Applications of Column Reversed-phase Partition Chromatography for the Determination of Actinides in Biological and Environmental Samples*

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Reversed phase partition chromatography (extraction chromatography) is a type of chromatography in which the stationary phase consists of a non-polar extractant absorbed on an inert support, while the mobile phase is a polar aqueous solution. The general principles of this separative technique have been widely described in a book by Braun and Ghersini [1]. Since 1960 column extraction chromatography has been used in Italy to separate many metal ions in simulated aqueous solutions for analytical purposes [2–5]. From 1964 to 1981 some applications of this technique were performed to isolate a certain number of actinides from biological samples before their radiometric determination [6–15]. Finally, since 1979 column extraction chromatography has been used for the determination of actinides in environmental and mineral samples [16–20].

Table I summarizes the experimental conditions (and the relevant references) used for the analyses of natural thorium, enriched uranium, plutonium, americium and neptunium in urine and faeces; Table II gives the same information as regards the determination of thorium, uranium, plutonium and americium in environmental samples (marine samples, sediments, soils, diets, sea water and zircon sands).

A recent example of the application of extraction chromatography for the determination of actinides in environmental samples is the separation and determination of uranium and thorium in zircon sands ($ZrSiO_4$) by a column consisting of 3 g of Microthene (50–100 mesh) supporting 3 ml of 0.5 M tri-n-octylamine (TNOA); Fig. 1 shows the relevant elution diagram. After the separation from zirconium (46% by weight), uranium was determined by fluorimetry and by alpha spectrometry of an electroplated source; thorium was determined by colorimetry with Arsenazo-III and by alpha spectrometry. The uranium content was found to be 0.023% fluorimetrically and 0.024% by alpha spectrometry; the thorium content was 0.019% by colorimetry and 0.018% by alpha spectrometry. The alpha spectra showed that the isotopes of the two actinides (^{232}Th–^{228}Th; ^{238}U–^{234}U) were in a secular radioactive equilibrium.

Some research is now in progress for the determination of radium-226 and uranium in phos-

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TABLE I. Determination of Actinides in Biological Samples by Extraction Chromatography

Actinide	Biological sample	Mobile phase (M HNO_3)	Stationary phase supported on Microthene[a]	Eluting solution	% Final yield	Reference
Th (natural)	urine	4	0.5 M TOPO	0.3 M H_2SO_4	98[b]	6
U (enriched)	urine	7.5	conc. TBP	water	91	7
	urine	4	0.5 M TOPO	1 M HF	70[b]	8
Pu	urine	2	0.1 M TNOA	conc. H_2SO_3	90	9
(238–239–240)	urine	4	0.3 M TOPO	6 M HCl + 0.01 M HI	77[b]	10
	urine	2	0.3 M HX-70	2 M HNO_3 + hydroquinone	74	11
	urine	5	conc. DHOA	0.02 M $NH_2OH \cdot HCl$	85	12
	faeces	2	0.3 M TOPO	6 M HCl + 0.01 M HI	64[b]	13
^{241}Am	urine	10^{-3}	1.5 M HDEHP	3 M HNO_3	86[b]	14
	faeces	10^{-3}	1.5 M HDEHP	3 M HNO_3	65[b]	13
^{237}Np	urine	6	0.1 M TOPO	6 M HCl + Cl_2	83[b]	15
	urine	2	0.3 M HX-70	0.1 M oxalic acid	82	11

[a]Microthene = microporous polyethylene (50–100 mesh); TNOA = tri-n-octylamine; TOPO = tri-n-octylphosphine oxide; HDEHP = di-(2-ethylhexyl)phosphoric acid; DHOA = *N,N'*-di-n-hexyloctanamide; TBP = tri-n-butyl phosphate. [b]Technique used as routine.

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TABLE II. Determination of Actinides in Environmental Samples by Extraction Chromatography

Actinide	Environmental sample	Mobile phase	Stationary phase supported on Microthene[a]	Eluting solution	% Final yield	Notes	Reference
Th (228–230–232)	zircon sands	10 M NH_4NO_3 + 0.1 M HNO_3	0.5 M TNOA	8 M HCl	75		16
U (234–235–238)	zircon sands	10 M NH_4NO_3 + 2 M HNO_3	0.5 M TNOA	6 M HNO_3	92		16
Pu (238–239–240)	sea water	4 M HNO_3	0.3 M TOPO	6 M HCl + 0.02 M HI	63		17, 18
	marine samples	4 M HNO_3	0.3 M TOPO	6 M HCl + 0.02 M HI	82	Double treatment	17, 18
	sediments	4 M HNO_3	0.3 M TOPO	6 M HCl + 0.02 M HI	45[b]	Double treatment	17, 18
	soils	4 M HNO_3	0.3 M TOPO	6 M HCl + 0.02 M HI	50[b]	Double treatment	18
	diets	4 M HNO_3	0.3 M TOPO	6 M HCl + 0.02 M HI	65		18
^{241}Am	sea water	I. 0.01 M HNO_3	1 M HDEHP	4 M HNO_3		After separation	19
	sediments	II. 0.02 M H_2SO_4 + 2 M NH_4CNS	0.7 M Aliquat-336	1 M HCl	~35%	of plutonium	
	marine samples						

[a]Microthene = microporous polyethylene (50–100 mesh); TNOA = tri-n-octylamine; TOPO = tri-n-octylphosphine oxide; HDEHP = di-(2-ethylhexyl)phosphoric acid; Aliquat-336 = tricaprylmethylammonium salt. [b]The use of ^{242}Pu as internal standard was necessary to calculate every single yield.

