Optimizing the Pratt-type titrimetric method to determine FeO in geochemical reference materials

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Determination of ferrous iron (FeO) is important across a wide breadth of disciplines in geochemistry. The certified values of FeO in geochemical reference materials have been determined mainly by wet chemistry. During this procedure, special attention is needed to prevent oxidation of Fe^{2+} to Fe^{3+} , which may lead to underestimations of FeO mass fractions. Here, we revisited a traditional titrimetric method to provide a better method of determining the FeO mass fractions in geochemical reference materials. We investigated the effect of duration of decomposition, sand bath temperature, and sample weight. Among these, we found that the effect of sample weight on the FeO values is most significant. The FeO values increase with increasing sample weight, indicating that vapor and foam effectively prevent oxidation. This is supported by yield tests and experiments involving the addition of SiO_2 powder to the samples. Thus, we suggest the use of greater amounts of sample to minimize oxidation. We further compare our results with the published recommended values for reference materials, demonstrating that the latter need be considered carefully. The approach described here is not only applicable to geochemical reference materials but also useful to unknown geological samples.

Keywords: titration, FeO, ferrous iron, wet chemistry, geochemical reference material

INTRODUCTION

Iron has two oxidation states, Fe^{2+} and Fe^{3+} , in silicate rocks. In general, instrumental analyses are not suitable for accurately detecting each oxidation state separately; therefore, FeO is usually analysed by traditional wet chemistry. While FeO mass fractions are determined by titration, Fe_2O_3 mass fractions are determined by subtracting those of FeO concentrations from the total Fe concentrations. The abundances of each oxidation state and their ratios are used widely in diverse disciplines in geochemistry; for example, they are essential for normative calculation (Middlemost, 1989; Verma *et al.*, 2002). The ratio of Fe_2O_3 to total Fe is also crucial for estimating the oxygen fugacity of the mid-ocean ridge basaltic glasses (Christie *et al.*, 1986; Bézou and Humler, 2005). Furthermore, it is a useful proxy with which to understand the great oxidation event during the history of the Earth that led to atmospheric oxygen reaching near-present levels (Stolper and Keller, 2018).

In wet chemical analysis, geochemical reference materials are treated as unknown samples. The measured

values are validated by comparisons with the measured value of the reference materials. Among various types of wet chemical analyses, titrimetric methods are one of the most classical methods used to measure FeO values. Although titrimetric methods yield accurate FeO values, it is time consuming. Much progress has been made on measuring FeO using analytical instruments; this includes new methods such as ion chromatography (Kanai, 1990; le Roex and Watkins, 1995), Mössbauer spectroscopy (Lalonde *et al.*, 1998), phenanthroline spectrophotometry (Husler *et al.*, 2011; Tarafder and Thakur, 2013), X-ray absorption near-edge structure (XANES) spectroscopy (Farges, 2001; Ohta *et al.*, 2006; O'Neill *et al.*, 2006, 2018; Berry *et al.*, 2010, 2018; Cottrell and Kelley, 2011; Zhang *et al.*, 2018), and electron probe microanalysis (EPMA) (Hughes *et al.*, 2018; Li *et al.*, 2019). In each of these developments, it is crucial to compare the results of unknown geological samples with geochemical reference materials; therefore, the importance of geochemical reference materials with certified values is increasing.

The certified values of geochemical reference materials have previously been determined mainly by a titrimetric method. During this method, samples are first decomposed by sulphuric acid (H_2SO_4) and hydrofluoric acid (HF) in crucibles. They are then titrated with a potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) solution to allow volumetric calculation of the amounts of FeO. The difficulty arises

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Fig. 1. Titrimetric analysis of FeO. (a) Weighing the sample. (b) Adding the deionized water and swirling. (c) Decomposition of the sample in H_2SO_4 and HF. (d) Masking HF with B(OH)_3 . (e) Adding H_2SO_4 , H_3PO_4 , and sodium diphenylamine-4-sulphonate. (f) Titration with $\text{K}_2\text{Cr}_2\text{O}_7$.

from the fact that Fe^{2+} is easily oxidized to Fe^{3+} during sample decomposition, leading to lower FeO values (Schafer, 1966a; Maxwell, 1968; Lalonde *et al.*, 1998; Bézos and Humler, 2005; Xue *et al.*, 2017). Thus, it is necessary to avoid oxidation of Fe^{2+} during the acid decomposition as much as possible. Here, we revisited the method to provide a better way to determine the FeO mass fractions in geochemical reference materials. We first examined the appropriate duration and temperature of

sample decomposition. We then investigated the effect of sample weight on the FeO values and demonstrated that treatment with larger sample sizes effectively prevents oxidation during decomposition. We confirmed this with yield tests on Fe^{2+} and experiments involving addition of pure SiO_2 powder to the samples. The approach described here is not only applicable to reference materials but also useful on unknown geological samples.

WET CHEMISTRY

Titrimetric determination of FeO

The mass fractions of FeO were measured by a modified version of the “Pratt method” (Maxwell, 1968). This titrimetric method has been applied to determine the certified values of FeO in geochemical reference materials issued by the Geological Survey of Japan (GSJ) (Terashima and Ando, 1987; Imai *et al.*, 1995). The method is the classical and simplest method among the various versions of the wet chemical method (Schafer, 1966a, 1966b). The details are slightly different from the original (Pratt, 1894), but the key concepts remain unchanged. We provide the full procedure here, because: (1) numerous versions of the “Pratt method” exist and none of these are the same and (2) the procedure at each step is often critical in wet chemistry, such that a detailed explanation is required to allow independent investigators to repeat the experiments.

