

Separation of Hafnium from Zirconium by Extraction Chromatography with Liquid Anionic Exchangers

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Abstract

The extraction chromatography behavior of zirconium and hafnium is studied using tri-*n*-octylamine (TNOA) and tri-caprylmonomethyl ammonium chloride (Aliquat 336) as the stationary phase supported on a styrene/divinylbenzene copolymer resin and hydrochloric acid as the mobile phase. The effects of hydrochloric acid concentration, extractant loading on the support, support particle size, column dimensions, and hydrofluoric acid are investigated. Microgram amounts of Zr and Hf are successfully separated on a small size ($\varnothing 5 \times 45$ mm) column, on which Zr is adsorbed and Hf is completely eluted with 8M HCl. The adsorbed Zr is then eluted with 2M HCl. Aliquat 336 is found to be superior to TNOA for the mutual separation of Zr and Hf. The stability of the extraction chromatography resin is also examined.

Introduction

It is well known that the mutual separation of zirconium and hafnium is very difficult because of the extreme similarity of these two elements. Both solvent extraction and ion-exchange techniques have been effectively applied to this mixture (1–5). However, the solvent extraction technique, which requires multi-stage counter-current mixer settlers using tributyl phosphate (TBP) as extractant, operating at the industrial scale, is not convenient for analytical separations. Ion-exchange technology is a very effective separation method for similar ions and has been extensively and successfully applied in analytical separations. The selectivity of the ion-exchange process depends on the properties of the ion-exchanger being used and the composition of the aqueous phase. In the case of two ions having the same charge and very similar radii, the selectivity resulting from the properties of the ion-exchanger (such as acidity or basicity and the degree of cross-linking) is not sufficient to ensure effective separation. In such a case, an appropriate complexing agent has to be added to the aqueous phase; the attained selectivity is then due to either the differences in the stability constants or the different charges

or structures of the complexes formed. An alternative is extraction chromatography, which combines the advantages of the high selectivity of solvent extraction and the high efficiency of ion-exchange chromatography. It has been extensively applied to separations in analytical chemistry. Extraction chromatography offers many opportunities for optimizing a separation by adjusting stationary phase parameters (type and size of support particles, type and concentration of the extracting agents used in diluents, or type and degree of the loading of liquid or solid extractants) and mobile phase parameters (flow rate, concentration of partitioning substances, type and concentration of complexing or salting out agents).

Crawley (6) used TBP on kieselguhr for the separation of zirconium and hafnium in the $\text{HNO}_3\text{--NH}_4\text{NO}_3$ system, and Ueno and Hoshi (7) reported the same agent adsorbed on a celite support for this separation in hydrochloric acid. TBP is a very good extractant for uranium, but the selectivity of TBP for zirconium and hafnium is not high. The separation factor of Zr–Hf using the TBP–celite–HCl system was approximately 4 (7). Zr and Hf were also separated in the system $\text{MIBK}[\text{NH}_4\text{SCN}+(\text{NH}_4)_2\text{SO}_4]$ (8). Although Wang et al. (9) studied the extraction chromatography behavior of Zr and Hf using sulfoxides as a stationary phase and an NH_4SCN –HCl solution as a mobile phase, the obtained separation factor of 3.6 was not large, and in addition, the introduction of NH_4SCN salt into the aqueous mobile phase causes complications.

As the selectivity of an extraction chromatography column is determined by the nature of the extractant used as the stationary phase, it is important to select a suitable extractant for effective separation. Moore (10) first reported the solvent extraction and separation of Zr and Hf with long-chain aliphatic amines (methyl-*n*-octylamine) in chloride solutions. The long-chain aliphatic amine compounds are also known as liquid ion-exchangers and have been widely used in the solvent extraction separation of various metal ions in nuclear fuel processing and fission product recovery. Cerrai and Testa (11,12) reported detailed investigations on the solvent extraction and separation of Zr and Hf using tri-*n*-octylamine (TNOA) and tri-

Table I. Physical Properties of Amberchrom and Levextrel Resins

Resin	Chemical structure	Surface area (m ² /g)	Porosity (% v)	Mean pore size (Å)	Mesh size (µm)	Approximate pore volume (mL/g)	Skeletal density (g/mL)
CG-300cd	polyaromatic	700	55–75	300	80–160	1.66	1.08
Levextrel	polyaromatic	80–345	65	180–800	125–200	NA*	NA*

* NA, data not available.

caprylyl-monomethyl ammonium chloride (Aliquat 336) in a hydrochloric medium, and later separated 9.7 mg of Zr from 0.3 mg of Hf using a TNOA–8M HCl–5% concentrated HNO₃ system on a cellulose powder column (13). However, high concentrations of HCl pose a problem for the cellulose powder support (14). Das and Chattopadhyay (15) reported briefly on the solvent extraction and chromatographic separation of niobium, zirconium, and hafnium with Aliquat 336. These earlier studies suggest that extraction chromatography using TNOA or Aliquat 336 is potentially promising for the mutual separation of Zr and Hf; however, systematic studies of the parameters affecting the separation are lacking. The aim of the present study is to systematically investigate the separation of Zr–Hf by extraction chromatography using TNOA and Aliquat 336. The studied parameters include the loading of the extractant, support particle size, column dimensions, composition of eluents, and stability of the resins in order to explore the potential application of the method for the separation of Zr–Hf from geological materials.

