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Non-Destructive Assay of Curium Contaminated Transuranic Waste Drums

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ABSTRACT

At the Plutonium Facility at Los Alamos National Laboratory, a series of non-destructive assays were performed on five transuranic waste (TRU) drums containing non-plutonium scrap metal that was potentially contaminated with weapons grade plutonium and trace quantities of curium. Typically, waste drums containing metal matrices are assayed for plutonium content using passive neutron coincidence counting techniques. The presence of trace quantities of Cm-244 prevents this type of analysis because of the strong coincidence signal created by spontaneous fission of Cm-244. To discriminate between the plutonium and curium materials present, an active neutron measurement technique was used. A Cf shuffler designed for measurement of uranium bearing materials was calibrated for plutonium in the active mode. The waste drums were then assayed for plutonium content in the shuffler using the active-mode calibration. The curium contamination levels were estimated from the difference between the active-mode measurement in the shuffler and a passive assay in a neutron coincidence counter. Far field gamma-ray measurements were made to identify additional radioactive contaminants and to corroborate the plutonium measurement results obtained from the active-mode assay. This report describes in detail the measurement process used for characterization of these waste drums. The measurement results and the estimated uncertainty will be presented.

INTRODUCTION

The Plutonium Facility at Los Alamos National Laboratory is a U.S. national defense facility that is involved in the recovery and processing of plutonium and other transuranic elements. Potentially contaminated wastes are routinely generated from many stages in the processing cycle as well as the decommissioning and decontamination of outdated equipment in the facility. Waste that is generated in the glovebox line is designated as transuranic waste (TRU) and must contain greater than 100 nCi/g. Items from this waste stream are typically packaged in 55 gal. drums that are destined for eventual emplacement in the Waste Isolation Pilot Plant waste disposal facility. Waste that is generated in Plutonium Facility laboratory rooms and support areas is considered low-level waste (LLW). This waste must contain less than 100 nCi/g.

Both waste streams must be nondestructively assayed to quantify the radioactive content of the waste both for accountability purposes and to verify that the waste is classified correctly as TRU or LLW. Low bulk-density TRU and LLW waste items such as paper, plastics, ash are assayed by gamma-ray analytical methods. More dense materials, such as non-actinide scrap metal and leaded gloves, are not amenable to assay by gamma-ray techniques due to the high attenuation of the emitted gamma rays. Measurement of items with dense matrices by gamma-ray techniques can lead to large uncertainties in the measurement results and inadequate detection sensitivities. Instead, these items are assayed by neutron measurement techniques. For high-density plutonium bearing waste drums, passive neutron coincidence counting is used. This technique measures the neutron emission rate from the spontaneous fission of even isotopes of plutonium: ^{238}Pu , ^{240}Pu and ^{242}Pu . The coincidence rate is then related to the quantity of plutonium present in the drum. The NDA Laboratory recently acquired a ^{252}Cf shuffler for active neutron measurement of high-density uranium contaminated waste drums.

One potential pitfall in the measurement of high-density plutonium waste is contamination of the waste from other radioactive isotopes that undergo spontaneous fission. One of these isotopes that has been used in various research activities at the Plutonium Facility is ^{244}Cm . Standard passive coincidence counting techniques can not discriminate between the neutrons from Pu and Cm. The spontaneous fission rate from ^{244}Cm is significantly greater than that from the even isotopes of plutonium. The spontaneous fission neutron production yields for the even plutonium isotopes and ^{244}Cm are shown in Table I.(ref) A small quantity of ^{244}Cm can greatly perturb the plutonium assay results. For example, the neutron emission rate of 1 mg of ^{244}Cm is equivalent to that of approximately 170 grams of weapons grade plutonium.

Table I. Spontaneous Fission Neutron Production Rates for Plutonium and Curium-244

Isotope	Half Life	Neutron Yield (n/s-g)	Multiplicity
Pu-238	87.74 y	2.59×10^3	2.21
Pu-240	6.56×10^3 y	1.02×10^3	2.16
Pu-242	3.76×10^5 y	1.72×10^3	2.15
Cm-244	18.1 y	1.08×10^7	2.72

EXPERIMENTAL

Five 55-gal. TRU waste drums containing potentially contaminated, high-density, non-actinide scrap metal were evaluated by non-destructive analysis at the Plutonium Facility NDA Laboratory. The drums were first assayed in a passive neutron coincidence counter according to standard assay practices for high-density waste matrices. After the passive neutron coincidence counting results were evaluated it was suspected that the drums were also contaminated with trace quantities of ^{244}Cm . The drums were then assayed in the active mode in a ^{252}Cf shuffler designed for analysis of uranium. A qualitative confirmation of the active assay results on the waste drums was performed by gamma-ray analysis.

