

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

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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. One molar CH_3COONa solution was used as an eluent. The heavier isotope of lithium was enriched in the solution phase, while the lighter isotope was enriched in the ion exchanger phase. The separation factor was calculated according to the method of Glueckauf from the elution curve and isotopic assays. The single stage separation factor of lithium isotope pair fractionation was 1.021.

Keywords : Lithium isotope separation, MnO_2 exchanger, Capacity, Isotope effects, Elution chromatography.

Introduction

The chemistry of the hydrous metal oxides has been studied in a large number of scientific fields, especially, ion exchange separation, scavenging by sorption and coprecipitation, separation of mineral, nuclear fuels, antiperspirants, radioactive contamination, and scavenging of trace metals.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 MnO_2 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 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. And 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. Ooi *et al.*⁶ reported that ion exchange chromatography of lithium was carried out to study the lithium isotope effect in an aqueous ion exchange system, using titanium phosphate exchangers granulated with polyvinyl chloride or an inorganic binder. The ion exchanger granulated with polyvinyl chloride showed significant isotope fractionations when a 0.05 M $(\text{NH}_4)_2\text{CO}_3$ solution was used as an eluent. They found that the lithium isotope separation factor was roughly evaluated as 1.007. They also found that the lighter isotope, $^6\text{Li}^+$ was preferentially fractionated into

the ion exchanger phase. Oi *et al.*⁷ investigated the lithium isotope effect in aqueous ion exchange systems by cation exchange chromatography. They obtained the value of the separation factor of 1.00089-1.00171 at 25 °C.

Kim *et al.*⁸ also investigated the separation of lithium isotopes with 1,7,13-trioxa-4,10,16-triazacyclooctadecane bonded Merrifield peptide resin by ion exchange elution chromatography, and obtained the impressibly larger value of the single stage separation factor of 1.068. The theoretical maximum value of the elementary separation factor for fractionation of lithium isotopes by molecular distillation is 1.080.⁹ Recently, Kim *et al.*¹⁰ reported that the separation of lithium isotopes by aminobenzo-15-crown-5 bonded Merrifield peptide resin was investigated, and obtained the value of the separation factor of lithium isotopes of 1.026. They also found that the heavier isotope, $^7\text{Li}^+$ was concentrated in the resin phase, while the lighter isotope, $^6\text{Li}^+$ was concentrated in the solution phase.

Naturally occurring element lithium consists of two stable isotopes, ^6Li and ^7Li , and each isotope plays an important role in nuclear science and industry. The heavy isotope of lithium, ^7Li could be used as a pH control agent ($^7\text{LiOH}$) of the coolant in nuclear fission reactors. And the lithium compounds rich in ^6Li will be required for the tritium breeder blanket in deuterium-tritium fusion power reactors in the future.⁷ Because of the large cross section for thermal neutron in the nuclear reaction, $^6\text{Li}(n, \alpha)\text{T}$ and $^7\text{Li}(n, \alpha)\text{T}$ in fast neutron, a variety of isotopic ratio of the element lithium have been proposed for releasing energy or production of tritium more effectively.¹¹

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

Experimental Section

Materials and Methods. Manganese(IV) oxide (-60 + 230 mesh, 99 + %) was purchased from Aldrich Chemical Company, Inc., USA. Lithium chloride and sodium acetate

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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 used to determine the isotope ratio in each feed solution.

Determination of the Total Weight Capacity. The capacity of the manganese(IV) oxide exchanger was determined by the method given in the literature.¹² Manganese(IV) oxide was washed to neutrality with distilled water, and dried in air. Of this quantity, 1.000 ± 0.005 g was weighed into a dry 250 mL Erlenmeyer flask containing exactly 200 mL 0.1 N NaOH with 5% sodium chloride, and was allowed to stand overnight. Amount of 1.0 g ion exchanger sample of the same material was separately weighed into a weighing bottle, dried at 110 °C overnight, and weighed again to determine the percentage of solids. Of the supernatant liquid in the Erlenmeyer flask, 50 mL aliquots are backtitrated with 0.1 N HCl against phenolphthalein. The capacity was then calculated by the formula:

$$\text{Capacity (meq/g)} = \frac{(200 \cdot \text{Normality}_{\text{NaOH}}) - 4(\text{mL}_{\text{Acid}} \cdot \text{Normality}_{\text{Acid}})}{\text{Sample Weight} \cdot (\% \text{ Solid}/100)} \quad (1)$$