First, the geochemical reference materials—which were supplied as ground rock powder—were weighed in 30 or 50 ml platinum crucibles (Fig. 1). To prevent caking during the following decomposition procedure, 3 ml of deionized water was added to these and the crucibles were swirled. This suspended the powders in the water. Second, 5 ml of 9 mol l⁻¹ H₂SO₄ and 8 ml of 50% HF were added for decomposition. The crucibles were placed immediately on a sand bath, the temperature of which was 150–170°C, for 3–20 minutes. Covers were placed on the crucibles during this procedure. While this was happening, mixtures of 50 ml of 4% boric acid and 130 ml of deionized water were prepared in plastic beakers. When the decomposition procedure was completed, the covered crucibles were grasped with platinum tipped tongs. The outside of the bottom part of the crucibles were rinsed with deionized water and then the crucibles were dropped into beakers in order to mask the HF. The crucibles were entirely immersed in the solution. The crucibles and the covers were then rinsed off with small amounts of deionized water. All the contents in the crucibles were washed into the beaker. Third, 10 ml of 9 mol l⁻¹ H₂SO₄ and 5 ml of 7.5 mol l⁻¹ phosphoric acid (H₃PO₄) were added for redox titration. The solutions were gently stirred with rods before and after the addition of 5 drops of 0.25% sodium diphenylamine-4-sulphonate as an indicator. Finally, the solutions were titrated with a K₂Cr₂O₇ solution prepared in advance. Depending on the amounts of FeO in the samples, the concentration of the K₂Cr₂O₇ solution was selected from 1/60, 1/120, or 1/240 mol l⁻¹. As the end point was being approached, the solutions turned a greenish colour. The end point was reached with the first appearance of a homogeneous violet colour. The change in colour to violet was drastic with only one drop of the K₂Cr₂O₇ solution, such that the end point was easily rec-

ognized. After making a note on the volume of titrant solution, another drop of the K₂Cr₂O₇ solution was added to determine whether the change in colour occurred or not. The K₂Cr₂O₇ solution was prepared from solid K₂Cr₂O₇ certified reference material for volumetric analysis supplied from Kanto Chemical Co. All other chemicals were analytical grade. We did not introduce a system to treat samples under an anoxic environment employing inert gas flow because we are determining FeO values of the reference materials in collaboration with eight other laboratories. In previous studies, much effort has been spent to prevent oxidation of Fe²⁺ by introducing specific apparatus enabling sample decomposition under an inert gas atmosphere (Cooke, 1867; Pratt, 1894; Hillebrand, 1907; Barnebey, 1915; Schafer, 1966a, b). The system of continuous gas flow has been further modified with the recent development of modern instruments (Xue *et al.*, 2017). Though we acknowledge these developments, the complex nature of the involved apparatus sometimes limits their use in laboratories, in addition to the fact that such systems are often too costly for most laboratories to employ. Instead, we aimed to optimize the method with an easy method of minimizing oxidation during sample decomposition, without employing specific apparatus.

The uncertainties propagated through to the combined standard uncertainties of the FeO mass fractions. The combined standard uncertainties include the uncertainties of sample weight, the uncertainties of the volume of the burette, the uncertainties of the read values of the burette, the uncertainties of the weight of K₂Cr₂O₇, and the uncertainties of the volume of the volumetric flask used to adjust the K₂Cr₂O₇ solution. The resultant uncertainties were mainly derived from the uncertainties of the volume of the burette and those of the read values of the burette.

Recovery yield measurements of Fe²⁺

We conducted two types of recovery yield tests. Solid ammonium iron(II) sulphate hexahydrate was used for the first type of tests, whereas Fe²⁺ solution was used for the second type of tests. The titrimetric procedure followed was the same as that described earlier. Amorphous SiO₂ powder supplied by Kanto Chemical Co. (high purity reagent, >99.9% purity, grain size of *ca.* 36 μm) was ground in a clean agate mortar to prepare fine pure SiO₂ powder that was easily suspended in deionized water. The grain size was measured using a laser scattering particle analyzer (HORIBA LA-920). The mean grain size of the ground SiO₂ powder was 14 μm. A quantity of 0–3 g of this SiO₂ powder was weighed in platinum crucibles for each type of recovery test. This was done to mimic increasing sample weights. In the first type of tests, 0.25 g of solid ammonium iron(II) sulphate hexahydrate was first

Fig. 2. Comparison of decomposition duration and FeO values for different sample weights. (a) 1.0 g of JG-3. (b) 1.5 g of JG-3. (c) 2.0 g of JG-3. (d) 2.5 g of JG-3. (e) 3.0 g of JG-3. (f) 1.0 g of JA-1. (g) 1.0 g of JB-1a. Range bars show combined standard uncertainties.

weighed in small quartz crucibles. The platinum crucibles were swirled with deionized water. After adding H_2SO_4 and HF, the platinum crucibles were placed on a sand bath. The quartz crucibles were then dropped into the platinum crucibles two minutes after HF was added

to the latter. Covers were quickly placed on the crucibles, which were then kept on the sand bath for a total of 13 min. This condition was employed to reproduce the conditions similar to those of the actual samples wherein minerals were decomposed and Fe^{2+} was released into

Fig. 3. Comparison of decomposition temperature and FeO values. Sample weights are 2.0 g of JG-3. Range bars show combined standard uncertainties.

Fig. 4. The effect of sample weight on FeO values. Sample sizes of JG-3 for analysis were doubled and quadrupled, while the concentrations of the $K_2Cr_2O_7$ solutions were also doubled ($1/120 \text{ mol l}^{-1}$) and quadrupled ($1/60 \text{ mol l}^{-1}$), respectively. This enabled the volume of consumed $K_2Cr_2O_7$ solution to be maintained approximately constant. Range bars show combined standard uncertainties.

the solution in hot HF. The procedure of titrimetric determining Fe^{2+} with $K_2Cr_2O_7$ solution was the same as that described earlier.

