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A rapid method for estimation of Pu-isotopes in urine samples using high volume centrifuge

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ABSTRACT

The conventional radio-analytical technique used for estimation of Pu-isotopes in urine samples involves anion exchange/TEVA column separation followed by alpha spectrometry. This sequence of analysis consumes nearly 3–4 days for completion. Many a times excreta analysis results are required urgently, particularly under repeat and incidental/emergency situations. Therefore, there is need to reduce the analysis time for the estimation of Pu-isotopes in bioassay samples. This paper gives the details of standardization of a rapid method for estimation of Pu-isotopes in urine samples using multi-purpose centrifuge, TEVA resin followed by alpha spectrometry. The rapid method involves oxidation of urine samples, co-precipitation of plutonium along with calcium phosphate followed by sample preparation using high volume centrifuge and separation of Pu using TEVA resin. Pu-fraction was electrodeposited and activity estimated using ^{236}Pu tracer recovery by alpha spectrometry. Ten routine urine samples of radiation workers were analyzed and consistent radiochemical tracer recovery was obtained in the range 47–88% with a mean and standard deviation of 64.4% and 11.3% respectively. With this newly standardized technique, the whole analytical procedure is completed within 9 h (one working day hour).

1. Introduction

In fuel fabrication and/or fuel reprocessing plants, isotopes of Pu, Am and U radionuclides present in the working environment may cause low levels of internal contamination. During routine plant operations and also under incidental situations, occupational workers may receive internal exposure through inhalation. Internally deposited Pu-isotopes are estimated with either or all of the techniques such as lung counting (in-vivo), urine and faecal bioassay (in- vitro) techniques. This paper deals with urine bioassay monitoring. A small fraction of internally deposited Pu-isotopes is excreted through urine whose content is dependent on time of inhalation, quantity and type of inhaled material. A standardized conventional method is generally used for estimation of Pu-isotopes in urine samples (Kumar et al., 2009). This methodology consumes about three and half working days and a relatively faster routine TEVA method takes about two and half working days for complete sample analysis (Kumar et al., 2013). A variety of methods have been reported in the literature for measurement of actinides in urine (Alvarez and Navarro, 1996).

For routine monitoring programme the period of analysis of about 3–4 days might be acceptable but in situations of special or incident related monitoring, it is necessary that the results are available at the earliest as they form an important input for decision making by the plant authorities. In view of the reducing radiochemical processing time, work was undertaken to standardize a technique for rapid estimation of Pu-isotopes in urine samples using multipurpose centrifuge, TEVA resin and alpha spectrometry. Earlier or rapid methods for processes and waste analyses were developed and implemented using rapid column extraction chromatography for a wide range of process analyses (Horwitz et al., 1995; Maxwell, 1997; Maxwell and Satkowski, 2001).

The important uses of multipurpose centrifuge are in its capacity to handle sample volume centrifuging for the precipitate. The precipitated sample is commonly allowed to settle overnight for subsequent siphoning of supernatant. The multipurpose centrifuge machine has of six 500 mL capacity centrifuge bottles ($6 \times 500 = 3000$ mL) and can therefore centrifuge 3000 mL of co-precipitated urine sample as shown in Fig. 1. The system is termed as multipurpose, as the bottles of lower than 500 mL (100, 250 mL) can be centrifuged.

2. Materials and methods

Certified ^{236}Pu tracer sourced from National Physical Laboratory (NPL) was purified to remove its daughter product ^{232}U. Purified activity was estimated by alpha spectrometry and stock solution of the tracer was prepared with known specific activity (mBq/g). All the

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Fig. 1. Multipurpose Centrifuge machine having maximum capacity of 6 numbers of 500 mL centrifuge bottle.

chemicals used during the study were procured locally and are of M/s. S.D.Fine Chemicals analytical reagents (AR) grade. Personnel from fuel reprocessing plant/fabrication plant were asked to collect 16 h (17.00 h to 9.00 h) urine sample at their residence to make sure that there is no cross contamination. For emergency situations, four samples, each 250 mL were also collected and analyzed as part of feasibility of handling four samples with the existing laboratory infra. Urine samples were spiked with ^{236}Pu tracer activity in the range of 7.84 mBq to 14.89 mBq. The samples were wet oxidized with Conc. HNO_3 and H_2O_2 to destroy the organic matter. Plutonium along with transuranics like Am, U and also Sr gets co-precipitated along with Calcium-phosphate $Ca_3(PO_4)_2$. Further the co-precipitated material was centrifuged to 3500 rpm for 5 min using multipurpose centrifuge and depending on the volume of the sample, it is divided into 4 or 6 bottles of 500 mL each. Supernatant was discarded and the precipitate was dissolved in Conc. HNO_3 with occasional addition of H_2O_2 and allowed to evaporate until dry. The white residue was dissolved in 10 mL, 3 M-HNO_3 −1 M-$Al(NO_3)_3$, slight heating and about 500 mg of $NaNO_2$ was added to adjust the valency of Pu in +4 state. The solution was filtered through Whatman filter paper No.41 (Particle size =20 μm) to remove silica or insoluble residue.

