

Waste reduction and process improvements in the analysis of plutonium by X-ray fluorescence: Results from multiple data sets

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To minimize waste, improve process safety, and reduce costs, modifications were implemented to a method for quantifying gallium in plutonium metal using wavelength dispersive X-ray fluorescence. These changes included reducing sample sizes, reducing ion exchange process volumes, using cheaper reagent grade acids, eliminating the use of HF acid, and using more robust containment films for sample analysis. Relative precision and accuracy achieved from analyzing multiple aliquots from a single parent sample were approximately 0.2 and 0.1%, respectively. The same precision was obtained from analyzing a total of four parent materials, and the average relative accuracy from all the samples was 0.4%, which is within programmatic uncertainty requirements. © 2011 International Centre for Diffraction Data. [DOI: 10.1154/1.3591160]

Key words: X-ray fluorescence, WDXRF, plutonium, waste minimization

I. INTRODUCTION

Gallium is an important plutonium metal alloying agent, and WDXRF is well established for quantifying the gallium content (Worley, 2002; Worley and Colletti, 2006). This method involves dissolving the plutonium, removing it with ion exchange solid phase extraction (SPE), and quantifying gallium in the eluate. Disposition of transuranic (TRU) waste is expensive; thus, process waste reduction substantially reduces costs as well as complies with environmental management waste minimization goals.

Several modifications were made to the XRF sample preparation method. The plutonium sample size was reduced by ~50%, which decreased the SPE acid volumes and resin by ~50%. Thus, fewer TRU-contaminated acid containers are generated, and disposal costs are greatly reduced. A prenitrate resin was also used, which required approximately half the amount of nitric acid currently necessary to condition the resin.

Several other process improvements were also implemented. Ultrahigh purity acid (ppt impurities) was replaced with considerably cheaper trace metal grade acid (ppb impurities). Hydrofluoric acid is used in the current method for historical reasons but was eliminated in the modified process, and Mylar specimen containment film was replaced with much more heat stable and robust Kapton to eliminate the possibility of film rupture during analysis of the specimen. Well-characterized plutonium from a Los Alamos National Laboratory Metal Exchange Program was used to determine the relative accuracy and precision for this modified process, and the results are discussed.

II. EXPERIMENTAL

A. Instrument

A PANalytical PW2404 WDXRF spectrometer with a 4000 W rhodium anode was used. Because the specimens

were solutions, the data were collected while flushing the analysis chamber with helium. A LiF (200) crystal was used for wavelength separation. A 150 μm collimator was used in front of a scintillation detector, and a 200 μm aluminum tube filter was employed. A 30 mm specimen collimator mask was used. Zinc was added as an internal standard. The gallium and zinc $K\alpha$ peak intensities were collected at 60 kV and 66 mA until a 0.1% relative counting statistical error was reached. One background channel was collected for each element. The total analysis time for each specimen was ~1.5 min.

B. Standards preparation

Eight standards were prepared using distilled, de-ionized water (18 M Ω) as the solvent containing 0, 100, 500, 1000, 1500, 2000, 2500, and 3000 μg of gallium, respectively. All volumes were measured gravimetrically. A 10 mg/ml gallium NIST-traceable standard (Inorganic Ventures) was used to prepare the above secondary standards. Zinc was added at 5000 μg to serve as an internal standard using a 10 mg/ml zinc NIST-traceable standard (Inorganic Ventures). Aliquots consisting of 5 ml of the standards were transferred to double open ended specimen cups (Chemplex Industries) sealed on the analysis end with 7.5 μm thick Kapton film (Chemplex). The open end was sealed with microporous Teflon (Chemplex). A 4 μm thick Prolene film (Chemplex) was used as secondary containment and placed over the primary film prior to analysis and calibration.

C. Test sample preparation

All acids were prepared from trace metal grade stock acids (ppb impurities; Fisher Scientific). All plutonium work was performed inside a radiological containment box. An initial set of plutonium test samples was prepared by cutting six 0.25 g pieces from a parent metal using wire cutters (pieces referred to as cuts here). Duplicate 0.25 g cuts were prepared from three additional plutonium parent metals and analyzed in subsequent months.

All plutonium cuts were dissolved in 1.5 ml of 6M HCl

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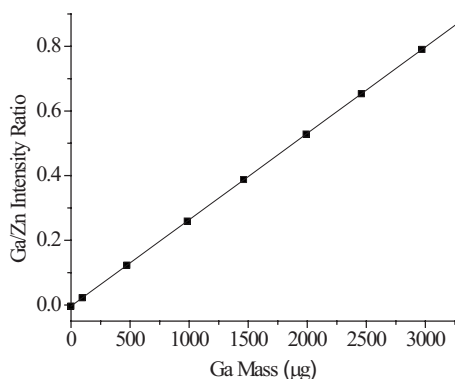


Figure 1. Calibration curve for gallium standards.

