



# Extraction-chromatographic behavior of Zr(IV) and Hf(IV) on TRU and LN resins in mixtures of HNO<sub>3</sub> and HF

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## Abstract

The behavior of group-4 homologs Zr and Hf on extraction-chromatographic sorbents LN resin and TRU resin in mixtures of HF and HNO<sub>3</sub> is considered. Distribution coefficients of the elements in the mixtures of  $5 \cdot 10^{-4}$  M–1 M HF and 0.01 M–5 M HNO<sub>3</sub> are determined. Strong retention of both elements was found on LN resin in the range of concentrations  $c(\text{HF}) \leq 0.01$  M for all concentrations of HNO<sub>3</sub>. Retention tends to gradually disappear while increasing  $c(\text{HF})$  to 0.5 M. On TRU resin retention is observed only in solutions with  $c(\text{HNO}_3) \geq 2$  M and  $c(\text{HF}) \leq 0.01$  M. The possibility of separating Zr(IV) and Hf(IV) on LN resin is illustrated in two different acid mixtures, whereas their separation on TRU resin under the conditions studied in this work is difficult. The results obtained can be used to isolate analytes from multicomponent mixtures during analytical tasks, as well as to separate them from each other.

**Keywords** Zirconium and hafnium · Extraction chromatography · Distribution coefficients measuring · HNO<sub>3</sub> and HF media · Radiochemical separation

## Introduction

Zirconium as metal finds application in production of parts of nuclear reactor, as it is highly resistant to corrosion, has a very low absorption cross-section of thermal neutrons and high melting point [1]. Hafnium's absorption cross-section of thermal neutrons is much greater, and its presence as impurity in zirconium leads to the degradation of anticorrosive properties. The acceptable quantity of hafnium in Zr metal, used in nuclear industry, should not exceed 100 ppm [2]. The separation of zirconium and hafnium can be a complicated task because of the similarity of chemical properties of these elements.

Three main methods are suitable for analytical separation, required for environmental and geochemical sciences: liquid extraction, ion-exchange chromatography and extraction chromatography.

One of the first systems for Hf(IV) and Zr(IV) separation using extraction chromatography was DMHP resin (di(1-methylheptyl)methylphosphonate) in HCl-NH<sub>4</sub>Cl media. Distribution coefficients of Zr(IV) and Hf(IV) reached 3664 and 629 respectively, showing a good result (SF 5.83) [3]. Systems of TNOA (tri-n-octylamine) and Aliquat 336 (tricaprylyl-monomethyl ammonium chloride) extractants in HCl media on Levetrel TNOA resin also allowed to successfully separate Hf(IV) and Zr(IV) [4]. To separate trace amounts of these elements TEVA resin in HCl media can be used—the maximum values of SF reached  $18 \pm 8$  [5].

Various sorbents are used for separating Hf(IV) and Zr(IV) by ion-exchange chromatography: Dowex 50 W-X8 in HCl media results in SF 8 [6], Marathon C also shows good results with oxalic acid as eluate, allowing to separate 99% Zr(IV) with 1% Hf(IV) as impurity [7].

Traditional system for separating Hf(IV) and Zr(IV) by liquid extraction consists of 60% TBP (tri-n-butyl phosphate) solution in kerosene and 6 M HNO<sub>3</sub> [8]. The main disadvantage of this method is the consumption of large quantities of chemical reagents, resulting in large amounts of wastes that are hard to dispose of [9]. Different ways of improving this technique are constantly being investigated. The use of various organophosphorus compounds (Cyanex-272, HDEHP (di-(2-ethylhexyl)phosphoric acid),

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etc.) and the implantation of membranes into the extraction system are considered in works [10, 11]. Mixtures of different organic extractants can result in increasing efficiency of extraction. For instance, use of TBP-Cyanex-272 instead of TBP leads to the highest SF 99.7, achieved in mixture of 0.5% (v/v) Cyanex-272 and 20% (v/v) TBP [9]. The mixture of TBP-Cyanex-923 allows to separate Zr and Hf with SF 186. The use of Alamine 336 results in less SF 9.6, but leads to less waste volumes [12].

