

164. Enrichment of Potassium Isotopes with Macrocylic Polyether Potassium Complexes

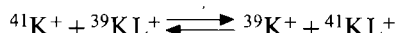
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Summary

Enrichment of the potassium isotopes is achieved by means of the chemical exchange reaction



where L represents a macrocylic polyether. Dicyclohexyl-18-crown-6 ((*cis-syn-cis*)-isomer) was investigated. The single stage-separation factor $\alpha = 1 + \varepsilon$ was determined according to the method of *Glueckauf* from the elution curve and isotopic assays. One obtains ε -values of 1.18, 0.84, and 0.74×10^{-3} ($\pm 5 \times 10^{-5}$) at -10 , 0 , and 10° respectively, in favor of the heavy isotope, indicating an enthalpy of isotopic exchange of -13 ± 4 Joule mol^{-1} .

The technical feasibility of a pre-enrichment process for ^{40}K starting with basic laboratory data is discussed.

1. Introduction and motivation. – The enrichment of the rare middle isotope ^{40}K among the K-isotopes (^{39}K 93.1%, ^{40}K 0.0117%, ^{41}K 6.88%) has remained a methodological challenge. Even preparative mass-spectroscopy has only produced minute samples of concentrations of up to 60% ^{40}K which were very expensive²⁾. Important applications of this isotope exist and others would become feasible if availability would increase. For example, the (^{40}K - ^{40}Ar)-scheme in geo-chronology uses ^{40}K as spike for the mass-spectrometric isotope-dilution assay of K in mineral fractions [1]. Precise ultramicro-analysis ($\pm 1\%$ in the range 10^{-6} to 10^{-12} g) of K is used frequently in biology where it is essential to measure K^+ -concentrations in single cells or cell-organelles like axons, membranes, and mitochondria [2].

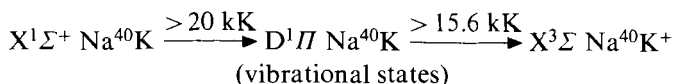
One of the well-known difficulties of K-isotope separation is the non-existence of molecular compounds which can be easily handled. Most attempts consider, therefore, the isotope effect in the spectral transitions of the atoms. One of the causes for this effect is the finite kinetic energy of the nucleus which gives slightly

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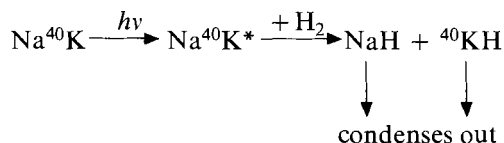
²⁾ Oak Ridge National Laboratory, now abandoned.

different electronic term energies for the different isotopic masses. It is on the order of 0.008 cm^{-1} for ^{39}K - ^{41}K . A second cause is the 'nuclear-volume' effect which includes the effect of nuclear size and shape on the ns-terms (mainly). It is below 10^{-3} cm^{-1} . Both effects together are minimal between $30 < M < 50$. Only very elaborate laser experiments in a *Doppler*-free arrangement can hope to make use of the atomic isotope effects. *Letokhov*³⁾ envisages a two-photon excitation to an atomic state high enough to be reactive in a scavenging reaction, e.g. hydride formation.

The isotopic vibrational energy differences in diatomic molecules are much larger, however. We have recently observed vibrational isotope effects from 10 to several 100 in the two-photon ionization efficiency between $^{39}\text{K}_2$, $^{39}\text{K}^{41}\text{K}$, and Na^{39}K , Na^{41}K via autoionizing *Rydberg* states in certain spectral regions [3]. We expect about half as high an effect in the respective ^{40}K -compounds. Na^{40}K would be the best suited molecule for a process utilizing this effect. It can be selectively ionized



and scavenged e.g. by an electric field or selectively excited to a neutral state and trapped by a chemical reaction, e.g.



This reaction does not proceed in dilute gas-phase without previous electronic excitation.

Isotope-discriminating photo-excitation or -ionization requires a collision-free time-interval between excitation and trapping events. This needs a low-pressure environment, typically below 0.1 Torr or molecular beam conditions. With only 117 ppm of ^{40}K present, one is confronted with handling, evaporating, trapping, and pumping of many kg of K (and Na). Hence, an efficient pre-enriching process, between 10 and 100 times the natural abundance, is mandatory for this endeavour.

