KERNFORSCHUNGSZENTRUM

KARLSRUHE

September 1976 KFK 2321

Institut für Angewandte Kernphysik
Projekt Spaltstoffflußkontrolle

Assay of Plutonium in Process Wastes from Fuel Fabrication Plants

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ABSTRACT

A gamma-spectrometric method for the assay of fissile plutonium in process wastes from fuel fabrication plants which are not mixed with fission products has been standardized. The method uses a multi-group-analysis of gamma spectra measured with a NaI detector from waste samples. The attenuation in matrix materials is corrected by making transmission measurements using an external plutonium source. The method also provides an internal check on the presence of plutonium bearing materials with significant self-absorption. The results are compared with that obtained using higher resolution spectrometry with a Ge(Li) detector.

Bestimmung von Plutonium in Abfallproben
aus Brennelement-Fabrikationsanlagen

ZUSAMMENFASSUNG

Es wird ein gammaspektrometrisches Meßverfahren zur quantitativen Bestimmung spaltbaren Plutoniums in spaltproduktfreien plutoniumhaltigen Abfällen aus Brennelementfabrikationsanlagen dargestellt. Die Meßmethode beruht auf einer Multi-Energiegruppen-Analyse von Gammaspektren, die mit einem einfachen NaJ-Detektor von Abfallproben gemessen werden. Zur Korrektur von Absorptionseffekten in Matrixmaterialien wird eine Transmissionsmessung mit einer externen Plutoniumquelle durchgeführt. Das Analyseverfahren läßt auch erkennen, ob Plutoniummaterialien mit beträchtlicher Selbstabsorption vorliegen. Die Ergebnisse der NaJ-Messungen werden mit Ge(Li)-Messungen verglichen.

CONTENTS

1. INTRODUCTION

A fast and relatively simple plutonium assay technique having reasonably good accuracy is necessary to scan the large number of bags and drums containing wastes from fuel fabrication plants and chemical laboratories for fissile material accountancy. Further, stringent limits (fractions of a gram) on the allowed plutonium content in wastes released for final disposal require sensitivities which cannot be normally attained by either the Ge(Li) or the neutron method. Both techniques - gamma spectrometry using a Ge(Li) detector and external transmission sources for effecting attenuation correction (cf. e.g. Ref. 1) as well as the neutron coincidence technique (cf., e.g. Ref. 2) are currently mainly used in waste monitors. The neutron method has the advantage that it can handle samples containing high levels of fission products and is less sensitive to matrix effects, but in general it has lower detection sensitivity than the gamma technique.

Since the wastes from fuel fabrication plants and chemical laboratories consist to a large extent of low density material (paper, rags, gloves etc.) and usually are not mixed with fission products, the higher sensitivity gamma technique for plutonium assay can be preferably applied to this category of wastes. In particular, gamma spectrometry using a NaI detector can be made use of, with the accompanying superiority in terms of sensitivity and simplicity over the higher resolution Ge(Li) detector.

The present work was aimed at standardizing the measurement of fissile plutonium in wastes using a NaI detector and establishing the feasibility and sensitivity for eventually adopting it as a computerized measurement system for routine use. The method is a multi-group one which can give the total fissile plutonium content (^{239}Pu and ^{241}Pu) after correcting for matrix attenuation by using an external plutonium source. It can check for the possibility of the presence of plutonium bearing materials with significant self-absorption, which cannot be corrected for by making a transmission measurement.

2. PRINCIPLE OF THE METHOD

Fig. 1 gives the typical gamma spectrum of a plutonium sample as obtained using a 3" dia. x 3" length NaI detector. The detector has been covered with a 1.5 mm thick cadmium absorber to reduce the high intensity of the 60 keV gamma rays from ^{241}Am and from plutonium x-rays, which otherwise would cause pulse pile-up and deadtime effects in the electronics and in the analyser. The electronics used in the measurements is the conventional one consisting of a high voltage unit, a linear amplifier and a multi-channel analyser. In addition a spectrum stabilizer which stabilizes on the alpha peak (3 to 4 MeV gamma equivalent peak) arising from a weak ^{241}Am source seeded into the NaI crystal ensures gain stability during data acquisition.

The characteristic peaks from a plutonium sample can be seen in the spectrum at 208 keV, ∿265 keV, ∿335 keV, ∿380 keV and ∿655 keV. The shape of the 400 keV complex may considerably vary with variation in isotopic composition. The peaks are composed of several gamma lines from the various plutonium isotopes. The relative contribution of the different plutonium isotopes to the different parts of the spectrum has been studied in detail in order to optimize the groupings for assay of plutonium in the samples. Computer simulated gamma spectra from plutonium of various isotopic compositions have been used for this purpose. The programme which uses as input the measured efficiency and resolution of the detector and the gamma-ray intensities from the various plutonium isotopes [3] calculates the spectrum as will be observed by using a NaI detector having a gaussian spread for the photo peak. The efficiencies are given at discrete points and the programme interpolates the value for a given photon energy, while the resolution for the particular detector used (3" x 3") is calculated from an empirically fitted function of FWHM (in percent of energy) vs energy of the photon:

$$\ln R = - 0.35134 \times \ln E + 4.2308$$

where R is the resolution at the energy E(keV). For the sake of comparison the calculated spectrum for the same plutonium as obtained by using the programme is shown along with the observed spectrum in Fig. 1. It may be noted that the calculated spectrum is for a sample with no self- or matrix-absorption and also does not include the contribution from

the compton scattered photons from higher energies. The measured spectrum on the other hand is taken through a cadmium filter of 1.5 mm surrounding the detector. Nevertheless, the calculated spectrum describes the gross shape as well as the fine structures of the measured spectrum very well. The percent contribution due to the various plutonium isotopes to the counts in any selected region of the spectrum can be directly obtained from the programme. The input required for any given sample is the isotopic composition and the time elapsed since separation of americium. The programme calculates the daughter product activity (^{237}U and ^{241}Am) buildup and takes into account the contribution from the photons belonging to these also.

High resolution Ge(Li) detectors have been used earlier for estimation of ^{239}Pu in wastes using discrete, well resolved gamma rays emitted by this isotope. The aim of the present method is to use the simpler NaI detector to assay the fissile plutonium content (^{239}Pu and ^{241}Pu) by selecting suitable windows. For this the following energy groups have been considered:

Group 1	375 to 470 keV
Group 2	290 to 470 keV
Group 3	180 to 240 keV

Setting a window limit on the slope of a spectrum will make it sensitive to gain variation. Hence the limits of Groups 2 and 3 have been taken as the limits of the respective peaks in the observed spectrum. The lower limit of Group 1 has been optimized to include counts due to ^{239}Pu preferentially. This is illustrated in Fig. 2 where the percent contribution of ^{239}Pu to the counts in the second half of the 400 keV complex as a function of the lower limit, keeping the upper limit at 470 keV, as calculated from the programme for some typical isotopic compositions corresponding to particular burn-ups is given. The contribution of various plutonium isotopes to the counts in the three energy groups are given in Table 1. Fig. 3 presents the contribution of ^{237}U and ^{241}Am to the counts in Group 1, in order to illustrate the extent to which the counts in this group can be taken as proportional to the ^{239}Pu content. The study leads to the following conclusions:

(i) For samples having more than 75 % ^{239}Pu the counts in Group 1 can be reasonably assumed to be proportional to the ^{239}Pu content.

