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IN-LINE MEASUREMENT OF TOTAL AND ISOTOPIC PLUTONIUM CONCENTRATIONS BY GAMMA-RAY SPECTROMETRY

R. Gunnink and J. E. Evans

February 7, 1977

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Contents

Abstract	1
Introduction	1
Discussion of Method	2
Direct Measurement Technique	2
Differential Attenuation Technique	5
Experimental Design	9
Cell Design	9
Detector System	11
Experimental Procedures	14
Discussion of Results	15
Experiment Using Recently Reprocessed Plutonium	15
Experiment Using Aged Plutonium	22
Conclusions.	29
References	31
Appendix	32

IN-LINE MEASUREMENT OF TOTAL AND ISOTOPIC PLUTONIUM CONCENTRATIONS BY GAMMA-RAY SPECTROMETRY

Abstract

This report describes preliminary experiments studying the feasibility of gamma-ray spectrometry for in-line measurements of plutonium in solutions. We measured the isotopic content of the plutonium by direct counting and the total plutonium

content by a differential attenuation technique. Two separate experiments on different solutions were performed with each technique. Our results show that both isotopic and total measurements can be made with precisions around 0.25 to 0.5%.

Introduction

Gamma-ray spectrometry methods have previously provided accurate assays of plutonium concentrations in solutions. Our objectives in the experiments described in this progress report were to investigate the feasibility of these techniques for in-line analyses of both total and isotopic plutonium content.

In-line analyses might be used in plutonium load-out accountability tanks and in the storage tanks of reprocessing facilities. Since gamma-ray spectrometry methods are nondestructive and can be automated and controlled by computers, these techniques could be used to analyze and inventory the tanks on a more timely basis without breaching the containment of the plutonium, thus

increasing plant operation efficiency while safeguarding the plutonium.

To assess the possibility of in-line plutonium assays, we designed an experimental configuration using two cells. One cell measured the plutonium isotopes directly by gamma-ray detection. The other cell measured total plutonium concentration by differentially attenuating two transmitted gamma rays whose energies were on either side of the K-shell binding energy for plutonium. The purpose of our experiments was to initially assess the accuracy with which isotopic and total plutonium analyses could be made on process streams, to determine the optimum values for the various experimental parameters, and to determine the limitations and

problems associated with the measurements.

We conducted two separate experiments, the first on concentrated plutonium nitrate solution from which the ^{241}Am and ^{237}Pu had been chemically removed (simulating the solution found in the product load-out

area of a reprocessing plant), and the second on a solution that simulated an "aged" plutonium solution (as would be found in storage areas).

Our results indicate that both isotopic and total measurements can be made with precisions in the range of 0.25 to 0.5%.

Discussion of Method

Our experimental design called for a direct measurement of gamma rays emitted by the plutonium in the solution and a separate measurement of two closely spaced gamma rays at 122 keV that had been transmitted through the solution.

DIRECT MEASUREMENT TECHNIQUE

The isotopes of interest in a plutonium solution are ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{242}Pu and ^{241}Am . ^{237}U is also present as a daughter product of ^{241}Pu . Of these, ^{242}Pu cannot be observed in the gamma spectrum and therefore cannot be measured by direct counting. The others all emit sufficiently abundant gamma rays to be detected using germanium detector systems.

The gamma-ray energies and intensities for these isotopes have been carefully characterized.^{1,2,3} These data are useful for designing spectroscopic procedures since different

procedures, or at least variations of them, are required depending on the type of material to be analyzed. For example, the low-energy spectra of recently processed plutonium (Fig. 1) are considerably different from spectra of the same material after it has been allowed to age (Fig. 2). As a result, the experimental counting arrangement should be tailored for the specific sample, and separate analysis programs must be written to interpret the spectra.

A general discussion of the spectral features and our approach to computer reduction of the data has been given in an earlier report.⁴ Although we have made several procedural improvements since the initial report, our discussions will emphasize experimental design and results, not details of methodology. However, we give here a brief review and discussions of some significant problems not described in earlier reports.

Fig. 1. Low-energy spectrum of recently separated reactor-grade plutonium solution.

Fig. 2. Low-energy spectrum of aged reactor-grade plutonium solution.

All of our analyses were made on the low-energy (below 210 keV) portion of the spectra. Table 1 summarizes the peaks in this region that are most prominent and amenable to interpretation. Recently processed solutions exhibit several intense peaks from which we can deduce isotopic abundances (see Fig. 1). Our procedure is to use the 43-keV peak for a measurement of ^{238}Pu , the 51-keV peak for ^{239}Pu , the 45-keV peak for ^{240}Pu , and the 148-keV peak for ^{241}Pu . We also analyzed the 94-keV and 129-keV peaks to confirm the results for ^{241}Pu and ^{239}Pu , respectively. The computer analysis is quite straightforward, but accurate results require some attention to details. For example, the analysis of 43- to 45-keV peaks requires removal of small interferences due to ^{239}Pu and ^{241}Pu peaks in the vicinity.³

Although the counting cell had a thickness of only 1 mm, significant attenuations of the gamma rays occurred in the sample. This is due to the high concentrations of plutonium in the solution (200-300 g/litre) and the high attenuation coefficient that plutonium has for low-energy gamma rays. Without knowing *a priori* the concentration of the plutonium, we cannot rigorously compute the attenuation that has occurred. Instead, an iterative approach must

be used, starting with an approximate measure of the concentration. Our procedure for this is detailed in the Appendix.