using a few drops at a time to allow for hydrogen liberation to subside between additions. Following dissolution, 0.5 ml of 10M HNO₃ was added. To prepare the anion-exchange resin for extracting the plutonium, a partially prenitrate and partially chloride form of Bio-Rad AG MP-1 200 to 400 mesh resin was fully nitrated by rinsing with 4M HNO₃. Complete nitration was verified by the absence of visible AgCl precipitate when 0.1M AgNO₃ was added to the final rinse. A 20 ml disposable chromatography column (Bio-Rad) was filled with ~8.5 ml of a slurry of the nitrated resin and 4M HNO₃ at a 1:1 ratio by volume. After the resin settled, it was compressed with a Teflon filter to the 4.5 ml level. The resin was rinsed with ~6 ml of 10M HNO₃. Columns were prepared in this fashion for each metal cut. The plutonium solution was poured onto the column, and the eluate was collected in a beaker containing 5 mg of Zn internal standard (measured gravimetrically). The plutonium was retained on the column resin. The sample container was rinsed with 1 ml of 10M HNO₃ and added to the column. The sample container was then rinsed four times with 2.5 ml each of 8M HNO₃ and added to the column after each rinsing when the previous rinse had passed through. The eluted solution volume was reduced to ~5 ml using a hot plate and heat lamp and brought up to 10 ml with 0.5M HNO₃. Two double open ended specimen cups sealed on one end with 7.5 µm Kapton were placed on a clean paper towel in the radiological containment box, and the two 5 ml aliquots of the 10 ml sample solution were transferred to the cups. This was repeated for all the samples. The cups were sealed on the open end with microporous Teflon. Using an alpha radiation monitor, each cup was verified to be free from any external contamination and then transferred to the instrument. A piece of 4 µm Prolene film was placed over the primary film to serve as secondary containment during analysis.

III. RESULTS AND DISCUSSION

A. Calibration

Because volumes were measured gravimetrically to prepare the standards and zinc internal standards, and the samples were ideal homogeneous solutions, the calibration curve was linear with a r^2 value of 1 (Figure 1).

TABLE I. Gallium relative precision and accuracy for the first plutonium test set.

Sample	RSD (%)	Relative accuracy (%)	RSD for all 6 cuts (%)	Relative accuracy for all 6 cuts (%)
Control	0.12	0.36		
1 and 2	0.18	0.21	0.18	0.10
3 and 4	0.11	-0.06		
5 and 6	0.11	0.14		

B. Test samples

Results from the first test set of six cuts from a single parent sample were excellent (Table I). The gallium RSD for all six sample cuts was 0.18%, which is comparable to the results obtained with the older, established method using sample cut sizes twice as large (Worley, 2002). The average relative accuracy from this first test batch was 0.1% as determined by comparing with the Metal Exchange Program consensus value [average of XRF and isotope dilution mass spectrometry (IDMS) qualified method measurements acquired over many years].

Test sample batches 2 and 3 were analyzed in approximately 1 month increments after batch 1. The relative precision and accuracy are presented for all three test sample sets in Table II. Although the average RSD for all the test samples of ~0.2% was the same as that observed from the first test set, the average relative accuracy for all test samples was 0.4%. There are no Plutonium Certified Reference Materials, but the parent metals used to prepare the test samples were part of the Plutonium Metal Exchange Program sponsored by Los Alamos National Laboratory, which include metals well-characterized for elemental content over the past decade (Tandon *et al.*, 2006). There appears to be some correlation between the relative accuracies obtained for each sample ID in test batches 2 and 3. Metal B has the poorest accuracies at 0.79 and 0.89, respectively. Metal C accuracies of 0.66 and 0.47% are better, and metal D values of 0.32 and 0.21% are the best (except for metal A). This could be an indication that metals A and D are more homogeneous than metals B and C. Thus, the gallium content of the cuts from metals B and C that were analyzed by established methods

TABLE II. Gallium relative precision and accuracy for all three plutonium test sets.

Batch No.	Sample ID	RSD (%)	Relative accuracy (%)
1	A	0.18	0.21
1	A	0.11	-0.06
1	A	0.11	0.14
2	B	0.14	0.79
2	C	0.29	0.66
2	D	0.15	0.32
3	D	0.06	0.21
3	B	0.20	0.89
3	C	0.49	0.47
Average		0.19	0.40

(IDMS and the previous XRF method) may have differed slightly from the gallium levels in the cuts analyzed using the new XRF method.

The programmatic relative precision requirement for gallium is <1% RSD; thus, the modified XRF sample preparation method more than satisfies that requirement. There is no programmatic accuracy requirement, but the established XRF process provides an average relative accuracy of $\pm 0.3\%$ based on NIST-traceable process controls and Metal Exchange Program consensus values. The modified process average relative accuracy of 0.4% is, therefore, not much worse than that obtainable with the current method.

C. Future plans

To examine potential parent metal heterogeneity issues and determine a more representative process accuracy, additional data will be collected from more samples over time. Additionally, high purity electrorefined plutonium solutions will be spiked with known amounts of gallium using NIST-traceable standards to assist in determining process accuracy.

IV. CONCLUSION

A number of sample preparation modifications were made to the currently certified method for quantifying gallium in plutonium metal by WDXRF. The driver for these changes was waste minimization, but cost savings and safety

improvements were also implemented. Four parent metals were analyzed over several months, and average relative precision and accuracy values of 0.2 and 0.4% were achieved, respectively. This is similar to what can be obtained using the current XRF sample preparation method, but the new method is cheaper, faster (half the acid volume to drain through the SPE columns), and safer than the previous process. Analysis of additional metals over time should provide ample data to indicate whether the new process can consistently provide this level of analytical uncertainty.

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