The tasks associated with the separation of hafnium generally relate to geochronology. For determination of age of different materials, the ratios  $^{176}\text{Hf}/^{177}\text{Hf}$  are measured by TIMS and MC-ICP-MS analysis. In such cases the separation of Hf(IV) are performed on extraction-chromatographic sorbent LN resin in 2 M HCl–0.2 M HF media with yield of 91% [13, 14]. This separation can also be carried out with extraction-chromatographic sorbent TRU resin with mixture of 6 M HCl + 0.2 M HF as eluate [15].

Observation of spent U–Zr fuel, buried deep underground, is performed by the determination of Zr and U in the groundwater, as it is the only way of radionuclide migration from the deep geological repository into the biosphere. The preconcentration of Zr is performed on TRU resin in 2 M HNO<sub>3</sub> media: Zr and U are eluted simultaneously with the mixture of HNO<sub>3</sub>/NH<sub>4</sub>HC<sub>2</sub>O<sub>4</sub> (0.02 M/0.05 M) with the yield of more than 80% [16].

It is known that LN resin and TRU resin are often used for separating zirconium and hafnium for different analytical tasks. Addition of various amounts of HF leads to elution of the analytes. No detailed study on the minimum quantities of HF for this purpose has been carried out until now. The aim of our work was to study the behavior of Zr(IV) and Hf(IV) in HNO<sub>3</sub> and HF on LN and TRU resins. The resulting concentrations of acids leading to low  $K_d$  values will determine the range for quick and quantitative elution of the analytes. This data will help to improve the methods used for isolating Zr(IV) or Hf(IV) from various multicomponent mixture and separating them from each other.

## Experimental

Extraction chromatographic materials TRU resin (based on TBP and carbamoylmethylphosphine oxide, 100–150 mesh), UTEVA (based on dipentyl pentylphosphate, 100–150 mesh) and LN resin (based on HDEHP, 100–150 mesh) were purchased from TrisKem Int.

All sorption experiments were carried out using radioactive tracers

Zirconium radiotracers for this work were obtained using the following procedure. 100 mg SrO target (99.5% purity) was sealed in molybdenum foil envelope and irradiated by 30 MeV  $\alpha$ -particles. The duration of irradiation was 2 h;

the average current was 2  $\mu\text{A}$ . Gamma spectrum of irradiated target was registered,  $^{88}\text{Zr}$  (83.4 d) and  $^{89}\text{Zr}$  (78.41 h) were detected. The target was dissolved in concentrated HCl under mild heating, then evaporated to dryness and dissolved in 4 M HNO<sub>3</sub>. Zr(IV) was separated from the target material using extraction chromatography on UTEVA resin according to the previously developed procedure [17]. Target solution was loaded to the column containing 3 mL of selected sorbent. Sr(II) and Y(III) were eluted by 4 M HNO<sub>3</sub>. Zr(IV) was eluted by 0.1 M HNO<sub>3</sub>. Fractions containing Zr(IV) were evaporated to wet salts and diluted with approximately 200  $\mu\text{L}$  of 0.1 M HNO<sub>3</sub>.

Hf(IV) radiotracer was also required to perform this work. Shavings of metallic hafnium, enriched by  $^{180}\text{Hf}$  (84%), were irradiated in nuclear reactor and kept for 200 days. This target was then dissolved in 10 mL HF + HNO<sub>3</sub> (3:1) media, the obtained solution was evaporated to wet salts and subsequently dissolved in 2 ml 1 M HF + 1 M HNO<sub>3</sub>.

Aliquots of zirconium and hafnium solutions were used in the further experiments

Measurements of the activity of hafnium and zirconium in experiments were carried out on gamma peaks of following isotopes:  $^{88}\text{Zr}$  (393 keV),  $^{89}\text{Zr}$  (909 keV) and  $^{181}\text{Hf}$  (42.39 d, 133 keV and 482 keV). Gamma spectra were registered on a gamma spectrometer with a high-purity germanium detector GR 3818 (Canberra Inc, USA). The detector was calibrated by certified reference point sources ( $^{22}\text{Na}$ ,  $^{60}\text{Co}$ ,  $^{241}\text{Am}$  and  $^{137}\text{Cs}$ ) and a  $^{152}\text{Eu}$  standard solution.

