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**LIMIT OF ERROR CALCULATIONS
USED IN INTEGRATED SAFEGUARDS EXPERIMENT**

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ABSTRACT

The Integrated Safeguards Experiment sponsored by the Atomic Energy Commission relied heavily on nondestructive assay techniques to attain a measured material balance on the mixed oxide fabrication process. This paper describes the calculations involved in determining the limit of error values for material measurements using calorimetry and neutron coincidence counting techniques as well as conventional chemical assay methods.

INTRODUCTION

The purpose of this paper is to present the computations of the limit of error (LE) that were used in the calculations of measured material balances in the Integrated Safeguards Experiment (ISE). The ISE, which was sponsored by the United States Atomic Energy Commission (AEC) with joint participation of their Office of Safeguards Materials Management (OSMM), Technical Support Organization (TSO) of Brookhaven National Laboratory, Technical Analysis Division of the National Bureau of Standards, and the General Electric Company (GE), was conducted at the General Electric Company, Vallecitos Nuclear Center, Pleasanton, California, on the mixed oxide (PuO_2 - UO_2) fabrication line in the plutonium fuels laboratory.

One of the goals of ISE was to obtain plutonium material balances which were based completely on measurement. To accomplish this it was necessary to use both destructive and nondestructive techniques (NDT) for determining the plutonium content of the various fabrication-line materials. Sampling, sample dissolution, and determination of the plutonium concentration by the destructive technique of coulometry was applied to the plutonium dioxide feed material and to sintered mixed oxide pellets representing the product. The Pu content of the feed material was also determined by calorimetry. For the scrap materials, both clean and dirty, and for the waste, which is classified as measured discards, the nondestructive technique of neutron coincidence counting was applied.

In this paper emphasis will be on the gPu LE* calculations associated with the four major flows of the fabrication process: feed, product, scrap and waste. The LE calculations will be illustrated using chemical assay (destructive) data for the feed and product materials and the non-destructive assay data associated with the feed (calorimetry) and scrap and waste (neutron coincidence).

LIMIT OF ERROR CALCULATIONS

Feed Material

Feed material quantities in the material balance were determined from both chemical assay and NDT calorimetry data. The chemical assay data were obtained by taking samples from each container of equilibrated feed material and determining the plutonium concentration by coulometry. The mean of the plutonium concentrations of the samples was used as the plutonium concentration value in the determination of the gPu in the feed. The variance obtained from the distribution of concentrations in the samples was used to compute the LE for the plutonium concentration value. This LE value includes variations due to sampling (main contributor is believed due to moisture), dissolution, and sample preparation, as well as the analytical variation. All feed material was equilibrated before weighing and sampling so that the samples would represent the material in the containers.

To obtain the LE on the total feed material, the LE associated with the weighings must be determined and combined with the LE associated with the mean plutonium concentration. The variance of the total weight of

* LE defined as boundaries within which the true value of the parameter being measured lies with a probability of 95 percent. Measurement error and sampling error are assumed to be normally distributed.

plutonium dioxide is the sum of the variances of the individual weighings. The variance of an individual weighing was determined from the balance calibration data obtained as part of the plant quality control program. The LE of the total weight was obtained by the standard formula of two times the square root of the total weight variance. The left hand column of Figure 1 shows the calculation of the LE for the total weight. The determination of the LE associated with the plutonium concentration value will now be explained. As stated before, the average concentration of Pu among the containers of feed material was used as the Pu concentration value to determine the gPu in the total feed material. Therefore, this LE calculation deals with a mean value, namely, the average plutonium concentration value. When dealing with average values and standard deviations computed from small sample sizes, a different statistical formula must be used than when treating individual values as was the case for weights. The standard deviation of the mean (generally called the standard error of the mean), $S(\bar{C})$, is obtained by the formula, $S(\bar{C}) = S(C) / \sqrt{n}$ where $S(C)$ is the standard deviation of the individual concentration assays. Also, the t distribution is used instead of the normal distribution, leading to the t factor. The value of the t factor depends on the confidence level desired and the number of samples involved. The t factor is then multiplied by the standard error to obtain the 95% CL limit of error value, $LE(\bar{C})$. The right hand column of Figure 1 illustrates this procedure to obtain the LE associated with the average plutonium concentration.

