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PRECISE ANALYSES BY GAMMA SPECTROMETRY

Raymond Gunnink and James B. Niday

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PRECISE ANALYSES BY GAMMA SPECTROMETRY*

Raymond Gunnink and James B. Niday

Lawrence Livermore Laboratory, University of California

Livermore, California 94550

ABSTRACT

An important application of Ge(Li) gamma-ray spectrometry is its use in nondestructive analysis. Highly precise results can be obtained by computer reduction of the data even though the spectra may be very complicated. However, this successful computer reduction requires a thorough understanding of the principles involved in the detection and acquisition techniques.

This report discusses some of the more important parameters that are involved in the making of accurate measurements. Included are discussions of proper methods for delineation of the background under the peaks and for precise characterization of the peak shapes, problems related to detector calibrations, and methods for quantitative interpretation of peak intensities.

Examples of gamma-ray analysis of plutonium on a small computer system are used to demonstrate that properly implemented techniques can give results to within 1% for the various isotopic constituents.

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INTRODUCTION

The Ge(Li) spectrometer system has become a widely used instrument since its advent some ten years ago. Application can be found wherever sources of gamma radiation exist. As a result, a wide variety of uses already exist and new ones are continually being found. Many of these only require identification of the nuclides present, or possibly some semi-quantitative information regarding the amounts present. Others, however, require a high degree of precision or accuracy.

Present day commercial instruments and techniques adequately cope with the former situations; however, highly precise analyses (i.e., better than 1 or 2%) require considerable attention to detail and also generally use computers to reduce and interpret the data. The ensuing discussion is based on the premise that if one understands the mechanisms that produce the observed spectrum, then one can probably write appropriate algorithms to describe the phenomena and use these in computer reduction and interpretation codes. Much of what will be presented stems from the development of a general purpose computer program which we call GAMANAL.¹ This code is routinely used at LLL to analyze ~6000 samples yearly. Automatic sample changers such as shown in Fig. 1 are used for counting the samples and the GAMANAL interpretation of the resulting spectra proceeds without man-machine interaction.

We will first discuss some of the important principles involved in the reduction and interpretation of Ge(Li) gamma-ray spectra, indicating techniques that have been developed to implement them. In the second part of the

presentation, we will illustrate some of these principles and techniques using specific examples drawn from our experience in developing techniques for measuring the isotopic ratios of plutonium.

DISCUSSION

Spectral analyses can generally be divided into two parts; first, the reduction of the spectral features into understandable entities such as photopeak energies and intensities and, secondly, the quantitative interpretation of these items as disintegration rates, atoms or grams of specific nuclides or materials.

Some of the spectral features we will now discuss are:

- The proper form of the background continuum under a peak or peak multiplet.
- The components of the observed peak shape.
- Methods for fitting peak multiplets.
- The calibration of detector systems.
- Schemes for interpreting the observed peaks.

Delineation of Backgrounds

If one were to consider a hypothetical detector system exhibiting no instrumental noise or line dispersions, all of the full-energy pulses corresponding to a given gamma ray would appear in one channel rather than as a broadened distribution (see Fig. 2). The background just before the peak presumably consists of degraded full-energy events resulting from such effects as "trapping" in the detector and low angle scattering by the source

or materials surrounding it. It would appear that these produce events that would continue right up to the full peak energy; the result being a discontinuity or step in the level of the "background". If this is so, any processes that disperse the original narrow gamma-ray line width will also smooth the background discontinuity in the manner shown in Fig. 2.

We believe this model closely represents the detection process and recommend one of two methods for computing the background curve.

1. Initially interpolate a step function as shown in Fig. 3 with the discontinuities occurring at the peak positions and with step heights proportioned according to the approximate peak heights. The region is subsequently smoothed with two or three cycles of linear smoothing. (This is the method used in GAMANAL).
2. An explicit function can be used for a point by point calculation of the background

$$B_i = B_n + (B_m - B_n) \cdot \left[\frac{\sum_{j=n}^{j=i} y_j}{\sum_{k=n}^{k=m} y_k} \right],$$

where

B_n = average background count in front of the peak

B_m = average background count in back of the peak

B_i = computed background at channel i

y_i = gross count in channel i .

This equation is more accurate than the first method described. Its application to a very complicated 100-keV multiplet from a plutonium spectrum can be seen in Fig. 4.

Characterization of Peak Shapes

There are at least three distinct components in the observed line shape of a gamma-ray photopeak. These are illustrated in Fig. 5. Additional structure may result from improper usage or alignment of the electronic components of the system. The major portion of the peak can be described by a Gaussian equation. However, accurate data interpretation requires that the "short-term" tailing in particular not be ignored. The "long-term" tailing may be important in the analysis of some complex multiplets. Otherwise it can frequently be treated as part of the "background" as is done in GAMANAL.

We found that the following algorithm adequately fits the observed peak shapes^{1,2}:

$$y_i = y_0 \left\{ e^{\alpha(x_i - x_0)^2} + \left[\underbrace{A \cdot e^{B(x_i - x_0)}}_{\text{short-term tail}} + \underbrace{D \cdot e^{E(x_i - x_0)}}_{\text{long-term tail}} \right] \cdot \left[1 - e^{C \cdot \alpha(x_i - x_0)^2} \right] \cdot \delta \right\},$$

where

y_i = net channel counts

y_0 = peak height

$\alpha = -\frac{1}{2\sigma^2}$ (σ = peak width parameter)

x_i = channel number of i^{th} point

x_0 = peak position

A, B, C, D, E are shape parameters describing the short- and long-term tailings

$\delta = 1$ for $x_i - x_0 < 0$

$\delta = 0$ for $x_i - x_0 > 0$.

