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CHROMATOGRAPHIC SEPARATION OF NITROGEN ISOTOPES USING PURE WATER AS ELUTING AGENT

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Aqueous solutions of ammonia were passed through ion-exchange columns. In some experiments the column was packed with a strongly acidic cation exchanger Diaion SK-IB in magnesium form, and in the others a weakly acidic cation exchanger composed of succinylated aminododecylcellulose with 3-aminobenzeneboronic acids was used. The ammonium bands formed in the columns were eluted with pure water. It was found that: (1) Nitrogen-15 was enriched in the rear part of the band, and depleted in the front part. (2) The ammonia charged to the column packed with Diaion SK-IB was completely eluted with pure water.

Since the first experiment on ion-exchange separation of isotopes was carried out by Taylor and Urey[1] in 1938, many experiments have been done on the separation of isotopes of nitrogen[2-7] and other elements[8-10] using similar methods. Recently the present authors[11-15] have found a simple chromatographic system for separating boron isotopes using weakly basic anion exchange resin in free base form, aqueous solution of boric acid, and pure water as eluting agent. This system is superior to other separation system, because the separation factor for boron isotopes between an ion-exchange resin and an external solution is as high as that for systems using strongly basic anion exchange resins, and boric acid charged to the column is absorbed in the resin to a high concentration, yet it can be completely eluted with pure water. The purpose of the present research is to develop a simple chromatographic system for separation of nitrogen isotopes in which pure water can be used as the eluting agent.

The ion-exchangers used were Diaion SK-IB and a special cellulose. Diaion SK-IB is a gel type strongly acidic cation exchange resin having sulfonic ion groups. The special cellulose is a weakly acidic cation exchanger composed of succinylated aminododecylcellulose and 3-aminobenzeneboronic acid as ionic groups. The reagents were analytical grade commercial materials, used without further purification. The columns used(20 cm in length and 1 cm in diameter in some cases, and 65 cm in length and 1 cm in diameter in others) were surrounded by jackets through which water from a thermostat was circulated so that the columns were maintained at a constant temperature with in ± 0.2°C. The ion-exchangers described above were packed in the columns, and subjected to ammonium-hydrogen or sodium-hydrogen cycles in the usual manner to ensure regeneration and uniform packing. The columns were throughly washed with distilled water after converting the ion-exchangers into the free acid or magnesium forms. Aqueous solutions containing ammonia were charged to the columns, and the ammonium bands formed were eluted with pure water. The flow rates of the

ammonia and eluting agents were controlled by screw cocks at the bottom of the columns. A number of fractions of the effluent were successively collected in graduate cylinders containing an excess of standard hydrochloric acid. The concentration of ammonia in each fraction was determined by back-titrating the excess acid with standard sodium hydroxide, using a mixed indicator. The indicator was prepared by mixing five parts of 0.1 % solution of bromocresol green and one part of 0.1 % solution of methyl red in methyl alcohol. Ammonium ion in each sample was converted to nitrogen gas by oxidation with sodium hypobromite. Isotopic analysis of the nitrogen gas was carried out using Hitachi RMI-2 mass spectrometer. The mass peaks used were those at m/e=28($^{14}N^{14}N^{+}$) and 29($^{14}N^{15}N^{+}$). This mass region was repeatedly scanned about 40 times for each sample, and the ratio of peak heights at m/e=28 to m/e=29 was calculated as an average of these scans. The atomic fraction of nitrogen-15 was determined from the ratio of the peak heights. The standard deviation of the isotope analysis of nitrogen-15 was less than ± 0.00001 in every case. The single-stage separation factor for nitrogen isotopes between resin phase(Diaion SK-IB in magnesium form) and external ammonia solution phase was determined by breakthrough operation. An ammonia solution was passed through a column(Diaion SK-IB in magnesium form, 1 x 50 cm bed) at a superficial velocity of 38 $ml \cdot h^{-1} \cdot cm^{-2}$. A number of fractions of the effluent were successively collected in measuring flasks, and the ammonia concentration and atomic fraction of nitrogen-15 in these fractions were determined by the method described above.

