

The Evaluation of Program Isotopic to Nondestructively Quantify Uranium and Plutonium Samples at the Joint Research Center in Ispra, Italy

Richard Hagenauer, AMETEK/ORTEC, Oak Ridge, TN
Pierre Funk, Institute of Nuclear Protection and Safety, Fontenay-Aux-Roses, France
Peter Schillebeeckx, and Michael Thornton, Joint Research Center, Ispra Italy

Abstract

In March, 2001 at the Joint Research Center in Ispra Italy, a measurement program was implemented by the Institute of Nuclear Safety and Protection (IRSN), Fontenay-Aux-Roses, France, for the nondestructive analysis of special nuclear material held by the Joint Research Staff of ISPN and ORTEC measured and analyzed well-characterized uranium and plutonium samples. Three of the software programs evaluated were, GammaVision (Version 5.1),¹ Program Isotopic (Version 2.0.4),² and PC/FRAM (Version 2.3).³ The GammaVision evaluation determined if the peak areas were adequately determined. Isotopic used modeling to compute correction factors for attenuation and geometry to determine gram-quantities of each nuclide. PC/FRAM was used to determine “isotopic ratios” or weight percent of the plutonium isotopes.

Samples were analyzed as unknowns and the average uncertainties determined for homogenous material consisting of: UO₂, U₃O₈, PuO₂ and MOX. Several nonhomogeneous samples were prepared in order to simulate containers of radioactive waste.

Results of these measurements are presented. Information from this exercise was used to determine accuracy estimates for inspection teams who would use these methods to measure and analyze uranium and plutonium samples of similar composition at French nuclear sites.

Introduction

Prior to inspections for verification of special nuclear material, it is good practice to check the accuracy of the analyses on known samples. Team members from the French Institute of Nuclear Protection and Safety, (IRSN) Fontenay-Aux-Roses, along with an experienced analyst from ORTEC measured a wide variety of samples from the PERLA laboratory of the Joint Research Center (JRC) in Ispra, Italy. Staff from the JRC facility assisted in sample movement and provided information about the container and sample matrix. The declared values of the quantities of the uranium and plutonium samples were not disclosed to measurement team until the analyses were completed. Then the declared values and the measured values were compared to establish accuracy.

The goals of this exercise were:

- (1) Establish the accuracy of Program Isotopic to nondestructively determination of gram quantities of uranium in UO₂ and U₃O₈ by determining the quantity of ²³⁸U and using the known weight percents of ²³⁸U.

¹ ORTEC® GammaVision®-32 Gamma-Ray Spectrum Analysis and MCA Emulator Software

² Radioactive Waste Characterization software Licensed from Lockheed Martin and Distributed by ORTEC

³ Plutonium and Uranium ISOTOPIC Analysis software Licensed from Los Alamos National Laboratory (The University of California) and Distributed by ORTEC

- (2) Establish the accuracy of Program Isotopic to nondestructively determine the quantities of plutonium in PuO₂ and MOX by determining the quantity of ²³⁹Pu and using the known weight percents of ²³⁹Pu.
- (3) Establish the accuracy of Program Isotopic to nondestructively determine the quantities of plutonium in PuO₂ and MOX by determining the quantity of ²³⁹Pu and using PC/FRAM to determine the weight percent ²³⁹Pu.
- (4) Estimate the accuracy of the software to nondestructively determine nonhomogeneous nuclear waste, by analyzing plutonium samples in simulated waste.

Description of data acquisition and analysis software

In general, multiple steps are necessary in order to quantify the activity in a measurement. Data must be acquired, the gamma-ray peaks analyzed, and corrections for gamma-ray attenuation and geometry must be made. The following describes a typical use of the GammaVision and Isotopic software to perform this type of measurement.

A high-purity high-resolution germanium detector is used to collect the data. GammaVision controls the multichannel analyzer and processes the spectra. In the versions tested, the peak areas from GammaVision provided the input to Isotopic (Reference 1) which corrects for the effects of geometry and attenuation. A new version of Isotopic in preparation is totally integrated, eliminating the multi-step process. The efficiency calibration for a HPGe detector is determined by positioning a traceable gamma-ray source at a known distance from the detector and determining the peak-area efficiency for gamma-rays through the energy ranges of interest for the analysis. In addition to detector efficiency, the peak width is computed at the same energies as the detector efficiency. The peak-width calibration is then used to accurately determine the actual peak width for the gamma-ray peak being measured. For gamma-ray multiplets this calibration is used directly for peak-area determinations. For a singlet, the peak-width calibration is used as the starting point for the fit.