Concentrations range from  $5 \cdot 10^{-4}$  M to 1 M for HF and from 0.01 M to 5 M for HNO<sub>3</sub>

Distribution coefficients under stationary conditions were determined by the following procedure. 10–50 mg of sorbent were weighed in the Eppendorf tube. 485–495  $\mu\text{L}$  HNO<sub>3</sub>, the same volume of HF and 10–30  $\mu\text{L}$  of solution containing Zr(IV) and Hf(IV) radiotracers were added to the sorbent. The mixture of sorbent and solution was centrifuged for an hour. Then 500  $\mu\text{L}$  of aqueous phase was filtered through a filter and gamma spectrum of it was registered. Temperature of 20–25 °C was maintained during all experiments. Distribution coefficients were determined by the formula (1),

$$K_d = \frac{A_0 - A_s}{A_s} \cdot \frac{V}{m} \quad (1)$$

where  $A_0$ —label activity before sorption (Bq),  $A_s$ —activity of the solution after sorption (Bq),  $V$ —volume of the solution (mL),  $m$ —mass of the sorbent (g),  $K_d$ —distribution coefficient (mL/g).

The experiment was performed at least three times at each selected concentration until convergence.

Under the selected conditions of gamma spectrum registration, the upper and lower limits of  $K_d$  values were established: 2000 and 10 respectively.

After determination of  $K_d$  values the separation of Zr(IV) and Hf(IV) was performed. The sorbent was preliminarily kept in diluted  $\text{HNO}_3$  solution for 24 h. The column (volume 3 mL, height 8 cm) was then packed with this sorbent and rinsed with 10 mL 0.1 M  $\text{HNO}_3$  solution. Aliquots of Zr(IV) and Hf(IV) solutions were mixed and brought to 1 mL volume. The resulting solution was loaded to the column and eluted with mixture of acids of selected concentration. The eluate was collected in 3 mL vials. The activity of Zr(IV) and Hf(IV) was compared to the activity of aliquots taken before the experiment. The elution profiles were drawn.

## Results and discussion

### LN resin

HDEHP, existing in solutions in the form of dimers, is the basis of the sorbent. Zirconium and hafnium bind to HDEHP via cation-exchange and solvate mechanisms. Compounds  $\text{M}(\text{NO}_3)_n\text{A}_{4-n}$  [18] are formed in a nitric acid medium. In mixtures of acids, the formation of  $\text{MA}_2(\text{HA}_2)_2$ ,  $\text{M}(\text{NO}_3)\text{A}(\text{HA}_2)_2$ ,  $\text{M}(\text{NO}_3)_2\text{A}_2 \cdot 2\text{HA}$ , and others [19] is possible (where M is  $\text{Zr}^{4+}$  or  $\text{Hf}^{4+}$  and HA is HDEHP). The structure of the complex always depends on the acidity of the medium. In dilute solutions, complexes with a greater number of ionic bonds predominate. In concentrated solutions, coordinate bonds form instead of ionic, since a high concentration of  $\text{H}^+$  in solution suppresses the dissociation of HDEHP. The complexation of  $\text{Zr}^{4+}$  and  $\text{Hf}^{4+}$  with the acid anions of the solution is a competing reaction. Hydrofluoric acid forms robust fluoride complexes  $\text{ZrF}_5^-$ ,  $\text{ZrF}_6^{2-}$ ,  $\text{HfF}_5^-$  and  $\text{HfF}_6^{2-}$  with analytes. Their formation constants are  $3.2 \cdot 10^4$ ,  $1.9 \cdot 10^3$ ,  $5.0 \cdot 10^4$  and  $3.2 \cdot 10^3$ , respectively. The literature describes a detailed study of the behavior of Zr(IV) and Hf(IV) on cation-exchange (Aminex A6 [20], CK08Y [21], CA08Y [22]) and anion-exchange sorbents (AG1X8 [20]), as well as on extraction chromatographic sorbent TTA [23] (based on 2-thenoyltrifluoroacetone). It was found that the ratio of  $K_d(\text{Zr(IV)})$  to  $K_d(\text{Hf(IV)})$  or vice versa slightly exceeds 1 in all the cases studied. Thus, the binding of analytes to HDEHP decreases with either increasing acidity of the solution or increasing the concentration of fluoride ions in it.

