Rapid Determination of Boron in 61 Soil, Sediment, and Rock Reference Materials by ICP-MS

Ting Liu^{a,b}, Tao He^a, Quanhui Shi^a, and Qian Ni^{*,a,b}

^a State Key Laboratory of Biogeology and Environmental Geology,
China University of Geosciences, Wuhan 430074, P.R. China

^b State Key Laboratory of Geological Processes and Mineral Resources,
China University of Geosciences, Wuhan 430074, P.R. China

INTRODUCTION

Boron in soils and sediments is essential to plant growth and crop yields (1). Deficient and excessive concentrations of B occur frequently, resulting in failure to meet internal growth needs and causing toxicity to the plants, respectively (2). Hence, chemical analysis of soils and sediments is valuable for monitoring the level of B to properly manage the environment (2). Besides, the fluid-mobile element B and its isotopes are efficient tracers of fluid-related processes. In the subduction zone processes, B and its isotopes were reported to define the link between subduction input and arc output (3-7). For terrestrial borate ore deposits, B as an indicator element was applied to investigate the relationship of its anomalies to completely delineate ore bodies by a soil geochemical study (8). Therefore, there is an urgent need for the accurate determination of the boron content in soil, sediment, and rock samples.

Several plasma-based techniques, including inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP mass spectrometry (ICP-MS) (9, 10), are commonly applied to determine the boron concentration in aqueous and solid samples (8, 11). ICP-OES detects B wavelengths typically monitored at 249.678 nm and 249.773 nm, which are near the wavelength of iron (9). If the sample has a high iron concentration, boron determination by ICP-OES is

ABSTRACT

Boron (B) is an important geochemical tracer for environmental and geological studies. This study presents a rapid acid digestion method with ammonia dilution to detect boron in soil, sediment, and rock samples using inductively coupled plasma mass spectrometry (ICP-MS). It took only 30 minutes of digestion time to completely recover B in 50 mg of soil (GSS-7), sediment (GSD-18), and rock (GSR-2) reference materials at a high digestion temperature of 190 °C using 1 mL HNO₃ and 1 mL HF in a PTFE-lined stainless-steel bomb. No loss of B was found at a digestion temperature of 190 °C for 30 hours. The well-known memory effect of B was eliminated by using an ammonia dilution method. Moreover, the alkaline sample solutions created by ammonia dilution also avoided the corrosiveness of HF in the ICP-MS sample introduction system. Rhodium is a more suitable internal standard element than In and Y in the alkaline medium. Compared to the standard sample cone + H skimmer cone (S + H cone), the standard sample cone + X skimmer cone (S + X cone) increases the sensitivity of B by a factor of 7.0-8.2 in ICP-MS. The proposed method was successfully applied for the rapid determination of B in soil, sediment, and rock reference materials.

affected by iron interference (9). Compared to ICP-OES, ICP-MS has been developed for the rapid determination of ultra-trace elements, including B, because of its higher sensitivity and reduced interference (12-17).

Precise and accurate determination of B in various solid samples by ICP-MS and ICP-OES requires complete extraction of B from the sample. Solid samples, especially rocks, require extraction of boron using alkali fusion, pyro-hydrolysis, or acid dissolution (18, 19). Generally, dissolution carried out by alkali fusion with fluxes, such as sodium carbonate (flux: rock 8:1) or sodium hydroxide (5:1) in a Pt or Ni crucible at 900-1500 °C, is an effective technique for relatively large samples (18-20). A 4:1 mixture of sodium carbonate and divalent cation oxides (e.g., ZnO) was suggested for the destruction of solid samples prior to analysis of volatile elements such as B (21). The major disadvantage of the technique is that less than 90% of total boron in the sample is extracted (18). However, pyro-hydrolysis separation of B is a successful method and does not require sample decomposition (9). Michel et al. (22) proposed a modified pyro-hydrolysis technique to fix the problem of high blank contribution and an incomplete B recovery from samples of low concentration. However, the issue remains that cleaning the pyro-hydrolysis apparatus is difficult (18); therefore, this technique is unsuitable for large batches of samples. Additionally, use of acid digestion (e.g., HF and HNO₃) for the extraction of B from solids other than biogenic carbonates is complicated (23), mainly because B volatilizes with HF (9). In order to effectively avoid the loss of B volatilization, Hlaváček et al. (24) found that phosphoric acid in a sample solution reduces the volatility of boric acid with water vapor. Ishikawa and Nakamura (25, 26) reported that the loss of boron

