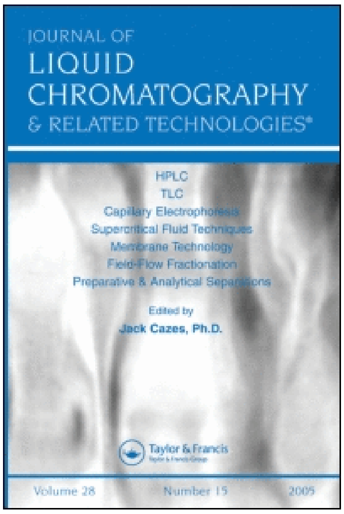

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Fedotov, P. S. , Maryutina, T. A. , Pukhovskaya, V. M. and Spivakov, B. Ya.(1994) 'Influence of Kinetic Properties of Extraction Systems on the Separation and Preconcentration of Some Elements by Countercurrent Chromatography', Journal of Liquid Chromatography & Related Technologies, 17: 16, 3491 — 3506

To link to this Article: DOI: 10.1080/10826079408013526

URL: http://dx.doi.org/10.1080/10826079408013526

JOURNAL OF LIQUID CHROMATOGRAPHY, 17(16), 3491-3506 (1994)

INFLUENCE OF KINETIC PROPERTIES OF EXTRACTION SYSTEMS ON THE SEPARATION AND PRECONCENTRATION OF SOME ELEMENTS BY COUNTERCURRENT CHROMATOGRAPHY

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ABSTRACT

The influence of kinetic properties of several extraction systems on the separation of some elements by countercurrent chromatography (CCC) has been studied. The chromatographic behaviour of Eu(III), Fe(III), Ta(V), Nb(V), Hf(IV), Zr(IV) has been investigated in two kinetically different extraction systems on the basis of di-2-ethylhexylphosphoric acid (D2EHPA) and tetraphenylmethylenediphosphine dioxide (DTPMDP). It has been shown that the values of mass transfer coefficients determine the type of elution (isocratic or step), which is necessary for the element separation. The data on batch extraction (mass transfer coefficients and partition coefficients) and parameters of chromatographic peaks (half-widths) can be interrelated by the expression proposed.

INTRODUCTION

Countercurrent chromatography (CCC) is based on retention (without solid support) of either phase (stationary) of a two-phase liquid system in a rotating column under the action of centrifugal forces while the other liquid phase (mobile) is being continuously pumped through [1]. A few devices providing the retention of the stationary phase in the field of mass forces in the absence of solid support have been suggested. The most successful device that gained acceptance is a planetary centrifuge [2]. A column (or a column unit) of a certain configuration rotates around the central axis of the device with the aid of a planetary gear.

So far, CCC has been mainly used for separation and determination of organic and bioorganic substances [3]. The studies of the last five years have shown that the technique can be successfully applied to separation and preconcentration of inorganic ions for their more selective and sensitive determination. The possibility of CCC separation of ortho- and pyrophosphate anions, Cs and Sr, rare earth and other elements in systems on the basis of extraction reagents of different types has been demonstrated [4-7].

The theory of CCC as a chromatographic separation method has being developed for a few last years. Equations for the calculations of partition coefficients, number of theoretical plates, separation factors, peak resolution have been set up on the basis of classical expressions used in extraction chromatography [8,9]. The influence of the flow rate of the mobile phase and the retention factor S_f (ratio of the stationary phase volume V_s to the total column volume V_c) on the separation efficiency and peak resolution has been studied [9-13]. A few procedures for optimization of chromatographic processes have been also proposed [8, 14-16].

The absence of solid support in CCC practically excludes the possibility of adsorbtion. It is assumed that the retention of substances in a separation column can be predicted with the help of partition coefficients. The partition coefficients D obtained under CCC conditions (dynamic) and determined from an elution curve (Eq. 1) are postulated to coincide with the partition coefficients estimated from batch extraction experiments [8].

$$D = \frac{V_r'}{V_s} = \frac{V_r'}{V_m}\frac{V_m}{V_s} = \frac{V_r'}{V_m}\frac{1-S_f}{S_f} = \frac{V_r-V_m}{V_m}\frac{1-S_f}{S_f} \qquad (1)$$

where V_r - retention volume, V_m - mobile phase volume in the column ($V_m = V_c - Vs$), V_r' - corrected retention volume ($V_r' = V_r - V_m$).

Examination of the reported data has shown that this approach is valid for physical distribution of substances between two liquid phases.

