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Separation of zirconium and hafnium using hollow fibres Part II. Membrane chromatography

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Abstract

A novel extraction chromatography system using hollow fibre membranes as supports is reported for separation of zirconium and hafnium. The effects of flow rate and flow mode, stationary phase concentration loaded on the hollow fibre membranes and fibre length on the separation were investigated. The separation performance of hollow fibre membrane chromatography can be analysed from existing theories of conventional extraction chromatography using particle supports.

Keywords: Hollow fibre; Membrane chromatography; Zirconium; Hafnium

1. Introduction

Liquid chromatography has very high efficiency in the traditional separation methods, since it is a multi-stage rather than a single stage process and a very high number of separation stages can be easily achieved in a low volume unit. However, this technology has been found only useful for laboratory and pilot scale production to produce small amounts of high purity products, for various economic and technical reasons [1]. One of the economic reasons is that column packing with the adsorbent particles is expensive. One of the technical reasons is that the scale-up of the chromatographic technique is accompanied by loss in the column efficiency (resolution). The simplest way of scale-up is to increase the column diameter, however, it is more difficult to pack large diameter columns uniformly than smaller ones. Even in analytical-scale columns (commonly 6–10 mm i.d.), the packing uniformity could still be a problem [2]. On the other hand, the use of small particle sizes means that the pressure drops in the bed are high.

Membrane technology has found increasing applications in separations and the combination of the membrane with chromatography has become an emerging new concept for the downstream processing of proteins and biomolecules in biochemical and molecular biology fields [3–5] because of its high throughput due to the height-to-diameter ratios as small as the separation requirements permits.

Membrane-based chromatography can generally be distinguished from particle-based chromatography by the fact that the interaction between a solute and a matrix (immobilised ligand or stationary phase) takes place mainly in the flow-through pores of the membranes in membrane chromatography and in the dead-end pores of the particles in particle-based chromatography [3]. The controlling transport resistance in conventional column chromatography using porous particles is the pore diffusion, while the main feature of chromatographic separations based on membranes is the absence of pore diffusion. The mass transport takes place mainly by convective flow through the pores of a membrane. Thus, the use of membranes in chromatography reduces the mass transport resistance for the solute to the matrix by eliminating pore diffusion, leaving film diffusion from the core of the liquid to the membrane surface in the interior of a through-pores process as the only transport resistance. As film diffusion is usually orders of magnitude faster than pore diffusion, mass transport limitations are drastically reduced in membrane chromatography. The chromatographic interactions in the membrane are usually identical to those in the particulate matrix (e.g. ion-exchange, hydrophobic, and bio- or pseudo-affinity interactions) and generally are very fast processes. Since single or even stacked membranes are very thin compared to gel beads, reduced pressure drops

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Nomenclature

C	solute concentration (mol/l)
d	diameter (m)
D	diffusion coefficient (m/s^2)
HETP	height of the equivalent theoretical plate (m)
k	distribution coefficient (−)
l	fibre length (m)
M_0	total amount of solute loaded (mol)
n	number of fibres (−)
N	number of plate (−)
p	pressure (atm)
R_s	resolution (−)
SF	separation factor (−)
t_m	residence time of mobile phase (s)
t_R	residence time of solute (s)
v	mobile phase velocity (m/s)
V_m	void volume/fibre lumen volume (m^3)
V_r	retention volume of solute (m^3)
W	width of elution peak (m)
z	position

Greek letters

β	separation coefficient (−)
ε	void fraction (−)
μ	viscosity
σ^2	variance

are found along the chromatographic bed, thus allowing increased flow rates and productivities. The scale-up of membrane-based chromatography with these properties may be easier than the scale-up of packed bed columns, which is usually carried out by increasing the diameter at constant height [3]. The membrane can be a form of shallow packed bed containing affinity ligands (by grafting) and rolled into the shape of a hollow fibre [5–7]. As such, this form of hollow fibre chromatography is analogous to adsorption in a very thin packed bed. However, it should be noted that the height of the equivalent theoretical plate (HETP) is very limited in this geometry because of the very thin wall.

