ACCURATE QUANTIFICATION OF DRIED RESIDUE THIN FILMS USING X-RAY FLUORESCENCE

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ABSTRACT

An XRF specimen preparation method was developed to quantify the concentration of gallium in plutonium metal while minimizing the risk of contaminating the instrument with radioactive material. To ensure that homogenous specimens are examined, plutonium is dissolved in dilute HCl and HNO₃ prior to analysis. In the preliminary work here, non-radioactive aqueous gallium standards were prepared, and zinc was added as an internal standard to improve the accuracy and precision. Aliquots from these solutions were cast on Mylar XRF films and air dried prior to analysis. Two methods of casting the solutions were evaluated: 1) casting as a thin layer using a surfactant to wet the support film and 2) casting multiple small spots on the support film. Aqueous gallium standards were prepared and cast as dried residue specimens using each method. These specimens were then analyzed, and calibration curves were prepared. Highly linear calibrations were obtained for each preparation method when zinc was used as the internal standard (RMS values ≤1% of the standards concentration range in both cases). Based on this preliminary work, this dried residue process appears very promising for the accurate quantification of gallium in plutonium.

INTRODUCTION

Accurately determining the concentration of gallium in plutonium metal is critical in the manufacturing of nuclear weapons. Wavelength-dispersive XRF is one method used to quantify the gallium content due to its wide concentration range and good precision and accuracy using matrix-matched standards. The established XRF specimen preparation method used to date entails dissolving the plutonium to prepare a homogenous specimen. Ion exchange chromatography is then employed to remove the plutonium prior to analysis for gallium.[1] This is done to minimize the amount of plutonium introduced into the instrument. However, some residual plutonium is still present in solution after the ion exchange process, and trace amounts of americium are also present. Due to these elements, the liquid specimen is radioactive, and the potential exists for the XRF specimen cup film to rupture during analysis. In addition to this safety concern, the ion exchange process and following preparation steps take approximately two days to complete, and copious amounts of aqueous radioactive waste are generated. Hence, an improved method for specimen preparation is needed.

The casting of solutions into dry residues for XRF analysis has been investigated in the past for preconcentrating trace elements to improve the detection limits.[2-6] In the current study, dried residues were cast from solution only to provide dry specimens for analysis; although, the advantage of sample preconcentration is present as well. While plutonium dissolution is necessary to ensure that the specimens are homogenous, utilizing dry residues eliminates the
possibility of radioactive solution leaking into the spectrometer. In addition the entire specimen preparation process can be completed in 1 to 2 hours instead of the 2 days necessary with the aqueous ion exchange method, and considerably less radioactive waste is generated with the dry residue process.

In the work presented here, non-radioactive aqueous gallium standards were prepared in which zinc was used as an internal standard. (Zinc is used as an internal standard with the traditional solution ion exchange process as well.) These standards were then cast as dry films using two different methods as discussed below. These dry residue standard specimens were then analyzed by XRF and used to calibrate the instrument.

**EXPERIMENTAL**

**Instrument.** A Philips Analytical PW2404 wavelength-dispersive XRF spectrometer with a 4000 W rhodium anode was used. The data were collected under helium. A LiF detector crystal and a 300 µm detector collimator were employed. Both the gallium and zinc intensities were collected using 50 kV and 60 mA. A 2θ channel of 38.8° was used to collect the gallium count rate, and a 2θ channel of 41.7° was used for the zinc count rate.

**Thin film standards analysis:** The gallium channel analysis time was 82 sec, and two background channels at 38.3° and 39.5° were collected for 22 sec each. The zinc channel analysis time was 34 sec, and two background channels at 41.3° and 42.3° were acquired for 20 sec each.

**Multiple spot standards analysis:** The gallium channel analysis time was 36 sec, and two background channels at 38.3° and 39.4° were collected for 12 sec each. The zinc channel analysis time was 36 sec, and two background channels at 41.1° and 42.3° were acquired for 12 sec each.

**Standards.** Thin film surfactant method. The following standards were prepared using 0.5 M HNO₃ as the solvent: 0, 50, 100, 500, 1000, 1500, 2000, 2250, and 2500 ppm gallium. A 10 mg/mL gallium NIST traceable stock solution (High Purity Standards) was used to prepare the above secondary standards. To serve as an internal standard, 1000 ppm zinc was used which was prepared from a 10 mg/mL zinc NIST traceable stock solution (High Purity Standards). To promote wetting of the XRF support film, 0.25% alconox (Alconox, Inc.) was used. (Note: An XRF qualitative analysis of an alconox solution did not reveal any impurities which would interfere in the gallium, zinc, or plutonium energy regions.) Dry residue thin film specimens were then prepared from the standards by casting a 500 µL drop on a 6 µm thick XRF Mylar support film (Somar International) mounted in a 40 mm diameter double open ended XRF specimen cup (Chempex Industries). The drop was cast on the interior side of the film in the cell and allowed to wet the entire film. The residual solution was extracted with a pipette, and the wet support film was air dried for ~15 min. The other end of the specimen cup was then capped with microporous Teflon film (Chempex Industries). A 3.6 µm thick Mylar film (Somar International) was used as secondary containment and placed over the primary 6 µm film through which the specimen was analyzed. This secondary film will serve as a barrier to prevent the release of any radioactive particles when real plutonium samples are prepared by this method at a later date. A specimen prepared in this manner from each standard solution was then analyzed to generate a dried residue thin film gallium concentration calibration.
Multiple spot method. The same materials (solvents, XRF film, etc.) used for the thin film method were also used here. The following gallium standards were prepared with 0.5 M HNO₃ and 1000 ppm zinc as an internal standard: 0, 50, 100, 250, 500, 750, 1000, 1250, and 1500 ppm. A 6 µm Mylar film was mounted on a double open ended specimen cup, and seven 15 µL drops of the standard solution were cast on the cell interior side of the film in a face-centered hexagonal arrangement spread across most of the film. This was repeated for each standard. The drops were air dried for 30 min using a heat lamp placed ~25 cm above the cells, and the open end of the cells were capped with microporous Teflon film for analysis. A 3.6 µm thick Mylar film was used as secondary containment and placed over the primary 6 µm film through which each specimen was analyzed. A gallium concentration calibration of the specimens prepared in this manner was then made.

