



Studies on the isotopic analysis of boron by thermal ionisation mass spectrometry using NaCl for the formation of Na_2BO_2^+ species

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ABSTRACT

Studies were carried out on the use of NaCl instead of sodium carbonate or sodium hydroxide for the formation of Na_2BO_2^+ ion used for the determination of isotopic composition of boron by TIMS. The addition of mannitol which forms an anionic complex with boron was found to be essential when using NaCl. The investigations show that when NaCl is used, B/Na molar concentration ratio need not be critically adjusted to 1 as required in case of sodium carbonate or sodium hydroxide. The $^{10}\text{B}/^{11}\text{B}$ ratio was found to be independent of B/Na molar concentration ratio in the range of 25–0.05. This aspect is extremely useful in carrying out isotopic analysis of B in unknown samples solutions. NIST boron isotopic standard SRM-951 having $^{10}\text{B}/^{11}\text{B}$ isotopic ratio of 0.2473 ± 0.0002 was used in these studies and a value of 0.24742 ± 0.00006 (1σ) was obtained.

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1. Introduction

Due to the large thermal neutron absorption cross-section of ^{10}B , boron is used in the form of homogenous solution of boric acid or boron trioxide in moderator systems of nuclear reactors to control the reactivity. Elemental boron, boron carbide and alloys of boron are other forms of the element which are used in various stages of the reactor operation. Since the extent of reactivity control is dependent on the amount of ^{10}B , accurate and precise knowledge on isotopic composition of boron is important. Measurements on small changes in the isotopic composition of B ($\delta^{11}\text{B}$ ranging from -30 to $+60$) are also required to understand the various geological and hydrological processes [1–4]. Isotopic composition of boron can be determined by various mass spectrometric techniques, e.g., thermal ionisation mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICPMS), secondary ion mass spectrometry (SIMS), laser vaporization mass spectrometry (LMS), glow discharge mass spectrometry (GDMS), etc. [5–9]. Amongst these, TIMS is the most widely used mass spectrometric technique due to its inherent capabilities of giving high precision in the isotope ratios. However, due to high ionisation potential of boron (8.3 eV), singly charged atomic ions of B cannot be obtained by TIMS. This problem has been circumvented by using different sample preparation and loading procedures to generate the molecular ions of boron in TIMS [8]. In the recent years, high resolution multi-collector

ICPMS has been gaining popularity for precise isotope ratio measurements of boron [5]. This has a relatively high mass bias but has been shown to give better precision compared to TIMS. In the present work, studies have been carried out for analysing boron as Na_2BO_2^+ ion using popular positive thermal ionisation mass spectrometry (PTIMS). This is normally used for determining $^{10}\text{B}/^{11}\text{B}$ atom ratio by carrying out a chemical reaction of boron containing compound with an alkali metal carbonate or hydroxide (lithium, sodium, potassium, rubidium or cesium) to form alkali tetraborate. Amongst the various alkali metals, cesium metaborate is preferred because high mass of Cs_2BO_2^+ ion leads to reduced mass fractionation [10,11]. Our laboratory was one of the first to develop the cesium borate method using the dynamic mode for data acquisition [10]. However, the method could not be adapted for multicollector detection because of restriction in moving the detectors due to the small dispersion of the Cs_2BO_2^+ ion at m/z 308 and 309. This required special arrangement of the Faraday cups at fixed spacing, which is not available in our present instrument [12]. Corrections for time-dependent variations in the ion current due to poor ion emissions and signal drifts are eliminated during simultaneous collection of the ions of different m/z and there is significant reduction in the time required for data collection. Determination of boron by PTIMS by monitoring the sodium metaborate ion was the first TIMS method to be developed. NIST standard SRM 951 and ^{10}B enriched SRM 952 [13] and CBNM boric acid [14] have been certified using this method. The method can be adapted for multicollection due to the lower mass of Na_2BO_2^+ ion (m/z 88 and 89). However, one of the main drawbacks of this method has been the dependence of the $^{10}\text{B}/^{11}\text{B}$ isotopic ratio on the B/Na molar concentration ratio

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in the loading solution. Shields and co-workers [13] have reported that at a constant filament temperature of 780 °C, the measured $^{10}\text{B}/^{11}\text{B}$ decreased by 0.85% as the B/Na was varied from 2 to 0.25 using Na_2CO_3 , with NaOH the $^{10}\text{B}/^{11}\text{B}$ ratio decreased by more than 1%. This necessitated a strict control of B/Na molar concentration ratio close to one to minimize the observed variations in the $^{10}\text{B}/^{11}\text{B}$ ratio. Further, to prevent the loss of boron [15,16] during preconcentration from very dilute solutions, mannitol has been added along with the alkali metal salt.

