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Effect of NO_3^- on the isotopic measurement of boron

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Abstract

The effect of NO_3^- on the isotopic measurements of boron based on the $Cs_2BO_2^+$ ion with graphite loading was investigated. The measured 309/308 ratio was considerably reduced by the presence of NO_3^- ion, especially in the presence of mannitol, due to the formation of the Cs_2CNO^+ ion producing ion peaks at masses of 308 and 309. The procedure of ion exchange using Amberlite IAR 743 resin, a boron-specific resin, and OH-Dowex 1 resin for extracting boron from sample solution was developed. The NO_3^- ion could be removed from sample solution during sample preparation by using this procedure. (Int J Mass Spectrom 178 (1998) 213–220) © 1998 Elsevier Science B.V.

Keywords: Boron; Isotopic measurement; Interference of NO_3^- ion

1. Introduction

Relatively few procedures for isotopic measurement of boron have been reported to date. A procedure based on the electron impact on gaseous BF_3 was first applied for boron isotope analysis [1]; this is rarely used nowadays because of the associated memory effect and the corrosive nature of BF_3. An alternative method, based on the measurement of $Na_2BO_2^+$, was first reported by Palmer [2] and has subsequently gained widespread acceptance. However, the precision based on the measurement of $Na_2BO_2^+$ is restricted by isotopic fractionation because of the relatively low mass of the $Na_2BO_2^+$ ion. A high precision procedure using the $Cs_2BO_2^+$ ion, which has a higher mass was developed by Spivack and Edmond [3] and Ramakumar et al. [4]. An improved method for the high-precision isotopic measurement of boron based on the $Cs_2BO_2^+$ was subsequently reported by Xiao et al. [5]. The enhanced sensitivity and stability of the $Cs_2BO_2^+$ ion were achieved by the addition of graphite in the sample loading step. Measurement of the $^{11}B/^{10}B$ ratio with a precision of 0.006% for NIST 951, a reference material for boron isotopes, was demonstrated. This procedure has since been applied by many laboratories worldwide [6–8]. A serious interference, however, from the NO_3^- ion was discovered by Xiao et al. [5]. The measured $^{11}B/^{10}B$ ratio was reduced by the presence of NO_3^- ion. Isobaric interference by ions with masses of 308 and 309 can result if the NO_3^- ion is loaded besides $Cs_2BO_2^+$ from the sample. In this case, the ion intensity of mass 308 is much higher than that of mass 309. Xiao et al. [5] postulated that Cs_2CNO^+ ion formation was the source of the problem. A relatively recent review of boron isotope analysis, including the extraction of boron from dif-

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ferent types of samples, purification of the extracted boron and mass spectrometry analysis of boron isotopes, was reported by Aggarwal and Palmer [9].

There are few published methods for separating boron from natural samples. Use of boron-specific resin was a successful and simple one [10,11]. Amberlite IRA 743 is a boron-specific resin in common use, which strongly adsorbs boron without the adsorption of other anions from alkaline solution. The adsorbed boron can be eluted by dilute HCl solution. In general, the HCl was removed by evaporation in the presence of mannitol but with the present risk of boron loss by volatilization [12]. Unpublished results by Swihart have suggested removing the HCl using Ag resin. In this case, NO_3^- ions may be released by the ion-exchange column and interfere with the isotopic measurement of boron.

The effect of NO_3^- ion on the isotopic measurement of boron has been systematically investigated in the present study and the sample preparation procedure was improved to eliminate the introduction of NO_3^-.

2. Experimental

2.1. Reagents

High-purity water with a boron blank of lower than 0.4 ng/mL, produced by sub-boiling distillation and use of boron-specific resin, was used in this study. 2 and 0.1 M HCl solutions were prepared from the high-purity reagent. A solution of mannitol with a concentration of 1.82% (wt/v) and a solution of Cs_2CO_3 containing of 12.3 mg Cs/ml were also prepared. In this case, addition of 1 μL of both the mannitol and Cs_2CO_3 solutions to the boron-bearing solution containing 1 μg B resulted in a B/mannitol/Cs molar ratio of 1/1/1. Spectroscopic-grade graphite was mixed with an 80% ethanol/20% water (v/v) solution to form a slurry. The working solutions were made using reagent grade boric acid (AR) and isotopic standard reference material NIST 951.