It is known that LN resin strongly binds both Zr(IV) and Hf(IV) in  $\text{HNO}_3$  media ( $K_d > 10^4$ ) [24]. Oxalate ions or fluoride ions tend to form soluble complexes with both Zr(IV) and Hf(IV) so they can be used to recover these elements from the column. On LN resin, recovering can be made with different concentrations of HF [13, 14, 25, 26], but no detailed research on behavior of Hf(IV) and Zr(IV) in mixtures of HF and  $\text{HNO}_3$  was ever made. As the precise values of  $K_d$  of Zr(IV) and Hf(IV) in  $\text{HNO}_3$  media is unknown, the

possibility of their separation in mixture of HF and  $\text{HNO}_3$  is yet to be discussed. To solve the above-mentioned tasks, sorption experiments under stationary conditions were carried out.

The following concentrations of  $\text{HNO}_3$  were selected for the experiment: 0.01, 0.05, 0.1, 0.5, 2 and 5 M. For each concentration of  $\text{HNO}_3$ , sorption in eight concentrations of HF was studied:  $5 \cdot 10^{-4}$ ,  $10^{-3}$ ,  $5 \cdot 10^{-3}$ , 0.01, 0.05, 0.1, 0.5 and 1 M. The results of the experiments are shown in Figs. 1, 2.

The results obtained correlate with theoretical predictions. It can be seen that both elements strongly bind to the sorbent in low concentrations of both acids. Strong nitric acid suppresses the dissociation of hydrofluoric acid and prevents the formation of fluoride complexes with metals, so the analytes bind strongly to the sorbent at concentrations of hydrofluoric acid  $\leq 0.01$  M for any concentrations of nitric acid. For the same reason,  $K_d$  in 0.05 M HF and 0.01 M HF media decreases with decreasing  $\text{HNO}_3$  concentration. Finally, HF concentrations  $\geq 0.5$  M lead to the lack of binding. In addition, hafnium binds to the sorbent stronger than zirconium at concentrations  $0.05 \text{ M} \leq c(\text{HF}) \leq 0.1 \text{ M}$ . This fact indicates the possibility of their separation under these conditions.

### TRU resin

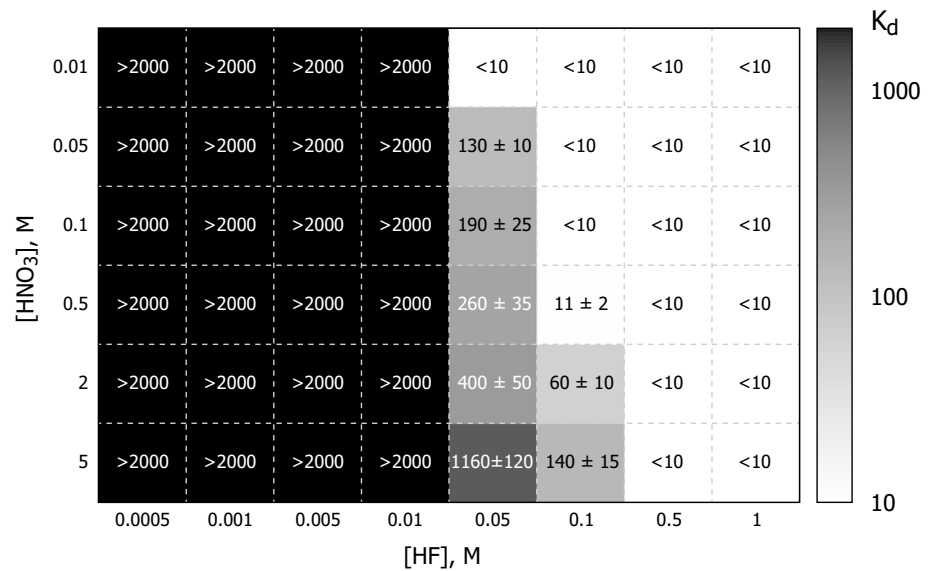
TRU resin is based on TBP and in nitric acid media forms  $\text{M}(\text{NO}_3)_4 \cdot \text{TBP}$  or  $\text{M}(\text{NO}_3)_4 \cdot 2\text{TBP}$  (here M is  $\text{Zr}^{4+}$  or  $\text{Hf}^{4+}$ ) complexes with analytes according to the solvation mechanism [27]. The formation of fluoride complexes is also a competing reaction for this process.

