DETERMINATION OF ISOTOPIC COMPOSITION OF BORON AS Rb$_2$BO$_2$$^+$ BY TIMS


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Introduction

The measurement of precise isotopic composition of boron is very important to nuclear industry, geochemistry, isotope hydrology and paleoceanography. PTIMS where boron is analyzed as polyatomic ions, Cs$_5$BO$_3$$^+$ or Na$_2$BO$_2$$^+$ and NTIMS where BO$_2^+$$^+$ ions are monitored, are the most widely used techniques. Analysis at low masses of 42 and 43 (BO$_2^+$) or 88 and 89 (Na$_2$BO$_2$$^+$) can lead to poor precision, due to high fractionation effects. Attempts have been made to reduce the mass discrimination by using improved loading techniques [1,2,3]. However, ion source isotope fractionation which causes variable systematic error, limiting the accuracy of the isotopic ratio cannot be eliminated. Isotopic fractionation has been observed even during analysis of heavy mass ion Cs$_5$BO$_3$$^+$ at masses 308 & 309 [4]. Though Rubidium is not monoisotopic like Sodium or Cesium, analysis of Boron as Rb$_2$BO$_2$$^+$ has certain advantages. 1) The mass of the molecular species Rb$_2$BO$_2$$^+$ is reasonably high (212-213) resulting in less isotopic fractionation. 2) Unlike Cs$_5$BO$_3$$^+$, simultaneous collection of ions is possible 3) There exists a possibility of correcting for isotope fractionation effects, using the known isotopic composition of Rubidium as internal standard. However as Rubidium has two isotopes, a number of species, 36 vs. 12 for Na$_2$BO$_2$$^+$ and Cs$_5$BO$_3$$^+$ are produced. A detailed theoretical study on the use of Rb$_2$BO$_2$$^+$ ions for isotopic analysis of Rubidium and Boron is discussed in [5]. A number of studies are reported for formation of Na$_2$BO$_2$$^+$, Cs$_5$BO$_3$$^+$ for analysis of boron in different samples and Li$_2$BO$_2$$^+$ for isotopic analysis of Li and B, but only a few studies have been carried out on the use of Rb$_2$BO$_2$$^+$ species [6,7]. In most of the cases, the observed ion intensity and isotope ratio of boron depends on Boron-to-alkali metal atom ratio. The loading technique and the reagent used also affects the ion intensity. For example, when isotopic standard of rubidium in the form of Rubidium chloride was used with boric acid, the ion current yield for Rb$_2$BO$_2$$^+$ was very low [6]. Xaio et al [7] reported reaction of rubidium carbonate with boric acid and use of graphite slurry on the tantalum single filament to give ion current of more than 10$^{-11}$ A, for 2 μg boron. This is expected as boric acid which is a weak acid can only react with a reasonably strong base, to produce borate salt and water.

The present work focuses on the experimental methods for generating Rb$_2$BO$_2$$^+$ ions and explores the possibility of a correlation between the K-factor (mass discrimination factor) for boron isotope ratios and the observed isotopic composition of rubidium. NIST-SRM-951 which is in the form of boric acid with $^{10}$B/$^{11}$B isotopic ratio of 0.2473 ± 0.0002 and Rubidium carbonate with natural isotope abundance of rubidium was used in this work.
Experimental

A state-of-the art, multicollector TIMS with nine adjustable Faraday cups was used for the analysis. Rubidium borate was obtained by reaction of boric acid with rubidium carbonate. Different mixtures of Rb(Natural) and boron(SRM-951) were prepared with boron/rubidium 10 to 0.05. The solutions were loaded as a boronmannitol complex on Ta filament. The filament was coated with about 100μg graphite slurry as a boronmannitol complex on Ta filament. The ion source, the filament was slowly heated to 1.6A in 85 minutes and after degassing for ten more minutes, the sample filament was further heated to obtain Rb B\textsuperscript{10}O\textsuperscript{17} ions. In the present experiment, the Faraday cups were adjusted to simultaneously collect ions from m/q 212 to 217. The ions were integrated for 5 seconds in each scan and typically the data was acquired in three blocks of 12 scans each. Two to three acquisitions of the same loaded sample at higher filament current, were also carried out.

Results and Discussion

For 1.5 to 2 μg boron on the filament, intensity of more than 1x 10\textsuperscript{11} A was obtained, for the \textsuperscript{18}O for all solutions, except B/Rb-10 and 0.05. The \textsuperscript{10}B/\textsuperscript{11}B ratio of the standard was found to vary from 0.2465 to 0.2470, depending on the filament current during analysis and on the B/Rb atom ratio.

The different species obtained at masses 212 to 217 are given in Table 1 along with their abundances for natural boron and rubidium. Though rubidium borate species upto m/q 221 are produced, Rb\textsubscript{2}B\textsuperscript{8}\textsuperscript{16}O\textsuperscript{2} species which constitute the major species are obtained only from m/q 212 to 217.

