THE RAPID DETERMINATION OF THE TRANSURANIUM ELEMENTS BY EXTRACTION CHROMATOGRAPHY IN URINES CONTAINING DTPA

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Abstract

Microporous polyethylene (Microthene-710) supporting tri-n--octylphosphine oxide (TOPO) and di(2-ethylhexyl) phosphoric acid (HDEHP) has been used successfully to extract respectively Th, Pa, U, Np, Pu, Am and Cm from the urine. As the extraction takes place in an HNO_3 medium, DTPA up to 2 g/l does not interfere. A particular investigation was carried out for Am in order to find out the best extraction pH. Finally it has been demonstrated that great losses of actinides occur when a coprecipitation with Ca and Mg phosphates are carried out in the presence of DTPA.

Introduction

During ten year experience in our laboratory several methods have been prepared for the determination of some actinide elements in the urine by means of extraction chromatography.

"Extraction chromatography" or "reversed phase partition chromatography" is a very useful tool to transform a liquid-liquid extraction into a chromatographic procedure by supporting some organic extractants on an inert microporous support[1-3]. By using Microthene-710 (microporous polyethylene) as the inert support and tri-n-octylphosphine oxide (TOPO) and di(2-ethylhexyl) phosphoric acid (HDEHP) as the extractants, many radiotoxicological determinations were performed; the urine was stirred with a slurry of Microthene-TOPO for Th, Pa, U, Np and Pu[4-9] and with Microthene-HDEHP for Am and Cm[10]; after this batch extraction, the slurry is transferred into a chromatographic column from which the radionuclide is eluted selectively with a suitable solution. Table I summarizes the experimental conditions and the relevant literature[4-10].

As it is well known, di-ethylentriaminopentacetic acid is widely used in case of acute contaminations with plutonium and americium. On the other hand, this complexing agent can seriously interfere with conventional radiotoxicological analyses: some authors recommend the complete destruction of DTPA by a wet ashing[11-12] and others claim a wet mineralization with HNO_3 and H_2O_2 would be sufficient before the coprecipitation of plutonium with Ca and Mg phosphates[13].

The aim of the present paper is to demonstrate that the techniques based on the extraction chromatography can be used successfully, and without any change, with urine containing large quantities of DTPA.

Experimental

Reagents and apparatus

TOPO was supplied by Eastman Organic Chemicals (USA) and HDEHP by K & K (USA).

Microthene-710, 50-100 mesh, was obtained by the Columbia Organic Chemicals (USA).

DTPA was supplied by Fluka (Switzerland).

Pa-233, U-233, Np-237, Pu-239, Am-241 and Cm-242 came from the Amersham Radiochemical Centre (England). Th-234 (UX_1) was prepared in our laboratory[6].

The other chemical reagents were of analytical grade.

An Intertechnique liquid scintillation apparatus connected to a Laben 400 channel analyzer was used for alpha counting after the batch extractions.

For the counting of Th-234 and Pa-233 a low background beta detector was employed.

The final recoveries of the alpha emitters were calculated by alpha counting with an Ortec solid state detector after electroplating the radionuclide.

The other apparatus (pHmeter, magnetic stirrer, chromatographic columns, etc.) were of conventional type.

Experimental results

To 500 ml of urine containing 6,000 dpm of Pu-239 (~44 ng), different quantities of DTPA (10 mg, 100 mg and 1000 mg) were added and the conventional chromatographic extraction procedure was performed; the final yields were 75.5%, 78.5% and 79.5%, respectively showing that large quantities of DTPA can be tolerated.

Taking into account these results, 1 g of DTPA was added to 500 ml of urine containing the other radionuclides and three analyses were carried out to check the effect of DTPA on the final yields. Table II summarizes the obtained results and it shows that DTPA does not interfere with the analysis, except for americium and curium for which the extraction takes place at pH 3.

TABLE I

DETERMINATION OF ACTINIDES IN THE URINE BY BATCH EXTRACTION WITH MICROTHENE SUPPORTING SOME ORGANIC EXTRACTANTS

NUCLIDE	HNO_3 CONC.	STATIONARY PHASE	ELUTING AGENT	RECOVERY %	SENSITIVITY LIMIT	METHOD (a)	TIME H.	REF.
Th	4.0 M	0.5M TOPO	0.3M H_2SO_4	98.2	0.2 µg/l	Col.	4	4
Pa	4.0 M	0.1M TOPO	6M HCl+0.2M HF	-	-	ZnS	4	5
U	4.0 M	0.5M TOPO	1M HF	70.0	1 dpm/l	ZnS	4	6
Np	6.0 M	0.1M TOPO	6M HCl+Cl_2	83.2	0.05 pCi/l	SSD	8	7
Pu	4.0 M	0.3M TOPO	6M HCl+0.01 HI	70.5	0.07 pCi/l	SSD	8	8
	4.0 M	0.3M TOPO	6M HCl+0.1 HI	76.5	0.10 pCi/l	ZnS	4	9
Am (Cm)	0.001M	1.5M HDEHP	3M HNO_3	85.9	0.05 pCi/l	SSD	8	10

