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ISOTOPE DILUTION ALPHA SPECTROMETRY FOR THE DETERMINATION OF PLUTONIUM CONCENTRATION IN IRRADIATED FUEL DISSOLVER SOLUTION : IDAS AND R-IDAS

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ABSTRACT

The report presents a new technique, Isotope Dilution Alpha Spectrometry (IDAS) and Reverse Isotope Dilution Alpha Spectrometry (R-IDAS) for determining the concentration of plutonium in the irradiated fuel dissolver solution. The method exploits ^{238}Pu in IDAS and ^{239}Pu in R-IDAS as a spike and provides an alternative method to Isotope Dilution Mass Spectrometry (IDMS) which requires enriched ^{242}Pu as a spike. Depending upon the burn-up of the fuel, ^{238}Pu or ^{239}Pu is used as a spike to change the ^{238}Pu / (^{239}Pu+^{240}Pu) α activity ratio in the sample by a factor of 10. This change is determined by α spectrometry on electrodeposited sources using a solid state silicon surface barrier detector coupled to a multichannel analyser. The validity of a simple method based on the geometric progression (G.P.) decrease for the far tail of the spectrum to correct for the tail contribution of ^{238}Pu peak (5.50 MeV) to the low energy ^{239}Pu + ^{240}Pu peak (5.17 MeV) is established. Results for the plutonium concentration on different irradiated fuel dissolver solutions with burn-up ranging from 1,000 to 100,000 MWD/TU are presented and compared with those obtained by IDMS. The values obtained by IDAS or R-IDAS and IDMS agree within 0.5%.

ISOTOPE DILUTION ALPHA SPECTROMETRY FOR THE DETERMINATION OF PLUTONIUM CONCENTRATION IN IRRADIATED FUEL DISSOLVER SOLUTION. IDAS AND R-IDAS

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1. INTRODUCTION

Determination of plutonium concentration in the irradiated fuel dissolver solution is one of the important measurements in the nuclear fuel cycle. Isotope Dilution Mass Spectrometry (IDMS) has been universally recognised[1,2] and used for this purpose. One of the chief requirements of this method is the availability of the enriched ^{242}Pu used as a spike for isotope dilution. ^{242}Pu is generally obtained through enrichment in calutrons or by burning other isotopes of plutonium and is thus not easily accessible.

Isotope dilution alpha spectrometry employing ^{238}Pu or ^{239}Pu as a spike provides an alternative method for the determination of plutonium concentration in the irradiated fuel dissolver solution. Depending upon the burn-up of the fuel, ^{238}Pu or ^{239}Pu is used to change the $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio in the sample by a factor of 10. This change is measured by α spectrometry on electrodeposited sources using a solid state silicon surface barrier detector coupled to a multichannel analyser. The method includes all the advantages as existing in IDMS and does not require enriched ^{242}Pu. Obviously, ^{238}Pu is not a desirable spike for routine use in IDMS as it has high α specific activity and

there is an inherent problem of isobaric interference due to ^{238}U during the mass spectrometric analysis while ^{239}Pu does not qualify as an ideal spike for IDMS.

A pre-requisite to the use of isotope dilution alpha spectrometry is that the $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio must be determined with high precision and accuracy. This is, however, limited by the inherent problem of tail contribution due to energy degradation from ^{238}Pu peak (5.50 MeV) to the low energy $^{239}Pu+^{240}Pu$ peak (5.17 MeV) in the α spectrum. A number of computer programmes are available in literature[3-8] to correct for this contribution. Further, two international intercomparison experiments ASET-74[9] and AS-76[10] have been conducted by Karlsruhe centre, Germany, to find out a suitable method for the evaluation of α spectrum and evaluate the precision and accuracy in the determination of $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio in the irradiated fuel dissolver solution. However, no simple method has been recognised so far which could be used routinely for a wide range of α activity ratios and give the desired precision and accuracy. A simple method based on the geometric progression (G.P) decrease for the far tail of the spectrum had been used earlier[11] for the determination of $^{234}U/^{238}U$ α activity ratio in natural uranium samples. This method has been tried for the first time for the determination of $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratios ranging from 0.01 to 10 and its validity has been established in the present work by making synthetic mixtures from solutions of ^{238}Pu and ^{239}Pu isotopes. The above range for α activity ratios was selected so that the isotope dilution alpha spectrometry could be employed for the various irradiated fuel dissolver solutions having different burn-up values.

This report presents the details of the investigations carried out in evaluating the precision and accuracy attainable in the determination of

$^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratios ranging from 0.01 to 10 and compares the results for plutonium concentration obtained by isotope dilution alpha spectrometry with those obtained by IDMS on different irradiated fuel dissolver solutions with burn-up ranging from 1,000 to 100,000 MWD/TU. ^{238}Pu is used as a spike in the case of low burn-up fuels and the method is referred to as IDAS (Isotope Dilution Alpha Spectrometry) while ^{239}Pu is used as a spike in the case of high burn-up fuels and the method is called as R-IDAS (Reverse Isotope Dilution Alpha Spectrometry).