The distribution of inorganic compounds is also dependent on the hydrodynamic properties of the system used, partition coefficients of substances to be separated and parameters of the planetary centrifuge operation (rotation and revolution speeds, direction and speed of the mobile phase pumping, sample volume). However, the systems for inorganic separations are very different from those for organic separations as in most cases they contain a complexing reagent (ligand). The complexation process, its rate and the mass transfer rate are the main factors that determine the separation efficiency. The kinetics is of particular importance, because CCC separation can be a non-equilibrium process. Thus, it has been shown for several systems that the batch partition coefficients for inorganic compounds are different from dynamic ones [17-19].

This work is an attempt to correlate kinetic properties of solvent extraction systems and results of separation of inorganic substances by CCC. Kinetic data, which could be used, are very limited. Freiser et al. studied the influence of kinetic factors on the separation efficiency in the centrifugal partition chromatography (CPC) [17, 18]. The kinetics of extraction of lanthanides by bis(2,4,4-trimethylpentyl)phosphinic acid in heptane was investigated and the data obtained were correlated with the results of the CPC separation of the elements [17]. The studies on the separation efficiency for the distributing species, a palladium complex and an organic solute (3-picoline) for the heptane - water phase pair were also reported [18].

It has become clear from our results as well as from the studies by Freiser et al. that the fundamentals of separation of substances in rotating coil columns need to be specially studied with respect to inorganic compounds.

EXPERIMENTAL

Apparatus

Chromatographic investigations were made on a device consisting of a planetary centrifuge with a vertical column drum fabricated in the Institute of Analytical Instrumentation, St. Petersburg, a peristaltic pump and a fraction collector.

The column of the device rotated around its axis and at the same time revolved around the central axis of the device. The rotation and revolution speeds were equal (ω = 350 r/min). The planetary centrifuge model had the following design parameters: revolution radius R = 140 mm, rotation radius r = 50 mm. The column was made of a teflon tube with an inner diameter of 1.5 mm and a wall thickness of 0.75 mm. The total inner capacity of the column was V_c = 24 ml.

A stirred diffusion cell was used for the investigation of the kinetics of batch extraction. The rotation speed of the motor-driver stirring rod was 150 r/min. The organic phase/aqueous phase interface had an area of 9 cm.

A γ-detector (Tesla, Czechoslovakia) was used for radiometric measurements of Eu and Fe concentrations (radioisotopes ^{154}Eu and ^{55}Fe).

Polychromator ICAP-61 ("Thermo Jarrell Ash Corp.", USA) with first order resolution 0.031 nm was used for ICP-AES determination of Hf, Nb, Ta, and Zr.

Reagents

Tetraphenylmethylenediphosphine dioxide (DTPMDP) was synthesized at the Institute of Organoelement Compounds, Moscow. Di-2-ethylhexylphosphoric acid (D2EHPA) was a high-purity grade (99.9%) reagent. The other chemicals were analytical grade reagents.

Measurement of batch extraction parameters

The equilibrium partition coefficients were determined under batch extraction conditions (using a separatory funnel). The volumes of aqueous and organic phases were equal to 5 ml. The initial concentration of an element under study in the aqueous phase was 5 ppm. Fe(III) in DTPMDP-based system and Eu(III) in both DTPMDP- and D2EHPA-based systems were equilibrated for 5 min. Zr(IV), Hf(IV) in D2EHPA-based systems required 15-min mixing to attain equilibrium. When Fe(III), Ta(V), Nb(V) were extracted in D2EHPA-based systems, test solutions were contacted for 5 hours to attain equilibrium.

When the kinetics of batch extraction in the stirred diffusion cell was investigated, the volumes of organic and aqueous phases were 10 and 30 ml, respectively. The initial concentration of the element in the aqueous phase was 5 ppm. The total volume of the aqueous phase fractions taken for concentration measurements were less than 3 ml.

The mass transfer coefficients were determined with the use of t-dependence of -ln(1-E_t) [20].

$$E_t = \frac{C_0 - C_t}{C_0 - C^*} \qquad (2)$$

where C_0 - initial, C_t - current, C^* - equilibrium concentration of the element in the aqueous phase, mol/l.

It is known that

$$-\ln(1-E_t) = k\,a \qquad (3)$$

where $a = S/V$ (S - phase interface area, cm²; V - aqueous phase volume, ml; k - mass transfer coefficient, cm/s). The tangent of an angle of t-dependence of -ln(1-E_t) is equal to ka.