There is another geometry for the use of hollow fibres in chromatography. A stationary phase coats the surface and the pores of the hollow fibres and a mobile phase flows through the fibres' lumen. A given amount of mixed solute is loaded and then eluted with mobile phases as peaks of separated solutes. In this case, the length of the hollow fibre can be as long as required in order to obtain the required HETP. As such, this form is a closer parallel to elution column chromatography very commonly used in analytical chemistry. Since hollow fibre chromatography does not have convection through the pores it foregoes the short diffusion path of membrane chromatography. This kind of hollow fibre chromatography offers one way to reduce the disadvantages of conventional liquid chromatography as mentioned above (high pressure drop along the column). Ding et al. [7–9] reported the separation of low molecular weight solutes (2-butanone, 2-pentanone, 2-heptanone) and some proteins (myoglobin and cytochrome-C) using hollow fibres impregnated with organic solvents (dodecanol, dodecane, octane, etc.) in which simple physical distribution occurred. It is interesting to investigate the separation behaviour of such systems in which chemical reactions are involved to expand the applications. In a previous short communication [10], we simply demonstrated the analytical separation of metal ions with extremely close chemical similarity such as adjacent lanthanide elements and zirconium and hafnium using a single hollow fibre coated with di (2-ethylhexyl) phosphate (HDEHP) and tri-*n*-octylamine (TNOA), respectively. For high throughput applications the bundle-packed hollow fibre column is recommended, and it is expected that the hydrodynamic conditions would play a more important role on the separation. Part I of this study has shown that under the same conditions chemical resistance could be a limiting factor for mass transfer in the configuration of the hollow fibre supported liquid membrane. The aim of this part is to investigate the effects of hydrodynamic conditions and chemical resistance on the separation of zirconium and hafnium using bundle-packed hollow fibres in the configuration of membrane chromatography.

2. Theoretical considerations

In the hollow fibre membrane chromatographic system, in general, an organic stationary phase coats the surface of the hollow fibres and is held within the pores of the wall of the fibres by capillary forces, and an aqueous mobile phase flows through the fibres' lumen. The stationary phase usually contains a specific organic extractant for a specific solute. The mixed solutes loaded onto the column are eluted as peaks of separated solutes. As a result, this arrangement is similar to the elution chromatography commonly used in analytical chemistry.

According to chromatographic theory [11], the mobile phase's residence time t_m in a single hollow fibre column is given by

$$t_m = \frac{l}{v} \tag{1}$$

where l is the column length and v the velocity within the single fibre. The average retention time in the column for a solute retained by the stationary phase is

$$t_R = \frac{l}{v}(1 + k') = \frac{l}{v}\left(1 + k\frac{V_s}{V_m}\right) \tag{2}$$

where k is the partition coefficient of the solute between the stationary and mobile phases; V_s, V_m the volumes of stationary and mobile phases, respectively. $k' = k(V_s/V_m)$ is the capacity factor.

In extraction chromatography, the variances (σ^2) of the peaks of the elution curves are applied to quantitatively

characterise the curves. For the hollow fibre column filled with a stationary phase, the variance is approximate by [12]:

$$\sigma^2 = \frac{d^2 l}{96Dv}(1 + 6k' + 11k'^2) + \frac{2\sigma^2 lk'}{3D_s v} + \frac{2Dl}{v^2}(1 + k')^2 \quad (3)$$

The first term on the right-hand side of this equation represents the generalisation of Taylor's dispersion. The second term denotes the diffusion in the stationary phase, described by the diffusion coefficient D_s, while the third represents axial diffusion. Most commonly, the spread of a peak in a cylindrical tube is attributed to the Aris–Taylor dispersion, which represents coupling between axial convection and radial diffusion.

For a hollow fibre column, the Reynolds number in the fibres is typically less than 5, so the relationship between the mobile phase flow rate (v) and the pressure drop is given by the Hagen–Poiseuille law [13]:

$$v_{\text{fiber}} = \frac{d^2}{32\mu}\frac{\Delta p}{l} \quad (4)$$

For a packed bed with Reynolds number below 10, the pressure drop is found from the Carman–Kozeny equation,

$$v_{\text{bed}} = \frac{d^2\varepsilon^3}{180\mu(1-\varepsilon)^2}\frac{\Delta p}{l} \quad (5)$$

For the solute concentration within a fibre, its distribution based on the mass balance is given by

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial z} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{\partial^2 C}{\partial z^2}\right) \quad (6)$$

The first term on the left-hand side of this equation represents solute accumulation within a differential volume of hollow fibre. The second term on this side describes axial convection.