For the second type of tests, $0.3 \text{ mmol g}^{-1} Fe^{2+}$ solution in $1 \text{ mol l}^{-1} H_2SO_4$ was prepared from solid ammonium iron(II) sulphate hexahydrate. After weighing 0–3 g of SiO_2 powder in platinum crucibles, the crucibles were swirled with deionized water and 2.2 g of the Fe^{2+} solution was then added to it. The decomposition procedure followed thereafter was the same. The second type of test reflected the worst-case scenario of having Fe^{2+} in solution from the beginning, which was not the case in the actual samples.

The molar concentration and the uncertainty of the

Fig. 5. The effect of sample weight on FeO values. FeO values increase with increasing sample weight until the sample weight reaches the weight that causes boil over and/or remaining undecomposed residues. (a) Plot of compiled FeO values for JG-3. Analyses with insufficient decomposition duration are not included. Samples heavier than 4 g resulted in boil over and/or remaining undecomposed residues. (b) Plot for JA-1. (c) Plot for JB-1a. Samples heavier than 3 g resulted in boil over for JA-1 and JB-1a. In the meantime, there were remaining undecomposed residues. Range bars show combined standard uncertainties.

Fe^{2+} solution was determined via five repeatable titrations with $1/120 \text{ mol l}^{-1} K_2Cr_2O_7$. The uncertainties of the added Fe^{2+} weight, the tolerance of the burette, the uncertainties in the read values of the burette, the uncer-

Table 1. Sample details and FeO determinations

Sample ^a	Sample weight (g)	Crucible size (ml)	Decomposition temperature (°C)	Decomposition duration (min)	K ₂ Cr ₂ O ₇ (mol l ⁻¹)	FeO (wt%) ^b	Remarks ^c
JG-3	1.0031	30	155	5	1/120	1.766 ± 0.003	
JG-3	1.0030	30	154	7	1/120	1.809 ± 0.003	
JG-3	1.0000	30	154	12	1/120	1.779 ± 0.003	
JG-3	1.0037	30	156	18	1/120	1.754 ± 0.003	
JG-3	1.0004	30	152	20	1/120	1.749 ± 0.003	
JG-3	3.0013	30	157	20	1/120	1.852 ± 0.003	
JG-3	1.0032	30	157	3	1/120	1.680 ± 0.003	undecomposed residue
JG-3	1.0016	30	154	10	1/120	1.758 ± 0.003	
JG-3	3.0026	30	157	3	1/120	1.583 ± 0.001	undecomposed residue
JG-3	3.0064	30	156	5	1/120	1.877 ± 0.002	
JG-3	3.0001	30	159	8	1/120	1.891 ± 0.002	
JG-3	3.0026	30	157	18	1/120	1.893 ± 0.002	
JG-3	1.0053	30	152	12	1/120	1.791 ± 0.003	
JG-3	1.0028	30	151	12	1/120	1.777 ± 0.003	
JG-3	1.0066	30	155	12	1/120	1.767 ± 0.003	
JG-3	1.0044	30	155	12	1/120	1.749 ± 0.003	
JG-3	1.0054	30	156	12	1/120	1.776 ± 0.003	
JG-3	1.0090	30	156	12	1/120	1.770 ± 0.003	
JG-3	1.0052	30	153	10	1/120	1.723 ± 0.003	
JG-3	1.0001	30	150	12	1/120	1.757 ± 0.003	
JG-3	1.0014	30	153	15	1/120	1.740 ± 0.003	
JG-3	1.0050	30	155	10	1/120	1.770 ± 0.003	
JG-3	1.0055	30	156	12	1/120	1.783 ± 0.003	
JG-3	1.0048	30	154	15	1/120	1.727 ± 0.003	
JG-3	1.5040	30	159	15	1/120	1.779 ± 0.002	
JG-3	1.5059	30	162	13	1/120	1.826 ± 0.002	
JG-3	1.5041	30	159	10	1/120	1.812 ± 0.002	
JG-3	1.5045	30	160	15	1/120	1.788 ± 0.002	
JG-3	1.5089	30	158	13	1/120	1.806 ± 0.002	
JG-3	1.5027	30	158	10	1/120	1.790 ± 0.002	
JG-3	2.0012	30	160	15	1/120	1.829 ± 0.002	
JG-3	2.0017	30	161	13	1/120	1.824 ± 0.002	
JG-3	2.0028	30	159	11	1/120	1.826 ± 0.002	
JG-3	2.0014	30	158	15	1/120	1.826 ± 0.002	
JG-3	2.0018	30	159	13	1/120	1.824 ± 0.002	
JG-3	2.0026	30	159	11	1/120	1.808 ± 0.002	
JG-3	2.5005	30	162	15	1/120	1.837 ± 0.002	
JG-3	2.5055	30	160	13	1/120	1.833 ± 0.002	
JG-3	2.5038	30	162	11	1/120	1.855 ± 0.002	
JG-3	2.0012	30	147	13	1/120	1.826 ± 0.002	
JG-3	2.0018	30	161	13	1/120	1.831 ± 0.002	
JG-3	2.0042	30	171	13	1/120	1.814 ± 0.002	
JG-3	3.0001	30	159	15	1/120	1.885 ± 0.002	
JG-3	3.0003	30	158	13	1/120	1.858 ± 0.002	
JG-3	3.0012	30	160	11	1/120	1.861 ± 0.002	
JG-3	3.5021	30	161	13	—	—	boiled over
JG-3	3.5055	30	160	11	—	—	boiled over
JG-3	1.0010	30	157	13	1/120	1.755 ± 0.003	
JG-3	0.6256	30	160	13	1/240	1.757 ± 0.002	
JG-3	0.6256	30	157	13	1/240	1.705 ± 0.002	
JG-3	1.2517	30	156	13	1/120	1.813 ± 0.002	
JG-3	1.2511	30	159	13	1/120	1.765 ± 0.002	
JG-3	2.5018	30	158	13	1/60	1.872 ± 0.002	
JG-3	2.5013	30	157	13	1/60	1.838 ± 0.002	