Chromatographic procedure

Before the chromatographic experiment was begun, the components of the two-phase liquid system were stirred and brought into equilibrium for mutual saturation of the phases, after which the aqueous phase was used as the mobile phase and the organic one as the stationary phase. The coil column in the stationary mode was filled with the organic phase. After that, while the column rotated, the aqueous phase was fed to its inlet. The mass force field, which arose during rotation, made it possible to retain a constant volume of the stationary phase V_s while the mobile phase was continually pumped through. The pumping speed was 1.0 ml/min. After equilibrium between the mobile and stationary phases had been established, a sample was introduced into the column; the concentration of Eu(III) or Fe(III) in the sample was 200 ppm, the sample volume was 0.1 ml. When the behaviour of Ta(V), Nb(V), Hf(IV), Zr(IV) under the preconcentration conditions was investigated, the sample volume was 10 ml and the concentration of each metal in the sample was 50 ppm.

The volume of the stationary phase retained in the column depends on the extraction system nature, the rotation speed of the column and the pumping speed of the mobile phase. When the influence of the quantity of the stationary phase in the column on the chromatographic peak shape was investigated, a fixed volume of the stationary phase V_s^f (less than V_s allowed by experimental conditions) was introduced with the flow of the mobile phase into the column in the stationary mode. After that, while the column was rotated, the aqueous phase was continuously fed to its inlet.

Table 1

Wavelengths and corresponding analytical ranges of ICP-AES determination of elements

Element	Wavelength, nm	Analytical range, ppm
Hf	282.022	0.010 - 1000
Nb	319.498	0.020 - 500
Ta	240.063	0.020 - 200
Zr	349.621	0.003 - 250

ICP-AES determination of elements

The operation conditions of the determination were the following: forward r.f. power - 1.1 kW; reflected r.f. power - less than 50 W; outer argon flow - 15 l/min, auxiliary argon flow - 0.29 l/min; carrier argon flow - 0.72 l/min; observation height - 16 mm above load coil; nebulizer - of cross-flow type; solution uptake rate - 1.5 ml/min. Operation system "Thermo SPEC" 4.20 on the basis of a personal computer IBM PC-AT 386 was used. The wavelengths and analytical ranges are presented in Table 1.

RESULTS AND DISCUSSION

Study of the kinetic properties of D2EHPA-based systems

D2EHPA is an effective extractant for separation and preconcentration of rare earth and other elements. Kinetic peculiarities of the interaction between D2EHPA and various metal ions have been relatively well studied. Eu(III) is known to be extracted much faster than Fe(III) in systems with D2EHPA [20].

However, for the chromatographic data interpretation additional studies of kinetic properties of the systems used and determination of Eu(III) and Fe(III) mass transfer coefficients are required. These studies were made by use of a stirred diffusion cell. Figure 1 illustrates t-dependences of $-\ln(1-E_t)$ for Eu(III) and Fe(III) extraction for the systems on the basis of D2EHPA. It can be seen that dependences *1* and *2* for Fe(III) extraction (systems containing 0.05 and 0.5 mol/l D2EHPA) and dependence *3* for Eu(III) extraction (system containing 0.5 mol/l D2EHPA) are straight lines, whereas the dependence *4* for Eu(III)

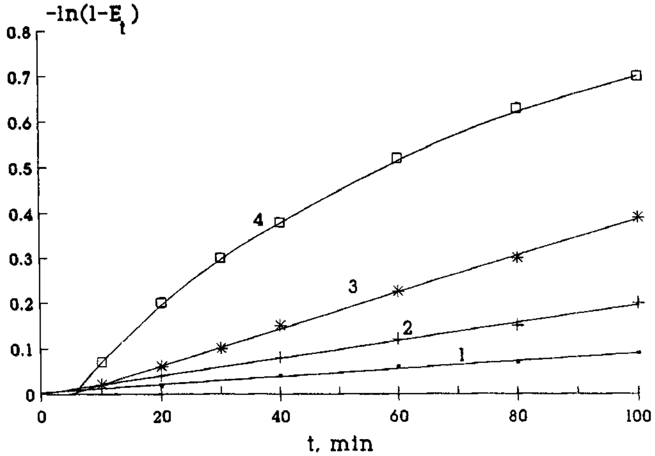

Fig. 1: Time-dependences of -ln(1-E_t) for Eu(III) and Fe(III) extraction in D2EHPA-based systems. *1* - Fe(III), 0.05 mol/l D2EHPA - n-decane - 0.2 HCl; *2* - Fe(III), 0.5 mol/l D2EHPA - n-decane - 3.0 mol/l HCl; *3* - Eu(III), 0.05 mol/l D2EHPA - n-decane - 0.2 mol/l HCl; *4* - Eu(III), 0.5 mol/l D2EHPA - n-decane - 0.5 mol/l HCl.