Two ^{244}Cm samples were obtained to verify that active analysis of plutonium in the ^{252}Cf shuffler could be performed in the presence of ^{244}Cm contamination. The Cm items were assayed by calorimetry to determine the quantity of Cm present in each item at the time of these experiments. The two Cm samples were also assayed by passive neutron coincidence counting and by active neutron analysis in the ^{252}Cf shuffler.

RESULTS AND DISCUSSION

The initial measurements on the five waste drums were performed in a passive neutron coincidence counter designed to assay 55-gal. drums containing plutonium contaminated materials.(ref) This instrument measures the neutron coincidence signature from spontaneous fission of the even plutonium isotopes. This coincidence count rate is then converted to total plutonium content using both a calibration curve based on plutonium standards and the plutonium isotopic ratios which are derived from measurement by gamma-ray spectroscopy or estimated from process knowledge. The results from the passive neutron assays are shown in Table II.

Table II. Passive Neutron Coincidence Results

Drum ID	Coincidence Rate (reals/sec)	Apparent Pu Content (g)
54375	97.41 +/- 0.91	87.46 +/- 0.81
54376	215.18 +/- 1.40	170.44 +/- 1.11
54981	29.10 +/- 0.47	28.08 +/- 0.45
54982	51.56 +/- 0.96	48.916 +/- 0.91
54997	197.22 +/- 1.35	158.89 +/- 1.09

The initial measurement results from the passive coincidence counter showed anomalously high results in the total plutonium content. There are two potential methods at this facility where measurement discrepancies will be discovered. The first is the knowledge of process from the operator that generated the waste. The waste generator estimates the plutonium content of each waste item delivered to the NDA Laboratory for plutonium assay and eventual disposal. This estimate is typically based on historical process performance or by inventory difference. The second method involves the near real time accounting system at the facility. The flow of nuclear material through the various processing areas of the facility is carefully monitored from the initial introduction of material to the production of product materials and associated waste by products. Any statistically significant discrepancies in the material balance are flagged and investigated.

Based on investigation of the processing history of the glovebox where this waste was generated, it was suspected that the high plutonium measurement results could be caused by contamination of trace quantities of ^{244}Cm . One method that is commonly used to resolve a discrepancy of this type is to perform a measurement using a segmented gamma scanner that can assay for plutonium. A gamma-ray assay of this type is specific to gamma rays from the isotope of interest and would not be effected by any curium that was present. Even on waste drums containing high-density matrices which would not normally be amenable to gamma-ray assay, this is often the best way to quickly resolve the issue. Unfortunately, the gross weight of four of the five waste drums in this evaluation significantly exceeded the weight limit for the drum-sized SGS available in the NDA Laboratory.

Another technique that has been demonstrated for discrimination between plutonium and curium neutrons is the use of multiplicity counting.(ref) As shown in the final column of Table I, the first moment of the neutron multiplicity distribution is significantly different for curium compared to the plutonium isotopes. Neutron multiplicity counting has been used to measure the $^{240}\text{Pu}/^{244}\text{Cm}$ ratio by looking at ratios of the higher order moments of the multiplicity distribution. This technique requires a well-characterized, high-efficiency neutron multiplicity counter. The NDA Laboratory does not a suitable instrument available that will accommodate 55-gal. drums.

