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PLUTONIUM ISOTOPIC MEASUREMENTS BY GAMMA-RAY SPECTROMETRY

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PLUTONIUM ISOTOPIC MEASUREMENTS BY GAMMA-RAY SPECTROMETRY*

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ABSTRACT

The assay of nuclear materials is generally characterized by both the elemental composition and the isotopic abundances. Traditionally, the isotopic measurements for plutonium have been made by mass spectrometry with measurements for ^{238}Pu and ^{241}Am being performed by alpha spectrometry.

We have developed techniques whereby the isotopic and total plutonium analyses can now be made by detecting and properly analyzing gamma rays emitted by the sample. A computerized prototype-system was developed and is now being routinely used at the Savannah River Plant for the nondestructive assay of solution samples. The analyses for ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and for ^{241}Am, when it is present, can be made in counting times as short as 11 to 15 minutes under optimum conditions. Comparison of isotopic ratio values with mass spectrometry generally shows agreement within 1% for ^{239}Pu and about 1% for ^{240}Pu and ^{241}Pu.

Some preliminary isotopic measurements on solids are also discussed.

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ISOTOPIC ANALYSIS TECHNIQUES
BY GAMMA-RAY SPECTROMETRY

Raymond Gunnink

The total assay of plutonium is generally characterized by two quantities, namely, the amount or weight of the element and the isotopic composition. Although many techniques are available for measuring amounts of materials, the ratio of isotopic abundances has been almost exclusively measured by the combination of mass spectrometry and alpha-pulse height analysis.

In this report, we describe two techniques for the measurement of plutonium isotopic abundances using gamma-ray spectrometry. We will emphasize the description of techniques involving homogeneous solutions and the results that we have obtained using a self-contained, computer-based spectrometer system which we have fielded at the AEC's Savannah River Plant for evaluation. At the conclusion, however, we will also describe some preliminary studies we have made on the isotopic assay of solids.

The spectrometer system we assembled is shown in Figure 1. The equipment is both an analyzer - it acquires and displays spectral data - and it is a computer - it reduces and interprets the data. The 12,000 word 12 bit minicomputer is interfaced to several I/O devices including two discs capable of storing 5.6 million words. These mass

storage devices are used for storing the large number of system and analysis software programs, for storing (and retrieval) of data files and for memory extension. The data acquisition and display routines are written in machine language. However, all of the data reduction and interpretation programs are written in FORTRAN. The longer programs are managed through a process of chaining-in, logical sections of program which had been previously stored as files on the discs. Calculations are generally under a minute with the more complex programs running for a few minutes.

The measurements of plutonium, in solution form, is best accomplished by detecting and analyzing the lower energy gamma rays, that is, those less than 210 keV. For this purpose, a small (~ 1 cc) germanium detector is used with an energy resolution of <600 ev FWHM measured at 122 keV.

The low energy portions of the gamma-ray spectra of the individual isotopes of interest are shown in Figures 2 through 6.[1] Figure 2 shows the peaks of ^{238}Pu, where the prominent peaks of interest are at 43, 99 and 152 keV. Figure 3 shows the low energy peaks due to ^{239}Pu. The main lines of interest here are at 51 and 129 keV as well as the E_α x-rays. The ^{240}Pu spectra, shown in Figure 4, exhibits prominent peaks at 45 and 104 keV and a weak peak at 160 keV. Figure 5 shows a ^{241}Pu spectrum. Some of the peaks are due to 6.75d ^{237}U which results from the alpha decay of ^{241}Pu. The x-rays and a peak at 148 keV are due to ^{241}Pu decay. If the ^{237}U is in equilibrium with the parent, the 208

keV peak is very useful. Finally, Figure 6 shows a spectrum due to ^{241}Am decay. The 59 keV radiation is very intense and an absorber must frequently be used to reduce its effects. The 26 and 103 keV radiations can also generally be seen.

Experimental Approach

Before proceeding with a discussion of analysis techniques, a distinction should be made between freshly reprocessed materials and older materials. In aged materials, the growth of ^{237}U and ^{241}Am from ^{241}Pu will significantly add to the spectral distributions. As a result, the spectral information below the 59 keV line of ^{241}Am becomes obscured and cannot be used. However, for recently processed material, as shown in Figure 7, the region below 59 keV contains very good information for ^{238}Pu, ^{239}Pu and ^{240}Pu. As one goes to a low reactor grade material, as shown in Figure 8, the peaks due to ^{239}Pu and ^{240}Pu become more prominent and can, therefore, be more precisely measured. The ^{240}Pu assay is made using higher energy lines at 104 and 148 keV.

In aged materials, this low energy information is no longer accessible and one must resort to using spectral regions at higher energies, as shown in Figure 9. Although clean peaks due to ^{239}Pu and ^{241}Pu are available for measurement, the analysis for ^{238}Pu, and particularly ^{240}Pu, are much more difficult. The position of the only prominent peak of ^{240}Pu at 104 keV in relation to the other members of the multiplet is shown more clearly in Figure 10. This

Figure also reveals the complexity of this multiplet and how each component contributes to the overall structure of this composite of peaks.

Obviously the proper analysis of such peak groupings require very precise peak fitting algorithms. The one we use very extensively in all our gamma analysis codes is shown in Figure II. It consists of a central Gaussian shaped component and a term describing the low side tailing. An additional term, similar to the tailing term but symmetric, is added for the line shape of x-rays to account for the influence of the broader intrinsic x-ray line width and its Lorentzian distribution. Techniques have been found and mathematically formulated whereby all of the parameters not of analytical interest, can be predetermined for a system and can, therefore, be calculated and held fixed in subsequent analyses.[2]

Results

In two similar experiments, samples were counted many times in succession. The purpose was to check the precision of the results and to compare the standard deviation with the average quoted error. The results of these two studies are shown in Table I. The samples had been recently processed so that spectral information below 5 keV was used for these analyses. After following one sample for two months, no significant bias in the results appeared although the general precision deteriorated somewhat.

Table II summarizes a comparison of some 20 gamma spectrometry measurements with mass spectrometry. The result, particularly for ^{241}Pu, could have been improved significantly by a longer count. We also feel that these analyses, which were for AEC grade plutonium, represent a worst case situation and that measurement precisions will generally improve as one goes to the more reactor grade materials.

