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A simple, rapid method has been developed for the sequential separation of actinide elements from samples with high salt content such as those resulting from efforts to characterize Hanford storage tank waste. Actinide elements in 9M HCl solution are introduced into an anion exchange column. U(VI), Np(IV) and Pu(IV) are retained on the column while Am(III) passes through. Plutonium is eluted first, reductively; after which neptunium and then uranium are eluted with mixtures of HCl and HF. The Am(III) is purified by cation exchange in a nitric acid system.

INTRODUCTION

Recently, the U.S. Environmental Protection Agency, the U.S. Department of Energy and the Washington State Department of Ecology agreed on a course of action for the environmental restoration of the Hanford Site in southeastern Washington. The formal agreement, called the Tri-Party Agreement was adopted in May 1989. This agreement requires the characterization of the highly radioactive defense waste stored in the 149 underground single shell carbon

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tanks and the 28 newer double shell tanks. Characterization of the waste in the tanks is needed to determine the appropriate disposal methodology. Important constituents of the waste are the major actinide elements, U, Np, Pu, Am and Cm; identifying the concentrations and abundances of their isotopes is an important part of the waste characterization effort.

At Pacific Northwest Laboratory (PNL), the concentration and isotopic abundance of the major actinide elements in a waste sample are ascertained by alpha activity measurements of Np, Pu, Am and Cm; laser fluorimetry measurements of U; and mass spectrometric isotopic composition measurements of U and Pu. Before these measurements can be performed, each of the actinide elements must be chemically separated from the sample matrix material and, except for Am and Cm, from each other.

Chemical separation and purification of the actinide elements are complicated by the fact that the sample matrix material consists of large amounts of inorganic salts and is highly radioactive.(1) In addition to the actinide elements, samples contain long-lived fission products such as ^{137}Cs and ^{90}Sr. Inorganic salts present are alkali metal salts, sodium aluminate and bismuth phosphate arising from the tank waste itself, along with large amounts of flux used for the dissolution of the sample. Common fluxes are either sodium peroxide or a mixture of potassium hydroxide and potassium nitrate.

Sample dissolution is accomplished in a shielded analytical hot-cell facility at PNL. Core samples are collected from the waste tanks by remote sampling techniques and are brought to this facility. Each sample is placed within a hot cell, and a nominal 0.25-g aliquot is taken. This aliquot is combined with flux, fused and then dissolved in hydrochloric acid. An aliquot is removed from the hot cell and taken to a conventional radiochemical laboratory for further processing in an open-faced hood.

This further processing consists of the separation and purification chemistry that is the topic of this paper. Classical procedures for the separation of actinide elements from samples containing high salt levels involve the use of combined techniques such as coprecipitation followed by organic solvent extraction. In the presence of salts, these techniques do not guarantee quantitative separations.(2) To compensate for this shortcoming, isotopic tracers are commonly employed. Other shortcomings of coprecipitation/solvent extraction techniques are that they are labor-intensive and time consuming and that they generate as waste a mixture of organic compounds, salts and radionuclides similar to those present in the waste tanks. Therefore, the disposal of the waste generated by coprecipitation/solvent extraction techniques requires special attention.

The shortcomings just described prompted the development of an ion exchange procedure for the separation and purification of actinide elements from samples containing high levels of salts. In this procedure, a coprecipitation operation is unnecessary and sample solution is introduced directly onto an ion exchange column. The actinide elements are eluted sequentially and collected with sufficient purity and high yield that isotopic tracers are not required. Furthermore, no additional processing is required for mass spectrometric measurements of U and Pu isotopic abundance. Separations are rapid, resulting in short sample turnaround times. A description of the procedure follows.

EXPERIMENTAL

CHEMICALS AND MATERIALS

Chemicals used were ACS reagent grade. Ultrex-grade acids (J. T. Baker Co.) were used. Ion exchange resins were AG-1, X-4, 100-200 mesh for anion exchange and AG-50, X-8, 200-400 mesh for cation exchange. Both of these resins were obtained from Bio-Rad Laboratories. Vials and other containers were leached before use with 8M HNO_3. All materials used in this work were disposable.

