

CHROM. 15,398

FACTORS AFFECTING SINGLE-STAGE SEPARATION COEFFICIENTS AND PROFILE OF THE CHROMATOGRAM IN URANIUM ISOTOPE ENRICHMENT BY CATION-EXCHANGE CHROMATOGRAPHY USING URANYL-CARBOXYLATE COMPLEXES

ATSUSHI NAKAGAWA, YOICHI SAKUMA and MAKOTO OKAMOTO*

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152 (Japan)

and

MASUNOBU MAEDA

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466 (Japan)

(Received September 27th, 1982)

SUMMARY

Cation-exchange chromatography was carried out at 25 and 60°C on the four systems of uranyl-tartrate, -citrate, -tricarballoylate and -phthalate. In each instance, the single-stage separation coefficient, ϵ , and the slope coefficient, k , which is one of the important factors determining the isotopic fraction profile of the isotope-enriched and -depleted zones of the chromatogram, were evaluated, and the influence of several experimental parameters on the ϵ and k values is discussed. The potential use of a large-scale enrichment process in ion-exchange chromatography is considered on the basis of the results.

INTRODUCTION

From the standpoint of a large-scale enrichment process for uranium isotopes using ion-exchange chromatography, some of the factors to be considered when choosing the most suitable system may be that (a) the single-stage separation coefficient, ϵ , should be large, (b) the isotopic fraction profiles of the isotope-enriched and -depleted zones in the chromatogram should be sharp and narrow and (c) the concentrations of the uranium isotopes in the enriched and depleted zones should be large.

In this investigation, we examined several experimental conditions such as the type of ligand, eluent concentration, displacement length and temperature that meet the above requirements in uranyl-carboxylate systems, in which the carboxylates were tartrate, citrate, carballylate and phthalate.

In a previous paper¹, it was reported that the ϵ values calculated in the cation-exchange chromatography of uranyl-acetate, -tartrate and -citrate complexes decreased in the order citrate > tartrate > acetate. In this work, the ϵ values for

carballylate and phthalate systems in addition to those for the tartrate and citrate systems were determined under experimental conditions different to those used in the previous work. In order to discuss requirement (b) above, the slope coefficient, k , which is one of the important factors determining the isotopic fraction profiles of enriched and depleted zones, was evaluated under different experimental conditions for each system. For requirement (c), if the eluent concentration is increased, the concentrations of uranium isotopes in the chromatogram would increase, but few data have been obtained to establish the influence of the eluent concentration on the ϵ and k values.

The potential use of a large-scale enrichment operation in the ion-exchange chromatography of uranium isotopes was considered by use of the data obtained in this study.

EXPERIMENTAL

Reagents

The ion-exchange resin used was LS-6 strongly acidic cation-exchange resin (100–200 mesh, degree of cross-linking 15%, highly porous type) supplied by Asahi Chemical Industry. Uranyl nitrate solution was prepared by dissolving U_3O_8 in concentrated nitric acid and recrystallizing the uranyl nitrate from solution. Uranyl nitrate stock solution was prepared by dissolving the salt in redistilled water. All other reagents were of analytical-reagent grade.

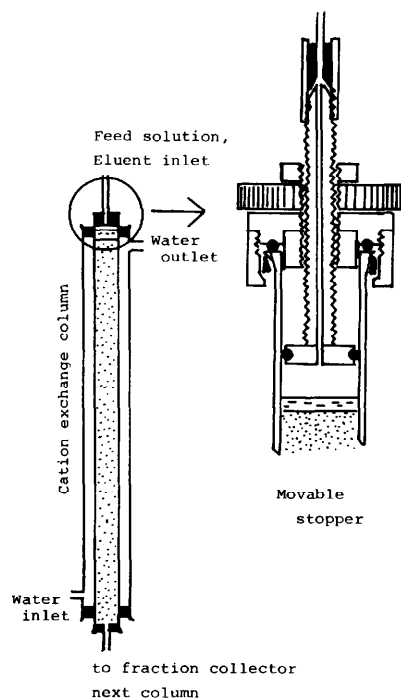


Fig. 1. Column and movable stopper.

