

# Radiochemical methods for the determination of plutonium, americium and curium in typical waste streams

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## Abstract

Accurate and reliable analytical methods have been developed for the measurement of Pu, Am and Cm in typical waste streams from nuclear power plants. Pu, Am and Cm were separated using anion exchange and coprecipitation techniques. The solution of Am and Cm was electrodeposited and measured by  $\alpha$ -particle spectrometry. In the case of Pu the solution was divided into two aliquots, one for liquid scintillation counting and the other for electrodeposition followed by  $\alpha$ -particle spectrometry. To determine the chemical recovery of  $\alpha$  emitters of the Pu fraction and the Am and Cm fraction, the sample was spiked with <sup>236</sup>Pu and <sup>243</sup>Am. The chemical recovery of <sup>241</sup>Pu was calculated using two different methods which gave reliable results. Analysis of every sample was carried out twice to examine the reproducibility of the analytical methods. The radiochemical yields of Pu and Am ranged from 80% to 100% and from 60% to 80% respectively.

## 1. Introduction

Characterization of the waste streams (ion exchange resins and evaporator concentrates) from nuclear power plants is needed to ascertain appropriate disposal methods. An important aspect of the characterization effort is determination of the concentrations in the waste of the major actinide elements, plutonium, americium and curium. The radionuclides of interest are  $\alpha$  emitters, except for <sup>241</sup>Pu which is a  $\beta$  emitter. Thus suitable techniques are  $\alpha$ -particle spectrometry (APS) to determine the concentrations of <sup>238</sup>Pu, <sup>239,240</sup>Pu, <sup>241</sup>Am, <sup>242</sup>Cm and <sup>244</sup>Cm, and liquid scintillation  $\beta$  counting (LSC) to determine the concentration of <sup>241</sup>Pu.

## 2. Experimental method

### 2.1. Pretreatment of samples

We analyzed two different kinds of samples: ion exchange resins and evaporator concentrates. Firstly, in both cases, it is necessary to dissolve the samples. Dissolution of the ion exchange resins consists of attack with H<sub>2</sub>O<sub>2</sub> in acid medium [1]. In the case of evaporator concentrates, the sample was attacked by a mixture of HNO<sub>3</sub>, HCl, HClO<sub>4</sub> and H<sub>2</sub>F<sub>2</sub>.

### 2.2. Methods for radiochemical analysis of Pu, Am and Cm

An aliquot of the dissolved sample was taken and the tracers <sup>236</sup>Pu and <sup>243</sup>Am were added. The separations of Pu, Am and Cm from fission products, rare-earth

and other elements have been carried out by coprecipitation and anion exchange techniques [2, 3]. The chemical procedures are shown schematically in Fig. 1.

After anion exchange purification the solution of Am and Cm was electrodeposited followed by APS. The solution of Pu was divided into two aliquots, one for LSC and the other for electrodeposition followed by APS.

### 2.3. Determination of $\alpha$ active radionuclides

The solution of Pu or Am and Cm was electrodeposited onto a stainless steel disc, following the method of Hallstadius [4]. The  $\alpha$  spectra were taken with 450 mm<sup>2</sup> silicon implanted detectors.

### 2.4. Determination of <sup>241</sup>Pu

The purified Pu fraction was transferred to a 22 ml glass liquid vial and 10 ml of counting cocktail (Instagel) was added.  $\beta$  and  $\alpha$  particle counting was done by liquid scintillation using the ranges 0-19 keV and 135-340 keV respectively. The efficiency of liquid scintillation  $\beta$  counting for <sup>241</sup>Pu is similar to that for <sup>3</sup>H (maximum 60%) and the efficiency of the liquid scintillation  $\alpha$  counting is practically 100% [5].

