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Development of radio analytical method for in-vitro monitoring of Pu in urine matrix

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ABSTRACT

A relatively less expensive and less time consuming radioanalytical technique for quantitative determination of Pu in urine at the mBq level was developed. In this new method, Pu in urine is co-precipitated with $Ca_2C_2O_4$ from wet oxidized urine matrix and oxalate ions is destroyed with $HClO_4$· Pu in +4 state is extracted into 0.01M PC-88A (2-ethyl hexyl phosphonic acid mono-2-ethylhexyl ester)dissolved in toluene from optimized 2M HCl aqueous phase. Pu is stripped into 5% oxalic acid solution and is evaporated with HNO_3–$HClO_4$ mixture to destroy oxalate ions. Finally, Pu is electro deposited in ammonium oxalate medium and counted in an alpha spectrometer. The detailed study of the work is presented in this paper. An interference study on elements that are normally present in urine and other actinides (if present) was performed and is also given.

Keywords: Bioassay; Plutonium; Solvent Extraction; PC-88A; Electrodeposition; Alphaspectrometry

1. Introduction

Estimation of Pu at mBq levels in urine provides an indirect assessment of internal dose received by radiation workers due to its intake while handling Pu in nuclear industries. The rate of Pu excretion in the urine decreases so markedly with time after intake and in parallel the derived investigation level (DIL) for Pu in urine also decreases [1,2].

Inhalation is the most likely route of occupational exposure to Pu and especially with M class compounds [1,2]. The DIL values for acute intake of ^{239}Pu due to M Class compounds are 8.1 mBq and 4.0 mBq for urine sample collected on 2nd and 3rd day of exposure respectively after intake. Moreover, the concentration of Pu excretes in each void of urine sample is variable [3]. Hence, 24 h urine sample is collected from radiation workers and the entire sample is processed to minimize the uncertainty in the dose assessment. Therefore, though, it is reported that alpha spectrometric technique involving extraction chromatographic separation is very fast [4–6], the volume of urine sample taken for analysis varies from 20 to 100 ml is not adequate to estimate low level exposure of Pu and the same extraction chromatographic technique applied to 400 ml urine sample and counted in an alpha spectrometer for 22 h is sensitive but expensive [7]. The technique that uses anion exchange separation requires seven days [8]. Sensitive techniques like ICPMS method with MDA 2.3 μBq/l, TIMS with MDA 6.0 μBq/l, AMS with MDA 6.0 μBq/l and automated flow injection system with MDA 2.3 μBq/l are suitable for low level estimation of Pu but expensive [9,10,11]. Finally FTA method with MDA 12.0 μBq/l requires reactor for irradiation of samples with an analysis time of 10 d [12].

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The present solvent extraction method is simple, less expensive and Pu is extracted into 2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester (PC-88A) dissolved in toluene.

2. Experimental: chemical procedure

The procedure developed involving various steps is shown in Fig. 1. Urine samples collected from unexposed personnel were pooled. To 1000 ml of each pooled urine sample, a known amount of Pu was spiked, mixed and heated with 25 ml of conc. HNO_3 and 5 ml of H_2O_2. The sample was covered with watch glass during heating of the sample for one hour. This treatment breaks metabolic complexes of Pu and other actinides (if present) in urine and keeps them in defined ionic state [13]. Pu in urine is pre-concentrated by a co-precipitation technique. A known amount of $(NH_4)_2C_2O_4$ (~3.0 g) and $NaNO_2$ (~2.0 g) were added and the sample was stirred. Pu was co-precipitated with calcium oxalate by adjusting the pH of the sample between 4 and 5 using 10% ammonia solution and 6 M HNO_3. The precipitate was centrifuged and again the precipitate was carried out in the supernatant for quantitative co-precipitation of Pu. The precipitate was washed with 5% ammonium oxalate solution with pH adjusted to 5.

