

The effect of instrumental mass bias on $\delta^{11}\text{B}$ measurements: a comparison between thermal ionisation mass spectrometry and multiple-collector ICP-MS

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Abstract

A series of synthetic samples which span the range of known $\delta^{11}\text{B}$ values have been measured by thermal ion mass spectrometry (positive and negative ion) and by multiple-collector ICP-MS (Axiom and IsoProbe) in order to assess the effects of mass bias on $\delta^{11}\text{B}$ values. The IsoProbe shows the highest mass bias, but yields $\delta^{11}\text{B}$ values identical to those obtained with the Axiom and by TIMS measurements, indicating that mass bias has no detectable effect on $\delta^{11}\text{B}$ values. Measurements carried out by multiple-collector ICP-MS yield higher precision than TIMS measurements. Typically multiple-collector ICP-MS measurements offer a 50% improvement in precision over positive ion TIMS and nearly one order of magnitude better than that for negative ion TIMS.

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1. Introduction

Traditionally isotopic measurements have been carried out by thermal ionisation mass spectrometry. Recent developments in mass spectrometry have given rise to the widespread use of multiple-collector ICP-MS instruments for the measurement of isotope ratios [1]. Isotope measurements for the light isotopes (e.g., B and Li) by multiple-collector ICP-MS show significantly higher instrumental mass bias than is exhibited by TIMS measurements [2]. In some multiple-collector ICP-MS instruments this mass bias can be as high as 70%. The aim of this study is to investigate if these large differences in mass bias can affect the accuracy of $\delta^{11}\text{B}$ measurements and therefore compromise interlaboratory comparisons.

Measurements of seawater by TIMS and MC-ICP-MS techniques show a spread of values (Table 1), which masks

any differences that may be attributed to instrumental mass bias. In this study a range of synthetic samples spanning the range of known $\delta^{11}\text{B}$ values have been measured by negative ion TIMS, positive ion TIMS and on multiple-collector ICP-MS instruments. For the latter, two different instruments have been employed, the ThermoElemental Axiom and the GV IsoProbe. Measurements on the IsoProbe have been carried out with different RF frequencies on the hexapole which alter the instrumental mass bias.

2. Methods

2.1. Negative ion thermal ionisation mass spectrometry

Negative ion TIMS measurements were carried out on the VG Sector 54-30 mass spectrometer located at the GFZ in Potsdam, Germany, using the technique developed by Kasemann et al. [10]. Ten nanograms of sample was loaded with 1 μl of B-free seawater prepared using the technique of Hemming and Hanson [4] onto recently outgassed Re filaments. The sample was dried

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Table 1

Comparison of seawater measurements using different instrumentation and analytical techniques

	Technique	$^{11}\text{B}/^{10}\text{B}$ for NBS	Seawater source	$\delta^{11}\text{B}$ for seawater (%)
Vengosh et al. [3]	Negative ion TIMS	3.986		39.0 ± 2.5
Hemming and Hanson [4]	Negative ion TIMS	4.0014		39.9 ± 1.1
Barth [5]	Negative ion TIMS	4.0013	Pacific	39.7 ± 1.4
Barth [5]	Negative ion TIMS	4.0013	Atlantic	39.5 ± 1.1
Spivack and You [6]	Negative ion TIMS			39.1 ± 1.5
Palmer et al. [7]	Negative ion TIMS	3.9873		39.7 ± 0.3
Spivack and Edmond [8]	Positive ion TIMS	4.04558	Atlantic	39.52 ± 0.13
Gaillardet and Allegre [9]	Positive ion TIMS	4.0510	Atlantic	39.8 ± 0.3
Aggarwal et al. [2]	Axiom MC-ICP-MS	4.2–4.4	Cook Straits, New Zealand	39.45 ± 0.38^a

See Aggarwal and co-workers [1] for a more complete discussion on error comparisons.

^a Note that the error calculated for the Axiom measurements is based on the error of calculated $\delta^{11}\text{B}$ values whereas the error for the TIMS measurements is based on the sample measurement and therefore represents an underestimate of the true error.

at 0.7 A and conditioned by heating the sample at 1.2 A for 30 s.