*Corresponding author.
E-mail: niq1981@163.com
Tel.: +86 27 67883452
Fax: +86 27 67883456

volatilization was avoided by using HF and HCl in the presence of mannitol because of the formation of a boron-mannitol complex. The method of mannitol plus HF to avoid boron loss has been widely used (27-30). Wei et al. (28) placed a mixture of 100 mg rock powder, 100 mL H₂O₂, 1 mL HF, and 100 mL mannitol on a hot plate at a temperature of 60 °C for three days in the acid digestion process and the rock powder was dissolved. In particular, Gaillardet et al. (31) found that no loss of boric acid occurred when 1 µg of B was evaporated in water, HCl, HF, and acetone solutions at 60-65 °C; however, boron was highly volatile when the dried residue of the evaporation was heated further. After these evaporation tests (31, 32), it was found that mannitol did not completely suppress B volatilization, particularly when the evaporation process was continued through dryness.

Admittedly, ICP-MS has some problems when measuring boron, including the resultant high memory effect. The boron memory effect originates from the tendency of boron to volatilize as boric acid from the sample solution layer that covers the inside surface of the spray chamber (33), resulting in a cross-contamination effect. In addition, B has a bad washout behavior. Sun et al. (34) found that dilute nitric acid did not reduce the B signals to blank levels with a 10-minute washout after 100 ng mL⁻¹ B was introduced over a period of 5 minutes. Some efforts have been made to eliminate or minimize the memory effect, including different washing solutions (e.g., sodium fluoride, mannitol, ammonia solution, and ammonia gas) (33-36). Al-Ammar et al. (33) indicated that only a 20-second washout was required to completely eliminate the boron memory effect and reduce boron signals to blank levels by injecting a small volume of ammonia solution into the spray chamber simultaneously with

the sample solution. Al-Ammar et al. (35) also noted that introduction of ammonia gas into the spray chamber within 2 minutes of washing efficiently removed the boron memory effect. In recent studies, practical applications have been reported (37, 38). In contrast to these studies, Vogl et al. (39) reported that the memory effect of B was minimized by washing with dilute HCl for 5.5 minutes, and matching the medium of all solutions for ICP-MS measurement without any additives.

This study presents a rapid closed-vessel acid digestion method for the ICP-MS determination of B in soil, sediment, and rock reference materials. Experimental digestion products before ICP-MS analysis were changed to alkaline medium by ammonia dilution. It should be noted that this method does not involve any sample evaporation or drying processes, thereby avoiding the loss of B volatilization. The analysis was focused on the effect of digestion time, ammonia matrix, different cone combinations, selection of internal standard elements, and the memory effect on B measurement. The method was also used successfully to detect B in 61 soil, sediment, and rock reference materials.

EXPERIMENTAL

Instrumentation and Data Acquisition

Experimental digestion products were analyzed using an Element XR sector field ICP-MS instrument (Thermo Fisher Scientific, Bremen, Germany) at the State Key Laboratory of Geological Processes and Mineral Resources, University of Geosciences in Wuhan, P.R. China. The high abundance isotope ¹¹B (80.1%) was utilized. The low abundance isotope of ¹⁰B (19.9%) was not selected because of spectral overlap interference from ²⁰Ne²⁺ and ⁴⁰Ar⁴⁺ at low resolution

(R = ~ 300). The instrumental parameters were optimized to obtain the stable signal intensity for ¹¹B while keeping the CeO⁺/Ce⁺ and Ce²⁺/Ce⁺ ratios below 2%. Two different combinations of cones were used, including an X skimmer cone + standard sample cone and an H skimmer cone + standard sample cone. The main operating conditions are listed in Table I.

Prior to sample analysis, the instrument was purged with ultrapure water for approximately one hour and then washed with 5% (w/w) ammonia solution for approximately one hour to clear any trace elements from the previous sample and to change the media to alkaline.

