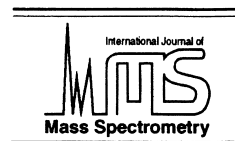




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Improvements of boron isotope analysis by positive thermal ionization mass spectrometry using static multicollection of Cs_2BO_2^+ ions

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Abstract

A static double collector system in the Finnigan-MAT 262 thermal ionization mass spectrometer was used to analyse different amounts of the boric acid standard NBS SRM 951 and natural samples. The main objectives of the study were to improve precision and accuracy of B isotope measurement, and to define the critical minimum amount of B for both standards and natural silicatic samples with which stable signals, and hence reliable measurements are obtained. A series of analyses were carried out using 1 μg , 100, 50, and 25 ng B for each NBS SRM 951 measurement, and 1 μg , 100, and 50 ng for measurement of natural silicatic samples. Stable runs could be obtained with this double collector package for both, the standard SRM 951 and for natural samples containing 100 ng of B on the filament. The internal analytical precision of measured $^{11}\text{B}/^{10}\text{B}$ ratios of 100 ng NBS SRM 951 boric acid is $\pm 0.006\%$. The reproducibility ($2\sigma_{\text{mean}}$) is $\pm 0.0002\%$, equivalent to an external uncertainty of 0.024%, both of which are more precise than previously published results from static measurements. Natural samples (two hemipelagic clays) analysed with 100 ng of B have an internal analytical precision of 0.009%–0.01% and a reproducibility ($2\sigma_{\text{mean}}$) of $\pm 0.004\%$ –0.007%, respectively. The external reproducibility for natural samples is $\pm 0.11\%$ –0.16‰, which demonstrates that the isotope ratio of small amounts of natural samples with low B contents can be measured reliably. Although smaller B concentrations of 50 ng have been measured with higher precision than that from earlier studies, the results of this study are in favour of 100 ng B being the optimum amount for static (multicollection) positive thermal mass spectrometry measurements. Given that the availability of B is often limited (i.e. trace contents) in natural samples, the precision gained with only 100 ng B can be viewed as a significant improvement in B isotope analysis. (Int J Mass Spectrom 206 (2001) 79–89) © 2001 Elsevier Science B.V.

Keywords: Boron isotope analysis; Positive TIMS; Static multicollection; Cs_2BO_2^+ ions; Small sample sizes

1. Introduction

Considering the boron analysis over the previous years, rapid improvements in analytical methods were gained. Positive thermal ionization mass spectrometry

(PTIMS) is considered to be the most precise method for B measurements with a precision of 0.1‰–0.4‰ e.g., [1,2]. However, the method of boron extraction of silicates is very time consuming, and extreme attention is required to avoid potential boron losses and/or contamination by boron of the ambient air. Boron isotopic analyses for silicatic rocks are therefore still scarce e.g. [2,3], especially for sample sizes

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<1 μg B. Also, it is difficult to assess interlaboratory biases as different boron extraction methods are used and no international rock standard has been employed [4]. For comparison, the negative thermal ionization mass spectrometry (NTIMS) method allows analysis in the nanogram range, e.g. [5], and in addition, samples can generally be measured directly. However, the NTIMS method has a lower $2\sigma_{\text{mean}}$ precision of between $\pm 1\%$ – 2% [6] and $\pm 0.5\%$ [7]. Nevertheless, NTIMS is not suitable for the analysis of silicatic rocks, as large isobaric mass interferences at $m/z = 42$ of CNO^- complexes are caused by organic material (e.g. from ion exchange resin and mannitol [8]). The Cs_2BO_2^+ method is usually applied for PTIMS, e.g. [3,9,10], because high mass numbers ($m/z = 308$ and 309) keep fractionation negligible. Good results were already obtained in earlier studies for sample sizes of $\sim 1 \mu\text{g}$ B, e.g. [2,3,9,11,12]. Also, some studies exist where smaller sample sizes of the SRM 951 (below $1 \mu\text{g}$ and as low as 50 ng of B) were analysed successfully, e.g. [4,8,10]. However, the only experimental studies analysing Cs_2BO_2^+ statically employing the multicollection technique have been published by Zuleger [12] and Nakano and Nakamura [8]. These studies only dealt with the analyses of SRM 951.

2. Compilation of previous studies

Due to the small relative mass difference between $m/z = 308$ and $m/z = 309$, simultaneous data collection was not possible with conventional multicollection mass spectrometers. Thus, several studies examined different sample concentrations, with dynamic data collection. Data acquisition time for $1 \mu\text{g}$ of B takes approximately 45 min [8] when data are collected in a single Faraday cup [2,10]. However, data acquisition should be kept short, because a decreasing ion beam is characteristic for the Cs_2BO_2^+ method. Hence, the multicollection method is superior to single data collection for small sample sizes with rapidly decaying signals [8]. Nakano and Nakamura [8] carried out the first study with varying sample concentrations (Table 1), which employed a double Faraday cup collector, especially developed for Cs_2BO_2^+ -ion mea-

surements. These authors considered 100 ng of B to be the critical minimum for precise B analyses with multicollection.

