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# Static multicollection of $Cs_2BO_2^+$ ions for precise boron isotope analysis with positive thermal ionization mass spectrometry

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## Abstract

Static multicollection of $Cs_2BO_2^+$ ions ($m/z$ = 308 and 309) for precise boron isotope analysis has been established by employing a newly developed double collector package in the modified Finnigan-MAT 261 thermal ionization mass spectrometer (TIMS). This method reduces the data acquisition time to 5 min which is approximately one order of magnitude shorter than conventional peak jumping method, and it is easier to measure small sample size as low as 0.1 $\mu$g of boron. The analytical precision for individual runs and reproducibility of measured $^{11}B/^{10}B$ ratios of NBS 951 boric acid with static multicollection, respectively, are ±0.007–0.025% ($2\sigma_{mean}$) and ±0.012% ($2\sigma_{mean}$), for 1 $\mu$g of B, and ±0.015–0.032% ($2\sigma_{mean}$) and ±0.023% ($2\sigma_{mean}$), for 0.1 $\mu$g of B. This analytical precision and reproducibility are essentially identical to those previous works with peak jumping method measuring sample amounts more than 1 $\mu$g of B. (Int J Mass Spectrom 176 (1998) 13–21) © 1998 Elsevier Science B.V.

*Keywords:* Boron isotope analysis; Static multicollection; $Cs_2BO_2^+$ ion; Positive thermal ionization mass spectrometry (PTIMS); Analytical precision and reproducibility

## 1. Introduction

The boron isotopic composition of meteoritic and terrestrial materials can provide important information to understand nuclear synthesis theories and many geological phenomena because of its unique physicochemical characteristics [1–3]. Many methods have been applied for determination of the isotopic composition of boron, and a number of different molecular ions ($M_2BO_2^+$: M is alkali metal, $BO_2^-$) have been used for this purpose with thermal ionization mass spectrometry (TIMS) [4–8]. These days, the $Cs_2BO_2^+$ method [7,9–11] and $BO_2^-$ method with negative thermal ionization mass spectrometry (NTIMS), [8,12–14] are commonly used.

In the $Cs_2BO_2^+$ method negligibly small isotopic fractionation is observed because of very high mass numbers of the ion ($m/z$ = 308 and 309) as compared to other molecular ions such as $Na_2BO_2^+$ ($m/z$ = 88 and 89), $Rb_2BO_2^+$ ($m/z$ = 213 and 214), and $BO_2^-$ ($m/z$ = 42 and 43). Furthermore, graphite activator in the $Cs_2BO_2^+$ method [10] achieves high signal intensity and stability, and thereby provides precise analysis of the boron isotopic composition with analytical reproducibility of 0.01% to 0.04% ($2\sigma$) for >500 ng B [9–11,15].

On the other hand, the $BO_2^-$ method with NTIMS

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is capable of analyzing a sample size of boron as small as 1 ng [16] because of extremely high ionization efficiency in mass spectrometry [8,12]. In this method, however, large isobaric mass interference at $m/z = 42$ ($^{10}B^{16}O_2^-$) is caused by CNO in the sample derived through chemical separation of boron [17] by using organic material like mannitol and ion exchange resin. The extent of such an isobaric interference is not reproducible so that the analytical reproducibility becomes 0.07% to 0.4% ($2\sigma$) even for a larger sample size (>1 $\mu$g of B) that is approximately one order of magnitude worse than that of the $Cs_2BO_2^+$ method [8, 12–14,16]. The use of organic materials cannot be avoided in the chemical separation of boron prior to the mass spectrometry, even for the $BO_2^-$ method. The $BO_2^-$ method with NTIMS, therefore, is not suitable for the studies of water/rock interaction and mantle/crust recycling that require precise boron isotope analysis with an analytical error smaller than 0.05% ($2\sigma$) (e.g. [18]).