RESULTS AND DISCUSSION

The XRF method of analyzing aqueous solutions for gallium concentration is well established in our laboratory and provides good precision and accuracy for plutonium samples. A precision RSD of 2.5% was measured for 6 samples of plutonium, and the average XRF gallium concentration value deviated by 1.2% from the known value determined by isotope dilution mass spectrometry. Further, a highly linear calibration curve was prepared from aqueous gallium standards with an RSD of 0.4% of the standards concentration range (see table 1).

<table>
<thead>
<tr>
<th>Type of Standard</th>
<th>RMS (% of concentration range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous, Zn internal standard</td>
<td>0.4</td>
</tr>
<tr>
<td>Thin film, no internal standard</td>
<td>7.3</td>
</tr>
<tr>
<td>Thin film, Zn internal standard</td>
<td>1.0</td>
</tr>
<tr>
<td>Multiple spot, no internal standard</td>
<td>3.2</td>
</tr>
<tr>
<td>Multiple spot, Zn internal standard</td>
<td>1.7</td>
</tr>
<tr>
<td>Multiple spot, linear concentration range</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 1. Calibration linearity for different standards types.

Thin film standards. In this preliminary study, the standard specimens were prepared to determine the linearity of the calibration. An attempt to calibrate using the raw gallium intensities without using the zinc intensities provided an unsatisfactory curve (see figure 1.) The RMS was 7.3% of the standards concentration range. However, when the Ga/Zn intensity ratio was applied, the calibration was much more linear (figure 2) with an RMS of 1% of the calibration range. Clearly, for these thin films, the specimens were not infinitely thick, and in addition the background was high. Hence, application of the internal standard was necessary to provide a linear calibration. Also, the signal-to-noise (S/N) was low due to the minimal amount of material analyzed. This will hinder the application of the method to real plutonium samples if trace gallium levels are present. The low RMS value of 1%, though, shows that this thin film preparation method may be applicable to analyzing plutonium where non-trace gallium analysis is required. Additionally, since there would be less radioactive material present in the specimen than in a multiple spot specimen, there would be less radioactive material released into the spectrometer in the unlikely event that the support and secondary Mylar films ruptured during
analysis. (The absence of any radioactive liquid greatly reduces the danger of contaminating the instrument should both these films break.)

Figure 1. Thin film standards gallium calibration without using zinc as an internal standard.

Figure 2. Thin film standards gallium calibration using zinc as an internal standard.
Multiple spot standards. As with the thin film standards, the calibration of the multiple spot standards was less linear when the zinc intensity was not used; the calibration RMS was 3.2% of the standards concentration range. When the internal standard was applied, the RMS was only 1.7%. There was some non-linearity at the highest concentration standard of 1500 ppm (see figure 3), presumably due to gallium self-absorption, but for the standards from 0 to 1250 ppm Ga, the curve was very linear with an RMS of 0.3% of the concentration range. This is comparable with the calibration RMS using aqueous standards (see table 1). The multiple spot specimens contain more material than the thin film specimens, so the S/N is higher, and better precision should be achieved. Thus, the multiple spot method appears to be a very promising means of analyzing real plutonium samples.

![Figure 3. Multiple spot standards gallium calibration using zinc as an internal standard.](image)

CONCLUSIONS

Both the thin film and multiple spot dried residue specimen preparation methods provided linear gallium calibrations. These dried residue methods are safer than analyzing radioactive liquids. Much less radioactive waste is generated with the dried residues, and the process is considerably faster than using ion exchange chromatography and preparing aqueous specimens. Due to the higher S/N, the multiple spot method will be better suited than the thin film method for analyzing low levels of gallium in plutonium samples. Also, no surfactant is required to prepare the specimens.

Since plutonium will absorb some of the gallium signal, the use of zinc as an internal standard will be essential in minimizing matrix effects when real plutonium is analyzed. However, studies need to be completed to determine if using the internal standard will be sufficient. As a
first step, depleted uranium will be used as a surrogate for plutonium to examine this matrix effect problem. Depleted uranium has an absorption edge near in energy to the absorption edge of plutonium but is less radioactive and considerably easier to handle for this preliminary testing phase. If the internal standard appears to mitigate the matrix effects, then the final stage will be to apply the dried residue method to real plutonium samples. However, if matrix effects are found to significantly hinder the accuracy and precision for gallium analysis, then high purity plutonium aqueous standards will be prepared and spiked with known amounts of gallium. Dried residue specimens will then be made from these standards and used for the gallium calibration.

ACKNOWLEDGMENTS

The authors thank the Department of Energy for funding this work.

REFERENCES