Applications of Liquid Anion Exchangers for the Separation of Zirconium and Hafnium

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Zirconium and hafnium were extracted with 0.1 M of Aliquat 336S in toluene from 0.005 M of ascorbic acid at pH 4.0. Both of the metals were stripped with 2 M hydrochloric acid. Zirconium from the aqueous phase was determined spectrophotometrically with Arsenazo III at 650 nm, while hafnium was determined with Xylenol Orange at 540 nm. The separation of zirconium from hafnium was achieved by stripping hafnium with 9 M hydrochloric acid followed by stripping zirconium with 2 M hydrochloric acid. They were also separated from associated elements in multicomponent mixtures.

Keywords Zirconium, hafnium, solvent extraction, Aliquat 336S, ascorbic acid

Because of lanthanide contraction, the chemical behavior of zirconium and hafnium is similar and, hence, the separation of zirconium from hafnium is somewhat difficult. Solvent-extraction methods, however, are most effective for the purpose of separation.

The separation of zirconium and hafnium was carried out with 60% tributyl phosphate¹ from either 6 M nitric acid or a thiocyanate media with isobutyl methyl ketone² or polyurethane³ as extractants. β -Diketones⁴ were also used. High molecular-weight amines were used in chloride⁵ or sulfate media with Primene JMT or Aliquat 336S⁶ used as the extractant.

Unfortunately, systematic investigations from organic acid solutions have been limited. Such a separation was effected from malonic acid with 0.05 M Amberlite LA-2 in xylene.⁷ The citrate buffered at pH 3.0–6.0 was also used with Amberlite LA-1.⁸ Separation from salicylate media was unsatisfactory, since it involved both masking and demasking reactions.⁹ Since studies involving ascorbic acid have been lacking, and endeavor was made to devise the separation of zirconium from hafnium from ascorbic acid with Aliquat 336S used as the extractant. It was possible to separate zirconium from hafnium as well as several other elements.

Experimental

Apparatus and reagents

The apparatus used was similar to that described earlier.¹⁰ A stock solution of zirconium was prepared by dissolving 2.50 g of zirconium nitrate pentahydrate (BDH, AnalR) in 50 ml of concentrated nitric acid. This solution was diluted to 500 ml with distilled water, and standardized complexometrically.¹¹ It contained

1 mg/ml of zirconium. A diluted solution containing 40 μ g/ml of zirconium was prepared by twenty-five fold dilution.

A stock solution of hafnium was prepared by dissolving 1.5 g of hafnium dioxide (BDH) in a mixture of hydrofluoric acid and sulfuric acid (1:1 v/v) in a platinum crucible. The dissolved solution was diluted with sulfuric acid and made up to 500 ml with distilled water. It was standardized gravimetrically with *N*-benzoyl-*N*-phenylhydroxyl amine.¹¹ It contained 2.54 mg/ml hafnium. A diluted solution containing 25.4 μ g of hafnium was prepared by hundred-fold dilution. Aliquat 336S (General Mills Ltd., UK), Amerlite LA-1 or Amerlite LA-2 or Primene JMT (Rohm and Hass Co., USA), trioctylamine (Riedel Haen, Germany) was used in the ascorbate form.

General procedure

To an aliquot of a solution containing 40 μ g of either zirconium or hafnium, 1 ml of a 0.005 M ascorbic acid solution was added. The pH of the resulting solution was adjusted to 4.0 with either 0.001 M ammonium hydroxide or 0.001 M ascorbic acid. In actual practice, less than 1 ml of these solutions were required for the pH adjustment. The solution was made up to 10 ml with distilled water; it was then transferred to a separatory funnel and shaken with 10 ml of 0.1 M Aliquat 336S in toluene for 10 min on a wrist-action flask shaker. The two phases were allowed to settle and separate. From the organic phase, either zirconium or hafnium was stripped with 2 M hydrochloric acid. The zirconium was then determined spectrophotometrically in the aqueous phase as its complex with Arsenazo III¹¹ at 660 nm; the hafnium was determined from the aqueous phase with Xylenol Orange¹¹ at 540 nm.

