

LEGIBILITY NOTICE

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

JUN 07 1989

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

LA-UR--89-1862

DE89 013465

TITLE POOR MAN'S DENSITOMETRY

AUTHOR(S) S.-T. Haue and R. Zhu

SUBMITTED TO Institute of Nuclear Materials Management
INMM Annual Meeting
Orlando, Florida
July 9-12, 1989
(FULL PAPER)

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By the acceptance of this article the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545



POOR MAN'S DENSITOMETRY

S.-T. Hsue and R. Zhu

Los Alamos National Laboratory

Los Alamos, NM 87545

ABSTRACT

We have developed two novel methods of determining plutonium concentrations (and isotopic distribution) that require no external radioactive sources or x-ray generators but rely only on the natural radiation from the plutonium. The methods are ideally suited to assay reasonably pure plutonium solutions, such as product solutions of reprocessing plants and eluate solutions from anion exchange columns. The methods can be applied to aged or freshly separated plutonium and can be used to measure plutonium concentrations in pipes or tanks. Because these methods do not require expensive equipment, we call them "Poor Man's Densitometry."

INTRODUCTION

An accurate measurement of plutonium concentration in a sample is always necessary for nuclear material control and accounting. This paper discusses two novel methods of determining plutonium concentration (and isotopic distribution) that require no external radioactive sources or x-ray generators but rely only on natural radiation. The methods are ideally suited to assay reasonably pure plutonium solutions, such as the product solutions of reprocessing plants and the eluate solutions from anion exchange columns. The methods can be applied to aged or freshly separated plutonium and can be used to measure plutonium concentrations in pipes or tanks.

The experimental work presented in this paper arises from an attempt to get as much information as possible from the natural radiation emitted by plutonium. There are several non-destructive assay (NDA) methods to determine the plutonium isotopic distribution,¹ which are highly successful with assay precision and accuracy approaching that of mass spectrometry. The question is, "Can the concentration also be determined from the natural radiation?"

Three NDA methods have been employed in the past to assay the plutonium concentration: (a) the passive counting technique,² (b) x-ray fluorescence,³ and (c) absorption-edge densitometry.⁴ For a wide concentration range (for example, 5 g/L to 300 g/L), both the passive-counting and the x-ray

fluorescence techniques require correction for the sample attenuation. This is usually accomplished by measuring the transmission of one or more gamma peaks from external source(s) through the solution. Both methods are also sensitive to rate loss variations in the counting rate; the rate loss correction is usually accomplished by monitoring the emission rate of a gamma ray from another external source. Absorption-edge densitometry measures the transmission above and below the edge; either radioactive sources or an x-ray generator is used to provide the source for the transmission measurement. In short, all existing NDA techniques require external radiation sources.

The purpose of this work is to explore the methods of determining the plutonium concentration from the gamma rays and x-rays emitted by plutonium without relying on external sources. Two methods have been developed: the densitometry method and the ratio method. In this paper, we discuss the experimental proofs of principle of these two methods with low-burnup samples. We also discuss the properties of these two techniques. Finally, we discuss the potential application of these techniques.

FIRST NOVEL METHOD--DENSITOMETRY

The first method of plutonium concentration determination without external sources utilizes the MGA2 isotopic program developed by R. Gunnink of Lawrence Livermore National Laboratory.⁵ In MGA2, a relative efficiency curve is fitted with 10 peaks (59, 94, 101, 103, 110, 129, 148, 165, 203, and 208 keV) from 59 keV to 208 keV, including the discontinuity at the plutonium K-absorption edge at 121.8 keV. Detailed discussion of the method can be found in Ref. 5. For a fixed-solution sample thickness, the magnitude of the discontinuity should be proportional to the plutonium concentration.

To test this hypothesis, a set of low-burnup plutonium solutions was prepared with concentrations ranging from 100 to 320 g/L. Each sample contained 18 mL of plutonium solution with a sample thickness of 1.772 cm in a cylindrical (3.5-cm-diam) vial. The solution was viewed by an

up-looking LEPS detector with a 2-cm³ active volume. The experimental setup is shown in Fig. 1. The measurement time for each sample to was 10 000 s, and was repeated eight times. The error quoted in this work is the standard deviation of the repeated runs. The results, shown in the top part of the Table I, indicate that the plutonium concentration could be determined reasonably well by the K-edge discontinuity determined by MGA2. Encouraged by the results, another four samples with the same isotopic distribution but different concentrations were prepared. These samples were measured in a second setup somewhat different from the first, shown in Fig. 2; the sample-to-detector distance was different, and the low-Z absorber between the solution and detector was also different. The results, shown in the bottom part of Table I, were in good agreement with the first four samples with the exception of the two samples with <30 g/L.

