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**A SYSTEM FOR PLUTONIUM ANALYSIS
BY GAMMA RAY SPECTROMETRY
PART 1: TECHNIQUES FOR ANALYSIS
OF SOLUTIONS**

R. Gunnink
J. B. Niday
P. D. Siemens

April 18, 1974

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FORWORD

This work was sponsored by the Office of Nuclear Materials Safeguards of the U.S. Atomic Energy Commission.

ABSTRACT

Procedures have been developed for analysis of the isotopic abundances and total amounts of plutonium in solution. The technique involves analysis of the gamma rays emitted from the sample and uses a computer-based spectrometer system.

A prototype system installed at the Savannah River Reprocessing Plant currently analyzes for ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu ,

and ^{241}Am when it is present. Precisions within 0.05% for ^{239}Pu and about 1% for ^{240}Pu and ^{241}Pu can be obtained in counting periods as short as 10 minutes.

This is the first in a series of reports which will describe the techniques, show the system components, list and describe the computer programs, and evaluate the operating performance.

I. INTRODUCTION

The total assay of plutonium is generally characterized by two quantities; namely, the concentration or amount of the element present, and the isotopic composition. Although several techniques are available for measuring the amount of plutonium present, the ratio of isotopic abundances has been measured almost exclusively by the combination of mass spectrometry and alpha-pulse height analysis on suitably prepared samples.

We have developed an analytical technique which determines the amount of ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{241}Pu present by measurement of their associated gamma rays. The system employs a computer-based spectrometer and can be used instead of the conventional analytical procedures. Some advantages of making the analysis by measuring gamma ray intensities are:

- The analysis is nondestructive.
- It is amenable to in-line monitoring.
- It is rapid (as short as 10 to 15 minutes.)
- It is less expensive than a good mass spectrometric system.
- It provides quantitative results.
- It also yields an assay for ^{241}Am when it is present.

It should be pointed out that the method is insensitive to ^{242}Pu . Furthermore, it requires a precise detector calibration and necessitated the development of some rather sophisticated data reduction and interpretation programs which would run on a small computer.

The prototype system we developed, which is shown in Figure 1, is now being field-tested at the Savannah River Plant on AEC weapons-grade plutonium. Sufficient data and experience have been acquired to conclude that the methods are sound and can be extended to other applications. For example, the precision of the analytical results can be better than 0.05% for ^{239}Pu and better than 0.5 to 1% for ^{240}Pu and ^{241}Pu . Rather than wait

until all of the relevant information has been gathered and assessed, an attempt will be made to issue a series of preliminary reports on various aspects of the plutonium analyses by gamma-ray measurement.

This report, which is the first in the series, presents an overview of the method, indicating its basis, describing the spectral analysis techniques, listing some of the system hardware and software requirements, and concluding with a summary of the initial results and some deductions that can be made from them.

Fig. 1. LLL computer-based spectrometer system for gamma-ray and x-ray fluorescence analysis.

II. BASIS OF THE TECHNIQUE

Our gamma analysis techniques use germanium detector systems whose characteristics will be described in the next section. Various detectors of differing efficiencies and resolution characteristics are available. One way to optimize the performance of a system is to select the proper detector for the particular application.

A complete isotopic analysis for plutonium requires measurements for all of the isotopes of interest, namely, ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , and ^{241}Am . The most abundant gamma rays for these isotopes are found in the low-energy region. (^{242}Pu is not included in the list because its low abundance and long half-life prevent it from being detected by gamma-ray spectrometry.) However, some of the peaks of interest must be resolved from close-lying neighbors. For these reasons, a small but high-resolution detector is best suited for the isotopic measurement of

homogeneous solutions of plutonium, using the spectral region from 40 to 210 keV.

Gamma-Ray Spectra of the Individual Isotopes

To better understand the data reduction techniques and the problems involved, it is worthwhile to review briefly some typical gamma-ray spectra corresponding to the isotopes of interest. Figures 2 and 6, showing such spectra, were taken with an ~ 1 cc detector at a gain of 0.075 keV/channel. The detector resolution at 122 keV was 525 eV.

The gamma rays of interest for ^{238}Pu are at 43, 99, and 152 keV, as Figure 2 indicates. The prominent gamma rays of ^{239}Pu , shown in Figure 3, are at 51 and 129 keV. The x-rays at 94 and 98 keV are also quite intense. The ^{240}Pu spectrum, shown in Figure 4, exhibits rather intense peaks at 45 and 104 keV and a

Fig. 2. Low-energy gamma-ray spectrum of ^{238}Pu .

Fig. 3. Low-energy gamma-ray spectrum of ^{239}Pu .

weak peak at 160 keV. ^{241}Pu decays principally by beta emission to the ground state of ^{241}Am . However, an alpha decay branching of 2.46×10^{-3} percent does occur and gives rise to measurable gamma ray signals at 103 and 148 keV, as shown in Figure 5. The 94 and 98 keV x-rays are also quite intense. The resultant daughter product of this decay, ^{237}U , has a half-life of 6.75 days. It, therefore, grows in quite rapidly and its decay rate comes into equilibrium with its formation rate after about eight weeks. The intense gamma ray at 208 keV and the x-rays at 97 and 101 keV then become useful for analysis. The gamma ray at 59 keV, while quite prominent, is nearly always dominated by the very intense gamma ray of exactly the same energy coming from the decay of ^{241}Am , as shown in Figure 6. ^{241}Am also has significant peaks at 99 and 103 keV.

Figure 7 shows the 59 keV intensity relationship for ^{237}U and ^{241}Am as a function of time.

Most of the samples encountered contain all of the isotopes we have just considered. The major spectral differences then arise from the extent to which each is present. Except for very unusual materials, the plutonium isotopic distributions follow certain ratio patterns which are somewhat predictable from their production history. One scheme of classification is to categorize plutonium according to the number of reactor cycles.² The corresponding grades of fuel would then resemble what is shown in Table 1.

In principle, the gamma-ray spectrometry technique of isotopic (and total) analysis will apply to all of these categories of plutonium. However, there are different alternative analytical procedures, and one must select

Fig. 4. Low-energy gamma-ray spectrum of ^{240}Pu (+ some ^{241}Pu .)

Fig. 5. Low-energy gamma-ray spectrum of ^{241}Pu .

Fig. 6. Low-energy gamma-ray spectrum of ^{241}Am .

Table 1. Approximate isotopic abundances corresponding to different burn-up categories.

Burn-Up (MWd/t)	Abundance (%)				
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Weapons Grade	0.01	93	6	0.5	0.04
8,000-10,000	0.10	87	10	2.4	0.3
16,000-18,000	0.25	75	18	4.5	1.0
25,000-27,000	1.0	58	25	9.0	7.0
38,000-40,000	2.0	45	27	15.0	12.0

the one that is most appropriate to the material to be measured.

