

가수된 산화 망간(IV)에 의한 리튬 동위원소의 크로마토그래피적 분리

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Chromatographic Separation of Lithium Isotopes by Hydrous Manganese(IV) Oxide

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요 약. 용리 크로마토그래피를 사용하여 가수된 산화 망간(IV) 이온교환체로 화학적 이온교환을 통하여, 리튬 동위원소를 분리하는 연구를 하였다. 산화 망간(IV) 이온교환체의 이온교환 용량은 0.5 meq/g이었다. 무거운 리튬 동위원소는 용액상에, 그리고 가벼운 동위원소는 이온교환 수지상에 농축되었다. 분리인자는, Glueckauf의 방법으로 용리곡선과 동위원소 분석 값들로부터 구하였다. ${}^6\text{Li}^+$ - ${}^7\text{Li}^+$ 동위원소쌍의 분별로부터 얻은 분리인자의 값은 1.018이었다.

ABSTRACT. Separation of lithium isotopes was investigated by chemical ion exchange with a hydrous manganese(IV) oxide ion exchanger using an elution chromatography. The capacity of manganese(IV) oxide ion exchanger was 0.5 meq/g. The heavier lithium isotope was enriched in the solution phase, while the lighter isotope was enriched in the ion exchanger phase. The separation factor was determined according to the method of Glueckauf from the elution curve and isotopic assays. The separation factor of ${}^6\text{Li}^+$ - ${}^7\text{Li}^+$ isotope pair fractionation was 1.018.

INTRODUCTION

The effect of pH on the extent of cation adsorption by hydrous metal oxides has been studied by many investigators. For most monovalent cations, such as the alkali metal cations, adsorption is usually nonspecific and therefore depends directly on the surface charge of the oxide as determined by the amount of H⁺/OH⁻ adsorption. At the point of zero charge, there is usually very little cation adsorption, but above the point of charge, cations are adsorbed to counterbalance the net negative surface charge. Part of the negative surface charge is also counterbalanced by the exclusion of anions, but this usually compensates for only a small fraction of the total charge, especially, at high electrolyte concentrations.¹

The high adsorptive capacity of colloidal hydrous manganese(IV) oxide for cations was demonstrated by Posselt *et al.*^{2,3} They noted that the pH of the isoelectric point of manganese oxide is quite low, ranging from pH 2.8 to pH 4.5. At higher pH, colloidal manganese(IV) oxide has a net negative charge. They demonstrated that the mechanism of adsorption by MnO₂ is primarily electrostatic by comparing the adsorption of cationic, anionic, and uncharged organic compounds. Only the organic cation showed any significant adsorption, and it was adsorbed to about the same extent as the metal cations examined. Gadde and Laitinen⁴ studied the adsorption of several metals on hydrous manganese(IV) oxide and hydrous ferric oxides. Takeuchi *et al.*⁵ reported that the sorbents are prepared by extracting lithium ions from

lithium manganese oxides with the lithium manganese mole ratio varying between 0.42 and 0.84. In addition, they investigated lithium isotope selectivity on these sorbents. They also found that all the sorbents are ^6Li -specific and the values of the ^7Li -to- ^6Li isotope separation factor are between 1.0040 and 1.0092 at 25 °C. Lithium isotopes play an important role in the nuclear science and industry due to the great difference in their nuclear characteristics. Highly enriched ^7Li in lithium hydroxide is used for adjustment of coolant pH in pressurized light water reactors,⁶ whereas ^6Li , in the form of Li_2H is employed as a shield against thermal neutrons.^{7,8}

In this work, it was examined in lithium isotope separation using a manganese(IV) oxide ion exchanger by ion exchange elution chromatography.

EXPERIMENTAL

Materials and methods The capacity of the MnO_2 ion exchanger was determined by the method given in the literature.⁹ Manganese(IV) oxide (-60-230 mesh, 99 +%) was purchased from Aldrich Chemical Company, Inc., USA. Lithium chloride and ammonium acetate were purchased from Sigma Chemical Co., USA. An Atomic Absorption Spectrophotometer (Hitachi Z-8000) was used to determine the lithium ion concentration in the solution. Measurement of the lithium isotope ratio was carried out using a Thermal Ionization Mass Spectrometer (Finnigan MAT 262) with a rhenium double filament. Amount of 1.0-2.0 μg lithium was loaded on an evaporation filament of the MAT 262. Ionization was then performed by passing a heating electric current through the ionization filament. After the ion beam intensities of ^6Li and ^7Li became sufficiently high, the Li-6 and Li-7 mass peaks were repeatedly recorded. And the mass scanning was repeated several times in a block, and several blocks were recorded as one measurement. The mole fraction of Li-6 of each feed solution was an average of three measurements.

Separation of lithium isotopes Manganese(IV) oxide ion exchanger was slurried in ammonium acetate solution. The slurried MnO_2 was packed in a water-jacketed glass column (0.2 cm I.D. 35 cm height). The temperature was maintained at 20 °C with using a Water Circulator (HAAKE A-80). The volume of 0.1 mL of 0.01 M

LiCl solution was loaded on the top of the MnO_2 bed. The 1.0 M $\text{CH}_3\text{COONH}_4$ (K_4-16) solution was used as an eluent. The lithium feed solution was then passed through the column by gravity flow. The flow rate was controlled by a fine stopcock to be 0.6 mL/hr. The effluent was collected as a fraction of 0.1 mL each with an Automatic Fraction Collector (Pharmacia LKB FRAC-100).

