

## ICP - Mass Spectrometry

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## Boron Isotope Ratio Analysis Using the NexION ICP-MS

abundant by a factor of four. While an earlier IUPAC report listed a fixed value (80.1%  $^{11}\text{B}$ ) for representative isotopic composition of boron<sup>1</sup>, the current edition of the report moved on to quote instead a natural abundance range of 79.6 – 81.1%  $^{11}\text{B}$ <sup>2</sup>, reserving the use of the former representative value in situations where the isotope composition is unknown for purely practical purposes. Accordingly, boron isotope ratios observable in nature can vary by about 100‰ (parts per thousand, or permil) or 10%<sup>3</sup> when expressed as the ratio of the deviation of the sample  $^{11}\text{B}/^{10}\text{B}$  ratio from an appropriate certified reference standard. The primary reference standard used for this purpose is NIST 951<sup>4</sup> with a  $^{11}\text{B}$  abundance of 80.17%. Special applications may require the measurement of wider ratios than occurring naturally. Examples include the use of  $^{10}\text{B}$  enriched boron in nuclear or medical applications<sup>5</sup> or the use of  $^{10}\text{B}$  depleted boron as a special impurity in Si microelectronics or diamond-based future electronics.

### Introduction

Boron (B) is studied for its isotope ratio composition in a range of paleoproxy, geochemical, nuclear, medical, and archeological applications. It has two stable isotopes,  $^{10}\text{B}$  and  $^{11}\text{B}$ , the latter being more

ICP-MS is recognized as a powerful technique for boron isotope analysis. For the most demanding paleoproxy applications, high-resolution multicollector ICP-MS (MC-ICP-MS) is frequently the technique of choice, providing precision and accuracy values for boron down to 0.2 – 0.4%.<sup>6</sup> Quadrupole ICP-MS (Q-ICP-MS) is used, sometimes also in combination with laser ablation, for various applications with less stringent requirements for precision and accuracy. However, also Q-ICP-MS can eliminate much of the noise in conventional measurements by means of collisional damping, yielding precisions close to the theoretical possible precision.<sup>7</sup> This requires using both appropriate instrument hardware and analysis conditions, as discussed further in this application note. Thus, despite essentially being a sequential instrument, Q-ICP-MS delivers performance that can approach that of MC-ICP-MS. Sufficient precision may be obtained even for demanding applications, and the analysis be fit for purpose at a small fraction of the cost of a multicollector instrument. With Q-ICP-MS also being more versatile and not exclusively dedicated to isotope ratio measurements, the appreciation of its isotope ratio capabilities can bring high-quality isotopic ratio analysis into the reach of laboratories with varied analysis needs. While Q-ICP-MS has been successfully used for boron isotope ratio analysis<sup>8</sup>, collisional damping is rarely used in the published literature, and published results therefore perhaps do not reflect the true potential of Q-ICP-MS. The purpose of this study is to investigate the performance attainable by Q-ICP-MS, using PerkinElmer's NexION® ICP-MS, when fully utilizing the instrument's capabilities.

This application note describes the analysis of boron isotope ratios using a sample depleted in <sup>10</sup>B isotope and a regular sample with natural ratio composition, in order to cover both the analysis scenario of samples close to the natural ratio and secondly the case of wide ratios. The content covers instrument setup, calibration, precision, drift and accuracy of isotope ratio measurements. Performance is discussed within the context of the theoretically attainable precision. While special attention is given to practical aspects relevant to boron analysis, the experimental setup is described with sufficient detail and background to also provide a useful starting point for users searching to maximize performance for other isotope ratio applications.

## Experimental

### Samples

Two different types of samples were analyzed:

- A general boron single-element concentration standard (non-certified isotopically) 1000 ppm (mg/L) in water (PerkinElmer Inc., USA) diluted to 100 ppb (µg/L) in deionized water
- Boric acid highly depleted in <sup>10</sup>B, dissolved in deionized water at a concentration of approximately 500 ppb B

### Calibration and Reporting of Results

A certified isotopic boron standard VHG-LIS11B-50 (LGC, Teddington, UK) was diluted to 100 ppb B and used to establish mass bias as part of the calibration routine. The <sup>10</sup>B/<sup>11</sup>B ratio in the general boron standard was measured against the isotopic boron standard. The <sup>10</sup>B depleted sample was measured against the general boron standard, whose isotope abundance was found to match that of the certified isotope standard. Calibration was established with abundance % (i.e. atom %) data of the isotopic composition of the reference standard, and isotope ratios are reported as abundance ratio (i.e. atomic ratio). All analyses took place using the dedicated isotope ratio analysis method within Syngistix™ for ICP-MS software. In this study, we report the ratio as <sup>10</sup>B/<sup>11</sup>B with the more abundant <sup>11</sup>B in the denominator. Precision and accuracy values are given in percent accompanied by occasional reference to the corresponding permit values in brackets.