It represents the total weight capacity of the exchanger in the dry H-form. The resin must be completely in the H-form before weighing of the sample, since difference in equivalent weights of different ions would lead to errors. The standard sodium hydroxide solution was treated with 5% sodium chloride to obtain a completely exchange equilibrium by the excess of sodium ions. A reproducibility of $\pm 1\%$ can consequently be obtained.

Separation of Lithium Isotopes. Manganese(IV) oxide ion exchanger was slurried in sodium acetate solution. The slurried MnO_2 was packed in a water-jacketed glass column (0.2 cm I.D. \times 35 cm height). The temperature was maintained at 20 °C with using an 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 CH_3COONa solution ($K_a = 25$) was used as an eluent. The lithium feed solution was then passed through the column under 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 from column operation with 1.0 M CH_3COONa solution at 20 °C as shown in Figure 1. From the elution curve, the number of theoretical plates in the column, was calculated by the equation:¹³

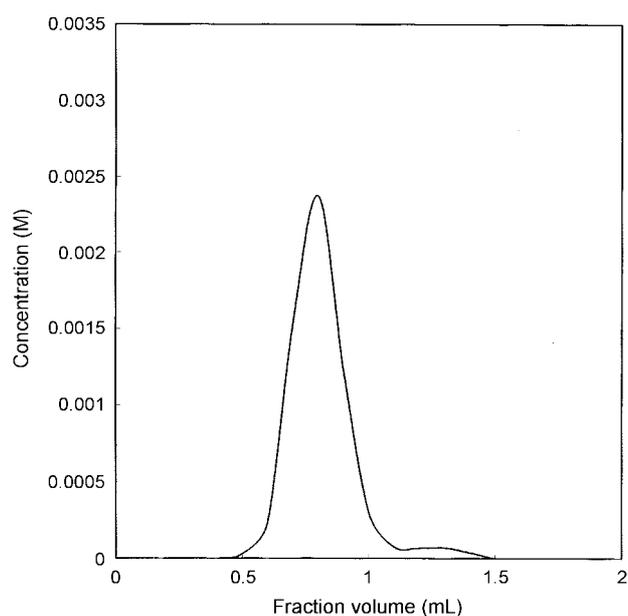


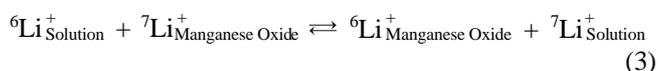
Figure 1. Elution curve for the separation of lithium isotopes.

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

where V_{max} is the peak elution volume, and β the band width at the concentration $C = C_{\text{max}}/e$, 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.¹⁴ The data were plotted on probability paper where the abscissa was a probability scale and the ordinate was a linear scale. The local enrichment percentage was the ordinate and the fraction of the eluted mixture was the abscissa. This gave a linear plot. The slope obtained will be $\epsilon \sqrt{N}$, and separation factor is $1 + \epsilon$. The separation factor, α , was determined from the slope of a least square line drawn through the points as shown in Figure 2. This is a typical plot of the isotopic assays in this experiment. In my experiment, the single stage separation factor of lithium isotopes was obtained as the value of 1.021. This value is larger than those of the values obtained by Takeuchi *et al.*,⁵ Ooi *et al.*,⁶ and Oi *et al.*⁷ The relatively larger separation factor obtained in this experiment can be explained by the fact that the difference in the adsorbabilities of the ions between ${}^6\text{Li}^+$ and ${}^7\text{Li}^+$ on the MnO_2 exchanger is significant. The larger the difference in the adsorbabilities of the ions between lithium isotopes, the larger the separation factor is obtained.

