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Determination of ferrous and total iron in refractory spinels

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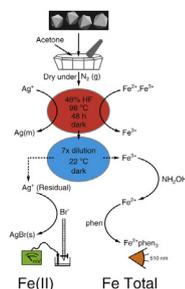
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HIGHLIGHTS

- Refractory samples, such as spinels, are the most difficult for Fe redox analysis.
- Oxidimetric(Ag⁺)/colorimetric (phen) method allows analysis of a single sample.
- Fe²⁺ measured by Ag⁺ potentiometry, total Fe by Fe-phen₃ absorbance at 510 nm.
- Excellent accuracy, relative differences of 0.4% for Fe²⁺ and 1.2% for total Fe.
- Modest precision, relative standard deviations of 3.7% for Fe²⁺ 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 ($(\text{NH}_2\text{OH})_2\text{–H}_2\text{SO}_4$, Aldrich 210250), ferrous ammonium sulfate hexahydrate ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2\text{–}6\text{H}_2\text{O}$, 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 ($\text{C}_2\text{H}_5\text{OH}$, 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

Table 1
Nominal compositions of reference materials and reagents analyzed.

Name	Description	Source	Nominal composition	
			Fe ²⁺	Total Fe
			--- weight % ---	
G-2	Rhode island granite (Split 100-7)	USGS ^a	1.13	1.86
BIR-1	Icelandic basalt (Split 396)	USGS	6.51	7.87
OREAS 700	Magnetite ore	OREAS ^b	9.38	15.57
OREAS 701	High grade magnetite ore	OREAS	13.49	23.02
ALP	Reagent magnetite (Product 518158, Lot MKBJ5645V, 99.99% metal purity)	Aldrich ^c	(23.93) ^f	71.8
ALNano	Nanosized reagent magnetite (Product 637106, Lot MKBD8421V, 97% metal purity, 50–100 nm particle size)	Aldrich ^c	(22.40) ^f	67.2
AAP	Reagent magnetite (Product 12962, Lot 22044, 99.997% metal purity)	Alfa Aesar ^d	(24.10) ^f	72.3
OQ	Magnetite synthesized in-house (Odetta Qafoku, BNW60373:71)	PNNL ^e	(24.12) ^g	(72.36) ^g

^a United States Geological Survey, Denver, CO, USA.

^b Ore Research & Exploration P/L, Bayswater North, VIC 3153, Australia.

^c Sigma-Aldrich Chemical Co., St. Louis, MO, USA.

^d Alfa Aesar, Ward Hill, MA, USA.

^e Pacific Northwest National Laboratory, Richland, WA, USA.

^f Stoichiometric estimate for magnetite based on Total Fe value provided by manufacturer.

^g Stoichiometric estimate for magnetite assuming 100% purity.

was described in Matyáš et al. [19], involved digesting 40 mg of spinel in 6 mL of N₂-sparged 48% HF for periods of 48 h or longer. This period of time was determined based on preliminary work that showed that digestion was incomplete at shorter times. After incubation, samples were cooled and weighed outside the chamber, then returned to the chamber where they were transferred quantitatively to 125-mL amber bottles and diluted with a N₂-sparged solution containing 12 mL of 10% H₂SO₄, 60 mL of 5% H₃BO₃, 2 mL of a 10% solution of phen in 95% ethanol, and 34 mL of deionized water. Two 0.5-mL aliquots of this solution were used to rinse the digestion vials, bringing the final volume of the diluted digestate to 115 mL. After dilution, the ferrous Fe concentration was stable and could be stored for several weeks if necessary.

To determine the concentrations of ferrous and total Fe in the diluted digestates, two further dilutions were made. One-mL aliquots of the diluted digestate were placed in separate 15-mL amber bottles, and diluted either with 9 mL of 1% trisodium citrate (for ferrous Fe determination) or 9 mL of a 1% trisodium citrate-1% NH₂OH solution (for total Fe determination). An aliquot of the ferrous Fe analyte was placed in a cuvette and the absorbance at 510 nm measured immediately. Absorbance of the total-Fe analyte was determined a minimum of 90 min after its preparation. A series of FAS standards, ranging from 0 to 70 mg of sample, were also carried through the procedure and used to calibrate the method.

2.4.2. Oxidimetric procedure

An argentometric method with potentiometric determination based on that of [28] was used with several significant modifications. Notably, during digestion and titration the samples are kept in the dark, or at very low light levels to minimize possible artifacts due to photoreduction, the spinel samples are pre-ground under acetone to facilitate decomposition, the digestion period is on the order of 48 h (and can be longer if needed), and the contents of each vial are titrated immediately after dilution to minimize reoxidation of Ag(m). Further, an aliquot of the digestate is taken prior to titration for determination of total Fe by colorimetry. Finally, because of interferences in the dissolved Ag(I) titer caused by sulfate ions present in the two common Fe(II) standards (FAS, and ferrous ethylenediammonium sulfate), KBr is used as the primary standard for measuring the titer of the initial AgF solution, as well

as that of the digested sample. A total Fe standard is still needed, however. A flow chart for the method is given in Fig. 1 and a detailed description follows.

Sample preparation: With most spinels, sample comminution is required to ensure complete digestion. Weigh out sufficient sample, allowing for 40 mg for each replicate and an additional 20% for transfer losses, into an agate mortar and pestle. Wet the sample with a few mL of acetone and grind gently until a very fine paste is obtained. When the appropriate particle size is obtained, the sample slurry should flow with the acetone when the mortar is tipped slightly and there should be no feeling of grittiness during grinding. Transfer the sample into a 20-mL glass scintillation vial using acetone and bring into a N₂-atmosphere chamber under continuous N₂ purge. Uncap the vial and let the sample dry overnight. When dry, recap the vial, remove it from the chamber, and weigh out sub-samples for replicate analysis as described below.

Digestion: Weigh out 40 mg of spinel (<32 mg Fe total) into a tared 7-mL Teflon reaction vial, cap and bring into a purged N₂-atmosphere chamber. Uncap to release all oxygen inside the vial. Using a calibrated automatic pipet, add 6 mL of N₂-sparged 0.030-M AgF in 48% HF, cap tightly, and place in a 98 °C sand bath in the dark to digest for 48 h. After 48 h, remove the vial from the sand bath and place in an opaque container to keep it in the dark while it cools. Remove the opaque container containing the vial from the N₂-atmosphere chamber.

