An optimized procedure for boron separation and mass spectrometry analysis for river samples

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Abstract

An optimized procedure for the separation of boron from natural river samples and an improved mass spectrometry determination of boron isotopic ratio are presented. The chemical procedure, based on the use of the boron-specific resin Amberlite IRA 743, is especially efficient in separating boron from natural organic matter-rich samples like river waters.

The properties of Amberlite IRA 743 have been investigated. The two factors important in determining the boron affinity for the resin are: the pH value and the ionic strength of the solution from which B is to be extracted. A logarithmic relationship between B partition coefficients and pH values is found. High ionic strength significantly lowers the fixation of B onto the Amberlite resin.

The knowledge of the factors controlling the affinity of the resin Amberlite IRA 743 for boron enables us to design a simple and miniaturized chemical separation procedure characterized by (i) three chromatographic steps using, respectively, 50, 10 and 3 μl of resin, (ii) no evaporation step between each column, and (iii) final separation of boron from residual organic matter by sublimation of boric acid at 75 °C.

Boron isotopic ratios are measured using an improved cesium metaborate technique, with graphite and mannitol. Adequate loading conditions enable us to obtain typical signal intensities of 5×10^{-12} A for 250 ng of boron. No in-run isotopic fractionation is observed, the external reproducibility for standards processed through the entire chemical procedure, as well as for samples, corresponds to 0.35‰ ($\pm 2\sigma$). According to this precision, a slight, but reproducible isotopic fractionation of 0.4‰ is observed for standards processed through the entire chemical procedure whose origin is discussed, but is still unclear. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Boron has two stable isotopes (^{10}B and ^{11}B) with a relative abundance of 19.8% and 80.2%, respectively. The determination of the ^{11}B/^{10}B ratios in natural samples was initiated by Inghram (1946) and Thode et al. (1948). Since these pioneering studies, analytical instruments and chemical procedures have been improved, allowing us today to analyze boron isotopes in nearly all kinds of geological material, with a precision in the order of 1‰ ($\pm \sigma$) or better. In nature, boron shows a large range of isotopic composition (up to 70‰), making it a powerful

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geochemical tracer. In particular, due the high solubility of boron, boron isotopes might be promisingly used in the field of low-temperature water–rock interactions, particularly in continental waters. So far, the boron isotopic composition of river waters has been rarely measured, because of analytical difficulties owing to the low boron concentration levels (of the order of ppb) and to the presence of soluble organic matter.

Analytical methods for boron isotopic ratio determination in natural materials have been reviewed by Aggarwal and Palmer (1995) and Palmer and Swihart (1996). Three different approaches for measuring the boron isotopic composition are used: TIMS, either as positive thermal ionization mass spectrometry (PTIMS) or negative thermal ionization mass spectrometry (NTIMS); inductively coupled plasma mass spectrometry (ICP-MS); and secondary ion mass spectrometry (SIMS). The PTIMS method, consisting of the thermal ionization of cesium metaborate ($Cs_2BO_2^+$) is, to date, the most precise and reproducible technique for boron analyses, leading to a precision as low as $\pm 0.2‰$ ($\pm 2\sigma$), (Xiao et al., 1988; Nakamura et al., 1992; Gaillardet and Allègre, 1995). This technique requires: (i) a relatively large amount of boron, in the order of 1–3 μg, (ii) a careful purification in order to remove alkali ions, (iii) boron separation from organic matter, which decreases the signal intensity and generates isobaric interference during the analyses. Therefore, the PTIMS procedure needs an improvement for precise determination of boron isotopic ratios for small amounts of samples and in the presence of organic matter.

Classically, boron extraction from aqueous samples is carried out by methyl borate distillation or by ion exchange using anion, cation or boron-specific resin (see review by Swihart, 1996). The use of the boron-specific resin Amberlite IRA 743 for boron purification has been exemplified by Kiss (1988) and Leeman et al. (1991). A typical volume of 1 ml of resin is used for the extraction of a few micrograms of boron.

The main objective for this study is to improve the PTIMS technique by (i) an enhanced signal intensity allowing us to analyze typical quantities of 250 ng of boron, (ii) a miniaturization of the extraction procedure using the boron specific resin Amberlite IRA 743 for small amounts of boron, (iii) a new procedure for separating boron from organic-rich media.

2. Reagents

High-purity water is obtained with a Millipore Milli-Q water purification system (specific resistivity: 18.2 $M\Omega$ cm^{-1}). Concentrated HCl is purified in the laboratory by subboiling distillation. NaOH, 0.5 M, solution is purified by exchange with boron-specific resin Amberlite IRA 743; NaCl powder was dissolved in water to obtained a 0.6 M solution and adjusted to pH = 8 by addition of boron-free NaOH. Reagent blanks are determined by the isotopic dilution method and are: H_2O (0.2 ppb), HCl (0.6 ppb), NaCl solution (0.7 ppb), NaOH solution (0.5 ppb). Aqueous mannitol (10 mg/g), and CsOH solutions (4.65 mg/g) are prepared by dissolution in Milli-Q water. NIST graphite is added to a mixture of 80% ethanol and 20% H_2O to obtain a final solution corresponding to 13 mg/g graphite. Note that alpha Ultra F' purity graphite can be used indiscriminately. A 250-ppm boron standard solution is prepared by dissolution of standard NIST SRM 951 boric acid powder in H_2O, and two spike solutions of 0.5 and 13 ppm are prepared with ^{10}B-enriched standard NIST SRM 952. For the boron chemical purification, we used the resin Amberlite IRA 743, which is crushed and sieved at the 100–200-mesh fraction.
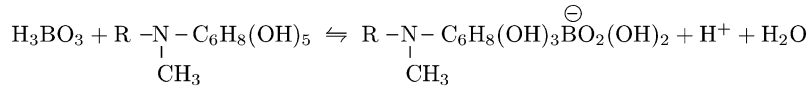
3. Boron extraction procedure