During the isotopic analysis of boron in ground water samples, we observed that after carrying out separation and purification of boron using boron specific resin, the amount of sodium carbonate added to the acidic eluent was not critical for isotope ratio measurements in TIMS. Since the addition of sodium carbonate in the acidic medium leads to the formation of NaCl, it was considered interesting to study the possibility of using NaCl directly instead of sodium carbonate or hydroxide since its addition will not lead to any change in the pH of the unknown solution. In alkaline or neutral solutions, the usage of alkali carbonate or hydroxide changes the pH of the solution. This results in the formation of different compounds of alkali metal borate on the filament thereby affecting the measured $^{10}\text{B}/^{11}\text{B}$ isotope ratio. Experiments were, therefore, carried out by using a neutral salt such as sodium chloride to study the effect of different B/Na molar concentration ratios on the determination of $^{10}\text{B}/^{11}\text{B}$ isotopic ratio using NIST certified isotopic reference material of boron.

2. Experimental

2.1. Instrument

A single focusing TIMS (Finnigan MAT 261 from Bremen, Germany) with 9 Faraday cups for multicollection was employed in the present work. An acceleration voltage of 8 kV was used and the Faraday cup numbers 5 (moveable) and 6 (fixed) were used to collect ions with m/z values of 89 and 88, respectively. The instrument has an inbuilt software for carrying out data acquisition and isotope ratio measurement on line. Tantalum single filament assembly having dimensions of 10 mm × 1 mm × 0.04 mm was used for loading of samples.

2.2. Reagents

NIST isotope reference material SRM 951 was used for the studies. Known amount of boric acid was dissolved in milliQ water to get a concentration of about 1 mg B/mL. Analytical grade NaCl was used to obtain a concentration of about 2.5 mg Na/mL.

Analytical grade mannitol procured from Merck was used for preparing solution of 10 mg/mL concentration.

Quartz ware was used for preparing the samples. All apparatus and flasks were thoroughly leached in 3 M nitric acid and

washed with milliQ water and dried before use. For transferring solutions, either polyethylene weight burettes or variable volume pipettes with disposable tips were used. No isobaric interference was observed at m/z values of 88 and 89.

2.3. Experimental details

Different mixtures of boron and sodium were prepared, using weighed aliquots, for B/Na molar concentration ratio ranging from 0.05 to 25. The amount of mannitol added was 40 times that of boron which corresponds to mannitol/boron mole ratio of 2. Evaporation experiments using mannitol to prevent volatilization of boron have shown that mannitol/boron mole ratio of at least 1 is required to prevent loss of boron from an acidic solution [15]. All mixtures were evaporated to dryness before use. Graphite coated Ta filament which has been shown to enhance the ion intensity of Cs_2BO_2^+ [17] was used. The graphite slurry for coating the Ta filament was prepared by mixing 40 mg graphite (spectroscopic grade) in 1 mL of 50% ethanol. 2–3 μL of the slurry was used for coating the Ta filament on which the solution of boron was loaded. B/Na molar concentration ratios of 25, 5, 2, 1, 0.5, 0.25, 0.1 and 0.05 were the different mixtures in which the boron isotopic ratios were determined. About 1.7 μg of boron containing about 70 μg of mannitol and varying amounts of Na were loaded on the filament. The solution was dried at 1 A and the current was slowly raised to 1.8 A and was maintained at this heating current for 5 min. In the ion source, the filament was programmed to heat to 1.6 A in 10 min and after a 10 min wait for degassing, the sample was further heated to obtain a steady signal for data acquisition. The data were acquired in 3 blocks of 12 scans each in static mode of multicollection.

