SHORT COMMUNICATION

Separation of Magnesium Isotopes by 1-Aza-12-Crown-4 Bonded Merrifield Peptide Resin

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Abstract—Magnesium isotope separation was investigated by chemical ion exchange with the 1-aza-12-crown-4 bonded Merrifield peptide resin using elution chromatography. The capacity of the novel azacrown ion exchanger was 1.0 meq/g dry resin. The heavier isotopes of magnesium were enriched in the resin phase, while the lighter isotopes were enriched in the solution phase. The single stage separation factor was determined according to the method of Glueckauf from the elution curve and isotopic assays. The separation factors of $^{24}Mg^{2+}$-$^{25}Mg^{2+}$, $^{24}Mg^{2+}$-$^{26}Mg^{2+}$, and $^{25}Mg^{2+}$-$^{26}Mg^{2+}$ isotope pairs were 1.012, 1.024, and 1.011, respectively.

INTRODUCTION

It was reported that crown ethers might also be applicable to the separation of isotopes. Macrocyclic polyethers and their analogues have the remarkable property of complexation with cations, especially, alkali and alkaline earth metal ions. Therefore, their unique ability to form stable complexes with various cations has been used to separate isotopes of alkali and alkaline earth metal ions. Jepson and De Witt [Jepson et al., 1976] attempted to separate $^{40}Ca^{2+}$ and $^{44}Ca^{2+}$ by the ion exchange reaction using dibenzo-18-crown-6 and dicyclohexyl-18-crown-6. In the liquid-liquid extraction of calcium chloride using chloroform or dichloroethane and dicyclohexyl-18-crown-6, the one step separation coefficient of the isotopes was 1.0010±0.0002 per 1 mass unit, which demonstrated that the enrichment of $^{44}Ca^{2+}$ isotope would be possible with this method. They also found that heavier calcium isotope, $^{44}Ca^{2+}$ was concentrated in the aqueous phase, while the lighter isotope $^{40}Ca^{2+}$ was concentrated into the organic phase [Hiraoka, 1982]. Konstantinov et al. [1965] investigated the separation of $^{24}Mg^{2+}$-$^{26}Mg^{2+}$ and $^{63}Cu^{2+}$-$^{65}Cu^{2+}$ isotope pairs in aqueous solutions of magnesium chloride and copper chloride using the method of countercurrent electromigration. Konstantinov et al. showed that, as the concentration of the magnesium chloride and copper chloride solutions increased, the relative difference in the mobilities of the isotope $^{24}Mg^{2+}$ and $^{26}Mg^{2+}$ ions and in the mobilities of the $^{63}Cu^{2+}$ and $^{65}Cu^{2+}$ ions increased, and concluded that, at the high concentrations, employed magnesium chloride and copper chloride may not be completely dissociated. Neu-

bert et al. [1961] also reported that the isotope enrichment of magnesium, calcium, strontium, and barium through the migration of ions in molten halides.

Aaltonen [1971] reported the separation of magnesium and calcium isotopes using a recycle ion exchange technique. He found that the separation factors of magnesium isotopes, $^{25}Mg^{2+}$-$^{26}Mg^{2+}$ and calcium isotopes, $^{40}Ca^{2+}$-$^{48}Ca^{2+}$ were 1.00016 and 1.00087, respectively. Ammonium lactate solution for magnesium and ammonium α-hydroxyisobutyrate solution for calcium were used as eluents. Nishizawa et al. [1996] obtained a separation factor of 1.0112 as a maximum value for the $^{24}Mg^{2+}$-$^{26}Mg^{2+}$ isotope pair by a liquid - liquid extraction system using the DC18C6. Nishizawa et al. [1996] reported that magnesium chloride was extracted into an organic phase including dicyclohexano-18-crown-6 (DC18C6), and showed that the partition coefficient had the largest value for liquid-liquid extraction system of 3.5 M $MgCl_2$ aqueous phase. They also found that the enrichment factors for a unit difference of mass numbers varied depending upon on the $MgCl_2$ concentration in the aqueous phase, and they obtained the isotope recognizing ability of DC18C6 was 1.0016, which is smaller than the separation factor due to an exchange of the aquua/dichloro complex formation constant of Mg^{2+}.