Assessment of Alternative Analysis Procedures

Table 2 lists the more prominent peaks in the low-energy region, along with the emission probability per decay associated with each. In addition to intensity variations, there are considerable differences with respect to interferences. Decisions on which peaks are most appropriate for a given analysis are made for the type of material and the complexity of the reduction program that one is willing to use.

A major division in experimental approaches can be made by making a distinction between recently processed or chemically separated materials and those which have aged. In the former, the ^{241}Am and ^{237}U daughter products of ^{241}Pu have been removed, resulting in substantial changes in certain regions of the observed spectrum. Specifically, the intense 59 keV radiation from ^{241}Am is nearly completely removed

permitting lower-energy gamma rays to be seen and analyzed, as Figures 8 and 9 show. The 100 keV peak is also affected because the 97 and 101 keV x-rays from ^{237}U and the 99 and 103 keV peaks of ^{241}Am are removed (see Figure 10). The spectral features caused by ^{237}U grow back in at a rate corresponding to its 6.75 day half-life.

For aged material (> 2 months since chemical processing for AEC-grade plutonium), the information below the 59 keV radiation becomes quite obscured. Consequently, either another chemical separation must be performed or the analysis must be based on higher-energy gamma rays. Although the data-reduction procedures then become more involved and the results less precise, advantage can be taken of the fact that ^{237}U grows into equilibrium with its parent after about eight weeks.

Using the peaks listed in Table 2, one can conceive of a variety of approaches and programs that could be tried, ranging from very simple to very complicated

Fig. 7. Relative contributions of ^{237}U and ^{241}Am to the intensity of 59 keV peak as a function of time.

Table 2. Prominent low-energy gamma rays associated with the isotopes of plutonium and ^{241}Am and the corresponding emission probabilities.

	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	(^{237}U)	^{241}Am
43.492	3.92×10^{-4}					
45.235			4.50×10^{-4}			
51.628		2.68×10^{-4}				
59.563						0.359
94.665	9.00×10^{-7}	4.00×10^{-5}	6.15×10^{-7}	2.98×10^{-6}		
97.095					(3.63×10^{-6})	1.13×10^{-5}
98.439	1.48×10^{-6}	6.43×10^{-5}	1.00×10^{-6}	4.70×10^{-6}		
98.81		1.40×10^{-5}				
99.00	7.40×10^{-5}					
101.085					(5.79×10^{-6})	1.88×10^{-5}
103.00						1.95×10^{-4}
103.03		1.91×10^{-6}				
103.67				1.04×10^{-6}		
104.233			7.00×10^{-5}			
129.28		6.44×10^{-5}				
148.60				1.90×10^{-6}		
152.77	1.01×10^{-5}					
207.98					(5.12×10^{-6})	

and sophisticated types. In general, one first wants to take advantage of well-isolated single peaks and, only as a last resort, to contend with complicated peak groupings. Unfortunately, there are times when a peak in a tight multiplet must be analyzed because it provides the only, or at least the best, information that is available.

Some additional considerations are discussed in the section on experimental approach. Part II in this series of reports contains some specific examples of different

approaches we have used from which one can infer programming complexity and precision of the results.

III. EXPERIMENTAL TECHNIQUES

Spectral Data Analysis

A careful analysis and interpretation of gamma-ray peaks involves many considerations, including the proper delineation of the peak shape, an accurate or

Fig. 8. Plutonium gamma-ray spectrum of the 35 to 55 keV region for AEC weapons-grade material.

Fig. 9. Plutonium gamma-ray spectrum of the 35 to 55 keV region for a reactor-grade material.

Fig. 10. Plutonium gamma-ray spectrum of the 100 keV region.
Upper curve is before chemical processing and lower curve after processing.

reproducible description of the background continuum under the peak or peak grouping, methods of unfolding peak multiplets or at least removing small interferences, good calibration constants for interpreting the observed peak areas, and various corrections such as for self-attenuation in the sample. There is, however, one basic equation that is used repeatedly in one form or another in nearly all the data reduction routines that we use. This equation is an algorithm describing the peak shapes³ and is written as follows:

$$y_i = y_0 \cdot e^{\alpha(x_i - x_0)^2} + A y_0 \cdot e^{-B(x_i - x_0)} \cdot \left[1 - e^{-C \alpha (x_i - x_0)^2} \right] \delta \quad (1)$$

where

y_i = net data counts,

y_0 = peak height,

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

x_i = channel value of i^{th} point,

x_0 = peak position,

A, B, C are shape parameters describing the tailing function,

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

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

Six parameters (y_0 , x_0 , α , A, B, and C) are used to completely characterize a particular gamma-ray peak (see Figure 11). The data points $\{Y(i)\}$ in an overlapping peak multiplet are then considered to be linear combinations of the contributions from each peak, so that

$$Y(i) = \sum_{j=1}^n y_{ji} \quad (2)$$

The parameters α , A, B, and C are needed to describe the peak shape, but otherwise are not generally of great interest by themselves. It is, therefore, useful to be able to predetermine their values for any given fit and to treat them as fixed rather than as free parameters in the fitting process. For this purpose, we have developed the following scheme.³

The peak width, σ , is normally the most sensitive shape parameter in a peak-fitting operation and is commonly specified by the full width at half maximum (FWHM = 2.355 σ). This is related to α by

$$\alpha = -1/(2\sigma)^2 \quad (3)$$

The width of a photopeak results primarily from the summing of the instrumental noise (ΔE_N) and an energy-dependent term (ΔE_E) resulting from statistical fluctuations in the number of ion pairs formed in the detector.⁴

To a first approximation, the statistical term is linear with energy, and the noise contribution is constant. Thus, the observed total peak width (ΔE_T) may be expressed as follows:

$$\Delta E_T^2 = \Delta E_N^2 + \Delta E_E^2 = k_1 + k_2 \cdot E \quad (4)$$

Although k_2 can, in principle, be calculated using the Fano factor for germanium, it is much better to treat it as a quantity which, along with k_1 , is determined for each detector system. This can best be accomplished using a low- and a high-energy peak in a spectrum. If more than two peaks are used, the constants can be determined by the method of linear least squares.

