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MGA: A Gamma-Ray Spectrum Analysis Code for Determining Plutonium Isotopic Abundances

Volume 1 Methods and Algorithms

R. Gunnink

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MGA: A Gamma-Ray Spectrum Analysis Code for Determining Plutonium Isotopic Abundances

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Abstract

Nondestructive measurements of x-ray and gamma-ray emissions can be used to analyze a sample for plutonium. This report describes the methods and algorithms we have developed for analyzing gamma-ray spectra obtained by using a germanium detector system to accurately determine the relative abundances of various actinide isotopes in a sample. Our methodology requires no calibrations and can be used to measure virtually any size and type of plutonium sample. Measurement times can be as short as a few minutes; measurements are frequently accurate to within 1%.

Our methods have been programmed into a computerized analysis code called MGA (Multi-Group Aalysis). Our current versions can be run on personal computers (IBM type) and on the DEC VAX microcomputer. Spectral analysis times are usually far less than a minute.

Introduction

As a special nuclear material, plutonium must be accurately accounted for and safeguarded at all times. This accountability usually requires a measurement of the isotopic abundances as well as the elemental weight or concentration. Although mass spectrometers historically have been used to measure isotopic abundances, methods using gamma ray spectrometry have been developed and are now increasingly being used. Our methods of analysis—using germanium detectors—were first applied to the measurement of solution samples.^{1,2} Later, we developed techniques and computer programs to accurately measure isotopic abundances of plutonium in various solid samples. Others have also developed analysis procedures and computer programs for measuring isotopic abundances.³⁻⁵ However, the methodology described in this report and embodied in the various versions of the MGA computerized analysis program for plutonium isotopic measurements is substantially different from those developed by others. MGA is an expansion of an earlier unpublished program called RATIO that was de-

veloped over 15 years ago. This early program was designed to measure the relative isotopic abundances of plutonium in 1- to 2-kg quantities of PuO₂ but worked well only for samples that were low (~0.5%) in ²⁴¹Pu abundance. To overcome this and other deficiencies, we later (1979) developed MGA.⁶ In the beginning, a satisfactory performance of this new program required two spectra, the first taken with a small high-resolution planar detector, and a second taken with a more efficient detector to measure the lower-intensity peaks in the energy regions from 332 to 345 and 367 to 380 keV. The added expense and inconvenience of the second detector have recently prompted us to further improve MGA, resulting in newer versions that can perform an accurate analyses without using the higher-energy regions.

Cursory descriptions of our methods have been published in previous reports.⁶⁻⁸ However, the purpose of this report is to describe our methodology in greater detail.

Discussion of Fundamentals

Basis of Gamma Ray Methods

The isotopes of plutonium that normally must be measured are ^{238}Pu through ^{242}Pu . Some decay products, particularly ^{241}Am and ^{237}U , are also always present and must be considered in the analysis process. All of these isotopes emit gamma rays; however, the gamma rays of ^{242}Pu are not observable in plutonium samples containing the other isotopes because of their comparatively low intensities.

The basis for the measurement of the amount of any radioactive isotope by gamma ray spectrometry is given by

$$I = E \cdot P \cdot X, \quad (1)$$

where

- I = the measured intensity of a peak corresponding to a gamma ray of specific energy,
- E = the overall detection or counting efficiency,
- P = the emission probability per decay of the gamma ray being measured, and
- X = the amount of the radioactive isotope present in the sample.

The measured peak intensity, I , and the quantity to be determined, X , are related by the values of E and P . The latter is a fundamental constant, related only to the nuclear decay properties of the isotope being measured. However, its exact value may be uncertain since it must be experimentally measured. The value of E , on the other hand, depends on a number of factors, some of which are quite complex or cannot be easily defined or determined.

How one develops a method based on the above fundamental equation depends on the type of analysis attempted. In deciding on a method, it is useful to separate samples into two broad categories: those whose counting geometry—and hence, counting efficiency—can be controlled (i.e., is reproducible or calculable) and those where this is not possible. The first group is illustrated by uniform solution samples whose volume and counting position can be controlled easily. For this type of sample, it is frequently easier to combine the terms E and P in Eq. (1) into

a single calibration constant for each peak that is analyzed. One or more appropriate sources are used to calibrate the spectrometer system, and the calibration constants that are generated can be used in an analysis program to interpret spectra obtained from unknown samples. Some of the analysis programs we have developed (e.g., LEPA and PUANAL)² use this approach for measuring the isotopic concentrations of plutonium in solution samples.

However, many other samples, particularly solid samples, are nondescript, possessing characteristics that are frequently unknown or uncontrolled. For such samples, this method usually will not work because the counting geometry or counting efficiency is not reproducible, or because gamma-ray attenuations by the (unknown) sample matrix or other absorbing materials are not known.

However, it was early recognized⁹ that a way to minimize the effects of these experimental problems was to take advantage of the similar counting efficiency with which neighboring-energy gamma rays are detected and counted. That is, when the energies are nearly equal, the efficiency and attenuation differences are small, and the ratio of the isotopic abundances can then be directly related to the peak intensities by

$$A/B = I_1/I_2 \cdot E_2/E_1 \cdot P_2/P_1 \cdot t_A/t_B, \quad (2)$$

where

- A/B = atom ratio of isotopes,
- I_1, I_2 = peak intensities of gamma rays from A and B , respectively,
- E_1, E_2 = counting efficiencies for the respective gamma rays,
- P_1, P_2 = gamma-ray branching probabilities, and
- t_A, t_B = decay half-lives of A and B .

Although it is difficult to obtain accurate individual values of E_i and P_i , it frequently is possible to obtain accurate ratios of these quantities, particularly when the energy differences are small. The half-lives are well known,¹⁰ and therefore the accuracy of calculated isotopic ratios is dependent largely on the statistical precision with which the peak intensities, I_i , are measured.

There are about ten energy regions in a plutonium gamma-ray spectrum that can be used to calculate isotopic abundance ratios. In a few of these regions the peaks are closely spaced, yet well-resolved and isotopic abundance ratios are easily calculated. In regions where, peaks are not closely spaced, a more careful delineation of a relative efficiency curve is required. Finally, other regions contain several, closely spaced and overlapping peaks. To properly analyze such regions, it is necessary to develop techniques for unfolding the overlapping peaks using algorithms that accurately describe the shapes of the gamma- and x-ray peaks.

Useful Energy Regions

We have previously reported the gamma-ray energies and emission probabilities of the various isotopes of plutonium and their daughter

products¹¹ and have also discussed many of the characteristics and interference problems that exist in various parts of a plutonium gamma-ray spectrum.¹² Therefore, in this report, we only summarize some of these characteristics and state briefly how they relate to analysis methods, problems, and measurement accuracies. (The reader may also want to consult other excellent summary reports that have been published on these topics.^{5,13})

The 38- to 59-keV Energy Region

This is the lowest usable energy region (see Fig. 1). It contains peaks due to ^{238}Pu (at 43 keV), ^{239}Pu (38 and 51 keV), and ^{240}Pu (45 keV). The peak at 59 keV is due to both ^{241}Am and ^{237}U .

Although these peaks represent the most intense gamma emissions for each of the respective isotopes, their usefulness is limited. First, in order to see these peaks, the samples must be low in ^{241}Am content because the 59-keV peak of

Figure 1. The 38- to 59-keV energy region. This is the lowest energy region that is useful for plutonium isotopic measurements. It is visible only in spectra of freshly processed materials (i.e., the Am has been removed). The solid curve is from a solution containing 73% ^{239}Pu , and the dashed curve is from a 93% ^{239}Pu sample.

^{241}Am is very intense and the attendant Compton distribution quickly obscures all peaks of lower energy. Also, these low energy radiations are easily attenuated by thick or highly absorbing containers. Finally, the 38-keV peak of ^{239}Pu is very weak, especially when analyzing low ^{239}Pu content samples, therefore limiting its usefulness in delineating the intrinsic efficiency curve in this region. Nonetheless, an option is available in the MGA program so that data from this region may be included in the analysis process.

It should be noted that the 38- to 51-keV region can be significantly enhanced by using a thin terbium foil to preferentially attenuate the 59-keV gamma rays of ^{241}Am . However, the analysis is now complicated by the presence of the terbium x rays.

The 94- to 104-keV Energy Region

This region contains peaks from all of the isotopes of interest (see Fig. 2). They are also the next most intense peaks after those of the 38- to 59-keV region. However, the more than 15 x rays and gamma rays of this region form a very tight

cluster of peaks, requiring a very sophisticated method of analysis. On the other hand, the fact that this region contains such a wealth of spectroscopic data gave us the incentive we needed to develop a method for deconvoluting this region and for including this region in the MGA analysis procedure.

The predecessor to the MGA program (RATIO program) used only this region to calculate relative isotopic abundances. The results were very good for samples that did not contain uranium and were relatively low in ^{241}Pu abundance. However, as predicted in our simulation studies,¹² the analysis precision obtained by using RATIO deteriorated for samples of higher ^{241}Pu content because the corresponding peaks of this isotope in the 100-keV region began to dominate the less-intense peaks of ^{239}Pu . One of the principal reasons for developing the MGA program was to overcome this deficiency.

The 110- to 120-keV Energy Region

This region is also very complex, containing all of the K-beta x rays of U, Np, Pu, and Am plus a few gamma rays from some of the isotopes

Figure 2. The 94- to 104-keV and 110- to 120-keV energy regions. The upper curve is from a 78% ^{239}Pu oxide sample. The lower (dashed) curve is from a 93% ^{239}Pu oxide sample.

(see Fig. 2). Therefore, the data in this region is not very useful for isotope measurements. However, we later describe how some of the data in this region is quite useful for accurately delineating the overall efficiency curve. We will also describe how this region can be used to determine the U/Pu ratio in sample.

The 123- to 129-keV Energy Region

This region can be used to measure the $^{241}\text{Am}/^{239}\text{Pu}$ abundance ratio (see Fig. 3). However, the 125-keV emission intensity of ^{241}Am is about 5 times less than the 99- and 103-keV gamma emissions found in the 100-keV group. Neighboring peaks at 123, 124, and 125 keV due to ^{239}Pu are present as interferences. Furthermore, the 125-keV peak is usually further suppressed because it resides just above the K-shell absorption edge of plutonium. Consequently, the information content in the 123- to 129-keV region is quite inferior to that in the 100-keV region, particularly for rather recently processed samples.

The 129- to 152-keV Energy Region

This region (see Fig. 3), contains peaks due to ^{238}Pu , ^{239}Pu , ^{241}Pu , and ^{241}Am . The 148- and 152-keV peaks are universally used in computer analysis codes to determine the relative abun-

dances of ^{241}Pu and ^{238}Pu . Although the 152-keV peak is included in MGA's analysis process, the ^{238}Pu abundance is predominantly determined by the much more intense 99-keV peak found in the 100-keV region.

Until recently, it was impossible to accurately relate the intensity of the 129-keV peak of ^{239}Pu to the 148-keV peak of ^{241}Pu . This was because the efficiency ratio [see Eq. (2)] needed to relate the two was quite uncertain because of (1) the large energy spacing, (2) the steepness of the efficiency curve in this region, and (3) the inability to accurately define the efficiency in the 129-keV region. Although problems related to (1) and (2) cannot be changed, we have been successful in developing a new method for delineating the overall efficiency curve so that the efficiency ratio of the 129- and 148-keV peaks can now be calculated very accurately. This breakthrough that now allows us to use these two peaks to relate the ^{239}Pu and ^{241}Pu abundances was particularly important for analyzing samples with high ^{241}Pu content that could otherwise be accurately analyzed only by using the 332- to 345- and 367- to 380-keV energy regions. As mentioned earlier, these regions usually require a second, more efficient detector to obtain sufficient counts in a reasonable counting period.

Figure 3. The 125- to 152-keV energy regions. The solid line curve is from a 78% ^{239}Pu sample. The dashed curve is from a 93% ^{239}Pu sample.

