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November 2, 1998 – November 6, 1998

Nuclear Waste Instrumentation Engineering

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Uncertainty analysis of nondestructive assay measurements of nuclear waste

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ABSTRACT

Regulatory agencies governing the disposal of nuclear waste require that the waste be appropriately characterized prior to disposition. The most important aspect of the characterization process, establishing radionuclide content, is often achieved by nondestructive assay (NDA). For NDA systems to be approved for use in these applications, measurement uncertainty must be established.

Standard “propagation of errors” methods provide a good starting point for considering the uncertainty analysis of NDA systems for nuclear waste. However, as compared with other applications (e.g., nuclear material accountability), using NDA systems for nuclear waste measurements presents some unique challenges. These challenges, stemming primarily from the diverse nature of the waste materials encountered, carry over into the uncertainty analysis as well. This paper reviews performance measures appropriate for the assessment of NDA uncertainty, describes characteristics of nuclear waste measurements that contribute to difficulties in assessing uncertainty, and outlines some statistics based methods for incorporating variability in waste characteristics in an uncertainty analysis.

KEYWORDS: uncertainty, non-destructive assay, nuclear waste, statistics

1. INTRODUCTION

Nondestructive assay (NDA) systems used to determine the quantity of radioactive material in nuclear waste are subject to various quality requirements and associated performance criteria. In particular, regulatory agencies such as the U. S. Department of Energy, the U. S. Environmental Protection Agency, and various state agencies require that uncertainty in NDA measurements be established prior to shipping and or disposal of nuclear waste.

Standard “propagation of errors” methods provide a good starting point for considering the uncertainty analysis of NDA systems for nuclear waste. However, as compared with other applications (e.g., nuclear material accountability), assessing uncertainty in NDA measurements of nuclear waste presents some unique challenges to the application of error propagation methods. These challenges stem primarily from the diverse nature of the waste. Nuclear waste is often heterogeneous in nature in terms of characteristics that can radically affect NDA measurement outcome. These matrix effects must be considered when assessing uncertainty of measurements. This paper reviews performance measures appropriate for the assessment of NDA uncertainty, describes characteristics of nuclear waste measurements that contribute to difficulties in assessing uncertainty using standard propagation of errors, and outlines some statistics based methods for incorporating variability in waste matrix characteristics in an uncertainty analysis.

2. MEASURES OF UNCERTAINTY

Uncertainty in NDA systems can be quantified by two basic measures: bias and precision. Bias is a measure of the systematic error in an NDA system, while precision is a measure of the random error. Bias and precision can be expressed in numerous forms. The most fundamental form for the calculation of bias is the difference between the mean of replicate NDA system measured values and the true quantity being measured. The fundamental precision measure is the standard deviation of replicate measurements.

For the purpose of this discussion, we need to distinguish between what might be termed nominal and matrix specific bias and precision measures. Nominal bias and precision refer to the calculated performance of an NDA system for a single ideal test item or container (e.g. 208-liter waste drum). Typically, the test item will comprise surrogate waste material whose properties are well known and in which known quantities of radioisotopes are placed. The waste matrix is typically homogeneous and non-interfering in the nominal case. (In fact it may consist of known sources suspended in an otherwise empty container.) Hence nominal uncertainty refers to measurement performance under ideal conditions, such as that

existing during instrument calibration. Counting statistics errors based on detector response values and an assumed Poisson distribution for counts comprise the largest component of error in regard to nominal uncertainty calculations. When standard propagation of errors methods are used based on component uncertainties estimated without regard to the influence of matrix effects etc., the end result is implicitly a measure of the nominal uncertainty of the NDA system.

Matrix specific bias and precision refer to the expected performance of the NDA system on a waste population of interest. To the extent that specific characteristics or properties of the waste affect measurements, matrix specific bias will be influenced by the average properties of the waste population. Similarly, matrix specific precision will be affected by the degree of variability of salient matrix characteristics in the population.

Except in a totally homogenous population, matrix specific uncertainty of an NDA system will always exceed the nominal uncertainty values. Some specific matrix characteristics found in real waste that can affect nuclear waste NDA measurements and produce larger uncertainties than the nominal values indicate are:

- Source isotopic/chemical composition variability
- Non-uniform matrix absorption
- Non-uniform matrix moderation
- Non-uniform source distribution
- Variations in source particle size
- Significant voids in the matrix
- Shadow shielding of one region by high neutron absorption in another region,
- Waste elemental composition not addressed by the calibration routine, and
- Excessive (α , n) source interference.