(ii) Group 2 has a higher contribution from the daughter products of ^{241}Pu. Of these, ^{237}U reaches equilibrium with ^{241}Pu within a short time ($\sim$ 30 days) and hence can be taken as a direct measure of ^{241}Pu. But ^{241}Am goes on slowly building up and is hence dependent on the age of the sample. For samples having less than 5 % of ^{241}Pu and ages less than 2 years, the contribution from ^{241}Am can be neglected and the counts may be regarded as due to ^{239}Pu and $^{237}U(^{241}Pu)$ only.

(iii) Group 3 can be seen to be essentially due to ^{237}U (proportional to ^{241}Pu) only, for samples of any age upto 6 years and having a wide range of isotopic compositions. Hence this can be taken as a quantitative measure of the ^{241}Pu content.

Thus in principle one can set up simultaneous equations with the ^{239}Pu, ^{241}Pu contents as unknowns. If c1, c2 and c3 are the counts per unit time (cps) in the respective groups and if P9, and P1 are the contents of ^{239}Pu and ^{241}Pu in the samples then,

$$A \times P9 + B = c1$$
$$C \times P9 + D \times P1 = c2$$
$$E \times P9 + F \times P1 = c3$$

The constants A,B,C,D,E and F can be solved for from c1, c2 and c3 corresponding to sources of known amounts of plutonium having standard isotopic compositions.

There are certain problems to be solved before the above principle can be directly applied for assay purposes. In an actual spectrum the counts c1, c2 and c3 have to be corrected for the compton contribution from higher energy gamma rays. All the three groups contain compton scattered gammas from the 655 keV complex which has significant contribution from isotopes other than ^{239}Pu and ^{241}Pu. The correction for this in the three groups can be done by taking a background window in the 520 keV region. Groups 1 and 2 also contain compton contribution from the 400 keV complex. It is rather difficult to correct for this by using a graphic procedure or by any suitable background windows. But once the correction for the contribution from the compton scattered photons of the 655 keV complex has been made, an analysis of the spectrum shows that the remaining compton contributions to Groups 2 and 3 are due to mainly ^{239}Pu and ^{237}U (^{241}Pu) and hence can be included in the constants of the equations. Thus if C1, C2 and C3 are the compton corrected (for 655 keV complex) counts, the equations can be rewritten as:

$$A \times P9 + B = C1$$
$$C \times P9 + D \times P1 = C2$$
$$E \times P9 + F \times P1 = C3$$

Another correction required is for the self-attenuation and matrix-attenuation in the samples. This is generally corrected for in two ways - by using external sources to measure the attenuation offered by the matrix of the sample or by using a differential absorption method which makes use of two different gammas emitted by the same isotope in the sample. These methods have been adopted for assay using a Ge(Li) detector[4]. While the former has the disadvantage that it cannot account for any localized shielding effect, the latter method, though in principle can correct for the attenuation exactly (both self and matrix), needs information on the ratio of the effective mass absorption coefficients of the two gammas and the density of the matrix. This information is rather difficult to know in practice.

By using an external plutonium source one can get the attenuation correction for the exact energies, but sufficiently strong sources are difficult to

obtain. In Ge(Li) spectrometry for correcting matrix attenuation of the 414 keV gamma ray from ^{239}Pu, the discrete gamma ray at 401 keV from a ^{75}Se source is generally made use of. For NaI measurements an external plutonium source may be more appropriate since it could take into account both the attenuation and scattering effects for the whole spectrum of gamma rays from plutonium. However, unlike in the case of Ge(Li) spectrometry using a ^{75}Se transmission source, the use of a plutonium transmission source in the NaI measurements requires a double scan.

In the present work an external plutonium source has been used to correct for the matrix attenuation of the counts in Groups 1 and 2 in the 400 keV complex. The corrected counts so obtained in Group 1 is used to estimate ^{239}Pu and counts in Group 2 gives a measure of ^{241}Pu. A transmission measurement for the 208 keV is not performed because usually the higher absorption coefficient at this energy involves the subtraction of two large quantities leading to low statistical precision. However, the ratio of the counts in Group 2 and 3 due to ^{241}Pu, after removing the contribution due to ^{239}Pu, correlates with the measured attenuation at 400 keV in the absence of large localized absorption. Any marked departure from this correlation indicates the presence of self absorption. If the matrix is known to have negligible attenuation as in the case of paper wastes etc., the 208 keV counts could be used to estimate the ^{241}Pu content directly, which leads to a higher sensitivity. This might be an advantage in certain cases as it can be shown empirically that the ^{241}Pu content is approximately proportional to the gross alpha activity, which is the consideration from waste disposal point of view.

3. CALIBRATION

A set of four samples containing plutonium of varying isotopic compositions have been used in the calibration of the system. The details of these samples are given in Table 2. The samples 1 to 3 were in form of powder and 4 in form of solution sealed in glass bottles and contained in sealed aluminium cans. The ^{241}Pu content in the samples as on April 1976 was measured using a high resolution Ge(Li) (active volume - 18 c.c.) detector and adopting a ratio technique as described in the Appendix. The measured $^{241}Pu/^{239}Pu$

ratio in the samples obtained are shown in Table A1 and these are used to calculate the ^{241}Pu content from the reported ^{239}Pu content in the samples. The ^{241}Pu values so obtained have been used for the calibration.