Libraries containing information about expected nuclide are developed using the gamma-ray branching ratios for every gamma ray expected in the spectrum. The branching ratio and the nuclide are selected from the energy of the gamma ray and used to compute the activity of the nuclide emitting the gamma rays. Reference gamma rays are selected for each nuclide. The activities of all the gamma rays are determined, but only the reference gamma ray is used for the reported results. The best reference gamma rays selected for reporting are gamma rays that are high energy, intense, and free from interference. In practice, many high-energy gamma rays are not intense and compromises are made between high energy and intensity. Usually, the importance of high energy for penetrability is greater than the importance of intensity when selecting a reference gamma ray.

During an analysis, the analyst can check the peak width by displaying the peak fit on the display of the spectrum. If the fitted peak is not accurate, then another peak shape calibration is determined using the identified peaks within the spectrum of the item being measured as the source of calibration.

The spectroscopy system is calibrated by positioning a point source, whose activity is traceable to a national standard, at a fixed distance from the detector. The activity results computed by GammaVision assume that the samples are point sources located at the calibration distance. Activities are determined for every gamma-ray peak identified in the spectrum using the following formula:

$$\text{Act} = \text{PA}/(\text{eff} \times \text{BR})$$

where:

- Act = activity of the nuclide (dis/s),
- PA = peak area (cts/s)
- eff = detector efficiency at the specified energy (cts/gamma ray emitted),
- BR = gamma ray branching ratio (gamma rays emitted/dis)

Program Isotopic then “post-processes” the results further to correct for the matrix, container, collimator, and geometry effects using operator-supplied information about the dimensions, weights, distances, and materials, along with internal collections of databases of geometry and matrix correction information. The same gamma-ray library used for GammaVision is then used for Isotopic to identify the gamma rays and establish the reference gamma ray. Program Isotopic is menu driven with selection by a mouse. Results are generated in units of grams and activity with activity units selected by the user. Hard-copy reports are available for summaries including gram and activity quantities of each nuclide, ²³⁵U enrichment, peak-area corrections, minimum detectable activity (MDA), and components of error estimates. A simplified formula for the conversion of activity computed from GammaVision to the reported activity is shown below:

$$\text{Act}_{\text{rep}} = \text{Act} \times \text{CF}_{\text{att}} \times \text{CF}_{\text{geo}}$$

where:

- Act_{rep} = reported activity configured as a point source (Bq),
- CF_{att} = correction factors for gamma-ray attenuation, and
- CF_{geo} = correction factor for geometry.

Program Isotopic is designed to allow the user to model the shape of the activity being measured. Once the activity is modeled, the activity of the item can be computed.

Geometry corrections are determined by dividing the item into small voxels and computing the geometry correction for each voxel. These geometry corrections are then averaged to determine the correction factor for the item being measured.

The geometry correction for each voxel is determined as follows:

$$\text{CF}_{\text{voxel}} = (\text{D}_{\text{voxel}}/\text{D}_{\text{cal}})^2$$

where:

- CF_{voxel} = geometry correction for a voxel,
- D_{voxel} = distance from the face of the detector to the center of the voxel (cm),
- D_{cal} = distance from the face of the detector to calibration point source (cm).

Attenuation correction factors are made for container, matrix, collimator, self absorption (for uranium and plutonium) and air. The correction factors for attenuation are as follows;

$$\text{CF}_{\text{cont}} = \text{Act} \times \exp(\mu\rho\chi)$$

where:

- CF_{cont} = correction factor for the container

- μ = mass attenuation factor of the container material (cm²/g),
- ρ = density of container material(g/cm³),
- χ = thickness of the container material(cm).

The correction factors for air, and collimator are computed in a similar manner.

The attenuation correction factor for matrix, CF_{matrix} , usually dominates the attenuation correction factors. The constant, A, shown in the formula below has a value of 1.0 for a box and 0.834 for a cylinder.

$$CF_{\text{matrix}} = A\mu\rho\chi/(1-\exp(A\mu\rho\chi))$$

Figure 1 is an example of a screen used to allow the user to model the activity. These models can be stored as templates, retrieved, and modified as necessary if any of the measurement parameters need adjusting. All the information is present to determine the correction factors from this configuration page.

Sample activity is computed using a reference gamma ray for the nuclide in question that is of high energy (if available) and high intensity. All the other gamma rays of a specific nuclide should have the same corrected activity if the modeling is correct. When the activity of the gamma ray is plotted referencing the activity of reference gamma rays, the percent difference can be plotted graphically as a function of energy. If a slope of the plotted points is noticeable, the user has an opportunity to adjust the matrix density or container thickness so that the points representing the nuclide activity line up; that is, reach a slope of zero. This is graphically shown in Figures 2 and 3. When the points are correctly adjusted, the results are ready to be reported. On this screen the reference gamma rays can be changed, if the peak was poorly fit or if interference activity of the reference gamma rays was present.

