Boron Isotope Separation by Ion Exchange Chromatography Using Weakly Basic Anion Exchange Resin

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Isotopic plateau displacement chromatography, a useful method for isotope separation is presented. The boric acid band formed in a column of weakly basic anion exchange resin Diaion WA21 can be eluted with pure water. In order to obtain good accumulation of the isotope effect, a series of experiments with different migration length were carried out. The boron-10 enriched part of the boric acid absorbed band was always preceded by the isotopic plateau part, in which the atomic fraction of boron-10 was maintained at its original value. The atomic fraction of boron-10 at the end of the chromatogram increased with migration length, and in the case of 256-m migration, boron-10 was enriched from its original atomic fraction of 19.84 to 91.00%, the separation factor S being constant irrespective of migration length: $S=1.0100\pm0.0005$.

The following conditions have been found to be favorable for effective isotope separation in chromatographic systems.[1,2] (1) The single stage separation factor should be large. (2) The rates of the ion exchange and isotope exchange reactions should be as high as possible. (3) When the separation factor is not so large as in the case of hydrogen-deuterium isotope separation, sharp band boundary such as characteristic of displacement chromatogram should be maintained at the front or at the rear, if possible at both ends of the chromatographic band. (4) Chromatography should be carried out in such a way that an "isotopic plateau zone" in which the atomic fraction of isotopes remains at its original value, always exists somewhere within the chromatogram. (5) Column operation should be as simple as possible.

Kotaka *et al.* reported that a boric acid band formed in a column packed with weakly basic anion exchange resin (Diaion WA21) can be eluted with pure water, resulting in good isotope fractionation.[3] The result seems to satisfy the five conditions mentioned above. (1) The separation factor is comparatively large (about 1.01). (2) The rates of ion exchange and isotope exchange reaction are not very low. (3) Under suitable conditions, a sharp boundary can be formed at the rear of the boric acid band, where boron-10 would be enriched. (4) An isotopic plateau zone can be maintained if the boric acid band is sufficiently long. (5) The operation is easy. The boric acid band can be eluted with pure water, and the eluted column can be used again with no special regeneration process.

These prospects were realized and the optimum experimental conditions to maintain the isotopic plateau displacement chromatography were found.[2] In the present paper we will report the results obtained with various migration lengths under the optimum conditions.

Experimental

A boric acid saturated band formed in a column of weakly basic anion exchange resin Diaion WA21 can be eluted with pure water, keeping the isotopic plateau displacement chromatogram at the rear part under certain conditions.[2] The optimum conditions are: concentration of boric acid solution, 0.1 mol dm^{-3}; temperature, 40 °C; rate, 20 $cm^3\ h^{-1}\ cm^{-2}$. Experiments were carried out with migration lengths of boric acid band 1—256 m.

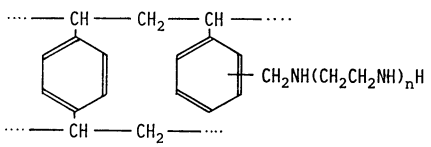

Fig. 1. Structure of Diaion WA21 resin.

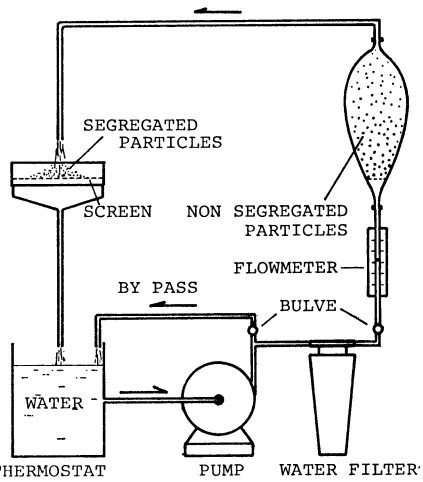

Fig. 2. An apparatus for segregating resin particle size.

Anion Exchange Resin. The structure of the weakly basic anion exchange resin Diaion WA21 is shown in Fig. 1. At first, the resin particles in chloride form were segregated by size (Fig. 2), and the particles between 80 and 100 mesh were packed into the column in chloride form.

Apparatus. The apparatus (Fig. 3) and method were the same as reported.[2] The height of the resin bed was 1 m and its diameter 21 mm. In order to detect the conductivity of the resin phase, a pair of platinum electrodes were inserted at the bottom of the resin bed. Since the conductivity of the boron band is much higher than that of the resin of free base form, the movement of boron band through column is effectively followed by the conductivity between the platinum electrodes.