### Instrument Setup

A NexION 2000 ICP-MS was used for this study. In addition to the analytical quadrupole, this instrument features a quadrupole Universal Cell for the controlled removal of interferences, plus multiple gas channels for maximum choice of cell gases. Isotope ratio analysis for best precisions is done in Reaction mode.<sup>7</sup> A cell gas (inert or reactive) is used to thermalize the ions from the plasma when determining their ratios by a process known as collisional damping. The key benefit of Reaction mode in isotope ratio applications is thereby to reduce fluctuations of the ion beam density, thus reducing measurement noise and allowing the optimal dwell time range to expand upwards from 0.1 ms to several ms.<sup>7</sup> The type of gas (e.g. argon, helium, or ammonia) and its flow are chosen such that enough collisions occur to minimize the energy spread of the analyte ions and by these means to improve measurement precision while maintaining sufficient sensitivity. Depending on the application, the measurement can additionally be conducted with removal of any on-mass interferences by means of reactive cell gases. For the case of boron, its isotopes do not suffer from spectral interferences and have very low mass. Using helium as an appropriate choice of collision gas, boron sensitivity remains relatively unaffected at flows up to 2 mL/min and declines at higher flows (Figure 1). Since only one gas channel is necessary for this application, the analysis could be equivalently implemented on a NexION 1000 instrument.

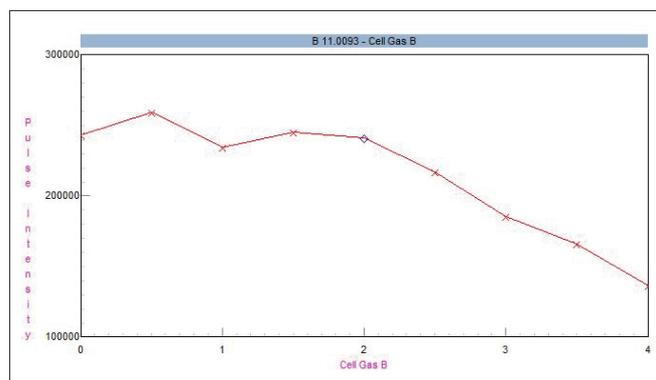


Figure 1. Impact of helium cell gas flow on <sup>11</sup>B sensitivity.

The NexION ICP-MS was set up with a PFA spray chamber with a self-aspirating PFA nebulizer and operated in Reaction mode using 2 mL/min helium. The nebulizer flow was optimized with the daily tuning solution using the default criteria for Ce double charged (<3%) and Ce oxide ratio (<2.5%). The cell voltages were optimized for maximum boron sensitivity; the complete setup is given in Table 1. A quadrupole settling time of 200  $\mu$ s was used. The ability of NexION instruments to achieve stable measurements at such low settling times is a further critical component for achieving superior isotope ratio precision, as it allows the use of very short dwell times while maintaining a high duty cycle, defined here as the fraction of total active counting time.

The isotope ratio method type was selected for data acquisition, using the settings reported in Table 2. Dwell times for  $^{10}\text{B}$  and  $^{11}\text{B}$  were set appropriately to account for the difference in the abundances of the boron isotopes. For best results, the number of ions counted for each isotope should be optimized, resulting in favorable counting statistics during reasonable measurement times. For this reason, the dwell time for  $^{10}\text{B}$  is longer than for  $^{11}\text{B}$ , and the dwell times for  $^{10}\text{B}$  are different between the standard and depleted samples. Duty cycle is high ( $\geq 94\%$ ), indicating that the instrument loses at most 6% of the analytical time to settle the electronics between mass jumps. Thus, the instrument works efficiently despite employing short dwell times down to 1 ms.

