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QUANTITATIVE ANALYSIS OF THORIUM IN PLUTONIUM USING REVERSED-PHASE LIQUID CHROMATOGRAPHY AND SPECTROPHOTOMETRIC DETECTION

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SUMMARY

We have developed a method for separating and quantitating trace amounts of thorium in plutonium using a C_{18} reversed-phase column, an eluent containing 2-hydroxyisobutyric acid as a complexant followed by post-column reaction with Arsenazo III, and an absorbance measurement at 656 nm. The method is linear over the range 1–50 $\mu g/ml$ thorium and can detect thorium as low as 0.2 $\mu g/ml$. Precision is 3% relative standard deviation at the 4 $\mu g/ml$ level. The method is simple, rapid, and precise and does not involve preliminary extraction or precipitation of thorium from plutonium or other potential contaminants.

INTRODUCTION

The separation of neutral metal chelates and organometallics by high-performance liquid chromatography (HPLC) is well documented[1–4], but the methodology has not been applied to the separation of actinides except in a few cases[5–9]. We have developed a reversed-phase liquid chromatographic analytical method for separating and quantitating thorium in plutonium to replace a precipitation method currently in use in our laboratory[10] as well as to continue our studies of actinide separations. Barkley *et al.*[5] reported that Th^{4+} and U^{6+} were selectively absorbed by reversed phases in the presence of 2-hydroxyisobutyric acid and, depending on the conditions of the mobile phase, could be well resolved from the rare earths and many transition metals. We studied the effect of modifying the mobile phase to optimize the resolution of thorium (4+) from plutonium (3+, 4+) to quantitate directly trace amounts of Th^{4+} in strong acid dissolutions of plutonium oxide and plutonium metal.

The chromatograph used for this work was configured so that the system components making contact with radioactive solutions, *i.e.* injection port, injection valve, separatory column, membrane reactor (Dionex, Sunnyvale, CA, U.S.A.), and photometer, were confined to an open-front radiation containment box. The eluent was pumped isocratically. Although gradient elution may provide better resolution of analytes, it was not studied as part of this work because the resolution obtained from isocratic elution was satisfactory and because this method was developed for

automated, routine analyses of many samples for which gradient equilibration periods are not desirable.

EXPERIMENTAL

Instrumentation

The chromatograph was a modified Dionex 4000 system consisting of various modules. The Dionex 4000 p.s.i. pump was operated isocratically at a flow-rate of 1.5 ml/min (1400–1600 p.s.i.). The sample was introduced by a Dionex 4000 p.s.i. injection valve plumbed for 50 μl sample uptake. The column was a μBondapak C_{18} reversed-phase column (300 × 3.9 mm I.D., Waters Assoc., Milford, MA, U.S.A.) used at room temperature. A Dionex reagent delivery module and a membrane reactor were used for delivery and post-column mixing of the color reagent, Arsenazo III, with the eluent stream. The flow-rate of the Arsenazo solution into the membrane reactor was 0.6 ml/min. The detector was a Dionex UV–VIS fixed-wavelength photometer monitoring at 656 nm with an Ealing 12.7-mm diameter, 11.5-nm band pass filter used in place of one of the standard photometer filters. Usual photometer attenuation was 0.2 a.u.f.s. A Spectra Physics 4270 integrator, operating with appropriate settings, was used to determine peak areas and retention times.

Reagents

The mobile phase was a 0.3 M solution of 96% 2-hydroxyisobutyric acid (HIBA, Aldrich, Milwaukee, WI, U.S.A.) in 0.2 M reagent-grade NH_4Cl, adjusted to pH 4.0 with reagent-grade NH_4OH. The concentration of Arsenazo III [2,2′-(1,8-dihy-droxy-3,6-disulfonaphthylene-2,7-bisazo)bisbenzenearsonic acid, Aldrich], was 1.5 · 10^{-4} M. Stock and working solutions were made by dissolving these reagents as received in 18 MΩ-cm deionized water. Before use, the working eluent was filtered first through a 0.45-μm pore cellulose acetate filter (Millipore, Bedford, MA, U.S.A.) then through a 0.2-μm polycarbonate filter (Biorad Labs., Richmond, CA, U.S.A.). The Arsenazo III solution was not filtered. The eluent reservoir was kept under nitrogen pressure of 3 p.s.i. to prevent the formation of bubbles in the pump and column. The Dionex reagent delivery module was pressurized with nitrogen at 40 p.s.i. to send the Arsenazo III to the membrane reactor for mixing with the column effluent stream.

