# Determination of americium in plutonium based nuclear fuel materials: An assessment of different methodologies

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## ABSTRACT

Determination of americium (Am) is one of the requirements of chemical quality assurance of plutonium (Pu) bearing fuel materials. Though many methods are published for determining Am at picogram to femtogram levels in environmental and biological matrices, yet a few of them are used routinely for Pu based nuclear fuel samples. This paper gives a brief summary of the different analytical methods available and presents results of our experiments on the determination of Am in Pu bearing fuels using gamma spectroscopy. The methods utilizing gamma emissions from $^{241}$Am and Pu isotopes are fast as they do not involve chemical separation of Pu and Am, do not require an accurate knowledge of the efficiency values of the detector systems and are not dependent on the availability of a radiometric standard for $^{241}$Am. In addition, for aged Pu samples containing large amounts of $^{241}$Am, there is no need for dilution and this reduces the volume of analytical radioactive waste solution. Future requirements of reference materials to validate different methodologies for determining Am isotopes are also highlighted.

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## 1. Introduction

Determination of americium (Am) in plutonium (Pu) bearing nuclear fuel materials is an important aspect of the chemical quality assurance of fuel materials. This is required in the starting materials used for fuel fabrication as well as after the fuel fabrication steps. The amount of Am present in the starting materials is required to decide about the shielding requirements during fuel fabrication whereas the finished product has to satisfy the specification limits before irradiation. The extent of Am present in any Pu sample depends upon several parameters including the initial atom% of $^{241}$Pu in Pu, time lapsed after last purification of Pu from Am and sometimes on fuel fabrication steps. For example, during the fabrication of carbide fuels, carbothermic reduction of uranium–plutonium oxides is one of the steps where Am gets preferentially volatilized. Therefore, determination of Am is one of the pre-requisites of chemical assurance of fuel materials. For example, a specification limit of 0.25 wt% of $^{241}$Am in Pu has been fixed mainly from point of view of dose during fuel fabrication.

The decay characteristics of $^{241}$Am and its parent $^{241}$Pu are well known. $^{241}$Pu is a soft beta emitter ($\beta_{max}$ of about 20 keV) with a half-life of 14.4 yr whereas $^{241}$Am gives alpha emission (5.486 MeV) followed by 59.6 keV gamma emission with a half-life of 432.6 yr. The other isotopes of Pu also emit alpha particles and low energy gamma rays (40–150 keV) with appreciable intensities.

Therefore, radiometric methods based on $\alpha$ and/or $\gamma$ counting/spectrometry are the obvious choices since these methodologies may not involve the separation and purification of $^{241}$Am from Pu, in view of the characteristic $\alpha$ and $\gamma$-energies of different Pu isotopes and $^{241}$Am. A recent manuscript [1] discusses different radiometric methods utilizing digital $\alpha$–$\gamma$ coincidence counting, liquid scintillation counting and defined solid angle counting for standardization of pure $^{241}$Am. Another review published recently discusses technological aspects of separation of americium from radioactive wastes and process solutions for purposes of partitioning of minor actinides [2].

There are a number of approaches published in literature [3–13] for the determination of $^{241}$Am in various matrices like environmental, biological, geological, waste materials, river water, nuclear fall out, etc. Since $^{241}$Am is present in low-ppt amounts, it becomes mandatory to separate and purify $^{241}$Am from bulk of the matrix. This step introduces additional uncertainty due to non-quantitative chemical yields (recoveries) which may vary depending upon sample type and matrix as well as the separation and purification procedure adopted. Considering the precision and accuracy desirable in the data from these complex matrices, the uncertainty in the chemical yield is not a big concern. However, this will not be acceptable in Pu based nuclear fuel materials due to various reasons mentioned above. The different methods reported can be broadly classified into mass spectrometry, radiometry, spectrophotometry, etc. The advent of high resolution magnetic sector based inductively coupled plasma mass spectrometry (ICPMS) has revolutionized the determination of actinides isotopes at femtogram concentrations in different environmental and biological matrices.

