SEQUENTIAL SEPARATION OF SOME ACTINIDE ELEMENTS BY ANION EXCHANGE

By

F. P. Roberts and F. P. Brauer

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INTRODUCTION

The methods for the separation of the elements from thorium to americium having wide use are those employing solvent extraction techniques⁽¹⁾⁽²⁾. During recent years the behavior of these elements on anion exchangers has been studied, resulting in the wide application of these resins to the separation of the actinides⁽³⁾⁽⁴⁾⁽⁵⁾⁽⁶⁾⁽⁷⁾.

Several of the actinide elements often occur together, either as the products of radioactive decay or neutron irradiation. Sequential separation of such mixtures by anion exchange offers a convenient means for tracer preparation, purification prior to radiochemical analysis and many other purposes. This paper describes two methods for sequential separation of the actinide elements from such mixtures.

SUMMARY AND CONCLUSIONS

Two methods are presented by which trace amounts of several actinide elements are separated. Use is made of the large differences in distribution coefficients, so careful chromatographic techniques are not necessary. Small columns are used, allowing the desired constituent to be obtained in 10 milliliters or less.

The first method separates americium, plutonium, and neptunium. These elements are sequentially eluted from columns of Dowex 1 resin in that order by 8 M HNO_3 , 0.02 M ferrous sulfamate in 4.5 M HNO_3 and 0.001 M ceric sulfate in 0.25 M HNO_3 . In the second method americium, thorium, plutonium and neptunium are sequentially eluted in that order by 8 M HNO_3 , 12 M HCl , 12 M HCl - 0.1 M NH_4I , and 4 M HCl . Protactinium and uranium follow the americium in both methods. The methods presented are characterized by a low degree of cross contamination. Yields are greater than 95 percent.

DISCUSSION

Theory

Neptunium(IV), plutonium(IV) and thorium(IV) are among the few elements strongly absorbed on anion exchangers from nitric acid solutions. Protactinium and uranium are absorbed, but to a much lesser extent. Trivalent plutonium, americium and curium are not absorbed. Table 1 shows distribution coefficients of these elements on anion exchange resins at various nitric acid concentrations.

In concentrated hydrochloric acid the quadrivalent and hexavalent ions of uranium, neptunium, plutonium and protactinium(V) are strongly absorbed. Thorium(IV), plutonium(III), americium(III) and curium(III) show no significant absorption. Table 2 lists some distribution coefficients for various HCl concentrations.

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TABLE 1

DISTRIBUTION COEFFICIENTS OF SOME ACTINIDES ON STRONG BASE ANION EXCHANGE
RESIN AT VARIOUS NITRIC ACID CONCENTRATIONS

<u>HNO₃ Moles/Liter</u>	<u>K_D</u>					<u>Reference</u>
	<u>2</u>	<u>4</u>	<u>6</u>	<u>8</u>	<u>10</u>	
Neptunium(IV)	300	600	1800	2000	2500	(8)
Plutonium(IV)		700	2100	3500		(7)
Thorium(IV)	15	50	200	300	200	(5)
Uranium(VI)	0.1	3	7	8	4	(4)
Protactinium(V)	2	8	10	10	4	(4)
Plutonium(III)		N o t	A b s o r b e d			
Americium-Curium(III)		N o t	A b s o r b e d			

TABLE 2

DISTRIBUTION COEFFICIENTS OF SOME ACTINIDE ELEMENTS ON STRONG BASE ANION
EXCHANGE RESIN AT VARIOUS HYDROCHLORIC ACID CONCENTRATIONS

<u>HCl Moles/Liter</u>	<u>D_V*</u>						<u>Reference</u>
	<u>2</u>	<u>4</u>	<u>6</u>	<u>8</u>	<u>10</u>	<u>12</u>	
Protactinium(V)		1	20	300		4000	(3)
Uranium(IV)			1	30	100		(9)
Uranium(VI)	8		300			1000	(9)
Neptunium(IV)	< 1	1	10		100		(9)
Neptunium(VI)	40	250	1000				(9)
Plutonium(IV)	< 1	1	10	100			(9)
Plutonium(VI)	40	250	1000		4000		(9)
Thorium(IV)		N o t	A b s o r b e d				
Plutonium(III)		N o t	A b s o r b e d				
Americium(III)		N o t	A b s o r b e d				

*These volume distribution coefficients are approximate values taken from curves published in the literature references cited.