Techniques have been found¹ whereby all of the peak shape parameters (α, A, B, C, D , and E) can be determined from two widely separated peaks in a spectrum. The resulting values will not change significantly in subsequent runs so that the determination of shape parameters simply becomes a part of the initial calibration of a system.

The above algorithm fits legitimate gamma-ray peaks very well; however, the 511-keV peak produced by positron annihilation and peaks due to x rays do not produce the predicted line shapes. The 511 radiation is Doppler broadened during the annihilation of the positronium. The x-ray line shape is broadened because of the very short lifetime of the x-ray transition. Figure 6 compares the intrinsic x-ray line shape with the instrumental distribution and shows how the two convolute. Only recently have we succeeded in finding an algorithm that adequately describes this convoluted distribution.⁵

The simultaneous fitting of several peaks in a multiplet is generally accomplished by some iterative method. In GAMAXAL we linearize the equations by using the first terms of a Taylor's expansion about the trial values and then use a Newton-Raphson or Gauss iterative technique. Very complicated unfoldings such as shown in Fig. 7 can be made using this approach.

In some specific and routine applications, it is possible to anticipate the isotopic contributions to a peak multiplet. If one has accurate gamma-ray energies and branching intensities corresponding to each of the components contributing to the grouping, then all of the peak positions relative to one another, and also the relative peak heights for each isotopic component, can be predetermined. With this foreknowledge, the number of unknowns in the fitting process can be reduced to be equal to the number of isotopic components. Furthermore, the equations are then linear and one can

avoid the iterative approach in fitting the set of equations. This approach is used extensively in our analyses of plutonium samples, which will be discussed in more detail later.

Detector Calibrations

If Ge(Li) detectors are to be used for quantitative measurements, they must be calibrated using appropriate sources. The counting efficiency at any particular gamma energy is dependent on a number of factors. Most of these are associated with the interaction process within the detector, the source-detector geometry, or with gamma-ray attenuations within the source or from surrounding materials. If the samples to be analyzed all have the same size, shape, set of radioactive components, and activity level, then it is possible to carry out a specific calibration for this sample type such that gamma-peak intensities can subsequently be directly converted to the desired units. This condition does not generally prevail in our case. As a consequence, a more flexible approach was developed. The one used in GAMANAL separates the overall efficiency into two components as follows:

$$\text{Efficiency} = \epsilon \times G,$$

where

ϵ = intrinsic efficiency

G = a geometry factor (includes attenuation factors).

This scheme requires only one efficiency curve, which can be used for all samples without regard for their shape, size, or activity level. A rather elaborate model has been developed to compute the geometry term.

In addition to calculating the simple geometry effect, it also corrects for sample size and volume and for attenuation by the sample matrix or by

other absorbers that may be present. Although the model has empirical components in it, it can be tuned to give very precise results as demonstrated by the following set of data:

	<u>Observed peak count^a</u>	<u>Count time (min)</u>	<u>Detector-to- source dist. (cm)</u>	<u>Difference from avg. value (%)</u>
1	518864	20	0.225	0.11
2	254690	20	0.540	-0.13
3	172517	20	1.180	-0.31
4	124862	20	1.825	-0.47
5	94278	20	2.450	-0.22
6	59168	20	3.750	0.35
7	80780	40	5.000	-0.03
8	58965	40	6.280	0.40
9	51500	80	10.650	-0.50
10	52850	160	20.750	-0.20

^adata are for ¹³⁷Cs (601-keV) counted on a 38-cm⁵ detector.

A description of the model and of many of the algorithms is given in a previous report.¹

Spectral Interpretation

A popular method of interpreting a spectrum is to hand pick one or more gamma-ray peaks for each nuclide represented and to compute nuclide abundances assuming that no interference exists. Although this is very practical for some situations, it generally means that much useful data is discarded and furthermore, unanticipated interference may cause errors.

A more generally applicable approach is to assume that the observed intensity of each peak is a linear addition of intensities from one or more components, i.e.,

$$Y_i = \sum_{j=1}^J A_j \cdot X_{ij},$$

where

Y_i = the intensity of the i^{th} peak in gammas/min

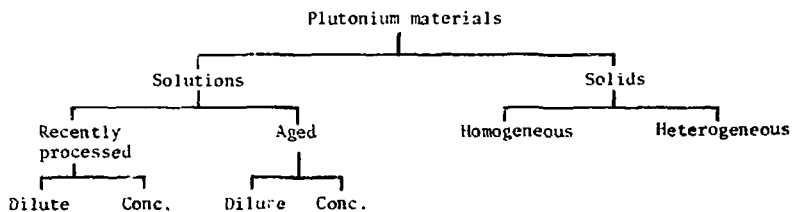
X_{ij} = the branching intensity of the j^{th} component at the i^{th} peak energy

A_j = the disintegration rate of the j^{th} component (a number that is to be determined).

The calculational method is to write the equations in matrix form as illustrated in Fig. 8, to find those sets of equations that are interdependent and then to solve them by the method of least squares. This approach becomes almost imperative for complex spectra, such as mixed-fission-product and some activation-analysis spectra, because of the large number of unresolved peak interferences. A typical interference resolved in this manner is illustrated in Fig. 9, which shows an 1175-keV peak that is generally attributed to ^{60}Co . However, small contributions of ^{56}Co and $^{132}\text{Te-I}$ are also present and must be properly considered for an accurate analysis. This illustration is representative of the detailed computer printout that provides a breakdown of contributions for each identified peak.