extraction (system containing 0.5 mol/l D2EHPA) is more complicated. The formation of thin condensed films at the interphase surface in Eu-containing systems with high D2EHPA concentration [20] may explain why the Eu(III) extraction retards with time.

t-Dependences of -ln(1-E_t) for Fe(III) extraction in D2EHPA-based systems are straight lines (Fig. 1) but mass transfer coefficients are much lower than in the case of Eu(III) (Table 2). Besides, the extraction of Fe(III) in the systems with D2EHPA is practically irreversible. For instance, the equilibrium partition coefficient (D_{bat}) of Fe(III) in the 0.05 mol/l D2EHPA - n-decane - 2.0 mol/l HCl system is about 1 in the extraction, whereas in the back-extraction this value is about 10. The mechanisms of the extraction and back-extraction of Fe(III) in the system under investigation are apparently different. It should be noted that the mass transfer coefficients for Eu(III) and Fe(III) extraction are not influenced by changing HCl concentration (from 0.2 to 3.0 mol/l), all other factors being the same.

Ta and Nb belong to elements kinetically more inert than Fe, that is why the investigation of their behaviour under batch extraction and CCC conditions is theoretically important. The 0.5 mol/l D2EHPA - n-decane - 2-3 mol/l HNO_3 systems are more selective to Ta(V), Nb(V), Hf(IV), Zr(IV) in comparison with the 0.5 mol/l D2EHPA - n-decane - HCl systems [21].

The results of the study on Ta(V), Nb(V), Hf(IV), Zr(IV) extraction kinetics in the 0.5 mol/l - n-decane - 2.0 mol/l HNO_3 system are presented in Fig. 2 and Table 2. *t* - Dependences of -ln(1-E_t) are straight lines for all elements, but mass transfer coefficients for Ta(V) and Nb(V) are appreciably lower than for Hf(IV) and Zr(IV).

Table 2

Mass transfer coefficients (*k*) and batch partition coefficients (D_{bat}) for Eu(III), Fe(III), Ta(V), Nb(V), Hf(IV), Zr(IV) in D2EHPA-based extraction systems

Element	Extraction system	*k*, cm/s	D_{bat}
Eu(III)	0.05 mol/l D2EHPA-n-decane-0.2 mol/l HCl	2.0 x 10^{-4}	0.8
	0.5 mol/l D2EHPA-n-decane-0.5 mol/l HCl	6.7 x 10^{-4}(a) 2.8 x 10^{-4}(b)	5.2
Fe(III)	0.05 mol/l D2EHPA-n-decane-0.2 mol/l HCl	4.0 x 10^{-5}	18.6
	0.05 mol/l D2EHPA-n-decane-2.0 mol/l HCl	1.2 x 10^{-4}(c)	10.9
	0.5 mol/l D2EHPA-n-decane-3.0 mol/l HCl	9.3 x 10^{-5}	3.1
Ta(V)	0.5 mol/l D2EHPA-n-decane-2.0 mol/l HNO_3	5.7 x 10^{-5}	12.1
Nb(V)		1.3 x 10^{-4}	33.8
Hf(V)		6.5 x 10^{-4}	>100
Zr(V)		7.1 x 10^{-4}	>100

(a) t < 30 min

(b) t > 60 min

(c) back-extraction

The chromatographic behaviour of Eu(III), Fe(III), Ta(V), Nb(V), Hf(IV), Zr(IV) in D2EHPA-based systems

The chromatographic behaviour of Eu(III) in the 0.05 mol/l D2EHPA - n-decane - HCl system at different HCl concentrations is shown in Fig. 3. It is seen that the elution of Eu(III) begins in all cases immediately after a volume of mobile phase equal to V_m has passed through the column. The peak width increases with the decrease in HCl concentration. Dynamic (D_{dyn}) and batch (D_{bat}) partition coefficients of Eu(III) in systems under investigation are given in Table 3. It is of interest that at a constant V_s value (12 ml) the shapes of elution curves of Eu(III) are not influenced by the rotation speed (from 350 to 500 r/min) and pumping speed of the mobile phase (from 0.4 to 1.0 ml/min). Therefore, the