The aged materials containing ^{237}U and ^{241}Am require a different analysis routine, as was pointed out earlier. Table III shows the precision that we have achieved for this kind of material.

In addition to samples taken from the final accountability tank, dissolved specimens taken from the final plutonium metal buttons are also routinely analyzed by gamma spectrometry. In fact, this is now the accepted analysis technique, with mass spectrometry being performed only on every tenth sample.

Plans are currently under way to install a detector "in-line" at the accountability tank so that sample taking can be eliminated and results can be obtained in just a few minutes.

Before moving on to a discussion on solids, I would like to summarize some of the advantages and disadvantages of our analysis techniques.

Some of the advantages are:

1) It is nondestructive (amenable to in-line monitoring).

2) Quite fast (as short as 10 minute counts).

3) Much low cost than a mass spectrometer.

4) Quantitative or total assay results can be obtained through proper calibration.

5) ^{241}Am is simultaneously assayed when it is present.

Some disadvantages include:

1) The analysis for ^{242}Pu is excluded.

2) It is difficult to achieve the precision that is attainable with high quality mass spectrometry.

3) The data reduction and interpretation methods are more involved and generally require a computer.

4) The initial calibrations are more involved and the detector must be routinely monitored for possible drifts.

Solids

We made some preliminary studies two years ago and made some suggestions as to how one might make isotopic measurements on solid materials.[3,4] We are now attempting a more critical assessment of what can be done by gamma-ray spectrometry.

This type of measurement generally involves large quantities of material (> 1 gram). The preferred procedure is to use one or more tightly grouped sets of peaks containing good representations of all of the isotopes of interest. The virtue of this approach is to minimize the effects of attenuation by the material and by the container so that these effects can be either calculated or accurately measured in the experiment.

^{239}Pu and ^{240}Pu are again the two isotopes that give the greatest difficulty. One group of peaks, shown in Figure 12, is in the 600 keV region. In addition to the three components shown in this figure, ^{238}Pu exhibits a peak at a 743 keV and a ^{241}Pu measurement can be made relative to ^{239}Pu in the 330-340 keV region.

Our approach here is again to compute the isotopic response functions for each isotope present and then to perform a least squares fit to the observed counts. Additional degrees of freedom can be allowed for slight variations in the background line and for slight changes in gamma-ray attenuation from that which is predicted.

The major problem with this approach is that the ^{95}Zr and ^{95}Nb content in recently processed plutonium is too high and its gamma emissions obscure the other features of this region of the spectrum. The data in this energy region can, therefore, be used only in analyzing older materials.

With this possibility removed, about the only other alternative that is left is to use the 100 keV region. As Figure 13 shows, this region contains information on all of the isotopes of interest. However, in comparison with Figure 10, this already complex region has now acquired two additional peaks. They are the K_{α_1} and K_{α_2} x-rays of plutonium which come from alpha induced x-ray fluorescence.

At this time we have only very preliminary experimental information on the feasibility of using the region. Since detailed experiments are difficult and time consuming, we have recently

written a computer program to [illegible] to the variety of conditions and problems that are anticipated for this spectral region, as well as any other region which is of interest. By running this code, we can predict the limiting precision that can be obtained for any given type of analysis assuming the principle source of error is a statistical one. In this way we are able to prejudge, to some extent, the success of an experiment before we attempt it. Furthermore, we are able to determine which parameters are the sensitive ones in the experiment and by varying them slowly, we can see how they affect the results.

Because of the preliminary nature of these studies, we are not prepared to elaborate on them at this time. However, we do not feel that the results are altogether discouraging but instead indicate that we can proceed with some of the verifying experiment. They do indicate that a great deal of attention will have to be devoted to experiment detail.

Acknowledgements

The author would like to acknowledge Miss Ann Gibbs of the Savannah River Laboratory who is presently evaluating the spectrometer system referred to in the text. Many of the results presented were obtained from this evaluation program.

References

1. R. Gunnink and R. J. Morrow, "Gamma-Ray Energies and Absolute Branching Intensities for $^{238,239,240,241}Pu$ and ^{241}Am", UCRL-51087, (1971).

2. R. Gunnink and J. E. Kiday, "Computerized Quantitative Analysis by Gamma-Ray Spectrometry", UCRL-51061 (1972).

3. R. Gunnink and J. F. Tinney, "Analysis of Fuel Rods By Gamma-Ray Spectroscopy", UCRL-51086 (1971).

4. R. Gunnink and J. F. Tinney "Total Fissile Content and Isotopic Analysis of Nuclear Materials By Gamma-Ray Spectrometry", IAEA-SM-149/29 (1972) pp. 573-586.

Figures

1. LLL computer-based spectrometer system for gamma ray and x-ray fluorescence analysis.
2. Low energy gamma ray spectrum of ^{238}Pu.
3. Low energy gamma ray spectrum of ^{239}Pu.
4. Low energy gamma ray spectrum of ^{240}Pu.
5. Low energy gamma ray spectrum of ^{241}Pu.
6. Low energy gamma ray spectrum of ^{241}Am.
7. Plutonium gamma ray spectrum of the 35 - 55 keV region for AEC grade material.
8. Plutonium gamma ray spectrum of the 35 - 55 keV region for a reactor grade material.

9. A typical low energy gamma ray spectrum of an aged AEC grade plutonium sample.

10. Typical gamma ray responses for the various isotopes in the 100 keV region and the resultant composite distribution for AEC grade plutonium.