The standard samples were thin samples offering no matrix or self attenuation. The sample-to-detector distance was kept as 50 cms and the 3" x 3" NaI detector was covered with 1.5 mm thick cadmium to reduce the intensity of the ^{241}Am gamma rays and x-rays at the detector. This does not attenuate the 208 keV and 400 keV gamma rays, which were of interest in the measurements, to any appreciable extent. The counts per second obtained for the four standards in the three windows (C1, C2 and C3), after correction for ambient background and for compton contribution from the 655 keV complex by using a window in the region of 520 keV, were used in calculating the constants. A least squares fitting procedure was used for deriving A and B. The procedure adopted for obtaining the two sets of constants C and D and E and F was as follows:

Consider the set of equations:

$$C \times P9_i + D \times P1_i = C2_i$$

where $P9_i$ and $P1_i$ are the quantities of ^{239}Pu and ^{241}Pu in the sample i(=1 to 4) and $C2_i$ is the counts per second in Group 2 for the particular sample. This results in a set of i (=4) equations in two unknowns C and D. Thus in matrix notation:

$$P \times \begin{vmatrix} C \\ D \end{vmatrix} = H$$

where P is a (4,2) matrix containing the $P9_i$ and $P1_i$ terms and H is a (4,1) matrix containing $C2_i$ terms. It can be shown that a solution of C and D consistent with all the four equations under the condition of the sum of the squares of the deviations being minimum is given by:

$$P' \times P \times \begin{vmatrix} C \\ D \end{vmatrix} = P' \times H$$

where P' is the transpose of P. A similar procedure was adopted for solving E and F also.

The countrates observed for the standard samples and the calculated constants are shown in Table 3.

4. MEASUREMENTS: RESULTS AND DISCUSSION

The system calibrated as described earlier was used in the estimation of ^{239}Pu and ^{241}Pu in some waste bags. The measurements were carried out on six waste samples. The samples were sealed in polyethylene bags and were about 30 cms in height and 20 cms in width, having no particular geometrical shape. One of the samples contained a known amount of plutonium (1.2 gms) of known isotopic composition (78.5 % ^{239}Pu and 2.6 % ^{241}Pu) distributed in a light matrix offering negligible attenuation to the 200 keV and 400 keV gamma rays. The other samples varied in the matrix and neither the amount of plutonium contained therein nor the nature of the matrix was known. These formed a sample population of the large number of waste bags which were scanned for plutonium earlier using a stabilized two-window analyzer unit (SAM 2) [5]. The samples were kept at a mean distance of about 50 cms from the detector. This gives a value of 1/6 for the ratio of the radius to the distance of the centre of the sample from the detector. This can lead to a difference of a factor of 1.44 in the counts due to variation of the location of the sample material within the container (Ref. 4). One has to choose the distance by compromising between the sensitivity and the inaccuracy due to the geometry variation. By rotating the sample this uncertainty could be brought down to 1.029. The present measurements were done with the sample stationary at two positions 180^{o} to each other. The average of the two readings reduces the uncertainty to some extent.

An external sealed 30 gm plutonium source was used to estimate the matrix attenuation correction for the 400 keV gamma rays. The gamma spectrum as analyzed by a 1024 channel analyser was recorded using a teleprinter for subsequent data processing. Suitable windows also could be chosen in the analyser to get the total counts in these. Each sample measurement consisted of four runs:

(a) with the sample in one position;

(b) with the sample rotated through 180^{o};

(c) with the sample and the transmission source located behind, such that it is viewed by the detector through the sample matrix and

(d) with only the transmission source in position.

The difference between the counts observed in Group 1 in runs (c) and (b) gives the counts due to the gammas from the transmission source after undergoing attenuation in the matrix of the sample. The transmission factor T is given by the ratio of this difference to the counts in run (d). The counts were taken for 500 sec. in each of the runs. The counting time selected are for standardizing the technique and by no means represent the typical time needed for actual measurements. As can be seen from the count-rates given in Table 4, a one or two minute counting should be able to estimate a fraction of a gram of ^{239}Pu and milli-gram quantities of ^{241}Pu with reasonable accuracy. The transmission measurements could be made more accurate by using a higher activity plutonium source. The correction factor to be applied to the observed sample countrate for attenuation is given by:

$$CF = \frac{-\ln T}{1 - T}$$

where T is the measured attenuation factor. The expression is taken from Ref. 4 and assumes a slab geometry for the sample. The degree of dependence of the correction factor on the geometry of the sample (slab or cylinder) is large only if T is less than 0.6. The correction factors were used to arrive at the countrates C1 and C2 after subtracting the ambient background and the compton background due to the 655 keV complex for the six samples. The means of the corrected countrates for the two positions of the sample are given in Table 4. The countrates C3 are un-corrected for attenuation. The ^{239}Pu content in each sample was estimated using the expression:

$$C1 = 0.0684 \times P9 - 0.1461$$

from the respective values of C1 for the sample. The estimated ^{239}Pu content in the samples are shown in Column 5 of Table 4. On the basis of the reported isotopic compositon of the 1.2 gm standard, the ^{239}Pu content works out to be 942 mgm. The measured value of 950 mgm compares well with this. For all the samples the ^{239}Pu content measured using the 414 keV gamma counts in the spectrum obtained using a Ge(Li) detector (active volume 37 c.c.) are

also shown for comparison. The Ge(Li) detector was calibrated using the standard samples listed in Table 2. The ^{241}Pu content in the samples were estimated from the counts C2 using the expression:

$$C2 = 0.1461 \times P9 + 0.8849 \times P1$$

and the already estimated ^{239}Pu content P9. The estimated values so obtained are shown in column 7 of Table 4. Again the measured value of 29 mgm agrees well with the calculated value of 31.7 mgm for the 1.2 gm sample. As far as the other samples are concerned the reported ^{241}Pu content roughly varies from 3.4 % to 6.4 % with the ^{239}Pu content constant nearly at 75 %. This amounts to a range of 0.045 to 0.085 for the values of $^{241}Pu/^{239}Pu$ ratio in the samples. The ratios calculated from the estimated ^{239}Pu and ^{241}Pu content given in the last column of Table 4 show that the values lie in this range.

Though the use of the 208 keV gamma ray for the estimation of ^{241}Pu can lead to a higher sensitivity for a given time of counting, it will in practice be difficult to correct the observed counts for matrix attenuation because of the higher absorption coefficient at this low energy, especially in samples having higher absorption. The present method, however, gives an internal check to the presence of plutonium bearing materials having significant self absorption. The counts due to ^{241}Pu in the 400 keV complex and that due to ^{241}Pu in the 208 keV region (un-corrected for attenuation) using the estimated ^{239}Pu content and the constants C and D and E and F give an idea of the presence of large matrix or self attenuation. These counts along with their ratios are given in Table 5 for the different samples and compared with the matrix attenuation factors for 400 keV measured using the external source. The two agree well in trend. The ratios can either be adopted to correct for the matrix and self attenuation by using a differential absorption method (Ref. 4) in which case the matrix nature and the density should be known or they can be used to indicate the presence of large self-attenuation in the sample. If the measured attenuation using the external source is not high but the ratios of counts in Group 2 and 3 indicate a high attenuation then the presence of self or localized attenuation should be suspected. The ^{239}Pu content estimated from the counts in Group 1 could be in error in such cases.