The production of isotopically pure ^{24}Mg is important because the magnesium-24 is a precursor of ^{22}Na through the nuclear reaction of $^{24}Mg(d, \alpha)$ ^{22}Na. The reaction product, ^{22}Na, is one of the rare β⁺ emitters and this isotope is used in various scientific fields as a source of annihilation radiation Nishizawa et al. [1996]. Recently, Kim et al. [2000] carried out an elution chromatographic separation of magnesium isotopes with N_3O_2 azacrown ion exchanger, and obtained the separation factors of 1.009 for the $^{25}Mg^{2+}$-$^{26}Mg^{2+}$ pair and 1.027 for the $^{24}Mg^{2+}$-$^{26}Mg^{2+}$ pair, respectively. They also

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found that the heavier isotopes were enriched in the resin phase, while the lighter isotopes were enriched in the solution phase. Ion exchange elution chromatography with macrocyclic compounds is a promising method for the separation of isotopes due to the ability of complexation with cations, especially, alkali and alkaline earth metal ions.

In this work, we have examined magnesium isotope separation using a novel 1-aza-12-crown-4 bonded Merrifield peptide resin by ion exchange elution chromatography.

EXPERIMENTAL

1. Materials and Methods

The novel 1-aza-12-crown-4 bonded Merrifield peptide resin was prepared by the method given in the literature [Bradshaw et al., 1993]. Synthetic route of the 1-aza-12-crown-4 bonded Merrifield peptide resin is shown in Scheme 1. Magnesium chloride and am-

Where R = $C_6H_5CH_2$
Yield : 60 %

H_2, Pd/C

Merrifield peptide resin
DMF, Triethylamine
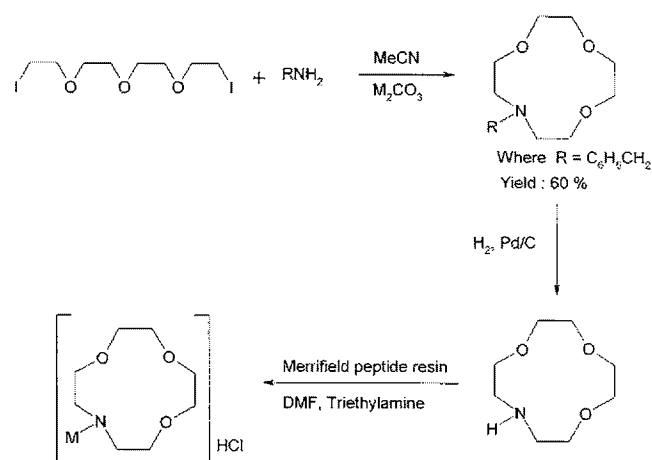
Scheme 1. Synthetic route of the 1-aza-12-crown-4 bonded Merrifield peptide resin.

monium chloride were purchased from Sigma Chemical Co., USA. An Atomic Absorption Spectrophotometer (Hitachi Z-8000) was used to determine the magnesium ion concentration in the solution. Magnesium isotope ratio was measured by using a Thermal Ionization Mass Spectrometer (Finnigan MAT 262) with a rhenium double filament. The amount of 1.0-2.0 μg magnesium with the MAT 262 was loaded on an evaporation filament. Ionization was then performed by passing a heating electric current through the ionization filament. After the ion beam intensities of $^{24}Mg^{2+}$, $^{25}Mg^{2+}$, and $^{26}Mg^{2+}$ became sufficiently high, the $^{24}Mg^{2+}$, $^{25}Mg^{2+}$, and $^{26}Mg^{2+}$ mass scanning was repeated several times in a block, and several blocks were recorded as one measurement. The mole fraction of $^{24}Mg^{2+}$, $^{25}Mg^{2+}$, and $^{26}Mg^{2+}$ of each feed solution was an average of three times in our measurement.

2. Ion Exchange Capacity

Ion exchange capacity was determined by the method given in the literature [Dorfner, 1991; Lee et al., 2001]. The 1-aza-12-crown-4 ion exchanger was transformed into the H-form by slow treatment with about 1.0 N HCl in the funnel. Subsequently, it 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. An exchanger sample of 1.0 g 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 were titrated with 0.1 N H_2SO_4 against phenolphthalein. The capacity was calculated by the formula:

$$Capacity(meq/g)$$
$$= \frac{\{(200 \cdot Normality_{NaOH}) - 4(ml_{acid} \cdot Normality_{acid})\}}{(Sample\ weight) \cdot (\%Solid/100)} \quad (1)$$

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 differences in equivalent weights of different ions would lead to errors, the standard sodium hydroxide solution was treated with 5% sodium chloride to obtain complete exchange equilibrium by the excess of sodium ions. A reproducibility of ±1% could consequently be obtained.