The quantities observed and measured, such as peak widths, are in terms of channels rather than energies. To accommodate different amplifier gains, it is desirable to separate the gain dependence from the equations that describe the shape parameters. For the width parameters, we write

$$\Delta E^2 = (\Delta CH^2 - C_3) \cdot (\text{GAIN})^2 \quad (5)$$

where gain is expressed in keV/channel and C_3 is a Sheppard's correction for the error resulting from treating all the counts in a given channel window as though concentrated at the channel center. It can be shown that the value of C_3 is approximately 0.46 when the resolution is expressed in terms of the full width at half maximum (FWHM). The above equation then becomes

$$[(\text{FWHM})^2 - 0.46] \cdot (\text{GAIN})^2 = k_1 + k_2 \cdot E \quad (6)$$

The quantities A and B in Eq. 1 characterize the amplitude and slope of an exponentially rising term used to describe the small amount of tailing that occurs on the low-energy side of peaks. It is multiplied by

$$\left[1 - e^{-C \alpha (x_i - x_0)^2} \right] \quad (7)$$

to reduce its contribution to the peak back to zero at the peak position. The quantity C is a rather insensitive parameter, quite easily influenced by poor statistics, and is, therefore, difficult to measure. A value of 0.4 appears to be suitable for all of our detector systems.

In our study of the other two tailing constants,³ we found that the slope parameter B is dependent only on the detector, whereas the amplitude A is both detector- and energy-dependent. The parameter A should be determined from a higher-energy peak where the tailing is most pronounced.

We have found a rather simple algorithm which

Fig. 11. A detail showing the components used to describe a peak shape.

approximates the relationship between the parameter A and the gamma-ray energy. It is given by

$$\ln A = C_1 + C_2 \cdot E \quad (8)$$

As in the case for determining α , two or more peaks are used to evaluate the constants C_1 and C_2 in the above expression.

Thus, by means of a few simple experimental measurements, the peak shapes for a system can be calibrated and specified in terms of six parameters: k_1 and k_2 (used to determine α), C_1 and C_2 (used to calculate A), B, and C (which is set equal to 0.4).

Although the above description can be applied to germanium spectra in general, there are additional considerations which apply to low-energy plutonium spectra. First, much of the observed peak shape at low energies is due to the first, or noise, term in Eq. 4. Since the tailing is generally to be associated with the statistical term of this equation, the low-energy peaks are quite symmetrical, possessing only a small amount of tailing. Second, one generally knows which component nuclides are present in a given analysis spectrum. Using appropriate reference peaks, one can then compute the exact positions of the peaks that are to be analyzed.

If the x_0 value in Eq. 1 is now also known (in addition to the other shape parameters), the set of equation represented by Eq. 2 will then no longer contain unknowns in the exponents, and the equations can be solved simply by the method of linear-least squares rather than by some iterative technique.

The line shapes of x-rays are an important exception to what has just been described. This is due to the fact that the intrinsic lifetime of heavy-element x-rays is quite short so that the attendant line width is of the order of 100 eV.⁵ Furthermore, since the intrinsic radiation process results in a Lorentzian distribution,⁶ the observed peak is both broadened and disturbed in peak shape.

Figure 12 shows qualitatively how these effects contribute to the overall line shape. To accommodate the increased peak width and the flaring of the peaks at the base, additional terms are added to Eq. 1. Our procedure has been to add the following terms:

$$+ D \cdot e^E \cdot |\Delta x| [1.05 - e^{C \cdot \alpha \cdot \Delta x^2}] \quad (9)$$

where

$$D = \frac{30 \cdot \Gamma^2}{(\text{FWHM})^2}$$

$$E = \frac{24.4 \cdot \Gamma \cdot \text{GAIN}}{\text{FWHM}}$$

Γ = intrinsic line width in keV (see Ref. 5),

FWHM = Equivalent-energy gamma-ray full width at half maximum expressed in keV.

This expression is quite adequate for most situations. However, we have recently re-examined the fit in greater detail and find that more terms should be added, particularly to account for the pronounced flaring.

There are several ways in which Eq. 1 is used. The first and obvious use is in fitting a peak in order to determine its position and area. Sometimes it is used to subtract (i.e. strip away) a small peak interference from a prominent peak of interest. It is also used to determine where a peak is considered to begin and to end. That is, using the net peak height and proceeding from the peak position, one calculates the approximate net count in each channel. By comparing this count with the square root of the variance of the observed count for that channel, a decision is made as to whether the net channel count is of statistical significance. In this way, a peak boundary channel can be found. A final use, which will be described in greater detail in a later section, is in the generation of isotopic component response functions. In this usage, a multiplet of peaks is being fitted. However, instead of allowing the amplitude of each peak in the composite to be free (i.e. to be a quantity to be determined by the fit), the relative amplitudes of all of the peaks belonging to a given isotopic component are fixed by a prior calibration. Hence, the response envelope for each isotope components, rather than for each peak, can be computed, thereby reducing the number of unknowns to the number of components.

The area of a peak is determined either by direct integration of the net count (as in the case of a single peak) or by integrating the algorithm used to fit the peak. Both methods require a precise technique for subtracting the background continuum. The scheme commonly used elsewhere for interpolating such a background has been to use a straight line or a polynomial function. However, we believe such a procedure is, in principle, incorrect and may lead to erroneous results and a poor fit for some peak multiplets.

If we consider a hypothetical detector system exhibiting no instrumental noise or statistical effects, all of the full-energy pulses corresponding to a given gamma ray could be made to appear in one channel rather than as a distribution. The background just before the peak (i.e. the additional counts that one observes between the Compton edge and the low-energy side of a peak) presumably consists of degraded full-energy events resulting from such causes as detector edge effects or small angle scattering by

Fig. 12. A detail showing the components contributing to the observed x-ray line shape.

the material between the source and the detector. If such processes continue to contribute pulses up to the full energy of the peak, then, in our hypothetical case, a sharp step would be observed at the peak location. It follows, then, that the same line-broadening processes that disperse the sharp peak will affect these pulses, which we have chosen to consider part of the Compton background. The resultant smoothed background step occurring under the peak is closely approximated by the following equation:

$$B(i) = B(n) + [B(m) - B(n)] \frac{\sum_{j=n}^i y(j)}{\sum_{k=n}^m y(k)} \quad (10)$$

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 ,
- $y(i)$ = spectrum count in channel i .

This same procedure works equally well for single peaks and for complex peak groupings. If the peak or peak grouping resides on a sloping background, Eq. 10 should be modified to account for this. This method of background interpolation is illustrated in Figure 13 for the complex 100 keV multiplet observed in plutonium spectra.

In the preceding discussions, methods have been described for obtaining net counts of single peaks and for peak shape fitting. The aim of the analysis is to interpret the spectral data in terms of disintegration rates or amounts of the isotopic components. This involves certain calibration constants and a procedure for interpreting the data. The approach we use is to form a set of linear equations, the number of unknowns being equal to the number of isotopic components. Each peak, then, can be considered to be composed of a linear combination of one or more components which may be written:

$$Y_i = \sum_{j=1}^J A_{ij} \cdot X_j \quad (11)$$

where

- Y_i = the intensity of the i^{th} peak in counts/min,
- A_{ij} = the calibration constant (e.g. in units of counts/disintegration) of the j^{th} component at the i^{th} peak energy,

X_j = the disintegration rate (or amount) of the j^{th} component—a number which is to be determined.

