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The Separation of Zirconium and Hafnium by Tributyl Phosphate - Celite Reversed-phase Partition Chromatography*

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The distribution ratios, K_d, for zirconium and hafnium were measured in the hydrochloric acid - TBP - celite system, the acid concentration being varied from 5 N to 8 N. The data obtained showed that the separation factor for the above elements, $K_{d_{Zr}}/K_{d_{Hf}}$, is fairly high, —4, in the 7—8 N hydrochloric acid range. Thus, the separation of these elements was carried out in 7.1 N hydrochloric acid by the use of a TBP-celite column.

Recently the technique of reversed-phase partition chromatography has been increasingly used for the separation of metal ions of similar chemical behavior. Fiedelis and Siekierski[1,2] demonstrated the application of this technique to the separation of the rare earth metals, using tributyl phosphate absorbed on kieselguhr as the stationary phase and nitric acid in various concentrations as the eluant. Crawley[3] used tributyl phosphate on kieselguhr for the separation of zirconium and hafnium in a nitric acid solution. The decontamination factor of zirconium in the recovery of 90% of the hafnium, calculated on the basis of his experimental data, was within 10^2, although hafnium was separated from zirconium excellently.

The present paper will show the mutual separation of zirconium and hafnium by reversed-phase partition chromatography, performed using tributyl phosphate absorbed on the celite as the stationary phase and hydrochloric acid as the mobile phase in order to obtain purified zirconium and hafnium.

Experimental

Reagents.—Commercial-quality tributyl phosphate was purified in the usual way.[4] Zirconium and hafnium chloride solution were prepared from analytical reagent-quality zirconium oxide and hafnium oxide respectively. All the other reagents used were of an analytical grade. hafnium-181 and zirconium-95 free from niobium-95 were chosen as the radioactive tracers for hafnium and zirconium respectively.

Batch Equilibrations.—A half grams of the TBP-celite was placed into a cylindrical vessel, then 5 ml. portions of hydrochloric acid in various concentrations were added, and finally a known quantity of zirconium-95 or hafnium-181 solution. The vessels were then closed and shaken vigorously at room temperature for 10, 30 and 60 min.

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1) S. Siekierski and I. Fidelis, *J. Chromatog.*, **4**, 60 (1960).

2) I. Fidelis and S. Siekierski, ibid., **5**, 161 (1961).

3) R. H. A. Crawley, *Nature*, **197**, 377 (1963).

4) D. F. Peppard, W. J. Driscoll and J. L. Maier, *J. Inorg. Nucl. Chem.*, **3**, 215 (1956).

After that, the aqueous layers were taken and centrifuged. Activities in 1 ml. aliquots of aqueous solutions, the equilibrium activities, C_f, were measured for the given systems. The distribution ratios, K_d, were obtained from the following equation: $K_d = \frac{C_0/5 - C_f}{C_0/5} \times 2$, where C_0 is the initial activity of the zirconium-95 or hafnium-181 added to the system. According to the equation given above, K_d values represent the ratios of activities of metal ions per gram of celite to that per milliliter of the solution.

Column Separation.—The column studies of zirconium and hafnium were carried out with a TBP-treated celite bed 0.8 cm. in diameter and 10.5 cm. high.

The material, TBP-celite, was transferred into a column, and the bed was pressed with a glass rod to eliminate air bubbles. The column was then conditioned with the same concentration of hydrochloric acid as the eluant. When one milliliter of the labeled zirconium or hafnium solution was placed on the top of the bed, it adsorbed completely. Then elution was started with eluants composed of various concentrations of hydrochloric acid. The elution rate was held at 1 ml./cm²/min.

The activity of 2 ml. samples of the eluate was determined by counting γ-rays with a well-type scintillation counter.

Results

The Separation Factor for Zirconium and Hafnium.—The first tests were made of the shaking-time dependence of the distribution ratios, K_d, between TBP-celite—hydrochloric acid with tracer-scale zirconium and hafnium in different concentrations of hydrochloric acid. As is shown in Fig. 1, the K_d values of these ions became almost constant in a shaking time of less than 10 min. Therefore, the batch equilibrium of both ions is attained in 10 min.