2.2. Ion exchange procedure

Amberlite IRA 743 (manufactured by Rohm and Hass Co., USA), a boron-specific ion-exchange resin, contains a hydrophobic styrene backbone and a tertiary amine group, which will only adsorb boron in alkaline solution. The ion exchange capacity for boron is 10.9 mg B/g [10]. The ground resins (80–100 mesh) were loaded into a polyethylene column with a diameter of 0.4 cm after soaking in water. The height of the resin bed was adjusted to 5.5 cm and conditioned by successive addition of 10 mL of 2.0 M HCl, high purity water, 3.0 M NH_4OH and, finally 10 mL of high purity water. A 1.8 mL volume of Dowex 1 (200 mesh) anion-exchange resin was placed in an ion-exchange column and was conditioned by 5.0 ml of 2 M HCl, 10 mL of high purity water, 5 mL of 2 M NaOH, followed by 10 mL of high purity water. The sample solutions first were loaded onto the conditioned Amberlite IRA 743 resin at a flow rate of 0.5 mL/min. The column was rinsed with 10 mL of high purity water, 10 mL of 2 M NH_4OH and 10 mL of high purity water to elute Cl^- and SO_4^{2-} off the resin. Finally, the boron held by the resin was eluted using approximately 10 mL of 0.1 M HCl at 75 °C. After cooling to room temperature, the eluate containing boron was passed through the Dowex 1 resin column and the column was eluted using 10 mL of HCl solution of pH 4.5. Equimolar mannitol and Cs_2CO_3 were added to the eluate, which was then was evaporated to produce a boron concentration of 1 mg B/mL, this being achieved in an oven at 60 °C under air drawn through four impregnated filters.

2.3. Analytical method

The concentrations of boron in some samples were examined using the azomethine-H spectrophotometric method described by Kiss [10]. One mL of boron-bearing solution, 2 mL of buffer solution (250 g of NH_4AC, 15 g EDTA, and 125 g glacial HAC, diluted to 400 mL, and 2 mL of azomethine-H solution (0.45 g azomethine-H and 1 g ascorbic acid in 100-mL water) were sequentially added into a quartz vessel. After mixing well, the solution was allowed to stand

Table 1
The variation of 309/308 ratio vs. time in the presence of NO_3^- alone

	Measured 309/308 ratios		
Time (min)	Without NO_3 loading	5.7 μg of NO_3 loading	11.4 μg of NO_3 loading
16			3.018 76 *
20		2.738 67 *	
24			3.418 02 *
30	4.050 24	3.662 30 *	3.607 09 *
40	4.050 01	3.789 10 *	3.839 18 *
50	4.051 68	3.904 26 *	3.991 60 *
60	4.051 10	4.052 04	4.050 51
70	4.050 17	4.050 93	4.051 66
80	4.049 90	4.052 32	4.048 93
90	4.050 11	4.051 63	4.050 13
100	4.050 91	4.049 95	4.051 14
110	4.050 53	4.049 10	4.051 81
120	4.051 24	4.051 49	4.050 33
130	4.050 98	4.051 31	4.051 03
140	4.051 53	4.049 89	4.049 06
150	4.050 66	4.050 88	4.049 76
160	4.050 56	4.050 07	
170	4.051 85	4.049 94	
180	4.050 54	4.047 88	
190	4.050 74	4.049 50	
200	4.051 56	4.045 48 *	
210	4.050 34	4.048 64	
220	4.050 43	4.050 08	
230	4.049 99	4.050 07	
240	4.049 60	4.050 82	
250	4.051 10	4.050 12	
260	4.050 02	4.049 20	
270	4.051 32	4.050 42	
280	4.050 41		
Average	4.050 67 ± 0.000 24	4.050 30 ± 0.000 48	4.050 43 ± 0.000 63

* These data were not included for the calculation of the average 309/308 ratios.

for 30 min and then the absorption of the boron-azomethine-H complex at 410 nm was measure using a 721 spectrophotometer (made in Shanghai Third Analytical Instrument Factory, China).