The calculational method is to form the matrix of linear equations and to solve it by the method of least-squares. That is, we minimize

$$\sum_{n=1}^N (W_i R_i)^2 \quad (12)$$

where

$$R_i = Y_i - \sum_{j=1}^J A_{ij} \cdot X_j \quad (13)$$

and

W_i = weighting factor.

Many of the coefficients A_{ij} will be zero; that is, the nuclide j cannot contribute to the observed count of peak i .

The form of the above equations implies that one must use the integrated count for each peak in performing this calculation. However, the net channel counts can be used equally well, provided the calibration coefficient A_{ij} is multiplied by a normalization value.

This normalization value can be computed with the aid of the appropriate peak shape equation. The value of y_0 in Equation 1 in this case must be considered to be the peak height-to-peak area ratio. This is dependent on the shape of the peak but is generally precalculated for a specific peak region at the time the shape parameters for the system are being determined.

As a result, each member in the set of equations may now either be equal to the integrated net count in a peak, or equal to the observed net count in the spectrum. The difference is that the coefficients in the latter case must be multiplied by factors which account for the dispersal of the total net count over a number of channels. The process is illustrated in Figure 14, in which equations representing the net counts of six isolated peaks are combined with a spectral distribution which includes three more overlapping peaks.

Before performing the least-squares fit, the equations must be appropriately weighted. This is done by dividing through each total net count equation by the square root of the variance associated with this count, and by dividing through each channel count equation by the square root of the variance of the gross channel count. In so doing, the diagonal matrix elements of the inverted matrix of the weighted normal equations can be used for assigning error values to the results of the fit.

Fig. 13. A detail showing how the background is drawn under a complex peak multiplet.

Fig. 14. Illustration of a heterogeneous set of equations to be solved for unknown isotopic abundances. Some of the equations are equated to net counts while others are equated to channel counts.

A correction to account for changes in sample self-attenuation must frequently be applied in interpreting the spectral information. The calibrations are generally made so that all sources of attenuations are included except for the plutonium content in the solution. The amount of plutonium and the attendant absorption is small enough so that the absorption can be approximated by

$$I/I_0 = 1 - 0.5 \cdot \mu \cdot a, \quad (14)$$

where

- I/I_0 = the attenuation factor,
- μ = the mass absorption coefficient expressed in cm^2/g ,
- a = the amount of Pu in g/cm^2 in the container.

The 0.5 comes from the fact that, on the average,

gamma rays need only traverse half of the sample thickness.

A difficulty arises as to how these corrections should be applied, since the least-squares analysis programs frequently use more than one peak per component to compute the isotopic amounts present. Each peak will, of course, be attenuated by a different amount, depending on its energy. Since the calibration is based on unattenuated data (i.e. unattenuated by plutonium), the appropriate quantities to be altered are not the final answers but the matrix of coefficients (i.e. the calibration constants which are used to convert peak intensities to amounts of material). However, this correction cannot be made in a rigorous manner since the correction requires a prior knowledge of the answers. To circumvent this problem, an approximate answer is obtained by interpreting certain key peaks and using this first estimate of the total plutonium amount to compute the attenuation corrections. This works very well simply

because the corrections are generally not greater than a few percent.*

The results of the least-squares solution of the matrix are generally in units of disintegration rate. Final calculations are then made to convert these values into atoms and weights from which the isotopic abundance ratios are determined.

Calibrations

There are two important types of calibrations which are required before routine spectral analyses can be initiated. The first is a characterization of the peak shape parameters described in the preceding section. This is accomplished by obtaining a spectrum containing a low- and a high-energy peak having good counting statistics. The higher-energy peak should contain at least 10^6 counts so that an adequate measure can be obtained of the amount of tailing that is occurring. The peaks should be located near the extremes of the energy range that is to be used for routine analyses. Care should also be exercised so that the counting conditions resemble those of the subsequent analyses. Zero and gain stabilization may be needed, the same approximate gain should be employed, and very high count rates should be avoided.

After the data have been acquired, appropriate computer codes can be used to generate the peak shape parameters, which are then stored as a disc file. (These programs will be more fully described in Part II.)

Once the peak shapes of the system have been characterized, one can proceed to the calibration of the detector efficiency. Since the measurements are generally of a very specific nature, it is more convenient and accurate to generate an efficiency value for each peak that is involved in subsequent analyses, rather than to work with efficiency curves.

We intend to develop a rather simple one-step process for performing this, which will be described and documented in a later report. For the present, a brief description will be given of the procedure that was used to calibrate the current operating systems.

We first obtained high isotopic purity samples of each of the materials of interest, i.e., 238, 239, 240, 241Pu and 241Am. The plutonium isotopes were

obtained from the ORNL research pool of calutron-separated isotopes and had the isotopic abundances shown in Table 3.

Table 3. Isotopic content (%) of source materials used for preparing solution standards.

Mass	238Pu	239Pu	240Pu	241Pu
238	90.39	<0.0002	0.002	<0.0005
239	9.21	99.978	0.762	0.07
240	0.607	0.021	98.30	0.131
241	0.029	0.0005	0.764	99.72
242	<0.01	—	0.171	0.077

These samples were dissolved, purified on an ion exchange column, and diluted to a specific activity of about 10^9 dpm/ml with 3M HCl solution.

The 238Pu was alpha-assayed using the 4π α-γ coincidence counting technique described in Appendix 1. Ten milliliters of the solution were then placed in the container that had been adopted for the subsequent analyses. After counting the sample, the peak intensities for the 43, 94, 98, 99, and 152 keV radiations were measured and divided by the absolute disintegration rate, thereby generating the necessary calibration constants for 238Pu.

Similarly, the 239Pu solution was alpha-counted, this time with three different counters: a 4π α-γ coincidence counter, a low geometry counter, and a 2π geometry counter (a counting efficiency of 51.7% was used for the latter.) The three methods gave agreement within the precision of the individual counts, which was about ± 0.25%. Again, 10 ml of the solution was then placed in a container and counted. The 51, 94, 98 (complex), 103, and 129 keV intensities were measured, from which the corresponding calibration constants were computed. This spectrum is also used to obtain a background profile in the 40 to 47 keV peaks of 238Pu and 241Pu.