3.1. The characteristics of the Amberlite IRA 743 resin

The extraction of boron from aqueous samples is accomplished by the ion exchange resin Amberlite IRA 743 (also called XE-243) produced by Rohm and Hass®. The resin consists of an *N*-methylglucamine group fixed on a polystyrenic backbone. This tertiary amine is a weak base with a p$K_A \approx 7$ (Pinon et al., 1968). Consequently, the resin behaves

as an anion exchanger at pH values < 7. According to Pinon et al. (1968), boron is strongly fixed onto the alcohol groups of the glucamine for pH values from neutral to alkaline, following the reaction:

$$H_3BO_3 + R-\underset{\underset{CH_3}{|}}{N}-C_6H_8(OH)_5 \leftrightharpoons R-\underset{\underset{CH_3}{|}}{N}-C_6H_8(OH)_3\overset{\ominus}{B}O_2(OH)_2 + H^+ + H_2O$$

A theoretical boron capacity, corresponding to the total number of *N*-methylglucamine groups, of 5.7 mg B/ml is given by Rohm and Hass[®]. Pinon et al. (1968) showed that the boron capacity of Amberlite IRA 743 depends on the boron concentration of the exchanging solution and follows a linear relationship. These authors propose a boron capacity of 4.9 mg B/ml for an infinitely diluted solution, and up to 15 mg B/ml for boron solution of 0.7 M. Kiss (1988) and Leeman et al. (1991) reported similar capacity values.

3.2. Chemical procedure

Due to the high partition coefficient for boron between the resin and the solution (see Section 4) and the rapid ion exchange with the resin Amberlite IRA 743, a miniaturization of the chemical procedure was set up. In order to isolate boron from natural water samples, characterized by B concentrations as low as 1 ppb, a maximum resin volume of 50 μl is necessary for a quantitative boron preconcentration. The purification of boron is then completed with two steps using columns containing 10 and 3 μl of resin. This allows us to minimize the final eluted volume to 40 μl. The exchange time between the solution and the resin is 3, 1 and 1 min, for resin volumes of 50, 10 and 3 μl, respectively.

The three extraction procedures are presented in Table 1. Prior to sample introduction, columns are conditioned with water. The pH of the loaded solution can be as low as 5.5, but should not exceed 9, because of the potential precipitation of hydroxide or carbonate species. For river water samples, the typical loaded volume is 25 ml and the flow rate of sample introduction onto the 50-μl column is accelerated up to about 50 μl/min under hydrostatic pressure (corresponding to an exchange time of 1 min). The introduction step is followed by a "wash-

ing" step using sequential rinses of ultrapure H_2O to eliminate residual sample volume, 0.6 M NaCl, at pH = 8 to exchange the anions fixed on the tertiary amine group of the resin with Cl^-, and finally H_2O to eliminate excess of Na^+. At this step, NaCl rinses show sometimes a brownish color for samples that are characterized by high concentration in dissolved organic matter, but they never contained boron. Boron is eluted from the column with 0.1 M HCl. H_2O, NaCl and HCl solutions are loaded in several steps in order to enhance the reaction time between the resin and the reagents and to avoid the resuspension of resin grains. Due to the potential volatility of boron from organic-rich media (Gaillardet et al., 2001), evaporation steps are avoided between different steps of the chemical procedure. Eluted solutions from the 50- and 10-μl columns are neutralized and adjusted to pH = 8 using boron-free NaOH.

The boron purification is then completed by sublimation. The final elution volume of 40 μl HCl, 0.1 M, is transferred into the cap of a 5-ml conical-shape Teflon beaker. The beaker is wrapped in an Al foil and sited on its cap onto a hot plate at a constant temperature of 75 °C for 12 h, and then allowed to