Columns

The column (210 × 1 cm I.D.) was made of pressure-resistant Pyrex glass, surrounded by a jacket through which thermostated water was circulated. Movable stoppers were attached at the tops of columns to regulate the liquid level above the resin bed. The column and its stopper are illustrated in Fig. 1. For long-distance migration three columns were connected in series by PTFE tubes of 1 mm I.D.

Chromatographic procedures

The cation-exchange resin was packed in the column and pre-treated with 2 mol/dm³ sulphuric acid to convert the resin completely into the H⁺ form, and then washed thoroughly with distilled water. The column (the first column in long-distance chromatography) was then loaded with a measured volume of 0.02 mol/dm³ uranyl nitrate solution to form a uranyl band of suitable length. The eluent solution was then introduced into the top of the column at a constant flow-rate using a peristaltic pump. The eluate was collected in fractions and for each fraction the pH, uranium content and uranium isotopic ratio were determined with a pH meter (TDA Electronic Model HM-513), by spectrophotometric measurements on a JASCO Uvidec 405 spectrophotometer and by mass spectrometric analysis on a Varian-MATCH-5 mass spectrometer, respectively. As organic "impurities" for mass spectrometric analysis was present in the fractions, they were pre-treated as follows for the quantitative and isotopic analyses of uranium. A measured portion of the fraction was placed in a porcelain crucible and concentrated nitric acid was added. The solution was evaporated to dryness on a hot-plate, then the uranyl sample was heated in a muffle furnace to convert it into U₃O₈. The solid U₃O₈ was dissolved in concentrated nitric acid and the resulting uranyl nitrate solution was evaporated to dryness on a hot-plate. The uranyl nitrate salt was ignited at ca. 1000°C in an electric oven to convert it completely into U₃O₈. The U₃O₈ thus prepared was again dissolved in concentrated nitric acid, then the salt solution was evaporated to dryness on a hot-plate, leaving solid uranyl nitrate. The solid salt was dissolved in redistilled water to give a sample solution for spectrophotometric and mass spectrometric analyses.

Calculation of single-stage separation coefficient, ϵ , and slope coefficient, k

Single-stage separation coefficient, ϵ . The isotope effect, evaluated as the single-stage separation coefficient, ϵ , is defined by the equation

$$\epsilon = \frac{[\overline{^{235}\text{U}}] [^{238}\text{U}]}{[^{235}\text{U}] [\overline{^{238}\text{U}}]} - 1 \quad (1)$$

The ϵ value defined by eqn. 1 can be determined from chromatographic data by means of the equation

$$\epsilon = \frac{\sum f_i (R_i - R_0)}{Q \cdot R_0 (1 - R_0)} \quad (2)$$

The larger the deviation of the ϵ value from zero, the greater is the isotope effect.

Slope coefficient, k . According to the theory of chromatographic separation of

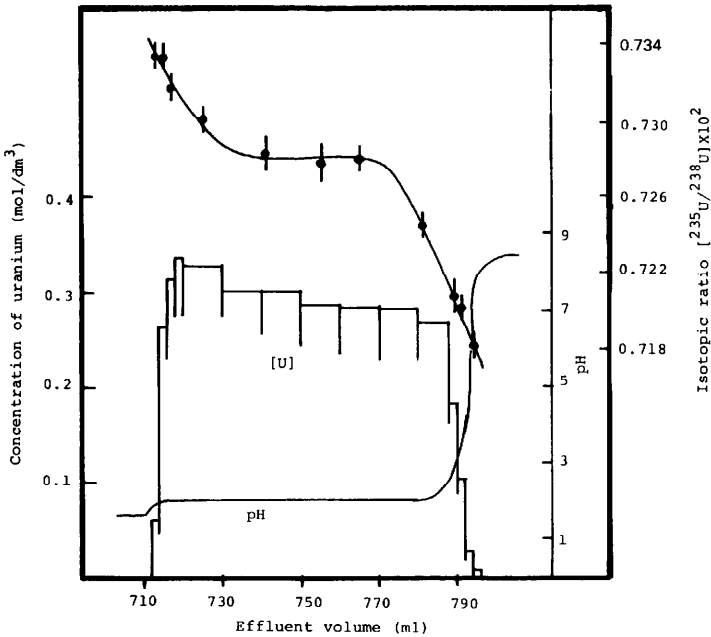


Fig. 2. Elution graph, pH and isotopic ratio for run 1. Eluent, $0.3 \text{ mol/dm}^3 (\text{NH}_4)_2\text{Tart.}$; temperature, 25°C ; displacement length, 398 cm; pH of eluent, 8.5.

