NUKLEONIKA 2015;60(1):181–186
doi: 10.1515/nuka-2015-0033

ORIGINAL PAPER

DE GRUYTER
OPEN

Validation of the method for determination of plutonium isotopes in urine samples and its application in a nuclear facility at Otwock

Katarzyna Rzemek, Andrzej Czerwiński, Małgorzata Dymecka, Jakub Ośko, Tomasz Pliszczyński, Zbigniew Haratym

Abstract. The studies aimed at determining low activities of alpha radioactive elements are widely recognized as essential for the human health, because of their high radiotoxicity in case of internal contamination. Some groups of workers of nuclear facility at Otwock are potentially exposed to contamination with plutonium isotopes. For this reason, the method for determination of plutonium isotopes has been introduced and validated in Radiation Protection Measurements Laboratory (LPD) of the National Centre for Nuclear Research (NCBJ). In this method the plutonium is isolated from a sample by coprecipitation with phosphates and separated on a AG 1-X2 Resin. After electrodeposition, the sample is measured by alpha spectrometry. Validation was performed in order to assess parameters such as: selectivity, accuracy (trueness and precision) and linearity of the method. The results of plutonium determination in urine samples of persons potentially exposed to internal contamination are presented in this work.

Key words: alpha radioactive elements • internal contamination • plutonium • urine

K. Rzemek✉, M. Dymecka, J. Ośko, T. Pliszczyński, Z. Haratym
Radiation Protection Measurements Laboratory,
National Centre for Nuclear Research (NCBJ),
7 A. Sołtana Str., 05-400 Otwock/Świerk, Poland,
Tel.: +48 22 273 1150, Fax: +48 22 273 1200,
E-mail: katarzyna.rzemek@ncbj.gov.pl

A. Czerwiński
Faculty of Chemistry,
University of Warsaw,
1 Pasteura Str., 02-093 Warsaw, Poland
and Department of Electrochemistry,
Industrial Chemistry Research Institute,
8 Rydygiera Str., 01-793 Warsaw, Poland

Received: 14 October 2014
Accepted: 19 January 2015

Introduction

Routine monitoring of internal contamination of the workers at a nuclear facility in Otwock is carried out by the accredited Radiation Protection Measurements Laboratory (LPD) of the National Centre for Nuclear Research (NCBJ). This monitoring is based on *in vivo* and *in vitro* measurements. Direct measurement of radionuclides in the human body is realized using a Whole Body Counter or a Thyroid Counter. *In vitro* measurements, which are routinely performed for the workers, include measurements of beta radioactive isotopes (HTO, ^{32}P, ^{35}S, ^{90}Sr, total beta activity) and alpha radioactive isotopes (total alpha activity) in urine samples. In the recent period, the Laboratory has broadened the range of procedures to include a procedure for the determination of activity of plutonium and americium isotopes in urine samples. These methods were developed due to the possibility of potential exposure to internal contamination of some groups of workers to these alpha emitters. In this paper a method for determining the activity of plutonium isotopes in urine samples is discussed. This method may be used to perform routine and accidental monitoring of potentially exposed persons. The aim of this work was to present the validation of the method for determination of plutonium activity and analyses of plutonium activity in urine which were carried out by LPD.

Studies aimed at determining the activity of plutonium isotopes are essential because of their high radiotoxicity [1]. Small amounts of these isotopes can cause a significant dose if internal contamination occurs. The way in which plutonium is adsorbed in the body depends on the routes of exposure to radiation and chemical forms of plutonium. Plutonium penetration into the body occurs mainly by inhalation. The element gets into the lungs along with atmospheric aerosols. Depending on the form in which plutonium occurs (soluble and insoluble) it can lodge in the lungs and lymph system or get into the bloodstream and is mainly deposited in the liver and bones [2].

Problem of the analysis of alpha emitters in urine is difficult due to very low activities of isotopes which are being determined (e.g. when it comes to intake of 1 Bq of plutonium by inhalation, assuming the absorption type M, plutonium activity in the urine after 1 day of intake is of the order of 10^{-4} Bq [3]). A suitable technique used for this type of measurement of low activity of alpha emitters is alpha spectrometry with silicon semiconductor detectors [4].