The K_d values of zirconium and hafnium as a function of the acid concentration are shown in Fig. 2. From these data, it may be seen that the K_d values of zirconium and hafnium increase linearly within the concentration of from 7 to 8 N of hydrochloric acid, and that hafnium is eluted more easily than zirconium by the eluant. The separation factor of these ions, $K_{d_{Zr}}/K_{d_{Hf}}$, is about 4 at each point of this acidity range.

The Loading Capacity of TBP-Celite.—The loading capacity of TBP-celite with the weight ratio of 1 : 2 was determined by the batch-equilibrium method described above. In this case, the

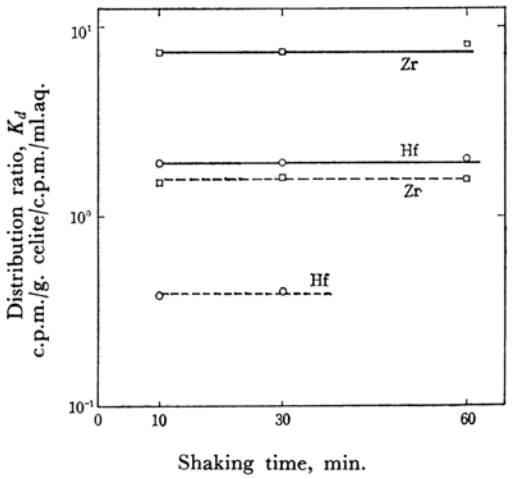

Fig. 1. Shaking time dependence of distribution ratio.
—— 7.35 N HCl
---- 6.85 N HCl
Weight ratio: TBP (1:2) celite

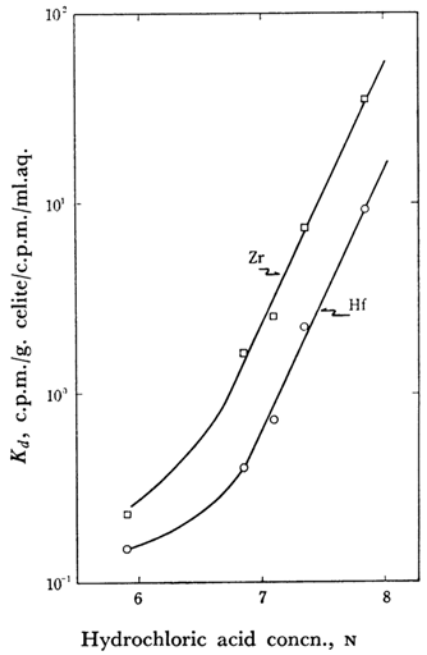

Fig. 2. K_d values of Zr and Hf dependent on HCl concentration.
Weight ratio: TBP (1:2) celite

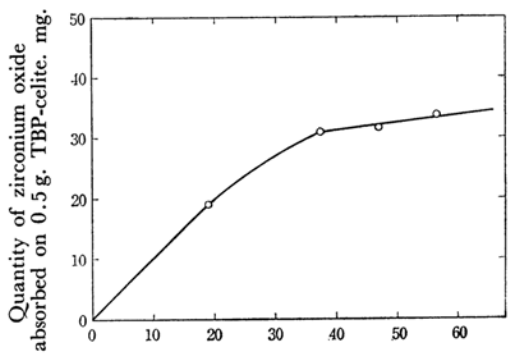

Fig. 3. The loading capacity of TBP-celite.
Weight ratio: TBP(1:2) celite

quantity of zirconium oxide in the solution was changed, while the acid concentration was kept at 9 N hydrochloric acid. As is shown in Fig. 3, the loading capacity is about 70 mg. zirconium oxide per 1 gr. TBP-celite. This number agrees with the value calculated on the assumption that the composition of the complex is $ZrO(NO_3)_2$-$(TBP)_2$.