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For example, recently Varga et al. [9] employed a sequential sample preparation method using co-precipitation for pre-concentration and a separation step applying extraction chromatographic resins. The method was applied for analysis of environmental samples from Chernobyl and Mayak region. The average recovery of sample preparation calculated using the tracer before and after sample treatment was reported to be better than 80%. The method also highlighted the elimination of possible isobaric interferences of molecular ions (e.g. $^{200}Hg^{40}Ar^+$, $^{204}Pb^{36}Ar^+$, $^{208}Pb^{16}O_2^+$ or $^{238}U^1H^+$) employing matrix separation and desolvation prior to ICPMS analysis. The effect of $N_2$ gas on signal intensity and oxide ratio was also reported. A twofold signal improvement was obtained by adding 5 mL min$^{-1}$ $N_2$ to the sample gas after the desolvation system. For $^{239}Pu$, $^{240}Pu$, $^{241}Pu$ and $^{241}Am$, limits of detection (LOD) of 15, 9.2, 14 and 104 fg g$^{-1}$ were achieved, respectively. Another publication [11] on the use of sector-filed ICPMS using a high efficiency nebulizer (APEX-Q) was reported and this was preceded by selective co-precipitation with $CaF_2$ followed by extraction chromatography using Eichrom TRU-resin. A detection limit of 0.32 fg/g or 0.041 mBq/g (for 1 g sediment) was reported in low-level marine sediment samples. However, to the best of our knowledge, ICPMS has not been routinely used for $^{241}Am$ determination in Pu based nuclear fuel materials, may be due to the risks associated with the generation of aerosols containing actinides in argon plasma.

An alpha spectrometric method preceded by co-precipitation and chemical separation of Pu and Am was reported recently [6] for determination of Am in large amounts (200 l) of sea water samples. In this method, the actinides were first pre-concentrated with combined $MnO_2$ and $Fe(OH)_3$ co-precipitation. Pu and Am were then separated from the large amounts of Mn by performing a second precipitation of $Fe(OH)_3$ at pH 6. The final separation of Pu and Am from interfering elements and from each other was achieved by using a single extraction chromatographic column of Eichrom TRU-resin. The sources for alpha spectrometry were prepared by $CeF_3$ co-precipitation. Chemical yields of 80–85% were reported and the procedure was claimed to be fast, simple and robust. However, this procedure would generate lot of analytical waste when applied routinely to nuclear fuel samples.

A second order derivative spectrophotometric method was reported [4] for the determination of Am(III) in $HNO_3$ medium in presence of U(VI) and Pu(IV) without separation, in MOX fuel materials. The zero point-to-trough measurement technique was used since Am(III) was observed to have two zero points at around 501 and 505 nm and a trough at 503.5 nm. Using absorbance of Am at 503.5 nm, it was reported that 100-fold of Pu and 600-fold of U could be tolerated for Am determination in this approach. A detection limit of 0.3 μg/mL for Am(III) was reported. At the specification limit of 0.25 wt% of Pu, Pu/Am amount ratio of 400 will be present in the sample and thus will not be applicable to the Pu based nuclear fuel materials.

There are two excellent reviews published by Warwick et al. [14] in 1996 and Wolf et al. [15] in 2005 for the determination of Am in soils and sediments, and high burnup spent nuclear fuel, respectively. In the latter, ICPMS was used for determining $^{241}Am$.

From our laboratory, we have reported different methods [16–18] from time to time for the determination of $^{241}Am$ in plutonium. These include alpha spectrometry, isotope dilution-thermal ionization mass spectrometry (ID-TIMS), isotope dilution alpha spectrometry (IDAS), gamma counting, etc. Amongst these, the isotope dilution approach based on the addition of enriched $^{243}Am$ as a spike is the best since the results are not affected by incomplete chemical recovery, if the sample and spike isotopes are chemically equilibrated prior to separation. This, however, depends upon the availability of enriched $^{243}Am$ which is accessible only to a few international laboratories. Another variation of isotope dilution approach is the use of isotope dilution gamma spectrometry (IDGS) which has not been quite popular, probably due to the fact that differences in the abundances and gamma counting efficiencies of the two gamma emitters viz. $^{241}Am$ and $^{243}Am$, need be accounted for. Though isotope dilution based methods have the potential of providing reference values, yet no reference materials of $^{241}Am/^{243}Am$ mixtures are commercially available to nuclear community for TIMS, alpha spectrometry or gamma spectrometry to validate these methodologies. In view of these facts, alpha spectrometry and gamma counting/spectrometry methodologies are attractive for Pu based fuel materials and have been used.