We found that the discontinuity is proportional to the plutonium concentration for a fixed sample thickness. Excluding the two samples with <30 g/L concentrations, the plutonium concentration can be determined by this method to 1.9% with a precision of ~1.5% in a 10 000-s assay. The rationale for excluding these two samples is that this method is similar to the regular densitometry method,⁴ which loses precision rapidly below 30 g/L. The 21% bias from this method could be due

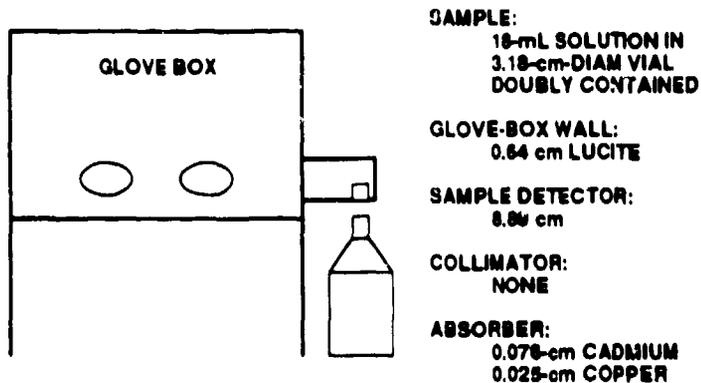


Fig. 1. First experimental setup for the measurement.

TABLE I. Comparison

Chemistry (g/L)	Densitometry (g/L)	Densit/Chem	Error (%)	
107.559	83.30	0.774	2.77	1st Setup
179.285	141.15	0.787	1.97	
243.703	195.88	0.804	0.78	
316.844	247.35	0.781	1.37	
12.67	6.49	0.512*	21.7	2nd Setup
27.880	18.06	0.648*	23.4	
63.370	48.53	0.766	1.70	
139.410	112.87	0.810	1.32	
107.559	84.09	0.782	1.38	
179.287	142.21	0.793	0.86	
	Av	0.787		
	RSD	1.87%		

* Excluded

SAMPLE:
18-mL SOLUTION IN
3.18-cm DIAM VIAL
DOUBLY CONTAINED

GLOVE-BOX WALL:
NONE

SAMPLE DETECTOR:
7.62 cm

COLLIMATOR:
NONE

ABSORBER:
0.076-cm CADMIUM
0.025-cm COPPER



Fig. 2. Second experimental setup for the measurement.

to the μ values used in the MGA2; different tabulations give different μ values by several percent.⁶⁻⁸ Another possible explanation of the bias could be due to the simplified model used in the MGA2 code to account for the absorption in the three-dimensional solution.

We should also mention that the MGA2 program was developed specifically to determine plutonium isotopic distribution and is therefore not optimized for concentration determination. If the program is tailored to concentration determination, both the method's bias and precision could improve.

SECOND NOVEL METHOD--RATIO METHOD

While the densitometry method can be used to determine the plutonium concentration, the assay time required is relatively long. The second method utilizes the ratio of a pair of gamma- or x-ray peaks--one above the K-absorption edge and one below the edge so that the absorption coefficients are substantially different. The μ values for plutonium of the 129-keV gamma (²³⁹Pu) and the 111-keV x ray (UK β from ²³⁹Pu and ²⁴¹Pu) differ by 2.2 cm²/g. Because of the substantial difference in the μ values, the ratio of the 111/129 peak intensities is a strong function of the plutonium concentration. For a fixed-solution thickness, this function can be used to determine the plutonium concentration. These two peaks are selected for low-burnup plutonium because they bracket the plutonium K-absorption edge and are only 18 keV apart; other peak pairs can also be selected, but the further apart they are in energy, the more sensitive the ratio will be to matrix variations. A typical plutonium spectrum in this energy range is shown in Fig. 3. Observe that the UK β ₁ and UK β ₃ peaks are well separated from the other peaks, and the sum of the these two peaks is used for the 111 x-ray peak.

Experimental Results

To test this method, the 111 net peak area and the 129 net peak area from the previous experimental data were also extracted with the MGA2 code. The experimental 111/129

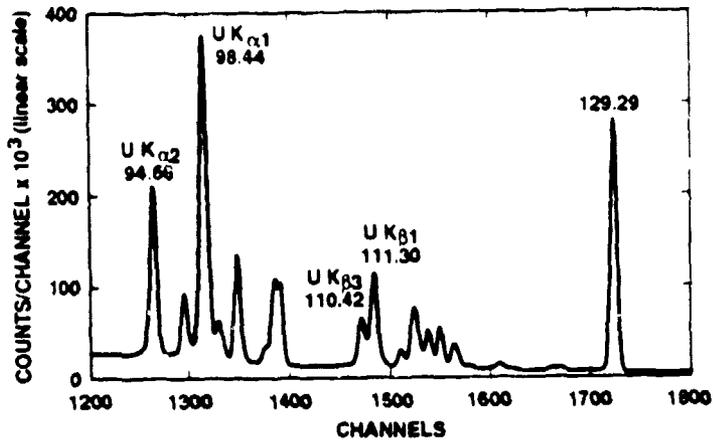


Fig. 3. Typical spectrum from low-burnup plutonium solution in the 94-keV to 129-keV region.