11. Algorithm used for fitting gamma ray peaks.

12. Gamma ray spectrum from 650 - 670 keV of an AEC grade plutonium sample.

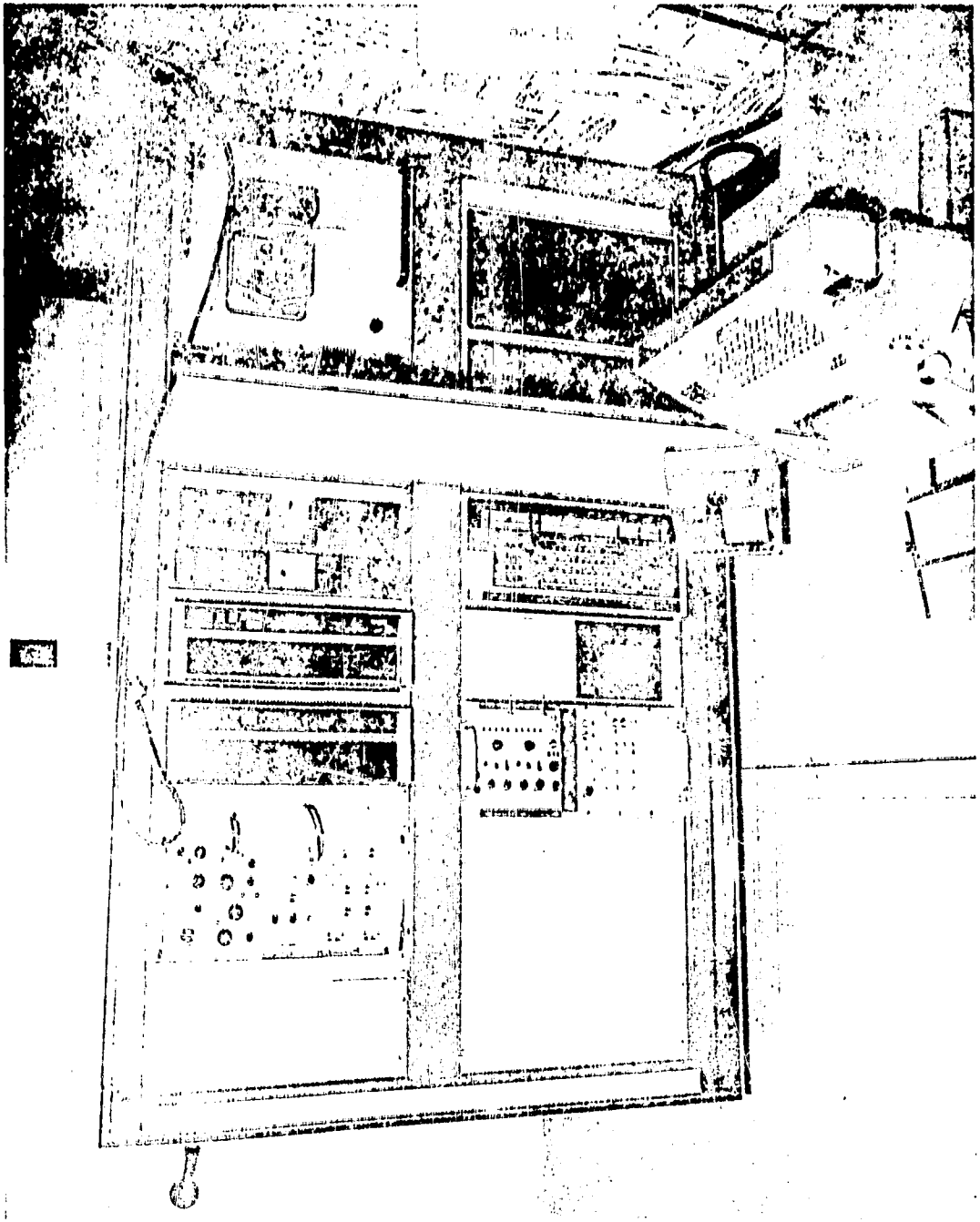
13. 100 keV spectral region for a solid plutonium sample. Alpha induced x-ray fluorescence produces radiations at 99 and 103 keV.

