

# Optimization of plutonium extraction with methyltrioctylammonium chloride preceding its determination by liquid scintillation spectrometry

Andrzej Komosa,  
Magdalena Piekarz

**Abstract.** Optimization of selective extraction conditions for separating plutonium from uranium and thorium standard solutions using methyltrioctylammonium chloride (Aliquat 336) as extracting agent is presented. Influence of such parameters as concentration of extracting agent and nitric acid, and kind of reducing agent on the efficiency of extraction were studied. The method was developed for standard solutions of Pu, Th and U. A Quantulus liquid scintillation spectrometer was used for determination of alpha activity of these isotopes. It was found that using HDEHP in the first stage of the elaborated procedure and Aliquat 336 in the next, it is possible to separate Pu from the mixture of U and Th. Optimal values of measuring parameters such as a PSA value and a scintillation cocktail volume were established as well.

**Key words:** Pu • LSC spectrometry • methyltrioctylammonium chloride • extraction

## Introduction

Plutonium isotopes are the most important radioelements due to their radiotoxicity, long half-life and global dispersion. Four long-lived Pu isotopes are concerned as long-term contaminants of the environment:  $^{238}\text{Pu}$  (87.7 y),  $^{239}\text{Pu}$  ( $2.41 \times 10^4$  y),  $^{240}\text{Pu}$  (6440 y) and  $^{241}\text{Pu}$  (14.4 y). Their presence in the environment is a result of atmospheric weapon testing and various accidents that caused worldwide contamination by Pu. For this reason, plutonium has been the subject of intensive biological and environmental research [9].

It was evaluated that former atmospheric tests involved dispersing of about 0.3 PBq  $^{238}\text{Pu}$ , 6.5 PBq  $^{239}\text{Pu}$ , 4.3 PBq  $^{240}\text{Pu}$  and 142 PBq  $^{241}\text{Pu}$ , mostly above the northern hemisphere [18, 19]. Accidental disintegration of satellites powered with plutonium sources introduced about 0.63 PBq  $^{238}\text{Pu}$  to global plutonium budget as well [3, 18]. This latter contamination was spread mainly above the southern hemisphere. The Chernobyl fallout in 1986 was also important, mostly for European countries. This catastrophe released to the atmosphere about 0.035 PBq  $^{238}\text{Pu}$ , 0.03 PBq  $^{239}\text{Pu}$ , 0.042 PBq  $^{240}\text{Pu}$  and 6 PBq  $^{241}\text{Pu}$  [10, 14].

Due to these facts, plutonium is still present in the environment. Long but diverse half-lives are a reason of plutonium isotopic ratio variation with time. In spite of rather small hazard for human health, plutonium isotopes can serve as tracers for environmental migra-

A. Komosa<sup>✉</sup>, M. Piekarz  
Department of Radiochemistry and Colloid Chemistry,  
Maria Curie-Skłodowska University,  
3 M. Curie-Skłodowskiej Sq., 20-031 Lublin, Poland,  
Tel.: +48 81 537 5631, Fax: +48 81 533 2811,  
E-mail: andrzej.komosa@umcs.lublin.pl

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tion of polyvalent ions. The importance of plutonium determination in environmental samples is connected with the existence of nuclear power plants and terrorist threat all over the world. Therefore, an elaboration of rapid method of Pu isotope determination in environmental samples is highly desirable.

Alpha emitting isotopes of plutonium can be relatively easily determined by alpha spectrometry after appropriate radiochemical treatment. However, determination of beta emitting  $^{241}\text{Pu}$  of low maximal beta energy, equal to 21 keV, is rather complicated. Its determination in environmental samples requires radiochemical separation from matrix material as well as proper, efficient method for measuring such low energy of beta radiation. The only possible radiometric method for activity determination is liquid scintillation (LS) spectrometry. Especially, the ultra-low level spectrometer Quantulus (Wallac-PerkinElmer) is the best choice for this purpose [21, 22].