Specific Examples from the Safeguards Program

One area where many of the above principles have been applied in considerable detail is in the gamma analysis of plutonium materials. The conventional methods here have been to perform chemical analyses using mass spectrometry and alpha pulse-height analysis. These procedures are rather lengthy, require expensive equipment and are destructive: hence they are not amenable to automation. We are finding that appropriately implemented techniques using gamma-ray spectrometry can provide accurate plutonium isotopic-ratio measurements.⁴ However, in contrast to the conventional approach, the gamma analyses must frequently be tailored to the type of sample that is to be assayed. One way of roughly cataloging plutonium-bearing materials is as follows:



Other factors are:

- Controlled vs uncontrolled geometry.
- Contamination of other activities (e.g., fission products).
- Grade of material (weapons vs reactor grade).

Dissolved Samples

Some of the sample types are, of course, much easier to analyze than others. Of these, the simplest form is the recently processed plutonium solution from which the ^{237}U and ^{241}Am have been removed. With the intense 59-keV peak from ^{241}Am largely removed, several abundant low-energy gamma rays, as shown in Figs. 10a and 10b, can be used to provide accurate assays for ^{238}Pu , ^{239}Pu , and ^{240}Pu . The ^{241}Pu content can be determined from higher energy radiations at 105 and 148 keV. The principles that must be considered in making these measurements were discussed earlier and are also presented in an earlier report.⁴ A prototype system for making this type of measurement on weapons-grade plutonium has been field tested at the Savannah River Plant (SRP) and has been operating satisfactorily for two years now. The system consists of a 1-cm³, high-resolution, Ge(Li) detector and associated electronics and a 12 000-word, 12-bit minicomputer equipped with mass storage. All data reduction is done in FORTRAN. A summary of results obtained at SRP on 91 samples is as follows:

<u>Isotope</u>	<u>Abundance</u>	<u>Avg. deviation from mass spec. (%)</u>
238	0.01	1.5 ^a
239	93.00	0.004
240	6.0	0.8
241	0.6	2.0 ^b

^aLab measurements made by α -pulse analysis.

^bMuch of this disagreement was in the form of a bias resulting from a drift in efficiency.

Another common solution sample is one in which the ^{237}U has grown into equilibrium with its ^{241}Pu parent and appreciable amounts of ^{241}Am are also present. The low energy spectrum of such a sample is shown in Fig. 11.

The gamma rays below 59 keV are now obscured and the 100-keV region has become very complex. However, all of the isotopes of interest are represented in this low energy region and with the aid of a somewhat more sophisticated computer program, analyses have been made with sufficient accuracy to replace certain mass spectrometric measurements.

The following table shows two sets of results which compare gamma spectrometry with mass spectrometry:

<u>Isotope^a</u>	<u>SRP avg. deviation for 105 samples (%)</u>	<u>LLL results (10 samples) std. dev. (%)</u>
^{238}Pu	-	3.1
^{239}Pu	-0.005	0.05
^{240}Pu	+0.4	0.3
^{241}Pu	+0.5	0.8
^{241}Am	-1.6	2.6

^aWeapons-grade plutonium.

Solid Samples

Until now we have been considering the rather specific case of measuring isotopic ratios of plutonium solutions. The optimum approach for solution samples is to select a convenient set of gamma rays that provide information on the isotopes of interest and then to calibrate the

spectrometer system for a fixed counting geometry. There is considerable advantage in finding an approach that is much more flexible and adaptable to different measurement conditions such as varying sample quantity or size, non-uniform packaging, sample inhomogeneity, variable counting geometry, and unknown attenuations by the sample matrix or other absorbing materials.

One way of minimizing the influences of these experimental problems is to compute the isotopic ratios by using the peak intensities observed in a set of neighboring peaks that are produced by the various isotopes in the sample. Since the energies are nearly equal, the efficiency and attenuation differences will be quite small, and the ratio of isotopic abundances is then, to a first approximation, directly related to the peak intensities as follows:

$$\begin{aligned} A/B &= \frac{I_1 \cdot t_A}{\epsilon_1 \cdot Y_1} \cdot \frac{I_2 \cdot t_B}{\epsilon_2 \cdot Y_2} \\ &= \frac{I_1}{I_2} \cdot \frac{\epsilon_2}{\epsilon_1} \cdot \frac{Y_2}{Y_1} \cdot \frac{t_A}{t_B}, \end{aligned}$$

where

A/B = isotopic ratio

I_1 and I_2 = observed peak intensities of the two gamma rays coming from isotope A and B, respectively

ϵ_1 and ϵ_2 = gamma-ray counting efficiencies

Y_1 and Y_2 = the gamma yield or branching intensities of the respective gamma rays

t_A and t_B = the respective half-lives of isotopes A and B.

Although it may not be possible to obtain accurate absolute values for ϵ_1 and Y_1 individually, it is possible to obtain accurate ratios over a small energy range. The accuracy of the calculated isotopic ratio is then largely limited by the precision with which the peak intensities are measured.

A search for peak groupings that can potentially provide information on isotopic ratios indicates that eight or nine such spectral regions do exist as shown in Fig. 12. Some of these regions are quite complex while others are simply doublets. The number of isotopic components and the accuracy with which ratio measurements can be made varies.

