) in spinels presents a significant challenge due to their refractory nature. The resultant extreme conditions needed to obtain complete dissolution generally oxidize some of the Fe(II) initially present and thus prevent the use of colorimetric methods for Fe(II) measurements. To overcome this challenge we developed a hybrid oxidimetric/colorimetric approach, using Ag(I) as the oxidimetric reagent for determination of Fe(II) and 1,10-phenanthroline as the colorimetric reagent for determination of total Fe. This approach, which allows determination of Fe(II) and total Fe on the same sample, was tested on a series of four geochemical reference materials and then applied to the analysis of Fe(Ni) spinel crystals isolated from simulated high-level-waste (HLW) glass and of several reagent magnetites. Results for the reference materials were in excellent agreement with recommended values, with the exception of USGS BIR-1, for which higher Fe(II) values and lower total Fe values were obtained. The Fe(Ni) spinels showed Fe(II) values at the detection limit (ca. 0.03 wt% Fe) and total Fe values higher than obtained by ICP-AES analysis after decomposition by lithium metaborate/tetraborate fusion. For the magnetite samples, total Fe values were in agreement with reference results, but a wide range in Fe(II) values was obtained indicating various degrees of conversion to maghemite. Formal comparisons of accuracy and precision were made with 13 existing methods. Accuracy for Fe(II) and total Fe was at or near the top of the group. Precision varied with the parameter used to measure it but was generally in the middle to upper part of the group for Fe(II) while that for total Fe ranged from the bottom of the group to near the top.

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1. Introduction

Quantitative determination of ferrous iron [Fe(II)] in minerals and related solid materials represents one of the most challenging procedures in analytical chemistry. Despite recent advances in and improved availability of spectroscopic methods such as Mössbauer and X-ray absorption near-edge (XANES), the majority of Fe(II) determinations continue to be made using wet-chemical methods due to their better precision, lower detection limits, and lower cost.

The chief difficulty in wet-chemical analysis arises from maintaining the Fe(II) titer during digestion and before its assay, whether by oxidimetry or colorimetry. Both of these approaches have a rich literature (see reviews by Refs. [23,2]) and many methods have been developed, principally for non-refractory minerals. Maintenance of the Fe(II) titer is made significantly more difficult when the material is refractory, due to the extreme conditions (high temperature, long duration, reagents) typically required to dissolve these materials. This is certainly the situation for Fe-bearing spinels, a common crystalline phase precipitating from high-level waste (HLW) glasses [17]. The spinel crystals do not affect the long-term durability of the glass; however, they settle and accumulate in the riser of the melter due to their high density and large size (up to 500 μm) and can potentially block the discharge of the molten glass into canisters [18,20]. Since redox state of the Fe plays an important role in their formation and growth there is a need to develop a fast and reliable analytical method to measure Fe(II) and Fe(III) in these materials.

As determination of mean Fe oxidation state is usually the parameter of interest, a value for Fe(II) must be balanced by one for Fe(III), which is usually obtained by subtraction of the Fe(II) value from that obtained for total Fe on a separate sample analyzed by other methods optimized for total elemental analysis. With the development of colorimetric methods for determination of total Fe in aqueous solutions that rely on complexation of Fe(II) by a chromophore such as 1,10-orthophenanthroline (phen) have come several methods for non-refractory minerals that allow determination of Fe(II) and total Fe on the same sample digest [8,26,16,4,14,27]. One fusion-decomposition method suitable for refractory minerals [6] has also been developed but requires a special apparatus and Pt/Au crucibles. These Fe(II)/total Fe methods are of great value where sample quantities are limited, and offer better estimates of the Fe(II)/Fe(III) ratio by avoiding sample to sample variability.

At the same time, however, methods that rely on oxidimetry (i.e., the change in quantity of an aqueous oxidant present during the decomposition of the sample) offer generally better precision and lower detection limits than those based on colorimetry. The strength of these methods often rests on the stability of the oxidant during the digestion, and as a result a temperature limit may be encountered or a specific mixture of acids may be required which, in turn, constrains the methods to non-refractory samples.