Fe(II) Analysis: For the steps described in this paragraph, work quickly and under reduced lighting conditions to decrease the potential for alteration of the Ag(I) titer either by photoreduction or reoxidation by the diluted digestate. Remove the vial from the opaque container and weigh it. Transfer the digest quantitatively to a tared 125-mL HDPE titration vessel using a total of 36 mL of H₂O. Reweigh the titration vessel. Tare a 15- to 50-mL polypropylene test tube and cap, add 10 mL of a 0.16 M (1%) H₃BO₃-1% NH₂OH solution, and reweigh. Using a calibrated pipet, transfer 1 mL of the diluted digestate into the test tube, add cap, and then record the weight. This solution is termed the total-Fe reductate. Add a stir-bar to the titration vessel containing the remainder of the diluted digestate and insert a combination Ag + -ion selective electrode. Titrate, while stirring, with 0.0200 M KBr, using a 10-mL Class A buret, until the endpoint (ca. 200 mV relative to a standard H₂ electrode) is reached. Record the titrant volume.

Total Fe determination: Let the total-Fe reductate sit for 8 h,

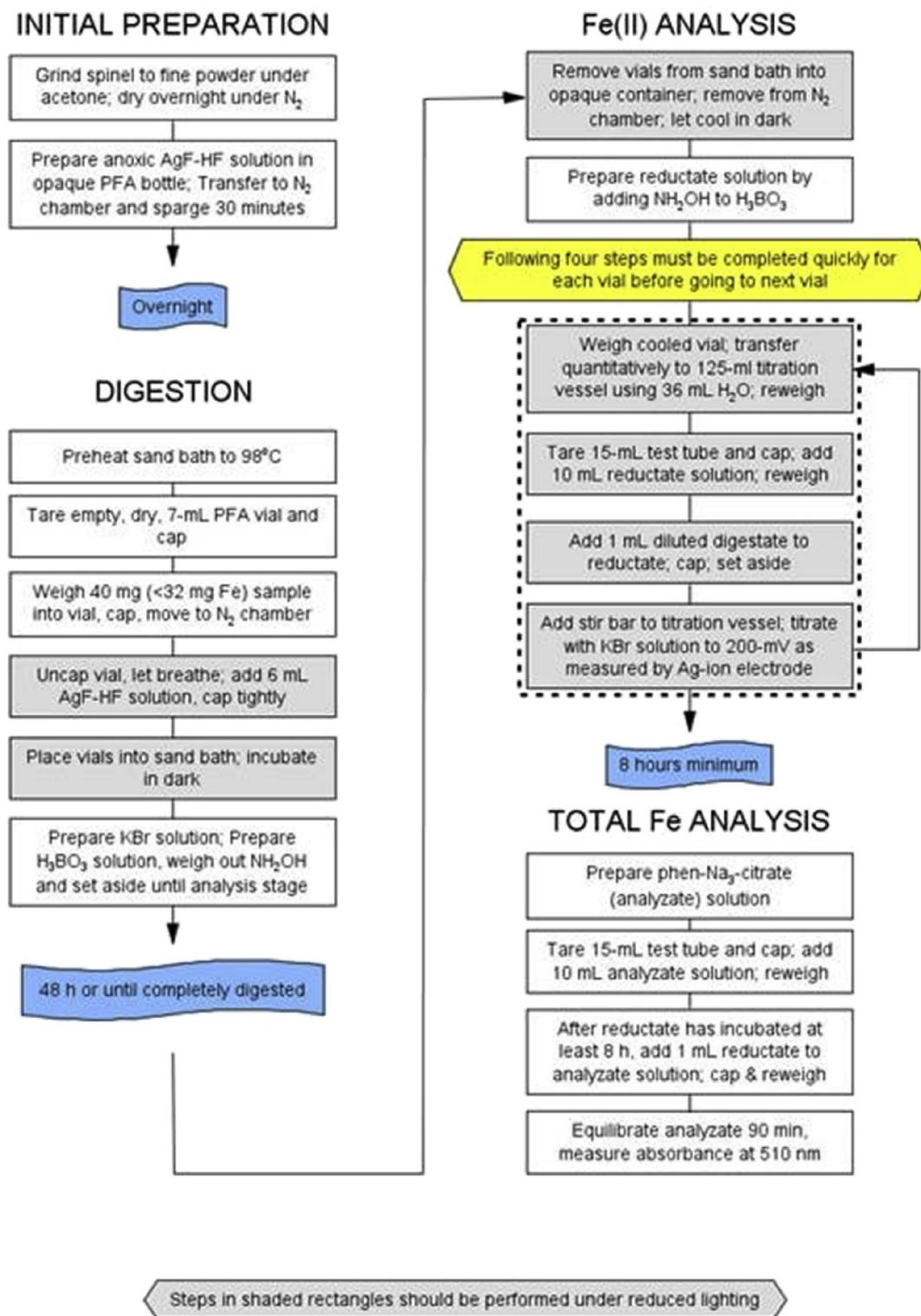


Fig. 1. Flow chart of hybrid oxidi-colorimetric method for Fe(II) and total Fe in refractory spinels.

preferably overnight, to reduce the remaining Ag(I). Tare a second 15- to 50-ml polypropylene test tube and cap, add 10-mL of a 1% Na_3 -citrate, 1 mM 1,10-orthophenanthroline solution and reweigh. Using a calibrated pipet add 1–2 mL (depending on expected Fe content) of the total-Fe reductate to the vial and reweigh. After 90 min, measure the absorbance at 510 nm.

