

Solvent and Reversed-Phase Extraction Chromatographic Separation of Niobium, Zirconium, and Hafnium with Aliquat 336

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(Received December 10, 1987)

Aliquat 336 has been employed as an effective anionic extractant for the radiochemical separation of niobium, zirconium, and hafnium in mixtures using solvent extraction and reversed phase extraction chromatography (RPEC). In solvent extraction, niobium and zirconium are extracted with reagent solutions in the respective concentration ranges <0.001 – 0.04 mol dm⁻³ and 0.5 mol dm⁻³ leaving hafnium in the aqueous phase. In RPEC, niobium and zirconium are extracted by the reagent impregnated column and hafnium is completely eluted with water. Zirconium and niobium subsequently are eluted successively with 0.5 mol dm⁻³ HNO₃ and 1 mol dm⁻³ HF solutions. Distribution studies indicate that the extracted species for niobium and zirconium are respectively mono- and dinegative in charge. The extent of separation and the purity of the separated species were verified by means of gamma-ray spectrometry.

Zirconium and hafnium constitute the most important congeneric pair of elements in the periodic system and their similarity, both in the metallic state and in their compounds, is greater than that of any other homologous elements. It is not surprising that they invariably accompany each other in nature. With respect to elemental purity, their mutual separation has always been problem for analytical chemists. Moreover, in radiochemical separations of zirconium from hafnium, the presence of niobium must be taken into account since ⁹⁵Zr always occurs in equilibrium with its daughter isotope, ⁹⁵Nb.

Amongst the analytical procedures generally used in their separation study, solvent extraction^{1–6} and reversed-phase extraction chromatography (RPEC) using various organic extractants^{7,8} are found to be very effective. Survey of literature⁹ reveals that the liquid exchangers, namely, the high-molecular-weight organo-nitrogenous compounds, in general, show very promising features in liquid-liquid extraction applications^{10–13,14a} such as nuclear fuel processing and fission product recovery.^{14b} Similarly, in RPEC^{15–17} also, the column loaded with strong organic base is mainly devoted to the use of quaternary ammonium compounds as the stationary phase for various separation studies. In this regard, the quaternary ammonium salt, Aliquat 336 (tricaprylmethylammonium chloride), although displaying very high selectivity for different elements under specific experimental conditions as an anion exchanger involving solvent extraction as well as RPEC, it has not yet been fruitfully utilized for the individual separation of the concerned elements in a mixture.

With these facts in view, in the present study, attempts have been made to develop effective solvent extraction and RPEC procedures for tracer scale separation of the critical element pair, zirconium–hafnium, in admixture with niobium using the quaternary ammonium compound, Aliquat 336, as the liquid anion exchanger.

Experimental

Reagents. Aliquat 336 of molecular weight 404.17 was procured from Aldrich Chemical Co., Inc. USA. All other reagents used were of analytical grade. The carrier-free radioisotopes, ⁹⁵Zr (65d) and ⁹⁵Nb (35d) in hydrochloric acid solution and ¹⁸¹Hf (44.6d) as HfO₂ of high specific activity were supplied by BARC, Trombay, India. HfO₂ powder was dissolved in the minimum quantity of a mixture of hydrofluoric and nitric acids and then diluted with water as required.

Solvent Extraction. Extractant stock solutions of desired concentrations were prepared by adding the necessary amount of Aliquat 336 to the nonpolar diluent cyclohexane, together with 3% (v/v) octanol as phase modifier. About 20 ml of the aqueous feed containing the mixture of the radio-tracers, ⁹⁵Zr–⁹⁵Nb and ¹⁸¹Hf ($<10^{-7}$ mol dm⁻³) in acid medium were shaken with equal volumes of the extractant solution for ten minutes. Following separation, elements present in both phases were measured radiometrically. The optimal condition for complete separation of the tracers were such that niobium was first extracted from 9 mol dm⁻³ HCl solution with Aliquat 336 in cyclohexane in the concentration range <0.001 – 0.04 mol dm⁻³ leaving zirconium and hafnium in the aqueous phase. In the second stage, zirconium was separated from hafnium with 0.5 mol dm⁻³ extractant solution, whereby hafnium remained entirely in the aqueous phase.

RPEC. For the separation of the tracer mixture, the extraction column of hydrophobised kieselguhr impregnated with the exchanger, Aliquat 336, was prepared and preconditioned.^{18,19} When the tracer species, i.e., ⁹⁵Zr–⁹⁵Nb and ¹⁸¹Hf in dilute hydrochloric acid solution was loaded on the top of the column, hafnium emerged without being extracted by the reagent, whereas zirconium and niobium remained completely absorbed on the column. Subsequently, zirconium and niobium were successively separated by elution with nitric (0.5 mol dm⁻³) and hydrofluoric (1 mol dm⁻³) acids respectively. A flow rate of 10–12 drops per minute was maintained with the aid of a peristaltic pump. Radioactivity present in different fractions of the effluents was measured by means of a GM counter.

