High Precision Boron Isotope Analyses

Negative Thermal Ionization Analysis and Static Multicollection

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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 $\text{BO}_2^-$ 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 $\text{BO}_2^-$ 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 x 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 $\text{BO}_2^-$ 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 $\text{BO}_2^-$ 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.

Key Words

- TRITON
- Boron
- Negative Ions
- TI-MS

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.
The δ¹¹B 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ¹¹B (‰, SRM951)</th>
<th>External Precision (1σ) n=4</th>
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</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>-21.10</td>
<td>0.46</td>
</tr>
<tr>
<td>Seawater</td>
<td>+39.71</td>
<td>0.50</td>
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</tbody>
</table>

Table 2: δ¹¹B values measured for four filaments of a groundwater laboratory standard and four filaments of a seawater laboratory standard. The δ¹¹B 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**