Experimental

Materials and reagents

TNOA, trioctylmethyl ammonium chloride (marketed as Aliquat 336, molecular weight 404.17), and cyclohexane were obtained from Aldrich Chemical (USA). The ready-to-use Levextrel resins contain TNOA or tricaprylylmethyl ammonium chloride (a mixture of C₈–C₁₀ chains with C₈ predominating; also marketed as Aliquat 336, but referred to as Aliquat 336M hereafter in order to distinguish it from the previous Aliquat 336). Levextrel resin is a copolymer of divinylbenzene (DVB) with styrene-containing organic extractant, where the organic extractant is added before the polymerisation reaction starts (17,18). The support for the preparation of solvent-impregnated resins (SIR) was Amberchrom CG-300cd, a highly crosslinked styrene/divinylbenzene copolymer, which was obtained from Supelco (USA). The spherical beads of Amberchrom resin offer exceptional mechanical and chemical stability. The physical properties of Levextrel resins and Amberchrom CG-300cd resin are listed in Table I.

The weight ratios of TNOA over the support in the Levextrel resins are 1:9, 1:2, and 1:1, and that of Aliquat 336M is 1:2. Zirconium and hafnium standard solutions (Aldrich) were 990

and 1002 µg/mL, respectively. All other chemicals were of analytical grade, and all the chemicals were used as received. Water with 18M Ω • cm resistivity that was purified using a Milli-Q (Millipore, Milford, MA) system was used throughout.

Apparatus

Polypropylene columns (inner diameter Ø3.5, 3.8, 5, and 9 mm) with a 30 µm polyethylene frit at the bottom were used for separation work. An inductively coupled plasma atomic emission spectrometry (ICP-AES) instrument (Jobin-Yvon 70 II, Longjumeau, France) was used for the measurement of Zr and Hf concentrations in the solutions collected fractionally from the columns.

Preparation of resins

The extraction chromatography resin was obtained using two approaches: the solvent impregnating method (direct adsorption of the extractant into macroporous polymeric supports), producing the SIR resin, and the suspension polymerisation method (polymerisation of styrene and divinyl copolymers in the presence of the extractant, developed by Kroebel and Meyer [17,18]), producing the Levextrel resin. The SIR resin was prepared by impregnating 10 g of Amberchrom CG-300cd resin in a 50–100-mL cyclohexane solution containing 5 g TNOA or Aliquat 336, stirring the mixture slightly, and evaporating it at room temperature (20°C) to dryness. This usually takes approximately 5 hours. The Levextrel resin was prepared at the Beijing Institute of Chemical Engineering and Metallurgy, Beijing, China. The Levextrel resin was sieved, and the 75–120 mesh size (125–200 µm) was used in this work.

Determination of the distribution and separation coefficients of Zr(IV) and Hf(IV) in an HCl medium using the batch-equilibrium method

Resin (0.20 g) was placed into a 10-mL cylindrical vessel, and 5.0-mL portions of aqueous solutions containing 50 µg/mL Zr and Hf in various HCl concentration were added. The vessel was closed and shaken vigorously for 30 min. After filtering, the concentrations of Zr and Hf in the aqueous phases were measured by ICP-AES. The distribution coefficient (*D*) of Zr and Hf can be calculated using the calculation

$$D = [(C_0 - C_e)C_e]/(V/m) \quad \text{Eq 1}$$

where *C*₀ and *C*_e are the initial and equilibrium concentrations of Zr and Hf in the aqueous solutions, respectively; *V* is the volume (mL) of aqueous solution; and *m* is the amount (g) of resin. The separation factor (*β*) is the ratio of distribution coefficients.

$$\beta = \frac{D_{\text{Zr}}}{D_{\text{Hf}}} \quad \text{Eq 2}$$

The purification factor (PF) corresponding to the initial solutions by the batch-equilibrium method can be calculated using

$$PF_{Zr} = \frac{[(C_0 - C_e)Zr/(C_0 - C_e)Hf]}{(C_0, Zr/C_0, Hf)} \quad \text{Eq 3}$$

$$PF_{Hf} = \frac{(C_e, Hf/C_e, Zr)}{(C_0, Hf/C_0, Zr)} \quad \text{Eq 4}$$

Determination of exchange capacity

A small-size column ($\varnothing 3.5 \times 50$ mm) and 0.1 g of resin were used for the determination of the exchange capacity of Zr by the breakthrough curve (i.e., the Zr concentration change of the effluent with effluent volume) that was obtained by loading the feed solution until the concentration of Zr in the effluent reached the same concentration of zirconium in the feed solution. Then, the feeding was interrupted, and the column bed was washed with an eluent that displaces the interstitial volume without stripping the Zr retained in the stationary phase. When no Zr was found in this eluate, another eluent (2M HCl) that was able to strip the Zr retained on the column was passed through the column until no Zr was detected in this stripping eluent. The equilibrium exchange capacity (EEC) for Zr was obtained by measuring the concentration of Zr in the collected volume of this stripping eluate:

$$EEC = \frac{CV}{m} \quad \text{Eq 5}$$

where C is the concentration of Zr in the eluate and V is the volume of eluate.

Column separation

The resin, suspended in water, was transferred into a chromatographic column, and the resin bed was pressed slightly with a glass rod to eliminate air bubbles. A 30- μ m polyethylene frit was placed on top of the column bed to prevent the disturbance of the resin during the elution phase. The column was preconditioned with 8–10 mL of the same concentration of hydrochloric acid as the first eluant. A solution containing a Zr–Hf mixture to be separated was then loaded into the column. The elution separation was carried out with eluants composed of various concentrations of hydrochloric acid as mobile phases using gravity flow. The concentrations of Zr and Hf in the fractions of the effluents were determined using ICP-AES, and the elution curves were drawn by plotting the concentration against the effluent volumes. The purification factor (PF) of the column method is calculated using

$$PF_{Hf} = \frac{(C_{Hf}/C_{Zr})(\text{eluate 1})}{(C_{Hf}/C_{Zr})\text{feed}} \quad \text{Eq 6}$$

$$PF_{Zr} = \frac{(C_{Zr}/C_{Hf})(\text{eluate 2})}{(C_{Zr}/C_{Hf})\text{feed}} \quad \text{Eq 7}$$

where eluate 1 is the Hf eluate obtained by passing 8M HCl through the column, and eluate 2 is the Zr eluate obtained by passing 2M HCl through the column.

