

Liquid-liquid Extractive Separation of Hafnium with Liquid Anion Exchangers from Malonate Solution

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Hafnium is quantitatively extracted with 0.05 *M* Amberlite LA-2 in xylene at *pH* 2.8-5.0 from 0.1 *M* malonic acid. It is stripped with 0.6 *M* perchloric acid and determined spectrophotometrically at 540 nm with xylenol orange. Hafnium has been separated from elements such as alkali and alkaline earths, silver, thallium(I), iron(II), arsenic(III), and yttrium since they are not extractable with hafnium; zinc, cadmium, nickel, cobalt, manganese(II), aluminium and chromium(III) are separated from hafnium by selective stripping with water. The separation of hafnium from zirconium is possible in a wide concentration range. Analysis of hafnium in high purity metal as well as in its ore, zircon, is also reported.

Although many extractants¹ have been developed for the solvent extraction of hafnium, invariably in most cases zirconium is co-extracted. As such liquid anion exchangers have scarcely been used². The primary and secondary amines³ are not efficient for the extraction of anionic chloro complexes of hafnium. Co-extraction of zirconium and hafnium with trioctylamine has been reported⁴, but by the process of multistage counter current extraction in the series could be eliminated. Methyl di-*n*-octylamine, is known to extract hafnium from concentrated hydrochloric acid⁵. The extractions with trioctylamine⁶ and Alamine 336⁷ from sulphuric acid are not quantitative but such extractions with Primene JM-T⁸ or Adogen 364⁹ are quantitative. Though the extraction of Hf(IV) from oxalate solution and nature of extracted species have been studied, so far no systematic investigations have been made for extractive separations from the dicarboxylic acid solutions.

This paper presents such studies with Amberlite LA-2 as an extractant from malonate solution. The new methods are suggested for the separation of mixtures; analysis of hafnium in its ore is also reported.

Materials and Methods

A digital *pH* meter, type 822 (ECIL, India) with glass and calomel electrodes, an ECIL GS 866 C spectrophotometer with matched 10 mm Corex glass cells and a wrist-action flask shaker, were used.

Hafnium oxide (0.45 g) was dissolved in a mixture of hydrofluoric and sulphuric acid (9:1). After digestion and evaporation, the cooled mass was leached with hot dil. sulphuric acid and made upto 100 ml with distilled water maintaining an acidity of 0.4 *M*. The solution was standardised gravimetrically¹¹ and was found to contain 3.4 mg/ml of hafnium. A solution,

containing 34 $\mu\text{g/ml}$ hafnium was prepared by appropriate dilution. Xylenol orange (BDH, AR), a 0.05% aqueous solution of xylenol orange in 0.3 *M* perchloric acid and malonic acid (Riedel-de Haen, Germany) were used. Amberlite LA-1 and LA-2, Primene JM-T (Rohm and Haas, Philadelphia, USA), Aliquat 336S (General Mills Ltd, USA), trioctylamine and triisooctylamine (Riedel-de Haen, Germany) were used as such and were converted into the malonate forms as per the procedure described earlier¹².

General procedure

An aliquot of solution containing 34 $\mu\text{g/ml}$ hafnium was mixed with 1 *M* malonic acid (1 ml), the *pH* of the solution adjusted to 4.0 with dil. sodium hydroxide or malonic acid and the solution made upto 10 ml. Amberlite LA-2 in xylene (0.05 *M*, 10 ml) was added and the mixture shaken for 5 min on a wrist-action flask shaker. After allowing the two phases to settle and separate, the organic phase was equilibrated with 0.6 *M* perchloric acid (10 ml) to back-strip hafnium. It was then mixed with 0.05% xylenol orange (3 ml) and the volume made upto 25 ml. The absorbance of the violet red coloured complex was measured spectrophotometrically at 540 nm against a reagent blank and the amount of hafnium computed from the calibration curve¹³.