The 160- to 165-keV Energy Region

The ^{240}Pu 160-keV peak in this region (see Fig. 4) is generally used by others³⁻⁵ to determine the ^{240}Pu isotopic abundance. However, the spectral data of this region is not used in MGA (except for determining the intrinsic efficiency curve) because (1) the 104-keV peak of ^{240}Pu is invariably far more intense than the 160-keV peak, as illustrated in Fig. 5; (2) the 160-keV peak, like the 104-keV peak, has interference problems, particularly as the ^{241}Pu content increases; (3) the 160-keV peak signal-to-background continuum is poor and tends to worsen with increasing ^{241}Pu abundance; and (4) the 165-keV peak to which the 160-keV peak is normally related is problematic when large amounts of ^{235}U are present or when the ^{237}U is not in equilibrium with ^{241}Pu .

The 203- and 208-keV Peak Region

This pair of peaks (see Fig. 6) is useful for determining the relative abundances of ^{241}Pu and ^{239}Pu . However, because the 208-keV peak is principally due to the decay of ^{237}U , a decay product of ^{241}Pu , the pair can be used only if secular equilibrium of the decay rates has been established. (This equilibrium is established about two months after complete removal of ^{237}U from a sample.) A small fraction of the 208-keV peak's intensity due to ^{241}Am must be considered in the analysis. The statistical uncertainty of the $^{241}\text{Pu}/^{239}\text{Pu}$ abundance ratio derived from this

Figure 4. The 160- to 165-keV energy region. The upper curve is from a 78% ^{239}Pu sample. The dashed curve is from a 93% ^{239}Pu sample.

Figure 5. Comparison of the relative intensities of the 104- and 160-keV peaks of ^{240}Pu in a spectrum of PuO_2 .

peak pair increases significantly for samples with high ^{241}Pu content because of the low intensity of the 203-keV peak relative to the 208-keV peak. Finally, the presence of ^{235}U or ^{239}Np (from the decay of ^{243}Am) in a sample complicates the

Figure 6. The 203- to 208-keV energy region. The upper curve is from a 78% ^{239}Pu sample. The lower, dashed curve is from a 93% ^{239}Pu sample.

analysis of this group. ^{235}U emits gamma rays of 202 and 205 keV, and ^{239}Np emits a gamma ray of 210 keV. These potential interferences are accounted for in the MGA program.

The 332- to 345-keV Energy Region

This region (see Fig. 7) provides useful data for measuring the relative abundances of ^{241}Pu and ^{239}Pu . ^{241}Am is also present, and some of the peaks overlap considerably. A reasonably large germanium detector should be used when measuring regions above the 208-keV peak in order to increase the efficiency for measuring these weaker gamma-ray groupings.

The 367- to 382-keV Energy Region

This region (see Fig. 7) is also useful for measuring the $^{241}\text{Pu}/^{239}\text{Pu}$ abundance ratio. However, whereas the precision of this ratio, when it is obtained from the 332- to 345-keV region, deteriorates with decreasing ^{239}Pu content (see Fig. 8), the opposite occurs when the 367- to 382-keV region¹² is used. Therefore, we include both of these regions in our analysis method. Although these regions were vital in older versions of MGA, the versions since 1986 have included the intense 129- to 148-keV peaks for determining the $^{241}\text{Pu}/^{239}\text{Pu}$ abundance ratio, thereby removing the need for including the

Figure 7. The 330- to 345-keV and 367- to 383-keV energy regions. The solid line curve is from a 78% ^{239}Pu sample. The dashed curve is from a 93% ^{239}Pu sample.

Figure 8. The solid lines show typical isotopic precisions obtained when analyzing the 330- to 345-keV region. The dashed lines are isotopic precisions using the 367- to 383-keV region. The 330- to 385-keV region is best for samples with high ^{239}Pu content. However, the 367- to 383-keV region is better when measuring samples low in ^{239}Pu .

higher-energy regions for most analyses. Although a second, larger detector should normally be used when analyzing the 300-keV regions, it is possible to alter the program to use a 8192-channel spectrum obtained from only the small detector. However, the lower counting efficiency will then greatly reduce the statistical precision of the data obtained from these regions.

The 632- to 664-keV Region

This region (see Fig. 9) contains peaks from ^{239}Pu , ^{240}Pu , and ^{241}Am . Although the region is somewhat complex, it can be used to measure the relative isotopic abundances of these isotopes. Because the radiations are so weak, a substantial amount of absorber, such as lead, must be used to attenuate the much more intense gamma rays of lower energy. The sample must also be relatively free of fission products. Freshly reprocessed plutonium, in particular, may contain significant quantities of ^{95}Zr and ^{95}Nb , which emit gamma rays that affect the data in the 600-keV region. ^{137}Cs , another fission-product contaminant, emits a 662-keV gamma ray that may compromise the ^{241}Am result derived from the measurement of a peak of about the same energy.

Although the 1001-keV peak of ^{238}U is quite removed in energy from the 632- to 664-keV

group of peaks, we have developed a method whereby we can relate its intensity to the peaks in this group so that the abundance of ^{238}U relative to plutonium can be determined. We discuss later how this group can also be used to determine the homogeneity of ^{241}Am in a sample.

Sample Variations

In standard "wet" chemical methods of analysis, the sample (or a representative portion of it) is conditioned and treated to make it conform to the measurement specifications of the instrument used to perform the analysis. For example, a mass-spectrometric measurement can be performed only after the sample has been chemically treated and reduced to a form acceptable to the spectrometer. The actual chemical procedures or steps used are frequently altered to take into account differences in the size, shape, or composition of the original sample, but the final form of the specimen loaded into the spectrometer is always the same.

In contrast, nondestructive analyses imply that the measurements be made without altering the sample. However, to properly analyze such a

Figure 9. The 630- to 665-keV energy region. This is the highest energy region that is useful for plutonium isotopic measurements.

sample, one should consider the isotopic, chemical, and physical characteristics of the sample that may have a bearing on the analysis.

Sample Size, Shape, and Composition

A good analysis method should accommodate any reasonable sample size. Obviously, the lower size limit is determined by the counting rate, the counting time, and the statistical accuracy required for the measurement. Although plutonium samples of less than 1 mg can be measured, a more practical lower limit is about 100 mg. There is no upper size limit. However, since the mean penetration of the radiations measured are very small, only the surface of a large sample is actually measured in the analysis. We should also point out that the size (or more specifically the thickness) of a sample significantly affects the relative efficiencies with which the various radiations are detected. However, as the sample thickness is increased, the radiations of the added material become increasingly absorbed until a so-called "saturation" thickness is reached. When this condition prevails, the radiations from the back side of the sample are completely absorbed, and the detected number of gamma rays will not increase. The saturation thickness is energy dependent but is approximately 5 g/cm² for 208-keV gamma rays. Variations of sample thickness less than this amount will significantly alter the relative efficiencies with which the lower-energy gamma rays are detected, hence changing the shape of the "intrinsic" efficiency curve.

The common chemical forms of plutonium are metals, oxides, and solutions. The chemical form has little effect on the analysis of the spectrum, with one notable exception. The alpha- and gamma-induced fluorescence of plutonium is related to the plutonium content (or concentration) in a sample. Consequently, there are dramatic differences in the observed x-ray intensities for metal, oxide, and solution samples. The qualitative differences can be used to distinguish between these forms.

Sample Age Since Processing

Recently processed plutonium samples are usually very low in ²³⁷U and ²⁴¹Am. The ²³⁷U increases in activity for about two months after processing, at which time it reaches equilibrium with the alpha-decay rate of its ²⁴¹Pu parent. Any analysis method that always assumes an established decay equilibrium between these two iso-

topes cannot be used to measure freshly processed samples.

The ²⁴¹Am content in a fresh sample initially increases linearly with time. As its activity level increases, the Compton distribution from its intense 59-keV peak soon begins to obscure the lower 38- to 51-keV energy peaks, thus making them useful only in special cases.

MGA has been programmed to analyze both freshly separated and aged samples.

Presence of Other Radioactive Materials

Other radioactive materials may be present in plutonium samples as decay products, as contaminants from previous processes, or as a result of blending. Uranium is one common radioactive material that is blended with plutonium to form mixed-oxide (MOX) fuels. The ²³⁵U/²³⁸U ratio may vary from about 0.002 to 20. The emissions of ²³⁸U and its daughter products are very weak; however, ²³⁵U and its daughter products emit several very observable radiations. They are found in nearly all of the low-energy regions discussed earlier and must be recognized and properly treated in the analysis process. However, the very presence of these radiations, particularly the very intense 185-keV gamma ray, allows one also to measure accurately the relative ²³⁵U content in a sample.

When uranium is present, the alpha and gamma rays of plutonium fluoresce the uranium as well as the plutonium in the sample. This increases the observed uranium x-ray intensity in the 100-keV region beyond that expected from the decay of the plutonium isotopes. We can take advantage of this fluorescence signal by comparing the enhanced uranium x-ray intensity (i.e., from the fluorescence process) with the plutonium alpha- and gamma-induced x-ray intensity (see Fig. 10). This ratio, for very homogeneous samples, directly reflects the relative abundances of the uranium and plutonium in the sample.

Another way of enhancing the fluorescence of these two elements is to expose the sample to an intense ⁵⁷Co source. In this way, one can achieve a more accurate measurement that is far less sensitive to inhomogeneities in the sample.

Other radioactive materials that may be encountered are ²³⁷Np-²³³Pa, ²⁴³Am-²³⁹Np, and low levels of some fission products such as ⁹⁵Zr-⁹⁵Nb and ¹³⁷Cs. The fission products are of little concern, except when analyzing the 600-keV region. ²³⁷Np-²³³Pa is nearly always present in aged plutonium because it is a decay product of

Figure 10. The highlighted curves are due to K_{α} x rays from the fluorescence of uranium and plutonium. Some of the uranium x-ray intensity is due to the decay of the plutonium isotopes. The remaining uranium x-ray intensity and all of the plutonium x-ray intensity are due to alpha-particle- and gamma-ray-induced fluorescence. The ratio of the uranium and plutonium fluorescence intensities is used as a measure of the elemental abundances.

^{241}Am . Although the presence of ^{237}Np does not create significant interference problems, it should be noted that neptunium is not always removed completely during the chemical processing of nuclear fuels; therefore, its 86-keV peak can sometimes be observed in spectra. The ^{233}Pa daughter ($t_{1/2} = 27$ d) emits several intense gamma rays of higher energy, but it takes several months to grow into decay equilibrium after separation.

Packaging and Use of Absorbers

The principal constraint for sample packaging is that the radiations must be able to penetrate the containers so that they can be detected. The lowest-energy peak usually used in our analysis is the 59-keV peak. Although an analysis can be performed without it, this peak is helpful in determining the cadmium absorber thickness. Ideally, the cadmium absorber used should attenuate the 59-keV peak's intensity to approximately the same height as that of the peaks found in the 100-keV region. Higher-mass-number absorbers, such as tantalum and lead, must be avoided.

Sample Homogeneity

Plutonium is a very dense and highly absorbing material. As a result, the gamma rays that are detected are principally from the first few millimeters of the sample surface. To infer that such a measurement is representative of the entire sample requires that the sample be homogeneous.

Caution must always be exercised when interpreting results obtained from an inhomogeneous sample. However, a few steps can be taken to improve the analysis of such a sample. One is to rotate (or better, to "tumble") the sample so that the portion of the sample viewed by the detector is constantly changing. In this way, a time-averaged spectrum is obtained that is much more representative of the entire sample than if only a small portion is viewed. Obviously, this method works only when the sample is composed of many smaller parts.

One method for detecting inhomogeneity is to compare isotopic results obtained from low-energy radiations with those from a higher-energy region, such as the 600-keV region.¹⁴ The results will differ if the sample material

associated with the more penetrating radiations has a different isotopic abundance than the material nearer the surface. Although this method can *sometimes detect* inhomogeneity, one cannot interpret the conflicting results without a model that adequately describes the characteristics of the inhomogeneity of a sample type. We are presently developing such models for several frequently encountered types of inhomogeneous samples.

Measurement System

It is beyond the scope of this report to treat in detail the many characteristics of the detector and electronic components of a good spectrometer system. However, a few salient comments and summary statements follow.