3. Experimental methods and mass spectrometry

3.1. Sample preparation

The procedure of the sample preparation is based on Nakano and Nakamura [8] with slight modifications. Sufficient sample was used to provide at least 100 ng of B for an individual analysis. Typically, 100 mg of powdered sample were digested with 30 M hydrofluoric acid (HF) in the presence of mannitol to prevent the volatilization of B. The liquid containing the B was evaporated on a hot plate after each step, at temperatures ranging from 60 to $65 \text{ }^\circ\text{C}$. Extreme care was taken to remove the sample from the hot plate when just dry to prevent potential B losses caused by continued heating. To remove cationic and anionic contaminants, one cation exchange and at least four anion exchanges were carried out. After the final ion exchange, a cesium–mannitol solution is added to the sample to get a B/Cs mole ratio of 2, and a B/mannitol ratio of $1/40$ by weight, respectively. For the boric acid standard SRM 951, a solution containing the required amount of B was prepared and CsCO_3 was added in the quantities described above. For mass spectrometry, samples were loaded on single tantalum (Ta) filaments. Prior to sample loading, the Ta filaments were degassed and allowed to oxidize for three days, protected from outside contamination in a plastic box. Compared to previous studies, e.g. [11,13], the loading procedure was slightly modified: First, the top of the filament was coated with the sample dissolved in $2 \mu\text{L}$ of distilled water and dried at 1.2 A . Before complete dryness, $1 \mu\text{L}$ of graphite–ethanol–water slurry (40 mg graphite/ml) was added to make a sample–graphite mixture. The filament was heated until the sample evaporated to dryness. The samples were then kept under an infrared heating lamp to retain complete dryness until all samples were immediately loaded into the mass spectrometer.

Table 1

Summary of some previous work for SRM 951 PTIMS measurements; original data or data gathered directly from literature are shown in roman type and data recalculated by the author of this study, (based on published results from literature) are presented in italics

Reference	Data collection	Sample size (μg)	Replicates	Mean value $^{11}\text{B}/^{10}\text{B}$	Internal precision for individual run		External reproducibility (sample)	
					$2\sigma_{\text{mean}}$ relative (%)	$2\sigma_{\text{mean}}$ absolute	$2\sigma_{\text{mean}}$ absolute	$2\sigma_{\text{mean}}$ relative (%)
A [3]	Dynamic	1–5	12	4.045 58	$\pm 0.019^{\text{a}}$	<i>0.000 77</i>	<i>0.000 28</i> (0.000 33) ^c	<i>0.007</i>
[10]	Dynamic	... ^d	10	4.050 4	$\pm 0.100^{\text{b}}$	<i>0.000 70</i>
		3	5	4.050 83	$\pm 0.007^{\text{b}}$	<i>0.000 35</i>
		1	5	4.050 91	$\pm 0.010^{\text{a}}$	<i>0.000 50</i>
		0.5	5	4.051 22	$\pm 0.007^{\text{b}}$	<i>0.000 35</i>
		0.1	5	4.050 78	$\pm 0.008^{\text{b}}$	<i>0.000 40</i>
		0.05	4	4.048 60	$\pm 0.010^{\text{b}}$	<i>0.000 40</i>
[2]	Dynamic	0.1–1	15	4.051 2	$\pm 0.012^{\text{b}}$	<i>0.000 47</i>	0.000 40	<i>0.009</i>
[11]	Dynamic	1	7	4.053 39	$\pm 0.009^{\text{a}}$	<i>0.000 36</i>	<i>0.000 40</i>	<i>0.010</i>
[4]	Dynamic	0.2–0.6	11	4.050 6	$\pm 0.009^{\text{a}}$	<i>0.000 37</i>	<i>0.000 24</i>	<i>0.006</i>
B [12]	Static	2	5	4.046 37	$\pm 0.009^{\text{a}}$	0.000 39
[8]	Static	1	18	4.052 8	$\pm 0.009^{\text{a}}$	<i>0.000 37</i>	0.000 40	0 011
		0.1	7	4.052 8	$\pm 0.015^{\text{a}}$ (0.014 ^a) ^e	<i>0.000 60</i>	0.000 97	0.024
		0.05	4	4.045 9	$\pm 0.063^{\text{a}}$	<i>0.002 53</i>	0.001 83	0.045
C This study	Static	1	7	4.053 03	$\pm 0.005^{\text{a}}$	0.000 18	0.000 34	0.008
		0.1	19	4.052 42	$\pm 0.003^{\text{a}}$	0.000 12	0.000 23	0.006
		0.05	4	4.052 26	$\pm 0.003^{\text{a}}$	0.000 11	0.000 76	0.019
		0.025	4	4.050 40	$\pm 0.008^{\text{a}}$	0.000 29	0.002 05	0.051