RESULTS AND DISCUSSION

The ion exchange capacity of the MnO_2 ion exchanger was found to be 0.5 meq/g. The chromatogram was obtained in the 1.0 M $\text{CH}_3\text{COONH}_4$ solution at 20 °C as shown in Fig. 1. From the elution curve, the number of theoretical plates, N , in the column, was calculated by the equation¹⁰:

$$N = 8 \cdot \left(\frac{V_{\text{max}}}{\beta} \right)^2 \quad (1)$$

where V_{max} is the peak elution volume, and β the band width at the concentration $C - C_{\text{max}}/c$, and C_{max} the concentration of solute at the maximum peak height of the elution curve.

From the elution curve and isotopic assay data, the separation factor of lithium isotopes was calculated by the Glueckauf theory.¹¹ The isotopic ratio of a fraction

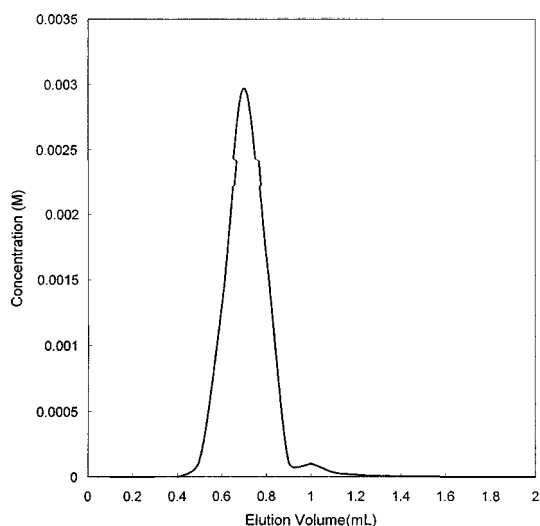


Fig. 1. Elution curve for lithium isotopes.

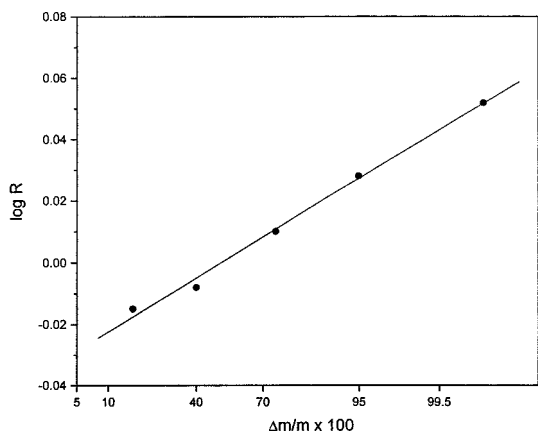
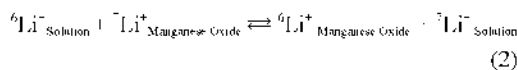


Fig. 2. Enrichment of lithium isotopes by cation exchange elution chromatography.

can be expressed by ${}^6\text{Li}^- / {}^7\text{Li}^+$, where ${}^6\text{Li}^-$ and ${}^7\text{Li}^+$ are the abundances of the light and heavy isotopes. The isotopic ratio of the lithium feed solution sample is denoted by $({}^6\text{Li}^- / {}^7\text{Li}^+)_0$ and the local enrichment factor, R , is given by $({}^6\text{Li}^- / {}^7\text{Li}^+) / ({}^6\text{Li}^- / {}^7\text{Li}^+)_0$. The $\Delta m/m$ is the proportion of lithium in the individual fraction. The $\log R$ vs. $\Delta m/m$ data were plotted on probability paper where the abscissa was a probability scale and the ordinate was a linear scale. The local enrichment factor ($\log R$) was the ordinate and the fraction of the eluted mixture ($\Delta m/m$) was the abscissa. This gave a linear plot. The slope of the straight line obtained will be $\epsilon\sqrt{N}$, and separation factor, α , is defined as $\epsilon+1$. The separation factor, α , was determined from the slope of a least square line drawn through the points as shown in Fig. 2. This is a typical plot of the isotopic assays in this experiment. In this experiment, the separation factor of lithium isotopes obtained was the value of 1.018. This value is larger than those obtained by Takeuchi *et al.*⁵ Kim *et al.*¹² investigated the separation of lithium isotopes by elution chromatography on an ion exchange resin having azacrown ether as an anchor group, and obtained the impressively larger value of the separation factor of 1.068. The theoretical maximum value of the elementary separation factor for fractionation of lithium isotopes by molecular distillation is 1.080.^{8,13} From the experimental data, it appears that the isotope exchange reaction can be represented by the following equation:



The subscripted symbols, such as solution and manganese oxide refer to the solution and manganese(IV) oxide ion exchanger phases in this chemical isotope exchange. Kondoh *et al.*¹⁴ Heumann *et al.*¹⁵ Oi *et al.*¹⁶ Ooi *et al.*¹⁷ Jepson *et al.*¹⁸ Kim *et al.*¹² and Fujine *et al.*¹⁹ also reported that the heavier isotopes were preferentially enriched in the solution phase in chromatography with strongly acidic cation, anion, titanium phosphate, and polymer-bound crown ether exchangers. These results well agree with my work. On the other hand, Oi *et al.*²⁰ Klinskii *et al.*²¹ Aaltonen *et al.*²² Heumann *et al.*²³ and Lee²⁴ reported that the heavier isotopes were preferentially enriched in the resin phase in cation and anion exchange chromatography. The metal species in the resin phase is less hydrated than the metal species in the solution phase. This contributes to a difference in bonding and subsequent enrichment of the lighter isotope in the ion exchanger phase.²¹ This effect well agrees with my work.

CONCLUUIONS

Lithium isotope separation was investigated by chemical ion exchange with the hydrous manganese(IV) oxide ion exchanger using an elution chromatography. The capacity of the MnO_2 ion exchanger was 0.5 meq/g. The heavier isotope of lithium was enriched in the solution phase, while the lighter isotope was enriched in the hydrous MnO_2 phase. The single stage separation factor was 1.018.

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