In the present work, we set out to explore possible ways of determining Fe(II) and total Fe in refractory Fe spinels, some of which (i.e., the spinel crystals isolated from the HLW glass) also contained Ni and Cr. Analysis of representative samples by Mössbauer spectroscopy suggested that the Fe(II) contents were below detection by that technique, and thus a wet-chemical approach was needed. As sample quantities were limited, a method that combined these two analyses on a single sample was desired. We started by modifying a colorimetric method [4] and then, based on the results, proceeded to develop a hybrid method that used oxidimetry for Fe(II) and colorimetry for total Fe. To our knowledge, this is the first method that combines oxidimetry and colorimetry for analysis of Fe(II) and total Fe in minerals and related Fe-bearing materials, whether refractory or not.

2. Materials and methods

2.1. Samples and standards

A set of four geochemical reference materials, as well as several iron reagents, were tested. The reference materials were a granite (G-2) and a basalt (BIR-1) from the U.S. Geological Survey, and two magnetite ores (OREAS 700 and OREAS 701) from Ore Research & Exploration Pty., Ltd., Victoria, Australia. The iron reagents were two high-purity magnetites (Alfa-Aesar 12962, Aldrich 518158), a nano-sized magnetite powder (Aldrich 637106), and an in-house-synthesized magnetite. This magnetite was prepared following the method of [24] with the slight modification of treating the starting $FeSO_4$ solution with a suspension of zerovalent Fe for one month to ensure complete reduction of any Fe(III) that may have been present. Subsequent oxidation of the $FeSO_4$ in an alkaline solution of KNO_3 at 90 °C under a N_2 atmosphere yielded the magnetite particles, which were dried and stored under N_2 until analysis. In addition to these reference materials, Fe(Ni) spinel crystals isolated from simulated waste glass samples were analyzed. Salient properties of the reference materials and samples are listed in Table 1.

2.2. Chemical reagents

Hydrofluoric acid (HF, 48%, Sigma–Aldrich 30107), sulfuric acid (H_2SO_4, 99.999%, Aldrich 339741), silver fluoride (AgF, Aldrich 226858), potassium bromide (KBr, Aldrich 378844), boric acid (H_3BO_3, Sigma–Aldrich B0394), hydroxylamine sulfate ($(NH_2OH)_2{-}H_2SO_4$, Aldrich 210250), ferrous ammonium sulfate hexahydrate ($Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$, FAS, 99.997% trace metals content, Aldrich, 203505) and trisodium citrate dihydrate (Sigma–Aldrich S4641) were used as received after dilution or dissolution in deionized water (as appropriate). A 1% or 10% solution of the analytical reagent for total Fe, 1,10-orthophenanthroline (phen, Aldrich 131377) was prepared in technical-grade ethanol (C_2H_5OH, 95%) before being mixed with the aqueous reagents.

2.3. Apparatus and instrumentation

Samples were digested in translucent 7-ml polyfluoroallomer (PFA) vials with gas-tight caps (Savillex, Eden Prairie, MN, No. 200-007-20). Vials were incubated in the dark in a sand bath that was heated to 98 °C and located inside a N_2-atmosphere filled chamber. Heat was maintained by a heat tape wrapped around the sand bath and controlled by a thermostatted power supply. Digests were diluted in a 125-mL titration vessel made from the bottom half of a 250-mL high-density polyethylene (HDPE) bottle. Subsamples were diluted in 15- or 50-mL polypropylene centrifuge tubes (total Fe) and 30-mL amber HDPE bottles. Absorbance readings were obtained using disposable plastic cuvettes and a Shimadzu UV-2501PC spectrophotometer.

2.4. Analytical procedures

Two analytical procedures were tested. The first was a modification of the colorimetric method of [4] in which both ferrous and total Fe were determined using complexation with phen. The second procedure combined an argentometric method for determination of ferrous Fe, modified from that of [28] with the colorimetric approach of [4] for determination of total Fe.

2.4.1. Colorimetric procedure

The modified colorimetric method, an early version of which