Radical convection is assumed to be small. The terms on the right-hand side result from radial and axial diffusion, respectively.This balance is usually solved for the case when the initial condition is a pulse of solutes and one boundary condition is a linear isotherm for each solute at the fibre wall. Diffusion within the wall is included in the radial direction but neglected in the axial direction. The result for each solute concentration averaged across the fibre's diameter can be written as [12,14]

$$C = c_0\, \mathrm{e}^{-(\tau-1)^2/2\sigma^2} \quad (7a)$$

where τ is a dimensionless time,

$$\tau = \frac{vt}{l(1+k')} \quad (7b)$$

The maximum concentration ($C_{\max}$) is given by [15]:

$$C_{\max} = \frac{M_0/(n\pi d^2/4)}{(2\pi)^{1/2} l\sigma(1+k')} \quad (8)$$

The HETP of a chromatographic column is defined by

$$\text{HETP} = \frac{1}{N} \quad (9)$$

where N is the number of plates,

$$N = \frac{8V_R^2}{W_e^2} \quad (10)$$

The separation coefficient for the two solutes is expressed by

$$\beta = \frac{(V_R - V_m)_2}{(V_R - V_m)_1} \quad (11)$$

Separation factor (SF) for the case of Zr/Hf is obtained by

$$\text{SF} = \frac{(C_{Zr}/C_{Hf})_{\text{eluate}}}{(C_{Zr}/C_{Hf})_{\text{feed}}} \quad (12)$$

Resolution is calculated by

$$R_s = \frac{2|V_{R2} - V_{R1}|}{W_1 + W_2} \quad (13)$$

3. Experimental

3.1. Reagents and materials

Tri-*n*-octylamine (TNOA), 2-ethyl-1-hexanol and cyclohexane were obtained from Aldrich (USA). Zirconium and hafnium stock solutions (Aldrich Chemical, USA) were 1000 mg/l (in 5% HCl). All chemicals used were reagent grade and used as received. Water purified using a Milli-Q (Millipore) system (resistivity 18 MΩ cm) was used throughout. The hollow fibre membranes, used as the support for the organic stationary phase, were kindly supplied by Akzo (Germany) and Memtec (Windsor, Australia). Table 1 lists the characteristics of the membranes used in this study.

3.2. Preparation of hollow fibre column and procedure

For single fibre columns, glass tubing (0.8–1.2 mm i.d. and 6 mm o.d.) or polyethylene tubing (Merck-Clevenot, France) with inner diameter 0.86–1.2 mm and outer diameter 1.3–1.7 mm was used as the shell for the hollow fibre. A single hollow fibre was inserted into the glass or polyethylene tubing and the two ends of the tubing were sealed with

Table 1
Characteristics of the membranes used

Membrane	Material	Outer diameter (μm)	Inner diameter (μm)	Pore size (μm)	Porosity (%)
Akzo (1#)	Polypropylene	1000	600	0.2	69
Memtec (2#)	Polypropylene	550	250	0.2	69

epoxy resin and joined to a connection tubing (0.76 mm i.d., Bioblock Scientific, Illkirch, France) for the pump. The effective length of fibre in the column was 460 mm. The organic solvent (TNOA + 2-ethyl-1-hexanol + cyclohexane) was pumped by a Gilson peristaltic pump (Minipuls 3, France) into the fibre until the fibre was completely wetted. Before use, the fibre was preconditioned with 0.5 ml of pure mobile phase (8 M HCl).

For multi-fibre columns, the fibres (number of fibres: Akzo fibre, 20 or Memtec fibre, 35) were arranged into a bundle in a glass tube (inner diameter 5 mm) and the ends were embedded using epoxy resin potting material. When the epoxy resin became hard, the plug was sliced open at the glass tube end. Special caution was taken to ensure that all the fibre bores at both ends of the fibre column were fully open. The column was positioned vertically and the organic solvent was pumped into the lumen of the fibres from the bottom of the module until all of the fibres were impregnated. The fibres were washed with 1–2 ml water at a flow rate of 0.2 ml/min to remove the excess organic solvent. Before use, the fibre was preconditioned with 2–4 ml of pure mobile phase (8 M HCl). Then, a mixture of metal ions to be separated was pumped into the column, followed by a suitable mobile phase (in upward flow from the bottom of the column, unless otherwise specified). The mobile phase (eluate) was collected in 5 ml polyethylene vessels in 0.1–1 ml fractions, in which the Zr and Hf concentrations were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Jobin-Yvon, Longumeau, France).

