Application Note: 30022

High Precision Boron Isotope Analyses

Negative Thermal Ionization Analysis and Static Multicollection

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Key Words

- TRITON
- Boron
- Negative Ions
- TI-MS

Introduction

Boron has two stable isotopes, ^{10}B and ^{11}B, that exhibit large isotope abundance variations in many biological and geological systems. Boron has been employed to determine if leachate from municipal waste sites has entered the groundwater system, to resolve the source of fluids in geothermal systems, and as a potential isotope indicator to ascertain the source of micronutrients in agricultural settings. In many systems, the amount of sample available is limited. Therefore, measurement strategies are required that are capable of analyzing nanogram quantities of material with high precision. One method is the analysis of BO_2^- ions by negative ion thermal ionization mass spectrometry. Using the Thermo Scientific TRITON, it is possible to measure 10 ng of boron as $^{10}B^{16}O_2^-$ (mass 42) and $^{11}B^{16}O_2^-$ (mass 43) ions with internal precisions better than 0.005% (1s) and an external reproducibility of typically 0.05% (1s).

Analytical Techniques

The TRITON is a multicollector thermal ionization mass spectrometer capable of delivering accurate and precise results for both positive and negative ion measurements. The high sensitivity ion source operates at -10 kV and focuses the negative ion currents onto Faraday cups machined from solid carbon. The multicollectors enable both isotopic ion currents of interest ($^{10}B^{16}O_2^-$ and $^{11}B^{16}O_2^-$) to be collected simultaneously (Figure 1).

A low temperature pyrometer allows accurate filament temperatures to be measured starting at 700 °C, which is essential for reproducible results when analyzing BO_2^- species. One microgram of Ca from a Ca solution ($Ca(NO_3)_2$ in 1% HNO_3) was deposited on single outgassed Re filaments. An aliquot of the sample (containing 5 to 10 ng of B) was then added to the filament and dried with 1.3 A for 60 s. No calcium activator was loaded on the filament for the seawater samples. The sample-coated filaments were loaded into the ion source and the analysis began once the source pressure was lower than 5.0×10^{-7} mbar. Filaments were heated automatically to 1200 mA at 200 mA/min and then stepwise to a temperature of 1000 °C. This typically resulted in a 5 V $^{11}B^{16}O_2^-$ signal. The beam was focused automatically and five blocks of 20 ratios were collected.

Results

One of the analytical challenges to measure boron isotope abundance ratios reproducibly using BO_2^- arises because the results are dependent on the sample loading technique, filament heating program, and measurement procedure employed. The sample can be fractionated during sample deposition and measurement due to the relatively light mass of the BO_2^- ions. It is not possible to apply a normalizing ratio to correct for mass dependent fractionation because boron has only two stable isotopes. Thus, the reproducibility over several filaments is dependent on the skill and experience of the operator.

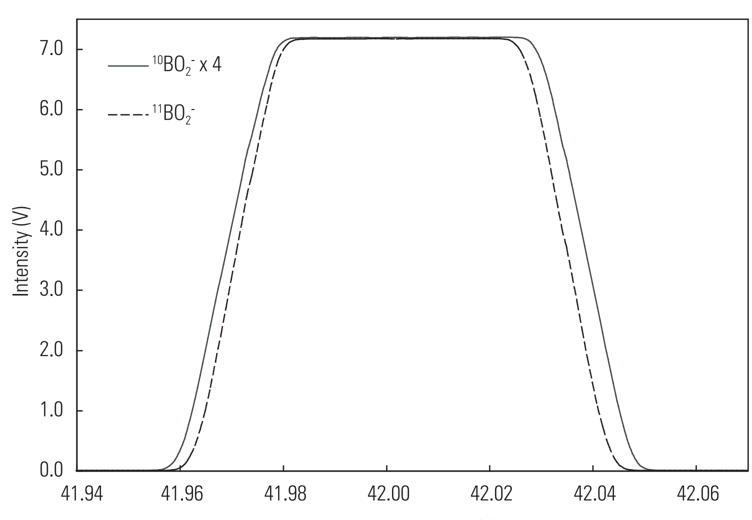

Figure 1: Overlap of $^{10}B^{16}O_2^-$ and $^{11}B^{16}O_2^-$ ion currents on the centre and H1 Faraday cups, respectively. Symmetric, flat-topped peaks are obtained in the negative ion mode.