Table 1
Boron extraction procedure using Amberlite IRA 743 resin

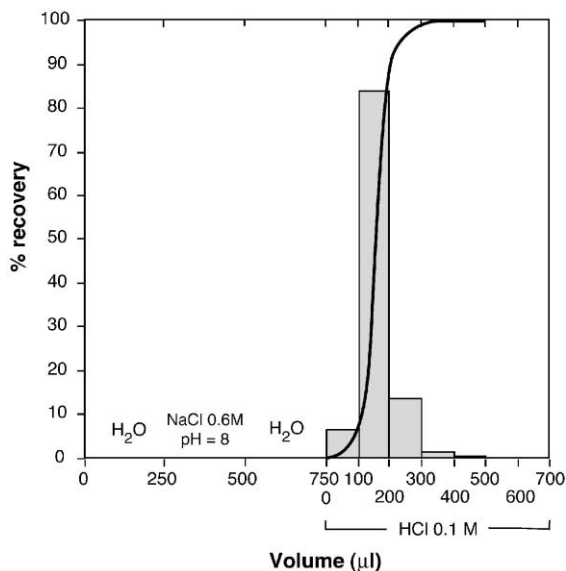|	50 μl	10 μl	3 μl
Column cleanup: 0.1 M HCl, H_2O, 0.5 M NaOH			
Conditioning			
H_2O (μl)	5×100	2×100	4×10
Loading sample: the pH of the solution is adjusted			
between 7 and 9			
"Washing" procedure			
H_2O (μl)	5×50	50	3×10
NaCl, 0.6 M pH = 8 (μl)	5×50	50	–
H_2O (μl)	5×50	2×50	–
Elution			
HCl, 0.1 M (μl)	5×100	2×50	4×10

Fig. 1. Elution curve of boron from a 50-μl column of Amberlite IRA 743 resin and cumulative curve of boron recovery.

cool for 15 min. Boron solution is then recovered at the top of the conical beaker and evaporated to dryness at a controlled temperature of 60 °C. The evaporation of the 40-μl solution takes about 75 min. Even if boron fractionation is not believed to occur during extra-heating of the dried residue (Gaillardet et al., 2001), heating is stopped within a couple of minutes after reaching dryness. The final crystallized residue is ready for loading onto the filament.

All beakers are washed with acetone and 6 M HCl at about 100 °C. The use of HNO_3 is prohibited because of isobaric interference at mass 308 is observed in some cases during analysis, probably due to the Cs_2CNO^+ compound. Such an isobaric interference is clearly observed by adding HNO_3 to the standard solution NIST SRM 951 before analysis.

3.3. Procedural blanks

Boron blanks were determined by isotopic dilution. The reagent blank corresponds to 1.5 ng. The procedural blank for the total chemical separation, including the microsublimation and the evaporation steps, is 3.5 ± 1.5 ng (i.e. less than 2% for a total mass of boron of 250 ng). It suggests that about 2 ng of this blank are attributed to the column and resin contamination and/or airborne boron. These blank levels are negligible for this procedure, but should be taken into account or improved for smaller amounts of loaded boron.

3.4. Boron recovery study

The yield of the boron recovery is quantified by isotopic dilution. The efficiency of the boron extraction procedure is tested by characterizing the elution curves (presented in Fig. 1 for the 50-μl column) and by evaluating the total chemical procedure recovery yield. The boron recovery yield for the extraction procedure from distilled water (pH = 5.5) ranges between 98% and 100%. It is likely that a slight loss of boron (less than 2%, corresponding to three steps of extraction) is consistent with the observed tails in the elution curves. No loss of boron is detected during the sample introduction and the washing steps (H_2O and NaCl). A loss of boron ranging between 5% and 10% occurs during microsublimation and evaporation. The addition of mannitol in the final volume prior to evaporation does not prevent this loss. Tests reported elsewhere (Gaillardet et al., 2001) show that evaporation or microsubli-

Table 2
Batch experiments of equilibration of boric acid solution with the B-specific resin Amberlite IRA 743

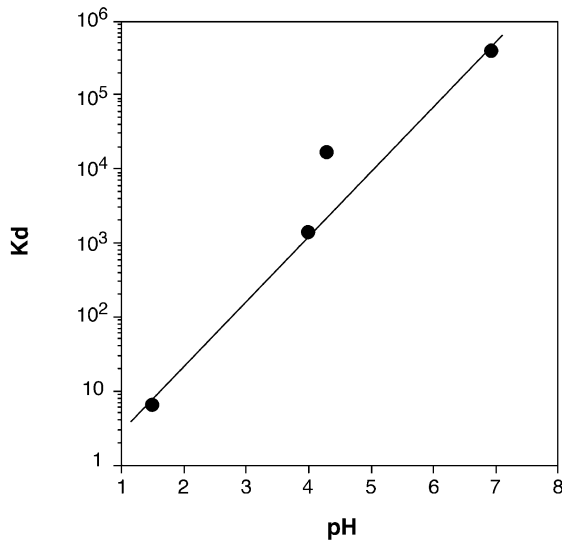| Test No.	$V_{sol.}$ (ml)	$V_{res.}$ (μl)	Initial pH	Final pH	Mass$_{total}^{B}$ (ng)	Mass$_{sol.}^{B}$ after equilibration	K_d
1	0.609	50	1.61	≈ 1	610	402	6
2	10.175	50	4.08	≈ 4	10,185	1318	1350
3	49.758	50	7.51	4.30	49,810	2876	16,250
4	51.726	50	9.85	6.93	51,780	137	389,800

Fig. 2. Partition coefficient (K_d, see text for details) between boron and the *N*-methyl-glucamine groups of Amberlite IRA 743 resin versus value of pH. Results from batch experiments.

mation of boric acid in HCl solution leads to a boron recovery of 100%. It suggests that the cause of this boron loss is to be found elsewhere. One hypothesis is the volatile nature of the organic compound coming from the slight breakdown of the resin.