3. Measurement of Distribution Coefficient

The batch method was employed for the determination of the distribution coefficients [Dorfner, 1970]. Each portion of 1.0 g of the 1-aza-12-crown-4 bonded Merrifield peptide resin, 200-400 mesh, which had been dried to a constant weight at 60 °C, was weighed out and transferred into a 100 ml polyethylene vial with a polyethylene screw top. Then, 1.0 ml of 0.01 M $MgCl_2$ solution was added, followed by 49 ml of ammonium chloride solution of the desired concentration to give a final volume of 50 ml. The reaction mixture was subjected to reciprocal shaking at 100 strokes/min for 24 h, and then centrifuged for 5 min at 5,000 rpm. The concentration of magnesium ions in the supernatant was determined by using an AA-Spectrophotometer (Hitachi Z-8000). The distribution coefficient, K_d, was calculated by the following equation:

$$K_d = \frac{(C_{st} - C_{eq})}{C_{eq}} \cdot \frac{V}{m} \quad (2)$$

where C_{st} is the metal ion concentration of the standard solution, C_{eq} the metal ion concentration after equilibrium, V the total volume in ml of the solution, and m the mass in g of dry resin.

4. Separation of Magnesium Isotopes

The 1-aza-12-crown-4 bonded Merrifield peptide resin was slurried in ammonium chloride solution. The slurried resin was packed in a water-jacketed glass column of 35 cm long with inner diameter of 0.2 cm. The temperature was maintained at 20 °C with an Water Circulator (HAAKE A-80). Five hundred ppm of magnesium ion in distilled water was loaded on the top of the resin bed. The 2.5 M NH_4Cl solution (K_d=198) was used as an eluent. The magnesium feed solution was then passed through the column under gravity flow. The flow rate was controlled by a fine stopcock to be 0.5 ml/h. 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 1-aza-12-crown-4 bonded Merrifield peptide resin was 1.0 meq/g dry resin. This value is comparable to those of the DIAION SK 102 (cation exchanger, 0.60 meq/g) and DIAION SK 103 (cation exchanger, 0.9 meq/g) [Dorfner,
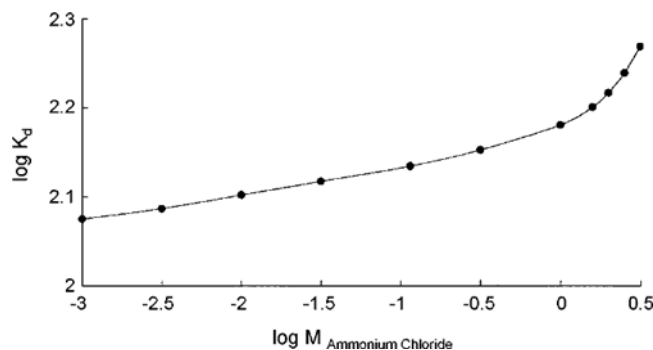
Fig. 1. Plot of log K_d for magnesium ions on the 1-aza-12-crown-4 bonded Merrifield peptide resin as a function of NH_4Cl solution concentration.

1970]. The distribution coefficients of magnesium ion on the resin were measured by changing the concentration of NH_4Cl solution from 1.0×10^{-3} to 6.0 M by using a batch method. The distribution coefficients were calculated with Eq. (2). As shown in Fig. 1, the distribution coefficients of magnesium ions on the 1-aza-12-crown-4 bonded Merrifield peptide resin increased in a non-linear manner with increasing concentration over a range from 1.0×10^{-3} to 6.0 M NH_4Cl solution. The elution time increased with increasing the distribution coefficient due to the high adsorption of ions on the resin phase in the column. For this reason, as expected, the eluents have the values of the distribution coefficients, ranging from 30 to 300, to separate isotopes in our laboratory. A 35 cm long ion exchange column was used to obtain a substantial total separation from which the single stage separation factor is calculated.