FIGURE 1. FEED MATERIAL

LE CALCULATIONS USING CHEMICAL ASSAY DATA

Weighings	Chemical Assay
N containers of PuO_2	n samples of PuO_2
X_1 (in grams of PuO_2)	C_1 (Pu/PuO_2)
X_2	C_2
$\vdots$	$\vdots$
X_N	C_n
$X_T = \sum_{i=1}^N X_i$ (total weight of feed in grams of PuO_2)	$\bar{C} = \sum_{i=1}^n C_i / n$ (average plutonium concentration)
Two weighings required for each container to determine amount of PuO_2 (gross-tare). The variance of the weighing balance, S^2 , is obtained from calibration data.	$S^2(C) = \sum_{i=1}^n \frac{(C_i - \bar{C})^2}{n-1}$
$LE(X_T) = 2 \left[\sum_{i=1}^N S_i^2 (\text{gross}) + \sum_{i=1}^N S_i^2 (\text{tare}) \right]^{1/2}$	$S(C) = S(C)/(n)^{1/2}$ (standard error)
If all weighing variances are the same, the expression reduces to $2S[2N]^{1/2}$	$LE(C) = t S(C)$
	where t is "t factor" at $\nu = n-1$ degrees of freedom at 95% CL.

$$LE \text{ of Feed Material in gPu} = [LE(X_T)/X_T + LE(C)/C] X_T$$

$$LE \text{ of Feed Material in gPu} = \bar{C} LE(X_T) + X_T LE(C)$$

The procedure used to obtain the LE for the total gPu for feed material, that is, combining the LE for the weighings and the LE for the chemical assay, was not based on the usual variance of a product of two variables. The variance of the product of two independent random variables, XY , is approximately $(XY)^2 \left(\frac{V_x}{X^2} + \frac{V_y}{Y^2} \right)$. In the ISE calculations, the average Pu concentration was used as a constant factor and therefore, the variance is obtained to account for the possible bias introduced by this procedure and the LE was obtained as follows. The total weight LE converted to a percentage was linearly added to the average plutonium concentration percentage LE; this sum was multiplied by the total gPu to obtain the total feed LE in gPu units. The LE values were combined because, first, the average plutonium concentration uncertainty would reflect how well the mean or average value was known. Secondly, the average plutonium concentration uncertainty was an order of magnitude larger than the total weight LE. If only the 68% CL uncertainty values were combined and then multiplied by 2, a 95% CL value would not be obtained since the plutonium concentration uncertainty value dominates. (Procedures* are available for determining the proper t factor in cases where 68% CL uncertainty values are used.) The procedure used to obtain the LE on feed material (in grams plutonium) is shown on the bottom of Figure 1.

* NBS Special Publication 300 Volume 1, "Precision Measurement and Calibration - Statistical Concepts and Procedures," page 339.

Calorimetry was the nondestructive technique employed for determining the plutonium in the plutonium dioxide feed material. The LE on feed material in grams plutonium from the calorimetry data has two components: that due to the reproducibility (precision) of the calorimeter, and that due to the uncertainties of the isotopic abundances and the specific power constants. The reproducibility LE was determined by taking repeated measurements on a typical feed can. The standard deviation, S , obtained from the values of the repeated measurements was multiplied by two to produce the LE associated with the variability of the calorimeter. If there are N containers of feed material then the total reproducibility LE would be $2S\sqrt{N}$. Note that this calorimeter reproducibility LE is essentially a parallel to the weighing balance LE, and similarly, both values came from the calibration data section of the plant quality control program.

The second component of the total LE is the systematic error that might be involved due to the uncertainty in the isotopic abundance values and the specific power constants that were used in the calculation of the grams plutonium. For each can of feed measured in the calorimeter, the same set of specific power constants (supplied by the calorimeter vendor - Mound Lab) was applied. Since an average value from the mass spectrometer data and alpha counting data was used to characterize the abundance of each isotope, the same set of isotopic abundance values was used in the calculation of the grams plutonium in each can of feed material. The errors in these two constants affect the gPu values for all of the feed cans in exactly the same way, thus giving the effects

of systematic error and is so labeled in the illustrations in Figure 2. To determine the magnitude of this second component the total uncertainty due to both abundance and specific heat was multiplied by the heat contribution for each of the isotopes. The sum of these products over all of the isotopes resulted in the total systematic effect. The main part of Figure 2 shows this procedure. The bottom part shows the formulation for total LE in grams plutonium for calorimetrically determined values.

