TITLE: Gamma Ray NDA Assay System for Total Plutonium and Isotopics and Plutonium Product Solutions


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Gamma Ray NDA Assay System for Total Plutonium and Isotopes in Plutonium Product Solutions

by

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ABSTRACT

A LASL-designed gamma-ray NDA instrument for assay of total plutonium and isotopes of product solutions at Tokai-Mura is currently installed and operating. The instrument is, optimally, a densitometer that uses radioisotopic sources for total plutonium measurements at the K absorption edge. The measured transmissions of additional gamma-ray lines from the same radioisotopic sources are used to correct for self-attenuation of passive gamma rays from plutonium. The corrected passive data give the plutonium isotopic content of freshly separated to moderately aged solutions. This off-line instrument is fully automated under computer control, with the exception of sample positioning and operates routinely in a mode designed for measurement control. A one-half percent precision in total plutonium concentration is achieved with a 15-minute measurement.

KEYWORDS: Reprocessing, product solutions, gamma-ray NDA, densitometry, transmission-corrected gamma-ray assay

I. INTRODUCTION

The Los Alamos Scientific Laboratory (LASL)-designed K-edge densitometer for plutonium product solutions accounting at the Power Reactor and Nuclear Fuel Development Corporation (PNC) fuel reprocessing facility in Tokai-Mura, Japan, was shipped to Tokai in summer of 1979 and installed and calibrated during September and October, 1979. The densitometer will continue to operate initially in a schedule that allows for testing and evaluation throughout the late fall and early spring reprocessing campaigns at Tokai. The instrument is intended to be used cooperatively by the PNC and the International Atomic Energy Agency (IAEA) for rapid, off-line assay. It will provide a means to bypass the time-consuming and costly destructive analytical methods for total plutonium measurement.

The densitometer is discussed below in sections describing the measurement principles and experimental design, III) hardware design, IV) software design, V) concepts of analysis, and VI) preliminary results.

II. MEASUREMENT PRINCIPLES AND EXPERIMENTAL DESIGN

Solution assay performed by K-edge densitometry provides the total concentration of an individual element in a well-defined geometry. The measured transmission of gamma radiation through recycles nuclear material (SNM) displays a discontinuity at the discrete energy corresponding to the binding energy of the K electrons. The transmissions, T1 and T2, just below and above the K edge, respectively, are related to the total concentration, \( \rho \), of the element by the relation

\[
T_1 = T_0 e^{-\frac{\rho}{10}}
\]
where \( \mu \) is the mass attenuation coefficient of the element for a given photon energy; \( x \) is the sample thickness and \( T_m \) is the transmission through the matrix. Thus, the ratio \( R \) of transmissions is logarithmically related to the elemental concentration, \( c \), independent of matrix by

\[
\ln \frac{T_2}{T_1} = \frac{\ln R}{\Delta x} = k
\]

where \( \Delta x = x - 1 \).

Discrete gamma-ray transmission sources can be used for K-edge measurements if the gamma-ray lines closely bracket the absorption edge of interest. For the plutonium case, the 121.1 and 122.1 keV lines of \(^{75}\text{Se}\) and \(^{57}\text{Co}\), respectively, are well located with respect to the 121.76 keV \( K \) electron binding energy. The measured transmissions of these two gamma-ray lines have previously been used with success to assay plutonium in solution.\(^1,2\) This technique is applied in the Tokai densitometer.

The densitometer design was optimized to measure plutonium solutions, freshly separated, with a total concentration of approximately 225 \( \mu \text{g Pu per liter} \). Even with less-than-ideal passive counting geometry, the measurement situation is well suited to transmission-corrected passive assays for isotopics determination. This type of assay has been applied in existing instrumentation\(^3\) to an extremely wide range of plutonium solution concentrations (0.5 to 500 \( \mu \text{g Pu per liter} \)) where self-attenuation corrections are based on transmission measurements performed with an external plutonium transmission source.

