Boron Separation by the Two-step Ion-Exchange for the Isotopic Measurement of Boron

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An improved procedure for extraction and purification of boron from natural samples is presented. The separation and purification of boron was carried out using a boron-specific resin, Amberlite IRA743, and a mixed ion exchange resin, Dowex 50W × 8 and Ion Exchanger II resin. Using the mixed ion exchange resin which adsorbs all cations and anions except boron, the HCl and other cations and anions left in eluant from the Amberlite IRA 743 were removed effectively. In this case, boron loss can be avoided because the boron-bearing solution does not have to be evaporated to reach dryness to dislodge HCl. The boron recovery ranged from 97.6% to 102% in this study. The isotopic fractionation of boron can be negligible within the precision of the isotopic measurement. The results show that boron separation for the isotopic measurement by using both Amberlite IRA 743 resin and the mixed resin is more effective than that using Amberlite IRA 743 resin alone. The boron in samples of brine, seawater, rock, coral and foraminifer were separated by this procedure. Boron isotopic compositions of these samples were measured by thermal ionization mass spectrometry in this study.

Keywords   boron, separation of boron, ion exchange, isotopic measurement

Introduction

Large variations in the isotopic composition of boron occur in nature. The boron is a useful tracer of the sources and evolution of aqueous fluids in the Earth's crust and hydrosphere.[1-6] Owing to improvements of analytical methods,[7,8] a rapid increase has been seen in many studies of the isotopic composition of boron in natural samples.[9-11] Sample preparation methods for boron isotopic analysis depend on the chemical nature of the material, its boron concentration, its physical state, and the instrumental technique to be used for isotopic analysis.[12] Extraction methods for boron isotopic analysis mainly used in many studies include methyl borate distillation and ion exchange. Boron separation has been carried out using boron-specific, anion, cation, and mixed resin. A mixed resin composed of a 1:1 V/V mixture of a weak anion resin, Bio-Rad AG3-×4 (OH⁻ form), and a strong cation resin, AG 50-×8 (H⁺ form) was used to extract boron from silicates and aqueous solutions by Spivach et al. (1986).[7] Similarly, Xiao et al. (1983) used a mixed resin prepared from a strong cation resin,[13] Shanghai No. 1 (made in Shanghai, China) in the H⁺ form, and a weak anion resin, Ion Exchanger II (made by Merck in Germany) in the HCO₃⁻ form, to extract boron from brine samples and seawater. But this procedure requires considerable caution and testing when it is applied to solutions of different compositions. The developed methods for separation of boron with boron-specific resin were described by many scientists.[14-17] Amberlite IRA 743 (manufactured by Rohm and Hass Co., USA) is a boron-specific resin in common use, which strongly adsorbs boron without the adsorption of other anions from alkaline solution. The boron is complexed by an N-methylglucamine functional group. The adsorbed boron can be eluted by dilute HCl solution. It is commonly used to separate boron from natural samples.

However, volatilization of boron from solution during evaporation was a very serious problem for boron iso-

topic studies because sample solutions with HCl must be often partially evaporated in order to concentrate boron prior to mass spectrometric analysis. So mannitol has been commonly adopted to suppress the volatilization of boron during evaporation of boron solution, especially in boron isotopic studies. Xiao and Vocke *et al*. (1997) studied the volatilization of boron during evaporation of boron solution, acid solution, and alkaline solution.[18] These results show that the presence of equimolar mannitol can reduce but not completely suppress the volatilization of boron. Especially when the solution was evaporated to dryness, the loss of boron is more serious. So the risk of boron loss exists by evaporating to reach dryness. Unpublished results by Swihart have suggested removing the HCl using Ag resin. But in this case, NO$_3^-$ ions may be released and interfere with the isotopic measurement of boron.[17] In order to remove the HCl, a mixed ion exchange resin, which strongly adsorbs other cations and anions except boron, was used in this study. The mixed resin can remove the HCl directly, and also effectively remove other cations and anions further. Therefore the boron-specific ion-exchange resin does not need to be rinsed with 5 mL of 3 mol/L NH$_4$OH to remove other cations and 10 mL of 2 mol/L NH$_4$OH to remove Cl$^-$ and SO$_4^{2-}$ of the resin before boron was eluted from the column with the diluted HCl.[15,17] Based on the composition of eluant from Amberlite IRA 743 resin, some properties of the mixed resin was investigated in this study.