(a) Col. = colorimetry; ZnS = alpha counting with a ZnS(Ag) detector;
SSD = alpha counting with a solid state detector after electroplating.

TABLE II

RECOVERIES OF ACTINIDES BY EXTRACTION CHROMATOGRAPHY WITHOUT AND WITH DTPA

RADIONUCLIDE	FINAL RECOVERY % WITHOUT DTPA (a)	σ %	FINAL RECOVERY % WITH 1 g OF DTPA IN 500 ML OF URINE (b)	σ %
Th	98.2	11.5	93.0(c)	1.7
Pa	-	-	91.1(d)	2.7
U	70.0	3.0	70.2	2.2
Np	83.2	6.5	79.8	4.7
Pu	76.5	5.7	76.7	2.5
Am(Cm)	85.9	7.6	0	-

(a) Average of 10 analyses; (b) Average of 3 analyses; (c) Th-234 radiometric determination; (d) % Recovery of the only extraction.

It appears that in 4-6 M HNO_3 the actinide elements are not complexed by DTPA.

A study was then performed to find out the possibility to extract also americium and curium in the presence of DTPA by decreasing the pH of the solution: in fact in this case there are two opposite effects, i.e. the extraction of Am which increases by increasing the pH value, and the complexing of Am by DTPA which also increases with the pH. Therefore it was decided to study the extraction of americium as a function of the DTPA concentration and of the pH of the solution. As Fig. 1 shows by stirring for 60 minutes 500 ml of urine without DTPA with 7 g of Microthene supporting 5 ml of 1.5 M HDEHP in xylene, the Am extraction is complete above pH 2.5; if some DTPA is present an extraction maximum takes place at a pH which decreases by increasing the quantity of DTPA. In any case it is always possible to obtain a sufficiently good extraction (56% to 86%) by using a suitable pH.

By fixing the pH at 2 and by increasing the DTPA concentration from 10 to 100 mg (fig. 2) the Am extraction decreased from 78 to 60%. Similar results were obtained with curium.

Discussion

From the experimental results it appears that by using the extraction chromatography it is always possible to obtain sufficiently good recoveries of the actinides from the urines, even in the presence of DTPA.

To be sure that the clearing of the urine by boiling with HNO_3 was not the cause of the DTPA removal[13], some analyses were carried out by adding the complexing agent after the wet mineralization of the urine: also in this case the actinides extractions were the same, showing that the DTPA present does not form complexes with these elements at high H^+concentrations[14-15].

On the other hand, the methods for the complete mineralization of the organic matter[11-12] are very time-consuming.

It has also been reported[13] that a wet-15 minute mineralization with 85 ml of conc. HNO_3 and 8 ml of H_2O_2 for 1.5 liter of urine could destroy the DTPA and permit plutonium to coprecipitate quantitatively at pH 8.5-9.0 with calcium and magnesium phosphates. On the contrary, we have found that this treatment is not sufficient to eliminate the effect of DTPA, as fig. 3 shows: in fact, boiling 500 ml of urine containing DTPA (0-1 g) with 100 ml of conc. HNO_3 and 20 ml of H_2O_2 for 60 minutes, the precipitation yield decreased from about 98% to about 39%. This is due to the precipitation pH (8.5-9.0) where the complex Pu-DTPA does take place.

Concluding, the described methods of extraction chromatography are very simple and rapid and they do not require any dry mineralization or coprecipitation.