In order to prepare a sample for alpha spectrometry measurement an appropriate radiochemical preparation should be performed. For this purpose, the determined isotopes are separated by the co-precipitation method and purified with an anion exchange resin. Afterwards, the source is being prepared for the measurement by electrodeposition on a steel disc.

For the purpose of validation of the procedure for plutonium determination in urine, the following parameters were assessed: selectivity, accuracy (trueness and precision) and linearity of the method. In order to evaluate these parameters the investigated procedure of plutonium determination was applied to the following urine samples: blank sample, urine sample with a ^{236}Pu tracer, urine samples spiked with a known activity of ^{238}Pu and a tracer of ^{236}Pu, urine sample containing ^{238}Pu, $^{239+240}$Pu and ^{236}Pu.

Materials and methods

Apparatus

Alpha spectra of the samples were measured with an Alpha Analyst Model 7200 spectrometer (Canberra, USA) equipped with passivated silicon planar implanted detectors of 450 mm^2 and 1200 mm^2 effective area. Alpha Appendix software was used to alpha spectra analyses.

Tracer

^{236}Pu standard solution, obtained from Isotrak, was used as tracer. Due to the high specific activity of this solution, its dilution was necessary. A specific activity of the prepared solution was 0.1038 ± 0.0010 Bq·g^{-1}.

Plutonium solution

Plutonium solution was obtained from PROCORAD (Association for the Promotion of Quality Control in Radiotoxicological Analysis) during the intercomparison exercise. PROCORAD provides a report summarizing the results obtained by participating laboratories and including referenced values. A specific activity of ^{238}Pu solution according to this report was 46.2 ± 2.0 Bq·dm^{-3} [5].

Chromatographic resin

The AG 1-X2 Resin (50–100 mesh, chloride form), purchased from Bio-Rad, was used for the procedure of plutonium isolation. The resin was placed in a glass column. Length and internal diameter of the column were 100 mm and 5 mm, respectively.

Electrodeposition device

The volume of electrodeposition cell, which was used in the procedure of determining plutonium activity in urine, was 50 cm^3. Cell was made of teflon. Plutonium isotopes, during the process, were electrochemically deposited on the cathode (stainless steel disc, thickness: 0.6 mm; diameter: 25 mm), which was placed at the bottom of the cell. The platinum electrode was used as anode. The effective area of electrodeposition on the disc was 2.84 cm^2. DC Regulated Power Supply (NDN, MODEL: DF173003C) was applied to electrodeposition process.

Samples

Urine samples for the validation of the procedure for determining plutonium activity were collected from people who were not exposed to contamination with alpha emitters (fourteen urine samples).

People who were occupationally exposed to plutonium isotopes were asked to collect daily urine samples into polyethylene vessels. Twenty two urine samples were analyzed.

Procedure

Plutonium separation (urine sample)

The method for plutonium determination in urine was developed on the basis of the literature data [e.g. 6–8]. Daily urine sample was acidified by the addition of 65% HNO_3 (130 cm^3 to 1 litre of urine). The known activity of ^{236}Pu tracer solution, 1 cm^3 of 85% H_3PO_4 and 1 cm^3 of 1.25 M $Ca(NO_3)_2$ were added to the sample. The sample was heated for about 3 h at a temperature of about 80°C. After this time, calcium phosphate was precipitated by the addition of 25% NH_3 to pH = 9. The next day, the precipitate was separated by decantation

and centrifugation. The precipitate was transferred by 65% HNO_3 to a glass beaker and after heating 30% H_2O_2 was added. Wet ashing was repeated until the color of the residue became white.

The AG 1-X2 Resin, which was suspended in water, was transferred into the column and pre-conditioned by 50 cm^3 of 8 M HNO_3. The sample was dissolved in 80 cm^3 of 8 M HNO_3, heated and 150 mg of $NaNO_2$ was added to adjust the +4 valency of plutonium. Then, the sample was passed through the resin and then, the resin was washed with 50 cm^3 of 8 M HNO_3. Next, the resin was washed with 40 cm^3 of 10 M HCl to remove thorium isotopes. In order to elute plutonium isotopes 250 mg of hydroxylamine hydrochloride was put on the top of the column and three fractions of 0.5 M HCl were added successively.