As can be seen from Table 1, measured ion intensity ratio of the molecular pair at m/q 212/213 (\textsuperscript{212}I/\textsuperscript{213}I) gives measured \textsuperscript{10}B/\textsuperscript{11}B atom ratio and the ion intensity ratio of the molecular pair at m/q 215/213, (\textsuperscript{215}I/\textsuperscript{213}I) = 2 x (\textsuperscript{85}Rb\textsuperscript{87}Rb + \textsuperscript{18}O/\textsuperscript{16}O), obtained by ignoring the negligible contributions of the molecular ions of very low abundance. Using natural isotopic composition of Rb (\textsuperscript{85}Rb\textsuperscript{87}Rb = 2.593) and O (\textsuperscript{16}O/\textsuperscript{18}O = 0.002), internal normalization technique was initially used, to correct for fractionation. However, no improvement in the precision of \textsuperscript{10}B/\textsuperscript{11}B was observed. This is because, the fractionation factor for a species is influenced by the individual elements constituting the molecular species. Therefore, the fractionation factor K for the molecular species \textsuperscript{85}Rb\textsubscript{2}\textsuperscript{11}B\textsuperscript{16}O\textsubscript{2} / \textsuperscript{85}Rb\textsubscript{2}\textsuperscript{16}B\textsuperscript{16}O\textsubscript{2} = \textsuperscript{11}B/\textsuperscript{16}B atom ratio and (\textsuperscript{85}Rb\textsuperscript{87}Rb\textsubscript{2}\textsuperscript{16}B\textsuperscript{16}O\textsubscript{2} + \textsuperscript{85}Rb\textsubscript{2}\textsuperscript{16}B\textsuperscript{16}O\textsubscript{2} / \textsuperscript{85}Rb\textsubscript{2}\textsuperscript{16}B\textsuperscript{16}O\textsuperscript{2} = (\textsuperscript{85}Rb\textsuperscript{87}Rb + \textsuperscript{18}O/\textsuperscript{16}O) atom ratio are different. Thus, in situ normalization is not possible. However, a correlation

<table>
<thead>
<tr>
<th>S.No.</th>
<th>m/q</th>
<th>Major species</th>
<th>Abundances (nat Rb &amp; nat B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>212</td>
<td>\textsuperscript{85}Rb\textsubscript{2}\textsuperscript{10}B\textsuperscript{16}O\textsubscript{2}</td>
<td>10.28</td>
</tr>
<tr>
<td>2</td>
<td>213</td>
<td>\textsuperscript{85}Rb\textsubscript{2}\textsuperscript{11}B\textsuperscript{16}O\textsubscript{2}, \textsuperscript{85}Rb\textsubscript{2}\textsuperscript{10}B\textsuperscript{16}O\textsubscript{2}</td>
<td>41.57</td>
</tr>
<tr>
<td>3</td>
<td>214</td>
<td>\textsuperscript{85}Rb\textsuperscript{11}B\textsuperscript{16}O\textsubscript{2}, \textsuperscript{85}Rb\textsuperscript{10}B\textsuperscript{16}O\textsubscript{2}, \textsuperscript{85}Rb\textsuperscript{11}B\textsuperscript{16}O\textsubscript{16}O, \textsuperscript{85}Rb\textsuperscript{10}B\textsuperscript{16}O\textsubscript{16}O</td>
<td>7.99</td>
</tr>
<tr>
<td>4</td>
<td>215</td>
<td>\textsuperscript{85}Rb\textsuperscript{11}B\textsuperscript{16}O\textsubscript{2}, \textsuperscript{85}Rb\textsuperscript{10}B\textsuperscript{16}O\textsubscript{2}, \textsuperscript{85}Rb\textsuperscript{11}B\textsuperscript{16}O\textsubscript{16}O, \textsuperscript{85}Rb\textsuperscript{10}B\textsuperscript{16}O\textsubscript{16}O, \textsuperscript{85}Rb\textsuperscript{87}Rb\textsuperscript{11}B\textsuperscript{16}O\textsubscript{17}O</td>
<td>32.11</td>
</tr>
<tr>
<td>5</td>
<td>216</td>
<td>\textsuperscript{85}Rb\textsuperscript{11}B\textsuperscript{16}O\textsubscript{2}, \textsuperscript{85}Rb\textsuperscript{10}B\textsuperscript{16}O\textsubscript{2}, \textsuperscript{85}Rb\textsuperscript{11}B\textsuperscript{16}O\textsubscript{16}O, \textsuperscript{85}Rb\textsuperscript{87}Rb\textsuperscript{11}B\textsuperscript{16}O\textsubscript{17}O</td>
<td>1.55</td>
</tr>
<tr>
<td>6</td>
<td>217</td>
<td>\textsuperscript{85}Rb\textsuperscript{11}B\textsuperscript{16}O\textsubscript{2}, \textsuperscript{85}Rb\textsuperscript{10}B\textsuperscript{16}O\textsubscript{2}, \textsuperscript{85}Rb\textsuperscript{11}B\textsuperscript{16}O\textsubscript{16}O, \textsuperscript{85}Rb\textsuperscript{87}Rb\textsuperscript{11}B\textsuperscript{16}O\textsubscript{18}O</td>
<td>6.32</td>
</tr>
</tbody>
</table>
between the fractionation pattern of the two monitoring pairs (m/q 213/212 for $^{10}$B/$^{11}$B) and (m/q 215/213 for $^{85}$Rb/$^{87}$Rb + $^{18}$O/$^{16}$O) could be achieved. Jason et al \[8\] had obtained a linear relationship between the measured $^{18}$O/$^{16}$O ion intensity ratios and measured $^{11}$B/$^{10}$B ion intensity ratios and used the linear relationship to correct for fractionation during BO$_2$ analysis. A similar linear relationship was also observed, during Rb$_2$BO$_2$ analysis.