The Tokai densitometer uses measured transmissions of the gamma-ray lines of \(^{75}\text{Se}\) and \(^{57}\text{Co}\) obtained during the densitometry measurement, in place of those from an external plutonium source, to correct for self-attenuation in the passive assay. The \(^{241}\text{Pu}\) and \(^{239}\text{Pu}\) isotopes are determined relative to \(^{239}\text{Pu}\), in this way using assay gamma rays at 149, 153, and 129 keV, respectively. The measurement of \(^{240}\text{Pu}\) and \(^{238}\text{Pu}\) are made by obtaining ratios of the respective peak areas (at 45.2 and 43.5 keV) to that of the \(^{239}\text{Pu}\) isotope at 51.6 keV. The latter technique is not effective for excessively aged solutions.

The solution assays are performed in two steps. The first is a transmission measurement of the \(^{75}\text{Se}\) and \(^{57}\text{Co}\) gamma rays utilizing strong sources and tight sample collimation. The second measurement is performed without sources, and the sample collimation is opened to maximize the passive counting geometry. The mechanical details of the measurements are discussed below.

Measurement control is an essential feature of the experimental design. This is a procedure, performed daily, to ensure that the calibration for total plutonium, based on previous measurements of solution standards, remains valid. A secondary standard is used in this exercise. The Tokai densitometer is designed to assay, on a daily basis, a plutonium foil of known characteristics for total plutonium. Agreement between this assay and the known result is required before routine assays can proceed. Measurement control on the isotopics analysis consists of a relative efficiency measurement performed with the \(^{75}\text{Se}\) transmission source. Since all isotopics data are analyzed relative to \(^{239}\text{Pu}\), it is the relative detector efficiency and not the absolute efficiency that is the critical factor.

### III. Hardware Design

The two-step (transmission and passive) assay performed in order to obtain results for total plutonium and isotopics is accomplished by rotation of the transmission sources in and out of the measurement position. The process is illustrated schematically in Fig. 1. Two motor-driven wheels containing collimators and sources are positioned synchronously by a Geneva mechanism such that the geranium detector counts, primarily, either transmission gamma rays from one of two \(^{75}\text{Se}\) or \(^{57}\text{Co}\) sources with tight sample collimation or the passive gamma rays from the sample with collimation open.

The mechanical system is mounted beneath a glovebox that is modified so that a measurement well extends down from the base of the box between the source and collimator wheels. Solution samples in plastic, disposable sample vials of well-defined dimensions...
are inserted into the well. The well fixes the position of the sample vial. Secondary standards are also prepared for measurement in this way.

The germanium detector sits beneath the glovebox, facing the sample and transmission sources, in a position downstream from the sample. The configuration at the measurement station is shown in Fig. 2. Figure 3 is a photograph of the measurement station before installation beneath the glove box. Figure 4 shows details of the measurement well and associated hardware appropriately to scale.

The optimum $^{75}$Se and $^{57}$Co source activities are approximately 50 and 25 mCi, respectively. Gamma rays from the sources are collimated to a diameter of 3 mm at the collimator wheel.

The sample well is a thin stainless steel canister which supports a thick tungsten shield. The tungsten shield is lined with a polyethylene boot into which the sample container fits securely. The stainless steel canister is the containment canister for the glovebox modification. The photon windows on this container are 0.5 mm thick at the entrance (transmission source) side and 0.25 mm thick at the exit side.

Solution sample volumes are a minimum of 10 ml. The photon transmission path length through the sample is approximately 2 cm. The sample cross sectional area viewed by the detector during passive measurements is 3 cm².

The germanium detector is a planar intrinsic which is chosen to be relatively thin (7 mm) to limit backgrounds due to Compton scattering of high energy protons. The crystal is located approximately 10 cm from the center of the sample. A 100 uCi $^{109}$Cd source is mounted just above the cryostat. This source is used for normalization to correct for losses due to differing count rates.

Pulses from the detector are amplified by a pulsed optical feedback preamplifier and further amplified and shaped with 1 µs time constants. Pulse-up rejection is employed to permit higher count rates. The optimized data throughput rate to the computer occurs at detector counting rates of approximately 20 kHz. At this rate, the resolution at 122 keV is approximately 500 eV, full width at half maximum (fwhm).