Table 1. (continued)

Sample ^a	Sample weight (g)	Crucible size (ml)	Decomposition temperature (°C)	Decomposition duration (min)	K ₂ Cr ₂ O ₇ (mol l ⁻¹)	FeO (wt%) ^b	Remarks ^c
JG-3	4.0012	50	159	13	1/60	1.905 ± 0.002	
JG-3	5.0035	50	159	13	—	—	undecomposed residue
JG-3	6.0001	50	157	13	—	—	undecomposed residue
JG-3	4.0031	50	160	13	1/60	1.887 ± 0.002	
JG-3	5.0043	50	157	13	—	—	undecomposed residue
JG-3	6.0047	50	158	13	—	—	undecomposed residue
JG-3	4.0001	50	157	13	1/60	1.887 ± 0.002	
JG-3	5.0008	50	160	13	—	—	boiled over
JG-3	6.0025	50	158	13	—	—	boiled over, undecomposed residue
JG-3	4.0020	50	160	13	—	—	undecomposed residue
JG-3	5.0016	50	158	13	—	—	undecomposed residue
JG-3	6.0027	50	156	13	—	—	undecomposed residue
JG-3	5.0006	50	150–160	15	—	—	boiled over
JG-3	6.0018	50	150–160	15	—	—	boiled over, undecomposed residue
JG-3	5.0004	50	150–160	15	—	—	boiled over, undecomposed residue
JG-3	6.0015	50	150–160	15	—	—	boiled over, undecomposed residue
JG-3	5.0011	50	150–160	15	—	—	undecomposed residue
JG-3	6.0001	50	150–160	15	—	—	boiled over, undecomposed residue
JA-1	1.0004	30	157	3	1/120	3.635 ± 0.004	undecomposed residue
JA-1	1.0037	30	154	5	1/120	3.401 ± 0.004	undecomposed residue
JA-1	1.0009	30	154	8	1/120	3.677 ± 0.004	undecomposed residue
JA-1	1.0035	30	155	10	1/120	3.789 ± 0.004	
JA-1	1.0002	30	156	13	1/120	3.791 ± 0.004	
JA-1	1.0022	30	155	15	1/120	3.744 ± 0.004	
JA-1	0.5000	30	152	13	1/60	3.677 ± 0.011	
JA-1	1.0010	30	153	13	1/60	3.818 ± 0.006	
JA-1	2.0023	30	154	13	1/60	3.853 ± 0.004	
JA-1	2.5010	30	154	13	—	—	boiled over, undecomposed residue
JA-1	3.0037	50	152	13	1/60	3.911 ± 0.003	
JA-1	4.0013	50	153	13	—	—	boiled over, undecomposed residue
JB-1a	1.0002	30	154	3	1/120	5.210 ± 0.005	undecomposed residue
JB-1a	1.0012	30	155	5	1/120	4.993 ± 0.004	undecomposed residue
JB-1a	1.0014	30	154	8	1/120	5.527 ± 0.005	
JB-1a	1.0015	30	156	10	1/120	5.555 ± 0.005	
JB-1a	1.0023	30	154	13	1/120	5.532 ± 0.005	
JB-1a	1.0058	30	155	15	1/120	5.467 ± 0.005	
JB-1a	0.5034	30	160	13	1/60	5.446 ± 0.011	
JB-1a	1.0009	30	157	13	1/60	5.543 ± 0.006	
JB-1a	1.9998	30	156	13	1/60	5.595 ± 0.005	
JB-1a	3.0042	30	157	13	—	—	boiled over
JB-1a	2.5004	30	158	13	1/60	5.652 ± 0.005	
JB-1a	3.0031	50	155	13	1/60	5.717 ± 0.004	
JA-1	1.0016	30	158	18	1/120	3.749 ± 0.004	
JA-1	1.0027	30	152	20	1/120	3.745 ± 0.004	
JB-1a	1.0035	30	155	18	1/120	5.479 ± 0.005	
JB-1a	1.0063	30	155	20	1/120	5.485 ± 0.005	
JG-3	2.0017	30	154	5	1/120	1.838 ± 0.002	
JG-3	1.9988	30	155	20	1/120	1.834 ± 0.002	
JB-1a	3.5022	50	159	13	—	—	boiled over, undecomposed residue
JA-1	3.5011	50	156	13	—	—	boiled over, undecomposed residue
JB-1a	2.0015	30	157	13	1/60	5.667 ± 0.005	
JB-1a	2.0038	30	158	13	1/60	5.682 ± 0.005	
JB-1a	2.0017	30	158	13	1/60	5.663 ± 0.005	
JA-1	2.0015	30	159	13	1/60	3.819 ± 0.004	

^a Six samples shown as a group are measured within a single batch. The order within a batch refers to their positions on the sand bath.

^b The uncertainties in the sample weight, the tolerance of the burette, the uncertainties in the read values of the burette, the uncertainties in the weight of K₂Cr₂O₇, and the tolerance of volumetric flask propagated through to the combined standard uncertainties in the FeO determinations.