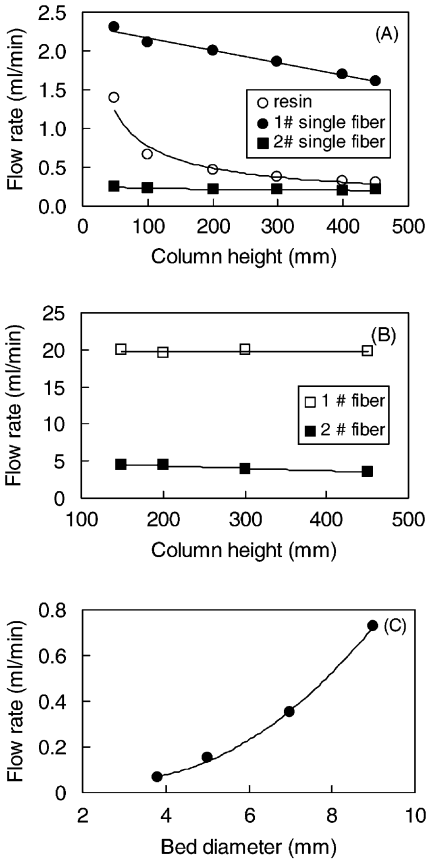

Fig. 1. Effect of length and diameter of the hollow fibre column and conventional extraction chromatographic resin column. Mobile phase: water. (A) Resin column: i.d. 5 mm, particle size, 125–200 μm and single hollow fibre columns; (B) multi-fibre column, 20 1# fibres; 35 2# fibres; (C) resin column: length = 45 mm, particle size = 80–160 μm.

4. Results and discussion

4.1. Flow resistance

If the fibre diameter equals the packing particle diameter, and if the pressure gradients ($\Delta p/l$) are the same, and the bed void fraction ε is 0.3, Eqs. (4) and (5) show that

$$\frac{v_{\text{fiber}}}{v_{\text{bed}}} = 102 \tag{14}$$

The ratio will be still larger if $\Delta p/l$ can be larger in the more rigid fibres.

The effect of length and diameter of the hollow fibre column and the conventional extraction chromatographic resin bed column on the gravity flow rate through the columns was experimentally examined and is shown in Fig. 1. It can be seen that the diameter and length of the resin bed have significant influence on the flow rate, while for the case of the hollow fibre column it can be neglected.

4.2. Breakthrough curve

Fig. 2 is the breakthrough, washing and elution curves for Zr in a single hollow fibre column. In the initial stage of loading (0–600 s, i.e. 2.5 ml), the Zr was completely retained on the fibre, then the Zr concentration in the effluent increased rapidly. After the initial stage, the adsorption of Zr was close to the saturation state and hence the Zr concentration in the effluent approached the loading concentration. After washing, the mobile phase was changed to 2 M HCl

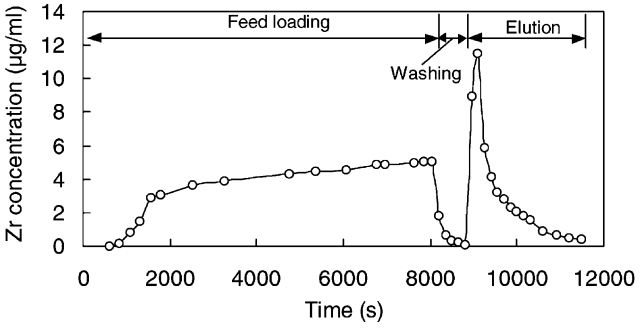

Fig. 2. Breakthrough, washing and elution curves of a single hollow fibre column. 1# fibre: length = 450 mm, 100% TNOA. Flow rate = 0.25 ml/min; feed, 5 ppm Zr in 10 M HCl. Washing 10 M HCl; elution, 0.5 M HCl.