For the realization of small enrichments in large quantities of K, statistical separation processes at or near ambient temperature have a high efficiency. Diffusion, thermal diffusion in gaseous K, or even multistage distillation of liquid K are such processes. For a university laboratory it is certainly not simple to solve the pertinent engineering problems. We therefore chose an isotope-exchange reaction in water solution between hydrated K-isotopes and their crown-ether complexes. The exchange medium is a cation-exchange resin. The two 'states' of K^+ , K_{res}^+ and

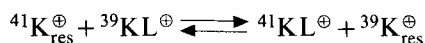
³⁾ Personal communication, Jan. 1982.

K^+ (crown-ether), are chemically not very different with the K^+ being bonded to about the same number of O-ligands with similar bond energies and vibrational (K–O)-frequencies in both cases. Small zero-point energy differences have their origin mainly in second neighbour O-atom interactions which perturb the (K–O)-vibrations slightly. Only small changes of the exchange equilibrium constant on the order of 10^{-3} are expected, similar to the findings with $^{40}Ca/^{48}Ca$ [4].

2. Choice of ligand. – Macrocycles such as crown ethers [5] and cryptates [6] have received considerable attention in recent years due to their unusual complexing properties which depend directly upon the size of their internal cavity [7]. Based on high selectivity for otherwise similar metal ions, the crown ethers were introduced into isotope-enrichment processes as promising complexing agents. This produces enhanced isotope effects [8] compared to other exchange processes.

X-ray data [9] show that among the 'crown' compounds the cavity size (2.6 to 3.2 \AA^4) of the 18-crown set of ligands fits best for incorporating the K^+ -ions (2.66 \AA^5).

The crown ether chosen in this study was the (*cis-syn-cis*)-isomer of dicyclohexyl-18-crown-6 named isomer A [5]. The mixture of both isomers A and B, the latter being *cis-anti-cis*, is commercially available at modest costs and methods of purification, and studies concerning its complexing properties have been well-specified for alkali metals in several solvents [10]. The operative separation process uses the ion-exchange equilibrium



where L is the macrocyclic polyether and K_{res}^{\oplus} indicates species in the resin phase.

3. Experimental. – *Reagents.* All acid solutions were prepared from *Suprapur* chemicals (*Merck*) dissolved in bidistilled water. The methanol was of HPLC.-grade. Dicyclohexyl-18-crown-6 (technical grade) was purchased from *Fluka*.

Separation of isomers. The isomers A and B were separated [11] by column chromatography using neutral Al_2O_3 (*Brockman*, activity grade I) and hexane/diethyl ether 1:1. Isomer B was stripped with CH_3OH . The product, isomer A (yield: 25%), was recrystallized from hexane or diethyl ether and its purity was checked by m.p. and 1H - and ^{13}C -NMR. spectra.

Column material and performance. The column was a *Pyrex* tube 1 cm in diameter and 45 cm in length. It was thermostated using a column jacket and a constant-temperature circulator filled with an (ethanol/water)-mixture. The end-fittings contained a 46μ frit. The resin used was the commercial 200–400 mesh *Dowex 50 W*, 8% cross-linked cation exchanger. It has an exchange capacity of 1.9 m-equiv. for protons per ml. The slurry packing was made up to a final bed-length of 43 cm.

Before each experiment the resin was conditioned by washing with 7M HCl, rinsing with water followed by CH_3OH , and then allowed to stand in the desired CH_3OH/H_2O mixture. A narrow band of K_{res}^{\oplus} was added to the top of the column and then eluted with 1M HNO_3 and 0.01M crown ether in CH_3OH/H_2O 4:1. The flow-rate was approximately 0.5 ml/min and maintained constant by pumping the eluents with an adjustable minipump. The effluent containing the complexed K was collected dropwise in polyethylene tubes by an automatic sampling device. Individual fractions of the K-elution band were selected for MS. analysis.

Measurements. The K^+ -content of each fraction was determined by flame atomic absorption spectrometry at a wavelength of 755.5 nm (*Beckman*, type 1248). The MS. work was performed on a

4) Smaller size from *Corey-Pauling-Koltun*, larger from *Fischer-Hirschfelder-Taylor* atomic models.

5) Crystal diameter. Of course, the coordination radius should be included for a precise discussion.