Analyte solutions

Thorium standard solutions were made from a 1000 μg/ml stock in 10% HNO_3 (Spex Industries, Edison, NJ, U.S.A.). Plutonium solutions were made from a dissolution of plutonium metal diluted to a concentration of 1017 μg/ml in 1% HNO_3. Americium (3+) and neptunyl (NpO_2^+) stock solutions were made from acidic dissolutions of the metal oxides. Uranyl (UO_2^{2+}) solutions were made from 1000 μg/ml uranium in 10% HNO_3 (Spex). All other metal solutions were prepared from commercially available acidic, aqueous standards by dilution in filtered eluent. A pH range of 3.0–3.5 was noted for the analyte solutions.

RESULTS AND DISCUSSION

The use of post-column derivatization and detection of Arsenazo III metal

complexes has several advantages over direct detection techniques. The color reagent provides favorable selectivity for detection because of its reactivity with the metals of interest at pH 4 and its lack of reactivity with many other metals. The high extinction coefficients of Arsenazo III complexes of thorium and plutonium give more than sufficient sensitivity at low concentrations of these analytes. Such high sensitivity is desirable so that the amounts of radioactive materials required for analysis can be kept to a minimum.

Initial absorbance measurements made with a diode array spectrophotometer showed an absorbance increase in the wavelength region 600–700 nm when a solution of thorium in Arsenazo III was measured against a solution of Arsenazo III. We used 656 nm as the detection wavelength because it is midway in this broad absorbance range. The Ealing 12.7-mm diameter, 656-nm interference filter was chosen for its small size as well as its 11.5-nm band pass, a feature we considered advantageous as it provides more signal than does a narrower band pass.

Selection of the mobile phase complexant, HIBA, was based on the work of Barkley et al.[5]. They found that the selective adsorption of thorium (4+) and uranium (6+) in the presence of only HIBA obviated the inclusion of an organic modifier in the eluent. We held the concentration of the complexant at levels which would insure that the thorium complex contained four ligands and would be a neutral species[11]. Addition of organic solvents such as acetonitrile or methanol decreased the retention times of both the thorium and plutonium peaks, as found by Barkley et al. Ammonium chloride was added to the eluent to increase mobile phase polarity and to reduce the tailing of the peaks, thereby increasing the resolution of thorium from plutonium. We altered the pH, the HIBA concentration, and the salt concentration in the mobile phase to optimize the resolution of thorium from plutonium. The conditions yielding the best resolution values were used for investigations of linearity, reproducibility, and interferences of the method.

Because the maximum buffer capacity of HIBA is at pH 4.04 (Beilstein Index, 3313), we began our evaluation at that pH. Results of eluent pH adjustments to pH 4.0 made with either NaOH or NH_4OH were compared using resolution values (Table Ia). The R value of 1.29 from the NH_4OH adjusted eluent was somewhat better than the R value of 1.08 from the NaOH adjusted eluent. This difference in R value may result from the effects of different ionic strengths.

The effect of varying eluent pH from 3.0 to 5.0 was determined by resolution value. Eluent at pH 4.0 yielded an R value of 1.39, whereas eluents at the other pH levels yielded R values from 0.76 to 1.12 (Table Ib). Thorium and plutonium peaks were not resolved at all when the eluent was at pH 5.0.

To determine which concentration of HIBA yielded the best resolution, we compared five HIBA complexant concentrations ranging from 0.15 M to 0.425 M. Resolution values ranged from 1.22 to 1.53 for HIBA concentrations of 0.2 M through 0.425 M (Table Ic). Although any HIBA concentration in this range can adequately resolve the thorium from the plutonium, the 0.3 M concentration was selected as the analytical concentration because it kept the system pressure below 1500 p.s.i. while providing reasonable retention times and peak shapes of the analytes (Fig. 1).

