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SEPARATION OF VARIOUS OXIDATION STATES OF NEPTUNIUM AND PLUTONIUM BY REVERSED-PHASE PARTITION CHROMATOGRAPHY

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SUMMARY

The application of reversed-phase partition chromatography, using tri-*n*-octyl phosphate as the stationary phase and nitric acid as the mobile phase, in the separation and determination of Pu(III), Pu(IV) and Pu(VI) and Np(IV), Np(V) and Np(VI) is described. The partition coefficients, separation factors and heights equivalent to a theoretical plate were determined as functions of the nitric acid concentration.

The separation of different oxidation states of plutonium in samples containing uranium was also investigated.

INTRODUCTION

The separation of Pu(III), Pu(IV) and Pu(VI)^{1,2} and Np(IV), Np(V) and Np(VI)³ by reversed-phase partition chromatography using tri-*n*-butyl phosphate (TBP) as the stationary phase, as well as the separation of Np(IV), Np(V) and Np(VI) using di-2-ethylhexylphosphoric acid (D2EHPA)⁴ as the stationary phase, has been reported earlier.

This paper describes investigations carried out on the separation of various oxidation states of neptunium and plutonium by reversed-phase partition chromatography using tri-*n*-octyl phosphate (TOP) as the stationary phase and nitric acid as the mobile phase.

EXPERIMENTAL

Reagents and radionuclides

Tri-*n*-octyl phosphate (Fluka, Buchs, Switzerland) was purified by a procedure reported previously for tri-*n*-butyl phosphate⁵. Fractionated silica gel "for column chromatography" (E. Merck, Darmstadt, G.F.R.) was used as a solid support. The fraction of particle size 0.063–0.071 mm was used, being settled several times from water during 10 min, treated with 1:1 hydrochloric acid, washed with double-distilled water and dried for several hours at 140°. The support was then treated for about 90 h with dichlorodimethylsilane^{2,6} (BDH, Poole, Great Britain). Other reagents used were of analytical-reagent grade.

The radionuclides ^{239}Pu and ^{237}Np were used as nitrates. The various oxidation states of plutonium were prepared from a plutonium solution previously purified by extraction with 2-thenoyltrifluoroacetone (TTA)⁷. Pu(III) was prepared by treating a solution of plutonium in 1–2 *M* nitric acid with 0.03 *M* iron(II) sulphamate. Pu(IV) was prepared by oxidation of Pu(III) (which in this case was obtained by reduction of plutonium in dilute nitric acid with 0.15 *M* hydroxylammonium chloride) with 0.3 *M* sodium nitrite solution. Pu(VI) was prepared by treating a plutonium solution in 5 *M* nitric acid with 0.15 *M* sodium bismuthate. A mixture of Pu(III), Pu(IV) and Pu(VI) was prepared by mixing a solution of pure unstabilized Pu(IV), which was disproportionated in 0.35 *M* nitric acid, and a solution of pure unstabilized Pu(IV), which was partially oxidized to Pu(VI) by heating it in dilute nitric acid.

Solutions of Np(IV), Np(V) and Np(VI) were prepared from a neptunium solution previously purified by extraction with TTA⁸. Np(IV) was prepared by reduction of neptunium in 1 *M* nitric acid with 0.03 *M* iron(II) sulphamate. Np(V) was prepared by oxidation to Np(VI) (heating it in dilute nitric acid) and reduction with 0.1 *M* sodium nitrite solution. Np(VI) was prepared by oxidation of neptunium with 0.01 *M* Ce(IV).

A mixture of Np(IV), Np(V) and Np(VI) was prepared by mixing a solution of unstabilized Np(V), a solution of Np(V) which was disproportionated in 4 *M* nitric acid and a solution of Np(VI) which was obtained by oxidation of Np(V) by heating in dilute nitric acid.

Column preparation and elution

TOP was adsorbed on the silica gel by an evaporation technique. The hydrophobized silica gel was added to a solution of TOP in acetone to give a slurry, and the acetone was evaporated at room temperature. The silica gel with adsorbed TOP was then heated for about 1 h at 60° in a drying oven. The amount of TOP on the silica gel was always 0.5 g/g.

Before filling the column, the silica gel–TOP mixture was added to 1–1.5 *M* nitric acid to give a slurry. Small portions of the slurry were successively filled into the 1 *M* nitric acid-filled column and compressed with a glass rod after each addition. The column was conditioned by passing several column volumes of the acid used for elution through it (*e.g.*, 1.5 *M* nitric acid).