^c Remarks only indicate insufficient decomposition.

tainties in the weight of $K_2Cr_2O_7$, and the tolerance of the volumetric flask were propagated to the combined standard uncertainties in the recovery yield determinations.

FeO measurements under the condition of SiO_2 addition

FeO values were measured under the condition of adding pure SiO_2 powder to the samples. While maintaining the weight of the samples at 0.5 or 1 g, we added 0–2.5 g of SiO_2 powder. The sample powder and SiO_2 powder were mixed via swirling with deionized water. This reproduces the decomposition conditions of larger sample volumes without changing the quantities of elements except for that of SiO_2 .

Design of study and experiments

The duration of sample decomposition plays a critical role in the method. Both shorter and longer decompositions cause the FeO values to be underestimated (Maxwell, 1968). While a shorter decomposition duration leads to residual undissolved FeO-bearing minerals, longer decomposition may oxidize Fe^{2+} to Fe^{3+} . The temperature of the sand bath also must be set properly. The temperature must be high enough to boil the solution, thereby excluding atmospheric oxygen, but not high enough for hot acid to oxidize Fe^{2+} . Given these constraints, we investigated the effect of the: (1) duration of decomposition; (2) temperature of the sand bath; and (3) sample size. First, the duration of decomposition was changed from 3 to 20 minutes, keeping the temperature at 150–160°C. This was applied for different sample weights ranging from 1 to 3 g, with particularly increased time resolution for the experiments for 1 and 3 g. The geochemical reference material JG-3 (granodiorite) was used as it is considered a representative geochemical reference material. The duration of decomposition for 1 g of JA-1 (andesite) and 1 g of JB-1a (basalt) was also tested. Second, the temperature was changed from 150 to 170°C in three steps, keeping the weight of the JG-3 at 2 g. To conduct this experiment in a single batch, the depth in the sand bath for the individual sample spots adjusted to obtain the target temperature. Finally, the effect of the weight of sample size on the FeO values was evaluated. We measured additional aliquots of JG-3 that were double and quadruple the size of the first while also doubling and quadrupling the concentrations of the $K_2Cr_2O_7$ solutions, respectively. This was intended to keep the volume of the titrated $K_2Cr_2O_7$ solution approximately the same to confirm that the effect of the sample weight is not indirectly controlled by the volume of the titrated solution. All results from JG-3 were compiled to investigate the effect of sample weight; these were then further tested on JA-1 and JB-1a. The intention was to examine whether the effect was common among the various sam-

Fig. 6. Relationships between recovery yield of Fe^{2+} and weight of SiO_2 powder. Circles show the recovery yield of Fe^{2+} when it is added as solid ammonium iron(II) sulphate hexahydrate. Grey squares show recovery yield of Fe^{2+} when it is added as a solution. Range bars show combined standard uncertainties.

ple types. Fifty-millilitre crucibles were used as using thirty-ml crucibles resulted in boil over. Further, recovery yield of Fe^{2+} was measured using solid ammonium iron(II) sulphate hexahydrate and Fe^{2+} solution. Finally, in order to support our findings, FeO values of JG-3 were measured under the condition of adding pure SiO_2 powder to the samples.

RESULTS AND DISCUSSION

The duration of sample decomposition

Overall, the FeO values are relatively constant once the samples are fully decomposed (Figs. 2a–g). While short decomposition durations yield undecomposed residues, which significantly underestimate FeO values, long decomposition durations do not show a significant loss of Fe^{2+} due to oxidation. Instead, higher FeO values are observed with increasing sample weight. The experiments with 1 and 3 g of JG-3 show that complete decomposition takes 5 minutes regardless of sample size (Figs. 2a and e). While the experiments with 3 minute decomposition durations yield undecomposed residues, 5 minute decomposition durations decompose FeO-bearing minerals completely. After samples are decomposed fully, broad and relatively flat peaks are sustained for 20 minutes of decomposition durations for 1, 2, and 3 g of JG-3 (Figs. 2a, c, e). The experiments spanning 3–8 minute decomposition durations for 1 g of JA-1 yield undecomposed residues, indicating that the duration for complete decomposition depends on the sample types (Fig. 2f). For 1 g of JB-1a, 3–5 minute decomposition

Table 2. Results of recovery yield of Fe^{2+}

SiO_2 weight (g)	Fe^{2+} addition	Ammonium iron(II) sulphate hexahydrate (g) ^a	Fe^{2+} solution in $1 \text{ mol l}^{-1} \text{H}_2\text{SO}_4$ (g) ^b	Added Fe^{2+} (mg) ^c	Crucible size (ml)	$\text{K}_2\text{Cr}_2\text{O}_7$ (mol l^{-1})	Recovery yield of Fe^{2+} (%) ^d
0.0000	added as solid	0.2520	—	35.89 ± 0.13	30	1/120	92.50 ± 0.35
1.0165	added as solid	0.2556	—	36.40 ± 0.14	30	1/120	97.58 ± 0.37
1.9997	added as solid	0.2573	—	36.64 ± 0.14	30	1/120	97.76 ± 0.37
2.9956	added as solid	0.2561	—	36.47 ± 0.14	30	1/120	98.46 ± 0.38
0.0000	added as solution	—	2.2295	36.69 ± 0.14	30	1/120	87.90 ± 0.34
1.0023	added as solution	—	2.2241	36.60 ± 0.14	30	1/120	91.23 ± 0.35
2.0150	added as solution	—	2.2364	36.80 ± 0.14	30	1/120	92.86 ± 0.36
3.0055	added as solution	—	2.2326	36.74 ± 0.14	30	1/120	94.76 ± 0.36

^a Shown as weight of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The correction factor of 1.0122 ± 0.0038 is determined by five repeatable titrations, employing $1/120 \text{ mol l}^{-1} \text{K}_2\text{Cr}_2\text{O}_7$, and multiplied to the measured weight.