(continued on next page)

3.2. Mass spectrometer and mass spectrometry

The Finnigan-MAT 262 (Finnigan, Bremen, Germany) is equipped with a double Faraday collector system with fixed spacing, to be used for the static analyses of Cs_2BO_2^+ . This mode allows isotope collection simultaneously, and no corrections for signal drifts need to be performed. Hence samples with unstable or poor emission are analysed more precisely, because signal variations occur on both collectors at the same time. The accelerating voltage is reduced from 10 to 8 kV. The Faraday cup collectors were used with a $10^{-11} \Omega$ feedback resistor and are automatically calibrated for amplifier gain, prior to analysis. For measurement of boron isotope ratios, the Cs_2BO_2^+ method of Nakano and Nakamura [8] was

applied with slight modifications. Most importantly, the heating procedure was modified, and is therefore described in more detail. When the vacuum reached 7×10^{-8} mbar, the filament current was quickly raised to 0.3 A, followed by a gradual increase of 0.050 A min^{-1} up to 1.1 A. At this current, the Cs^+ signal could usually be detected on the Faraday cup, and was used to focus the ion beam. The filament current was then increased in smaller increments of 15 mA min^{-1} until a Cs_2BO_2^+ signal became detectable ($m/z=309$). At an ion beam intensity of 1×10^{-11} , the ion beam was focused again and the measurement was started when the beam was stable or slowly decreasing. At this time, the filament current ranged typically around 1.2–1.3 A. This current corresponds to a temperature below 600 °C, which is too low to be detected by the

Table (continued)

VI	VII	VIII	IX	X	XI
External reproducibility (population)		External uncertainty (sample)		External uncertainty (population)	
$2\sigma_{\text{mean}}$ absolute	$2\sigma_{\text{mean}}$ relative (%)	$2\sigma_{\text{mean}}$ absolute	$2\sigma_{\text{mean}}$ relative (%)	$2\sigma_{\text{absolute}}$	$2\sigma_{\text{relative}}$ (%)
0.000 27	0.007	0.000 98	0.024	0.000 94	0.023
0.000 14	0.003	0.000 43	0.011
0.000 79	0.019	0.001 76	0.043
0.000 44	0.011	0.000 98	0.024
0.000 64	0.016	0.001 44	0.036
0.000 20	0.005	0.000 40	0.010
0.001 50	0.037	0.003 00	0.074
0.000 34	0.008	0.001 40	0.035	0.001 37	0.034
0.000 37	0.009	0.001 10	0.026	0.000 99	0.024
0.000 21	0.005	0.000 78	0.019	0.000 74	0.018
...
0.000 40	0.010	0.001 84	0.045	0.001 84	0.044
0.000 90	0.022	0.002 56	0.063	0.002 37	0.059
0.001 60	0.039	0.003 66	0.090	0.003 17	0.078
0.000 32	0.008	0.000 89	0.022	0.000 84	0.021
0.000 22	0.005	0.000 99	0.024	0.000 96	0.024
0.000 66	0.016	0.001 52	0.038	0.001 32	0.032
0.001 78	0.044	0.004 11	0.101	0.003 56	0.088

^a Average value.

^b Median value.

^c [3] states that 2σ standard deviation is 0.000 33, but it is unclear, if it is referred to the external uncertainty, as numbers in this table do not match 0.000 33.

^d Not possible to recalculate as individual measurements were not provided.

^e Original data from [8]. Columns IV, V, VIII, and IX: standard deviation calculated based on a sample ($n - 1$) and columns VI, VII, X, and XI: standard deviation calculated based on the entire population (n).

optical pyrometer. Ratios of $^{11}\text{B}/^{10}\text{B}$ are measured in blocks of 20 individual ratios (scans) and measurements were envisaged to be optimal when reaching a standard mean deviation ($2\sigma_{\text{mean}}$) of at least 0.01% for the standard, and 0.015% for natural samples. This analytical precision was often reached after three blocks (60 scans) for a single run, but sometimes up to five blocks (100 scans) were measured, corresponding to a data acquisition time of 15–25 min. Peak centering is performed for each isotope at the beginning of each block. Isotope ratios are collected by measuring masses of 309 and 308 for 4 s and the baseline is determined at a mass of 306.5.

4. Data reduction

$^{11}\text{B}/^{10}\text{B}$ ratios measured were routinely corrected for oxygen isotopes (^{17}O), following Spivack and Edmond [3]: $(^{11}\text{B}/^{10}\text{B}_{\text{corrected}}) = (^{11}\text{B}/^{10}\text{B}_{\text{measured}}) - 0.00079$. The oxygen corrected results from natural samples are then normalized to that of SRM 951 ($^{11}\text{B}/^{10}\text{B} = 4.05163$) to facilitate interlaboratory comparisons, and are reported as $\delta^{11}\text{B}$ in permil (‰) deviation from the standard (SRM 951 boric acid), as follows: $\delta^{11}\text{B} = 1000([R_{\text{sample}}/R_{\text{standard}}] - 1)$.