Aged plutonium is generally characterized by the presence of ^{237}U and ^{241}Am resulting from the decay of ^{241}Pu . The concomitant 59-keV peak of ^{241}Am is quite intense and obscures the spectral features of lower energy. We therefore analyze higher energy peaks which must now include the complex 94- to 104-keV peak multiplet shown in Fig. 3 to get good measurements for ^{238}Pu and ^{240}Pu . This peak grouping consists of up to 14 x rays and gamma rays. However, since x rays of this energy have a significant intrinsic line width (about 100 eV), the observed peak shape distribution is noticeably different from that of a gamma-ray peak of equivalent energy^{5,6} (see Fig. 4). We made considerable effort to develop an algorithm that would adequately describe the shape of x-ray peaks. A description of the problem and its mathematical solutions are treated in a separate report.⁷

DIFFERENTIAL ATTENUATION TECHNIQUE

The principle underlying this technique is simply that the transmission, T , of a gamma ray by a material is related to 1) the amount of the material present, x , and 2) the absorption coefficient, μ , of the

Table 1. Prominent low-energy gamma rays associated with isotopes of plutonium and ^{241}Am and the corresponding emission probabilities.

Energy	Isotopes					
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	$(^{237}\text{U})^a$	^{241}Am
43.477	3.92×10^{-4}	---	---	---	---	---
45.232	---	---	4.53×10^{-4}	---	---	---
51.629	---	2.70×10^{-4}	---	---	---	---
59.536	---	---	---	---	---	0.359
94.660	1.05×10^{-6}	4.22×10^{-5}	6.36×10^{-7}	3.03×10^{-6}	---	---
96.15	---	2.23×10^{-7}	---	---	---	---
97.071	---	---	---	---	(3.89×10^{-6})	1.18×10^{-5}
98.441	1.69×10^{-6}	6.76×10^{-5}	1.02×10^{-6}	4.85×10^{-6}	---	---
98.780	---	1.22×10^{-5}	---	---	---	---
98.951	---	---	---	---	---	2.03×10^{-4}
99.53	----- Pu K_{α_2} x ray from induced fluorescence -----					
99.864	7.24×10^{-5}	---	---	---	---	---
101.066	---	---	---	---	(6.20×10^{-6})	1.90×10^{-5}
102.966	---	---	---	---	---	1.95×10^{-4}
103.02	---	2.17×10^{-6}	---	---	---	---
103.680	---	---	---	1.01×10^{-6}	---	---
103.748	----- Pu K_{α_1} x ray from induced fluorescence -----					
104.244	---	---	6.98×10^{-5}	---	---	---
129.294	---	6.26×10^{-5}	---	---	---	---
148.567	---	---	---	1.87×10^{-6}	---	---
152.680	9.56×10^{-6}	---	---	---	---	---
208.000	---	---	---	---	(7.91×10^{-6})	---

^aThe branching intensities shown for ^{237}U include the α -branching probability of ^{241}Pu . The values therefore represent photon emission probability per decay of ^{241}Pu , assuming a decay equilibrium has been established.

Fig. 3. The 94- to 104-keV peak multiplet of a weapons-grade Pu oxide sample. This is a very complex region, consisting of up to 14 x rays and gamma rays that must be interpreted for the isotopic analysis of aged plutonium samples. For solutions, the Pu x-ray contribution from α -induced fluorescence will be substantially less than is shown here.

Fig. 4. The Lorentzian x-ray energy distribution combined with the Gaussian shaped curve for instrumental broadening result in the convoluted distribution line shown. The modified peak shape which results differs from that of a gamma ray of equivalent energy.

material. The relationship is expressed by

$$T = I/I_0 = \exp[-\mu \cdot x] \quad (1)$$

where I_0 and I are the initial and final intensities and μ and x are expressed in units that are the reciprocal of each other.

If the absorption coefficient μ is known and the reduction of intensity of a gamma ray (I/I_0) can be measured, then the concentration, x , can be calculated.

For composite materials, the total attenuation is given by the same expression except that $\mu \cdot x$ now can be

considered to be the sum of its component elements, that is

$$(\mu \cdot x)_{\text{total}} = \sum \mu_i \cdot x_i \quad (2)$$

In principle, one additional constituent can now be determined for every additional gamma-ray intensity ratio that is measured with a corresponding knowledge of the appropriate absorption coefficient. In practice, the technique is limited to measuring the concentration of a heavy element in a low-Z matrix. This is done by observing the reduction in intensity of two transmitted gamma rays, one at low energy where the differences in absorbance between low- and high-Z materials are large and the other at higher energy where the absorption coefficients are similar. This approach, using 60 keV from ^{241}Am and 662 keV from ^{137}Cs , has been the basis of systems developed by F. Cartan⁸ for plutonium analysis in product streams. The technique cannot, however, distinguish plutonium from other heavy elements such as uranium.

An alternative to the above procedure was first reported by Canada et al.⁹ This approach takes advantage of the abrupt discontinuity in the absorbancy that occurs at the K-shell binding energy of an element — for plutonium, at 121.80 keV. Normally, two gamma rays of nearly equal energy are attenuated to the same extent because the differences in the

absorption coefficients at the two energies are nearly equal. However, gamma rays of energies just below and above the K-shell binding energy of an element show considerably different rates of attenuation.

We can take advantage of this phenomenon in the assay of plutonium solution. The solution can be considered to be a two-component system described simply as a concentration of plutonium in some other generally (though not necessarily) low-Z material. The ratio of the transmission for the two gamma rays, E_1 and E_2 , is given by

$$T_1/T_2 = \exp \left[- \left(\mu_{Pu}^1 - \mu_{Pu}^2 \right) \cdot x_{Pu} \right] \cdot \exp \left[- \left(\mu_m^1 - \mu_m^2 \right) \cdot x_m \right]. \quad (3)$$

Since μ_m^1 and μ_m^2 for the matrix are nearly the same, the last exponential term in the equation approaches unity. As a result, the logarithm of the transmission ratio is linearly related to the plutonium concentration,

$$\ln(T_1/T_2) = - \left(\mu_{Pu}^1 - \mu_{Pu}^2 \right) \cdot x_{Pu}. \quad (4)$$

Experimentally, two gamma rays must be found that have energies slightly below and above 121.80 keV and that have sufficient energy separation so that they are at least partially resolved by a high-resolution germanium gamma-ray spectrometer. One pair of isotopes suggested by Canada et al.⁹ satisfying these criteria is ⁷⁵Se and ⁵⁷Co. We used these isotopes, which emit gamma rays at 121.05 and 122.05 keV, respectively, in our experiments.