Matrix effects (and other effects such as varying background levels) add a whole new dimension to an uncertainty analysis in that conditions external to the measurement system itself can become major determinants of measurement uncertainty. A good way to think of nominal vs. matrix specific bias and precision of an NDA system is to consider what the expected bias and precision are for a single “ideal” drum vs. that for a randomly selected item from the population of interest. Suppose 20 measurements of a single 208-liter waste drum containing 50g of plutonium in a non-interfering matrix are obtained. The difference between the mean of those 20 measurements and the true value of 50g Pu is an estimate of the nominal bias of the NDA system. The standard deviation of the 20 measurements is an estimate of the nominal precision. Now suppose 20 different drums all containing different configurations of a particular waste type (e.g. glass, combustibles, or process sludge) but all containing 50g of plutonium are measured using the same NDA system. The difference between the mean of the measurements on the 20 different drums and the true value of 50g Pu is an estimate of the matrix specific bias for that waste type. Similarly, their standard deviation is a measure of the matrix specific precision.

3. IMPLICATIONS OF MATRIX EFFECTS

Note that matrix specific bias and precision can only be measured relative to a specific population of waste. That is, while nominal uncertainty measures are characteristics of the measurement system only, matrix specific uncertainty is a characteristic of a NDA system used on a particular waste type. When detector response is influenced by characteristics of the waste other than the amount of radionuclides present, only matrix specific measurement uncertainty will provide a realistic estimate of true measurement error.

In the presence of significant matrix effects it becomes just as important to adequately characterize the makeup of the population of interest (in terms of the distribution of important matrix parameters) as it is to characterize the measurement system itself. Uncertainty analysis results become waste type specific and are valid only to the extent that they properly reflect the distribution of important matrix effects in the population of interest. Failure to adequately characterize the distribution of the population matrix parameters can produce misleading or erroneous results.

Figure 1 contains a very simple example of the importance of establishing matrix specific measurement uncertainty. Consider two waste form populations of 3 drums each. All drums in both populations contain 10g Pu, but the quantity of a matrix component with a shielding effect varies from drum to drum within a population as well as between the two populations. In addition, the degree of drum to drum matrix heterogeneity varies between the two populations. The results

show that the bias and precision can differ considerably between the two populations. Hence any estimates of uncertainty must be population specific.