The only drawback which exists for the americium and curium determination is to know roughly the DTPA concentration in the

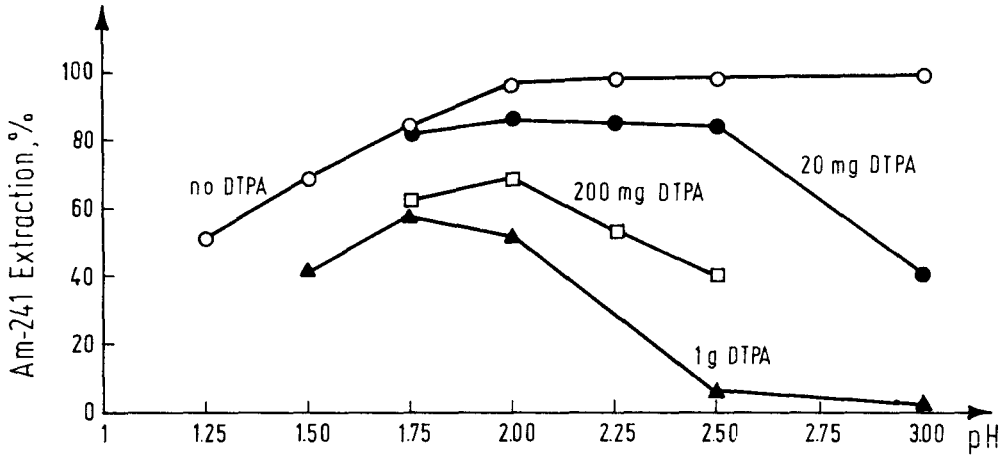

Fig 1 Extraction of Am-241 from 500 ml of urine by Microthene-HDEHP as a function of the DTPA concetration

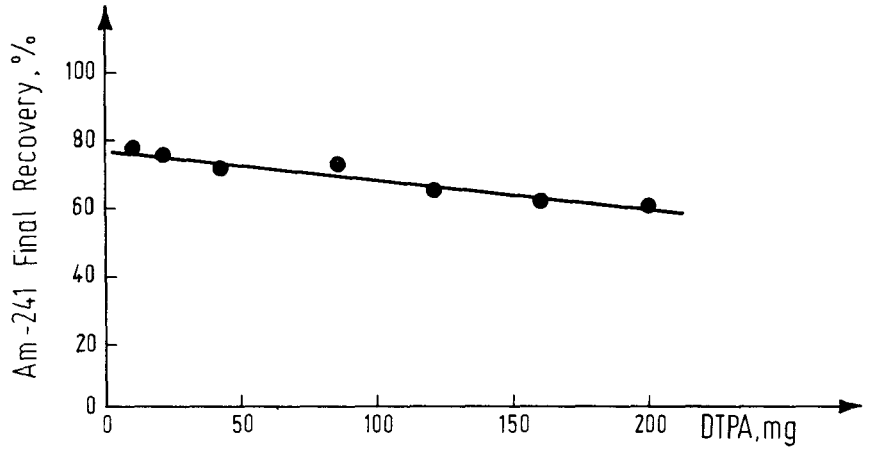

Fig. 2 Am-241 final recovery with Microthene-HDEHP from 500 ml of urine at pH 2 as a function of the DTPA concentration

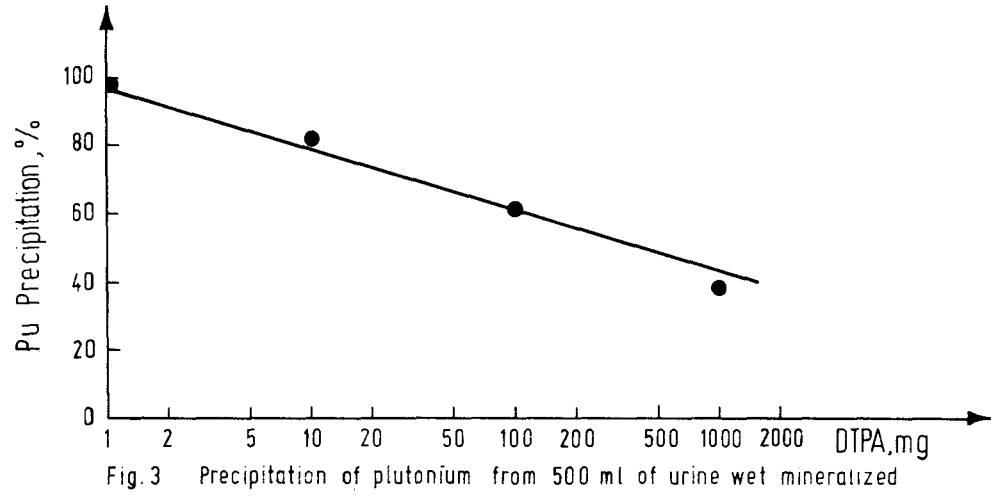

Fig. 3 Precipitation of plutonium from 500 ml of urine wet mineralized with HNO_3 and H_2O_2 as a function of DTPA concentration

urine; however this is easily estimated by considering that almost all the injected DTPA is excreted in the first 24 hour urine sample[16].

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