Results and Discussion

Effect of HCl concentration on distribution coefficient and separation factor

The distribution coefficient as a function of HCl concentration ranging from 6 to 10M obtained by the batch method is shown in Figure 1. The plots of $\log D$ versus $\log [HCl]$ give linear relationships. It has been assumed that the extraction mechanism of Zr(IV) and Hf(IV) by tertiary amine (TNOA) and quaternary ammonium salt compound may be represented as TNOA:

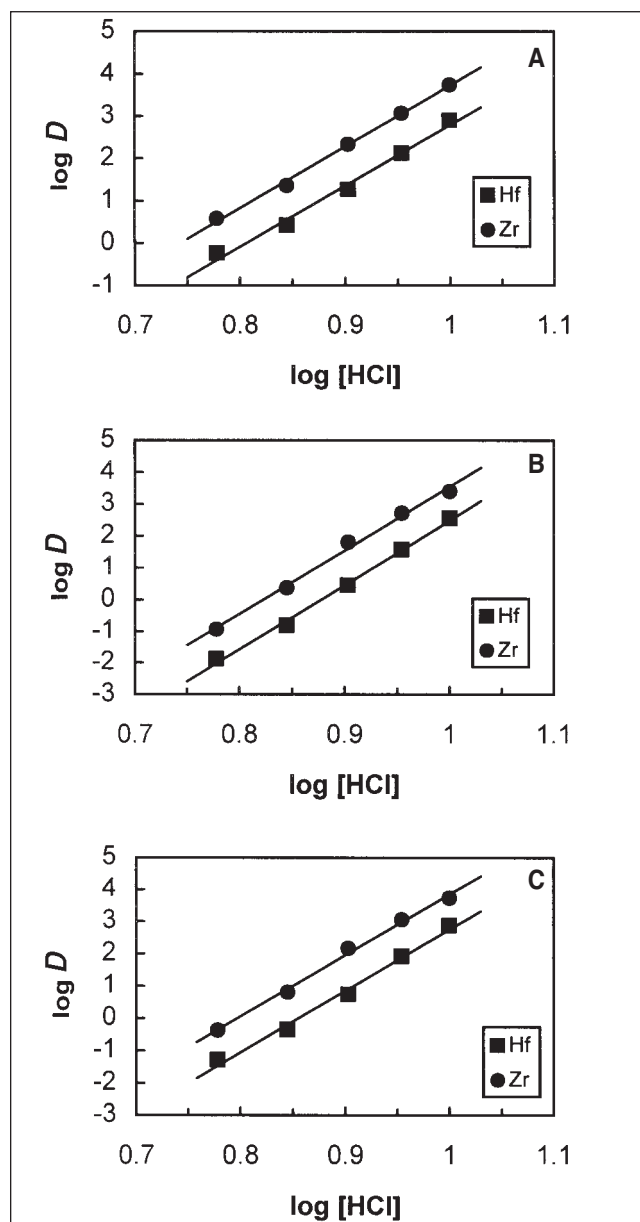
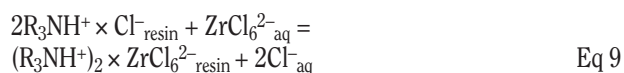
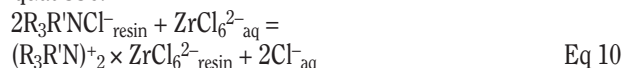


Figure 1. Dependence of $\log D$ on $\log [HCl]$. 1:2 Levextrel TNOA resin (A), 1:2 SIR Aliquat 336 resin (B), 1:2 Levextrel Aliquat 336M resin (C). Aqueous phase, 5 mL of 50 μ g/mL Zr and Hf in various HCl concentrations; resin phase, 0.20 g.



Aliquat 336:



where "resin" refers to the resin phase, "aq" is the aqueous phase, R_3N is TNOA, $R_3R'N^+Cl^-$ is Aliquat 336, R is the octyl group, and R' is the methyl group. The distribution coefficients at a given HCl concentration are in the order TNOA > Aliquat 336M > Aliquat 336, showing that the extraction power is in this order. It has been demonstrated that the extraction power of Aliquat 336 is generally lower than that of TNOA and thus of tri-*i*-octylamine (TIOA) (16). The separation factor as a function of HCl concentration is given in Figure 2. The maximum separation is obtainable at an HCl concentration of 8M, and the separation factor is in the order Aliquat 336M ($\beta = 27$) > Aliquat 336 ($\beta = 23$) > TNOA

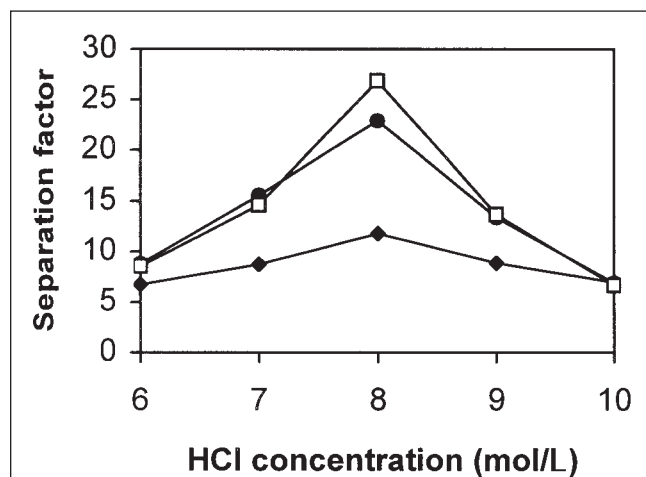


Figure 2. Separation coefficients as a function of HCl concentration: \square TNOA; \circ , Aliquat 336; \bullet , Aliquat 336M.