Blanks and Standards: Reagent-grade KBr is sufficiently stable that, after drying for 2 h at $110^\circ C$ followed by cooling to room temperature in a desiccator, it can serve as a primary standard. If additional calibration of the KBr is desired, prepare a 4.5 mM solution of reagent grade $AgNO_3$ (again after drying the reagent for 2 h at $110^\circ C$ followed by cooling to room temperature in a

desiccator). Using a calibrated pipet, transfer 40 mL of the AgNO_3 solution to the 125-mL titration vessel, and titrate with the KBr solution as described above for the diluted digestate samples. To calibrate the total Fe determinations, prepare a set of 6 standards [FAS, for example] ranging from 0 to 32 mg Fe and carry them through the digestion, dilution, and determination stages for total Fe.

Quantities of reagents and samples are best determined by gravimetry, and require determination of the densities of the AgF-HF , $\text{NH}_2\text{OH-H}_3\text{BO}_3$, and citrate-phen solutions at the laboratory temperature.

3. Results and discussion

3.1. Modified colorimetric method

A number of modifications were made to the method of [4] in an attempt to preserve the ability to measure Fe(II) and total Fe on the same digested sample by colorimetry. Preliminary experiments showed that 1) the samples could only be digested in neat 48% HF at near-boiling temperatures and 2) a typical incubation period was 48 h if the samples were pre-ground to maximize the available surface for acid attack. The presence of H_2SO_4 , and even the ethanol/phen solution, in the digesting solution prevented dissolution of the spinels, presumably by a combination of dilution of HF and interference with attack of the spinel surface by HF. With the inability to have phen present during digestion, the analysis had to be moved into an anoxic chamber to minimize oxidation of Fe(II) during the digestion, and to allow addition of the H_2SO_4 and phen after the digestion stage. Moreover, the bath used to heat the samples needed to be a sand bath to avoid the moisture issues associated with a water bath inside an anoxic chamber.

However, even with these changes, and careful sparging of all reagents with N_2 inside the anoxic chamber prior to use, analysis of the geochemical standards and FAS showed that significant oxidation of Fe(II) occurred (Fig. 2). Thermodynamically, this would be expected due to the formation of a suite of strong Fe(III)-fluoride complexes and the lack of Fe(II)-fluoride complexes of comparable strength to maintain the initial Fe(II)/Fe(III) ratio. A time study of the rate of Fe(II) oxidation showed that it occurred during the first

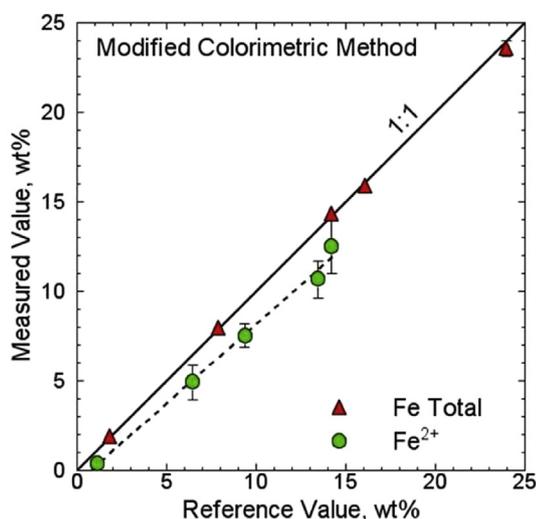


Fig. 2. Comparison of measured and reference values for analysis of four geochemical reference materials and ferrous ammonium sulfate by the modified colorimetric method. Solid line indicates exact agreement (1:1). Dashed line is regression of Fe(II) results [$\text{Fe}(\text{measured}) = 0.884 * (\text{Fe}(\text{reference})) - 0.734$, $r^2 = 0.993$]. Error bars are one standard deviation.

4 h of digestion (see Supplemental Information). Thereafter, no further oxidation occurred, suggesting that a new equilibrium had been obtained. Despite the disappointing results obtained for Fe(II), values for total Fe were in excellent agreement with the reference values (Fig. 2).

3.2. Hybrid oxidi-colorimetric method

Having established a way to digest the spinels and measure their total Fe content we turned our attention to finding a way to assay the Fe(II) content reliably. Clearly, the only option was to measure the Fe(II) by oxidimetry, but the challenge was to find an oxidant that was stable in neat 48% HF at near-boiling temperatures for extended periods of time. Methods involving vanadate (e.g., [29,31]) could not be used due to the instability of the vanadate in the absence of H_2SO_4 . With the exception of the IO_3^-/I_2 system [7,31,32], similar issues were expected with the other oxyanion-based oxidants, presumably due to the different degrees of complexation of the reduced form of the reagent (e.g., VO^{2+} , Cr^{3+}) by fluoride ions, which yielded a situation similar to that encountered for Fe(II) and Fe(III) in HF.

The Ag(I)/Ag(m) couple, however, avoids this differential complexation issue. Ag(I) is readily soluble in HF and forms only a very weak complex with fluoride ($\log K = -0.32$, Smith and Martell, 1989), whereas Ag(m) is insoluble in HF, and by virtue of being a solid does not form any fluoride complexes. Further, the formal reduction potential of the Ag(I)/Ag(m) couple (+0.79 V) is the same in concentrated HF as it is in water whereas that of the Fe(III)/Fe(II) couple is more than 0.4 V lower in concentrated HF making Fe(II) susceptible to oxidation by Ag(I) under those conditions. These features had been appreciated and a method published for analysis of Fe(II) in silicate minerals by Ag(I) by Ref. [28]. To ensure the suitability of the Ag(I) method in combination with the colorimetric method for measurement of total Fe, we had to adjust volumes analyzed and select the counter ion to eliminate any potential interferences with the phen complexation approach. Fortunately, the amount of sample needed for total Fe colorimetric analysis was very small, less than 1% of the total Fe present, and that left the rest of the digestate available for the titrimetric analysis of Fe(II).

During the course of the testing of the hybrid oxidi-colorimetric method, several improvements were made to Ungethüm's original approach. We conducted all work with Ag(I) solutions in the dark, or under reduced lighting, to avoid the potential for photoreduction (and a resultant high Fe(II) titer). We substituted AgF for the AgClO_4 originally called for, to eliminate the possibility of any oxidation of Fe(II) by the anion. After an initial dilution with H_2O , which altered the formal reduction potential of the Fe(III)/Fe(II) couple such that it could oxidize Ag(m), we took a subsample for total Fe analysis and then immediately titrated the rest of the digest thus minimizing any loss of Fe(II) titer. And, after several failed attempts, we eliminated titration of standard samples containing FAS because the sulfate in the FAS oxidized Ag(m) making the results unreliable. Instead, we relied on the primary standard quality of the KBr titrant both to quantify the initial Ag(I) titer of the blank samples, and the final Ag(I) titer of digested samples.