Special correction factors are available for uranium and plutonium. These elements have a high atomic weight and gram quantities of these elements can cause extra self absorption. When the gamma rays interact with a mixture of these heavy atoms plus the matrix material, the attenuation will increase. Lump corrections are possible by adding a weight percent of uranium or plutonium to the matrix content. Usually the weight percent is impossible to know before hand, but this correction can be determined within the plot screen. Figures 4 and 5 show the benefit of the lump corrections to this analysis procedure. The scattered points indicate areas determined from complicated multiplets.

Figure 6 shows a typical Results screen for user to observe the analysis results before they are printed or archived.

PC/FRAM

In this series of measurements, PC/FRAM software (Reference 2) was used to accurately determine the plutonium isotopic content. This software computes the weight percent ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu and ²⁴²Pu. Special attention is given for complicated gamma-ray and X-ray multiplets. In this exercise, only the ²³⁹Pu weight percent was used to compute the quantity of plutonium. In other applications, the additional weight percent information is critical for the determination of total plutonium activity.

System calibration and setup

The high purity germanium detector (HPGe) was calibrated using an ^{152}Eu point source. The activity of the source was traceable to a national standard. The point source was positioned 25 cm from the face of the detector with a cadmium foil covering the face of the detector to reduce the low-energy activity anticipated from ^{241}Am .

A library used by GammaVision and Isotopic to identify the gamma rays was prepared containing the isotopes from americium, plutonium, neptunium and uranium. The gamma-ray identification of the short-lived daughters of these isotopes was identified as belonging to the parents. For example, the gamma rays emitted from ^{234}Pa and ^{234}Th were identified as ^{238}U gamma rays. Chemical separation had not occurred for these samples for several years and secular equilibrium between the parents and daughters had been established.

Reference gamma rays for the Isotopes of interest are shown in Table 1.

Table 1. Reference Gamma Rays Used to Quantify Nuclides in Program Isotopic	
Nuclide	Energy (keV)
^{235}U	185.7
^{238}U	1001.0
^{239}Pu	413.7
^{240}Pu	160.3
^{241}Pu	208.0
^{237}Np	311.6
^{241}Am	662.89

Description of the hardware

A portable HPGe with an efficiency of 80% relative to an 7.6-cm \times 7.6-cm (3-in. \times 3-in.) NaI detector, was used to collect the data. This detector was positioned on a table whose height was adjustable. Thus, the detector could be raised and lowered to measure the item at the center of the sample container. It was not known at the time of the measurement where the top of the sample material was located, however, this inability to center the detector on the center of the activity did not contribute to a significant error. A DSPEC + digital signal processor, controlled by GammaVision software, was used to provide the high-voltage to the germanium detector provide the signal processing from the detector.

Analysis of results

To help establish accuracy the measured results were compared to declared values using the following formula:

$$\%Diff = (Val_{decl} - Val_{meas}) * 100 / Val_{ref}$$

where:

Val_{decl} = declared value
 Val_{meas} = measured value

In all cases, the declared values were considered to have no significant errors.

The average (abs) values represented an average of differences without any positive or negative value. This gave an indication of the uncertainty that can be assigned to a value. The average difference of a series of measurements gave an indication if there was a significant bias present.

Description of the uranium samples

Powders of U_3O_8 , UO_2 , mixed oxide (UO_2 and PuO_2), and PuO_2 were measured in containers of different shapes and wall thickness. These materials have been well characterized by the Joint Research Center and the container dimensions well documented.

Measurements of Uranium Samples

Nine containers of U_3O_8 , UO_2 were analyzed by positioning the sample 100 cm from the face of the detector. Samples were counted for 20 minutes or longer. The samples were analyzed two ways: (1) the ^{238}U content was determined using Isotopic and the declared ^{235}U enrichment for uranium was used to compute total uranium and (2) the values of ^{235}U and ^{238}U were determined by Isotopic and summed. Only one set of data was taken as shown in Table 2.

The quantity of ^{234}U was considered insignificant for this exercise. In method 1, whatever errors were present in the ^{235}U analysis would directly affect the ^{235}U weight percent result. The measured uranium results in this table represent the sum of ^{235}U and ^{238}U quantities.