ratio as a function of the plutonium concentration are plotted in Fig. 4. The data can be fitted well with a quadratic curve. The average deviation from the curve is 0.26% for concentrations from 10 g/L to 300 g/L, and the deviation would be <0.2% if we exclude the data from the tilted sample (tilted with respect to the outer vial and, therefore, to the detector). We should emphasize that no normalization or adjustment is required between the data from the two different experimental setups. Figure 5 shows the precision from the ratio method as well as from the previous densitometry method. In general, the precision for the ratio method is a factor of 10 better than the densitometry method. Observe that the precision of the ratio method at 12 g/L is still reasonable--0.8% for a 10 000-s assay or 2.5% for a 1 000-s assay--indicating that the ratio method has a broader useful dynamic range when compared with the densitometry method.

The ratio method should be less sensitive to geometry changes because many factors that affect the absolute counting are cancelled in the ratio method. To test this hypothesis, an experiment was carried out to measure the 111/129 ratio as a

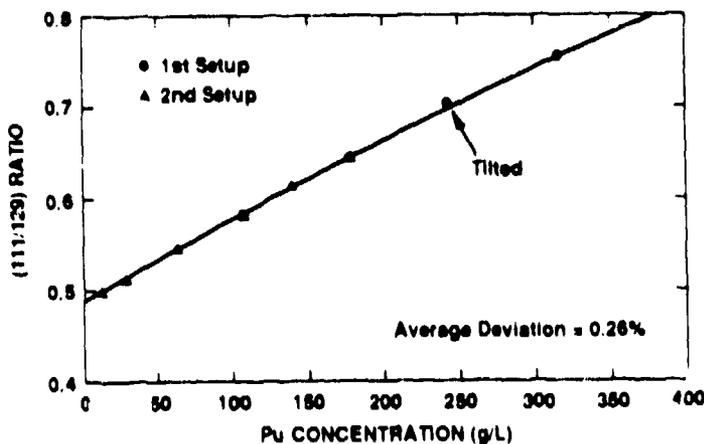


Fig. 4. The measured 111/129 ratios from two different experimental setups. The sample-to-detector distance was 8.9 cm for the first setup and 7.6 cm for the second setup.

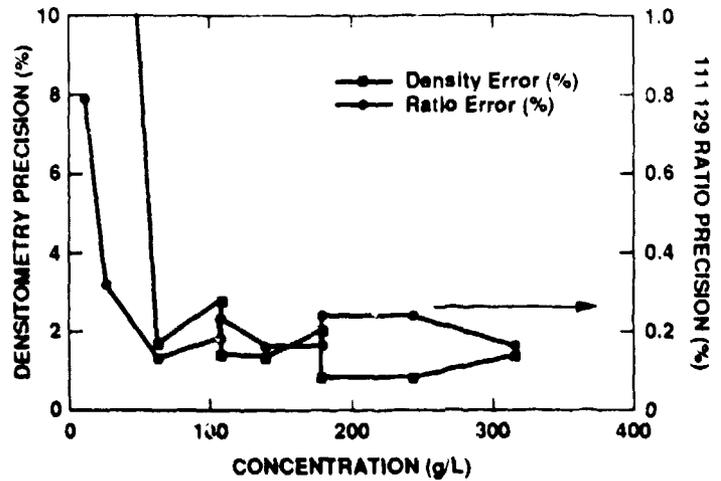


Fig. 5. Precision of the ratio method and the densitometry method. The precision is obtained from the repeatability of eight 10 000-s runs.

function of the sample-to-detector distance. Measurements were made at 2.5-cm increments. The results are summarized in Fig. 6. We observe that the measured ratio remains constant within the experimental precision beyond 7 cm when the diameter of the solution vial is 3.5 cm. Therefore, if the sample-to-detector distance exceeds 2 times the sample diameter, the ratio remains the same, but the measurement precision does degrade as the sample-to-detector distance increases.

Mathematical Model

To understand the behavior of the ratio technique, a simple model has been developed. In this model, the detector is assumed to be far away from the solution sample as shown in Fig. 7.

- ρ = density of plutonium in g/cm^3 .
- μ_{111}, μ_{129} = mass absorption coefficients of plutonium.
- μ_{111}, μ_{129} = mass absorption coefficients of matrix.

