MASTER

AN ANALYTICAL INVESTIGATION OF PLUTONIUM OXIDE

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An Analytical Investigation of Plutonium Oxide

Franklin L. Oetting and Yvonne M. Ferris

Abstract. An analysis of plutonium in 36 samples of scrap plutonium oxide, each weighing approximately one kilogram, has been performed. Each sample was investigated by four separate analyses. Wet chemical analyses were performed on three of the samples taken from different locations within the container of plutonium material. The fourth analysis was a calorimetric technique which non-destructively analyzed the complete contents of the container. The results of all analyses are compared.

INTRODUCTION

A problem associated with the transfer of plutonium materials is the accountability of the exact amount of plutonium in the material being transferred. The plutonium may be in the form of metal, oxide, or scrap; the latter being a mixture of metal and oxide. The standard practice has been to chemically analyze a composite taken from a number of 1-kilogram batches of the material, and use this analytical result to establish the amount of plutonium being transferred. The transferred plutonium is primarily scrap material which implies some degree of heterogeneity. Therefore there is no assurance that the composite sample, and the chemical analysis of it, is a representation of the entire material. If there is a considerable amount of heterogeneous material there could be a large error in the recorded amount of plutonium being transferred.

Recently, a new method for plutonium analysis by calorimetry has been developed.¹ This calorimetric method is unique because it non-destructively analyzes the complete contents of the container of material. The result, therefore, is an analysis for plutonium in the total material to be transferred. The calorimetric analyses are compared with the result obtained by routine analytical procedures.

SUMMARY AND CONCLUSIONS

Thirty-six small containers of plutonium material were analyzed for plutonium by both calorimetry and

wet chemical procedures. Samples for chemical analysis were taken from material in 3 different sections of the container, whereby the entire container of material was submitted for the non-destructive calorimetry analysis. The results from the three chemical analyses and the calorimetric analysis were statistically evaluated.

The evaluation disclosed that the plutonium material was heterogeneous. This indicated a degree of uncertainty in the plutonium content results, which were derived from the wet chemical analysis owing to sampling techniques. Since calorimetry is not susceptible to sampling difficulties, this method is considered accurate for analysis of scrap plutonium. It was also shown that given a homogeneous material, the plutonium analytical results obtained by calorimetry and chemical means are not significantly different.

EXPERIMENTAL

To compare the calorimeter results with those obtained from the chemical analysis, a complete investigation was made on 18 containers of impure plutonium oxide, each weighing approximately 2 kilograms. This material had accumulated during a period of one month and was scheduled to be transferred for reprocessing.

The 18 containers, called large containers, were subdivided into two parts each, hereafter called small containers. A scoop of material was taken off the top of each small container and submitted to the analytical laboratory for determination of plutonium content by a volumetric ceric sulfate titration method. The analytical result on the scoop of material taken off the top of the container is called the foundry analysis.

Two core-samples were also obtained from each small container. The first core-sample was taken from near an edge at the top of the container. The second core-sample was taken near an edge opposite to the first, but from the bottom of the container. Samples submitted to the analytical laboratory (the foundry sample and the two core-samples)

¹F. L. Oetting, *J. Inorg. Nucl. Chem.* 27, 2151 (1965).

were each divided into two portions. The analytical results are given in Table I.

The small containers were then analyzed for plutonium by calorimetry. This was accomplished by measuring the power emission from each container. The emitted power is related to the plutonium content by the isotopic composition.¹ Accordingly, an isotopic analysis was made on each foundry sample from the 36 small containers. Details of the calculation relating emitted power and isotopic composition are found elsewhere.^{1,2} The plutonium content of the 36 containers as determined by calorimetry is shown in Table I.

¹F. L. Oetting, *J. Inorg. Nucl. Chem.* 27, 2151 (1965).

²F. L. Oetting, R. G. White, Unpublished report. The Dow Chemical Company, Rocky Flats Division, Golden, Colorado.

In addition to this sampling procedure, plutonium analysis was also made on a composite sample by the analytical laboratory. This sample consisted of a small portion of material taken from the top of each container after which all 36 portions were thoroughly mixed. Since the composite sample is a routine sampling procedure, the plutonium analysis on this sample indicated the amount of plutonium that was shipped during that month in a routine operation. The plutonium analysis on the composite sample was also compared to the mean of the analytical results from the foundry and core samples.

It is possible to derive a calorimetric composite result for the plutonium content of the 36 containers. To accomplish this derivation, it is necessary to know the total power being emitted

Table I. Individual results on foundry scoop-samples, laboratory core-samples, and the calorimeter.