Alpha spectrometric determination of $^{241}Am$ in plutonium is based on the preparation of sources from unpurified and purified Pu samples. This has limitations from the point of view of preparing electrodeposited sources, from a solution containing both Pu and Am and ensuring quantitative electrodeposition yield for both the actinides. However, if isotope dilution is used, differences in the electrodeposition yields do not matter. In addition, the commonly encountered problem of tailing contribution at low energy peak of $^{239}Pu + ^{240}Pu$ due to energy degradation of high energy $^{238}Pu + ^{241}Am$ peak always remains. This tail contribution depends upon number of parameters including the source thickness, activity ratio of counts in high energy peak to that of low energy peak, quality of the source and the detector. The method has been used in our laboratory for more than three decades, but direct evaporated sources were prepared from unpurified Pu sample containing Am. However, the separation of Pu and Am by ion exchange procedure not only leads to the generation of radioactive analytical waste, but is also time-consuming. Another attractive and promising approach is based on the gamma counting of solution containing $^{241}Am$, taking advantage of the very low abundances of the gamma emissions of Pu isotopes. This approach has several advantages. Firstly, it does not require any chemical separation of Pu and Am thereby avoiding the problem of waste generation. Secondly, it does not demand the availability of any standard for $^{241}Am$, unlike those required for ID-TIMS, IDAS. Thirdly, the approach is very simple and does not depend upon the knowledge of isotopic composition or alpha specific activity of Pu. Considering the above factors, $\alpha/\gamma$ ratio method was developed for the determination of percentage alpha activity of $^{241}Am$ with respect to plutonium in different types of nuclear fuel samples. It offers simplicity of sample preparation, does not require preparation of thin and weightless sources for alpha spectrometry and results can be reported in 3–4 h for a given sample. This methodology uses gamma scintillation counting with NaI(Tl) detector for gamma counting and liquid scintillation detector for alpha counting [17].

Since NaI(Tl) detector is characterized by poor resolution, it cannot discriminate among different gamma emitters of close lying gamma energies and one has to assume that there are no other gamma emitters present in the sample. On the contrary, gamma ray spectrometry with semiconductor detectors like high purity germanium (HPGe) is characterized by low efficiency and high energy resolution. It was, therefore, considered worthwhile to compare the results obtained using NaI(Tl) detector with those from HPGe detector for a few of the Pu based nuclear fuel samples. $\alpha/\gamma$ ratio approach was followed with both the detector systems using liquid scintillation counting for gross alpha activity. This paper presents the results of the comparative data obtained by using gamma counting and gamma spectrometry.

## 2. Experimental

### 2.1. Reagents and sample preparation

All reagents were of analytical grade. For liquid scintillation counting, sample aliquots were diluted with 1 M $HNO_3$ on weight

basis to obtain alpha activity in the range of $10^4$–$1.5 \times 10^6$ cpm for achieving good counting statistics with low dead time. Di-isopropyl naphthelene (DIN) based scintillator cocktail was used for alpha liquid scintillation counting. Five millilitres of the scintillation cocktail was used for each sample. For gamma scintillation counting, the weighed aliquot was diluted to 2 mL with 1 M $HNO_3$. The measured activities were corrected for background in all the cases. The same aliquots were counted in HPGe detector at standard fixed geometry (at a distance of 10 cm from detector). The background subtracted peak areas at 59.6 keV were determined for $^{241}$Am using PHAST software developed at Electronics Division, BARC, India [19]. $^{241}$Am was generated in-house during purification of Pu and its radiochemical purity was confirmed by $\alpha$ as well as $\gamma$-spectroscopy.

## 2.2. Instruments

(i) Alpha liquid scintillation counter supplied by ECIL, Hyderabad, India was used to measure gross alpha activity with nearly 100% efficiency.
(ii) Gamma scintillation counter consisted of a well type 3″ × 3″ NaI(Tl) detector with pulse height analyzer and was used for determining gross gamma activity. The gamma counting was done in the window mode for $^{241}$Am peak, using a discriminator setting of 1.0 V, low level discriminator (LLD) at 1, upper level discriminator (ULD) at 10.
(iii) High purity germanium (HPGe) detector from ORTEC (USA) with a resolution of 550 eV (FWHM) at 122 keV was used for gamma spectrometric analysis. It had a diameter of 25 mm, length 10 mm, end cap to detector distance 7 mm and absorbing layer of beryllium 0.254 mm. The detector was coupled to a PC based 4 K multichannel analyzer.