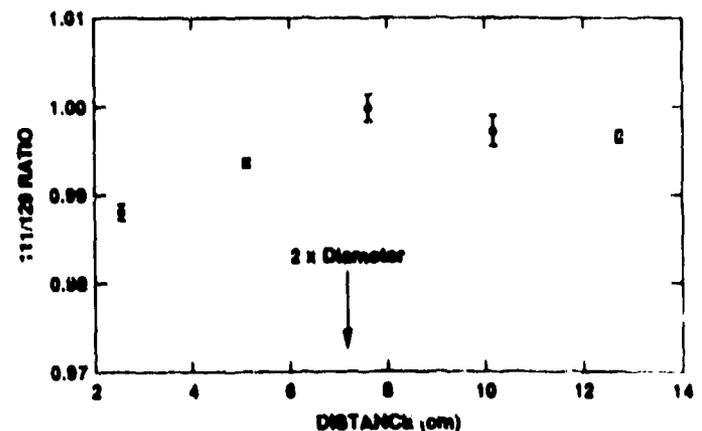


Fig. 6. The 111/129 measured ratios vs distance from the front of the sample vial.

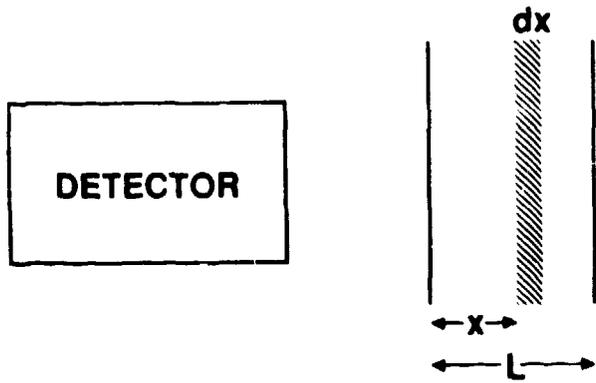


Fig. 7. Simple mathematical model of the measurement.

- ρ_m = density of matrix.
- $\epsilon_{111}, \epsilon_{129}$ = detection efficiencies.
- f_8, f_9, f_0, f_1, f_2 = weight fractions of plutonium isotopes.
- g_9 = γ /s-g of ^{239}Pu .
- x_8, x_9, x_0, x_1, x_2 = x/s-g of K (111 keV) of plutonium isotopes.
- A = cross-sectional area.

Detection of 129-keV gamma ray:

$$I(129) = \epsilon_{129} \rho g_9 f_9 A \int_0^L \exp[-(\mu_{129} \rho + \mu_{129}^m \rho_m)x] dx$$

$$= \epsilon_{129} \rho g_9 f_9 A \frac{1}{\mu_{129} \rho + \mu_{129}^m \rho_m} \cdot \left\{ 1 - \exp\left[-(\mu_{129} \rho + \mu_{129}^m \rho_m)L\right] \right\}$$

$$= \epsilon_{129} \rho g_9 f_9 AL \frac{1 - T_{129}}{-\ln(T_{129})}$$

The above expression is correct for the far-field approximation. The more accurate expression is given below, where CF(AT) is the correction factor for attenuation.

$$I(129) = \epsilon_{129} \rho g_9 f_9 AL \frac{1}{\text{CF(AT)}_{129}}$$

Similarly, detection of 111-keV x ray:

$$I(111) = \epsilon_{111} \rho L \left(\sum_i x_i f_i \right) A \frac{1}{\text{CF(AT)}_{111}}$$

The ratio 111:129 is

$$\frac{I(111)}{I(129)} = K \frac{\sum_i x_i f_i}{g_9 f_9} \frac{\text{CF(AT)}_{129}}{\text{CF(AT)}_{111}}$$

where $K = \frac{\epsilon_{111}}{\epsilon_{129}}$,

$$= K^* \cdot \left(1 + \frac{f_8 x_8}{f_9 x_9} + \frac{f_1 x_1}{f_9 x_9} \right) \cdot \frac{\text{CF(AT)}_{129}}{\text{CF(AT)}_{111}}$$

where $K^* = \frac{x_9 \epsilon_{111}}{g_9 \epsilon_{129}}$,

$$= K^* \cdot \text{CF(ISO)} \cdot \frac{\text{CF(AT)}_{129}}{\text{CF(AT)}_{111}}$$

where the CF(ISO) is the isotopic correction factor.

To test the validity of the model, we have calculated the correction factors using the simple far-field slab approximation with the sample thickness of 1.772 cm and a 3-M-HCl matrix. The comparison between the model and the experimental data is summarized in Fig. 8. This simple model can reproduce the quadratic fit between the ratio and the concentration, but there is ~3% deviation from 10 g/L to 300 g/L. This deviation could be due to the μ values⁶ used in the model, or it could be due to a far-field approximation used to calculate the correction factors. Although the model cannot predict the experimental data accurately, it is sufficient to be used for parametric studies.