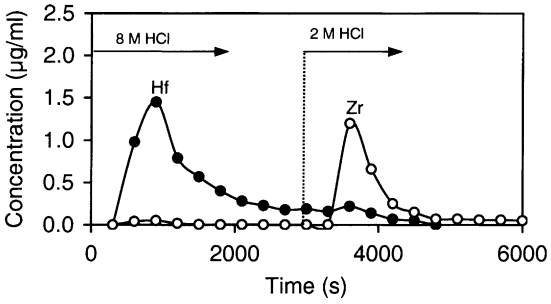

Fig. 3. Typical separation of Zr and Hf by a multi-fibre column. Column i.d. = 5 mm, packed with 35 fibres (2#), length = 450 mm, feed loading, 1 ml 10 μg/ml Zr and Hf each in 8 M HCl; stationary phase 100% TNOA; flow rate = 0.25 ml/min.

where the distribution coefficient is zero, and as a result, a sharp elution peak occurred. This is very similar to a typical separation in resin chromatography.

4.3. Typical separations

Typical chromatographic separations using single hollow fibre columns for lanthanide elements and zirconium/hafnium have been reported in previous work [10]. Fig. 3 shows separation profiles for Zr and Hf using a multi-fibres column. As expected, it shows different retention times for Hf and Zr in 8 M HCl, because they have different distribution coefficients between the stationary phase and 8 M HCl [2]. Zr has a much larger distribution coefficient than Hf and, as a result, it was retained on the fibre and Hf was eluted. When the mobile phase was changed to 2 M HCl where the distribution coefficient for Zr is very low, the retained Zr was then eluted.

4.4. Effect of flow rate

In liquid chromatography, the flow rate of the mobile phase generally has a significant effect on separation performance, because it affects the retention time of the solute within the column and in turn the distribution. Fig. 4 shows the elution curves as a function of flow rate, indicating that the separation was improved with decreasing the flow rate. When the flow rate was greater than 0.25 ml/min, two peaks of Zr elution occurred, which lead to poor separation. The retention times vary linearly with l/v showing that the lower the flow rate, the longer the retention time (Fig. 5). The SF and the HETP variation as a function of flow rate are shown in Fig. 6A and B, which clearly indicate the effect of flow rate on the separation and emphasise the advantage of low velocity operation. Fig. 6B also shows that the smaller diameter fibre has lower HETP, which is similar to the situation in resin chromatography in which smaller diameter beads have lower HETP. However, it should be pointed out that lower flow rate will potentially lead to larger variance of an elution peak, as predicted

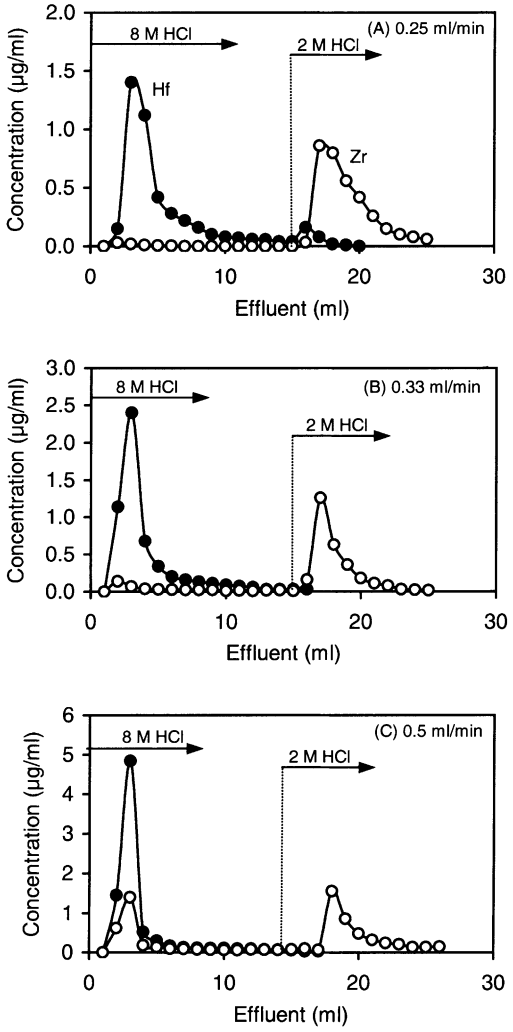

Fig. 4. Separation profiles as a function of flow rate. Column i.d. = 5 mm packed with 20 fibres (1#). 50% TNOA–cyclohexane. (A) 0.25 ml/min; (B) 0.33 ml/min; (C) 0.50 ml/min.