isotopes presented by Kakihana and co-workers²⁻⁵, the isotopic fraction profile of, say, the isotopically enriched zone in the band displacement chromatogram, $R(x,t)$, can be expressed by the equation

$$R(x,t) - R_0 = A'(t)\{\exp[k(x - x_p)] - 1\} \quad (3)$$

Differentiation of eqn. 3 against x leads to

$$\Delta R(x,t)/\Delta x = k[R(x,t) - R_0 + A'(t)] \quad (4)$$

The k value can be determined by plotting $\Delta R(x,t)/\Delta x$ against $R(x,t)$, using the chromatographic data.

With increasing k , the isotopic fraction profile of the isotope enrichment zone shows a sharp increase, and thus the width of the enrichment zone diminishes and the degree of accumulation of ^{235}U at the front part of the zone increases. In addition, when the enrichment zone is narrow, one can form a narrow band of the isotope mixture in the column, and hence increase the degree of the utilization of the column.

RESULTS

The chromatograms, pH variation and isotopic ratios for some typical runs are illustrated in Figs. 2-6. Satisfactory displacement chromatograms were obtained for all the runs except run 8 (Fig. 5), where the isotopic plateau region between the front and rear sections of the chromatogram was not maintained horizontal. It can be

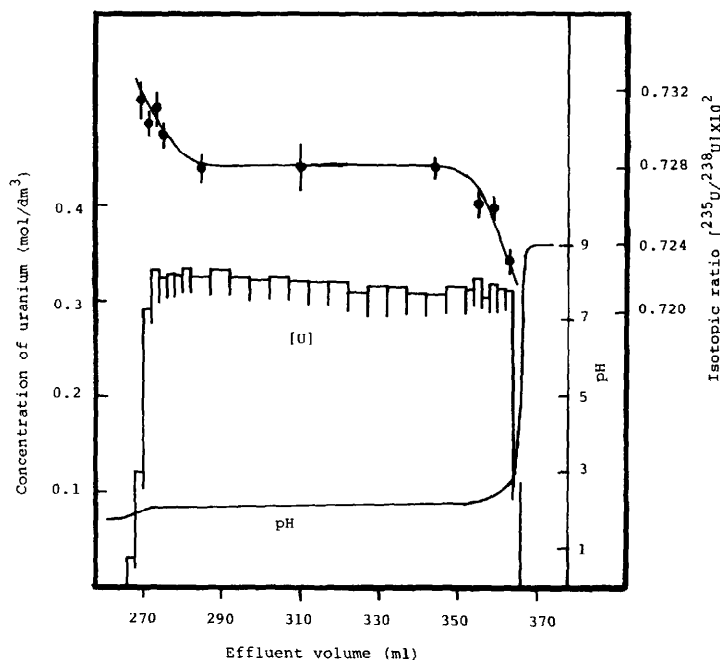


Fig. 3. Elution graph, pH and isotopic ratio for run 2. Eluent, 0.3 mol/dm³ (NH₄)₂Tart.; temperature, 60°C; displacement length, 188 cm; pH of eluent, 9.0.