After assessing the potential of each of the groupings using a computer program we wrote⁵ to simulate various conditions for each grouping, the 100-keV multiplet was selected for additional study. Although this region is very complex, as Fig. 13 shows, it cannot be ignored because it contains a wealth of information not otherwise available. In order to manage the complexity, it is important to precharacterize the region as much as possible. The relative gamma-ray energies and branching intensities were very carefully measured. Errors of 1- or 2-eV in the energy of a peak, relative to other peaks in the multiplet, clearly affect the quality of fit and may also significantly affect the results obtained for minor constituents.

The fitting procedure here is not that of individually fitting the 14 or more peaks in the multiplet, but rather to generate response functions or envelopes; one for each component (i.e., isotope) represented in the grouping. This reduces the number of unknowns in the least-square fitting from 14 to 6. That is, the unknowns now are the relative amounts of ^{258}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{241}Am , and α -induced x-ray fluorescence. The response function corresponding to each isotope is computed from energies and

branching intensities, which are provided as input. Also note how the ^{238}Pu signal appears to be nearly buried.

We have made some preliminary measurements aimed at verifying the analytical precision predicted by the simulator code. We repeatedly analyzed the same sample to study the reproducibility of the analysis and the stability of the detector system. Some of the results of these experiments are summarized in the following table:

<u>Isotope</u>	<u>Abundance (%)</u>	<u>Precision (1σ)</u> <u>(ten 10-h spectra)</u>	<u>Precision (1σ)</u> <u>(Fourteen 2-h spectra)</u>
^{238}Pu	0.01	0.6%	2.0%
^{239}Pu	93.7	0.015%	0.028%
^{240}Pu	5.8	0.2%	0.45%
^{241}Pu	0.44	0.06%	0.17%
^{241}Am	0.10	0.40%	0.44%

These results compare very well with those obtained from the study using the simulator code.⁵

We are presently comparing the analytical results from direct gamma measurements with those obtained by more conventional techniques. Thus far, they have generally agreed within the combined limits of error for these techniques and actually have been close to those shown in the last column of the table above.

As expected with any developing technique, many unsolved problems remain, but there are also many potential areas of application. In the past much of the data reduction involved hand calculations, or, at best,

man-machine interaction with a computer. However, significant progress has now been made in the development of good methodology for completely automatic analysis. Since there has been a simultaneous increase in the power and sophistication of minicomputer systems, we feel that gamma-ray spectrometry applications will become much more automated and, thus, more amenable to routine and on-line usage.

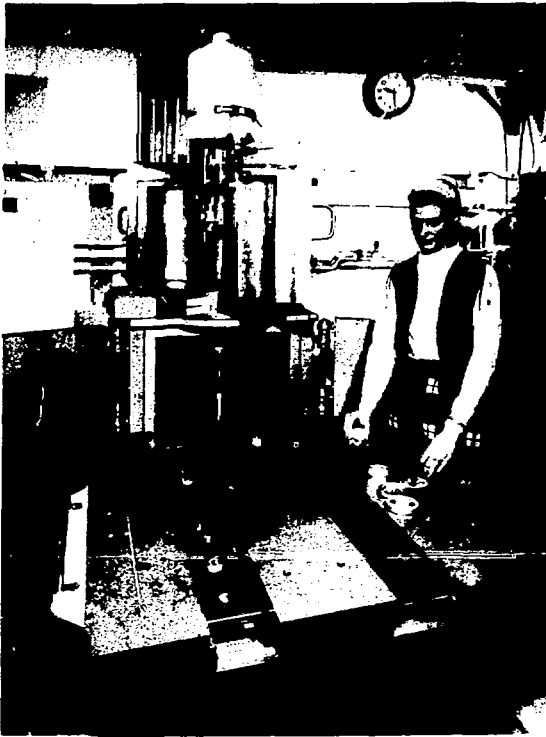


Fig. 1. Changers used at LLL to automatically change and position radioactive samples for counting.

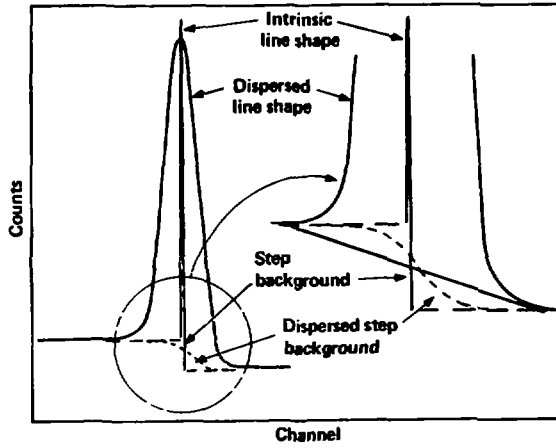


Fig. 2. The idealized background shape under a gamma-ray peak is a smoothed step.

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METHOD OF BACKGROUND INTERPOLATION

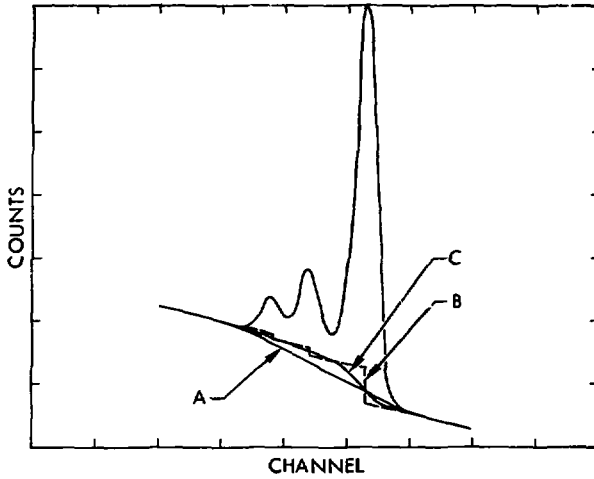


Fig. 3. An illustration of how a smoothed step function can be used to describe the background continuum.