The reported ratios are based on block averages of 20 scans. Single run data were corrected for outliers

Table 2
Summary of some previous work of analytical reproducibility for natural samples

Reference	Sample	Sample size (μg)	$\delta^{11}\text{B}(\text{‰})$	External uncertainty	External reproducibility	External reproducibility
				2σ (‰)	$2\sigma_{\text{absolute}}$	$2\sigma_{\text{mean}}$ (%)
[2]	JB-2	~1	7.08	± 0.19	0.000 76	0.009
[4]	JB-2	4–1.5	7.23	± 0.49	0.002 00	0.014
This study	1 clay	0.1	2.36	± 0.16	0.000 59	0.007
	2 clay	0.1	3.01	± 0.11	0.000 44	0.005

using the two-sigma-criterion. Estimates of precision vary considerably in the literature (i.e., onefold or twofold standard deviation (σ) is given, or the standard deviation of the mean ($2\sigma_{\text{mean}}$ is used)). Another discrepancy between previous presentations is the calculation of the standard deviation. Either, it is based on the entire population (n), or it is based on a sample ($n-1$). In general, due to the use of ($n-1$) instead of (n), results give slightly higher errors when small data sets are regarded. Nevertheless, for small data sets ($n < 20$) the use of ($n-1$) gives a better estimate of σ [14]. In this study, either way of calculation is given to allow intercomparison of all results gathered from literature (see Table 1, and explanations in the caption). The external uncertainty (2σ) and the external reproducibility (as two mean standard deviations of the mean; i.e. $2\sigma_{\text{mean}}$) are reported both as absolute and relative (%) numbers. Comparisons between different methods are based on published analyses of SRM-951 (Table 1) and natural samples (Table 2) which were recalculated if required.

5. Results and discussion

5.1. Filament loading and signal intensities

Some key improvements of B isotope measurement appear to be related to the sample loading technique onto the filament and to the heating procedure of the sample in the TIMS. Consequently, these two procedures were varied to optimise the precision of the results.

As previously reported [4,8,11], in the common loading procedure the filament was coated by 1 μL of

graphite–ethanol mixture, and the sample was loaded on the graphite layer. In this study, however, the sample was loaded first, followed by the graphite. This loading procedure yielded better results (Table 1). In the first case, the Cs_2BO_2^+ signal was less stable, fractionation occurred, and consequently, precision was almost two orders of magnitudes worse ($2\sigma_{\text{mean}} = 0.014\%$, Table 3). Hence, to guarantee precise analysis of small sample sizes (see Sec. 5.2, and Table 1) the graphite mixture was loaded onto the filament after the sample.

Another interesting finding was the generally better signal stability when the sample was loaded first. This allowed isotope analyses with signal intensities of up to 4×10^{-11} A ($m/z = 309$, i.e. a signal of about 1×10^{-11} A for $m/z = 308$). The ion beam remained stable over more than ten blocks (i.e. about an hour). Also, very stable runs were obtained for the standard SRM 951 (between 0.001% and 0.002% internal precision, $2\sigma_{\text{mean}}$), which hardly showed any fractionation (see Table 4). At ion beam intensities of 1×10^{-11} A ($m/z = 309$), the internal precision was usually between 0.001% and 0.007% (average 0.003%, $2\sigma_{\text{mean}}$). This intensity is approximately one order of magnitude higher than previously reported by Nakano and Nakamura [8] (Fig. 1). Vice versa, considerably lower $^{11}\text{B}/^{10}\text{B}$ ratios and decaying signal stabilities were observed when the graphite was loaded first, which probably resulted from fractionation during heating. This coincides with problems reported in Nakano and Nakamura [8], where a quickly decaying signal during analysis of 100 ng B in SRM 951 has been described. These authors stated that a signal of $m/z = 308$ was difficult to raise up to 5×10^{-13} A with their multicollecion method. If

Table 3
NBS SRM 951 standard, graphite loaded first

Sample No.	$^{11}\text{B}/^{10}\text{B}$ measured	$2\sigma_{\text{mean}}$ (%) relative	$2\sigma_{\text{mean}}$ absolute	$^{11}\text{B}/^{10}\text{B}$ corrected for ^{17}O
1	4.015 242	0.029	0.0012	4.014 452
2	4.045 062	0.022	0.0009	4.044 272
3	4.039 245	0.045	0.0017	4.038 455
4	4.045 520	0.022	0.0009	4.044 730
Average	4.036 267	0.030	0.0012	4.035 477
$2\sigma_{\text{absolute}}$				0.029
External uncertainty (%)				0.71
$2\sigma_{\text{mean}}$				0.014
Reproducibility 2σ mean (%)				0.35