We thought that making the eluent more polar might improve the resolution of thorium from plutonium. Comparisons were made of the R values calculated from 0.2 M concentrations of NaCl and NH_4Cl in the eluent. Because 0.2 M NH_4Cl yielded the

TABLE I

RESOLUTION VALUES OF Th^{4+} FROM Pu^{4+} FOR VARIOUS CONDITIONS OF THE ELUENT

Parameter	R Value
(a) pH Adjuster	
NH_4OH	1.29
NaOH	1.08
(b) Eluent pH	
3.0	0.76
3.5	1.12
4.0	1.39
4.5	0.93
(c) HIBA concentration	
0.15 M	1.22
0.2 M	1.49
0.3 M	1.39
0.375 M	1.40
0.425 M	1.53
(d) Eluent salt	
NH_4Cl (0.2 M)	1.39
NaCl (0.2 M)	1.29

higher R value of 1.39, it was used as the eluent for the linearity, sensitivity and precision studies (Table Id).

Increasing the temperature in the separation column from room temperature to 40°C had no effect on the resolution of Th^{4+} from Pu^{4+}. Because no changes were seen, further temperature studies were not pursued. Also, no improvement in sensitivity was noted when the concentration of Arsenazo III was doubled from $1.5 \cdot 10^{-4}$ M to $3.0 \cdot 10^{-4}$ M.

Once optimum mobile phase conditions were determined, linearity studies of Th^{4+} concentration versus integrated peak areas were done at three photometer sensitivity settings. A minimum of five concentrations of thorium was used to calculate the correlation coefficients at each sensitivity setting. In all cases, the correlation coefficients were greater than 0.99 for thorium concentrations between 1.0 and 50.0 $\mu g/ml$ (Table II).

The lowest detectable concentration of thorium was determined by analyzing Th^{4+} solutions to the level at which Th^{4+} could no longer be discerned from the baseline. The lowest concentration detectable was 0.2 $\mu g/ml$ at the 0.1 a.u.f.s. photometer setting.

Reproducibility of thorium quantitation was established by analyzing a 4.0 $\mu g/ml$ Th^{4+} control solution for 12 days over a period of 3 weeks. Variables in the system during the time these data were collected included a column replacement and three eluent batch changes. For the twelve determinations, an average concentration of 4.06 mg/ml with an S.D. of 0.12 $\mu g/ml$ and a relative standard deviation (R.S.D.) of 2.96% were calculated.

Analyses of 5 $\mu g/ml$ solutions of thorium in increasing amounts of plutonium showed that interference of thorium quantitation by plutonium begins when the
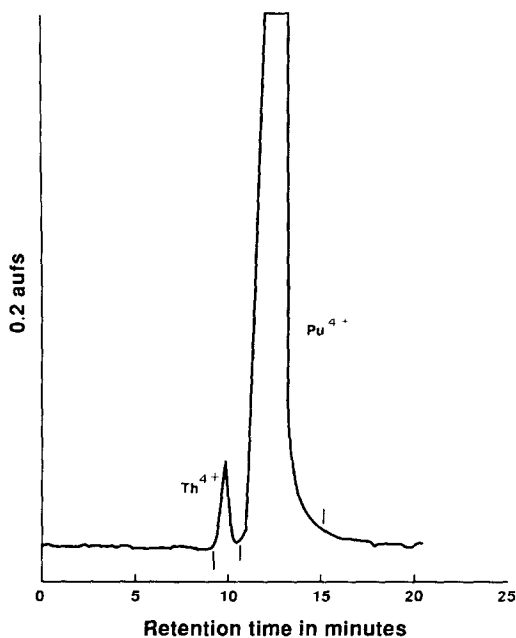
Fig. 1. Chromatogram of 5 μg/ml Th^{4+} and 470 μg/ml Pu^{4+} in 0.3 M HIBA in 0.2 M NH₄Cl, pH 4 with NH₄OH. Post-column reaction with 1.5 · 10⁻⁴ M Arsenazo III; detection at 656 nm, 0.2 a.u.f.s.

plutonium concentration exceeds 500 μg/ml. At this point, the increasing base width of the plutonium peak begins to affect the base of the thorium peak (Fig. 1). Although appropriate integrator settings can correct this problem, analyses for thorium in greater than 500 μg/ml plutonium should be done by using standards containing matching amounts of plutonium or by standard additions of thorium.

The efficiency of the column as measured by the height equivalent to a theoretical plate (HETP) of the thorium peak is not as high a might be expected, with values *ca.* 0.2 mm being the average HETP seen with the analytical conditions. We believe the reason for the relatively low efficiencies lies in several factors, which include the mass transfer rate of the complex onto the column, the labile nature of the adsorbed thorium complex arising from the dynamic equilibrium between the adsorbed species and the ligand in the mobile phase, and peak broadening arising from the apparatus necessary for post column derivatization. In spite of the relatively low column efficiency, the degree of resolution between thorium and plutonium is sufficient for high precision analysis.