4. Partition coefficient of Amberlite IRA 743

We carried out batch experiments to evaluate the influence of the pH and the ionic strength of the loaded solution for boron retention by the resin. The boron retention is related to the affinity of the resin for boron, which is described by the partition coefficient K_d:

$$K_d = \frac{[B]_{res.}}{[B]_{sol.}} \tag{1}$$

where $[B]_{res.}$ is expressed in mass of boron per volume of wet resin, and $[B]_{sol.}$ in mass of boron per volume of solution. The batch experiments have been processed as follows: a solution of 1 mg/l boric acid was equilibrated with a precise volume of wet resin during 2 days with shaking. The pH value of this solution was adjusted by adding NaOH or HCl. The boron concentration of the solution was then measured after equilibration by isotopic dilution. The K_d values are calculated using the mass budget equation:

$$K_d = \frac{\left(\text{mass}_{total}^{B} - \text{mass}_{sol.}^{B}\right)V_{sol.}}{\text{mass}_{sol.}^{B} V_{res.}}. \tag{2}$$

The results, listed in Table 2 and illustrated in Fig. 2, vary by 5 orders of magnitude for solutions whose pH values range between 1.5 and 7. The K_d values increase with the pH values of the solution and follow a linear relationship between $\log(K_d)$ and pH with a slope of 0.9. This supports the chemical reaction written in Section 3.1 for the fixation of boron onto the resin. Palmer et al. (1987) also reported a linear relationship between K_d and pH values of seawater equilibrated with riverine sedi-

Table 3

Retention of boron on the resin Amberlite IRA 743 as a function of ionic strength and pH value of the loaded solution (5 μg B/ml)

Volume of resin within the column	pH of the loaded solution	Ionic strength of the loaded solution	Volume of solution loaded before B elution (ml)	Corresponding amount of B fixed on the column (μg B)	Amount of B fixed (μg B/ml of resin)
Resin conditioned with H$_2$O (anionic form)					
2 ml	5.5	0.6 M NaCl	20–24	100–120	50–60
200 μl	5.5	0.6 M NaCl	4	20	100
200 μl	6.5	0.6 M NaCl	6–8	30–40	150–200
20 μl	6.5	0.6 M NaCl	0.8	4	200
200 μl	8.6	0.6 M NaCl	60–64	300–320	1500–1600
20 μl	8.6	0.6 M NaCl	6	30	1500
Resin conditioned with NaOH (0.5 M) followed by H$_2$O (free base form)					
200 μl	5.5	H$_2$O	46–48	230–240	1150–1200
200 μl	8.6	0.6 M NaCl	47–57	230–285	1200

ments. However, their absolute K_d values vary between 2 and 4.

In a practical view, to test how much boron can be retained by the resin in different media, solutions of NIST SRM 951 boric acid concentrated at 5 mg B/l, adjusted to different pH- and salinity values, were continuously loaded onto preconditioned columns. The presence of boron in the eluted fraction was tested sequentially.

The total volume loaded on the resin column before elution of boron gives the total amount of boron effectively adsorbed on the resin. The volumes indicated in Table 3 corresponds to the volumes of eluant in which boron was detected by colorimetric determinations. The amount of boron effectively retained on the resin is reported. This table shows that the retention of boron by Amberlite IRA 743 is strongly affected by ionic force, because a 10 times decrease is observed between pure water and 0.6 M NaCl at pH = 5.5. Such a decrease can be counterbalanced by increasing the pH value. The retention by Amberlite IRA 743 is identical at pH = 5.5, salinity = 0 M and pH = 8.6 salinity = 0.6 M.
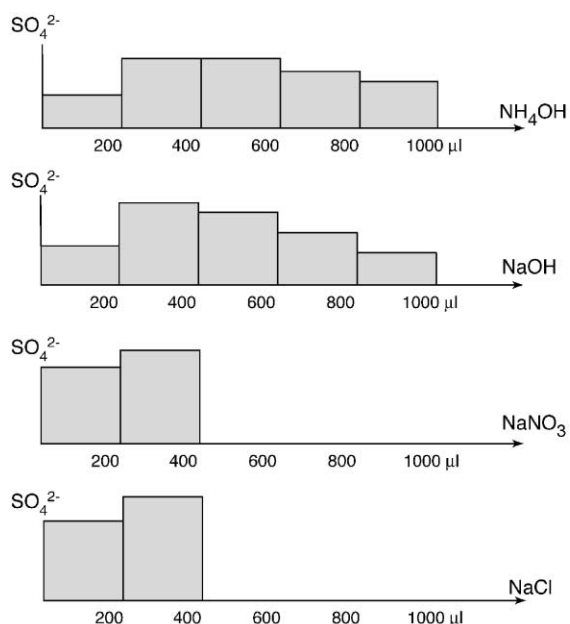

Fig. 3. Histograms showing the removal of sulfate ions fixed onto the Amberlite IRA 743 resin using different rinsing solutions. This experiment is the measure of the relative affinity of major anions on the amine groups Amberlite IRA 743 resin: $Cl^- = NO_3^- >$ OH^-.