### Effect of Dead Time on Accuracy

For accuracy, it is necessary to characterize the dead time of the detector system. At high signal intensities ( $> 10^5$  cps) using the correct detector dead time setting becomes highly critical for isotope ratio accuracy. The reason for this is that with increasing signal, there is a higher chance that an ion arrives at the detector while the system is still processing the preceding ion. When this occurs, the second ion will not be counted. Therefore, the observed signal measured by the detector may be several % lower than the true signal of ions arriving at the detector. The deviation of the true count rate from the observed count rate for three different detector speed scenarios is shown in Figure 2.

Table 2. Method Parameters.

Parameter	General Boron Standard (Natural Abundance)	Boric Acid with Depleted $^{10}\text{B}$
Method Type	Isotope Ratio	Isotope Ratio
Sweeps per Reading	200	300
Readings per Replicate	10	10
Replicates	10	10
Dwell Time $^{10}\text{B}$	5 ms	10 ms
Dwell Time $^{11}\text{B}$	1 ms	1 ms
Duty Cycle	94%	96%
Total Analytical Time	128 s	6 min 4 s

The effect of dead time can be and must be corrected. The software comes with a predefined acquisition workspace for this purpose, supported by instructions in the Help menu. With the dead time set correctly, the raw signal is accurately and automatically corrected by the software, meaning that the measurement of standard and samples can be made at different signal intensity levels without introducing bias.

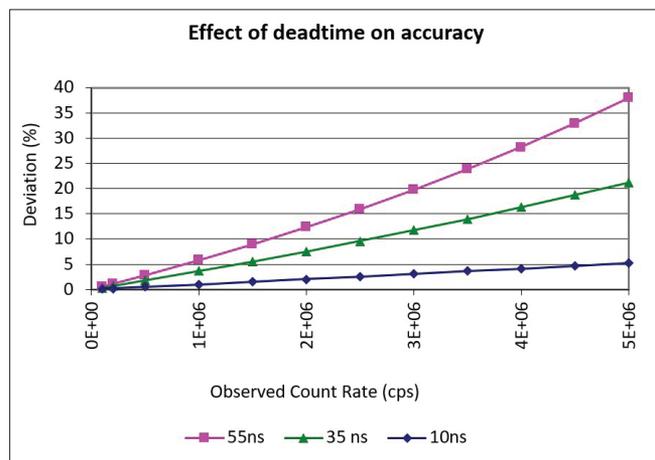


Figure 2. Calculated percent deviation of true count rate from observed count rate for three dead time scenarios.

Table 1. NexION ICP-MS Instrument Setup.

Parameter	Value
Nebulizer	PFA-ST
Sample Uptake	100 $\mu$ L/min, Self Aspirating
Spray Chamber	PFA Scott at Room Temperature
Injector	2 mm Sapphire
Cones	Pt
Plasma Power	1600 W
Plasma Gas	15 L/min
Aux Gas	1.2 L/min
Neb Gas	1.0 L/min
QID	Fixed at -15.5V
Cell Mode	Reaction
Cell Gas	Helium, 2 mL/min
RPq	0.45

## Dual Detector Calibration

Depending on the circumstances, it may be important for accuracy to additionally consider dual detector calibration (detection ranges cross calibration). This is relevant if measurements cross over between the pulse and analog stages of the detector, such as when determining ratios  $< 10^{-4}$ . Attainable precisions would be severely limited by the low abundance of the minor isotope if detection is restricted exclusively to the pulse stage. Dual detector calibration was utilized in this study for the  $^{10}\text{B}$  depleted sample due to the wide ratio of this sample when measured intensities exceeded the pulse stage. However, in order to avoid any potential inaccuracies due to dual detector calibration, a common approach is to limit measurements to the pulse stage of the detector when possible, as was used in this work for the general (natural) boron standard. Pulse detector shutdown occurs at 2 Mcps for a detector with correctly optimized detector voltages, with a safe operating level chosen somewhat below that value to ensure all readings are collected on the pulse stage at all times. The absence of a 'detector shutdown' symbol in the Realtime window (set to "pulse detector only" view) allows the user to verify that all measurements occurred on the pulse stage.

## Boron Washout

Boron is renowned for being a 'sticky' element, because of its difficulty washing out from the sample introduction system, particularly the spray chamber. Direct injection nebulization, which avoids the use of a spray chamber altogether, can successfully address this issue<sup>9</sup> and, where available, might be considered as a promising alternative sample introduction type.