2. PRINCIPLE

The principle of IDAS and R-IDAS is similar to that of IDMS but for the measurement of $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio by α spectrometry instead of $^{242}Pu/^{239}Pu$ atom ratio by mass spectrometry. A known aliquot W_{Sp} of the precalibrated spike (say ^{238}Pu) is added to an aliquot W_S of the irradiated fuel dissolver solution. After ensuring chemical exchange between the plutonium isotopes, the $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio is determined in the spiked mixture. Knowing the α activity ratio in the unspiked sample and the isotopic composition of plutonium in the sample and the spike, the concentration of plutonium in the irradiated fuel dissolver solution can be calculated.

Let R_S, R_{Sp} and R_M be the $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratios in the sample (dissolver solution), spike and spiked mixture respectively.

$$R_S = \left(\frac{A_8}{A_9 + A_0}\right)_S \qquad (1)$$

$$R_{Sp} = \left(\frac{A_8}{A_9 + A_0}\right)_{Sp} \qquad (2)$$

$$R_M = \frac{(A_8)_S + (A_8)_{Sp}}{(A_9+A_0)_S + (A_9+A_0)_{Sp}} \qquad (3)$$

where A_8, A_9, A_0 denote the α activity due to ^{238}Pu, ^{239}Pu, ^{240}Pu respectively and the subscripts S, Sp and M stand for sample, spike and spiked mixture respectively.

Substituting the values of $(A_8)_S$ and $(A_9+A_0)_{Sp}$ from Eqs.(1) and (2) in Eq.(3) and rearranging,

$$\frac{(A_9+A_0)_S}{(A_8)_{Sp}} = \frac{1 - R_M/R_{Sp}}{R_M - R_S} \qquad (4)$$

$(A_9 + A_0)_S$ and $(A_8)_{Sp}$ in Eq.(4) can be written in terms of aliquot weights, concentrations and atomic fractions.

$$(A_9+A_0)_S = \frac{C_S W_S 6.022 \times 10^{23}}{(At.Wt)_S} \left[(A.F.239)_S \lambda_{239} + (A.F.240)_S \lambda_{240} \right] \qquad (5)$$

$$(A_8)_{Sp} = \frac{C_{Sp} W_{Sp} 6.022 \times 10^{23}}{(At.Wt.)_{Sp}} \left[(A.F.238)_{Sp} \lambda_{238} \right] \qquad (6)$$

Here C's denote the concentrations, W's the aliquot sizes, (At.Wt.) the average atomic weight of plutonium, (A.F.) the atomic fraction and λ's the decay constants. Substituting the values of $(A_9 + A_0)_S$ and $(A_8)_{Sp}$ from Eqs.(5) and (6) in Eq.(4) and rearranging,

$$C_S = \frac{C_{Sp} W_{Sp}}{W_S} \frac{R_{Sp} - R_M}{R_M - R_S} \frac{(At.Wt.)_S}{(At.Wt.)_{Sp}} \frac{(A.F.\ 238)_{Sp} \lambda_{238}}{(A.F.\ 239)_S \lambda_{239} + (A.F.\ 240)_S \lambda_{240}} \qquad (7)$$

In the case of R-IDAS where ^{239}Pu is used as a spike, the concentration of plutonium in the irradiated fuel dissolver solution is given by :

$$= \frac{C_{Sp} W_{Sp}}{W_S} \frac{R_{Sp} - R_M}{R_M - R_S} \frac{(At.Wt.)_S}{(At.Wt.)_{Sp}} \frac{(A.F.239)_{Sp} \lambda_{239} + (A.F.240)_{Sp} \lambda_{240}}{(A.F.\ 238)_S \lambda_{238}} \qquad (8)$$

As is seen from the decay characteristics of various plutonium isotopes given in Table-1, the α energies of ^{239}Pu and ^{240}Pu are very close and cannot be resolved by the presently available detectors. Thus it is mandatory to measure the ratio of ^{238}Pu α activity to the combined α activity due to ^{239}Pu + ^{240}Pu.

3. CHOICE OF SPIKE

The choice of spike is governed by the initial $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio in the irradiated fuel dissolver solution. The estimates of $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio at different burn-up values are given in Table-2. The α activity ratio is, however, also dependent on the various other parameters like the type of reactor, initial enrichment of the fuel, moderation ratio, neutron spectrum and void fraction (in case of BWR's) etc. and may range from 0.01 to 10 for burn-up varying from 1,000 to 100,000 MWD/TU. Our experiece in the field of α spectrometry shows that as the $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio increases, the tail contribution due to energy degradation from the high energy ^{238}Pu peak (5.50 MeV) to the low energy $^{239}Pu+^{240}Pu$ peak (5.17 MeV) increases. This contribution as observed from the α spectrum on ^{238}Pu source was found to be approximately 0.70% of the α activity under ^{238}Pu peak.