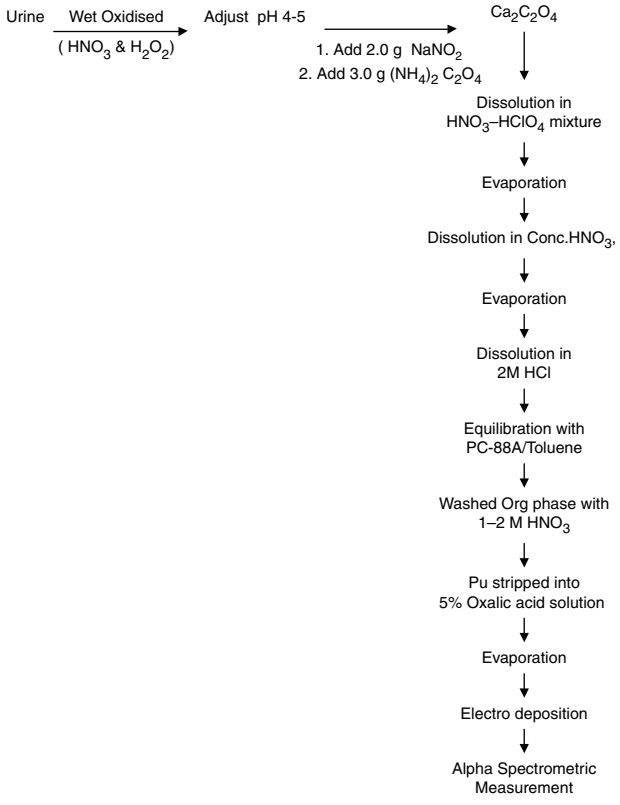

Fig. 1. Scheme of chemical method for in-vitro monitoring of plutonium.

Pu is pre-concentrated through isomorphous replacement mechanism. The precipitate was dissolved in 25 ml of 8 M HNO_3 and 2 ml of conc. $HClO_4$ and kept for evaporation. This step is repeated again to destroy the oxalate ions completely. To remove ClO_4^- ions completely, the residue was dissolved in 25 ml of conc. HNO_3 and kept for evaporation. It is found that without adding $NaNO_2$, this step keeps Pu into +4 state. To remove nitrate ions completely, 25 ml conc. was added and kept for evaporation. Finally, the content of the beaker was dissolved in 25 ml of 2 M HCl solution and filtered. The filtrate was equilibrated with 15 ml of 0.01 M PC-88A/toluene for 30 min and the phase was separated using separatory funnel. This step was repeated again with fresh PC-88A for quantitative extraction of Pu. Then the organic phase was collectively washed with 25 ml of 1–2 M HNO_3 by equilibration with 0.01M PC-88A/toluene for 30 min. This step was repeated again with fresh 1–2 M HNO_3. Finally, the organic phase was equilibrated with 25 ml of 5% oxalic acid for 30 min. This step was repeated again with fresh 25 ml of 5% oxalic acid solution for quantitative elution of Pu into oxalic acid solution. The eluate was evaporated to dryness with HNO_3 – $HClO_4$ mixture to destroy $C_2O_4^{2-}$ ions. Pu present in the eluate was electrodeposited in ammonium oxalate medium on a stainless steel planchette, at 0.6 Amp for 3 h [14] and sample was counted for 20000 s in an alpha spectrometer contains PIPS detector (active area 450 mm^2) with FWHM for ^{242}Pu tracer is 93.5 keV and for ^{239}Pu is 78.5 keV when source to detector distance is 10 mm.

3. Results and discussion

Table 1 shows accuracy and precision obtained for 12.34 mBq of ^{242}Pu tracer spiked in an unexposed pooled urine sample divided into 10 equal parts of each one liter. The average radiochemical recovery obtained is

Table 1
Percentage Recovery of ^{242}Pu (12.34 mBq) spiked in 1000 ml urine

Sl. No	Urine Sample Code	^{242}Pu tracer recovered (mBq)	Recovery (%)
1	US-1	11.30	91.6
2	US-2	10.24	83.0
3	US-3	10.95	88.7
4	US-4	11.30	91.6
5	US-5	9.18	74.4
6	US-6	9.89	80.1
7	US-7	11.30	91.6
8	US-8	8.83	71.6
9	US-9	10.60	85.9
10	US-10	9.89	80.1
		Average Recovery	(84.0 ± 2.0)%

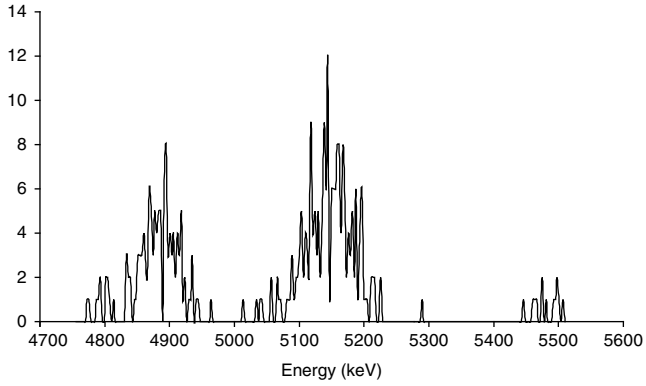

Fig. 2. Alpha spectrum for radiochemical recovery of ^{239} Pu and ^{242} Pu.