The amplified pulses are digitized by a digitally stabilized analog-to-digital converter (ADC). The converted data is stored and processed by an LSI-11 microcomputer, part of the LSI-11 data acquisition system utilized in this instrument.

The computer control of the data acquisition system includes all hardware mechanical operations (except sample positioning) and some electronics adjustment (such as selection of gain stabilization channels), measurement control, and data acquisition and analysis. The control software uses the DEC RT-11 version 30 foreground-background operating system, the Nuclear Data foreground process, NDD60, which controls acquisition and display, and FORTRAN-callable subroutines provided by Nuclear Data for communication between foreground and the background control programs. The background code is overlaid in segments that are accessed from floppy diskette. Spectral data are stored on floppy diskette along with measurement parameters, constants, and file identification information. The code is also capable of reanalyzing data stored previously on disk.

Special interfaces to the LSI-11 that are accessed by the code are those for the ADC, the source-collimator-wheel drive mechanism and position sensing mechanism, three thermocouples for equipment temperature monitoring, and the gain stabilizer.

Figure 5 is a photograph showing the measurement well (extreme right), control hardware (middle), and the rack-mounted electronics. The electronics are (top to bottom), a dual floppy diskette unit, an oscilloscope, the control electronics for the Geneva mechanism and temperature sensors, the computer display terminal, the LSI-11 microcomputer, and the NI4 electronics for processing the signals from the detector preamplifier.

IV. SOFTWARE DESIGN

The computer program for automatic data acquisition and analysis and measurement control is written in overlaid form so that the executive routine, any one of three major control routines, and any one of twenty utility routines are resident in core at once. As much as 11.4 K of core is available for the control program. The remainder of the LSI memory is used by the NDD foreground program, the 4 K spectrum, and the RT-11 operating system.

This program requires a minimum of operator interaction since the program itself performs diagnostic tests and executes the assay providing the outcome of these tests is positive. Other modes of program operation give the user more flexibility to exercise
diagnostic procedures, but these modes are designed for setup, calibration, testing, and other nonroutine measurements, and are not intended for regular use with the instrument package.

Routine use of the program requires the daily execution of a measurement control sequence. Measurement control establishes the unattenuated gamma-ray intensities used for compiling fractional transmissions, it checks for changes in relative detector efficiencies, and it verifies that the source strengths are sufficient to obtain the statistics required. These 75Se and 57Co spectra are also used to verify the energy resolution and gain of the spectrometer, which must agree with the original values that are stored. Furthermore, the known thickness of a secondary standard plutonium foil must be reproduced by a densitometry measurement to satisfy measurement control requirements.

A successful completion of measurement control allows the user the option to assay a sample. The assay proceeds automatically with the accumulation and storage (on floppy disk) of 75Se and 57Co spectra, calculation of total plutonium concentration and of transmission values that apply to the passive assay, accumulation and storage of the passive spectrum and calculation of the isotopic weight fractions.

V. CONCEPTS OF ANALYSIS

Techniques for extraction of peak areas using straight line background subtraction have been described previously. The reduction of raw data before analysis is accomplished using these techniques both for the active and passive spectra. No peak fitting is employed.

For all analyses which requires the absolute area of a peak in a given spectrum, normalization is accomplished by dividing by the area of the 88 keV 106Cd peak. This normalization is applied to peak areas used for the transmission measurements, both for densitometry and for attenuation corrections.

All peak areas used for transmission measurements are corrected for the decay of the source since the time of measurement of the unattenuated intensities.

Analysis of the transmission data for the densitometry assay is straightforward and has been discussed in sufficient detail in Sec. 2. The predicted fractional uncertainty in the measured plutonium concentration is

\[
\frac{dR}{R} = \frac{dR}{R} + R \frac{dR}{R}
\]

where \( R \) is the transmission ratio as defined in Sec. 2. The results of the densitometry analysis on standard plutonium solutions appear in the next section.

Analysis of the passive data for isotopics is more complex in that different analysis techniques are used in the two energy regions discussed previously. The two techniques are discussed separately below.