The isotopic composition of boron in the solution was measured by thermal ionization mass spectrometry, using a VG 354 instrument [5]. For mass spectrometry, the samples were loaded onto a single outgassed tantalum filament. First, 2.5 μL of graphite slurry was spread across the whole filament. Next, approximately 1 μL of sample solution containing 1 μg B and equimolar mannitol and Cs_2CO_3 was loaded. The NO_3^- (as $CsNO_3$) was then loaded during testing of the effect of NO_3^-. The loaded sample was dried by heating the filament by a current of 1.0 A for 3 min. Isotope ratio data were collected by switching magnetically between the masses of 309 ($^{133}Cs_2{}^{11}B^{16}O_2^+$) and 308 ($^{133}Cs_2{}^{10}B^{16}O_2^+$).

3. Results and discussion

3.1. Interference of NO_3^- ion on the isotopic measurement of boron

The intensity of $Cs_2BO_2{}^+$ ion was enhanced by graphite coating the filament, which forms the basis of the high-precision isotopic measurement of boron by

Table 2
The variation of 309/308 ratio vs. time in the presence of NO_3^- and 2 μl of 1.82% mannitol solution

	Measured 309/308 ratios				
Time (min)	Without NO_3	0.1 μg NO_3	0.5 μg NO_3	1.0 μg NO_3	5.7 μg NO_3
20		4.053 25	3.965 67	3.863 33	3.790 75
30		4.053 43	4.017 25	3.964 15	3.998 74
40	4.058 85	4.054 00	4.034 15	3.991 01	4.014 83
48	4.058 50				
50		4.054 78	4.042 00	4.007 73	4.017 92
52	4.058 27				
56	4.057 98				
60		4.056 37	4.042 15	4.021 78	4.021 32
62	4.057 85				
70	4.056 79	4.055 82	4.049 38	4.025 24	4.023 55
80	4.057 08	4.056 75	4.048 77	4.031 32	4.028 65
90	4.058 50	4.054 80	4.050 52	4.034 80	4.028 21
100	4.056 52	4.055 23	4.049 20	4.034 08	4.032 47
110	4.055 47	4.051 31	4.049 69	4.038 42	4.028 04
120	4.056 44	4.053 79	4.050 74	4.037 10	4.031 15
130	4.057 14	4.054 97	4.053 07	4.041 30	4.031 28
140	4.057 33	4.056 58	4.049 42	4.039 81	4.032 04
150	4.057 24	4.052 86	4.050 65	4.038 48	4.032 98
160	4.056 73	4.052 37	4.049 52	4.048 41	4.032 57
170	4.057 33	4.056 12	4.050 32		4.032 22
180	4.055 52	4.056 78	4.052 14	4.043 52	4.033 58
190	4.056 30	4.053 80	4.053 54	4.046 92	4.029 48
200	4.057 56	4.052 97	4.052 57	4.045 88	4.025 97
210	4.055 42		4.054 01	4.045 28	4.028 13
220	4.055 79	4.053 95	4.053 03	4.047 70	4.026 11
230	4.055 98	4.053 87	4.051 21	4.046 08	4.024 68
240	4.055 74	4.053 87	4.053 04	4.047 68	4.023 14
250	4.055 97	4.053 79	4.052 314.047 83	4.009 94	
260	4.055 01	4.055 05	4.050 99	4.048 59	4.007 94
270	4.055 16	4.053 82	4.049 95	4.045 86	4.001 77
280			4.051 80		

thermal ionization mass spectrometry as developed by Xiao et al. [5]. These authors discovered that $CsNO_3$ produced significant peaks at masses 308 and 309, besides at mass 312 and that the intensity of mass 308 is higher than that of mass 309. Apparently the presence of NO_3^- causes a serious interference on the isotopic measurement of boron based on the measurement of $Cs_2BO_2^+$ using graphite loading technique.