Although the $Cs_2BO_2^+$ method has improved the analytical precision and reproducibility available for the geochemical studies as mentioned above, decrease in ion beam intensity during mass spectrometry is rapid as in the case of Pb isotope analysis. Therefore, multicollection mass spectrometry is desirable for the $Cs_2BO_2^+$ method for the analysis of a small sample size (<500 ng B) that has the following advantages in comparison to the peak switching mass spectrometry: (1) the data acquisition time is shorter so that the smaller sample size can be analyzed before ion beam intensity decays, and (2) the time drift correction for ion beam decay is not necessary. In the $Cs_2BO_2^+$ method, however, the relative mass difference between $m/z = 308$ and 309 is too small to allow simultaneous collection in the general multicollector mass spectrometer. Therefore, data acquisition has been obliged to employ peak switching by using a single Faraday cup collector.

In this article, we describe a static multicollection technique employing a newly developed double collector package for the collection of $Cs_2BO_2^+$ ions for the determination of precise boron isotopic composition with a shorter acquisition time and smaller sample size.

## 2. Experimental

### 2.1. Mass spectrometer

A modified Finnigan-MAT 261 (Finnigan, Bremen, Germany) mass spectrometer, originally the same as the one used in [11], was employed in this study. This mass spectrometer is equipped with six movable platforms for Faraday cup collectors, including the special double collector package for $Cs_2BO_2^+$ ($m/z = 308$ and 309), a piggyback double collector for Pb ($m/z = 207$ and 208) and a fixed central one. The double collector package for boron is located in the lower mass side on a movable platform. A schematic design of the double collector package is shown in Fig. 1 together with some cup configurations in the modified multicollection system of MAT 261. Because the masses of $Cs_2BO_2^+$ ($m/z = 308$ and 309) ions are very high, they can only be deflected by reduced accelerating voltage of 8 kV. A Faraday cup collector was used with a $10^{11}$-$\Omega$ resistor.

### 2.2. Reagents

*Water.* Boron selective resin (0.5 mL) [Amberlite IR-743 (XE-243) (Sigma, MO)] and mannitol (2 g) were added to 5 L of water deionized with mixed-bed ion-exchange resin. After intermittent agitation for 3 days, the supernatant was finally subboiled by using a two-bottle Teflon (DuPont, DE) still [19] at a temperature of less than 80°C. Blank of the distilled water for boron was found to be 10 pg $mL^{-1}$ by using isotope dilution mass spectrometry (IDMS).

*Cesium solution.* Analytical grade cesium carbonate was dissolved in 0.1 M HF to get a $9.25 \times 10^{-3}$ M Cs solution. The solution was subsequently passed through 1 mL of anion-exchange resin bed to remove a trace amount of boron [11].

*Mannitol solution.* Analytical grade mannitol powder was dissolved in 0.1 M HF to obtain a 1% solution. This solution was passed through anion-exchange resin bed in the same way as employed for the cesium solution [11].