Boron ion beams were detected as the BO_2^- species in the mass spectrometer. Samples were heated under pyrometer control to 850°C over 5 min, focussed and heated until the ^{11}B gave an ion beam of 200 mV. This time was recorded as t_0 . Using an accelerating voltage of 8260 V, simultaneous detection of the ^{11}B and ^{10}B ion beams was carried out in the Axial and Low 2 Faraday collectors, respectively. The sample was heated up to 920°C (or more if the ^{11}B ion beam was less than 1 V) and measurement was initiated. The measurement consisted of baseline measurements at masses 42.5 and 43.5 for 5 s each, followed by peak measurements over 5 s. A total of 82 blocks consisting of 12 ratios were measured over ~ 4 h for each sample.

Negative ion measurements of B show considerable at the beginning of an analysis partly due to the formation of inter-

fering CNO^- ions on $^{10}\text{BO}_2^-$, and due to Rayleigh fraction occurring on the filament. These effects can be corrected by plotting the cumulative ion beam produced over the course of an analysis against measured B isotope ratios (Fig. 1). The true ratio is calculated as the intercept on the y axis of the extrapolated linear region of the slope. The cumulative ion beam produced is calculated by integrating the ion beam intensity (A) over time starting from t_0 (min). This integration is summed for each additional block of data measured [10].

2.2. Positive ion thermal ionisation mass spectrometry

Positive ion TIMS measurements were carried out in Münster on the Micromass Sector 54 instrument using the technique described in Aggarwal and Palmer [11]. One microlitre of a graphite slurry was loaded onto outgassed Ta

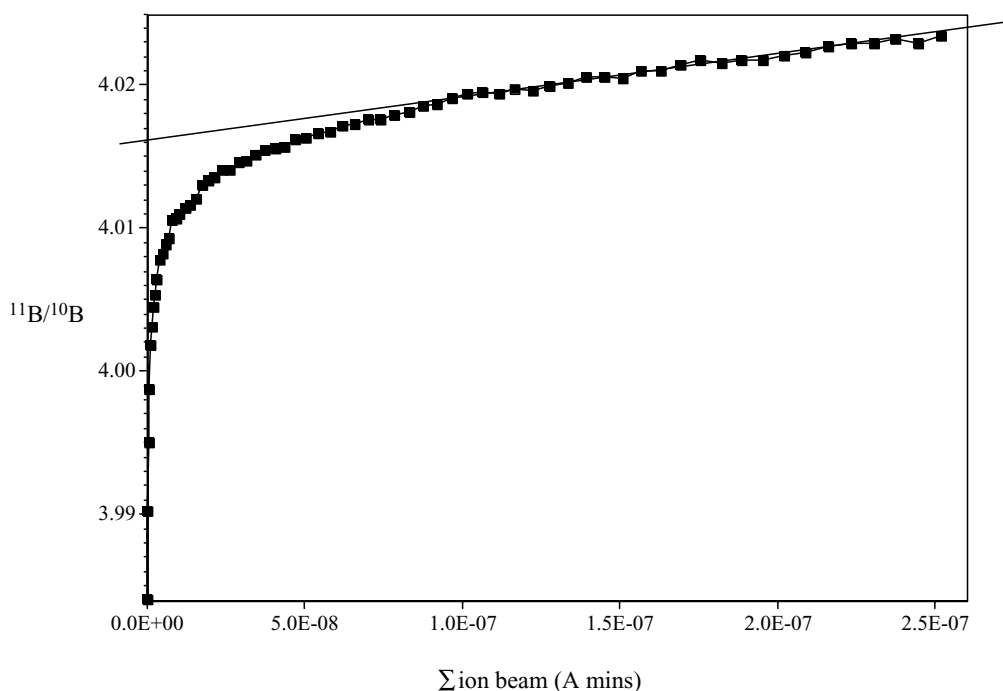


Fig. 1. Determination of $^{11}\text{B}/^{10}\text{B}$ by negative ion TIMS. Line shows intercept of stabilised signal on y axis to give $^{11}\text{B}/^{10}\text{B}$ of the sample.

filaments, followed by 1 μl of 7.62 mmol/kg CsCl solution and 2 μl of 1000 ppm B sample. The sample was dried at 0.8 A and conditioned at 1.2 A for 5 min.