^b Molar concentration of the solution is $0.2947 \pm 0.0011 \text{ mmol/g Fe}^{2+}$. This is determined by five repeatable titrations with $1/120 \text{ mol l}^{-1} \text{K}_2\text{Cr}_2\text{O}_7$.

^c Added Fe^{2+} is calculated from added ammonium iron(II) sulphate hexahydrate or added Fe^{2+} solution.

^d The uncertainties of added Fe^{2+} weight, the tolerance of the burette, the uncertainties in the read values of the burette, the uncertainties in the weight of $\text{K}_2\text{Cr}_2\text{O}_7$, and the tolerance of the volumetric flask propagated through to the combined standard uncertainties in the recovery yield determinations.

Fig. 7. Schematic representations of acid decomposition in platinum crucibles. (a) A sample of 0.5 g is decomposed in a 30 ml crucible. Fe^{2+} is oxidized to Fe^{3+} by atmospheric oxygen. (b) A sample of 2.5 g is decomposed in a 30 ml crucible. The vapor and foam on the acid solution prevent loss of Fe^{2+} due to oxidation.

durations yield undecomposed residues (Fig. 2g). Considering the uncertainty of repeatability, we do not overinterpret the distinct high FeO values at 7 minutes for JG-3, 10 minutes for JA-1, and 10–13 minutes for JB-1a. The relative standard deviation of 0.7%, which is calculated from 9 duplicate measurements at the decomposition time of 12 minutes for the 1 g of JG-3, exceeds the individual combined standard uncertainties. Consequently, we conducted the rest of the experiments with decomposition durations of 12–13 min, for consistency. This does not influence our conclusions regarding the relationship between sample weight and FeO values.

The temperature of decomposition

The FeO values are relatively constant throughout the variations of the temperature of the sand bath in the range

Fig. 8. Effect of sample weight on FeO values for JG-3. FeO values of JG-3 was measured under the condition of adding pure SiO_2 powder to the samples. While maintaining the weight of the JG-3 at 0.5 or 1 g, SiO_2 powder was added. Range bars show combined standard uncertainties.

of our experiments. Hence, we maintained the temperature at $150\text{--}160^\circ\text{C}$ for the rest of the experiments. This supports the view that increasing FeO values associated with the increasing sample weight is not due to insufficient decomposition duration nor due to insufficient decomposition temperature. The optimum temperature of the sand bath is likely specific to be that of the laboratory, because the actual temperature of the crucibles is balanced between the heat from the sand bath and the cooling wind within the fume hood used in the laboratory.

Table 3. FeO in JG-3 with addition of pure SiO₂ powder

Sample	Sample weight (g)	SiO ₂ weight (g)	Sample + SiO ₂ weight (g)	Crucible size (ml)	K ₂ Cr ₂ O ₇ (mol l ⁻¹)	FeO (wt%)*
JG-3	0.4988	0.0000	0.4988	30	1/120	1.513 ± 0.005
JG-3	0.4994	1.5054	2.0048	30	1/120	1.806 ± 0.005
JG-3	0.4995	2.5039	3.0034	30	1/120	1.928 ± 0.005
JG-3	0.5020	0.0000	0.5020	30	1/120	1.553 ± 0.005
JG-3	0.5012	1.5033	2.0045	30	1/120	1.821 ± 0.005
JG-3	0.5008	2.5012	3.0020	30	1/120	1.873 ± 0.005
JG-3	1.0071	0.0000	1.0071	30	1/120	1.768 ± 0.003
JG-3	1.0276	1.0330	2.0606	30	1/120	1.789 ± 0.003
JG-3	1.0053	2.0257	3.0310	30	1/120	1.872 ± 0.003

*The uncertainties in the sample weight, the tolerances of the burette, the uncertainties in the read values of the burette, the uncertainties in the weight of K₂Cr₂O₇, and the tolerance of the volumetric flask propagated through to the combined standard uncertainties in the FeO determinations.

Fig. 9. Recommended values of the geochemical reference materials. All data is from Terashima et al. (1994). Solid hexagons show the recommended values for (a) JG-3, (b) JA-1, and (c) JB-1a. These were determined by averaging all reported values (Terashima et al., 1994). The reported values include those determined by the titrimetric method, "Titr.", conventional chemical method, "Chem.", photometric method, "Photom.", and atomic absorption spectrometry, "AAS". One value for JA-1 is reported as the "X-ray fluorescence (XRF) and conventional chemical method" (Terashima et al., 1994). The quantities of the reported values are shown below each box plot. The boxes define the areas of the first and third quartiles and the solid lines are the medians. The whiskers are data ranges excluding outliers, which are presented as circles. Uncertainties for the recommended values given below the figures are at the 1s level.

Relationship between sample weight and FeO values

Figure 4 shows the FeO values increased as the sample weight was increased. We measured additional sample aliquots that were double and quadruple in size, while the concentrations of the K₂Cr₂O₇ solutions were also doubled and quadrupled, respectively. This enabled the volume of consumed K₂Cr₂O₇ solution to be maintained approximately constant as the sample weight was increased. The changes in the volume of the consumed solution could vary the invisible amounts of solution remaining attached to the wall of the burette, thereby affecting the meniscus. Therefore, the results demonstrate

that the volume of the consumed solution did not affect the relationship between the sample weight and FeO values.