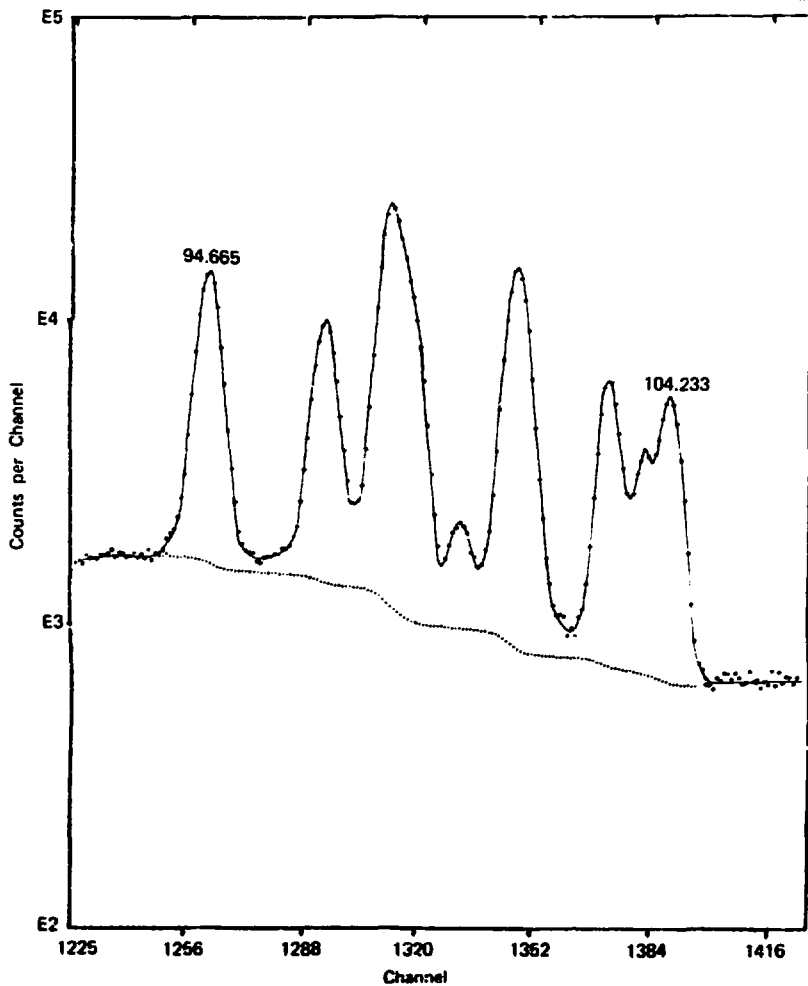


Fig. 1. The background continuum for this complex multiplet was calculated using the explicit function given in the text.

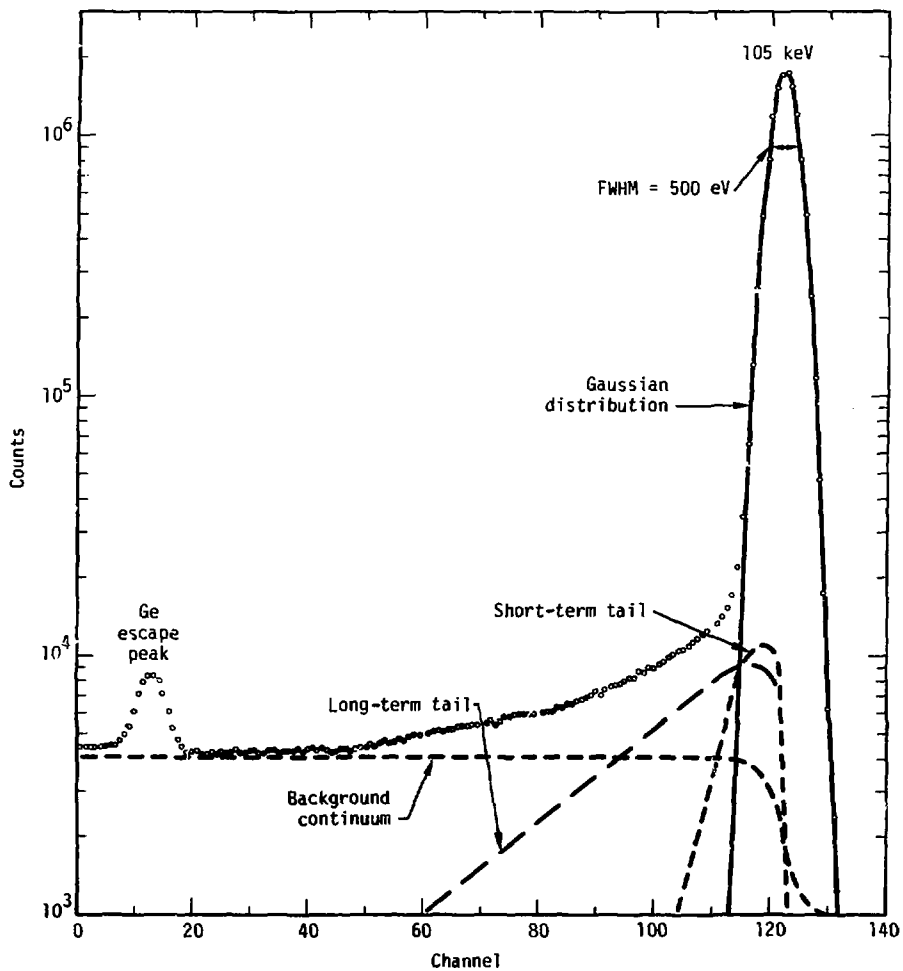


Fig. 5. Three components can be used to characterize the instrumental peak shape of a 105-keV gamma ray.