We obtained a chromatogram from column operation with 2.5 M NH_4Cl solution (K_d=198) at 20 °C as shown in Fig. 2. From the elution curve, the number of theoretical plates, N, in the column was calculated by the equation [Glueckauf, 1955]:

$$N = 8 \cdot \left(\frac{V_{max}}{\beta}\right)^2 \qquad (3)$$

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

From the elution curve and isotopic assay data, the single stage separation factors, $(^{24}Mg^{2+}/^{25}Mg^{2+})_{Resin}/(^{24}Mg^{2+}/^{25}Mg^{2+})_{Solution}, (^{24}Mg^{2+}/$

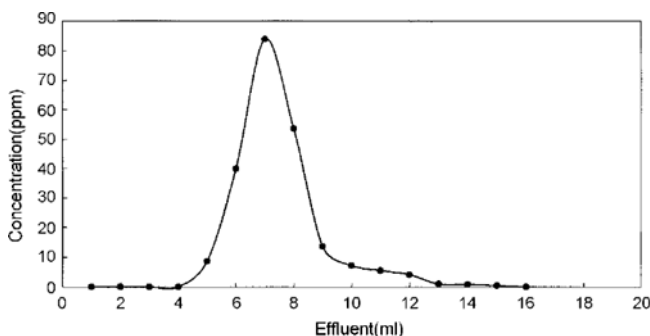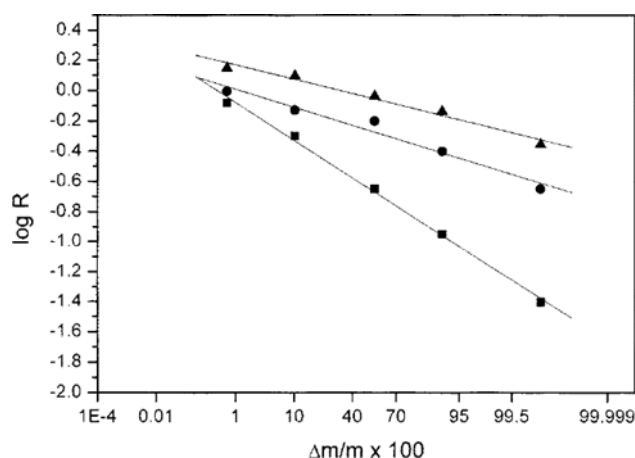**Fig. 2. Elution curve for magnesium isotope separation with 2.5 M NH_4Cl.**

Fig. 3. Separation of magnesium isotopes by cation exchange elution chromatography. ●; $^{24}Mg^{2+}$-$^{25}Mg^{2+}$, ■; $^{24}Mg^{2+}$-$^{26}Mg^{2+}$, ▲; $^{25}Mg^{2+}$-$^{26}Mg^{2+}$.

$^{26}Mg^{2+})_{Resin}/(^{24}Mg^{2+}/^{26}Mg^{2+})_{Solution}$, and $(^{25}Mg^{2+}/^{26}Mg^{2+})_{Resin}/(^{25}Mg^{2+}/^{26}Mg^{2+})_{Solution}$, were determined by the Glueckauf theory [1958]. The isotopic ratio of a fraction can be expressed by C_1/C_2, where C_1 and C_2 are the relative abundances of the light and heavy magnesium isotopes. The isotope ratio of the natural abundances is expressed by C_1^o/C_2^o, and the local enrichment factor for a fraction is given by $R=(C_1/C_2)(C_2^o/C_1^o)$. The 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 is $\varepsilon\sqrt{N}$, and separation factor is $1+\varepsilon$. The separation factor, α, was determined from the slope of the least squares line drawn through the points as shown in Fig. 3. In our experiment, the magnesium isotope separation factors for $^{24}Mg^{2+}$-$^{25}Mg^{2+}$, $^{24}Mg^{2+}$-$^{26}Mg^{2+}$, and $^{25}Mg^{2+}$-$^{26}Mg^{2+}$ were obtained as values of 1.012, 1.024 and 1.011, respectively. These values are larger than that of the factor determined by Aaltonen [1971]. Separation factors for our system were considerably greater, perhaps hundredfold more, than 1.00016 for the $^{25}Mg^{2+}$-$^{26}Mg^{2+}$ pair obtained by Aaltonen [1971]. Aaltonen [1971] carried out an elution chromatographic separation of magnesium isotopes with a strongly acidic cation exchanger, Dowex 50×8, and reported that the value of the separation factor for the $^{25}Mg^{2+}$-$^{26}Mg^{2+}$ pair was 1.00016. Nishizawa et al. [1996], reported the separation factor for the $^{24}Mg^{2+}$-$^{26}Mg^{2+}$ pair of 1.0112 as a maximum value in a liquid-liquid extraction system including the dicyclohexano-18-crown-6(DC18C6). Separation factor of 1.0112 obtained by Nishizawa et al. [1996] is same order of our results. Separation of isotopes of some divalent elements by ion exchange is shown in Table 1, and it was shown that, for the separation of isotopes, the magnesium isotope effect was about hundredfold larger than that achieved on Dowex ion exchangers. From the experimental data, it appears that the isotope exchange reaction can be represented by the following equations:
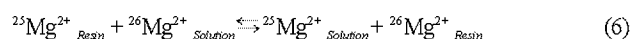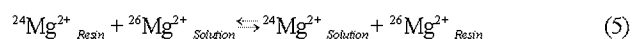
$$^{24}Mg^{2+}{}_{Resin} + {}^{25}Mg^{2+}{}_{Solution} \xrightarrow{\longleftarrow} {}^{24}Mg^{2+}{}_{Solution} + {}^{25}Mg^{2+}{}_{Resin} \qquad (4)$$