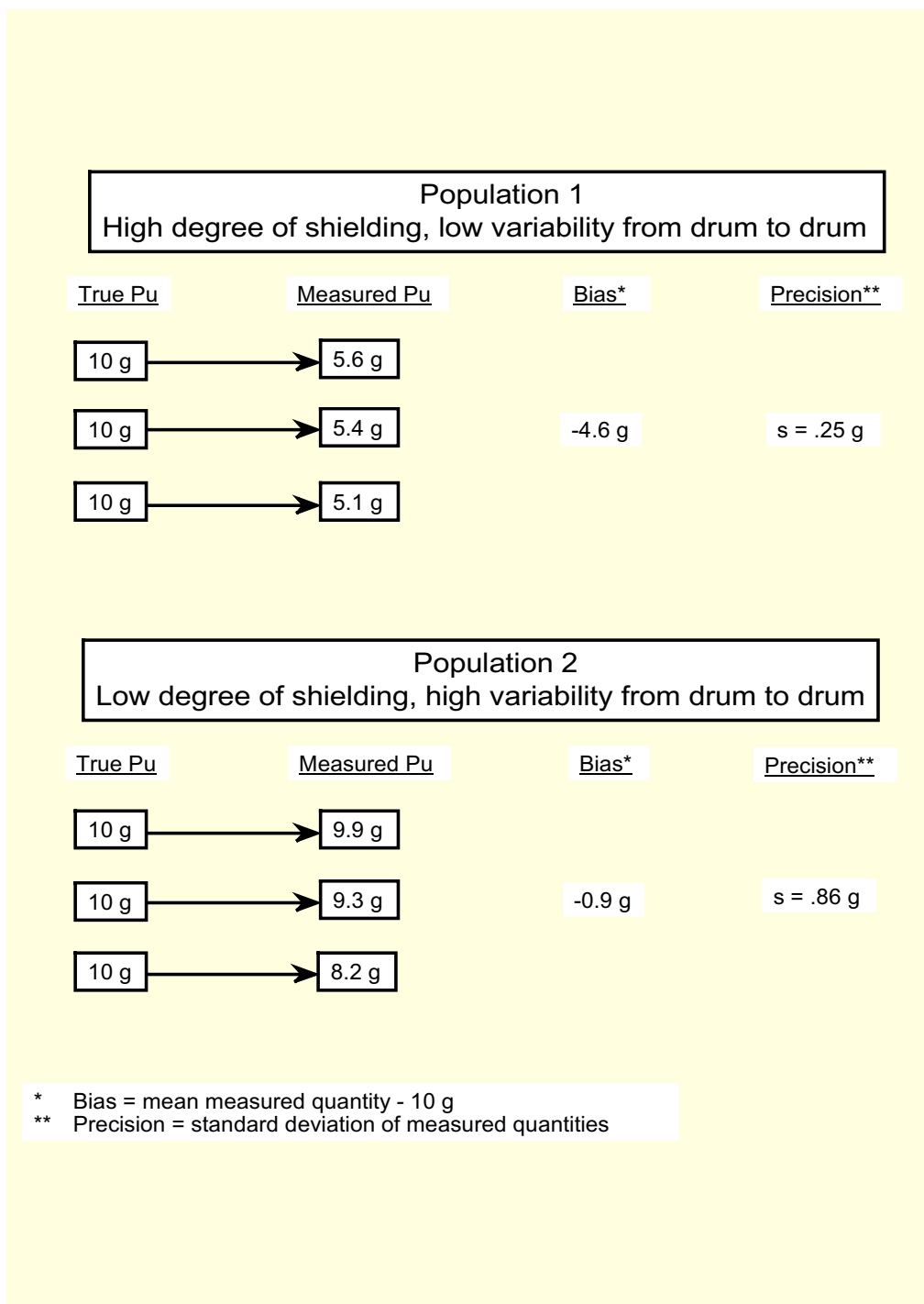


Figure 1. A simple example of matrix specific uncertainty.

One might ask why include bias in the discussion of uncertainty. If we have a known bias, then it is standard procedure to correct for it. In this case the expected bias is zero. However, the bias correction is generally estimated rather than known exactly, thus there is some unknown error in the bias adjustment. Tracking bias uncertainty allows estimation of the uncertainty in the bias correction. This can be important in subsequent calculations involving summing multiple measurements in which the relative precision error tends to get smaller but the bias error will not.

A bias error in one situation can become a random error in another. For example, replicate measurements of a single waste drum establish the bias of an NDA system for that drum. However, in a random selection of drums from the same waste type, each drum will have a unique bias value. The average of these bias values becomes the bias estimate for the waste type population, but the standard deviation of the bias values contributes to the overall precision error for the NDA system for measurements of that waste type.

It is also important to note that bias can be a major component of the total uncertainty in a measurement. For example, using a NDA system calibrated using standards in a non-interfering matrix to measure nuclear waste with high absorption or other significant matrix effects, large bias in measurements may result.

Combining bias and precision uncertainties gives an estimate of the total uncertainty in a measurement. While a measure of total error is useful, care must be taken in using total uncertainties in certain applications. Suppose two or more waste drums from the same measurement system are combined in a single container for shipment and estimates of the uncertainty components in the total Pu content for the shipment are required. The random components of the uncertainties for each drum will generally be uncorrelated. Hence the relative precision error of the total Pu content will be reduced compared to the values for the individual drums. The bias errors on the other hand may be perfectly correlated. Hence there is no reduction in the bias error for the combined value. If the bias and precision components are kept separate, these calculations are easy. If only the total uncertainty for each drum is available, then the correlation between the errors induced by the bias components will be difficult to take into account. Simply combining the total uncertainties as if they were uncorrelated will underestimate the total uncertainty for the combined shipment.

4. STANDARD PROPAGATION OF ERROR METHODS

In most NDA systems, measurement results are not obtained directly. Instead they are derived as the result of calculations performed on a set of input components or parameters. The system uncertainty is then a function of the uncertainties in the input parameters. A typical propagation of errors approach to deriving the final uncertainty values involves the following four basic steps.

1. Identify all input parameters and formulas required for calculating the final measurement value.
2. Assess the uncertainty of the individual input parameters.
3. Obtain the correlation structure of the parameter errors.
4. Propagate the results to obtain final uncertainty.

Examples of the input parameters for the NDA measurements are detector counts, gate times, calibration coefficients, etc. The final measurement outcome is expressed as a mathematical function of these input parameters.

Once all the input parameters are identified, estimates of their individual uncertainties (bias and standard deviation) are obtained. Various methods are used to obtain the component uncertainties. Suitable values are sometimes available from the manufacturer's specifications. Otherwise laboratory evaluations may be performed. Calibration coefficient uncertainties are usually a by-product of the analysis (e.g., least squares regression) used to derive the coefficients themselves.

For some components in a NDA system, measurement errors are correlated. For example, calibration intercept and slope coefficients based on least squares regression are always correlated. The correlation (or alternatively the covariance) of the errors for all pairs of interrelated input parameters must be estimated. These estimates are typically obtained through laboratory experiments.

Once the uncertainties of the various components of a measurement system have been characterized, they are combined, i.e. propagated, to produce the uncertainty for the system output. The formula used for combining the uncertainties depends on the mathematical function or functions used to calculate the system output. In other words it depends on the form of data reduction used to process the input parameters to obtain the final measurement result.