3.3. Reference standards

When applied to analysis of the standard reference materials in two separate 6-replicate runs, the new hybrid oxidi-colorimetric method yielded precise results in excellent agreement with published values for all but one sample (Table 2, Fig. 3). Analysis of the Icelandic basalt standard, BIR-1, however, yielded higher Fe(II) values and lower total Fe values than the corresponding reference values (Table 2, Fig. 4). This sample was unique among the reference materials in that it contained significant quantities of Mg (about 70% more Mg than Fe on a molar basis). Given the well-

Table 2
Results of analysis of reference standards using the new hybrid oxidi-colorimetric method. All values are weight percent.

Sample	Run	Measured Values				Reference Values ^a	
		Fe(II)		Fe total		Fe(II)	Fe total
		Mean (CI) ^b	n	Mean (CI)	n	Mean (CI)	Mean (CI)
G-2	1 ^c	1.22 (0.25)	5 ^d	1.78 (0.28)	5 ^e	1.13 (0.12)	1.86 (0.14)
BIR-1	1	7.30 (0.48)	5 ^d	6.82 (0.33)	5 ^f	6.51 (0.20)	7.87 (0.33)
OREAS 700	1	9.41 (0.33)	6	16.28 (0.22)	5 ^f	9.38 (0.62)	16.06 (0.35)
OREAS 701	1	13.47 (0.25)	5 ^d	24.22 (0.31)	5 ^f	13.49 (0.99)	23.98 (1.09)
G-2	2 ^g	1.07 (0.16)	6	1.87 (0.52)	6	1.13 (0.12)	1.86 (0.14)
BIR-1	2	6.86 (0.26)	5 ^d	7.02 (0.07)	5 ^f	6.51 (0.20)	7.87 (0.33)
OREAS 700	2	9.44 (0.21)	6	16.21 (0.31)	6	9.38 (0.62)	16.06 (0.35)
OREAS 701	2	13.54 (0.05)	5 ^f	24.06 (1.80)	5 ^f	13.49 (0.99)	23.98 (1.09)

^a Refs. [11,12], and datapacks provided by OREAS.

^b CI is 95% confidence interval.

^c SRM-8, 28 March 2015.

^d Rep lost due to titration overshoot.

^e Rep not analyzed.

^f Outlier data point removed using Q test at $p = 0.95$ [22].

^g SRM-9, 25 April 2015.

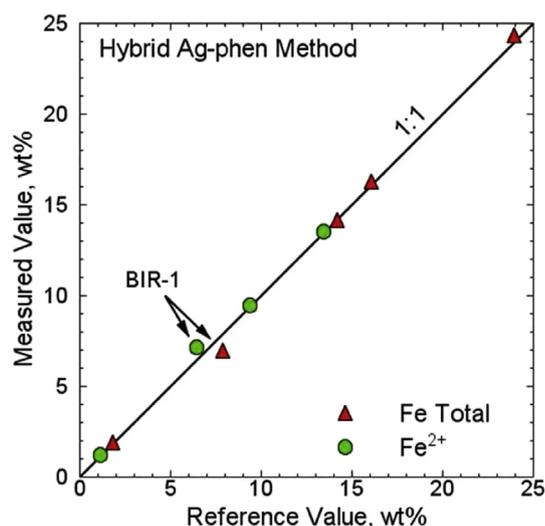


Fig. 3. Comparison of measured and reference values for analysis of four geochemical reference materials and ferrous ammonium sulfate by the hybrid oxidi-colorimetric method. Solid line indicates exact agreement (1:1). Error bars of one standard deviation are smaller than the symbols plotted.

known limited solubilities of MgF_2 and FeF_3 ($\log K_{sp} = -8.18$ and -6.95 , respectively [33]) and the generally observed problems with dissolution of high-Mg materials in HF solutions [3,10], one can explain the low total Fe results as due to some form of co-precipitation of Fe(III) with MgF_2 to form (Mg,Fe) fluoride solid solutions. Evidently, the boric acid added to the aliquot taken for total Fe was insufficient to completely dissolve these precipitates.

As for the high values for Fe(II) obtained with BIR-1, we think it likely that the values we measured are real, and that most of the previous analyses have not measured this Fe(II) due to issues associated with the formation of the (MgFe)-fluoride precipitates. In those instances, the precipitates likely contained Fe(II) as well as Mg and Fe(III). In the present instance, the ability of Ag(I) to react with Fe(II) as soon as it is released from the oxide matrix eliminates this concern.

Due to the significant Cu content of the magnetite ore reference standards, Fe(II) values obtained for OREAS-700 and OREAS-701 were adjusted downward by the reported Cu concentrations for

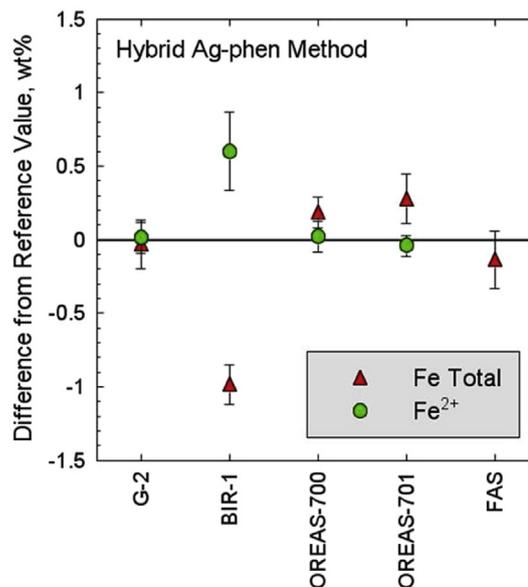


Fig. 4. Differences from the reference values for Fe(II) and total Fe obtained by the hybrid oxidi-colorimetric method for each geochemical reference material and for FAS (total Fe only). Error bars are one standard deviation.

these two standards. Monovalent Cu is oxidized by Ag(I) in the same way as Fe(II).