Samples were heated gradually until a Cs^+ beam could be found on the Faraday detector using an accelerating voltage of -5500 V. Once a 1 V Cs^+ beam had been focussed, the Cs_2BO_2^+ was examined on the Daly detector. Measurements were carried with peak jumping on the Daly detector once the Cs_2BO_2^+ signal was greater than 1×10^6 cps. Measurements consisted of a baseline measurement at half mass unit between the $\text{Cs}_2^{11}\text{BO}_2^+$ and $\text{Cs}_2^{10}\text{BO}_2^+$ ion beams for 1 s followed by measurement at 260.12 and 259.20 for 5 s each. Ratios were measured for five blocks consisting of 20 ratios with a typical ion beam of 2×10^5 cps.

2.3. Axiom measurements

Measurements by the Axiom MC-ICP-MS have been previously reported by Aggarwal et al. [2]. Typically, 100 μl of sample containing 2 ppm B was required for each sample measurement. A direct injection nebuliser (Cetac MicroNeb 2000) was used to reduced the memory effects which plague ICP-MS techniques. Correction for mass bias was carried out by bracketing sample measurements with standards. An accelerating voltage of -5000 V was used with ^{11}B and ^{10}B being detected in High 4 and Low 4 Faraday detectors. Baseline measurements were carried out at masses 9.5 and 10.5 for 7.5 s each, followed by peak measurements for 8 s. A measurement comprised of one block of 10 ratios. A $\delta^{11}\text{B}$ ratio for the sample was obtained by bracketing sample measurements with standards measurements in the order: standard, sample, standard, sample and standard. This technique gave three $\delta^{11}\text{B}$ ratios which were then used to calculate the mean and standard deviation. Uncorrected measurements of NBS 951 over a 2-year period yield $^{11}\text{B}/^{10}\text{B}$ of 4.20–4.36.

2.4. IsoProbe measurements

The Micromass IsoProbe is a single focussing multiple-collector inductively coupled plasma mass spectrometer with the source held at ground potential and the analyser floated up to 6 kV. Prior to passing into the magnetic sector analyser,

the ions are directed through a hexapole collision cell, which serves to reduce the energy spread of the ions from 20–30 eV to ~ 1 to 2 eV. (A complete discussion on collision cells can be found in Feldmann et al. [12,13].) A collision gas of Ar or He is fed into the centre of the hexapole ion guide, and the analyte ions collide with the gas atoms. The energy transfer that occurs in these collisions serves to thermalise the analyte ions and to reduce their energy spread. A further benefit of the hexapole is that reactions between the ions and the collision gas can be exploited to eliminate or reduce interferences.

Typical B isotope measurements were carried out with an accelerating voltage of 6100 V. Flat-topped peaks for B^+ were produced with the IsoProbe using He collision gas flowing at 6.2 ml/min and a hexapole DAC set at 7%. A single analysis comprised of a 30-s baseline measurement at mass 9.5, followed by 10 measurements over a 10-s integration period each, centred with $^{10}\text{B}^+$ and $^{11}\text{B}^+$ in Low 3 and High 5 Faraday detectors, respectively. Sample was introduced using a direct injection nebuliser (Cetac MicroNeb 2000), using the same techniques employed for the Axiom. Measurements were carried out on 100 μl of solution containing 2 ppm B. $\delta^{11}\text{B}$ values were calculated by alternating standard measurements with sample measurements. Over a 2-year period measurements of uncorrected NBS 951 samples yielded $^{11}\text{B}/^{10}\text{B}$ between 4.8 and 6.5.

3. Results

A series of solutions with $\delta^{11}\text{B}$ values spanning all known B isotope ratios was prepared gravimetrically mixing a ^{10}B -rich spike with an ^{11}B -rich spike. These solutions were then analysed along with NBS 951 on the different instruments. Results of the analyses are shown in Table 2 and Fig. 2 along with their uncertainties.