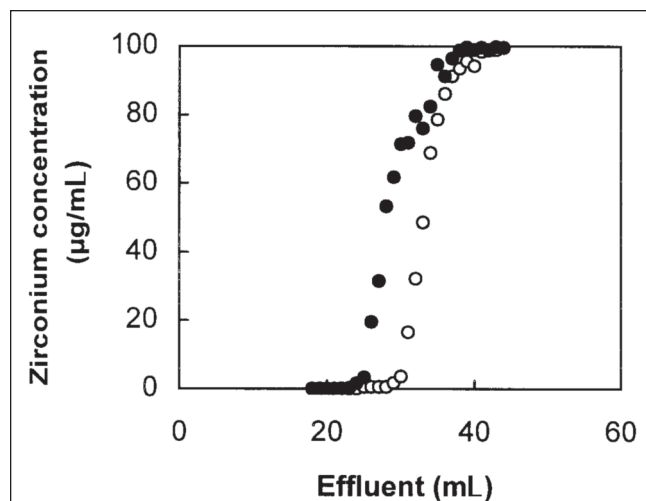


Figure 3. Breakthrough curves of zirconium on the Levextrel Aliquat 336M resin and SIR Aliquat 336 resin columns (0.1 g of resin). \circ Levextrel Aliquat 336M resin; \bullet SIR Aliquat 336 resin.

($\beta = 12$), which is much larger than the literature values obtained by TBP ($\beta = 4$) (7) and sulfoxides ($\beta = 3.6$) (9). The Zr and Hf concentrations in the 8M HCl aqueous solution after the batch equilibrium using Levextrel Aliquat 336M were 7.51 and 42.3 $\mu\text{g/mL}$, respectively (initial concentration, 50 $\mu\text{g/mL}$). Therefore, the purification factors obtained by the batch method in 8M HCl were 5.52 for Zr and 5.63 for Hf. It is expected that the separation will be greatly improved by the column method, because numerous equilibria occur in the column during the elution. The column separation will be discussed later.

Breakthrough curve and exchange capacity

The breakthrough curves for Zr with Aliquat 336M and Aliquat 336 resin are shown in Figure 3. Using Equation 5, the exchange capacities of Levextrel Aliquat 336M resin and Aliquat 336 SIR

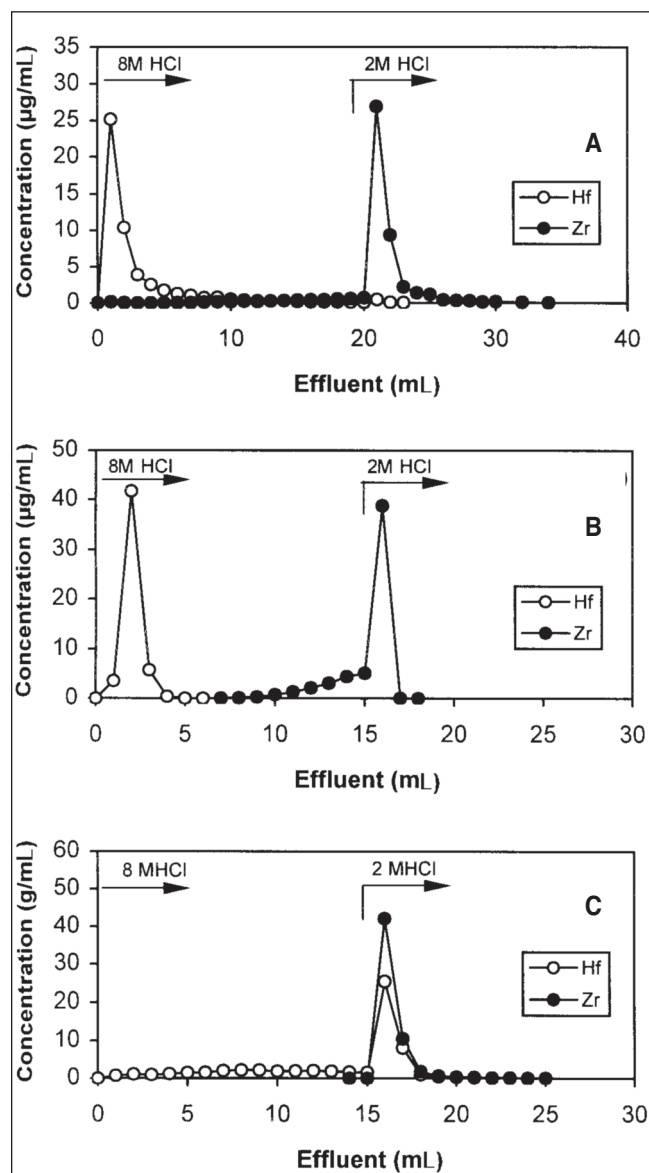


Figure 4. Separation profiles of Hf and Zr on a $\varnothing 5 \times 45$ -mm column (loading, 50 μg Zr and 50 μg Hf): 1:1 Levextrel Aliquat 336M (flow rate, 0.24 mL/min) (A); 1:2 SIR Aliquat 336 (flow rate, 0.24 mL/min) (B); 1:1 Levextrel TNOA (flowrate, 0.2 mL/min) (C).

resin are 24.3 and 30.8 mg Zr/g of resin, respectively.