The columns used were 0.31 cm in diameter and the bed height was 10 cm. The amounts of solutions of Np ($8 \cdot 10^{-2}$ mole/l) or Pu ($2 \cdot 10^{-3}$ mole/l) transferred to the top of the column were 5 or 10 μl .

The elutions were carried out at room temperature ($21 \pm 3^\circ$) using nitric acid of appropriate concentration, pre-equilibrated with TOP.

^{237}Np and ^{239}Pu were measured with a Tracerlab Model P-12 alpha scintillation detector. Samples were prepared on discs of stainless steel.

RESULTS AND DISCUSSION

The partition coefficient, K_D , is defined⁹ by

$$K_D = \frac{V}{X} - a$$

where \bar{V} is the peak elution volume, X is the total column volume and α is the void fraction of the column.

The term X was used instead of X' , where $X' = X - 1/2 x_0$, x_0 being the volume of the initial band⁹. Because x_0 was considered to be negligible in comparison with X , it was assumed that $X = X'$.

The number of plates in the column, N , was calculated from

$$N = 8 \left(\frac{\bar{V}}{W} \right)^2$$

where W is the width of the elution curve at the solute concentration $c = c_{\max.}/e = 0.368 \cdot c_{\max.}$ (ref. 9). The height equivalent to a theoretical plate (h) is the bed height divided by N .

The void fraction of the column, α , was obtained by dividing the peak elution volume of $^{137}\text{CsNO}_3$ (a salt which is not retained by the column) by the total column volume, X .

TABLE I

K_D , β AND h DATA FOR Pu(IV) AND Pu(VI) ON A TOP-SILICA GEL COLUMN
 Column, 10 cm \times 0.078 cm²; flow-rate, 0.35 ml/cm²·min; $\alpha = 0.53$.

HNO_3 (M)	K_D		β , Pu(IV)/Pu(VI)	h (mm)	
	Pu(IV)	Pu(VI)		Pu(IV)	Pu(VI)
1.0	2.79 (3)*	1.16 (3)	2.40	0.60 (3)	0.58 (3)
1.5	4.70 (4)	1.66 (8)	2.83	0.54 (4)	0.68 (8)
1.8	—	2.06 (2)	—	—	0.55 (2)
2.0	8.67	2.57	3.37	0.21	0.65

* Average values for several different runs are given. Numbers in parentheses indicate the number of different runs.

The partition coefficients, K_D , separation factors, β , and heights equivalent to a theoretical plate, h , for Pu(IV) and Pu(VI) and for Np(IV) and Np(VI) on TOP-silica gel columns are given in Tables I and II, respectively. The relative standard deviations of the K_D values for Pu(IV), Pu(VI) and Np(IV) were 1.0, 2.4 and 2.1 %, respectively.

The order of extraction of plutonium and neptunium ions from nitric acid solution by TOP was Pu(IV) > Pu(VI) \gg Pu(III) and Np(VI) > Np(IV) \gg Np(V).

TABLE II

K_D , β AND h DATA FOR Np(IV) AND Np(VI) ON A TOP-SILICA GEL COLUMN
 Column, 10 cm \times 0.078 cm²; flow-rate, 0.35 ml/cm²·min; $\alpha = 0.53$.

HNO_3 (M)	K_D		β , Np(VI)/Np(IV)	h (mm)	
	Np(IV)	Np(VI)		Np(IV)	Np(VI)
1.0	0.25	—	—	—	—
1.5	0.94 (7)*	6.87	7.30	0.99 (7)	0.59

* Average values for several different runs are given. Numbers in parentheses indicate the number of different runs.

The same order of extractability of plutonium¹⁰ and neptunium¹¹ ions was obtained for the TBP–nitric acid system. Pu(III) and Np(V) are not extracted to a significant extent by TOP. The peak elution volume (\bar{V}) for Pu(III) and Np(V) was equal to the free volume of the column.

In general, TOP and TBP are very similar extractants. However, the separation factor for Np(VI)–Np(IV) on the TOP–silica gel column ($\beta = 7.30$ using 1.5 M nitric acid, Table II) was higher than on the TBP–Kieselguhr column ($\beta = 1.99$ –1.88 using 0.96–1.98 M nitric acid³).