$$^{24}Mg^{2+}{}_{Resin} + {}^{26}Mg^{2+}{}_{Solution} \xrightarrow{\longleftarrow} {}^{24}Mg^{2+}{}_{Solution} + {}^{26}Mg^{2+}{}_{Resin} \qquad (5)$$

$$^{25}Mg^{2+}{}_{Resin} + {}^{26}Mg^{2+}{}_{Solution} \xrightarrow{\longleftarrow} {}^{25}Mg^{2+}{}_{Solution} + {}^{26}Mg^{2+}{}_{Resin} \qquad (6)$$
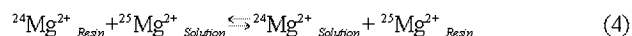
Table 1. Separation of isotopes of some divalent elements by cation exchange

Atomic number	Isotopic pair	Separation factor $(\alpha=1+\varepsilon)$	Enrichment factor$\times10^3$ $(\varepsilon=\alpha-1)$	$\varepsilon/\Delta m\times10^3$	Method	Reference
12	$^{25}Mg^{2+}$-$^{26}Mg^{2+}$	1.00016	0.16	0.16	Elution, Dowex50×8	Aaltonen, 1971
	$^{24}Mg^{2+}$-$^{26}Mg^{2+}$	1.0112	11.2	5.6	Extraction, DC18C6	Nishizawa et al., 1996
	$^{24}Mg^{2+}$-$^{25}Mg^{2+}$	1.012	12	12	Elution, Azacrown	This Work
	$^{24}Mg^{2+}$-$^{26}Mg^{2+}$	1.024	24	12	Elution, Azacrown	This Work
	$^{25}Mg^{2+}$-$^{26}Mg^{2+}$	1.011	11	11	Elution, Azacrown	This Work
20	$^{40}Ca^{2+}$-$^{44}Ca^{2+}$	1.00047	0.47	0.12	Elution, Dowex50×8	Aaltonen, 1971
	$^{40}Ca^{2+}$-$^{48}Ca^{2+}$	1.00087	0.87	0.11	Elution, Dowex50×8	Aaltonen, 1971
	$^{40}Ca^{2+}$-$^{47}Ca^{2+}$	1.00026	0.26	0.04	Elution, Dowex	Lee, 1976
	$^{40}Ca^{2+}$-$^{44}Ca^{2+}$	1.019	19	5	Elution, Dowex50×12	Heumann et al., 1972
	$^{40}Ca^{2+}$-$^{48}Ca^{2+}$	1.040	40	5	Elution, Dowex50×12	Heumann et al., 1972
38	$^{84}Sr^{2+}$-$^{88}Sr^{2+}$	1.0000036	0.0036	0.00090	Breakthrough Asahi LS-6	Oi et al., 1992
	$^{86}Sr^{2+}$-$^{88}Sr^{2+}$	1.0000023	0.0023	0.00115	Breakthrough Asahi LS-6	Oi et al., 1992
	$^{87}Sr^{2+}$-$^{88}Sr^{2+}$	1.00000097	0.00097	0.00097	Breakthrough Asahi LS-6	Oi et al., 1992
56	$^{130}Ba^{2+}$-$^{138}ba^{2+}$	1.000041	0.041	0.0052	Breakthrough Asahi LS-6	Kondoh et al., 1996
	$^{135}Ba^{2+}$-$^{138}ba^{2+}$	1.000016	0.016	0.0055	Breakthrough Asahi LS-6	Kondoh et al., 1996
	$^{137}Ba^{2+}$-$^{138}ba^{2+}$	1.0000053	0.0053	0.0053	Breakthrough Asahi LS-6	Kondoh et al., 1996