The activity of <sup>241</sup>Pu in the sample C<sub>41</sub> is given by the following expression:

$$C_{41} = \frac{A_{41}}{R_s MF}$$

where *M* is the amount of sample (g or ml) analyzed, *F* is the fraction of the sample solution used for LSC,

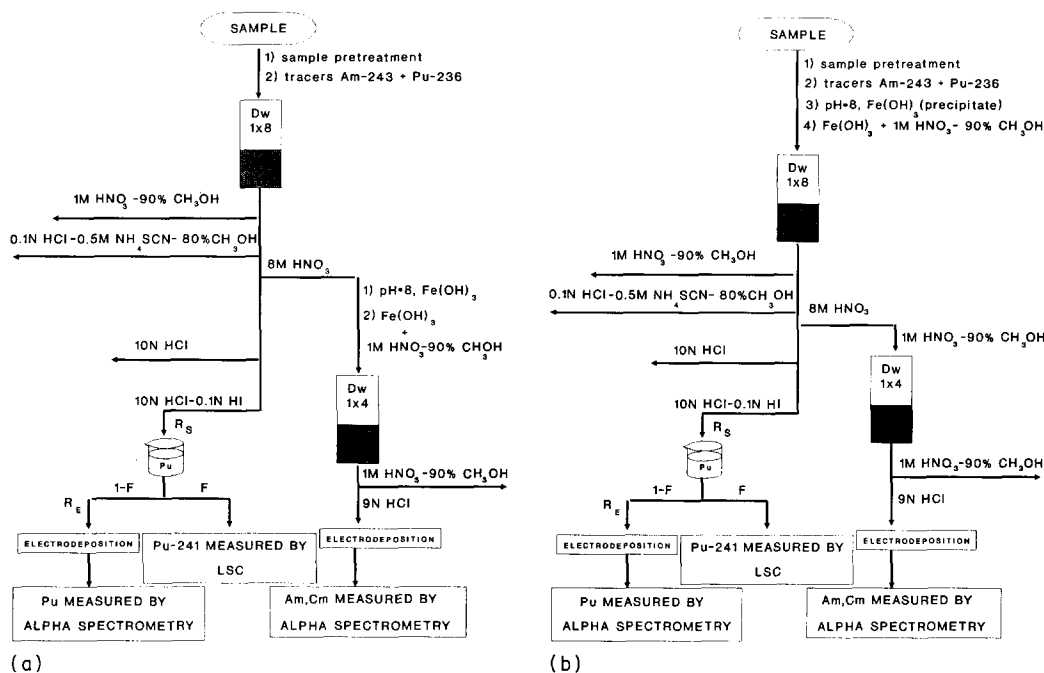


Fig. 1. Separation scheme of Pu, Am and Cm for ion exchange resin (a) and evaporator concentrate (b) samples.

TABLE 1. Results of the plutonium analysis of ion exchange resins and evaporator concentrates

Reference	$^{238}\text{Pu}$	$^{239, 240}\text{Pu}$	$^{241}\text{Pu}$ (Method A)	$^{241}\text{Pu}$ (Method B)
R-1	$44 \pm 1$	$7.9 \pm 0.2$	$869 \pm 54$	$776 \pm 42$
R-1	$45 \pm 2$	$8 \pm 1$	$847 \pm 94$	$758 \pm 54$
R-2	$86 \pm 5$	$46 \pm 3$	$2388 \pm 143$	$2399 \pm 96$
R-2	$89 \pm 5$	$48 \pm 3$	$2550 \pm 204$	$2348 \pm 141$
R-3	$91 \pm 7$	$48 \pm 2$	$2806 \pm 224$	$2600 \pm 156$
R-3	$98 \pm 8$	$53 \pm 5$	$2700 \pm 162$	$2800 \pm 280$
C-1	$0.26 \pm 0.02$	$0.19 \pm 0.01$	$16 \pm 4$	$17 \pm 3$
C-1	$0.23 \pm 0.02$	$0.18 \pm 0.02$	$15 \pm 2$	$14 \pm 1$
C-2	$0.215 \pm 0.004$	$0.083 \pm 0.004$	$34 \pm 3$	$36 \pm 3$
C-2	$0.219 \pm 0.004$	$0.079 \pm 0.003$	$35 \pm 4$	$37 \pm 4$
C-3	$0.14 \pm 0.01$	$0.070 \pm 0.008$	$10.0 \pm 0.06$	$9.0 \pm 0.5$
C-3	$0.16 \pm 0.02$	$0.086 \pm 0.01$	$9.7 \pm 0.04$	$9.5 \pm 0.4$

R, ion exchange resin sample ( $\text{Bq g}^{-1} \pm 2 \sigma$ ); C, concentrate evaporator sample ( $\text{Bq ml}^{-1} \pm 2 \sigma$ ).