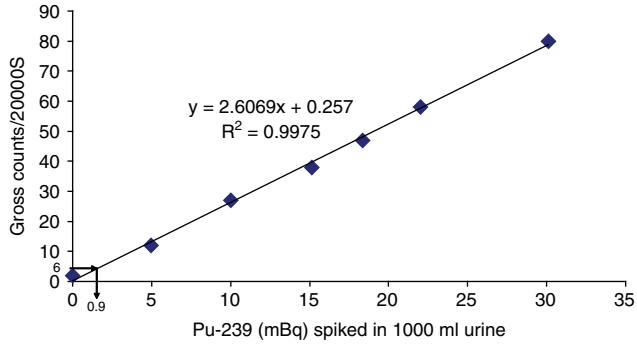

Fig. 3. Derivation of minimum detectable amount of the method.

84% with a range 71–91% and standard deviation 2%. The radiochemical recovery of the method for a known amount of ^{242}Pu (12.34 mBq) and ^{239}Pu (19.0 mBq) were added together in 1000 ml of unexposed urine sample and processed by the present method and counted for 24 h in the alpha spectrometer gave 81% recovery for ^{242}Pu and 83% for ^{239} Pu. A small peak due to ^{238}Pu was also obtained which is present along with ^{239}Pu standard solution as shown in Fig. 2. For each experiment 30 ml organic waste is produced. It is being collected in a glass bottle and will be sent to radio active waste management facility situated within our IGCAR complex.

3.1. Validation of the method

Urine samples collected from unexposed personnel were divided into 12 equal parts of each one liter. Each set consists of six samples. In each set, different amounts of ^{239}Pu was spiked ranging from 4.96 –30.11 mBq. One set was processed by a standard anion exchange method and the other set by the new developed method [8]. Average recovery obtained by anion exchange method is 84% with a standard deviation 7% and the average recovery obtained by the present method is 85% with a standard deviation 7.4%. This anion exchange method was validated during national inter-comparison exercise conducted in 2005.

3.2. Minimum detectable activity of the method

Minimum detectable activity was derived from a graph obtained by plotting gross counts versus sample activity for various concentration of ^{239}Pu spiked in each one liter of pooled unexposed urine sample (Fig. 3). The activity corresponding to ten average blank values plus 3σ computed from the graph was considered as MDA of this method. Average blank value for 20000 s is 2 and the activity corresponds to blank value plus 3σ is 0.9 mBq/l.

MDA is obtained from the following relation [15]:

$$\mathrm{MDA} = \frac{(4.65\sqrt{C} + 2.7)}{T} \times \frac{100}{E} \times \frac{100}{R} \times \frac{TV}{V} \quad (1)$$

where, C is the background counts, T is the counting time in seconds, E is the efficiency of the counter, R is the radiochemical recovery, TV is volume of the urine sample and V is the volume of the sample taken for analysis. However, if there is information on variance parameter in replicate measurements of blank samples and of samples spiked with known amounts of Pu close to the estimated MDA, the same may be obtained more accurately as follows [15]:

$$\mathrm{MDA} = \frac{1.645(\sigma^2 b + \sigma^2 b)^{\frac{1}{2}} + 1.645(s^2 b + \sigma^2 b)^{\frac{1}{2}}}{T} \times \frac{100}{E} \times \frac{100}{R} \times \frac{TV}{V} \quad (2)$$

where, $\sigma^2 s+b$ is the observed variance in the spiked samples and $\sigma^2 b$ is the observed variance in the blank samples. The MDAs for Pu by the present method computed by making use of the above mentioned relation (1) and (2) are 3.85 mBq/l and 6.53 mBq/l respectively. The MDA (1 mBq/l) of this method computed from the graph is an experimentally determined value and hence should be a more appropriate one.