Often the data reduction functions are not linear. Since exact error propagation for nonlinear functions is complex, a linear approximation of the functions is employed. The linearization is achieved mathematically by the use of a Taylor series expansion, which re-expresses the function as a polynomial sum of linear and higher order terms. Under the assumption that the measurement errors in the input parameters are small, the higher order terms in the expansion are set to zero, leaving only

the linear terms. Given the variances and covariances of the input parameters, uncertainty is then easily estimated. For a k input parameter system with an arbitrary (i.e. potentially nonlinear) form

$$z = f(x_1, x_2, \dots, x_k), \quad (1)$$

the Taylor series expansion produces the following expression for the variance of the final measurement

$$\sigma_z^2 = \sum_{i=1}^k \left(\frac{\partial f}{\partial x_i} \right)^2 \sigma_i^2 + 2 \sum_{i=1}^k \sum_{j=1}^{i-1} \left(\frac{\partial f}{\partial x_i} \right) \left(\frac{\partial f}{\partial x_j} \right) \sigma_{ij} \quad (2)$$

where $\frac{\partial f}{\partial x_i}$ is the partial derivatives of f with respect to x_i , σ_i^2 is the variance of x_i , and σ_{ij} is the covariance of the errors in the input parameters x_i and x_j .

Similarly the bias is propagated as

$$B_z^2 = \sum_{i=1}^k \left(\frac{\partial f}{\partial x_i} \right)^2 B_i^2 + 2 \sum_{i=1}^k \sum_{j=1}^{i-1} \left(\frac{\partial f}{\partial x_i} \right) \left(\frac{\partial f}{\partial x_j} \right) B_{ij}^2 \quad (3)$$

where B_i is the bias for x_i and B_{ij} is that portion of the bias terms B_i and B_j that arise from identical error sources.

Propagation of errors can proceed separately for bias error and for precision error, or they can be combined when only total uncertainty is desired. Parameters contributing to bias error only are considered constants in the propagation of precision error. Similarly, parameters contributing only to precision error are treated as constants in the propagation of bias error. Bias parameters are often uncertainty parameters from a calibration etc. that were originally calculated as variances in the context of the calibration, but become bias errors in implementation because the calibration error is constant in application.¹

5. ERROR PROPAGATION EXAMPLE: PASSIVE-ACTIVE NEUTRON RADIOASSAY SYSTEM ACTIVE MODE NET ACTIVITY CALCULATION

At the Idaho National Engineering and Environmental Laboratory (INEEL) the Passive-Active Neutron (PAN) radioassay system is used to certify 208 liter nuclear waste drums in terms of quantifying plutonium and other transuranic elements activities. In the active mode, the net activity (in nCi/g) in a waste drum is calculated as

$$NetActivity = c_1 * EGSC - c_2 * LGSC - c_3 * IB \quad (4)$$

where:

$EGSC$ = early gate shielded count

$LGSC$ = late gate shielded count

IB = interrogation background

The terms in c_1 , c_2 , and c_3 are combinations of correction and calibration factors that have been estimated at some previous point. The errors in these estimates will be the same for all measurements with this system (until such time that new correction factor estimates are introduced e.g. at recalibration). Thus these contribute to the bias error in the measurements. The variables unique to each drum measurement, $EGSC$, $LGSC$, and IB are count data containing random errors, thus contributing to the precision uncertainty.

Given that the terms c_1 , c_2 , and c_3 are constants in the sense that they do not change from one measurement to the next, the precision error for the net activity, expressed as a variance, is

$$\sigma_{NetActivity}^2 = c_1^2 \sigma_{EGSC}^2 + c_2^2 \sigma_{LGSC}^2 + c_3^2 \sigma_{IB}^2 \quad (5)$$

where σ^2 is the variance for the parameter indicated in the subscript. Since the three count measurements $EGSC$, $LGSC$, and IB are obtained independently of each other, all the covariance terms in the calculation are zero.

Bias error is propagated in a similar manner as

$$B_{NetActivity}^2 = EGSC^2 B_{c_1}^2 + LGSC^2 B_{c_2}^2 + IB^2 B_{c_3}^2 + 2 \left(EGSC \cdot LGSC \cdot B_{c_1, c_2}^2 + EGSC \cdot IB \cdot B_{c_1, c_3}^2 + LGSC \cdot IB \cdot B_{c_2, c_3}^2 \right) \quad (6)$$

Since the terms c_1 , c_2 , and c_3 have several terms in common, their bias “covariance” values are nonzero. The values of these terms are obtained by further propagation of the formulas for c_1 , c_2 , and c_3 (not shown).

In the nominal case (i.e., a non-interfering matrix), the variance of $EGSC$, $LGSC$, IB can be estimated by the values $EGSC$, $LGSC$, and IB themselves since they represent count data following Poisson distributions. However, for estimating matrix specific precision other estimates of the variances of these terms must be obtained. These estimates must contain the additional variability due to matrix effects. Matrix effects in 208-liter drums can be quite large, as waste heterogeneity within and between drums (even of a particular waste type) can be considerable. The additional variability created by this heterogeneity can be much larger than the simple counting statistics error values used in the nominal case.