## 2.3. Procedure

The $\alpha/\gamma$ ratio method for determination of $^{241}$Am in Pu involves calculating wt% of $^{241}$Am using $\alpha$-specific activity of $^{241}$Am. Following steps are involved.

### 2.3.1. Determination of alpha activity of $^{241}$Am solution

Five weighed aliquots of $^{241}$Am solution in glass scintillation vials were used for liquid scintillation counting to obtain $\alpha$-activity (cpm g$^{-1}$). These vials with $^{241}$Am solution were also used for recording gamma spectra with HPGe detector to check for linearity of response function of HPGe detector.

### 2.3.2. Determination of $\alpha/\gamma$ ratio of $^{241}$Am using NaI(Tl) detector

Four weighed aliquots of the $^{241}$Am solution were taken in glass tubes for gamma scintillation counting of 60 keV peak to determine $\gamma$-activity (cpm g$^{-1}$). Knowing the $\alpha$-activity (cpm g$^{-1}$) from liquid scintillation counting, $F_{NaI(Tl)}$ ($\alpha$ cpm g$^{-1}$/$\gamma$ cpm g$^{-1}$) was calculated.

### 2.3.3. Determination of $\alpha/\gamma$ ratio of $^{241}$Am using HPGe detector

The glass tubes containing weighed aliquots of $^{241}$Am solution, employed in 2.3.2 above, were used for recording the gamma spectra using HPGe detector and determining the gamma activity ($\gamma$ cpm g$^{-1}$) of peak at 59.6 keV. These data were used to calculate $F_{HPGe}$ ($\alpha$ cpm g$^{-1}$/$\gamma$ cpm g$^{-1}$).

### 2.3.4. Preparation of nuclear fuel samples for the determination of $^{241}$Am

Weighed amounts ($W$ gm) of different types of solid samples such as plutonium oxide/carbide/alloy were dissolved in different mineral acids ($HNO_3$ for $PuO_2$, $HNO_3 + H_2SO_4$ for PuC and $HCl + HF + H_2SO_4$ for Pu alloy). Weighed aliquots ($Y$ gm) of diluted solutions of the dissolved nuclear fuel samples were taken in gamma tubes. These gamma tubes were used for gamma counting with NaI(Tl) detector and gamma spectrometry with HPGe detector.

### 2.3.5. Determination of wt% of $^{241}$Am by $\alpha/\gamma$ ratio method using NaI(Tl) detector

Weighed aliquot of dissolved sample solution was taken in a gamma tube, which was used for gamma scintillation counting to determine gamma activity, $A_\gamma(S)$, cpm g$^{-1}$ of unpurified sample solution. The $\alpha$-activity $A_\alpha(S)$ (cpm g$^{-1}$) due to $^{241}$Am in the sample was obtained by multiplying background corrected $\gamma$-activity $A_\gamma(S)$ (cpm g$^{-1}$) of the sample with $F_{NaI(Tl)}$.

$$A_\alpha(S) = A_\gamma(S) \times F_{NaI(Tl)} \tag{1}$$

Then wt% of $^{241}$Am was calculated as

$$\text{Wt\% of } ^{241}\text{Am} = \left[A_\alpha(S) \times Y \times \text{specific activity of } ^{241}\text{Am} \times 100\right]/W \tag{2}$$

Specific activity of $^{241}$Am = $7.6074 \times 10^{12}$ dpm g$^{-1}$ ($T_{1/2}$ of $^{241}$Am = 432.6 yr).

### 2.3.6. Determination of wt% of $^{241}$Am by $\alpha/\gamma$ ratio method using HPGe detector

The weighed aliquots of different sample solutions, taken in step 2.3.5, in gamma tubes, were used for $\gamma$-spectrometry with HPGe detector to determine gamma activity, $A_\gamma(S)$ cpm g$^{-1}$ of unpurified sample solution. The alpha activity due to $^{241}$Am, $A_\alpha(S)$, in cpm g$^{-1}$ of unpurified sample solution was then calculated as

$$A_\alpha(S) = A_\gamma(S) \times F_{HPGe} \tag{3}$$

The wt% of $^{241}$Am was calculated as

$$\text{Wt\% of } ^{241}\text{Am} = \left[A_\alpha(S) \times Y \times \text{Specific activity of } ^{241}\text{Am} \times 100\right]/W$$