Detectors

A good analysis of the low-energy region of a spectrum requires a high-resolution germanium detector. The nominal size of the detector used most frequently is 200 mm² by 10 to 16 mm deep. The counting rate obtained with this small detector is usually adequate except for very small (<0.1-g) plutonium samples. The principal asset of the small detector is its excellent resolution of about 500 eV at 122 keV. Because our methods depend on accurately analyzing the complex 100-keV region, it is quite important that the resolution and other characteristics of the peak shape meet certain standards. We prefer that the full-width at half-maximum (FWHM) resolution at 122 keV be less than 525 eV; however, we have successfully analyzed spectra with resolutions in excess of 600 eV. Such high resolutions are encountered when using large detectors or when using a short amplifier-shaping time constant. The effects of these conditions are discussed later. It should be noted that if the measurement times are to be kept quite short (less than 10 to 20 minutes), the counting rate should be maximized even if there is some loss in resolution. In this case, the detector manufacturer should be told that the detector is to be used for high-counting-rate measurements so that the proper feedback resistance is used in the detector preamplifier. Furthermore, the detector, when viewed on an oscilloscope, should exhibit very few "slow" collection pulses. These slow pulses produce high-side peak distortions, thus making it more difficult to accurately characterize the peak shape. Methods for removing or reducing the causes for

these slow pulses are currently being investigated by some manufacturers and researchers.

Another concern is the amount of damage a detector receives as a result of energetic neutrons emitted by the sample. A high fluence of such neutrons produces damage sites in the detector that have a deleterious effect on the peak shapes. We are currently performing a study of the neutron damage process and its effects on the spectrum by irradiating germanium detectors with ²⁵²Cf neutrons.

The new versions of MGA do not require the energy regions above 300 keV, except possibly for purposes of measuring ²³⁸U or detecting isotopic inhomogeneities in samples. Should the higher-energy regions be important, a standard coaxial germanium detector approximately 50 cm³ in size with good resolution will suffice.

Pulse Electronics

Excellent commercial products are available; however, some care must always be taken when selecting the electronic components or specifying an analyzer system. The amplifier should be of high quality and preferably should include pulse-pileup-rejection circuitry. It is important that the amplifier and analyzer ADC be very stable because even small drifts of 0.01 to 0.02 in channel gain or zero level cause peak-shape distortions and potentially affect the results. Gain and zero level stabilizers may be added to prevent such drifts. The amplifier/ADC system must also exhibit good differential and integral linearity. However, only once in recent years have we encountered a system with unacceptable linearity.

If high counting rates are to be used, a fast ADC will improve the throughput rate. Shorter amplifier-shaping time constants of 1 or 2 μ s should be used for such measurements.

Computer

MGA is structured as a set of subroutines called in sequence. Various versions have been written to run under RT and RSX operating systems on Digital Equipment Corporation PDP-11 computers and under the VMS operating system of the VAX computer. It has also been implemented on an IBM-compatible personal computer. However, future enhancements and expansions of the capabilities of the code will be limited to the versions on the VAX and IBM PC computers because the PDP-11 systems have limited memory and are becoming obsolescent.

Methods and Algorithms for Measuring Peaks

If we consider an ideal, noiseless detector system, then all pulses from the "full-energy" absorption of gamma rays of a given energy will appear in one channel of a spectrum, rather than as a broadened distribution (see Fig. 11). Energy-degrading effects, such as low-angle scattering and incomplete charge collection, produce pulses of lower energy. The result is a discontinuity in the continuum at the peak.

This ideal cannot be realized because several sources for energy dispersion are always present in germanium spectrometer systems. The principal sources are electronic noise, statistical processes in the detector associated with the conversion of gamma-ray energy into electron-hole pairs, and energy degradation caused by trapping sites in the detector. These processes largely determine the shape of the observed peak and the underlying background continuum.

Describing the Peak Shape

Some peaks in plutonium spectra are well resolved so that their intensity can be simply determined by integrating the counts in selected channels and subtracting related backgrounds to obtain the net peak areas. However, the peaks in other regions overlap severely, requiring a more involved procedure to interpret the data. To

Figure 11. The change in background levels in going from one side of a peak to the other is ideally a step. However, it is smoothed by the detector/amplifier line broadening processes.

start, one must have an analytic function or algorithm that adequately describes the shapes of the peaks in the regions of interest. This shape is mainly described by a Gaussian function; however, some tailing does occur, particularly on the low-energy side. Therefore, the following equation we have formulated to fit a peak,¹⁵ as shown in Fig. 12, not only contains the central Gaussian component but also includes a "short-term" (and sometimes a "long-term") tailing component:

$$y_i = y^0 [\exp[\alpha (x_i - x^0)^2] + T(x_i)] \quad (3)$$

where

- y_i = net counts in channel x_i ,
- y^0 = peak height at the peak position, x^0 ,
- α = peak-width parameter, and
- $T(x_i)$ = tailing function, which is given by

$$T(x) = [A \cdot \exp(Bx) + C \cdot \exp(Dx)] \cdot [1 - \exp(0.4 x^2)]\delta \quad (4)$$

where $x = x_i - x^0$, $A \cdot \exp(Bx)$ accounts for short-term tailing and $C \cdot \exp(Dx)$ accounts for long-term tailing. We refer to A and C as

Figure 12. The principal shape components of a gamma-ray peak are described by a central Gaussian distribution and two tailing components.

"tailing-amplitude parameters," and B and D are parameters that describe the two tailing slopes. The final term involving δ reduces the effect of $T(x)$ to zero at the peak position ($\delta = 1$ for $x < 0$ and 0 for $x > 0$ to limit the tailing contributions only to the low-energy side of a peak).

We later discuss how these equations are used to unfold the data in complex peak regions. For now, it is important to note that some of the variables enter linearly in the equations (such as y_0 , A , and C), whereas the others are in one of the exponents. We have found that the variables appearing in the exponents usually can be predetermined and therefore treated as constants. The equations then become linear in form so that they can be solved by a one-pass least-squares calculation rather than by iterative calculations. No prior peak-shape characterization is required. Instead, the variables are all determined from the spectrum that is analyzed.

The peak resolution parameter, α , is related to the peak width, σ_t , by the equation

$$\alpha = -1/2\sigma_t^2, \quad (5)$$

where σ_t is given by

$$\sigma_t^2 = \sigma_n^2 + \sigma_s^2, \quad (6)$$

and where

- σ_t = the total peak width at half-maximum,
- σ_n = contributions due to the system "noise," and
- σ_s = detector contribution related to the statistical process of electron-hole production.

Because σ_n is a constant for a given spectrum and σ_s is directly related to the energy,¹⁵ Eq. (6) can be written as

$$\sigma_t^2 = S_1 + S_2 E. \quad (7)$$

The shape constants S_1 and S_2 are determined by measuring the peak width of two "clean" peaks in a spectrum. The two resulting equations of the above form are solved to determine values for S_1 and S_2 . The peaks used in MGA are the 59.5-keV peak of ^{241}Am for the lower-energy peak and a weighted average of the widths calculated for the 129.29- and 148.567-keV peaks. If the 59.5-keV peak is very weak, a default value for S_2 is used. Default values for A , B , and D are also written into the program.

Although Eqs. (3) and (4) are useful for describing gamma-ray peak shapes, they do not accurately describe the observed distribution of K-series x-ray peaks associated with the actinide elements.¹⁶ Because of the short lifetime of the virtual x-ray state associated with the electron conversion process, the Lorentzian distribution of K x rays emitted have an FWHM of about 100 eV. When this energy distribution of radiations is convoluted with the instrumental dispersion, the resulting peak shape, as shown in Fig. 13, is substantially different from that of an equivalent-energy gamma ray. A special subroutine, based on the algorithms reported in Ref. 16, is used to compute the altered response.

The above equations are adequate for describing peaks in a spectrum taken at modest counting rates. Additional peak-shape distortions may occur when using high counting rates. These manifest themselves as protrusions or tails on the high-energy side of the peaks. The magnitude and shape of this distortion is not predictable. However, a relatively crude procedure has been implemented in MGA to account for this distortion when generating peak shape profiles. In this procedure, the Gaussian portion of the 59- and 208-keV peaks is first stripped out. The net counts left on the high-energy side of these peaks are used to determine an approximate magnitude and shape of any distortion caused by

Figure 13. The Lorentzian-broadened energy distribution of x rays both increases the FWHM of a peak and significantly alters its line shape.

pulse pileup. This profile is stored and used when calculating the shape responses of the peaks in the 94- to 104-keV region.

Delineating the Background

The data of a low-energy spectrum can be broadly considered to result from either single interactions or multiple interactions that deposit all of the energy of the gamma rays in the detector, or from Compton-scattering events in which some of the energy is lost. The first process produces the distinct peaks in the spectrum, the second simply produces an underlying continuum that is of little worth. It is therefore usually removed by subtraction to give the "net" counts of a region of interest. The net-count intensity is then analyzed to yield isotopic results.

The energy boundaries for each peak or peak grouping used in the analysis are specified in the MGA code. The continuum intensities, referred to as background levels, are determined for each of the boundaries. An explicit function is then used to interpolate the channel-by-channel continuum or background level from one boundary point to the other. The function we use is given by

$$B_i = b_n + (b_m - b_n) \frac{\sum_{j=n}^i y_j}{\sum_{k=n}^m y_k}, \quad (8)$$

where

- B_i = computed background at channel i ,
- y_i = spectrum count of channel i ,
- b_n = background level of the low-energy side of the peak, and
- b_m = background level of the high-energy side of the peak.

This expression works equally well for single peaks and for complex peak groupings, such as is shown in Fig. 17, and produces the expected form of the continuum response when the ideal detection responses are smeared by the system noise.

The above expression is quite simple and yet rigorous. However, it assumes that the smooth steps are superimposed on an otherwise

flat, nonsloping background. In practice, it is found that the background level at one or both boundary positions may be sloping. The subroutine we use in MGA accounts for these sloping conditions in its process of interpolating the background continuum.

Another question that must be addressed is, "Where does the peak region begin and where does it end?" The functions that describe the peak shape are continuous functions [see Eqs. (3) and (4)]. Therefore, a pragmatic approach must be used to define the boundaries. Since the high-energy side of a gamma-ray peak is described by a Gaussian function, the upper energy boundary can be determined easily by calculating the position where the peak intensity has become negligible. For example, the peak intensity will be only 0.0005 of the peak height at an energy that is 1.66 times the FWHM above the peak centroid.

It is more difficult to apply this simple procedure to calculate the low-energy-side boundary because of the presence of tailing. Our procedure is to subtract 0.1 to 0.2 keV from the position calculated by using the method just described for determining the high-energy-side boundary. This generally will include all of the short-term-tailing area associated with the peak. Long-term tailing is considered to be part of the background continuum.

Not all peaks are amenable to this simple treatment. In some cases, the peak or peak grouping is bounded by a region that is not truly background. In such cases, a more remote region must be chosen to define the background level.

The 94- to 104-keV region presents an additional problem. This region contains several intense x rays. The energy dispersion of x rays is Lorentzian in shape. The extremities of the shape function extend a great distance from the peak centroid and therefore may contribute significantly to the background levels at the boundary positions (see Fig. 14). However, the x-ray intensities at the boundaries can be computed by using

$$f_a = 1 - \frac{2}{\pi} \tan^{-1} \left(\frac{2\delta}{\Gamma} \right), \quad (9)$$

where

- f_a = fraction of peak area outside of $\pm$ distance from centroid of peak,
- δ = distance from peak centroid, and
- Γ = Lorentzian width of x-ray peak.

Figure 14. Equation (8) accurately delineates the background continuum under complex peak clusters, as shown here. Note that the entrance and exit background slopes are also considered in our background-calculation routine.

Appropriate adjustments can be made to the background levels by using this equation. Additional adjustments are made to the lower background level because of the long-term tailing of the peaks in the region.

Another problem is the rather large energy span of the 94- to 104-keV region (usually encompassing about 170 channels). Small unpredictable changes in the background shape may be present because of Compton scattering of higher-energy gamma rays. To treat these and other possible background perturbations, we have implemented

a background-correction process in the final calculational stage. In this process, after the initial least-squares fit of the data, the residual vector is examined to determine significant positive or negative trends in certain regions of the 94- to 104-keV data. Significant trends in the residuals corresponding to the beginning and ending equations representing the data in this region are used to make adjustments in the beginning and ending background levels.