5. Removal of anions

As described in the Section 3.1, the tertiary amine fixed on the polystyrenic backbone of the resin has the property to exchange anions with solution for pH ≤ 7. Kiss (1988) and Leeman et al. (1991) used a 3-M ammonia solution for removing anions fixed on the anion exchange sites of the resin. We observe that the wash with NH_4OH is not completely efficient for sulfide-rich solutions. Traces of sulfuric acid (resistant to evaporation) were found in some cases in the final eluted volume and the final solid residues after chemical procedure often contained crystals of NH_4Cl. Therefore, we tested other rinsing solutions: NaOH, NaCl and $NaNO_3$. About 4 ml of mineral water "Contrexeville" was loaded onto 200 μl of resin preconditioned with H_2O. Contrexeville water was selected for its relatively large proportion of SO_4^{2-} ($SO_4^{2-}/Cl^- = 120$). The presence of sulfate anions in the eluted solution was detected by precipitation of $Ba(NO_3)_2$. Results are illustrated in Fig. 3. This figure shows that Cl^- and NO_3^- anions are

more efficient than OH^- in exchanging with SO_4^{2-}. This result is in agreement with the order of affinity of anion-exchange resins (Trémillon, 1965). Because of the delicate use of nitrogen compounds that may induce isobaric interferences during the TIMS analyses, we advocate the use of a 0.6 M NaCl solution for removing the anions. The pH value of this solution is increased to 8 for counterbalancing the decrease of the partition coefficient with the high salinity of the solution. A final wash with H_2O is then necessary to remove Na ions present in the interstitial volume.

6. Removal of organic matter

During the procedure of boron purification, soluble organic matter and boron are closely associated. This organic matter originates from the sample itself or from the slight breakdown of the resin, and usually leads to a decrease of signal intensity during

TIMS analyses, and in some cases, result in isobaric interference.

We investigated a number of techniques to separate boron from organic matter, including UV irradiation, the use of organic matter specific resins, activated carbon and hydrogen peroxide. None of these attempts was completely satisfactory. We propose here a new procedure for separating boron from organic-rich media. Based on the recently developed technique of microsublimation (Gaillardet et al.,

2001), we extract boron from organic matter by sublimation. The procedure is based on the aptitude of boron for sublimation at low temperature, (see details in Section 3.2). A typical mass of boron of 1 ng, but never exceeding 5 ng, is measured in the organic residue remaining at the bottom of the beaker. Separate analyses of organic-rich rivers do not show any relationship between boron content in the organic residue and the isotopic composition of the recovered boron.

Table 4
Boron isotopic composition of standard NIST SRM 951 and natural samples (250 ng of B are processed for each determination)

Date	$^{11}B/^{10}B$	$\pm 2 \times RSD$	$\delta^{11}B$ (‰)	$\pm 2 \times RSD$
Standard NBS SRM 951 with HCl directly loaded onto the filament				
Mean value	4.05288	0.00019		
Error ($2\sigma/\sqrt{n}$)		$n = 22$		
Standard NBS SRM 951 processed through chemistry including microsublimation				
08/12/98	4.05480	0.00035	0.47	0.10
08/01/99	4.05523	0.00044	0.58	0.12
09/01/99	4.05463	0.00040	0.43	0.11
19/01/99	4.05461	0.00035	0.43	0.10
27/01/99	4.05503	0.00056	0.53	0.15
27/01/99	4.05374	0.00100	0.21	0.25
30/04/99	4.05431	0.00052	0.35	0.14
02/05/99	4.05412	0.00061	0.31	0.16
07/05/99	4.05411	0.00038	0.30	0.11
18/11/99	4.05592	0.00080	0.75	0.20
19/11/99	4.05424	0.00050	0.34	0.13
20/11/99	4.05486	0.00043	0.49	0.12
20/11/99	4.05496	0.00084	0.51	0.21
06/02/00	4.05556	0.00048	0.66	0.12
Mean value	4.05472	0.00120	0.45	0.30
Error ($2\sigma/\sqrt{n}$)		0.00032		0.08
Seawater standard CASS2				
30/10/98	4.21538	0.00044	39.62[a]	0.11
31/10/98	4.21536	0.00144	39.62[a]	0.36
09/01/99	4.21529	0.00062	39.60[a]	0.16
20/01/99	4.21533	0.00068	39.61[a]	0.17
17/11/99	4.21505	0.00071	39.54[a]	0.18
Mean value	4.2154	0.00030	39.60[a]	0.07
Amazon river [B] = 6.1 ppb				
20/03/99	4.10286	0.00053	11.87[a]	0.14
11/12/99	4.10290	0.00095	11.88[a]	0.24
11/12/99	4.10447	0.00049	12.27[a]	0.13
13/12/99	4.10333	0.00097	11.99[a]	0.25
Mean value	4.10339	0.00150	12.00[a]	0.37

[*] Normalized to standard mean value $^{11}B/^{10}B = 4.05288$.
[a] Normalized to standard processed through chemistry mean value $^{11}B/^{10}B = 4.05473$.

7. Elution and associated boron fractionation

Boron is eluted with HCl solution. We tested different molarities for HCl solutions and show that the thinnest elution curves are observed for 0.1 M HCl. At higher molarities, the volume of acid necessary for a complete B recovery increases. The elution curve for column containing 50 μl of resin Amberlite IRA 743 is illustrated Fig. 1; 99.4% of the total boron are recovered with 500 μl of 0.1 M HCl. The results for NIST SRM 951 processed through chemistry are reported in Table 4 and show a slight, but reproducible isotopic fractionation of 0.4‰ relative to results when NIST SRM 951 is directly loaded onto the filament and analyzed.