Basically, TRU resin is used for separating various actinides. The possibility of Zr(IV) and Hf(IV) separation in HCl and HF media was recently investigated [15]. In our previous work the behavior of Zr(IV) in  $\text{HNO}_3$  media was examined [17]. Distribution coefficients of Hf(IV) on TRU resin in  $\text{HNO}_3$  media are unknown; however, they are determined in the presence of 0.02 M HF [15]. Zr(IV) binds well to the sorbent, and similarity of Zr(IV) and Hf(IV) properties suggests that the  $K_d$  values are quite similar too.

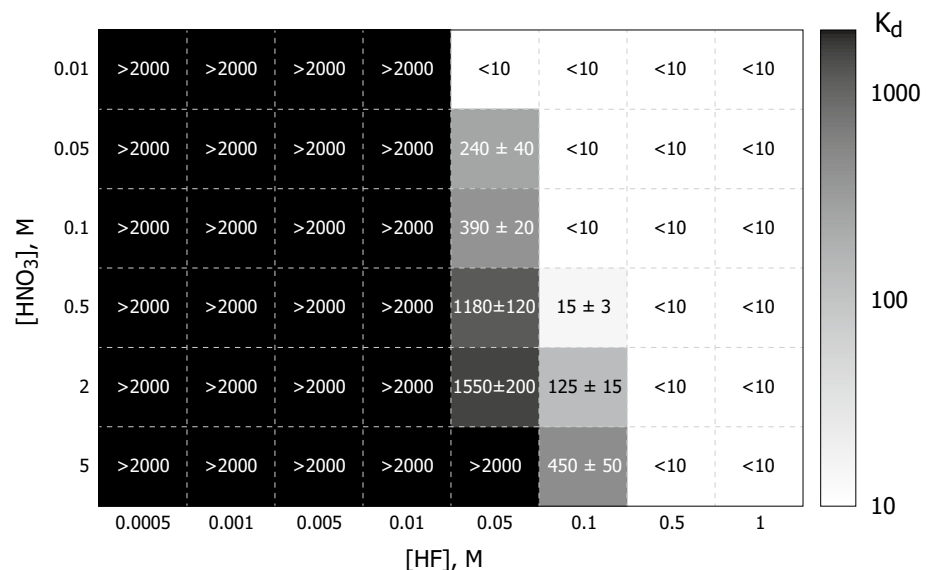
We selected the same range of HF and  $\text{HNO}_3$  concentrations for investigating the possibility of separating the elements (Figs. 3, 4).

Unlike LN resin, the elements are not retained by TRU resin in  $\text{HNO}_3$  with concentration up to 2 M in all range of HF concentrations. The only  $K_d$  values exceeding 10 was observed in 2 M and 5 M  $\text{HNO}_3$ , where nitric acid strongly suppresses the dissociation of hydrofluoric. No retention can be seen for all other selected concentration combinations of acids. The addition of even the small amounts of HF, such as  $5 \cdot 10^{-4}$  M, is sufficient for quantitative elution of analytes.