6. MATRIX EFFECTS AND PROPAGATION OF ERRORS

Using propagation of errors methods to estimate matrix specific uncertainty is problematic compared to calculation of nominal uncertainty. The variance terms used in a propagation of errors uncertainty analysis are often based on theoretical calculations or limited laboratory tests. For example the variance of the early gate shielded count in the previous example can be calculated theoretically to be equal to the measured count since counts typically follow a Poisson probability distribution (for which the variance is equal to the mean). However, such a theoretical calculation does not take into account the degree to which the matrix characteristics can affect the overall performance of the NDA system. The material used in laboratory tests may or may not duplicate the important matrix characteristics of the population of interest. Even if test items for laboratory experiments are constructed to be generally similar to those in the population of interest, they can still vary considerably in terms of matrix complexity compared to the real items. This will also result in underestimation of variance terms used in propagation of error calculations. For the uncertainty analysis results to be truly applicable to a population of nuclear waste whose matrix characteristics are expected to affect measurement results, error terms must reflect the bias and variability that would have been obtained on samples from that specific population.

An additional limitation to the standard propagation of errors methods for uncertainty analysis when matrix effects are present is due to the magnitude of the errors in measurements induced by the matrix effects. The propagation of errors formulas used for nonlinear measurement functions are based on the assumption that the measured values are close to the true values. That is the relative measurement error is small. As long as this is true, the linear approximation to the measurement function obtained by setting the higher order terms in the Taylor’s series expansion to zero is justifiable. However, in NDA systems measurement errors can be very large (e.g. even orders of magnitude) so the linear approximation can be invalid.

When matrix effects are a significant component of the uncertainty of an NDA measurement, quoted uncertainty results are population specific. In other words, the results are only valid in the context of the population of waste items for which the uncertainty analysis duplicates the matrix effects. Thus laboratory derived variance components are only valid for a population of waste that matches the same matrix characteristics as used in the laboratory tests. The only way to verify this equivalence is to perform some sort of characterization process of the real waste that delineates the important matrix parameters. Even if all the relevant matrix characteristics are identified and evaluated, it may not be possible to duplicate the complexity of the real waste in a laboratory setting. A prime example is source size effects. While it is recognized that the source particle size distribution can have major effects on NDA measurements, lack of knowledge of the actual particle size distribution can lead to problems.

7. UNCERTAINTY ANALYSIS BY DIRECT SAMPLING AND VERIFICATION

In the presence of matrix effects the importance of the representativeness of sampled items used to estimate bias or variance components is clear. In a waste drum radioassay system for example, results from an uncertainty evaluation using drums filled with a benign matrix cannot be legitimately used to infer the uncertainty for drums containing large quantities of shielding material such as lead. An alternative approach to propagation of errors that directly addresses the issue of representativeness is direct sampling and verification. The basic steps in this method are:

1. Draw a random sample of actual items from the waste population of interest.
2. Measure the items using the NDA measurement system being evaluated.
3. Perform a confirmatory measurement using a different (unbiased) method.
4. Use regression analysis and variance component analysis to obtain estimates of bias and precision.

By directly calculating bias and variability of the final NDA measurement of real waste (rather than evaluating each component of the system separately and then combining them as in the propagation of errors method), many assumptions and approximations required in the propagation of errors method or in the construction of test items for laboratory evaluations are avoided. For example, any issues related to the Taylor's series approximations in the propagation of error calculations are no longer relevant. Also eliminated are any concerns of potentially misleading results due to constructing laboratory test items that fail to reflect the diversity of matrix characteristics in the real waste. By drawing a random sample, the matrix characteristics of the items evaluated will be representative of the population of interest. It will also by default automatically include all relevant matrix effects. Thus bias and precision estimates for the sample will apply directly to the entire population.

Typically the confirmatory method will be a more precise but perhaps more expensive method than the NDA method under study. The primary requirement of the confirmatory measurements is that they must be unbiased for the true values of the quantity of interest. Otherwise, it would not be possible to establish the exact bias of the NDA system (only its bias relative to the confirmatory measurement method).

Often it will be the case that the uncertainty, particularly the precision error or standard deviation of the errors in measurement, will increase with the amount of the quantity of interest that is present in an item being measured. In this case bias and precision must be defined as a function of the quantity of interest. For bias, this most often simply means expressing it as a constant relative bias (i.e. bias is a fixed percentage of the measured value). It is also possible for there to be both absolute and relative bias terms. A regression of the confirmatory measurements on the quantity of interest will yield estimates of both components. For variable precision, an additional regression fit involving residuals from the bias regression model will give an indication of trends in standard deviation.

Estimates of the bias components are obtained by linear regression analysis. A weighted least squares regression is appropriate in the usual case where the random error changes as a function of the values measured. It is possible that a more complicated bias relationship exists than that expressed by a linear model, i.e., the bias may be a nonlinear function of the quantity being measured.) This can be checked in the regression analysis, by testing for significant quadratic effects for example.

Precision estimates are obtained by analysis of the residuals from the regression performed to estimate the bias components. If there is no indication of varying precision values, then precision can be estimated simply by calculating the standard deviation of the residuals (i.e., the mean square error from the regression). However, if the residuals themselves appear to follow a trend as a function of the measured values, then that must be estimated using additional regression analysis or other appropriate techniques. Also, in the case where there is appreciable measurement error in the confirmatory measurements as well as the NDA measurements, analysis separating the variability due to these two sources is required.