The boron isotopic composition of each eluted fraction was measured in order to constrain boron isotopes behavior during exchange with resin. Results are illustrated in Fig. 4. We observe a strong isotopic effect: ^{11}B is enriched at the head of the elution. Between the first few percents of recovered boron and the end of the elution, an important isotopic fractionation, corresponding to about 100‰, is observed. Similar fractionation trends are reported by
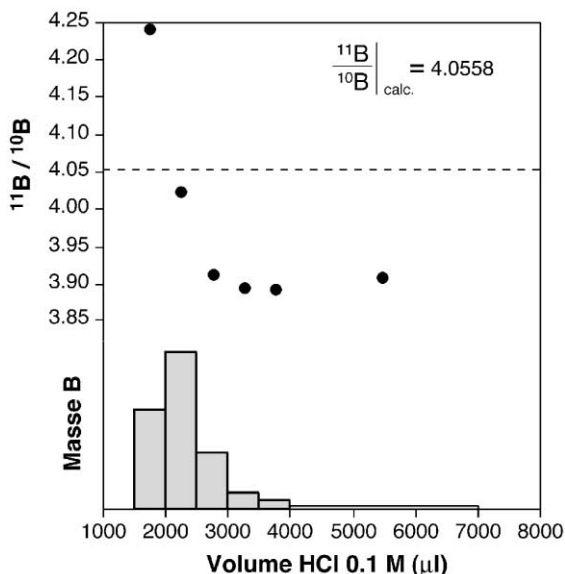

Fig. 4. Isotopic composition and relative mass of recovered boron for each volume of 0.1 M HCl loaded to elute boron from a 1-ml column of Amberlite IRA 743 resin. Black circles are arbitrary centered on each *X*-axis interval.

Conrard et al. (1972) for boron isotope fixation on Dowex 2×10 anion exchange resin. As a consequence, the extraction procedure must assure a complete and quite reproducible recovery of boron.

The results shown in Fig. 4 allow us to calculate an empirical separation factor K ($K = 1 + \varepsilon$) between the two isotopes. From the ion exchange theory, it follows that:

$$V_m = V_0 + K_d M_0 \tag{1}$$

where V_m is the eluent volume for maximum concentration, V_0 corresponds to the interstitial volume of the resin (about 35% of the volume of resin), K_d is the partition coefficient, and M_o is the mass of the resin (Trémillon, 1965). Eq. (1) gives for each isotope:

$$V_m^{10_B} = V_0 + K_d^{10_B} M_0 \tag{2}$$

$$V_m^{11_B} = V_0 + K_d^{11_B} M_0 \tag{3}$$

Eqs. (2) and (3) give:

$$K = \frac{K_d^{10_B}}{K_d^{11_B}} = \frac{V_m^{10_B} - V_0}{K_m^{11_B} - V_0} \tag{4}$$

Conrard et al. (1972) showed a linear relation between the molar percentage of ^{10}B in each eluted fraction and the cumulative mass of recovered boron. Based on this empirical relation, we modeled in Fig. 5 the elution for each boron isotope as two different species with its own partition coefficient. As a result, Eq. (4) gives $K = 1.0009$ ($\varepsilon = 0.9 \times 10^{-3}$) and $K = 1.0014$ ($\varepsilon = 1.4 \times 10^{-3}$) for 50 μl and 1 ml of resin, respectively. These results are one order of magnitude lower than the fractionation factor, calculated using a column length of 11.63 m as studied by Conrard et al. ($\varepsilon = 12 \times 10^{-3}$). This discrepancy is difficult to explain solely by the different number of theoretical plates, and may be due to a non-equilibrium state of boron fixation onto the resin.

An incomplete elution and the loss of boron during the final evaporation may account for the 0.4‰ isotopic shift that occurs during the chemical procedure. The determination of the boron isotopic composition along the elution curve shows that the tail of the elution has a very low $^{11}B/^{10}B$ ratio of about 3.9 ($\delta^{11}B = -35‰$). A loss of 1% of boron at the end of the elution should cause a shift of 0.2 ‰ for the recovered solution. The total range of the
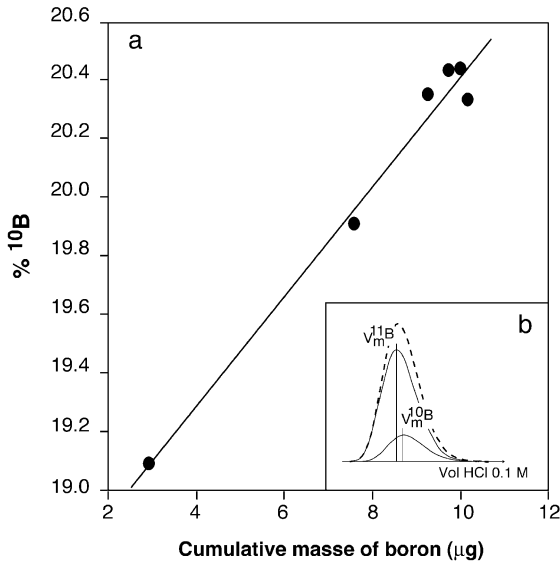
Fig. 5. (a) Percentage of [10]B in each 0.1 M HCl elution fraction (corresponding to 1 ml of resin) expressed as a function of the cumulative mass of recovered boron. (b) Representation of boron isotopes peak separation during purification with the resin Amberlite IRA 743 (see text for more details).