Examples of the experimental results obtained are shown Figures 1 through 3. The following can be seen from the results under the present experimental conditions:

(1) Nitrogen-15 was considerably enriched in the rear part of the ammonium band, and depleted in the front part.

(2) The ammonia charged to the column packed with Diaion SK-IB was completely eluted with pure water.

(3) The flow rate had little influence on the elution curve in the case of Diaion SK-IB.

A separation factor $^{15}_{14}S$ for nitrogen isotopes between the resin and the external phases was calculated from the breakthrough-experimental data by means of the following equation[16],

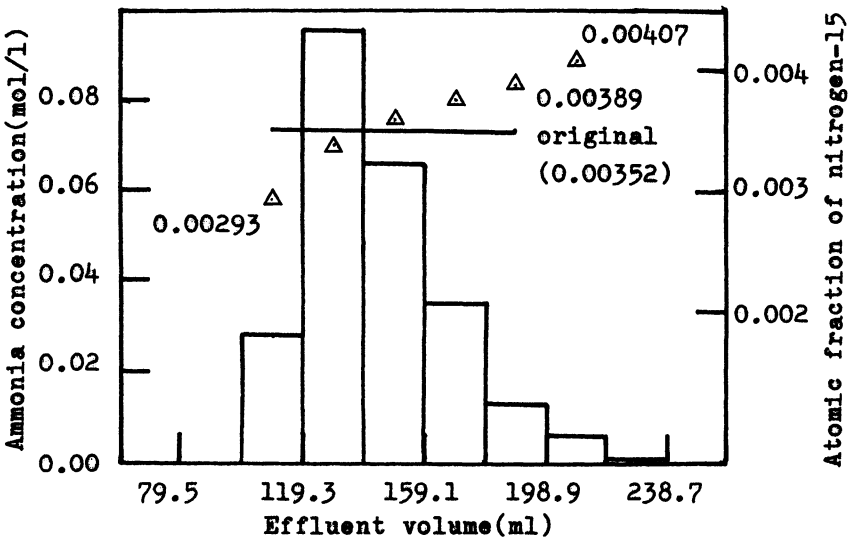


Fig. 1 Elution graph

Column: Diaion SK-IB, magnesium form, 20-50 mesh, 0.8 cm^2 x 50 cm bed.

Charge: 50 ml of 0.101M NH_4OH.

Eluting agent: H_2O

Temperature: 25°C

Flow rate: 38 $ml \cdot h^{-1} \cdot cm^{-2}$

□ : Ammonia concentration.

△ : Atomic fraction of nitrogen-15

Fig. 2 Elution graph

Column: Diaion SK-IB, magnesium form, 20-50 mesh, 0.8 cm^2 x 50 cm bed.
Charge: 50 ml of 0.101M NH_4OH.
Eluting agent: H_2O
Temperature: 25°C
Flow rate: 76 $ml \cdot h^{-1} \cdot cm^{-2}$
▭ : Ammonia concentration.
△ : Atomic fraction of nitrogen-15.