raised to this intensity, they also reported that the ion beam decayed rapidly. However, the general observation of this study is, that a signal intensity of 1×10^{-11} A ($m/z=309$; and approximately 2.5×10^{-12} A for $m/z=308$), can be obtained for sample and standard without difficulty. Repeat analyses of SRM 951 yielded no significant changes in measured ratios when using different ion beam intensities (see Table 4). For natural samples, higher ion beam intensities than 1×10^{-11} A ($m/z=309$) could not be obtained easily probably due to matrix effects, and a stable signal could not be kept up long enough to get an acceptable run. Natural samples worked best at 1×10^{-11} A to 2×10^{-12} A. Therefore, standard measurements were conducted at 1×10^{-11} A to allow comparison of SRM 951 and natural samples, as temperature was not detectable by the optical pyrometer. As a result of the collection of 60–100 scans (three to five blocks), static data acquisition in this study is more durable than previously reported for the multicollection method [8]. Isotopic analyses sometimes took a few scans to stabilize and reach a plateau with negligible fractionation (Fig. 2). When reaching the plateau, data acquisition was continued for three more blocks. Once the signal stabilised, the following analyses were generally of higher quality. Therefore, a longer duration of data acquisition time was preferred, as results improved with time.

5.2. Results and analytical precision and reproducibility for SRM 951 standard

Analyses with sample concentrations of 1 μg , 100, 50, and 25 ng B for each measurement were conducted (Tables 1 (Part C) and 4 and Fig. 3). Seven samples of 1 μg B in SRM 951 were analysed to check for systematic biases in the isotopic ratios when measuring different B contents. For these samples, ratios were slightly higher than for 100, 50, and 25 ng B in SRM 951. For 1 μg the ion beam took longer to stabilize than for smaller sample concentrations. At least five blocks, (i.e. 100 scans) were measured until the ion beam stabilised and the internal precision was better than 0.01% ($2\sigma_{\text{mean}}$). Analytical precision of the averaged $^{11}\text{B}/^{10}\text{B}$ ratio is 4.05224 ± 0.0003 ($2\sigma_{\text{mean}}$) and the reproducibility is 0.008% ($2\sigma_{\text{mean}}$) which corresponds to an external uncertainty of 0.022%. 19 analyses of 100 ng NBS SRM 951 were carried out. Typically the measurement of three blocks (60 scans) was enough to reach an internal precision better than 0.01% ($2\sigma_{\text{mean}}$). A slightly lower ratio of 4.05163 ± 0.0002 ($2\sigma_{\text{mean}}$), but a better in-run precision (of 0.003%) was obtained for 100 ng of B per measurement. The reproducibility of 0.006% ($2\sigma_{\text{mean}}$) and external uncertainty (2σ) of 0.024% are similar to the results of 1 μg . 50 ng of B gave a similar $^{11}\text{B}/^{10}\text{B}$ ratio to 100 ng of 4.05147 ± 0.0008 ($2\sigma_{\text{mean}}$),

Table 4
Boron isotope analyses of NBS SRM 951

Sample No.	$^{11}\text{B}/^{10}\text{B}$ measured	$2\sigma_{\text{mean}}$ (%) relative	$2\sigma_{\text{mean}}$ absolute	$^{11}\text{B}/^{10}\text{B}$ corrected for ^{17}O	Intensity (10^{-11} A)
Sample size 1 μg					
1	4.053 042	0.002	0.000 10	4.052 252	1
2	4.053 021	0.009	0.000 19	4.052 231	1
3	4.053 509	0.004	0.000 18	4.052 719	1
4	4.052 851	0.003	0.000 10	4.052 061	1
5	4.053 663	0.007	0.000 25	4.052 873	1
6	4.052 751	0.006	0.000 24	4.051 961	1
7	4.052 352	0.004	0.000 18	4.051 562	
Average	4.053 027	0.005	0.000 18	4.052 237	
$2\sigma_{\text{absolute}}$				0.000 89	
External uncertainty (%)				0.022	
$2\sigma_{\text{mean}}$				0.000 34	
Reproducibility $2\sigma_{\text{mean}}$ (%)				0.008	
Sample size 100 ng					
1	4.051 880	0.002	0.000 06	4.051 090	1
2	4.052 127	0.001	0.000 05	4.051 337	4
3	4.051 897	0.002	0.000 03	4.051 107	4
4	4.053 506	0.001	0.000 06	4.052 716	4
5	4.052 504	0.002	0.000 10	4.051 714	0.1
6	4.053 161	0.002	0.000 17	4.052 371	0.1
7	4.052 603	0.002	0.000 06	4.051 813	1
8	4.051 897	0.007	0.000 26	4.051 107	1
9	4.052 324	0.005	0.000 17	4.051 534	1
10	4.052 324	0.005	0.000 21	4.051 534	1
11	4.051 905	0.002	0.000 07	4.051 115	1
12	4.053 037	0.002	0.000 06	4.052 247	1
13	4.053 152	0.003	0.000 10	4.052 362	1
14	4.052 200	0.006	0.000 24	4.051 410	1
15	4.051 905	0.007	0.000 25	4.051 115	1
16	4.052 731	0.003	0.000 10	4.051 941	1
17	4.052 222	0.003	0.000 11	4.051 432	1
18	4.052 479	0.002	0.000 10	4.051 689	1
19	4.052 167	0.003	0.000 11	4.051 377	1
Average	4.052 422	0.003	0.000 12	4.051 632	
$2\sigma_{\text{absolute}}$				0.000 99	
External uncertainty (%)				0.024	
$2\sigma_{\text{mean}}$				0.000 23	
Reproducibility $2\sigma_{\text{mean}}$ (%)				0.006	
Sample size 50 ng					
1	4.051 304	0.004	0.000 18	4.050 514	1
2	4.053 141	0.002	0.000 07	4.052 351	1
3	4.052 157	0.003	0.000 11	4.051 367	1
4	4.052 440	0.002	0.000 07	4.051 650	1
Average	4.052 261	0.003	0.000 11	4.051 471	
$2\sigma_{\text{absolute}}$				0.001 5	
External uncertainty (%)				0.038	
$2\sigma_{\text{mean}}$				0.000 76	
Reproducibility $2\sigma_{\text{mean}}$ (%)				0.019	
Sample size 25 ng					
1	4.0507 63	0.008	0.000 31	4.049 973	1
2	4.0514 13	0.007	0.000 25	4.050 623	1
3	4.0520 09	0.01	0.000 39	4.051 219	1
4	4.0474 15	0.008	0.000 19	4.046 625	1
Average	4.0504 00	0.008	0.000 28	4.049 610	
$2\sigma_{\text{absolute}}$				0.004 1	
External uncertainty (%)				0.101	
$2\sigma_{\text{mean}}$				0.002 05	
Reproducibility $2\sigma_{\text{mean}}$ (%)				0.051	