3.3. Optimization of the method

In this developed method, the following observations were found: Pu^{4+} is quantitatively co-precipitated with $Ca_2C_2O_4$ from wet oxidized urine matrix with pH adjusted from 3 to 6. During removal of oxalate ions with perchloric acid, Pu in +4 state would have oxidized to PuO_2^{2+}. To remove ClO_4^- ions completely, the residue was dissolved in 25 ml of conc. HNO_3 and kept for evaporation to convert Pu into +4 state. It is found that there is no change in the percent chemical recovery

of Pu whether $NaNO_2$ was added or not with conc. HNO_3 to the beaker and kept for evaporation after destroying the oxalate ions with $HClO_4$. The percent extraction of Pu^{4+} state is maximum between pH 1.5 to 2.5 HCl solution. Among various stripping agents used in the study such as 5% hydroxylamine hydrochloride, 5% ammonium sulphate, 5% citric acid, 5% ascorbic acid and 5% oxalic acid, it is found that, 100% elution of Pu from PC-88A extractant was obtained only with 5% oxalic acid solution. Pu is eluted as anionic complex oxalate ion.

3.4. Interference study

A known amount of ^{233}U (481 mBq), ^{241}Am (73.6 mBq) and Nat. Th (50 mBq) were spiked separately in each 25 ml of 2 M HCl solution and each solution was equilibrated with PC-88A extractant followed by back-extraction with 5% oxalic acid solution and subsequently electroplated and counted in alpha spectrometer for 20000 s. The spectral analysis revealed that the above said radio nuclides are not co-eluted with Pu. It was also observed that the presence of Ca^{2+} (400 mg), Mg^{2+} (400 mg) and Fe^{3+} (5 mg) ions together in 2 M HCl aqueous phase did not interfere during extraction of Pu into PC-88A extractant. This clearly indicates high tolerance ratio for these ions and hence this method is very much suitable for Pu estimation from urine matrices. It is also found that there is no change in the percent recovery of Pu when the same amount of Ca^{2+}, Mg^{2+} and Fe^{3+} ions were present together in the urine matrix. A known amount of salt of each ion was added to the required amount in urine after determining the ions originally present in urine matrix.

3.5. Extraction of Pu from different aqueous phases

In order to optimize the acidity of aqueous phase at different molar concentrations of HNO_3, HCl and $HClO_4$, a known amount of ^{239}Pu (114.8 mBq) was spiked in each 25 ml of aqueous phase of varying molar concentration of the above said acids from 0.001 M to 4 M. In HNO_3 medium, the percent extraction of ^{239}Pu increases as the molar concentration of the acid increases and attained maximum (100%) when the molar concentration of the aqueous phase is 4.0 M. In an HCl medium, the percent extraction of ^{239}Pu increases as the molar concentration of the aqueous increases up to 2 M HCl and then decreases to 85% when the concentration of the acid is 4 M. In $HClO_4$ medium, the percent recovery of ^{239}Pu was maximum (100%) when the molar concentration of the acid is 0.01 M and then decreases to 80% for 1.0 M and remained the same thereafter up to 4 M as shown in Fig. 4. The variation in the percent extraction of Pu from PC-88A organic phase into stripping agent may be depends up on stability constant of the complex formed between Pu^{4+} and anions like Cl^-, NO_3^-, ClO_4^- for a given acidity of the aqueous phase.

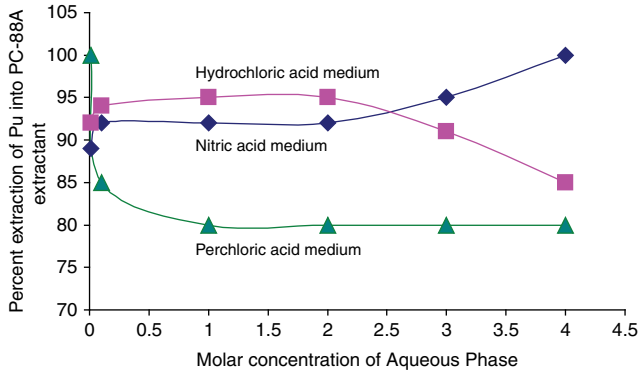

Fig. 4. Extraction of Pu from different aqueous phases.

4. Conclusions

The radioanalytical method for Pu developed reduces the analysis time to 4 d compared to seven days taken by the conventional anion exchange method. It is less expensive and quite useful for the 'special' and 'routine' monitoring of Pu in urine samples. In this present work, the solvent extraction technique that established using HCl is applied to Pu, after separated from urine matrix. Very soon, the solvent extraction technique that was established using HNO_3 and $HClO_4$ as aqueous phase will be applied for Pu separated from urine matrix.

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