A variable amount of HNO_3 was loaded together with NIST 951 containing Cs, in order to study the interference of NO_3^-. The results are list in Tables 1 and 2 and also shown in Figs. 1 and 2. The data in Table 1 and Fig. 1 indicate that in the presence of NO_3^-, the measured 309/308 ratios are obviously low initially and then increase toward the accepted value. The rate of increase of the measured 309/308 ratio decreased with increasing HNO_3 burden; in general, the effect of NO_3^- will decay away after heating the filaments for 1 h.

Mannitol was widely used in the preparation of samples for the isotopic measurement of boron because mannitol suppresses the volatilization of boron during the evaporation of boron-bearing solution due to the formation of a mannitol–boron complex. However, the interference of NO_3^- ion on the isotopic measurement of boron can be enhanced by the presence of mannitol. The results indicated in Table 2 and Fig. 2 show that the measured 309/308 ratios in the presence of 1.0 μg of NO_3^- are much lower than that in the absence of NO_3^- and that the measured 309/308

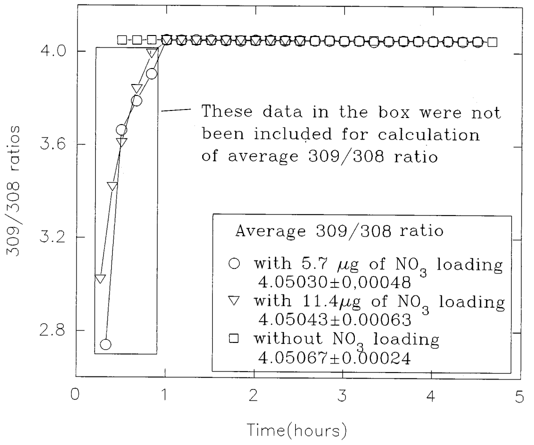

Fig. 1. The variation of 309/308 ratio vs. time, in the presence of NO_3^- alone.

ratios slowly rise. However, the measured 309/308 ratios do not reach the accepted value even after 5 h heating of the filament. When the amount of NO_3^- was 5.7 μg, the measured 309/308 ratios stabilized after the first hour, but at much lower values than accepted and decreased again after 3 h heating of the filament.

Xiao et al. [5] argued that the peaks at masses of 309 and 308 would be partially produced by Cs_2CNO^+ ions formed in the presence of NO_3^-. To confirm this, 1 μL of 0.5 M KCNO solution, rather than a boron sample was loaded with the graphite. Peaks at masses 308 and 309 were not detected when the heating currents through the filament reached 1.6 A. This is, however, very interesting in that a very strong ion beam ($6-8 \times 10^{-12}$ A) at masses of 308 and 309 were produced if boron was present at the same time, furthermore, the measured 309/308 ratio was 0.019 46, which does not agree with $^{11}B/^{10}B$ from the $Cs_2BO_2^+$ ion, but may be attributed mainly to the presence of the Cs_2CNO^+ ion. The peaks of masses 309 and 308 deriving from Cs_2CNO^+ ion could result from $^{133}Cs_2{}^{12}C^{15}N^{16}O^+$, $^{133}Cs_2{}^{13}C^{14}N^{16}O^+$ and $^{133}Cs_2{}^{12}C^{14}N^{17}O^+$ and $^{133}Cs_2{}^{12}C^{14}N^{16}O^+$ ions, respectively.