Reagents and Standard Solutions

The ultrapure water (resistivity, 18.2 MΩ/cm) used throughout the experiments, was obtained from a Milli-Q[®] water purification system (Millipore Corporation, USA). Concentrated HNO₃ and HF (GR grade, SCR, Shanghai, P.R. China) were further distilled using a DST-1000 acid purification system (Saville, Eden Prairie, USA). Chromatographic grade ammonia reagent (Aladdin, Shanghai, P.R. China) was used. The 1000 mg mL⁻¹ stock solutions of single elements (Li, Be, B, Na, Al, Cu, Rb, Y, Rh, In, Te, Ce, Hf, Pb, and U) were purchased from the National Center for Analysis and Testing of Steel Materials, Beijing, P.R. China. The ammonia solutions (1%, 3%, 5%, and 7% w/w) were prepared by directly diluting the ammonia reagent with ultrapure water. Calibration was made using standard solutions of B (0, 5, 10, 15, and 20 ng mL⁻¹) with 5% (w/w) ammonia. We tested three internal standard elements (Y, Rh, and In) in the ammonia matrix. The calibration blank and a series of working standards of B contained 1 ng mL⁻¹ Y, Rh, and In.

TABLE I
Operating Parameters for ICP-MS

RF power	1200 W
Cooling gas flow rate	16 L min ⁻¹
Auxiliary gas flow rate	0.9 L min ⁻¹
Sample gas flow rate	1.10 L min ⁻¹
Sample cone	Standard sampler cone, Nickel
Skimmer cone	X skimmer cone, Nickel H skimmer cone, Nickel
Spray chamber temperature	4 °C
Nebulizer	Micro Mist nebulizer, 200 µL min ⁻¹
Mass resolution	Low
Mass window	50%
Sample time	10 ms
Samples per peak	30
Integration window	20%
Integration type	Average
Scan type	EScan
Detection system	Triple
Runs	3
Passes	3

Using Class 100 clean laboratory conditions, the high-density polyethylene bottles and tubes were cleaned in 5% (w/w) HNO₃ for 24 hours and rinsed 3 times with ultra-pure water before use. Great care was taken to prevent B contamination.

Reference Materials

To investigate the accuracy and precision of the proposed method, a series of international geological reference materials, including soils, sediments, shales, basalts, an andesite and granites were analyzed. Sixty-one geological reference materials were obtained from the United States Geological Survey (AGV-2, BCR-2, BHVO-2, BIR-1a, and SCO-1) and the Institute of Geophysical and Geochemical Exploration. Detailed sample information is listed in Table II.

Sample Digestion Procedure

Approximately 50 mg of sample powder was weighed and soaked with 1 mL HNO₃ and 1 mL HF in a homemade PTFE-lined stainless-

steel bomb. Subsequently, the bomb was heated in an electric oven at 190 °C. After cooling, the slurry was diluted with 5% (w/w) ammonia solution to a final weight of 50 g and stored in polyethylene bottles. Then, 1 mL of supernatant solution was transferred to a polyethylene tube and 10 µL of 1 µg mL⁻¹ Y, Rh, and In standard solution were added to the sample solution. A reagent blank solution was simultaneously prepared for each group in the same way.

RESULTS AND DISCUSSION

Effect of Digestion Time

It is clear that decomposition of the samples is controlled by the synergistic effect of temperature and time. Due to the limitations of the physical and chemical properties of the PTFE-lined stainless-steel bomb and for the sake of efficiency, the digestion temperature of 190 °C is usually used in routine geological sample analysis (16). Figure 1 summarizes the effect of digestion time on the recovery of B in three differ-

ent types of geological materials (soil, GSS-7; sediment, GSD-18; rock, GSR-2) at 190 °C. It can be seen from Figure 1 that B in these three geological materials was completely recovered at all given digestion times (0.5-30 hours). For the complete recovery of B in GSS-7, GSD-18, and GSR-2, the digestion time required only 30 minutes, which is approximately 144 times faster than a conventional mannitol-added HF digestion (28).

