NDA Analysis of Legacy INL Wastes for disposal at WIPP

D.C. Warner, R.N. Ceo, D.E. Gulbransen
Canberra Industries, Inc.

Abstract

This paper discusses Nondestructive Assay (NDA) of legacy radioactive wastes at the Idaho National Laboratory, but focuses chiefly on expert analysis techniques that may be applied to most defense-related wastes. A brief history of the waste is included, and typical waste matrices and analytes are described. Several analytical problems are used as examples to illustrate the difficulties faced by the expert analyst in reducing the data to meaningful results.

Introduction

Legacy radioactive wastes exist at several sites around the United Sates, and pose interesting analysis and disposal challenges as the wastes are unearthed, analyzed, and disposed of. The current work at Idaho National Laboratory (INL) is typical of such cleanup efforts, and experiences there illustrate the difficulties analysts must overcome to produce worthwhile analytical results.

INL wastes came mostly from Rocky Flats operations, but also include items generated locally or from other sites. The waste drums have either been buried or stored above ground. The Rocky Flats wastes originated from many different processes there during the past forty years or so, and not all the waste streams have been well characterized. As far as possible, information about each waste stream has been gleaned from existing records and interviews with people who worked on the different processes; this summary information is referred to as “acceptable knowledge” or AK. Further information, particularly net waste weight and fill height, is gained by real-time radiography (RTR) or in some cases visual examination (VE). All this information is provided as a starting point to the Nondestructive Assay (NDA) analyst.

Nondestructive Assay Techniques

Several NDA instruments are used for waste measurements at INL, and these are typical of those found at other sites across the country. In general, the NDA instruments utilize passive neutron techniques, quantitative gamma ray spectrometry, and gamma ray isotopic analysis. Each instrument has advantages and shortcomings, and is selected depending on the nature of the waste.

Neutron methods are preferred when measuring lumpy or inhomogeneous wastes containing more than a few hundred mg of Pu. However, uncorrected neutron measurements are subject to bias if the waste matrices contain neutron moderators or absorbers.

Quantitative gamma spectrometry is preferred when the wastes contain low concentrations of plutonium, and the plutonium is distributed evenly throughout the matrix. If the matrix density is low, transmission correction is normally used to reduce bias due to gamma attenuation. If the matrix is dense, an efficiency multi-curve technique yields better results.

Gamma ray isotopic measurements are applied to both neutron and gamma assay results to quantify those plutonium isotopes which cannot be directly measured.

Typical Wastes

Although INL wastes originate from many waste streams, it is sometimes useful to consider the wastes as three generalized forms: sludge, soil and gravel, or debris. Each waste matrix poses its own set of challenges.

Sludges are usually by-products of liquid waste treatment facilities. Because they are precipitated from solutions, they are generally homogeneous and fairly dense with significant hydrogen content. Typical sludge densities range from 1.1 to 1.4 g/cm^3. Because sludges are dense, they are not generally amenable to transmission-corrected gamma spectrometry. The homogeneous nature of sludges does allow measurement using the multi-curve gamma efficiency technique. Sludges may be measured with a passive neutron counter, provided that the matrix does not contain high concentrations of fluoride compounds, but gamma measurements are often preferred.

Contaminated soil and gravel is recovered and packaged when buried wastes are unearthed or when spills occur. Soil and gravel wastes may or may not be homogeneous. Typical bulk densities range from about 0.4 to 1.2 g/cm^3. Radionuclides are usually not very concentrated in soil and gravel, so low detection limits are important when measuring them.

Waste that is neither sludge, nor soil and gravel, is considered debris. Debris may be broken equipment, contaminated clothing and paper, glove box trash and residue, or something completely unexpected. It is probably not homogeneous. Typical bulk densities range from about 0.02 to 0.4 g/cm^3. Sometimes RTR or VE will provide valuable information regarding the nature of the waste matrix. For example, if a drum contains lead bricks or big chunks of steel, and that information is made known to the NDA analyst, corrections can be made that will significantly improve the result.

Analytes

Defense-related wastes typically contain uranium, plutonium, and other transuranic radionuclides. The wastes may also contain fission products or activation products used as radiotracers or for calibration.

If uranium is present in waste, it is considered to be depleted, enriched, or a mixture of both. Uranium U-235 may be measured directly by gamma spectrometry. U-238 is measured indirectly, using gamma rays from its decay product Pa-234 and assuming secular equilibrium. U-234 cannot be measured by gamma spectrometry, so its presence is inferred whenever U-235 or U-238 is detected.