**Fig. 1** Distribution coefficients for Zr(IV) in mixtures of HF and HNO<sub>3</sub> on LN resin



**Fig. 2** Distribution coefficients for Hf(IV) in mixtures of HF and HNO<sub>3</sub> on LN resin



The similarity of  $K_d$  values from Figs. 3, 4 demonstrates the impossibility of separating Hf(IV) and Zr(IV) in the presence of HF on TRU resin. Nevertheless, it is determined that in HF concentration range from 0.01 M both cations can be eluted quantitatively. This may be important for separating multicomponent mixtures on this sorbent.

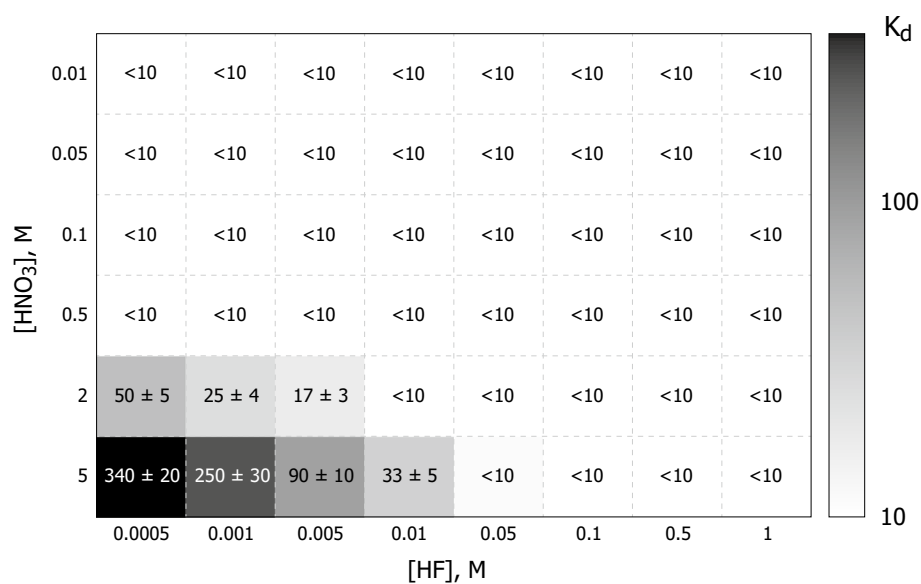
### The possibility of separating Zr(IV) and Hf(IV)

Zr(IV) and Hf(IV) can be successfully separated in HNO<sub>3</sub> + HF media on LN resin, but separation of these elements on TRU resin can hardly be achieved.

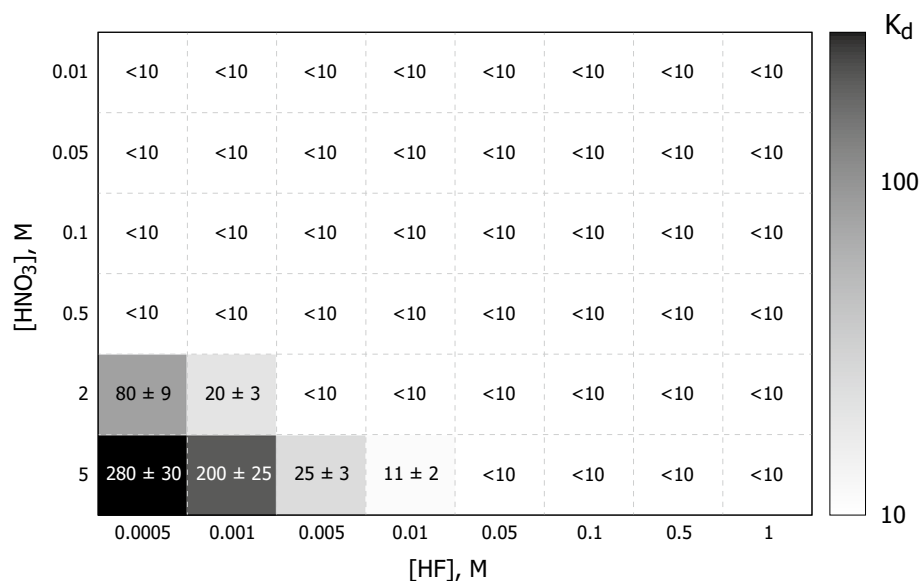
Our purpose was to illustrate the possibility of separating Zr(IV) and Hf(IV) in small (2–3 ml) columns, simulating possible analytical tasks.