Tables

1. Typical analysis precisions which were obtained for recently processed samples.

2. Summary of a comparison of gamma and mass spectrometry results.

3. Typical analysis precision which was obtained on aged plutonium samples.



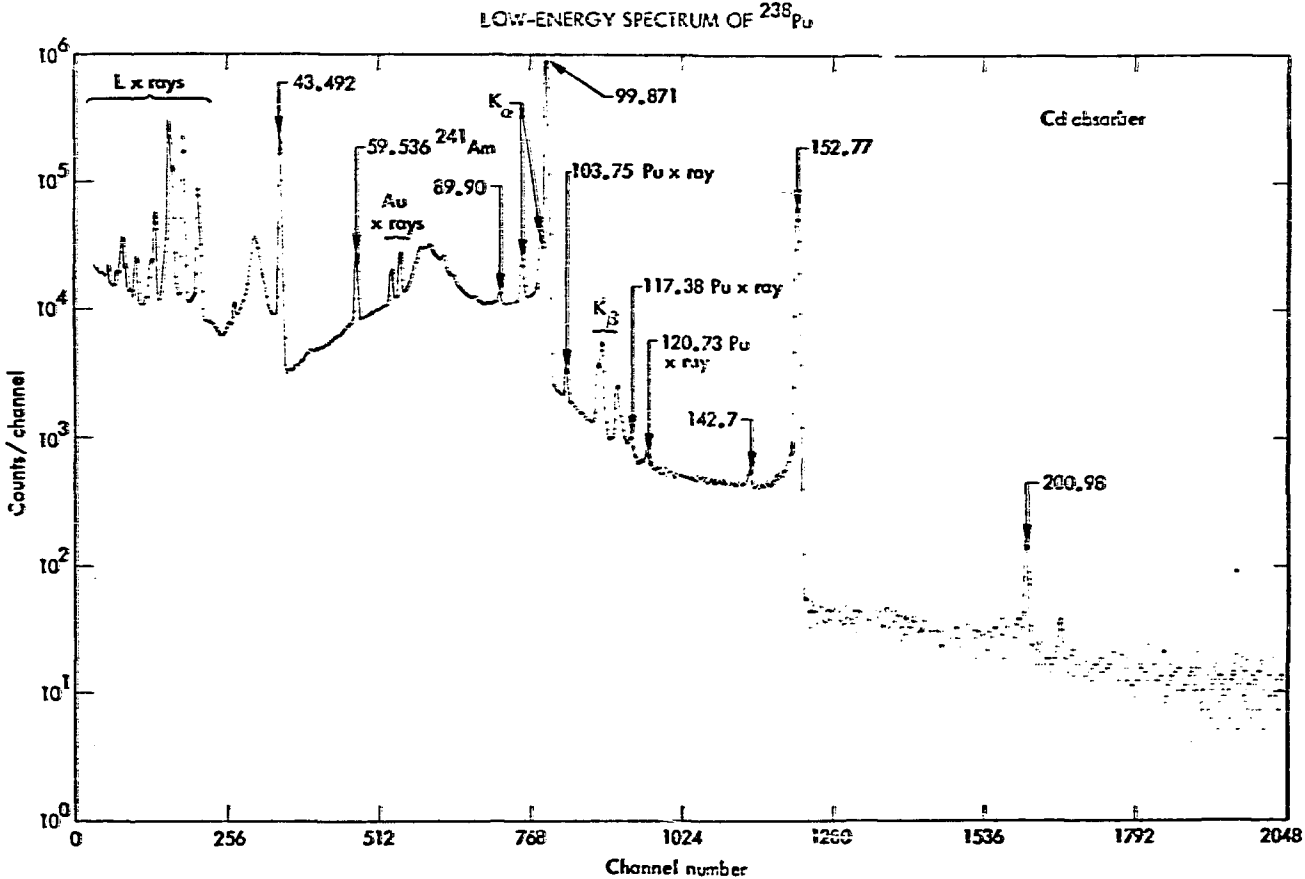

LOW-ENERGY SPECTRUM OF ^{238}Pu
L x rays
43.492
59.536 ^{241}Am
Au x rays
69.90
K_α
99.871
103.75 Pu x ray
K_β
117.38 Pu x ray
120.73 Pu x ray
142.7
152.77
Cd absorber
200.98
Counts / channel
Channel number
0
256
512
768
1024
1280
1536
1792
2048

Figure 2

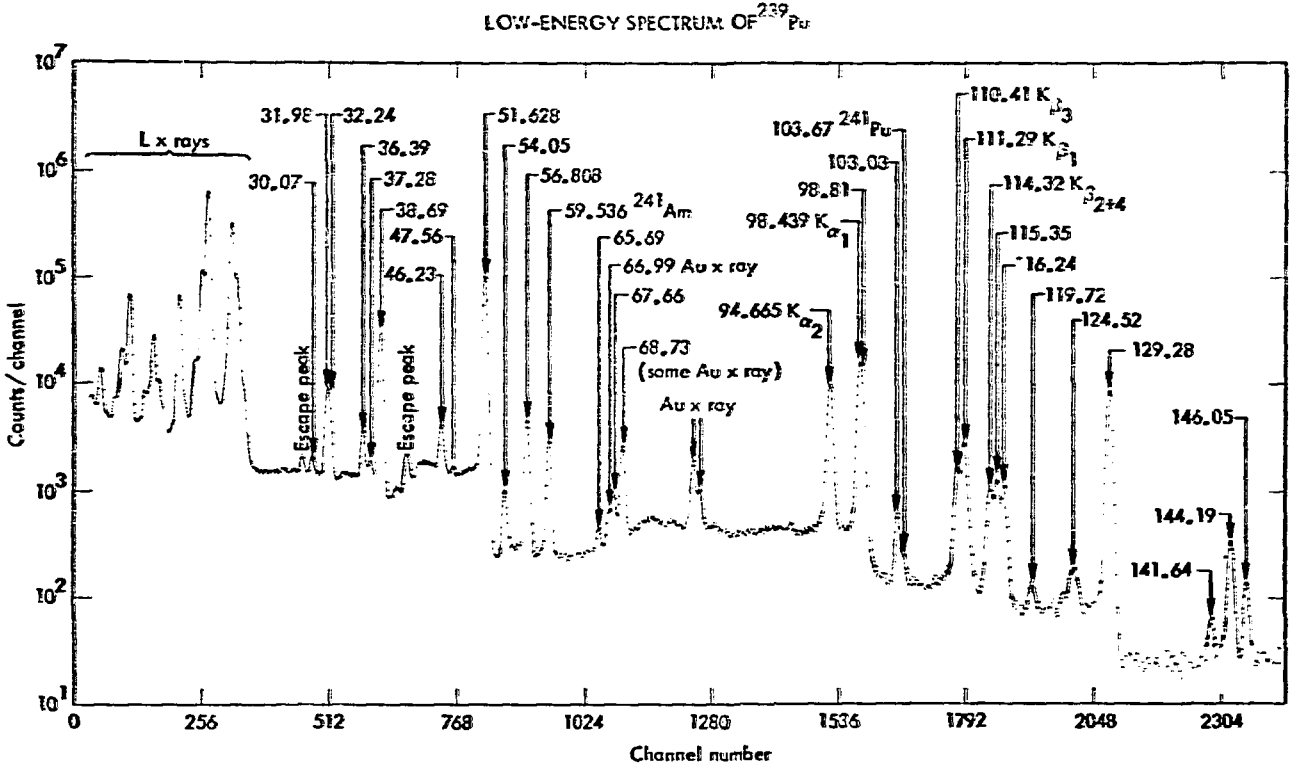

LOW-ENERGY SPECTRUM OF ^{239}Pu
L x rays
31.98
32.24
30.07
36.39
37.28
38.69
47.56
46.23
Escape peak
Escape peak
51.628
54.05
56.808
59.536 ^{241}Am
65.69
66.99 Au x ray
67.66
68.73
(some Au x ray)
Au x ray
94.665 K_{α_2}
98.439 K_{α_1}
98.81
103.03
103.67 ^{241}Pu
110.41 K_{β_3}
111.29 K_{β_1}
114.32 $K_{\beta_{2+4}}$
115.35
116.24
119.72
124.52
129.28
146.05
144.19
141.64
Counts / channel
Channel number
10^7
10^6
10^5
10^4
10^3
10^2
10^1
0
256
512
768
1024
1280
1536
1792
2048
2304