Plutonium in waste is usually weapons-grade material (93% - 95% Pu-239), but heat sources (68% Pu-238) and other isotopic ratios are sometimes encountered. If plutonium is assayed using a neutron coincidence counter, the result is expressed as Pu-240 effective, and the individual plutonium isotopes are quantified from that result and the appropriate isotopic fractions. Pu-239 may also be quantified directly by gamma spectrometry. Other Pu isotopes are usually quantified

indirectly by ratio to Pu-239. Heat source waste is a special case where enough Pu-238 exists to allow its direct measurement. There is no typical Pu mass loading for these waste drums – some Pu results are below the lower limit of detection (< LLD), and some Pu results approach the upper permissible limit with most results distributed between these extremes.

Other transuranic radionuclides may include Am, Cf, Cm, and Np isotopes. These nuclides are usually quantified by gamma spectrometry, but some of them (e.g. Cf-252, Cm-244) may severely bias passive neutron analyses since they decay by spontaneous fission.

Data Analysis

Data analysis is rarely straightforward, since each combination of analyte and matrix poses its own problems. Several examples of analytical problems are presented here, along with techniques for resolving them.

Undetectable radionuclides

U-234 is not quantifiable by neutron assay, and emits only a very few low-energy gamma rays. It is more practical to estimate U-234 from either U-235 or U-238 as follows:

If U-235 is detected, but not U-238, then the uranium in the waste is assumed to be highly enriched, with no depleted uranium present. U-234 is computed from mass fractions normally present in HEU:

$$M_{U\text{-}234} = (1.02 \times 10^{-2} M_{U\text{-}235})/9.317 \times 10^{-1} \quad (1)$$

Conversely, if U-238 is detected, but not U-235, then the uranium in the waste is assumed to be depleted, with no highly enriched uranium present. U-234 is computed from typical DU mass fractions:

$$M_{U\text{-}234} = (1 \times 10^{-5} M_{U\text{-}238})/ 9.978 \times 10^{-1} \quad (2)$$

If both U-235 and U-238 are detected, the waste may contain either DU or a combination of DU and HEU. In this case, the U-234 mass is determined from the measured mass of U-235 using equation (1) above. This approach provides an upper limit to the U-234 content.

If neither U-235 nor U-238 is detected, then U-234 is reported as <LLD.

Sr-90 emits only beta particles, and cannot be detected by normal NDA techniques. It is assumed to be present in wastes along with Cs-137, so if Cs-137 is detected, then both Sr-90 and Cs-137 are reported. For the waste project at INL, Sr-90 activity is estimated as 110% of Cs-137 activity. Quantification of Cs-137 poses its own problems, discussed later in this paper.

Pu-242, like U-234, emits only a very few low-energy gamma rays. It is not directly measurable in quantities normally encountered in waste. Instead, Pu-242 is estimated from its isotopic fraction

and the Pu-240 effective mass (neutron assay) or its isotopic fraction and the Pu-239 mass (gamma ray assay).

It is meaningless to define a lower limit of detection (LLD) for these three radionuclides, since they are not normally detectable in any quantity. Instead, we define a related quantity called "typical reporting threshold" based on the LLD of the measurable nuclide (e.g. U-235, Cs-137, and Pu-239) and the related scaling factors.

Isotopic Fractions

Isotopic fractions are routinely applied to gamma and neutron results to quantify Pu radionuclides that would otherwise be difficult or impossible to detect. For example, Pu-238, Pu-240, and Pu-241 emit low-energy, low-intensity gamma rays so they are difficult to quantify by direct measurement. Pu-242 gamma rays are very low in intensity, and virtually impossible to detect.

Site acceptable knowledge usually provides information about plutonium and uranium isotopic fractions, but if there are several possible combinations, isotopic AK may be of limited use. In general, a direct measurement is preferred.

There are several analytical techniques that can be used to determine Pu isotopic fractions from gamma spectra. Of these, MGA and FRAM are in regular use at INL, and give good results for most wastes. Occasionally, the waste may contain enhanced Am-241 or some other radionuclide that interferes with isotopic analysis, and in these cases the expert analyst must evaluate the gamma spectrum to determine the most probable isotopics.

In the worst case, measured isotopics are inconsistent with isotopics specified by AK. The expert analyst must resolve the conflicting information or reject the assay. It should be noted that small inaccuracies in the isotopic fractions will not affect the gamma assay results very much, but can severely bias neutron assay results.