In order to compare the TIMS and multiple-collector ICP-MS data, TIMS measurements of the synthetic samples were bracketed with standard measurements to give $\delta^{11}\text{B}$ values in a similar technique to that used for the multiple-collector ICP-MS measurements [2]. This was carried out for two mean measurements of the sample with

Table 2
Comparison of measurement of synthetic samples by different instrumental techniques and from gravimetric preparation

	Gravimetric	Negative ion TIMS		Positive ion TIMS		IsoProbe 6 MHz		IsoProbe 8.9 MHz		Axiom	
	$\delta^{11}\text{B}$ (%)	$\delta^{11}\text{B}$ (%)	$\pm 2\sigma$	$\delta^{11}\text{B}$ (%)	$\pm 2\sigma$	$\delta^{11}\text{B}$ (%)	$\pm 2\sigma$	$\delta^{11}\text{B}$ (%)	$\pm 2\sigma$	$\delta^{11}\text{B}$ (%)	$\pm 2\sigma$
Sample 1	-13.9	-13.26	0.30	-13.46	0.52	-13.81	0.56	-14.18	0.34	-14.01	0.24
Sample 2	12.1	13.34	0.89	12.86	0.73	12.08	0.36	12.03	0.42	11.95	0.22
Sample 3	37.6	38.46	1.86	38.62	0.93	37.37	0.16	37.39	0.24	37.83	0.24
Sample 4	52.7	53.10	1.26	54.22	1.08	52.39	0.51	52.27	0.38	52.85	0.34
Sample 5	77.7	78.70	0.51	79.1	1.24	77.36	0.48	77.08	0.46	77.72	0.40
Sample 6	101.3	100.90	0.14	104.11	1.36	100.74	0.56	100.77	0.22	102.04	0.42
$^{11}\text{B}/^{10}\text{B}$ for NBS 951		4.011		4.045		5.6–6.8		4.8		4.2	

$\delta^{11}\text{B}$ values for gravimetrically determined samples calculated assuming a $^{11}\text{B}/^{10}\text{B}$ for NBS 951 of 4.04558.