Experimental Design

Since one of the objectives of the experiments was to simulate on-line measurements of plutonium in process streams, a small flow system was built and set up in a glove box as shown in Fig. 5. A horizontally mounted germanium detector was located outside the box and viewed the cells through a rubber diaphragm mounted in one of the ports of the glove box. The remaining part of the

system was a computer-based gamma spectrometer system which was used to acquire and interpret the spectra (see Fig. 6).

CELL DESIGN

Since two types of measurements were required, a configuration containing two cells was designed. The cells were made of quartz glass and connected with tubing. The solution

Fig. 5. Photograph of the experimental arrangement in the glove box. The detector is located outside of the box at the left side of the figure.

was circulated through the cells and the dilution reservoir by a peristaltic pump.

The direct counting cell was placed closest to the detector and had a volume of 0.3 millilitres and an inside thickness of 0.11 cm. The transmission cell had a diameter of

0.8 cm i.d. and was 3.57 cm long. An approximate length between 3 and 4 cm was arrived at by considering two competing parameters of the transmission measurement. One was the sensitivity of change in peak height ratio to change in plutonium concentration (dR/dC increases with concentration as shown in Fig. 7). The other was the limited range for which accurate peak height ratios can be measured, which limits the concentration range that can be assayed. We chose to conduct our experiments in the 150- to 300-g/litre concentration range with a sensitivity of about 2 to 3% change in peak height ratio for a 1% change in concentration.

We also needed to design a shutter that would selectively discriminate between the cells. The configuration is schematically shown in Fig. 8; a picture of the partially assembled

Fig. 6. Computer-based gamma spectrometer used for acquiring and reducing the spectral data.

Fig. 7. The plutonium concentration is linearly related to the logarithm of the 122/121-keV peak intensity ratios. The sensitivity, $\Delta R/\Delta C$, increases with total plutonium content.

apparatus is shown in Fig. 9. In the first position, the detector views the entire area of the small thin cell but is shielded from all other sources of radiation. A spectrum taken in this configuration provides data on the isotopic content of the solution by direct counting of the solution. In the second position, the viewing aperture for the small cell is reduced to a 0.5-cm diameter, and a collimating port of the same dimension is opened to the transmission cell. In this mode, the total gamma radiation level from the source is reduced by the collimation to enhance the measurement of the two transmission gamma rays. A 0.6-g/cm^2

Cd absorber was used in front of the detector to further reduce low-energy radiation originating in the solution. The ^{75}Se - ^{57}Co source for the transmission gamma rays contained approximately 0.4 mCi of ^{75}Se and 1.6 mCi of ^{57}Co . The gamma rays from the source were directed toward the transmission cell and detector by a 0.5-cm-diameter collimation hole in the lead shield surrounding the source.

DETECTOR SYSTEM

The gamma-ray system consisted of a small, high-resolution Ge detector and a computer-based pulse height analyzer. The detector was about 1 cm^3 in volume and had a resolution of 530 eV FWHM at 122 keV. The system was operated with a shaping time constant of 6 μs and a gain of 0.075 keV per channel. The pulse height distribution was accumulated in 4096 channels. A pulse height stabilizer was used to minimize zero and gain shifts, and a Camberra model 1468 livetime corrector/pileup rejector was also incorporated to improve the performance of the system. The measured livetime error as a function of count rate is shown in Fig. 10. The count rate in the experiments did not exceed 14 000 counts per second. At this count rate, the resolution deteriorated to 545 eV FWHM. These small changes in resolution are accounted for in the analysis programs.

Fig. 8. Schematic of the experimental arrangement. (a) shows the direct counting configuration and (b) shows the configuration for the transmission measurement.

Fig. 9. Photograph of the component parts of the experimental arrangement. The solution is loaded into the mixing reservoir and pumped through the two counting cells. The lead shutter differentiates between the two counting arrangements.

Fig. 10. System error in measuring the true livetime of a count as a function of count rate.

Experimental Procedures

We dissolved approximately 5 g of plutonium oxide and measured the isotopic abundances shown in Table 2 by mass spectrometry. For the first experiment, the ^{237}U and ^{241}Am were removed with chemical procedures using ion exchange columns to produce a solution simulating reprocessing plant conditions. The resulting solution had a concentration of 360 g/litre in 3N HNO_3 . Eight millilitres of this solution was accurately pipetted into the reservoir of the system, and the solution was circulated by a peristaltic pump. After the solution in the cells was counted, a known dilution of the solution was made using 3N HNO_3 to permit a measurement at a new concentration. Four separate spectra were generally taken during each counting period, two counts for each cell configuration. That is, two duplicate spectra were taken of the thin cell and similarly, two transmission measurements were made. Many replicate spectra were taken during nighttime periods, and these were used to study the precision of the analyses as well as drifts in the system.

In this way spectral measurements were taken at plutonium concentrations ranging from about 350 g/litre down to about 140 g/litre. The spectra

were analyzed using computer programs that had been specifically written to reduce and interpret them.