Am-241 Analysis

Am-241 is present in all Pu waste to some extent, and in some cases it is the most significant component. Am-241 grows into a waste as Pu-241 decays, and may be enhanced in the waste as a by-product of plutonium purification. Am-241 is fairly easy to detect by gamma spectrometry, but accurate quantification presents several challenges. Table 1 is a list of selected gamma rays useful for Am-241 determinations.

The 60 keV gamma ray is by far the easiest to detect, but its low energy makes it very susceptible to self-attenuation and to attenuation within the matrix. The 662 keV and 722 keV gamma rays are the least susceptible to attenuation, but their intensities are rather low. If the waste contains enough Am-241, these gamma rays should be used for quantification. In general, it is best to quantify Am-241 using higher-energy gamma rays, or by ratio to Pu-239 using measured isotopics.

Table 1: Selected Am-241 gamma rays

Energy (keV)	Intensity (%)
59.54	35.9
125.30	4.08×10^{-3}

662.40	3.64×10^{-4}
722.01	1.96×10^{-4}

In cases where the waste contains very little Am-241 and no detectable Pu, it may be necessary for the expert analyst to quantify Am-241 using only the 60 keV gamma ray.

It should be noted that Cs-137 emits a single useful gamma ray at 661.7 keV. This gamma ray is similar in energy to the Am-241 emission at 662.4 keV, and interference is likely if a waste contains both Am-241 and Cs-137. In a typical assay, Am-241 is quantified using the 662 keV and 722 keV gamma rays. Alternatively, Am-241 can be quantified using the 125 keV and 662 keV gamma rays. In either case, any counts in the 662 keV part of the spectrum that are not attributed to Am-241 are attributed to Cs-137 decay. As mentioned earlier in this paper, the computed Cs-137 activity is used to infer Sr-90 activity. Therefore, some care must be taken in Am-241 analysis because the accuracy of three reported values depends on it.
Some wastes contain 0.5 Ci of Am-241 or even more. In these cases excessive dead time and pulse pileup occurs, causing interference with quantitative analysis and problems with isotopic analysis as well. It is good practice to attach a Cd or Sn filter to the face of the gamma ray detector to attenuate the 60 keV gamma rays, thereby reducing dead time and pulse pileup to acceptable levels. A filter thickness of about 0.7 g cm^{-2} is usually sufficient for this purpose.

Heat Source Assays

Heat source waste may be assayed using passive neutron and gamma techniques. In either case, a reliable estimate of the plutonium isotopic fractions is necessary. These values may be obtained from gamma ray analysis using programs like MGA or FRAM, from direct measurement of Pu-238 and Pu-239 masses, or from AK. Under most circumstances, it is assumed that drums containing heat source waste were originally packaged without other Pu present. However, if the original drum has disintegrated and its contents have been repackaged, other Pu waste may have been added so that AK isotopics are no longer applicable.

Table 2: Comparison of selected Pu-238 and U-238* gamma rays

Pu-238		U-238	
Energy (keV)	Intensity (%)	Energy (keV)	Intensity (%)
152.720	9.37×10^{-4}		
766.39	2.20×10^{-5}	766.36	2.94×10^{-1}
1001.03	9.9×10^{-7}	1001.03	8.37×10^{-1}

*Gamma rays actually emitted by Pa-234 in equilibrium with U-238

Pu-238 and U-238 emit similar gamma rays, as shown in Table 2. Unless the nuclide library has been carefully defined, heat source waste could appear to contain U-238 even if none were present. If Pu-238 is quantified based on the 153 keV gamma ray alone, the result will probably suffer a negative bias due to attenuation of the gamma ray in the matrix and in the source itself. A better method is to use all three gamma rays for quantifying Pu-238, correct for self-attenuation, and compute U-238 (if any) based on the 766 keV and 1001 keV peak areas remaining after interference correction.

Determining U-232 and Th-232

U-232 and Th-232 both emit only a few low-intensity gamma rays, so they are normally quantified indirectly by gamma rays from their decay progeny. However, both U-232 and Th-232 decay through the same chain starting with Th-228, so many of the same gamma rays (see Table 3) will be observed whether the parent is U-232 or Th-232. It is possible to mistakenly infer the existence of one of these two parent nuclides when the other is actually the one present. Th-232 decays through Ac-228 as an intermediate, and U-232 does not, so existence of all four gamma ray peaks is a reliable indicator that the parent is Th-232. Absence of both 911 keV and 969 keV peaks indicates that U-232 is the likely parent.

Table 3: Comparison of selected gamma rays, if parents are in equilibrium with their decay products.