So

$$309/308 = {}^{15}N/{}^{14}N + {}^{13}C/{}^{12}C + {}^{17}O/{}^{16}O \qquad (1)$$

The ratios of $^{15}N/^{14}N$, $^{13}C/^{12}C$, and $^{17}O/^{16}O$ in nature are 0.003 673, 0.011 12, and 0.000 38, respectively [13].

Therefore

$$\begin{aligned} 309/308 &= 0.003\,673 + 0.011\,12 + 0.000\,38 \\ &= 0.015\,17 \end{aligned} \qquad (2)$$

The average measured value of 309/308 for three loads was 0.019 46, which is a little higher than the calculated value of 0.015 17. This may represent the minimum amount of $Cs_2BO_2^+$ ion yielded. It is considered very probable that the ion beams at masses of 309 and 308 contained a significant contribution from the Cs_2CNO^+ ion, which shows that a minimum amount of cyanate could be formed when the NO_3^- and graphite are heated on the filament. The result reported by Xiao et al. [14] indicates that mannitol affects the isotopic measurement of boron based on the measurement of $Cs_2BO_2^+$ ion. The measured 309/308 ratio should be higher than the true ratio, if mannitol is present. Therefore, the enhancing interference of NO_3^- on isotopic measurement of boron in the presence of mannitol is not derived from mannitol itself. The formation of cyanate could be catalyzed by mannitol.

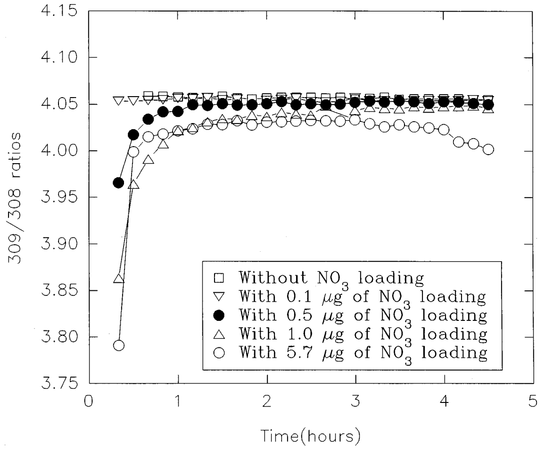

Fig. 2. The variation of 309/308 ratio vs. time in the presence of NO_3^- and mannitol.

Table 3
The recovery of boron from OH Dowex 1 resin column (elution: pH 4.5 HCl; 6 ml solution)

Loaded B, μg	4.92	25.01	49.50	74.93	98.25
Recovered B, μg	4.94	24.40	50.38	74.00	99.31
Recovering efficiency, %	100.4	97.6	101.8	98.8	101.1

3.2. Ion-exchange separation of boron

Ion-exchange using boron-specific resin (Amberlite IRA 743) is a simple and effective method for separating boron from natural samples. Recently, Xiao et al. [11] reported that Amberlite 743 strongly adsorbs boron in alkaline solution and also adsorbs a small amount of strong anion in weak acid solution. The adsorbed anion, however, can be easily eluted by NH_4OH. Similarly, Cl^-, SO_4^{2-}, and NO_3^- ions can also be removed from the sample by Amberlite 743. The adsorbed boron may be eluted by a strong acid. More than 10 mL of 2 M HCl solution was generally used hitherto to elute boron from Amberlite 743 resin column, whereas Xiao et al. [11] used 10 mL of 0.1 M HCl solution at a temperature of 75 °C. It is necessary to remove the HCl from the eluate, usually by evaporation to dryness in the presence of mannitol, before loading onto a filament. It is possible that some boron would be volatilized during the evaporation process [12]; furthermore it is difficult to collect boron from the dry residue, using a small volume of water. Therefore, Swihart et al. used Ag-resin prepared by passing $AgNO_3$ solution through a column filled by cation ion-exchange resin to remove the HCl (unpublished results). The eluate containing HCl needed to be evaporated only for reducing the volume, not to dryness. The drawback, however, is the introduction of NO_3^-, which derives from $AgNO_3$ used in the preparation of Ag-resin columns. Because of this, we have investigated the use of an OH-resin to remove the HCl.