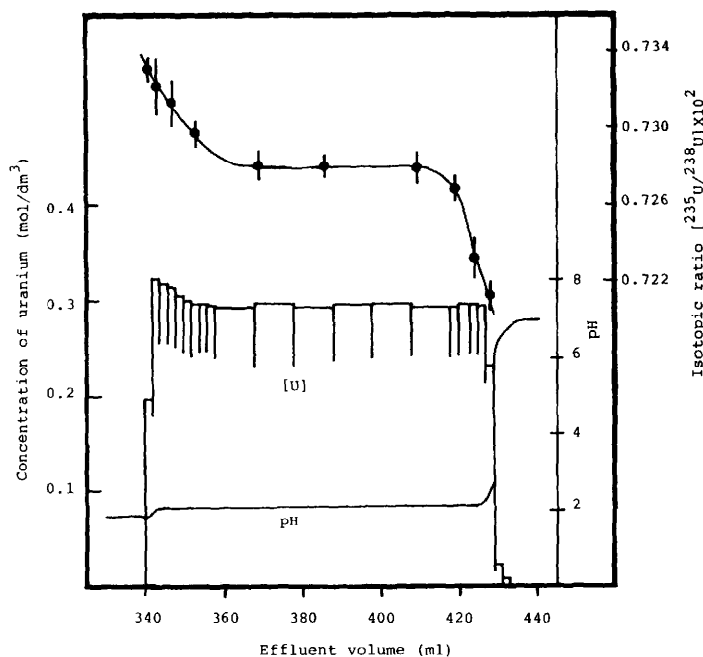


Fig. 4. Elution graph, pH and isotopic ratio for run 7. Eluent, 0.2 mol/dm³ (NH₄)₃Cit.; temperature, 60°C; displacement length, 200 cm; pH of eluent, 7.0.

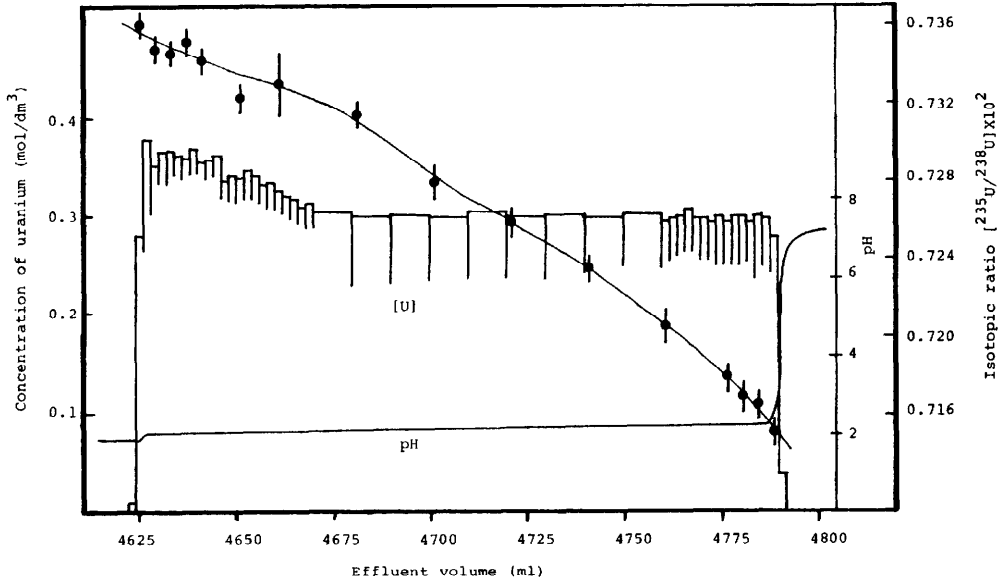


Fig. 5. Elution graph, pH and isotopic ratio for run 8. Eluent, 0.2 mol/dm³ (NH₄)₃Cit.; temperature, 25°C; displacement length, 2131 cm; pH of eluent, 7.2.