This solution was loaded on TEVA resin of Eichrom's make. The resin column was pre-conditioned with 3 M- HNO_3, at the rate of 0.6–0.7 mL/min. The column was sequentially washed with 30 mL, 3 M- HNO_3 and then 25 mL of 8 M-HCl at the rate of 0.7 mL/min. Plutonium was eluted with 30 mL of 1.5 M-NH2OH·HCl (hydroxylamine hydrochloride) solution in 1 M-HCl at the rate of 0.6 mL/min. The flow rate of elution was maintained at the rate of 0.6–0.7 mL/min so as to allow sufficient contact time for the reduction of Pu^{+4} to Pu^{+3} oxidation state. The eluted Pu-fraction was electrodeposited on stainless steel planchette in ammonium sulphate, $(NH_4)_2SO_4$ medium at 2.2 pH, 300 mA current at 6 V for 2 h (Rudran, 1969). The entire analytical procedure gets completed within 8–9 h (one working day hour).

Pu content was assessed by Eight Chamber Alpha Spectrometer consisting of passivated ion implanted planar silicon detector (PIPS detector) of 100 μm depletion and 450 mm^2 surface area. The data acquisition and analysis were performed using standard alpha spectrometry software. The electro-deposited samples are counted initially for a counting duration of 25000 s and activity is quantitatively assessed. Depending on the precision requirement, counting period is increased to 86400 s to obtain uncertainty levels of about 10% for tracer nuclide. The efficiency of the alpha spectrometric system was 22.5% for electroplated ^{239}Pu source placed at ~5 mm distance (1st slot of sample holder) from the face of detector. The efficiency calibration has traceability to ^{236}Pu primary standard obtained from NPL Ref. No. (E05090391/01).

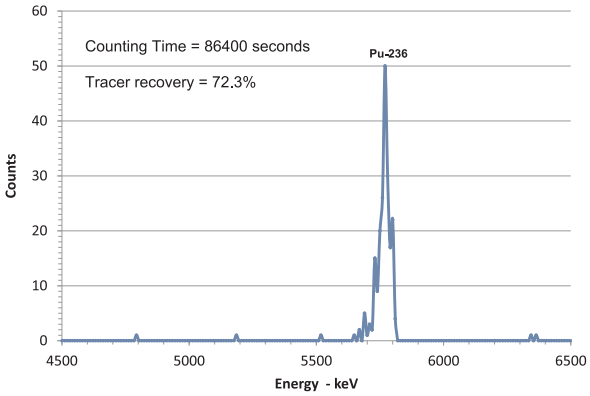

Fig. 2. Typical plutonium spectrum of a urine sample (FU-7) with ^{236}Pu tracer.

Fig. 2 shows a typical alpha spectrum of Pu-isotopes in urine samples analyzed with ^{236}Pu tracer. Fig. 2 is a spectra relating to a urine sample (FU-7 of Table 1) having Pu-isotopes counts less than lower limit of detection or, equal to background counts. The photo peak areas of all the isotopes of plutonium including ^{236}Pu tracer are evaluated by summing of the counts of each channel of the respective isotope peak as the peaks are generally distinctly distinguished.

3. Quantification of alpha nuclide concentration

The activity recovered of ^{236}Pu tracer and activity of Pu-isotopes is determined by the following formulae:

$$RF = \frac{N_T}{\mathrm{T} \times \mathrm{EF} \times \mathrm{TA}}$$

$$A = \frac{N_s \times 24 \times 1000}{T \times \mathrm{EF} \times \mathrm{RF} \times 16}$$

Table 1
Comparison of time required for each major analytical steps for methods like Ion exchange method, Routine TEVA method and Rapid TEVA method.

Analytical steps	Ion exchange method	Routine TEVA method	Rapid TEVA method (Present study)
Oxidation & Co-precipitation with $Ca_3(PO_4)_2$	6–7 h (one WD)	6–7 h (one WD)	1 h
Siphoning/ Centrifuge/ Evaporation of white precipitate/ Column preconditioning and loading	6–7 h (one WD)	3–4 h (0.5 WD)	2 h
Anion exchange resin/TEVA column for separation	6–7 h (one WD)	2–3 h (0.5 WD)	2 h
Evaporation of eluted Pu fraction, destroy with Conc. HNO_3, Fumed off with Conc. H_2SO_4, Cool and electro-deposition	3–4 h (0.5 WD)	3–4 h (0.5 WD)	3–4 h
Counting by alpha spectrometry	As required	As required	As required
Total time required in working days excluding counting time	25 h (3.5 WD)	18 h (2.5 WD)	8–9 h (1 WD)

WD: working day of 8 h.