Ion exchange columns were prepared from 7.5-ml plastic transfer pipets (#14670-103, VWR). The top 0.5 cm was trimmed from the pipet bulb. The tip of the column was fitted with a small wad of glass wool. The resin volume in the column was 1 ml and was established by introducing 1 ml of water into the column and marking the resultant level. Resin was introduced into the columns just before use as a slurry in deionized water.

SAMPLES

Samples used for this work consisted of aliquots of a solution containing known amounts of U, Np, Pu and Am isotopes along with potassium hydroxide/potassium nitrate flux acidified with hydrochloric acid. Curium was not employed. The U used was Natural Uranium Standard SRM-950A. The Pu was 99.99% pure in the ^{239}Pu isotope and was obtained from Oak Ridge National Laboratory, Isotopes Division. The Np and Am isotopes were ^{237}Np and ^{241}Am and were obtained from Hanford stocks.

PROCEDURE

The procedure is outlined in Figure 1 and has already been described in detail elsewhere.(3) A shorter version is presented in this paper.

The sample was evaporated to near dryness under a heat lamp. The residue was dissolved in 9M HCl-0.05M HNO_3 and warmed for 10 minutes at 80°C. The sample solution was then cooled and introduced into an anion exchange column previously activated with 9M HCl. The U, Np, and Pu were retained in the column. Americium, which is trivalent and consequently not amenable to anion exchange in a chloride system, passed through. The Am fraction was retained for subsequent processing by cation exchange.

The column was then washed with five column volumes of 9M HCl. This wash, which in practical applications contains major impurity cations such as alkali metals, alkaline earths and aluminum and, in addition, traces of Am, was combined with the Am fraction. Plutonium was eluted from the column first. This was accomplished by introducing eight, one-column volume increments of 9M HCl-0.05M NH_4I, allowing the column to drain completely before the introduction of the next increment. Incremental addition of the 9M HCl-0.05M NH_4I results in improved separation. Plutonium does not begin to elute until iodide breakthrough occurs.(4) Neptunium was eluted next, with four column volumes of 4M HCl-0.1M HF. Finally, U was eluted with three column volumes of 0.5M HCl-1M HF. The Np and U fractions were collected in plastic receivers because of the presence of HF

The Am fraction was evaporated to near dryness under a heat lamp and the residue was dissolved in 1.85M HNO_3. The solution was introduced into a cation exchange column previously activated with 1.85M HNO_3. Americium was retained on the column and salts were washed from the column with twelve column volumes of 1.85M HNO_3. In practice, the salts of major concern that are removed in this operation are the alkali metals (including the gamma emitter ^{137}Cs), alkaline earths (which include the beta emitter ^{90}Sr) and aluminum.(5) Americium was eluted from the column with ten column volumes of 8M HNO_3.

After separation, all fractions were dried under a heat lamp. Concentrated HNO_3 and H_2O_2 were added to oxidize iodide to iodine to rid the Pu fraction of iodide. This was done before the Pu fraction was dried.

Next, residues from the dried fractions were dissolved with 1M HNO_3 and aliquots were taken for the various measurements. The aliquot of the uranium fraction was placed in the cuvette for laser fluorimetry. For alpha activity measurements of Np, Pu and Am, the aliquots were deposited and baked on stainless steel planchets. Aliquots for mass spectrometry measurements of U and Pu isotopic abundance were deposited and dried on rhenium mass spectrometer filaments.

RESULTS AND DISCUSSION

In the HCl concentration range from 8 to 12M, Pu(IV) is present as the hexacoordinated chloride complex $PuCl_6^{2-}$.(6) This complex is strongly retained by anion exchange resin. To ensure that all plutonium was in the Pu(IV) state, mildly oxidizing conditions were created by adding nitric acid to the 9M HCl.(4,7) Rapid elution of plutonium was achieved by reduction of Pu(IV) to Pu(III) through the addition of ammonium iodide to the 9M HCl. Pu(III), like Am(III) and other trivalent actinides and lanthanides, is not retained on anion exchange resin in aqueous HCl. Neither Np nor U can be reduced to the trivalent state by iodide, and so both remain on the column. Uranium is maintained in the U(VI) state by maintaining the HCl concentration below 10M.(4)