In both methods, the extraction or elution of each species

was first tested with individual tracers under identical experimental conditions.

Results and Discussion

Solvent extraction and RPEC procedures, though independent, appear to be inter-related in that they follow similar types of extraction mechanisms. In solvent extraction, elements which have a higher affinity for the extractant are easily extracted in the organic phase, leaving others in the aqueous phase. In the RPEC system, a mixture of metal ions is percolated through the column of inert material impregnated with an organic exchanger, and elements which are readily bound to the extractant molecules are extracted in the column by the extractant and subsequently eluted by means of suitable agents. Elements with low affinity for the reagent come out of the column by simple washing with water. Depending on experimental conditions, both procedures may thus be applied to the separation of the critical pair of elements, zirconium and hafnium in the presence of niobium.

Aliquat 336 is amphiphilic in nature, i.e., the molecule has a polar end and a long hydrophobic alkyl chain. The simultaneously hydrophobic-hydrophilic nature of the extractant is essential in maintaining both a high solubility in diluents with low dielectric constant and a high complexing power with respect to inorganic metal species. These reagents are accordingly characterized by high interfacial activity and enhanced extracting power. Reaction of the surface-active reagent with the metal ion takes place at the interface. The nonpolar alkyl groups surround the metal complex formed at the interface and solubilize it in the bulk organic phase. In this case the extractant and the extractant metal complex can undergo aggregation and disaggregation processes which can affect

the distribution ratio value appreciably.

The higher efficiency of the quaternary salts is understandable for conditions under which the extraction mechanism is of the ion-association or ion-exchange type; in such instances, the charge of the metal anionic complexes in aqueous medium is balanced by salts which results in the formation of neutral species.²⁰⁾

Niobium and zirconium, unlike hafnium, tend to form negatively charged species in the acidic medium and are extracted to a different extent by Aliquat 336, depending upon the types of the acids and their acidities. In the present study, it was observed that the difference in the extent of extraction is especially pronounced in hydrochloric acid medium. It is also evident from Fig. 1 that the extent of extraction of zirconium along with its niobium daughter increases with increasing acid concentration, complete extraction occurring at 9 mol dm^{-3} HCl. However, hafnium has a lower tendency to form anionic complexes under these conditions, and remains unextracted by Aliquat 336 in the concentration region where niobium and zirconium are extracted. At higher acid concentrations viz., at about 10 mol dm^{-3} HCl, hafnium is extracted to a slight extent.

The concentration of the reagent is important, 0.5 mol dm^{-3} reagent solution extracting both niobium and zirconium completely from the aqueous solution and leaving hafnium in the aqueous phase. Niobium can be separated from the mixture with a lower concentration of the reagent. Extraction of niobium begins at $<0.001 \text{ mol dm}^{-3}$ reagent and is complete at 0.04 mol dm^{-3} reagent. Whereas the extraction of zirconium starts at about 0.05 mol dm^{-3} reagent, other conditions remaining same (Fig. 2).

It is evident from Fig. 3 that under conditions of RPEC, the extractional behavior of these elements corresponds closely to that of the solvent extraction. When the mixture is absorbed on the column impregnated with Aliquat 336, hafnium elutes quantitatively

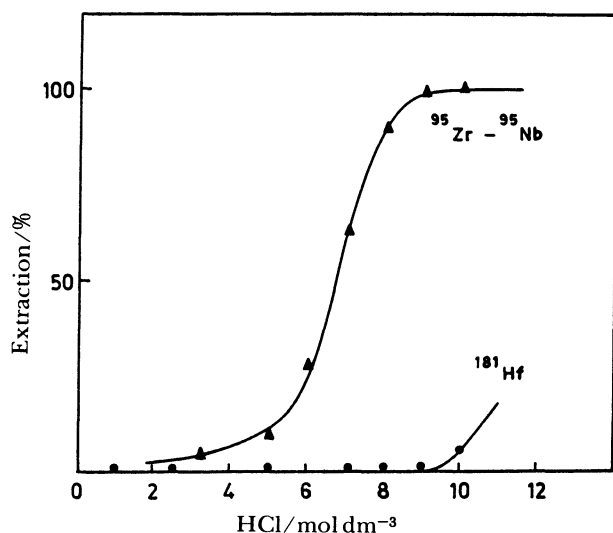


Fig. 1. Extraction dependence of ^{95}Zr - ^{95}Nb and ^{181}Hf on HCl concentration using 0.5 mol dm^{-3} Aliquat 336 solution.