Container Number	Plutonium Concentration (g/g)						Calorimeter
	Foundry Scoop Samples	Laboratory Core Samples					
		Top		Bottom			
1A	0.8647	0.8649	0.8773	0.8751	0.8619	0.8629	0.85935
B	0.8635	0.8590	0.8686	0.8626	0.0469	0.8502	0.85278
2A	0.8671	0.8671	0.8495	0.8509	0.8554	0.8508	0.85974
B	0.8567	0.8536	0.8636	0.8528	0.8634	0.8678	0.85829
3A	0.8437	0.8421	0.8785	0.8725	0.8798	0.8764	0.85942
B	0.8458	0.8441	0.8658	0.8640	0.8668	0.8638	0.84206
4A	0.8687	0.8700	0.8536	0.8575	0.8497	0.8508	0.84783
B	0.8710	0.8773	0.8222	0.8280	0.8280	0.8259	0.87301
5A	0.8745	0.8730	0.8544	0.8544	0.8551	0.8549	0.86154
B	0.8776	0.8696	0.0556	0.8363	0.8648	0.8618	0.87546
6A	0.8767	0.8742	0.8479	0.8400	0.8373	0.8339	0.86765
B	0.8704	0.8667	0.8385	0.8465	0.8384	0.8362	0.86950
7A	0.8716	0.8672	0.8376	0.8343	0.8368	0.8437	0.86907
B	0.8696	0.8709	0.8499	0.8491	0.8373	0.8408	0.87133
8A	0.8299	0.8340	0.8612	0.8627	0.8572	0.8544	0.87663
B	0.8645	0.8646	0.8565	0.8566	0.8409	0.8420	0.87760
9A	0.8656	0.8580	0.8618	0.8621	0.8416	0.8450	0.86455
B	0.8658	0.8665	0.8582	0.8610	0.8595	0.8549	0.87297
10A	0.8679	0.8694	0.8419	0.8454	0.8455	0.8427	0.87636
B	0.8710	0.8693	0.8470	0.8465	0.8446	0.8446	0.88687
11A	0.8586	0.8700	0.8624	0.8665	0.8599	0.8635	0.86766
B	0.8560	0.8573	0.8737	0.8690	0.8708	0.8728	0.86325
12A	0.8685	0.8676	0.8418	0.8421	0.8424	0.8466	0.88223
B	0.8588	0.8682	0.8404	0.8398	0.8426	0.8449	0.89068
13A	0.8716	0.8770	0.8591	0.8623	0.8611	0.8606	0.88173
B	0.8775	0.8710	0.8558	0.8552	0.8689	0.8651	0.87455
14A	0.8485	0.8499	0.8576	0.8559	0.8542	0.8556	0.88647
B	0.8542	0.8425	0.8450	0.8441	0.8321	0.8404	0.88453
15A	0.8317	0.8418	0.8311	0.8348	0.8169	0.8354	0.88159
B	0.8346	0.8519	0.8193	0.8167	0.8193	0.8234	0.88219
16A	0.8776	0.8697	0.8624	0.8646	0.8613	0.8578	0.88116
B	0.8815	0.8756	0.8559	0.8570	0.8518	0.8569	0.88011
17A	0.7824	0.7845	0.8644	0.8625	0.8633	0.8622	0.88075
B	0.8408	0.8425	0.8643	0.8628	0.8605	0.8595	0.88183
18A	0.7647	0.7723	0.8614	0.8630	0.8552	0.8534	0.87884
B	0.8137	0.8159	0.8515	0.8548	0.8320	0.8371	0.82961

from the 36 containers and the isotopic composition of the material. The total power being emitted from the 36 containers is simply the summation of the individual powers which had been determined for each container. The isotopic composition was taken from the composite sample described earlier. The calorimetric composite differs from the mean of the calorimeter results in that the calorimetric results rely upon isotopic analysis from each container, whereas the calorimeter composite result relies on an "average" isotopic analysis, i.e., that taken from the composite sample.

RESULTS AND DISCUSSION

To comprehensively evaluate the data presented in Table I, a statistical analysis was made. The results are given in Tables II, III, and IV.

Table II. Statistical results on the foundry samples (chemical analysis).

Source of Variation	Standard Deviation (g/g)
Between Means of Large Containers	0.00204
Between Means of Small Containers	0.01362
Analytical	0.00419
Total Variation of Individual Results	0.02488
Total Variation of Mean of All Results	0.00534
Mean = 0.85592 g/g	

Table III. Statistical results on core samples (chemical analysis).

Source of Variation	Standard Deviation (g/g)
Between Means of Large Containers	0.01052
Between Means of Small Containers	0.00724
Between Sampling Location in Small Container	0.00390
Interaction between Sampling Location and Small Container	0.00334
Analytical	0.00298
Total Variation of Individuals Results	0.01408
Total Variation of Mean of All Results	0.00287
Mean = 0.85213 g/g	

Table IV. Statistical results on the calorimeter.

Source of Variation	Standard Deviation (g/g)
Between Means of Large Containers	0.00860
Between Means of Small Containers	0.01046
Total Variation of Individual Results	0.01354
Total Variation of Mean of All Results	0.00267
Mean = 0.87081 g/g	

A comparison of the mean of the three methods of determining the plutonium content of the impure oxide shows that the calorimeter results are significantly higher than those obtained by volumetric methods used on the foundry samples or the core samples. The mean of the foundry samples is 0.85592 g/g. The mean of the core samples (both top and bottom) is 0.85213 g/g. The mean of the calorimeter results is 0.87081 g/g.