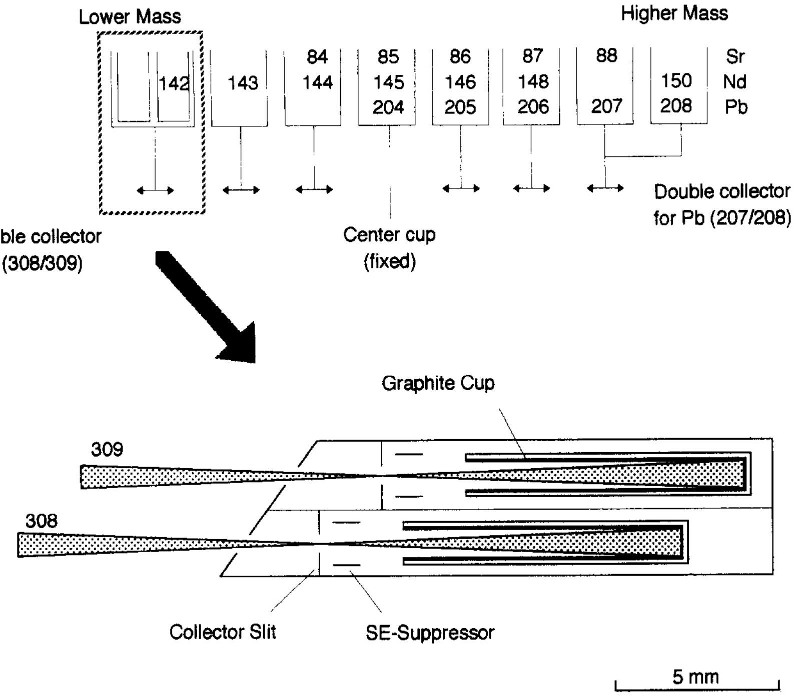

Fig. 1. Schematic design of the double collector Faraday cup package for $Cs_2BO_2^+$ ions and some cup configurations for Sr, Nd, and Pb isotope analysis in the modified multicollection system of MAT 261. There are six movable platforms that lie along the focal plane and are equipped with Faraday cup collectors. Two cups are doubled on the platforms of lower and higher mass side for boron and lead isotopes, respectively. Arrows indicate adjustable multicollectors.

*Graphite.* Spectroscopic grade graphite was repeatedly cleaned with an ethanol-3 M HF solution and finally suspended in 50% ethanol–50% $H_2O$ solution (v/v) to prepare 40 mg graphite/mL [11].

*Boric acid.* We analyzed U.S. Department of Commerce, National Institute of Standards and Technology (NIST), Standard Reference Material (SRM) 951 boric acid as sample in this study. A solution of 10 ppm NIST SRM 951 was prepared and used for a series of experiments.

### 2.3. Procedure

#### 2.3.1. Sample preparation

Cesium and mannitol solution were added to boric acid solution to get the B/Cs mole ratio of 2 and 40–50 $\mu$g of mannitol to 1 $\mu$g B, respectively. The mixed solution was finally evaporated to dryness at 70°C. The dried sample was then loaded onto a Ta filament for mass spectrometry.

#### 2.3.2. Mass spectrometry

The sample loading method onto the Ta filament is essentially the same as described in [20]. Prior to sample loading, the trapezoidal Ta filaments (2 mm top × 0.025 mm × 0.75 mm) were degassed for 30 min with a filament current of 3.0 A at $10^{-6}$ Torr in a degassing unit that is independent of mass spectrometer. The filaments were then allowed to oxidize by the ambient atmosphere for 3 days in a plastic box protected against outside contamination.

First, the top of the filament was coated by 1 $\mu$L of graphite–ethanol–water slurry containing ≈40 $\mu$g of graphite. Just before the complete dryness of graphite, the boron sample dissolved in 1 $\mu$L of the distilled water was loaded on the graphite layer to make a sample–graphite mixture. The filament was then dried

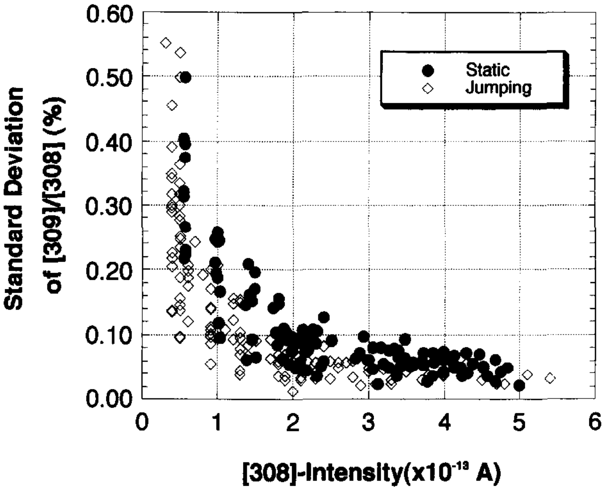

Fig. 2. Ion beam [308] intensity vs. standard deviation of [309]/[308] ratio diagram for static and jumping methods. The plotted symbols show the standard deviation of block ratios that are the means of 10 ratios (scan). A sample of 1 μg of B was measured repeatedly.

under a heating lamp. The sample was then introduced into the mass spectrometer.