As can be seen from Fig. 3 the assumption that the counts in the 375 - 470 keV window is proportional to the ^{239}Pu content is valid for plutonium of any age from burn-ups upto 20,000 Mwd/t and upto 2 years of age for plutonium from burn-ups upto 30,000 Mwd/t, if the over-estimation is to be kept below 10 %. If the approximate burn-up category of plutonium is known a factor to correct for this can also be incorporated. For high burn-ups a narrower window of about 30 keV centered at 415 keV should (cf. Fig. 2) involve less inaccuracy at the expense of better sensitivity.

5. CONCLUSION

The present work was aimed at standardizing a technique using the simpler NaI detector for the estimation of fissile plutonium (^{239}Pu and ^{241}Pu) in waste samples and to compare it with the more elaborate Ge(Li) measurements. The comparison of the ^{239}Pu measured in the samples using the two methods shows reasonably good agreement. The counts in the 375 - 470 keV window obtained using a NaI detector (3" x 3") detector is roughly 50 times more than the counts under the 414 keV peak in the Ge(Li) (active volume 32 cc) spectrum. This results in an increased sensitivity. By using a bigger area NaI crystal this can further be increased.

The hardware for a computerized assay system using the above technique would be the same as the ones currently available using a Ge(Li) detector. Suitable software for the data processing procedures as outlined in this report has to be incorporated. In NaI measurements it is also essential to ensure the absence of interference from other gamma rays, for instance from fission products. This can be accomplished by checking the spectrum using a suitable software for any extra peaks and for the width of the various peaks in the spectrum. Thus the simpler NaI detector can be used with advantage for assay of fissile plutonium (^{239}Pu and ^{241}Pu) in process wastes.

Appendix

Determination of Plutonium Isotopic Ratios Using High Resolution Gamma Spectrometry

A rather accurate determination of plutonium isotopic ratios can be made by high resolution gamma-ray spectrometry. The isotopic ratio N_i/N_k of two different isotopes i and k deduces from the simple relation

$$\frac{N_i}{N_k} = \frac{P_i}{P_k} \frac{I_k \cdot \lambda_k}{I_i \cdot \lambda_i} \frac{\varepsilon_k}{\varepsilon_i}$$

where P, I, and λ are the measured peak area, the absolute branching intensity, the decay constant and the overall efficiency for gamma rays with energies E_i and E_k from isotopes i and k, respectively. If the energies of the two gamma rays are very close to each other, then the overall efficiency which includes both the effect of attenuation in the sample and the external absorbers and the detector efficiency, can be taken approximately as same for both the gamma rays. The ratio of the counts under the two peaks after due correction for the underlying compton continuum then gives a direct measure of the isotopic ratio provided the relevant nuclear data, i.e. the photon yields of the two gamma rays and the half-lives of the two isotopes are well known. For very accurate measurements the differences in the relative efficiency even for gamma rays very close in energy has to be taken into account. This is best done by establishing the relative efficiency curve in the energy region of interest by means of gamma rays with known photon yields emitted by the *same* isotope.

For the present purpose of estimating the $^{241}Pu/^{239}Pu$ ratios in the samples used for calibrating the NaI measurements on the waste samples as described in this report the following pairs of gamma rays have been used:

Peak	Energy (keV)	Emitting Isotope	Photon yield (Ref.3)
1	203.52	^{239}Pu	5.630-06
2	207.97	^{237}U (^{241}Pu)	5.117-06
		^{241}Am	7.600-06
3	419.19	^{241}Am	2.760-07
4	422.54	^{239}Pu	1.190-06

In all the samples ^{237}U has been in equilibrium with ^{241}Pu, hence its 207.97 keV gamma ray could be used as a direct measure for the ^{241}Pu content. The photon yield given for the 207.97 keV gamma ray includes the alpha-branching ratio of 2.46-05 [6] for ^{241}Pu decaying to ^{237}U.

The 207.97 keV peak from ^{237}U (^{241}Pu) has an interfering contribution of a gamma ray with the same energy emitted by ^{241}Am. To correct for this contribution which amounts to a few percent for older samples, the relative ^{241}Am content must be known. This correction has been made using the pair of gamma rays at 419 keV (^{241}Am) and 422 keV(^{239}Pu).

The spectra in the region of the four energies 203, 208, 419 and 422 keV obtained for two samples using a 18 cc Ge(Li) detector are shown in Fig. A1. The detector has a resolution of 795 eV FWHM at 208 keV and 1110 eV FWHM at 422.54 keV. A step function has been used for subtraction of the compton background. If P_{203}, P_{208}, P_{419} and P_{422} are the counts under the peak due to photons of the four energies, then

$$P_{203} = N_{239} \cdot \lambda_{239} \cdot I_{203} \cdot \varepsilon_{203}$$

$$P_{208} = N_{241} \cdot \lambda_{241} \cdot I_{208}(241) \cdot \varepsilon_{208} + N_{Am} \cdot I_{208}(Am) \cdot \varepsilon_{208}$$

$$P_{419} = N_{Am} \cdot \lambda_{Am} \cdot I_{419} \cdot \varepsilon_{419}$$

$$P_{422} = N_{239} \cdot \lambda_{239} \cdot I_{422} \cdot \varepsilon_{422}$$

To a first approximation the efficiencies at the two energies within each pair has been taken to be the same, i.e. $\varepsilon_{203} = \varepsilon_{208}$ and $\varepsilon_{419} = \varepsilon_{422}$.

The error involved in this assumption turned out to be less than 2 % (see below). Taking ratios:

$$\frac{P_{208}}{P_{203}} = \frac{\lambda_{241} \cdot I_{208}\,(241)}{\lambda_{239} \cdot I_{203}} \cdot \frac{N_{241}}{N_{239}} + \frac{\lambda_{Am} \cdot I_{208}\,(Am)}{\lambda_{239} \cdot I_{203}} \cdot \frac{N_{Am}}{N_{239}}$$

$$\frac{P_{419}}{P_{422}} = \frac{\lambda_{Am} \cdot I_{419}}{\lambda_{239} \cdot I_{422}} \quad \frac{N_{Am}}{N_{239}}$$

from which N_{241}/N_{239} can be solved for. The counts in the four energies after correction for the compton continuum are shown in Table A1 along with the $^{241}Pu/^{239}Pu$ weight ratios evaluated therefrom using the photon yields given above and half-lives of 24,400 years for ^{239}Pu and 15.16 years for ^{241}Pu.