Measurement of PuO2 and MOX samples

Twelve PuO_2 and MOX samples in a variety of containers were measured in a similar manner. The declared values corrected for the decay of ^{241}Pu are shown in Table 3. Total grams of plutonium were nondestructively analyzed by using PC/FRAM to compute the weight percent of each of the Pu isotopes and Isotopic to determine the ^{239}Pu .

Table 2. NDA Results for Homogeneous Uranium Measurements

Item #	Material	Declared				Measured Isotopic				% Difference from Declared			
		²³⁵ U (g)	²³⁸ U (g)	Wt % ²³⁵ U	U (g)	²³⁵ U (g)	²³⁸ U (g)	Wt % ²³⁵ U	U (g)	²³⁵ U	²³⁸ U	Wt % (Rel)	U % Diff
LU-12	U ₃ O ₈	23.28	2352.72	0.98	2376	23.3	2350	0.98	2373.3	0.07	-0.12	-0.18	0.11
LU-25	U ₃ O ₈	73.83	2323.27	3.08	2397.1	69.4	2180	3.09	2249.4	-6.00	-6.17	-0.17	6.16
LU-27	U ₃ O ₈	73.84	2323.56	3.08	2397.4	33.2	2160	1.51	2193.2	-55.04	-7.04	50.85	8.52
LU-29	U ₃ O ₈	155.07	4879.63	3.08	5034.7	65.7	4460	1.45	4525.7	-57.63	-8.60	52.87	10.11
LU-32	U ₃ O ₈	390.23	12279.57	3.08	12669.8	162	13100	1.22	13262	-58.49	6.68	60.34	-4.67
LU-44	U ₃ O ₈	118.19	2259.91	4.97	2378.1	97	2610	3.58	2707	-17.93	15.49	27.90	-13.83
U-47	UO ₂	248.72	1002.38	19.88	1251.1	233	964	19.47	1197	-6.32	-3.83	2.09	4.32
U-50	UO ₂	348.20	1403.30	19.88	1751.5	335	1310	20.36	1645	-3.79	-6.65	-2.44	6.08
U-127	UO ₂	1027.13	84.24	92.42	1111.37	1020	78.8	92.83	1098.8	-0.69	-6.46	-0.44	1.13
Average % Difference (abs)													
Average % Difference													

Table 3. NDA Results for Homogeneous Plutonium Measurements

Item #	Material	Declared			Measured PC/FRAM and Isotopic			% Difference from Declared.	
		²³⁹ Pu (g)	Wt % ²³⁹ Pu	Pu (g)	²³⁹ Pu (g)	Wt % PC/FRAM	Pu (g) NDA	²³⁹ Pu	Pu
1	PuO ₂	5.72	72.15	8.01	5.44	71.37	7.61	-4.84	-3.31
102	PuO ₂	36.96	72.15	51.46	43.50	71.84	60.55	17.68	19.67
104	PuO ₂	71.38	72.15	98.49	87.50	72.47	120.74	22.59	25.17
107	PuO ₂	214.54	72.15	298.81	234	71.80	325.91	9.07	10.91
109	PuO ₂	369.46	72.15	501.98	359	73.60	487.77	-2.83	-1.19
114	PuO ₂	1079.68	72.15	1503.34	806	71.82	1122.25	-25.35	-24.09
11	MOX	1.40	69.46	1.92	1.61	72.98	2.21	15.14	17.62
16	MOX	1.98	72.08	2.69	2.48	73.56	3.37	25.24	26.80
21	MOX	0.52	66.63	0.78	0.59	66.24	0.83	14.20	9.71
46	MOX	1.41	75.13	1.79	1.09	78.62	1.83	-22.68	-0.24
ENEA01	MOX	114.39	70.92	168.00	134	68.09	196.80	17.15	7.92
ENEA02	MOX	130.53	67.01	191	103	68.34	150.72	-21.09	-20.54
Average % Difference (abs)								12.50	13.90
Average % Difference								6.53	5.70

Measurement of Simulated Waste Samples

Ispra personnel simulated the nonhomogeneous waste samples by preparing waste containers ranging in size from 2.8 liter to 118 liter and densities 0.1 to 1.0. For containers with ID numbers 73240 and 82015 small plutonium samples were positioned in the center of the container. For samples D00185 (LD) and D00185 (HD) three plutonium sources were arranged at the vertices of an equilateral triangle for Sample D00185 (LD) the sample was positioned at the half-height of the container. For sample D00185(HD) the sample was positioned in a random vertical height. Total grams of plutonium were determined nondestructively analyzed by using PC FRAM to compute the weight percent of each of the Pu isotopes as was done with the homogenous samples. Results of the measurement are shown in Table 4.