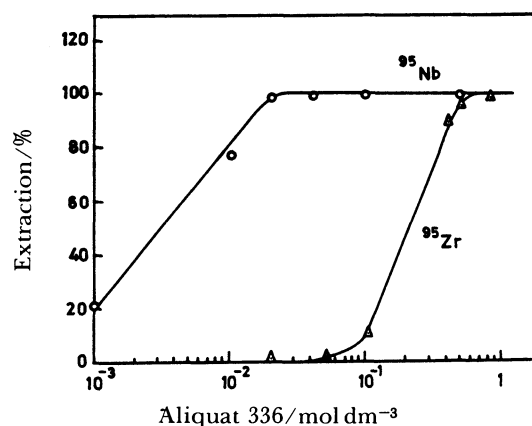


Fig. 2. Extraction dependence of ^{95}Nb and ^{95}Zr on Aliquat 336 concentration in 9 mol dm^{-3} HCl solution.

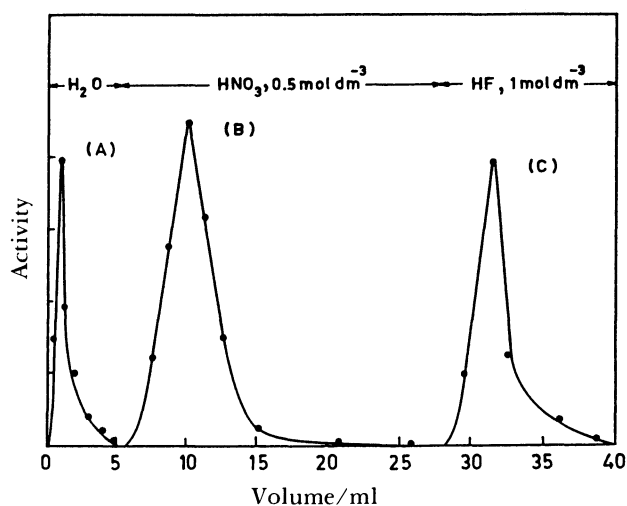
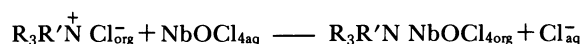


Fig. 3. Separation of ^{95}Zr , ^{95}Nb , and ^{181}Hf in the RPEC method (A) ^{181}Hf by water, (B) ^{95}Zr by $0.5 \text{ mol dm}^{-3} \text{ HNO}_3$, and (C) ^{95}Nb by $1 \text{ mol dm}^{-3} \text{ HF}$.

since it does not form anionic species in this case. Zirconium can be eluted with dilute nitric acid since it is bound by the reagent less firmly than niobium, which is finally eluted with dilute hydrofluoric acid.

Although both niobium and zirconium can form anionic species in aqueous medium, the difference in extraction of these species results from their competitive association with the bulky reagent cation. The preferential extraction of niobium with respect to zirconium may be attributed to the fact that the former primarily forms singly charged oxo- and hydroxy-chlorocomplexes such as NbOCl_4^- , $\text{Nb}(\text{OH})_2\text{Cl}_4^-$,²¹⁾ etc., which are readily extracted by the reagent. Zirconium in aqueous solution generally forms dinegative species like ZrCl_6^{2-} and hence it requires two molecules of the reagent to form a neutral complex. Moreover, it tends to form polymerized species^{22,23)} of the form $(\text{ZrOCl}_4)_n^{2-}$ resulting in an overall hindrance in its extraction.

This behavior is evident from the results shown in Fig. 4 for which the values of the distribution ratio for niobium and zirconium were measured at various concentrations of Aliquat 336 in the organic phase. For niobium, it is observed that D values increase with increasing extractant concentrations, and the slope of this increment is 1. It follows that niobium forms uninegative species in the aqueous phase, and is easily extracted into the organic phase. In the case of zirconium, however, the increment in D -values with the increase in concentration of Aliquat 336 is characterized by a slope of about 2, indicating that zirconium forms dinegative species in the aqueous phase. Hence, the mechanism of extraction of niobium and zirconium may be represented as



and

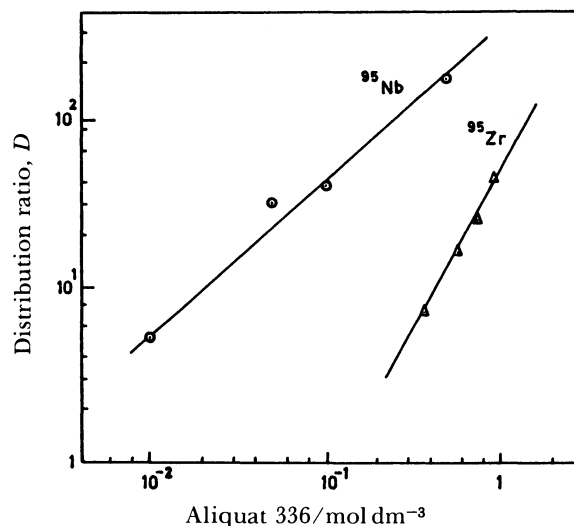
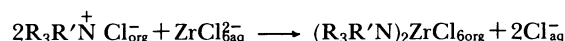