The Separation of Zirconium and Hafnium by the Column Method.—*Acid Dependence.*—Figure 4 shows elution curves for both hafnium and zirconium. The curves for hafnium were obtained with 6.85, 7.10 and 7.35 N hydrochloric acid, and those for zirconium, with 6.85 and 7.10 N. Factors other than the acidity were kept constant. With an increase in the hydrochloric acid concentration, the curve becomes broader and the peak eluate positions are shifted to the right. Figure 5 shows the linear relationship between the peak eluate volumes in TBP-celite-reversed phase chromatography and the corresponding distribution ratio, K_d, obtained by the batch method. The values obtained fall along straight lines, with very little deviation. This fact shows the good reliability of the TBP-celite reversed-phase chromatography.

The Effect of the Amount of TBP Absorbed on the Celite.—In order to check this effect, TBP-celite absorbents with the weight ratios of 1 : 1, 1 : 2 and 1 : 4 were prepared. Figure 6 shows the relationships between the weight ratio of TBP-celite and the peak eluate volumes in this reversed-phase chromatography. The column with increasing TBP weight ratios makes the elution curve broader, and the peak eluate position shifts right for both zirconium and hafnium. This results is

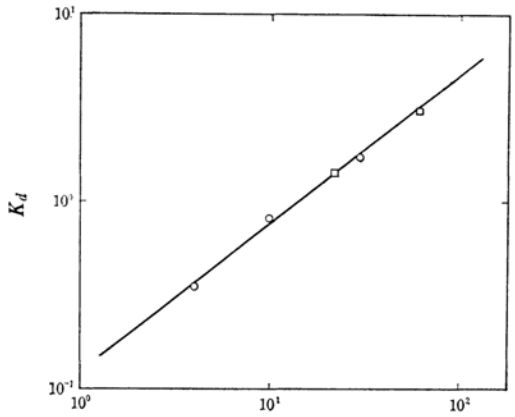

Fig. 5. Relationship between K_d values and peak eluate volume.
○ Hf □ Zr

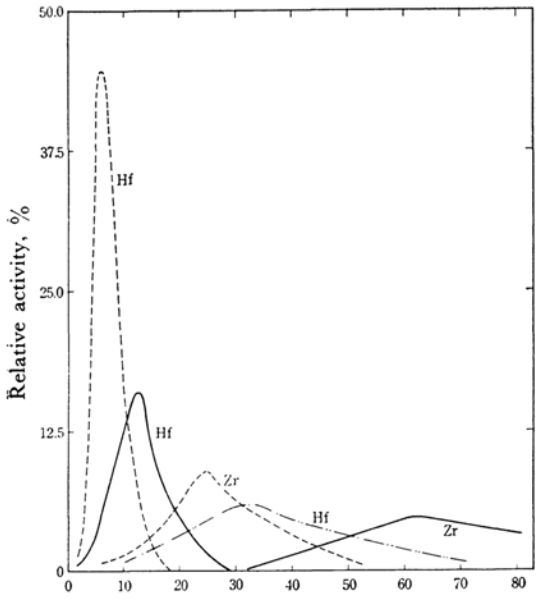

Fig. 4. Elution curves of Zr and Hf from TBP-celite with 6.85—7.35 N HCl.
Eluant
---- 6.85 N HCl
—— 7.10 N HCl
-·-·- 7.35 N HCl
Column $\phi=0.8$ cm. $h=10.5$ cm. weight ratio, TBP (1:2) celite

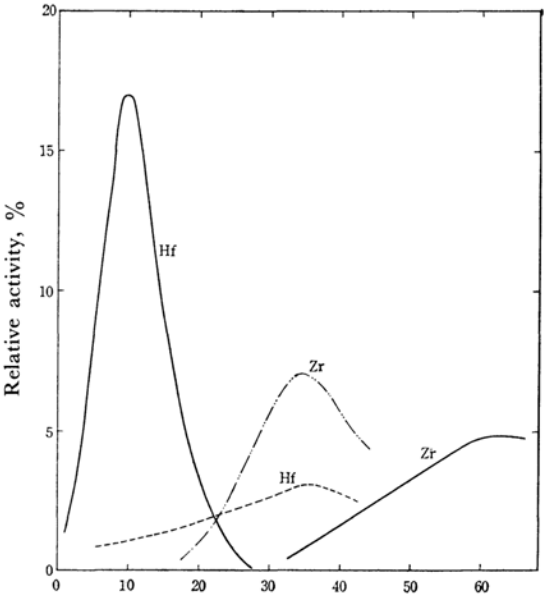

Fig. 6. Elution curves dependent on the weight ratio of TBP to celite.
Weight ratio of TBP to celite
—— TBP (1:2) celite
---- TBP (1:1) celite
-·-·- TBP (1:4) celite
Column $\phi=0.8$ cm. $h=10.5$ cm. eluant, 7.10 N HCl

similar to those obtained from a study of the hydrochloric acid concentration dependence on the elution curves.