The $Cs_2BO_2^+$-graphite method [10,11] was used in the measurement of the boron isotope ratio. The procedures for boron isotope measurement are the same as those described in [11]. When the vacuum reached $3 \times 10^{-7}$ Torr, the filament current was rapidly raised to 0.5 A and then increased further to 0.8–0.90 A at a rate of 0.05 A $min^{-1}$. In this range, $Cs^+$ ($m/z = 133$) signal appeared and was used to focus the ion beam. When the ion current of $Cs^+$ was (1–5) $\times 10^{-12}$ A, $Cs_2^{11}BO_2^+$ ($m/z = 309$) became detectable with the Faraday cup collector. The filament current was then slowly increased at a rate of 0.01 A $min^{-1}$ until the ion current of $Cs_2^{11}BO_2^+$ reached $1 \times 10^{-12}$ to $1 \times 10^{-11}$ A; at that time the filament current was typically 0.91 to 1.20 A. This current produces a temperature too low to be measured accurately by using an optical pyrometer. The ratio of $Cs_2^{10}BO_2^+$ ($m/z = 308$) to $Cs_2^{11}BO_2^+$ ($m/z = 309$) was measured against a baseline and the result was corrected for oxygen isotopes following Spivack and Edmond [9]: $(^{11}B/^{10}B_{corr.}) = (^{11}B/^{10}B_{meas.}) - 0.00079$.

Generally, the baseline is determined at $m/z = 306.5$ in the $Cs_2BO_2^+$ method [10,11]. However, the noise level at baseline of $m/z = 306.5$ with no ion beam by closing the ion source valve is essentially identical in the modified multicollection system. Therefore, the baseline was determined by closing the ion source valve which allows one to fix the magnetic field using the static multicollection technique during data collection and to avoid magnetic hysteresis.

Four isotopic measurements were carried out in order to examine analytical precision with different integration times of 4 and 8 s. There was no significant difference observed in isotope ratio and precision between these different integration times. Therefore, we used the integration time of 4 s in this study, whereas 16 s was given to baseline collection.

## 3. Results and discussion

### 3.1. Relationship between intensity and standard deviation

In order to examine the relationship between ion beam intensity and deviation for the measurement of boron isotopes by applying static multicollection and peak jumping methods, 1 μg of B sample was analyzed repeatedly with changing ion beam intensity. The standard deviation for the isotopic measurement is shown against the ion beam intensity of $m/z = 308$ in Fig. 2. Because the ion beam intensity

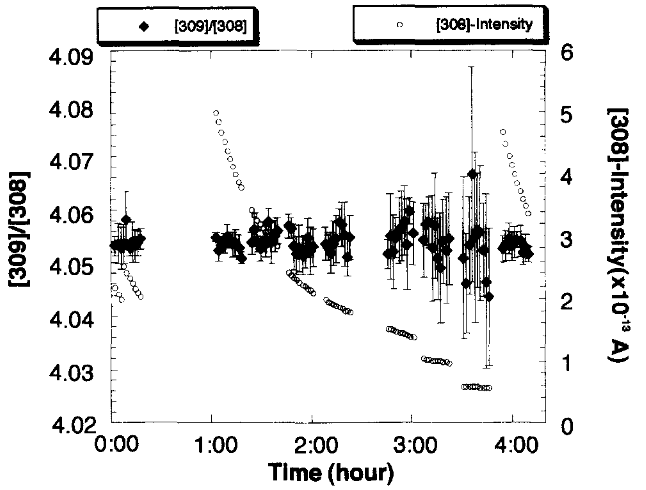

Fig. 3. Time vs. [309]/[308] ratio and intensity of [308] ion beam diagram. The plotted symbols show one block of data of [309]/[308] ratio (filled diamond) and intensity of [308] (open circle). The vertical bar shows the analytical error in standard deviation of each block ratio. The same 1 μg of B sample was measured repeatedly.

of $Cs_2BO_2^+$ decays to half of the starting ion currents by the end of data acquisition in the 1 μg B analysis within 45 min that is taken by the conventional peak jumping method, the standard deviation in $^{11}B/^{10}B$ analysis is given by using one block of data containing 10 scans. The ion beam intensity presented in Fig. 2 is a starting value in each block. The standard deviations decrease exponentially with increasing intensity and the standard deviations are essentially identical in terms of ion beam intensity between static collection and peak jumping method. This indicates that the linearity between ion beam intensity and sensitivity of Faraday cup with amplifier is properly maintained in the newly developed double Faraday cup collector package for $Cs_2BO_2^+$ ions. There appears to be a sharp increase of standard deviation at an ion beam intensity of less than $2 \times 10^{-13}$ A at $m/z = 308$, and the deviation is fairly constant at less than 0.1% when the ion beam intensity exceeds $2 \times 10^{-13}$ A. Therefore, the ion beam intensity of $m/z = 308$ is required to be more than $2 \times 10^{-13}$ A for precise isotopic measurement of boron.