8. SAMPLING AND VERIFICATION EXAMPLE: PAN RADIOASSAY SYSTEM ACTIVE MODE PU MASS MEASUREMENTS OF SOLIDIFIED AQUEOUS SLUDGE WASTE

A major waste type being measured using the INEEL's PAN radioassay system is solidified aqueous sludge stored in 208-liter drums. Sampling and verification was used to determine measurement uncertainty for the PAN active mode sludge measurements. The confirmatory measurements for the sludge waste were obtained from destructive radioassay of core

samples from selected drums. A facility has been built at the INEEL for coring and sampling sludge waste drums. Originally developed for sampling for Resource Conservation Recovery Act (RCRA) listed hazardous constituents, core sampling plans were modified to include sampling for radioassay analysis as well. While the comparative drum core radioassay data contain a certain amount of uncertainty themselves, they are expected to be unbiased. So by comparing the mean core sample results to the mean PAN results, the bias of the PAN system can be easily established. Furthermore, applying the proper variance component analysis allows the standard deviation of errors to be estimated as well.

8.1 Basic steps in performing the uncertainty analysis

The basic steps used in performing the sampling and verification uncertainty analysis for the solidified aqueous sludge waste were as follows:

1. Select 125 sludge waste drums for which PAN measurements are available and which are being sent to the coring facility for RCRA evaluation.
2. Send samples from the cores for each of the selected drums to the INEEL Analytical Chemistry Laboratory for radiochemical assessment.
3. Convert the chemical radioassay results (pCi/g) to the equivalent total drum contents (i.e., total grams of Pu).
4. Compare the radiochemical analysis results with the PAN Pu measurement results for the same drums. From these data, estimates of matrix specific bias and precision for the PAN system sludge drum measurements can be obtained.

A minimum of two cores was obtained from each of the 125 waste drums used in the uncertainty analysis. Coring locations for each drum were selected at random from seven possible ports in a template placed over the drum prior to coring. Once the cores were removed from the drum, a slice of the recovered material, running the full length of the core, was obtained and homogenized. One aliquot was randomly sampled from each homogenized core slice and sent to the lab for analysis.

8.2 Data

The total Pu mass as determined by radiochemistry analysis and the corresponding PAN measurements for each of the 125 drums in the uncertainty analysis are plotted in Figure 2. The line of perfect agreement specified in the plot (i.e., the solid line) indicates where the data would fall if there were no measurement bias or precision error. The second line in the plot (i.e., the dashed line) is a regression line fit to the data using the method described below. The regression line indicates the degree of bias in the PAN system. That the regression line (and most of the data) falls above the line of perfect agreement indicates that the PAN Pu measurements are biased low compared to the confirmatory radiochemistry results. The degree of scatter in the points about the regression line is an indicator of the degree of precision in the measurements. Since both the PAN system and radiochemistry data are subject to precision error, the precision of the PAN system must be estimated by the decomposition of variance components in the regression model. The appropriate treatment of the variance components is determined by consideration of measurement models in the next section.

8.3 Measurement models

Let ξ_η be the theoretical mean of the PAN measurements of all drums in the population of sludge drums that contain η g Pu. If the PAN system is unbiased, $\xi_\eta = \eta$. If there is constant and/or relative bias in the PAN system then the relevant model is

$$\eta = \alpha + \beta \xi_\eta \quad (7)$$

where α is the constant bias effect and β is the relative bias effect. If $\alpha \neq 0$ and $\beta = 1$, then there is a constant bias in the measurement system. If $\alpha = 0$ and $\beta \neq 1$, then there is constant relative bias in the system. It is also possible to have both constant and relative bias terms at the same time. To estimate the bias terms as well as address the precision error in the PAN system, we need to compare the measured Pu values from the PAN system and the radiochemistry data.

The observed PAN measurement for a randomly selected drum from those containing η g Pu is equal to the theoretical mean ξ_η plus random errors due to matrix effects, counting statistics, etc. That is, if x_i is the PAN measurement for drum i and η_i the true Pu value for drum i then



Figure 2. Comparison of PAN and radiochemistry Pu measurement results

$$x_i = \xi_{\eta i} + \delta_{pi} \quad (8)$$

where δ_{pi} is the random error in the measurement of drum i , and

$$E(\delta_{pi}) = 0 \quad (9)$$

$$\text{Var}(\delta_{pi}) = \sigma_{pi}^2 \quad (10)$$

$E(\cdot)$ and $\text{Var}(\cdot)$ are the expected value and variance of the indicated terms. The i in the subscript of the σ^2 terms indicates that the variance values can change from drum to drum. (Below we show that the error variances can be modeled as functions of the measured Pu quantity in the drum.)