Figure 5

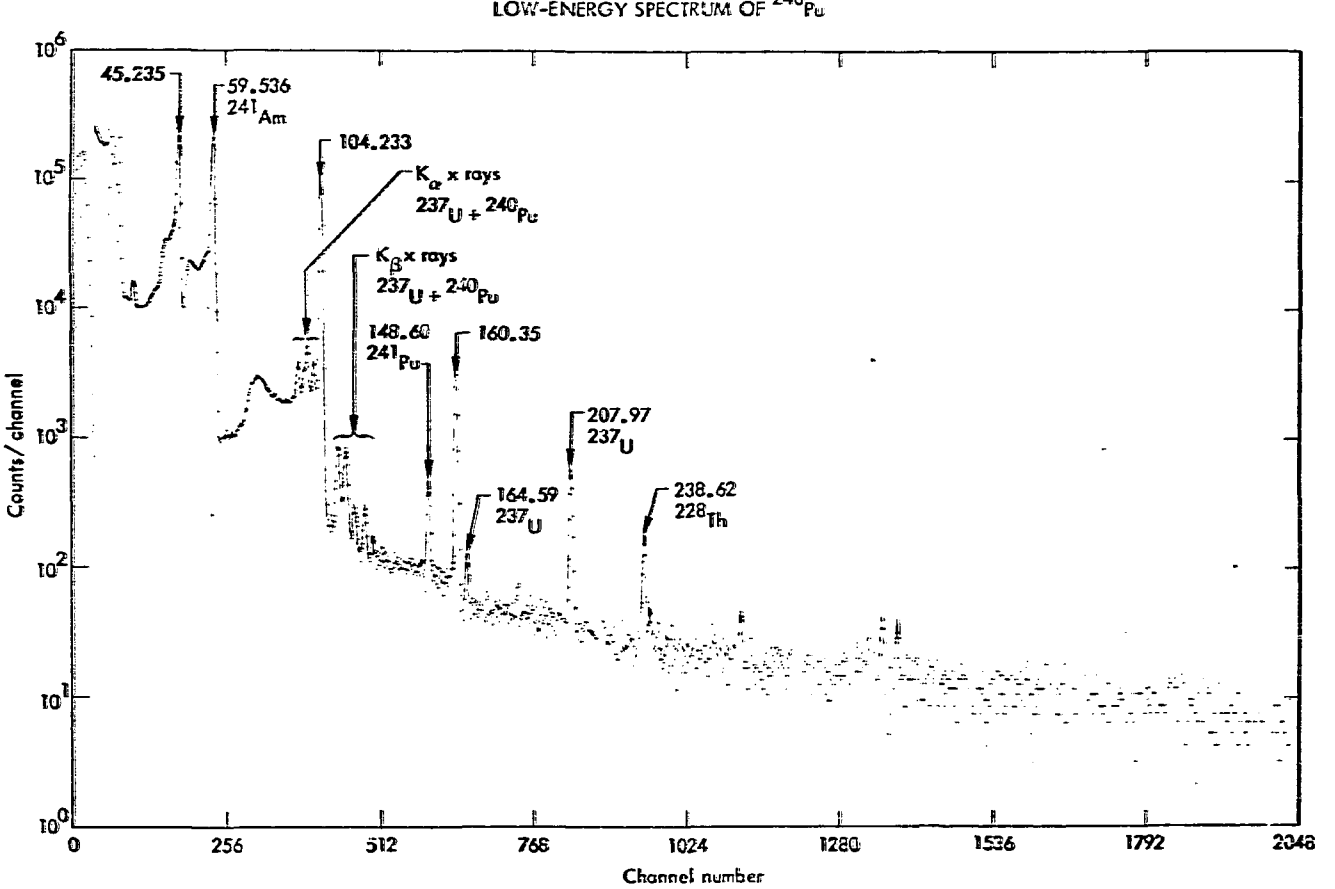

LOW-ENERGY SPECTRUM OF ^{240}Pu
45.235
59.536
^{241}Am
104.233
K_α x rays
$^{237}U + ^{240}Pu$
K_β x rays
$^{237}U + ^{240}Pu$
148.60
^{241}Pu
160.35
207.97
^{237}U
164.59
^{237}U
238.62
^{228}Th
Counts / channel
Channel number
10^0
10^1
10^2
10^3
10^4
10^5
10^6
0
256
512
768
1024
1280
1536
1792
2048