3. Results and discussion

3.1. Effect of B/Na molar concentration ratio on isotopic ratio of boron

Table 1 gives the $^{10}\text{B}/^{11}\text{B}$ isotopic data obtained for different molar concentration ratios of B/Na. The approximate filament current at which stable ion intensity for data acquisition was obtained is also given in this Table. The $^{10}\text{B}/^{11}\text{B}$ isotopic data obtained were corrected for ^{17}O contribution. A mean of average values of 0.24742 ± 0.00006 was obtained for B/Na molar concentration ratios ranging from 25 to 0.05. This compares well with the certified $^{10}\text{B}/^{11}\text{B}$ ratio of 0.2473 ± 0.0002 in the standard [13]. Fig. 1 gives a graphical representation of $^{10}\text{B}/^{11}\text{B}$ isotope ratio data using B/Na molar concentration ratio of 0.05–5. In this figure, each data point represents results obtained during a typical mass spectrometric analysis.

It was observed that for the same amount of boron on the filament, stable ion current that could be obtained for a block increases with increase in the amount of sodium corresponding to B/Na molar

Table 1
Effect of B/Na molar concentration ratio on the $^{10}\text{B}/^{11}\text{B}$ isotope ratio in NIST-SRM-951

B/Na molar concentration ratio	$^{10}\text{B}/^{11}\text{B}$ ratio	Approximate filament heating current (A)	Amount of boron on the filament (μg)
25	0.24750 (0.028) ^a	2.2	5
5	0.24741 (0.024)	2.01	1.75
2	0.24739 (0.032)	2.09	1.75
1	0.24742 (0.040)	1.82	1.75
0.5	0.24747 (0.032)	1.86	1.75
0.25	0.24740 (0.032)	1.96	1.75
0.1	0.24741 (0.036)	1.88	1.75
0.05	0.24745 (0.040)	2.26	1.75
Mean of average values			0.24742 ± 0.00006 (1σ), $N=8$

^a External standard deviation in percentage with four independent analysis.

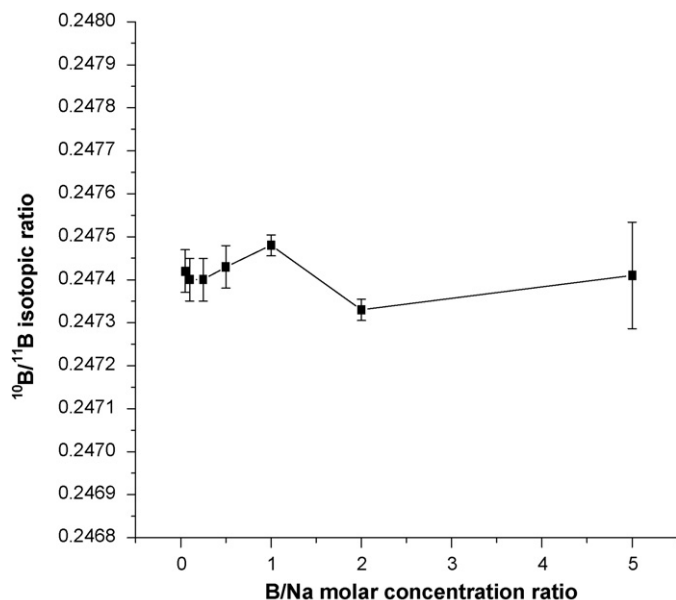


Fig. 1. Effect of B/Na ratio on the isotopic ratio of boron using NIST-SRM-951; the error bars indicate external standard deviation calculated from data obtained in three blocks during a mass spectrometric analysis.

concentration ratio of 25–0.1. Even at B/Na molar concentration ratio of 0.05, consistent $^{10}\text{B}/^{11}\text{B}$ isotopic ratio was obtained though the ion intensity was found to decrease. Therefore, except for B/Na molar concentration ratios of 5 and 2, where the ion currents were about 2×10^{-12} A (ion intensity of ^{11}B at m/z 89) during analysis, for the remaining mixtures, the data were acquired at ion currents of about 1×10^{-11} A. For B/Na ratio of 25, at least 5 μg of boron was required on the filament for getting a stable ion current. There was no noticeable trend in the filament heating current during the mass spectrometric analysis, though filament heating current for B/Na ratio of 1–0.1 appeared to be lower than for other boron + sodium mixtures. Increase in the mannitol amount on the filament can