Experimental

Reagents and apparatus

High-purity water with a boron blank of lower than 0.4 ng/mL, produced by sub-boiling distillation and then passing through Amberlite IRA 743, was used in this study. Sodium chloride (1.0 mol/L, 0.1 mol/L NaCl), hydrochloric acid (0.5 mol/L, 0.1 mol/L, 0.05 mol/L HCl), sodium hydroxide (0.5 mol/L, 0.1 mol/L, 0.05 mol/L NaOH) and boric acid (1 mg/mL H$_3$BO$_3$) were used to investigate recovery of boron. HCl solution was prepared from the sub-boiling reagent. Hg(NO$_3$)$_2$ was used to measure the concentration of Cl$^-$ by titration. Sodium carbonate and hydrochloric acid were used to condition the Ion Exchanger II and Dowex 50W × 8. Azomethine-H solution was prepared freshly as re-

quired by dissolving the azomethine-H (0.5 g) in 100 mL of water containing ascorbic acid (1 g). The buffer solution was 50% (*W/V*) ammonium acetate adjusted with acetic acid to pH 5.1 ± 0.1. A series of boron calibration standards were prepared from NBS 951 boricacid and stored in Teflon bottles. A solution of mannitol with a concentration of 18.2% (*W/V*) and a solution of Cs$_2$CO$_3$ containing 12.3 mg of Cs per mL were also prepared. Graphite (Johnson Matthey) was mixed with an 80% ethanol/20% water (*V/V*) solution to form slurry.

A 721 spectrophotometer made in Shanghai was used to measure the concentration of boron. Teflon bottles and beaker were used as required.

Determination of boron with azomethine-H

The concentrations of boron were measured using the azomethine-H spectrophotometric method. It is similar to that described by Kiss (1988),[14] but slightly altered.

Calibration amount of boron-bearing solution was weighed out and transferred to a 25 mL beaker, to which was added 5 mL of ammonium acetate buffer followed by 5 mL azomethine-H reagent. The solution was mixed, diluted to full capacity with water and weighed (± 0.0001 g). A blank reference was prepared in the same manner. The colored solutions were kept in a dark place for 70 min. Calibration standards (0.3—10 µg of B) were prepared simultaneously with every batch and the absorbencies were measured at 415 nm in a 20-mm or a 30-mm quartz cell. The boron concentration was calculated, using a polynomial curve-fitting equation (the third or fourth order).

Preparation of ion exchange column

The ion exchange capacity of Amberlite IRA-743 for boron in alkaline solution is 10.9 mg of B per g.[14,15,17] The resin was ground and screened to 60—100 mesh. The ground Amberlite IRA 743 resin was loaded into a polyethylene column with an internal diameter of 4 mm after being soaked in water. The height of the resin bed was adjusted to 5 cm and conditioned by successive addition of 10 mL of 2 mol/L HCl, 10 mL of high purity water, 10 mL of 3 mol/L NH$_4$OH, and 10 mL of high purity water.