Operation. A column packed with the Diaion WA21 resin in chloride form was converted into free base form by passing NaOH solution (Fig. 4-i), and was washed with pure water (Fig. 4-ii). To the column was fed excess (*ca.* 1.2 dm^3) 0.1 mol dm^{-3} H_3BO_3 solution to form a band saturated with boric acid and boron-10 depleted effluent from the column was discarded (Figs. 4-iii,iv); a few columns

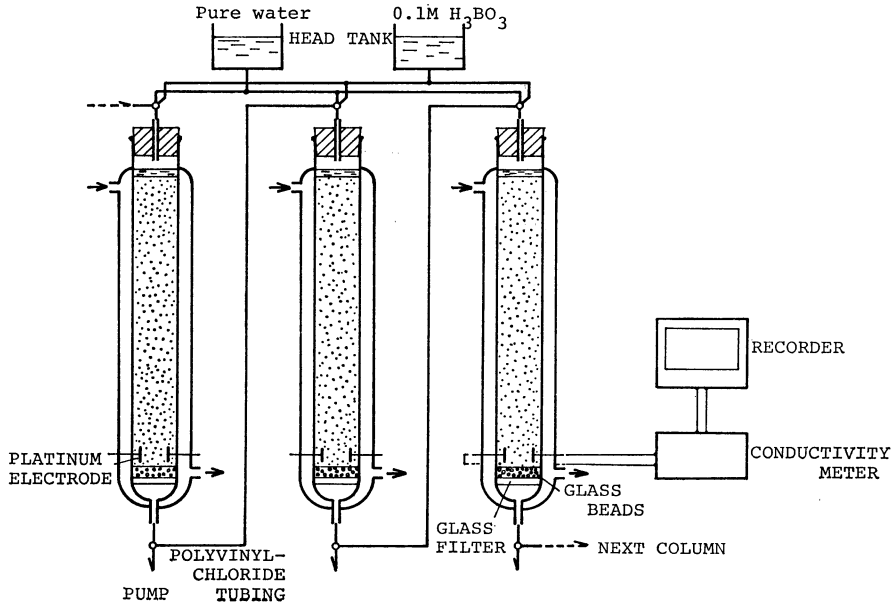

Fig. 3. Experimental apparatus.

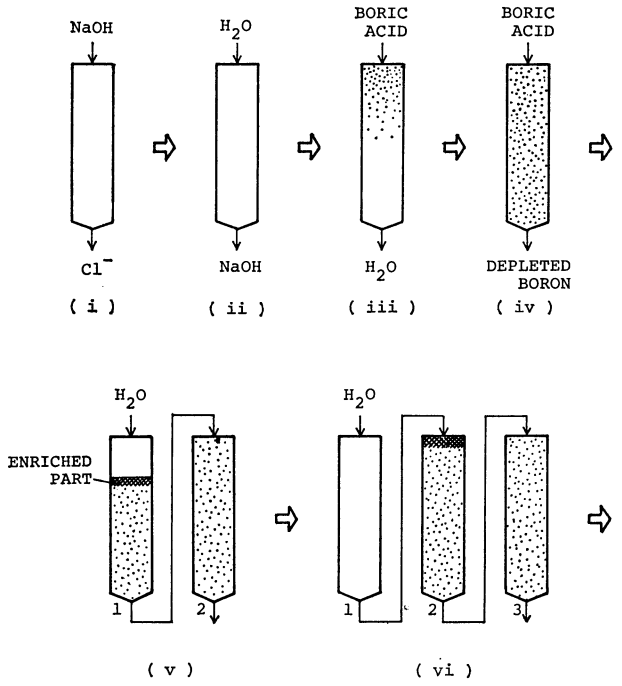

Fig. 4. Column operation.

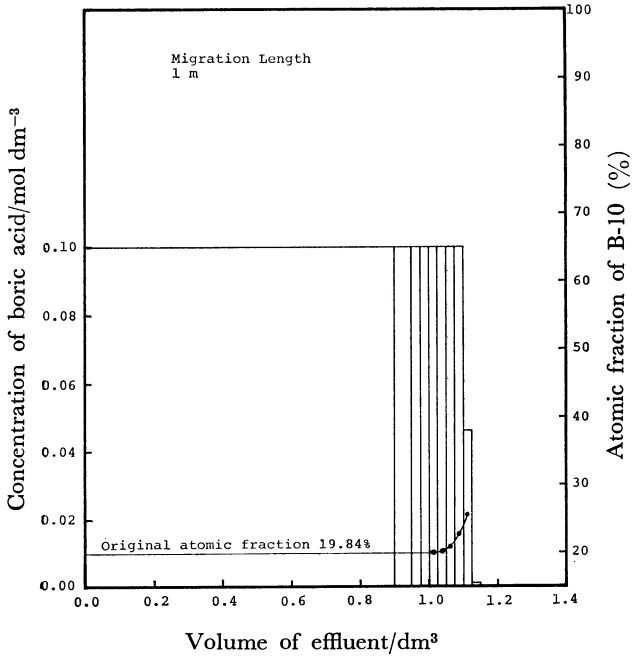

Fig. 5. Elution curve and isotope distribution curve of 1 m migration.