3.4. Spinel samples

To demonstrate applicability of the method to the analysis of spinel samples, a set of five samples of Fe(Ni) spinel crystals (Fig. 5) isolated from a simulated glass being considered for storage of nuclear waste was analyzed in triplicate. Also analyzed were four reagent magnetite (Fe_3O_4) specimens. Two of these (ALP, AAP) were high-metal-purity nominally stoichiometric magnetite, and a third (ALN) was a nano-sized magnetite. The fourth (OQ) was synthesized in-house and had seen minimal processing or handling under atmospheric conditions.

The results of these analyses showed levels of Fe(II) at the detection limit for the spinel crystals, consistent with the earlier Mössbauer results, and values of total Fe slightly, but consistently, higher than those obtained by separate elemental analysis

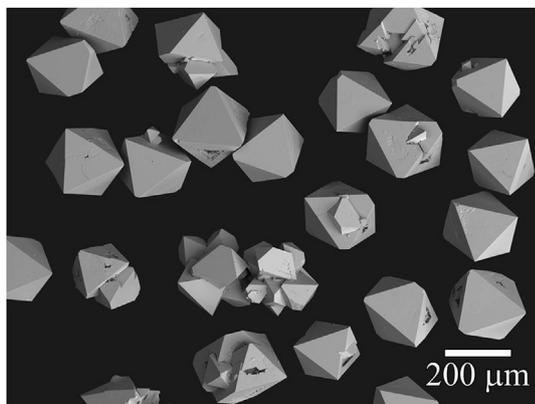


Fig. 5. Backscattered electron SEM image of crystals of Spinel 15. Crystals were isolated from Ni_{1.5}/Fe_{17.5} glass heat-treated at 900 °C for 4 days [19].

(Table 3). The magnetites yielded a wide range of Fe(II) values, with the in-house sample (OQ) being closest to stoichiometric magnetite (about 92% magnetite), and the nano-sized magnetite (ALN) having only about 20% stoichiometric magnetite. The two high-purity samples showed more oxidation than the in-house sample, but came from containers that had been opened a few months earlier and had not been stored under N₂. Total Fe results were in good agreement with values reported by the manufacturers (Table 3).

3.5. Accuracy and precision

The accuracy of the hybrid method was formally assessed by calculation of four parameters that compare the measured and reference data. Thus, the assessment of accuracy depends not only on the quality of the measurements made by the hybrid method, but also on the quality of the measurements contributing to the reference value.

The first and simplest parameter, d , is the size of the difference between the measured and reference data for a given sample (i.e., $d = \text{measured value} - \text{reference value}$). By its sign, this parameter gives an idea of whether the method is giving results that are higher or lower than the reference values. The second parameter, $|d|$, is the absolute value of d , which gives an idea of the overall size of the difference without assessing whether it is higher

or lower than the reference value. This parameter is most useful for calculating the mean difference obtained for a particular method or set of samples. The third parameter, RD, is the relative difference (i.e., $RD = 100 * |d| / RV$, where RV is the reference value for a given sample). This parameter normalized the size of the analytical difference to the amount of analyte present in the sample. The fourth, and most complex, parameter is $|t'|$, which is similar to the Student's t , but has a complex denominator that accounts for separate variances and sample sizes in the measured and reference data populations. This value can be compared against a slightly modified value of Student's t (again to account for separate variances and lack of sample pairing) for a given probability and number of degrees of freedom (determined by the number of replicates in the measured and reference values) to test whether the populations of measured and reference values have similar means [25, p. 81], [30, p. 100–102]. We chose to do the test at the 95% probability level.

The values for these four parameters are listed in Table 4 for each of the spinel and SRM samples analyzed by the hybrid method along with means calculated across all samples for each parameter. In general, the lower the value for each of these parameters, the more accurate the method, recognizing that “accuracy” is simply a measure of the degree of agreement between the values obtained by the hybrid method and those obtained by other well-regarded methods and laboratories. The possibility of experimental artifacts, even in the well-regarded methods, is always present.

For Fe(II) measurements, the method accuracy was excellent for three of the four SRMs with mean differences of 0.02 wt%, an RD of 0.4% and a $|t'|$ value less than 0.5. The exception was BIR-1, for which large positive d values were obtained along with a $|t'|$ value that was significant at the 95% probability level. As discussed in Section 3.3, it is likely that these differences reflect an artifact common to most methods employing HF digestion and thus the reference value for Fe(II) in BIR-1 is likely too low. As a result, in addition to calculating parameter means for all four SRM samples, we calculated a separate set of means for the other three SRMs to more truly reflect the accuracy of the hybrid method.

For total-Fe measurements, we calculated accuracy parameters for the five spinel samples as well as for the SRMs since we had an independent set of total-Fe data for the spinels that we could use as a reference. As for Fe(II), the results showed good accuracy for three of the SRMs and considerably poorer accuracy for BIR-1. In this instance, however, the formation of MgFe(III) fluoride complexes

Table 3

Results of analysis of spinel samples using the new hybrid oxidi-colorimetric method. All values are weight percent.

Sample	Run	Measured values				Reference values	
		Fe(II)		Fe total		Fe(II)	Fe total
		Mean (CI) ^a	n	Mean (CI)	n	Mean	Mean (CI)
Spinel 13 ^b	3 ^c	0.16 (3.15)	3	45.29 (0.71)	3	NA	43.5 (1.78) ^d
Spinel 14	3	0.19 (0.32)	3	45.66 (2.41)	3		43.9 (1.78) ^d
Spinel 15	3	0.13 (0.51)	3	44.88 (5.27)	3		43.9 (1.78) ^d
Spinel 16	3	0.17 (1.78)	3	46.15 (2.13)	3		43.3 (1.78) ^d
Spinel 17	3	0.06 (1.64)	3	45.71 (14.89)	3		43.5 (1.78) ^d
OQ	3	21.84 (2.92)	2 ^e	70.96 (1.76)	3	[24.12] ^f	[72.36] ^f
ALP	3	20.37 (5.25)	3	71.48 (1.68)	3	[23.93] ^f	71.8 ^g
ALNano	3	4.61 (0.34)	3	69.03 (2.84)	3	[22.40] ^f	67.2 ^g
AAP	3	18.19 (0.82)	3	71.65 (1.81)	3	[24.10] ^f	72.3 ^g

^a CI is 95% confidence interval.