240Pu likewise was alpha-counted and a spectrum taken with the germanium detector. Here the 45, 94, 98, and 104 keV peaks were measured and the corresponding calibration constants calculated. Since the source material contained small amounts of 239Pu and 241Pu, it was necessary to make small corrections in the spectral analysis.

241Pu decays principally by beta minus emission to 241Am, although a small fraction of alpha branching (to the extent of 0.00246%) does occur, producing the 237U daughter product. Since the beta emissions are

*Solutions measured at the Savannah River Laboratory are quite dilute compared with the product concentration in commercial plants, which is about 200 mg/ml. As a result, the attenuation will be more severe, requiring a more exact calculation of the corrections.

low energy, it is difficult to assay the ^{241}Pu solution by counting techniques. Instead, we assayed it by first mixing accurately measured volumes of the ^{239}Pu and ^{241}Pu solutions and then submitting the resulting mixture for a mass isotopic ratio measurement. Knowing the ^{239}Pu concentration, one can then easily calculate the ^{241}Pu content of the stock solution.

The radiations of importance are at 94, 98, 103, and 148 keV. However, there is an additional complication in that the ^{237}U daughter rapidly starts to grow back in after it is first removed. Its x-rays at 97 and 101 keV must be considered in the spectral analysis. It is, indeed, wise to isolate a ^{237}U fraction and count it separately to characterize the relative counting efficiencies of its radiations at 59, 97, 101, and 208 keV. This information can be used to determine the calibration constants used in the codes which analyze aged materials.

The information regarding ^{241}Am is needed only if analyses will be made on aged materials. A calibration similar to that above is carried out, and measurements should be made for the 59, 97, 99, 101, 103, and 208 keV radiations.

An important consideration should be stressed at this point. In aged materials, the most intense radiation, by far, is the 59 keV gamma ray of ^{241}Am . In order to reduce its effect in relation to the higher-energy radiations of interest, an absorber should be used which consists typically of 30 mil cadmium. The corresponding calibrations should be made with the absorber in place.

In the case of ^{239}Pu and ^{240}Pu , small corrections should be made in the computed calibration coefficients to account for attenuation by the plutonium (see Eq. 4).

Although it was our intention to perform the above calibrations quite rigorously, we were thwarted in our attempt because of some changes that occurred in the efficiency of the detector. (This is discussed in more detail in the section on performance.) Therefore, the initial calibrations could be treated only as approximate at the time the spectrometer system was placed into operation at the Savannah River Plant. However, by comparing the isotopic results obtained by gamma measurement with those obtained by mass spectrometry, it was not difficult to note the magnitude of the differences (which were quite small) and to make appropriate changes in the file of calibration constants. At present, this would also be our recommended approach to calibration; that is, first to make a rough calibration of the system to provide approximately correct answers, and then to fine-tune the calibrations by comparing them with a number of corresponding measurements made by mass spectrometry.

Detector Requirements

The analytical techniques we have been describing

use the energy region from about 40 to 210 keV. The spectra of interest require state-of-the-art resolution for this region. A small (~ 1 cc) germanium detector, either intrinsic or lithium-drifted, best fulfills these needs. The specifications for such a detector are summarized in Regulatory Guide 5.9, which was issued by the Directorate of Regulatory Standards of U.S.A.E.C. in June of 1973. The salient specifications are that the detector should have a resolution of about 550 eV FWHM at 122 keV and produce peaks with a very small tailing component.

It is very important that the efficiency of the detector not change with time. It was disconcerting to find in our experience that the efficiency of even an intrinsic germanium detector can change with time. It is not clear what can be done to avoid such a problem. It is obvious, however, that the efficiency should be routinely monitored, preferably by using a very long half-life source. In our case, some of the high isotopic purity ^{238}Pu and ^{239}Pu source material was used to make permanent sealed sources, which were then used for monitoring the detector.

System Hardware Requirements

The electronic components separate into two general categories: the pulse amplification and pulse height measurement hardware, and the computer with its associated peripherals. Figure 15 presents a block diagram of the system which was assembled at LLL. Its features are sufficiently unique so that no comparable spectrometer system is commercially available. Although its intended use was initially quite specific, the system was designed as a general purpose spectrometer with a high degree of flexibility. The complete system design will be described in a separate report. The discussion here will be concerned with some general requirements with respect to adequate system performance.

There are several problems that are related to the count rate. At higher count rates, precautions should be taken to prevent pulse pile-up and peak shape distortion. Furthermore, at higher count rates, corrections must be made to the real-time clock to account for system "dead" time. Commercial modules are available that will inhibit the analysis of a pulse which is riding on the tail of a previous pulse. Consequently, this feature should definitely be included in even a minimum system. A more elaborate system would also include leading-edge pile-up rejection.

The amount of pile-up can obviously be reduced by lowering the count rate, but it can also be reduced by decreasing the "peaking" time* of the pulse. However,

*The time required for a pulse to reach its maximum amplitude.

Fig. 15. Block diagram of LLL computer-based spectrometer system.

the penalty for doing this is a loss in resolution. Consequently, it is generally not advisable to operate with "peaking" times less than 5 μ sec.

Even with systems which are designed for both "leading-edge" and "tail" pile-up rejection, there is a minimum time resolution for the discrimination of two pulses. When the events are too close together, the resulting pulse will indeed nearly correspond to a linear addition of the individual pulses. In rare instances, these spurious "sum-peaks" may cause problems. For example, in one of our programs we take into account the small amount of 51.628 - 51.628 pulse addition that occurs at high count rate; this is a 103.256 keV sum-peak which, in this case, happens to lie in a sensitive region.

Most commercial pulse height analyzers are equipped to correct for analog-to-digital conversion (ADC) dead-time, i.e., those pulses lost because the ADC was busy processing another signal. However, if pulse rejection circuitry is employed in front of the ADC, additional logic is required to correct the timer for these pulse losses. Frequently, the signals from the two sources of rejection are simply "ORed" together. This works quite well but may lead to an overcorrection because the two sources do not work on the same pulse at the same time. That is, it is possible for the

amplifier to begin processing a pulse even though the ADC is busy.

Because of the many complications that set in, we generally limit the count rate to < 5000 cps. It also happens that, in our system, the amplifier recovery time is sufficiently long so that the 100 MHz ADC can completely measure a pulse before the amplifier is able to accept a new one. Thus, there is no ADC contribution to the dead time. Fortunately, isotopic ratio measurements are not dependent on accurate live-time measurements.

Gain stability of the system is also important. Although the stability of the electronic components has improved considerably, we prefer to stabilize the spectrum with respect to both the zero energy intercept and the gain by using a hardwired stabilizer unit which "locks" onto a selected low- and high-energy peak in the spectrum. The compensation rate on the stabilizer unit should be kept quite low so as not to degrade the peak resolution significantly.