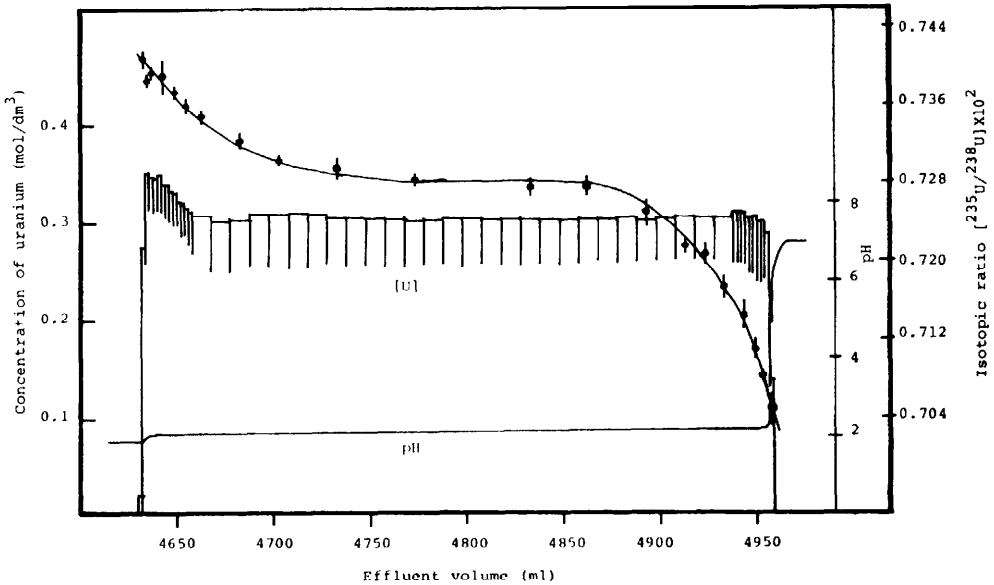


Fig. 6. Elution graph, pH and isotopic ratio for run 9. Eluent, 0.2 mol/dm³ (NH₄)₃Cit.; temperature, 60°C; displacement length, 2173 cm; pH of eluent, 7.0.

clearly seen in each instance that ^{235}U is enriched at the frontal boundaries of the chromatograms, whereas ^{238}U is enriched at the rear.

The experimental conditions and the ϵ and k values calculated according to eqns. 2 and 4, respectively, based on the chromatographic results are collected in Table I. The ϵ and k values were calculated by use of the data for the isotope enrichment zones (front parts of the chromatograms).

DISCUSSION

The influence of the experimental conditions on the ϵ and k values was examined, and the potential use of a large-scale enrichment process in ion-exchange chromatography, is considered below.

Influence of ligands on ϵ and k values

The results in Table I indicate, although not conclusively, because the experimental conditions differed from run to run, that ϵ decreases in the order citrate > tartrate > phthalate > acetate¹ > tricarallylate, whereas the k value is little affected by the ligand, having a value of about 0.3 except for 0.72 for the tricarallylate system. This means that of the systems studied the citrate system may be the most suitable for the enrichment of uranium isotopes by the cation-exchange chromatography of uranyl complexes.

Influence of eluent concentration on ϵ and k values

This was examined with ammonium citrate as the eluent. The eluent concentration was varied over the range 0.1–0.6 mol/dm³, while other parameters such as temperature (25°C) and migration length (*ca.* 2 m) were kept constant. The ϵ and k values obtained in this work and reported in a previous paper¹ are compared in Table II. It is obvious that the ϵ value decreases as the eluent concentration increases and thus the uranyl citrate concentration in the external solution increases. On the other hand, the k value has a slight tendency to increase with increasing eluent concentration.

As reported in a previous paper⁶, the ϵ value in ion-exchange chromatography involving the formation of uranyl acetate complexes was evaluated as a function of the uranyl acetate concentration in the external solution according to the two-phase distribution theory⁷ by use of the data for the compositions and concentrations of uranyl acetate species in the resin phase measured by equilibrium experiments and for the reduced partition function ratios for uranyl acetate species in solution obtained by the analysis of Raman spectroscopic data. It was found that the ϵ value decreases with increase in the uranyl acetate concentration in the external solution. This was attributed to the reduction of the ideal ion-exchange behaviour because of the increase in the concentrations of uranyl acetate species in the external solution, *i.e.*, the concentration of the uncharged uranyl acetate species $\text{UO}_2(\text{CH}_3\text{COO})_2$ increased in the resin phase with increase in the uranyl acetate concentration in the external solution, which led to the decrease in the ϵ value. The decrease in the ϵ value in the present uranyl citrate system may also be ascribed to the reduction of the ideal ion-exchange behaviour because of the increase in the uranyl citrate concentration in the external solution. In order to permit a quantitative discussion on this phenomenon, the com-