A mixture of ion exchange resin was prepared from the strong cation resin, Dowex 50W × 8 (200—400 mesh) and a weak alkaline anion resin, Ion Exchanger II. The individual resins are conditioned with HCl and NaHCO$_3$ to convert them to their H$^+$ and HCO$_3^-$ forms before they are mixed. Ion Exchanger II was also ground and screened to 60—100 mesh before use. Because of the difference sizes, Ion Exchanger II and Dowex 50W × 8 can be separated each other by sieving (100 mesh sifter) so that they can be regenerated for further use. A mixed ion exchange resin column composed of 1 : 1 V/V Ion Exchanger II and Dowex 50W × 8 was prepared. 6 mL of mixed resin was loaded into a 10 mL polyethylene column showed in Fig 1. In order to remove HCl completely from the Amberlite IRA 743 eluate, the column was connected to a polyethylene column with an internal diameter of 4 mm and height of 6 cm at its bottom. The mixed resin bed was rinsed with 10 mL of high purity water.
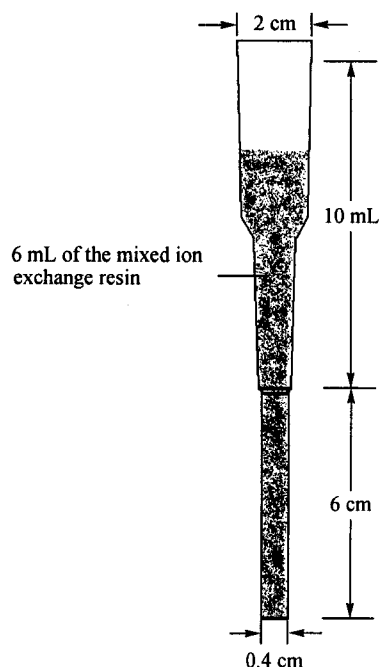

Fig. 1 Column shape of the mixed resin.

A procedure of ion exchange

The sample solutions were first loaded into the conditioned Amberlite IRA 743 resin at a flow rate of less than 0.5 mL/min. The column was rinsed with 15—20 mL of high purity water. Then, the boron held by the resin was eluted using 10 mL of 0.1 mol/L HCl at 75 ℃. After being cooled to room temperature, the eluant from the column of Amberlite IRA 743 was passed through a mixed ion exchange resin column at a flow rate of less than 0.3 mL/min, and after that, the column was eluted using 10—15 mL of high purity water. The final eluent was collected in a clean Teflon beaker. The proper amount of Cs$_2$CO$_3$ was added into the final eluent (B/Cs molar ratio of 1/2). The final eluent was evaporated in an oven at 60 ℃ under clean air drawn through four KOH impregnated filters. After volume reduction to less than 1 mL, the solution was transferred to clean jars, and evaporation continued to reach an approximate concentration of 1 mg of B per mL. The jar was capped tightly and stored for mass spectrometric analysis.

Mass spectrometry

The ^{11}B/^{10}B ratio was measured based on the measurement of the Cs$_2$BO$_2^+$ ion by the thermal ionization technique.[8] A single magnetic sector (equivalent to 54 cm of radius), the thermal ionization mass spectrometer, VG-354, was used. Flat single Ta filaments (7.5 × 0.76 × 0.025 mm^3) were used. Filaments were first treated with a slurry of spectroscopic grade graphite mixed with an 80% ethanol/20% water (V/V) solution to coat the filaments with approximate 100 μg of graphite. The sample solution containing the boron amount of about 1-2 μg was added finally. The loaded sample was then dried with a current of 1.0 A passing through the filament and maintained for 3 min. Isotopic ratio data were collected by switching magnetically between the masses of 309 (^{133}Cs$_2$^{11}B^{16}O$_2^+$) and 308(^{133}Cs$_2$^{11}B^{16}O$_2^+$). The δ values are calculated relative to NBS 951 boron standard as $\delta^{11}B_{sample}$ (‰) = [(^{11}B/^{10}B)$_{sample}$/(^{11}B/^{10}B)$_{standard}$ − 1] × 1000.

Results and discussion

Effect of solution pH *on exchange capacity of Ion Exchanger* II

The exchange capacity of Ion Exchanger II in the mixed exchange resin was measured firstly. A series of solutions, 5.0 mmol of NaCl with different pH, were prepared in beakers. The pH of the solutions were ad-