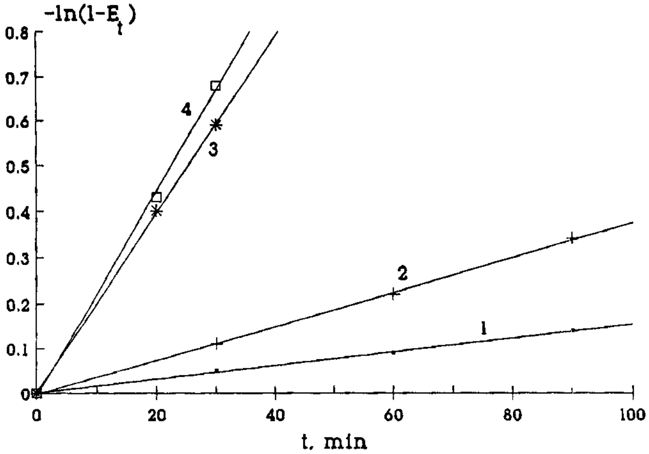

Fig. 2: Time-dependences of -ln(1-E_t) for Ta(V), Nb(V), Hf(IV), Zr(IV) in 0.5 mol/l D2EHPA - n-decane - 2.0 mol/l HNO_3. *1* - Ta(V), *2* - Nb(V), *3* - Hf(IV), *4* - Zr(IV).

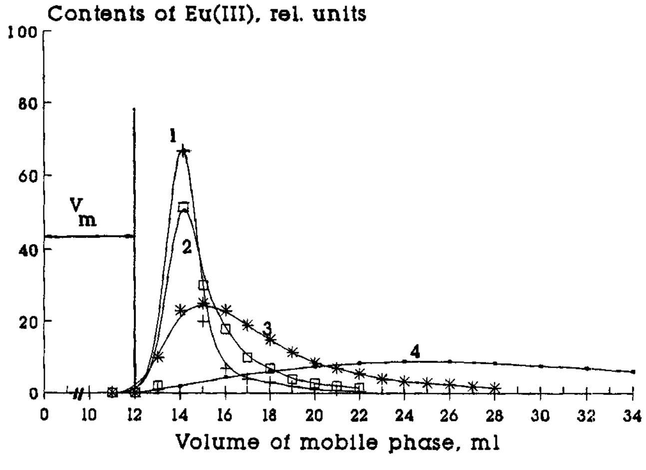

Fig. 3: Chromatographic behaviour of Eu(III) in 0.05 mol/l D2EHPA - n-decane - HCl systems. S_f = 0.5. Mobile phase: *1* - 0.70, *2* - 0.40, *3* - 0.25, *4* - 0.20 mol/l HCl.

Table 3

Batch and dynamic partition coefficients for Eu(III) in the 0.05 mol/l D2EHPA - n-decane - HCl system

C_{HCl}, mol/l	D_{bat}	D_{dyn}
0.70	0.06	0.12
0.40	0.12	0.12
0.25	0.20	0.18
0.20	0.80	1.20

nature of the extraction system, its kinetic properties may have a greater effect on the chromatographic process than the hydrodynamic parameters of the planet centrifuge operation.

D_{dyn} = 1.0 is considered to be the optimal value for obtaining a well-resolved peak of an individual component [8]. A significant broadening of the peak at D_{dyn} = 1.2 does not make it possible to use the chosen extraction system under the chosen experimental conditions for isocratic separation of Eu(III) from other elements.

The isocratic separation of some rare earth elements in the 0.02 mol/l D2EHPA - n-heptane - 0.02 mol/l HCl system was carried out using high-speed CCC [7] (a planetary centrifuge with three identical multilayer coiled columns connected in series; rotation speed 900 r/min, pumping speed 5 ml/min, total column volume 270 ml). Such a device allows one to increase the efficiency of the mass exchange between the mobile and stationary phases. However, a considerable increase in the total column capacity leads to an increase in the time required for the separation (several hours) and to a large volume (about 100 ml) of the mobile phase needed for the elution of each element. Hence, the practical use of these techniques may be very limited.

The equilibrium for Fe(III) extraction in D2EHPA - n-decane - HCl systems is achieved within several hours under the batch extraction conditions. When the chromatographic behaviour of Fe(III) in these systems is examined, it would not be correct to discuss dynamic partition coefficients since under the same conditions a part of Fe(III) is eluted from the column, whereas the other part is extracted into the stationary phase and is not eluted even after the volume of the mobile phase equal to 10 V_m is passed through the column. Consequently, the first part of Fe(III) should have the partition coefficient about 0.1