Because boron does not rinse out well with water, the following four solutions were used to improve washout: 1% methanol (v/v), 1% mannitol (w/v), 0.5% HF (v/v), and 10%  $\text{NH}_4\text{OH}$  (v/v). Figure 3 shows an example of how 10%  $\text{NH}_4\text{OH}$  improves boron washout compared to water. Washout to a low and reproducible level is of critical importance for accurate, stable isotope ratio analyses. For the depleted  $^{10}\text{B}$  sample in particular, a change in blank level of just 10 cps could introduce a bias of 1% in the measured isotope ratio. Therefore, for this analysis, the  $^{10}\text{B}$  blank level was monitored closely and kept below 50 cps prior to calibration and before sample measurement.

## Results and Discussion

### Analysis of a Sample with Natural Abundance Ratio

Following calibration with the certified isotopic standard to correct for mass bias, a 100 ppb solution of the general B standard was analyzed five times in alternation with the certified isotopic standard

in order to determine precision and accuracy. The results are displayed in Table 3 and Figure 4. It can be seen that the means are close, and the overlap of the standard deviations is large. The certified isotopic standard had a certified  $^{10}\text{B}/^{11}\text{B}$  ratio of  $0.2473 \pm 0.0003$  ( $2\sigma$ ). When read back against itself, it produced a group average ratio of  $0.2476 \pm 0.0003$  ( $1\sigma$ ) for five measurements. The accuracy of the average readback was 100.10% (i.e. 1.0% deviation), well within the range of the  $1\sigma$  measurement precision (0.14% or 1.4%). The  $^{10}\text{B}/^{11}\text{B}$  ratio for the general boron standard was determined to be  $0.2475 \pm 0.0002$  ( $1\sigma$ ). The measured difference in the isotope ratio between the general boron standard and the certified isotopic standard is very small (0.03% or 0.3%) and not statistically significant, implying that the isotopic abundance of  $^{10}\text{B}$  and  $^{11}\text{B}$  in the two solutions can be taken as being identical. Taken together, these results show that boron isotope ratios were measured with both high accuracy and high precision.

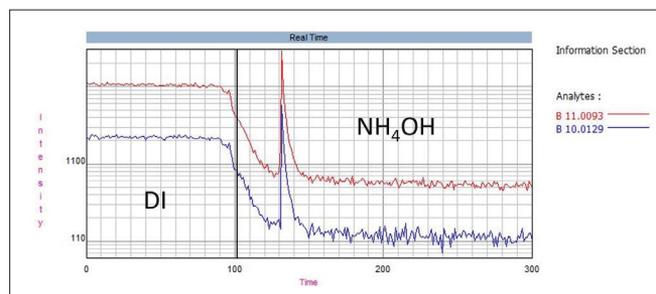


Figure 3. Boron washout, showing the effect of 10%  $\text{NH}_4\text{OH}$  (v/v) compared to DI water.

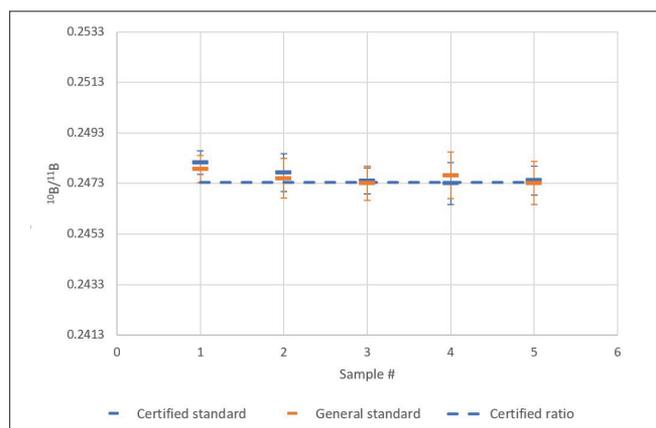


Figure 4. Comparison of certified isotopic standard and general boron standard  $^{10}\text{B}/^{11}\text{B}$  ratio mean and standard deviation ( $1\sigma$  error bars) for five repeat sample analyses.

Table 3. Accuracy and Precision for Five Repeat Measurements of 100 ppb B Solutions.