On the basis of the results in Tables I and II, the separation of Pu(III), Pu(IV) and Pu(VI) (Figs. 1 and 2) and Np(IV), Np(V) and Np(VI) (Fig. 3) was carried out. As can be seen in Fig. 1, a clean separation of Pu(III), Pu(IV) and Pu(VI) may be obtained using TOP as the stationary phase and 1.5 M nitric acid as the mobile phase. Because the elution of Pu(IV) takes too long, and the elution curves are flat, the elution of Pu(IV) was carried out with 1.5 M nitric acid + 0.03 M iron(II) sulphamate (Fig. 2).

Colloidal or hydrolytic products of plutonium are also eluted in the Pu(III) inextractable fraction. In our plutonium solution, they were not present.

A very clean separation of Np(V), Np(IV) and Np(VI) was also obtained. After elution of Np(V) and Np(VI) with 1.5 M nitric acid, the Np(VI) was eluted with 0.1 M nitric acid (Fig. 3).

By using TOP–silica gel columns, we never found less than 0.2–0.5% of Pu(III) in pure Pu(IV) and Pu(VI) solutions or in their mixtures. Approximately the

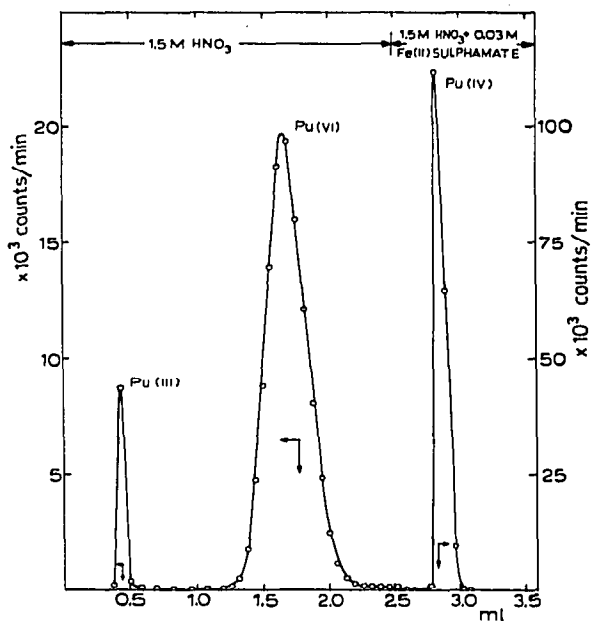
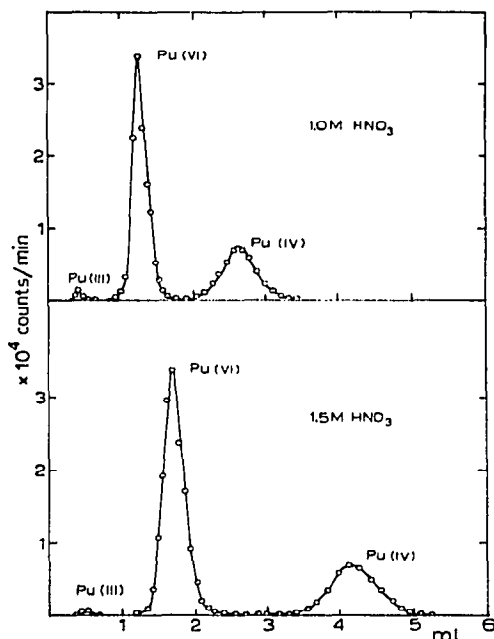


Fig. 1. Separation of Pu(III), Pu(IV) and Pu(VI) on a TOP–silica gel column with 1.0 and 1.5 M HNO_3 . Column: 10 cm \times 0.078 cm². Flow-rate: 0.38 ml/cm²·min.

Fig. 2. Separation of Pu(III), Pu(IV) and Pu(VI) on a TOP–silica gel column. Pu(IV) is eluted after reduction with iron(II) sulphamate. Column: 10 cm \times 0.078 cm². Flow-rate: 0.35 ml/cm²·min.

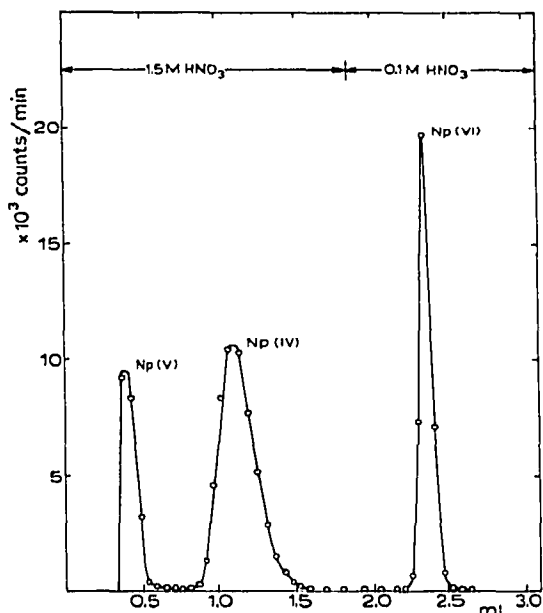


Fig. 3. Separation of Np(IV), Np(V) and Np(VI) on a TOP-silica gel column. Column: 10 cm \times 0.075 cm². Flow-rate: 0.34 ml/cm²·min.