The concentration of a given isotope, \( \nu_1 \), measured by gamma-ray spectroscopy can be expressed as

\[
\nu_1 = A \cdot CF
\]

where \( A \) is the normalized peak area corresponding to a gamma ray emitted by the isotope of interest. The correction factor, \( CF \), takes into account the energy- and concentration-dependent sample attenuation effects on the gamma ray of interest. The proportionality constant is dependent upon quantities such as branching ratios, half lives, counting efficiencies, the atomic mass, and a calibration factor that disappears if relative peak area results are analyzed as is the case here.

The calculation of \( CF \) is performed in order to measure the isotopic contents of 238Pu, 239Pu and 241Pu using the assay gamma-ray peaks at 153, 129 and 149 keV, respectively. Measured transmissions at 122 keV (from 57Co), 136 keV and 279 keV (from 75Se) are linearly interpolated or extrapolated based on both the 122-136 keV pair and on the 136-279 keV pair. Therefore, two transmission values are determined for each of the three plutonium gamma-ray energies. The average of the two is the value used in the calculation...
of CF, since this has been shown to give a more realistic result than a quadratic fit to three measured transmissions, two of which are closely spaced in energy.

A slab sample with finite thickness, D, which remains small compared to the sample-to-detector distance, x₀, has a correction factor that can be expressed as an integral over the sample thickness

\[ \text{CF} = \frac{K_0 \int_0^D dx}{\int_0^D T_x dx} \]

where

\[ T_x = e^{-\mu x} \]

and \( \mu \) is the linear attenuation coefficient. In this case, the integral has an exact solution. However, if D is not negligible compared to x₀, geometry effects due to sample thickness must be included in the integration over sample thickness

\[ \text{CF} = \frac{K_0 \int_0^D dx}{\int_0^D \frac{T_x}{(x + x_0)^2} dx} = \frac{K}{x_0(x_0 + \ell)} \]

This integral has no exact solution, and thus a numerical evaluation is appropriate. The known (measured) transmission values \( e^{-\mu D} \) are used to empirically evaluate the quantity \( K \) at each energy for each sample. The slab assumption proves to be a valid approximation in this case.

The fractional error in the average extrapolated transmission propagates to one-half that in \( K \).

The approach to isotopic analysis in the low-energy region is less cumbersome, primarily because there is no need to determine the correction factor for sample attenuation. The relative efficiencies, \( R_{\text{eff}} \), of two gamma-ray lines for \( ^{239}\text{Pu} \) at 39 and 51 keV are determined from the respective measured peak areas, \( A \), and the branching ratios (BR) known for these gamma-ray lines. Thus

\[ R_{\text{eff}} = A \cdot \text{BR} \]

The dependence in \( n R_{\text{eff}} \) versus \( n (n E) \) is interpolated linearly between 39 and 51 keV to obtain \( R_{\text{eff}} \) at 43 and 45 keV, the energies of the two gamma rays due to \( ^{239}\text{Pu} \) and \( ^{240}\text{Pu} \) respectively. The ratios of the weight fractions, \( f_i \), of each of these two isotopes to that of the \( ^{239}\text{Pu} \), \( f^{239} \), are then given by

\[ f_i = \frac{A (43 or 45)}{R_{\text{eff}} (43 or 45)} \cdot \frac{R_{\text{eff}} (51)}{R_L (43 or 45) A (51)} \]

where \( R_L \) accounts for the ratios of half-lives and branching ratios and atomic masses associated with the \( ^{239}\text{Pu} \) (51 keV line) and each of the other two.
VI. RESULTS

A. Calibration at LASL

Primary standard solutions of reactor grade plutonium have been used for preliminary calibration of the Tokai densitometer at LASL for total plutonium. Total plutonium concentrations range between 150 and 300 g per liter. The 241Pu isotopic content of the solutions was 13% although the calibration was also verified with solutions of low burnup material.