analyses of standards NIST SRM 951 processed through the whole chemical procedure may be thus explained by extraction recovery yields ranging between 97.9% and 99.5%. This explanation is likely, but it implies that no isotopic fractionation of boron occurs during evaporation and microsublimation. This hypothesis is confirmed by the study of Gaillardet et al. (2001), showing that no isotopic fractionation occurs during evaporation of HCl solutions. In addition, no relation exists between boron staying in cap and isotopic composition of recovered boron during microsublimation. Tests on boron extraction procedure show that long time storage of resin Amberlite IRA 743 in 1 M HCl solution damages the resin properties. NIST SRM 951 processed through the chemical procedure after a storage a several weeks of the resin leads to boron recovery yields after final microsublimation and evaporation as low as 80%, although recovery yields higher than 99% are measured before the microsublimation and evaporation step. The isotopic ratios corresponding to these low recovery yields are fractionated up to +2‰. Repeated procedures enhance the efficiency of the extraction procedure and decrease the isotopic

fractionation to the typical value of +0.4‰. We suggest that a boron volatile compound is present in the eluted solution, probably derived from the breakdown of the resin. It is likely that the reaction is enhanced by UV photo-oxidation of the *N*-methyl glucamine. This volatile compound may be an ester of low molecular weight or a methylborate.

8. Mass spectrometry

8.1. Filament loading

Single tungsten V-shaped filaments are used for isotope analyses. They are previously outgassed at 5 A for 4 h, then stored in a clean room for several days to avoid a spreading load. The boron loading procedure follows that of Xiao et al. (1988), later modified by Leeman et al. (1991), with slight modifications allowing to analyze only 250 ng of boron. A mixture of 1 μl of CsOH solution (31 nmol), 1 μl of mannitol solution (55 nmol), and 2 μl of 0.1 M HCl containing 250 ng of boron is prepared. The B/Cs and B/mannitol molar ratios are 3:4 and 1:2, respectively. Prior loading the boron solution, 1 μl of a graphite suspension is used to coat the filament and heated nearly to dryness at 1 A. Special care is taken for not spreading graphite under the filament that causes a decrease of the signal intensity and in-run boron isotopic evolution. The load onto the filament of higher amounts of graphite leads to a decrease of the signal intensity. Boron solution is added step by step, and dried under a heating lamp. Evaporation to dryness of the 4 μl of the boron solution takes about 6 min. The loading procedure is stopped exactly after 15 min under the heating lamp.

It is shown that this loading procedure is also suited for analyzing 50 ng of NIST standard solution (see Fig. 6).

8.2. Isotopic composition determination

All determinations of boron isotopic composition are performed with a thermal ionization mass spectrometer (Thomson-CSF type THN 206), with a single magnetic sector (60°, 30-cm radius). Measurements are made with a single Faraday cup detector, coupled to a 10^{11} Ω resistor, and ion currents of
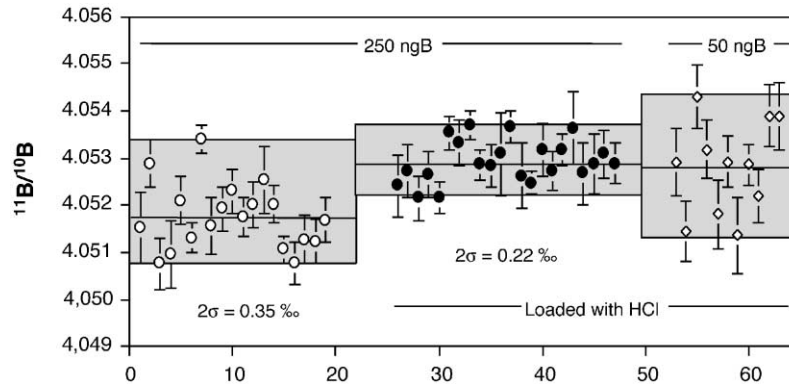
Fig. 6. Reproducibility of standard NIST SRM 951: (○) 250 ng of boron loaded without free HCl; (●) 250 ng of boron loaded with free HCl; (◇) 50 ng of boron loaded with free HCl. Lines indicate the mean value. Shaded areas indicate the total range of variation.

10^{-13}–10^{-10} A are available for isotopic determinations. The accelerating voltage is fixed at 6 kV. The filament is heated to 2 A at the rate of 0.5 A/min, then adjusted (at the rate of 0.05 A/min) to obtain the typical ion current of 5×10^{-13} A for the mass 309.