In the anion exchange separation of americium-curium, plutonium and neptunium in HNO_3 solutions, it is necessary to have the plutonium and neptunium in the +4 valence state simultaneously. This condition is met by first reducing the higher oxidation states of neptunium and plutonium to neptunium(IV) and plutonium(III) with ferrous sulfamate and then reoxidizing plutonium(III) to plutonium(IV) in 8 M nitric acid with an excess of sodium nitrite. Under these conditions no oxidation of neptunium(IV) takes place. When a solution of americium(III), neptunium(IV) and plutonium(IV) in 8 M HNO_3 is passed through a column of Dowex 1 resin the plutonium and neptunium are absorbed. The americium and curium are readily removed by washing with 8 M HNO_3 . Plutonium is selectively eluted by reduction on the column to the non-absorbable plutonium(III) with a strong reducing agent such as ferrous sulfamate in nitric acid. The rate of elution of plutonium increases with decreasing nitric concentration but at 4.5 M HNO_3 the rate of elution is rapid and no significant loss of neptunium occurs. Neptunium(IV) can be eluted with dilute nitric acid; however, the rate of elution is much faster with the use of an oxidant such as cerium(IV) in dilute HNO_3 ⁽¹⁰⁾.

Thorium can be separated from all other actinide elements by making use of its high distribution coefficient in 8 M HNO_3 and low distribution coefficient in HCl . In this scheme thorium is absorbed with neptunium(IV) and plutonium(IV) from 8 M HNO_3 . Washing with 8 M HNO_3 removes protactinium(V), uranium(VI) and the transplutonium elements. Thorium is then selectively eluted by 12 M HCl . Plutonium can be readily eluted from the Cl^- form resin with 12 M HCl - 0.1 M NH_4I and the neptunium finally eluted by dilute HCl .

In the separation schemes suggested by the previous remarks, protactinium and uranium will accompany the americium. Further separation of these elements can be accomplished by the well known solvent extraction techniques or by the anion exchange technique suggested by Kraus⁽¹¹⁾. In the latter method the solution is made 9 to 12 M HCl and passed through Dowex 1 resin. The uranium(VI) and protactinium(V) are absorbed. Protactinium(V) can be eluted with 9 M HCl - 0.004 M HF . The uranium is readily eluted with dilute HCl .

EXPERIMENTAL

Reagents and Material

Analytical grade Dowex 1 x 4 (100 to 200 mesh) resin was used throughout the study. The resin was converted to the nitrate form by washing with 8 M nitric acid just prior to use. No other purification steps were necessary.

Neptunium-239 tracer was obtained by thermal neutron irradiation of uranium-238 and separation from the uranium and fission products by anion exchange techniques. The purity of the neptunium-239 was confirmed by its gamma energy spectrum.

Thorium-234 was separated from natural uranium. Its gamma spectrum showed no detectable impurities.

Americium-241 and plutonium-239 tracers were obtained in a high degree of purity. Their alpha energy spectrum showed less than one percent impurity.

Protactinium-233 was separated from neptunium-237 by anion exchange. Its purity was confirmed by its gamma spectrum.

Apparatus

Glass columns three millimeters by four centimeters were used in all experiments.

The alpha energy analyzer used was a four-place gridded chamber⁽¹²⁾. A scintillation counter with a three-inch NaI(Tl) crystal was used as a gamma detector. A 256-channel pulse height analyzer⁽¹³⁾ was used with the gamma and alpha detectors.

Sequential Separation, Americium-Curium, Plutonium and Neptunium

Trace quantities of americium-241, plutonium-239, neptunium-239, uranium-233 and protactinium-233 were individually passed through Dowex 1 x 4 (100-200 mesh) columns 0.3 x 4.0 centimeters at the rate of from three to five drops per minute. The samples in 8 M HNO_3 were first made 0.03 M ferrous sulfamate and then 0.1 M sodium nitrite. After loading, the columns were washed with ten milliliters of 8.0 M HNO_3 followed by ten milliliters of 4.5 M HNO_3 - 0.02 M ferrous sulfamate, and finally by five milliliters of 0.25 M HNO_3 - 0.001 M ceric sulfate. One-half milliliter fractions were collected and either alpha or gamma counted, depending on the isotope. Figure 1 shows typical elution curves obtained for these isotopes. The degree of cross contamination and the quantitativity are shown in Table 3. The recoveries are quantitative within the expected experimental errors.