With a view to reducing the uncertainty on the factor (R_M-R_S) in Eqs.(7) and (8), it was considered essential to change the α activity ratio (R_M) in the spiked sample by at least ten times of the initial value (R_S) in the unspiked sample. Thus ^{238}Pu was selected as a spike for low burn-up fuels where the initial α activity ratio ranges from 0.01 to 1 and final α activity ratio in the spiked sample will be less than 10 which can be determined accurately. In the case of high burn-up

fuels, where the initial α activity ratio could be between 1 to 10, the use of ^{238}Pu as a spike would necessitate the ratio to be increased to a value of 10 to 100. At such high values of the α activity ratios, the tail contribution becomes very high (7 to 70% of the activity due to $^{239}Pu+^{240}Pu$) and it is not desirable to evaluate the α spectrum with such a large correction. Thus in the case of high burn-up fuels, ^{239}Pu was selected as a spike to reduce the initial α activity ratio (R_S) in the sample by a factor of ten in the spiked mixture (R_M). It is worth mentioning that ^{238}Pu to be used as a spiked need not be isotopically pure. ^{238}Pu prepared by neutron irradiation of ^{237}Np and ^{239}Pu obtained from low burn-up fuel of a CANDU type reactor can be conveniently used as spikes in IDAS and R-IDAS respectively.

^{238}Pu has earlier been used as a spike in Process Analysis Field Experiment[12] (PAFEX-I) by laboratory with Code No.3 for determining the concentration of plutonium in PuO_2 powder, UO_2-PuO_2 pellet and SRM-949 d where the initial $^{238}Pu/(^{239}Pu + ^{240}Pu)$ α activity ratios were ≤ 0.5. However, the method was not used for $Pu(NO_3)_4$ solution where the initial α activity ratio was greater than two. ^{236}Pu[13] and ^{240}Pu[14] have also been tried as spikes but no detailed investigations were carried out. Further, enriched ^{240}Pu and ^{236}Pu are not easily accessible.

4. EXPERIMENTAL DETAILS

4.1 Precision and accuracy in the determination of $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio by α spectrometry

The precision and accuracy in the determination of $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio was evaluated by making synthetic mixtures using ^{238}Pu and ^{239}Pu isotopes. The nitrate solutions of these plutonium isotopes were purified from traces of ^{241}Am and fission products, if any, using an ion

exchange procedure. The complete removal of ^{241}Am was confirmed by taking a γ spectrum on an intrinsic germanium detector. The small percentage (less than 1%) of the α activity due to $^{239}Pu+^{240}Pu$ in ^{238}Pu solution and of ^{238}Pu in ^{239}Pu solution was determined by using mass spectrometry and α spectrometry respectively. Master solutions of the plutonium isotopes were prepared in volumetric flasks using 1 M HNO_3. The α specific activity of these solutions was determined by liquid scintillation counting with a precision of 0.05% (1σ). Duplicate dilutions and replicate samples for counting were prepared to check for any systematic error. Various dilutions and preparation of samples for counting were done on weight basis using polyethylene weight burettes rather than on volume basis so as to avoid errors in calibration of glass ware and in pipetting. The liquid scintillation vials were counted for a time sufficient to accumulate more than 10^5 counts. The count rate for each sample was about 20,000 dpm so that the dead time correction was negligible.

Thirteen synthetic mixtures (referred to as SM-89) with $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratios ranging from 0.01 to 10 were prepared by mixing the precalculated and accurately weighed aliquots from the solutions of ^{238}Pu and ^{239}Pu. The α activity ratios (referred to as the true values) of these mixtures were calculated by using the α spetific activity of the master solutions, the aliquot weights, the contribution of $^{239}Pu+^{240}Pu$ activity in ^{238}Pu solution and that of ^{238}Pu activity in ^{239}Pu solution. The uncertainty on these calculated α activity ratios was computed by considering the uncertainties on the various components and was found to be 0.10% (1σ).

The synthetic mixtures were evaporated to near dryness, treated with Conc. HNO_3 to break the polymer, if any, and finally subjected to a redox

treatment using H_2C_2 in 3 M HNO_3. Triplicate sources for α spectrometry from each of mixtures were prepared by electrodeposition in aqueous HNO_3 medium (pH about 2) and using electropolished stainless steel planchet as the backing material. The α activity on each source was about 2×10^5 dpm so as to eliminate the distortion and pile-up effects. The α spectrum from the sources was recorded by using a 50 mm^2 silicon surface barrier detector coupled to a 4 K analyser (TN-1700) and the pressure in the source chamber was less than 10^{-2} torr. The system has a resolution of 20 KeV full width at half maximum (FWHM) at 5.50 MeV. The source to detector geometry was such that about 3% of the α particles emitted (in 4π) by the source were counted. Triplicate spectra were recorded from each source. The sources were counted for a sufficiently long time to accumulate more than 10^5 counts under each of the two peaks.