It was observed that larger amounts of Rb on the filament and higher filament current, resulted in higher fractionation for both $^{87}$Rb/$^{85}$Rb and $^{10}$B/$^{11}$B atom ratios. The data obtained from the analysis of SRM-951 with different B/Rb ratios, was used for obtaining the relationship between the fractionating $^{213}$I/$^{212}$I and $^{215}$I/$^{213}$I. As shown in Figs. 1 and 2, it was observed that both $^{213}$I/$^{212}$I (i.e. $^{11}$B/$^{10}$B) and $^{215}$I/$^{212}$I = $^{213}$I/$^{212}$I x $^{215}$I/$^{213}$I \{i.e. $^{11}$B/$^{10}$B x 2 x ($^{85}$Rb/$^{87}$Rb + $^{18}$O/$^{16}$O)\} vary linearly with $^{215}$I/$^{213}$I. A correlation between the mass discrimination factor, $K = (^{10}$B/$^{11}$B)$_{true}$ / (^{10}$B/$^{11}$B)$_{observed}$ and the $^{215}$I/$^{213}$I could be obtained, by using isotope reference material SRM-951. Fig. 3 shows the correlation between $K$ and $^{215}$I/$^{213}$I and Fig. 4 which

![Fig. 1: Relationship between the ion intensity ratios $^{213}$I/$^{212}$I vs $^{215}$I/$^{213}$I](image1)

![Fig. 2: Relationship between the ion intensity ratios $^{215}$I/$^{212}$I vs $^{215}$I/$^{213}$I](image2)

![Fig. 3](image3)

![Fig. 4](image4)

Figs. 3 and 4: Based on the linearity observed in Figs. 1 & 2 showing the linearity of K-factor of boron with the observed $^{215}$I/$^{213}$I
shows improved regression coefficient, is a plot of $K \times \frac{215I}{213I}$ Vs $\frac{213I}{211I}$. The certified value of 0.2473 for $\frac{10^B}{11^B}$ was used for obtaining the K factor. Using the equation obtained, a correction for fractionation can be carried out, to improve the precision of the analysis. It should be noted that since the same rubidium solution is used in all samples, it is not necessary to obtain the K-factor for $\frac{87^{Rb}}{85^{Rb}} + \frac{18^{O}}{16^{O}}$, thus eliminating the need for isotopic standard of rubidium. The equation obtained from the plot of Fraction Factor for Boron vs $\frac{215I}{213I}$ also makes the calculation for corrected $\frac{10^B}{11^B}$ atom ratio in unknown samples easy and simple. Also because of high abundance of the molecular ion beam of interest at m/q 212, 213, 214, 215 and negligible abundance of the isobaric species at these masses, the equation $\frac{213I}{212I} = \frac{10^B}{11^B} R$ & $\frac{211I}{213I} = 2 \times (\frac{87^{Rb}}{85^{Rb}} + \frac{18^{O}}{16^{O}})$ is easily derived with minimum uncertainty leading to increased reliability of the method [9].