The efficiency of alpha liquid scintillation counting was assumed to be 100%. However, this will not have any effect on the comparative evaluation of the two different detector systems used for measuring gamma activity. Using the above formulae, $^{241}$Am

**Table 1**
Alpha and gamma activities of $^{241}$Am in vials using liquid scintillation counter and HPGe detector.

| Sample no. | Weight of solution (g) | Alpha count rate (cpm) | Alpha activity (cpm g$^{-1}$) | Gamma count rate (cpm) | Gamma activity (cpm g$^{-1}$) | $F_{HPGe}$ ($\alpha/\gamma$ ratio) |
|---|---|---|---|---|---|---|
| 1 | 0.1227 | 58,912 ± 543 | 4,80,127 ± 4423 | 145 ± 2.7 | 1181 ± 22 | 406 |
| 2 | 0.1464 | 70,354 ± 593 | 4,80,563 ± 4051 | 173 ± 2.9 | 1182 ± 20 | 406 |
| 3 | 0.2021 | 97,238 ± 697 | 4,81,139 ± 3450 | 244 ± 3.8 | 1208 ± 19 | 398 |
| 4 | 0.2359 | 112,934 ± 751 | 4,78,735 ± 3185 | 284 ± 5.1 | 1205 ± 21 | 397 |
| 5 | 0.2776 | 133,196 ± 816 | 4,79,812 ± 2940 | 328 ± 5.4 | 1182 ± 20 | 406 |

Mean alpha activity of $^{241}$Am solution = 480,075 cpm g$^{-1}$, rsd = 0.19%.
Mean gamma activity of $^{241}$Am solution using HPGe = 1191 cpm g$^{-1}$, rsd = 1.14%.
Mean $\alpha/\gamma$ ratio = 403, rsd = $\sqrt{[(0.19)^2 + (1.14)^2]}$ = 1.16%.

was determined in different types of nine nuclear fuel samples such as plutonium oxide, plutonium carbide and plutonium alloy samples.

### 2.3.7. Evaluation of precision on determination of wt% of $^{241}$Am in a nuclear fuel sample

To evaluate precision of $\alpha/\gamma$ ratio method using gamma scintillation counting technique and high resolution gamma spectrometry, the above procedures were carried out with four weighed aliquots of one of the Pu alloy samples and wt% of $^{241}$Am in the four aliquots of the same sample was calculated, using both the detectors.

## 3. Results and discussion

Table 1 presents results of alpha and gamma activities determined from replicate aliquots of $^{241}$Am, in glass vials, using alpha liquid scintillation counting and gamma spectrometry with HPGe detector. Relative standard deviations of 0.19% and 1.14% were obtained for alpha and gamma activities, respectively and these are as per the statistical uncertainties based on the counting. An $F_{HPGe}$ value of 403 with an RSD of about 1.2% was obtained. Though this $F_{HPGe}$ ($\alpha/\gamma$ ratio) was not used in determining $^{241}$Am in unknown samples, but it was of interest to confirm the linear relation between the alpha and gamma activity, in view of quenching effects which can vary during liquid scintillation counting of samples with varying amounts of aqueous solutions. A plot of gamma activity $^{241}$Am in each aliquot using HPGe detector and alpha activity using liquid scintillation counter is shown in Fig. 1. A regression coefficient close to unity ($R^2 = 0.999$) demonstrates a linear response and the absence of significant differences due to quenching.

Table 2 gives the results obtained for gamma activity of $^{241}$Am, using replicate aliquots in glass tubes by using gamma scintillation counting with NaI(Tl) and gamma spectrometry with HPGe detector, respectively. Using data from Tables 1 and 2, the $F_{NaI(Tl)}$ and $F_{HPGe}$ were calculated for $^{241}$Am. These results on $F_{NaI(Tl)}$ and $F_{HPGe}$ are shown in Table 3.