The α activity ratios were computed from the α spectra by a method based on the geometrical progression (G.P) decrease for the far tail of the spectrum. In this method, two assumptions are made (a) the difference of self absorption between the α particles of ^{238}Pu, ^{239}Pu and ^{240}Pu is negligibly small and (b) the counts in the far tail of the spectrum decrease in the geometric progression. The procedure comprises of dividing the α particle energy spectrum into four regions A,B,C and D; each region having equal number of channels. Firstly, the high energy end of region A is selected from the α spectrum. The low energy end of region B is fixed at 4.95 MeV so as to exclude the small α activity due to $^{241}Pu+^{242}Pu$. The high energy end of region B is obtained by subtracting from the high energy end of A, the number of channels corresponding to the separation of ^{238}Pu and $^{239}Pu+^{240}Pu$ peak tops. The low energy end of region A gets automatically fixed since the number of channels is

kept the same as in region B. Regions C and D are fixed in a similar way. Then $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio R is calculated from :

$$R = \frac{A}{B - \frac{AC}{B + \frac{AD}{C}}} \qquad (9)$$

The region C contains about 0.5% of the total counts in the regions A and B and will include about 70% of the α activities from $^{241}Pu(T_{1/2}=6\times10^{5}$ yr) and $^{242}Pu(T_{1/2} = 3.754 \times 10^{5}$ yr), which may range from 0.01% to 0.1% of the total counts in the regions A and B depending upon the isotopic composition of plutonium. It is, therefore, desirable to subtract the counts due to $^{241}Pu+^{242}Pu$ from the region C while determining $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratios greater than unity. In the case of IDAS, this small contribution can be subtracted by knowing the counts in the region B and the $(^{241}Pu+^{242}Pu)/(^{239}Pu+^{240}Pu)$ α activity ratio computed from the isotopic ratios determined mass spectrometrically and the half-life values. In the case of R-IDAS, the same can be accomplished by knowing the counts in region A and the $(^{241}Pu+^{242}Pu)/ ^{238}Pu$ α activity ratio. This α activity ratio can be calculated by knowing the $(^{241}Pu+^{242}Pu)/(^{239}Pu+^{243}Pu)$ α activity ratio from the mass spectrometric data and $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio from the α spectrum in the case of unspiked sample.

A typical α spectrum along with the selection of regions A,B,C and D is shown in Fig.1. The results on $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratios evaluated from the α spectra are compared with the true values in the synthetic mixtures in Table-3. It is seen that an accuracy of better than 0.5% can be achieved in the determination of $^{238}Pu/(^{239}Pu+^{240}Pu)$

α activity ratios ranging from 0.01 to 10 and using the G.P. method for α spectrum evaluation. Details of this work have been published elsewhere[15].

4.2 Isotope Dilution Alpha Spectrometry (IDAS) using ^{238}Pu as a spike

4.2.1. Calibration of ^{238}Pu spike : The isotopic composition of ^{238}Pu used as a spike was determined mass spectrometrically and the data are given in Table-4. ^{238}Pu spike used for IDAS was calibrated against a chemical assay standard of plutonium SRM-949d obtained from National Bureau of Standards. The spike calibration was carried out by two independent methods viz. IDMS and IDAS. The chemical exchange between the sample and the spike isotopes was ensured by using H_2O_2 as a redox reagent. In IDMS, the isobaric interference due to small traces of uranium at ^{238}Pu peak was eliminated by preferential evaporation and ionisation technique[16]. Traces of enriched ^{233}U were added to the spiked plutonium sample. The absence of ^{233}U peak during mass spectrometric analysis of plutonium served as an indicator for the complete elimination of traces of uranium. In IDAS, the amount of standard added to ^{238}Pu spike was such as to obtain the $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio close to unity. The spike calibration values obtained by IDMS and IDAS were in good agreement (within 0.1%).

4.2.2 Determination of plutonium concentration in irradiated fuel dissolver solution : Ten different irradiated fuel dissolver solutions with burn-up ranging from 1,000 to 10,000 MWD/TU were taken. Replicate samples were taken from each of the irradiated fuel dissolver solutions and were spiked with precalibrated ^{238}Pu spike. The amount of ^{238}Pu to be added was precalculated so as to increase the α activity ratio by ten times the initial value in the irradiated fuel dissolver solution.

A typical calculation is given in Appendix-I. Replicate samples were also taken for IDMS[17] and spiked with ^{242}Pu. The $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratios in the samples spiked with ^{238}Pu were determined by α spectrometry while in the case of samples spiked with ^{242}Pu, $^{242}Pu/^{239}Pu$ atom ratios were obtained mass spectrometrically. The results of plutonium concentration on different irradiated fuel dissolver solutions by IDAS and IDMS are given in Table-5. An example for the calculation of plutonium concentration in irradiated fuel dissolver solution by IDAS is given in Appendix-II.

4.3 Reverse Isotope Dilution Alpha Spectrometry (R-IDAS) using ^{239}Pu as a spike :

4.3.1 Calibration of ^{239}Pu spike : The isotopic composition of ^{239}Pu used as a spike was determined by employing mass spectrometry and α spectrometry and the data are given in Table-6. ^{239}Pu spike used for R-IDAS was a plutonium nitrate solution working standard[18] which had been calibrated using electrochemical methods and simultaneously analysing the chemical assay standard of plutonium SRM-949d. The calibration was further checked by two methods viz. by IDAS using precalibrated solution of ^{238}Pu and by IDMS using precalibrated solution of ^{242}Pu. The spike calibration values obtained by IDAS and IDMS were in good agreement with the working standard value (within 0.1%)

4.3.2 Determination of plutonium concentration in simulated dissolver solution: Due to the non-availability of irradiated fuel dissolver solution with burn-up in the range of 50,000 to 100,000 MWD/TU, three simulated dissolver solutions were prepared by mixing precalculated amounts of

^{238}Pu with one of the irradiated fuel dissolver solutions (burn-up=20,000 MWD/TU) used earlier. The initial $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratios in these simulated fuel dissolver solutions were 4,6 and 10 respectively. Replicate samples were taken from each of the three simulated fuel dissolver solutions and spiked with ^{239}Pu to decrease the $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio by ten times the initial value. Replicate samples were also taken for IDMS and spiked with ^{242}Pu. The results on plutonium concentration obtained by R-IDAS and IDMS are given in Table-7.