Another approach was taken for the analysis of these waste drums. A combination of active and passive neutron assay techniques can be used to discriminate between the two materials. The NDA Laboratory recently purchased a ^{252}Cf shuffler for measurement of ^{235}U bearing materials.(ref) Since uranium does not have a significant spontaneous fission neutron yield, it is necessary to use active neutron assay techniques to quantify uranium. The ^{252}Cf shuffler operates by using an intense isotopic ^{252}Cf source to activate some of the fissile material in the waste drum. The source is then withdrawn to a shielded storage location and the delayed neutrons from the induced fissions are measured. This process is repeated many times as the neutron source is "shuffled" between the assay chamber and the storage location. The delayed neutron count rate is proportional to the quantity of uranium in the waste drum. The active shuffler-type measurement techniques are not typically used for measurement of plutonium. Passive neutron coincidence counting generally has a higher sensitivity and better precision for plutonium materials. However, the ^{252}Cf shuffler will also induce fissions in the fissile ^{239}Pu component in weapons grade plutonium. The delayed neutrons are detected and again an appropriate calibration can then be used to relate the delayed neutron yield to the quantity of ^{239}Pu present. The induced fission cross-sections for ^{244}Cm are significantly smaller than the induced fission cross-sections for ^{239}Pu , the main isotope in weapons grade plutonium. Since the interrogating neutrons have a relatively low probability of inducing fissions in ^{244}Cm , the ^{244}Cm contamination will be transparent to the active neutron measurement technique. This technique can be used to quantify the plutonium in the presence of curium contamination. This combination of active and passive measurement techniques is used in Europe for the measurement of wastes generated in spent fuel reprocessing facilities.(ref)

The first step required was to generate an active calibration curve for weapons grade plutonium. A set of small can standards ranging from 10 to 240 g total plutonium was used for this purpose. The calibration curve is shown in Figure 1. The delayed neutron yield, in counts/sec, is related to the quantity of fissile mass, primarily ^{239}Pu , in the standards. The observed relationship is not linear. There are contributing factors from self-shielding and multiplication that complicate the shape of the curve. However, there is a clearly one-to-one correspondence between the observed delayed neutron yield and the fissile mass. The

response is, however, nearly linear in the lower mass range (< 50 g), where plutonium content of most waste drums would be expected. For this data set, the total count time per measurement was approximately 25 minutes. The first five minutes of each assay is devoted to a background measurement. The remainder of the assay time is divided between neutron activation time, source movement, and the actual measurement of the delayed neutron yield following each source shuffle. The one-sigma relative standard deviation of the 10 g standard was 41 % over a set of 10 measurements. For a comparable assay time in the passive neutron coincidence counter, the measurement results would have a relative standard error of a few percent for this same 10 g standard. One reason for the increased uncertainty in the active measurement of plutonium is the large neutron background created by the plutonium. The delayed neutron yield must be measured on top of the relatively large spontaneous fission and (α, n) neutron yield from the plutonium. By comparison, there is very little additional background introduced from uranium samples, making active assay of uranium an easier task.

Table III. Active Neutron Assay Results from the ^{252}Cf Shuffler

Drum ID	Number of Runs	Active Result (g)	Peak Area (413.7 keV)
54375	10	23.10 +/- 2.38	57493
54376	13	2.74 +/- 1.62	14220
54981	10	4.15 +/- 1.01	12718
54982	5	43.69 +/- 3.77	239996
54997	5	20.34 +/- 1.36	34993

The five TRU waste drums were assayed in the shuffler using the same measurement parameters. The shuffler measurement results for the five drums are shown in Table III. Each drum was assayed from 5 to 13 times. The result shown is the average from the repeat measurements performed for that drum. The error quoted for each drum is the standard deviation of the mean. To try to qualitatively confirm the measurement results from the shuffler, a 10 hr gamma-ray spectrum was taken on each drum using a high-resolution Ge detector. The area of the 413.7 keV ^{239}Pu peak is shown for each drum in the final column of Table III. No attempt was made to correct this data for matrix attenuation. However, the count rates clearly show a rough correlation with the total plutonium as measured by the shuffler.

One of the drums, 54982, showed an active measurement result of 43.69 +/- 3.77 g total plutonium. The result from the passive neutron coincidence count on this drum was 48.916 +/- 0.91. The shuffler result is statistically indistinguishable from the passive assay at the 95% confidence level. For this drum, the curium content was assumed to be zero and the passive neutron measurement result was used to derive the plutonium accountability value since this is the superior measurement technique for plutonium assay.

To demonstrate that the active measurement technique is not effected by the curium contamination, two curium samples were located to test the active measurement. The curium content in the items was derived from calorimetry measurements. Curium has a very high specific heat, producing 2.83 watts per gram ^{244}Cm , allowing very small quantities of ^{244}Cm to be detected by calorimetric assay. The calorimetry results for the two items were 90 mWatts and 125 mWatts, corresponding to 31.8 and 44.2 mg ^{244}Cm respectively.