Ratio vs Sample Thickness. This model has been used to calculate the ratio of 111/129 as a function of solution thickness. The results of the calculation are shown in Fig. 9. Observe that for 1-cm solution thickness, the ratio vs concentration is almost a straight line, but the ratio is not very sensitive to the concentration variations. For thicker samples, the response is no longer a straight line, but the ratio is more sensitive to the plutonium concentration.

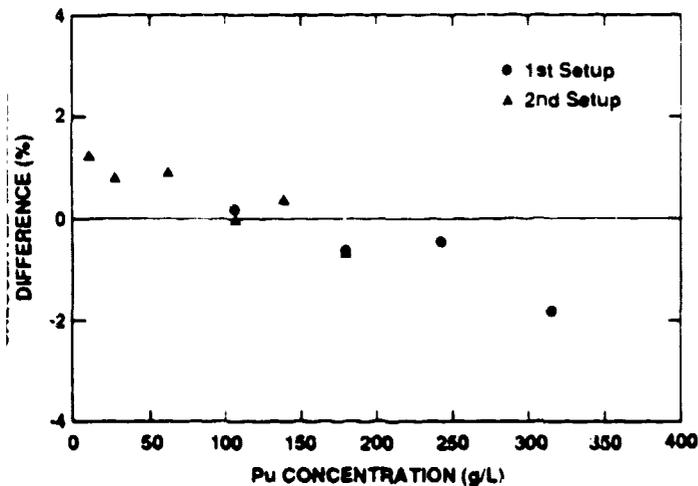


Fig. 8. The agreement between the simple model and the experimental data. The data show that the agreement is within 3% from 10 g/L to 310 g/L.

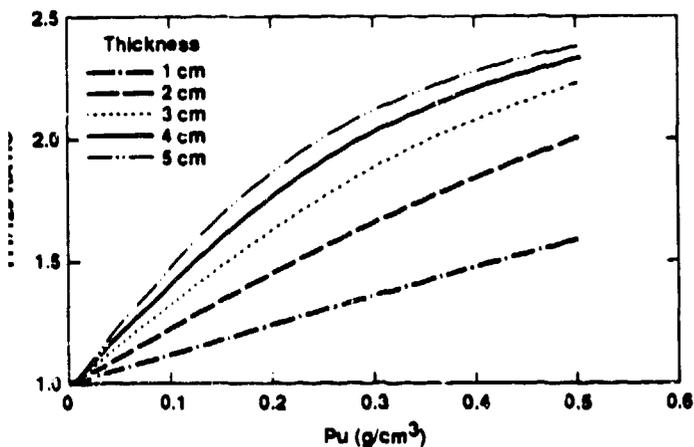


Fig. 9. A 111/129 ratio as a function of sample thickness from 1 cm to 5 cm.

Ratio vs Acid Molarity. The same model is used to calculate the ratio when the acid molarity changes. Three molar HCl was considered the reference case, and calculations were performed for 1-M, 6-M, and 9-M solutions. The results are summarized in Fig. 10. The ratio is not very sensitive to the acid molarity variations: from 1- to 9-M acid, the ratio changes <0.5% from 0 to 300 g/L. This is reasonable because 111 and 129 are only 18 keV apart, and the μ values of the low-Z matrix do not change much from 111 keV to 129 keV; therefore, the ratio method is relatively insensitive to low-Z matrix variations.

Ratio vs Medium-Z Matrix. The same model is used to calculate the 111/129 intensity ratio when the amount of medium-Z matrix varies. For our calculation, molybdenum ($Z = 40$) is mixed into the solution. Plutonium solution with no molybdenum is used as the reference; different amounts of molybdenum with respect to the plutonium concentration are introduced, and the results are summarized in Fig. 11. Assuming that we want to limit the bias to <0.5%, we found that

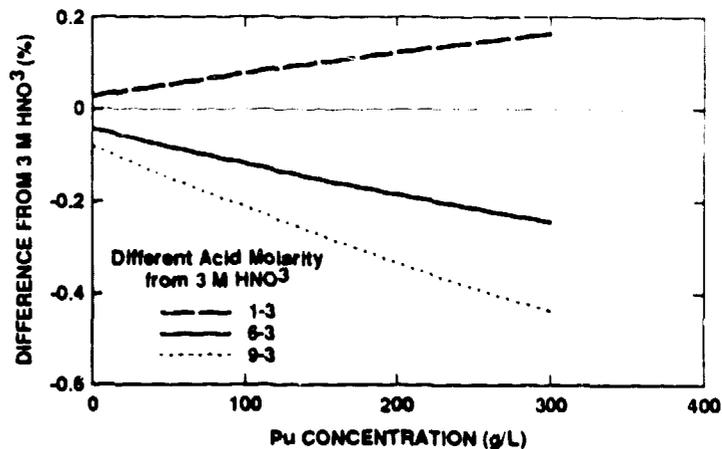


Fig. 10. The ratio as a function of the HNO_3 acid molarity. Three-molar HNO_3 is used as the reference solution.