Although great care has been taken to evaluate properly the 203 and 208 keV peak areas, the measured $^{241}Pu/^{239}Pu$ weight ratios for the two standards NBS 946 and NBS 947 deviate by approximately 7% from the values derived from the mass-spectrometric data. This inconsistency still remained after the 203 keV and 208 keV peak areas had been corrected in addition for the differences in the relative overall efficiency at these two energies. For this purpose the relative efficiency in this energy region was established from the counts under the 148.60 keV peak of ^{241}Pu and from counts under the peaks at 164.59 keV, 207.97 keV and 267.50 keV of ^{237}U along with the gamma branching ratios from Ref. 3. The measured relative efficiencies for each sample were fitted to a parabolic curve and the efficiency ratio for 203 - to - 208 keV was obtained from this. This procedure was applied to the gamma spectra from samples NBS 946 and NBS 947 and to gamma spectra previously measured from samples NBS 948 and NBS 949 a [7]. The maximum variation in efficiency between energies 203 keV and 208 keV was found to be 2%.

In view of the high energy resolution attained and the great care taken in the peak area analysis, it appears very unlikely that the

observed inconsistency between mass-spectrometric and gamma-spectrometric $^{241}Pu/^{239}Pu$ weight ratios can be attributed to an improper peak area evaluation. The deviation is most likely due to uncertainities in the nuclear data used, i.e. the alpha and gamma branching intensities and the half-lives. The errors associated with the branching intensities as taken from Ref. 3 are 2 % for the 203 keV gamma rays from ^{239}Pu, 2 % for the 208 keV gamma rays from ^{237}U and 4 % for the alpha branching from ^{241}Pu to ^{237}U [6] which could indeed account for the observed bias between mass spectrometry and gamma spectrometry if they all add in the same direction. Alternatively, a variation in the half-life of ^{241}Pu which seems not yet unambiguously settled, brings both data sets closer together. This is shown in Table A2 which gives a comparison of $^{241}Pu/^{239}Pu$ weight ratios obtained from gamma spectrometry and mass spectrometry using two different half-lives for ^{241}Pu. Apparently the bias between gamma spectrometry and mass spectrometry reduces from ~ 9% to ~ 2.5 %, changing from the recent reported value of 15.16 years [6] for the half-life of ^{241}Pu to the previously measured value of 14 years.

In order to eliminate the present uncertainties in the half-lives as well as alpha and gamma branching intensities, very accurately known isotopic standards should be rather used for calibration purposes in high-accuracy isotopic analysis work using gamma-ray spectrometry. In this way isotopic ratios are directly related to *ratios* of peak areas which can be much more accurately determined than *absolute* branching intensities.

Using the isotopic ratios $^{241}Pu/^{239}Pu$ from the standards NBS 946, NBS 947, NBS 948 and NBS 949a, a relationship has been obtained between the ratio $^{241}Pu/^{239}Pu$ and the peak area ratios P_{208}/P_{203}. The data used and the relationship obtained are shown in Table A3. The values P_{208}/P_{203} are corrected for ^{241}Am contribution and relative efficiency. The uncertainty associated with the half-life of ^{241}Pu is not completely eliminated because the mass-spectrometric isotopic data have to be corrected for decay. As can be seen from Table A2 this can give rise to an error of up to 2 % using the two half-lives quoted in literature.

From the fitted expression given in Table A3 $^{241}Pu/^{239}Pu$ ratios can be obtained from gamma spectrometry with accuracies of better than 1 %

for samples containing less than 4 to 5 % ^{241}Pu. For samples having higher ^{241}Pu isotopic content, the peak area determination under the 203 keV peak becomes rather inaccurate due to the unfavourable peak to background ratios at this energy in the spectrum. In such cases other spectral regions should be made use of. Detailed investigations on the isotopic analysis by high resolution gamma spectroscopy is being undertaken.

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Table 1

The Contribution of the Various Plutonium Isotopes to the Counts in the 3 Energy Groups

Group	^{239}Pu	^{241}Pu	Contribution from ^{239}Pu (in percent)				Contribution from ^{237}U+^{241}Am (in percent)+)			
			t = 0.1 Yr	t = 2 Yr	t = 4 Yr	t = 6 Yr	t = 0.1 Yr	t = 2 Yr	t = 4 Yr	t = 6 Yr
Group 1	87 %	2.4 %	98.33	97.53	96.82	96.18	1.67	2.47	3.18	3.82
375 to 470							(0.05)	(0.96)	(1.81)	(2.58)
keV	75 %	4.5 %	96.43	94.79	93.33	92.05	3.57	5.22	6.67	7.95
							(0.11)	(2.02)	(3.80)	(5.37)
	58 %	9.0 %	91.26	87.54	84.40	81.74	8.73	12.45	15.60	18.26
							(0.26)	(4.82)	(8.88)	(12.32)
	45 %	15.0 %	82.94	76.59	71.59	67.58	17.05	23.41	28.42	32.42
							(0.51)	(9.07)	(16.18)	(21.88)
Group 2	87 %	2.4 %	79.64	78.84	78.86	78.12	20.36	21.16	21.54	21.88
290 to 470							(0.12)	(2.35)	(4.46)	(6.36)
keV	75 %	4.5 %	64.26	63.14	62.61	62.14	35.74	36.86	37.39	37.86
							(0.22)	(4.09)	(7.74)	(11.00)
	58 %	9.0 %	41.02	39.85	39.30	38.82	58.99	60.15	60.70	61.18
							(0.36)	(6.67)	(12.56)	(17.78)
	45 %	15.0 %	24.45	23.57	23.16	22.81	75.55	76.42	76.84	77.19
							(0.46)	(8.47)	(15.90)	(22.43)
Group 3	87 %	2.4 %					96.30	96.09	95.75	95.39
180 to 240							(0.03)	(0.53)	(1.10)	(1.76)
keV	75 %	4.5 %					98.26	98.15	97.99	97.83
							(0.03)	(0.54)	(9.13)	(1.76)
	58 %	9.0 %					99.31	99.26	99.20	99.13
							(0.03)	(0.55)	(1.14)	(1.78)
	45 %	15.0 %					99.06	99.64	99.61	99.58
							(0.03)	(0.55)	(1.15)	(1.79)

+) The value in the brackets is the countrate from ^{241}Am

Table 2

Samples Used in Calibrating the System

Sample	Amount	Age	Isotopic Compos. (weight percent)				
			^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
NBS 946	152 mgm	4.5 years	0.246	83.052	12.109	4.021	0.572
NBS 947	237 mgm	4.5 years	0.294	75.600	18.341	4.572	1.193
S3	91.4 mgm	∿6 years	-	91.2	8.0	0.8	0.004
S4	500 mgm	2 months	1.08	62.09	23.18	9.84	3.81

Table 3

Observed Countrates From the Standards

Sample	C1 (cps)	C2 (cps)	C3 (cps)
NBS 946	8.501	23.512	96.405
NBS 947	12.001	35.097	155.865
S3	5.610	11.545	13.636
S4	21.134	95.111	841.100