Varian MAT CH4. The preliminary treatment of the fractions consisted in destruction of the organic matter with H_2SO_4 and subsequent conversion to K_2SO_4 in a Pt-crucible. A drop of the extracted K_2SO_4 -solution was placed onto one ribbon (Re-filament) of a two-ribbon surface-ionization source. After evaporation of the solvent and a short flash to dull red heat in air, the ($^{39}\text{K}/^{41}\text{K}$)-ratios were determined. The standard deviation of the average values in the relative measurements of $^{39}\text{K}/^{41}\text{K}$ was in the range of ± 0.4 to 0.6% .

Evaluations. An elution curve was obtained by plotting the concentration of K in the samples vs. the sample number or elution volume. From the elution curve the number of theoretical plates was computed [12].

The separation factor a (defined as the ratio of the light to heavy isotope in the solution phase divided by the ratio of the light to heavy isotope in the resin phase) was determined from the slope of a least-squares line drawn through the points using the equation of *Glueckauf*

$$\ln R = -N\varepsilon \frac{\bar{v} - v}{\sqrt{\bar{v}v}}$$

In the above equation R is the local isotopic enrichment at point v of the elution curve, N is the theoretical plate number, $\varepsilon = a - 1$, and \bar{v} is the maximum of the elution curve.

4. Results and discussion. – *Figur 1* shows the bell-shaped elution curve for the K-isotopes taken at a temperature of 0° in a typical run. The elution curve for other runs and under different conditions did not differ markedly from that shown. Those taken at -10° exhibited a longer tail, and those at room temperature showed an asymmetric profile indicating that the rate of exchange is slow. From the elution curve the number of theoretical plates was determined by standard methods [12].

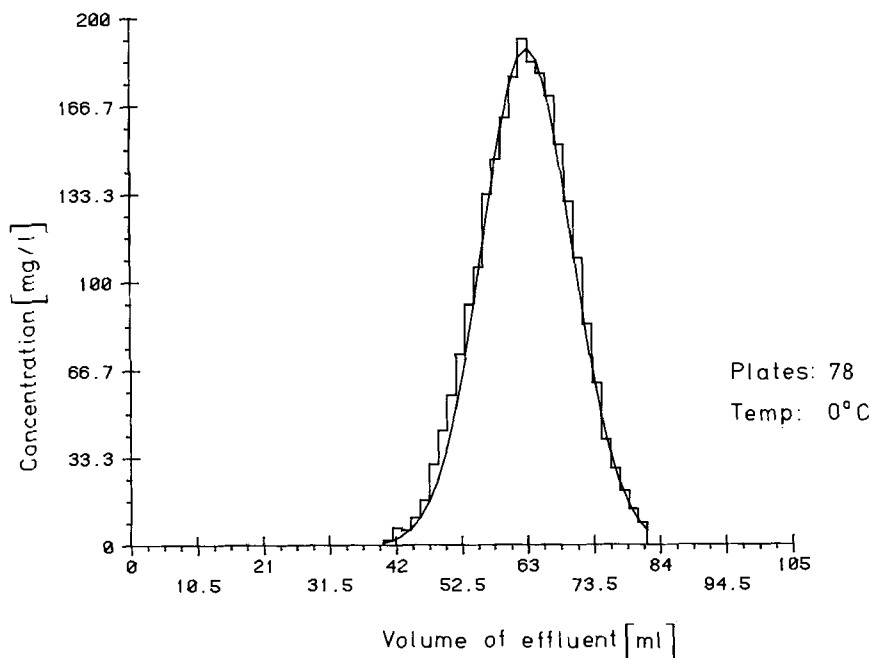


Fig. 1. *K*-elution curve at 0° (the histogram plot represents the measured values, overlaid with a fitted *Gaussian* profile)

This treatment gave a value of approximately 2 plates per cm, far less than expected from the resin-bead size in a diffusion-rate-limited process. The *Table* summarizes the main results of the present work. It represents the basic data sheet for a process designer.