were treated in a similar way. The columns were equilibrated with boric acid aqueous solution having natural abundance ratio of boron isotopes (boron-10 content 19.84%); the columns were slightly enriched with boron-10. Two columns were connected in series by a thin polyvinyl chloride tubing.

Pure water was fed to the first column in order to elute the boric acid band, boron-10 being enriched at the rear boundary (Fig. 4-v). The effluent from the second column (the column holding isotopic plateau) was discarded. The third column was connected to the second column in series when the boric acid band of the first column had been completely transferred to the second column (Fig. 4-vi). The first column was again saturated with 0.1 mol dm^{-3} H_3BO_3 aqueous solution having natural abundance ratio of boron isotopes and used for another plateau holding column (the fourth column, Figs. 4-iii,iv). In the case of a longer migration length about 50 m, it was necessary to use three columns in series to hold the isotopic plateau region. In this way the chromatogram was migrated to the required length; 1, 2, 4, 8, 16, 32, 64, 128, and 256 m. The effluent of each experiment was collected in fraction.

Measurements. The samples were analyzed in a similar way to that reported.[1,2] The concentration of boric acid was determined by neutralization titration using mannitol and the atomic fraction of boron-10 by the surface ionization method using a Variant MAT CH-5 mass spectrometer.[4]

Reabents. All the chemicals used were of reagent grade.

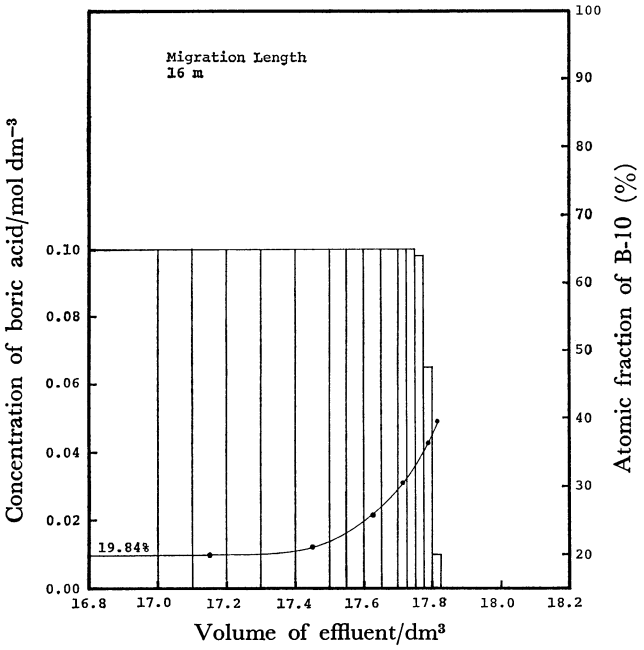

Fig. 6. Elution curve and isotope distribution curve of 32 m migration.

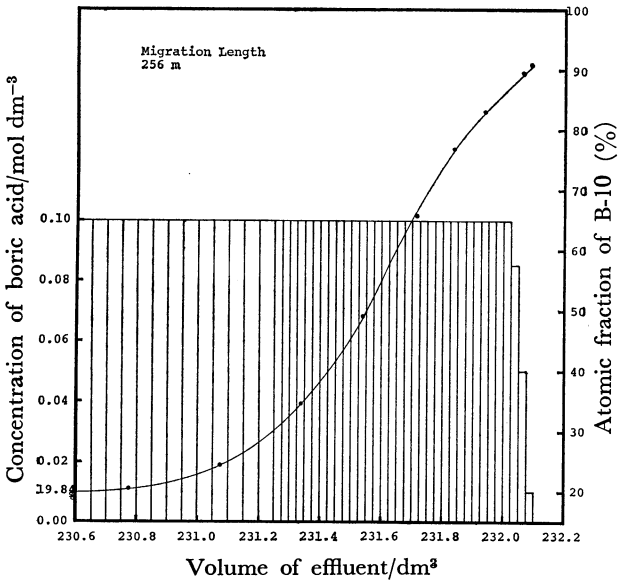

Fig. 7. Elution curve and isotope distribution curve of 256 m migration.