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

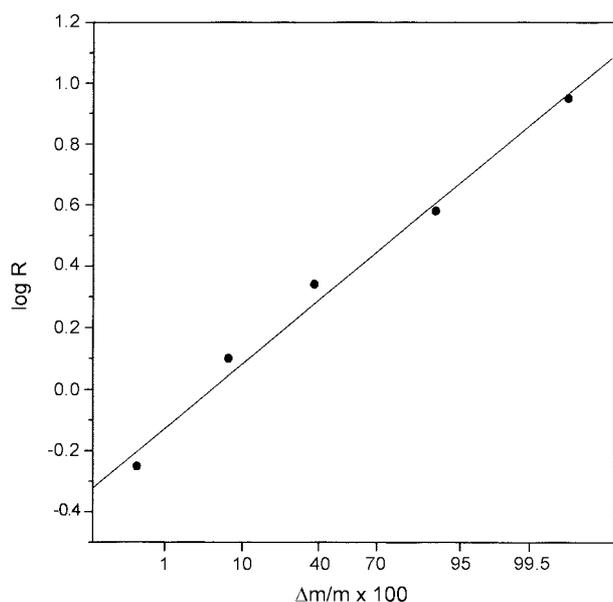


Figure 2. Enrichment of lithium isotopes by cation exchange chromatography. The isotopic ratio of a fraction can be expressed by ${}^7\text{Li}/{}^6\text{Li}$, where ${}^6\text{Li}$ and ${}^7\text{Li}$ are the relative abundances of the light and heavy lithium isotopes. The isotopic ratio of the standard used in the mass analysis is denoted by $({}^6\text{Li}/{}^7\text{Li})_0$. The local enrichment factor, R , is defined as $({}^7\text{Li}/{}^6\text{Li})/({}^6\text{Li}/{}^7\text{Li})_0$. The $\Delta m/m$ is the proportions of lithium in the individual fractions.

exchanger phases in this chemical isotope exchange. Kondoh *et al.*,¹⁵ Heumann *et al.*,¹⁶ Oi *et al.*,¹⁷ Ooi *et al.*,⁶ Jepson *et al.*,¹⁸ and Fujine *et al.*¹⁹ also reported that the heavier isotopes were preferentially enriched in the solution phase of chromatography using strongly acidic cation exchangers, anion exchanger, titanium phosphate exchangers, and polymer-bound crown ether. These results well agree with my work. On the other hand, Oi *et al.*,⁷ Klinskii *et al.*,²⁰ Aaltonen *et al.*,²¹ Heumann *et al.*,²² and Lee²³ reported that the heavier isotopes were preferentially enriched in the resin phase of cation and anion exchange chromatography. The separation factor depended upon the mass of the isotope as well as the difference in the masses of the isotope pairs. The cation species in the exchanger phase is less hydrated than

Table 1. Separation of lithium isotopes of some investigations by ion exchange chromatography

Separation Factor	Method	Exchanger	Reference
1.0092	Extraction	Lithium manganese oxide	5
1.007	Elution	Titanium phosphate	6
1.00171	Displacement	Asahi LS-6, fiber	7
1.026	Elution	Crown resin	10
1.068	Elution	Azacrown resin	8
1.014	Displacement	Cryptand resin	19
1.0026	Breakthrough	Dowex 50 × 24	24
1.0016	Breakthrough	Cubic antimonic acid	25
1.014	Extraction	LiMn_2O_4	26
1.021	Elution	MnO_2	This Work

the cation species in the solution phase. This contributes to a difference in bonding and subsequent enrichment of the lighter isotope in the exchanger phase.²³ These phenomena well agree with my work. Some investigations for the separation of lithium isotopes by ion exchange chromatography are listed in Table 1. As shown in Table 1, the crown, cryptand, LiMn_2O_4 , and manganese(IV) oxide exchangers are more significant to separate lithium isotopes than the other exchangers.

Conclusions

Separation of lithium isotopes was investigated by chemical ion exchange with the hydrous manganese(IV) oxide ion exchanger using an elution chromatographic technique. The capacity of the MnO_2 ion exchanger was 0.5 meq/g. One molar CH_3COONa solution was used as an eluent. The heavier isotope of lithium was enriched in the solution phase, while the lighter isotope was enriched in the MnO_2 ion exchanger phase. The single stage separation factor was calculated according to the method of Glueckauf from the elution curve and isotopic assays. The single stage separation factor of lithium isotopes was 1.021.

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