### *3.2. Relationship between intensity and isotope ratio*

The relationship between ion beam intensity and isotope ratio ($^{11}B/^{10}B_{meas}$) was investigated by doing repeat analysis of the same 1 μg of B sample (NIST SRM 951). Fig. 3 illustrates the change in ion beam intensity within the same sample run, as well as the measured isotopic ratio vs. time. In this experiment, ion beam intensity was arbitrarily increased by increasing filament current during a long run exceeding 4 h, and the isotopic compositions of each block were measured. In the range of intensity investigated from $0.5 \times 10^{-13}$ to $5 \times 10^{-13}$ A, there is no difference in isotopic ratio within the analytical error in each block, though deviation of isotope ratios and individual block errors increase with decreasing intensity. Moreover, no significant isotopic fractionation is observed within the same sample run during 4 h. This indicates that the boron isotope ratio obtained by static multicollection is not affected by the ion beam intensity at least in the observed range. It is, therefore, suggested that ion beam intensity can be changed by changing filament current during data acquisition, i.e. between the blocks.

### *3.3. Relationship between boron amount and the isotope ratio*

NIST SRM 951 was also repeatedly analyzed with varying amounts of B from 0.05 to 1 μg. Ion beam

Table 1
Boron sample size and $^{11}B/^{10}B_{corr}$ ratios of NIST SRM 951 collected in 10 blocks for single run

| No. | $^{11}B/^{10}B_{corr}$ | $2\sigma_{mean}$ |
|---|---|---|
| 1 μg of boron | | |
| 1 | 4.0531 | 0.0002 |
| 2 | 4.0527 | 0.0003 |
| 3 | 4.0539 | 0.0003 |
| 4 | 4.0539 | 0.0003 |
| 5 | 4.0539 | 0.0003 |
| 6 | 4.0533 | 0.0003 |
| 7 | 4.0521 | 0.0003 |
| 8 | 4.0519 | 0.0005 |
| 9 | 4.0523 | 0.0005 |
| 10 | 4.0526 | 0.0004 |
| 11 | 4.0538 | 0.0006 |
| 12 | 4.0523 | 0.0005 |
| 13 | 4.0523 | 0.0005 |
| 14 | 4.0513 | 0.0004 |
| 15 | 4.0512 | 0.0005 |
| 16 | 4.0541 | 0.0002 |
| 17 | 4.0528 | 0.0003 |
| 18 | 4.0519 | 0.0005 |
| Average | 4.0528 | 0.0004 |
| 0.1 μg of boron | | |
| 1 | 4.0537 | 0.0008 |
| 2 | 4.0515 | 0.0007 |
| 3 | 4.0522 | 0.0006 |
| 4 | 4.0540 | 0.0006 |
| 5 | 4.0537 | 0.0005 |
| 6 | 4.0534 | 0.0004 |
| 7 | 4.0507 | 0.0006 |
| Average | 4.0528 | 0.0010 |
| 0.05 μg of boron | | |
| 1 | 4.0476 | 0.0015 |
| 2 | 4.0468 | 0.0031 |
| 3 | 4.0456 | 0.0028 |
| 4 | 4.0434 | 0.0027 |
| Average | 4.0459 | 0.0018 |

intensities of $m/z$ = 308 for 0.05 and 0.1 to 1 μg were more than $4 \times 10^{-14}$ and $2 \times 10^{-13}$ A, respectively, at the beginning of data acquisition. One hundred ratios were collected in 10 blocks for a single run taking approximately 20 min, including a gain calibration of amplifier. The corrected $^{11}B/^{10}B$ ratios ($^{11}B/^{10}B_{corr}$) for oxygen isotopes are given in Table 1, and are shown in Fig. 4. For the sample size of 0.1 and 1 μg, the isotope ratios obtained are scattered within ±0.03% relative standard deviation (RSD), although some deviate with exceeding analytical precision. On the other hand, the ratios of 0.05 μg sample size are clearly lower than those of large sample size analysis. This manner is the same (see Table 2) as observed in [10]. In the measurement for 0.05 μg of sample size, the ion beam intensity of $m/z$ = 308 could not increase to $2 \times 10^{-13}$ A, and the ion beam intensity decayed rapidly during data collection, causing an increase of analytical errors. Such a rapid decay could cause a peculiar mass fractionation for small sample size during the increase of filament current before data acquisition. These observations indicate that the sample size of 0.1-μg B is the critical minimum amount to get the precise boron isotopic measurement in this multicollection mass spectrometry with analytical error better than 0.02%, and also may suggest that this sample size is close to a limit of capability in the boron isotopic analysis by using the $Cs_2BO_2^+$ method with TIMS.

