

## HIGH PRECISION ISOTOPE DETERMINATION OF SMALL BORON SAMPLES

- Inert sample introduction system
- Use of different pre-amplifier resistors
- Excellent mass fractionation stability
- Precise isotope determination of small boron samples

An international boron standard NIST SRM 951 (boric acid) was used in this study. Solution was introduced into the mass spectrometer in 2% HNO<sub>3</sub> under 'wet plasma' conditions. In view of the well-known boron washout issue related to instrumental analysis, an introduction system including a quartz torch, a PFA cyclonic spray chamber and a PFA concentric nebuliser was used instead of the standard glassware, of which borosilicate is a main constituent.

Data was collected using static analysis. Each analysis consisted of one block of 60 integrations of 2 seconds on-peak measurements. The blank was obtained by a 60 seconds on-peak measurement of a 2% HNO<sub>3</sub> solution at the beginning of the measurement sequence. The analysis duration was approximately 2.4 minutes. 137 repeat analyses were performed, equating to approximately 5.5 hours of data collection. No tuning of the instrument was made once the measurements had started. The experiment was repeated for a 50 ppb SRM 951 solution and a 10 ppb SRM 951 solution. For the analysis of the 50 ppb solution, <sup>10</sup>B and <sup>11</sup>B were measured in Faraday cups connected to pre-amplifiers each fitted with a 10<sup>11</sup> ohm resistor. For the analysis of the 10 ppb solution, <sup>10</sup>B and <sup>11</sup>B were measured in Faraday cups connected to pre-amplifiers each fitted with a 10<sup>12</sup> ohm resistor, in order to reduce the measurement uncertainties of small signals. With a nebuliser uptake rate of 140 µL/min, approximately 16.8 ng and 3.4 ng of B were consumed during a single analysis of the 50 ppb and 10 ppb SRM 951 standard solutions, respectively.

Similar to Li isotopes (see Nu Instruments Application Note AN34), the relatively large mass difference (10%) between the two B isotopes can result in significant mass fractionation during the instrumental analysis. A previous study (Foster, 2008) had suggested that the optimal condition for B measurements can be achieved when tuning the MC-ICP-MS for best mass fractionation stability rather than maximum sensitivity. In this experiment, the optimal fractionation stability was tuned for on a daily basis by monitoring the measured <sup>11</sup>B/<sup>10</sup>B ratio whilst changing the nebuliser pressure in steps of 0.3 Psi. A plateau of nebuliser pressure between 29.2 and 29.8 Psi was identified (Fig. 1), where variations in nebuliser pressure would induce the smallest changes in the measured <sup>11</sup>B/<sup>10</sup>B ratio. The middle of this plateau, a nebuliser pressure of 29.5 Psi was therefore chosen for the measurements. A test with the instrument being tuned up for maximum sensitivity was also performed for comparison, the external reproducibility achieved when using the approach mentioned above was better by a factor of 4.

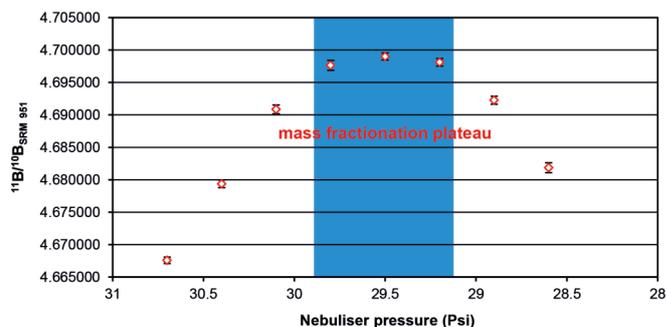


Fig 1: Variations in the measured <sup>11</sup>B/<sup>10</sup>B ratio of a 50 ppb SRM 951 solution as a function of nebuliser pressure (Psi). Error bars are 2SE. A plateau of between 29.2 and 29.8 Psi (highlighted in blue) was identified.

The zoom optics maintain good peak shapes (Fig. 2), allowing precise measurements of B isotope ratios. It is noticed that the <sup>40</sup>Ar<sup>4+</sup> interference was partially resolved from <sup>10</sup>B in the low resolution mode and did not affect the isotope ratio measurement at the peak centre. Interference of the boron hydride <sup>10</sup>BH on <sup>11</sup>B was negligible, as suggested by a mass scan in the high resolution mode.

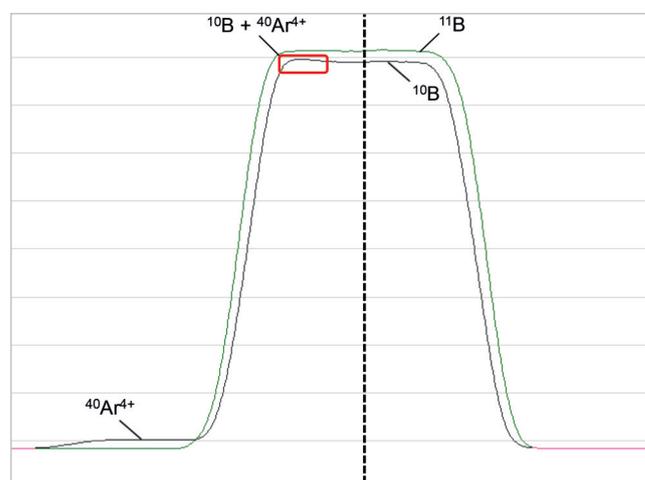


Fig 2: B isotopes <sup>10</sup>B and <sup>11</sup>B in coincidence. Interference <sup>40</sup>Ar<sup>4+</sup> was partially resolved from the <sup>10</sup>B peak. The centre of the flat peaks was chosen as the mass analysis position.