$A_{41}$  is the activity of  $^{241}\text{Pu}$  (Bq) measured by LSC, and  $R_s$  is the chemical separation yield of  $^{241}\text{Pu}$  which can be calculated using two different methods.

#### 2.4.1. Method A

$R_s$  of  $^{241}\text{Pu}$  is the same as that of  $^{236}\text{Pu}$  before electrodeposition:

$$R_s = \frac{R_T}{R_E(1-F)}$$

where  $(1-F)$  is the fraction of sample solution used for APS,  $R_T$  is the total recovery of  $^{236}\text{Pu}$  that can be calculated by APS, and  $R_E$  is the electrodeposition recovery,

$$R_E = \frac{A_{6D}}{A_{6D} + A_{6N}}$$

where  $A_{6D}$  is the activity of electrodeposited  $^{236}\text{Pu}$ , calculated by APS, and  $A_{6N}$  is the activity of  $^{236}\text{Pu}$  which is not electrodeposited. To determine this activity it is necessary to do a second electrodeposition with the solution left after the first electrodeposition and an added known amount of a tracer. The best tracer would be  $^{242}\text{Pu}$  but it was not available in our laboratory. We had a standard  $^{238}\text{Pu}$  sample which could be used as tracer. This tracer has the advantage that its half-life and its immediate daughter product  $^{234}\text{U}$  are both long lived, thus once purified, the tracer remains substantially pure for a long time.

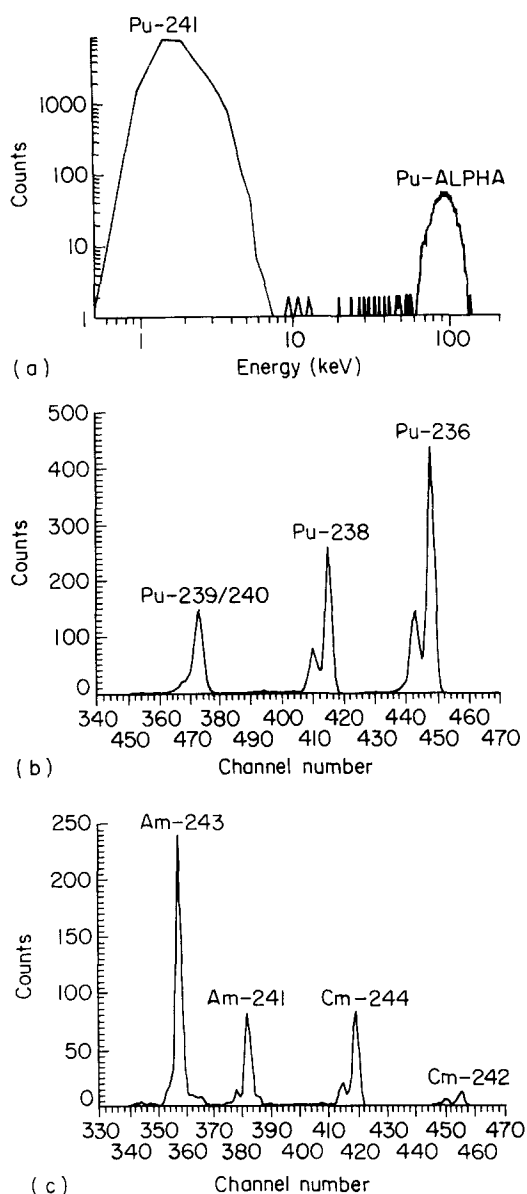


Fig. 2. Liquid scintillation  $\beta$  counting spectrum of Pu (a),  $\alpha$  spectrum of Pu (b) and  $\alpha$  spectrum of Am and Cm (c).