TABLE I
EXPERIMENTAL CONDITIONS AND ϵ AND k VALUES

Run No.	Eluent*	Concentration of eluent (mol/dm ³)	pH	Temperature (°C)	Displacement length (cm)	Flow rate (ml/h)	Band velocity (cm/h)	$\epsilon \times 10^4$	k (cm ⁻¹)	Remarks
1	(NH ₄) ₂ Tart.	0.3	8.5	25	398	5.1	2.5	1.2	0.21	Fig. 2
2	(NH ₄) ₂ Tart.	0.3	9.0	60	188	4.8	2.4	1.2	0.26	Fig. 3
3	(NH ₄) ₂ Tart.	0.3	5.0	60	186	4.6	2.3	1.2	0.23	
4	(NH ₄) ₃ Cit.	0.1	7.2	25	183	7.3	2.0	1.8	0.24	
5	(NH ₄) ₃ Cit.	0.4	7.2	25	199	3.1	2.1	1.4	0.27	
6	(NH ₄) ₃ Cit.	0.6	7.2	25	200	2.2	2.2	1.1	0.28	
7	(NH ₄) ₃ Cit.	0.2	7.0	60	200	4.5	2.1	1.8	0.22	Fig. 4
8	(NH ₄) ₃ Cit.	0.2	7.2	25	2131	4.4	1.9	1.6		Fig. 5
9	(NH ₄) ₃ Cit.	0.2	7.0	60	2173	4.3	1.9	1.8	0.061	Fig. 6
10	(NH ₄) ₃ Tri.	0.1	4.0	25	198	9.4	1.9	0.83	0.63	
11	(NH ₄) ₃ Tri.	0.08	3.5	25	200	10.0	1.9	0.66	0.72	
12	(NH ₄) ₂ Phth.	0.1	5.25	60	187	14.7	2.0	1.1	0.36	

* Tart. = tartrate; Cit. = citrate; Tri. = tricarballate; Phth. = phthalate.

TABLE II
INFLUENCE OF ELUENT CONCENTRATION ON ϵ AND k VALUES

Eluent concentration (mol/dm ³)	pH in external solution	Concentration of UO ₂ ²⁺ in external solution (mol/dm ³)	$\epsilon \times 10^4$	k (cm ⁻¹)	Remarks
0.1	2.25	0.148	1.8	0.24	Run 4
0.2	2.15	0.283	1.8	0.25	Ref. 1
0.4	2.0	0.565	1.4	0.27	Run 5
0.6	1.9	0.850	1.1	0.28	Run 6

positions and concentrations of the uranyl citrate species in the resin phase and the spectroscopic data for the uranyl citrate species in solution must be obtained^{8,9}.

Influence of eluent pH on ϵ and k values

The ϵ and k values for eluents with different pH values in the uranyl tartrate system are compared in Table III. The eluent concentration (0.2 mol/dm³) and the displacement length (2 m) were kept approximately constant for all the runs. It is apparent from Table III that the isotope effects are not affected by changes in the eluent pH. These findings are reasonable as the pH values in the external phase are maintained approximately constant irrespective of changes in the eluent pH value, as is shown in Table III. The decrease in pH may be caused by the hydrolysis of UO₂²⁺ ions.

Influence of operating temperature on ϵ and k values

The ϵ and k values at 25 and 60°C for the systems with ammonium citrate and tartrate as eluents are given in Table IV. The experimental conditions other than temperature were kept approximately constant. Little influence of temperature can be seen, probably because the temperature range covered was narrow.

Influence of displacement length on ϵ and k values

The ϵ and k values for the citrate system at 25 and 60°C are shown in Table V. The concentration and the pH of the ammonium citrate eluent were kept at 0.2 mol/dm³ and 7.2, respectively, and the band velocity was about 2 cm/h in all of the runs. As illustrated in Fig. 5, the isotope plateau region was not maintained in the 20-

TABLE III
INFLUENCE OF ELUENT pH ON ϵ AND k VALUES

Eluent pH	pH in external solution	Temperature (°C)	$\epsilon \times 10^4$	k (cm ⁻¹)	Remarks
9.0	2.2	60	1.2	0.26	Run 2
5.0	2.0	60	1.2	0.23	Run 3
8.5	2.0	25	1.2	0.21	Run 1
6.5	1.7	25	1.3		Ref. 1
5.0		25	1.2		Ref. 1

TABLE IV
INFLUENCE OF OPERATING TEMPERATURE ON ϵ AND k VALUES

Eluent*	Temperature (°C)	$\epsilon \times 10^4$	$k(\text{cm}^{-1})$	Remarks
A	25	1.2	0.21	Run 1
A	60	1.2	0.26	Run 2
B	25	1.8	0.3	Ref. 1
B	60	1.8	0.22	Run 7

* A, 0.3 mol/dm³ ammonium tartrate solution; B, 0.2 mol/dm³ ammonium citrate solution.