3.3. Ion-exchange characteristics of Dowex 1 resin

Dowex 1 ion-exchange resin is strongly basic anion-exchange resin and was converted into the OH and Cl forms by the use of NaOH and NaCl, respectively. The ion-exchange characteristics of Dowex 1 for boron were tested as follows: 1 mL of boron-bearing solutions, containing 50.02 and 49.97 μg B, were loaded onto a column filled with OH Dowex 1 resin. The column was then eluted by 10 mL of water. No boron was found in the eluate, which indicates that boron was completely absorbed by resin. A similar experiment using Cl Dowex 1 resin was also performed. The result showed that the adsorbed boron could be completely recovered from the column by only 6 mL of water, thereby showing that the boron was only very weakly absorbed by Cl Dowex 1 resin. As is well known, anions in acid solution can be adsorbed by strongly basic (hydroxyl-bearing) anion exchange resin and the released OH^- ion neutralized by H^+ ion to form H_2O. This implies that OH Dowex 1 resin may be used for removing HCl from the boron-bearing solution eluted from Amberlite 743 resin. Cl^- ion from the HCl will be adsorbed by Dowex 1 resin; the H^+ ion will be neutralized by released OH^-.

3.4. Elution and recovery of boron

It is necessary to quantitatively recover boron from the column after HCl is removed by OH Dowex 1 resin. To achieve this, the required amount of Dowex 1 is estimated from the volume of solution used to elute boron from the Amberlite 743 resin and the

Table 4
The measured 309/308 ratios in boron working solution preparing from reagent grade boric acid (AR)

	Measured 309/308 ratios			Avg. 309/308 ratio
Direct loading	4.0970	4.0962	4.0964	4.0965 ± 0.0004
Loading after ion exchange procedure	4.0950	4.0960	4.0971	4.0960 ± 0.0010

Table 5
The isotopic measurement of boron in natural samples

Samples	Measured $^{11}B/^{10}B$ ratios [a]			Avg. $^{11}B/^{10}B$ ratio
Brine of Da Qaidam Lake	4.0719	4.0743	4.0730	4.0731 ± 0.0012
Brine of De Zhongmahai Lake	4.0616	4.0635	4.0630	4.0627 ± 0.0010
Saline water of Gahai Lake	4.1108	4.1102	4.1096	4.1102 ± 0.0006
Coral	4.1457	4.1473		4.1465

[a] The $^{11}B/^{10}B$ ratios were corrected for the contribution of ^{17}O to the 309 peak by subtracting 0.000 79 from measured 309/308 ratios.

concentration of HCl in eluate. In principle, the quantity of OH Dowex 1 resin used needs to be just sufficient to completely remove HCl from the Amberlite 743 eluate. If significant excess is used, some boron could be adsorbed by the OH Dowex 1 resin. The adsorbed boron can be sequentially eluted by dilute acid. The test results showed that the boron adsorbed by OH Dowex 1 resin could be eluted by 6 mL of pH 2.5–4.5 HCl when 10 mL of 0.1 M HCl was used to elute the boron adsorbed by Amberlite 743 resin and the eluate subsequently passed through a column loaded with 1.8 mL of wet OH Dowex 1 resin. In this study a pH 4.5 HCl solution was adopted for eluting boron. The recovery results of 4.92–98.25 μg of boron are shown in Table 3, which indicates that this quantity of boron on a column of OH Dowex 1 resin can be quantitatively recovered by 6 mL of pH 4.5 HCl solution. Under these conditions, the concentration of HCl in the eluate was reduced to 10^{-4} M, which does not need to be removed before sample loading onto a filament for the analysis of boron isotopic composition. Table 4 shows the measured $^{11}B/^{10}B$ values using the procedure reported by Xiao et al. [5] before and after the boron-bearing working solutions prepared from reagent grade boric acid (AR) were subjected to the complete preparation procedure. The results show that the fractionation is negligible, within the precision of the isotopic measurement using our ion exchange procedure for boron separation.