Results and Discussion

Optimum conditions for quantitative extraction of Hf(III)

The optimum *pH* for quantitative extraction of hafnium was 2.8-5.0 with Amberlite LA-2, 4.0-4.5 with Amberlite LA-1, 2.0-4.0 with Primene JM-T, 3.0-4.0 with Aliquat 336S. The extraction was incomplete with

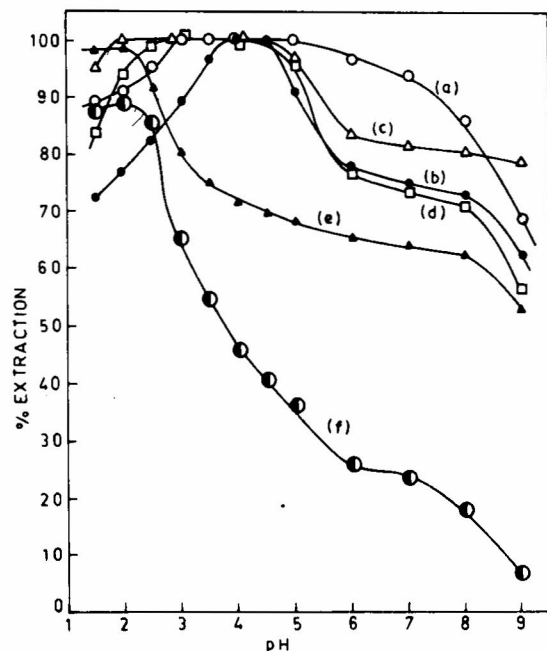


Fig. 1—Extraction of Hafnium(IV) from Malonate Media with various 4% solutions of Liquid Anion Exchangers in Xylene [(a) Amberlite LA-2, (b) Amberlite LA-1, (c) Primene JM-T, (d) Aliquat 336S, (e) TOA, (f) TIOA]

trioctylamine and triisooctylamine. Extraction with Amberlite LA was quantitative (Fig. 1). There was problem of emulsification with Primene JM-T or Aliquat 336S but it was circumvented by separating two phases on a high speed centrifuge (4000 rpm).

Extraction was quantitative in the presence of xylene, toluene, hexane, cyclohexane and kerosene as the diluents (Table 1). Extraction per cent decreased with increase in the dielectric constant of the diluent (Table 1). Isobutyl methyl ketone was a poor diluent due to its high dielectric constant. Xylene was found to be the best diluent for all practical purposes.

Varying the concentration of malonic acid from $0.5 \cdot 100 \times 10^{-2} M$ showed that the extraction commenced from $0.5 \times 10^{-2} M$ malonic acid and it was quantitative with $8 \cdot 30 \times 10^{-2} M$ malonic acid. At higher concentration, the per cent extraction decreased on account of the existence of the competitive equilibria between anionic malonato complex of hafnium and excess of free malonate anion.

The hafnium was extracted at pH 4.0 from 0.1 M malonic acid with varying concentrations of Amberlite LA-2 in the range $0.4 \cdot 5 \times 10^{-2} M$ with xylene as the diluent (Table 2). The extraction with $1.6 \times 10^{-2} M$ of Amberlite LA-2 was 90% and 100% from $4.4 \times 10^{-2} M$ of the exchanger.

After the extraction, hafnium was stripped with various mineral acids and bases. Stripping was quantitative with 2-4 M hydrochloric acid, 4-8 M nitric acid or sulphuric acid, 0.5-8 M perchloric acid, 0.2-1 M

Table 1—Effect of Various Diluents on Extraction of Hafnium

Hf(IV) = 34 μ g; [Amberlite LA-2] = 0.05 M; pH = 4.0; [Malonic acid] = 0.1 M

Diluent	Dielectric constant	Extraction, (%)	Distribution ratio (D)
Hexane	1.89	100.0	∞
Cyclohexane	2.05	100.0	∞
Kerosene	2.13	100.0	∞
Carbon tetrachloride	2.24	94.1	15.95
Benzene	2.28	97.8	44.46
Xylene	2.30	100.0	∞
Toluene	2.38	100.0	∞
Chloroform	4.80	96.3	26.03
Isobutyl methyl ketone	13.10	49.3	0.97

