Use of Inductively Coupled Plasma-Mass Spectrometry in Boron-10 Stable Isotope Experiments with Plants, Rats, and Humans

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boron concentrations and isotope ratios in a large number of samples with minimal sample preparation. A typical analytical sequence for fecal sam-

Table 1. Offline calculations summary.

1	$^{9}I, ^{10}I, ^{11}I$	Raw peak integrals
2	$I_{Nor} = I_n \times (^{9}I_1 / ^{9}I_n)$	Normalize / run
3	I_{Avg}, RSD	Average and statistics
4	$I_{Corr} = (I_{Smpl} - I_{Ablk}) - (I_{Dblk} - I_{Ablk})$	Blank subtraction (acid and digestion)
[redacted]		
6	$R_{Corr} = {}^{Smpl}R_{Obs} \times ({}^{SRM}R_{lit} / {}^{SRM}R_{Obs})$	Bias correction
7	$^{11}B = (^{11}I_{Corr} - b) / m$	Regression curve and nmole / ml
8	$^{10}B_{Tot} = {}^{11}B \times (^{10}B / {}^{11}B)$	nmole / ml ^{10}B
9	$^{10}B_{NA} = {}^{11}B_{NA} \times (^{10}B / {}^{11}B)_{NA}$	nmole / ml NA ^{10}B
10	$^{10}B_{Sk} = {}^{10}B_{Tot} - {}^{10}B_{NA}$	nmole / ml ^{10}B spike

Abbreviations: ^{9}I, raw peak integral, ^{9}beryllium (Be); ^{10}I, raw peak integral, ^{10}Be; ^{11}I, raw peak integral, ^{11}Be; I_{Nor}, normalized integral, I_{Avg}, average integral for each isotope; I_{Corr}, corrected integral; I_{Smpl}, integral of sample; I_{Ablk}, integral for acid blank, I_{Dblk}, integral for digestion blank; R_{Obs}, isotope ratios; $^{11}I_{Corr}$, corrected integral for ^{11}boron

passed through a Scott double bypass spray chamber of borosilicate glass to remove larger aerosol particles and some of the water load as the spray chamber is cooled to 6 °C. Boron contamination from the glass spray chamber seems to be minor [redacted]

in acid blanks (see below). The aerosol then flows into a quartz torch where a radio-frequency (RF) field supports an argon plasma in which the sample is ionized in a 7500-K plasma and is extracted from the plasma with the use of two cones, a sample and a skimmer cone. The cones feed the sample into a vacuum system and through a lens stack, which

Table 3. Dwell and precision.[a]

Dwell	Scans	Time	%RSD (n = 20) [b]			
µsec	per min	sec	^{9}Be	^{10}B	^{11}B	$R_{(11/10)}$
10240	450	100	1.5	1.1	1.2	0.6
5120	490	60	1.6	1.5	1.3	0.6
2560	530	40	1.8	1.7	1.7	0.9
1280	560	35	2.0	1.8	1.7	1.3
80	1100	10	2.3	3.1	2.8	2.4

R, isotope ratio. RSD, Relative standard deviation. [a] 50 ppb beryllium (Be) and 50 ppb boron (B) (National Institute of Standards and Technology Standard Reference Material 951); average of 20 accumulations per isotope for an average ^{9}Be peak integral of 16,891 ± 200. [b] n = 10 for 5120 µsec dwell.

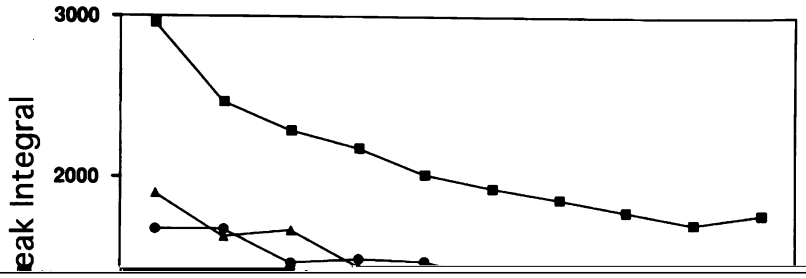
coefficient, *R*, was greater than 0.999 for the calibration curve. The 1% HNO_3 blank used in the calibration ranged from 3 to 5 ppb with much of the boron contamination coming from the laboratory prepared subboiling distilled HNO_3. Detection limits were determined as three times the standard deviation ($3 \times 1\sigma$) of an acid blank by collecting 10, 1-min counts in single ion monitoring. The detection limit for ^{11}B was calculated at

[redacted]

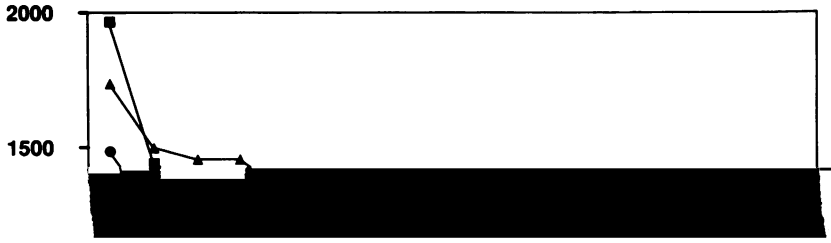
Table 4. Inductively coupled plasma-mass spectrometry autosampler load sequence for fecal sample.[a]