The maximum B sensitivity achieved was approximately 22 volts/ppm. Signal intensity remained stable over the course of measurement, with a decrease of less than 3% after 5.5 hours.

It has been reported (Foster et al., 2013) that a main source of B blank accumulation for instrumental analysis is the airborne contamination. In this study, a piece of Parafilm was used to prevent each solution bottle from being exposed to the laboratory

atmosphere during the measurements. An identical bottle (same material, size and also covered with the Parafilm) containing the same volume of SRM 951 solution was placed next to the analyte bottles, and was analysed for B content before and after each measurement sequence, with no significant B blank accumulation being found. The measured B blank was approximately 100 ppt in this study, with a relative contribution of 0.2% and 1.0% to the 50 ppb and 10 ppb SRM 951 standard solutions, respectively. The isotope composition of this B blank was measured, showing an insignificant difference from the SRM 951 standard. In this case, the B blank correction was within measurement uncertainties.

The measured  $^{11}\text{B}/^{10}\text{B}$  ratios of the 137 repeat analyses for both the 50 ppb and 10 ppb SRM 951 standard solutions are plotted in Fig. 3.

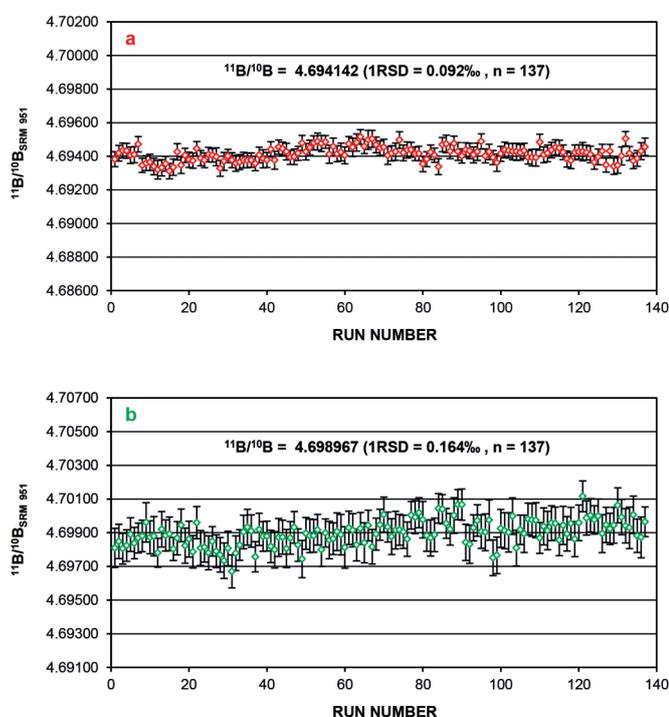


Fig 3:  $^{11}\text{B}/^{10}\text{B}$  ratios of the a) 50 ppb, b) 10 ppb SRM 951 standard solutions measured over the course of 5.5 hours. Error bars are 2SE.

For each analysis of 60 integrations of 2 seconds, the internal  $^{11}\text{B}/^{10}\text{B}$  precision was 0.06‰ (1RSE) for the 50 ppb solution and 0.10‰ (1RSE) for the 10 ppb solution, demonstrating the low noise of the pre-amplifiers, stability of baselines and excellent peak flatness. The external precision was 0.092‰ (1RSD,  $n = 137$ ) for the 50 ppb and 0.164‰ (1RSD,  $n = 137$ ) for the 10 ppb measurements, exhibiting the excellent stability of the plasma conditions and instrumental mass fractionations. The observed B mass fractionation was approximately 16‰ per amu.

Boron only has two stable isotopes, it is therefore not possible to use the internal normalisation or double spike approach to correct for the instrumental mass fractionation. A standard bracketing approach has been adopted for mass fractionation correction. This approach assumes a linear mass fractionation drift over the course of measurement. Results are reported in Table. 1, where  $\delta$  denotes the per mil deviation of a ratio relative to the average of the two ratios measured before and after. For the measured  $^{11}\text{B}/^{10}\text{B}$  ratios of the 50 ppb and 10 ppb SRM 951 standard solutions, the average  $\delta$  values of 68 brackets were both within measurement uncertainties of the theoretical 0‰.

Table 1: Standard bracketing results of 137 repeat analyses of a 50 ppb and a 10 ppb SRM 951 standard solution.

	50 ppb	10 ppb
Average $\delta$ (‰)	-0.005	0.008
1SD (‰)	0.082	0.144

The Nu Plasma II Multi Collector ICP-MS instrument exhibits the capability of high precision isotope determination of small boron samples.

### Reference

Foster, G.L., 2008. Seawater pH,  $\text{pCO}_2$  and  $[\text{CO}_2^{-3}]$  variations in the Caribbean Sea over the last 130 kyr: A boron isotope and B/Ca study of planktic foraminifera. *Earth and Planetary Science Letters*, 271, (1-4), 254-266.

Foster, G.L., Hönisch, B., Paris, G., Dwyer, G.S., Rae, J.W., Elliott, T., Gaillardet, J., Hemming, N.G., Louvat, P., Vengosh, A., 2013. Interlaboratory comparison of boron isotope analyses of boric acid, seawater and marine  $\text{CaCO}_3$  by MC-ICPMS and NTIMS. *Chemical Geology*, 358, 1-14.