Sequential Separation of Americium-Curium, Thorium, Plutonium and Neptunium

Trace quantities of thorium-234, plutonium-239 and neptunium-239 in 8 M HNO_3 were individually passed through Dowex 1 x 4 (100 - 200 mesh) 0.3 x 4.0 centimeter columns after reduction with ferrous sulfamate and oxidation with sodium nitrite as in the previous section. After washing the column with ten milliliters 8 M HNO_3 , the thorium was eluted with 12 M HCl using five milliliters. The plutonium was eluted with five milliliters of 12 M HCl - 0.1 M NH_4I and the neptunium was eluted with five milliliters 4 M HCl . One-milliliter fractions of each elutriant were collected for gamma or alpha counting. Typical elution curves for these elements are shown in Figure 2.

Several similar runs were made on samples containing mixtures of tracer amounts of americium-241, thorium-234, plutonium-239 and neptunium-239. Table 4 shows the results of these runs. Again, the results are quantitative within the expected experimental errors.

TABLE 3

CROSS CONTAMINATION IN VARIOUS FRACTIONS

Element	Run	Elutriants and Percents of Elements Eluted		
		8 M HNO ₃	4.5 M HNO ₃ -0.02 M Fe ⁺⁺	0.25 M HNO ₃ -0.001 M Ce(SO ₄) ₂
Americium	1	99.5	0.6	Not Detectable
	2	100.7	Not Detectable	Not Detectable
	3	100.0	Not Detectable	Not Detectable
Uranium	1	98.2	0.06	Not Detectable
	2	101.6	0.09	Not Detectable
	3	96.4	0.02	Not Detectable
Protactinium	1	96.5	0.90	Not Detectable
	2	96.3	0.25	Not Detectable
	3	100.9	0.67	Not Detectable
Plutonium	1	0.04	96.7	0.2
	2	0.05	100.8	0.06
	3	0.02	102.0	0.04
Neptunium	1	0.4	0.20	99.0
	2	0.6	0.18	97.9
	3	0.2	0.15	102.0

TABLE 4

SEPARATION OF SOME ACTINIDES USING HNO₃ AND HCl ELUTRIANTS

Element	Run	Elutriants and Percents of Elements Eluted			
		8 M HNO ₃	12 M HCl	12 HCl-0.1 M NH ₄ I	4 M HCl
Americium	1	100.8			
	2	98.2			
	3	98.4			
Thorium	1		96.7		
	2		101.1		
	3		97.0		
Plutonium	1			101.7	
	2			95.7	
	3			100.9	
Neptunium	1				99.8
	2				102.0
	3				99.6

REFERENCES

1. Katz, J. J. and G. T. Seaborg, The Chemistry of the Actinide Elements, John Wiley and Sons, Inc., New York (1957).
2. Morrison, G. H. and H. Freisen, Solvent Extraction, Analytical Chemistry, John Wiley and Sons, Inc., New York (1957).
3. Kraus, K. A., and F. Nelson, Am. Soc. Testing Materials Special Technical Publication No. 195 (1958).
4. Bunney, L. R. et al., Anion Exchange Behavior of Several Metal Ions in HCl, HNO₃ and H₂SO₄ Solutions with Dowex 2, USNRDL-TR-228 (1958).
5. Danan, J., "Separation of Thorium and Rare Earths in Nitric Acid by Anion Exchange", J. Inorg. and Nuclear Chem. 5 237-9 (1958).
6. Tober, F. W., "Concentration and Purification of Pu and Np by Ion Exchange in Nuclearly Safe Equipment", Second United Nations Int'l. Conf. on the Peaceful Uses of Atomic Energy, P-520 (1958).
7. Ryan, J. L. and E. J. Wheelwright, "Application of Anion Exchange to Reprocessing of Plutonium", Second United Nations Int'l. Conf. on the Peaceful Uses of Atomic Energy, P-1915 (1958).
8. Sheppard, J. C. and G. V. Becker, Progress Report HW-49825 (1957) (Secret).
9. Nelson, F. and K. A. Kraus, Progress Report ORNL-2584, Page 59 (1958).
10. Roberts, F. P., An Analytical Method for Np-237 Using Anion Exchange, HW-59032 (1959).
12. Brauer, F. P. and R. E. Connally, Report in Preparation.
13. Shumann, R. W. and J. P. McMahan, "Argonne 256-Channel Pulse Height Analyzer", Rev. Sci Instr. 27 675-687 (September, 1956).
11. Kraus, K.A. Anion Exchange Studies III Protoactinium in Same HCL-HF Mixtures ORNL-673 (1950).

FIGURE 1

Elution of Several Actinides with HNO₃ from Dowex 1 x 4 (100-200 mesh)
Flow Rate 1.5 ml cm⁻² min.⁻¹

FIGURE 2

Elution of Several Actinides with HCl from Dowex 1 x 4 (100-200 mesh)
Flow Rate 1.5 ml cm⁻² min.⁻¹

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