Using these determined alpha/gamma ratios, the wt% of $^{241}$Am in nine plutonium bearing nuclear fuel samples was determined and the results are given in Table 4. Precision on $\alpha/\gamma$ ratio method using gamma scintillation counting technique was found to be better than that obtained using high resolution gamma spectrometric method as shown in Table 5. Though gamma scintillation counting technique gives precise results, the NaI(Tl) detector suffers from
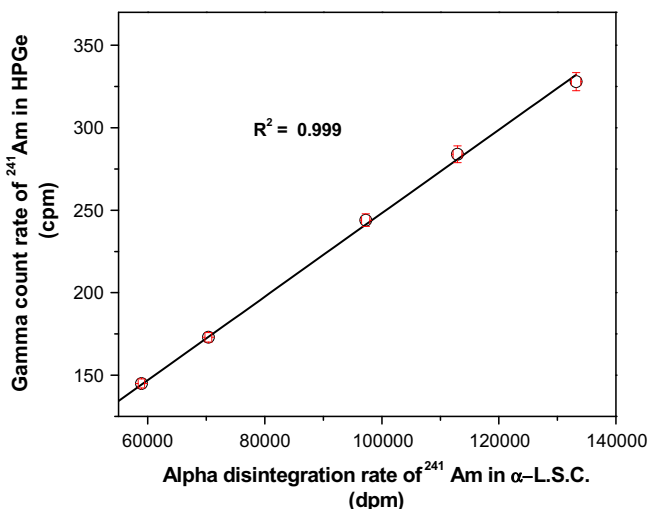


**Fig. 1.** Correlation of gamma activity of $^{241}$Am in HPGe detector with alpha activity of $^{241}$Am using $\alpha$-liquid scintillation counting (LSC).

**Table 2**
Gamma activity of $^{241}$Am in gamma tubes using NaI(Tl) and HPGe detectors.

| Sample no. | Weight of solution (g) | Gamma count rate by NaI(Tl) (cpm) | Gamma activity by NaI(Tl) (cpm g$^{-1}$) | Gamma count rate by HPGe (cpm) | Gamma activity by HPGe (cpm g$^{-1}$) |
|---|---|---|---|---|---|
| 1 | 0.0799 | 11,063 ± 235 | 138,456 ± 2944 | 116 ± 2 | 1448 ± 30 |
| 2 | 0.1595 | 23,082 ± 340 | 144,712 ± 2130 | 232 ± 3 | 1456 ± 20 |
| 3 | 0.3577 | 50,196 ± 501 | 140,329 ± 1400 | 518 ± 6 | 1449 ± 16 |
| 4 | 0.4903 | 67,739 ± 582 | 138,158 ± 1187 | 699 ± 6 | 1427 ± 13 |

Mean gamma activity by NaI(Tl) = 1,40,414 cpm g$^{-1}$, rsd = 2.15%.
Mean gamma activity by HPGe = 1445 cpm g$^{-1}$, rsd = 0.87%.

**Table 3**
Determination of alpha/gamma ratio of $^{241}$Am.

| Sample no. | $\gamma$ cpm g$^{-1}$ (NaI) | $\gamma$ cpm g$^{-1}$ (HPGe) | $F^{*}_{NaI}$ | $F^{*}_{HPGe}$ |
|---|---|---|---|---|
| 1 | 144,712 | 1456 | 3.32 | 330.0 |
| 2 | 140,329 | 1449 | 3.42 | 331.6 |
| 3 | 138,158 | 1427 | 3.48 | 336.7 |
| 4 | 138,456 | 1448 | 3.47 | 331.8 |

$^{*}$ Using alpha activity data from Table 1: Mean $F_{NaI(Tl)} = 3.42$; rsd = $[(0.19)^2 + (2.15)^2]^{1/2} = 2.16\%$, mean $F_{HPGe} = 332.5$; rsd = $[(0.19)^2 + (0.87)^2]^{1/2} = 0.89\%$.

**Table 4**
Results of $^{241}$Am determination in plutonium samples using NaI(Tl) and HPGe detectors.

| Sample no. | $^{241}$Am ($\alpha$ cpm g$^{-1}$) using NaI(Tl) | $^{241}$Am ($\alpha$ cpm g$^{-1}$) using HPGe | Wt% of $^{241}$Am using NaI(Tl) (A) | Wt% of $^{241}$Am using HPGe (B) | A/B |
|---|---|---|---|---|---|
| 1 | 229,172 ± 4380 | 236,810 ± 2764 | 0.037 | 0.039 | 0.97 |
| 2 | 397,667 ± 8865 | 418,640 ± 11,832 | 0.051 | 0.054 | 0.95 |
| 3 | 1024,382 ± 15,585 | 1073,950 ± 18,951 | 0.058 | 0.061 | 0.95 |
| 4 | 2120,020 ± 24,063 | 2175,293 ± 46,715 | 0.476 | 0.489 | 0.97 |
| 5 | 2728,878 ± 15,996 | 2778,758 ± 56,946 | 0.050 | 0.051 | 0.98 |
| 6 | 3278,363 ± 31,061 | 3449,541 ± 58,828 | 0.470 | 0.500 | 0.95 |
| 7 | 4369,336 ± 18,545 | 4483,580 ± 85,296 | 0.630 | 0.650 | 0.97 |
| 8 | 5630,408 ± 37,740 | 5465,819 ± 74,051 | 0.066 | 0.064 | 1.03 |
| 9 | 10,154,835 ± 58,454 | 9760,643 ± 98,956 | 0.309 | 0.297 | 1.04 |