^b Spinel crystal isolated from a simulated HLW glass having an initial Ni/Fe ratio of 1.5/17.5 and treated at 900 °C for 2–10 days [19].

^c Spinel-Fe₃O₄-3, 5 September 2015.

^d Determined by ICP-AES analysis after lithium metaborate/tetraborate fusion, 95% confidence interval estimated from one set of duplicates and applied to all samples [19].

^e Rep lost due to titration overshoot.

^f Nominal value calculated assuming ideal purity and stoichiometry.

^g No value for uncertainty provided by manufacturer.

Table 4
Several measures of the accuracy of the hybrid oxidi-colorimetric method.

Sample	Fe(II)				Total Fe			
	d ^a	d ^b	RD ^c	t' ^d	d	d	RD	t'
	-- wt% --	--	%		-- wt% --	--	%	
Spinel 13 ^a	– ^e	–	–	–	2.28	2.28	5.2	21.405
Spinel 14	–	–	–	–	0.21	0.21	0.5	0.631
Spinel 15	–	–	–	–	1.58	1.58	3.6	2.217
Spinel 16	–	–	–	–	2.93	2.93	6.8	9.705
Spinel 17	–	–	–	–	1.27	1.27	2.9	1.526
G-2	0.01	0.01	0.6	0.195	–0.03	0.03	1.7	0.620
BIR-1	0.57	0.57	8.7	6.326	–0.95	0.95	12.1	19.161
OREAS 700	0.04	0.04	0.5	0.872	0.19	0.19	1.2	4.829
OREAS 701	0.02	0.02	0.2	0.371	0.16	0.16	0.7	1.161
Means	0.16	0.16	2.5	1.941	0.85	1.07	3.9	6.806
SRM means	0.16	0.16	2.5	1.941	–0.16	0.33	3.9	6.443
w/o BIR-1	0.02	0.02	0.4	0.479	0.11	0.13	1.2	2.203

^a Difference between measured and reference values (i.e., measured value minus reference value).

^b Absolute value of difference between measured and reference values.

^c Relative difference (i.e., (|d|*100)/R, where R is the reference value).

^d Calculated *t* statistic for unpaired samples from populations having unequal variances (see p. 81 in Ref. [25] or p. 100–102 in Ref. [30]; bold entries indicate values of *t* that are significant at *P* = 0.95 (i.e., the null hypothesis, *H*₀, that measured and reference populations have equal means is likely to be false).

^e Not applicable (no reference data exist for these samples).

may have been responsible for the lower total Fe results with BIR-1 obtained by the hybrid method. Accuracy for the spinel samples was roughly comparable to that for the four SRMs with RD values of 3.9% and |*t*'| values averaging 6.4–6.8, well above the level of significance at 95% probability. The reference values for the spinels were not “certified” and represented, at most, the results of duplicate analyses, but the generally positive trends in the *d* values suggested that the hybrid method was more successful in achieving complete dissolution and recovery of Fe from these samples than the reference method. Because of the uncertainty in the spinel reference data and the problem with the BIR-1 analysis, our overall interpretation of the accuracy for total Fe focuses on the remaining three SRM samples. For G-2, excellent accuracy was obtained. For the two OREAS samples, generally higher total-Fe values were measured (by 0.16–0.19 wt%) than for the reference method (borate fusion with XRF analysis), and for OREAS 700 the difference was significant (*P* = 0.95) by the |*t*'| test. The OREAS datapacks also give values for total Fe obtained by two acid-dissolution methods that were substantially lower than the fusion/XRF values. It is unclear, therefore, whether the true values for total Fe in these two SRMs are those obtained by the hybrid method or by the fusion/XRF method. Taken as a whole, RD values averaged 1.2% and the mean |*t*'| value was below the level of significance (*P* = 0.95) for the three SRM samples indicating that adequate accuracy was obtained for total Fe by the hybrid method.

Formal assessment of precision of the hybrid method involved calculation of three parameters, the standard deviation (SD), the relative standard deviation (RSD), and the 95% confidence interval. As these calculations did not require reference data, all of the samples analyzed were included in the assessment. The results (Table 5) showed a mean SD of 0.23 wt%, a mean RSD of 6.3%, and a 95% confidence interval of 1.38% for Fe(II). Corresponding values for total Fe were 0.48 wt%, 1.8%, and 2.72 wt%. The much higher RSD for Fe(II) was driven by Fe(II) levels in the spinels that were at or near the detection limit. For the SRM samples, SD values ranged from 0.1 to 0.4 wt%, RSD values from 0.5 to 9.3%, and 95% confidence intervals from 0.2 to 0.9 wt% for both Fe(II) and total Fe. The results for

Table 5
Several measures of the precision of the hybrid oxidi-colorimetric method.

Sample	Fe(II)			Total Fe		
	SD ^a	RSD ^b	CI ^c	SD	RSD	CI
	wt%	%	wt%	wt%	%	wt%
Spinel 13	0.25	77.9	3.15	0.06	0.1	0.71
Spinel 14	0.03	–196	0.32	0.56	1.3	2.41
Spinel 15	0.12	47.1	0.51	1.23	2.7	5.27
Spinel 16	0.14	80.9	1.78	0.49	1.1	2.13
Spinel 17	0.13	47.1	1.64	1.17	2.6	14.89
OQ	0.23	1.1	2.92	0.41	0.6	1.76
ALP	1.22	6.0	5.25	0.39	0.5	1.68
ALNano	0.08	1.7	0.34	0.66	1.0	2.84
AAP	0.19	1.0	0.82	0.42	0.6	1.81
G-2	0.11	9.3	0.24	0.16	9.0	0.37
BIR-1	0.27	3.8	0.61	0.13	1.9	0.30
OREAS 700	0.10	1.1	0.23	0.11	0.7	0.24
OREAS 701	0.07	0.5	0.16	0.39	1.6	0.89
Means	0.23	6.3	1.38	0.48	1.8	2.72
SRMs only ^d	0.14	3.7	0.31	0.20	3.3	0.45

^a SD is the standard deviation.

