Inorganica Chimica Acta, *94* (1984) 223–227

Separation and Sequential Determination of Americium and Plutonium in Urine Samples

R. GIACOMELLI and P. SPEZZANO

E.N.E.A., Fuel Cycle Department, Health Physic and Radiotoxicological Service, CRE, Saluggia 13040, Ve, Italy

Received October 5, 1983

Introduction

Simultaneously determining low levels of americium and plutonium in complex matrixes poses serious problems, owing to the different chemical behaviour of the two actinides, which makes it difficult to establish one simple analysis method for separating them sequentially. Because the alpha emission of ^{238}Pu is close to that of ^{241}Am, the two actinides must first be isolated and separated before the final alpha spectrometry test can be performed.

Determining Am and Pu in biological samples taken from personnel exposed to a risk of internal contamination is of vital importance, considering the high degree of radiotoxicity involved both for excluding internal contamination during routine control analysis and for evaluating the extent of incorporation if internal contamination is actually detected.

In view of the low levels involved (0.2 pCi/24 h for ^{239}Pu and 0.25 pCi/24 h for ^{241}Am), an extremely fast, sensitive method is required for the necessary therapeutical steps (chelant, *i.e.* DTPA treatment) to be taken in time, in the event of accidental contamination.

It is also important for Am and Pu to be determined simultaneously from a single sample, to avoid sensitivity loss caused by dividing samples and also to lighten the laboratory work load by providing a simple analytical procedure. Though available literature offers numerous methods of determining Am and Pu in urine samples [1–11], these have not been successful in simultaneously determining both from the same sample without dividing it into two parts, or subjecting it to long, complex handling procedures.

The advantage of reagents with molecules comprising two binder groups, such as bidentate compounds, is that they can be successfully employed for extracting trivalent or higher valency actinides from solutions with high HNO_3 concentrations.

Various bidentate compounds, particularly dibutyl N,N–diethyl carbamyl phosphonate (DBDECP) and dibutyl N,N–diethyl carbamylmethylene phosphonate (DBDECMP) were first synthesized and used by Siddall [12, 13] for extracting trivalent elements.

These extractants have already been applied to analysis [11, 14] and used on a large scale [15, 16] for extracting actinides from various matrixes. A detailed report [17] has been published on the extraction of various elements using DBDECP and DBDECMP in nitric solutions.

This paper describes a method of separating and determining Am and Pu sequentially from urine samples by means of liquid-liquid extraction using DBDECP as a reagent. The possibility of separating the two actinides by partition chromatography has also been taken into consideration.

Experimental

Reagents and Equipment

The DBDECP used for the purpose of this analysis (Columbia Organic Chemicals) was not subjected to further purification. The radioisotopes used were supplied by the Amersham Atomic Centre and by C.E.A.

All the other reagents were analytical grade. The alpha activity tests were performed using an Intertechnique SL32 liquid scintillation spectrometer. Insta-Gel (Packard) was used as the scintillation liquid. The alpha spectrometry tests were performed using a chain consisting of a Tennelec TC 256 alpha spectrometer with a 450 mm^2 Ortec surface barrier detector connected via a Tennelec TC 306 Mixer Router to a Silena System BS/27 multichannel analyzer.

Actinide Extraction in DBDECP

Extraction of some actinides in tracer concentrations by 50% solution of DBDECP in toluene was