The significant difference in the means of these results suggests that either the chemical or calorimetric method or both of these methods of analysis may be in error. The first impression is that there may be a significant difference in the analysis for plutonium between the two methods. This does not appear to be the case (see Appendix).

Heterogeneity of the material under investigation and thus sampling techniques may be the reason for the significant difference in means of the analytical results. A thorough comparison of the analytical results indicates that the difference in means is caused by heterogeneity of the material.

The analytical error of the samples obtained from the foundry is 0.00419 g/g. The analytical error of the core samples is 0.00298 g/g. There is a significant difference between these two results. A significant difference between these two results would not be expected if the material was homogeneous.

There is a lack of consistency in the amount of variability in the method for analysis. For example, the variability between large containers is considerably less for the foundry samples than the other samples yet the variability between the small containers is less for the core samples than the other two systems of analyses. This can be explained by improper sampling, such as heterogeneity of the material.

The results on the core samples between sampling locations in the small containers show a standard deviation larger than the analytical standard deviation on these same samples indicating again that sampling techniques are improper.

The most informative comparison between the three analyses lies in the total variation of the individual results and the total variation of the means of all results. If the variations were identical, one could assume comparable results from the respective

techniques, which in turn would indicate that these analyses were performed on homogeneous material. However, there is a significant difference in the variation in the three analyses, with the calorimeter showing the lowest variation in results. If non-homogeneity is a factor, the calorimetric variation should be the lowest since the calorimeter non-destructively analyzes the complete sample. This eliminates the factor of heterogeneity.

The analytical results on the composite sample are given in Table V.

Table V. Comparison of composite sample

Analytical Composite	0.8757 g/g
Calorimeter Composite	0.8703 g/g
Mean of Foundry	0.8559 g/g
Mean of Core	0.8521 g/g
Mean of Calorimeter	0.8708 g/g

The two aliquots taken on the analytical composite sample gave 0.8828 g/g and 0.8707 g/g for an average of 0.8757 g/g. This does not agree with the mean of the foundry sample of 0.8559 g/g or the mean of the core samples 0.8521 g/g. The analytical composite result is in good agreement with the result of the calorimeter composite of 0.8703 g/g which, in turn, is in good agreement with the mean of the calorimeter results 0.8708 g/g. The agreement between the calorimeter composite and calorimeter mean indicates very little difference between the isotopic content of the composite and the individual samples as indeed was the case. It is difficult to explain the large difference in the results of the foundry and core samples as compared to the calorimeter and analytical composite results unless it is a factor of homogeneity.

It is interesting to make a comparison on the amount of plutonium as determined by the various methods. The amount is calculated from each of the preceding analyses with the assumption that each one of the 36 small containers weigh exactly 1 kilogram. (Actual weights did not vary more than $\pm 1\%$ from 1 kilogram.) The results are given in Table VI.

Table VI. Plutonium analysis comparison.

Foundry	30.813 kg
Core	30.677 kg
Calorimeter	31.349 kg
Composite	31.525 kg
Calorimeter Composite	31.331 kg

This table indicates that there can be a discrepancy of approximately 800 grams of plutonium in a shipment of approximately 31 kg or about 2.6 percent, depending on which analysis is selected to determine the amount of plutonium being transferred.

Since there is apparently a degree of heterogeneity associated with this type of material, the most accurate method of analysis is the calorimetric method because it does not rely on sampling techniques.

APPENDIX

There are two independent cases where calorimetric and laboratory analysis have been compared. Case one is from a report entitled, "Measurements Involved in Shipping Plutonium Oxide" (RFP-502). Fourteen containers of homogenous plutonium oxide were analyzed for plutonium by both the laboratory and by calorimetry. The percent difference was not significant.

Recently, a comparison of analytical results has been made on a homogeneous sample of PuO_2 weighing approximately 900 grams. This material was analyzed identically to the containers involved in this work. The results of this comparison are given in Table A.

Table A. Comparison of Plutonium Analysis (g/g Pu).

	Calorimeter	Laboratory		
		Core (Top)	Core (Bottom)	Foundry
Determination	1. 0.8742	1. 0.8728	1. 0.8697	1. 0.8703
	2. 0.8717	2. 0.8767	2. 0.8706	2. 0.8695
	3. 0.8700		3. 0.8792	
	4. 0.8709			
	5. 0.8697			
Mean	0.8713	0.8747	0.8748	0.8699
			0.8734	
Std. Deviation	0.0018		0.0037	

There is no significant difference between the mean of the calorimeter results and the mean of the analytical results. This appears to be sufficient evidence to state that given a homogeneous sample of plutonium oxide, the calorimetric-plutonium analysis is not significantly different from the laboratory plutonium analysis.