Fig. 1 Extraction of zirconium as a function of pH with various liquid anion exchangers. ●, 0.1 M Aliquat 336S; △, 0.1 M Amberlite LA-1; ○, 0.08 M Amberlite LA-2; ×, 0.1 M trioctylamine; □, 0.1 M Primene JMT.

Fig. 2 Extraction of hafnium as a function of pH with various liquid anion exchangers. ●, 0.1 M Aliquat 336S; △, 0.1 M Amberlite LA-1; ○, 0.08 M Amberlite LA-2; ×, 0.1 M trioctylamine; □, 0.1 M Primene JMT.

Results and Discussion

The optimum pH for a quantitative extraction of zirconium or hafnium was ascertained by extracting between pH 0.5–8.0 with various liquid anion exchangers (Figs. 1 and 2). Zirconium was quantitatively extracted with 0.1 M each Aliquat 336S at (pH 2.5–6.5), Amberlite LA-1 (pH 3.0–5.0), Amberlite LA-2 (pH 3.5–4.0), trioctylamine (pH 3.0–4.0) and Primene JMT (pH 2.0–6.0). However, the extraction of hafnium was quantitative only with 0.1 M Aliquat 336S (pH 3.0–7.5). Thus, 0.1 M Aliquat 336S was preferred as the extractant for zirconium as well as for hafnium at pH 4.0.

Extraction as a function of the Aliquat 336S concentration

Zirconium or hafnium was extracted at pH 4.0 with 0.01 to 0.1 M of Aliquat 336S in toluene (Table 1). Zirconium was extracted with 0.07–0.1 M Aliquat 336S, while hafnium was extracted with 0.06–0.1 M of Aliquat 336S. Hence, 0.1 M Aliquat 336S in toluene was used for both metals.

Extraction as a function of the ascorbic acid concentration

With other factors kept constant, zirconium or hafnium was extracted from 0.0005–0.005 M of ascorbic acid as the complexing agent. The optimum concent-

Table 1 Effect of the Aliquat 336S concentration

Aliquat 336S/M	Zirconium		Hafnium	
	%E	D	%E	D
0.01	54.0	1.1	60.0	1.5
0.02	56.0	1.2	64.0	1.7
0.03	65.1	1.8	70.0	2.3
0.04	79.0	3.7	79.0	3.7
0.05	85.2	5.7	85.0	5.6
0.06	92.1	11.6	99.0	99
0.07	99.7	332.6	99.0	249
0.08–0.1	99.7	>332	99.6	>249

Table 2 Effect of the ascorbic acid concentration

Ascorbic acid/M	Zirconium		Hafnium	
	%E	D	%E	D
0.0005	42.0	0.72	30.0	0.42
0.0006	50.0	1.0	40.0	0.66
0.0007	59.1	1.4	51.0	1.0
0.0008	62.0	1.6	59.0	1.4
0.0009	66.8	2.0	62.0	1.6
0.001	75.0	3.3	70.0	2.3
0.002	82.1	4.5	75.0	3.0
0.003	91.0	10.1	86.0	6.1
0.004	95.6	21.7	95.0	19.0
0.005–0.05	99.7	>332	99.6	>249

ration of ascorbic acid for the extraction of zirconium, as well as for hafnium, was 0.005 M (Table 2).

Effect of diluents

Various nonpolar solvents (benzene, toluene, xylene, chloroform and carbon tetrachloride) were used as the diluents (Table 3). The volume of the organic-to-aqueous phase was maintained at 1:1 in order to avoid any third-phase formation and emulsification. Zirconium was quantitatively extracted with benzene, toluene and xylene as the diluents, while hafnium was extracted with toluene and xylene. Due to the non-toxicity nature and absence of emulsification, and a clear-cut phase separation, toluene was preferred as the diluent for both metals.