Like Pu(IV), Np(IV) in 9M HCl is strongly absorbed onto anion exchange resin as a hexacoordinated complex, $NpCl_6^{2-}$.(8) No special effort is required to ensure that Np is maintained in this state.(9) Np(IV) was eluted with 4M HCl-0.1M HF.(4) The rapid desorption is attributable to the tendency of Np to form a complex with fluoride even at concentrations as low as 0.1M. The complex formed is NpF_6^{2-}, which is very weakly sorbed and therefore elutes easily.(8)

U(VI) forms an anionic complex of the composition $UO_2Cl_3^-$, in the HCl concentration range from 6 to 12M, which is absorbed on anion exchange resin.(8) Since this complex forms only at high HCl concentrations, dilute HCl (e.g., 0.5M) is commonly used to elute U(VI).(10, 11) However, it was decided to perform the elution with 0.5M HCl-1M HF, the use of which results in improved resolution and more rapid separation.(12)

The anion exchange separation in 9M HCl of actinide elements from inorganic salts is effective because the actinide elements are strongly retained on the column and most of the salts readily wash off. An important salt cation that does not wash off is bismuth. Bismuth is present in many waste tanks because it was employed in the bismuth phosphate coprecipitation process for separating plutonium from uranium and fission products.(1) Bismuth is strongly absorbed on anion exchange resin over a wide HCl concentration range.(13) Fortunately, the absorption behavior of bismuth is unaffected by the addition of HF and bismuth remains on the column while the actinide elements are eluted.(14)

Although trivalent actinides, except for nobelium, are not absorbed on anion resins, they are very strongly absorbed on cation exchange resin from dilute acid solution according to the following reaction:

$$An^{3+} + 3HR \rightleftharpoons AnR_3 + 3H^+$$

where An = actinide and R = resin anionic site. The third-power dependence on hydrogen ion activity in the above equilibrium expression can be utilized for absorption of transplutonium elements at low acidity and elution at higher acidity.(9) In this procedure, this principle was applied to absorption of the Am onto the cation exchange column from dilute HNO_3 (1.85M) followed by elution with more concentrated nitric acid (8M).

The chemistry underlying the separation and purification of actinide elements by the procedure just presented is well understood. Therefore, well-resolved, quantitative separations were anticipated. That such separations were achieved is confirmed by the analytical results presented in Table 1. This table describes the actinide element chemical recoveries obtained from four replicate analyses. The recoveries for Pu, Np and Am were essentially quantitative. For U, the recovery was 95 percent with an uncertainty of 3 percent. As expected, quality separations were achieved for U and Pu isotopic abundance measurements. Mass spectrometry measurements were performed on two samples; measurement results and actual values are compared in Table 2.

Samples prepared for alpha counting were also subjected to alpha pulse height analysis. For each element analyzed, the alpha spectra were free of measurable activity arising from radionuclides of other elements. This is further evidence that separations were well resolved.

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TABLE 1

RECOVERY OF PLUTONIUM, NEPTUNIUM, AMERICIUM AND URANIUM

Sample	Recovery %			
	^{239}Pu	^{237}Np	^{241}Am	^{238}U
1	99.0	99.0	100.0	98.0
2	99.0	102.0	99.0	92.0
3	98.3	102.0	103.0	97.0
4	99.3	100.0	99.0	92.0
Average	99.0	101.0	100.3	95.0
%RSD*	0.4	1.5	1.9	3.4

*RSD = relative standard deviation.

TABLE 2

MASS SPECTROMETRY MEASUREMENT RESULTS OF URANIUM AND PLUTONIUM ISOTOPIC COMPOSITION

Sample	Uranium Atom %		Plutonium Atom %	
	^{238}U	^{235}U	^{239}Pu	^{240}Pu
1	99.271 ±0.007	0.720 ±0.007	99.98 ±0.02	<0.05
2	99.273 ±0.006	0.720 ±0.005	99.98 ±0.02	<0.04
Actual Values*	99.275	0.720	99.998	0.001

*The uranium had natural composition.
The plutonium isotopic composition was determined by Oak Ridge National Laboratory.

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