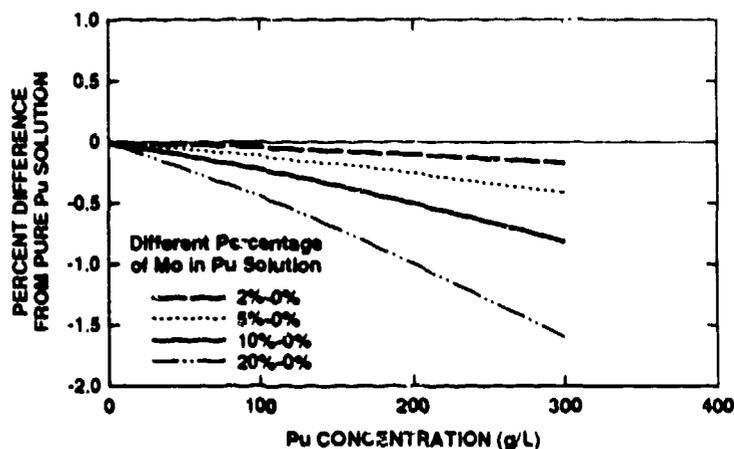


Fig. 11. This figure shows the effect of mixing medium-Z material in the matrix. Each curve shows the effect of mixing a fixed percentage of molybdenum relative to the plutonium in the solution. Percentage difference is plotted against the plutonium concentration using pure plutonium solution as the reference.

the amount of molybdenum should be <6% of the plutonium ranging from 0 to 300 g/L. If the plutonium concentration range is more limited, then the tolerance of the medium-Z matrix variation is even greater.

Ratio vs High-Z Matrix. The plutonium product solution of the reprocessing plant sometimes has a small amount of uranium, and it is interesting to find out how sensitive the ratio method is to the presence of uranium. The results of the calculation are shown in Fig. 12. Assuming again that we want to limit the bias to <0.5%, the amount of uranium should be <3% for plutonium ranging from 0 to 300 g/L.

Second Experiment

The previous experiment was carried out with low-burnup plutonium solutions of the same isotopic distribution. A second experiment was carried out with various isotopic distributions. Solutions with three different isotopic distributions, ranging from 6% ^{240}Pu to 12% ^{240}Pu , and 13 plutonium concentrations were measured. The sample cells used were

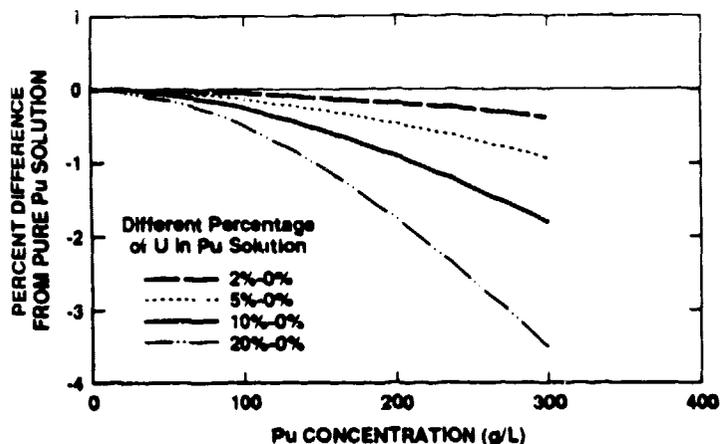


Fig. 12. The effect of the presence of uranium in plutonium solution. Pure plutonium solution is considered the reference solution.

spectrophotometric cells with a solution thickness of 2 cm and a 2-cm diam that held 6 mL of solution; the detector was a side-looking detector (also 2-cm³ active volume) located 7 cm from the flat surface of the cell. Each measurement consisted of a 20 000-s assay repeated 4 to 8 times. The data are summarized in Fig. 13. We should point out that some sample solutions were freshly separated samples such that the ²⁴¹Pu and ²³⁷U were not in equilibrium. The measured 111/129 ratio, corrected by dividing with the isotopic factor $(1 + f_1/f_9 \cdot x_1/x_9)$, where $x_1/x_9 = 118.58$, is plotted against the plutonium concentration in Fig. 13. The data can be fitted well with a quadratic equation, indicating that if the plutonium isotopic distribution is known or measured, the 111/129 ratio can be used to determine the plutonium concentrations.

SUMMARY

The ratio method has certain properties that are summarized below:

- The method is insensitive to the sample-to-detector distance, as long as the distance exceeds 2 times the diameter of the sample. Precise positioning of the sample vial with respect to the detector is not required.
- It is insensitive to absolute detector-efficiency changes. Therefore, less-frequent calibration is required for in-plant instruments. Because the calibration includes determining the response curve, once the sample size and the detector are fixed, the response is fixed. Therefore, an inspector can calibrate the system in a host facility and employ the method for field inspection.
- The method is insensitive to low-Z matrix variations and the insertion of low-Z absorbers; it is fairly insensitive to the medium-Z matrix variations; and it is insensitive to the small amount of high-Z matrix.