Extraction as a function of the stripping agents

Zirconium or hafnium was stripped after extraction with 0.01–10 M of various mineral acids (Table 4). Zirconium was stripped with (0.5–3.0) M hydrochloric, (2.0–8.0) M nitric, and (0.1–3.0) M perchloric acids. Hafnium was quantitatively stripped with (0.5–8.5) M hydrochloric, (1.0–8.0) M nitric, (4.0–7.0) M sulfuric and (1.0–8.0) M perchloric acids. In general, 2 M hydrochloric acid was preferred as the stripping agent, since it facilitated dry ashing before a quantitative analysis.

Separation from binary mixtures

Zirconium or hafnium was extracted in the presence

of various ions. The tolerance limit was calculated in the usual way.¹⁰ The alkali and alkaline earths were tolerated in ratios of 1:125. The transition elements, however, were tolerated in ratios of 1:50; since scandium, molybdenum, uranium, thorium were coextracted, they showed a smaller tolerance limit (Table 5).

Table 5 Effect of diverse ions

Element	Added as	Tolerance limit/mg	
		Zr	Hf
Li ⁺	LiCl	5.0	5.0
Na ⁺	NaCl	5.0	5.0
K ⁺	KCl	5.5	5.0
Be ²⁺	Be(NO ₃) ₂ ·3H ₂ O	0.7	0.8
Ca ²⁺	Ca(NO ₃) ₂	5.0	5.0
Mg ²⁺	MgSO ₄ ·7H ₂ O	6.0	6.0
Sr ²⁺	Sr(NO ₃) ₂ ·2H ₂ O	4.9	4.0
Al ³⁺	Al(NO ₃) ₃ ·9H ₂ O	1.0	1.0
Ti ³⁺	Ti ₂ (SO ₄) ₃ ·7H ₂ O	2.0	2.0
Zn ²⁺	ZnSO ₄ ·7H ₂ O	2.5	2.5
Cd ²⁺	Cd(NO ₃) ₂ ·6H ₂ O	2.5	2.5
Cu ²⁺	CuSO ₄ ·5H ₂ O	0.9	1.0
Sc ³⁺	Sc(NO ₃) ₃	0.5	0.4
Ce ³⁺	Ce(NO ₃) ₃	1.0	1.0
Y ³⁺	Y(NO ₃) ₃	1.0	1.0
Ti ⁴⁺	Ti(SO ₄) ₂	0.25	0.4
V ⁵⁺	NH ₄ VO ₃	0.3	0.4
Co ²⁺	CoCl ₂ ·6H ₂ O	0.8	0.9
Cr ³⁺	Cr(NO ₃) ₃	0.9	0.8
Cr ⁶⁺	K ₂ Cr ₂ O ₇	0.8	1.2
Mo ⁶⁺	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	0.5	0.5
UO ₂ ²⁺	UO ₂ (NO ₃) ₂ ·6H ₂ O	0.3	0.2
Th ⁴⁺	Th(NO ₃) ₄	0.4	0.5
Hf ⁴⁺	Hf(NO ₃) ₄	0.4	—
Zr ⁴⁺	Zr(NO ₃) ₄	—	0.4
Cl ⁻	NaCl	1.0	1.0
SO ₄ ²⁻	Na ₂ SO ₄	1.0	1.0
NO ₃ ⁻	NH ₄ NO ₃	3.0	3.0
SeO ₃ ²⁻	Na ₂ SeO ₃	0.8	0.8
TeO ₃ ²⁻	Na ₂ TeO ₃	0.8	0.8
Cit ³⁻	citric acid	1.0	1.5
Tart ³⁻	tartaric acid	2.0	2.0
Mal ²⁻	malonic acid	2.0	2.0

Table 3 Effect of the various diluents

Diluent	ϵ	Zirconium		Hafnium	
		%E	D	%E	D
Benzene	2.28	99.0	99.0	90.0	9.0
Toluene	2.30	99.6	249.0	99.6	249.0
Xylene	2.30	99.1	110.0	99.6	249.0
Hexane	1.89	98.0	49.0	96.0	24.0
Chloroform	4.80	97.0	32.0	89.0	8.0
CCl ₄	2.24	60.0	1.5	80.0	4.0

ϵ , dielectric constant.