RESULTS AND DISCUSSION

From the results given in Tables-5 and 7, it is seen that the plutonium concentration in the irradiated fuel dissolver solution determined by IDAS and R-IDAS is in good agreement with that obtained by IDMS. Further, as seen from Table-8, the factor IDAS/IDMS is 1.00087 ± 0.0035 which shows that the method is free from any bias and can be used for the determination of plutonium concentration in the irradiated fuel dissolver solution from fuels having a wide range of burn-up values. The method not only provides an alternative to the ^{242}Pu spike but brings forth an independent technique for determining the concentration of plutonium in the irradiated fuel dissolver solution. However, it may be pointed out that the mass spectrometer is indispensable in the case of IDAS and R-IDAS as the isotopic composition of the sample and the spike required in these cases has to be determined mass spectrometrically.

As seen from Eqs.(7) and (8), though the calculation of plutonium concentration in IDAS and R-IDAS involves the half-lives of ^{238}Pu, ^{239}Pu and ^{240}Pu, but the uncertainty on these plays an insignificant role as these are involved both in the spike calibration as well as while determining the plutonium concentration in the samples and hence are cancelled to a

great extent. The estimates of various error components in IDAS are listed in Table-9. An overall error of 0.61% is calculated for the plutonium concentration obtained by IDAS. The total uncertainty in the case of R-IDAS is also the same. It is seen that the determination of $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio by α spectrometry is the major source of error in the method. It may be possible, in future, to improve upon the precision and accuracy in the determination of $^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio and thereby the concentration of plutonium in the irradiated fuel dissolver solution by making a better source, improving on the α spectrometry set up and a better understanding of the exact nature of the tail contribution due to energy degradation.

It is worthmentioning that a demonstration experiment on IDAS for determining the concentration of plutonium in two irradiated fuel dissolver solutions having approximate burn-up 1,000 and 10,000 MWD/TU was conducted. Five different groups of the Radiochemistry Division, BARC, took part in this experiment. Each group was provided with three spiked and one unspiked sample from each irradiated fuel dissolver solution. The weights of the sample and spike aliquots were kept confidential. The results for plutonium concentration were calculated in the presence of all the participants and the data were compiled. The values obtained by different groups were within 0.5% of that obtained by IDMS using ^{242}Pu as a spike.

In conclusion, it may be stated that an accuracy of 0.50% can be achieved, at present, for determining the plutonium concentration in irradiated fuel dissolver solution by IDAS and R-IDAS using replicate samples.

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25. Y.A. Ellis and R.L. Haese, Ibid, 21, 615 (1977).

Table-1

HALF-LIVES, α PARTICLE ENERGIES, RELATIVE INTENSITIES AND SPECIFIC ACTIVITY OF PLUTONIUM ISOTOPES AND AMERICIUM -241

Isotope	Half-life (yr)	α energy (MeV)	Abundance (%)	α specific activity (dpm/ μg)
^{238}Pu	87.74[19]	5.4992[21]	71.6	3.80×10^{7}
		5.4565	28.3	
		5.3577	0.10	
		5.2056	0.003	
^{239}Pu	24110[19]	5.1564[22]	73.3	1.377×10^{5}
		5.1429	15.1	
		5.112	< 0.03	
		5.1046	11.5	
		5.076	0.036	
		5.054	0.025	
^{240}Pu	6553[19]	5.1683[23]	73.4	5.045×10^{5}
		5.1238	26.5	
		5.014	0.091	
		4.851	0.002	
^{241}Pu	6.0×10^{5}[19]	5.054[24]	0.35	5.487×10^{3}
		5.042	1.02	
		4.998	0.41	
		4.972	1.3	
		4.8965	83.2	
		4.9535	12.1	
		4.799	1.2	
		4.784	0.2	
^{242}Pu	3.754×10^{5}[20]	4.9009[25]	77.0	8.734×10^{3}
		4.8566	23.0	
^{241}Am	432.6[19]	5.5443[24]	0.34	7.612×10^{6}
		5.512	0.20	
		5.4857	85.2	
		5.469	< 0.04	
		5.4429	12.8	
		5.417	0.01	
		5.388	1.4	

Table-2

ESTIMATES OF $^{238}Pu/(^{239}Pu+^{240}Pu)$ $\propto$ ACTIVITY RATIO WITH BURN-UP

S.No.	Burn-up (MWD/TU)	Approximate $^{238}Pu/(^{239}Pu+^{240}Pu)$ $\propto$ activity ratio
1	1,000	0.1
2	5,000	0.2
3	10,000	0.4
4	25,000	3.0
5	50,000	5.0
6	100,000	10.0