Calculated Constants:

A = 0.0684

B =-0.1461

C = 0.1461

D = 0.8849

E = 0.1151

F = 14.2944

Table 4

Results of Estimation in Some Samples

Sample No.	C1[+)] (cps)	C2[+)] (cps)	C3 (cps)	Estimated Pu-239 from C1 (gm)	Estimated Pu-239 using Ge(Li) (gm)	Estimated Pu-241 from C2 (gm)	Pu-241/Pu-239 weight ratio
164	270.1	687.6	1600.4	3.95	4.24	0.125	0.032
18	723.4	2242.6	4410.6	10.58	8.66	0.789	0.075
28	546.2	1672.7	5436.3	7.98	7.64	0.573	0.072
32	1857.2	4728.6	3421.5	27.15	26.12	0.863	0.032
132	462.7	1185.7	2130.1	6.77	7.82	0.223	0.033
1.2 gm Standard	65.0	164.92	657.8	0.95	1.05	0.029	0.031

[+)] Counts corrected for matrix attenuation using an external plutonium source.

Table 5

Attenuation of the 208 keV Gammas in the Samples

Sample No.	Pu-241 counts in C2 (1)	Pu-241 counts in C3 (2)	Ratio (1) / (2)	Attenuation Factor by Transmission (for 400 keV)
164	110.7	1145.6	0.097	0.709
18	697.4	3192.5	0.219	0.341
28	507.2	4517.6	0.112	0.781
32	763.3	295.7	2.581	0.131
132	196.9	1350.7	0.146	0.699
1.2 gm standard	26.2	548.4	0.048	0.928

Table A1

Estimation of $^{241}Pu/^{239}Pu$ ratios in standards from Ge(Li) spectra

Sample	P_{203}	P_{208}	P_{419}	P_{422}	$\frac{Pu\ 241}{Pu\ 239}$ Activ. Ratio	$\frac{Pu\ 241}{Pu\ 239}$ Weight Rat.	Reported weight of Pu-239 (mgm)	Estimated weight of Pu-241 (mgm)
NBS 946	6.5165+5	4.1125+7	0.1076+5	0.6008+5	68.2916	0.04243	126.24	5.356
NBS 947	6.4222+5	5.1112+7	0.1191+5	0.6042+5	86.3070	0.05362	179.17	9.607
S3	3.4242+6	3.1179+7	0.1617+5	0.2974+6	9.6706	0.00601	83.36	0.501
S4	1.7840+5	4.7411+7	0.7312+3	0.1755+5	292.1460	0.18151	310.45	56.350
S5	9.8679+5	9.7093+7	0.4024+4	0.9692+5	107.9946	0.06710	601.61	40.366

Table A2

Comparison of $^{241}Pu/^{239}Pu$ Weight Ratios Obtained from Gamma Spectrometry and Mass Spectrometry Using two Different Values for the Half-Life of ^{241}Pu

Standard	Date of Gamma Measurement	$^{241}Pu/^{239}Pu$ Using $T_{1/2}$ = 15.16 y			$^{241}Pu/^{239}Pu$ Using $T_{1/2}$ = 14 y		
		Mass Spectr.	Gamma	Percent Deviation	Mass Spectr.	Gamma	Percent Deviation
NBS 946	3/76	3.965-02	4.339-02	8.62	3.900-02	4.007-02	2.74
NBS 947	3/76	4.953-02	5.466-02	9.36	4.871-02	5.048-02	3.63
NBS 948	5/74	4.740-03	5.193-03	8.76	4.707-03	4.796-03	1.89
NBS 949a	5/74	1.609-03	1.751-03	8.51	1.592-03	1.617-03	1.57
				Mean 8.81			Mean 2.46

Table A3

Data Used for Obtaining the Relationship $^{241}Pu/^{239}Pu$ vs P_{208}/P_{203}

Standard	Date of Gamma Measurement	P_{208}/P_{203}	$^{241}Pu/^{239}Pu$ Weight Ratio		Percent Deviation
			Mass Spectr.+)	Gamma ++)	
NBS 946	3/76	6.348 + 01	3.965 - 02	3.945 - 02	- 0.50
NBS 947	3/76	7.996 + 01	4.953 - 02	4.968 - 02	+ 0.30
NBS 948	5/74	7.596 + 00	4.740 - 03	4.759 - 03	+ 0.40
NBS 949a	5/74	2.561 + 00	1.609 - 03	1.633 - 03	+ 1.49

+) Half-life of ^{241}Pu is taken as 15.16 years

++) Fitted Expression:

$$^{241}Pu/^{239}Pu = (6.2085 \pm 0.0261)10^{-4} \ (P_{208}/P_{203}) + (4.274 \pm 13.377) \cdot 10^{-5}$$