In addition to these two regions, there are three other positions—at 96, 100, and 102 keV—where the peak intensities are quite low and the corresponding net counts approach the background level (see Fig. 2). The residuals in these regions are also examined for trends. The background (and the resulting net counts) are adjusted so that the residuals in these three regions and at the two ends of the 94- to 104-keV region will be near zero when the calculation is repeated a second time.

Determining the Energy Scaling

Early versions of MGA required that the low-energy spectrum be taken at a gain of close to 75 eV per channel, with a zero energy intercept at channel zero. Current versions are more forgiving with respect to the energy scaling, but we still strongly recommend that the spectrometer be set up to approximate these conditions. The peak positions of the 59-, 129-, and 148-keV peaks are used to refine the zero intercept and gain values. Exact placement of the peaks in the 94- to 104-keV region requires a further refinement of the energy scaling. A new gain is calculated for this region based on the measured positions of the 94.66- and 101.063-keV x rays.

Calculational Methods Used in MGA

Although many analysts refer to the “algorithm” used in an analysis program, the term “methodology” is perhaps more appropriate because the total analysis process is much more than a few well-defined steps or easily written equations. It is true that most plutonium isotopic analysis methods, including MGA, begin with some variant of Eq. (2). However, the methods used in MGA differ from other programs in at least the following ways:

- It uses the most intense peaks of a spectrum—for example, the 94- and 104-keV region and the 129- and 148-keV peaks. Although these regions are more difficult to analyze, they can provide measurement precisions of 1% or better and also reduce the measurement times to only a few minutes.
- The technique for delineating the “intrinsic” efficiency curve for the region from 59 to 208 keV is based on the physical processes

governing the change in detection efficiency with energy and enables us to relate accurately the intensities of peaks belonging to the different isotopes in this region. This procedure is particularly important for relating the intensities of the widely separated peaks at 129 and 148 keV due to ^{239}Pu and ^{241}Pu , respectively. However, similar principles are employed to define the efficiency from 208 to 1000 keV when a second detector is used to augment MGA's analysis capability.

- We treat the data differently. The spectroscopic data used to perform an analysis are represented by a large number of equations, which are made compatible and internally consistent. Some equations represent integrated peak areas (e.g., equations for well-resolved peaks), while others represent channel-by-channel counts. The equations are linear in form and when properly weighed by the variance of the data they represent, they are easily solved in a single computational step by the method of least-squares to give the relative isotopic abundances of interest along with the attendant measurement uncertainties.
- We have attempted to include in the methodology the capability to analyze a wide range of sample types. For example, samples may vary in size, isotopic and chemical composition, and age since chemical purification, and they may contain other activities such as ^{235}U , ^{238}U , ^{237}Np – ^{233}Pa , ^{243}Am – ^{239}Np , or fission products.

Basis of the Method

The basic method for determining the relative abundance of plutonium isotopes is to measure the intensity of two or more peaks from gamma rays of similar energy, but arising from different isotopes [see Eq. (2)]. Because the gamma-ray-emission probabilities and half-lives are known, the atom ratios can be calculated if relative detection efficiencies for the peaks can be estimated. The local intragroup relative efficiencies can be determined accurately by delineating intergroup efficiencies. The curve describing intergroup efficiencies, commonly known as the "intrinsic" efficiency curve,¹⁷ is determined by fitting observed peak intensities (divided by the gamma branching intensity) to a function used to describe the relative efficiency with energy. The functions that are commonly

used are adequate to determine the efficiency relationships of closely spaced peaks; i.e., those separated by less than 5 to 10 keV. However, it is difficult for these functions to accurately relate the 129- and 148-keV peak efficiencies. One reason is that the energy spacing is so large. Another is that the efficiency slope in this region is very steep, and the K-shell absorption edge precludes peaks of lower energy from being used to define the curve.

The "Intrinsic" Efficiency Function Used

We have developed a function that is related to the three basic physical processes that predominantly determine the overall shape of the relative detection efficiency curve (see Fig. 15):

- The gamma-ray interactions with the detector.
- Attenuations caused by absorbers (cadmium is usually used).
- Sample self-attenuation.

The advantage of basing the functional form on known processes is that its shape is determined not only by the data but also by the *known* physical-interaction processes. Because the variables involved in the three processes are not usually controlled or known, they must be determined from the gamma-ray spectrum itself. We have developed an equation involving these processes that describes the relative detection efficiency as a function of energy:

$$A_j = \sum_{k=1}^{3/4} (B_{jk} \cdot X_k) \cdot e^{-\mu_j^{\text{Cd}} \cdot \text{CD}} \times \frac{1}{\mu_j^{\text{Pu}} \cdot \text{PU}} (1 - e^{-\mu_j^{\text{Pu}} \cdot \text{PU}}) \times \text{eff} \cdot (1 + bE_j + cE_j^2) , \quad (10)$$

where

- A_j = area of peak j ,
- B_{jk} = gamma-ray branching probability of peak j of component k ,
- X_k = disintegrations per minute of component k ,
- μ_j^{Cd} = mass absorption coefficient of cadmium for peak j ,
- CD = mass (g/cm^2) of cadmium absorber used,
- μ_j^{Pu} = mass absorption coefficient of plutonium for peak j ,

- PU = mass (g/cm^2) of plutonium in the sample,
 eff = estimated detector efficiency for peak j obtained from a "standard" efficiency curve,
 E_j = energy (keV) of peak j , and
 b, c = coefficients in a quadratic function used to account for small deviations in the efficiency from the "standard" value.

To solve Eq. (10) for the variables involved, we have chosen to use the measured intensity of the ten ^{239}Pu , ^{241}Pu , ^{241}Am , and ^{237}U peaks* that are identified and highlighted in Fig. 15. Since the ^{237}U decay rate is usually in equilibrium with

* In the most recent versions of MGA, the 267-keV peak of ^{241}Pu - ^{237}U is also measured and included in the analysis process.

its ^{241}Pu parent activity, the two components can then be treated as one, thus reducing the maximum number of variables to seven. An additional degree of freedom must be allowed when analyzing samples containing uranium.

Since the equations representing the peak intensities are very nonlinear, an iterative least-squares method is used that involves a Taylor series expansion about trial values of the variables. The trial values are improved following each iteration until all incremental improvements are negligible.

Considerable effort has been devoted to ensuring that the iterative process used to solve the set of equations converges properly for all of the different analysis situations that are encountered. The reasons for the success of the new method can be better understood by using Fig. 16, which represents the matrix of coefficients of the equations representing the

Figure 15. The intensity of x-ray and gamma-ray peaks in a spectrum are determined principally by three factors: the intrinsic detection efficiency, attenuation by absorbers such as cadmium, and sample self-attenuation. The general effect of each factor on the intensity of the peaks is shown superimposed on a typical spectrum that highlights the 10 peaks used to determine the exact shape of the overall efficiency curve.

Figure 16. The relative intensities of the 10 peaks used to determine the intrinsic efficiency curve are governed by the components of this matrix. The isotopic origins of the peaks are shown in the first four columns. The effect of the other four variables are illustrated in the remaining columns.

intensities of the 10 peaks that are used. From this figure, one can see first that many of the peaks result from more than one isotope. Next, it is easy to sense that the relative intensities of the 59- and 103-keV peaks (caused principally by ^{241}Am) will strongly determine the value of CD in Eq. (10) because the 59-keV peak intensity is so predominantly determined by the thickness of the cadmium absorber. The plutonium thickness, PU in Eq. (10), is mainly determined by the 94-, 111-, 129- and 148-keV peaks because the plutonium K-shell discontinuity at 121.8 keV greatly alters their relative intensities. That is, ^{239}Pu and ^{241}Pu emit intense peaks at 129 and 148 keV, respectively, whereas the 94- and 111-keV peaks are uranium x rays coming from both of these isotopes. The x rays lie below the K-shell absorption discontinuity, whereas the gamma rays lie

above it. The magnitude of the abrupt change in the intensity pattern of the two sets of peaks strongly determines the value of PU in Eq. (10).

We found that special calculational procedures were required to handle certain measurement conditions, particularly as parameter boundaries are approached. For example, special action is required when the value for the plutonium sample thickness approaches either zero or the "saturation" thickness, where the gamma-ray peak intensities remain invariant with increasing sample thickness. Finally, it should be pointed out that the quadratic (final) term in Eq. (10) not only corrects for small deviations from the computed "generic" efficiency curve (denoted by "eff" in the equation), but this term also accounts for other slowly varying effects, such as attenuation due to low-Z materials. As a result of considerable study and many evaluations, our method now appears to converge satisfactorily for all sample types.

Calculational Methods and Equations

The area of a peak in a spectrum is related to the isotopic components in a sample by

$$A_j = \epsilon_j B_{j,k} X_k, \quad (11)$$

where A_j , $B_{j,k}$, and X_k are defined as in Eq. (1), and ϵ_j is the relative efficiency for detecting this gamma ray. This linear equation can be used directly to represent well-resolved peak pairs such as the 129/148-, 148/152-, and 203/208-keV peak pairs. To illustrate, consider the 203/208-keV peak pair belonging to ^{239}Pu , ^{241}Pu , ^{237}U , and ^{241}Am . If A^{203} and A^{208} represent the net areas of the two peaks, the following equations can be written to relate their intensities to these isotopes:

$$A^{203} = \epsilon^{203} B_2^{203} X_2, \quad (12)$$

and

$$A^{208} = \epsilon^{208} (B_4^{208} X_4 + B_5^{208} X_5), \quad (13)$$

where the indices 2, 4, and 5 represent ^{239}Pu , ^{241}Pu , and ^{241}Am , respectively. Note that peak-shape factors have not been included in these equations because the peaks are well-resolved; and, therefore, only total net counts need be used.

A single linear equation can now be formed by dividing Eq. (13) by Eq. (12):

$$0 = B_2^{203} X_2 - \frac{A^{203}}{A^{208}} \frac{\epsilon^{208}}{\epsilon^{203}} (B_4^{208} X_4 + B_5^{208} X_5) . \quad (14)$$

The ratio $\epsilon^{208}/\epsilon^{203}$ is the intragroup efficiency correction, which can be determined accurately from the slope of the "intrinsic" efficiency curve in this energy region. Although the efficiency of this group, in relation to other groups used in the analysis, does not explicitly appear in Eq. (14), it can be shown that the approximate intergroup efficiency ($\epsilon^{203}/\epsilon^{100}$ in this case) must be used to properly weight this equation relative to the equations that represent the 100-keV peaks, prior to solving them by the method of least squares. Equations similar to Eq. (14) can be developed to represent other peak pairs such as the 129/148- and 148/152-keV pairs. After all of the equations have been assembled and properly weighted, they are solved by the standard method of least-squares. Appendix A contains the x rays and gamma rays used in the low-energy region and their branching intensities.

For unresolved peaks, such as those shown in Fig. 14, Eq. (11) must be expanded to include overlap of the peak distributions. This can be done by allowing the branching intensity in Eq. (11) to be altered by a peak-shape dispersal factor S_{ij} , which is a computed shape factor that describes the dispersion of the area of peak j into channel i . The peak-shape function we use is similar to Eq. (3):

$$S_i = h [\exp \alpha (x_i - x_i^0)^2 + \text{tailing terms}] , \quad (15)$$

where S_i is the counts in channel i relative to the peak height, h , at the peak centroid x^0 ; and α is a peak-width parameter. Methods have been developed whereby all of the variables not appearing as linear terms in the peak-shape function can be predetermined and, therefore, treated as constants when this expression is used to calculate peak shapes.

When the dispersion function is applied to a peak of area A_j , we no longer have a single equation but several equations that encompass

the width of the peak (or peaks). Instead of using peak areas, as described by Eq. (11), we now treat each channel count, y_i , separately:

$$y_i = \sum_{k=1}^m \left(\sum_{j=1}^n \epsilon_j \cdot B_{jk} \cdot S_{i,j} \right) X_k . \quad (16)$$

This equation forms the basis for analyzing the highly overlapping 94- to 104-keV peak region.

Since we are interested only in determining *relative* isotopic abundances, we have chosen, arbitrarily, to set the detector efficiency to be 1.0 at 100 keV. The shape of the spectral response of isotopic component X_k is represented by the channel-by-channel calculated coefficients of component k . This method greatly simplifies the analysis process, since there is now only one degree of freedom per isotopic component. These component-response distributions are illustrated in Fig. 17.