Using LS spectrometry is necessary to prepare sample in such a way that it meets measuring requirements: measuring isotope should be in the form of solvent easily mixed with scintillation cocktail and do not involve marked quench effect. Therefore, a liquid-liquid extraction method during sample preparation is the best one.

Commercially available scintillation cocktails for non-aqueous solutions give better counting efficiency due to a maximal light yield [11, 20] than other ones destined to aqueous samples. Aim of this study was to choose a proper extracting agent for separation of plutonium from environmental sample (usually by a few steps). This agent should be characterized by a high distribution coefficient and a small quenching influence [1].

During determination of beta emitting plutonium by LS one should note that the main disadvantage of this method is a low resolution of the alpha peaks. Thus, using liquid scintillation spectrometry it is possible to determine only a total alpha activity (if several alpha emitters are present) [8]. However, the measurement of low energy beta radiation together with total alpha activity is possible from the same spectrum. This possibility is very important due to the fact that  $^{241}\text{Pu}$  is a beta emitter, and in this way it can be measured simultaneously with other plutonium isotopes, if other  $\beta$ -emitters are absent [15]. Sometimes, especially in the case of overlapping spectra, a pulse shape discrimination option of Quantulus can be chosen (PSA), which allows distinguishing pulses from alpha and beta decays.

For extraction of uranium and transuranides, various reagents can be used. The most frequently applied are salts of organophosphoric acid or quaternary ammonium salts.

As it is known from the literature, a methyltrioctylammonium salt (Aliquat 336) is very efficient extracting agent for tetravalent elements, but can extract other ions. It was found that extraction ability decrease in the order:  $\text{M}^{4+} > \text{MO}_2^{2+} > \text{M}^{3+}$  [5]. This extractant was used for plutonium separation during its determination in tissue samples by alpha spectrometry [6]. Aliquat 336 was used also as extractant for purification of uranium, separating it from thorium [4] or for separation uranium(VI) from americium(III) [13]. This reagent was a good extractant for  $\text{Np(VI)}$  [12] or radium-226 [2] as well.

The aim of this work was to find optimal conditions of plutonium extraction from solutions containing also uranium and thorium isotopes using methyltrioctylammonium chloride as extracting agent. At the beginning, the study was performed using standard solution of alpha emitting plutonium. In the next stage, beta emitting plutonium is planned to apply.

## Experimental

For measurements, a ultra-low level spectrometer Quantulus (Wallac-PerkinElmer) was used with a  $^{14}\text{C}$  or an alpha/beta option. All experiments were conducted using a standard  $^{242}\text{Pu}$  (alpha emitter) tracer solution of specific activity 0.7327 Bq/g. Usually 0.02Bq  $^{242}\text{Pu}$  was added to the solution to form the experimental sample. Thorium and uranium nitrate were used to prepare standard solution in 3 M  $\text{HNO}_3$ . Concentration activity of thorium was found by alpha spectrometry to be 0.17 Bq/sample and uranium 0.18 Bq/sample.

Three various concentrations of methyltrioctylammonium chloride were prepared by dissolution in xylene: 0.2 M, 0.1 M and 0.05 M. Nitric acid solutions of concentration ranging from 0.5 M to 8 M were prepared by dissolution of concentrated  $\text{HNO}_3$  in distilled water. Sodium nitrite was used as an oxidizing agent and ascorbic acid dissolved in 1 M hydrochloric acid as reducing agent. Scintillation cocktail was prepared by dissolving 7 g of Permablend III (Packard) which consists of 91% 2,5-difenyloxazole (PPO) and 9% 1,4-bis (2-methylstyryl) benzene (*bis*-MSB) in 1 dm<sup>3</sup> of toluene.

Preliminary extraction experiments were conducted with a single isotope to find the best extraction conditions of these nuclides into the organic phase and establish conditions of possible separation of these isotopes. In the next step, a separating extraction procedure was studied to assure conditions for a separate determination of plutonium from other isotopes.