An equilibration period of up to 2 days was needed for some concentrated solutions of plutonium which contained both Pu^{3+} and Pu^{4+} to allow time for oxidation from Pu^{3+} to Pu^{4+}. Chromatograms of fresh plutonium solutions made from a stock solution in 1% HNO₃ showed two peaks: a small, early peak eluting between 2 and 3 min and a much larger peak eluting after thorium. When the same solution was analyzed the next day, the early Pu^{3+} peak was diminished, whereas the later Pu^{4+} peak had increased proportionately (Fig. 2). Because the dilutions were made in the pH 4 eluent, it appears that it took some time for any Pu^{3+} to oxidize to

TABLE II
LINEARITY RESULTS

	0.1 a.u.f.s.	0.2 a.u.f.s.	0.5 a.u.f.s.
Range (μg/ml)	10–10.0	1.0–20.0	2.0–50.0
Correlation coefficient	0.9939	0.9988	0.9995

Pu^{4+}. In the presence of HIBA at pH 4, evidence of plutonium polymerization was not seen.

Studies of interferences by other metals were done using most of the Group IIIB–Group IVA metals at concentrations of 10 μg/ml, and fourteen lanthanide metals at concentrations ranging from 2 to 50 μg/ml. Interferences by the actinides, UO_2^{2+}, NpO_2^+, Pu^{3+}, Pu^{4+}, and Am^{3+} were also studied (Fig. 3). Arsenazo III complexes were observed with Y^{3+}, Fe^{3+}, Pb^{2+}, the actinides and the lanthanides (Table III), though the detection sensitivity of lanthanides decreased with increasing atomic number (Fig. 4). All metals reacting with Arsenazo III eluted well before the Th^{4+} peak except Pu^{4+} and UO_2^{2+}, which eluted later.

The possibility of thorium hydrolysis and polymer formation was considered. The method for preparing the solutions for analysis was intended totally to preclude the formation of polymeric species. The solutions were prepared by acid dissolution of the metals, where the acid concentrations were at least 10%. An aliquot of this solution was added to the eluent solution, which contained 0.3 M HIBA. The formation
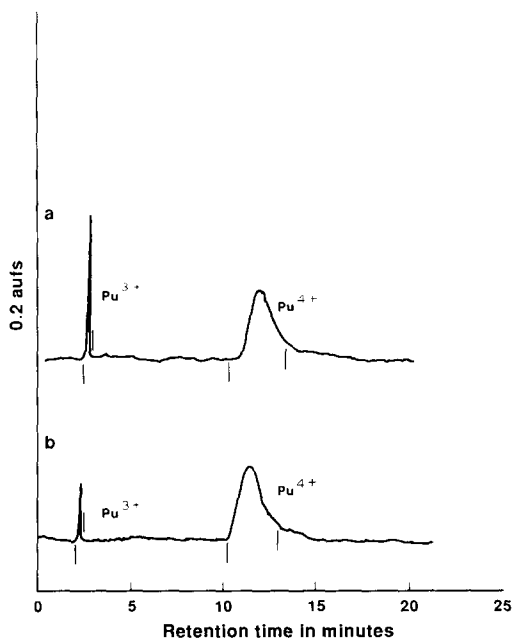

Fig. 2. (a) Chromatogram of 10 μg/ml plutonium in eluent; (b) chromatogram of same dilution analyzed the next day. Conditions as in Fig. 1.
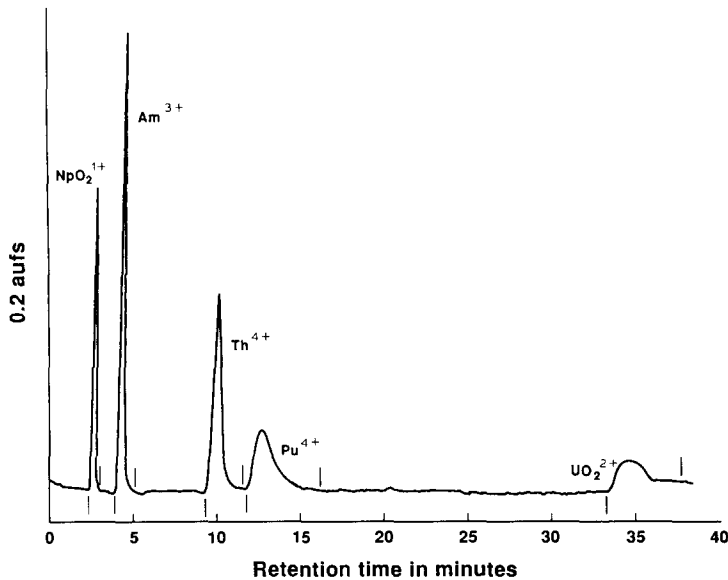
Fig. 3. Chromatogram of 6 $\mu g/ml$ NpO_2^+, 5 $\mu g/ml$ Am^{3+}, 10 $\mu g/ml$ Th^{4+}, Pu^{4+}, and UO_2^{2+} in eluent. Conditions as in Fig. 1.