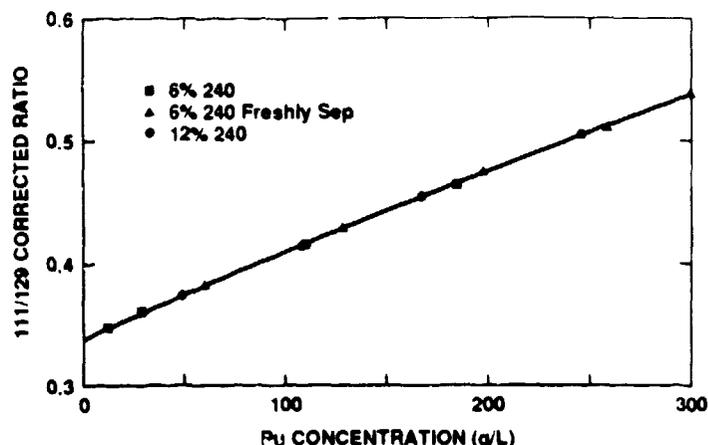


Fig. 13. Experimental data from the second experiment in which the plutonium isotopic distribution is also allowed to vary. After the isotopic distribution correction factor is applied, the 111/129 ratio is plotted against the plutonium concentrations.

- The method does require a plutonium isotopic measurement. The isotopic distribution can be determined simultaneously with the same detector and electronics. The method, therefore, is not for waste solutions for which the isotopic measurement is difficult.

CONCLUSIONS AND APPLICATIONS

The main advantage of the two methods described is that no external radioactive source or x-ray generator is required. The experimental data in this work demonstrate that, for low-burnup plutonium, the concentration can be determined by the densitometry method to 1.9% from 50 g/L to 300 g/L. For similar burnup solutions, the ratio method can determine the concentration to better than 1% from 10 g/L to 300 g/L. However, these methods are not for all plutonium solutions; if the solution is reasonably pure, the methods can be used to determine the plutonium concentration. The product solution of a reprocessing plant and the product solution from anion exchange are ideal candidates for these methods.

Because the methods rely only on the natural radiation from plutonium, the assay setup can be extremely simple, and the methods have several important applications:

- They can be used by inspectors to verify the reprocessing plant product solutions (both the isotopics and the concentration). The fact that the methods require no external source is a tremendous operational convenience.
- They can be used to monitor plutonium isotopics and concentration in pipes.
- The ratio method can be used to monitor plutonium isotopics and concentrations in tanks. We observe that for thick samples, the plutonium concentration and the

111/129 ratio approaches a unique function. The 111/129 ratio vs thick samples are shown in Fig. 14. Observe that the response between the 15-cm sample and 20-cm sample is very nearly the same. In Fig. 15, we use the response from a 100-cm sample as the reference and calculate the differences between the response from a 15-, 20-, 25-, 30-, and 35-cm sample from that of a 100-cm sample. Observe that the difference is <0.1% between 35 cm and 100 cm for the entire concentration range. This calculation indicates that if the calibration was performed with 35-cm-thick solutions, then the same calibration can work for any solution thickness beyond 35 cm. Therefore, the ratio method can be used to monitor tanks of plutonium solution without drawing samples or building bypass loops, which will make tank monitoring considerably simpler.

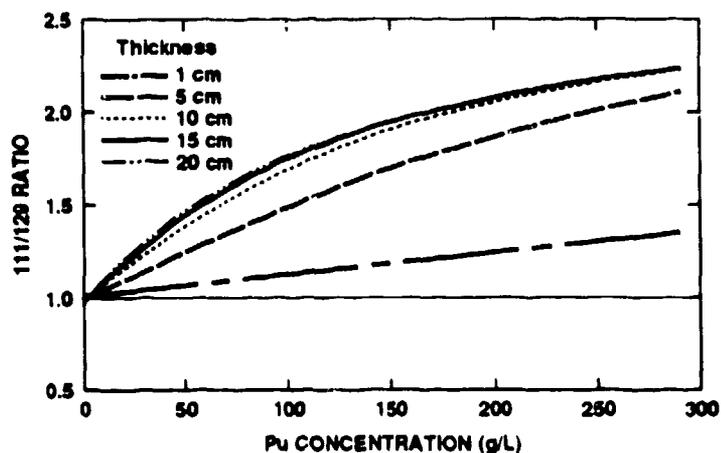


Fig. 14. The calculated 111/129 ratio vs concentration for thick-solution samples. Observe that the 15-cm response and the 20-cm response are nearly the same.