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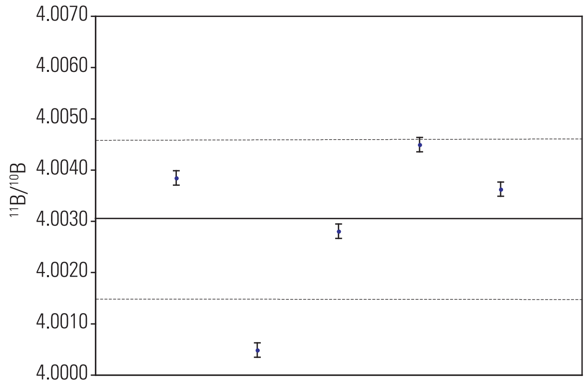

Figure 2: $^{11}B/^{10}B$ isotope abundance ratios of SRM951. The internal precision of each individual measurement is typically 0.005% (1s). The scatter over the five filaments is the result of the relatively rapid isotope fractionation of BO_2^- from the hot filament during analysis.

This is seen in Figure 2, where the internal precision of the individual measurements for each of the five filaments of SRM951 is significantly better than the ability of the operator to reproduce the measured ratio. One possibility to improve the reproducibility over several filaments is to analyze boron as the heavier $Cs_2BO_2^+$ ions (mass 308 u vs 42 u). In this case, isotope fractionation of the sample on the filament is less severe and it is possible to achieve an external reproducibility of better than ±0.01 % over several filaments (Xiao et al., 1988; Deyhle, 2001). However, this method requires the addition of both Cs and graphite activators and is not as simple to apply as the BO_2^- analyses. Since isotope abundance variations encountered in many settings may be several times greater than the analytical precision reported here, negative ion analysis is an acceptable and more practical method. The $^{11}B/^{10}B$ isotope abundance ratios measured for a standard reference material (SRM951) and groundwater and seawater laboratory standards are summarized in Table 1. These data were corrected for the isobaric interference of $^{10}B^{16}O^{17}O^-$ at mass 43 (i.e. $R_{corr}=R_{meas}$-0.00076). The internal precisions of the individual measurements are typically better than 0.005% (1s). The $^{11}B/^{10}B$ isotope abundance ratio for the five measurements of SRM951 is plotted in Figure 2. The average for the five measurements is 4.0031 ± 0.0016 (1s). Isotope abundance variations are reported as relative deviations (in parts per thousand) compared to the boric acid Standard Reference Material SRM951 distributed by the National Institute of Standards and Technology (NIST), in Gaithersburg, USA. Delta values ($\delta^{11}B$) are calculated according to Equation 1 and reported in per mil.

Sample	$^{11}B/^{10}B$	Internal Precision (1s)
SRM951	4.00384	0.00014
SRM951	4.00048	0.00030
SRM951	4.00280	0.00027
SRM951	4.00449	0.00015
SRM951	4.00362	0.00042
Groundwater	3.91726	0.00044
Groundwater	3.92088	0.00006
Groundwater	3.91698	0.00003
Groundwater	3.91925	0.00002
Seawater	4.16036	0.00006
Seawater	4.16475	0.00009
Seawater	4.16222	0.00010
Seawater	4.16077	0.00006

Table 1: Results of the analyses of individual filaments of SRM951 boron isotope standard, a groundwater laboratory standard and a seawater laboratory standard.

Equation 1:
$$\delta\,^{11}B\,(‰) = \left(\frac{\left({}^{11}B / {}^{10}B \right)_{sample}}{\left({}^{11}B / {}^{10}B \right)_{SRM\ 951}} - 1 \right) \times 1000$$

The $\delta^{11}B$ values for each of the groundwater and seawater measurements were calculated using the average value of the five SRM951 filaments and are reported in Table 2.

Sample	δ11B (‰, SRM951)	External Precision (1s) n=4
Groundwater	-21.10	0.46
Seawater	+39.71	0.50

Table 2: $\delta^{11}B$ values measured for four filaments of a groundwater laboratory standard and four filaments of a seawater laboratory standard. The $\delta^{11}B$ values are calculated relative to the average measured value of SRM951 reported above.

Summary

Precise and rapid analyses of nanogram quantities of boron can be achieved using negative ion techniques on the Thermo Scientific TRITON thermal ionization mass spectrometer. The use of a Ca loading agent enhances ion production at low temperatures and results in a stable ion beam and precise isotope abundance data.

References

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