Sample	Certified Isotopic Standard		General B Standard	
	$^{10}\text{B}/^{11}\text{B}$ Ratio	RSD	$^{10}\text{B}/^{11}\text{B}$ Ratio	RSD
1	0.2481	0.19%	0.2479	0.22%
2	0.2477	0.31%	0.2475	0.32%
3	0.2474	0.21%	0.2473	0.27%
4	0.2473	0.34%	0.2476	0.38%
5	0.2474	0.23%	0.2473	0.35%
Group Avg and Group RSD	0.2476	0.14%	0.2475	0.09%

It is instructive to compare the attained precision to the theoretically possible precision as predicted by Poisson counting statistics calculations.<sup>7</sup> The theoretically attainable precision (i.e. RSD) for an individual isotope equals the inverse of the square root of collected counts, with the corresponding RSD for the ratio of two isotopes being dictated by simple error propagation. The respective calculation for the experiment discussed above shows the theoretically attainable precision is 0.19%, with both isotopes contributing equally to attainable precision, comparing well to the achieved values ranging from 0.19-0.38%, as shown in Table 3. Being within 30% of the counting statistics limit is typically achievable with the collision damping approach employed here.<sup>7</sup> Group RSDs (0.15% and 0.09% for certified and general standard, respectively) are substantially below the 0.19% theoretical RSD for individual samples, in line with statistical expectations.

A further experiment with the general standard was conducted in order to evaluate the best attainable precision over a wider range of acquisition times, by varying the number of sweeps per reading from 5 to 1000. The dwell times shown in Table 2 were used again to allow acquisition of roughly equal number of counts for both isotopes over the acquisition period. As in the previous experiment, five sample determinations were carried out for each sweep setting. The corresponding analytical time and theoretical RSD expected from counting statistics are listed in Table 4, together with the measured sample RSD and group RSDs. In line with the previous experiment, sample RSD refers to the distribution of individual replicates about the sample mean – reported is the average RSD for five repeat sample analyses – and group RSD refers to the distribution of a sample analysis result around the group average of all samples. Figure 5 shows the same data as a graphical display of the relationship of precision with counting time as indicated by the number of sweeps. It can be seen that the measured sample RSD tracks counting statistics RSD closely, down to a measured RSD of 0.066% RSD vs. a theoretically possible RSD of 0.052% for the longest acquisition time in the series. Corresponding group RSDs show a similar trend with the best value of 0.037% (or 0.37‰) achieved for the longest counting time. The tight group RSD of 0.037% for the longest measurement series implies there was no significant drift over the hour it took to acquire the five determinations of the group. Minimization of drift is a key benefit of the Triple Cone Interface/Quadrupole Ion Deflector design used in the NexION instrument series, evidenced also by the superior four-hour drift specification for NexION. Since Q-ICP-MS does not measure at flat top mass peaks as compared to MC-ICP-MS, superior mass spectrometer stability is required for accurate and precise measurements.

Table 4. Dependence of Measured Precision on Counting Time.

Sweeps/Reading	Sample Analysis Time	Counting Statistics RSD	Measured Sample RSD	Group RSD (n = 5)
5	3 s	0.74%	1.22%	0.44% (4.4‰)
25	16 s	0.33%	0.53%	0.11% (1.1‰)
100	64 s	0.17%	0.29%	0.083% (0.83‰)
500	5 min 20 s	0.073%	0.13%	0.081% (0.81‰)
1000	10 min 40 s	0.052%	0.066%	0.037% (0.37‰)

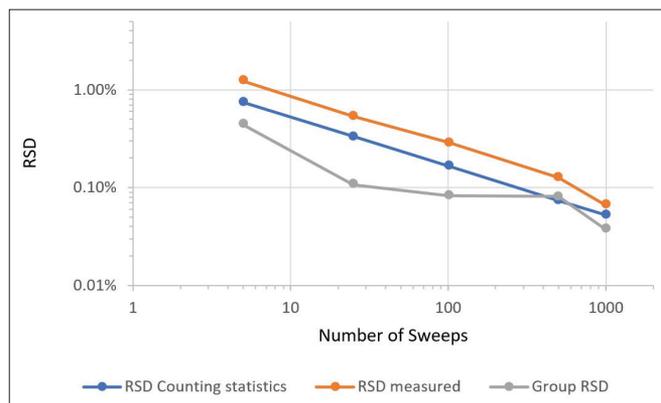


Figure 5. Dependence of precision on counting time, as indicated by number of sweeps.