justed by using HCl and NaOH. Then 2 mL ± 0.1 of Ion Exchanger II and 2.0 ± 0.1 mL of Dowex 50W × 8 of were added to each beaker above. The volumes of all solutions were diluted to full 20.0 mL. Chloride was equilibrated with mixed resin for 24 h. Excess of chloride was determined by titration with $Hg(NO_3)_2$. Results are shown in Fig 2. The exchange capacity of Ion Exchanger II almost kept constant (1.22 mmol per mL of wet resin) if pH of solutions was less than 7, and the exchange capacity of Ion Exchanger II decreased quickly when pH was higher than 12. Thus, the pH of solution loaded into a mixed exchange resin should be less than 7. Fortunately, the eluent from Amberlite IRA 743 was 0.1 mol/ L of boron-bearing HCl, so the HCl could be removed effectively. It is important to quantitatively recover boron from the solution. To achieve this, the required amount of mixed resin used for removing HCl must be sufficient to completely remove HCl from the Amberlite IRA 743 eluate. 6 mL of mixed resin was used to remove the HCl in eluent from Amberlite IRA 743 resin column in this study.
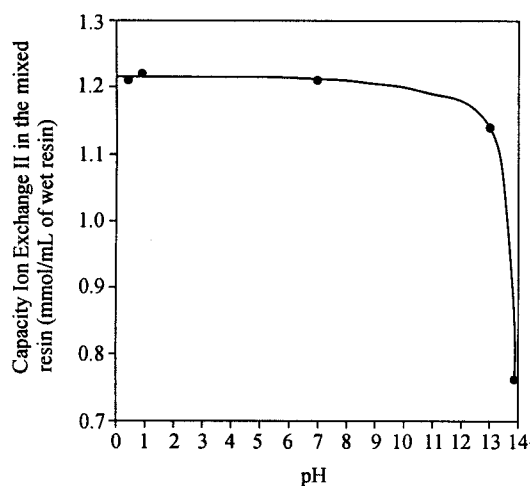

Fig. 2   Capacity of Ion Exchanger II in the mixed resin in different pH solution.

Effect of acidity and salinity on recovery of boron from the mixed exchange resin

These parameters were examined in following experiments: 1) columns were loaded with known amounts of boric acid (5—50 µg) and sodium chloride (0—1.2 mmol); 2) columns were loaded with known amounts of boric acid (5—50 µg) and HCl (0—1 mmol). Results

are shown in Fig 3. The group 1 and 2 experiments showed that recovery of boron in solutions ranged from 98.7% to 102.4%, and boron could be recovered satisfactorily. No significant recovery difference was found with variation of salinity and acidity. Boron recoveries were determined in each batch by spectrophotometer with azomethine-H.
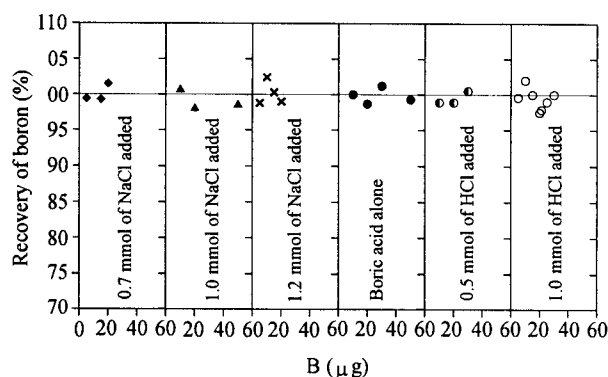
Fig. 3   Recovery of boron with different salinity and acidity.

Recovery of boron throughout experiment procedure

Recovery of boron throughout experiment procedure was also examined by imitated sample solutions. The solutions were prepared from boric acid and sodium chloride. The contents of boron in the solutions ranged from 5 to 25 µg. Recovery of boron-bearing solutions ranged from 97.6% to 102%. The results are listed in Table 1.