Since the radiochemistry data are unbiased but measured with error, the measured radiochemistry value for drum i is the true value plus a random measurement error term, i.e.,

$$y_i = \eta_i + \delta_{ri} \quad (11)$$

$$E(\delta_{ri}) = 0 \quad (12)$$

$$\text{Var}(\delta_{ri}) = \sigma_{ri}^2 \quad (13)$$

where y_i is the measured radiochemistry value for drum i and δ_{ri} is the measurement error in the radiochemistry value for drum i . The term δ_{ri} comprises all the error in the radiochemistry data (e.g., analytic error and core to core variability in the radiochemistry measurements).

A measurement model relating the radiochemistry data to the PAN data from which bias and precision estimates can be obtained via regression is created by first replacing the η_i term in Equation 11 with Equation 7:

$$y_i = \alpha + \beta \xi_{\eta i} + \delta_{ri} \quad (14)$$

Next, solve for ξ_{η_i} in Equation 8 and substitute into Equation 14 to get

$$\begin{aligned}
 y_i &= \alpha + \beta(x_i - \delta_{pi}) + \delta_{ri} \\
 &= \alpha + \beta(x_i) + \delta_{ri} - \beta(\delta_{pi}) \\
 &= \alpha + \beta(x_i) + \varepsilon_i
 \end{aligned} \tag{15}$$

where

$$\varepsilon_i = \delta_{ri} - \beta(\delta_{pi}). \tag{16}$$

The model in Equation 15 is in terms of the observed PAN and radiochemistry measurements so estimates of α and β can be obtained using statistical regression analysis techniques. Since the residual values (the differences between actual and predicted y_i values) from this regression are estimates of the ε values, the residuals, along with additional information, can be used to obtain precision component estimates. (Note, since the independent variable values in the regression analysis are measured with error, a violation of standard regression assumptions, special statistical analysis techniques may be required to prevent bias in the regression parameters.^{2,3})

8.4 Matrix specific bias

A regression analysis was performed to estimate the parameters α and β in Equation 15. Since the variability of the data increases with increasing Pu quantity (see Figure 7-1), a weighted least squares analysis was performed.⁴ Ideally, the weights used in the analysis should be $1/\sigma_x^2$ where σ_x is the standard deviation of ε for a given value of x . True values of σ_x are unknown but can be estimated by estimating ε , since $s_x = |\varepsilon|$ is an estimate of σ_x .

Equation 16 cannot be used directly to estimate ε . While we have estimates of the radioassay measurement error δ_{ri} independent estimates of the remaining two components β and δ_{pi} are not available. (We have estimates of the counting statistics error component of δ_{pi} , but not the matrix error component.) Hence, both the weights and the regression coefficients were estimated by an iterative method.

In the first iteration of the weighted least squares analysis the weights were all set to 1.0 (i.e., an ordinary least squares analysis was performed). To obtain new weight estimates, the estimated values of α and β from this regression were first substituted into Equation 15. Solving for ε_i and taking absolute values gives the new s_x value for each of the x_i data points. While each of the s_x values is an estimate of the corresponding σ_x value, taken individually they are highly inaccurate estimates. Better estimates of the weights can be obtained by considering the whole set of s_x estimates in terms of their relationship to the PAN measured mass values. A scatterplot of the s_x values and the measured PAN mass values showed the relationship to be linearly increasing on a log-log scale. A numerical estimate of this increasing relationship was obtained by regressing the logarithms of the s_x values on the logarithms of the PAN mass values. New estimated values for s_x obtained from this regression equation were then squared and, after taking reciprocals, used as weights in the second iteration of the weighted least squares analysis. This yielded new estimates of α and β , from which new estimates of the ε could be obtained. This iterative process was repeated until the estimates of α and β and ε did not change in the first three significant digits.

The final equation used for calculating s_x and hence the weights in the final iteration of the weighted least squares analysis was

$$s_x = .365(PAN\ Pu\ mass)^{.931}. \tag{17}$$

The weighted least squares analysis for the measurement model in Equation 15 produced an estimate for α that was not significantly different from zero, so that term was dropped from the model. The estimated value for β is $\hat{\beta} = 1.55$. To check the adequacy of a linear model for the data, a quadratic term was also tested. The quadratic term was not statistically significant; indicating the linear model is sufficient to represent the data. Therefore, the only applicable bias term is the relative bias term β . That is, the model relating the PAN system measurements to the radiochemistry results is simply

$$y = \beta x \quad (18)$$

which is estimated as

$$y = 1.55x. \quad (19)$$

Under the assumption that the radiochemistry data are unbiased, Equation 19 becomes an expression for quantifying the bias in the PAN system. Based on this analysis, a 1.55 bias correction is being applied to all aqueous sludge drum measurements. Hence, the expected bias in measurements of aqueous sludge waste is now zero. There is still uncertainty in the result associated with the bias adjustment. An approximate 95% confidence interval for the true relative bias of PAN measurements after the bias adjustment was calculated to be (-27%, 27%). (A detailed description of the analysis is available elsewhere.⁵)

8.5 Matrix specific precision

An expression for calculating matrix specific precision error for the sludge waste can be found by calculating the variance of both sides of Equation 16 and solving for the error term associated with the PAN measurements, σ_{pi} . This gives the precision error as

$$\sigma_{pi} = \sqrt{\frac{\sigma_{ei}^2 - \sigma_{ri}^2}{\beta^2}} \quad (20)$$

where σ_{ei} is the residual standard deviation (i.e., the standard deviation of the ε values) and all the other terms are defined as before.