The measured FeO values of JG-3 are compiled in Fig. 5a. This compilation does not include measurements with insufficient decomposition duration (Table 1). The FeO values increases from *ca.* 1.7 to 1.9 wt% with increasing sample weight. One-way analysis of variance (ANOVA) supports the view that the FeO values vary between sample clusters with different sample weights ($p < 0.01$). Measurements with sample sizes of 3.5 g using 30 ml crucibles resulted in boil over (Table 1). Although we

obtained some successful results with 50 ml crucibles for 4 g samples (Fig. 5a), measurements with sample sizes of 5 and 6 g all failed (Table 1). Large samples caused intense reactions in the crucibles, thereby producing large amounts of foam, which raised the covers and overflowed the crucibles. Large samples caused undecomposed residues to become caked on the bottom of the crucibles and the underside of the covers. As a result, 4 g is the maximum sample weight of JG-3 that can be treated with this method. The increase in FeO values with increasing sample weight was also observed for JA-1 and JB-1a (Figs. 5b and c), indicating this trend is general among majority of reference materials. Samples heavier than 3 g result in boil over and remaining undecomposed residues for JA-1 and JB-1a (Table 1), implying 3 g is the maximum sample weight for these two reference materials.

Effect of vapor and foam

The results of the recovery yield tests show increasing recovery of Fe^{2+} with increasing weight of SiO_2 powder (Fig. 6, Table 2). The recovery yield of Fe^{2+} from solid ammonium iron(II) sulphate hexahydrate increased significantly under the condition of 1 g SiO_2 powder, compared to that of the experiment that did not utilize SiO_2 powder. The recovery yield then increased gradually to $98.46 \pm 0.38\%$ when decomposed with 3 g of SiO_2 powder. This demonstrates that loss of Fe^{2+} is reduced to 1.5% in the ideal case. The increase in recovery yields with increasing SiO_2 weight was also observed when Fe^{2+} was added in the form of solution. However, the values were low compared to those of the experiments where Fe^{2+} was added in the form of solid salt. Given that Fe^{2+} is released into solution gradually in hot HF in the case of actual silicate minerals, we consider that Fe^{2+} addition in the solid phase resembles the treatments of actual samples more. The experiments involving Fe^{2+} addition in the form of solution represent the worst-case scenarios wherein all the Fe^{2+} in samples is released into the solution before addition of the decomposing acid, which is not likely to be the case for actual samples. Nonetheless, the results of Fe^{2+} addition in the form of solution suggest that insufficient treatments in wet chemical analysis may cause non-negligible loss of Fe^{2+} , which is 5% for the yield test when decomposed with 3 g of SiO_2 powder.

From our observations, the increase in FeO values with increasing weight of the reference materials, which is supported by the recovery yield tests, is most likely due to the fact that the vapor and the foam on the acid solution prevent oxidation (Fig. 7). Larger samples generate more continuous vapor flow of H_2O , HF, and H_2SiF_6 , shutting out the atmospheric oxygen. Larger samples also produce larger amounts of foam that prevent the solution from contacting with the atmospheric oxygen. The amount of oxidized Fe^{2+} is minimized with larger samples that re-

duce the open spaces in the crucible as much as possible. Maximum FeO is therefore obtained with sample weights that are slightly less than the weight that causes boil over (Fig. 5, Table 1). Similarly, the relationship between the weight of SiO_2 powder and the recovery yield of Fe^{2+} implies that oxidation of Fe^{2+} in solution is significant until the vapor and the foam on the acid solution prevent contact with atmospheric oxygen.

Low concentrations of carbon in igneous rock series of reference materials suggest that the increase in FeO values with sample weight is not due to the consumption of $\text{K}_2\text{Cr}_2\text{O}_7$ by the organic matter contained in the samples. For example, carbon mass fractions are only 120, 271, and $312 \mu\text{g g}^{-1}$ for JG-3, JA-1, and JB-1a, respectively (Imai *et al.*, 1995), indicating that the consumption of $\text{K}_2\text{Cr}_2\text{O}_7$ is negligible. The results are not affected by the presence of sulphide because sulphur mass fractions are only 54.7, 21.6, and $10.2 \mu\text{g g}^{-1}$ for JG-3, JA-1, and JB-1a, respectively (Imai *et al.*, 1995). This is supported by the recovery yield tests. Furthermore, this is also supported by the results of adding pure SiO_2 powder to JG-3 (Fig. 8, Table 3). The experiments permitted us to examine the effect of the vapor and the foam without changing the amount of organic matter in the samples. Addition of pure SiO_2 powder effectively increased FeO values for 0.5 and 1 g of JG-3 (Fig. 8). Increasing the amount of pure SiO_2 powder enhanced the reactions in the crucibles, thereby producing large amounts of vapor and foam preventing oxidation. The trend of increasing FeO values with increasing total weight of the samples (Fig. 8) is the same, as is observed from the experiments that simply employ increasing sample weights (Fig. 5a). Additionally, we note that $\text{K}_2\text{Cr}_2\text{O}_7$ consumes much less organic matter compared to permanganate that is sometimes used for titrimetric solutions (Sarver, 1927).

Comparison with the recommended values

We compared our results with the recommended values of the geochemical reference materials (Fig. 9, Supplementary Table S1). The reference materials we measured in this study are those that had been issued early-on in the program. The recommended values at that time were determined by averaging reported values from researchers following wide distribution of the materials (Terashima *et al.*, 1994). The reported values were mainly obtained by titrimetric method, but include values determined by other methods such as conventional chemical method, the photometric method, and atomic absorption spectrometry (AAS). In Terashima *et al.* (1994), wet chemical values that was not clearly reported as titrimetric values were classified as the conventional chemical method. We note that the certified values of FeO in recently issued reference materials from the GSJ are collaboratively determined using the titrimetric method only

(Okai, 2016).