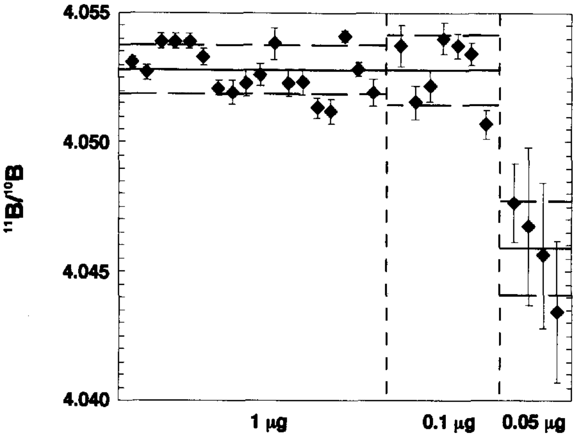

Fig. 4. Boron sample size and isotopic ratio ($^{11}B/^{10}B$) of SRM 951. The plotted symbols show the isotopic ratio for one run. The vertical bar and horizontal broken line shows the analytical error in $2\sigma_{mean}$ of each run and reproducibility (RSD), respectively.

### 3.4. Analytical precision, reproducibility, and accuracy

The analytical precision ($2\sigma_{mean}$) for 10 blocks of data collection in the individual runs of 1, 0.1, and 0.05 μg of B sample size are given in Table 1 and the

Table 2
Summary of some precisions and reproducibilities reported for boron isotopic analysis of SRM 951 boric acid standard by PTIMS by using the $Cs_2BO_2^+$ method

| Reference | Sample size ($\mu$g) | Replicates | Mean value $^{11}B/^{10}B$ | Mean value $2\sigma_{mean}$ | Precision for individual run $2\sigma_{mean}$(%) | Reproducibility $2\sigma_{mean}$(%) |
|---|---|---|---|---|---|---|
| Spivack and Edmond (1986) | 1–5 | 12 | 4.04558 | ± 0.00097 | 0.019[a] | 0.024 |
| Xiao et al. (1988) | 3 | 5 | 4.05083 | ± 0.00079 | 0.007[b] | 0.019 |
| | 1 | 5 | 4.05091 | ± 0.00044 | 0.010[b] | 0.011 |
| | 0.5 | 5 | 4.05122 | ± 0.00064 | 0.007[b] | 0.016 |
| | 0.1 | 5 | 4.05078 | ± 0.00018 | 0.008[b] | 0.004 |
| | 0.05 | 4 | 4.04860 | ± 0.00150 | 0.010[b] | 0.037 |
| Nakamura et al. (1992) | 0.1–1 | 15 | 4.0512 | ± 0.0004 | 0.012[a]<br>(0.007–0.019) | 0.009 |
| Leeman et al. (1991) | 1 | 7 | 4.05339 | ± 0.00040 | 0.009[a]<br>(0.001–0.013) | 0.010 |
| This study | 1 | 18 | 4.0528 | ± 0.0004 | 0.009[a] | 0.011 |
| | 0.1 | 7 | 4.0528 | ± 0.0010 | 0.014[a] | 0.024 |
| | 0.05 | 4 | 4.0459 | ± 0.0018 | 0.063[a] | 0.045 |

[a] Average value.
[b] Median value.

results are compared in Table 2 with those of peak jumping methods investigated in the previous studies. The precision in the individual runs for 1, 0.1, and 0.05 $\mu$g of B sample size are ±0.0002 to 0.0006 (0.005 to 0.015%), 0.0004 to 0.0008 (0.010 to 0.020%), and 0.0015 to 0.0031 (0.038 to 0.076%), respectively.