Th-232			U-232	
Energy (keV)	Intensity (%)		Energy (keV)	Intensity (%)
911.2	25.8			
969.0	15.8			
238.6	43.6		238.6	43.6
583.2	30.3		583.2	30.3

Note that the intensities listed in Table 3 are correct only if the parent is in secular equilibrium with its daughters, a valid assumption if the waste is at least 30 years old.

Self-Attenuation Corrections

Depleted U may be present in multi-kg quantities, and the U-235 content in that case may be significant from a regulatory standpoint, even if no real criticality safety issue exists.
It is noted that U-238 has a very low specific activity, and is normally quantified using only a few high-energy, low-abundance gamma rays. On the other hand,U-235 is normally quantified using a few low-energy, relatively high-intensity gamma rays.

The U-238 analytical result is not particularly susceptible to self-attenuation bias, but if there is a significant amount of U-238 in the waste, any U-235 gamma rays will be severely self-attenuated and its result will be negatively biased. The expert analyst may choose to quantify U-235 based on an isotopic ratio rather than on a direct measurement in this case.

A recent case provides a good example of depleted uranium assay. The initial assay result for U-235, calculated directly from the gamma spectrum, was too low based on the reported mass of U-238 (66.6 kg) and the measured isotopics (99.49% U-238, 0.51% U-235). The expert analyst applied self-attenuation correction to the U-235 gamma rays and the U-235 result was improved, but still too low. Instead, the reported U-235 result was based on the measured U-238 mass and measured isotopics. Results from all three computations are shown in Table 4.

Table 4: Gamma ray assay of waste containing depleted uranium. Results are shown in grams.

	Uncorrected Results	Results with U-235 Self-attenuation	Results based on Isotopic Ratio
U-234	1.80×10^{-1}	9.96×10^{-1}	3.72×10^{0}
U-235	1.64×10^{1}	9.10×10^{1}	3.41×10^{2}
U-238	6.66×10^{4}	6.66×10^{4}	6.66×10^{4}

Spectral interferences

In some cases, two or more radionuclides emit gamma rays that are similar in energy. If the spectral peaks are imperfectly resolved, bias may be introduced. For example, if a significant quantity of Np-237 is present along with Pu-239, the Pu-239 result may have positive bias. The bias is caused by Pa-233 gamma rays at 375.45 keV and 415.76 keV, interfering with the Pu-239 gamma rays at 375.05 keV and 413.7 keV respectively. If multiplet peaks are imperfectly deconvoluted, the peak search software will report a reduced χ^2 that is too large. The interactive peak fit software will show a positive residual where the missing peak should be located. The expert analyst can then interactively fit the peaks and reduce the bias as shown in Figures 1a and 1b.

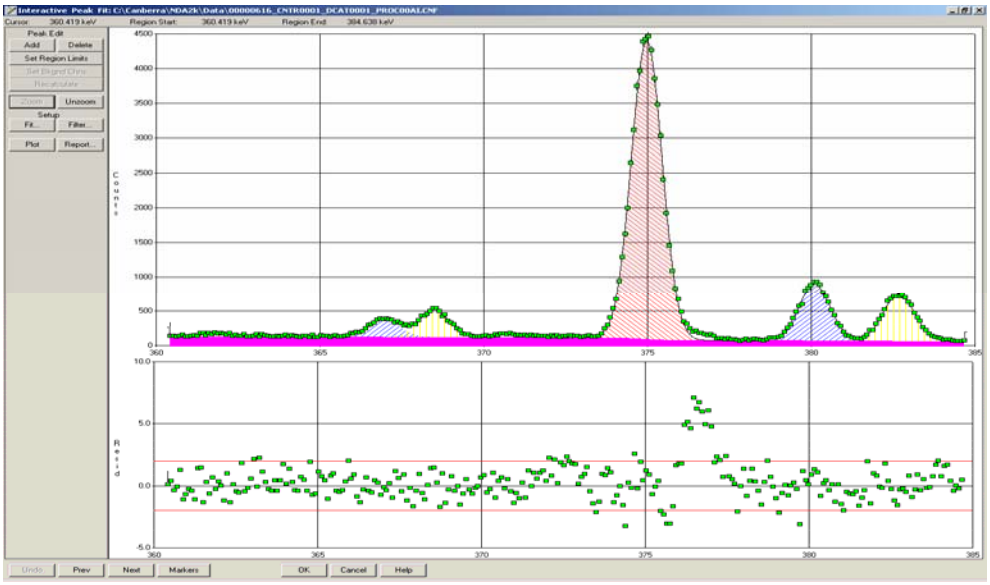

Figure 1a: Spectral region showing overlap of Pa-233 and Pu-239 gamma ray peaks. Note the large positive residual at the bottom of the figure, showing the location of the unresolved 375.45 keV peak.