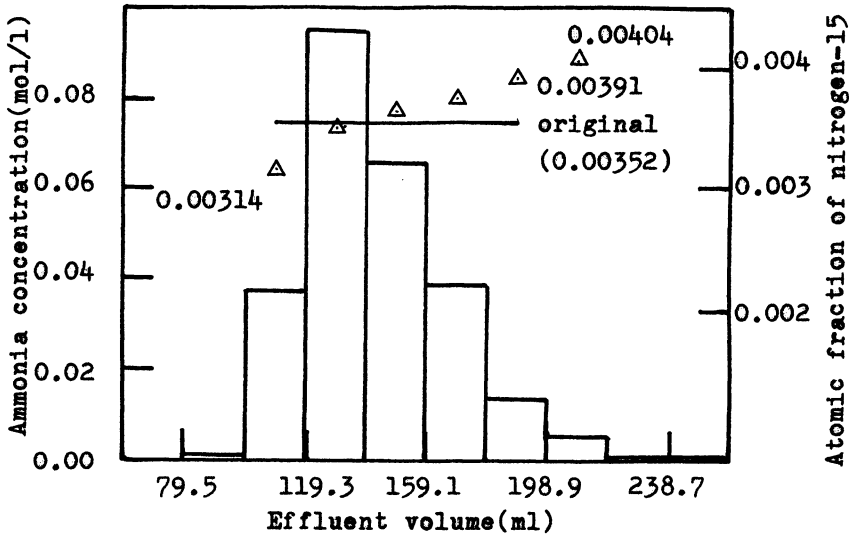
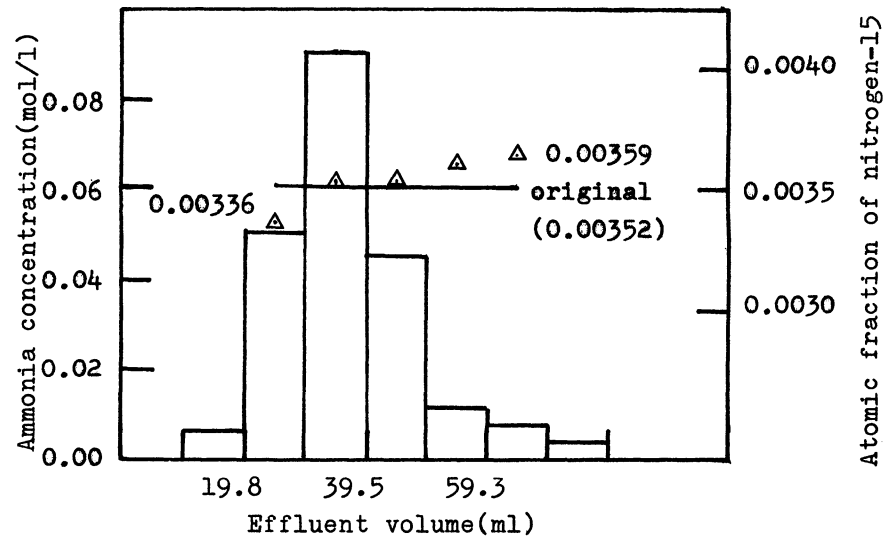


Fig. 3 Elution graph

Column: Weak acid cation exchanger, free acid form($RB(OH)_2$), 0.8 cm^2 x 17 cm bed.
Charge: 25 ml of 0.100M NH_4OH
Eluting agent: H_2O
Temperature: 25°C
Flow rate: 14 $ml \cdot h^{-1} \cdot cm^{-2}$
▭ : Ammonia concentration.
△ : Atomic fraction of nitrogen-15.



$$^{15}_{14}S = 1 + \frac{1}{Q} \cdot \frac{1}{R_0(1 - R_0)} \cdot (R_0 - R_i) \cdot f_i$$

where Q is the total amount of nitrogen in the resin phase(m mol), R_0 the atomic fraction of nitrogen-15 in the feed solution, R_i the atomic fraction of nitrogen-15 in fraction i of the effluent, and f_i the total amount of the nitrogen isotopes in fraction i(m mol). The value obtained for the NH_4OH-Diaion SK-IB(magnesium form) system was 1.009, which is smaller than the value(1.025) for an NH_4OH-strong acid cation exchange resin(hydrogen form) system[2]. The small separation factor may be due to the fact that the structure of an ammonia molecule changes very little as it transfers from the external solution to the resin phases. The separation system of nitrogen isotopes by means of a more weakly acidic cation exchanger having o-toluneboronic acid as the ionic functional group would be one of the best separation

systems, because (1) this system would make use of the nitrogen isotope exchange reaction between NH_4^+ and NH_3(whose equilibrium constant is large; 1.025), so that nitrogen isotopes could be enriched more efficiently; (2) the ammonia charged to the column could probably be completely eluted with pure water, and the elution curve would be sharper. The advantages of the ammonia charged to the column being easily eluted with pure water are that it is scarcely necessary to regenerate the resin in the column, and that the ammonia is free from contamination by any other chemicals.

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