Table 4. NDA Results for Nonhomogeneous Plutonium Measurements

Item ID	Volume (liter)	Density (g/cc)	Declared			Measured Isotopic and PC/FRAM			% Difference from Declared	
			²³⁹ Pu (g)	Wt % ²³⁹ Pu	Pu (g)	²³⁹ Pu (g)	Wt % ²³⁹ Pu	Pu (g)	²³⁹ Pu	Pu
73240	2.8	0.553	15.28	93.88	16.28	14.5	93.898	15.44	-5.13	-5.15
D00185 (LD)	100	0.106	12.20	75.66	16.12	12	74.853	16.03	-1.61	-0.55
D00185 (HD)	100	0.368	12.20	75.66	16.12	13.1	74.853	17.50	24.76	8.57
82015	12.6	1.01	0.66	76.187	0.86	0.426	75.758	0.56	-34.98	-34.61
Average % Difference (Abs)									16.3	12.22
Average Difference									-4.24	-7.94

Discussion of Results

The gamma-rays from ²³⁸U were used to fine tune the fill density and uranium self attenuation because the intense gamma rays from this isotope range in energy from 92 keV to 1001-keV. Under these conditions, the percent difference from the declared values was 6.8% with no significant bias. When the ²³⁵U enrichment declared values were not used, the grams of uranium determined from the addition of the ²³⁵U and ²³⁸U quantity differences from declared averaged only 6.1% - not much different from the ²³⁸U values. This is because the ²³⁸U quantities dominate the analysis. There seemed to be no significant difference in the analysis between U₃O₈ and UO₂ materials.

Because of the heavy sample attenuation the ²³⁵U values determined nondestructively were be biased low. This bias is the reason for the large difference between nondestructively measured values and declared values for the ²³⁵U enrichment determinations for sample of low ²³⁵U percentage. It is recommended that ²³⁵U not be used to quantify the similar samples. For low enriched samples this bias is not significant when summing the ²³⁵U and ²³⁸U quantities to compute the total quantity of uranium because the ²³⁵U quantities are such a small fraction of the overall uranium quantity.

For ²³⁹Pu analyses in homogeneous samples the average absolute percent difference was 12.5% for PuO₂ and mixed oxide samples. No significant bias was detected. In a similar manner, if the known isotopic content were used to determine the plutonium content then the plutonium analysis would be of the same uncertainty. When PC/FRAM was used to determine the weight percentage of ²³⁹Pu, the uncertainty between the declared value and the nondestructively determined values was 13.9%.

It is difficult to compute the quantity of plutonium by summing the results from ²³⁹Pu, ²⁴⁰Pu and ²⁴¹Pu. Significant quantities of ²⁴⁰Pu were present in the sample but the 104-keV and 160-keV gamma rays which can be used to determine the ²⁴⁰Pu content have interference from ²³⁹Pu activity. The best method to nondestructively analyze these samples is to quantify the ²³⁹Pu and divide by the weight percentage to determine the total quantity of plutonium.

The results from the measurements simulating nonhomogeneous waste showed an average percent difference of 16.3 %. When PC/FRAM was used to determine the weight percent of all the plutonium isotopes, the average difference between measured and declared values of plutonium was reduced to 12.2 %

Summary

It has been shown that the combination of GammaVision, Program Isotopic nondestructively determined homogeneous uranium samples in the form of U_3O_8 and UO_2 to an average percent difference of 6.1% with no significant bias. The most accurate method to quantify uranium is to determine the ^{238}U isotope and use the declared weight percent ^{235}U to determine the uranium quantity. In a similar manner homogeneous plutonium was nondestructively determined to an average percent difference of 12.5% by analysis of the ^{239}Pu if the plutonium isotopic content is known. If the weight percent is determined using PC/FRAM, the average percent difference in plutonium measurement increased slightly to 13.9%. For nonhomogeneous plutonium samples it appears that these also can be verified to a similar average percent difference. It should be noted however that a very small sampling of nonhomogeneous material types was measured and care should be taken in extrapolation of these uncertainties to measurements of other nonhomogeneous waste streams.

Acknowledgement

The authors appreciate the staff of JRC for their assistance in providing sample helpful the development of this exercise. Peter Schillebeeckx, Andrea Ravazzani, and Michael Thornton were especially helpful for their technical insight and program implementation. Additional team members from IRSN including Nicolas Pepin, and Thierry Lambert were very cooperative.

