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COMPARISON OF DESTRUCTIVE AND NONDESTRUCTIVE ASSAY OF HETEROGENEOUS SALT RESIDUES

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ABSTRACT

To study problems associated with nondestructive assay (NDA) measurements of molten salt residues, a joint study was conducted by the Rocky Flats Plant, Golden, CO and Mound Laboratories, Miamisburg, OH. Extensive NDA measurements were made on nine containers of molten salt residues by both Rocky Flats and Mound followed by dissolution and solution quantification at Rocky Flats. Results of this study verify that plutonium and americium can be measured in such salt residues by a new gamma-ray spectral analysis technique coupled with calorimetry. Biases with respect to the segmented gamma-scan technique were noted.

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John G. Fleissner and Merril W. Hume

INTRODUCTION

The conversion of americium-bearing plutonium metal to high-purity plutonium metal is accomplished at Rocky Flats by the molten salt extraction process in Pyrochemical Operations. This process produces a molten salt residue containing plutonium and americium interdispersed in chloride salts of magnesium, potassium, and calcium. Some of the plutonium exists as metal fines. Material accountancy measurements for these salt residues at Rocky Flats are by a segmented gamma-scan technique.

Synthetic standards were constructed using plutonium oxide to calibrate the segmented gamma-scan systems for their plutonium and americium response. These synthetic standards consisted of an RTV matrix with 100 to 300 g of plutonium and 10 to 30 g of americium. The segmented gamma-scan technique, however, is susceptible to measurement errors due to sample non-homogeneity and self absorption effects caused by the finite-sized plutonium metal fines. Because of these inherent measurement problems (heterogeneity, particle size), an assessment of the gamma-scan measurement technique for molten salts using the synthetic standard calibration was deemed desirable.

A calorimetric assay measurement, which provides a total assay value for the plutonium and americium, was chosen as an NDA comparison (referee) technique. However, reliable results by this technique depend on an accurate determination of the americium-to-plutonium ratio, since these salts contain high levels of americium, which is a primary heat producer. The relative amount of heat produced by the americium in these samples is typically 50% or more. These measurement concerns for both the segmented gamma-scan and the calorimetric assay technique prompted this study to assess NDA measurement capability for molten salt residues.

MEASUREMENTS

For the purpose of this joint study, nine containers of molten salt residues, which contained a wide range of both plutonium and americium, were selected from the inventory at Rocky Flats. Multiple measurements of each container were made at Rocky Flats using the segmented gamma-scan technique (referred to hereafter as Can Scan). The containers were shipped to Mound where gamma-ray isotopic spectral analysis and calorimetric heat measurements were performed. The salts were then returned to Rocky Flats for dissolution and solution quantification. The measurement results for grams of plutonium and americium for each container are presented in Table 1. Both the Mound and Dissolution results shown are decay corrected to June 1, 1984.

Can Scan

The Can Scan technique for measuring molten salt residues is presented in Reference 1. The results presented in Table 1 are averages of five measurements on each residue. These measurements were made in the late summer of 1982. It is clear from the results of this study, as well as others, that this measurement technique is biased for both plutonium and americium.[2,3] Bias corrections have been incorporated into Can Scan measurements as a result of these studies. However, the justification for applying an overall bias correction to Can Scan based on the limited results of this study is somewhat questionable, and it is based on the assumption that the average plutonium particle size remains constant and does not vary from sample to sample or with time. This assumption would be difficult to verify for actual production salt residues.

TABLE 1. Molten Salt Results in Grams

Container Number	Can Scan	Mound	Dissolution	Ratios to Dissolution: Can Scan/ Dissolution	Ratios to Dissolution: Mound/ Dissolution
Plutonium					
1	194	212	214	0.907	0.991
2	225	258	253	0.889	1.019
3	300	334	326	0.920	1.024
4	242	250	251	0.964	0.996
5	280	296	291	0.962	1.017
6	340	377	377	0.902	1.000
7	392	421	414	0.947	1.016
8	379	439	423	0.896	1.037
9	365	394	380	0.961	1.036
			Mean:	0.928	1.015
			Standard Deviation:	0.031	0.017
Americium					
1	4.4	5.4	5.4	0.815	1.000
2	3.9	4.8	4.8	0.813	1.000
3	21.0	24.1	23.8	0.871	1.013
4	13.8	16.3	16.1	0.857	1.012
5	6.3	7.3	7.5	0.840	0.973
6	20.9	23.9	23.5	0.889	1.017
7	24.8	27.1	26.3	0.943	1.030
8	14.0	16.2	16.3	0.859	0.994
9	8.5	9.6	9.8	0.867	0.980
			Mean:	0.862	1.002
			Standard Deviation:	0.040	0.018

Mound

Gamma-ray spectral isotopic analysis coupled with calorimetry was performed at Mound on each can of salt. The purpose was to demonstrate new hardware and software techniques developed at Mound for the measurement of plutonium and americium in heterogeneous salt residues. Reference 2 presents complete details of the Mound effort.

Results of the Mound measurements are summarized in Table 1 in grams per container for both plutonium and americium. The relative standard deviations range from 0.32 to 0.50% for plutonium values and 0.23 to 0.39% for americium values.

These measurement uncertainties vary from container to container and were determined by propagating the uncertainties due to counting statistics and the thermal power measurement. The gram values were calculated using isotopic stream averages for the plutonium isotopes 238, 240, and 242. These stream values supplied by Rocky Flats were 109, 61775, and 322 ppm, respectively, relative to plutonium-239. Stream averages were used for these isotopes since the critical measurement is the americium-to-plutonium ratio, because of the high heat content of the americium.

