WASTE REDUCTION AND PROCESS IMPROVEMENTS IN THE ANALYSIS OF PLUTONIUM BY X-RAY FLUORESCENCE

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ABSTRACT

Significant modifications were made to a sample preparation process for quantifying gallium in plutonium metal by wavelength dispersive X-ray fluorescence. These changes were made to minimize waste and improve process safety and efficiency. Sample sizes were reduced, cheaper sample preparation acids were used, and safety improvements were implemented. Using this modified process, results from analyzing a batch of test samples indicated that relative precision and accuracy were ~0.2% and ~0.1% respectively, which is comparable to that obtained using the older, established sample preparation method.

INTRODUCTION

Gallium is an important alloying agent in certain types of plutonium metal, and wavelength dispersive X-ray fluorescence (WDXRF) is an established method for quantifying the gallium content (Worley, 2002; Worley and Colletti, 2006). The currently certified method entails dissolving the plutonium, removing it with ion exchange solid phase extraction (SPE), and quantifying the eluate for gallium content. Because disposing transuranic (TRU) waste is expensive, waste reduction in this process would substantially reduce costs as well as comply with environmental management waste minimization goals.

Several modifications were made to the XRF sample preparation method. The sample size was reduced by 50%, which reduced needed SPE acid volumes and resin by ~50%. Consequently, fewer expensive TRU-contaminated acid containers needed to be disposed. Also, a pre-nitrated resin was used, which required approximately half the amount of nitric acid currently necessary to fully condition the resin.

In addition to these waste minimization practices, several additional cost savings and safety improvements were employed. Ultra high purity acid (ppt impurities) is used in the currently certified method for historical reasons, but considerably cheaper trace metal grade acid (ppb impurities) was used in the modified process. Toxic hydrofluoric acid is used in the current method for historical reasons but was eliminated in the modified process. Finally, Mylar specimen containment film was replaced with more robust Kapton to reduce the possibility of film rupture during analysis of the specimen.

Well-characterized plutonium from a national Metal Exchange Program was analyzed using this modified method, and the relative accuracy and precision results are presented here.
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EXPERIMENTAL

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 Kα 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.

Standards preparation. Eight standards were prepared using distilled, deionized water (18 MΩ) 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 5,000 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 (Chempex Industries) sealed on the analysis end with 7.5 μm thick Kapton film (Chempex). The open end was sealed with microporous Teflon (Chempex). A 4 μm thick Prolene film (Chempex) was used as secondary containment and placed over the primary film prior to analysis and calibration.

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. A set of plutonium test samples were prepared by cutting six ~0.25 g pieces from a parent metal using wire cutters (pieces referred to as cuts in the present work). The cuts were dissolved with 1.5 mL of 6 M HCl using a few drops at a time to allow for hydrogen liberation to subside between additions. Following dissolution 0.5 mL of 10 M HNO₃ was added. To prepare the anion-exchange resin for extracting the plutonium, a partially pre-nitrated and partially chloride form of Bio-Rad AG MP-1 200 to 400-mesh resin was fully nitrated by rinsing with 4 M HNO₃. Complete nitration was verified by the absence of visible AgCl precipitate when 0.1 M 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 4 M 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 10 M 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 10 M HNO₃ and added to the column. The sample container was then rinsed four times with 2.5 mL each of 8 M 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 0.5 M 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
of 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.

RESULTS

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

![Figure 1. Calibration curve for gallium standards.](image)

Test Samples. Results of the first of three planned test sample batches were excellent (Table 1). The gallium RSD for all six sample cuts was 0.18 %, which is comparable to results that can be obtained with the older, established method using sample cut sizes twice as large (Worley, 2002). The relative precision requirement for gallium is <1% RSD; thus, this improved method more than satisfied that requirement. The parent material used to prepare the test sample cuts was obtained from the Plutonium Metal Exchange Program sponsored by Los Alamos National Laboratory and has been well-characterized for elemental content over the past decade (Tandon et al., 2006). The test samples average relative error was only 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).
This is actually a little better than that obtained with the established larger cut size method. The established process provides an average relative error of ±0.3% based on NIST-traceable process controls and Metal Exchange Program consensus values. In conclusion, this modified sample preparation method is cheaper, faster (half the acid volume to drain through the SPE columns), and safer than the previous process, and comparable method relative uncertainty is still obtained.

<table>
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<tr>
<th>Specimen Number</th>
<th>RSD (%)</th>
<th>Relative Accuracy (%)*</th>
<th>RSD for all 6 cuts</th>
<th>Rel accuracy for all 6 cuts**</th>
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<td>6-B</td>
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</table>

*Control accuracy based on NIST-traceable standard value.
**Pu cut accuracy based on consensus value compiled from IDMS and XRF qualified method data.

Table 1. Gallium relative precision and accuracy for plutonium test sample set.

Future Plans. Two more plutonium test sample sets will be prepared and analyzed but using three different parent materials for each set. The test sets will also be prepared and analyzed several months apart to evaluate the method over time.

CONCLUSION

A number of sample preparation modifications were made to the currently certified method to quantify gallium in plutonium metal by WDXRF. The driver for these changes was waste minimization, but cost savings and safety improvements were also implemented. A test batch consisting of six 0.25 g plutonium pieces were analyzed, and the relative precision and accuracy were comparable to that obtained using the currently certified method. Once additional data from future test samples are collected and compiled, this modified process will be incorporated as the standard for quantifying gallium in plutonium.
ACKNOWLEDGEMENTS

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REFERENCES