### Analysis of Boric Acid with Highly Depleted <sup>10</sup>B

With the instrument calibrated using the general boron standard (whose isotopic composition matched that of the certified isotopic standard), the isotope ratio of the boric acid sample was measured with the acquisition parameters given in Table 2, using increased <sup>10</sup>B dwell time and increased number of sweeps/reading on account of the depleted <sup>10</sup>B level of the sample. The sample was aspirated for 15 min for maximum stabilization prior to being measured 10 times successively, with the results reported in Table 5. The group average <sup>10</sup>B/<sup>11</sup>B ratio is 0.0008109 ± 0.0000019 (1σ) with a group RSD of 0.23% (2.3‰). Individual sample RSDs obtained (Table 6) compare well to the theoretically attainable precision of 0.53% (Table 6). The close agreement demonstrates that the NexION ICP-MS is capable of measuring at the highest precision theoretically attainable. The limiting factor for the attainable precision was <sup>10</sup>B isotope abundance, owing to the low intensity of the <sup>10</sup>B isotope (Table 6). From the graphical display of the data in Figure 6, it is evident there was no drift.

Table 5. 10 Repeat Measurements of a Sample Highly Depleted in <sup>10</sup>B.

Sample #	<sup>10</sup> B/ <sup>11</sup> B Ratio	RSD
1	0.0008102	0.75%
2	0.0008090	0.58%
3	0.0008100	0.73%
4	0.0008113	0.42%
5	0.0008085	0.67%
6	0.0008119	0.35%
7	0.0008144	0.31%
8	0.0008117	0.44%
9	0.0008128	0.49%
10	0.0008095	0.60%
Group	0.0008109	0.23%

Table 6. Counting Statistics for Acquisition of a Sample Highly Depleted in <sup>10</sup>B.

Isotope	Integration Time (s)	cps	cts	RSD
<sup>10</sup> B	30	1195	35844	0.53%
<sup>11</sup> B	3	1809435	5428306	0.04%
<sup>10</sup> B/ <sup>11</sup> B				0.53%

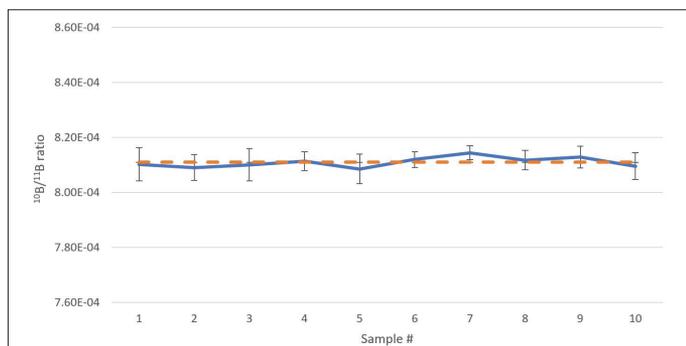


Figure 6. Boron isotope ratios of a boric acid sample depleted in <sup>10</sup>B, analyzed 10 times in direct succession. Error bars indicate standard deviation of the measurements. The dashed orange line indicates the average ratio of the 10 analyses. Analysis time 6 min 4 sec per sample.

## Conclusion

In this study, a boric acid sample highly depleted in <sup>10</sup>B has been analyzed with the NexION ICP-MS operated with collisional damping. Ten repeat analyses yielded a <sup>10</sup>B/<sup>11</sup>B group average of  $0.0008109 \pm 0.0000037$  ( $2\sigma$ ). The measured precision is at the level predicted by counting statistics, demonstrating that the NexION ICP-MS is measuring at the best possible level of precision. Furthermore, this result demonstrates superior blank control on account of the low levels of <sup>10</sup>B involved. The instrument was able to read back a solution of known natural abundance with high accuracy, averaging 0.10% (1.0‰) deviation, well within the measurement precision of that experiment (0.14% or 1.4‰). No drift was evident during any of the batch measurements. When the attainable precision was not limited by low abundance of an individual isotope, very good precisions were achieved at moderate counting times (ca. 10 min), down to 0.066% (0.66‰) for individual measurements, 0.037% (0.37‰) for measurement groups, and within 30% of the counting statistics limit. This is not far (factor of 2-3) from the performance of multicollector ICP-MS at less than 30% of the price. In summary, the advanced instrumental features of the NexION ICP-MS, operated in Reaction mode at high scan speeds with exceptional duty cycle, delivered superb performance for boron isotope ratio measurements.

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## Consumables Used

Component	Part Number
PFA-ST Nebulizer	N8145368
PFA Scott Spray Chamber	N8152390
2 mm Sapphire Injector	N8152447
Platinum Sampler Cone	W1033614
Platinum Skimmer Cone	W1026907
Boron Standard, 1000 ppm	N9303760 (125 mL) N9300106 (500 mL)
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)