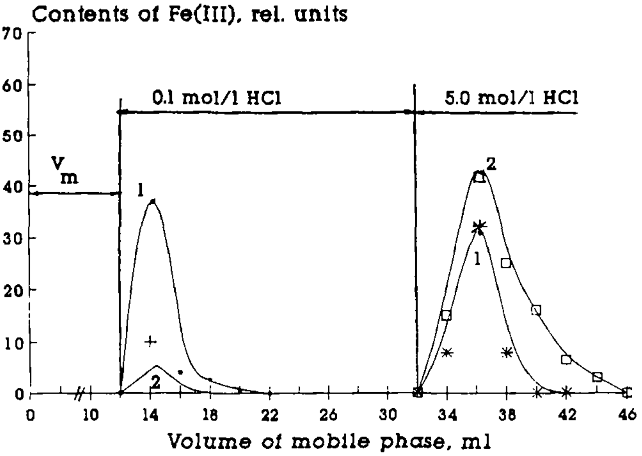

Fig. 4: Chromatographic behaviour of Fe(III) in D2EHPA - n-decane - HCl systems. S_f = 0.5. Step elution. Stationary phase: *1* - 0.05, *2* - 0.5 mol/l D2EHPA.

and the second part of Fe(III) about 10 or higher. About 50% of Fe(III) is eluted in the case of 0.05 mol/l and 5% in the case of 0.5 mol/l D2EHPA. The corresponding values of mass transfer coefficients are 4.0 x 10^{-5} and 9.3 x 10^{-5} cm/s (Table 2). Hence, the less the magnitude of mass tranfer coefficient, the greater the quantity of Fe(III) eluted immediately after the V_m volume is passed through the column. Fe(III) retained by the stationary phase can be eluted only by a highly concentrated HCl solution, since the mechanism of back-extraction of Fe(III) is different from that of extraction.

Similar curves circumscribe the chromatographic behaviour of Ta(V) and Nb(V) in the 0.5 mol/l D2EHPA - n-decane - 2.0 mol/l HNO_3 system (Fig.5). As is seen, a part of Ta(V) (40%) and Nb(V) (35%) is not extracted and eluted after the V_m volume has passed through the column. Zr(IV) and Hf(IV) are extracted quantitatively.

The extraction system used provides relatively high values of the equilibrium partition coefficients for Ta(V) and Nb(V) (Table 2). However, the quantitative extraction is not attained because of a low rate of the mass transfer process. The comparison of the chromatographic behaviour of elements under investigation and their mass transfer coefficients allows us to assume the following. To concentrate species with mass transfer coefficients $k < 10^{-4}$ cm/s under experimental conditions used (V_c = 24 ml), their partition coefficients must be 100 or higher. Otherwise, the species will be partly eluted after the V_m volume is passed through the column.

Therefore, when kinetically inert compounds are concentrated in the stationary phase under CCC conditions, a column with a larger total volume can be used. However, in the separation of any species, a larger column volume results in a longer separation time and broader chromatographic peaks [7].

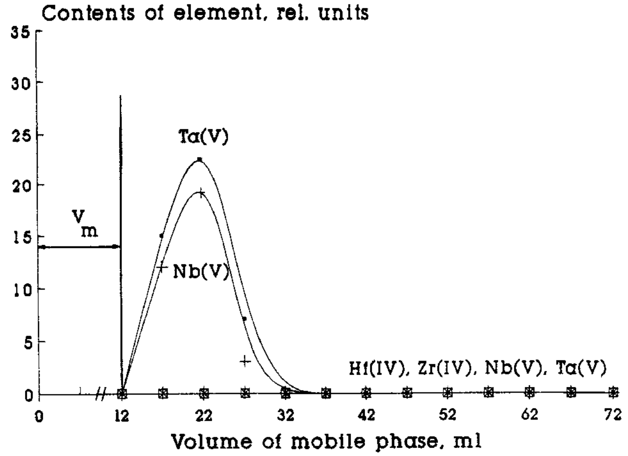

Fig. 5: Chromatographic behaviour of Ta(V) (·), Nb(V) (+), Hf(IV) (■), Zr(IV) (*) in 0.5 mol/l D2EHPA - n-decane - 2.0 mol/l HNO_3 system. $S_f = 0.5$.

Study of the kinetic properties of DTPMDP-based systems

Neutral organophosphorous compounds (NOC) are known to be advantageously distinguished from acidic organophosphorous compounds by kinetic properties. Thus, the equilibrium attainment in an extraction system on the basis of NOC is faster and the mass transfer is more efficient. The values of mass transfer coefficients of Eu(III) and Fe(III) in DTMPDP - chloroform - HCl - NH_4SCN systems are given in Table 4. Both *t*-dependences are straight lines. NH_4SCN was used as complexing agent, which increased the extraction of Eu(III) and Fe(III) and enabled one to work with low DTPMDP concentrations [22]. The results obtained demonstrate that the mass transfer coefficients of Eu(III) and Fe(III) in the systems on the basis of DTPMDP are significantly higher than those for the systems with D2EHPA.