Suppression of Ammonia Matrix Effect

In ICP-MS, matrix effects are usually known to cause signal suppression with an increase in matrix concentrations. To the best of our knowledge, the effect of the ammonia matrix on the B signal in ICP-MS was never studied or reported. Figure 2 illustrates the ¹¹B signal intensity as a function of nebulizer gas flow rate in 1%, 3%, 5%, and 7% (w/w) ammonia solutions. Clearly, the optimum sample gas flow rate (corresponding to the maximum signal intensity of B) shifted to a lower gas flow rate when the ammonia concentration was increased from 1% to 7%. The maximum signal intensity of ¹¹B also gradually decreased with an increase in ammonia concentration. Generally, the suppression of the maximum signal intensity for ¹¹B by the increase in ammonia concentration became more significant at higher nebulizer gas flow rates (>1.12 L min⁻¹). These phenomena may be attributed to the local cooling effect of ammonium in the central channel of the plasma so that the aerosol particles are less effectively converted to atomic ions. It can be seen in Figure 2 that the B signal intensity was not affected by the change in ammonia concentration from 1% to 7% at nebulizer gas flow rates of 1.06-1.12 L min⁻¹. It seems that the ammonia matrix effect on B can be overcome by using a low sample gas flow rate of

TABLE II
Experimental and Reference Values
in 61 Geological Reference Materials

Materials	Abbreviation	Sample Type	ICP-MS ($\mu\text{g g}^{-1}$)	Ref. ($\mu\text{g g}^{-1}$)
GBW07401	GSS-1	Podzolic soil	45.0 $\pm$ 2.4	50 $\pm$ 3
GBW07402	GSS-2	Soil	35.8 $\pm$ 0.3	36 $\pm$ 3
GBW07403	GSS-3	Soil	23.3 $\pm$ 0.4	23 $\pm$ 3
GBW07404	GSS-4	Soil	97.3 $\pm$ 3.7	97 $\pm$ 9
GBW07405	GSS-5	Soil	69.8 $\pm$ 5.1	53 $\pm$ 6
GBW07406	GSS-6	Soil	68.4 $\pm$ 3.6	57 $\pm$ 5
GBW07407	GSS-7	Laterite	10.0 $\pm$ 0.3	10
GBW07408	GSS-8	Loess	64.6 $\pm$ 1.0	54 $\pm$ 4
GBW07423	GSS-9	Sediment	53.6 $\pm$ 0.7	52 $\pm$ 4
GBW07424	GSS-10	soil	34.8 $\pm$ 0.5	35 $\pm$ 3 ^a
GBW07425	GSS-11	Soil	39.7 $\pm$ 0.5	36 $\pm$ 3 ^a
GBW07426	GSS-12	Soil	48.0 $\pm$ 1.2	55 $\pm$ 5 ^a
GBW07427	GSS-13	Soil	50.5 $\pm$ 0.8	53 $\pm$ 3 ^a
GBW07428	GSS-14	Soil	44.6 $\pm$ 0.8	46 $\pm$ 3 ^a
GBW07429	GSS-15	Soil	58.4 $\pm$ 1.0	63 $\pm$ 2 ^a
GBW07430	GSS-16	Soil	61.7 $\pm$ 1.1	63 $\pm$ 4 ^a
GBW07446	GSS-17	Sandy soil	20.9 $\pm$ 0.4	24 $\pm$ 3
GBW07447	GSS-18	Saline-alkali soil	67.4 $\pm$ 0.9	62 $\pm$ 7
GBW07448	GSS-19	Soil	50.2 $\pm$ 1.2	51 $\pm$ 4
GBW07449	GSS-20	Saline-alkali soil	163 $\pm$ 2	143 $\pm$ 38
GBW07450	GSS-21	Soil	50.8 $\pm$ 2.9	48 $\pm$ 6
GBW07451	GSS-22	Tidal flat sediment	50.4 $\pm$ 1.6	52 $\pm$ 7
GBW07452	GSS-23	Tidal flat sediment	76.5 $\pm$ 3.2	77 $\pm$ 8
GBW07453	GSS-24	Tidal flat sediment	81.6 $\pm$ 1.2	83 $\pm$ 7
GBW07454	GSS-25	Soil	57.2 $\pm$ 0.6	54 $\pm$ 6
GBW07455	GSS-26	Sediments	54.7 $\pm$ 1.1	52 $\pm$ 8
GBW07456	GSS-27	Sediments	67.7 $\pm$ 1.4	64 $\pm$ 7
GBW07457	GSS-28	Sediments	77.8 $\pm$ 1.1	80 $\pm$ 10
GBW07301	GSD-1	Stream sediments	5.84 $\pm$ 0.51	4.6 $\pm$ 0.9
GBW07302	GSD-2	Stream sediments	9.81 $\pm$ 0.89	10.8 $\pm$ 2.5
GBW07303a	GSD-3a	Stream sediments	52.7 $\pm$ 1.3	57 $\pm$ 7
GBW07304	GSD-4	Sediments	58.1 $\pm$ 1.1	52 $\pm$ 6
GBW07305	GSD-5	Stream sediments	53.1 $\pm$ 0.6	51 $\pm$ 6
GBW07306	GSD-6	Stream sediments	48.6 $\pm$ 2.1	50 $\pm$ 7
GBW07307a	GSD-7a	Stream sediments	220 $\pm$ 4	195 $\pm$ 32
GBW07308a	GSD-8a	Stream sediments	4.73 $\pm$ 0.18	5.3 $\pm$ 1.1
GBW07308	GSD-8	Stream sediments	3.14 $\pm$ 0.25	3.6 $\pm$ 0.7
GBW07309	GSD-9	Stream sediments	56.0 $\pm$ 3.2	54 $\pm$ 6
GBW07310	GSD-10	Stream sediments	19.5 $\pm$ 0.4	26 $\pm$ 4
GBW07311	GSD-11	Stream sediments	61.6 $\pm$ 3.5	68 $\pm$ 5
GBW07312	GSD-12	Stream sediments	22.6 $\pm$ 0.6	24 $\pm$ 2