m displacement chromatogram at 25°C. The ϵ value calculated by means of eqn. 2 should be the true separation coefficient for the system in question and ought to be constant and independent of the displacement length as long as the isotope plateau region remains in the displacement chromatogram in which the atomic fraction R_i is equal to the original value R_0 . It is apparent from Table V that in the three instances where the isotope plateau-holding chromatography was successfully performed, the ϵ values are $1.8 \cdot 10^{-4}$, independent of the displacement length. With the 20-m chromatogram at 25°C the ϵ value is lower than in the other instances because of the partial mixing of the front and rear parts. The long-distance chromatographic experiments revealed that the ϵ value is independent of the displacement length as long as the isotope plateau region is maintained. It is obvious that the k values are much smaller in the 20-m chromatograms than in the 2-m chromatograms. In principle, the k value should be independent of the displacement length so long as the chromatography is performed in an ideal fashion. The decrease in the k value with increase in the displacement length may be ascribed mainly to the phenomena of mixing of the external solution at the tops of the columns and within the tubes connecting the columns in series. The mixing at the tops may be reduced by making the height of the solution phase as low as possible, and the mixing within the tubes by making them as short and narrow as possible.

Calculation of isotope separation power in chromatography

The separation power of uranium isotopes in the chromatography of uranyl-carboxylate complexes was considered on the basis of the theory of the chromatographic separation of isotopes^{2-5,10}. According to the theory, the maximum amount

TABLE V
INFLUENCE OF DISPLACEMENT LENGTH ON ϵ AND k VALUES

Displacement length (cm)	$\epsilon \times 10^4$	$k(\text{cm}^{-1})$	Temperature (°C)	Remarks
200	1.8	0.3	25	Ref. 1
2131	1.6	0.07	25	Run 8
200	1.8	0.22	60	Run 7
2173	1.8	0.061	60	Run 9

of ^{235}U product per unit time per uranium band volume, U_p^{\max} , can be expressed by eqn. 5.

$$U_p^{\max} = \frac{C_0 dx_e^*/dt}{x_e^* + x_d^*} \quad (5)$$

where

$$dx_e^* = \frac{\eta \varepsilon \bar{V}}{\Delta R^{\max} [1 + \varepsilon(1 - R_0)]} \quad (6)$$

$$\eta = \frac{R_0 (1 - R_0)}{1 + \alpha/d} \quad (7)$$

$$x_e^* = \frac{1}{k_e} \cdot \ln \left(\frac{\Delta R^{\max}}{A'_e} + 1 \right) \quad (8)$$

$$x_d^* = \frac{1}{k_d} \cdot \ln \left(\frac{\Delta R^{\min}}{A'_d} + 1 \right) \quad (9)$$

The plant equilibrium time, *i.e.*, the operating time before the product of the design enrichment can be withdrawn, t_s , can be defined by

$$t_s = \frac{1 + \varepsilon(1 - R_0)}{\eta \varepsilon \bar{v} k_e} \left[\Delta R^{\max} - A'_e \ln \left(\frac{\Delta R^{\max}}{A'_e} + 1 \right) \right] \quad (10)$$

The U_p^{\max} and t_s values to attain 3% ^{235}U enrichment were estimated according to eqns. 5 and 10, respectively, as follows. In the estimation the following characteristics were assumed in view of the results from the long-distance chromatography: (a) $\Delta R^{\max} = 0.0228$; (b) $\Delta R^{\min} = 0.0062$; (c) $\varepsilon = 1.8 \cdot 10^{-4}$; (d) $\bar{v} = 2$ cm/h; (e) $k_e = 0.061$ cm $^{-1}$; (f) $A'_e = 1 \cdot 10^{-6}$; (g) $k_d = 0.085$ cm $^{-1}$; (h) $A'_d = 1 \cdot 10^{-6}$; (i) $C_0 = 0.8$ mol/dm 3 . By use of these assumed values, the x_e^* and x_d^* values were calculated to be 160 and 100 cm, respectively. In practice, a plateau region in which the isotopic ratio is maintained at the original level is needed between the enriched and depleted zones in order to prevent their mixing. Thus, additional assumptions were introduced: (j) the isotope plateau region = 100 cm; (k) a column length three times the band length is required to displace the uranium band, which results in *ca.* 1000 cm as the column length. Based on assumptions (a)–(k), the U_p^{\max} and t_s values were estimated to be 0.71 kg/m $^3 \cdot$ year and 19 years, respectively. Here, U_p^{\max} is expressed in units of the column volume instead of the uranium band volume. In a practical operation, it may be possible to increase \bar{v} , k_e and k_d to 10 cm/h, 0.10 cm $^{-1}$ and 0.15 cm $^{-1}$, respectively. In this case, it is calculated that $U_p^{\max} = 1.1$ kg/m $^3 \cdot$ year and $t_s = 2.3$ years. On the other hand, for comparison, the amount of product per unit time per unit area of barrier for the gaseous diffusion process is estimated to be *ca.* 1 kg/m $^2 \cdot$ year. It may be said that the U_p^{\max} value estimated in ion-exchange chromatography is comparable to that in the