A summary of the results of the densitometry measurements on the solution standards is shown in Fig. 6. Count times for each transmission measurement were 1000 seconds. Since the data were obtained with solutions of known concentration, the calibration factor was derived from each measurement. Plotted is the percent deviation from the mean value for each run. The error bars reflect the statistical precision (+1σ) in the densitometry measurement. The precision of 0.1 percent (1σ) in the reference concentrations is not included but has very little effect on these error bars. The scatter in the data is consistent with the statistical prediction shown by the ±1 statistical error bars. The data shows no evidence of a concentration effect on the calibration factor. It should be noted that the 131Cd source rate was sufficiently low for these measurements (because of positioning) to increase the statistical uncertainty by 60 percent compared to measurements performed with optimized count rates.

Calibration with solution standards was carried out along with routine assays of the plutonium foil. The foil is equivalent to approximately 235 g Pu per liter. The statistical precision on the foil assay for a 1000-s count time is 0.029%. The experimental precision agrees with this as is shown in Fig. 7. These data were obtained in a four-week period after measurement of the solution standards as a demonstration of the stability of the calibration for total plutonium.

Isotopic results have been obtained from passive measurements of the reactor-grade plutonium standard solutions. The results are all based on measurements of peak areas relative to the 239Pu peak area, as described in Secs. II and V. Relative peak area measurements appear to be immune to any shifts in gain, resolution, or detector efficiency, since these measurements use ratios of areas of peaks closely spaced in energy.

Thus, the data analysis involves obtaining the ratio of each isotopic fraction, fj, to that for 239Pu, f239. This ratio, fj/f239, is defined by Eq. (2) for the low-energy data, and is identical to the ratio, fj/f239, obtained using Eq. (1) and the high-energy data. The experimental ratios can be combined with a result for 242Pu obtained by isotopic correlations using the experimental value for f240/f239 [5]. The fraction of 239Pu is derived from the equation

\[ f_{239} = \frac{1}{(1 + R_{238} + R_{240} + R_{241} + R_{242})} \]

where

\[ R_1 = f_1/f_{239} \]

This result for f239, is used to obtain the other isotopic fractions:

\[ f_j = R_j f_{239} \]

The solution standards were used first to determine the relative counting efficiencies for assay peaks in the high-energy region. They were also used to verify (and correct if necessary) the literature values that make up the constants Rj(43) and Rj(45) (see Eq. (2)) for the low-energy analysis. Once the relative efficiencies and constants were established, the isotopic fractions, f239 and f1, were determined for thirteen passive measurements performed on the four solutions listed previously (refer to Fig. 6), all with the same isotopic content (namely 0.349%, 79.65%, 14.30%, 4.56%, and 0.933% for the 238, 239, 240, 241, and 242 isotopes, respectively). The reference values for isotopic content were obtained from mass spectrometric measurements. These initial measurements were performed within several days of the 241Am separation so the 241Am content was approximately 100 ppm. All passive count times were 2000 seconds.

The results for the early measurements are shown in Columns 2 and 3 of Table I. Column 2 compares the average calculated measurement precision with the experimental
TABLE
SUMMARY OF ISOTOPIC FRACTION RESULTS
FOR REACTOR-GRADE Pu SOLUTIONS

<table>
<thead>
<tr>
<th>ppm americium</th>
<th>100</th>
<th>100</th>
<th>1000</th>
<th>3000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1c calc.</td>
<td>1c exp.</td>
<td>CALCULATED 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Isotopic</td>
<td>Total Pu</td>
<td>Isotopic</td>
<td>Total Pu</td>
</tr>
<tr>
<td>238Pu</td>
<td>1.2</td>
<td>0.9%</td>
<td>0.003%</td>
<td>1.2%</td>
</tr>
<tr>
<td>239Pu</td>
<td>1.0</td>
<td>0.45%</td>
<td>0.36%</td>
<td>0.45%</td>
</tr>
<tr>
<td>240Pu</td>
<td>1.2</td>
<td>1.0%</td>
<td>0.14%</td>
<td>1.3%</td>
</tr>
<tr>
<td>241Pu</td>
<td>0.7</td>
<td>0.9%</td>
<td>0.04%</td>
<td>0.9%</td>
</tr>
<tr>
<td>242Pu</td>
<td>40%</td>
<td>0.37%</td>
<td>40%</td>
<td>0.37%</td>
</tr>
<tr>
<td>FISSILE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FERTILE</td>
<td>2.6%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

scatter in the weight fraction for each isotope. The results are close to unity indicating no observable contributions to the measurement precision beyond the statistical contributions. (This result is not shown for 242Pu, since the calculated error in this case is derived from the correlation data rather than counting statistics.)