From Equation 20, estimates of the matrix specific error can be calculated using reported radiochemistry measurement error values to estimate σ_{ri} , and estimates of β and σ_{ei} produced in the weighted least squares regression above.

The matrix specific precision error is related to the mass of Pu in the drum, as can be seen in Figure 3, which plots the calculated precision error terms as a function of the bias adjusted PAN Pu mass. A weighted least squares regression was applied to these data, resulting in the following formula for estimating the matrix specific error:

$$s_m = .33 * (\text{bias adjusted PAN Pu mass}). \quad (21)$$

Equation 21 indicates a relative precision error of approximately 33%. It should be noted that the regression fit is affected somewhat by several high uncertainty values. If the relative precision error is calculated separately for each of the 125 individual drums the mean value is 31%, which agrees closely with the regression parameter estimate of 33%. However, the median relative uncertainty value is 19%, a considerably lower value.

9. DISCUSSION

The previous example has shown how an uncertainty analysis can proceed based on direct sampling and verification of nuclear waste. This method was ideal for the sludge waste because verification of PAN measurements could be reasonably obtained by destructive radiochemical analysis of core samples. This may not be the case for other waste types, particularly debris waste where coring is not a practical means of obtaining confirmatory measurements. Some modifications of the sampling and verification method can be used on such waste types. Computer simulation of direct sampling and verification methods has been used successively at the INEEL.

In the computer simulation approach, computer models of real waste drums and of the PAN system performance were developed. After benchmarking the process by comparing real and simulated measurements of surrogate waste drums, the computer-simulated measurements of the real waste drums were analyzed as if they had come from real measurements of the waste type of interest. For the computer simulation method to work requires specific knowledge of both the important matrix

characteristics and the distribution of these characteristics in the population of interest. At the INEEL the simulation based approach was made possible by:

- the previous existence of computer programs simulating both the neutron transport properties of a simulated waste drum and the subsequent PAN system performance,
- a large collection of real-time radiography tapes for waste drums at the INEEL (so that actual waste drums could be modeled), and
- an extensive database of actual PAN measurements on waste drums and background drums (from which other parameters important to measurements (e.g. background levels) could be determined.

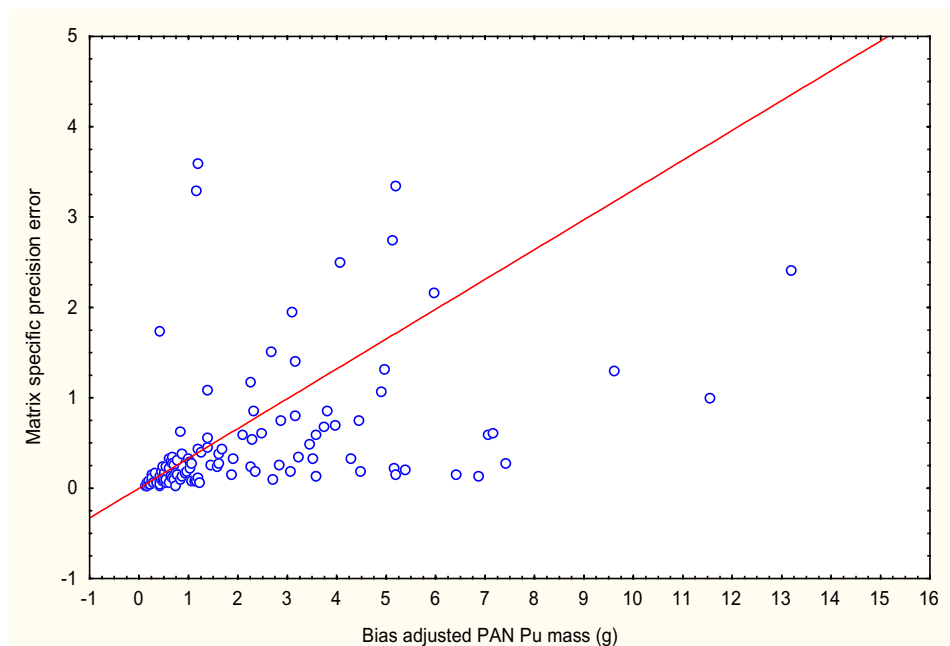


Figure 3. Estimated matrix specific error as a function of bias adjusted Pu PAN Pu mass.

10. ACKNOWLEDGEMENTS

This document was prepared for the U. S. Department of Energy Office of Environmental Restoration and Waste Management under DOE Idaho Operations Office Contract DE-AC07-94ID13223.

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