The second experiment was conducted in essentially the same way. However, in this case, the ^{237}U was in secular equilibrium with its ^{241}Pu parent, and ^{241}Am was added to the solution so that it simulated plutonium that had aged about 1.5 years since chemical processing.

A ^{238}Pu monitor was also added to the experimental setup because small drifts in detector efficiency were noted in the first experiment (see later discussions). The ^{238}Pu was periodically counted to monitor changes in the counting efficiency.

Table 2. Isotopic content of plutonium used in experiments.

Isotope	Abundance (%) ^a
^{238}Pu	0.230
^{239}Pu	76.06
^{240}Pu	19.09
^{241}Pu	2.98
^{242}Pu	1.64

^aDetermined by mass spectrometry.

Discussion of Results

EXPERIMENT USING RECENTLY REPROCESSED PLUTONIUM

The starting volume in both experiments was 8 millilitres. In the first experiment, the initial concentration was 360 g/litre, and eleven subsequent dilutions were made so that the final concentration was 130.1 g/litre. The measurements and dilutions were made over three days and two nights.

Gamma Transmission Results

Figure 11 shows the spectral region of the two transmission gamma rays. We observed a rather high and sloping background in front of the peak doublet, but we did not discover the cause for this until the experiment had been completed. At that time, we found that if the ^{75}Se - ^{57}Co source was backed away from the collimating hole of its container, then the background level dropped considerably. The obvious conclusion was that the 122-keV gamma rays of ^{57}Co were being scattered through low angles from the surfaces of the collimator. The slightly degraded Compton radiations were now below the absorption edge of plutonium and were no longer severely attenuated by the solution. Figure 12 shows this effect when only a ^{57}Co source is used in two differing

positions with respect to the collimating hole.

The fact that the above phenomena had occurred in this experiment, and indeed will always occur to some extent, complicated the exact shape of the background continuum under the peaks. The two essential components of this continuum are shown in Fig. 13. Qualitatively, the first component describes smoothed discontinuities in the background, centered at the respective peak positions with step proportional to the intensities. This component is related to the gamma-ray interaction process in the detector. The second is due to the differential transmission of the gamma-ray continuum. It results in an increasing background level with a smoothed discontinuity occurring at the K-shell absorption edge of plutonium.

To remove the effects of the background continuum, we wrote an algorithm so that the resulting net counts for the peak doublet could be fitted by our standard peak fitting techniques. We achieved calibration by taking the peak height ratios (R) corrected for isotopic decay of the ^{75}Se and ^{57}Co sources and the concentrations (C) calculated from known dilution factors ("book" values).

Fig. 11. Typical intensity distributions of transmitted peaks as a function of plutonium concentration.

Fig. 12. The upper spectrum shows the effect of scattering material around the transmission source. The resulting high continuum level can be reduced, as shown by the lower spectrum, by minimizing the sources of low-angle scattering.

Fig. 13. The background continuum under the gamma-ray doublet is quite complex, consisting of steps at the peak positions (a) and (c) as well as a step at the absorption edge itself (b).

These were fitted by the method of least squares using the equation

$$C_i = a + b \ln (K_1). \quad (5)$$

The resulting calibration constants, a and b , were used to calculate the

experimental concentrations from each peak height ratio measurement. These values are compared to the book values shown in Table 3. With a few exceptions, the differences do not greatly exceed the statistical uncertainty

Table 3. Results of differential transmission measurements on recently separated plutonium solutions.

Run No.	Count time (min)	Peak height ratio (122 keV/121 keV)	Pu concentration (g/litre)		
			Book value	Measured	% difference
1a	20	0.1097 (1.3) ^a	360.0	355.1 (0.4) ^a	-0.26
1b		0.1121		357.1	-0.80
2a	20	0.1497 (1.0)	331.0	331.4 (0.35)	0.12
2b		0.1500		331.2	0.07
3a	20	0.1954 (0.85)	306.4	307.8 (0.3)	0.45
3b		0.2000		305.7	-0.23
4a	20	0.2490 (0.75)	285.1	286.2 (0.25)	0.37
4b		0.2507		285.6	0.16
5a	60	0.3091 (0.4)	266.7	267.0 (0.15)	0.12
5b		0.3078		267.4	0.26
5c		0.3075		267.4	0.29
5d		0.3073		267.5	0.31
5e		0.3072		267.5	0.32
6a	20	0.3703 (0.5)	250.4	250.9 (0.25)	0.20
6b		0.3710		250.8	0.13
7a	20	0.4406 (0.5)	236.1	235.5 (0.25)	-0.25
7b		0.4374		236.1	0.03
8a	20	0.5739 (0.4)	211.8	212.0 (0.2)	0.11
8b		0.5777		211.4	-0.17
9a	20	0.7261 (0.35)	192.0	191.1 (0.2)	-0.48
9b		0.7292		190.7	-0.68
10a	20	0.8602 (0.35)	175.6	176.0 (0.2)	0.23
10b		0.8622		175.8	0.11
11	40	1.173 (0.3)	149.4	148.4 (0.2)	-0.67
12	40	1.471 (0.3)	130.0	128.2 (0.2)	-1.37
Relative standard deviation (σ) = 0.44					

^aNumbers in parentheses show approximate % error for the indicated values in the group.

assigned to the measurement. However, there does appear to be a small but definite nonlinearity to the fit as Fig. 14 shows. This phenomenon was also observed in some of the other experimental measurements; possible

explanations will be presented later. If an additional degree of freedom is permitted in the least-squares fitting, the relative standard deviation of the error can be reduced to approximately 0.3%.

Fig. 14. Comparison of the total plutonium concentration in recently separated solutions as determined from transmission measurements with values calculated from known dilution factors. Small but definite nonlinearity is noted at the extremes of the range. $\sigma = 0.44\%$ linear fit, 0.30% cubic fit.