Column 3 of Table I gives the calculated values of the precision error in the isotopic fractions for the same data. These are shown as percentages of the isotopic weight fraction ("isotopic") and percentages of the total plutonium concentration ("total Pu").

As the solutions age and 241Am grows in, the statistical uncertainty on the low-energy data increases because of increased Compton background from the 60-keV gamma ray. Data from the more aged solutions were obtained and analyzed as described for Column 3 of Table I. These are shown in Columns 4 and 5, the latter corresponding to the two-month-old LANS solutions. Clearly, the 241Am growth has affected the measurement precision of the even isotopes.

As the 241Pu content of spent fuel varies with fuel burnup, the level of americium grown in will vary for a given aging time. A passive measurement on samples with 14 percent 241Pu is permitted for samples aged up to six months.

The isotopic analysis is also appropriate for the assay of low burnup materials. The plutonium foil is an example of this (0.022%, 93.71%, 5.95%, 0.29%, and 0.03% for the 238Pu, 239Pu, 240Pu, 241Pu, and 242Pu weight percents, respectively). Thirteen passive assays on the foil give the results shown in Table II. Here again the experimental precision (scatter) agrees with the calculated precision for the 2000-s passive measurements. The calculated results are shown in Columns 2 and 3 as the percent of the isotopic fraction and the percent of total plutonium, respectively, for each of the five isotopes. Although the errors on the isotopic fractions other than 239Pu are larger than for the high burnup plutonium in the solutions, they translate into small uncertainties in total plutonium since these isotopes are now significantly lower in content.

It should be noted that the effect of the 241Am grow-in is less pronounced for the isotopic analysis of low burnup material. The foil data in Table II were obtained from plutonium aged more than six months after americium separation.
The recent calibration at Tokai-Mura was accomplished with solutions of high burnup plutonium provided as reference materials. Total plutonium concentrations were precise to ±0.5 percent. Figure 6 shows these calibration results for densitometry plotted as the percentage deviation from the analytical chemistry values (used as reference values) versus plutonium concentration. The plotted results were obtained between two and four weeks after the americium separation. The error bars reflect only the precision in the densitometry measurement as in Fig. 6. The error is significantly increased by inclusion of the precision in the reference concentrations. Furthermore, three of the four outlying data points agree with independent measurements obtained using a second NDA instrument.

Determination of the parameters for isotopics assay was accomplished using the same plutonium solutions. Reference values were obtained from mass spectrometric results. The experimental precisions in the isotopic parameters are in agreement with the expected statistical precision in the measurements and are comparable to those quoted in Table I. The absolute results agree with those determined at LASL.

Further calibration data will be obtained at PNC before the first reprocessing campaign commences.

REFERENCES

5. Private communication with S.-T. Bue.
Fig. 1. Conceptual view of measurement configuration. The sample is shown between the source (\(^{75}\text{Se}\), in this case) and the collimator in the detector line of sight. Sources and collimators are mounted on separate wheels driven synchronously.
Fig. 2. Schematic view of measurement station extending below and positioned beneath glovebox.
...cross-sectional view of the measurement well extension from the glovebox base.
Fig. 5. Complete R-edge densitometer including computer, MCA, terminal, and measurement well.
Fig. 6. Total Pu measurements of solution standards at LASL.
FOIL RESULTS OBTAINED DURING FOUR-WEEK TEST PERIOD
(CALCULATED 1σ PRECISION = ±.28%)

CONSECUTIVE RUN NUMBER

Fig. 7. Foil results obtained during four-week test period.
Fig. 8. Total Pu measurements of solution standards at Tokai. "Fresh" and "aged" correspond to two and four weeks, respectively, after americium separation.