Table 4 Effect of the stripping agent concentration on the %recovery

Conc./M	HCl		HNO ₃		H ₂ SO ₄		HClO ₄	
	Zr	Hf	Zr	Hf	Zr	Hf	Zr	Hf
0.1	90.0	—	89.0	90.0	—	—	98.0	96.0
0.5	99.0	99.0	90.0	98.0	0	0	99.6	98.0
1.0	99.6	99.6	98.4	99.0	45.0	40.0	99.6	99.0
2.0	99.6	99.6	99.6	99.6	63.0	95.0	99.6	99.4
4.0	89.6	99.6	99.6	99.6	45.0	99.6	98.0	99.5
6.0	52.0	99.6	99.6	99.6	35.0	99.6	90.0	99.6
8.0	10.0	99.6	99.6	98.0	35.0	98.0	80.0	99.0
9.5	0.0	99.0	—	—	—	—	—	—

Table 6 Separation from multicomponent mixtures

	Metal	Taken/ μg	Found/ μg	Stripping agent/M	%Recovery	Chromogenic ligand	$\lambda_{\text{max}}/\text{nm}^{12}$
1	Ti(IV)	100	96.0	0.1 H_2SO_4 3% H_2O_2	96.0	Tiron	380
	Th	50	48.6	0.5 H_2SO_4	95.8	Arsenazo III	650
	Hf	40	39.1	9 HCl	99.1	Xylenol Orange	540
	Zr	20	19.8	2 HCl	99.0	Arsenazo III	650
2	Zr	40	39.6	6 HCl	99.6	Arsenazo III	650
	In	80	79.4	1 HNO_3	99.6	PAN	540
	Al	150	149.0	—	99.0	Alizarin Red S	520
3	Hf	100	99.6	6 HCl	99.6	Xylenol Orange	540
	Mo(VI)	100	99.1	1 HNO_3	99.1	Tiron	380
	Cr(III)	200	199	—	98.0	<i>sym</i> -diphenyl carbazide	570
4	Sc	80	79.4	0.5 H_2SO_4	99.6	Arsenazo III	670
	Zr	40	39.6	2 HCl	99.6	Arsenazo III	650
	Y	100	99.0	—	99.6	Arsenazo III	660
5	Hf	40	39.6	8 HNO_3	99.6	Xylenol Orange	540
	U(VI)	100	99.6	0.5 NaOH	99.6	Arsenazo III	665
	Fe(III)	250	248	—	99.2	1,10-phenanthroline	510
6	Zr	40	39.6	8 HNO_3	99.6	Arsenazo III	650
	Th	80	79	5 HCl	99.0	Arsenazo III	650
	U(VI)	100	99.0	0.5 NaOH	99.0	Arsenazo III	665
	Al	150	149.0	—	99.0	Alizarin Red S	510
7	Ti(IV)	100	96.4	0.5 H_2SO_4	99.6	Tiron	380
	Hf	40	39.4	9 HCl	98.6	Xylenol Orange	540
	Zr	20	19.2	2 HCl	98.4	Arsenazo III	650
	Fe(III)	250	249	—	99.6	1,10-phenanthroline	510

Separation of zirconium and hafnium

Although zirconium and hafnium were coextracted, there was a significant difference in their stripping behaviors. Thus, when hafnium was stripped with 9 M hydrochloric acid, zirconium was not stripped at all. It was stripped later with 2 M hydrochloric acid. For such a separation, the separation factor was quite large. At 2 M hydrochloric acid, the distribution ratio for both metals was 999; at 9 M hydrochloric acid the distribution ratio of zirconium was 0, while that of hafnium was 999. Consequently, the separation factor (α) was ∞ facilitating their separation (Fig. 3).