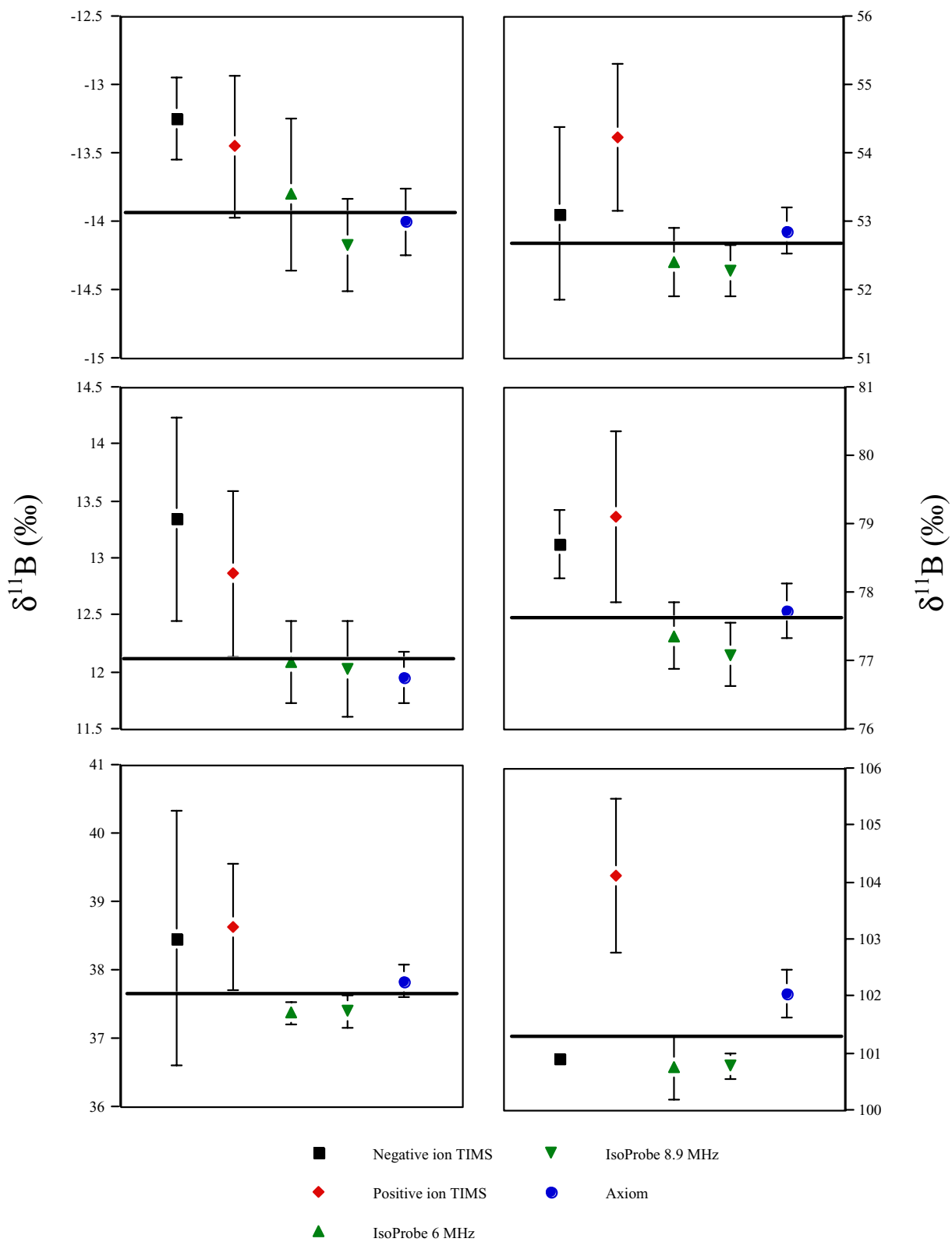


Fig. 2. Comparison of $\delta^{11}\text{B}$ values measured by positive and negative ion TIMS, Axiom and IsoProbe for the suite of synthetic samples. Solid lines indicate gravimetrically calculated $\delta^{11}\text{B}$ values. Error bars shown in the figures are 2σ .

three measurements of the standard. In this technique $\delta^{11}\text{B}$ values are calculated by normalising the sample measurement to the mean of adjacent standard measurements. This enables three $\delta^{11}\text{B}$ values to be calculated. Whilst this is not the usual technique for calculating $\delta^{11}\text{B}$ values for TIMS measurements it does allow direct comparison of the precision of all of the different techniques.

4. Discussion

Measurements by multiple-collector ICP-MS yield data that are more precise than that by TIMS techniques despite showing the highest mass bias. The errors for the TIMS techniques mask any fine structure in the data, but indicate that despite the significant mass bias, all the measurements tend to concur. Comparison of the Axiom and IsoProbe data which offer the highest precision, show that despite the range in mass bias from 7 to 70%, $\delta^{11}\text{B}$ values appear to be unaffected. The relative differences between samples and standards do not yield anomalous data except in the case of sample 6, which gives different $\delta^{11}\text{B}$ values. However, since this effect is observed only in sample 6 this is more likely to be due to poor analysis and may be reflected in the poorer precision of the data.

5. Conclusions

Data gathered by the Axiom and IsoProbe, which display the highest precision and a large range in mass bias, show identical $\delta^{11}\text{B}$ values to those measured by TIMS techniques which show much lower mass. This suggests that instrumental mass bias has no detectable effect on the natural isotope variations measured. Even with a large mass bias, $\delta^{11}\text{B}$

values measured by different techniques on different instruments are identical within analytical uncertainties. Measurements of seawater by the Axiom yield $\delta^{11}\text{B}$ values that are identical to measurements by other techniques. This indicates that it is valid to compare data from different data sets especially, including data gathered from multiple-collector ICP-MS instruments that show the highest mass bias.

Acknowledgements

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