[redacted]

cally 10 ppb, so sample concentrations



show fecal samples and boron standards are the most difficult to rinse from the ICP-MS system. Basic washes have been reported for boron and other elements such as bromine (*7*). However, a basic rinse requires the ICP-MS acid rinse system be changed and the acid digested samples converted to a basic pH. Mannitol represents another option; but when using 1% mannitol in both samples and wash, a rapid



To examine the effects of signal loss, a set of 10 fecal samples was run to verify the increased RSD for the last three samples in an analysis. A pooled set of fecal samples was prepared and isotope ratios determined

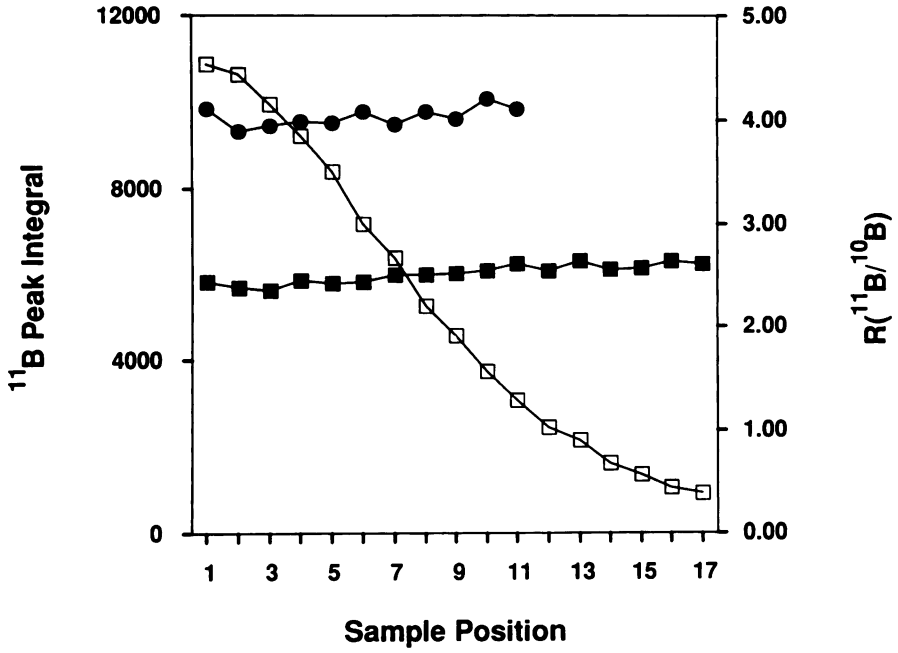


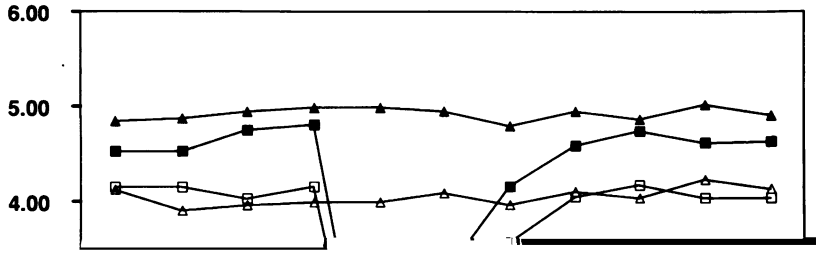
Figure 7. Boron signal loss and isotope ratios effects. Sequential determination of 12 aliquots of pooled fecal digests with cones showing signal loss caused by contamination from previous analysis. Blank corrected ^{11}B peak integral, $^{11}I_{Corr}$, (□) showing a 91% drop in signal; boron isotope ratios for each sample (■) showing a 3.6% RSD over the run and 1.8% for samples 1 to 7. For comparison the urine isotope ratios (●) collected from a metabolic cage from a single animal showing a 2.4% RSD over the entire run.

digestion blank, and bias standard. The loading sequence in Table 4 was based on samples digested in a 12-position microwave turntable. The microwave digestion procedure consisted of 10 samples, 1 digestion blank, and 1 NIST SRM biological standard. The single SRM was diluted into the 4 SRM standards shown in Table 4. For the bias standard, the 50 ppb boron standard in the calibration curve was used.

Several quality control checks were used during data analysis. The average peak integrals, I_{Avg}, and RSD for each isotope were examined. Typically, the RSD within a run was consistent. An RSD of ≤2% for the isotope ratios indicates acceptable variability in an analysis. Finally, calculation of the boron concentration (ng/g) in the bias standard and the SRM biological standard using the mean ^{11}B molar concentration and the measured isotope ratio permits a final check within the run and comparison to previous runs.

Fractionation

Geochemists have shown boron isotope ratios are variable; therefore, there is not a single natural abundance ratio for boron,



nmole/ml of $^{10}B_{St}$ would be simply the difference between the total nmole/ml of ^{10}B in the sample and nmole/ml of naturally occurring ^{10}B in the sample ($^{10}B_{Tot} - {}^{10}B_{NA}$). Because the ^{11}B in the sample was not spiked, it was considered natural abundance, $^{11}B_{NA}$, and when multiplied by the inverse of the sample's natural abundance isotope ratio ($^{10}B/^{11}B$) ... it gave the ^{10}B

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inductively coupled plasma-mass spectrometry. Appl Spectrosc 41:01–806 (1987).

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