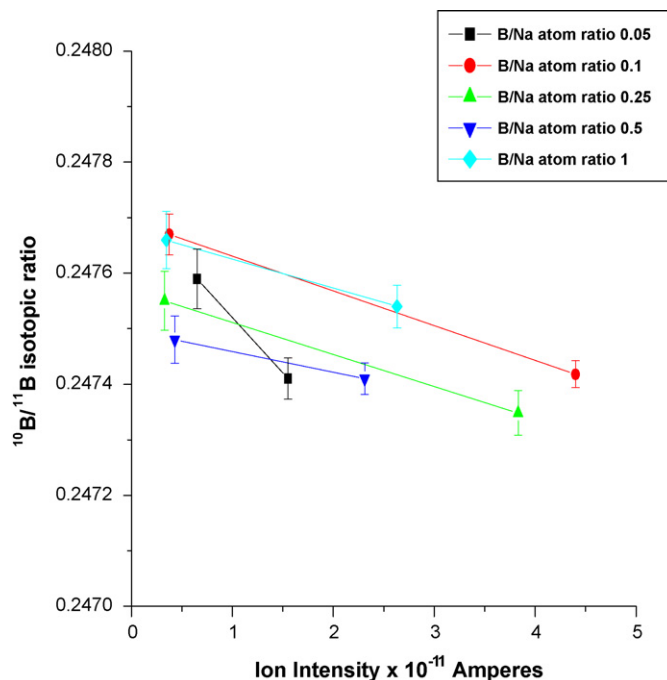


Fig. 2. Change in isotopic ratio of boron with increase in ion intensity (i.e., filament heating temperature). Boron amount on filament about 1.7 μg and NIST SRM-951 sample was employed.

also lead to analysis at higher filament current. As can be seen, the $^{10}\text{B}/^{11}\text{B}$ isotopic ratio obtained remained constant irrespective of the B/Na ratio on the filament. It may be noted that the presence of mannitol is crucial for the formation of metaborate ion as boric acid itself has a weak dissociation constant, $K_a = 6.4 \times 10^{-10}$ but with mannitol, it becomes a much stronger acid, $K_a = 1.5 \times 10^{-4}$ due to which it can react with a neutral salt such as NaCl leading to the formation of Na_2BO_2^+ in the ion source. As shown in this Table, the $^{10}\text{B}/^{11}\text{B}$ ratio obtained using sodium chloride instead of sodium

Table 2

Effect of boron amount loaded on the filament on the isotopic composition of boron (B/Na molar concentration ratio 0.5)

Boron amount on filament (μg)	$^{10}\text{B}/^{11}\text{B}$ ratio	Ion current (A)	Filament heating current (A)
0.1	0.24742 (0.040) ^a	1×10^{-12}	2.1
0.5	0.24739 (0.040)	2×10^{-12}	2.1
1.75	0.24748 (0.024)	5×10^{-12}	1.8
5	0.24745 (0.028)	5×10^{-12}	2.1

^a External standard deviation in percentage with four independent analyses.

Table 3

Comparison of $^{10}\text{B}/^{11}\text{B}$ isotopic ratios in NIST SRM-951 using TIMS