The same items were assayed in the passive neutron coincidence counter as plutonium items with weapons grade isotopic composition. The results were 1.45 and 1.73 kg total plutonium equivalent for the two items. The passive neutron results from the two curium test samples were used to calibrate the passive neutron counter for curium. The curium content in the waste drums could then be estimated after the signal from the plutonium was subtracted from the coincidence rate. The plutonium content derived from the shuffler assay was combined with the passive plutonium calibration curve to estimate the plutonium coincidence signal. The remaining coincidence signature was assumed to be from ^{244}Cm . The range of curium contamination for the four drums that contained curium was from 0.15 mg to 1.28 mg ^{244}Cm .

The curium test samples were assayed in the shuffler in the active mode as plutonium unknowns. The results for the two samples were 0.52 ± 7.0 and 8.71 ± 23.5 g equivalent total plutonium. The samples were counted seven and five times respectively to obtain these composite results. The uncertainty on the measurement is quite large because of the very high neutron background created by the significant quantities of ^{244}Cm . However, the results are significant in that they show that even for quantities of ^{244}Cm equivalent to kg quantities of plutonium, the active neutron measurement can effectively discriminate between plutonium and curium. The results of the test samples are statistically indistinguishable from zero in both cases.

Identification of curium by gamma-ray assay is difficult at the contamination levels sufficient to perturb passive neutron assay, i.e. mg quantities of ^{244}Cm . However, it can be detected and used as supporting evidence in some cases. Gamma-ray spectra were taken on the curium test items and on the waste drums. The spectra from one of the curium items and the waste drum containing the largest quantity of ^{244}Cm contamination are shown in Figure 2. The curium sample was counted for 30 minutes while the spectra on the waste drum was collected for 10 hours. The spectra have been arbitrarily normalized for presentation purposes. The gamma-ray lines that are most useful for detection of ^{244}Cm are identified in the figure. Even these gamma rays are subject to possible interference from other radioactive contaminants and care must be taken to rule out the presence of these other isotopes. Of the four waste drums containing ^{244}Cm contamination, only two had curium levels that were positively identifiable by gamma-ray analysis after a 10 hr measurement.

As previously mentioned, the measurement of plutonium by active neutron analysis is complicated by the passive neutron emission from the plutonium. The measurement is made even more difficult by the presence of Cm contamination, which also contributes to the neutron background. A theoretical study was performed to illustrate the effects on the assay precision and detection limits. For this study, conditions were chosen that were similar to those under which the waste drums were assayed. No attempt was made to estimate the overall error from other sources such as count time, Cf source strength, or matrix effects. The assay precision as a function of plutonium content for several levels of ^{244}Cm contamination is shown in Figure 3. The driving factor in the change in the estimated precision is the neutron background. The background has contributions from several sources. The first is the room background, which is essentially constant. Next is the neutron signal from the plutonium which has two sources, spontaneous fission and (α, n) neutrons, both increase with plutonium content. The third contribution to the background in this model is the spontaneous fission of the ^{244}Cm contamination, which increases with increasing Cm content. Finally, the estimated minimum detectable quantity of plutonium is shown as a function of the ^{244}Cm content in Figure 4. Here, the definition of the detectable quantity is assumed to be the quantity for which the relative assay precision is 33%, which is a generally accepted definition for detection limits in the non-destructive assay community.

CONCLUSIONS

Very small quantities of curium can produce a relatively large neutron coincidence signature, which if not interpreted correctly could be identified as plutonium. An active neutron technique using a ^{252}Cf shuffler designed for uranium assay was used for analysis of plutonium in the presence of curium contamination. This technique was applied to five high-density transuranic waste drums. Of the five drums, four were found to contain significant quantities of ^{244}Cm , where significant means sufficient to measurably perturb a passive coincidence neutron measurement. The technique can be used to derive plutonium accountability values under circumstances where there was previously no other assay technique available. The assay precision and detection limits are significantly effected by the curium contamination. Contamination of ^{244}Cm at the 10 mg level will increase the plutonium detection limit by nearly an order of magnitude.

REFERENCES

Fig. 1

Shuffler - Active Assay of Pu-239

Fig. 2

Fig. 3

Fig. 4