Figure 4

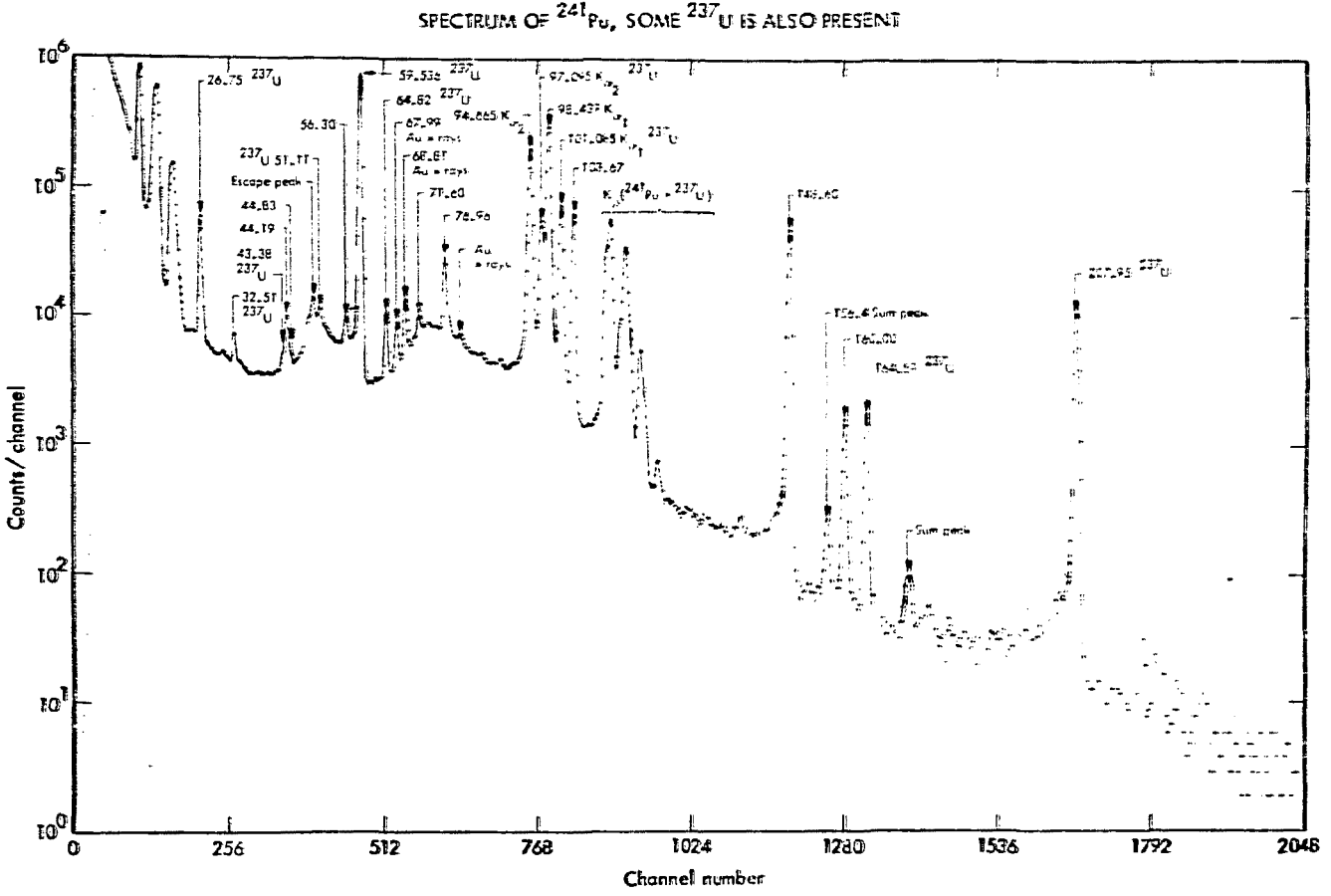

SPECTRUM OF ^{241}Pu, SOME ^{237}U IS ALSO PRESENT
Counts / channel
Channel number
0
256
512
768
1024
1280
1536
1792
2048
10^0
10^1
10^2
10^3
10^4
10^5
10^6
26.75 ^{237}U
56.30
59.53s ^{237}U
64.62 ^{237}U
94.665 K_{α_2}
98.439 K_{α_1}
101.05 K_{β_1}
103.67
K_{α} (^{241}Pu + ^{237}U)
146.46
Sum peak
Sum peak
^{237}U 51.77
Escape peak
44.83
44.19
43.38
^{237}U
32.51
^{237}U

Figure 5

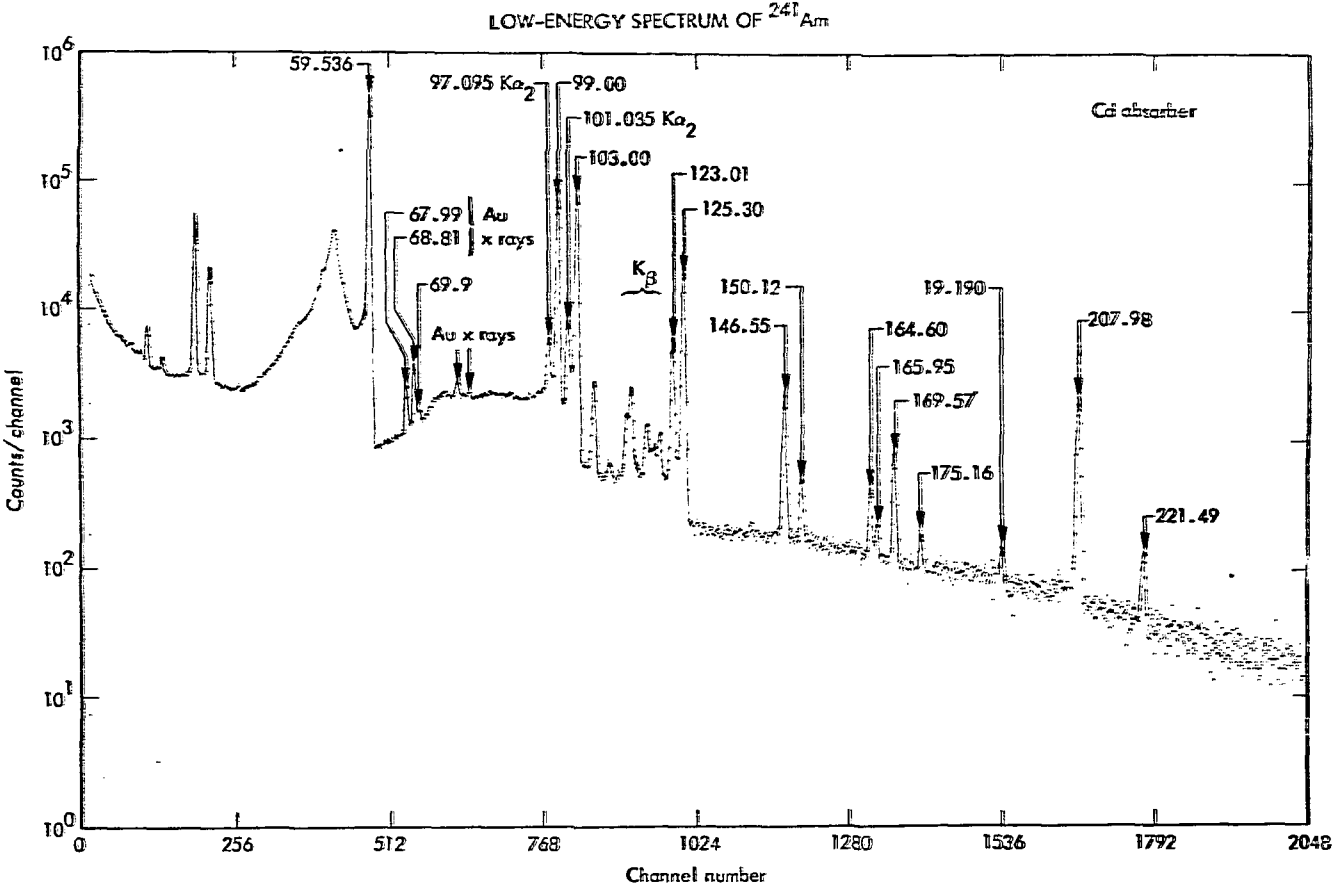

LOW-ENERGY SPECTRUM OF ^{241}Am
59.536
97.095 Kα2
99.00
101.035 Kα2
103.00
123.01
125.30
67.99
68.81
Au x rays
69.9
Au x rays
Kβ
150.12
146.55
164.60
165.95
169.57
175.16
190.19
207.98
221.49
Cd absorber
Counts/channel
Channel number
10^6
10^5
10^4
10^3
10^2
10^1
10^0
0
256
512
768
1024
1280
1536
1792
2048