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1.06–1.12 L min⁻¹. Taking into consideration both the ammonia matrix effect and the B signal intensities, the nebulizer gas flow rate for sample analysis was set at 1.10–1.12 L min⁻¹.

Effects of Different Cone Combinations on Signal Intensity

Two different combinations of cones were used in this study, such as an H skimmer cone + standard sample cone and an X skimmer cone + standard sample cone. Both skimmer cones were made of nickel. However, their tip angles were different. The H skimmer cone has a cylindrical entrance and a trumpet-shaped exit, while the X skimmer cone has a completely trumpet-shaped form (14). As shown in Figure 3, a significant improvement in analytical sensitivity was observed for most of these investigated elements when using the S + X cone combination compared to the S + H cone combination. The enhancement factors are negatively correlated with the mass number of elements. The light mass elements (e.g., Li, Be, and B) have an enhancement factor of 7.0–8.2. The results show that the use of the S + X cone combination is very beneficial for the determination of low content B in the samples. The X skimmer cone with the trumpet-shaped entrance provides more space for the ion beams to enter the skimmer orifice. This difference may partly explain the observed signal enhancement effects.

Selection of Internal Standard Elements

When using ICP-MS measurements, internal standard elements are usually used to correct signal drift and matrix effect (9, 30). The elements Y, Rh, and In are very stable in acid media and often used as internal standard elements during ICP-MS analysis. However, it is possible that these elements may not be a suitable internal standard ele-

TABLE II (cont'd)
Experimental and Reference Values
in 61 Geological Reference Materials