Similarly, the sequential separation of titanium, zirconium, hafnium, and thorium was accomplished after coextraction by stripping titanium with 0.1 M sulfuric acid containing 10% (v/v) of hydrogen peroxide, then thorium with 0.5 M sulfuric acid, hafnium with 9 M hydrochloric acid, and finally zirconium with 2 M hydrochloric acid (Table 6).

Separation from multicomponent mixtures

A mixture of zirconium, indium and aluminum was separated by stripping zirconium with 6 M hydrochloric acid, and indium with 1 M nitric acid when aluminum was not extracted. The mixture of hafnium, molybdenum and chromium(III) was separated by stripping hafnium with 6 M hydrochloric acid, and molybdenum with 1 M nitric acid when chromium was not extracted. Scandium, zirconium and yttrium were

Fig. 3 %Recovery of zirconium and hafnium at various concentrations of hydrochloric acid. X, hafnium; O, zirconium.

separated by stripping scandium with 0.5 M sulfuric acid, and zirconium with 2 M hydrochloric acid when yttrium was not extracted. The separation of hafnium, uranium (VI) and iron(III) was effected by stripping hafnium with 8 M nitric acid, and uranium with 0.5 M sodium hydroxide, when iron was not extracted.

The quaternary mixture of zirconium, thorium, uranium and aluminum was separated by stripping zirconium with 8 M nitric acid, thorium with 5 M hydro-

chloric and, finally, uranium with 0.5 M sodium hydroxide, when aluminum was not extracted. A mixture of titanium, zirconium, hafnium, and iron(III) was separated by stripping titanium with 0.5 M sulfuric acid, hafnium with 9 M hydrochloric acid, and zirconium with 2 M hydrochloric acid when iron was not extracted (Table 6).

The total time required for the separation and determination was just 30 min. The significant features concerning this method are the sequential separation of titanium, zirconium, thorium and hafnium. Separation from chromium, vanadium, uranium and molybdenum is important since they are associated in minerals. This method is simple, rapid, selective and reproducible. The relative standard deviation is $\pm 1.2\%$.

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References

1. J. Hure, M. Rastiox, R. Saint-James, *Anal. Chim. Acta*, **25**, 1 and 118 (1961).
2. W. Fischer, B. Deierling, H. Meitsch, G. Otto, H. P. Pohlmann and K. Reinhardt, *Angew. Chem., Int. Ed. Engl.*, **5**, 15 (1966).
3. J. Liu and A. Chow, *Talanta*, **34**, 331 (1987).
4. A. K. De, S. M. Khopkar and R. A. Chalmers, "Solvent Extraction of Metals", Van Nostrand Reinhold, London, 1970.
5. E. Cerrai and C. Testa, *Energia Nucleare*, **6**, 707 and 768 (1959); Chem. Abstr., **54**, 10713h.
6. I. S. El-Yamani, M. Y. Farah and F. A. Abd El-Aleim, *Talanta*, **25**, 534 (1978).
7. R. R. Rao and S. M. Khopkar, *Indian J. Chem.*, **23A**, 504 (1984).
8. C. P. Vibhute and S. M. Khopkar, *Anal. Chim. Acta*, **193**, 387 (1987).
9. N. M. Sundaramurthi and V. M. Shinde, *Analyst* [London], **114**, 201 (1989).
10. M. A. Karve and S. M. Khopkar, *Anal. Sci.*, **8**, 77 (1992).
11. A. K. Mukherji, "Analytical Chemistry of Zirconium and Hafnium", pp. 51, 23, 75, 76, Pergamon Press, Oxford, 1970.
12. F. D. Snell, "Photometric and Fluorimetric Methods of Analysis", Part I and II, Wiley Interscience, New York, 1978.

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