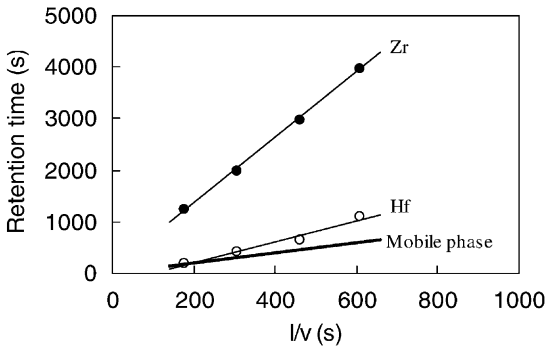

Fig. 5. Retention times of Hf, Zr and mobile phase in a hollow fibre column packed with 20 fibres (1#). Mobile phase, 8 M HCl.

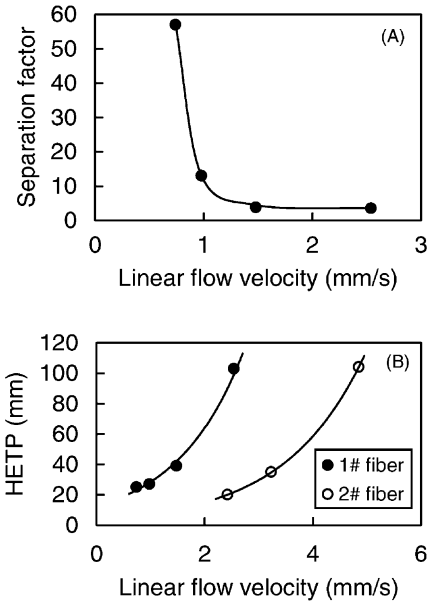

Fig. 6. SF of Zr and Hf and HETP of Hf as a function of flow velocity. (A) Column (i.d. 5 mm) packed with 20 fibres (1#); (B) (●) column (i.d. 5 mm) packed with 20 fibres (1#); (○) column (i.d. 5 mm) packed with 35 fibres (2#).

by Eq. (3). The axial diffusion within the membrane wall will result in tailing of the elution peaks, as shown in Figs. 2–4.

4.5. Effect of flow mode

So far the elution has been reported in the upward flow and it has been shown that the flow rate has a significant effect on the separation. As the diameter of the fibres and the swelling of the fibres when impregnated with organic solvent could not be identical it is expected that the flow distribution within the fibres would not be identical when the elution is carried out in the downward flow. The separation was carried out using the same column as used in Fig. 4 at a flow rate of 0.25 ml/min but the elution was in downward flow (the column was positioned vertically). It was observed that the Zr peak occurred even within 2 ml of 8 M HCl elution and the peaks of Hf and Zr overlapped (there was only a very small peak when the mobile phase was changed to 2 M HCl). The SF as a function of column flow rate (upward and downward flows) is shown in Fig. 7. At a flow rate of 0.1 ml/min, the SF of the upward flow mode was 12 times that of the downward flow mode. With increase in flow rate, the difference became smaller. The explanation could be that there are big differences in flow rates among the individual fibres in the downward flow mode, possibly because slight changes in the fibre diameters and the density effects exacerbate flow maldistribution. It was observed that flow maldistribution in the fibres became significant when the flow rate was below 0.1 and 1 ml/min for upward and downward flow, respectively. It is expected that

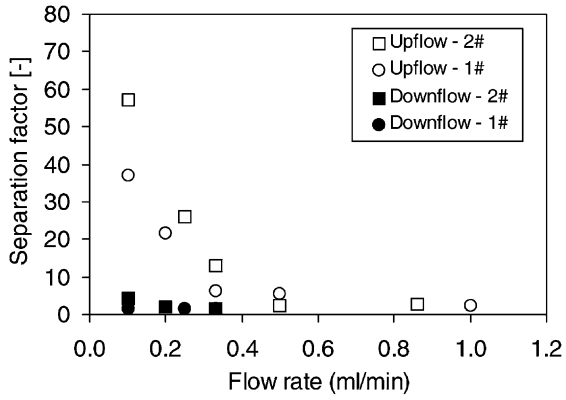

Fig. 7. Effect of flow mode (upward and downward) on the SFs of multi-fibres column. Column i.d. 5 mm packed with 20 fibres (1#) or with 35 fibres (2#), length = 450 mm; 50% TNOA.

there should be no significant difference in separation for single hollow fibre columns between the upward and downward flows mode. As expected, the differences were found to be less than 25%. Therefore, the individual fibre flow rates seriously compromise the separation in multi-fibre columns.