^b RSD is the relative standard deviation, i.e., (100*SD/mean).

^c CI is the 95% confidence interval.

^d SRMS are G-2, BIR-1, OREAS 700 and OREAS 701.

BIR-1 were not substantially different from the other three SRMs. Although there were no sample-specific trends in SD values for Fe(II), for total Fe the SD and CI values obtained for the spinel and magnetite samples were generally larger than those for SRM samples, perhaps as a result of the higher total-Fe levels measured. In general, precision of the hybrid method was adequate for both Fe(II) and total Fe.

3.6. Comparison with existing methods

As discussed by Ref. [1] assessing the accuracy of different methods, even when analyzing the same SRM, represents a formidable challenge. And trying to compare different methods analyzing different SRMs may well be impossible. Nevertheless, we think some insight can be derived from applying a consistent statistical approach to the results obtained by a range of methods analyzing well-characterized SRMs, so long as we recognize that 1) “accuracy” is a continuously evolving relative term, and 2) comparing methods developed for different purposes and types of samples in general terms may overlook the special attributes that these methods have for their original purpose.

To compare the performance of the hybrid method with that of comparable existing methods for silicates and refractory materials, assessments of accuracy and precision identical to those described in Section 3.5 were completed for 13 published methods, five of which determined both Fe(II) and total Fe. Of these methods, three [6,9,21] were specifically aimed at refractory samples and involved decomposition by borate fusion followed by Fe(II) determination using oxidimetry or colorimetry. Only that of [6] however, also determined total Fe. The remaining 10 methods were designed for analysis of non-refractory minerals and rocks, and four of these measured both Fe(II) and total Fe. A total suite of 47 SRMs were analyzed by these methods, and the reference values for these (means, standard deviations, and numbers of analyses) were obtained primarily from Ref. [13] and references cited therein. A full listing of the SRMs, the individual results obtained for each method, and the literature used for reference values is given in the Supplemental Information. In order to compare the methods, however, only the means of the results obtained for each of the four

accuracy parameters (d , $|d|$, RD, and $|t'|$) and the three precision parameters (SD, RSD, and CI) are provided here. In addition to mean values for each method/parameter combination, grand means for all the existing methods were also calculated along with a “percentile score” that placed the mean obtained for the hybrid method in the range of those obtained by all the methods. The worst mean at one end of the range of values was assigned a percentile score of 0 and the best mean at the other end of the range a score of 100. The mean for the hybrid method was then compared to these two means, and its position in the range of values normalized on a scale of 0–100. Thus, a percentile score of 90 indicates the mean for the hybrid method was 90% along the range between the worst and the best means.

In terms of accuracy (Table 6), the hybrid method performed extraordinarily well for Fe(II), with percentile scores near 90 for $|t'|$ and RD and, when the BIR-1 data was excluded, scores of 99–100 for all four parameters. Two other methods were comparable to the hybrid method in terms of Fe(II) accuracy. The fusion/colorimetric method of [6] and the rapid HF–H₂SO₄ decomposition method of [8] with colorimetric determination of Fe(II) yielded almost identical accuracy ratings. Of the two, however, only [6] would be applicable to analysis of refractory spinel samples. Very good accuracy for Fe(II) was obtained by method [14] which also employed a rapid acid-decomposition approach followed by colorimetric analysis. The hybrid method clearly represents an improvement in accuracy over the original method employing Ag(I) [28] although lack of replicate data did not allow estimation of the $|t'|$ parameter for Ungethüm's method.

For total-Fe accuracy, the hybrid method performed very well with RD and $|t'|$ percentile scores of 99 and 85, respectively, when the BIR-1 data were not considered. The methods of [14] and [6]

yielded comparable results to the hybrid method. The measured and reference total-Fe data presented by Ref. [14] however, are incorrect due to a unit-conversion error. Correct values were kindly supplied by E. A. D. Ferriss (personal communication, 10 December 2015).

In terms of precision (Table 7), the performance of the hybrid method was mixed. When compared on the basis of SD and RSD values, it was not as strong a performer as most of the other methods with SD values as much as twice the grand mean and RSD values 1.6 times higher. As a result, the percentile scores for SD were 35 for Fe(II) and only 11 for total Fe. Percentile scores for RSD were near 45 for both Fe(II) and total Fe. However, when compared on the basis of 95% confidence intervals, the method performed well, with a lower CI than the grand mean, and percentile scores near 80 for both Fe(II) and total Fe. The methods of [3,4] and the acid dissolution method of [9] yielded better precision. The mixed performance of the hybrid method in terms of precision is likely due to the long digestion period and more extensive sample handling employed.

One method not included in our analysis was the iodine monochloride method of Hey [31,32], which when combined with fusion decomposition using Ayranci's approach [6] would seem to be an excellent method. Unfortunately, neither of Hey's papers provide the SRM data needed for a statistical analysis and so we could not include the method in our comparison. We were able to include an acid-dissolution method using iodine monochloride by Ref. [7] in which the author notes the chief difficulty was in obtaining complete decomposition of the samples.

Overall, the main strengths of the hybrid method relative to the existing methods are the high accuracy for Fe(II) and total Fe, and the ability to analyze refractory spinels. This is achieved with

Table 6

Comparison of accuracy of the hybrid oxidi-colorimetric method with that of other selected wet-chemical methods when applied to standard reference materials (SRMs). Values are overall means for all the SRM samples analyzed by a particular method.