In this procedure, an additional extracting reagent was adopted for the first stage: HDEHP (*bis* (2-ethylhexyl) phosphate) and TOPO (trioctylphosphine oxide). These reagents should easily transfer all studied isotopes into an organic phase [1, 16, 21].

## Simple extraction of Pu and a sum of U and Th

A procedure of single isotope extraction was elaborated basing on Toribio *et al.* results [17]. Given amounts of the tracer standard solutions ( $^{242}\text{Pu}$ ,  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  nitrate) were added into separate 25 cm<sup>3</sup> beakers containing 10 cm<sup>3</sup> of nitric acid. Next, a small amount of solid  $\text{NaNO}_2$  was added to the solution to oxidize Pu to  $\text{Pu}^{4+}$  or to stabilize uranium and thorium in their oxidation states. Different concentrations of  $\text{HNO}_3$  (0.5 M to 8 M) were used. Concentrations of extractive agents were 0.05 M, 0.1 M and 0.2 M. Extraction was performed as follows: 10 cm<sup>3</sup> of an aqueous solution was transferred to a separatory funnel, and then was shaken with 5 cm<sup>3</sup> of Aliquat 336 for 5 min. The 4.5 cm<sup>3</sup> sample of organic phase was transferred by pipetting to a polyethylene, teflon coated scintillation vial (low-diffusion vial, Packard) and 5 cm<sup>3</sup> of the scintillation

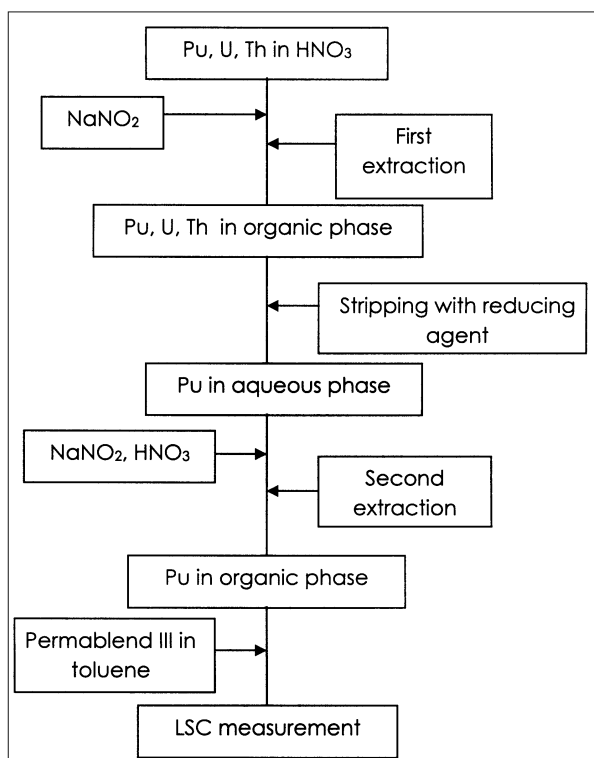
cocktail was added. After few hours of conditioning in the dark, the sample was measured inside the apparatus in the LS spectrometer during 5 h at high energy beta option ( $^{14}\text{C}$ ).

Blank samples were prepared in the same way, except that the tracer solution was replaced by pure 3 M nitric acid.

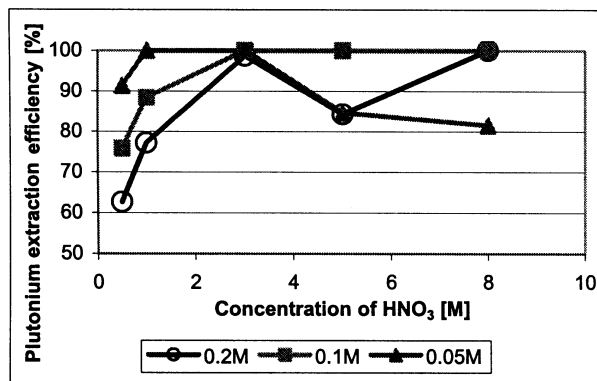
### Procedure of selective extraction of Pu from U and Th mixture