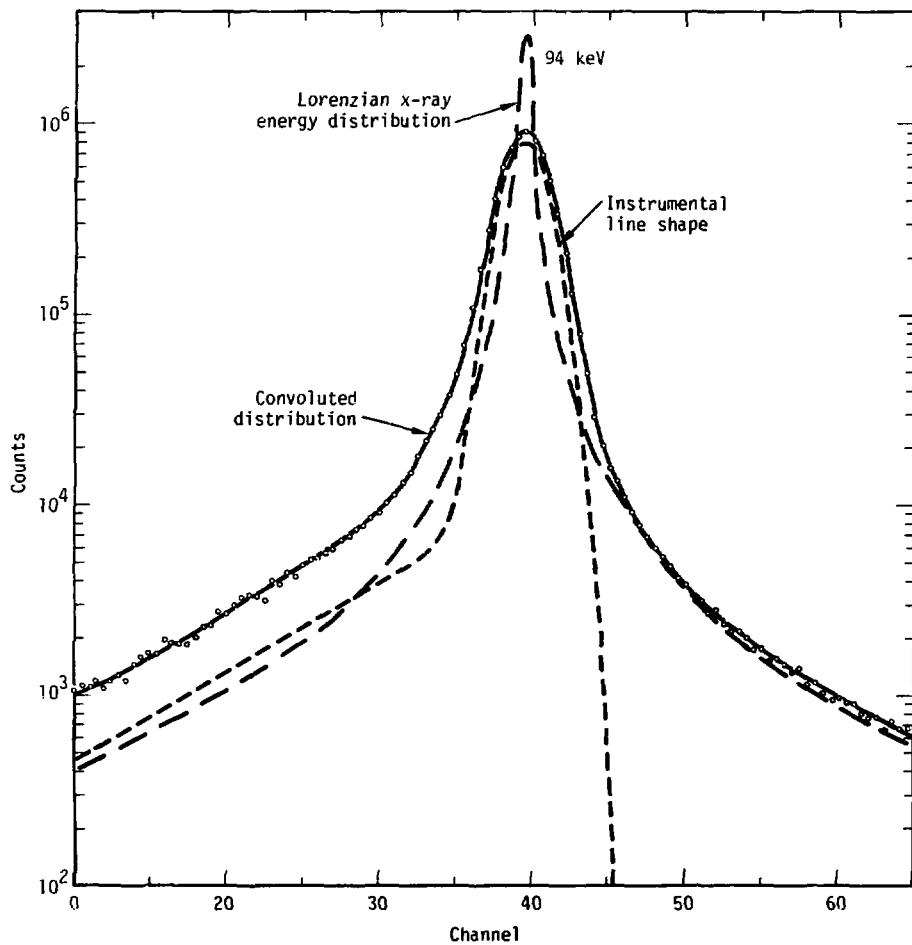


Fig. 6. The Lorentzian x-ray energy distribution convolutes with the instrumental line shape resulting in a modified peak shape.

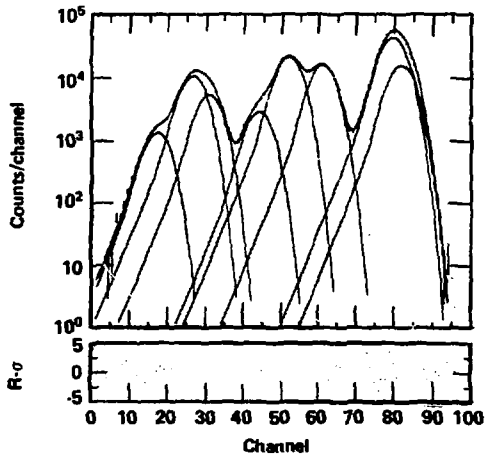


Fig. 7. The close lying peaks illustrated here can be unfolded using iterative fitting techniques.

Component nuclides

	A	B	C	D	E	F	G	H	I	
1	X	X								
2					X	X				
3					X					
4		X								
5		X								
6			X	X						
7		X		X						
8							X	X	X	
9								X		
10								X		
11								X		

Gamma peak intensities (γ/min)

Branching intensities

Row flags

Column flags

Fig. 8. An illustration of a matrix containing data and coefficients for a set of equations that describe the observed peak intensities. Three interference sets are illustrated.

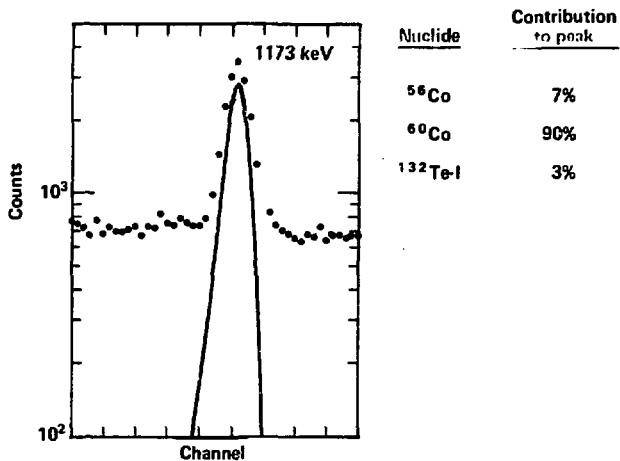


Fig. 9. This 1173-keV peak cannot be resolved by peak-shape fitting, but its components can be quantitatively resolved in the final matrix calculation.