Method	N ^a	n ^b	Fe(II)				Total Fe			
			d^c		RD ^e	$ t' ^f$	d		RD	$ t' $
			wt%				wt%			
Hybrid (this method)	4	43	0.16	0.16	2.5	1.94	–0.16	0.33	3.9	6.44
Hybrid (w/o BIR-1 data)	3	33	0.02	0.02	0.4	0.48	0.11	0.13	1.2	2.20
[3]	5	47	0.07	0.09	2.8	3.83	– ^g	–	–	–
[4]	5	29	0.07	0.17	2.4	4.04	–0.03	0.12	2.7	4.94
[5]	9	49	0.01	0.12	18.3	1.77	–	–	–	–
[6]	7	12	–0.02	0.03	3.2	– ^h	0.05	0.06	3.6	1.46 ^h
[7]	11	44	0.03	0.13	1.9	2.39	–	–	–	–
[8]	5	30	0.02	0.02	0.6	0.51	–0.12	0.19	3.4	7.56
[9] acid dissolution	8	30	0.09	0.11	3.6	4.29	–	–	–	–
[9] fusion	8	30	0.35	0.37	18.2	15.7	–	–	–	–
[14]	8	21	–0.03	0.09	1.3	1.19	0.02	0.14	1.1	1.28
[15]	2	8	0.06	0.24	4.1	2.67	–	–	–	–
[21]	4	8	0.17	0.30	5.8	8.22	–	–	–	–
[27]	13	65	–0.19	0.28	13.8	2.20	0.08	0.18	7.5	2.30
[28]	5	5	0.06	0.06	6.5	– ⁱ	–	–	–	–
Grand means (except for Hybrid method)			0.05	0.16	6.3	4.25	0.00	0.14	3.6	4.02
Hybrid percentile score			60	60	89	91	0	0	56	18
Hybrid percentile score w/o BIR-1			99	99	100	100	49	49	99	85

^a Number of SRMs analyzed.

^b Total number of samples analyzed.

^c Difference between measured and reference values (i.e., measured value minus reference value).

^d Absolute value of difference between measured and reference values.

^e Relative difference (i.e., $(|d| \cdot 100)/R$, where R is the reference value).

^f Calculated t statistic for unpaired samples from populations having unequal variances (see p. 81 in Ref. [25] or p. 100–102 in Ref. [30]; bold entries indicate values of t' that are significant at $P = 0.95$ (i.e., the null hypothesis, H_0 , that measured and reference populations have equal means is likely to be false).

^g No total Fe data measured.

^h Insufficient reference-value replication data reported to calculate $|t'|$.

ⁱ Insufficient measured-value replication data reported to calculate $|t'|$.

Table 7

Comparison of precision of the hybrid oxidi-colorimetric method with that of other selected wet-chemical methods when applied to standard reference materials (SRMs). Values are overall means for all the SRM samples analyzed by a particular method.

Method	N ^a	n ^b	Fe(II)			Total Fe		
			SD ^c	RSD ^d	CI ^e	SD	RSD	CI
			wt%	%	wt%	wt%	%	wt%
Hybrid (this method)	4	43	0.14	3.7	0.31	0.20	3.3	0.45
[3]	5	47	0.02	0.4	0.05	– ^f	–	–
[4]	5	29	0.03	0.6	0.09	0.04	0.6	0.11
[5]	9	49	0.11	6.5	0.30	–	–	–
[6]	3	8	0.04	1.4	0.33	0.04	1.9	0.24
[7]	11	44	0.04	2.2	0.14	–	–	–
[8]	5	30	0.07	3.0	0.18	0.07	1.9	0.19
[9] acid dissolution	8	30	0.02	1.0	0.08	–	–	–
[9] fusion	8	30	0.06	1.6	0.19	–	–	–
[14]	8	21	0.15	1.8	1.42	0.21	1.6	1.69
[16]	2	8	0.20	3.4	0.64	–	–	–
[21]	4	8	0.06	1.1	0.82	–	–	–
[27]	13	65	0.12	5.0	0.34	0.22	5.5	0.61
Grand means (except for Hybrid method)			0.08	2.3	0.38	0.12	2.3	0.57
Hybrid percentile (continuous)		35		46	81	11	44	78

^a Number of SRMs analyzed.

^b Total number of samples analyzed.

^c SD is the standard deviation.

^d RSD is the relative standard deviation, i.e., (100*SD/mean).

^e CI is the 95% confidence interval.

^f No total Fe data measured.

somewhat poorer, though still adequate, precision. Only one existing method, that of [6], can determine Fe(II) and total Fe in refractory samples with apparently comparable accuracy, and that method requires a special apparatus for fusion decomposition under an inert atmosphere and the use of Pt/Au alloy crucibles. However, even with the use of Pt/Au crucibles, the ability of fusion decomposition to obtain accurate values for Fe(II) has been questioned by Ref. [9] on the basis of high-temperature equilibrium considerations. The hybrid method also has the advantage of a much smaller-volume waste stream than many of the existing methods, such as those of [6,3,4] and the ability to completely recover the Ag precipitated as Ag(m) or AgBr. The chief disadvantages of the hybrid method are the long digestion period required, the maintenance of low lighting conditions during the digestion and Fe(II) titration steps, and the need to perform both potentiometric and colorimetric analyses. And, as noted for BIR-1, the hybrid method does not obtain accurate total Fe values for samples with high Mg contents.

4. Conclusions

The hybrid oxidi-colorimetric method resolves most of the problems associated with Fe(II) and total Fe analysis of Fe-bearing spinels. Although the time for digestion is quite lengthy, results obtained for a series of geochemical reference materials, including two magnetite ores, as well as for reagent magnetites, are consistent with expectations. Anomalous values for a Mg-rich basalt (BIR-1), however, yielded higher Fe(II) and lower total Fe values than expected. These results can be attributed to the formation of MgFe(III)-fluoride precipitates that were not completely re-dissolved by boric acid after digestion, and by the likely presence of Fe(II) in similar precipitates analyzed by other groups that was not counted in the Fe(II) titers they obtained. The presence of Ag(I) in the digestate ensures that all Fe(II) is reacted upon dissolution of the oxide matrix, and the “noble” stability of Ag(m) in concentrated HF maintains the Fe(II) titer for at least 48 h at near-boiling

temperatures. Provided that evaporation of the digestate does not occur, it is likely that much longer digestions are possible, if needed, for highly recalcitrant samples. Because of its very high accuracy for Fe(II), we expect this method to be fully applicable to non-refractory samples as well, and thus of wide utility in the wet-chemical determination of iron redox states.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.aca.2015.12.024>.

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