Column separation

Figure 4 shows the column separation of Hf from Zr using Aliquat 336, Aliquat 336M, and TNOA as stationary phases and 8M HCl as the mobile phase to elute Hf. The separations of Hf from Zr with Aliquat 336 and Aliquat 336M are excellent using 10 mL

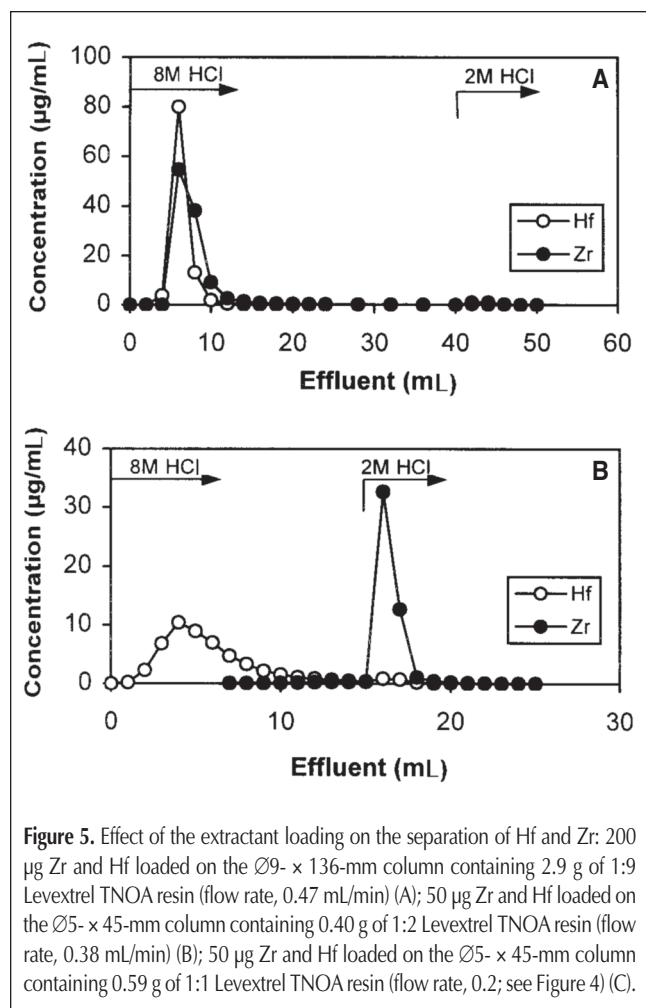


Figure 5. Effect of the extractant loading on the separation of Hf and Zr: 200 µg Zr and Hf loaded on the Ø9- × 136-mm column containing 2.9 g of 1:9 Levestrel TNOA resin (flow rate, 0.47 mL/min) (A); 50 µg Zr and Hf loaded on the Ø5- × 45-mm column containing 0.40 g of 1:2 Levestrel TNOA resin (flow rate, 0.38 mL/min) (B); 50 µg Zr and Hf loaded on the Ø5- × 45-mm column containing 0.59 g of 1:1 Levestrel TNOA resin (flow rate, 0.2; see Figure 4) (C).

of 8M HCl. However, the elution curve with Aliquat 336M seemed to show more tailing than with Aliquat 336, and the elution peak of Hf was very broad (only approximately 50% of the amount of Hf loaded was eluted with 15 mL of 8M HCl from the TNOA resin column). This can be explained by the higher distribution coefficient of the TNOA resin than that of the Aliquat 336 resin (Figure 1). Hence, a larger volume of 8M HCl will be needed to separate Hf from Zr on the TNOA column. The recovery and purification factors in different initial Zr/Hf ratios of the feed solutions obtained by the Aliquat 336M columns are summarized in Table II (10 mL of 8M HCl eluate was collected for recovering Hf, and 10 mL of 2M HCl eluate was collected for Zr). The purification factors are much larger than those obtained by the batch-equilibrium method.

It should be noted that the 5–8 mL of effluent of the conditioning phase (10 mL of 8M HCl) became turbid, and white spots were observed in the columns during the course of elution/separation. The turbidity was assumed to be caused by the drainage of some of the extractant from the column. Many more spots appeared in the SIR resin columns than in the Levestrel resin columns. As a result, the flow rate decreased gradually. This could be attributed to the instability of the resin (i.e., the losses of the organic substance from the support). The stability of the SIR and Levestrel resins will be discussed in more detail later.

Effect of extractant loading on the support

The effect of extractant loading on the column separation was examined using 1:9, 1:2, and 1:1 Levestrel TNOA resin, and the results are shown in Figures 4 and 5. The separation of Hf from Zr can be effectively performed with 1:2 TNOA (Figure 5B), whereas the extractant loading of 1:9 is not enough to retain Zr on the column (Figure 5A). Using a 1:1 ratio, only approximately 50% Hf loading was eluted with 15 mL of 8M HCl (Figure 4C), reflecting the high affinity of the extractant for Hf and Zr. These results show that 1:2 extractant loading has the optimum column efficiency. Grosse-Ruyken and Bosholm (19) reported that the minimum heights of the equivalent theoretical plate (HETP) values at different di-(2-ethylhexyl) phosphoric acid (HDEHP) loadings on the 0.09-mm diameter silica gel were obtained at the HDEHP/