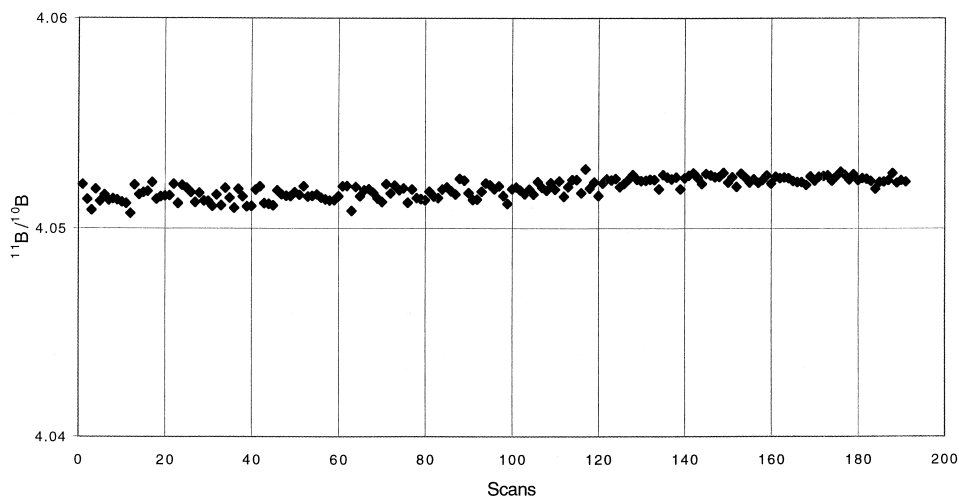


Fig. 1. Plotted symbols show isotope ratios vs. scans, representing a typical run for 100 ng of SRM 951 at an ion beam intensity of 1×10^{-11} A (mass 309), with an internal precision of 0.003% (2σ mean).

with a reproducibility of 0.019% ($2\sigma_{\text{mean}}$) and an external uncertainty of 0.038%. A small bias exists to a lower $^{11}\text{B}/^{10}\text{B}$ ratio for 25 ng of 4.04961 ± 0.0021 ($2\sigma_{\text{mean}}$) with a reproducibility of 0.051% ($2\sigma_{\text{mean}}$), and an external uncertainty of 0.101%, indicating that this amount is the minimum concentration to be measured on the double collector. Both, 50 and 25 ng did not run as stable as 100 ng, and at least five blocks (100 scans) had to be measured until the measurement

reached an internal precision of approximately 0.01% ($2\sigma_{\text{mean}}$). In summary, all measured $^{11}\text{B}/^{10}\text{B}$ ratios are significantly higher than the certified value of 4.04362 [15]. However, this shift corresponds well with other publications, where e.g. values of 4.0451 [4] and 4.04528 [8] were reported. The ratios $R_{\text{certified}}/R_{\text{measured}}$ of 0.99787 (1 μg) to 0.99852 (25 ng) are also in agreement with previous studies using the Cs_2BO_2^+ –graphite method (0.99773, [8]; 0.99812,