Table-I

COMPARISON OF THE $^{238}Pu/(^{239}Pu+^{240}Pu)$ α ACTIVITY RATIOS EVALUATED FROM THE α SPECTRA WITH THE TRUE VALUES IN VARIOUS SYNTHETIC MIXTURES

S.No.	Synthetic mixture code No.	$^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio		Difference (%)
		True Value	Evaluated from the α spectrum	
1	SM-89-24	0.023584±0.000068 (a)	0.023390±0.000064 (b)	-0.82
2	SM-89-25	0.04632±0.00010	0.046326±0.000007	+0.01
3	SM-89-26	0.10121±0.00020	0.10108±0.000046	-0.13
4	SM-89-13	0.27322±0.00064	0.27436±0.00026	+0.04
5	SM-89-14	0.54874±0.00076	0.55169±0.00075	+0.54
6	SM-89-15	0.74533±0.00089	0.7480±0.0020	+0.36
7	SM-89-16	0.9207±0.0010	0.9194±0.0016	-0.14
8	SM-89-17	1.2305±0.0012	1.2363±0.0014	+0.47
9	SM-89-18	2.0395±0.0011	2.0431±0.0011	+0.18
10	SM-89-19	2.5269±0.0023	2.5235±0.0018	-0.13
11	SM-89-20	4.0097±0.0035	4.0213±0.0083	+0.30
12	SM-89-22	6.3339±0.0071	6.3336±0.0073	-0.05
13	SM-89-23	9.6063±0.0087	9.5580±0.0053	-0.50
			Mean error =	0.28%

(a) Uncertainty (1σ) on the true value computed by combining uncertainties on the α activities of the master solutions, the aliquot weights and contributions of ^{239}Pu, ^{240}Pu and ^{238}Pu α activities in ^{238}Pu and ^{239}Pu isotopes respectively.

(b) External standard deviation computed from $s^2 = \sum_{i=1}^{n} (\bar{x}_i - \bar{\bar{x}})^2/(n-1)$ with n=3, as three sources were prepared from each synthetic mixture.

Table-4

ISOTOPIC COMPOSITION OF ^{238}Pu SPIKE USED IN IDAS

Mass number	Abundance		% α activity[a]
	Atom%	Weight %	
238	93.8882	93.8631	99.9737
239	5.8398	5.8628	0.0226
240	0.2546	0.2567	0.0036
241	0.0172	0.0174	0.0000027
242	--	--	--

Average atomic weight = 238.113

(a) Calculated from the abundances and the latest recommended half-life values[19].

Table-8

PLUTONIUM CONCENTRATION IN THE IRRADIATED FUEL DISSOLVER SOLUTIONS DETERMINED BY IDAS AND IDMS

Dissolver Solution No.	Approximate Burn-up (MWD/TU)	$^{238}Pu/(^{239}Pu+^{240}Pu)$ α activity ratio		Concentration of plutonium µg/g			
		Initial	Final	By IDAS		By IDMS	
1	1,000	0.15	1.50	12.749±0.019[a]	(6)	12.757±0.019[a]	(6)
2	1,000	0.03	3.00	83.890±0.110	(8)	83.736±0.056	(4)
3	1,000	0.15	1.50	12.865±0.022	(3)	12.844±0.073	(3)
4	5,500	0.26	2.80	10.566±0.013	(3)	10.559±0.022	(3)
5	7,400	0.25	0.85	30.868±0.040	(6)	31.050±0.055	(6)
6	8,300	0.44	5.20	15.689±0.026	(3)	15.668±0.029	(3)
7	8,600	0.44	1.30	6.487±0.010	(5)	6.493±0.008	(5)
8	9,000	0.41	2.50	5.638±0.021	(5)	5.625±0.007	(4)
9	10,000	0.40	4.00	5.779±0.005	(5)	5.768±0.010	(5)
10	20,000	2.[illegible]0	9.60	52.181±0.127	(3)	52.447±0.021	(3)

(a) Standard error of the mean computed as $s/\sqrt{n}$ where $s^2 = \sum_{i=1}^{n} (x_i - \bar{x})^2/(n-1)$; the number in the parenthesis specifies the value of n where n denotes the number of replicate samples.

Table-6

ISOTOPIC COMPOSITION OF ^{239}Pu SPIKE USED IN R-IDAS

Mass number	Abundance		% α activity[a]
	Atom %	Weight %	
238	0.0136[b]	0.01354	3.1723
239	94.362	94.339	80.0981
240	5.354	5.375	16.7200
241	0.2543	0.2564	0.00867
242	0.0158	0.01599	0.00086

Average atomic weight = 239.110

(a) Calculated from the abundances and the latest recommended half-life values[19]

(b) Determined by α particle pulse height analysis.