Calculating Measurement Uncertainties

Equations (11) and (16) can be rewritten in a number of different ways. However, in their present forms, the least-squares solution of the equations results in *relative* abundances of the various isotopes. (That is, these are *un-normalized* abundances.) It should be understood that there may be several variables in addition to the isotopic abundances implied by Eqs. (11) and (16). The 16 possible variables or components currently allowed in MGA are given in Vol. 2 of this report. These are treated as independent variables. Consequently, the diagonal elements of the inverse matrix of the weighted equations represent the variances of the relative abundances. The square roots of the variances are a measure of the standard deviations associated with the relative abundances.

The relative isotopic abundances resulting from the least-squares calculation are better understood if they are ratioed to one of the isotopes (e.g., ^{239}Pu) or if they are summed and then ratioed to the sum, producing a fractional or percentage abundance. The standard deviations corresponding to these new representations of the isotopic abundances also involve the off-diagonal or covariance matrix. For example, to calculate

Figure 17. The spectral response of each isotopic component in the 94- to 104-keV region can be calculated by using known and measurable parameters. The relative isotopic abundances are then determined by fitting these responses to the data in this energy region.

the standard deviation of the ratio of one isotope A to another B , we have

$$\sigma_{A/B}^2 = \left(\frac{A}{B}\right)^2 \left[\left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_B}{B}\right)^2 - \frac{2\sigma_{AB}^2}{A \cdot B} \right], \quad (17)$$

where σ_A and σ_B are the standard deviations of the relative abundances of A and B , respectively, and $\sigma_{A/B}$ is the standard deviation of the ratio of A to B .

The propagation of the standard deviations of the isotopic abundances that have been normalized to unity is more complex, but it can be shown to be given by¹⁸

$$\sigma_r^2(f_A) = (1 - f_A) \sigma_r^2(A) + \sum [f_x \cdot \sigma_r^2(x)], \quad (18)$$

where $\sigma_r(f_A) = \sigma_A/A$ represents the relative standard deviation of isotope A when its abundance is represented as a fraction f_A of the total and $\sigma_r(x)$ and f_i are the relative standard deviation and fractions of the other isotopes.

Equations (17) and (18) are derived from a standard treatment of statistical data. However, it must be recognized that there are many sources of measurement uncertainty that do not derive from such a simple treatment of counting statistics. Some sources are random or fluctuating, and others persist, at least for certain measurement conditions, thereby producing a bias. These sources of measurement error are usually difficult to find and to treat properly. They also become more apparent when high-statistical-precision spectra are taken so that peak areas and even channel counts contain 10^6 or more counts.

Particularly in such instances, nonstatistical sources of error dominate the measurement error. We have implemented some pragmatic methods to account for these sources of error. For example, we add 0.1% of the peak area or channel count to its normal statistical uncertainty. That is, these uncertainties can never be less than 0.1%. There are other places in the analysis program where it was impossible to rigorously determine the uncertainty that a calculation or operation introduced into the final results. However, where possible, we made an estimate of the error and included it in the calculations.

Many of the constants, parameters, and algorithms used in the program are assumed to be perfect. For example, we assume that the gamma-ray branching intensities and the absorption coefficients have no uncertainty. We also assume that the peak-shape algorithm [Eqs. (3) and (15)] is perfect in form and that the parameters used to calculate the peak-shape profiles have no uncertainty associated with them. This is an ideal that is rarely attained, particularly as the statistical precision of the data becomes very good. One test of the adequacy of the peak-shape function is to calculate the reduced Chi-squared or "goodness-of-fit" ("QFIT" in the printout). This quantity is defined as

$$QFIT = \frac{\sum_{i=1}^n R_i^2}{n - m} , \quad (19)$$

where

- R_i = weighted residuals following the least-squares fitting operation,
- n = number of equations, and
- m = number of variables.

The most probable value of QFIT for an ideal least-squares fit is 1.0. A value >1 signals an imperfect fit. However, its absolute value is frequently not very useful because it is correlated with the statistical precision of the data.

To circumvent this correlation, we have implemented a modification to the quantity QFIT, suggested by Sekine and Baba.¹⁹ This new procedure attempts to remove most of the dependence on intensity. We have therefore named the new quantity "NQFIT" to represent the intensity-normalized goodness-of-fit defined by

$$NQFIT = 1.0 + \frac{100[(n - m)(QFIT - 1.0)]}{\Sigma Y_i} , \quad (20)$$

where ΣY_i = sum of the net counts in the region. Since NQFIT is insensitive to the spectral intensity, the degree of its departure from a value of 1.0 can be used to warn the analyst of a problem in the fitting process.

Ancillary Measurements and Analyses

Determining the ²⁴²Pu Abundance

The ²⁴²Pu isotope cannot be observed in a gamma-ray spectrum, and, therefore, a *direct* determination of its abundance cannot be made. The analyst is given a couple of options to account for its presence. One is to enter a known or estimated value that will simply be used without change during the calculation and reporting processes. The other option is to calculate the ²⁴²Pu abundance by using algorithms based on the measured abundances for the other plutonium isotopes. The one algorithm available is based on an earlier study,²⁰ which showed that the ²⁴²Pu abundance could be estimated by

$$[242] = 53 \cdot [240] \cdot [241] / [239]^2 , \quad (21)$$

where quantities in brackets are the abundances of the 239, 240, and 241 mass isotopes. This correlation (see Fig. 18) was found to be independent of the reactor origin of the plutonium. The largest problem with this algorithm is its sensitivity to the ²⁴¹Pu isotope ($t_{1/2} = 14.35$ y). Since the sample history is not always known or available, any uncertainty in the decay of ²⁴¹Pu prior to the last separation of ²⁴¹Am will be directly reflected in the calculated ²⁴²Pu abundance.

Other attempts have been made to develop an algorithm that is less sensitive to this decay problem. Patrick Lewis²¹ has suggested using

Figure 18. An isotopic correlation that can be used to determine the ^{242}Pu abundance.

the following simple polynomial form to calculate the ^{242}Pu abundance:

$$[242] = a + b [239] + c [240] + d [241] \quad (22)$$

We have tried this equation and several modifications of it but have had only limited success in using this general form to fit the wide range of isotopic measurements we have in our data base. The best results were obtained by adding higher order terms to the above equation and by applying the equation only to limited regions of isotopic data. A separate set of coefficients is determined and subsequently used for each region. This algorithm is also implemented in MGA. The coefficients currently used are given in Vol. 2 of this report.

Measurement of Other Actinide Isotopes

Plutonium samples invariably contain isotopes of other actinide elements, some as products of the isotopic decay process and others as a result of incomplete chemical processing or of intentional additions. For example, ^{237}U and ^{241}Am are both decay products of ^{241}Pu . The ^{237}U activity is usually in equilibrium with the ^{241}Pu decay (i.e., about 2 months after its separation), and, therefore, its presence is not usually

reported. ^{241}Am is also always present, and its determination is usually required as part of a complete measurement of a sample. Its abundance in a sample is reported relative to the total plutonium abundance.

^{237}Np is also sometimes detected because it is a natural decay product of ^{241}Am and is not always completely removed during chemical processing. MGA will attempt to detect its weak, but only, peak at 86 keV. (Lead x rays interfere with the detection of this peak and therefore any lead used for detector shielding should be carefully lined with cadmium.) If a two-detector system is used, the ^{237}Np in a sample can be detected down to about the 50-ppm level by analyzing the 312-keV peak due to ^{233}Pa , the daughter product of ^{237}Np . However, this analysis assumes that ^{233}Pa ($t_{1/2} = 27$ d) is in decay equilibrium with ^{237}Np . It is also important to account for the intensity of the 311.7-keV peak of ^{239}Pu that appears in the same location in the spectrum.

The MGA analysis also accounts for the presence of interference coming from ^{243}Am – ^{239}Np , from the fluorescence x rays of thorium in a sample, and from fission-product ^{137}Cs that is sometimes present in the second spectrum of a two-detector system.

Uranium is another actinide element that is frequently mixed with plutonium, particularly for the purpose of preparing nuclear fuels for power reactors. These MOX materials usually have low enriched uranium content, but samples high in ^{235}U content are also sometimes encountered.

The ^{235}U content of a sample is easily measured by analyzing the 185-keV peak in the spectrum (see Fig. 19). This gamma ray is conveniently located in the low-energy portion of a plutonium spectrum and can still be detected when the amount of ^{235}U present in a sample is only about 1% of the amount of plutonium in that sample. With higher abundances of ^{235}U (and its ^{231}Th daughter product), several other gamma rays appear in the spectrum as shown in Figs. 20 and 21. The interferences from these peaks must be taken into account in the analysis process.

The presence of ^{238}U is much more difficult to detect and measure. This results, in part, from its very long half-life and the corresponding low disintegration rate and also from the rather low emission probability of its gamma rays. The most tractable gamma ray is at 1001 keV, which is not a direct result of the decay of ^{238}U , but rather of the decay of ^{234}Pa , a daughter product that is assumed

Figure 19. The abundance of ^{235}U in plutonium samples is best determined by measuring the 185-keV gamma-ray intensity. Other ^{235}U peaks in the 200-keV region produce interferences that must be accounted for in the analysis program.

to be in decay equilibrium with ^{238}U . The emission probability of this gamma ray is less than 1%, and its relatively high energy requires that a large germanium detector be used to increase the counting efficiency.

We have implemented a procedure for directly measuring its abundance by using the weak peak at 1001 keV that can be observed in a two-detector system. This procedure is described in the next section, which discusses the analysis enhancements provided by the second detector of a two-detector system.

A few other methods can be used to measure the total uranium content and, indirectly, the ^{238}U content of a sample. One of these uses the uranium and plutonium x rays generated by the self-fluorescence in a sample (see Fig. 10). We infer the relative elemental abundances to be directly related to the measured intensities of the two sets of x rays. However, this implies that the uranium and plutonium are being fluoresced with equal probability. Two known processes affect this direct relationship. We must first point out that the observed fluorescence is induced both by alpha and by gamma rays that are emit-

ted principally by the plutonium in the sample. (The proportions resulting from each radiation have not been quantitatively determined.) The alpha rays have a very short range, and therefore, any significant differentiation of the uranium and plutonium components in the mixture will cause the plutonium to be preferentially fluoresced. This will result in a low measurement of the U/Pu ratio by this technique. Only when the sample is intimately mixed at the molecular scale, such as in coprecipitated materials, can the measurement of the U/Pu ratio by internal fluorescence be trusted.

The second process that perturbs the relative uranium and plutonium fluorescence probabilities is related to x-ray and gamma-ray self-fluorescence. First, we recall that the K-shell absorption edge for uranium and plutonium are at 115 and 121 keV, respectively. This means that the x rays and gamma rays in this energy interval can excite only the uranium in the sample, not the plutonium. Most of these radiations are K_{β} x rays, some of which belong to plutonium. This preferential excitation of the uranium is most prominent when the U/Pu ratio is low. We have

Figure 20. ^{235}U and its daughter products also produce interference peaks in the 100-keV region. Note the enhanced uranium x-ray intensities due to self-induced fluorescence.

Figure 21. ^{235}U interference peak in the 160- to 165-keV region.

written the following empirical relationship to correct the observed U/Pu x-ray-intensity ratio:

$$\text{U/Pu} = R [1 - 0.3/(R + 1)] \quad , \quad (23)$$

where R is the observed U/Pu x-ray-intensity ratio.

The problem with the alpha-induced component of self-fluorescence can probably be greatly reduced by using an external excitor source such as ^{57}Co . The fluorescence signal thus produced should be far less dependent on the particle size of the uranium and plutonium components of the sample.

Another method we have attempted is based on measuring the abrupt change in spectrum intensity pattern near the K-shell absorption

of uranium, as shown in Fig. 22. The presence of uranium produces a discontinuity in the intensities of the $K\beta$ x rays found in the 110- to 120-keV region. This discontinuity is caused by the abrupt change in absorbance at the binding of the K-shell binding energy of uranium at 115.6 keV. The U/Pu ratio can be inferred from the size of the intensity shift.

We have written a test subroutine that utilizes this technique to measure the U/Pu ratio. Although we could not obtain good quantitative results in our initial attempts, the method could be used to provide qualitative estimates.