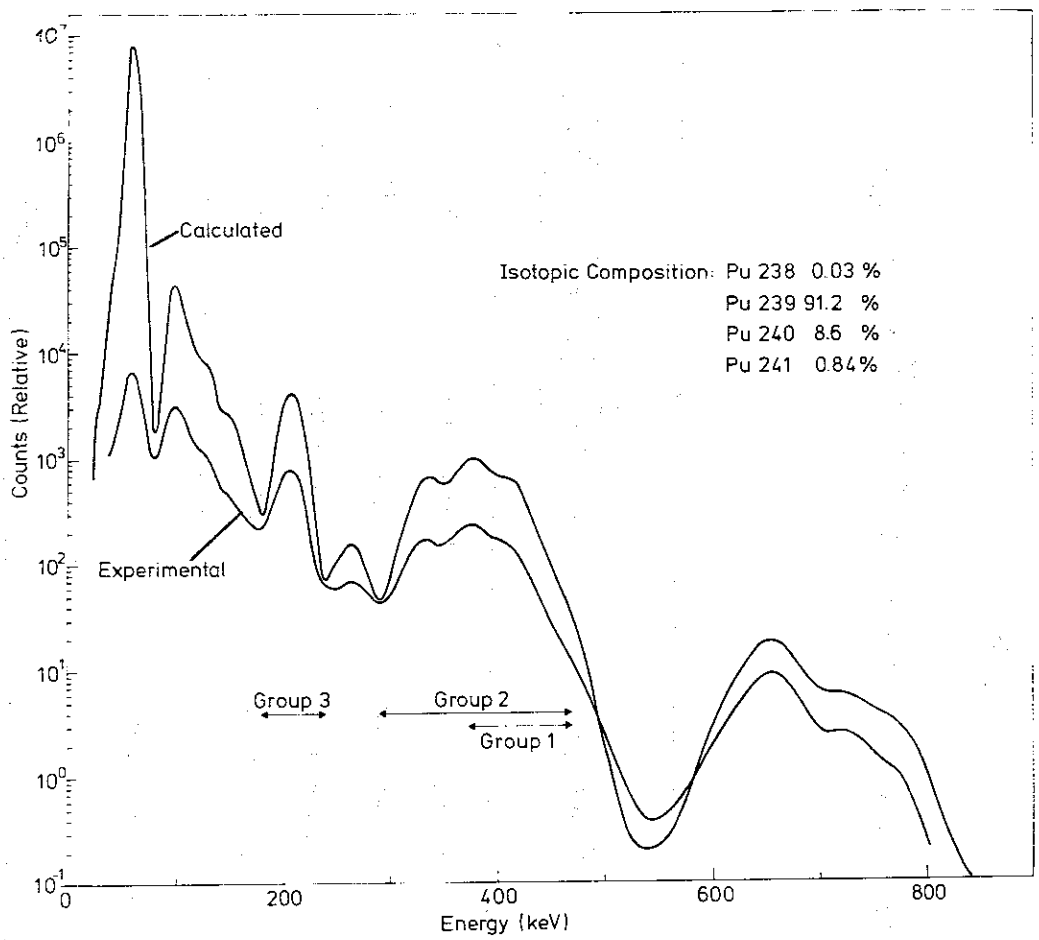

Fig. 1 Typical Gamma Spectrum of a Plutonium Sample

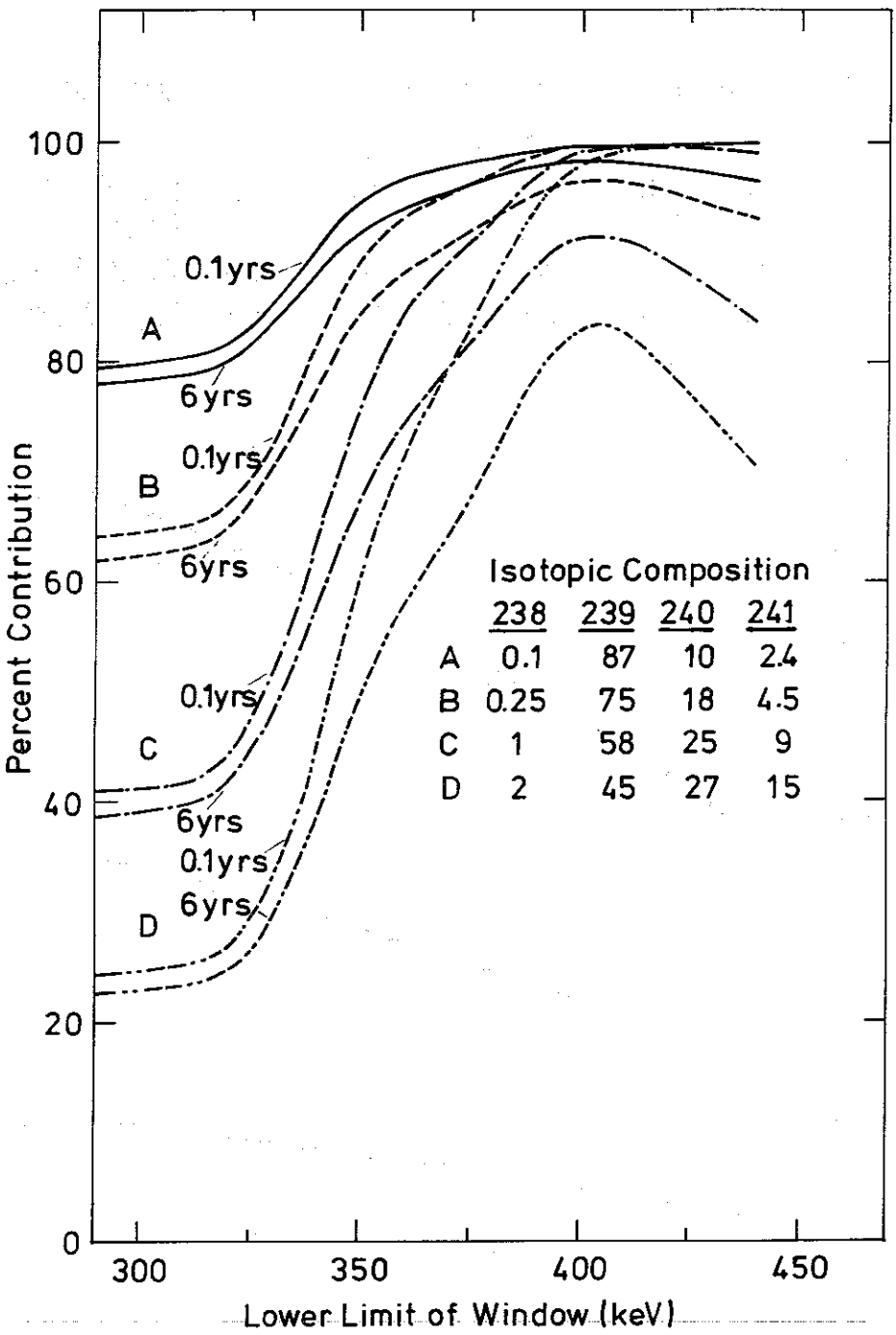

Fig. 2 Percent Contribution of ^{239}Pu to the Counts in the 400 keV Complex. Upper Window Limit Fixed at 470 keV.