Method	Loading procedure	M_1/M_2	$^{10}\text{B}/^{11}\text{B}$	Reproducibility (2σ)	Reference/year
PTIMS(Na_2BO_2^+)	B/Na ^a mole ratio-1 B/Na ^a mole ratio 2–0.25	88/89	0.24730 0.24678 ^c	0.033% 0.77%	[13]/1970
PTIMS(Na_2BO_2^+)	pH adjusted to 9.4 ^a	88/89	0.24724	0.25%	[11]/1986
PTIMS(Rb_2BO_2^+)	B/Rb ^a mole ratio-1	212/213	0.24699	0.1%	[18]/1991
PTIMS(Cs_2BO_2^+)	B/Cs ^a mole ratio-2 B/Cs mole ratio 5–0.33	308/309	0.24727 0.24713 ^c	0.12% 0.20%	[10]/1985
PTIMS(Cs_2BO_2^+)	B/Cs ^a mole ratio-2	308/309	0.24718	0.008%	[11]/1986
PTIMS(Cs_2BO_2^+)	B/Cs ^a mole ratio-0.5 graphite slurry on filament B/Cs mole ratio 2–0.25	308/309	0.24689 0.24684 ^c	0.011% 0.071%	[17]/1988
PTIMS(Cs_2BO_2^+)	B/Cs ^a mole ratio-2 graphite slurry on filament	308/309	0.24674	0.012%	[12]/1998
PTIMS(Cs_2BO_2^+)	B/Cs ^a mole ratio-2 graphite slurry on filament	308/309	0.24677	0.024%	[19]/2001
NTIMS(BO_2^-)	pH less than 5. Boron free Sea water on filament	42/43	0.24991	0.07%	[20]/1994
NTIMS(BO_2^-)	Ba(OH) ₂ + MgCl ₂ on filament	42/43	0.24957	0.30%	[3]/1996
NTIMS(BO_2^-)	Boron free sea water on filament	42/43	0.24841	0.10%	[21]/2002
PTIMS(Na_2BO_2^+)	B/Na ^b mole ratio 25–0.05 (Table 1)	88/89	0.24742	0.05%	Present work

^a Alkali metal added as carbonate.

^b Sodium chloride added.

^c Calculated from data available in literature.

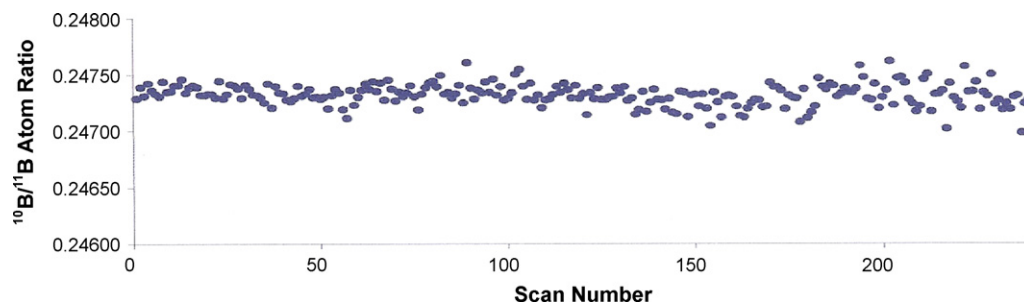


Fig. 3. Change in isotopic ratio of boron with scan number for B/Na molar concentration ratio of 2, ^{11}B ion intensity was about 4×10^{-12} A with boron amount on filament about 1.7 μg and NIST SRM-951 sample was employed.

carbonate yielded nearly a constant value of 0.2474 ($1\sigma < 0.05\%$) for B/Na molar concentration ratio of 25–0.05. This is because, irrespective of the B/Na molar concentration ratio, the pH of the loading solution being same, ions may be forming from the same salt on heating in the ion source. However, it was observed that the best results in terms of ion intensity (10^{-11} A) and precision (better than 0.02%) are obtained for B/Na molar concentration ratio in the range of 1–0.1.

3.2. Effect of boron amount on the filament on the $^{10}\text{B}/^{11}\text{B}$ ratio

The NIST standard was also analysed with varying amounts of B from 0.1 to 5 μg on the filament for B/Na molar concentration ratio of 0.5. It was observed that even for 100 ng of boron on filament, stable ion current of 1×10^{-12} could be obtained giving good precision for the $^{10}\text{B}/^{11}\text{B}$ ratio. Table 2 gives the data for different amounts of boron on the filament. When 5 μg or more of boron was loaded, a cake was formed on the filament which resulted in slow decreasing signal at the temperature of data acquisition. However, this signal increased with the increase in filament current and lasted for a long period. As can be seen from the data given in this Table, external precision values of 0.024–0.040% were obtained using boron amounts ranging from 0.1 to 5 μg . The precision achieved in the present work is comparable to a precision value of 0.035% using boron amount of 0.25 μg when analysing B as Cs_2BO_2^+ [22]. However, the analysis of B as Na_2BO_2^+ ion by using the methodology described in this paper has an advantage that one need not strictly control the B/Na ratio in contrast to that required for B/Cs ratio (0.5–2) in Cs_2BO_2^+ method. This is possible since the intensity of Na^+ ions produced is much lower than that of Cs^+ ions due to high ionisation potential (5.14 eV) of Na compared to that of Cs (3.89 eV). In the latter case, the presence of large amounts of Cs on the filament may lead to suppression in the intensity of Cs_2BO_2^+ .