Calculation of Specific Heat, ^{240}Pu Effective, and Sample Age Since ^{241}Am Removal

Relative isotopic-abundance results by gamma-ray spectrometry are frequently used to interpret the measurement results produced by other nondestructive techniques, such as calorimetry and neutron-coincidence counting. The total specific power that a sample produces is easily calculated from the isotopic abundance results by

$$P = \sum_i k_i f_i, \quad (24)$$

where

P = sample specific power (W/g),
 k_i = specific power of the i^{th} isotope (a constant related to the energy released per gram of the isotope), and
 f_i = isotopic fraction of the i^{th} isotope in the sample.

The uncertainty in P is related to the uncertainties in the relative isotopic abundances by

$$\sigma^2(P) = \sum_i [(P - k_i) f_i \sigma_r(i)]^2, \quad (25)$$

Measurement of Groups Outside the 59- to 300-keV Region

The preceding discussions are largely oriented to the analysis of the 59- to 300-keV region of a spectrum. The spectrum of this region should be collected with a small high-resolution

Figure 22. In a sample containing both uranium and plutonium, the x rays and the gamma rays lying between the K-shell absorption edges of the two elements—115.6 and 121.8 keV, respectively—will be attenuated in a significantly different fashion than the radiations outside these bounds. The change in attenuation can be used to determine the approximate U/Pu ratio.

where $\sigma_r(i)$ is as defined in Eq. (18).

The ^{240}Pu effective value is used to interpret neutron-coincidence-measurement results. It is calculated by

$$^{240}\text{Pu}_{\text{eff}} = 2.49 \cdot f_{238} + f_{240} + 1.57 \cdot f_{242}. \quad (26)$$

It is also sometimes useful to know the age of a sample since the time it was chemically processed and stripped of its ^{237}U and ^{241}Am . For freshly separated samples (i.e., less than about 10 days) the program will calculate a separation date based on the extent of ^{237}U ingrowth. Thereafter, the time since separation is calculated only from the ingrowth of ^{241}Am resulting from the decay of its ^{241}Pu parent.

germanium detector, using a gain of approximately 75 eV per channel. This precludes analysis of peaks above 300 keV when using a 4096-channel spectrum. Furthermore, the efficiency of

small planar detectors is very low for higher-energy gamma rays. Fortunately, the gamma-ray groupings above 300 keV do not usually add significantly to the content or accuracy of the low-energy results, with perhaps two exceptions. Sample homogeneity is one characteristic that can be detected by including higher-energy groupings. The easily absorbed low-energy radiations determine only a surface analysis of the sample, whereas the more penetrating higher-energy gamma rays also represents sample material from greater depths. Any differences in the results for the low- vs high-energy regions are easily detected in the analysis of the data from a two-detector system. A quantitative interpretation of the data from heterogeneous samples is more difficult, requiring a model to properly describe the characteristics of heterogeneity. (Strictly speaking, it is somewhat incongruous to model or uniquely describe a sample that is not homogeneous.)

The high-energy region of a spectrum can also be used to measure the abundance of ^{238}U in a sample. This is done by measuring and interpreting the 1001-keV peak that is principally caused by ^{238}U , with a small contribution coming from ^{238}Pu .

Finally, ^{237}Np is an isotope that can be measured more accurately by including the 312-keV peak of the ^{233}Pa daughter nuclide in the analysis. However, there is an interference from ^{239}Pu , as shown in Fig. 23.

The high-energy spectrum should be taken with a standard coaxial germanium detector, using a gain of about 0.25 keV per channel. Lead and cadmium absorbers should be used to attenuate the low-energy gamma rays (<150 keV) so that they do not dominate the counting rate. However, the absorber thickness should not be so great as to completely remove the 208-keV peak from the spectrum.

Intrinsic Efficiency Curve for the Second Detector

The energy region of interest in the second spectrum is from 300 to 1000 keV. Figure 24 shows six prominent peaks resulting from ^{239}Pu that are used to delineate the intrinsic efficiency curve for this region. It is important to note that the energy of the last peak is at 769 keV. The problem then is to find a functional form for the efficiency curve that will accurately extrapolate to

1001 keV, where the peak caused by ^{238}U is found. After some experimentation and modeling, we found that a fit of the six efficiency values with a simple polynomial function could not be trusted to accurately describe the overall efficiency curve, particularly when extrapolated to 1001 keV. Instead of using an arbitrary function, it became apparent that we needed an equation that accounted for and properly described the various physical processes that govern the detection efficiency as a function of energy. In fact, the same three principal processes that govern the efficiency of the low-energy detector system discussed previously also apply here—namely, the detector efficiency and the two absorption processes, one by the sample itself and the other by external absorbers. Each of these three processes, as Fig. 24 shows, has its own effect on the overall efficiency curve in the low-energy region. However, these effects are far less unique and distinguishable in the higher-energy regions. As a result, fitting the six relative-efficiency values with nonlinear equations of the form shown in Eq. (10) will not usually converge to a unique and correct determination of the variables. To overcome this problem, we have made use of additional data to estimate, and thereby fix, some of the variables in the equation.

This is done in a three-step process. We begin by deriving an approximate lead absorber thickness by using the observed intensities of the 208- and 267-keV peaks. These two peaks are caused by the decay of ^{241}Pu – ^{237}U in a sample. To calculate the lead thickness, we first correct the relative 208/267-keV intensities for the plutonium sample self-absorption by using the plutonium-thickness value calculated during the low-energy analysis. An examination of the efficiency curves of typical coaxial germanium detectors also allows us to estimate and correct for the detector-efficiency difference between 208 and 267 keV. After their intensities are corrected for sample self-attenuation, relative detector efficiency, and relative branching intensities, the lead thickness can be calculated by

$$\text{Pb} = [\ln(R)]/(\mu_{208} - \mu_{267}) \quad , \quad (27)$$

where R is the corrected 267/208 peak intensity ratio, and μ_{208} and μ_{267} are the lead absorption coefficients at 208 and 267 keV, respectively.

The plutonium sample thickness is the next variable that is refined. The initial value obtained from the low-energy spectrum cannot exceed 5 g/cm² because this corresponds to the

Figure 23. The ^{237}Np abundance in a sample is best determined by measuring the 312-keV peak of its ^{233}Pa daughter product, assuming the two isotopes are in decay equilibrium. If they are not in equilibrium, the 86-keV gamma ray of ^{237}Np can be analyzed, but the measurement sensitivity is reduced by an order of magnitude.

saturation thickness for a 208-keV gamma ray. However, the saturation thickness at 769 keV is approximately 40 g/cm². We therefore enter an iterative process to determine the approximate plutonium thickness by using only the 345- and 769-keV peaks caused by ^{239}Pu . The process terminates if the upper-limit constraints for the 345- to 769-keV relative efficiencies and for the plutonium sample thickness are exceeded.

After adjusting the six peak intensities for lead absorption, sample self-attenuation, and the respective branching intensities, the final step is a least-squares fitting of these corrected values to a quadratic equation of the form

$$\ln(\text{eff}_i) = \sum_{j=1}^3 a_j \cdot (\ln E_i)^{j-1}, \quad (28)$$

where

- eff_i = the peak intensity of the i^{th} peak, corrected for lead-absorber and plutonium-sample attenuation and for branching intensity,
- E_i = energy of the peak, and
- a_j = polynomial coefficient determined by the fitting process.

Figure 24. The most intense gamma-ray peak arising from the decay chain of ^{238}U occurs at 1001 keV. The extrapolation of an accurate efficiency curve (defined by lower-energy peaks of ^{239}Pu) to 1001 keV required the development of an equation that described the three major physical processes that determine the efficiency vs energy, namely, the detector efficiency, attenuation due to absorbers (cadmium and lead), and self-attenuation by the U/Pu sample.

Methods for Analyzing the High-Energy Regions

The three most useful high-energy peak groupings are in the regions from 332 to 345, 367 to 383, and 637 to 664 keV. There are other isolated peaks, such as the 312-keV peak of ^{237}Np - ^{233}Pa and the 1001-keV peak of ^{238}U , that are also of interest. Discussions of these groups and corresponding plots showing their spectroscopic features are given on pages 2 through 11.

The groupings are all quite compact and therefore must be resolved by a peak-fitting process. In an earlier version of MGA, a separate equation of the form given by Eq. (13) was formed for each net channel count in a group. These equations were ratioed to one of the intense peaks in the grouping so that the resulting equation had the form of that given by

Eq. (14), except that these equations now included the peak shape factor, S_i . These equations were linear in form and, when weighted, could be added to the previous set of equations that had been developed from the low-energy spectrum. The final least-squares calculation then included all of the relevant data from both the low- and high-energy spectra.

This procedure, which we used for many years, worked very well, but it did require a peak-shape characterization for the second detector. In an effort to minimize this requirement, we have now modified the analysis method so that we now first fit each grouping separately by using a routine similar to one we developed for our GRPANL analysis program.²² Although this approach requires a far greater calculational effort by the computer, the increase in analysis time on VAX and 386-based personal computers

is not excessive. The advantages of this approach over the older method are not great; however, the coding is greatly simplified, and the program is now more forgiving of changing measurement conditions.

Since some of the peaks in the high-energy groupings overlap severely, it is not prudent to allow all of the peak position and amplitude variables to be treated as free parameters during the fitting process. The method we use instead allows us to interrelate nearly all of the peak positions and also to selectively relate some of the peak amplitudes. That is, the exact gamma-ray energies and branching intensities are known from prior studies and characterizations of the nuclear-decay scheme of each isotope.¹¹ Because the system gain is easily measured, the relative positions of the peaks in a group can be predetermined and held constant during the fitting process. Similarly, the relative peak intensities of a given isotope can be calculated and also fixed during the fitting. This procedure greatly reduces the number of variables that need to be determined in the fitting process, thereby also increasing the speed and accuracy of the convergence.

Tables A-3 and A-4 in Appendix A list the peaks considered in each high-energy group. These tables also indicate the position and intensity relationships we have imposed on the various peaks in each group.

Relative peak intensities are determined by the fitting process. These are similar to the integrated counts of resolved peaks discussed on pages 15 through 21. Therefore, equations of the form given by Eq. (14) can be generated and added to the set of equations obtained from the low-energy spectrum. The entire set is then solved by least-squares to determine the relative abundances of the isotopes.

Analysis of the 38- to 59-keV Energy Region

The 38- to 59-keV region, shown in Fig. 1, is usable only when measuring a freshly processed plutonium sample. The 43-, 45-, 51-, and 59-keV peaks caused by ^{238}Pu , ^{240}Pu , ^{239}Pu , and ^{241}Am , respectively, are usually quite intense in such samples. However, these gamma rays are easily absorbed by the sample container or other absorbing materials because their energies are so low. It is also quite difficult to determine an accurate relative efficiency curve in this region. The 38- and 51-keV peaks of ^{239}Pu can be used to establish the slope of the efficiency in this region. However, the 38-keV peak becomes very weak when measuring thick samples where the ^{239}Pu content is less than 70 to 80%. The slope of the efficiency curve is also very steep and therefore needs to be determined very accurately. Finally, the shape of the efficiency curve is governed by the type and amount of the absorbers that are present.

In spite of these limitations, the 38- to 59-keV region at times contributes useful data to the analytical determination of the isotopic content of a sample. An option provided in MGA causes this region to be included in the analysis process. Equations of the form of Eq. (14) are generated to relate the intensities of the 43-, 45-, and 59-keV peaks to the ^{239}Pu 51-keV peak.

It is obvious that a cadmium absorber should not be used when measuring these low-energy gamma rays. However, about 0.1 to 0.2 mm of copper absorber should be used to attenuate the intense L-shell x rays. The accuracy of the efficiency curve that MGA calculates for this region can be greatly enhanced by including the copper thickness as a parameter in the detector peak-shape parameter file.

User Experience and Attainable Accuracies

The only user input required to perform an MGA analysis of a spectrum is the file name of the spectrum. Other optional inputs include

- The name of the peak shape parameter file. If it not specified, the built-in default values will be used.
- Sample ID or other descriptive information.
- The measurement date.

- The operator declaration date. That is, the date to which the analysis results must be decay-corrected.
- The declared ^{242}Pu value. If not provided, the program calculates a value by using an algorithm discussed in an earlier section.