Basing on the literature data, the following procedure was proposed for the separation of plutonium from a mixture of two other nuclides [7, 8, 22]. In the first extraction step, three various reagents were tested with the purpose to extract all isotopes: Pu, Th and U from aqueous solution to organic phase. The solutions of 0.1 M and 0.05 M Aliquat 336 in xylene, 0.2 M HDEHP in toluene and 0.2 M TOPO in cyclohexane were used for this purpose. Extraction was performed from 2 M nitric acid, in the way as described above. Organic phase was retained in a separatory funnel. Afterwards Pu was stripped 2 times with 5 cm<sup>3</sup> of 5% ascorbic acid in 1 M HCl or 0.1 M NH<sub>4</sub>I in 6 M HCl. In these conditions plutonium was reduced to trivalent oxidation state and transferred to the aqueous phase, whereas Th and U still remained in the organic phase.

The aqueous phase was then boiled with nitric acid and solid NaNO<sub>2</sub> was added to oxidize Pu. Next, plutonium was extracted again by 0.1 M Aliquat 336 in xylene, 5 cm<sup>3</sup> of the scintillation cocktail added and LS measurement performed during 5 h. A scheme of the procedure described above is given in Fig. 1.



**Fig. 1.** Scheme of procedure used for selective plutonium extraction from uranium and thorium.



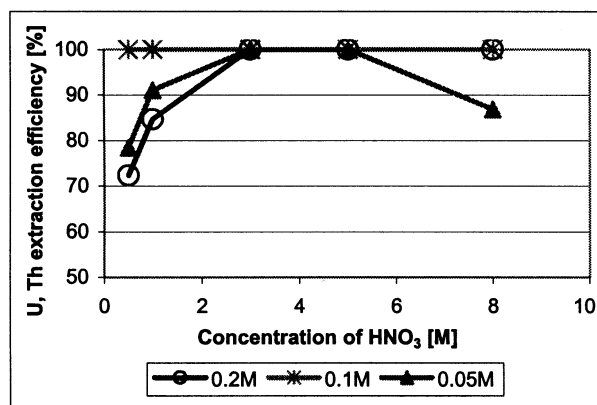
**Fig. 2.** Extraction efficiency of plutonium as a function of nitric acid concentration for 3 various Aliquat 336 concentrations.

## Results and discussion

### Optimization of extraction procedure

Results of single extraction of plutonium were shown in Fig. 2 and that of uranium and thorium mixture in Fig. 3. As it is seen, Aliquat 336 is a good extracting agent for plutonium, uranium and thorium. It was proved that the best conditions of Pu extraction were assured by applying 0.1 M Aliquat 336 and the nitric acid concentration ranging from 3 M to 8 M. If the extracting agent concentration varies from 0.05 M to 0.2 M the concentration of 3 M HNO<sub>3</sub> assures a 100% yield of plutonium extraction (see Fig. 2). At higher HNO<sub>3</sub> concentrations (above 3 M), the extraction yield of plutonium, at 0.05 M Aliquat 336, decreases to about 80%. It is probably connected with shifting of the reaction equilibrium state to a less extractable form. However, the observed decrease of plutonium extraction yield in 5 M HNO<sub>3</sub> and the highest Aliquat 336 concentration, i.e. 0.2 M, is hard to explain (see Fig. 2). Effect of experimental error cannot be excluded.

Figure 3 presents the influence of nitric acid concentration on the extraction efficiency of the sum of thorium and uranium at various concentration of the extracting agent Aliquat 336. In Fig. 3, one can observe that the sum of uranium and thorium is effectively extracted to organic phase at all concentrations of Aliquat 336 from 3–5 M nitric acid. A slight decrease of the efficiency is observed only in 8 M HNO<sub>3</sub> and 0.05 M Aliquat 336 what



**Fig. 3.** Extraction efficiency of a sum of thorium and uranium as a function of nitric acid concentration for 3 various Aliquat 336 concentrations.