Materials	Abbreviation	Sample Type	ICP-MS ($\mu\text{g g}^{-1}$)	Ref. ($\mu\text{g g}^{-1}$)
GBW07317	GSD-13	Stream sediments	5.25 $\pm$ 0.45	5.3 $\pm$ 0.7
GBW07318	GSD-14	Stream sediments	27.1 $\pm$ 0.4	27 $\pm$ 4
GBW07358	GSD-15	Stream sediments	52.8 $\pm$ 1.1	53 $\pm$ 7
GBW07359	GSD-16	Stream sediments	45.3 $\pm$ 0.6	48 $\pm$ 6
GBW07360	GSD-17	Stream sediments	61.3 $\pm$ 0.3	62 $\pm$ 6
GBW07361	GSD-18	Stream sediments	5.65 $\pm$ 0.80	5.5 $\pm$ 1.2
GBW07362	GSD-19	Stream sediments	16.0 $\pm$ 0.9	14 $\pm$ 3
GBW07363	GSD-20	Stream sediments	29.5 $\pm$ 1.9	28 $\pm$ 2
GBW07364	GSD-21	Stream sediments	31.4 $\pm$ 4.4	35 $\pm$ 6
GBW07365	GSD-22	Stream sediments	47.8 $\pm$ 0.6	46 $\pm$ 10
GBW07366	GSD-23	Stream sediments	63.2 $\pm$ 0.2	70 $\pm$ 8
GBW07103	GSR-1	Granite	22.9 $\pm$ 0.6	24 $\pm$ 3
GBW07104	GSR-2	Andesite	4.51 $\pm$ 0.16	4.7 $\pm$ 0.8
GBW07105	GSR-3	Basalt	1.50 $\pm$ 0.37	3.5 $\pm$ 1
GBW07107	GSR-5	Shale	174 $\pm$ 5	154 $\pm$ 11
	AGV-2	Andesite	6.21 $\pm$ 0.28	6.45 $\pm$ 0.52 ^b
	BHVO-2	Basalt	2.41 $\pm$ 0.16	2.95 $\pm$ 0.26 ^b
	SCO-1	Cody shale	71.1 $\pm$ 0.7	72 $\pm$ 6 ^b
	BIR-1a	Basalt	0.211 $\pm$ 0.182	0.25 ^b
	BCR-2	Basalt	3.42 $\pm$ 0.31	4.4 ^b

ICP-MS = Experimental values determined by ICP-MS.

Ref. = Reference values.

Reference values (uncertainty: 1 s) are taken from Wang et al. (40).

^a Reference values (uncertainty: 95% CL) are taken from Gu et al. (41).

^b Reference values (uncertainty: 95% CL) are taken from Jochum et al. (42).

ment in alkaline media. Figure 4 shows the variation in the signal intensities of the internal standard elements (1 ng mL⁻¹ Y, Rh, and In) in 44 different sample solutions. The signal of Rh was very stable for all of these different sample solutions, while the signal of Y was relatively stable in most of these different sample solutions. In contrast, the signal of In fluctuated drastically. This could be related to the formation of In(OH)₃ in the aqueous ammonia solution (15). Therefore, Rh was a much more suitable internal standard element than Y and In for correcting the signal variation for B during ICP-MS analysis.

Memory Effect

The memory effect is one of the main obstacles for the accurate determination of B in samples using ICP-MS analysis. In this study, three washing solutions [H₂O, 5% (w/w) HNO₃, and 5% (w/w) ammonia] were tested. The time-resolved signal response for ¹¹B was continuously monitored when the washing solution and the B standard solution were injected in turn. First, the signal was collected with the reagent blank within approximately 30 seconds, then the standard solu-

Fig. 1. Recovery of B in GSD-18, GSS-7, and GSR-2 as a function of digestion time at 190 °C.

Fig. 2. Signal intensity of ¹¹B as a function of sample gas flow rate in 1%, 3%, 5%, and 7% (w/w) ammonia solutions.

Fig. 3. Sensitivity enhancement factors for 14 elements using the X skimmer cone + standard sampler cone compared to the standard arrangement (H skimmer cone + standard sample cone).

Fig. 4. Signal intensities of the internal standard elements (1 ng mL^{-1} Y, Rb and In) in 44 different sample solutions.

tion was introduced for approximately 100 seconds, and finally the reagent blank was reintroduced as the washing solution for approximately 60 seconds (Figure 5). It is clear that the memory effect of B observed in these three different washing solutions was different. The H_2O and 5% (w/w) ammonia washing solutions are very effective for washout of the residual B. The memory effect of B observed in these two washing solutions was negligible (Figure 5). However, over time, the background signals of ^{11}B in H_2O gradually increased from 55,000 to 115,000 cps. In contrast, the memory effect of B is very significant using the 5% (w/w) HNO_3 solution. It required about 100 seconds for the B signal to drift from 600,000 to 200,000 cps. In addition, the background signal intensity of ^{11}B was approximately 4 times that of 5% (w/w) ammonia solution. The ammonia washing solution together with the sample solution in the alkaline media also eliminated the corrosiveness of HF on the sample introduction system and the torch. Therefore, 5% (w/w) ammonia solution was used as the washing solution in our experiments.