Figure 6

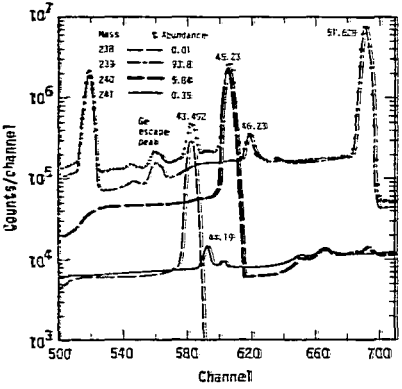

Mass
% Abundance
238 0.01
239 93.8
242 5.86
241 0.35
45.23
57.62
Ge escape peak
43.472
46.23
63.19
Counts/channel
Channel
500
540
580
620
660
700

Figure 7

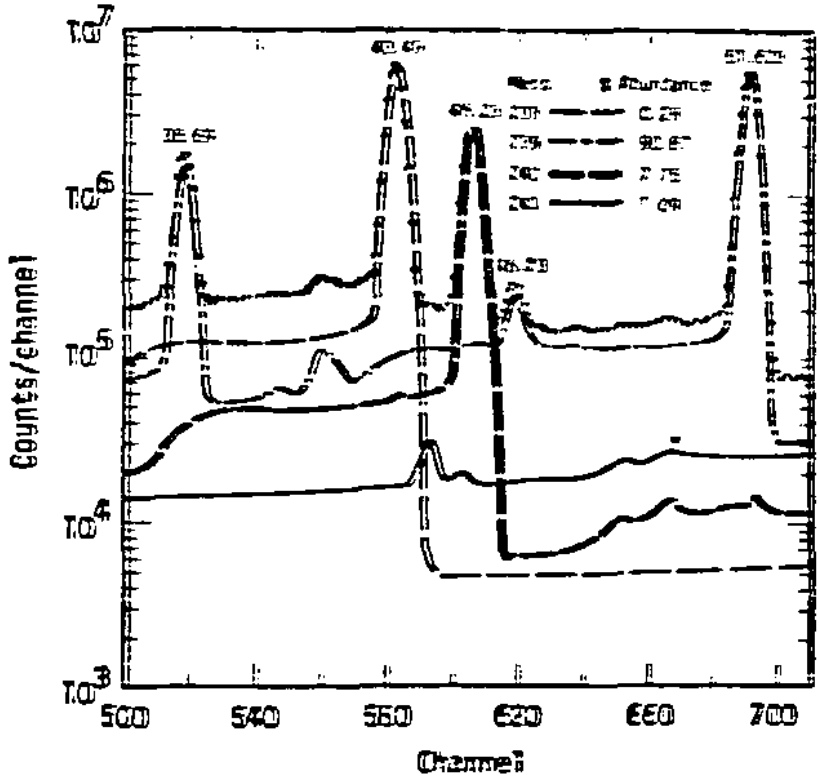


Figure 8

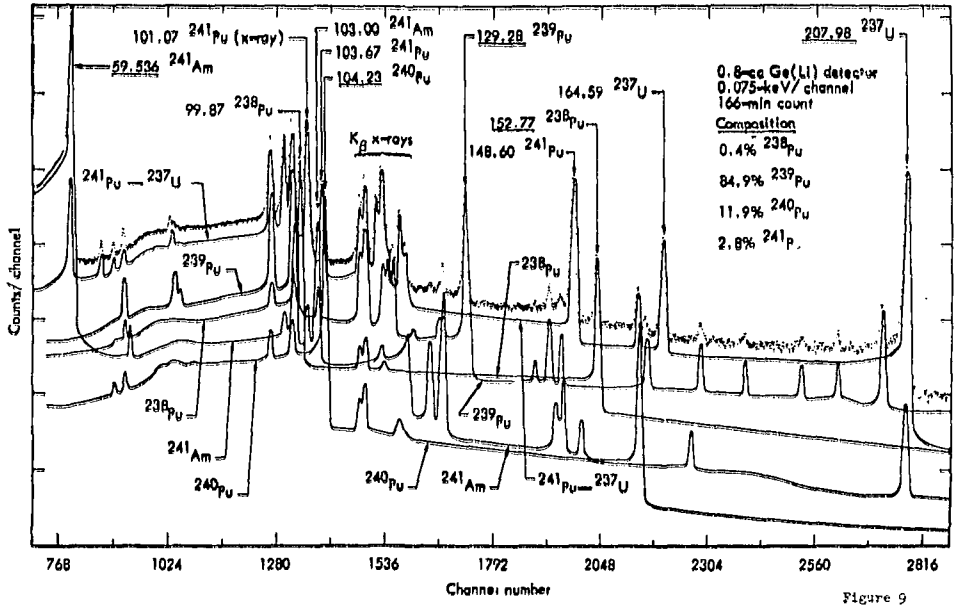

101.07 241Pu (x-ray)
59.536 241Am
99.87 238Pu
241Pu — 237U
239Pu
238Pu
241Am
240Pu
103.09 241Am
103.67 241Pu
104.23 240Pu
Kβ x-rays
129.28 239Pu
152.77 238Pu
148.60 241Pu
238Pu
239Pu
240Pu
241Am
241Pu — 237U
164.59 237U
207.98 237U
0.8-cc Ge(Li) detector
0.075-keV/ channel
166-min count
Composition
0.4% 238Pu
84.9% 239Pu
11.9% 240Pu
2.8% 241Pu
Counts/ channel
768
1024
1280
1536
1792
2048
2304
2560
2816
Channel number