**Table 1.** Total efficiency of extraction of the single isotopes in two extraction steps from 3 M nitric acid

First extraction	Stripping	Second extraction	Extraction efficiency (%)		
			Pu	U	Th
0.1 M Aliquat 336	0.1 M NH <sub>4</sub> I/6 M HCl	0.1 M Aliquat 336	95	22	100
0.05 M Aliquat 336	0.1 M NH <sub>4</sub> I/6 M HCl	0.05 M Aliquat 336	87	20	83
0.1 M Aliquat 336	5% ascorbic acid/1 M HCl	0.1 M Aliquat 336	77	21	100
0.05 M Aliquat 336	5% ascorbic acid/1 M HCl	0.05 M Aliquat 336	86	18	100
0.2 M TOPO	0.1 M NH <sub>4</sub> I/6 M HCl	0.1 M Aliquat 336	6.3	17	53
0.2 M HDEHP	5% ascorbic acid/1 M HCl	0.1 M Aliquat 336	96	3.1	1.9

can be explained as above. As it is seen, a concentration of 0.1 M of extracting agent ensures a complete extraction of both isotopes at the studied concentration range of HNO<sub>3</sub> (i.e. 1–8 M). From these results, it follows that it is impossible to find such a range of nitric acid and extracting agent concentrations in which separate, selective extraction of plutonium from uranium and thorium could be achieved. Therefore, another procedure was tested, which comprised of extraction of all nuclides into organic phase, and then plutonium was stripped by changing its oxidation state, followed by the second extraction of plutonium.

The results of selective extraction study of Pu from U and Th using this procedure are shown in Table 1. As it is seen, using Aliquat 336 in the first and second extractions the recovery of plutonium achieved value as high as 77–95%, that of uranium being around 20%. In these conditions, however, thorium was also strongly extracted, i.e. the figure being almost 100%. If extracting agent in the first step was changed to a TOPO solution, enough satisfactory results were still not achieved. A small recovery of Pu (about 6%) and high of Th (above 50%) was observed. At the end, the best results were obtained when 0.2 M HDEHP was used in the first step of extraction, 5% ascorbic acid in 1 M HCl as reducing agent and 0.1 M Aliquat 336 as the second step of extraction. In this way, it was possible to reach a high recovery of Pu (96%), whereas thorium and uranium remained in the aqueous phase.

### Optimization of LS measurement

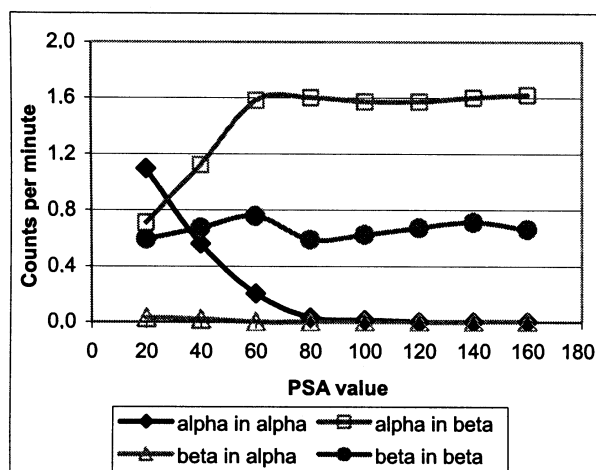
During determination of plutonium, the measurement conditions are very important, especially, in the case of applying this method for the determination of beta emitting <sup>241</sup>Pu. Such measurement parameters as a PSA (pulse shape analyzer) level, quenching and the volume of scintillation cocktail have a large influence on the precision and uncertainty of activity measurement. Therefore, in our study these parameters were tested.