Table-7

PLUTONIUM CONCENTRATION IN THE SIMULATED FUEL DISSOLVER SOLUTIONS DETERMINED BY R-IDAS AND IDMS

Dissolver Solution No.	Approximate Burn-up (MWD/TU)	$^{238}Pu/(^{239}Pu+^{240}Pu)$ ∝ activity ratio		Concentration of plutonium (µg/g)	
		Initial	Final	By R-IDAS	By IDMS
1	50,000[a]	4	0.50	6.7218±0.046[b](6)	6.6945±0.011[b](6)
2	70,000[a]	6	0.60	6.4150±0.009(6)	6.3666±0.057(6)
3	100,000[a]	10	0.65	5.9052±0.006(6)	5.8905±0.007(6)

(a) Simulated fuel dissolver solution

(b) Standard error of the mean computed as $s/\sqrt{n}$ where $s^2 = \sum_{i=1}^{n} (x_i - \bar{x})^2/(n-1)$; the number in the parenthesis specifies the value of n.

Table-8

COMPARISON OF IDAS AND R-IDAS WITH IDMS

Spike used	Dissolver Solution No.	Approximate Burn-up (MWD/TU)	IDAS or R-IDAS / IDMS
^{238}Pu	1	1,000	0.9994±0.0021 (a)
	2	1,000	1.0018±0.0015
	3	1,000	1.0016±0.0059
	4	5,500	1.0007±0.0024
	5	7,400	0.9941±0.0024
	6	8,300	1.0013±0.0025
	7	8,600	0.9991±0.0020
	8	9,000	1.0023±0.0019
	9	10,000	1.0019±0.0019
	10	20,000	0.9949±0.0024
^{239}Pu	1	50,000 (b)	1.0041±0.0071
	2	70,000 (b)	1.0076±0.0091
	3	100,000 (b)	1.0025±0.0016
		Mean =	1.00087±0.00[illegible] (c)

(a) The uncertainty has been evaluated by considering the uncertainty on the concentration values obtained by IDAS or R-IDAS and by IDMS (given in Tables 5 and 7)

(b) Simulated fuel dissolver solution

(c) Standard deviation computed from $s^2 = \sum_{i=1}^{n} (x_i - \bar{x})^2/(n-1)$ with $n = 13$

Table-2

ESTIMATES OF ERROR COMPONENTS IN IDAS (%)

S.No.	Quantity	Error (%)	Remarks
1	C_{Sp}	0.10	Spike calibrated against SRM-949d
2	W_{Sp} (~250 mg)	0.02	Error of 0.00005 g
3	W_S (~ 250 mg)	0.02	Error of 0.00005 g
4	$R_M - R_S$ ($R_M \simeq 10\ R_S$)	0.66	Error of 0.50% in both R_M and R_S
5	$(At.\ wt.)_S$	0.10	Obtained from the isotopic composition data
6	$(At.\ wt.)_{Sp}$	0.10	Obtained from the isotopic composition data
7	$(A.F.\ 238)_{Sp}\ \lambda_{238}$	0.14	Error of 0.10% in $(A.F.\ 238)_{Sp}$ and error of 0.10% in λ_{238}
8	$(A.F.\ 239)_S\ \lambda_{239}$ $+(A.F.240)_S\ \lambda_{240}$	0.10	Errors of individual components are $(A.F.\ 239)_S$=0.05%, λ_{239} = 0.10%, $(A.F.240)_S$=0.10% and λ_{240} = 0.10%

Combined error = 0.61% [Computed by error propagation in Eq.(7)]