Table. Data from three series of experiments (α = Isotope-exchange equilibrium constant $\epsilon = \alpha - 1$; $\Delta m = 2$ atomic mass units; C.I. = Confidence interval. System: crown ether; support: Dowex X8-200/400; plates/cm: approximately 2; flow rate: 0.5 ml/min)

T [°C]	$\epsilon/\Delta m \cdot 10^4$ (95% C.I.)	α ($^{39}\text{K}/^{41}\text{K}$) (95% C.I.)
-10	5.9 ± 0.5	1.00118 ± 0.0001
0	4.2 ± 0.2	1.00084 ± 0.00005
10	3.7 ± 0.2	1.00074 ± 0.00005

As expected, the single-stage factors are larger at lower temperatures. An enrichment plot for the isotopic exchange at 0° is shown in *Figur 2*. A large mass fractionation of the K-isotopes developed between the front and tail of the elution curve, whereas central fractions emerge essentially unchanged in isotopic composition. The direction of the isotope effect is the same as found in other systems [13]. The light isotope is preferentially retained by the resin, with maximal variations in $^{39}\text{K}/^{41}\text{K}$ between the leading and trailing fractions of up to 6.9% (for $T = -10^\circ$). The flow rate and particle size have not been optimized during this study. The temperature dependence ($\log K_c$ vs. $1/T$) of the isotopic-exchange equilibrium yields an enthalpy of exchange of $-13 \pm (4)$ Joule mol^{-1} .

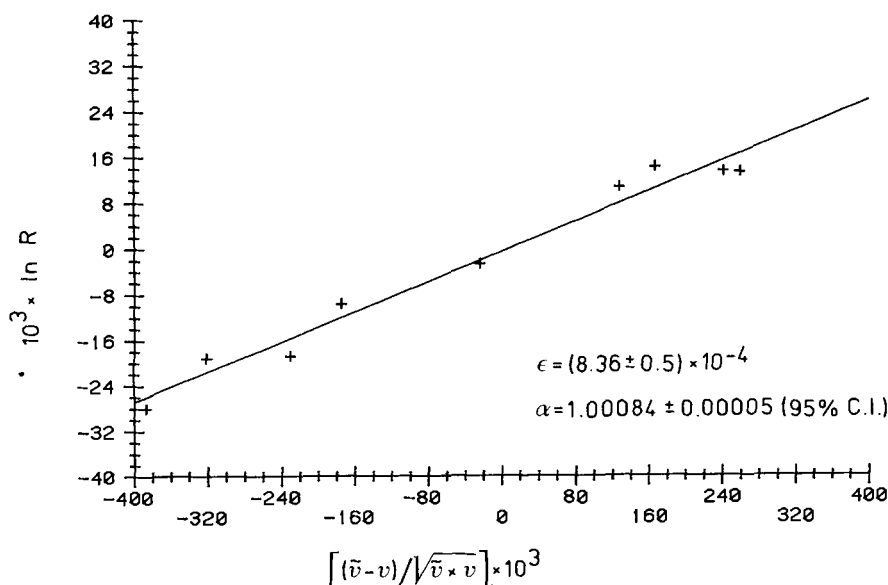


Fig. 2. Enrichment of ^{39}K relative to ^{41}K at 0° by ion-exchange chromatography (the ordinate $10^3 \times \ln R$ corresponds to $R = [(^{39}\text{K}/^{41}\text{K}) / (^{39}\text{K}_0/^{41}\text{K}_0)]$)

Application and technical feasibility of an enrichment for ^{40}K . A desirable first separation stage should increase the ^{40}K from 117 ppm to between 0.1 to 1%. With a good approximation the observed single-stage factor of 1.00118 for $^{39}\text{K}/^{41}\text{K}$ will be halved for $^{39}\text{K}/^{40}\text{K}$ and $^{40}\text{K}/^{41}\text{K}$. This requires a minimum of 4000 plates resulting in a column length of approximately 20 m, assuming 5 mm as the height equivalent to a theoretical plate and total reflux.

Tradition in ion-exchange separation processes [14] would suggest using several smaller columns in a cascade arrangement with the possibility of regenerating one set of the columns while the K-band is moving in the other half. A complete phase transfer from complex to K^+ -solution is necessary between the two sets. This will preserve the ligand for the next cycle.