3.5. Measurement of the isotopic composition of boron in natural samples

The isotopic composition of boron in salt lake brine and in coral coming from the India Ocean have been measured, following the ion-exchange procedure for separation of boron as described previously. The coral samples, dissolved by the procedure reported by Gaillarde [15], were loaded into the column filled with Amberlite 743 resin after being neutralized by NaOH solution. The brine samples could be directly loaded into the column. The column was sequentially washed by H_2O, NH_4OH, and H_2O and the adsorbed boron was eluted using 10 mL of 0.1 M HCl at a temperature of 75 °C. Finally, the eluate containing boron was passed through OH Dowex 1 resin column to remove HCl. The amount of boron in the collected solution was determined using the azomethine-H spectrophotometric method [10].

The collected solution was evaporated to minimum volume after equimolar quantities of mannitol and Cs_2CO_3 were added. The isotopic composition of boron in the samples was measured using the procedure based on the measurement of $Cs_2BO_2^+$ ion with graphite loading [5]. The results are shown in Table 5.

4. Conclusions

The NO_3^- ion seriously affects the isotopic measurement of boron based on the measurement of $Cs_2BO_2{}^+$ ion with graphite loading. In particular, it causes the measured $^{11}B/^{10}B$ ratio to be lower than the true value, especially, in the presence of mannitol. Therefore the NO_3^- ion should be removed from the sample and its introduction during sample preparation must be avoided. An ion exchange procedure using Amberlite 743 resin and OH Dowex 1 resin together was used to extract boron from samples. First, Amberlite 743 resin was adopted for removing all ions except for boron, then 0.1 M HCl of eluate containing boron was passed through OH Dowex 1 resin to remove HCl. Finally, the near neutral solution was evaporated to minimum volume for isotopic measurement of boron. This procedure of sample preparation for boron separation removed other ions, including NO_3^-, and avoided introducing NO_3^- again when Ag resin was used to remove HCl from the final eluate. Thus, this is an improved procedure for the quantitative recovery of boron from natural samples. It avoids isotopic fractionation and hence permits high accuracy of isotopic measurement of boron to be achieved.

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References

[1] Y.F. Liu, Q. Liu, S.J. Wang, Yuan Zi Neng Kexue Jishu 4 (1964) 381.
[2] G.H. Palmer, J. Nucl. Energy 7 (1958) 1.
[3] A.J. Spivack, J.M. Edmond, Anal. Chem. 58 (1986) 31.
[4] K.L. Ramakumar, et al., J. Radio Anal. Nucl. Chem. 94 (1985) 53.
[5] Y.K. Xiao, E.S. Beary, J.D. Fassett, Int. J. Mass Spectrum. Ion Processes 85 (1988) 203.
[6] W.P. Leemam et al., Geochim. Cosmochim. Acta 55 (1992) 3901.
[7] E. Nakamura et al., Chem. Geol. 94 (1992) 193.
[8] G.H. Swihart, E.H. McBay, H.S. David, W.S. Joseph, Chem. Geol. 127 (1996) 241.
[9] J.K. Aggarwal, M.R. Palmer, Analyst 120 (1995) 1301.
[10] E. Kiss, Anal. Chem. Acta 211 (1988) 243.
[11] Y.K. Xiao, Y. Xiao, G.H. Swihart, W.G. Liu, Acta Geosci. Sin. 18 (1997) 286.
[12] Y.K. Xiao, R.D. Vocke, G.H. Swihart, Y. Xiao, Anal. Chem. 69 (1997) 5203.
[13] IUPAC, Pure Appl. Chem. 63 (1991) 991.
[14] Y.K. Xiao, B.D. Vocke, Geochim. Cosmochim. Acta, in press.
[15] J. Gaillarde, C.J. Allégre, Earth Planet. Sci. Lett. 136 (1995) 665.