References

- (1) Hagenauer, R.C. "Nondestructive Assay Quantification of Poorly Characterized Radioactive Isotopes," Proceedings of the 4th Nondestructive Assay and Nondestructive Waste Characterization Conference, Salt Lake City, 1995.
- (2) Sampson, T.E., Kelley, T.A., "The Los Alamos PC/FRAM Code for the Nondestructive Analysis of the Isotopic Composition of Plutonium and Other Actinides" LA-UR-96-1220, Los Alamos National Laboratory, Los Alamos, NM, 1996

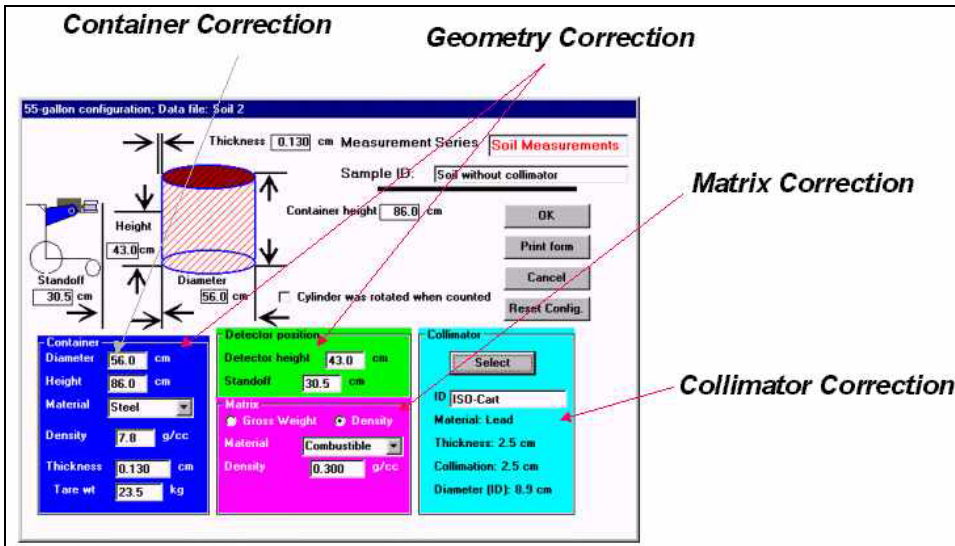


Figure 1 Configuration Screen used to compute the correction factors

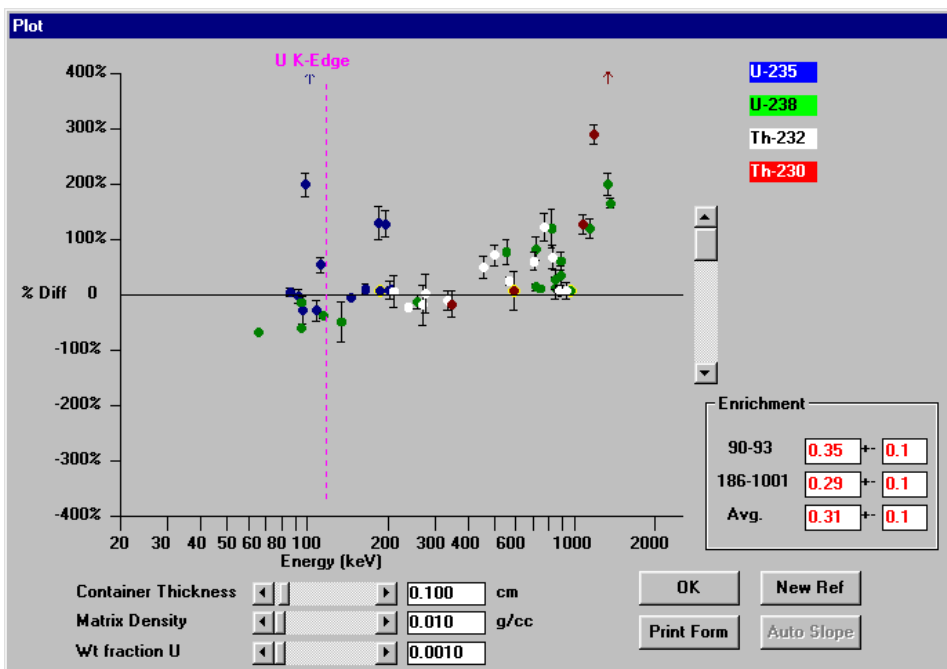


Figure 2 Fine-Tune Correction Screen showing under-corrected data

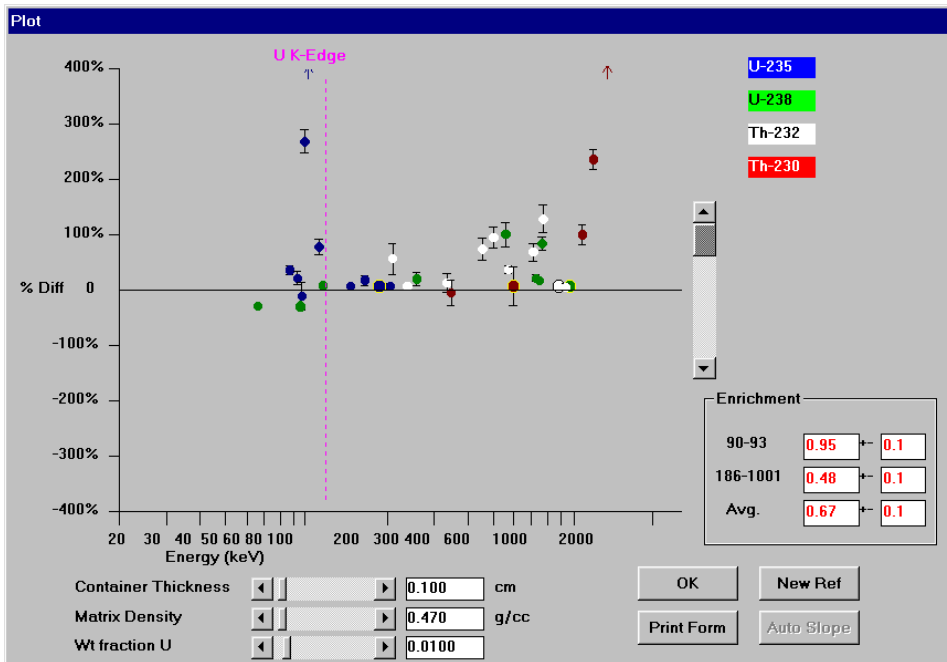