Figure 9

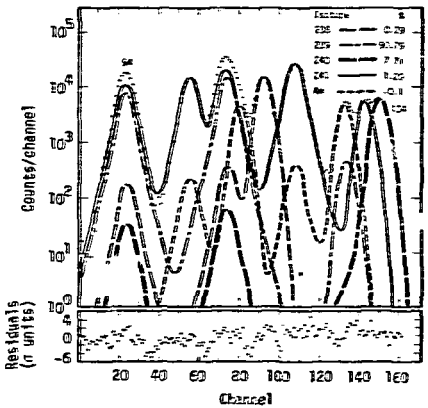

Counts/channel
Residuals (σ units)
Channel
20
40
60
80
100
120
140
160

Figure 10

EQUATION USED TO DESCRIBE PEAK SHAPE

$$y_i = y_o \cdot e^{\alpha(x_i - x_o)^2} + A y_o \cdot e^{B(x_i - x_o)} \left[1 - e^{C \cdot \alpha (x_i - x_o)^2}\right]^{\delta}$$

where

y_i = NET DATA COUNTS

y_o = PEAK HEIGHT

$\alpha = -\frac{1}{2\sigma^2}$ (σ = PEAK WIDTH PARAMETER)

x_i = CHANNEL VALUE OF i^{th} POINT

x_o = PEAK POSITION

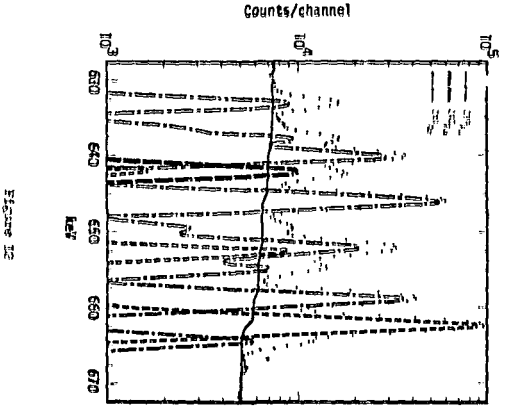
A, B, C ARE SHAPE PARAMETERS DESCRIBING THE TAILING FUNCTION

$\delta = 1$ FOR $x_i - x_o \leq 0$

$\delta = 0$ FOR $x_i - x_o > 0$

Figure 11

02607/Blade/10-6/we



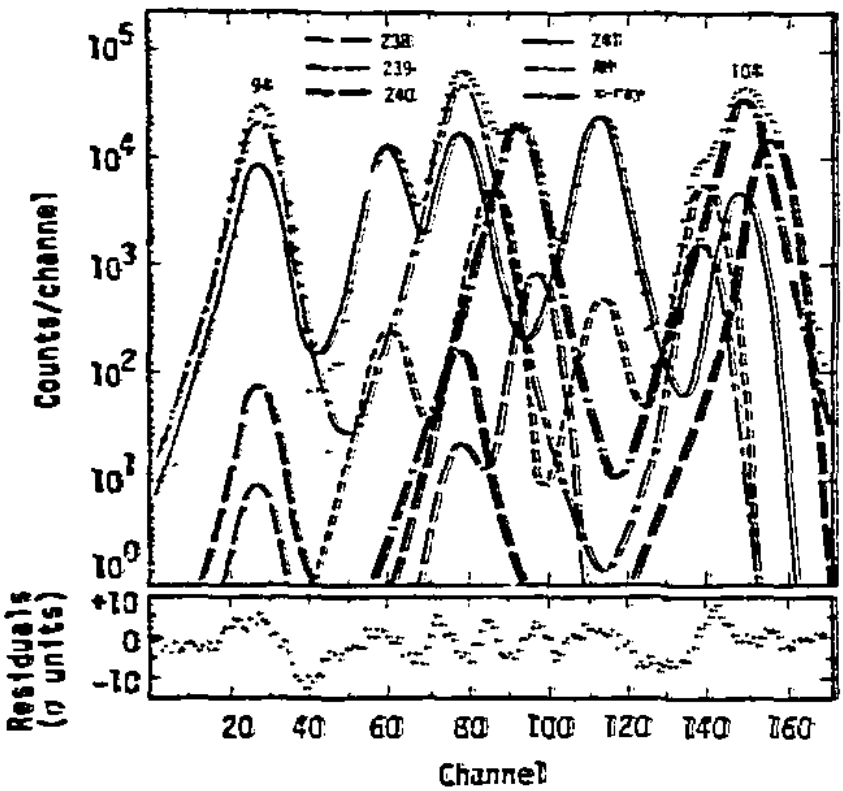

Counts/channel
Residuals (σ units)
Channel
20
40
60
80
100
120
140
160
+10
0
-10

Figure 13

TABLE 1

ANALYSIS PRECISION OF RECENTLY REPROCESSED SAMPLES USING >10 REPLICATE RESULTS

Isotope	Abundance (%)	Ave. computed error (%)		Precision (%)	
		10 minute*	60 minute*	10 minute	60 minute
238	0.008	5.6	2.7	4.7	2.0
239	93.46	0.048	0.05	0.049	0.032
240	5.88	0.75	0.40	0.72	0.043
241	0.65	0.96	0.38	1.9	0.37
Total assay	(3 mg/ml)	0.16	0.11	0.36	0.22

*Counting time at optimum counting rate

TABLE I

COMPARISON OF GAMMA AND MASS SPECTROMETRY RESULTS
(10 min. counts on 20 samples of AEC grade Pu)

Isotope	Std. dev. (%)	Bias (%)	Std. dev. (%) bias removed
239	0.056	-0.019	0.052
240	1.0	+0.46	0.65
241	1.8	-0.5	1.6

TABLE 5

ANALYSIS PRECISION OF "OLDER" SAMPLES
USING 13 REPLICATE RESULTS
(60 min. counting time at optimum counting rate)

Isotope	Abundance (%)	Ave. computed error (%)	Precision (%)
^{238}Pu	0.0176	7.6	5.7
^{239}Pu	90.92	0.14	0.09
^{240}Pu	8.40	1.6	0.94
^{241}Pu	0.661	0.64	0.61
^{241}Am	–	0.08	0.26
Total assay	5.44 mg/ml	0.46	0.35