The variation of the FeO values associated with sample weight is within the variation of the recommended values (Fig. 9). Thus, the dependency of the FeO values on sample weight is a variation within a very narrow range. The average and the standard deviation of 3 values from our study with 4 g samples (Fig. 5a) provides 1.89 ± 0.01 wt% for JG-3. This value is consistent with the recommended value of 1.83 ± 0.20 wt% (Terashima *et al.*, 1994) (Fig. 9a), and close to the original value of 1.91 wt% reported by the GSJ (Terashima and Ando, 1987). The titrimetric and photometric methods are indistinguishable with respect to JG-3. The highest FeO value of 3.91 wt% for JA-1 from our measurements (Fig. 5b) is consistent with the recommended value of 3.98 ± 0.20 wt% (Terashima *et al.*, 1994) (Fig. 9b). Revisiting the original values reported using the Kruskal-Wallis test, we observe that the photometric method provides higher values compared to the titrimetric method ($p < 0.05$). If we compile the reported values by titrimetric method only, the FeO value is 3.94 ± 0.17 wt%. The highest FeO value of 5.72 wt% for JB-1a from our measurements (Fig. 5c) is consistent with the recommended value of 5.78 ± 0.24 wt% (Terashima *et al.*, 1994) (Fig. 9c), although it is slightly lower than the original value of 5.92 wt% reported by the GSJ (Terashima and Ando, 1987). No statistical difference was observed between the methods, although the conventional chemical method provides visually lower values for JB-1a.

Modification of the method and applications

We suggest that using greater amounts of sample provides an easy means to minimize oxidation during sample decomposition, thereby allowing for more accurate determination of FeO in geochemical reference materials and unknown geological samples. We also stress that a slight loss of Fe^{2+} is unavoidable, as shown by the recovery yield tests. The maximum sample weight that can be treated within typical 30 ml crucibles is 2.5 or 3 g, depending on the sample type. In contrast, the typical sample weight in the literature is *ca.* 0.5–1.0 g (Maxwell, 1968; Jeffery, 1970; Bennett and Reed, 1971; Saikkonen and Rautiainen, 1993). To the best of our knowledge, trials to test larger samples have never been reported. Similarly, adding pure SiO_2 powder to samples helps to minimize oxidation. While just using greater quantities of sample is simpler, adding pure SiO_2 powder proves effective when the FeO value is large enough to prevent usage of large samples size in terms of the concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ solution and the maximum volume of a burette.

Some studies use the “Wilson method” to measure FeO (Wilson, 1960; Whipple, 1974; Amonette and Scott, 1991; Andrade *et al.*, 2002). In that method, Fe^{2+} is deliberately oxidized to Fe^{3+} by an oxidizing agent such as am-

monium metavanadate, the excess of which is determined using a titrimetric method. Discrepancies in the FeO values obtained from the “Pratt method” and “Wilson method” are often reported, and are attributed either to unexpected oxidation of Fe^{2+} in the “Pratt method” or to complex interference of the sample matrix with the oxidizing agent in the “Wilson method” (Saikkonen and Rautiainen, 1993; Lalonde *et al.*, 1998; Yokoyama and Nakamura, 2002; Amonette and Matyas, 2016; Xue *et al.*, 2017). Although the “Wilson method” has been developed to overcome the disadvantage of unexpected oxidation of Fe^{2+} in the “Pratt method”, the behaviour of the oxidizing agent in the sample matrix is partly still unclear. Whipple (1974) reported that oxidation of Fe^{2+} or V^{4+} occurs in the “Wilson method”. The degree to which the oxidizing agent is being consumed by sulphur and other elements such as Ti^{3+} in the samples remains uncertain (Schafer, 1966a; Saikkonen and Rautiainen, 1993). Our simple modification of the “Pratt method” using a greater amount of the sample will therefore provide opportunities to evaluate the difference between these two methods.

CONCLUSIONS

We have presented the optimization of a titrimetric method to determine FeO in geological materials. We tested the effect of the duration of decomposition, the temperature of a sand bath, and the sample weight. A duration of 12–13 min at 150–160°C is sufficient for the acid decomposition using a mixture of 5 ml of 9 mol l^{-1} H_2SO_4 and 8 ml of 50% HF. The FeO values increase with increasing sample weight until the sample weight reaches the weight that causes boil over. This is most likely owing to the fact that the vapor and the foam on the acid solution prevent loss of Fe^{2+} due to oxidation. We suggest that using a greater amount of sample provides an easy means to minimize oxidation during sample decomposition, thereby allowing a better determination of FeO in geochemical reference materials and unknown geological samples. The maximum sample weight that can be treated within typical 30 ml crucibles is 2.5 or 3 g, depending on the sample type. In contrast, 50 ml crucibles are sufficient to treat 3 to 4 g samples. We also note, however, that slight loss of Fe^{2+} is unavoidable; therefore, and FeO values with low sample weight obtained from the modified version of the Pratt method need to be carefully considered. The recovery yield tests with 3 g of SiO_2 powder demonstrate that loss of Fe^{2+} is 1.5% in the ideal case and 5% in the worst case. Previously published recommended values of FeO for geochemical reference materials are averages, including those determined using several methods; therefore, they need to be considered carefully.

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SUPPLEMENTARY MATERIALS

URL (<http://www.terrapub.co.jp/journals/GJ/archives/data/54/MS605.pdf>)
Table S1