The sample was evaporated to dryness and mineralized with 2.5 cm^3 of 65% HNO_3 and 2.5 cm^3 of 35–38% HCl. The final step was plutonium electrodeposition on a steel disc.

Electrodeposition procedure

Electrodeposition was performed following the modified procedure of Hallstadius [9]. In the beginning, 1.5 cm^3 of 1 M Na_2SO_4 was added to the sample and evaporated to dryness. In the next step, 0.5 cm^3 of 96% H_2SO_4 was added and the sample was heated. After fuming, deionized water was added to the sample to a volume of approximately 30 cm^3 and the sample was boiled. After addition of 1 cm^3 of saturated solution of EDTA and a drop of 1% thymol blue idicator, the value of pH was adjusted to 2.5÷2.8. The solution was transferred to the electrodeposition cell, and the required current of 1 A was set. After three hours, at the end of electrodeposition, approximately 1.5 cm^3 of 25% NH_4OH was added to the sample and power supply was turned off. After dismantling of the cell, the stainless steel disc was removed and rinsed with deionized water.

Alpha counting

For standard measurement, the counting time of the sample depends on the plutonium (^{238}Pu or $^{239+240}Pu$) activity, the sample was measured until the uncertainty of peak area was in the range of 2–10%.

Results and discussion

The analysis of the main parameters which characterize the validated method are shown below.

Selectivity

The method is selective if the determined element is clearly identified in the presence of other elements that may occur in the sample [10]. In the case of identification of plutonium isotopes, the method is considered to be selective if all the interfering isotopes are, as a result of the application of column chromatography process, removed from the sample and if in the alpha spectrum of the determined isotopes can be distinguished. The selectivity of the method for the determination of plutonium isotopes was assessed by examining the alpha spectra of three samples: those with ^{236}Pu, ^{238}Pu, $^{239+240}Pu$, a sample with a tracer of ^{236}Pu and a blank sample (Fig. 1). Alpha spectra show that the method is appropriate for selective separation of the isotopes ^{238}Pu, $^{239+240}Pu$ from the matrix. The measurement of blank sample (Fig. 1c) showed that during the radiochemical procedure no contamination occured.

Accuracy (trueness and precision)

The accuracy of the method is a parameter that expresses the closeness of obtained results to the reference (true) value. The method is accurate if the conditions for both, trueness and precision, are fulfilled [10].

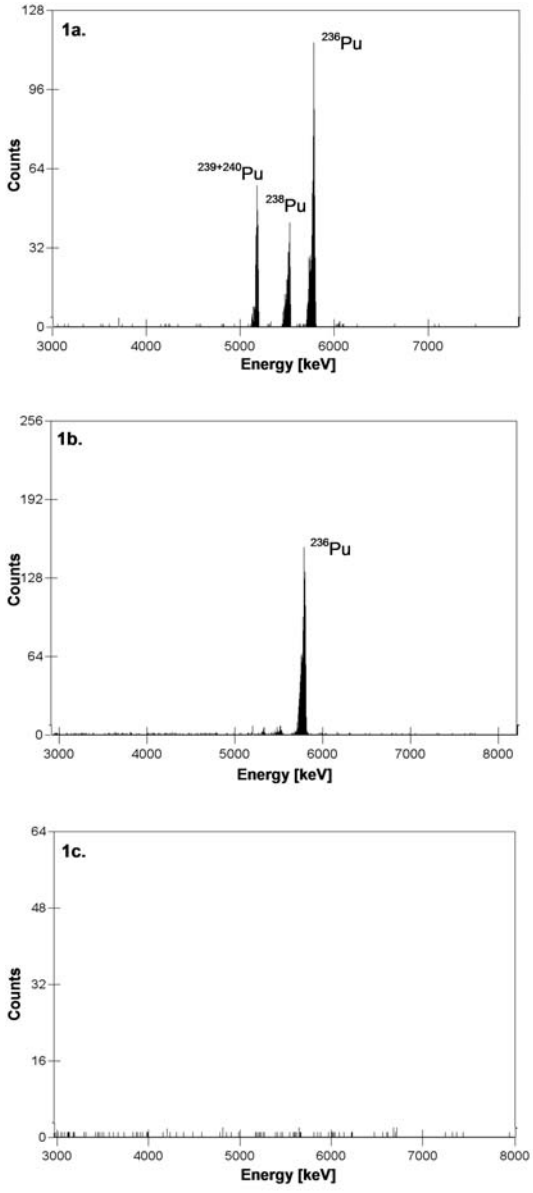

Fig. 1. Alpha spectra of a) urine sample with plutonium isotopes (^{236}Pu, ^{238}Pu, $^{239+240}Pu$), b) urine sample with tracer (^{236}Pu), c) blank sample.