During the first nighttime period, we took repetitive counts of the transmission measurement. The results are included in Table 3 as entries 5a through 5e. These counts indicate that a precision approaching 0.1% can be achieved if sufficiently good counting statistics are acquired.

Direct Counting Results

Our experiment was designed not only to obtain data for isotopic ratio measurements but also to obtain quantitative assays for the measurable plutonium isotopes. Because ^{242}Pu is not directly measurable by gamma spectrometry, we planned an indirect estimate of its abundance by subtracting the directly counted values of ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{241}Pu from

the total assay obtained by the differential transmission technique. This required considerable care in calibrating the detector, in characterizing the operating performance of the system hardware and in writing analysis software that would properly interpret the resulting spectra.

One detail we did not consider in the first experiment was that the detector efficiency might drift slightly with time. We had experienced changes of several percent in the efficiency of small intrinsic and lithium-drifted detectors in the past, but we had noted that these occurred when the detectors were new and that the effects were over considerable time periods. To our knowledge, small changes in efficiency of 1% or less over short periods of time (i.e., a few days) have not been studied.

During the second nighttime period, we took repeated counts of the thin, direct-counting cell. The change in the counting results is shown in Fig. 15. Subsequent experiments seem to confirm that the efficiency of small detectors can vary with time (see Fig. 16). We believe this is due to small changes in the surface states of the detector that affect the efficiency with which events occurring near the surface are collected.^{4,10}

Having noted that the detector efficiency did apparently drift during

Fig. 15. Repetitive counts of the direct counting cell indicate an efficiency drift of about 0.5% during an overnight period of time.

Fig. 16. Repetitive counts of a ^{238}Pu monitor over several days confirm that efficiency drifts of about 1% can occur.

the course of the experiment, we renormalized the original data so that the last count of one day agreed with the beginning count of the succeeding day taken at the same concentration.

An approximate calibration was made for the various detector efficiency parameters, and the resulting analyses

were fitted by least squares to the true concentration value. A linear fit made in this way gave agreement, as shown by Table 4 and Fig. 17. Two results to be noted in the fit are that there is a definite nonlinear component in the measurement and that the intercepts are not at the origin. Several possible causes can be postulated for these results and additional experiments will be required to fully understand the problem. Even so, the results are encouraging and, as Table 4 and Fig. 17 show, the fit improves significantly with one additional degree of freedom.

Results of Isotopic Ratio Measurements

The experiment also allowed us to study the precision with which isotopic ratio measurements can be made as a function of plutonium concentration. The measurements are summarized in Table 5. The isotopic abundances show very little change with concentration. The standard deviation calculated from the reproducibility, however, appears to be somewhat worse than that permitted by statistical error alone, implying that either the procedures used for determining the uncertainties in the measured values are not exact or that nonstatistical sources of error are present.

The ^{242}Pu isotopic content reported in Table 5 was not determined by direct counting but was calculated

Table 4. Results of direct gamma counting of recently separated plutonium solutions.

Run No.	Count time (min)	Book value	Pu concentration excluding ^{242}Pu (g/litre)			
			Measured ^a	% difference	Measured ^a	% difference
1a	10	354.1	353.0	-0.32	354.1	0.00
1b			353.9	-0.05	355.1	0.28
2a	10	325.6	324.1	-0.47	324.4	-0.37
2b			324.9	-0.20	325.3	-0.09
3a	10	301.3	300.2	-0.39	300.0	-0.44
3b			301.6	0.09	301.5	0.05
4a	10	280.5	281.8	0.48	281.4	0.34
4b			280.7	0.09	280.3	-0.07
5	10	262.3	263.2	0.34	262.6	0.12
6a	12	246.3	247.3	0.40	246.7	0.13
6b			247.5	0.48	246.9	0.22
7a	12	232.2	233.6	0.58	232.9	0.30
7b			233.1	0.41	232.5	0.13
8a	15	208.3	208.6	0.16	208.1	-0.09
8b			208.8	0.25	208.3	0.00
9a	15	188.9	188.18	-0.05	188.5	-0.20
9b			188.6	-0.13	188.3	-0.28
10	60	172.7	172.4	-0.19	172.4	-0.19
11	30	147.0	145.8	-0.80	146.4	-0.39
12a	30	128.0	127.0	-0.77	128.1	0.14
12b	15		127.4	-0.46	128.5	0.44
Relative standard deviation $\sigma = 0.41$						$\sigma = 0.26$

^aThe first column of measured values shows a linear fit whereas the second column shows a cubic fit. The error in the measured values due to counting statistics is about 0.1%.

from the difference in value between the total plutonium concentration measured by the differential attenuation technique and the isotopic sum value of measurable plutonium isotopes by direct counting.

EXPERIMENT USING AGED PLUTONIUM

The experiment using aged plutonium solution was conducted in much the same way as the preceding experiment. However, in this experiment, we counted a ^{238}Pu sample periodically

Table 5. Isotopic ratio measurements of recently separated plutonium solutions.