gaseous diffusion process. However, their direct comparison is, of course, misleading, because other factors such as energy requirement, hold-up and cost must be taken into consideration.

SYMBOLS

$A'(t)$	$c \exp(k\kappa t) \exp(kx_p)$;
A'_c	$c \exp(k_c \kappa t) \exp(kx_p)$;
A'_d	$c \exp(k_d \kappa t) \exp(kx_p)$;
c	constant;
C_0	original total concentration of uranium in the column;
d	distribution coefficient of uranium ions between resin and solution phases;
D_{235}, D_{238}	diffusion coefficients of ^{235}U and ^{238}U , respectively;
f_i	amount of uranium in the i th fraction;
k	slope coefficient, $(v_{235} - v_{238}) / (D_{235} - D_{238})$;
k_e, k_d	slope coefficients in enriched and depleted zones, respectively;
Q	total exchange capacity of the resin bed;
R_0	^{235}U atomic fraction in the originally loaded solution = 0.0072;
R_i	^{235}U atomic fraction in the i th fraction;
ΔR^{\max}	maximum degree of enrichment of ^{235}U ;
ΔR^{\min}	maximum degree of depletion of ^{235}U ;
$R(x, t)$	^{235}U atomic fraction at a distance x and time t from the start;
t_s	plant equilibrium time defined by eqn. 10;
U_p^{\max}	maximum amount of ^{235}U product per unit time per uranium band volume defined by eqn. 5;
\bar{v}	velocity of the uranium band;
v_{235}, v_{238}	velocities of ^{235}U and ^{238}U , respectively;
x	distance from original point;
x_p	distance from original point ($x = 0$) to the point where the value of $R(x, t)$ starts to deviate from R_0 ;
α	void fraction of chromatographic column;
ε	single-stage separation coefficient defined by eqn. 1;
η	defined by eqn. 7;
κ	$(v_{235} D_{238} - v_{238} D_{235}) / (D_{235} - D_{238})$;
$\left[\frac{\quad}{\quad} \right]$	concentration of isotope in the external solution divided by concentration of isotope in the resin phase.

REFERENCES

- 1 M. Okamoto, R. Goda, A. Nakagawa, Y. Sakuma and H. Kakahana, *Isotopenpraxis*, 16 (1980) 293.
- 2 H. Kakahana, T. Oi and T. Nomura, *J. Nucl. Sci. Technol.*, 14 (1977) 672.
- 3 H. Kakahana, T. Oi and T. Nomura, *J. Nucl. Sci. Technol.*, 15 (1978) 272.
- 4 H. Kakahana, T. Oi and T. Nomura, *J. Nucl. Sci. Technol.*, 15 (1978) 835.
- 5 T. Oi and H. Kakahana, *J. Nucl. Sci. Technol.*, 15 (1978) 941.
- 6 M. Okamoto, Y. Tanaka, Y. Fujii and M. Maeda, *Isotopenpraxis*, 18 (1982) 285.
- 7 H. Kakahana and M. Aida, *Bull. Tokyo Inst. Technol.*, 116 (1973) 39, and references cited therein.
- 8 Y. Tanaka, J. Fukuda, Y. Fujii and M. Okamoto, *J. Phys. Chem.*, 86 (1982) 1015.
- 9 Y. Tanaka, J. Fukuda, M. Okamoto and M. Maeda, *J. Inorg. Nucl. Chem.*, 43 (1981) 3291.
- 10 H. Kakahana, *Separ. Sci. Technol.*, 15 (1980) 567.