The $2\sigma_{mean}$ values of repeat analyses (reproducibility) of 1, 0.1, and 0.05 $\mu$g sample size are also shown in Table 1. The mean values and reproducibility ($2\sigma_{mean}$) for 1, 0.1, and 0.05 $\mu$g of B sample size are 4.0528 ± 0.0004, 4.0528 ± 0.0010, and 4.0459 ± 0.0018, respectively. The analytical precision and reproducibility are in good agreement with those of previous works (Table 2). Analytical precision of individual runs were sometimes better than the analytical reproducibility. Practically, precision for individual runs need not be better than reproducibility. Therefore, precision for individual runs for 0.1 $\mu$g of sample size requires 0.024% ($2\sigma_{mean}$). Fig. 5 illustrates the relationship between the number of blocks and analytical error [$2\sigma_{mean}$ (%)] in six different 1 $\mu$g of sample size and three different 0.1 $\mu$g of sample size analyses. The analytical error decreases with increasing number of blocks, and a sharp increase in $2\sigma_{mean}$ (%) = 3 blocks is clear. Therefore, three blocks are practically enough to measure precisely the boron isotope ratio for 0.1 to 1 $\mu$g of sample size, when analytical reproducibility is taken into account. Table 3 shows the precision of three blocks of data for

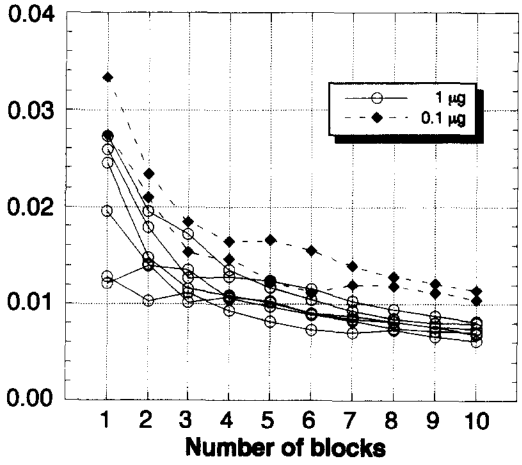

Fig. 5. Number of blocks vs. analytical precision [$2\sigma_{mean}$ (%)] diagram. Open circle and filled diamond represent the runs of 1 and 0.1 $\mu$g sample size of boron, respectively. The ion beam intensity of [308] for 1 and 0.1 $\mu$g of boron at the beginning of data acquisition were more than 5 × $10^{-13}$ and 4 × $10^{-13}$ A, respectively.

Table 3
Boron sample size and $^{11}B/^{10}B_{corr}$ ratios of NIST SRM 951 collected in three blocks for a single run

| No. | $^{11}B/^{10}B_{corr}$ | $2\sigma_{mean}$ |
|---|---|---|
| 1 μg of boron | | |
| 1 | 4.0532 | 0.0004 |
| 2 | 4.0524 | 0.0005 |
| 3 | 4.0545 | 0.0007 |
| 4 | 4.0540 | 0.0005 |
| 5 | 4.0543 | 0.0005 |
| 6 | 4.0539 | 0.0005 |
| 7 | 4.0528 | 0.0004 |
| 8 | 4.0526 | 0.0006 |
| 9 | 4.0517 | 0.0008 |
| 10 | 4.0526 | 0.0006 |
| 11 | 4.0538 | 0.0010 |
| 12 | 4.0526 | 0.0010 |
| 13 | 4.0515 | 0.0009 |
| 14 | 4.0518 | 0.0007 |
| 15 | 4.0520 | 0.0007 |
| 16 | 4.0545 | 0.0003 |
| 17 | 4.0528 | 0.0004 |
| 18 | 4.0520 | 0.0008 |
| Average | 4.0529 | 0.0005 |
| 0.1 μg of boron | | |
| 1 | 4.0550 | 0.0017 |
| 2 | 4.0525 | 0.0011 |
| 3 | 4.0525 | 0.0010 |
| 4 | 4.0547 | 0.0011 |
| 5 | 4.0534 | 0.0008 |
| 6 | 4.0544 | 0.0006 |
| 7 | 4.0519 | 0.0013 |
| Average | 4.0535 | 0.0009 |

individual run and the reproducibility for 1- and 0.1-μg sample size. The values are essentially identical with the values for 10 blocks (Table 1).