The measured plutonium and americium-241 results are given in Table 2. The relative standard

TABLE 2. Isotopic Results - Relative to Plutonium-239

Container Number	Pu-241/Pu-239 Mound (ppm)	Pu-241/Pu-239 Dissolution (ppm)	Am-241/Pu-239 Mound (ppm)	Am-241/Pu-239 Dissolution (ppm)
1	2344	2431	27192	26855
2	2408	2613	19706	20235
3	2059	2123	76190	77703
4	2450	3004	69006	68224
5	3001	2932	26047	27419
6	1752	1901	66797	66244
7	2048	2039	67976	67593
8	2916	2989	38913	41104
9	2313	2279	25734	27448

deviations range from 0.46 to 1.72% for plutonium and 0.46 to 0.63% for americium; the deviations were propagated from the counting statistics of the gamma-ray measurement.

Dissolution and Solution Quantification

Dissolution and solution quantification for plutonium and americium content of the nine molten salt residues was performed at Rocky Flats. This work commenced in late summer 1983 and was completed in early summer 1984. Dissolution of the salts, standards preparation for quality control, and blind submission of all samples for analysis by the Analytical Laboratories were performed by the Chemistry Standards Laboratory.

The integrity of each of the nine salts was maintained throughout the dissolution and solution quantification process. Each salt was treated similarly with occasional slight variations to the following process.

Grinding was accomplished by transferring a salt to a grinding can with two or three 1.25-inch steel balls and placing the can in a paint shaker for about 45 minutes. Each pulverized salt was treated as a unit or split into two or three batches; each batch was dissolved in three liters of 2*N* HCL, then diluted to four liters. Multiple (at least five) 5-mℓ samples were taken from each four-liter batch and submitted for analysis along with three or four special liquid standards. These standards were prepared to approximate the unknown samples. The set of samples and standards were submitted blindly as a group for analysis.

Quantitative plutonium and americium analyses were performed on each sample and standard. Plutonium was measured by x-ray fluorescence using yttrium as an internal standard. Americium was determined by gamma counting volume dilutions of the liquid samples using a sodium iodide detector in conjunction with known standards. Heel samples from each batch were individually pyrosulfate-fused, dissolved, and treated as above.

All these analyses were performed by a single technician in the Building 371 Analytical Laboratory. Results from the standards submitted with a batch were used for bias corrections for that batch when appropriate. Final dissolution gram values for each container are presented in Table 1. The relative standard deviations of these results are 1 to 2% for plutonium and half that for americium.

The plutonium-241 values reported in Table 2 by dissolution are averages of three or four analyses. These analyses were performed using plutonium separation by ion exchange coupled with mass spectrometry. The relative standard deviations of these results ranged from less than 1% to nearly 17%. Details of these analyses are given in Reference 3. The americium-241 values by dissolution reported in Table 2 were not measured directly, but were based on the gram values in Table 1 and weight percent plutonium-239 as reported in Reference 3. The relative standard deviation for these results is approximately 4%.

Isotopic values for plutonium-240 and plutonium-242 were determined as the plutonium-241 discussed above. These results are reported in Table 3 along with plutonium-238 values obtained by alpha spectroscopy. The uncertainty associated with plutonium-242 is similar to that of plutonium-241. The plutonium-240 and plutonium-238 have relative standard deviations of less than 1%.

TABLE 3. Isotopic Results - Relative to Plutonium-239

Container Number	Pu-238/Pu-239 (ppm)	Pu-240/Pu-239 (ppm)	Pu-242/Pu-239 (ppm)
1	100	61466	255
2	112	63632	257
3	97	61872	224
4	94	60207	256
5	91	60541	246
6	91	60450	200
7	96	61624	220
8	117	63257	315
9	94	61582	249
Mean:	99	61626	247
Standard Deviation:	9	1191	32
Stream Values used by Mound	109	61775	322

CONCLUSIONS

The primary objective of this study was to verify that a molten salt process residue could be certified as to total plutonium and americium content by a gamma-ray spectral analysis technique coupled with calorimetry. A comparison of the Mound and Dissolution values of Table 1 establishes this capability. No biases or statistical differences between pairs of measurements are noted. The bias and inherent measurement problems associated with Can Scan have been previously mentioned.

A comparison of isotopic values in Table 2 shows quite favorable agreement for dissolution and the gamma-ray isotopic values. No biases or statistical differences between pairs of measurements are noted. The obvious bias of plutonium-242 noted in Table 3 is inconsequential to total plutonium or americium.

REFERENCES

1. F. X. Haas et al., "Measurement of Plutonium and Americium in Molten Salt Residues," *Proceedings American Nuclear Society Topical Conference on Measurement Technology for Safeguards and Materials Control, Kiawah Island, SC, November 26-29, 1979,* NBS Special Publication 582, 1980.

2. J. G. Fleissner, "Nondestructive Assay of Plutonium in Isotopically Heterogeneous Salt Residues," ANS-INMM Safeguards Technology Conference, Hilton Head, SC, November 28, 1983, MLM-3124 (OP), Mound Laboratories, Miamisburg, OH.

3. M. Bergeron, Rockwell International, Rocky Flats Plant, Golden, CO, Private Communication, July 31, 1984.