Trueness defines the closeness of set of results obtained by the method to the true value. It was tested by examining nine urine samples at three different levels of ^{238}Pu activity (approximate activity added to the samples: 15, 30, and 45 mBq). The trueness of the result is satisfactory if [11]:

$$(1) \qquad \left|C_{lab} - C_{ref}\right| \le 2.58 \cdot \sqrt{u_{lab}^2 + u_{ref}^2}$$

where C is the activity concentration of ^{238}Pu [Bq·dm^{-3}] and u is the measurement uncertainty ($k = 1$). It was verified that the acceptance criterion is met in the case of each of the results obtained, regardless of the level of activity (Table 1).

Precision characterizes the scattering of results which are obtained by multiple determination using the same method [10]. Evaluation of the precision of the method was carried out on the basis of the results obtained from measurements of six samples with the same concentration activity of ^{238}Pu. Precision is usually assessed in terms of relative standard deviation or the following formula [11]:

$$(2) \qquad 100\% \cdot \sqrt{\left(\left(\frac{u_{ref}}{C_{ref}}\right)^2 + \left(\frac{u_{lab}}{C_{lab}}\right)^2\right)}$$

The Laboratory has accepted the criteria that the values of RSD and the above expression should not exceed 15%. Values calculated according to Eq. (2) for each measured sample did not exceed 4.4%. The result of RSD test is shown in Table 2. Based on the analysis of the obtained results it can be concluded that the validated method is precise.

Additionally, the accuracy of the method was verified through participation in interlaboratory comparisons organized by PROCORAD in 2013 – "Actinides in the urine" and "Plutonium solution". Results obtained for plutonium isotopes fulfilled the acceptance criteria of the organizers. Activities of ^{238}Pu and ^{239}Pu determined by LPD in samples B and C and plutonium solution were close to the target values [5]. In this case the accuracy was expressed in terms of relative bias (Table 3).

Linearity

The linearity of the validated method was investigated by analyzing the results of the measured activity of the samples in which plutonium concentration was at various levels (approximately 20, 40, 60, 100% of applicability range of the method). Samples were measured in an alpha spectrometer with detectors of 450 mm^2 effective area. The graph (Fig. 2) shows the relation between the plutonium reference concentration in urine and the net area of plutonium peak divided by the measurement time. It was assumed that the method is linear if the correlation coefficient is greater than 0.98. The adopted criterion is met,

Table 1. Assessment of accuracy (trueness) of the plutonium activity determination method

Approximate activity of ^{238}Pu added [mBq]	$\lvert C_{lab} - C_{ref}\rvert$ [Bq·dm^{-3}]	$2.58 \cdot \sqrt{u^2_{lab} + u^2_{ref}}$ [Bq·dm^{-3}]	Accuracy (trueness)
	0.002	0.003	+
15	0.002	0.003	+
	0.001	0.003	+
	0.004	0.007	+
30	0.002	0.007	+
	0.004	0.007	+
	0.008	0.010	+
45	0.005	0.010	+
	0.010	0.011	+

Table 2. Assessment of accuracy (precision) of the plutonium activity determination method – RSD test

Approximate activity of ^{238}Pu added [mBq]	Number of samples	RSD [%]	Precision
30	6	5.4	+

Table 3. Determination of ^{238}Pu and ^{239}Pu activity in urine samples – PROCORAD 2013 Intercomparison: "Actinides in urine" and "Plutonium solution"

Sample	Isotope	Activity determined by LPD	Reference value	Relative bias [%]
Urine sample A	blank	blank	blank	–
Urine sample B	^{238}Pu	4.51 ± 0.64 [mBq·sample^{-1}]	4.29 ± 0.20 [mBq·sample^{-1}]	5.13
Urine sample C	^{238}Pu	2.26 ± 0.36 [mBq·sample^{-1}]	2.15 ± 0.10 [mBq·sample^{-1}]	5.12
	^{239}Pu	2.91 ± 0.45 [mBq·sample^{-1}]	2.58 ± 0.12 [mBq·sample^{-1}]	12.8
Plutonium solution	^{238}Pu	48.3 ± 5.6 [Bq·dm^{-3}]	46.2 ± 2.0 [Bq·dm^{-3}]	4.55