The PSA parameter enables to separate alpha and beta pulses from the same sample collecting them in separate channels. If one can measure simultaneously beta <sup>241</sup>Pu and alpha emitting Pu isotopes, this option of Quantulus is very useful. To establish the optimum PSA level a sample was prepared by a single extraction of Pu with 0.1 M Aliquat 336 from 3 M HNO<sub>3</sub>, next 5 cm<sup>3</sup> of scintillation cocktail was added and measurements were performed with a PSA level ranging from 20 to 160. Results are given in Fig. 4. Because of the absence of beta radiation in our sample (alpha emitting nuclides were only introduced) in beta channel only beta pulses

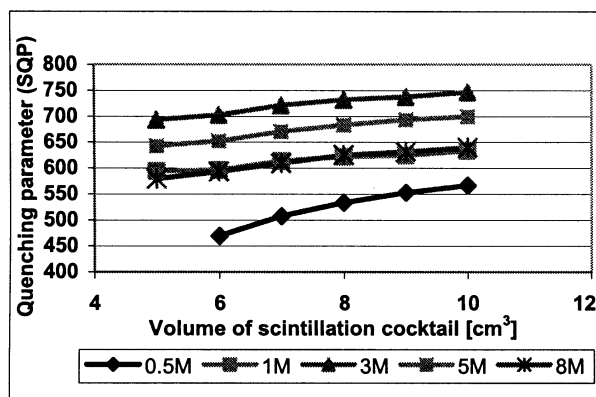
of background were recorded. As it is seen, with an increase in PSA level, the alpha count rate diminishes and the rate of beta pulses misclassified as alpha increase. Therefore, PSA value of 30 proved to be optimal.

During LS measurement, the quenching is the most important factor. Our study showed that this parameter was changed with both nitric acid concentration and volume of scintillation cocktail used. Quench level is described by SQP value (which ranged from 0 for total quench to 1000 for no quench condition). The results of SQP values vs. volume of scintillation cocktail added for five various HNO<sub>3</sub> concentrations and 0.2 M Aliquat 336 were presented in Fig. 5.

In the examined range of cocktail volume, the SQP values slightly decreased with decreasing volume. It seems that the best measurement conditions (the high-



**Fig. 4.** Count rate [cpm] in the alpha and beta channels vs. the PSA value (conditions: 0.1 M Aliquat 336, 3 M HNO<sub>3</sub>). Open points – misclassified pulses.



**Fig. 5.** Influence of volume of scintillation cocktail on the quench parameter value (PSA) at various HNO<sub>3</sub> concentrations (0.2 M Aliquat 336).

est SQP value) can be achieved by adding 10 cm<sup>3</sup> of scintillation cocktail to the extracted sample. However, such a large total sample volume resulted in a high background; therefore, in our study usually 5 cm<sup>3</sup> of the cocktail was used. As it is seen from Fig. 5, no simple correlation between nitric acid concentration and the SQP value was observed, but the highest SQP values were obtained at 3 M HNO<sub>3</sub>.

## Conclusions

Methyltrioctylammonium chloride dissolved in xylene reveals a good extracting power for plutonium, uranium and thorium from a wide range of nitric acid concentration. The optimal extraction condition was obtained using 3 M HNO<sub>3</sub> and 0.1 M Aliquat 336. Concentration of nitric acid was found to influence both extraction efficiency and quench, the optimal concentration being 3 M HNO<sub>3</sub>.

Increase in volume of scintillation cocktail caused an increase in the SQP quench parameter value. It was found that the optimal PSA value for measuring alpha and beta pulses separately was equal to 30. The highest selectivity of plutonium separation from both uranium and thorium can be achieved using 0.2 M HDEHP in the first step and 5% ascorbic acid in 1 M HCl as reducing agent for Pu stripping, and 0.1 M Aliquat 336 for the second extraction. In these conditions, 96% of plutonium can be found in the organic phase with only traces of thorium and uranium present.

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