Fig. 4. Distribution ratio, D , of ^{95}Nb and ^{95}Zr as a function of Aliquat 336 concentration in $9 \text{ mol dm}^{-3} \text{ HCl}$.



where,

R = capryl (C_8 – C_{10} -alkyl) group,
 R' = methyl group.

The absence of any anionic species of hafnium as indicated by its extraction behavior towards the anionic extractant may be attributed to its electronic configuration. Hafnium ions are very weakly polarizing and as a result the formation of the complex compounds is very unusual.

The purity of the separated elements in both methods was monitored by gamma ray spectrometry at each stage of separation. The elements were identified by their characteristic gamma ray spectral lines using the following energies, 765.8 keV for ^{95}Nb , 724.0 and 756.6 keV for ^{95}Zr and 133.1, 345.7, and 482.2 keV for ^{181}Hf (Fig. 5).

In RPEC, kieselguhr was selected as a support because of its high resistance to nuclear radiation. This property is essential for radiochemical studies^{24,25)} of this kind. Moreover, kieselguhr is sufficiently porous, has a large capacity for absorbing the organic extractant with which it is impregnated and is chemically inert.

It is considered that the RPEC procedure is preferable to solvent extraction owing to its simplicity and selectivity. In liquid-liquid extraction, fresh portions of the reagent are repeatedly necessary, whereas in RPEC, the column can be impregnated with the reagent and used for several runs. In liquid-liquid extraction sometimes a phase modifier is required to prevent the formation of emulsions. But in RPEC, where the extractant is used as a stationary phase in the extraction columns the addition of the phase modifier is not required. Furthermore, the latter process is less time-consuming and results in a quantitative and

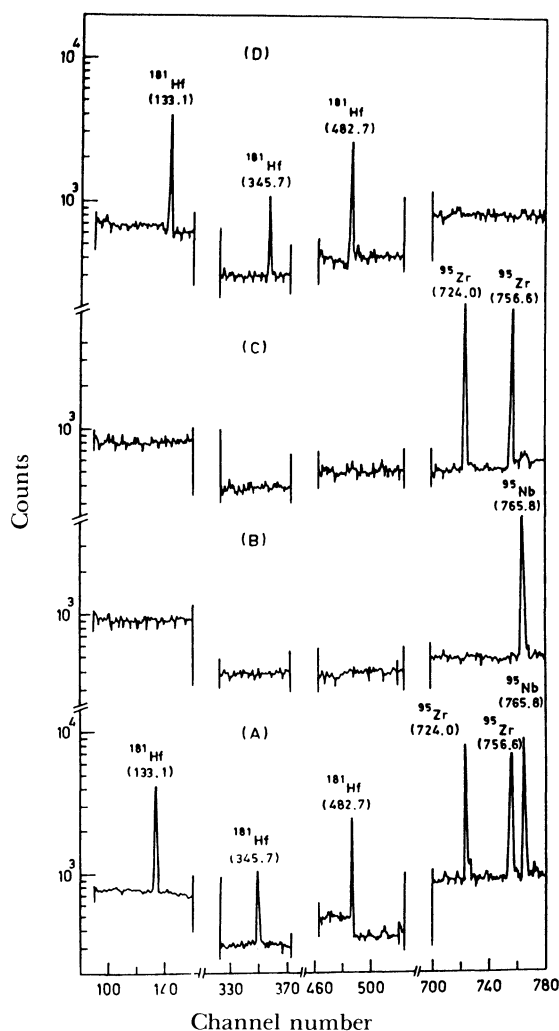


Fig. 5. Gamma spectra of ^{95}Nb , ^{95}Zr , and ^{181}Hf separated by solvent extraction. (A) Mixture of ^{95}Nb , ^{95}Zr , and ^{181}Hf before separation (B) ^{95}Nb separated in Aliquat 336 (0.02 mol dm^{-3}) (C) ^{95}Zr separated in Aliquat 336 (0.5 mol dm^{-3}) and (D) ^{181}Hf in aqueous phase.

clear-cut separation with minimal contamination.

Grateful acknowledgement is due to Professor S. N. Bhattacharyya, Head, Nuclear Chemistry Division, for his encouragement in the work.

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