Validation of the Correction method

A few irradiated alloy samples analyzed by $Na_2BO_2^+$ method for $\frac{10^B}{11^B}$ were also analyzed by $Rb_2BO_2^+$ method and correction for fractionation carried out using the linear equation obtained. The observed $\frac{215I}{213I}$ and $\frac{213I}{211I}$ during analyses were used, for obtaining the correction. The correction was carried out for each analysis and not on individual scans. The results are given in Table 2. The Table also gives the data obtained for a natural boric acid sample and boron isotopic standard SRM-951 with different B/Rb atom ratio. Each sample was analyzed at two or more filament currents, with each analysis consisting of 3 blocks with a total of 36 scans. Column 3 of the Table gives the $\frac{215I}{213I}$ ratio obtained for each analysis with the uncertainty given in parenthesis. Column 4 gives the agreement among the different analyses of the same sample loading. As can be seen, the analysis at higher filament current leads to increased isotope fractionation and increases the uncertainty of the isotopic ratio. Column 5 gives observed $2 \times (\frac{87^{Rb}}{85^{Rb}} + \frac{18^{O}}{16^{O}})$ ratio obtained during each analysis with the uncertainty in the ratio given in parenthesis. Column 6 gives the $\frac{10^B}{11^B}$ ratio obtained through internal normalization

Table 2: $\frac{10^B}{11^B}$ ratio observed and corrected for fractionation in different samples

<table>
<thead>
<tr>
<th>sample</th>
<th>Fil. Current(A)</th>
<th>$m/q$-212/213 $\frac{10^B}{11^B}$ observed</th>
<th>Deviation w.r.t mean</th>
<th>$m/q$-215/213 $2 \times (\frac{87^{Rb}}{85^{Rb}} + \frac{18^{O}}{16^{O}})$</th>
<th>$\frac{10^B}{11^B}$ obtained from internal norm</th>
<th>$\frac{10^B}{11^B}$ Corrected with present method</th>
<th>Deviation w.r.t mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>b-alloy-1</td>
<td>1.9 1.95 2</td>
<td>0.2486(0.12) 0.2469(0.04) 0.2441(0.03)</td>
<td>0.01%</td>
<td>0.7783(0.08) 0.7815(0.03) 0.7835(0.02)</td>
<td>0.2452(0.12) 0.2469(0.04) 0.2492(0.01)</td>
<td>0.24546 0.24538 0.24546</td>
<td>0.03%</td>
</tr>
<tr>
<td>b-alloy-2</td>
<td>1.8 1.85</td>
<td>0.2451(0.02) 0.2447(0.02)</td>
<td>0.14%</td>
<td>0.7721(0.02) 0.7814(0.02)</td>
<td>0.2454(0.03) 0.2488(0.02)</td>
<td>0.24552 0.24544</td>
<td>0.03%</td>
</tr>
<tr>
<td>b-alloy-3</td>
<td>2 2.05</td>
<td>0.2470(0.09) 0.2468(0.07)</td>
<td>0.1%</td>
<td>0.7807(0.06) 0.7872(0.05)</td>
<td>0.2479(0.1) 0.2487(0.05)</td>
<td>0.24777 0.24770</td>
<td>0.05%</td>
</tr>
<tr>
<td>Boric acid</td>
<td>1.82 1.87</td>
<td>0.2499(0.05) 0.2498(0.03)</td>
<td>0.044%</td>
<td>0.7781(0.05) 0.7810(0.03)</td>
<td>0.2504(0.03) 0.2508(0.02)</td>
<td>0.25056 0.25056</td>
<td>0.002%</td>
</tr>
<tr>
<td>SRM-951</td>
<td>2 2.05</td>
<td>0.2468(0.01) 0.2467(0.01)</td>
<td>0.02%</td>
<td>0.7735(0.01) 0.7737(0.01)</td>
<td>0.2465(0.01) 0.2464(0.01)</td>
<td>0.24729 0.24726</td>
<td>0.01%</td>
</tr>
<tr>
<td>SRM-951 B/Rb-0.5</td>
<td>2.1 2.15</td>
<td>0.2465(0.04) 0.2464(0.04)</td>
<td>0.04%</td>
<td>0.7813(0.03) 0.7834(0.03)</td>
<td>0.2475(0.03) 0.2477(0.04)</td>
<td>0.24726 0.24722</td>
<td>0.02%</td>
</tr>
</tbody>
</table>
using the value of 0.77531 for $2 \times (^{87}\text{Rb}/^{85}\text{Rb} + ^{18}\text{O}/^{16}\text{O})$ and the observed value at m/q 215/213. As can be seen, the in situ normalization does not result in any improvement in the precision between the different analyses. Column 7 gives the corrected $^{10}\text{B}/^{11}\text{B}$ ratio obtained from the linear equation from either Fig. 3 or 4. The correction improves the precision between the analysis by a factor of 2 to 3 as can be seen from columns 4 and 8.

Conclusion

$\text{Rb}_2\text{BO}_4^-$ method is an attractive viable alternative to $\text{Cs}_2\text{BO}_3^+$ method as its mass is reasonably high and also suitable for simultaneous collection of different ionic species. In addition to this, the fractionation effects on the isotopic ratio of boron can be corrected, by using the linear relationship between the fractionation factors of boron isotopic ratio and rubidium isotopic ratio.

References


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