The selection of the appropriate mini-computer was based on both hardware and software considerations. A general purpose system for germanium spectroscopy requires about 4000 channels of 20- to 24-bit data. The software requirements (particularly the data reduction and interpretation programs) force constraints on

system speed. It should be noted that this speed is determined both by the computer execution speed and the efficiency of the particular software being used. We decided that the power of the computer, which takes in such things as the memory cycle-time and the power of the instruction set, must be sufficient to allow the analytical programs to execute within a few minutes time.

Certain peripherals are required to support the above functions. A mass-storage device is required for program and data storage (and subsequent retrieval). A cathode-ray tube display is required for the pulse height analysis function, and a paper-tape reader is necessary for initial program loading.

Our selection of a 12,000-word 12-bit computer (PDP-8E or DCC-112H) tended to fill not only these requirements but the software requirements as well. The software aspects divide into three categories: general system software, data acquisition and display software, and data analysis and interpretation software.

The general system software is very complex (hence, too costly to develop at LLL). Therefore, the requirement that this software be available in the public domain or from the vendor was an important consideration in the selection of the mini-computer. The system software we adopted was PS-8, which consists of an operating system, including a keyboard and an I/O monitor, and of a high-level language. The keyboard monitor allows easy operation of the system by personnel who are not computer specialists. The I/O

monitor provides system services to a problem program such as I/O requests, file management, and program chaining, thus decreasing the software effort required to implement the problem program.

The data acquisition and display software was written in a machine-level language. It operates principally in conjunction with the function box which allows the user to acquire and to transfer or manipulate the display of spectral or digital data on the cathode-ray tube. The features of this software and the source listings will appear in a separate report.

The third type of software is in the form of a high level language because of the complexity of some of the data analysis codes. A requirement was that this language be reasonably fast, indicating the use of a compiler rather than an interpreter, and be capable of generating a fairly large code. As a result, we chose to use FORTRAN language, because it was available as part of the system software operating package and because of its prevalent use.

A large variety of FORTRAN programs have been written and tested which are useful for both set-up purposes or for the reduction and interpretation of the spectral data resulting in specific analyses. The more lengthy programs are very easily accommodated by chaining, in rapid sequence, logical sections of program which have been previously written, compiled, and stored as files on one of the discs.

The features of the specific programs and the source listings will appear in Part II of this series of reports.

IV. SUMMARY OF PERFORMANCE

A more detailed evaluation of the performance of the spectrometer system will be presented in a separate report. However, a summary of the performance, the usage that is made of the system at the Savannah River Plant, and some results will be described here.

The germanium detector used in the SRP system was made of intrinsic material and was fabricated at the Lawrence Berkeley Laboratory by R. Pehl and D. Landis. The dimensions of the detector were 1.4 x 1.6 x 0.65 cm. The preamp used pulsed opto feedback electronics which are described in Ref. 7. A FWHM resolution at 525 eV at 122 keV was obtained using a 17 μ sec pulse shape "peaking time."

The electronic components of the system and the resolution obtained were very good. However, there were two, probably related, problems with the efficiency of the detector. First, even though the volume of the detector was calculated to be considerably larger than 1 cc, its measured efficiency at 59 and 122 keV was less than that of a nominal 1 cc germanium (lithium) commercial detector that was also tested. Second, this efficiency initially decreased with time.

Some of the reasons for such phenomena are just now beginning to be understood.⁽⁸⁾

Referring to Figure 16, it is generally assumed that the field lines for a planar detector are parallel surfaces or junctions. However, a detector is not like an air gap condenser but possesses physical edges with surface impurities and imperfections which cause a leakage current. If the resistivity of this surface varies, then the field lines may terminate into the edge rather than at the opposite surface. One of the components of an electron-hole pair produced near such field lines, as the result of a gamma ray interaction in the vicinity, may migrate to the edge, become temporarily trapped and, therefore, become part of the leakage current rather than appear as a legitimate pulse. In effect, part of the detector volume is dead. Furthermore, if the surface states are changed by jarring, system outgassing, or leaks, the surface resistivity may change, and, as a result, the field lines and the efficiency may change.

It is apparent that such a phenomenon would be most noticeable in small planar detectors because such detectors exhibit the largest surface-to-volume ratio.

Fig. 16. Diagram of field lines in a small planar detector. The decrease in active volume is postulated to be due to field lines terminating into the edge.

Also, it may be possible to observe different changes in the efficiency at different gamma ray energies since low-energy radiations interact only at the front surface while higher-energy gamma rays interact throughout the entire volume of the detector. Such an effect was indeed noted with our intrinsic detector. The efficiency at ~ 50 keV changed by only a few percent whereas the efficiency at ~ 150 keV changed by $>20\%$.

If this continues to be the pattern of behavior for small detectors, it may be necessary to resort to a guard-ring design so as to remove edge effects. However, there seems to be some progress made in "setting" the surface states. (8)

The system hardware has performed very well. Although the equipment is in a laboratory environment, there were times when it functioned well in spite of nonideal conditions. For example, no problems were encountered during an 8-hour period when the air-conditioning failed and the temperature rose to 88°F , accompanied by high humidity.

The system is routinely used for plutonium isotopic measurements on materials taken from several points

in the plant. Most of the samples originate at the product accountability tank or are portions of dissolved specimens taken from the plutonium metal buttons. Some samples originate from storage tanks containing aged plutonium.

Samples from the accountability tank are invariably checked by mass spectrometry for the purposes of the evaluation program. However, in the case of metal button samples, only every tenth one is checked by mass spectrometry. Aged samples from storage tanks are checked in those instances in which an assurance of accuracy is required.

In addition to the routine samples, some controlled experiments were conducted to assess certain aspects of the analytical results. For example, in one series of measurements, the same sample was counted repeatedly to verify the reproducibility of the results. Table 4 summarizes the data and indicates the precision that can be achieved by using a 10- or 60-minute counting time. The peaks that were analyzed to obtain these results were at 43, 45, 51, 94, 103, 103.67, 104.23, 129, and 148 keV.

Table 4. Analytical precision of recently reprocessed samples using >10 replicate results (counting time at optimum counting rate).

Isotope	Abundance (%)	Average 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	(3 mg/ml)	0.16	0.11	0.36	0.22

We continued to count the above sample for about two months to see how the ingrowth of ^{237}U and ^{241}Am would affect the results. Table 5 summarizes the isotopic and total Pu assays obtained from those counts. It appears that this data reduction program introduced very little bias into the results as a function of time.

Table 6 shows a comparison of a set of twenty separate gamma-ray and mass-spectrometry results. The standard deviation is consistent with the quoted errors of the two methods. Some of the precision in the gamma-ray measurements was significantly affected by counting statistics which could have been improved by a longer count.