**Table 5**
Precision data for determination of wt% of $^{241}$Am using NaI(Tl) and HPGe detectors.

| Sample aliquot no. | Wt% of $^{241}$Am using NaI(Tl) detector | Wt% of $^{241}$Am using HPGe detector |
|---|---|---|
| 1 | 0.050 | 0.051 |
| 2 | 0.051 | 0.052 |
| 3 | 0.051 | 0.052 |
| 4 | 0.052 | 0.054 |
| Mean | 0.051 | 0.052 |
| rsd (%) | 1.08 | 2.34 |

significant dead time at higher count rate (>150,000 cpm) of (Pu + Am) sample. As shown in Table 6, only on sufficient dilution of sample aliquots, count rate of samples obtained with gamma scintillation counting technique could give results comparable to those obtained by high resolution gamma spectrometry. Therefore, high resolution gamma spectrometry is useful for the determination of $^{241}$Am in Pu solutions containing significantly large amounts of americium. Due to low background activity, HPGe detectors are comparatively free from background maintenance compared to NaI(Tl) detectors.

**Table 6**
Effect of dilution of sample aliquot on counting characteristics using NaI(Tl) and HPGe detectors.

| S. no. | NaI(Tl) before dilution (cpm) | NaI(Tl) after dilution (cpm) | NaI(Tl) before dilution (dpm/g) A | HPGe before dilution (dpm/g) B | A/B | NaI(Tl) after dilution (dpm/g) A1 | A1/B |
|---|---|---|---|---|---|---|---|
| 1 | 182,371 | 26,223 | 1,955,067 | 2,181,390 | 0.90 | 2,120,020 | 0.97 |
| 2 | 490,024 | 69,765 | 5,015,561 | 5,481,211 | 0.92 | 5,630,408 | 1.03 |

It can be seen that results obtained with HPGe detector are in good agreement with those obtained by gamma scintillation counter, within the experimental uncertainties. Since efficiency of HPGe detector is lower by a factor of about 100 than that of gamma scintillation detector, under the present experimental conditions, samples with high radioactivity can be analysed using HPGe detector. Hence use of HPGe detector in place of NaI(Tl) detector will not require dilution of the samples with high activity thereby reducing the volume of radioactive liquid waste. Further, a good agreement in the results obtained by the two independent detector systems would enhance the confidence in the data, since there are no reference materials available with known amounts of Am in Pu, to validate the methodologies.

## 4. Conclusions

The studies carried out in the present work show that $\alpha/\gamma$ ratio method (without separation of Pu and Am) can be applied for the determination of $^{241}$Am in various types of nuclear fuel samples using high purity germanium detector as well as NaI(Tl) scintillation detector. This methodology does not require any elaborate sample preparation procedure, provides comparable results with the two detector systems, and obviates the need of dilution, especially when employing HPGe detector in samples with higher wt% of $^{241}$Am. In addition, there is no need to have any radiometric standard for $^{241}$Am and chemical separation of plutonium and americium is also not required. There is a strong need to have reference materials for $^{241}$Am/$^{243}$Am atom ratios and alpha activity ratios, prepared by mixing enriched isotopes on weight basis. The availability of these reference materials will provide traceability to the experimentally determined values and would also allow to validate mass spectrometric data on isotope ratios and alpha spectrometric data on alpha activity ratios. In view of the nuclear renaissance world-wide, large amounts of $^{241}$Am and $^{243}$Am will get generated along with Pu, which would have to be assayed experimentally with high reliability. These would also be highly useful for nuclear forensics applications since the amount of $^{241}$Am present in any Pu sample depends upon the time elapsed after last Pu purification from Am as well as on the amount of $^{241}$Pu present in the Pu sample.

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