We do not intend to present a flow-diagram for such a separation scheme at this stage. However, it is important to point out that ion-exchange techniques with complex formation as the discriminating reaction have never been applied to a rare middle isotope such as ^{40}K . It has been known for many years that it is not feasible to obtain higher concentrations of this product by withdrawal of a (1:1)-mixture of the two flanking isotopes while working near total reflux. In the present case this would lead to a maximum enrichment of a factor of 2 according to the relationship [15]:

$$\gamma_{2\max} = \frac{\gamma_2}{\gamma_1 \left(\frac{f_{32}\gamma_3}{f_{21}\gamma_1} \right) f_{21}/f_{31} + \gamma_3 \left(\frac{f_{21}\gamma_1}{f_{32}\gamma_3} \right) f_{32}/f_{31} + \gamma_2}$$

indices: 1: ^{39}K ; 2: ^{40}K ; 3: ^{41}K

γ_i initial concentration of the component i

f_{ik} single-stage separation factors between the components i and k

Assuming $f_{21} = f_{32} = \frac{1}{2} f_{31}$, $\gamma_{2(\max)} = 231$ ppm

Higher enrichments are easily possible if the withdrawal of the product is carefully adjusted to the total material circulation in the counter-current mode of the band-movement. The best point to harvest the product is still near the location of the (1:1)-mixture of $^{39}\text{K}/^{41}\text{K}$, but the milking rate should be near but below the maximum transport capacity of ^{40}K to this location. An extensive theoretical treatment of this case will be published elsewhere.

5. Conclusions. – The enrichment factor per unit mass is found to be 3 to 4 times larger with macrocyclic ligands compared to some of the recently reported systems with other ligands [13]. Assuming a negligible entropy of isotope exchange, the measured enthalpy of -13 ± 4 Joule mol^{-1} leads to an estimated frequency difference of the relevant vibrational modes of 2 cm^{-1} . The isotope effect of $\varepsilon = 1.18 \times 10^{-3}$ at -10° is still very small for a preparative isotope separation of K-isotopes.

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REFERENCES

- [1] *E. Jäger & J. C. Hunziker*, in: *Lectures in Isotope Geology*, Springer-Verlag, Heidelberg 1981.
- [2] *P. Karlson*, *Lehrbuch der Biochemie*, 11. Aufl., p. 396ff., Georg-Thieme-Verlag, Stuttgart 1980.
- [3] *S. Leutwyler, A. Herrmann, L. Wöste & E. Schumacher*, *Chem. Phys.* **48**, 253 (1980).
- [4] *K. G. Heumann & H. P. Schiefer*, *Angew. Chem.* **92**, 406 (1980).
- [5] *C. J. Pedersen*, *J. Am. Chem. Soc.* **89**, 7017 (1967).
- [6] *B. Dietrich, J. M. Lehn & J. P. Sauvage*, *Tetrahedron Lett.* **1969**, 2885.
- [7] *J. J. Christensen, D. H. Eathough & R. M. Izatt*, *Chem. Rev.* **74**, 351 (1974).
- [8] *B. E. Jepson & R. DeWitt*, *J. Inorg. Nucl. Chem.* **38**, 1175 (1976).
- [9] *M. R. Truter*, *Struct. Bond.* **16**, 71 (1973).
- [10] *H. K. Frensdorff*, *J. Am. Chem. Soc.* **93**, 600 (1971); *R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet & J. J. Christensen*, *ibid.* **98**, 7620 (1976); *W. H. Delphin & E. P. Horwitz*, *Anal. Chem.* **50**, 843 (1978).
- [11] *R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore & J. J. Christensen*, *J. Am. Chem. Soc.* **93**, 1619 (1971).
- [12] *E. Glueckauf*, *Trans. Faraday Soc.* **54**, 1203 (1958).
- [13] *R. H. Betts, H. E. Harris & M. D. Stevenson*, *Can. J. Chem.* **34**, 65 (1956); *J. Aaltonen*, *Suom. Kemistil.* **B44**, 1 (1971); *G. D. Klinski, D. A. Knyazev & G. I. Vlasova*, *Russ. J. Phys. Chem.* **48**, 380 (1974); *E. P. Horwitz, W. H. Delphin, C. A. A. Bloomquist & G. F. Vandegrift*, *J. Chromatogr.* **125**, 203 (1976).
- [14] *Proc. Intern. Symp. of Isotope Separation*, North Holland Publishing Company, Amsterdam 1958.
- [15] *E. Schumacher*, *Helv. Chim. Acta* **36**, 949 (1953).