For the ISE, the reproducibility LE for the calorimeter was very small compared to the isotopic uncertainties (systematic component) and was ignored. A comment is in order concerning the total uncertainty for calorimetry resulting from the abundance and specific power aspects of the Pu isotopes. The Pu 238, Pu 239, Pu 240, and Am 241 isotopes are the main contributors to the heat. Of these 4 isotopes the abundance determinations for the Am 241 and Pu 238 are the poorest. The specific power uncertainties for these two isotopes are small in comparison to the abundance uncertainties and can usually be ignored. So what one usually ends up with for the total systematic effect is due mainly to the abundance uncertainties for the Am 241 and Pu 238 isotopes.

FIGURE 2. FEED MATERIAL

IE CALCULATIONS USING CALORIMETRICALLY DETERMINED DATA

Isotope	Abundance	Specific Power Watts/Gram/Isotope	Watts/Gram	Heat Contribution	Isotopic and Specific Power Uncertainty	Systematic Effect
Pu 238	X_1	W_1	$X_1 W_1$	$H_1 = X_1 W_1 / XW$	$U_1 (\%)$	$H_1 U_1 (\%)$
Pu 239	X_2	W_2	$X_2 W_2$	H_2	U_2	$H_2 U_2$
Pu 240	X_3	W_3	$X_3 W_3$	H_3	U_3	$H_3 U_3$
Pu 241	X_4	W_4	$X_4 W_4$	H_4	U_4	$H_4 U_4$
Pu 242	X_5	W_5	$X_5 W_5$	H_5	U_5	$H_5 U_5$
Am 241	X_6	W_6	$X_6 W_6$	H_6	U_6	$H_6 U_6$
$XW = \sum X_i W_i$				Total Systematic Effect is $\sum H_i U_i$		

Total feed IE from calorimetry = Reproducibility IE + Total Systematic Error

$$= 2S/\sqrt{N} + (\sum H_i U_i) (\text{total gPu})$$

Product Material

The quantity of Pu in the product material and its associated LE were determined from weight data and the chemical assay of samples taken from the product, sintered mixed oxide pellets. For a given campaign or job in the ISE, there usually were more than one enrichment (percent of plutonium in the mixed oxide) and more than one blend or batch within an enrichment. It was important to verify that the distribution of plutonium concentrations for each blend (these data came from sintered samples sent to analytical lab) within a given enrichment was the same since it could affect the resulting LE on the product material. If the t and F tests for the means and variances of the Pu concentrations indicated that the blends came from the same population, then the Pu concentration data were pooled into one distribution for each enrichment. If the tests showed otherwise, the LE was obtained by using the Pu concentration of the batches. In either case the calculations are similar to that used for the feed material. Figure 3 illustrates the computational procedures. Note that whenever a constant was used, such as the average Pu concentration, the variability measures were combined as though a systematic effect was present. Again, as pointed out in the discussion on the feed, the LE(C) value includes the variations due to dissolution, sample preparation, technicians, standards, and coulometry uncertainty.

Scrap and Measured Discards

The plutonium content of scrap and discarded materials (waste) was determined by neutron coincidence counting. This NDT method utilizes standards for the determination of Pu in the samples. The standards used in the ISE were fabricated from known quantities of mixed oxide in the existing inventory materials.

FIGURE 3. PRODUCT MATERIAL

LE CALCULATIONS USING CHEMICAL ASSAY DATA.

For each enrichment the following calculations were performed:

M weighings of pellet groups

X_1 (g mixed oxide)

X_2

$\vdots$

X_M

$$X_T = \sum_{i=1}^M X_i$$

$$LE(X_T) = 2 \left[\sum_{i=1}^M S_i^2 (\text{gross}) + \sum_{i=1}^M S_i^2 (\text{tare}) \right]^{1/2}$$

m samples of pellets

C_1 (Pu/mixed oxide)