Run No.	Total concentration	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	$^{242}\text{Pu}^a$
1a	360.0	0.2229	76.070	19.08	3.022	1.39
1b		0.2305	76.064	19.11	2.992	0.56
2a	331.0	0.2313	75.919	19.22	3.032	2.11
2b		0.2306	76.028	19.13	3.009	1.78
3a	306.4	0.2317	75.947	19.20	3.017	2.54
3b		0.2306	76.009	19.16	3.005	1.37
4a	285.1	0.2317	76.101	19.09	2.997	1.68
4b		0.2327	75.992	19.13	3.042	1.86
5a	266.7	0.2305	75.987	19.16	3.022	1.83
5b		0.2315	76.037	19.10	3.034	-
6a	250.4	0.2313	75.987	19.17	3.008	1.68
6b		0.2309	76.081	19.09	2.997	1.56
7a	236.1	0.2310	76.058	19.10	3.009	1.40
7b		0.2309	76.112	19.04	3.017	1.52
8a	211.8	0.2316	76.009	19.16	2.996	1.84
8b		0.2302	76.052	19.09	3.030	1.46
9a	192.0	0.2321	76.003	19.14	3.026	1.35
9b		0.2301	76.054	19.09	3.023	1.25
10a	175.6	0.2316	76.119	19.04	3.009	2.00
10b		0.2316	76.088	19.05	3.011	-
10c		0.2322	76.088	19.06	3.009	-
10d		0.2319	76.112	19.05	2.998	-
10e		0.2330	76.088	19.06	3.012	-
10f		0.2323	76.114	19.04	3.005	-
10g		0.2329	76.131	19.03	2.992	-
10h		0.2325	76.051	19.09	3.008	-
10i		0.2335	76.093	19.06	3.004	-
10j		0.2336	76.023	19.10	3.016	-
11	149.4	0.2330	76.004	19.15	3.018	1.34
12a	130.0	0.2327	76.002	19.16	3.007	-0.23
12b		0.2291	76.001	19.16	3.010	-
Average		0.2317	76.046	19.10	3.011	1.51
Relative standard deviation		±0.46%	±0.07%	±0.26%	±0.45%	±38%

^aThe isotopic values for ^{242}Pu were not obtained by direct measurements but by subtracting the direct counting measurements of Table 4 from the differential transmission measurements of Table 3.

Fig. 17. Comparison of plutonium isotopic sum (exclusive of ^{242}Pu) from direct counting of recently separated solution with values calculated from known dilution factors. A nonlinearity similar to that shown in Fig. 14 appears to be present. $\sigma = 0.41\%$ linear fit, 0.26% cubic fit.

to monitor the stability of the counting efficiency. The results of these counts are shown in Fig. 18. The data are somewhat ambiguous but, as in the first experiment, small changes in counting efficiency are apparent. The starting concentration for this experiment was 350.4 g/litre. Eleven dilutions were made resulting in a final concentration of 146.0 g/litre.

Gamma Transmission Results

In this experiment, the ^{75}Se - ^{57}Co source was backed away from the collimating hole of its shield. This

Fig. 18. Results of the ^{238}Pu monitor during the second experiment.

reduced but did not completely eliminate the low-angle scattering of the 122-keV radiation of ^{57}Co . The analysis and interpretation of the two transmission gamma rays was similar to that described for the first experiment. The peak height ratios

and true values of the concentration were again fitted by least squares to Eq. (5), resulting in a fit as shown in Table 6 and Fig. 19. The relative standard deviation of the error of 0.35 is similar to that obtained in the first experiment and appears to

Table 6. Results of differential transmission measurements on aged plutonium solutions.

Run No.	Count time (min)	Peak height ratio (122 keV/121 keV)	Pu concentration (g/litre)		
			Book value	Measured	% difference
1a	20	0.3472 (1.0) ^d	350.4	349.0 (0.3) ^a	-0.40
1b		0.3513 (0.8)		347.9 (0.2)	-0.71
2a	30	0.4656 (0.6)	322.2	322.3 (0.2)	0.02
2b		0.4628		322.8	0.19
3a	30	0.6040 (0.6)	298.2	298.6 (0.2)	0.12
3b	15	0.6031 (0.7)		298.7	0.17
4	60	0.7519 (0.3)	277.5	278.6 (0.1)	0.40
5a	45	0.9095 (0.3)	259.5	261.3 (0.2)	0.68
5b	51	0.9142		260.8	0.50
6a	26	1.107 (0.4)	243.7	243.4 (0.1)	-0.12
6b	28	1.096		244.3	0.23
7a	30	1.288 (0.4)	229.8	229.6 (0.1)	-0.10
7b	35	1.285		229.8	-0.01
8a	32	1.663 (0.3)	206.1	206.3 (0.1)	0.09
8b	21	1.664 (0.4)		206.2 (0.2)	0.07
9a	72	2.052 (0.2)	186.9	187.2 (0.1)	0.14
9b	97	2.052		187.2	0.14
10a	200	2.450 (0.1)	170.9	171.0 (0.05)	0.07
10b	200	2.448		171.1	0.11
10c	182	2.450		171.0	0.07
11a	15	2.869 (0.3)	157.5	156.6 (0.2)	-0.55
11b	20	2.874		156.5	-0.65
12a	60	3.246 (0.2)	146.0	145.4 (0.1)	-0.42
12b		3.245		145.4	-0.40

Relative standard deviation (σ) = 0.35

^aNumbers in parentheses show approximate % error for the indicated values.

Fig. 19. Comparison of total plutonium concentration from transmission measurements of aged solution with values calculated from known dilution factors. $\sigma = 0.35\%$.

be only slightly greater than the statistical uncertainties associated with the individual measurement. The most pronounced deviations appear to be at the extremes of the concentration range, indicating that the non-linearity may be due to the imbalance in the relative intensities of the two peaks.

Direct Counting Results

Direct measurement of plutonium isotopes in aged material is more difficult than it is for recently processed solution. This is because the presence of ^{237}U and ^{241}Am obscures the low-energy part of the spectrum and complicates other parts. To compensate, longer counting periods are required to obtain the desired accuracy, and a more sophisticated computer program is necessary to interpret the spectra.

