

Title:

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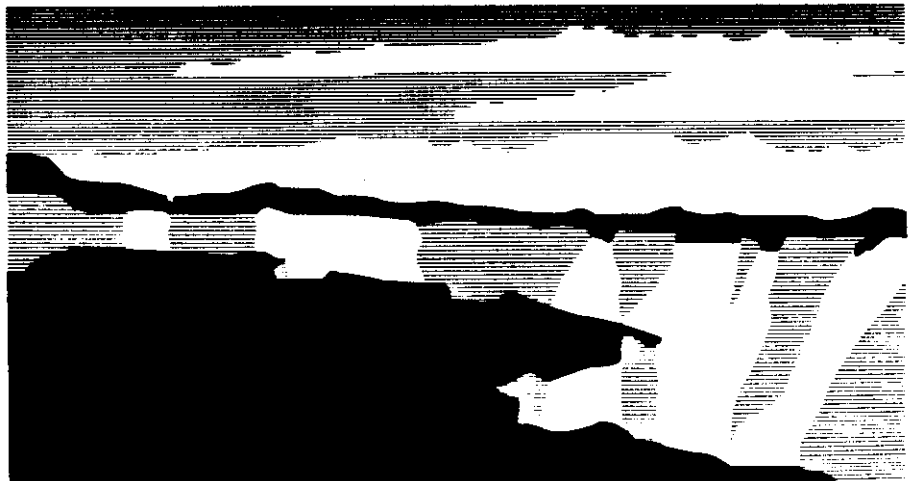
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SELECTION OF NON-DESTRUCTIVE ASSAY METHODS: NEUTRON COUNTING OR CALORIMETRIC ASSAY?

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ABSTRACT

The transition of DOE facilities from production to D&D has lead to more measurements of product, waste, scrap, and other less attractive materials. Some of these materials are difficult to analyze by either neutron counting and calorimetric assay. To determine the most efficacious analysis method, a variety of materials, impure salts and hydrofluorination residues have been assayed by both calorimetric assay and neutron counting. New data will be presented together with a review of published data. The precision and accuracy of these measurements are compared to chemistry values and are reported. The contribution of the gamma ray isotopic determination measurement to the overall error of the calorimetric assay or neutron assay is examined and discussed. Other factors affecting selection of the most appropriate non-destructive assay method are listed and considered.

INTRODUCTION

The increased emphasis on clean-up and waste recovery at DOE facilities has lead to an increased demand for assays of hard to measure materials. These items include americium extraction residues, crucible and hydrofluorination residues (metal halides and oxides). In the past, these materials have been measured by calorimetric assay, neutron coincidence counting, and neutron multiplicity counting. The measurement results obtained by different techniques for these materials have been published in different places and are frequently difficult to reconcile. In addition to the nondestructive assay data, there are a few of these materials which have been analyzed by chemical mass spectroscopy. These data can be very useful in the evaluation of the precision and accuracy of nondestructive assay methods.

RESULTS

Americium is removed from plutonium by the molten salt extraction process. This process produces residues which are inhomogeneous mixtures of alkaline earth halides, americium and plutonium halides and americium and plutonium metal. Generally, the americium is present as americium halide dissolved in the salt and the plutonium occurs as metal particles distributed throughout the salt. Plutonium concentrations average fifteen percent of the total weight of the salt. Average americium concentration is 0.5% of the total weight of the salt. The americium to plutonium ratio ranges from 0.2 to 5.0 percent. The MSE residues are formidable analysis problems for both destructive and nondestructive assay practitioners. The heterogeneous nature of the material and the difficulty of dissolution make assay by traditional chemical methods difficult. The presence of the alkaline earths and potentially high americium concentrations make measurement by traditional neutron counting methods difficult because the large numbers of (α , n) neutrons overwhelm traditional coincidence counting techniques. More advanced neutron techniques, such as multiplicity counting, are unproven. Although the heat measurement

necessary for calorimetric assay is easy, the necessary determination of the plutonium isotopic distribution by gamma ray spectroscopy is made difficult by the high ratio of americium to plutonium and the heterogeneous nature of the material. The analysis of the gamma ray spectrum is also necessary to obtain ^{240}Pu effective fraction for neutron coincidence counting.