Table II. Purification Factor Obtained by the Column Method*

Mixture (µg)		Found (µg)				Recovery (%)		Purification factor	
		8M HCl (10 mL)		2M HCl (10 mL)		8M HCl	2M HCl		
Hf	Zr	Hf	Zr	Hf	Zr	Hf	Zr	Hf	Zr
Column 1									
50	50	48.4	0.41	0.56	49.9	96.7	99.9	118	89.2
100	5	102	0.13	0.58	4.77	102	95.4	40.4	164
50	2.5	51.2	0.07	0.38	2.34	102	94.0	36.6	123
Column 2									
10	100	9.50	1.18	0.25	94.5	95.0	94.5	80.5	38.3
10	50	9.74	0.49	0.12	48.7	97.4	97.0	99.4	81.2
1 [†]	40 [†]	0.93	0.27	0.05	40.8	93.0	102	138	20.4

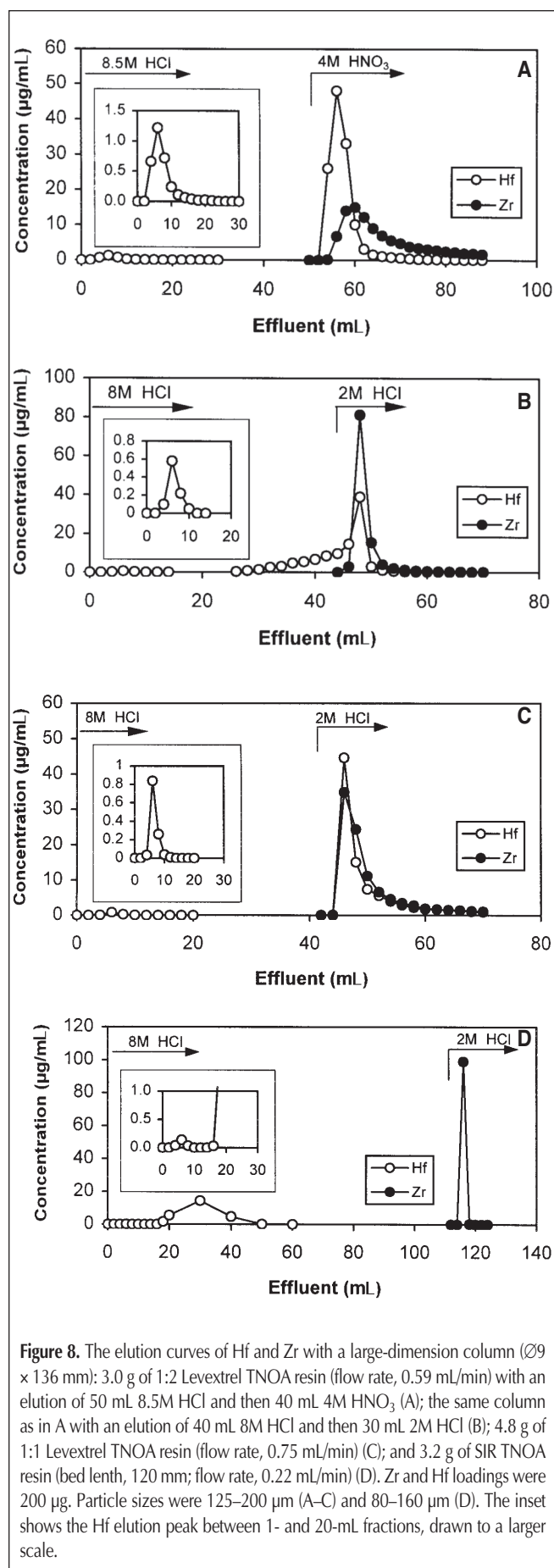
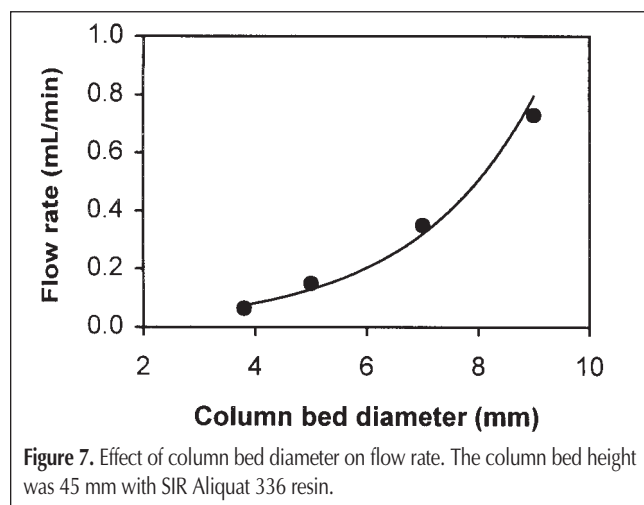
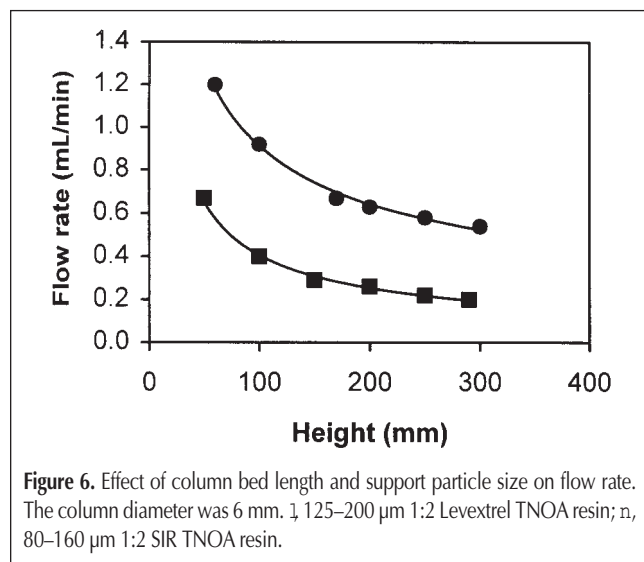
* Column dimension, 80 mm × 3.8-mm i.d.; resin type, Levestrel Aliquat 336M; amount, 0.4 g; conditioning, 8 mL 8M HCl. The purification factors by the batch-equilibrium method were 5.52 for Zr and 5.63 for Hf.