constants for the complexation reaction dominate the chemistry of the solution and completely block polymerization reactions of the thorium[11]. It has been reported that in the pH range used for analysis, the formation of $Th(OH)^{3+}$ ($\beta 1 = 2.98$) occurs slowly and that polymeric species are minor constituents[12]. In the presence of HIBA ligand, which has a higher formation constant than hydroxide with Th^{4+}, ($\beta 1 =$

TABLE III

REACTIONS OF METALS ANALYZED IN REVERSED-PHASE SYSTEM

Rx: ($-$), no complex forming reaction with Arsenazo III; ($+$) complex forming reaction with Arsenazo III.

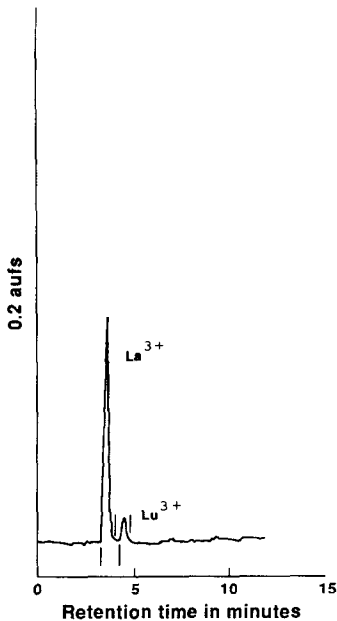| Metal	Rx	Metal	Rx	Metal	Rx
Sc^{3+}	$-$	In^{3+}	$-$	Nd^{3+}	$+$
Ti^{4+}	$-$	Sn^{4+}	$-$	Sm^{3+}	$+$
V^{5+}	$-$	Sb^{3+}	$-$	Eu^{3+}	$+$
Cr^{6+}	$-$	Hf^{4+}	$-$	Gd^{3+}	$+$
Mn^{2+}	$-$	Ta^{5+}	$-$	Tb^{3+}	$+$
Fe^{3+}	$+$	W^{6+}	$-$	Dy^{3+}	$+$
Zn^{2+}	$-$	Re^{7+}	$-$	Ho^{3+}	$+$
Ga^{3+}	$-$	Pt^{4+}	$-$	Er^{3+}	$+$
Ge^{4+}	$-$	Tl^{1+}	$-$	Tm^{3+}	$+$
Y^{3+}	$+$	Pb^{2+}	$+$	Yb^{3+}	$+$
Zr^{4+}	$-$	Bi^{3+}	$-$	Lu^{3+}	$+$
Nb^{5+}	$-$	Al^{3+}	$-$	Np^{5+}	$+$
Mo^{6+}	$-$	La^{3+}	$+$	Am^{3+}	$+$
Rh^{3+}	$-$	Ce^{3+}	$+$	U^{6+}	$+$
Pd^{2+}	$-$	Pr^{3+}	$+$	$Pu^{3+,4+}$	$+$
Ag^+	$-$				

Fig. 4. Chromatogram of 2 μg/ml La^{3+} and 50 μg/ml Lu^{3+} in eluent. Conditions as Fig. 1.

4.43)[11], no polymerization occurs. Integrated areas from peaks from our reproducibility study remained constant over a 3-week period, which when considered with the pH of the stock solution and the probable thorium species present, precludes any significant loss of the thorium due to polymerization.

CONCLUSION

        The data obtained from this HIBA reversed-phase separation system indicate that it is very useful for detecting thorium in plutonium because of its simplicity, sensitivity, and precision. Continued work may provide better understanding of the complexations and column interaction which occur, and may lead to improved routine separations of the actinides and lanthanides.

ACKNOWLEDGEMENTS

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