Fig. 5. Time-resolved signal intensity (cps) of ^{11}B : (I) with reagent blanks [(1) H_2O , (2) 5% (w/w) HNO_3 , and (3) 5% (w/w) ammonia solution], (II) B standard solution, and (III) with reagent blanks as the washing solutions.

Detection and Quantification Limits

A reagent blank (5% w/w ammonia) and a procedure blank were used to measure the limits of detection and quantitation, respectively. The limits of detection, calculated as three times the standard deviations of 10 measurements of $^{11}\text{B}^+$ concentration was 0.0224 ng g^{-1} . The limit of quantitation, which was calculated as 10 times the standard deviation of 10 measurements of $^{11}\text{B}^+$ concentration and then multiplied by the dilution factor used for sample preparation (50 mg of sample/50 g) was $0.0355 \text{ } \mu\text{g g}^{-1}$.

Analysis of Reference Materials

Table II summarizes the results and reference values in 61 international soil, sediment, and rock reference materials. The reference values are taken from what has been published in GeoReM (<http://georem.mpch-mainz.gwdg.de/>) (40-42). Figure 6 compares the results for B between our measured values and the reference values in these reference materials. It was clearly shown that the measured values were generally in good agreement with the reference values with correlation coefficients of 0.98 for B. The results showed

Fig. 6. Comparison of measured results and reference values for B in 61 reference materials. Horizontal bars and vertical bars show one standard deviation for measured values and reference values, respectively.

agreement between our data obtained and the reference values were better than 10% for most of these soil, sediment, and rock materials, demonstrating the accuracy of the method (Table II). The obvious discrepancies for the basalt reference materials were as follows: GSR-3, BHVO-2, and BCR-2.

The discrepancies in the basalt reference materials are probably due to resistant minerals containing B that are not being effectively attacked with a digestion time of only 30 minutes. In particular, the relative deviation of the B concentration in GSR-3 was 57%. Therefore, we increased the digestion time from 0.5 hours to 24 hours at 190 °C. These three newly measured values of B (1.28 ± 0.05 , 1.38 ± 0.40 , and $1.24 \pm 0.38 \mu\text{g g}^{-1}$, respectively) agreed with our previous measured values ($1.50 \pm 0.37 \mu\text{g g}^{-1}$) and were still significantly lower than the reference value ($3.5 \pm 1 \mu\text{g g}^{-1}$) (40). It seems that a longer digestion time has no effect on the recovery of boron. Another reason for the discrepancies is that these reference values in GeoReM could be incorrect. Because most of the reference values are means of multiple analyses carried out by dif-

ferent institutions using different methods, the values are not necessarily 'true'. We found that the determined values of B in BHVO-2 and BCR-2 (2.41 ± 0.16 and $3.42 \pm 0.31 \mu\text{g g}^{-1}$, respectively) agreed better with recently published data, which were 2.8 ± 0.3 and $4.1 \pm 0.6 \mu\text{g g}^{-1}$, respectively (43).

CONCLUSION

A new method was developed for the direct determination of B in soil, sediment, and rock samples by ICP-MS using a rapid acid digestion, followed by ammonia dilution. It took only 30 minutes of digestion time to completely recover B in 50 mg of the soil (GSS-7), sediment (GSD-18), and rock (GSR-2) reference materials at a high digestion temperature of 190 °C and using 1 mL HNO_3 and 1 mL HF in a PTFE-lined stainless-steel bomb. No loss of B was found in this study. The alkaline sample solution together with the ammonia washing solution not only eliminates the memory effect of B, but also avoids the corrosiveness of HF on the ICP-MS sample introduction system. The presented method is considerably simpler than conventional methods and has great potential for the

direct ICP-MS determination of boron in environmental and geological samples.

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