C_2

$\vdots$

C_m

$$\bar{C} = \sum_{i=1}^m C_i / m \text{ (average concentration)}$$

$S(\bar{C})$ = computed standard error

$$LE(\bar{C}) = t S(\bar{C})$$

$$\text{gPu LE for Enrichment } j = LE(j) = [LE(X_T)/X_T + LE(\bar{C})/\bar{C}] X_T \bar{C}$$

$$\text{For the total job of } K \text{ Enrichments the product gPu LE} = \left[\sum_{j=1}^K LE^2(j) \right]^{1/2}$$

From the counting data collected on the known standards a calibration curve was fitted by using the least squares technique. The y axis or ordinate represented the coincidence counts for a fixed time corrected for accidental counts, dead time losses and background counts. The x axis or abscissa represented the grams of plutonium 240 equivalent in the standards. The weighting of calibration data had no significant effect on the resulting calibration parameters. From the least squares fit of the standards data the slope, intercept, standard deviations of the slope and intercept, and the covariance between the slope and intercept were obtained. The standard deviation of the slope and intercept represented the uncertainty associated with the standards provided that all the standards did not come from the same isotopic and enrichment lot. When the scrap and discarded materials were coincidence counted, the count, Σy_i , was obtained with information for the counting variance. Figure 4 shows the pertinent expressions used to obtain the grams of plutonium 240 equivalent, X , and the associated variance, σ^2_X . Note that the summation of the individual gPu 240 equivalent values, X_i , takes place before the error propagation is applied. If this procedure is carried out in reverse order, the covariance effects among the individual counts would have to be accounted for. The X_i values for all of the material counted within a given calibration period were related through the use of the same calibration parameters. In other words, the variances associated with the individual X_i values are not independent and cannot be summed to obtain the variance on the total, σ^2_X . On the other hand, variances from different periods based on independent

FIGURE 4. SCRAP AND WASTE
LE CALCULATIONS USING DATA FROM NEUTRON
COINCIDENCE COUNTING

$y = ax + b$ general equation

From calibration data:

a - slope

b - intercept

σ_a^2 - slope variance

σ_b^2 - intercept variance

cov (a,b) - covariance between slope and intercept

$$x_i = (y_i - b)/a$$

$$X = \sum x_i = (\sum y_i - nb)/a$$

y_i - net corrected coincidence counts of sample i.

x_i - calculated gPu 240 eq. of sample i.

$$\frac{\sigma_X^2}{X^2} = \frac{\sigma^2(\sum y - nb)}{(\sum y - nb)^2} + \frac{\sigma_a^2}{a^2} - \frac{2 \text{Cov}(\sum y - nb, a)}{(\sum y - nb)(a)}$$

$$= \frac{\sigma_{\sum y}^2 + n^2 \sigma_b^2}{(\sum y - nb)^2} + \frac{\sigma_a^2}{a^2} - \frac{2[\text{cov}(\sum y, a) - n \text{cov}(b, a)]}{(\sum y - nb)(a)}$$

$$\sigma_X^2 = \left(\frac{\sum y - nb}{a} \right)^2 \left[\frac{\sigma_{\sum y}^2 + n^2 \sigma_b^2}{(\sum y - nb)^2} + \frac{\sigma_a^2}{a^2} \pm \frac{2n \text{cov}(a, b)}{(\sum y - nb)(a)} \right]$$

If there was one calibration curve for the waste (measured discards) and J calibration periods for the scrap the limit of error expressions would be:

$$LE(\text{waste}) = 2\sqrt{\sigma_X^2(\text{waste})}$$

$$LE(\text{scrap}) = 2\sqrt{\sum_{k=1}^J \sigma_{X_k}^2}$$

calibrations can be summed together in the normal manner since they are not related. The procedure followed in the ISE is shown at the bottom of Figure 4.

A point that should be emphasized concerns the gPu 240 equivalent of the standards. If the standards used to generate a calibration curve all came from the same isotopic and enrichment lot, the abscissa may be biased. This systematic error would not show up in the standard deviation of the intercept and slope values. It would then be necessary to account for this systematic error separately.

SUMMARY

This paper has presented the LE calculations that were involved in the Integrated Safeguards Experiment. With the neutron coincidence NDT method one had to be aware of the several covariance effects especially where the same standards were used. With the chemical assay method the problem was with the use of average values used as constants in connection with other measured values.

The intent of this paper is to provide a useful guide to persons in safeguards and accountability for use in computing limit of error values using both destructive and nondestructive techniques.