same amount of Pu(III) was found on the TBP columns². It is difficult to explain whether this is due to the real equilibrium conditions in these solutions, or to a slight reduction on the column.

In Table III, the results of four analyses of the oxidation states of plutonium in a given plutonium sample are presented.

TABLE III

DETERMINATION OF THE OXIDATION STATE OF PLUTONIUM IN A PLUTONIUM SAMPLE

Expt. No.	Amount (%)		
	Pu(III)	Pu(IV)	Pu(VI)
1	2.9	32.0	65.1
2	2.7	31.5	65.9
3	2.1	32.5	65.4
4	2.6	32.2	65.5

In the presence of excess of uranyl nitrate in Pu(IV) and Pu(VI) solutions, most of the plutonium was reduced to Pu(III) on the TOP column, exposed to light, and eluted just after the first free column volume. In the absence of light, this reduction did not occur. The reduction is caused by trace amounts of photochemically produced U(IV)². The same effect was observed on the TBP column². Much slower reduction also occurred in U + Pu solutions exposed to daylight. The results are given in Table IV.

TABLE IV

EFFECT OF LIGHT ON THE REDUCTION OF Pu(VI) AND Pu(IV) IN A NITRIC ACID SOLUTION IN THE PRESENCE OF URANYL NITRATE

Storage time in daylight	Column exposed to daylight, U not present*			Column in the dark, U present**			Column exposed to daylight, U present***		
	Pu(III) (%)	Pu(IV) (%)	Pu(VI) (%)	Pu(III) (%)	Pu(IV) (%)	Pu(VI) (%)	Pu(III) (%)	Pu(IV) (%)	Pu(VI) (%)
1 min	0.8	61.9	37.3	0.9	67.8	31.4			
2.5 h				2.2	66.9	30.9	94.6		~5
71 h	0.8	61.8	37.4	2.9	90.4	6.6			
120 h	0.8	61.7	37.6						
648 h	1.5	63.0	35.5						

* Pu $1.3 \cdot 10^{-3}$ M, HNO₃ 1.5 M.** Pu $9.7 \cdot 10^{-4}$ M, U $6.0 \cdot 10^{-1}$ M, HNO₃ 1.5 M.*** Pu $9.7 \cdot 10^{-4}$ M, U $6.0 \cdot 10^{-1}$ M, HNO₃ 1.5 M.

CONCLUSION

It can be seen from the results that very clean separations of the oxidation states of plutonium and neptunium were obtained by reversed-phase partition chromatography using TOP as the stationary and nitric acid as the mobile phase.

The separation and determination of the plutonium (and neptunium) oxidation states in samples containing uranium should be carried out in the dark.

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REFERENCES

- 1 R. Gwózdź and S. Siekierski, *Nukleonika*, 5 (1960) 671.
- 2 M. Bonnevie-Svendsen and V. Martini, Rep. KR-81, Institutt for Atomenergi, Kjeller, 1966.
- 3 H. Eschrich, *Z. Anal. Chem.*, 226 (1967) 100.
- 4 V. N. Ushatskii, L. D. Preobrazhenskaya and M. G. Omel'chenko, *Radiokhimiya*, 14 (1972) 892.
- 5 J. Kennedy and S. S. Grimley, Rep. AERE CE/R 968, Atomic Energy Research Establishment, Harwell, 1957.
- 6 S. Siekierski and I. Fidelis, *J. Chromatogr.*, 4 (1960) 60.
- 7 F. L. Moore and J. E. Hudgens, *Anal. Chem.*, 29 (1957) 1767.
- 8 F. L. Moore, *Anal. Chem.*, 29 (1957) 941.
- 9 E. Glueckauf, *Trans. Faraday Soc.*, 51 (1955) 34.
- 10 J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements*, Methuen, London, 1957, p. 257.
- 11 K. Watanabe, JAERI Rep. No. 1132, 1967.