0020-1693/84/$3.00

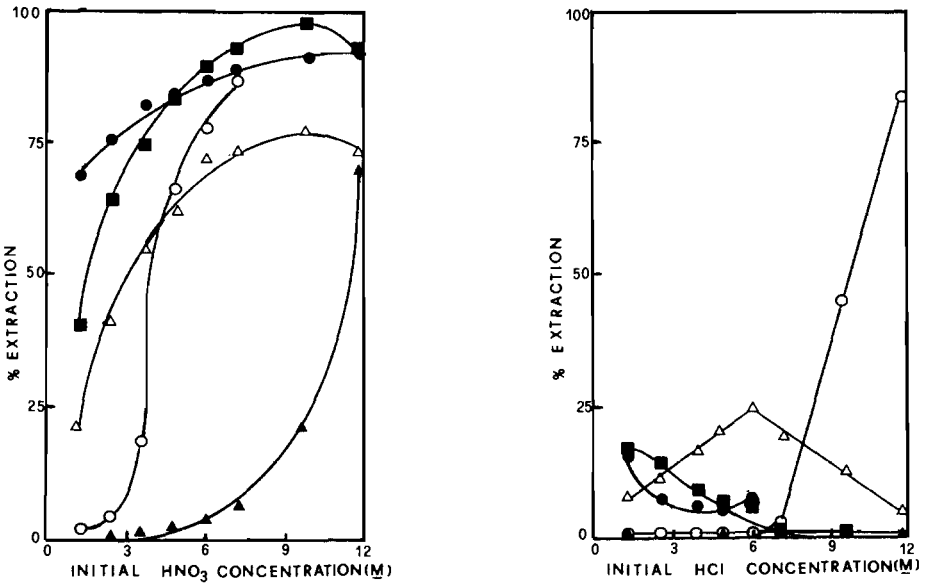

Fig. 1. Extraction of Am, Pu, U, Th in tracer concentration, by DBDECP as a function of initial HNO_3 and HCl concentration. DBDECP - 50% in toluene, 1 ml; Phase ratio - aqueous/organic, 50; Extraction time - 1 minute; Pu(III) - Pu reduced with Fe(II) plus sulphamic acid; Pu(IV) - Pu reduced with hydroxylamine, reoxidized and stabilized with $NaNO_2$. ▲ Am; ○ Pu(III); ● Pu(IV); △ U(VI); ■ Th.

first studied in dependence of initial concentrations of HNO_3 and HCl. The extraction was performed at an aqueous–organic phase ratio of 50:1, the volume of the organic phase being 1 ml. Time contact was 1 minute.

After separation, the organic phase and the part of the aqueous phase containing the examined radionuclide were measured by liquid scintillation counting to determine the extraction percentages.

The results are shown in Fig. 1. Pu(III) was prepared by reduction with Fe(II) in excess sulphamic acid and Pu(IV) by reducing Pu with NH_3OH^+, followed by oxidation and stabilization to valency IV using $NaNO_2$.

The reason for the curve relative to Pu(III) in HNO_3 may be an increase in extraction coefficient or gradual oxidation to Pu(IV) along with an increase in the HNO_3 concentration.

Actinide extraction by DBDECP is always poor in HCl. Only Pu(III) proved to be highly extractable in strong HCl solutions, whereas Am(III) is practically unextractable at any concentration.

Actinide extraction in HNO_3 solutions increases in proportion with the strength of the solution. For all practical purposes, however, it is advisable to use undiluted DBDECP for the extraction step, in that dilution in the solvent reduces the actinide extraction. Only during the back-extraction step is it advisable to add solvent, to improve stripping and to reduce the solubility of DBDECP which is high in diluted solutions of nitric acid.

Chromatographic Separation of Am and Pu

To remove any intereference and improve the Am and Pu separation as compared with the liquid–liquid extraction method, a test was run to determine whether they could be separated by partition chromatography.

The stationary phase consisted of 3 g of Microthene 651/50 (60–100 mesh) supporting 2 cc of 25% DBDECP, cyclohexane solution previously conditioned in HNO_3 12 *M*. The column had an inside diameter of 1 cm and was 10 cm in height. A few cc of HNO_3 12 *M* containing the actinides being studied were passed through the column at a flow rate of 0.5–1 cc/min, then washed with 100 cc of HNO_3 12 *M* at the same speed.

The Am was eluted with 20 cc of 4 *M* nitric acid the the Pu with 30 cc of 1 *M* nitric acid containing 0.02 *M* ascorbic acid as a reducing agent. The elution graph plotted by collecting 5 cc fraction of each elution is shown in Fig. 2. Under these conditions, uranium and radium are washed out while thorium remains in the column. Less than 1% of Pu follows Am, while Pu is practically free from any contamination by Am.

Alternatively, a column with an inside diameter of 1 cm by 20 cm in height was filled with 6 g of Microthene supporting 4 cc of 25% DBDECP, cyclohexane solution. In this case, after putting through the sample in 20 cc of HNO_3 12 *M* and washing with another 20 cc of HNO_3 12 *M*, Am was eluted with HNO_3 4 *M*, uranium with HNO_3

TABLE I. Overall Recovery of ^{241}Am and ^{239}Pu from 'Spiked' Urine Using the DBDECP Procedure.