All studies on the calorimetric assay of MSE salts have focussed on the gamma ray measurement of the plutonium isotopic distribution (used for calculation of effective specific power, P_{eff} , and ^{240}Pu effective fraction, $^{240}\text{P}_{\text{eff}}$, and the americium concentration. In two of the references, the effective specific power and ^{240}Pu effective fraction obtained by gamma ray isotopic distributions are compared with chemical assay and mass spectroscopy.^{1,2} The MSE salts measured were identical, and were very inhomogeneous and resembled rocks. The americium and plutonium concentrations spanned the range indicated above. In these studies two different and independent gamma ray codes, FRAM and GRPAUT were used to determine specific power. The results from both of these studies are consistent and are presented in Table I.

Table I. Determination of plutonium isotopic distribution and ^{240}Pu effective fraction as measured by gamma ray spectroscopy compared to chemical mass spectroscopy. The uncertainties calculated are the standard deviations of the mean ratios ($\sigma_{\text{mean}} = \sigma_{\text{single measurement}}/\sqrt{N}$, where N is the number of measurements). The percent standard deviation of a single measurement is also given.

Reference	Number of Items Measured	Ratio Gamma ray/chemistry P_{eff}	Ratio Gamma ray/chemistry $^{240}\text{P}_{\text{eff}}$
1 (GRPAUT)	10	0.970 ± 0.006 (1.72%)	0.958 ± 0.0065 (2.1%)
2 (FRAM)	5	0.975 ± 0.011 (2.54%)	

The data presented in Table I show that the specific power can be measured on an MSE salt to an accuracy of two to three percent with comparable precision. The heat output of plutonium items can therefore be measured to an accuracy and precision of a few tenths of percent.³ Thus, the dominant error component for these items is contributed by the specific power. This type of MSE residue can be measured with an accuracy and precision of about two to three percent.

Calorimetric assay, although accurate, is a very slow measurement method, a typical assay takes about four to six hours. Neutron counting techniques were investigated as a possible faster assay method. A group of inhomogeneous MSE salts were measured by calorimetric assay and neutron counting. These salts were similar to those measured in the above studies and thus it can be inferred that calorimetric assay is capable of measuring them to a precision and accuracy of two to three percent. The calorimetric assay value was used as the reference measurement for the neutron counting. The americium concentration was obtained from the gamma ray analysis used for the calorimetric assay. The results of these measurements are presented in Table II.

Table II. Neutron coincidence counting results of MSE salts.

Item	²⁴¹ Am (μg/g Pu)	Calorimetric Assay (g Pu)	Ratio: Neutron/Calor	Single Measurement Precision (% RSD)	
				P _{eff}	²⁴⁰ Pu _{eff}
XBLP268	26064	115.3	1.24	0.3	2.7
XBLP280	26578	158.6	1.21	0.2	2.0
XBLP272	30380	109.9	1.27	0.3	3.0
ARF876700	33651	221.8	1.44	0.2	2.4
XBLP265	35671	168.7	1.39	0.3	3.1
XBLP260	42876	108.4	1.41	0.3	3.0
XBLS96	66942	86.5	1.17	0.3	5.0
XBLS97	91649	42.1	1.30	0.3	5.0
XBLS95	105642	130.6	1.80	0.4	6.1

The results show that neutron coincidence counting must be used only with great caution for measurement of MSE salts. The ratio of grams of plutonium as determined by neutron counting to calorimetric assay varies from 1.17 to 1.80. The ratio does not correlate with either plutonium mass or americium concentration.

The single measurement precisions for P_{eff} and ²⁴⁰Pu_{eff} predicted by the gamma ray isotopic analysis software are also reported in Table II. These values were obtained from the gamma ray isotopic analysis software. Not enough spectra were obtained for the MSE salts to verify these values, but our experience with a wide variety of materials indicates that the precisions estimated by gamma ray isotopic codes are accurate. This is verified by the data presented in Reference 4. These precision estimates are important for evaluating the overall expected precision of both calorimetric assay and neutron coincidence counting. Specific power is combined with the heat measurement obtained by calorimetry by dividing the measured watts by P_{eff}. The ²⁴⁰Pu effective fraction is used similarly with the data from neutron counting. The precision of the calorimetric determination of heat and the precision of the neutron counting results are often the same, about 0.2% - 0.3% one standard deviation. Thus, the major component of the error for either calorimetric assay or neutron coincidence counting resides in the measurement of specific power or ²⁴⁰Pu effective fraction. For low burnup material (6% ²⁴⁰Pu), the error in specific power is about 0.3% and for ²⁴⁰Pu_{eff} the error is about 1.8%. The error in ²⁴⁰Pu_{eff} is about six times that of the error of specific power. As shown in Table II, above, the errors in ²⁴⁰Pu_{eff} range from ten to fifteen times that of P_{eff}. Therefore, the precision expected from assay by neutron coincidence counting for these materials can never be better than that expected by calorimetric assay.