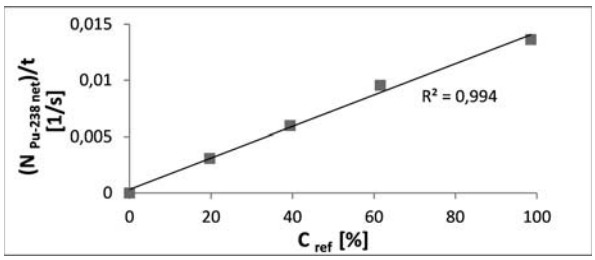

Fig. 2. Assessment of linearity of the determination method of plutonium activity.

therefore, this method is linear over the range of investigated concentrations of ^{238}Pu.

Study of internal contamination

Development of the method for plutonium determination method allowed to conduct analyses of urine samples of persons occupationally exposed to internal contamination with alpha emitters. Analyses of plutonium isotopes activity in twenty two urine samples from employees of the nuclear facility at Otwock were performed.

Table 4 shows the results of conducted analyses. Chemical recovery of ^{236}Pu ranged from 70.6% to 90.4% with an average of 81.9% with a standard deviation of 5.8%. Its average value is comparable to the values presented in the literature [12]. In order to determine the tracer recovery R the following equation was used:

$$R = \frac{N_{tr}}{t \cdot E \cdot A_{tr}} \tag{3}$$

Table 4. Determination of plutonium activity in urine samples

Urine sample code	Added activity of ^{236}Pu [mBq]	Recovery [%]
Sample 1	6.95	90.4
Sample 2	7.04	82.0
Sample 3	7.97	73.6
Sample 4	7.65	93.1
Sample 5	7.96	81.8
Sample 6	8.00	82.8
Sample 7	8.02	78.8
Sample 8	7.92	84.5
Sample 9	7.92	81.6
Sample 10	8.01	77.5
Sample 11	9.15	82.6
Sample 12	9.04	76.1
Sample 13	9.03	76.1
Sample 14	9.19	74.6
Sample 15	7.65	89.8
Sample 16	7.67	84.3
Sample 17	7.74	83.0
Sample 18	7.61	88.5
Sample 19	7.24	87.5
Sample 20	7.28	81.4
Sample 21	7.28	70.6
Sample 22	7.22	82.0
Avarage recovery: 81.9 ± 5.8		

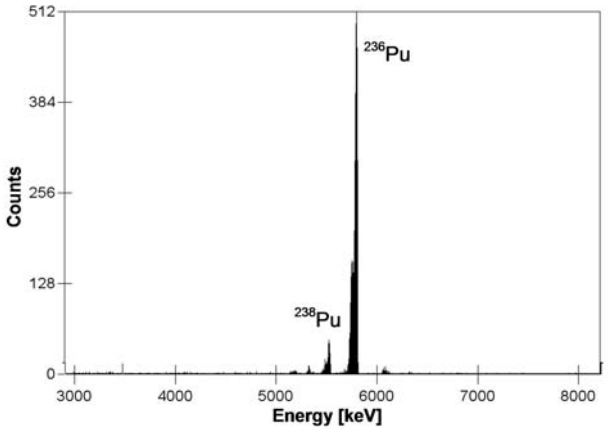

Fig. 3. Alpha spectra of a urine sample with ^{238}Pu activity above MDA.

where, N_{tr} – net area counts of the ^{236}Pu tracer peak (–), t – sample counting time [s], E – counting efficiency of the detector (–), A_{tr} – tracer activity (^{236}Pu) added [Bq].

The analyses showed that twenty one samples were below the minimum detectable activity (MDA) of plutonium isotopes, which was calculated by the following equation [13]:

$$\mathrm{MDA} = \frac{4.66 \cdot \sqrt{B} + 3}{t \cdot E \cdot R} \tag{4}$$

where, B – net area counts of background (–), t – sample counting time [s], E – counting efficiency of the detector (–), R – tracer recovery (–).