One or more additional options can also be set to determine the type of report that will be

generated or the way the analysis will be performed. These options are selected by appending their letter designation to the spectrum file name. These options are explained more fully in Vol. 2 of this report.

A typical "short-form" analysis printout is shown in Fig. 25, resulting from a "one-detector" measurement of a U/Pu MOX sample containing uranium depleted in ^{235}U . The presence of ^{235}U is nonetheless detected, although the uncertainty of its measurement is quite high. A longer printout can also be requested to provide the user with additional details about the analysis process and parameters.

A key feature of the MGA methodology is the analysis of the 94- to 104-keV region. This is admittedly a very complex region, but we have had much experience and considered many details in developing our analysis of this region. (See Appendix B for a discussion of one of the more interesting "details" of this region.) This region is very intense and permits us to obtain significantly better statistical precisions that can be obtained by using other regions of the spec-

trum. We must hasten to add that this increased statistical precision also causes us to observe more readily many of the biases and interferences that are otherwise easily masked by statistical uncertainties.

Our experience in using the new method for determining the "intrinsic" efficiency curve is of less duration. We initially experienced occasional difficulties in obtaining the proper convergence and a good solution of the set of equations, particularly for poor or unusual measurement conditions. However, we continued to improve the method and have now successfully tested it for a wide range of measurement conditions, such as variations in sample size (from milligrams to kilograms), isotopic abundances, and ^{241}Am and uranium content.

We do not attempt, in this report, to make a comprehensive or detailed analysis of the measurement precisions and accuracies associated with the MGA methodology. Instead we give only some examples that we believe illustrate and can serve as a guide to the precisions and accuracies that can be obtained. Even this general

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MGApC (IAEA Version 6.3 17-Aug-89)  Date: 11-Sep-89

Spec. ID: Test.spc                      LT: 12.3 Mins  DT:35%
Measurement Date: 28-Jun-89  Declared Date: 1-Nov 87

Sample ID: MOX rod 40208      Detector: B1  Total Counts: 2.000E+07

PU g/cm2 = 5.000    CD g/cm2 = 1.553          FWHM at 122 keV = 555 eV
QFIT = 1.00                      at 208 keV = 684 eV
NQFIT= 1.000

ISOTOPIC ANALYSIS AT
      RELATIVE %      %*      MEAS. DATE      DECLARED DATE      SPECIFIC POWER
      ABUNDANCE ERR  ERR  WT.PCT.  %ERR  WT.PCT.  %ERR  (MILLIWATTS/GM)
Pu238 = .004960  .6  .9  .35448  .79  .35804  .78  2.03216
Pu239 = 1.000000  .8  .0  71.46925  .28  71.25284  .28  1.37432
Pu240 = .324370  .5  .9  23.18247  .68  23.11521  .68  1.63711
Pu241 = .049821  .2  .7  3.56067  .56  3.84519  .56  2.26732
Pu242 = (NEW ALGORITHM) 1.433 1.429 (10) .13120
Am241 = .031898  .2  .8  2.27975  .60  1.98539  .70  2.26732
U235 = .02126  24.0 24.1 1.5196 24.05 1.5149 24.05
      * = Error in Ratio                      TOTAL = 7.444 +/- .46%

Approx. U/Pu ratio by fluorescence x rays = 1.81+/- .98%

Am/Pu241 Wt. Ratio = .64026 +/- .26%

241Am Separated About 10.245+/- .212 Years Ago.