Figure 3 Fine-Tune Correction Screen with proper corrections

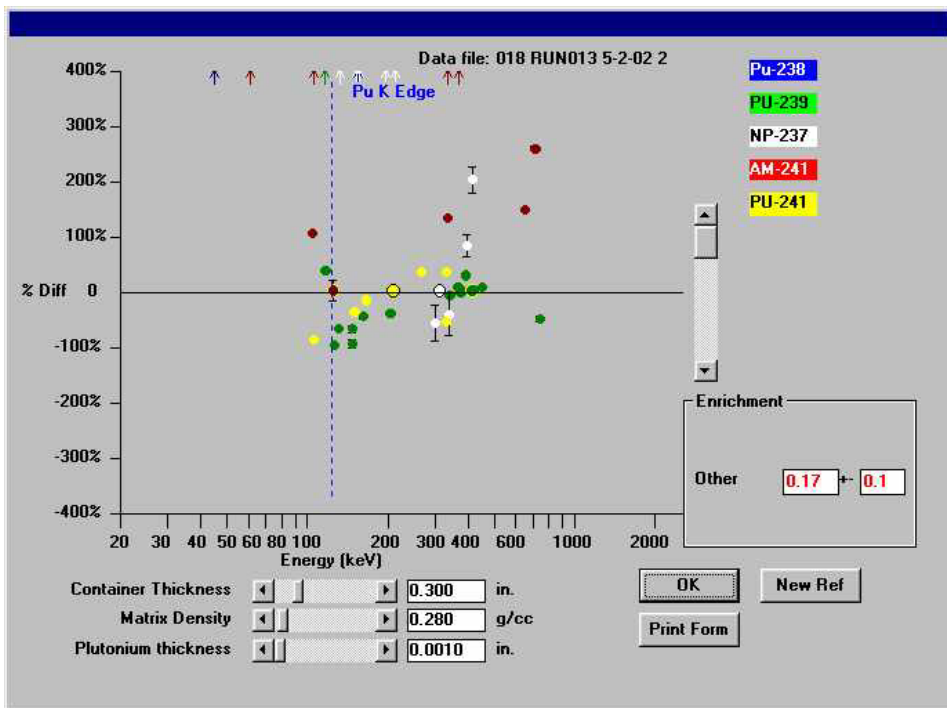


Figure 4 Configuration modeled without lump corrections

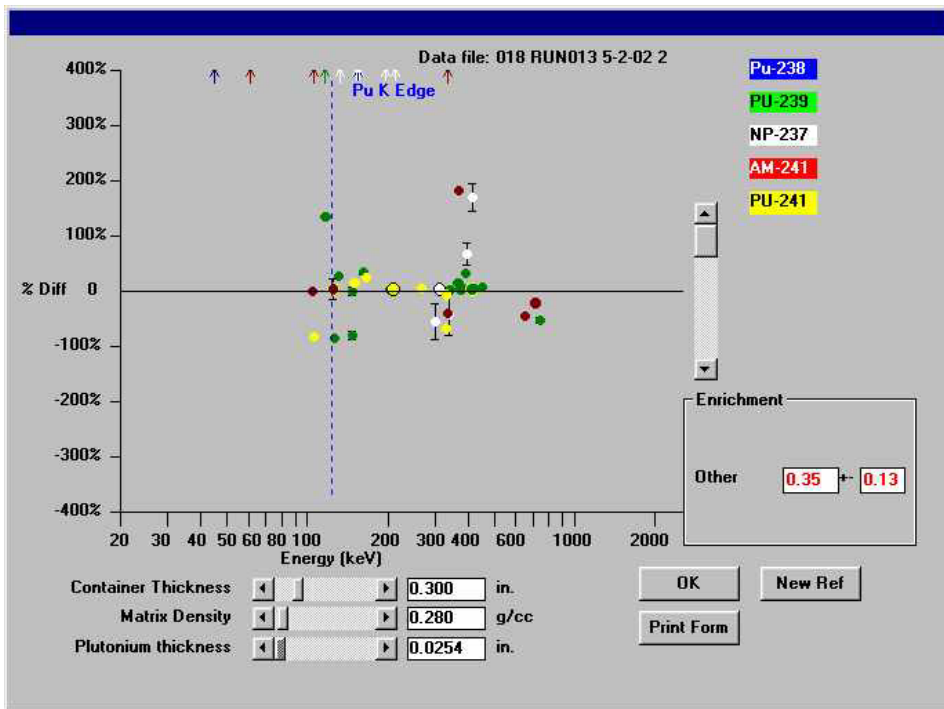


Figure 5 Same configuration with lump correction

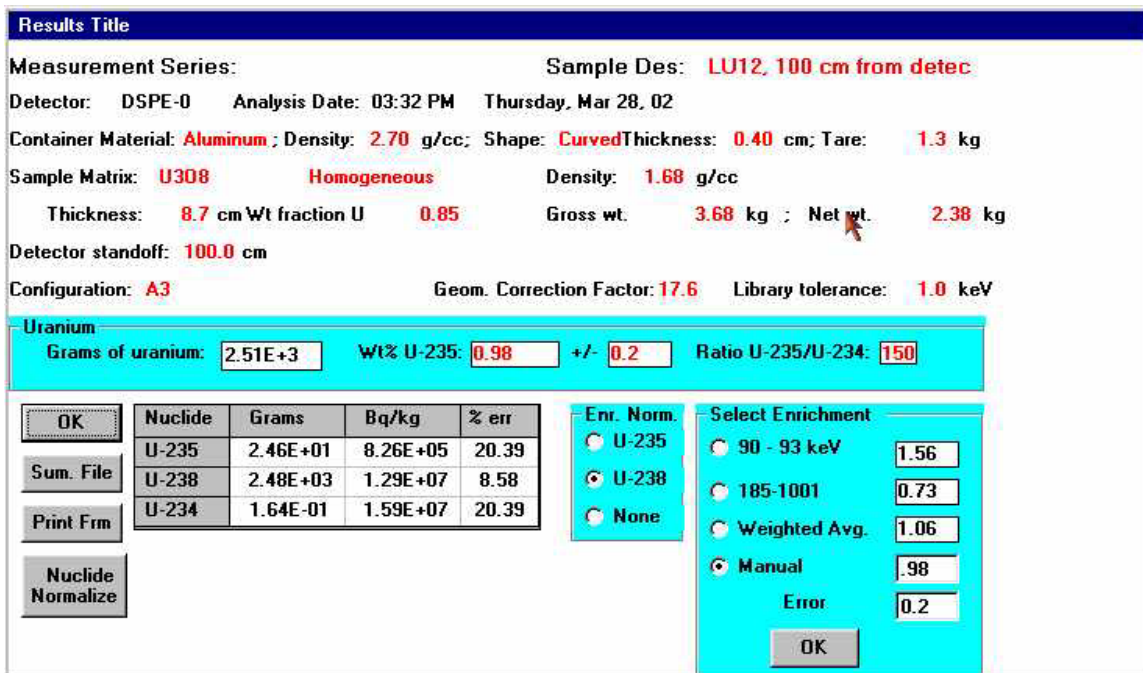


Figure 6 Typical Result Screen for Uranium