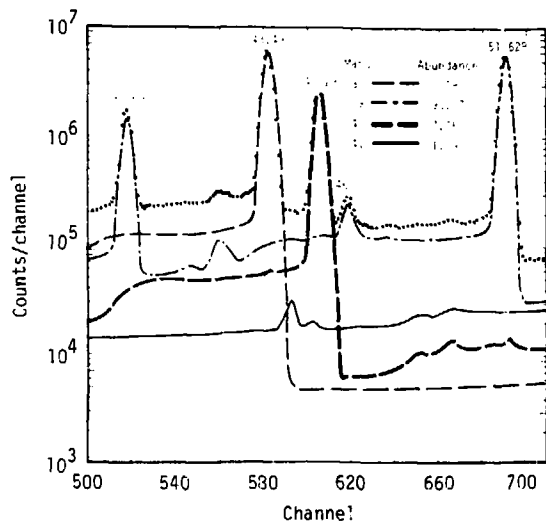
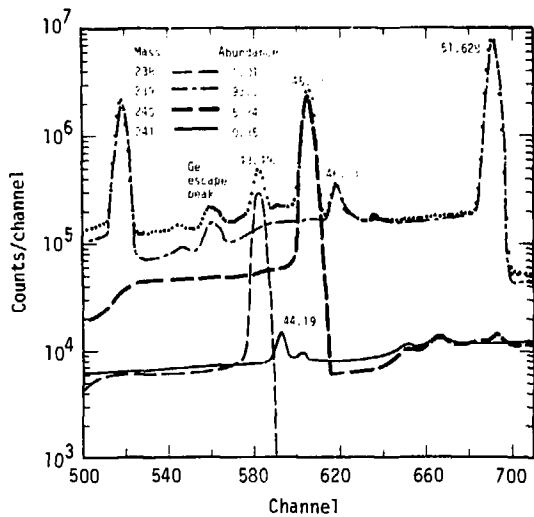


Fig. 10. Portions of low-energy spectra of recently processed plutonium showing strong signals for ^{238}Pu , ^{239}Pu , and ^{240}Pu .

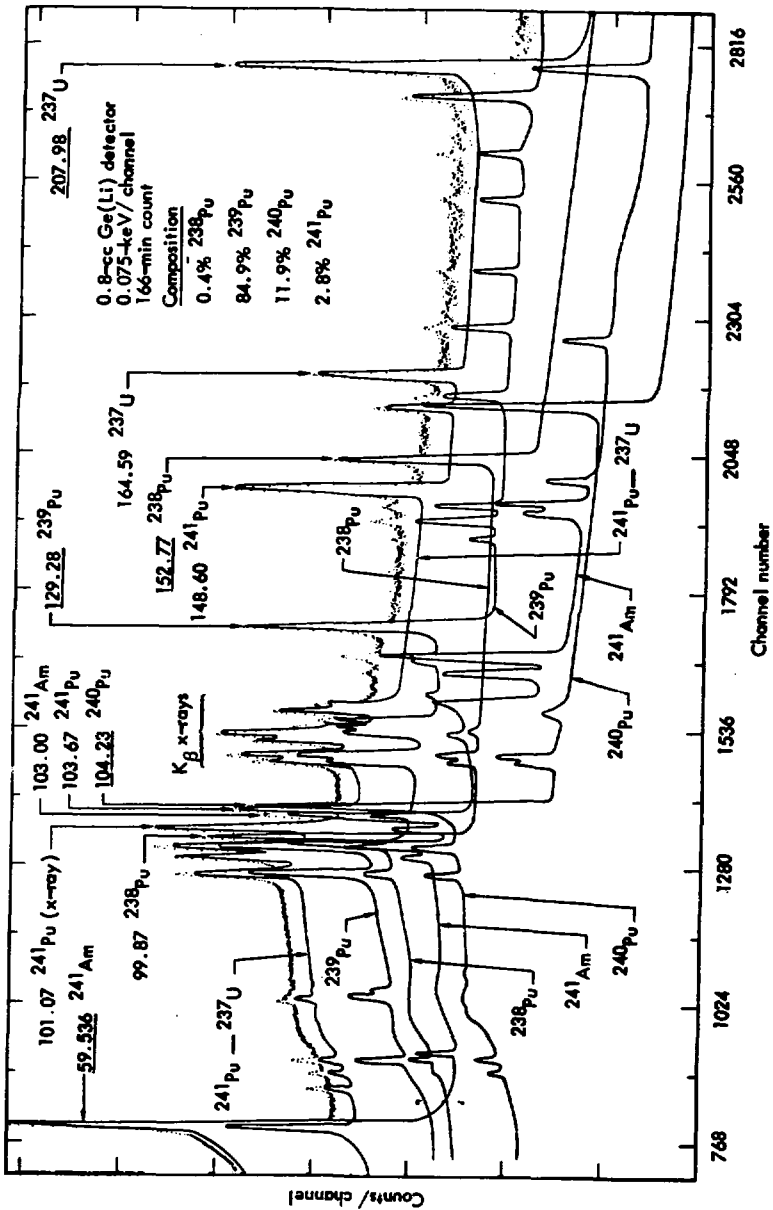


Fig. 11. The low-energy spectra of "aged" plutonium solutions consists of contributions from various isotopic components.