3.3. Mass discrimination effect in boron isotopic ratio

In TIMS, preferential evaporation of the lighter isotope leads to isotope fractionation which results in positive bias in the $^{10}\text{B}/^{11}\text{B}$ isotope ratio, during the initial stages of mass spectrometric analysis. As the sample on the filament gets depleted in the lighter isotope, this isotope ratio decreases with the amount of sample consumed. This effect is generally known as mass discrimination when using Faraday cup as the detector system. The mass discrimination is dependent on many factors including mass difference between the isotopes being analysed, sample amount, sample composition, heating temperature of the filament, etc. and has been recognised as a source of variable systematic error.

Fig. 2 shows the effect of increase in ion current on the boron isotopic ratio for B/Na molar concentration ratio 1–0.05 for 1.75 μg of B on the filament. It was observed that a similar isotopic variation

pattern was obtained for all samples irrespective of B/Na ratio. Two points on each line show the $^{10}\text{B}/^{11}\text{B}$ ratios acquired at ion currents of about 2.5×10^{-12} A at m/z 89, which was subsequently increased to obtain stable ion currents of 1×10^{-11} A or higher for data acquisition. As expected, analysis at higher ion currents resulted in better precision in the isotopic ratio. An overall mass discrimination of about 0.1% per mass unit was observed for boron isotope ratios determined in the present work.

3.4. $^{10}\text{B}/^{11}\text{B}$ isotope ratios in NIST-SRM 951 reference material

Table 3 gives a comparison of the $^{10}\text{B}/^{11}\text{B}$ isotopic ratio in NIST SRM-951 obtained by different methods in different laboratories. The Table includes the isotope ratios determined using different alkali metals for PTIMS and also the data reported using negative ions. Owing to different fractionation behaviour patterns, the $^{10}\text{B}/^{11}\text{B}$ isotope ratios obtained by different methods are not the same. Therefore, when studying small changes in boron isotope ratios for geological and hydrological applications, $\delta^{11}\text{B}$ values w.r.t. certified value in NIST SRM 951 are used. By making the analysis independent of B/Na molar concentration ratio, the reliability of the $\delta^{11}\text{B}$ values obtained by this method would improve.

Figs. 3 and 4 give plots of $^{10}\text{B}/^{11}\text{B}$ isotope ratios obtained in different scans for B/Na molar concentration ratios of 2 and 0.1, respectively. As can be seen, in spite of significant difference (4×10^{-12} A vs. 10^{-11} A) in the ion intensities of ^{11}B , the $^{10}\text{B}/^{11}\text{B}$ isotope ratios observed in 200 scans remain nearly constant and unfractionated. Hence for repeated analysis of samples reported in this paper, data acquired in three blocks were used. Table 4 gives the data on the reproducibility obtained after repeated analysis of NIST-SRM-951 standard. It is seen that precision values of 0.016–0.024% are obtained for different B/Na molar concentration ratios.

Table 4

Results on the reproducibility of the method during repeated analysis of NIST SRM-951 using B/Na molar concentration ratios of 1, 0.5 and 0.1

Analysis no.	$^{10}\text{B}/^{11}\text{B}$ atom ratio using B/Na molar concentration ratio of		
	1	0.5	0.1
1	0.24745 (0.02) ^a	0.24745 (0.02) ^a	0.24747 (0.01) ^a
2	0.24748 (0.02)	0.24737 (0.01)	0.24748 (0.02)
3	0.24748 (0.01)	0.24748 (0.01)	0.24752 (0.02)
4	0.24738 (0.01)	0.24741 (0.01)	0.24742 (0.01)
5	0.24735 (0.01)	0.24743 (0.01)	0.24749 (0.01)
6	0.24753 (0.01)	0.24743 (0.02)	0.24736 (0.02)
7	0.24740 (0.01)	0.24742 (0.02)	0.24748 (0.02)
8	0.24750 (0.02)	0.24751 (0.006)	0.24736 (0.02)
Mean value	0.24745 \pm (0.024%) ^b	0.24744 \pm (0.016%) ^b	0.24745 \pm (0.024%) ^b

^a External standard deviation in percentage based on data from different blocks.