Pu-240 effective = 26.308 +/- 1.04%

```

Figure 25. Typical "short-form" printout of MGA. This output results from a one-detector measurement of a U/Pu mixed-oxide sample containing uranium depleted in ^{235}U .

guidance is difficult to give without specifying many details related to the measurement conditions, such as the characteristics of the sample, the instruments used, and the counting configuration.

Our own experience at LLNL largely has been in analyzing metals, oxides, and solutions that are high in ^{239}Pu content. Various versions of MGA have evolved and used over the past 15 years. Our isotopic results are frequently used to interpret calorimetry measurements of samples so that an accurate accountability of the plutonium inventory can be maintained. The limits of uncertainty in our plutonium accountability requires that our isotopic measurements be accurate to about 0.5 to 1%, depending, of course, on the relative abundances of the isotopes.

How well does MGA compare to other codes and methods for measuring isotopic abundances? This question is difficult to answer. The reports of the Calorimetry Sample Exchange Program issued by the Mound Laboratory²³ are one source for comparisons. They contain results generated by seven U.S. Department of Energy contract laboratories, including the LLNL results determined by MGA. In the calorimetry exchange program, each participating laboratory makes several measurements of a sample of PuO_2 obtained from a common homogeneous batch of stock material. The quarterly reports, containing the measurement results of the different laboratories, are primarily intended to verify that measurements taken during the quarter meet certain control criteria. Some results for a typical quarter are shown in Fig. 26. Caution must be exercised in comparing the results of the various laboratories because counting conditions may differ. Nonetheless, the reported data consistently displays the differences shown in Fig. 26. The mea-

surement bias shown for ^{241}Am is believed to reflect an error in the original characterization of the stock material, and this bias is currently being investigated.

Another series of comparisons, the results of several highly characterized standards, is tabulated in Table 1. The measurements were taken during the past few years, under varying conditions and using different analyzer systems. Since the measurement conditions were not carefully controlled, the data presented in Table 1 are intended only to provide estimates of precisions and accuracies that are attainable, and do not represent a rigorous evaluation of the MGA methodology. The data indicate that better than 1% precisions and accuracies are attainable for a wide variety of samples, even with measurement times as short as 10 minutes.

The uncertainties shown in Table 1 reflect the measurement errors calculated by the code. However, in a number of separate studies, we have also found that measurement uncertainties calculated by the code are in good agreement with the standard deviations from the mean that can be determined from a series of replicate measurements.

The Euratom Safeguards Inspectorate has also evaluated the MGA code. Their preliminary studies, taken under field inspections conditions, confirm many of the observations summarized in Table 1.^{26,27} The Euratom safeguards community is also performing a carefully controlled evaluation of various isotopic codes at the Perla facility of the Joint Research Center in Ispra, Italy.²⁸ Several hundred measurements have been made, and several statistical tests will be applied to evaluate the results and determine the characteristics of the various codes.

Summary

We cannot claim that we have solved all of our measurement problems or removed all sources of bias or error. However, we believe that the methodology we have developed and incorporated in the MGA computer code is among the most advanced yet developed and that it is capable of making highly accurate measurements on a wide variety of samples in a reasonably short counting time. We conclude by summarizing some of the more salient features of our methodology and code that make it unique:

- MGA uses the most intense peaks in a plutonium spectrum—for example, the 94- and 104-keV region and the 129- and 148-keV peaks. Although these regions are more difficult to analyze and interpret accurately, they enable us to make measurements that are accurate to within 1% and also reduce the measurement time to only a few minutes.
- A unique and accurate technique for delineating the “intrinsic” efficiency curve was developed. It now enables us to relate the

Figure 26. The gamma-spectrometer measurement results of reference sample RH1979 taken by seven different DOE laboratories. At the time these measurements were taken, only our (LLNL's) measurements made use of the 100-keV region in the analysis process, resulting in generally higher precision.

Figure 26. (Continued)

intensities of widely separated peaks such as the 129- and 148-keV peaks. Consequently, only the energy region ≤ 208 keV is required for analysis. However, the code does not preclude data from the higher-energy regions (≤ 1 MeV) from being included in the analysis process.

- The data obtained from a spectrum are incorporated into a single set of internally consistent and appropriately weighted equations. Some equations represent integrated peak areas (e.g., equations representing well-resolved peaks), while others represent

channel-by-channel counts. The equations are *linear* in form and are therefore easily solved by the method of least-squares, resulting directly in relative isotopic abundances and their attendant measurement uncertainties.

- A wide range of sample types may be analyzed. These include samples varying in isotopic composition and in size; samples that are freshly separated (^{237}U not in equilibrium) and aged; and samples containing other radioactive isotopes such as ^{235}U , ^{238}U , ^{237}Np , ^{233}Pa , ^{243}Am – ^{239}Np , and small amounts of fission products.

Table 1. Some comparisons of MGA results with declared values of NBS, CBNM, PIDIE, and PERLA isotopic standards.

Source	Measured time (min)	Isotope									
		238		239		240		241		Am	
		Declared (%)	% Diff. ⁽¹⁾	Declared (%)	% Diff. ⁽¹⁾	Declared (%)	% Diff. ⁽¹⁾	Declared (%)	% Diff. ⁽¹⁾	Declared (%)	% Diff. ⁽¹⁾
NBS 948	>100	0.010 ⁽²⁾	10 (2)	91.76	0.03 (0.03)	7.95	-0.4 (0.04)	0.245	-0.8 (0.4)	0.495 ⁽²⁾	3.6 (0.3)
NBS 946	>100	0.225	0.4 (0.4)	84.80	0.08 (0.08)	12.35	-0.5 (0.04)	2.041	-0.9 (0.3)	2.365	-1.1 (0.3)
NBS 947	>100	0.271	0.0 (0.4)	77.43	0.10 (0.08)	18.76	-0.4 (0.03)	2.322	-0.8 (0.3)	2.562	-1.1 (0.3)
NBS 122	>100	0.0523	-0.8 (0.4)	87.35	-0.06 (0.02)	11.50	+0.4 (0.02)	0.918	+0.5 (0.4)	—	—
CBNM 93 ⁽³⁾	10	0.0119	-4.4 (4.0)	93.42	0.03 (0.05)	6.32	-0.5 (0.7)	0.223	0.3 (0.5)	0.1047	-0.4 (0.8)
CBNM 84	10	0.0704	-0.6 (1.4)	84.33	-0.05 (0.07)	14.21	0.3 (0.4)	1.028	-0.1 (0.5)	0.2173	0.5 (0.4)
CBNM 70	10	0.847	0.5 (0.8)	73.32	-0.50 (0.40)	18.30	1.6 (1.6)	5.457	0.6 (0.3)	1.171	-0.8 (0.5)
CBNM 60	10	1.198	1.2 (1.2)	62.21	-0.51 (0.54)	25.40	0.9 (1.4)	6.68	1.0 (1.0)	1.445	0.5 (1.0)
PIDIE 1 ⁽⁴⁾	10	0.0109	3.0 (4)	93.82	-0.10 (0.05)	5.97	1.5 (0.7)	1.98	-0.5 (0.6)	0.2261	0.7 (0.6)
	>100	(10) ⁽²⁾	-1.0 (1.5)		-0.01 (0.02)		0.3 (0.3)		0.0 (0.2)	(1.0) ⁽²⁾	0.0 (0.2)
PIDIE 2	10	0.0233	4.0 (2.5)	89.46	-0.02 (0.07)	10.07	0.0 (0.6)	0.443	-0.2 (0.5)	0.264	-1.9 (0.6)
	>100	(1.4)	3.0 (0.8)		-0.04 (0.02)		0.5 (0.2)		0.2 (0.2)	(1.4)	-1.5 (0.2)
PIDIE 3	10	0.0474	-0.2 (2.4)	84.83	-0.12 (0.12)	14.13	0.6 (0.7)	0.992	0.2 (0.6)	0.618	-0.2 (0.6)
	>100	(0.8)	1.7 (0.7)		-0.13 (0.04)		0.7 (0.2)		0.3 (0.2)	(1.3)	-0.2 (0.2)
PIDIE 4	10	0.1089	1.0 (1.4)	78.23	-0.05 (0.18)	19.82	0.2 (0.7)	1.839	-0.3 (0.6)	1.563	0.4 (0.6)
	>100	(0.5)	2.0 (0.5)		-0.13 (0.07)		0.5 (0.3)		0.2 (0.2)	(1.8)	0.4 (0.2)
PIDIE 5	10	0.1328	0.4 (1.3)	76.50	0.20 (0.20)	21.31	0.8 (0.7)	2.065	0.2 (0.5)	1.727	1.3 (0.6)
	>100	(0.8)	0.9 (0.5)		0.20 (0.07)		0.6 (0.3)		0.4 (0.2)	(4.4)	1.3 (0.2)
PIDIE 6	10	0.969	-0.4 (1.1)	68.89	-0.38 (0.50)	24.70	0.3 (1.2)	5.44	-0.4 (1.0)	3.767	2.6 (1.0)
	>100	(0.8)	0.7 (0.3)		-0.55 (0.20)		1.4 (0.4)		0.4 (0.3)	(4.1)	3.2 (0.3)
PIDIE 7	10	1.324	0.2 (1.1)	65.12	-0.10 (0.60)	26.78	0.4 (1.3)	6.77	-0.4 (1.1)	3.60	3.0 (1.1)
	>100	(1.8)	0.3 (0.4)		-0.20 (0.20)		0.5 (0.5)		-0.3 (0.4)	(4.1)	3.0 (0.4)
PERLA 118 ⁽⁵⁾	12	0.1993	-0.6 (1.2)	70.95	0.01 (0.30)	24.58	0.0 (0.7)	3.29	0.0 (0.6)	1.021	-1.0 (0.8)
PERLA 105	>100	1.493	0.5 (0.6)	60.99	-0.30 (0.40)	23.44	0.6 (0.7)	9.25	0.2 (0.6)	1.364	-0.7 (1.0)
PERLA 1007	>100	1.721	0.1 (0.9)	58.09	0.15 (0.60)	24.77	-0.3 (1.1)	9.77	-0.1 (0.9)	1.424	-1.2 (1.5)
PERLA 16 ⁽⁶⁾	12	0.348	0.6 (0.7)	71.19	0.15 (0.20)	23.04	-0.6 (0.6)	3.81	0.3 (0.5)	1.985	-1.0 (0.7)
PERLA 68 ⁽⁶⁾	12	1.413	1.9 (0.8)	59.52	0.08 (0.50)	24.73	-0.4 (0.9)	9.44	1.1 (0.7)	0.914	-0.1 (1.6)

⁽¹⁾ The percent difference = $100 \times (\text{measured} - \text{declared}) / \text{declared}$. The uncertainty (%) associated with the measured abundance is in parentheses following the % difference.

⁽²⁾ The uncertainty associated with the declared abundance for ²³⁸Pu and ²⁴¹Am is usually much higher than the uncertainty in the other isotopic values. These uncertainties for the PIDIE standards are shown in parentheses below the reported values.

⁽³⁾ The CBNM standards are 6-g sintered PuO₂ pellet standards produced by the Central Bureau of Nuclear Measurement, Geel, Belgium.

⁽⁴⁾ See Ref. 24.

⁽⁵⁾ See Ref. 25.

⁽⁶⁾ These samples are mixed uranium/plutonium oxide samples.

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Appendix A

The Gamma-Ray Energies and Branching Intensities Used by MGA

Table A-1. Branching intensities for single peaks in the low-energy (<208-keV) region.

Energy (keV)	Branch	Isotope
43.477	3.830×10^{-4}	^{238}Pu
45.232	4.430×10^{-4}	^{240}Pu
51.629	2.670×10^{-4}	^{239}Pu
59.536	3.590×10^{-1}	^{241}Am (^{237}Pu)
129.294	6.290×10^{-5}	^{239}Pu
148.567	1.870×10^{-6}	^{241}Pu
152.680	9.260×10^{-6}	^{238}Pu
185.720	5.610×10^{-1}	^{235}U
203.537	5.600×10^{-6}	^{239}Pu
205.330	4.870×10^{-2}	^{235}U
208.000	5.330×10^{-6}	^{241}Pu - ^{237}U

Table A-2. Energies and branching intensities for x rays and gamma rays in the 100-keV region.

Energy (keV)	Isotope						
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{241}Am	Pu x ray	^{237}Np ^{235}U
86.500	—	—	—	—	—	—	0.144 —
93.360	—	—	—	—	—	—	— 0.050
94.660	1.15×10^{-6}	4.200×10^{-5}	6.80×10^{-7}	3.009×10^{-6}	—	—	0.0958 —
95.858	—	—	—	—	—	—	0.03 —
95.880	—	—	—	—	—	—	— 0.008
96.160	—	3.68×10^{-7}	—	—	—	—	— —
97.071	—	—	—	3.841×10^{-6}	1.222×10^{-5}	—	— —
98.443	1.85×10^{-6}	6.820×10^{-5}	1.00×10^{-6}	4.892×10^{-6}	—	—	0.1437 —
98.790	—	1.22×10^{-5}	—	—	—	—	— —
98.956	—	—	—	—	2.011×10^{-4}	—	— —
99.270	—	—	—	—	—	—	— 0.0025
99.533	—	—	—	—	—	4.13×10^{-5}	— —
99.864	7.10×10^{-5}	—	—	—	—	—	— —
101.063	—	—	—	6.180×10^{-6}	1.97×10^{-5}	—	— —
102.275	—	—	—	—	—	—	— 0.0042
102.963	—	—	—	—	1.945×10^{-4}	—	— —
103.035	—	2.12×10^{-6}	—	—	—	—	— —
103.679	—	—	—	9.95×10^{-7}	—	—	— —
103.742	—	—	—	—	—	6.60×10^{-5}	— —
103.860	—	—	—	—	—	—	0.0083 —
104.242	—	—	6.960×10^{-5}	—	—	—	— —
104.820	—	—	—	—	—	—	— 0.0052
105.610	—	—	—	—	—	—	— 0.011

Table A-3. Energies and branching intensities for the 300-keV region.

	Energy (keV)	Isotope				Energy Ref. No. ^a	Intensity Ref. No. ^a
		²³⁷ Np	²³⁹ Pu	²⁴¹ Pu	²⁴¹ Am		
1	311.896	0.38	—	—	—	—	—
2	332.390	—	—	2.977×10^{-7}	1.450×10^{-6}	—	—
3	332.853	—	5.054×10^{-6}	—	—	9	9
4	332.390	—	—	2.494×10^{-8}	4.830×10^{-6}	2	—
5	336.116	—	1.135×10^{-6}	—	—	9	9
6	337.760	—	—	2.120×10^{-9}	—	2	—
7	340.470	—	—	—	—	9	—
8	341.526	—	6.62×10^{-7}	—	—	9	9
9	345.014	—	5.590×10^{-6}	—	—	—	—
10	367.052	—	8.74×10^{-7}	—	—	15	15
11	368.547	—	9.08×10^{-7}	—	—	15	15
12	368.600	—	—	1.074×10^{-8}	2.12×10^{-6}	15	—
13	370.933	—	—	2.731×10^{-8}	5.125×10^{-7}	15	—
14	372.470	—	2.1×10^{-8}	—	—	15	15
15	375.039	—	1.57×10^{-5}	—	—	—	—
16	376.600	—	—	—	1.348×10^{-6}	15	—
17	379.050	—	1.05×10^{-8}	—	—	15	—
18	380.160	—	3.051×10^{-6}	—	—	15	15
19	382.732	—	2.587×10^{-6}	—	—	15	15
20	383.744	—	—	—	2.82×10^{-7}	15	16

^a The reference number indicates the peak to which the energy or intensity is tied. For example, the position of the 332.853-keV peak is held fixed relative to the position of peak number 9 (345.014 keV). The intensity of this peak is also held fixed relative to peak number 9.

Table A-4. Energies and branching intensities for gamma rays in the 600-keV and high-energy regions.

	Energy (keV)	Isotope					Energy ref. no.	Intensity ref. no.
		²³⁸ U	²³⁸ Pu	²³⁹ Pu	²⁴⁰ Pu	²⁴¹ Am		
1	637.862	—	—	2.56×10^{-8}	—	—	5	5
2	640.096	—	—	8.20×10^{-8}	—	—	5	5
3	641.436	—	—	—	—	7.10×10^{-8}	5	13
4	642.500	—	—	—	1.260×10^{-7}	—	5	—
5	645.969	—	—	1.489×10^{-7}	—	—	—	—
6	647.296	—	—	1.90×10^{-9}	—	—	5	5
7	649.377	—	—	7.12×10^{-9}	—	—	5	5
8	650.529	—	—	2.60×10^{-9}	—	—	5	5
9	652.052	—	—	6.55×10^{-8}	—	—	5	5
10	652.990	—	—	—	—	3.77×10^{-7}	5	13
11	654.890	—	—	2.25×10^{-8}	—	—	5	5
12	658.919	—	—	9.900×10^{-8}	—	—	—	5
13	662.456	—	—	—	—	3.67×10^{-6}	—	—
14	664.587	—	—	1.657×10^{-8}	—	—	5	5
	766.	3.15×10^{-3}	2.19×10^{-7}	—	—	—	—	—
	1001.2	9.10×10^{-3}	1.05×10^{-8}	—	—	—	—	—

Appendix B

Anomalous X-Ray Line Shapes from the Decay of ^{239}Pu

The 94- to 104-keV region of germanium-detector spectra of plutonium samples contains x-ray and gamma-ray peaks from all of the isotopes of plutonium, as well as ^{237}U and ^{241}Am (see Fig. B-1). However, we have long noted an anomalous negative dip in the residuals of the fit of this region just above the 94-keV peak. This uranium $K_{\alpha 1}$ peak is largely the result of internal conversions of the states of ^{235}U and ^{237}U following the decay of ^{239}Pu and ^{241}Pu . We have found that this anomalous dip can be explained as the result of an interplay between atomic and nuclear processes.

The anomaly was first dismissed as being a problem in the algorithm used to fit the Lorentzian-broadened shape of the x-ray peaks. However, when we re-examined the 94- to 104-keV energy region of isotopically pure sources of plutonium, we found that the fit of the x-ray and gamma-ray peaks from ^{239}Pu showed residuals above both the 94- and 98-keV peaks [see Fig. B-2(a)] but did not show such behavior for the fit of the same region of peaks from the decay of ^{241}Pu to ^{237}U [see Fig. B-2(b)].

We concluded that the ^{239}Pu nuclear-decay process must have an effect on the x-ray energy distribution. We then realized that an anomalous line shape could result from an interplay between atomic and nuclear transitions. The K x rays result primarily from internal conversion of nuclear transitions. If the energy of a nuclear transition is only slightly greater than the binding energy of the K-shell electrons, the usual Lorentzian line intensities of the resulting x rays are damped out at energies above the peak and must indeed vanish entirely at the energy corresponding to that of the internal-conversion transition. For a single x-ray line, a good approximation of the spectral shape is given by

$$I(E) \propto \frac{E(E_n - E_{2p} - E)}{[E - (E_{1s} - E_{2p})]^2 + \frac{\Gamma^2}{4}}, \quad (\text{B-1})$$

Figure B-1. The 94- to 104-keV energy region of a germanium spectrum of plutonium. A careful fitting of the x-ray and gamma-ray peaks in this region shows an anomalous negative dip in the residuals just above the 94-keV peak.

Figure B-2. The anomalous negative dip in the residuals is very pronounced when a spectrum of isotopically pure ^{239}Pu is analyzed (a), but it is absent when ^{241}Pu is analyzed (b).

where E is the x-ray energy, E_n is the energy of the internally converted nuclear transition, $E_{1s(2p)}$ is the binding energy of the 1s(2p) electron, and Γ is the natural line width of the x-ray transition.

An examination of the decay scheme showed that there is a 116.24-keV transition from the 129.29-keV state in ^{235}U that is very close in energy to the 115.61-keV binding energy of the K-shell electrons of uranium. Therefore, the energy spectrum associated with the intermediate x-ray state [see Fig. B-3(a)] cannot have the symmetric Lorentzian shape it normally has. Rather, it now is bounded on the upper-energy side by the available energy of the nuclear state feeding it. In fact, for transitions lower

Figure B-3. The energy of the 116.24-keV transition in ²³⁵U is only 0.63 keV above the binding energy of the K shell of uranium. (a) The intermediate x-ray state formed during internal conversion is bounded on the high-energy side by the energy of the nuclear state. (b) The resulting x-ray line shape is asymmetric and terminates 0.63 keV above the x-ray energy.

than the 115.61-keV binding energy, no K x-ray peaks are possible. Figure B-3(b) shows the resulting suppression and eventual cutoff of the intensity of the K_{α1} and K_{α2} x-ray distributions. The anomalous negative dips in the residuals shown in Figs. B-1 and B-2(a) are then due to the neglect of this expression. The standard fit, using symmetric Lorentzian peak shapes, overestimates the intensity above the peaks and thus produces negative residuals.