The results shown in Tables 4, 5, and 6 are typical of what can be achieved on recently processed weapons-grade plutonium. If the material has aged so that there

is an appreciable ingrowth of ^{237}U and ^{241}Am , the peaks below 59 keV become obscured. The 100 keV peak region now becomes more complex, as indicated in Figure 10, and the remaining useful peaks are less intense than the low-energy peaks; hence, the counting statistics are less. Therefore, longer counting times are generally needed, and, as Table 7 indicates, some loss in precision is observed.

Until now, the samples were placed in plastic vials and counted in a holder placed above the detector. Plans are in progress to install a detector on a sample line leading from the product accountability tank. This will not only reduce much work in sampling and provide a more rapid analysis of the material, but, by eliminating errors due to sampling and to positioning of the source in the holder, there may also be some improvement in the absolute accuracy.

Table 5. Isotopic results as a function of time after initial separation (counting times of 10 minutes at optimum count rate).

Time from separation (days)	^{238}U % Error	^{239}Pu % Error	^{240}Pu % Error	^{241}Pu % Error	Total (mg/ml) Error
1	0.0080 (4.7)	93.46 (0.05)	5.88 (0.7)	0.651 (1.9)	0.528 (0.36)
10	0.0085 (6.6)	93.39 (0.06)	5.92 (0.9)	0.685 (1.2)	0.528 (0.22)
14	0.0085 (6.8)	93.45 (0.06)	5.87 (0.9)	0.671 (1.2)	0.533 (0.23)
17	0.0091 (5.1)	93.45 (0.05)	5.85 (0.7)	0.660 (1.0)	0.532 (0.18)
22	0.0088 (4.2)	93.49 (0.04)	5.86 (0.6)	0.645 (0.8)	0.530 (0.16)
31	0.0096 (7.3)	93.53 (0.07)	5.80 (1.0)	0.659 (1.3)	0.522 (0.28)
36	0.0096 (4.3)	93.51 (0.04)	5.83 (0.6)	0.649 (0.8)	0.528 (0.16)
38	0.0090 (5.0)	93.48 (0.04)	5.85 (0.7)	0.662 (0.9)	0.525 (0.20)
43	0.0093 (5.7)	93.49 (0.05)	5.86 (0.8)	0.638 (1.0)	0.528 (0.22)
50	0.0090 (7.0)	93.44 (0.06)	5.88 (0.9)	0.673 (1.1)	0.523 (0.25)
57	0.0099 (6.2)	93.51 (0.06)	5.83 (0.9)	0.642 (1.1)	0.527 (0.26)
62	0.0111 (6.0)	93.51 (0.06)	5.84 (1.0)	0.641 (1.2)	0.531 (0.28)
Average	0.0092	93.48	5.85	0.657	0.528
Standard deviation (%)	± 8.7	± 0.04	± 0.5	± 2.2	± 0.64

Table 6. Comparison of gamma and mass-spectrometry results (10-minute counts on 20 samples of AEC grade Pu).

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

**Table 7. Analytical precision of "older" samples using
13 replicate results
(60-minute counting time at optimum counting rate).**

Isotope	Abundance (%)	Average 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

V. INFERENCES FOR THE ANALYSIS OF REACTOR-GRADE PLUTONIUM

Virtually all of our experience to date has been with the analysis of AEC weapons-grade plutonium, which is nominally 93% ^{239}Pu . What can be inferred from these results and applied to the analysis of reactor-grade plutonium is dependent on the changes in the material itself. These are twofold, namely, changes in isotopic abundance ratios and changes in total concentration. (Fission product contamination levels may be a third, but it is not anticipated to present a problem.)

Referring to the isotopic abundances shown in Table 1, it is generally agreed that plutonium of the Categories III and IV types will become quite common. This means that the amount of ^{238}Pu , and its attendant signals, will be 100 to 200 times that for weapons-grade material. Similarly, the ^{240}Pu will be four times more, and ^{241}Pu from 20 to 30 times more. The only signal that will decrease is that from ^{239}Pu . Correspondingly, the analysis errors for ^{238}Pu , ^{240}Pu , and ^{241}Pu will decrease; however, the error for ^{239}Pu will increase somewhat. In many respects, then, we feel that the gamma analysis technique is even better suited for reactor-grade material than for weapons-grade plutonium.

The second significant difference is in total plutonium concentration. The final product concentration of commercial reprocessing plants is from 200 to 250 g/l, which is considerably greater than at the Savannah River Plant. Again, some advantage is gained in that we are currently count-rate limited. However, it is anticipated that, in going to reactor-grade material, the combination of isotopic and concentration changes will require that a much smaller sample be used (<1 ml). The sample cell will have to be very shallow

(<0.1 cm), to minimize sample self-attenuations which become quite pronounced at such high-plutonium concentrations.

It may be possible to gain an advantage from the high concentration. It has been demonstrated* that the total plutonium concentration can be measured by gamma-ray absorbance techniques to within 0.5% for such solutions. This means that, if the gamma spectrometer system is calibrated very accurately, it may be possible to determine the ^{242}Pu content by difference to an accuracy of $\pm 10\%$. It is certainly true that the counting statistics warrant such a judgment. However, extreme care will have to be used in designing and in calibrating the necessary hardware and computer programs.

The above remarks and inferences pertain to recently reprocessed material. There are several complications which will arise when analyzing reactor-grade material which has been aged.

- 1) The ^{239}Pu analysis will have a greater error because of the poorer counting statistics in the 129 keV peak.
- 2) The ^{241}Am growth from the large amount of ^{241}Pu will soon tend to flood the detector with the ^{241}Am signal.
- 3) The ^{240}Pu accuracy will be reduced in spite of its increasing isotopic concentration. This is due to the severe interference between the 104.23

*Experimental work performed at the National Reactor testing facilities in Idaho by Cartan and Shaw.

keV ^{240}Pu gamma ray and the 103.67 keV gamma ray of ^{241}Pu , whose concentration increase with burnup is much greater than that of ^{240}Pu .

- 4) Although no direct measurement has yet been made, it is anticipated that the 200 g/l concentration will produce a significant amount of alpha-induced plutonium x-ray fluorescence. The $K_{\alpha 1}$ and $K_{\alpha 2}$ x-rays have energies of 99.536 and 103.750 respectively. In reference to the

preceding complication, the 103.750 keV radiation will present further problems in resolving the 103-104 keV multiplet.

More developmental work must be performed to determine the extent to which these complications affect the analyses. As a last resort, a chemical separation can be performed to remove the ^{241}Am and ^{237}U interferences, permitting the cleaner peaks at lower energies to be detected and analyzed (see Appendix 2).