[†] The natural Zr/Hf ratio in geological materials is about 40:1.

support weight ratio of 1:2. Ueno and Hoshi (7) investigated the effect of the TBP-celite weight ratios of 1:1, 1:2, and 1:4 on the separation of Hf from Zr and also found that the 1:2 ratio was the optimum extractant loading for Hf-Zr separation.

Effect of column dimension and support particle size

Bed length is one of the most important parameters in extraction chromatography; elution volumes, separation time, and the number of theoretical plates increase linearly with bed length, and column resolution increases with its square root. Extraction chromatographic experiments are usually run under gravity flow. When very similar ions are involved, very long lengths of column are usually necessary to obtain a satisfactory resolution. An increase in bed length leads to a proportional increase in pressure needed to force the mobile phase through the column. Most columns used in chromatography for analytical purposes have bed lengths ranging between 50 and 150 mm, mainly determined by the resolution needed and the time that can be tolerated for analysis. The support particle size is of importance to the column performance in both gas and liquid chromatography (LC), because it significantly affects the surface area and the HETP. However, the particle size of the support also has a significant influence on the flow resistance. Figure 6



shows the effect of column bed length and support particle size on the flow rate. The particle size of the Levextrel resin ranged from 125 to 200- μm diameter, and that of the support for the SIR TNOA resin ranged from 80 to 160- μm diameter; the smaller resin (SIR TNOA) gave a lower flow rate as expected. Figure 7 shows the effect of bed diameter on the flow rate. The flow rate decreased drastically when the bed diameter decreased from 9 to 3.8 mm.

Figure 8 shows the separation chromatogram for the larger-dimension column ($\varnothing 9 \times 150$ mm) using different diameter resins (125–200- μm diameter for 1:1 and 1:2 Levextrel TNOA resins and 80–160 μm diameter for 1:2 SIR TNOA resin). For the diameter of 125–200 μm resins (Figure 8, flow rate = 0.6–0.75 mL/min), in the first effluent fraction of 15 mL of 8M HCl, a portion of 1–3% of the Hf amount loaded on the column was detected, whereas in the following fraction of 10 mL, no Hf was detected, indicating that Hf leakage occurred at the beginning of elution. This elution of Hf amounting to 1–3% of the loaded amount was presumably caused by channeling in the column due to the larger size of resin and column diameter and the low distribution coefficient of Hf. The bulk of the Hf was eluted together with the Zr (i.e., no separation occurred) when the mobile phase was changed to 2M HCl. In the case of smaller size resin (80–160 μm diameter) (Figure 8D, flow rate = 0.22 mL/min, much smaller than the previous cases), no obvious peak for Hf in the first fraction of 15 mL was observed, indicating that there was no leakage of Hf. Following this, the Hf was eluted separately from Zr with 8M HCl, resulting in excellent separation. It can be concluded that for efficient operation, smaller resins, smaller diameter columns, and slower mobile phase flow rates are preferred. In general, the channeling phenomena led to the loss of resolution and may occur when large-diameter columns and large support particle sizes are used, because in such a case it is difficult to pack the columns uniformly and homogeneously. Therefore, it is good practice to reduce column diameters as much as allowed by experimental limitations. A bed diameter of approximately 5–50 particle diameter (i.e., column internal diameters from 2.5 to 7.0 mm) for 50–150- μm particles is a compromise used frequently (16). Recently, a more detailed investigation on the reproducibility of column performance in LC and the role of the packing density was reported by Stanley et al. (20).

Effect of hydrofluoric acid on separation

Hydrofluoric (HF) acid is commonly used as a complexing agent to stabilize Zr and Hf solutions. In addition, when dealing with geological materials and minerals, HF acid is the most convenient way to create the decomposition. The main purpose of this study was to explore the possibility of the present extraction chromatographic system to separate of Zr and Hf from geological materials and minerals. Therefore, the effect of HF acid on the elution behavior of Hf and Zr was investigated and is shown in Figure 9. It can be seen that no separation was achieved when a small amount of HF acid was present in the solution; the elution peaks of Zr and Hf completely overlapped (the amounts eluted in the 8M HCl were 99.8% for Hf and 97.3% for Zr). This is because Hf and Zr form much more stable complexes with the fluoride ion than the chloride ion, and the fluoride complexes are not extractable by the amine compounds. This system was applied to “real world” sam-

ples (e.g., geological materials) and found that the successful separation could be obtained in the case of complete removal of fluoride ions from the solution. On the other hand, the separation became very complex because of the presence of the major elements Al, Fe, and Ti, which are difficult to separate from Zr and Hf. The details will be published elsewhere (21).