Table 2—Effect of Varying Amberlite LA-2 Concentration on Extraction of Hafnium

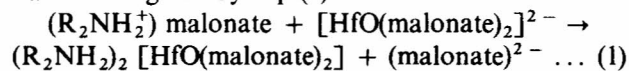
Hf(IV) = 34 μ g; pH = 4.0; [Malonic acid] = 0.1 M

[Amberlite LA-2] $1 \times 10^{-2} M$	Extraction, (%)	Distribution ratio (D)
0.4	39.9	0.66
0.8	74.3	2.89
1.2	86.5	6.41
1.6	91.9	11.35
2.0	94.6	17.52
2.4	96.3	26.03
2.8	97.3	36.04
3.2	98.0	49.00
3.6	98.7	75.92
4.0	99.2	124.00
4.4	100.0	∞
5.0	100.0	∞

of sodium or potassium carbonates and 4 M of potassium chloride or potassium nitrate. The hydroxides of ammonium or sodium were poor stripping agents due to hydrolytic precipitation of hafnium. For practical purposes 0.6 M perchloric acid was most effective stripping agent.

Nature of the extracted species

The possible mechanism for the extraction of hafnium is given by Eq. (1).



This was also confirmed by the plots of $\log D$ versus $\log$ [Amberlite LA-2] (from 0.1 M malonic acid) and $\log D$ versus $\log$ [malonic acid] (by 0.08 M Amberlite LA-2). The slopes were 2.03 and 1.85 respectively, indicating the probable composition of the extracted species as $(R_2NH_2)_2 [HfO(\text{malonate})_2]$.

Table 3—Separation of Hafnium from Tertiary Mixtures

[Amberlite LA-2] = $8 \times 10^{-2} M$; pH = 4.0

No.	Mixture	Hf(III) (μ g)		Recovery, (%)	Eluent
		Taken	Found		
1.	Cr(III)	1400	1396.0	99.7	Water
	Ti(IV)	550	549.2	99.8	0.5 M H_2SO_4
	Hf(IV)	34	34.0	100.0	2 M HCl
2.	Cr(III)	1240	1236.5	99.7	Water
	Fe(III)	3000	2994.6	99.8	0.5 M H_2SO_4
	Hf(IV)	34	34.0	100.0	2 M HCl
3.	Ni(II)	1500	1497.4	99.8	Water
	Fe(III)	3000	2992.5	99.7	0.5 M H_2SO_4
	Hf(IV)	34	34.1	100.3	2 M HCl
4.	Co(II)	1100	1098.2	99.8	Water
	V(V)	800	799.4	99.9	0.5 M H_2SO_4
	Hf(IV)	34	34.0	100.0	2 M HCl
5.	Ti(IV)	1100	1098.6	99.9	0.5 M H_2SO_4
	Hf(IV)	34	34.0	100.0	9 M HCl
	Zr(IV)	800	798.4	99.8	2 M HCl
6.	Sc(III)	1200	1199.2	99.9	0.5 M H_2SO_4
	Hf(IV)	34	34.1	100.3	9 M HCl
	Zr(IV)	800	797.0	99.6	2 M HCl
7.	Fe(III)	2500	2494.8	99.8	0.5 M H_2SO_4
	Hf(IV)	34	34.2	100.5	9 M HCl
	Zr(IV)	1240	1235.1	99.6	2 M HCl
8.	Hf(IV)	34	34.0	100.0	8 M HNO_3
	Th(IV)	740	739.0	99.8	6 M HCl
	U(VI)	1200	1197.6	99.8	0.5 M HCl

Separation of hafnium from binary mixtures

Hafnium was separated from alkali and alkaline earths, thallium(I), iron(II), silver, arsenic(III), tin(IV) and yttrium as at pH 4, these metal ions formed malonato complexes and hence were not extracted with hafnium; zinc, cadmium, nickel(II), cobalt(II), manganese(II), aluminium and chromium(III) formed weak malonato complexes and were subsequently scrubbed with water before stripping hafnium.