The area in which the precision and accuracy of neutron counting might be expected to be better than that of calorimetry is for the assay of items which contain very little plutonium and concomitantly produce little heat. The error in the heat measurement will become the dominant source of error in the calorimetric assay. The precision and accuracy of the heat measurement made with the calorimeters used to measure these items has been shown to be about ten percent for a 27 milliwatt heat source.⁵ The MSE salts reported here have specific powers which range from 5.14 to 14.3 milliwatts/g Pu. This corresponds to a range in grams (at heat output of 27 milliwatts) of 5.25 to 1.9 grams. Thus, the lower limit of calorimetric assay for MSE salts is two to five grams, with a precision and accuracy of about ten percent. As the heat output increases the calorimeter precision and accuracy improves dramatically. At 100 milliwatts of heat, the precision and accuracy have improved to about one percent. At 500 milliwatts the heat measurement has a precision and accuracy of about 0.3%.

For small amount of plutonium oxide (~ 1g ²⁴⁰Pu effective fraction) with low (α, n) yields, measurement accuracy and precision are typically 2.0% and 2.5%, respectively. However, these values increase substantially for MSE and hydrofluorination residues with α values (the ratio of (α, n) neutrons to spontaneous fission neutrons) ranging from ten to thirty.⁶ For these materials accuracies with 20% and precisions between 4% and 10% are more typical.

Many of these MSE salts have been measured by multiplicity techniques.⁶ The results for multiplicity measurements for the ratio of calorimetric assay to neutron assay was 1.01 ± 0.048 , where the error reported is the standard deviation of the mean. The standard deviation of a single measurement is 14.8%. The multiplicity measurements are unbiased, but the lack of precision suggest that caution must be exercised before application of the technique to MSE salts.

Next, a series of sand, slag, and crucible items were measured by neutron coincidence counting and the results compared with calorimetric assay. The results of these measurements are presented in Table III.

Table III. Neutron coincidence counting results of sand, slag, and crucible items.

Item	²⁴¹ Am (μg/g Pu)	Calorimetric Assay (g Pu)	Ratio: Neutron/Calor	Single Measurement Precision (% RSD)	
				P _{eff}	²⁴⁰ Pu _{eff}
MPX2640	359	178.0	1.137	0.36	1.72
MPX2581	1099	163.0	1.131	0.48	2.38
MPX2601	272	142.2	1.172	0.57	2.63
MPX2572	443	118.3	1.121	0.37	1.75
MPX2569	678	113.6	1.083	0.38	1.82
MPX2608	441	113.2	1.121	0.40	1.98
MPX2583	976	88.04	1.109	0.42	2.06
MPX2609	527	68.16	1.111	0.42	2.09
MPX2607	677	67.75	1.206	0.43	2.10
MPX2698	1107	13.93	1.013	0.78	3.86
MPX2696	1094	12.75	1.365	0.58	2.78
MPX2697	1372	11.64	1.175	1.26	6.44

The comparison data for the sand, slag, and crucible samples yield slightly different results than the MSE salt measurements. For the samples which contain over 100 g of plutonium the ratio of the neutron measurement to the calorimetric assay is 1.128 ± 0.0118 (the error is the mean standard deviation). The consistent results for these items suggest that a bias correction could be applied to the neutron measurement. There is more scatter in the neutron to calorimetry ratio data for the samples under 100 g. However, the heat produced by these samples ranges from 31 to 213 milliwatts. The error in the heat measurement for the smallest items is about ten to twenty percent. Thus, for these samples with small amounts of plutonium the comparison is as good as can be expected from the combined calorimetric assay and neutron counting errors for low level materials.

The differences in the estimated precision of the gamma ray measurement of P_{eff} and ²⁴⁰Pu_{eff} are not as large as those observed for the MSE salts. The error in P_{eff} is about 0.3% and the error in ²⁴⁰Pu_{eff} is about 2.0%. This is consistent with data observed for plutonium oxide standards and although the differences in precision are not as great as observed for the MSE salts, the data indicate that calorimetric assay will generally be better than neutron counting.

CONCLUSIONS

Although calorimetric assay provides greater precision and accuracy than passive neutron coincidence counting for these materials, neutron measurements may be the preferred nondestructive assay technique. If reliable bias correction factors can be obtained for neutron counter measurements, then assay accuracies are comparable to those from calorimetric assay for wastes and leaner residues. In these cases, neutron coincidence assay may be preferred because of their shorter duration.

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