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APPENDIX 1

ABSOLUTE CALIBRATIONS USING A 4π α - γ COINCIDENCE TECHNIQUE

A standard method for the absolute standardization of beta-emitting radioactivities has been the so-called β - γ coincidence technique^(9,10). The technique is quite easily extended to include alpha emitters, provided a prominent coincident gamma ray is present. The problem with any absolute counter is to know what fraction of the emissions is actually being detected. The coincidence counting technique, shown below, corrects for those events which are not detected.

$$N_{\alpha} = N \cdot \epsilon_{\alpha}$$

$$N_{\gamma} = N \cdot \epsilon_{\gamma}$$

$$N_{\alpha-\gamma} = N \cdot \epsilon_{\alpha} \cdot \epsilon_{\gamma}$$

Therefore:

$$N = N_{\alpha} \cdot \frac{N_{\gamma}}{N_{\alpha-\gamma}}$$

where

N_{α} , N_{γ} , and $N_{\alpha-\gamma}$ are the observed α , γ , and α - γ coincidence counts respectively,
 ϵ_{α} and ϵ_{γ} are the counting efficiencies for the alpha and gamma radiations,
 N is the absolute number of disintegrations.

The equipment consists of a 4π proportional flow counter which is viewed by a NaI scintillation crystal for detecting the gamma emissions. Three scalars are used to record the alpha, gamma, and coincidence counts.

The method is ideally suited for standardizing ^{241}Am solutions since the abundant 59 keV gamma ray can be conveniently detected. Typical results for such a standardization are tabulated below.

	Count duration (minutes)	Alpha count	Net gamma count	Coincidence count	Correction factor	Absolute dpm	
1)	110	1,190,696	18,610	18,591	1.0011	10,837	$\pm 0.25\%$
2)	935	10,095,197	160,575	159,849	1.0045	10,845	$\pm 0.08\%$
3)	120	1,294,485	20,841	20,727	1.0055	10,847	$\pm 0.23\%$
4)	110	1,185,466	18,580	18,499	1.0043	10,823	$\pm 0.24\%$

Average = 10,838

The technique cannot, however, be directly applied to the assay of the plutonium solutions since the decay of these isotopes is not accompanied by abundant gamma transitions. To circumvent this problem, a small but known amount (usually 5 to 15% by activity) of a previously calibrated ^{241}Am solution was added as a tracer. The coincidence to gamma count ratio still indicates the efficiency of the alpha counter. In this way, precisions within $\pm 0.3\%$ could be obtained on assay results for ^{238}Pu , ^{239}Pu , and ^{240}Pu .

APPENDIX 2

CHEMICAL SEPARATION OF Am AND U FROM Pu*

Procedure 1 (Chloride System)

1. Prepare an anion exchange bed of Dowex-1X10 (10% cross-linked with DVB) with a length-to-diameter ratio of at least 10:1. Assume the chloride complex ion to be PuCl_6^- , and load the resin bed to only 30% of capacity. Dowex-1X10 contains approximately 200 milliequivalents per gram of dry resin. The resin mesh size should be chosen to give a flow rate of approximately 5 ml/min/cm² of column area.
2. Load the column to be used with the above resin in the chloride form from an H_2O slurry. Wash the bed with 3 column volumes (CV) of $\sim 12.5 \text{ M HCl}$, and then with 5 CV of $12 \text{ M HCl} + 0.1 \text{ M HNO}_3$ (the last to oxidize any residual low-molecular-weight organic residues in the bed). Do not allow air to enter the resin bed, as it will both lower the bed capacity and cause tailing of the ionic species during loading and washing.
3. Load the solution containing the Pu, Am, and U in approximately $10 \text{ M HCl} + 0.1 \text{ M HNO}_3$ (warm to 50°C and let stand for 5 minutes to insure that the Pu is oxidized to +4 state); $0.1 \text{ M NH}_4\text{NO}_2$ may be used instead, if available. After passing all the loading solution through the bed, wash the bed with at least 15 CV of 10 M HCl , one CV at a time, taking care to wash all

* Edited by M. S. Coops of LLL Radiochemistry Division

droplets or resin that may be on the sides of the column down onto the resin bed. (Separation efficiency is directly dependent on the care that is used to make sure all Am is rinsed from the column walls.)

4. Eluate from step 3 contains all Am in the 10 M HCl fraction (expect DF from Pu to be $> 10^6$).

5. If separation from U is desired, pass 10 CV of 10 M HCl + 0.2 M HI through the column to elute the Pu^{+3} from U and Fe (DF from Am $> 10^4$).

6. If separation from U is not required, skip step 5 and elute the column with 0.5 M HCl, starting by adding $\frac{1}{2}$ CV fractions to the column. After passing 3 CV through the column, elute with an additional 5 to 7 CV batch of $\frac{1}{2}$ M HCl. This fraction contains Pu, U, Fe, etc.

Procedure II (Nitrate System)

1. Prepare the column per I-1 above [$\text{Pu}(\text{NO}_3)_6 =$].

2. Wash the Dowex-1X10 column with 13 to 15 M HNO_3 to convert resin to nitrate form if the resin was in chloride form. Wash with 3 to 5 CV of H_2O to remove aqua regia. Unload the resin from the column, stir to expel any air of chlorine, and reload the column as a water slurry. Wash the resin bed with 5 CV of

8 M HNO_3 .

3. Load the Pu, Am, and U fraction onto column in 8 M HNO_3 . Wash the resin column with 1 CV fractions of 8 M HNO_3 : Am will elute in the first 3 CV beyond free volume. U will start to elute starting ~ CV-11. To wash all Am and U off the column, 20 to 25 CV of 8 M HNO_3 are required.

4. Am will be contained in the 8 M load and wash. If large volumes are used to load the column, some U will be found in the Am fraction.

5. Elute column with 1.0 M HNO_3 , approximately 10 CV to elute the Pu^{+4} fraction. Note: If aqua regia or chloride ion was present in the loading solution, not all Pu will elute in 1.0 M HNO_3 ($\text{PuO}_2(\text{NO}_3)_4$ is formed). In such case, convert the resin to chloride form with 10 M HCl, 5 to 10 CV, and then strip with 0.5 M HCl, 5 to 10 CV.

Note: $\text{Pu}(\text{NO}_3)_6$ = absorbed on Dowex 1X10 will show a forest green absorption bond. Efficiency of loading and stripping can be readily determined visually. $\text{Pu}(\text{Cl})_6$ = is brick red-orange, as is $\text{Fe}(\text{Cl}_4)^-$. Elution bands can also be followed visually in the chloride system.