Our averaged $^{11}B/^{10}B$ value of NIST SRM 951 for 1 and 0.1 μg of B is significantly higher than the certified value of 4.04362 ± 0.00137 [21] and those of 4.045–4.046 obtained by using the $Cs_2BO_2^+$ method without graphite [7, 9]. However, the $R_{certified}/R_{measured}$ ratio of 0.99773 for $^{11}B/^{10}B$ is identical within analytical errors to the previous results (0.99833 [10] and 0.99812 [11]) determined by the $Cs_2BO_2^+$ method with graphite. Thus, this study also supports that the higher $^{11}B/^{10}B$ ratio is a characteristic of $Cs_2BO_2^+$-graphite method [11].

No difference was observed within the analytical errors between the results obtained by peak jumping method (4.0531 ± 0.0023; $n = 4$) and static multicollection method (4.0528 ± 0.0010; Table 1). This indicates that the Faraday cup efficiencies (FCE) of these cups are essentially identical as reported by Makishima and Nakamura [22] with relative FCE factors ranging 0.99999–1.00001 for normal Faraday cups in MAT 261. It is, therefore, confirmed that the higher $^{11}B/^{10}B$ ratio observed in graphite loading method is not due to the differences in the cup efficiencies of the two Faraday cups.

### 3.5. Acquisition time

Typically, one isotopic measurement run took 20 min including the gain calibration for 10 blocks (100 ratio values) in the multicollection method. This acquisition time is shorter than half of the works [10, 11] done previously. Moreover, the number of blocks can be reduced to three, which will make the acquisition time even shorter. And the gain factors can use old values, since the deviation of gain factors is negligibly small as 0.0002% ($2\sigma_{mean}$). Therefore, acquisition time for three blocks without the gain calibration can be reduced to 5 min. In the measurement for 0.1 μg of sample size, the ion beam intensity of $m/z = 308$ is difficult to raise up to $5 \times 10^{-13}$ A, and if it does so, the ion beam intensity decays rapidly during data collection (Sample A in Fig. 6). So it is not easy to measure an isotope ratio of 0.1 μg of sample size by the peak jumping method as it requires 45 min for acquisition. However, the static multicollection technique established in this study can facilitate boron isotope measurement in a difficult condition like a small sample size.

## 4. Conclusions

We have established the conditions for precise boron isotopic measurement using the multicollection technique at PML, Misasa. This technique enables us to do speedy analysis of boron isotopes by using the $Cs_2BO_2^+$-graphite method with mannitol as it reduces the acquisition time to 5 min. Therefore, reducing

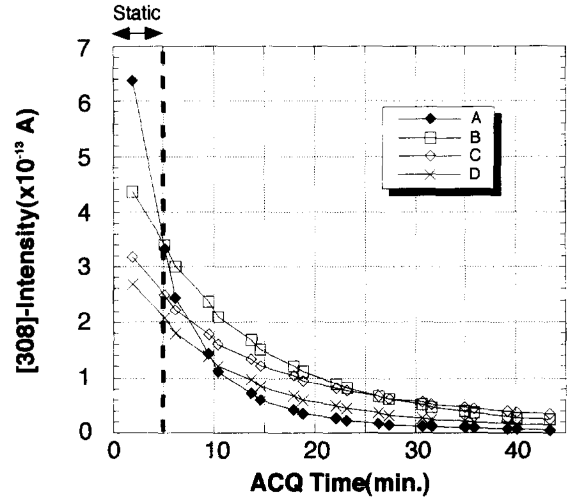

Fig. 6. Acquisition time vs. intensity of [308] ion beam diagram for 0.1 $\mu$g of sample size. The vertical dashed line shows acquisition (ACQ) time of static mode with data of three blocks without gain calibration.

acquisition time, the static multicollection technique makes it easier to measure a small sample size as low as 0.1 $\mu$g of boron, and will extend the application of boron isotopes to boron-poor silicate samples such as mafic minerals, mantle materials, and meteorites.

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