Sample number	Americium added Bq	Plutonium added Bq	Americium recovery %	Plutonium recovery %
1	0.80	–	89.8	–
2	0.80	–	72.8	–
3	0.80	–	91.3	–
4	0.80	–	70.7	–
5	0.80	–	80.2	–
6	0.80	–	77.0	–
7	0.40	–	90.2	–
8	4.00	2.06	79.7	82.3
9	0.80	1.03	84.1	64.0
10	0.80	1.03	76.8	65.4
11	0.80	1.03	72.9	64.4
12	–	1.03	–	75.3
13	–	1.03	–	63.0
14	–	1.03	–	60.4
15	–	1.03	–	63.0
16	–	1.03	–	72.8
Mean and S.D.			80.5 ± 7.4	67.8 ± 7.3

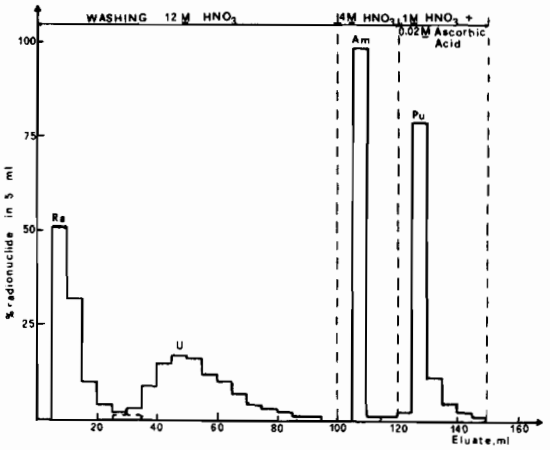

Fig. 2. Elution diagram of Ra, U, Am, Pu from a 3 g Microthene - DBDECP column.

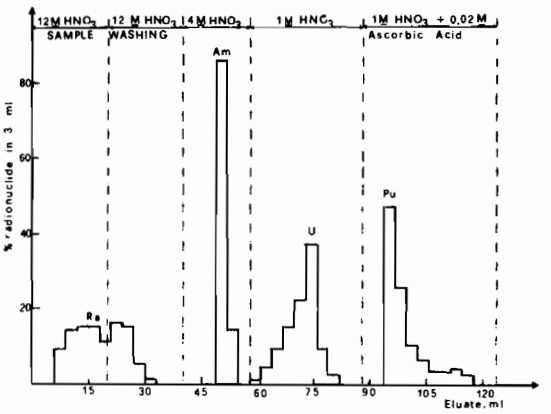

Fig. 3. Elution diagram of Ra, Am, U, Pu from a 6 g Microthene - DBDECP column.

1 *M* and Pu with HNO_3 1 *M* + 0.02 *M* ascorbic acid (Fig. 3). In this test, however, there was greater interference by Pu in the Am fraction, probably caused by the presence of Pu(VI) in the solution.

These separation methods can be included in any analytical method for determining Am and Pu, probably after pre-concentration by precipitation with a suitable carrier.

Method used for Determining Am and Pu in Urine Samples

To 500 ml of urine in a 1000 ml beaker, 150 ml of 70% HNO_3 and 50 ml of H_2O_2 were added. The mixture was brought to boiling point and was evaporated to 200 ml. The solution should thus give roughly 12 *M* in HNO_3. A few ml of H_2O_2 were added. After cooling the solution was poured into a 300 ml separatory funnel and 3 ml of DBDECP was added. The mixture was shaken vigorously for 1 minute and the phases allowed to separate.

The aqueous phase was discarded and the organic phase washed with 5–10 ml of HNO_3 12 *M*. The aqueous phase was discarded. Toluene (5 ml) was added and Am in the aqueous phase extracted by shaking for 1 minute with 30 ml of HNO_3 2 *M*. The operation was repeated once more.

Plutonium was extracted by shaking for 1 minute with 30 ml of HCl 3 *M* + NH_4I 0.1 *M*. The operation was repeated and then the two aqueous extracts were dried.

TABLE II. Results of Americium and Plutonium Determination on Urine Samples from non-Exposed Personnel Using the DBDECP Procedure.

Sample number	Americium activity Bq/l	Plutonium activity Bq/l
1	$3.7 \cdot 10^{-4}$	$13 \cdot 10^{-4}$
2	$8.5 \cdot 10^{-4}$	$4.8 \cdot 10^{-4}$
3	$6.7 \cdot 10^{-4}$	$5.2 \cdot 10^{-4}$
4	$5.2 \cdot 10^{-4}$	$9.9 \cdot 10^{-4}$
5	$8.5 \cdot 10^{-4}$	$7.4 \cdot 10^{-4}$
6	$6.3 \cdot 10^{-4}$	$9.9 \cdot 10^{-4}$
7	$8.8 \cdot 10^{-4}$	$5.2 \cdot 10^{-4}$
8	$4.1 \cdot 10^{-4}$	$4.8 \cdot 10^{-4}$
9	$9.6 \cdot 10^{-4}$	$7.4 \cdot 10^{-4}$
10	$5.5 \cdot 10^{-4}$	$7.0 \cdot 10^{-4}$
Mean and S.D.	$6.7 \cdot 10^{-4} \pm 2.1 \cdot 10^{-4}$	$7.4 \cdot 10^{-4} \pm 2.7 \cdot 10^{-4}$

TABLE III. Decontamination Factors of Americium and Plutonium from Some Natural Alpha Emitters Using the DBDECP Procedure.