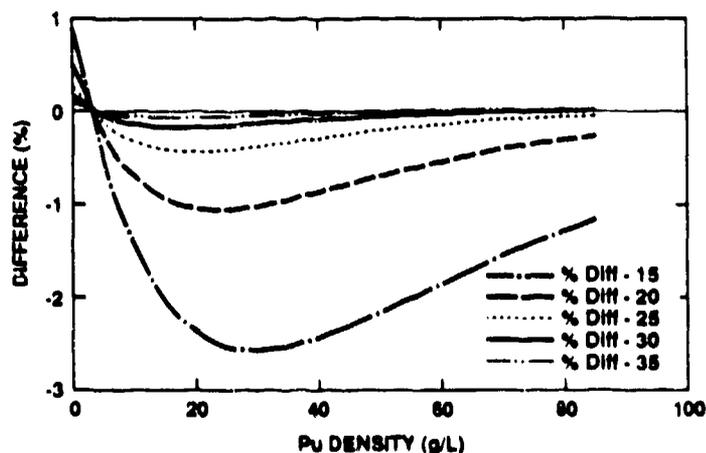


Fig. 15. In this figure, the 100-cm-thick sample is considered the norm, and the percent difference between other thicknesses is calculated against that of the 100-cm sample.

If we use the far-field model, the 111/129 ratio for thick-solution samples becomes

$$\frac{I(111)}{I(129)} = \frac{\epsilon_{111} \sum_i x_i f_i}{\epsilon_{129} g_9 f_9} \frac{\mu_{129} \rho + \mu_{129}^m \rho_m}{\mu_{111} \rho + \mu_{111}^m \rho_m}$$

This is somewhat similar to the enrichment principle⁹ situation; the major difference is that the matrix terms $\mu_{129}^m \rho_m$ and $\mu_{111}^m \rho_m$ are not negligible with respect to the plutonium terms $\mu_{129} \rho$ and $\mu_{111} \rho$. In fact, in many cases, they are comparable in magnitude. Therefore, when ρ varies (and because of the substantially different μ_{129} and μ_{111}) the ratio of mu times density also changes, giving rise to different $I(111)/I(129)$ ratios.

In our future efforts, we will try to perform experiments with high-burnup plutonium solutions and demonstrate the applicability of these methods. A tank-monitoring experiment is also being planned.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Dr. R. Gunnink of Lawrence Livermore National Laboratory for providing the MGA2 program and various discussions, and to A. Smith for helping in calculating and plotting the data.

REFERENCES

1. T. E. Sampson, "Plutonium Isotopic Composition by Gamma-Ray Spectroscopy: A Review," Los Alamos National Laboratory report LA-10750-MS (September 1986).
2. J. L. Parker, "A Plutonium Solution Assay System Based on High-Resolution Gamma-Ray Spectroscopy," Los Alamos Scientific Laboratory report LA-8146-MS (January 1980).
3. W. D. Ruhter and D. C. Camp, "Transmission-Corrected X-Ray Fluorescence Analysis of Uranium and Plutonium Solutions Using a Dual Transmission Source," in *Proc. Third International Conference on Facility Operations--Safeguards Interface* (American Nuclear Society, Inc., La Grange Park, Illinois, 1988), ANS Order No. 700132, pp. 300-305.
4. P. A. Russo, S.-T. Hsue, D. G. Langner, and J. K. Sprinkle, Jr., "Nuclear Safeguards Applications of Energy-Dispersive Absorption-Edge Densitometry" in *Proc. 21st Institute of Nuclear Material Management*, Palm Beach, Florida, June 30-July 2, 1980, pp. 730-772.

5. R. Gunnink, "MGA2: A One-Detector Code for Rapid High-Precision Plutonium Isotopic Measurement," in *Proc. 28th Institute of Nuclear Material Management Meeting*, Newport Beach, California, July 12-15, 1987, *Nucl. Mater. Manage.* XVI, Proc. Issue, 352-358 (1987).
6. E. Storm and H. I. Israel, "Photo Cross Section From 1 keV to 100 MeV for Elements Z = 1 to Z = 100," *Nuclear Data Table A7*, 565-681 (1970).
7. W. H. McMaster, N. Kerr Del Grande, J. H. Mallett, and J. H. Hubbell, "Compilation of X-Ray Cross Section," Lawrence Livermore National Laboratory report UCRL-50174, Sec. II, Rev. 1.
8. J. H. Hubbell, "Photo Cross Sections, Attenuation Coefficients, and Energy Absorption Coefficients From 10 keV to 100 GeV," National Bureau of Standards report NSRDS-NBS 29 (August 1969).
9. L. A. Kull and R. O. Ginaven, "Guidelines for Gamma-Ray Spectroscopy Measurements of ²³⁵U Enrichment," Brookhaven National Laboratory report BNL 50414 (1974).