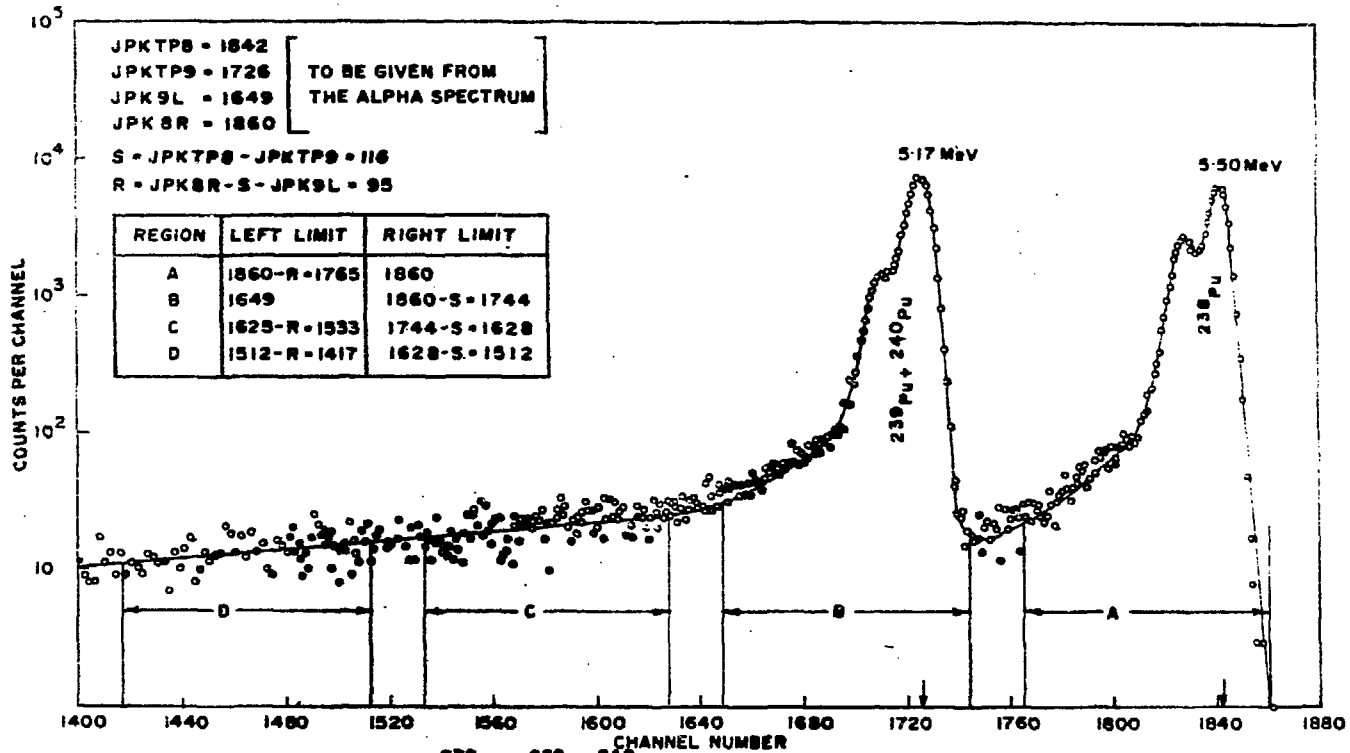

FIG.-1 SELECTION OF REGIONS FOR $^{238}Pu/(^{239}Pu+^{240}Pu)$ α - ACTIVITY RATIO COMPUTATION BY G.P. METHOD

APPENDIX I

A TYPICAL CALCULATION FOR SPIKING IRRADIATED FUEL DISSOLVER SOLUTION WITH ^{238}Pu

Approximate burn-up = 1000 MWD/TU

Initial α activity ratio $R_s = \frac{A_s}{A_g + A_s} = 0.15$

Approximate concentration of plutonium in the dissolver solution (D.S) = 12 μg Pu/g solution [U/Pu = 1000 Feed contains 300 mg of U/g solution and therefore 300 μg of Pu/g solution. 1 g of dissolver solution diluted to 25 g]

Mass number	Atom %	Weight %	% α activity
238	0.0637	0.0634	13.18
239	91.933	91.895	69.02
240	6.435	6.459	17.77
241	1.150	1.159	0.0346
242	0.418	0.423	0.0201

α specific activity = 1.834×10^5 dpm/μg of plutonium (calculated from the isotopic composition data)

Concentration of plutonium in D.S. = 12 μg Pu/g of solution

dpm/g of ^{238}Pu in D.S. $= 1.834 \times 10^5 \times 12 \times 0.1315 = 2.8940 \times 10^5$

dpm/g of $^{239}Pu + ^{240}Pu$ in D.S $= 1.834 \times 10^5 \times 12 \times (0.6902 + 0.1777)$

$= 19.101 \times 10^5$

If 250 mg of D.S. is weighed, then α activity due to ^{238}Pu in the aliquot = $2.894 \times 0.25 \times 10^5 = 0.72 \times 10^5$ dpm

α activity due to $^{239}Pu+^{240}Pu$ in the aliquot = $19.101 \times 0.25 \times 10^5 = 4.77 \times 10^5$ dpm

Final α activity ratio required, (R_M) = 1.5

α activity due to ^{238}Pu required in the spiked mixture = $4.77 \times 1.5 \times 10^5 = 7.15 \times 10^5$ dpm

^{238}Pu α activity to be added = $(7.15 - 0.72) \times 10^5$

= 6.43×10^5 dpm

Concentration of ^{238}Pu spike = 88.3175 ng/g (precalibrated)

= $88.3175 \times 3.80 \times 10^7$ dpm/g solution

= 3.356×10^6 dpm/g solution

aliquot size of spike solution to be taken = $\frac{6.43 \times 10^5}{3.356 \times 10^6}$

= 0.191 g

Thus 250 mg of D.S. is to be spiked with about 190 mg of ^{238}Pu spike for increasing the α activity ratio from 0.15 to 1.5

APPENDIX II

A TYPICAL CALCULATION FOR DETERMINING PLUTONIUM CONCENTRATION IN THE IRRADIATED FUEL DISSOLVER SOLUTION BY IDAS

Sample Data	Spike Data
C_S = ?	C_{Sp} = 88.3175 ng Pu/g solution
A.F. of ^{239}Pu = 0.91933	A.F. of ^{238}Pu = 0.93888
A.F. of ^{240}Pu = 0.06435	$(At.\ Wt.)_{Sp}$ = 238.1132
$(At.\ Wt.)_S$ = 239.1509	R_{Sp} = 3758.41 (From Table-4)
R_S = 0.1491	

W_S = 0.30065 g, W_{Sp} = 0.27130 g, R_M = 1.4595

Substituting the values in Eq.(7)

$$C_S = \frac{88.3175 \times 0.27130}{0.30065 \times 3758.41} \frac{3758.41-1.4595}{1.4595-0.1491} \frac{239.1509}{238.1132} \frac{0.93888/87.74}{(0.91933/24110)+(0.06435/6553)} 10^{-3}$$

$$= 13.626\ \mu g/g$$