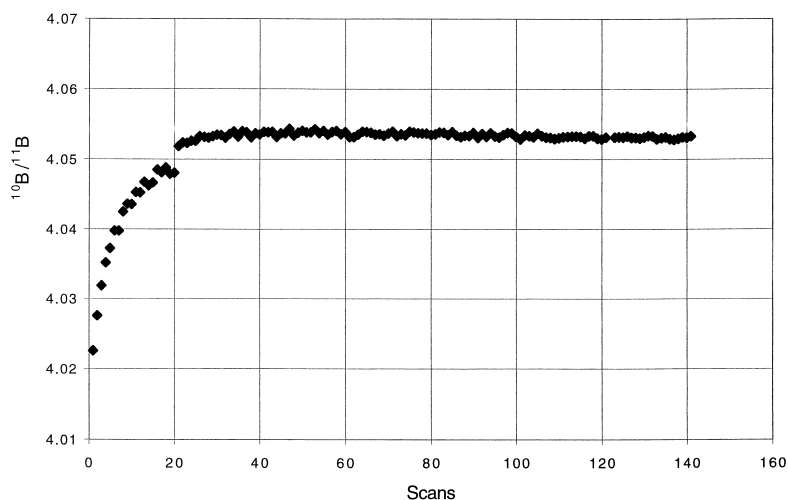


Fig. 2. Plotted symbols show isotope ratios vs. scans, representing a typical run for 100 ng of SRM 951. During the first block (20 scans) considerable fractionation occurs, stabilizing with time.

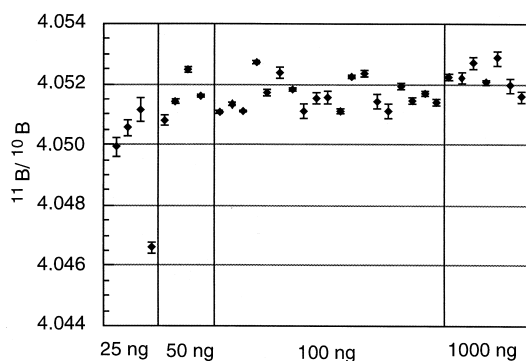


Fig. 3. Boron sample size and isotopic ratio ($^{11}\text{B}/^{10}\text{B}$) of SRM 951. The symbols show the averaged isotopic ratios for one block and the vertical bars show the analytical error $2\sigma_{\text{mean}}$ of each run.

[10]). $^{11}\text{B}/^{10}\text{B}$ ratios determined with the Cs_2BO_2^+ –graphite method seem to be systematically higher and therefore are a characteristic of the Cs_2BO_2^+ –graphite method [8]. Hence, 100 ng is considered to be the optimum amount of SRM 951 for isotopic measurements with Finnigan MAT 262 TIMS, gaining best results both in measurement precision and the shortest data acquisition time (approximately 15 min). Considering the averaged standard $^{11}\text{B}/^{10}\text{B}$ ratios and reproducibility, the results from this study are superior to previous results using multicollection [7,8], and better than [1,2,11] or similar to [4,10] results obtained by dynamic data collection (see Table 1). Moreover, data reported by Xiao et al. [10] were collected over a period of one week under highly reproducible conditions (as stated in Leeman et al. [11]), whereas data of this study were collected over a period of approximately one year. The internal analytical precision is better compared to previous studies, which owes to the improvements of the loading, heating, and measuring technique. As internal precision practically needs to be better than reproducibility, this requirement is met in this study. External reproducibility, on the opposite, is also influenced by changes within the TIMS with time. The broad use of the mass spectrometer for measuring different element systems, can cause lower cup efficiencies, deteriorating reproducibilities [16]. It can be safely assumed that even a better reproducibility might have been obtained if the analyses of this study

were carried out in a shorter period of time. The analysis of sample sizes as small as 25 ng B for a single PTIMS measurement has not been reported before. Despite the errors are reasonable, the results of this study suggest that 50 ng of B is the minimum amount for a reliable isotope analysis. For 25 ng B, analytical errors are significantly higher, and the $^{11}\text{B}/^{10}\text{B}$ ratio decreases.

In summary, the results show that 100 ng of B can be measured as precisely, or even more precisely, than larger amounts of B. This result is also supported by the results of Xiao et al. [10], who analysed 2–0.05 μg B, and also obtained the best results for 100 ng of B.