The chromatographic behaviour of Eu(III) and Fe(III) in DTPMDP-based systems

The chromatographic behaviour of Eu(III) in the 0.005 mol/l DTPMDP - chloroform - 0.5 mol/l NH_4SCN - HCl system at different HCl concentrations is shown in Fig.6. D_{dyn} and D_{bat} of Eu(III) in the systems under investigation are given in Table 5. The values of D_{dyn} are lower than those of D_{bat}. This fact testifies that the elution of Eu(III) is not an equilibrium process. The width of the chromatographic peaks increases with a decrease in HCl concentration. However, in contrast to systems with D2EHPA, Eu(III) was retained in the separation column after a volume of V_m had passed off.

Figure 7 (the origin of the coordinates corresponds to the volume of the mobile phase in the column) shows the curve shape and position as a function of the stationary phase

Table 4

Mass transfer coefficients (k) and batch partition coefficients (D_{bat}) for Eu(III) and Fe(III) in DTPMDP-based extraction systems

Element	Extraction system	*k*, cm/s	D_{bat}
Eu(III)	0.005 mol/l DTPMDP - $CHCl_3$ - 0.4 mol/l HCl - 0.5 mol/l NH_4SCN	1.8×10^{-3}	3.8
Fe(III)	0.003 mol/l DTPMDP - $CHCl_3$ - 1.0 mol/l HCl - 0.5 mol/l NH_4SCN	8.6×10^{-4}	2.7

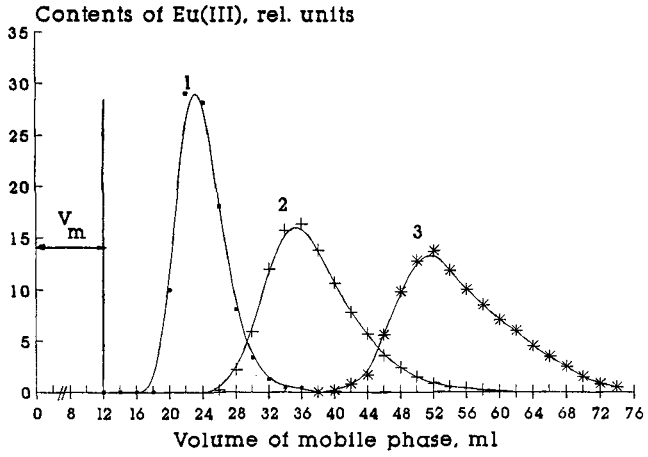

Fig.6: Chromatographic behaviour of Eu(III) in the 0.005 mol/l DTPMDP - chloroform - HCl - 0.5 mol/l NH_4SCN system. S_f = 0.5. HCl concentration in the mobile phase: *1* - 1.0, *2* - 0.6, *3* - 0.4 mol/l.

Table 5

Batch and dynamic partition coefficients for Eu(III) in the 0.005 mol/l DTPMDP - chloroform - HCl - 0.5 mol/l NH_4SCN system

C_{HCl}, mol/l	D_{bat}	D_{dyn}
1.0	1.8	0.9
0.6	2.7	1.8
0.4	3.8	3.0

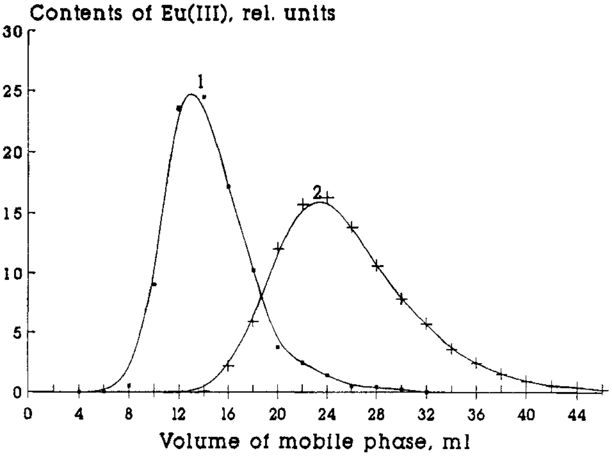

Fig. 7: Influence of the stationary phase volume on the shape of the elution curves of Eu(III) in the 0.005 mol/l DTPMDP - chloroform - 0.6 mol/l HCl - 0.5 mol/l NH_4SCN system. *1* - $S_f = 0.25$ (V_s = 6 ml), *2* - S_f = 0.5 (V_s=12 ml).