After we determined the detector system parameters and efficiency coefficients required by the analysis program, the spectra were interpreted by the computer and the results were compared with known concentration values. As in the first experiment, we had to renormalize the data at certain points in the experiment. In this experiment, the ^{238}Pu monitor indicated the direction and magnitude of the drift of counting efficiency. The only renormalization that appeared justified was after a weekend, during which repetitive counts were taken. A linear fit of the experimentally measured values and true values is shown in Table 7 and Fig. 20. The relative standard deviation approached 0.25% in this experiment with very little indication of nonlinearity. The first coefficient of the linear fit was not, however, equal to zero, indicating that the line did not quite pass through the origin.

Results of Isotopic Ratio Measurements

The analysis program for this case computes assay results for ^{241}Am as well as for the isotopes of plutonium. The individual results are given in Table 8 from which relative standard deviations can be calculated. As with the first experiment, there is very little bias in isotopic results with change in plutonium concentration.

Table 7. Results of direct gamma counting of aged plutonium solutions.

Run No	Count time (min)	Pu concentration excluding ^{242}Pu (g/litre)		
		Book value	Measured	% difference
1a	30	344.8	345.5 (0.3) ^a	0.19
1b	20		344.1 (0.4)	-0.22
2a	180	317.1	317.4 (0.15)	0.11
2b			317.3	0.07
2c			318.0	0.28
3a	30	293.4	293.8 (0.3)	0.14
3b			292.2	-0.40
4	75	273.0	272.7 (0.2)	-0.13
5a	180	255.3	254.7 (0.15)	-0.25
5b			254.7	-0.22
5c			255.0	-0.12
6a	76	239.8	239.8 (0.2)	0.02
6b	75		240.4	0.24
7a	200	226.1	225.6 (0.15)	-0.24
7b			225.9	-0.09
7c			226.2	0.06
8a	144	202.7	202.7 (0.2)	0.01
8b	90		203.9	0.61
9a	300	183.9	183.4 (0.1)	-0.30
9b			183.8	-0.04
10a	83	168.2	168.9 (0.2)	0.40
10b	76		168.9	0.42
11a	214	155.0	154.5 (0.15)	-0.30
11b	153		154.9 (0.2)	-0.08
12a	300	143.7	143.7 (0.15)	0.02
12b			143.5	-0.16
Relative standard deviation (σ) = 0.25				

^aNumbers in parentheses show approximate % error for the indicated values.

Fig. 20. Comparison of plutonium isotopic sum (excluding ^{242}Pu) from direct counting of aged solution with values calculated from known dilution factors. $\sigma = 0.25\%$.

Table 8. Isotopic ratio measurements of aged plutonium solutions.

Run No.	Total Pu concentration	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{241}Am	$^{242}\text{Pu}^a$
1a	350.4	-	76.08	19.12	2.970	0.1759	1.00
1b		-	76.00	19.19	2.986	0.1769	1.09
2a	322.2	-	76.12	19.11	2.970	0.1758	1.52
2b		-	76.17	19.06	2.973	0.1764	1.71
2c		-	76.24	19.00	2.970	0.1763	-
3a	298.2	0.2320	76.06	19.18	2.967	0.1753	1.61
3b		0.2322	76.05	19.18	2.986	0.1766	2.18
4	277.5	0.2319	76.02	19.21	2.980	0.1760	1.73
5a	259.5	0.2312	76.13	19.10	2.982	0.1760	2.54
5b		0.2296	76.13	19.10	2.982	0.1765	2.35
5c		0.2313	76.07	19.16	2.984	0.1765	-
6a	243.7	0.2311	76.14	19.10	2.980	0.1757	1.48
6b		0.2303	76.08	19.16	2.977	0.1754	1.60
7a	299.8	0.2304	76.11	19.12	2.989	0.1761	1.74
7b		0.2307	76.12	19.11	2.985	0.1761	1.70
7c		0.2304	76.11	19.12	2.982	0.1760	-
8a	206.1	0.2298	76.18	19.06	2.975	0.1753	1.75
8b		0.2286	76.11	19.14	2.965	0.1748	1.11
9a	186.9	0.2307	76.08	19.16	2.988	0.1754	2.00
9b		0.2296	76.16	19.08	2.980	0.1753	1.82
9c		0.2292	76.12	19.11	2.985	0.1757	-
9d		0.2296	76.06	19.17	2.982	0.1750	-
9e		0.2295	76.16	19.07	2.989	0.1755	-
9f		0.2294	76.13	19.10	2.982	0.1751	-
9g		0.2305	76.13	19.10	2.988	0.1757	-
9h		0.2288	76.20	19.04	2.984	0.1755	-
9i		0.2304	76.15	19.08	2.982	0.1751	-
9j		0.2295	76.12	19.11	2.978	0.1751	-
10a	170.9	0.2291	76.15	19.10	2.971	0.1741	1.23
10b		0.2284	76.13	19.11	2.976	0.1745	1.23
11a	157.5	0.2291	76.23	19.00	2.983	0.1746	1.33
11b		0.2288	76.17	19.06	2.982	0.1751	1.02
12a	146.0	0.2293	76.14	19.09	2.985	0.1751	1.16
12b		0.2293	76.15	19.08	2.986	0.1754	1.30
		0.2339	76.12	19.11	2.980	0.1755	1.57
Relative standard deviation = $\pm 0.44\%$			$\pm 0.065\%$	$\pm 0.26\%$	$\pm 0.23\%$	$\pm 0.38\%$	$\pm 26\%$

^aThe isotopic values for ^{242}Pu were not obtained by direct measurements but by subtracting the direct counting measurements of Table 7 from the differential transmission measurements of Table 6.

Conclusions

The overall results of these experiments are very encouraging. They demonstrate that plutonium concentration and isotopic measurements can be made to within 0.25 to 0.5%. However, the results only indicate the applicability of the technique. Many more experiments must be made to investigate the effect of changing parameters held constant in these experiments, e.g., the isotopic abundances, and to improve upon those parts of the experimental design or procedures that we know to be weak or not adequately understood.