Results and Discussion

Three examples of the elution curve and isotope distribution curve of each run are shown in Figs. 5—7. The profiles of enriched zone of boron-10 are surveyed with regard to migration length in Fig. 8.

Migration Length and Extent of Boron-10 Enrichment. The most enriched boron-10 was always obtained at the most rear part of the chromatogram. The atomic fractions of boron-10 at the end of each chromatogram increased steadily with increase of migration length (Table 1). This indicates that an ideal chromatogram is accomplished in each run.

In the case of 256-m migration, boron-10 was enriched to 91.00% from its original atomic fraction of 19.84.

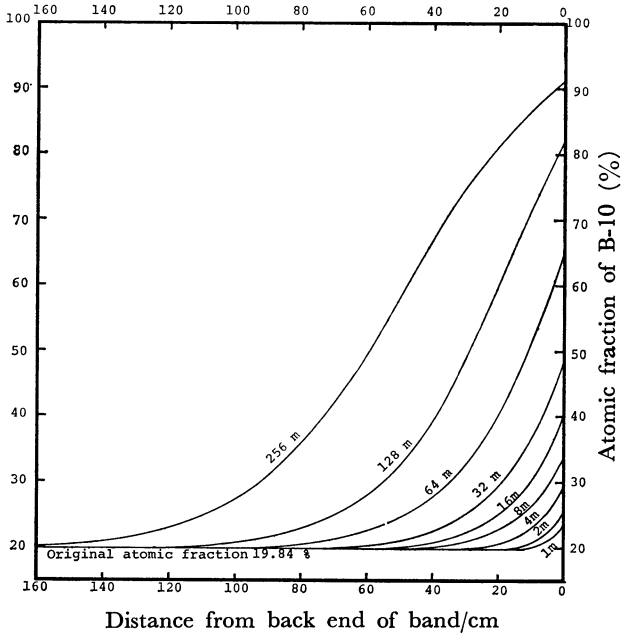

Fig. 8. Dependence of atomic fraction of boron-10 on migration length.

Table 1. Migration length *vs.* separation factor S and maximum atomic fraction of boron-10

L[a] / m	S[b]	R_m[c] / %
1	1.0096	25.62
2	1.0099	26.91
4	1.0095	27.76
8	1.0098	33.26
16	1.0105	39.62
32	1.0100	48.12
64	1.0101	62.43
128	1.0104	81.62
256	1.0105	91.00
S_a[d]	1.0100±0.0005	

a) Migration length of each run. b) Separation factor. c) Maximum atomic fraction of boron-10 obtained. d) Average value of S.

Migration Length and Separation Factor. The single stage separation factor S is defined by

$$S = \frac{[\overline{^{10}B}][^{11}B]}{[^{10}B][\overline{^{11}B}]} \quad (1)$$

where [ ] denotes the concentration of isotopes in the aqueous phase and [$\overline{\ }$] the concentration of the isotopes in the resin phase. The value of separation factor S can be obtained from the data by means of

$$S = \frac{\Sigma f_i(R_i - R_0)}{QR_0(1-R_0)} + 1 \quad (2)$$

where f_i is the total amount of boron in the i-th fraction, R_0 the original atomic fraction of boron-10, R_i the atomic fraction of boron-10 in the i-th fraction and Q the total capacity of ion exchange column. The

calculated values are given in Table 1. The separation factor S is constant irrespective of migration length. This is quite different from the results obtained by Hagiwara *et al.* on lithium isotope separation[5] and by Aida *et al.* on boron isotope separation,[1] in which the separation factor decreases with increase of migration length. The experiments were carried out without holding the isotopic plateau part in the chromatogram, the depleted part being mixed with an enriched part during the course of migration, making it impossible to obtain a reliable value of separation factor. In the present study, an isotopic plateau region in which the atomic fraction of isotopes remains unchanged always existed, no mixing taking place. The value obtained by means of Eq. 2 gives a satisfactory separation factor.

Conclusion

(1) Boron-10 was enriched from its original atomic fraction of 19.84 to 91.00% by the simple process of eluting a boric acid band with pure water through columns of weakly basic anion exchange resin Diaion WA21.

(2) The steady increase in atomic fraction of boron-10 with migration length indicates the merit of isotopic plateau displacement chromatography.

(3) At 40 °C a constant value 1.010 was obtained for the separation factor irrespective of migration length 1—256 m.

References

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