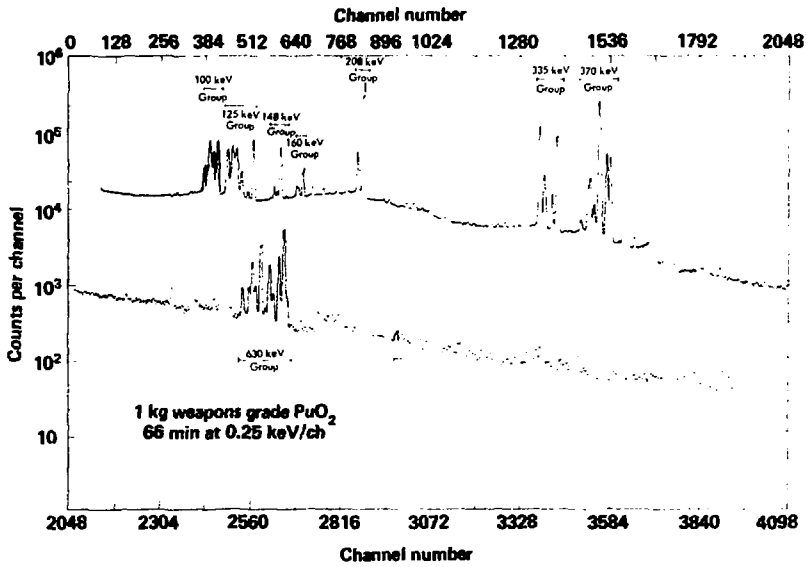


Fig. 12. This Ge(Li) spectrum of PuO₂ shows eight peak groupings that can be used to yield isotopic information.

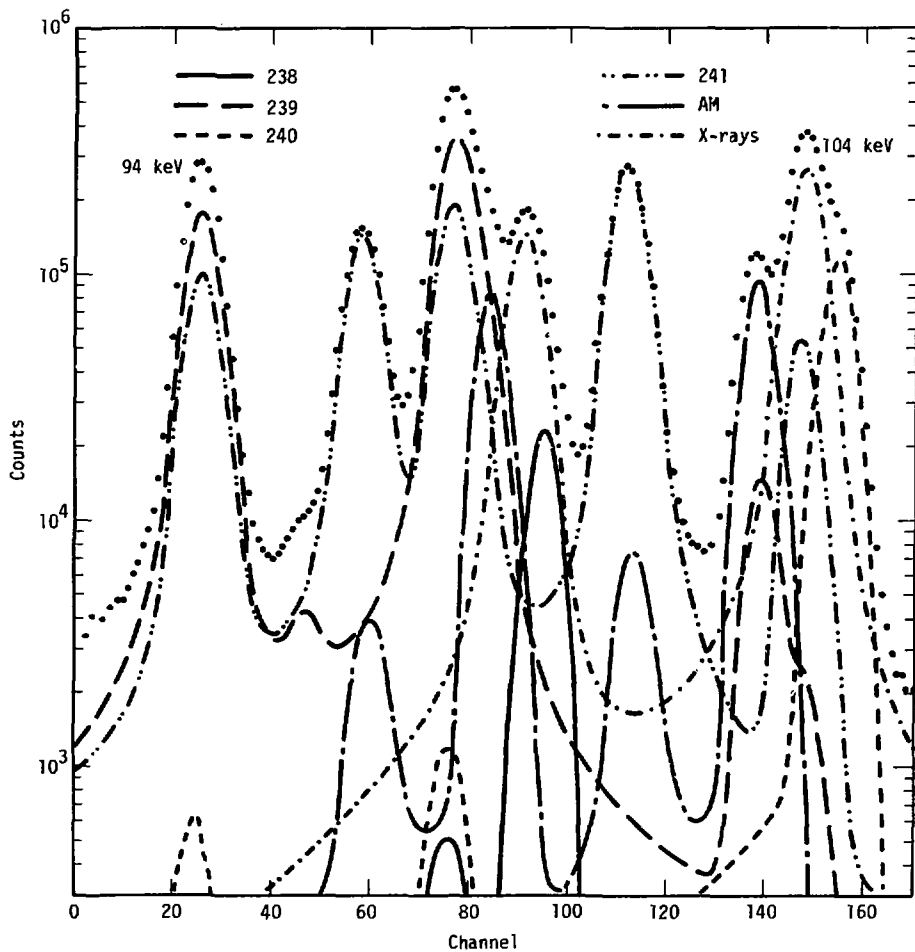


Fig. 13. This detail shows how the isotopic components contribute to the 100-keV peak multiplet.

REFERENCES

1. R. Gunnink and J. B. Niday, Computerized Quantitative Analysis by Gamma-Ray Spectrometry, Lawrence Livermore Laboratory Rept. UCRL-51561, Vol. 1, (1972).
2. W. M. Sanders and D. M. Holm, An Analytical Method for Unfolding Gamma-Ray Spectra, Los Alamos Scientific Laboratory Rept. LA-493 (1969).
3. D. L. Wilkinson, Nucl. Inst. and Methods 35, p. 259 (1971).
4. R. Gunnink, J. B. Niday, and P. D. Siemens, A System for Plutonium Analysis by Gamma-Ray Spectrometry Part I: Techniques for Analysis of Solutions, Lawrence Livermore Laboratory Rept. UCRL-51577, Part 1 (1971).
5. R. Gunnink, A Simulation Study of Plutonium Gamma-Ray Groupings for Isotopic Ratio Determinations, Lawrence Livermore Laboratory Rept. UCRL-51605 (1974).

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