After the extraction of hafnium with either bismuth, antimony, mercury, thallium or gold, hafnium was first stripped with 2 M hydrochloric acid, while other elements were subsequently stripped with 0.5 M sodium hydroxide. The separation of hafnium from uranium(VI) or gallium, was achieved by first stripping hafnium with 6 M hydrochloric acid followed by stripping uranium or gallium with 0.5 M hydrochloric acid.

The most interesting separation was that of hafnium from zirconium in the ratio of 1:80. Thus after extraction, hafnium was first stripped with 9 M hydrochloric acid while zirconium was back-extracted later with 2 M hydrochloric acid.

After extraction of indium and thorium alongwith hafnium, hafnium was first stripped with 4-8 M nitric

acid; indium or thorium were later stripped with 0.5 M nitric acid.

After extraction of copper, scandium, titanium, vanadium, iron or cerium, all these elements were stripped with 0.5 M sulphuric acid and hafnium was later stripped with 0.6 M perchloric acid. All above separations were possible in the ratio of 1:10.

Separation from tertiary mixtures

The results of separation of ternary mixtures containing hafnium as one of the component are presented in Table 3. The separation of hafnium from ternary mixtures containing (i) chromium(III), titanium(IV) and hafnium(IV), and (ii) chromium(III), iron(III) and hafnium(IV) was affected as follows: Chromium was stripped with water, followed by stripping of titanium or iron with 0.5 M sulphuric acid and hafnium with 2 M hydrochloric acid (Table 3).

Similarly, ternary mixtures of nickel(II), iron(III) and hafnium(IV), or cobalt(II), vanadium(V) and hafnium(IV), were separated by stripping nickel or cobalt with water, iron or vanadium with 0.5 M sulphuric acid and finally hafnium was stripped with 2 M hydrochloric acid.

The separation of either titanium(IV), hafnium(IV)

and zirconium(IV) or scandium(III), hafnium(IV) and zirconium(IV) or iron(III), hafnium(IV) and zirconium(IV) was achieved by first stripping titanium or scandium or iron with 0.5 M sulphuric acid, followed by that of hafnium with 9 M hydrochloric acid and finally zirconium was stripped with 2 M hydrochloric acid.

Hafnium(IV), thorium(IV) and uranium(VI) were separated by first stripping hafnium with 8 M nitric acid, then thorium with 6 M hydrochloric acid and finally uranium with 0.5 M hydrochloric acid. Invariably the volume of stripping agents was 10 ml and the elements in the aqueous phase were determined spectrophotometrically with appropriate chromogenic ligand¹⁴.

Analysis of hafnium in zircon

A sample of finely powdered zircon (0.5 g) was fused with a mixture (5 g) of sodium hydroxide and sodium peroxide in a platinum crucible. The mass was cooled and water (50 ml) added, and digested on a steam-bath. The solution was filtered to remove soluble silicates. The precipitate was dissolved in conc. sulphuric acid (2 ml) and the volume made upto 200 ml with distilled water. An aliquot of sample solution was taken and extracted as per the general procedure. The extracted titanium and iron were stripped with 0.5 M sulphuric acid, hafnium with 9 M hydrochloric acid and finally zirconium with 2 M hydrochloric acid. From quadriplate determinations, the amount of hafnium

was found to be 1.38, 1.41, 1.42 and 1.39% against the reported value of 1.4%.

The proposed method is rapid, simple and selective and applicable at trace concentrations. The separation of hafnium from elements of the same group like titanium, zirconium and thorium is significant. The separation of hafnium from scandium, uranium, thorium and zirconium is also significant as they are generally associated in fission products.

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