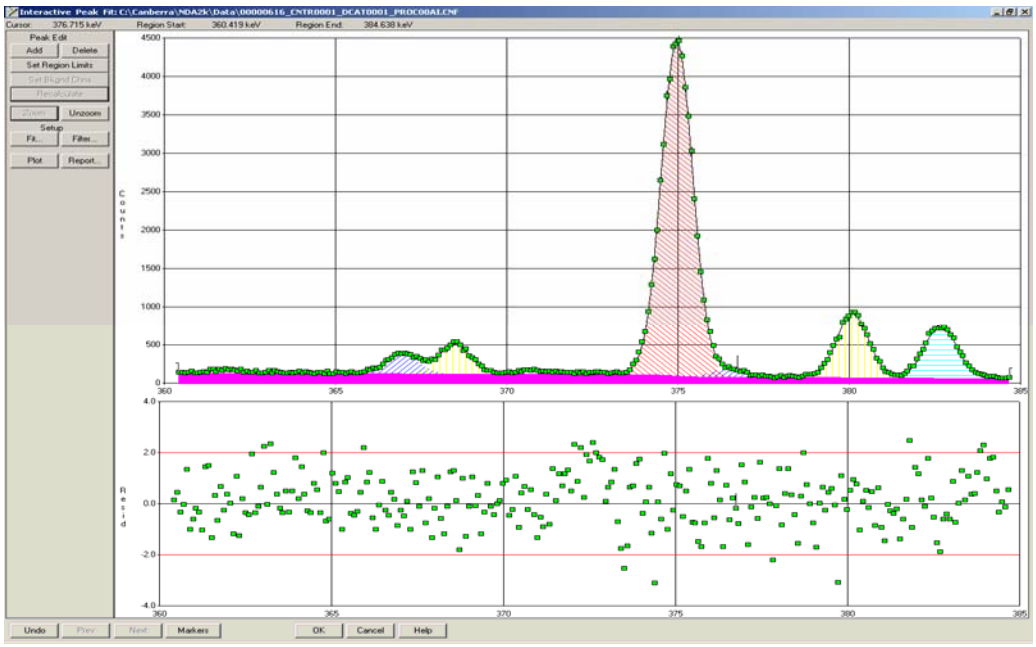

Figure 1b: The same spectral region, showing addition of the missing peak at 375.45 keV, and the improved residual plot.

Matrix Corrections for Neutron Assays

Neutron assays in particular are susceptible to bias caused by variations in the waste matrix. The bias may be positive if the waste contains fluorides, or metals like iron and lead. Negative bias may occur if the waste contains bound water or certain plastics. Correction techniques have been developed to reduce such bias.

Some waste matrices, particularly sludges, may contain significant amounts of fluoride compounds. Alpha-emitting radionuclides interact with the fluorine atoms to release uncorrelated neutrons from (α, n) reactions. Neutron sources such as Am/Li and Pu/Be also emit uncorrelated neutrons. These uncorrelated neutrons greatly increase the totals and accidental coincidence rates, worsening the instrument's LLD. In extreme cases, they also introduce positive bias.

High-Z materials such as lead and iron interact with cosmic rays and release bursts of neutrons that increase the real coincidence rate and cause positive bias. These spallation reactions are more problematic at high-elevation sites, since the atmosphere is thinner and does not absorb cosmic rays as effectively. High-Z interactions are characterized by higher-order neutron multiplicities, so the software can estimate the identity and amount of high-Z material present, and apply a bias correction. If real-time radiography or visual examination of the waste can provide accurate information about the type and amount of high-Z material present, the expert analyst can improve the bias correction further.

Some matrix constituents absorb or moderate neutrons, reducing the neutron yield per gram of Pu-240 effective and introducing negative bias. Graphite and sludge are a few examples of these. To correct the bias, neutron coincidence counters may be equipped with an Add-a-Source option, an external Cf-252 source that exposes the waste drum to additional neutrons at the beginning of each

assay. Interactions of these external neutrons with the waste matrix are measured and used to correct for variations in the waste matrix.

Summary

Experience with waste NDA measurements has given insight into several analytical pitfalls, most of which can be resolved by expert analysis. Neutron and gamma modalities each pose their own problems. A thorough understanding of the measurement process is indispensable when reviewing the data. Knowledge of the waste matrices and potential analytes can provide valuable clues to reducing interferences, minimizing bias and improving precision.