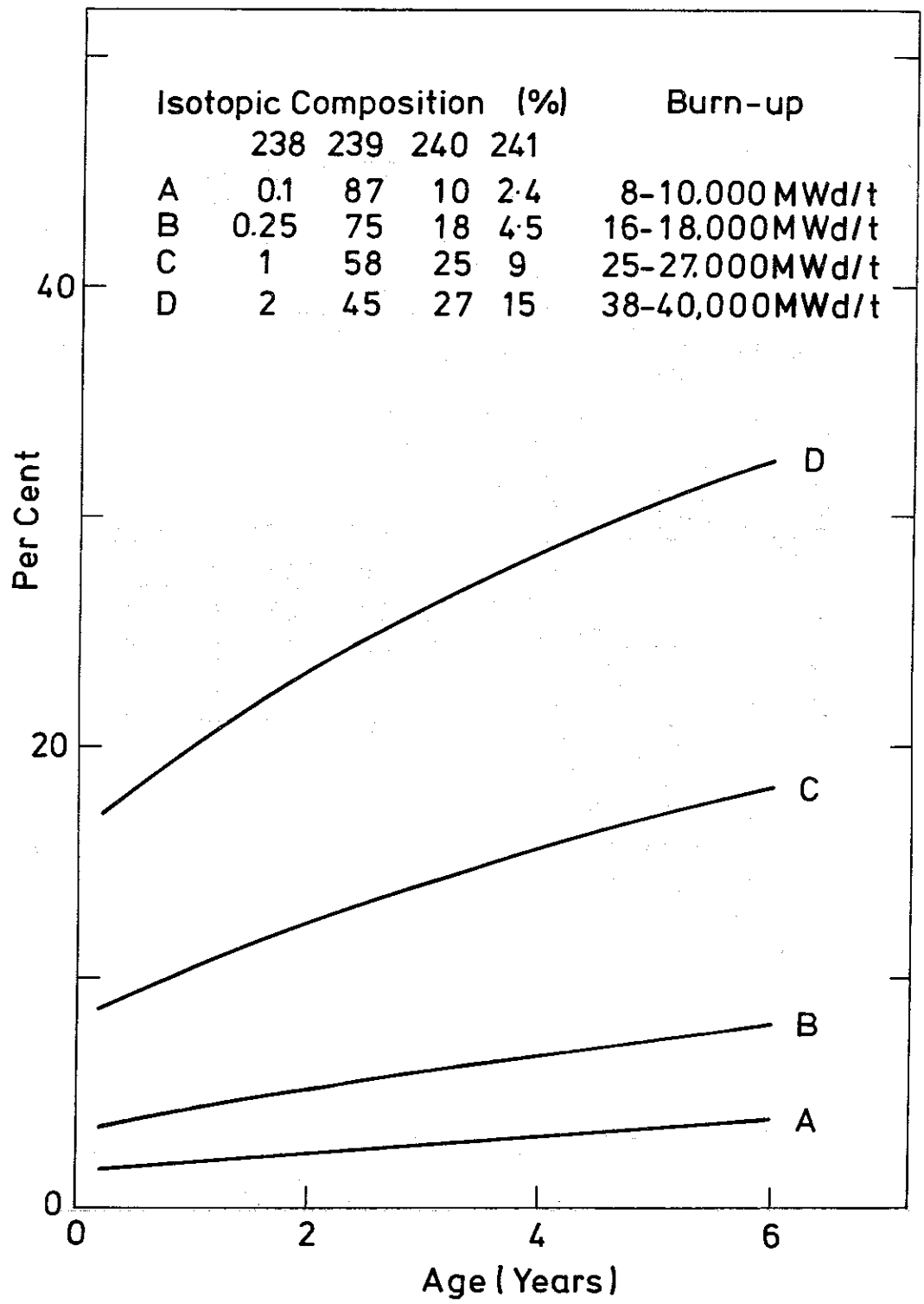

Fig. 3 Contribution of ^{237}U + ^{241}Am to Counts in Group 1 (375 to 470 keV) vs Sample Age.

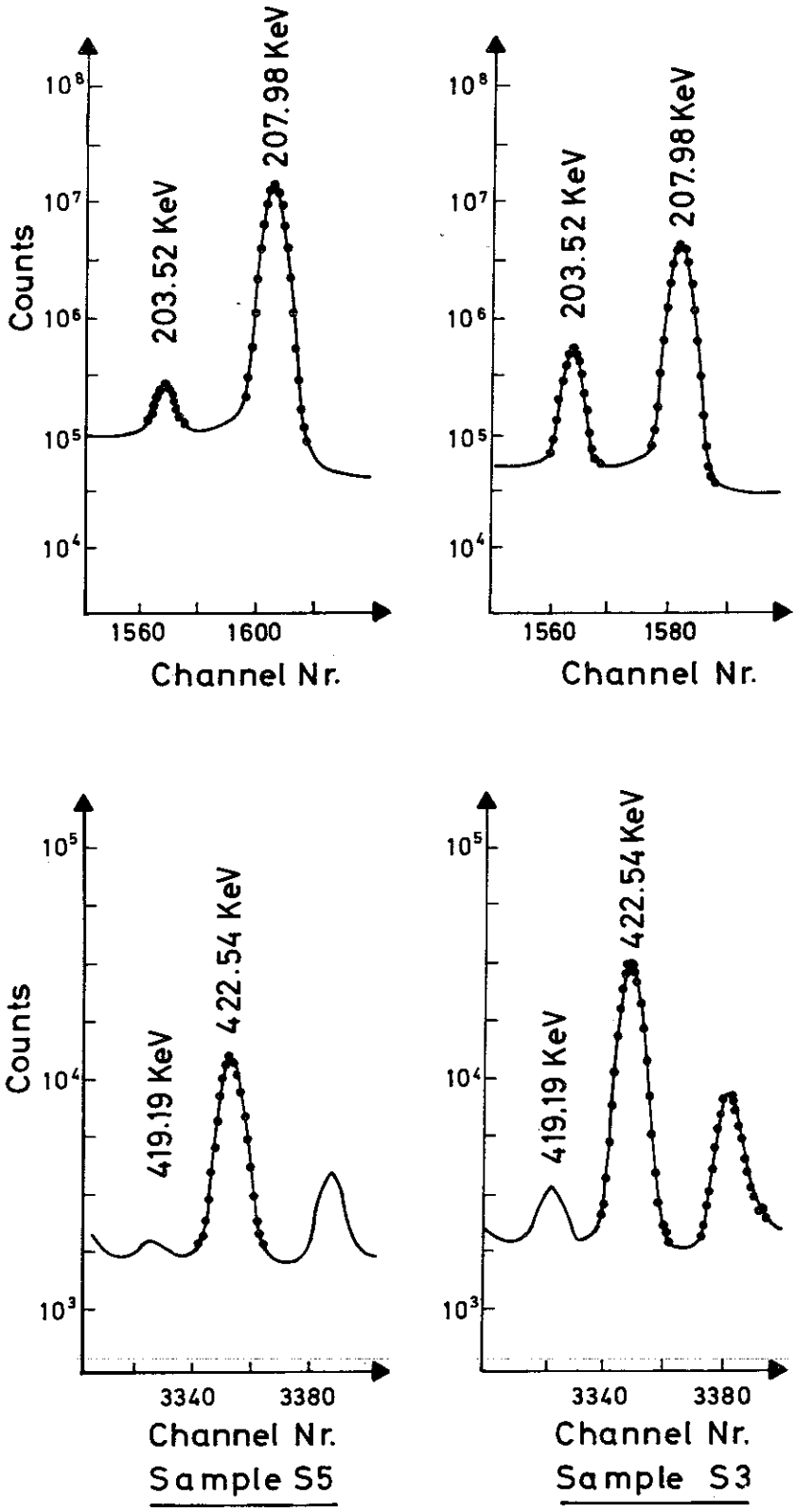

Fig. A1 Gamma Spectra of Plutonium Samples Taken Using a 18 cc Ge(Li)-Detector - 200 keV and 420 keV Regions.