The subscripted symbols such as solution and resin refer to the solution and 1-aza-12-crown-4 bonded Merrifield peptide resin phases in this chemical isotope exchange. Eqs. (4), (5), and (6) stated that the heavier isotopes of magnesium were enriched in the resin phase, while the lighter isotopes were enriched in the solution phase. Aaltonen [1971] reported that the heavier isotopes of magnesium are enriched in the front parts of magnesium adsorption bands formed in chromatographic separation columns, packed with strongly acidic cation exchanger, Dowex 50×8, 400 mesh. Kondoh et al. [1996], Heumann et al. [1972], Oi et al. [1992], Ooi et al. [1999], Jepson et al. [1991], and Fujine et al. [1983], also reported that the heavier isotopes were preferentially concentrated into the solution phase of chromatography by using strongly acidic cation exchangers, anion exchanger, titanium phosphate exchangers, and polymer-bound crown ether. These results are in contrast with our work. On the other hand, Oi et al. [1991], Klinskii et al. [1974], Heumann et al. [1980], Aaltonen et al. [1974], and Lee [1976] reported that the heavier isotopes were enriched in the resin phase of cation and anion exchange chromatography.

Lee [1976] has shown that the metal ion species in the resin phase is less hydrated than the metal ion species in the solution phase. This contributes to a difference in bonding and subsequent enrichment of the lighter isotopes in the resin phase. These phenomena are in contrast with our system. The enrichment factor $(\varepsilon=\alpha-1)$ for isotopes separated by ion exchange or extraction chromatography depended upon the mass of the isotope as well as the difference in the masses of the isotope pairs [Lee, 1976]. It was shown in Table 1 that the separation factor decreased as the mass of the isotopes increased, and increased as the difference in the masses (Δm) of the isotope pairs increased [Kondoh, 1996; Lee, 1976]. Isotopes within approximately the same mass range may have an increase or decrease in factor due to ion complexation, but the mass effect is more significant [Lee, 1976] as shown in Table 1. The magnesium isotope separation system in our work, therefore, can be explained by

the fact that the hydration and complexation effects are less than the isotope mass effect.

CONCLUSIONS

Separation of magnesium isotopes was investigated by chemical ion exchange with the 1-aza-12-crown-4 bonded Merrifield peptide resin by using an elution chromatographic technique. The capacity of the novel monoazacrown ion exchanger was 1.0 meq/g dry resin. The heavier isotopes of magnesium were enriched in the resin phase, while the lighter isotopes were enriched in the solution phase. The single stage separation factor was determined according to the method of Glueckauf from the elution curve and isotopic assays. The separation factors of $^{24}Mg^{2+}$-$^{25}Mg^{2+}$, $^{24}Mg^{2+}$-$^{26}Mg^{2+}$, and $^{25}Mg^{2+}$-$^{26}Mg^{2+}$ were 1.012, 1.024, and 1.011, respectively.

ACKNOWLEDGEMENT

NOMENCLATURE

C_{eq} : metal ion concentration of the standard solution [mole/l]
C_{st} : metal ion concentration after equilibrium [mole/l]
K_d : distribution coefficient
M : mass of ion exchanger [g]
N : number of theoretical plated in the column
V : total volume of solution [ml]
V_{max} : peak elution volume [ml]

Greek Letters
α : separation factor $[1+\varepsilon]$

Δm   : isotope mass difference unit

ϵ/Δm : enrichment factor per mass unit

ϵ : enrichment factor $[\alpha-1]$

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