Stability and lifetime of resin

As mentioned above, instability phenomena were observed with the resin used. The stability characterisation of Levextrel and SIR resins were further examined by measuring the capacity variations of resin during operation. Figure 10 shows the capacity of Levextrel Aliquat 336M resin and SIR Aliquat 336 resin as a function of elution cycle number. In the capacity measurement, no preconditioning was carried out for the first run. It can be seen that the capacity for Zr drops 29% for the Levextrel Aliquat 336M resin and 50% for the SIR Aliquat 336 resin between runs 1 and

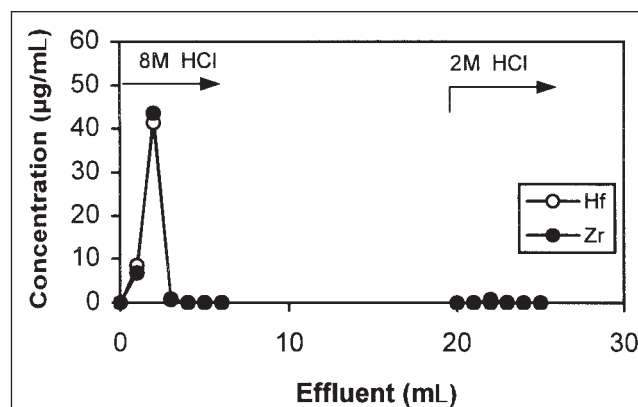


Figure 9. Effect of hydrofluoric acid on the elution behavior of Hf and Zr. Conditions: column, $\varnothing 5 \times 45$ mm; 1:2 Levextrel TNOA resin; loading, 1 mL of 8M HCl–0.05M HF containing 50 μg Zr and Hf; flow rate, 0.36 mL/min.

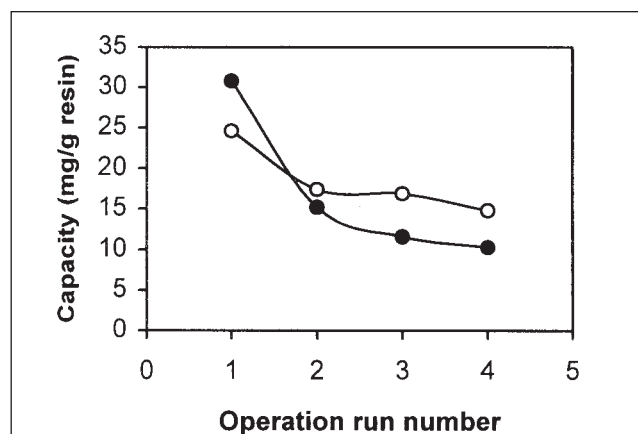


Figure 10. Exchange capacity for Zr as a function of operation run number. The column was $\varnothing 3.5 \times 30$ mm filled with 0.1 g resin. Each run included 8 mL of 10M HCl for conditioning (except the first run), 40 mL of feed solution in 10M HCl of 100 $\mu\text{g}/\text{mL}$ Zr, 10 mL of 2M HCl for eluting Zr from the column, and 10 mL of water for washing the column. 1, SIR Aliquat 336 resin (the flowrate decreased from 0.43 mL/min at the beginning to 0.12 mL/min at the end); 2, Levextrel Aliquat 336M resin (the flowrate decreased from 0.18 mL/min at the beginning to 0.05 mL/min at the end).

2, and thereafter there was little change in capacity. One of reasons for this difference between runs 1 and 2 could be the preconditioning prior to run 2. As has been mentioned previously that at the preconditioning stage, some emulsion formation in the effluent was observed, indicating loss of extractant. The flow rate of the Levestrel Aliquat 336M resin column decreased from 0.43 to 0.12 mL/min, and that of the SIR Aliquat 336 resin column decreased from 0.18 to 0.05 mL/min. The decreases in flow rate and capacity reflect the loss of extractant from the support. The stability of a chromatographic column includes physical stability and chemical stability. Losses of extractant from the column may derive either from dissolution into the eluants or drainage by the eluant of undissolved portions of extractant scarcely retained on the supporting material. They may result in the undesirable presence of extractant in the eluate and also in the variation of the characteristics of the column. When a second, more retained element is involved (in the case of this work, Zr) and loaded at a high ratio, leakages of extractant could also include losses of the extracted compound and give rise to contamination of the eluate and decreases in the purification factor of the first, less retained element or incomplete recovery of the second element in the subsequent steps. In general, a maximum loading of no more than 20% of the column capacity is recommended in extraction chromatography. In the experiments shown in Table II, the resin amount in the column was 0.4 g, hence the Zr loading was between 0.003–1%. In addition, 10 mL of conditioning phase (8M HCl) aged the column. Therefore, the instability of the resin has no significant effect on the purification factors when the metals loading is very low (no more than 1% of the maximum capacity) and aging action is taken.

From Figure 10, it can also be seen that the Levestrel resin is more stable than the SIR resin. This may be attributed to the different ways the extractant was introduced and held on the support. For the Levestrel resin, the extractant was added before the polymerisation started, and as a result, a large amount of the extractant was adsorbed and fixed in the network or matrix of the porous copolymer. Figure 6A may be further evidence of this, because no adsorption of Zr was observed on the 1:9 Levestrel TNOA resin. For the SIR resin, which was prepared "in house", a large amount of the extractant was adsorbed onto the surface of the resin by physical adsorption, and some of the extractant entered the cavities of the porous support by capillary forces. Consequently, the Levestrel resin should be more stable than the in-house SIR resin. From Levestrel Aliquat 336M resin (Figure 4A) and SIR Aliquat 336 resin (Figure 4B) and Figure 8, it can be seen that the tailing of Hf and Zr on the Levestrel resin is more serious than on the SIR resin. This verifies the above analysis.

Conclusion

The experimental results showed that TNOA and Aliquat 336 are good extractants for the zirconium–hafnium separation in an extraction chromatography system. Aliquat 336 is more selective than TNOA. The separation factors obtained ranged between 36 and 164 for 1–100 µg of Hf and 2.5–100 µg of Zr. Channeling in

the column is more serious with larger column dimensions and support particle sizes. An optimum extractant loading ratio of 1:2 (the weight ratio of extractant over the support) was identified for separation purposes. No separation can be achieved when the feed aqueous solution contains hydrofluoric acid. The stability of the Levestrel resin is better than the solvent impregnated resin prepared in house using the conventional method.

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