In each source, the activity ratio  $^{238}\text{Pu}/^{236}\text{Pu}$  is calculated by APS then  $A_{6N}$  is

$$A_{6N} = \frac{T_8}{R_{86}^T - R_{86}}$$

where  $T_8$  is the activity of  $^{238}\text{Pu}$  (Bq) added to the solution,  $R_{86}^T$  is the activity ratio  $^{238}\text{Pu}/^{236}\text{Pu}$  for the second source, and  $R_{86}$  is the activity ratio  $^{238}\text{Pu}/^{236}\text{Pu}$  for the first source.

#### 2.4.2. Method B

Another method to calculate  $R_s$  is measurement of the relations  $^{238}\text{Pu}/^{236}\text{Pu}$  and  $^{239,240}\text{Pu}/^{236}\text{Pu}$  by APS using the total  $\alpha$  activity of Pu isotopes found by LSC:

TABLE 2. Results of the americium and curium analysis of ion exchange resins and evaporator concentrates

Reference	$^{241}\text{Am}$	$^{242}\text{Cm}$	$^{244}\text{Cm}$
R-1	$6.2 \pm 0.4$	$81 \pm 4$	$33 \pm 1$
R-1	$5.6 \pm 0.2$	$80 \pm 4$	$32 \pm 1$
R-2	$10.3 \pm 0.6$	$56 \pm 3$	$28 \pm 2$
R-2	$11.6 \pm 0.9$	$59 \pm 5$	$29 \pm 2$
R-3	$12.6 \pm 0.8$	$58 \pm 3$	$30 \pm 2$
R-3	$11.3 \pm 0.7$	$55 \pm 3$	$28 \pm 2$
C-1	$0.076 \pm 0.001$	$0.0018 \pm 0.0002$	$0.024 \pm 0.002$
C-1	$0.080 \pm 0.007$	$0.0017 \pm 0.0004$	$0.025 \pm 0.004$
C-2	$0.057 \pm 0.002$	$0.230 \pm 0.005$	$0.161 \pm 0.003$
C-2	$0.054 \pm 0.002$	$0.220 \pm 0.004$	$0.160 \pm 0.003$
C-3	$0.040 \pm 0.002$	$0.0005 \pm 0.0001$	$0.013 \pm 0.001$
C-3	$0.043 \pm 0.004$	$0.0007 \pm 0.0002$	$0.012 \pm 0.001$

R, ion exchange resin sample ( $\text{Bq g}^{-1} \pm 2 \sigma$ ); C, concentrate evaporator sample ( $\text{Bq ml}^{-1} \pm 2 \sigma$ ).

$$R_s = \frac{A_T}{(1 - R_{86} + R_{96})T_6 F}$$

where  $F$  is the fraction of the sample solution used for LSC, and  $A_T$  is the total  $\alpha$  activity (Bq) in the fraction  $F$  determined by LSC,  $T_6$  is the activity of  $^{236}\text{Pu}$  (Bq) added to the sample,  $R_{86}$  is the activity ratio  $^{238}\text{Pu}/^{236}\text{Pu}$  determined by APS, and  $R_{96}$  is the activity ratio  $^{239,240}\text{Pu}/^{236}\text{Pu}$  determined by APS.

### 3. Discussion

The procedures described for the separation of Pu, Am and Cm are efficient methods. This is indicated by the liquid scintillation counting spectrum of Pu and the good resolution of the peaks of Pu, Am and Cm in the  $\alpha$ -ray spectra (Fig. 2). The results of the analysis are given in Tables 1 and 2. To examine the reproducibility of the present method, the analyses were carried out twice. The radiochemical yields of Pu and Am ranged from 80% to 100% and from 60% to 80% respectively.

The results of the analysis of  $^{241}\text{Pu}$  obtained by methods A and B are given in Table 1. Experience of both methods has shown that the results are generally reliable.

### References

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