5.3. Analytical reproducibility of natural samples

For natural samples, sample sizes analysed during previous studies were reported to be typically over or $\sim 1 \mu\text{g}$ [2–4,9–11,17]. Therefore, it is difficult to compare the data quality of this study (using 100 ng of B) to literature data. As impurities in the boron extracted from natural silicate samples may contribute to poorer in-run precision, and as lower ion beam intensities might be caused from organic material derived from the ion-exchange resins [18], measurements of natural samples containing 100 ng of B did not run as well as the SRM 951 standard. Two natural samples (hemipelagic clays from the Costa Rican margin) were repeatedly analysed to reliably estimate the reproducibility for natural samples. These samples have average B contents of 60 ppm. Results from individually prepared (i.e. whole chemistry) replicate analyses, natural silicatic samples are listed in Table 4. Internal analytical precision of 0.004%–0.014% ($2\sigma_{\text{mean}}$), reproducibility of 0.005%–0.007% ($2\sigma_{\text{mean}}$) and external uncertainty of 0.011%–0.016% (2σ) obtained for the clays were not as accurate as the SRM 951 standard analyses without chemical treatment. Nevertheless, 100 ng of B were sufficient to obtain high quality data, and maintain the ion beam stable over five blocks and more. Data of silicatic samples in literature (were more than replicate analysis were carried out, or single measurements were listed), are very scarce and the only studies which can

Table 5
Analytical reproducibility for natural samples and standards put through full chemistry

Sample	Sample size	$^{11}\text{B}/^{10}\text{B}$ corrected for ^{17}O	Internal precision for individual run		$\delta^{11}\text{B}$
			$2\sigma_{\text{mean}}$ (%)	$2\sigma_{\text{mean}}$	
1. Hemipelagic clay	1 μg	4.060 69	0.014	0.000 58	2.24
	100 ng	4.061 62	0.010	0.000 55	2.46
	100 ng	4.061 16	0.007	0.000 28	2.35
	100 ng	4.061 26	0.011	0.000 58	2.38
	50 ng	4.061 16	0.009	0.000 38	2.35
	Average		4.061 18	0.010	0.000 47
2σ absolute		0.000 66			
External reproducibility (%)					0.16
2σ mean		0.000 3			
Reproducibility		0.007			
2. Hemipelagic clay	1 μg	4.063 722	0.013	0.000 54	2.98
	100 ng	4.064 201	0.004	0.000 18	3.10
	100 ng	4.063 887	0.004	0.000 18	3.02
	100 ng	4.063 623	0.008	0.000 31	2.96
	50 μg	4.063 805	0.010	0.000 40	3.00
	Average		4.063 848	0.009	0.000 47
2σ absolute		0.000 44			
External reproducibility (%)					0.11
2σ mean		0.0002			
Reproducibility 2σ mean (%)		0.005			
JB-2	100 ng	4.079 30	0.028	0.001 4	6.83
JB-2	100 ng	4.079 48	0.020	0.000 9	6.87
Average		4.079 39	0.240	0.001 2	6.85
SRM 951	100 ng	4.050 35	0.010	0.000 4	-0.32
SRM 951	100 ng	4.050 63	0.009	0.000 4	-0.25
Average		4.050 64	0.010	0.000 4	-0.28

be used for comparison are from Nakamura et al. [2] and Tonarini et al. [4]. Taking the $\delta^{11}\text{B}$ values for the calculation of the standard deviation (2σ) in permil these authors have lower external reproducibilities of 0.19‰ and 0.49‰, respectively, although, they used higher boron concentrations for their analysis (Table 2). To check for efficiency in the boron extraction, SRM 951 and the rock standard JB-2, were analysed twice (after processing through whole chemistry separately). The gained $^{11}\text{B}/^{10}\text{B}$ ratio for SRM 951 is slightly lower than for the standard without chemical treatment (Table 4). This effect was also observed by Tonarini et al. [4] and might be explained by small B losses, (i.e. fractionation during chemistry), or caused by organic compounds from the resin, lowering the isotopic ratio during data acquisition. JB-2 with a

$\delta^{11}\text{B}$ of 6.85‰ is also found slightly lower than values obtained by Tonarini et al. [4] ($\delta^{11}\text{B}=7.23\text{‰}$) and by Nakamura et al. [2] ($\delta^{11}\text{B}=7.08\text{‰}$). Nevertheless, replicate analyses of SRM 951 and JB-2 are identical within the analytical precision. Compared to values from the literature, differences of $\delta^{11}\text{B}$ values obtained for the JB-2 and SRM 951 in this study are within analytical reproducibility, and suggest that 100 ng of B are sufficient to analyse natural samples with satisfactory precision. Generally speaking, observations made for the analyses of SRM 951 are similar to those of natural samples. In either case, 100 ng of B in the samples yielded better results than higher amounts of B (see Tables 4 and 5). This finding is attributed to more profound matrix effects, which increase with an increasing sample amount loaded.

This effect can be seen in Tables 4 and 5, where errors for in-run precision are higher for larger amounts of sample.

6. Conclusions

Improvements of B analysis by multicollection technique could be achieved by modifications in PTIMS procedures. The minimum range of B contents in samples analysed was further diminished. 100 ng of B is considered to be the optimum amount for an individual B isotope measurement on the Finnigan MAT 262 double collector mass spectrometer, yielding very precise analyses of both standards and natural samples. Nevertheless, sample sizes as small as 50 ng can be analysed precisely, if not enough B is available. This method allows precise analysis of natural samples with B concentrations almost one order of magnitude lower than previously reported.

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