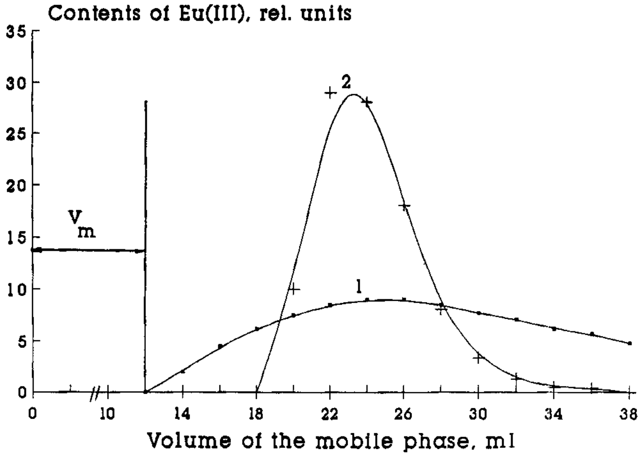

Fig. 8: Influence of the mass transfer coefficient on the Eu(III) peak shape. *1* - 0.05 mol/l D2EHPA - n-decane - 0.20 mol/l HCl system. S_f=0.5. D_{dyn}=1.2. k=2.0 x 10^{-4} cm/s. *2* - 0.005 mol/l DTPMDP - chloroform - 1.0 mol/l HCl - 0.5 mol/l NH_4SCN system. S_f = 0.5. D_{dyn} = 0.9. k = 1.8 x 10^{-3} cm/s.

volume in the column. The chromatographic peak shifts to the left and narrows if the extractant quantity is twice lower (V_s^f =6 ml, peak *1*), all the other factors being the same. The values of D_{dyn} calculated from the chromatograms are the same and equal to 1.8.

Figure 8 illustrates once more the importance of the contribution from chemical kinetics to the separation process. Two peaks are quite different due to the kinetic peculiarities of the extraction systems used, although the corresponding values of dynamic partition coefficients are close (1.2 and 0.9).

Hence, the mass transfer coefficients determine the type of elution, which is necessary for the element separation under given experimental conditions. The systems providing high values of k (about 10^{-3} cm/s) are suitable for isocratic separation as well as for separation by step elution, whereas kinetically more inert systems (k is about 10^{-4} cm/s) require only step elution.

It should be noted that the solvent extraction and chromatographic characteristics for the substances to be separated can be linked by empirical expression 4 [19].

$$\frac{\dfrac{D_{(1)}^{bat} V_{s(1)}}{W_{1/2(1)}}}{\dfrac{D_{(2)}^{bat} V_{s(2)}}{W_{1/2(2)}}} \approx \frac{k_{(1)}}{k_{(2)}}, \qquad (4)$$

where $W_{1/2}$ - half-width of chromatographic peak, indices (1) and (2) relate to two different extraction systems.

Thus, having the batch extraction data (partition coefficients and mass transfer coefficients) for two systems and the results of a chromatographic experiment for one of them, one can estimate $W_{1/2}$ of a chromatographic peak obtained by use of the second system. However, Eq. 4 is valid for partition coefficient values in the range of 1 - 10 and for reversible processes of extraction and back-extraction. The hydrodynamic conditions of both experiments should be identical. Theoretical estimation of $W_{1/2}$ allows one to avoid a time-consuming experimental selection of chromatographic conditions. Thus, if the estimated value is relatively high when $D_{(2)}{}^{bat}=1$, elution of the component of interest begins with the V_m volume and the chosen system is unsuitable under given conditions for isocratic separation from other components. An acceptable magnitude of $W_{1/2}$ can be achieved by changing the extraction system, choosing concentrations of its constituents, changing V_s volume.

CONCLUSION

The systems for CCC inorganic separations in most cases contain a complexing reagent (ligand). Because of the necessity of taking into account metal-ligand interaction and distribution of the complexes formed, the fundamentals of inorganic separations should be very different from organic ones. The contribution from some chemical kinetics factors to the separation of inorganic species by CCC has been estimated.

It has been shown that the kinetic properties of extraction systems on the basis of complexing reagents have a greater influence on the separation (preconcentration) process than hydrodynamic parameters of the planet centrifuge operation (rotation and pumping speeds). It has been demonstrated that the systems providing high values of mass transfer coefficients (about 10^{-3} cm/s) are suitable for isocratic separation as well as for separation by step elution. When complex formation and mass transfer rates are lower (k is about 10^{-4} cm/s), only step elution is required. If the elements under investigation are kinetically very inert (k is about 10^{-5} cm/s), some difficulties arise even when these elements are being concentrated. High partition coefficients (about 10^{2}) are necessary for the quantitative extraction of such elements into the stationary phase.

Acknowledgements

The authors are grateful to Dr. A. A. Pichugin and Dr. M. K. Chmutova for useful discussions and help.

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Received: August 31, 1993
Accepted: April 5, 1994