For example, we do not fully understand the slight nonlinear response in some of the data. One possible explanation is that the dilution procedures were not sufficiently accurate, or that evaporation or temperature changes affected the concentration of the solution. Some credibility is given to this possibility by the fact that a 200-microlitre portion of solution was removed from circulation toward the end of the first experiment. When it was analyzed in the same way that the initial starting solution was analyzed, we obtained a somewhat higher value of 176.9 g/litre as compared to a book value of 175.6 g/litre. This evidence was not used to renormalize any data. However, it does indicate that the

actual concentrations may indeed be different from those calculated from dilution factors.

Greater attention must also be given to the proper way of measuring peak height ratios from the transmission experiments. Although we are confident that our methods of peak fitting are accurate, we need to study in greater detail the change in the intensity of the Compton continuum at the K-shell binding energy of plutonium. An improper delineation of the continuum source under the peak doublet may be responsible for some of the nonlinearity in this measurement, particularly at the extremes of the range where the peak height ratio is quite different from 1.

In future experiments we will also try to make independent measurements for each of the two gamma rays. This will reduce the problem in describing the background and eliminate the imbalance in peak height ratio at the extremes of the concentration range. However, it will require two separate counts for which we will need highly stable detector and counting systems.

Other sources of nonlinearity in the direct measurement technique may be inaccuracies in the livetime correction or inaccurate algorithms used for making self-attenuation corrections. However, these possible

sources of error have been carefully checked and found to present no obvious problems.

In general, the sizes of the cells and dimensions used in the experiment were approximately correct. However, the count rate experienced in measuring the chemically separated plutonium solution in the first experiment was initially too high. Therefore the distance between the detector and the cell was increased from about 0.5 cm to about 1.5 cm to reduce the count rate to an acceptable level. Also, in future experiments of this type, it would be helpful to increase the signal level of the two gamma rays in the transmission measurement. This can be done by increasing the source strength and by making a corresponding reduction in the area of the collimating hole.

We believe that the most difficult assay in our experiments is the quantitative measurement of the four

plutonium isotopes observed by direct counting. Our principal reason for making the measurements rigorously quantitative is so that the ^{242}Pu isotopic content could be deduced from the difference between the direct isotopic counting and the differential transmission measurements. However, studies are in progress to develop algorithms which can compute the ^{242}Pu content based on isotopic correlation techniques.¹¹ If this approach is successful, quantitative isotopic measurements will not be required and the measurement will be reduced to determining isotopic ratios, a measurement quite easily and accurately made by gamma spectrometry.

It therefore appears possible to perform a complete and quantitative in-line measurement for plutonium using a combination of techniques and methods that are nondestructive and can be automated.

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Appendix

Plutonium isotopic concentrations can be assayed by direct counting of the gamma rays that are emitted by the solution. A problem arises, however, in determining the attenuation of the gamma rays in traversing a relatively thick sample without knowing *a priori* the plutonium concentration of the solution. We developed the following approximate solution to the problem using the intensities of the peaks representing the respective isotopes present, the respective absorption coefficients (μ_i) and the counting efficiencies (ϵ_i) corresponding to a plutonium concentration approaching zero. Ignoring geometric considerations, we can express the observed counting activity as follows:

$$\text{Activity (A)} = \epsilon \int_0^X \exp(-\mu l) dl \quad (1)$$

$$(A) = \epsilon/\mu [1 - \exp(-\mu X)] \quad (2)$$

where X = amount of plutonium present. The true total activity, A° , is given by

$$A^\circ = \epsilon X . \quad (3)$$

Therefore,

$$A/A^\circ = (1/\mu X) [1 - \exp(-\mu X)] \quad (4)$$

or

$$A^\circ = A\mu X/[1 - \exp(-\mu X)] . \quad (5)$$

The total concentration of plutonium is simply the sum of the isotopic components, hence,

$$X = \sum_{i=1}^n x_i = \sum_{i=1}^n \frac{A^\circ_i}{\epsilon_i} . \quad (6)$$

Substituting Eq. 5, we obtain

$$X = \sum_{i=1}^n \frac{A_i \mu_i X}{\epsilon_i [1 - \exp(-\mu_i X)]} \quad (7)$$

or

$$1 = \sum_{i=1}^n \frac{A_i \mu_i}{\epsilon_i [1 - \exp(-\mu_i X)]} \quad (8)$$

We now assume that one of the components, hence one term in Eq. (8), is dominant and therefore isolate it from the other terms. For example,

$$1 = \frac{A_1 \mu_1}{\epsilon_1 [1 - \exp(-\mu_1 X)]} + \sum_{i=2}^n \frac{A_i \mu_i}{\epsilon_i [1 - \exp(-\mu_i X)]} \quad (9)$$

Solving for X, we derive

$$X = -\frac{1}{\mu_1} \ln \left[1 - \sum_{i=1}^n \frac{A_i \mu_i}{\epsilon_i} \frac{1 - \exp(-\mu_i X)}{1 - \exp(-\mu_1 X)} \right] \quad (10)$$

The solution of this equation requires an initial estimate of the plutonium concentration, X, that can be used in the exponential terms in the righthand portion of the equation. We estimate this concentration by assuming that $\mu_i = \mu_1$. Then

$$X \text{ (estimated)} = -\frac{1}{\mu_1} \ln \left(1 - \mu_1 \sum \frac{A_i}{\epsilon_i} \right) \quad (11)$$

After summing the A_i/ϵ_i values, an initial estimate for X can be used in Eq. (10). The final value of X is then calculated using Eq. (10).