Table 1   Recovery of boron throughout experiment procedure

No.	NaCl content (g)	Added boron (µg)	Recovery of boron (µg)	Recovery rate of boron (%)
1	1.1	5.0	4.98	99.6
2	1.1	10.0	10.2	102
3	1.1	15.0	15.0	100
4	1.1	20.0	20.3	101.5
5	1.1	25.0	24.7	98.8
6	1.1	21.2	21.4	101
7	1.1	21.1	20.6	97.6
8	1.1	21.2	21.4	101
9	1.1	21.2	21.0	99

Isotopic fractionation of boron

Due to that recovery of boron from imitated sample

solutions is more than 97%, the isotopic fractionation of boron throughout experiment procedure can be neglected. In further tests, NBS 951 was used to examine the isotopic fractionation of boron as imitated solution. The isotopic compositions of boron in a series of imitated solution, following the two-step ion exchange procedure for separation of boron as described above, were measured

preciously. At the same time, NBS 951 was also loaded into the filament directly and the isotopic composition of NBS 951 was measured. Results listed in Table 2 demonstrate that the fractionation of boron can be negligible, within the precision of the isotopic measurement for boron separation.

Table 2 Isotopic measurement of boron in imitated sample solution and NBS 951

No.	B (μg)	Measured ratio $^{11}B/^{10}B^a$				Averaged ratio $^{11}B/^{10}B$
1	11.1	4.04993	4.05122			4.05057
2	21.2	4.05288	4.05319			4.05303
3	32.5	4.05570	4.04926			4.05248
4	42.6	4.05208	4.05418			4.05313
Total Averaged ratio $^{11}B/^{10}B$ of the imitated solution						4.05230 ± 0.00200
NBS 951		4.05211	4.0520	4.05164	4.05257	4.05208 ± 0.00033

^{a} The ratio $^{11}B/^{10}B$ was corrected for the contribution of ^{17}O to the peak 309 by subtracting 0.00079 from measured ratio 309/308.

Measurement of the isotopic composition of natural samples

Boron separation of some natural samples including brine of Da Qaidam Lake, seawater from Southern China Sea, coral, foraminifer and rock was carried out by the two-step ion exchange method. The brine and the seawater were diluted and loaded into the column of Amberlite IRA 743 directly. The coral was dissolved in the dilute HCl. The rock sample was fluxed with Na_2CO_3 at a Na_2CO_3: sample proportion of 5:1. The fusion took 4—8 h in a covered Pt crucible in a muffle furnace at 900°C,

then the cooled fusion cake was dissolved in dilute HCl. The rock fusion is very similar to that described by Kiss (1988).[14] After separation, the final eluant was evaporated to reach an approximate concentration of 1 mg of B per mL in an oven at 60°C under air drawn through four impregnated filters. The isotopic compositions of boron of these natural samples were measured. Results of all natural samples are listed in Table 3. We also successfully separated the boron from shell and measured the isotopic composition with about 0.7 μg of boron loaded onto each single filament.

Table 3 Isotopic measurement of boron in natural samples

Samples	Total B (μg)	Measured $^{11}B/^{10}B$ value (σ_{ex})^a	$\delta^{11}B$ (‰)
Brine of Da Qaidam	18.6	4.07635(28)	+ 5.9
Sea water	44.8	4.20267(11)	+ 37.1
Rock	103	4.03268(14)	− 4.8
Coral	28.0	4.15271(2)	+ 24.8
Foraminifer	5.4	4.13547(25)	+ 20.5

^{a} The ratio $^{11}B/^{10}B$ was corrected for the contribution of 17O to the peak 309 by subtracting 0.00079 from measured ratio 309/308.

Conclusion

The sufficient amount of the mixed resin can remove HCl from the Amberlite IRA 743 eluant completely and also effectively remove other cations and anions left in eluant except boron for further purity.[13] According to the study of boron volatilization and its isotopic fractiona-

tion during evaporation of boron solution by Xiao et al. (1997),[18] the final eluant can be also evaporated to a concentration of 1 mg/mL without mannitol at an oven, through which filtered air was passed, at a temperature of 60°C, and the recovery of boron from the final eluant is more than 98.7%.[18] Thus, boron separation by the two-step ion exchange for the isotopic measurement of

boron is a more effectively improved procedure for the quantitative recovery of boron from natural samples. It achieves high accuracy of isotopic measurement of boron.

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(E0105282   JIANG, X. H.; DONG, L. J.)