Fig. 1. Elution diagram for the separation of uranium and thorium from zirconium by a Microthene–TNOA column.

phorites [$Ca_3(PO_4)_2$] and related compounds (H_3PO_4, $CaSO_4$) by using a column of Microthene–TOPO; the phosphorite (100 mg) is dissolved by a 6 M HNO_3 leaching, the HNO_3 concentration is brought to 2 M and the solution is passed through the column. ^{226}Ra present in the first eluate is co-precipitated with $BaSO_4$ and counted by a ZnS(Ag) alpha detector; then uranium is eluted with 1 M HF or 1 M $(NH_4)_2CO_3$ and determined both by solid fluorimetry and by alpha spectrometry of an electroplated source. The equilibrium or the non-equilibrium of the uranium isotopes can finally be derived from these alpha spectra.

A recent example of the application of extraction chromatography for radiotoxicological purposes was the checking of plutonium in the urine and faeces of four Italian workers living near Kiev during the Chernobyl nuclear accident and for whom a certain internal radiocontamination from fission products was detected at the Medical and Radiotoxicological Service of the C.R.E.-Casaccia, E.N.E.A. (Rome).

After the mineralization of the biological samples, a known activity of ^{242}Pu was added as the internal standard and a solution 4 M in HNO_3 was prepared; plutonium was brought to Pu(IV) by adding some $NaNO_2$ and the solution was passed through the Microthene–TOPO column. After washing with 4 M HNO_3, plutonium was eluted by reduction to Pu(III) with a 6 M HCl + 0.01 M HI solution. The plutonium electrodeposition was then carried out for 5 h from $(NH_4)_2SO_4$ at 400 mA; the alpha spectra obtained by counting for a week with a solid state alpha detector were then considered in order to obtain the plutonium (238–239–240) concentration and the final yield (^{242}Pu).

Figure 2 shows that these concentrations were lower than the method detection limits (0.37 mBq for urine and 1.85 mBq for faeces): the final recov-