The mass ratio 309/308 is measured by determining alternatively ion current intensities at mass 306.5, 308, 309. The integration time for each mass corresponds to 5, 5 and 2 s, respectively. A typical analysis consists of 15 blocks of 12 ratios each, and a linear interpolation is used during peak jumping. Errors are calculated as the two mean standard deviation $\sigma_m = 2\sigma/\sqrt{N}$, where N is the number of averaged blocks. Measured ratios are corrected for ^{17}O contribution ($Cs_2{}^{10}B^{16}O^{17}O$) at mass 309 as follows: $^{11}B/^{10}B = 309/308_{measured} - 0.00078$. Assuming a natural variation of 5% for the $^{17}O/^{16}O$ ratio, this does not exceed a correction error of 0.02‰ on the $^{11}B/^{10}B$ ratio that is small relative to the analytical error (Spivack and Edmond, 1986).

8.3. Analytical precision and accuracy

The external reproducibility for standard NIST SRM 951 is presented in Fig. 6. The oxygen corrected mean value corresponds to 4.05174 ± 0.00032 (0.08‰, $n = 19$). This value is significantly higher than the certified value 4.04362 ± 0.00137 (Catanzaro et al., 1970), but close to previously published analyses using graphite and/or mannitol procedure (Leeman et al., 1991; Nakamura et al.,

1992; Gaillardet and Allègre, 1995). Adding HCl during loading onto the filament improves the external reproducibility, as shown by separate analyses of standard solution, giving an oxygen corrected mean value of 4.05288 ± 0.00019 (0.05‰, $n = 22$), and generally increases the signal intensity allowing to load only 50 ng of boron. The explanation of the increase of the signal intensity by addition of HCl on the filament is, at the present day, still not clear. One assumption could be the enhancement of the work
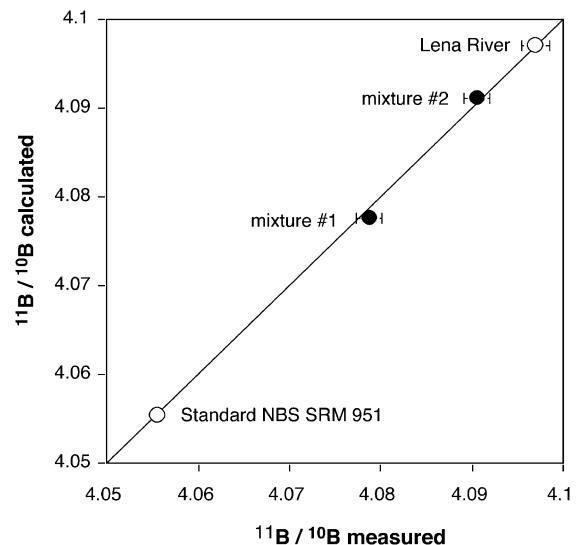

Fig. 7. Comparison between calculated and measured boron isotopic composition of a standard solution NIST SRM 951 mixed with different proportions of natural sample (Lena river). Errors are deduced from the external reproducibility (0.3‰, 2σ).

function of tungsten filament by addition of an halogen element.

Separate analyses of a standard solution processed through the whole chemistry were carried out. The oxygen corrected mean value corresponds to 4.05472 $\pm$ 0.00032 (0.08‰, $n = 14$), Table 4. This value is used as a reference for determining sample isotopic composition. The external precision expressed in $2 \times$ relative standard deviation (RSD), i.e. the true reproducibility, is then 0.30‰, close to the results of separate analyses for standard solution NIST SRM 951 carried out by Leeman et al. (1991), with an external precision expressed in $2 \times$ RSD of 0.39‰. The assessment of the analytical precision for natural samples have been carried out on separate analyses of the Amazon river ([B] = 6.1 ppb) and seawater standard CASS2 (see Table 4). The results show an external reproducibility of 0.37‰ (in 2 RSD) for Amazon river close to the reproducibility for the standard solution and of 0.07‰ for seawater CASS2 ($\delta^{11}B = 39.60$‰).

Finally, we tested the accuracy of the total procedure presented here by analysing the isotopic composition of mixtures between standard NIST SRM 951 and the Lena river, selected for its relative large amount of dissolved organic matter. Results are presented in Fig. 7. We show a remarkable consistency, within external reproducibility, between calculated and measured isotopic compositions.

9. Conclusions

The improved sensitivity for boron isotopic ratio determination using positive TIMS with $Cs_2BO_2^+$ method makes it possible to analyze 250 ng boron from natural samples and 50 ng for standard solution NIST SRM 951. The high partition coefficient of the boron-specific resin Amberlite IRA 743 allows us to miniaturize the volume of the resin. After riverine boron preconcentration using 50 μl of resin, the purification of boron requires two steps with 10 and 3 μl of resin. The blank level is typically 3 ng. This study shows that the boron extraction by ion exchange with the resin Amberlite IRA 743 requires recovery yields close to 100% on account of the important boron isotopic fractionation during exchange with resin. The technique of microsublima-

tion is efficient for the removal of boron from organic-rich media. The precision deduced from the external reproducibility for separate analyses of standards processed through the chemical procedure and natural samples corresponds to 0.35‰ ($\pm 2\sigma$). We show that precise determination of boron isotopic ratio is possible for river water samples characterized by boron concentration as low as a few ppb. We suggest that it can be applied for each measurement method either TIMS or ICP-MS or after alkali fusion.

Acknowledgements

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