Obtained values of  $K_d$  on LN resin demonstrates the possibility of separating Zr(IV) and Hf(IV) in concentration range  $0.05 \text{ M} \leq c(\text{HF}) \leq 0.1 \text{ M}$ . To illustrate this, two mixtures of acids were selected: 0.05 M HF + 0.05 M HNO<sub>3</sub> and 0.1 M HF + 5 M HNO<sub>3</sub>. Under these conditions, the difference in  $K_d$  reaches 2 and 3, and  $K_d$  take values of 130–450, which allows the analytes to be eluted fairly quickly from small columns. According to the experimental data,  $K_d$  values in these mixture differ by two–three times and the volume of solution for elution

**Fig. 3** Distribution coefficients of Zr(IV) in mixture of HF and HNO<sub>3</sub> on TRU resin



**Fig. 4** Distribution coefficients of Hf(IV) in mixture of HF and HNO<sub>3</sub> on TRU resin



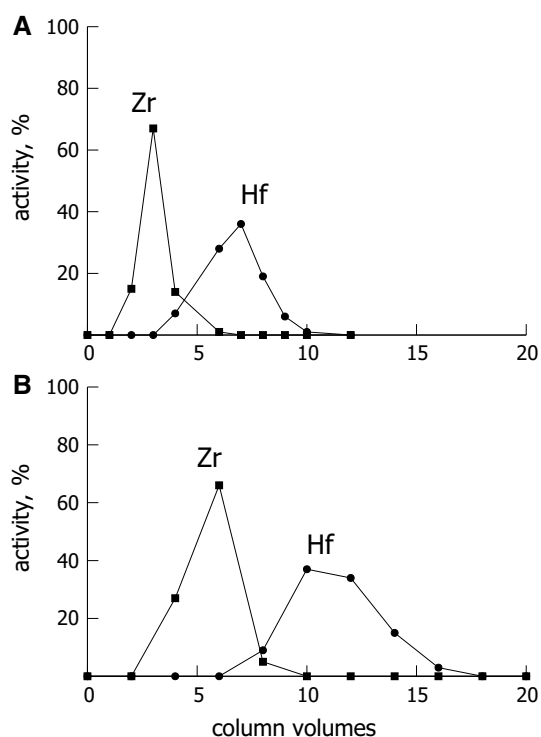
is relatively small. The results of these experiments are presented in Fig. 5.

Up to 90% of purified Zr(IV) or 85% of purified Hf(IV) can be separated in selected mixtures of acids. Quantitative separation of Zr(IV) and Hf(IV) on LN resin can probably be achieved, but require either an increased column length or larger volume of eluate in case of media change.

## Conclusions

The determination of  $K_d$  values for Zr(IV) and Hf(IV) under stationary conditions on LN resin and TRU resin in mixtures of HF and HNO<sub>3</sub> in wide range of concentrations was carried out. It is established for LN resin that the increase of HF concentration to 0.05–0.1 M caused the weakening of bonds between elements and sorbent. Quantitative separation of target element can be achieved by the proper selection of HNO<sub>3</sub> concentration in above-mentioned range of HF concentration. In case of TRU resin the elements are retained only in HNO<sub>3</sub> concentration





**Fig. 5** Elution profiles of Zr(IV) and Hf(IV) on LN resin in a mixture of **a** 0.05 M HF and 0.05 M HNO<sub>3</sub> and **b** 0.1 M HF and 5 M HNO<sub>3</sub>

higher than 2 M in low HF concentrations; otherwise, even the smallest quantities of HF prevent the elements from binding with sorbent. The separation of Zr(IV) and Hf(IV) on TRU resin in HNO<sub>3</sub> + HF media is almost impossible. Nevertheless, the determined distribution coefficients can be quite useful for separating these analytes from the elements from other groups.

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