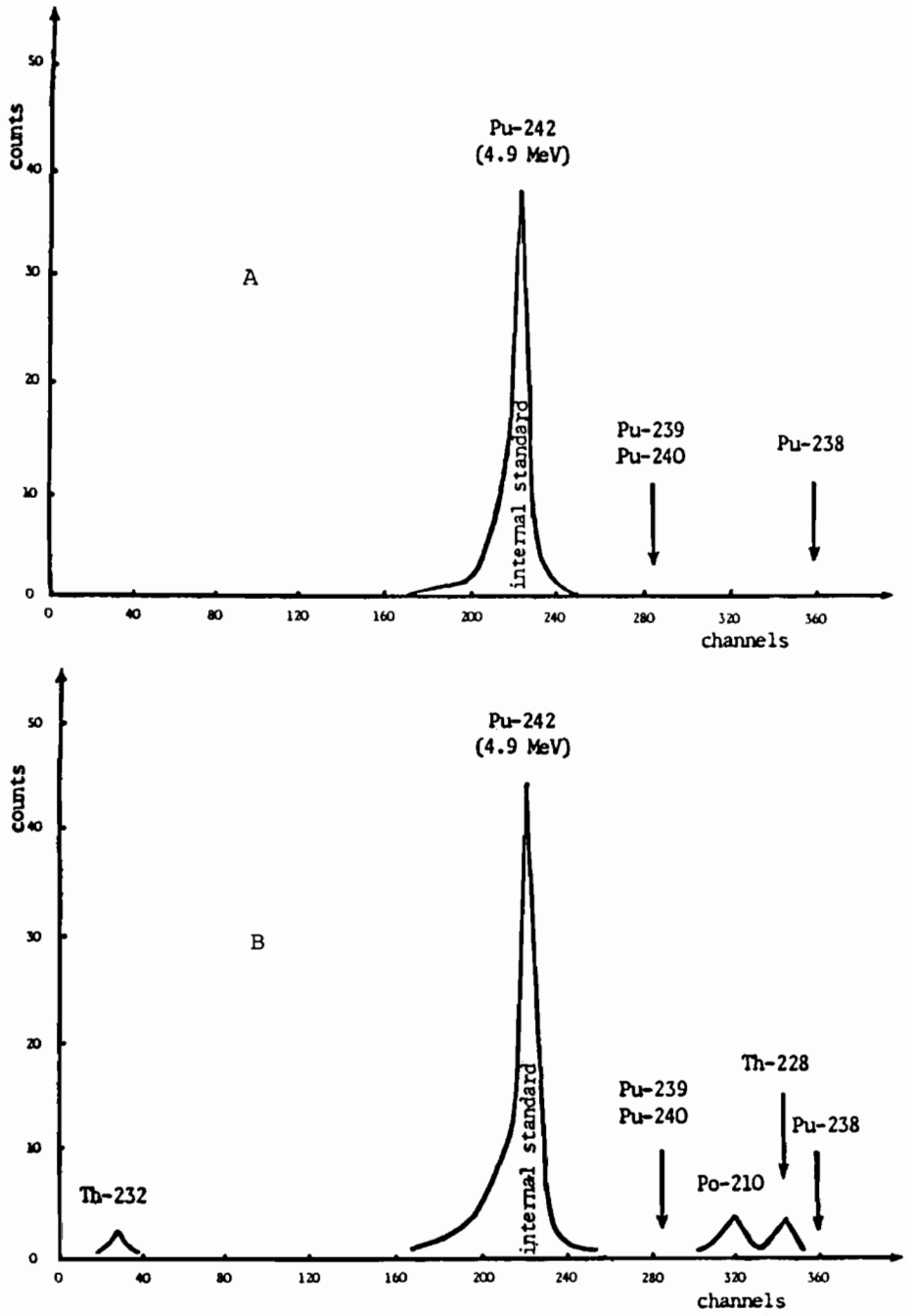

Fig. 2. Plutonium alpha spectra of an electroplated source after chemical separation by a Microthene–TOPO column from biological samples (A = urine; B = faeces).

eries were 91% and 45% respectively. As a conclusion, the absence of any significant internal radiocontamination was derived as regards plutonium.

Finally, it has to be said that the reliability of these chromatographic techniques was checked by two intercalibration programmes organized by I.A.E.A. (Vienna), which provided standardized biological and environmental samples containing very low quantities of actinides (analytical quality control of actinides). The first one [21] regarded urine samples containing natural thorium (11.2 μg/l), natural uranium (33.6 μg/l) and plutonium (23 mBq/l); the second one [22] was related to sea water containing 50 μBq/l $^{239(240)}$Pu and 10 μBq/l ^{238}Pu, and to marine sediments containing 15 mBq/g $^{239(240)}$Pu and 0.7 mBq/g ^{238}Pu. The

values obtained by utilizing extraction chromatography as a separation technique were found to be very close to the true and unknown values.

References

1 T. Braun and G. Ghersini, 'Extraction Chromatography', Elsevier, Amsterdam, 1975.
2 E. Cerrai and C. Testa, *J. Chromatogr., 6*, 443 (1961).
3 E. Cerrai and C. Testa, *Energ. Nucl., 8*, 510 (1961).
4 E. Cerrai and C. Testa, *J. Chromatogr., 9*, 216 (1962).
5 E. Cerrai and C. Testa, *J. Inorg. Nucl. Chem., 25*, 1045 (1963).
6 C. Testa, 'Radiological Health and Safety in Mining and Milling of Nuclear Materials'. Vol. 2, IAEA, Vienna, 1964, p. 489.
7 C. Testa and G. Masi, *Minerva Nucl., 9*, 22 (1966).
8 C. Testa, D. De Rosa and A. Salvatori, *Technical Report CNEN RT/PROT 68*, 1968, p. 6.
9 C. Testa, *Minerva Fisiconucl., 10*, 202 (1966).
10 C. Testa and G. Santori, *G. Fis. Sanit., 1*, 16 (1972).
11 A. Delle Site, *J. Radioanal. Chem., 14*, 45 (1973).
12 C. Testa and S. Torcini, *Proc. XXIIIth Congress AIRP*, Brescia, Italy, 1981, p. 585.
13 A. Delle Site, G. Santori and C. Testa, *Technical Report CNEN RT/PROT 76*, 1976, p. 6.
14 A. Delle Site, G. Santori and C. Testa, *Technical Report CNEN RT/PROT 81*, 1981, p. 6.
15 G. Santori and C. Testa, *J. Radioanal. Chem., 14*, 37 (1973).
16 S. Bazzarri, D. Desideri, L. Staccioli and C. Testa, *J. Radioanal. Nucl. Chem., 107*, 165 (1986).
17 A. Delle Site, V. Marchionni, C. Testa and C. Triulzi, *Anal. Chim. Acta, 117*, 217 (1980).
18 A. Delle Site, V. Marchionni and G. Santori, *Technical Report CNEN RT/PROT 79*, 1979, p. 12.
19 A. Delle Site and V. Marchionni, *Rapp. Comm. Int. Mer Medit., 47*, 3 (1981).
20 A. Delle Site, 'Chromatography in Biochemistry, Medicine and Environmental Research', Elsevier, Amsterdam, 1983.
21 J. Heinonen, L. Górski and O. Suschny, *IAEA/RL/18*, IAEA, Vienna, 1973.
22 R. Fukai, S. Ballestra and M. Thein, *IAEA-TECDOC-265*, IAEA, Vienna, 1982.