Radionuclide	D.F. for Americium	D.F. for Plutonium
Radium Ra-226	$>3 \cdot 10^4$	$>3 \cdot 10^4$
Polonium Po-210	600	$1 \cdot 10^4$
Thorium Th-228	160	90
Uranium U-232	10	5
Americium Am-241	–	500
Plutonium Pu-239	30	–

To the extracted Am and Pu residues sulphuric acid was added, and electrodeposition on a stainless steel cathode from $(NH_4)_2SO_4$ 0.5–1 *M* at pH 4–4.5 was made, using methyl red as indicator [18].

Results and Discussion

A number of urine samples were analysed after adding small quantities of ^{241}Am and ^{239}Pu. After electrodeposition, the discs were examined under an alpha spectrometer using a 450 mm^2 surface barrier detector with a background value of 0.001 cpm and 27% detection efficiency. The results are shown in Table I.

Chemical yield for Am can be considered good. Though lower, the chemical yield for Pu can be said to be acceptable. With these chemical yields, background values and count efficiencies, the lower limit of detection (LLD) at the 95% confidence level can be calculated for a count time of 300′ as $1.6 \cdot 10^{-3}$ Bq/l (0.04 pCi/l) for ^{239}Pu and $1.3 \cdot 10^{-3}$ Bq/l (0.03 pCi/l) for ^{241}Am.

'Urine whites' were also determined in the same way by analysing ten urine samples from individuals not exposed to risk of contamination by Pu and Am. The results are shown in Table II.

Decontamination factors for a number of natural emitting alpha radionuclides were also determined by adding 10^4–10^5 dpm of each radionuclide to urine samples, which were then analysed (Table III). As the decontamination factor of Am by Pu is not very high, in the event of combined contamination activity due to ^{241}Am may be overestimated on account of interference by ^{238}Pu.

From the results, it can safely be concluded that the proposed method can be used successfully in laboratories conducting control analysis of personnel exposed to internal contamination. The main advantages of the method are that it is simple and quick,

thus enabling a large number of samples to be analysed in a short time, and provides for determining the two actinides sequentially from a single sample. Using chromatography, it may even be possible to improve Am–Pu separation even further.

References

1 T. Y. Toribara, C. Predmore and P. A. Hargrave, *Talanta, 10,* 209 (1963).
2 E. E. Campbell and W. D. Moss, *Health Physics, 11,* 737 (1965).
3 C. Testa, *Gior. Fis. San. Prot. Rad., 10,* 202 (1966).
4 C. Testa and G. Santori, *Gior. Fis. San. Prot. Rad., 16,* 1 (1972).
5 W. B. Silker, *Health Physics, 11,* 965 (1965).
6 F. E. Butler, *Health Physics, 15,* 19 (1967).
7 A. Delle Site, G. Santori and C. Testa, CNEN-RT/PROT. (81) 6 (1981).
8 F. E. Butler, *Analytical Chemistry, 37,* 340 (1965).
9 I. F. Horn, *Health Physics, 20,* 664 (1971).
10 F. Patti and D. Bullier, *Radioprotection, 6,* 2 (1972).
11 F. E. Butler and R. M. Hall, *Analytical Chemistry, 42,* 1073 (1970).
12 T. H. Siddall, *J. Inorg. Nucl. Chem., 25,* 883 (1963).
13 T. H. Siddall, *J. Inorg. Nucl. Chem., 26,* 1991 (1964).
14 S. Ballestra and R. Fukai, *Talanta, 30,* 45 (983).
15 W. W. Schulz, Richland, ARH-SA-203 (1974).
16 W. W. Schulz and L. D. Mc Isaac, Richland, ARH-SA-217 (1975).
17 H. Petržílová, L. Kuča and J. Binka, UJV 5093-CH (1980).
18 N. A. Talvitie, *Analytical Chemistry, 44,* 280 (1972).