4.6. Effect of stationary phase concentration loaded on the fibres

In conventional extraction chromatography using particle supports, the extractant loading on the support has a significant effect on the column efficiency. Grosse-Ruyken and Bosholm [16] obtained minimum HETP values for the HDEHP/silica gel support (0.09 mm diameter) weight ratio of 1:2. Ueno and Hoshi [17] 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 found that the 1:2 ratio was the optimum extractant loading for Hf–Zr separation. In previous work [2], it has been found that the TNOA/support weight ratio of 1:2 was the optimum condition for the separation of Hf and Zr using TNOA extraction chromatographic resin. In fact, the extractant/support weight ratio in resin chromatography refers to the extractant "concentration" in the solid support particle. Therefore, it is expected that the TNOA concentration loaded on the hollow fibre membrane would have a significant influence. Fig. 8 shows the effect of TNOA concentration loaded on the hollow fibre membrane on the HETP and SF. It can be seen that at about 80% TNOA concentration there is minimum HETP for Zr and maximum SF for Hf/Zr.

The higher TNOA concentration gives higher distribution coefficient, but is more significant for Zr, which could lead to better separation. However, higher TNOA concentration has higher viscosity and this would tend to decrease the mass transfer rate more significantly of Zr than Hf. As a result, there is a compromise between increasing the TNOA concentration and improving separation.

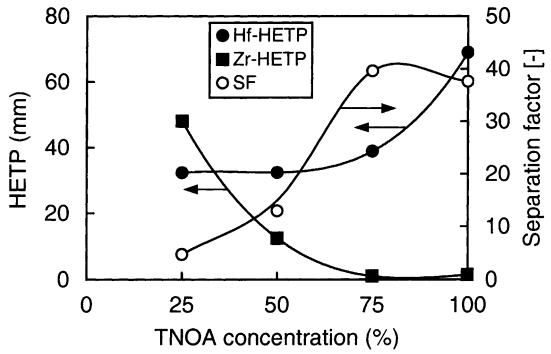

Fig. 8. Effect of TNOA concentration. Column i.d. 5 mm packed with 35 fibres (2#), fibre length = 450 mm; flow rate = 0.2 ml/min; upward flow. The varied TNOA concentrations loaded on the fibres were obtained by impregnating the fibres with different TNOA–cyclohexane solutions.

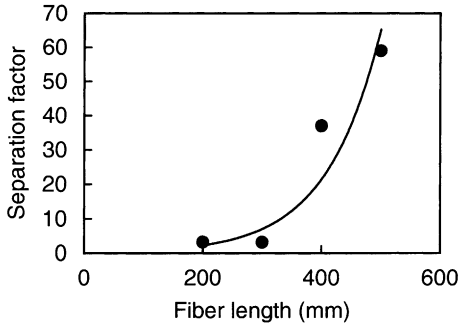

Fig. 9. Effect of fibre length on SF. 50% TNOA; 20 1# fibres, column i.d. = 5 mm; flow rate = 0.2 ml/min; Zr and Hf loading: 10 μg.

4.7. Effect of column height

Fig. 9 shows the effect of fibre length on the separation. The fibre length has a significant effect on the SF. This trend is similar to that of conventional resin chromatography. When the length increases, the partition steps between the solute and the stationary phase increases. Consequently, numerous multi-stage partition processes are obtained along the column (i.e. the numbers of theoretical plates increases). Therefore, in this case excellent separation can be obtained even for the solutes with extreme similarity. In Part I of this study that assessed the selective transport of Zr and Hf through the hollow fibre supported liquid membranes using the same organic solvent as used in this part, it was found that separation was not improved when the length of the hollow fibre was increased. This demonstrates that mass transfer processes between hollow fibre membrane chromatography and hollow fibre supported liquid membranes are different.

5. Conclusions

Hydrophobic hollow fibres impregnated with an organic extracting agent have been successfully used as a novel extraction chromatography system for the separation of Zr and Hf. The extractant was TNOA and achieved a maximum SF of 60. Fibres with a small i.d. (250 μm) had a smaller HETP than a larger fibre (600 μm i.d.). Several factors influence separation, including mobile phase flow rate (increase reduces separation) and fibre length (increase improves separation). Upflow operation worked effectively whereas downflow was unsuccessful due to flow maldistribution and density effects. Scale-up from single to multi-fibre columns will require particular attention to flow distribution.

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