Background counts in the energy range of $^{239+240}$Pu were 1–6 counts for one week measurement. Background counts from ^{236}Pu in the energy range of ^{238}Pu depend on the tracer activity, for 1000 counts from ^{236}Pu there were about 35 counts. MDA values for the performed measurements were within the range of 0.04–0.28 mBq per sample.

Figure 3 relates to the urine sample containing ^{238}Pu whose activity was above the MDA. Activity content of ^{238}Pu in sample 13 was 0.46 ± 0.10 mBq per sample. The minimum detectable activity for this measurement was 0.13 mBq per sample.

Conclusions

On the basis of the literature data analysis, a method for plutonium determination in urine samples was developed. The selected method was validated. Reliability of the procedures was proved by assessing the validation parameters which met the established criteria. The method is used for radiological monitoring of workers of the nuclear facility at Otwock, which is carried out by LPD. Analyses of urine samples of persons occupationally exposed was performed using the discussed method, have shown that there was no internal contamination with plutonium isotopes in almost all the cases. In one urine sample ^{238}Pu was detected, which indicates that analyses of plutonium isotopes activity concentration should be carried out in the future, according to the developed method.

Acknowledgment. This work is partly supported by the funds of The National Centre for Research and Development as a part of project no. SP/J/6/143339/11: "Technologies supporting development of safe nuclear power engineering".

References

1. Qiao, J., Xu, Y., Hou, X., & Miro, M. (2014). Comparison of sample preparation methods for reliable plutonium and neptunium urinalysis using automatic extraction chromatography. *Talanta*, *128*, 75–82.
2. Voelz, G. L. (2000). Plutonium and health – how great is the risk? *Los Alamos Science*, 26, 74–89.
3. ICRP. (1997). Individual monitoring for internal exposure of workers. ICRP Publication 78. Ann. ICRP, *27*(3/4).
4. Vajda, N., & Kim, C. -K. (2009). Determination of Pu isotopes by alpha spectrometry: a review of analytical methodology. *J. Radioanal. Nucl. Chem*., *283*, 203–223.
5. Lecoix, G., & Chevalier, C. (2013). Actinides in urine. PROCORAD Radiotoxicological Intercomparison Exercises, 19–21 June 2013, Bucharest, Romania, Retrieved September 11, 2014 from https://procorad.mysps.net/SiteAssets/SitePages/en/News/Lecoix_actinides_urines.pdf
6. Alvarez, A., & Navarro, N. (1996). Method for actinides and Sr-90 determination in urine samples. *Appl. Radiat. Isot*., *47*, 869–873.
7. Arginelli, D., Berton, G., Bortoluzzi, S., Canuto, G., Groppi, F., Montalto, M., Nocente, M., Ridone, S., & Vergo, M. (2008). Purification and separation of Pu and Am in biological samples by anion-exchange and extraction chromatography for high resolution alpha-spectrometry analyses. *J. Radioanal. Nucl. Chem*., *277*, 65–71.
8. Robredo, L. M., Navarro, T., & Sierra, I. (2000). Indirect monitoring of internal exposure in decomissioning of a nuclear power plant in Spain. *Appl. Radiat. Isot*., *53*, 345–350.
9. Hallstadius, L. (1984). A method for the electrodeposition of actinides. *Nucl. Instrum. Methods Phys. Res*., *223*, 266–267.
10. EURACHEM-Guide. (1998). The fitness for purpose of analytical methods – a laboratory guide to method validation and related topics.
11. Shakhashiro, A., Fajgelj, A., & Sansone, U. (2007). Comparison of different approaches to evaluate proficiency test data. In: A. Fajgelj, A. Belli & U. Sansone (Eds.), *Combining and reporting analytical results* (pp. 220–228). Cambridge: RSC Publishing.
12. Kumar, R., Yadav, J. R., Rao, D. D., & Chand, L. (2010). Determination of plutonium isotopes in urine samples from radiation workers using ^{236}Pu tracer, anion exchange resin and alpha spectrometry. *J. Radioanal. Nucl. Chem*., *283*, 785–788.
13. American National Standards Institute. (1996). Performance criteria for radiobioassay. ANSI N 13.30. New York.