^b External standard deviation.

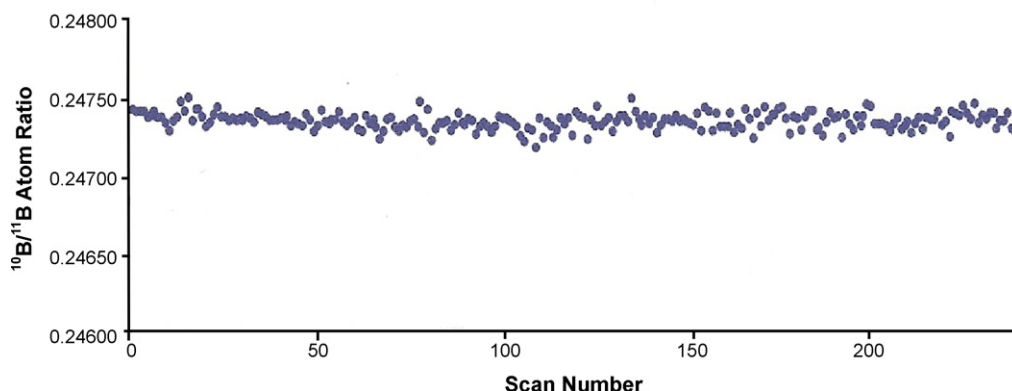


Fig. 4. Change in isotopic ratio of boron with scan number for B/Na molar concentration ratio of 0.1, ^{11}B ion intensity was about 10^{-11} A with boron amount on filament about 1.7 μg and NIST SRM-951 sample was employed.

Table 5

Results of a few samples analysed using the present method (NaCl with the boron-mannitol complex)

Filament loading ^a	$^{10}\text{B}/^{11}\text{B}$ atom ratio	Internal standard deviation (1σ)	External standard deviation (1σ)	Relative external standard deviation (%)
B_2O_3 powder-1				
Analysis 1	0.25098	0.00011	0.00078	0.03
Analysis 2	0.25097	0.00009		
Analysis 3	0.25109	0.00009		
B_2O_3 powder-2				
Analysis 1	0.25054	0.00008	0.00028	0.01
Analysis 2	0.25065	0.00003		
Analysis 3	0.25058	0.00003		
$\text{Li}_2\text{B}_{10}\text{O}_{16}$ powder				
Analysis 1	0.24775	0.00003	0.00064	0.03
Analysis 2	0.24774	0.00003		
Analysis 3	0.24766	0.00006		
Heavy water moderator				
Analysis 1	0.15261	0.00010	0.00002	0.01
Analysis 2	0.15234	0.00010		
Analysis 3	0.15263	0.00009		

^a The sample preparation was done independently for each TIMS analysis.

3.5. Application of the method to real samples

Table 5 gives the results of $^{10}\text{B}/^{11}\text{B}$ isotope ratios measured in a few nuclear samples. During sample preparation, mannitol and NaCl solution were added to each of the samples as described in Section 2 given above. No effort was made to adjust the boron/sodium molar concentration ratio to any particular value. The resulting solution was evaporated to dryness, redissolved in 50 μL of deionised water. From this, 2–3 μL solution was loaded on Ta filament using the graphite method. Three mixtures were prepared from each sample and were analysed by TIMS. The analysis show very good agreement with a reproducibility of 0.03%.

4. Conclusion

B/Na molar concentration ratio does not have to be maintained strictly at one when boron is loaded from neutral solutions. As demonstrated, NaCl could be used instead of sodium carbonate to form neutral solutions of boromannitol complex. NIST SRM 951 analysed by this method gives $^{10}\text{B}/^{11}\text{B}$ ratio in close agreement with the certified value. B/Na molar concentration ratio of 1–0.1 gave maximum ion intensity when graphite activator was used during loading and should be the preferred working range for determination of isotopic composition of boron using boromannitol complex.

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