Miscellaneous Conditions for the Separations of Zirconium and Hafnium.—In the course of this work it has been observed that the peak eluate volumes of zirconium and hafnium for a 1 : 2-weight-ratio TBP-celite column are almost independent of the amounts of these elements in the range from tracer scale to 50 mg./ml. of hydrochloric acid. After these experiments, using 7.1 N hydrochloric acid as the eluant, the separation was checked in detail with 10 mg. of zirconium and a small quantity of hafnium labeled with Hf-181. The radioactivities of hafnium in the eluate became detectable at 4 ml.; the concentration in the eluate rose to a maximum at 14 ml. and then fell off roughly symmetrically to an undetectable level.

The mutual separation of 10 mg. of hafnium and a small amount of zirconium labeled with zirconium-95 was effected, using 7.1 N hydrochloric acid as the eluant. The activities of zirconium in the eluate began to come through at 30 ml., reaching a maximum at 65 ml. and then falling gradually.

These elution curves of hafnium or zirconium are very similar to the curves obtained with pure hafnium or zirconium respectively. Several column tests like these two showed that mixtures of the two ions in weight ratios, Zr/Hf, from 1 : 1000 to 1000 : 1 bring about no change in the shapes and locations of the elution curves of zirconium and hafnium.

Finally, other factors, such as the grain size of the celite or the conditioning time with water or hydrochloric acid, were also examined. No remarkable difference caused by these factors was observed. Hafnium is separated with hydrochloric acid, leaving zirconium in the column; the zirconium remaining is easily eluted with less than

Table I. Decontamination factor

Column: $\phi = 0.8$ cm. $h = 10.5$ cm.
Weight ratio: TBP(1:2) celite

Eluant	Taken		Recovery, %		Decontamination factor	
HCl concn., N	HfO_2, mg.	ZrO_2, mg.	Hf	Zr	Zr for Hf	Hf for Zr
6.95	10	10	100		1.8×10	
			99		7.0×10	
			98		1.5×10^2	
			96		5.8×10^2	
			95		$>10^3$	
6.95	10	10		100		1.1×10
				99		7.2×10
				98		2.0×10^2
				96		$>10^3$
				95		$>10^3$
7.10	100	0.01	100		8.7×10	
			99.5		4.5×10^2	
			99		$>10^3$	
7.10	100	0.01		100		9.9×10
				99.5		9.9×10^2
				99		$>10^3$
7.10	10	10	100		1.6×10^2	
			99.5		$\sim10^3$	
			99		$>10^3$	
7.10	10	10		100		2.2×10^2
				99.5		7.1×10^2
				99		$>10^3$
7.10	0.01	100	100		1.3×10^2	
			99.5		6.6×10^2	
			99		$>10^3$	
7.10	0.01	100		100		7.2×10
				99.5		8.3×10^2
				99		$>10^3$
7.10	0.01	0.01	100		5.7×10	
			99.5		1.1×10^2	
			99		2.0×10^2	
7.10	0.01	0.01		100		2.5×10
				99.5		1.1×10^2
				99		3.6×10^2

0.01 N of oxalic acid, which is also very effective in stripping zirconium from the TBP-celite column.

From the results described above, the decontamination factors of zirconium or hafnium were calculated. These values are shown in Table I, in which values higher than 10^3 indicate that no detailed calculations could be made because of the statistical error of the counting method.

Conclusion

The mutual separation of zirconium and hafnium with reversed-phase partion chromatography, using 7.1 N hydrochloric acid as the eluant and 1 : 2-weight-ratio TBP-celite as the stationary phase, can be carried out very simply.

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