Glow Discharge Optical Emission of Plutonium and Plutonium Waste

by

W. A. Spencer
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

R. K. Marcus
Clemson University

DOE Contract No. DE-AC09-89SR18035

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.
Final Report

WSRTC/SCUREF Task Order #174

Glow Discharge Optical Emission of Plutonium

and Plutonium Waste

Submitted November 9, 1995

by

R. Kenneth Marcus
Associate Professor

Department of Chemistry
Howard L. Hunter Chemical Laboratory
Clemson University
Clemson, SC 29634-1905
INTRODUCTION

The application of glow discharges to the analysis of nonconducting materials such as glasses and ceramics is of great interest due to the number of advantages afforded by their direct solids capabilities. These types of samples, by their chemical nature, pose difficulties in dissolution for their subsequent analysis by common spectroscopic instrumental methods such as inductively coupled plasma atomic emission (ICP-AES). The ability of the glow discharge to sputter-atomize and excite solid nonconducting materials greatly reduces sample preparation time, cost, and complexity of an analysis. In comparison with x-ray spectroscopies, GD also provides the advantage of a relatively uniform sample atomization rate, resulting in a lowering of matrix effects.

In a traditional direct current glow discharge (dc-GD), the material to be analyzed must first be ground and thoroughly mixed with a conductive host matrix and pressed into a solid pellet [1-3]. Although the GD offers many advantages as described above, the sample preparation involved in dc-GD analyses can produce undesirable effects. Mixing with a conductive host matrix may result in decreased sensitivity and contamination of the sample. Additionally, atmospheric gases which are often trapped in the sample upon pressing can degrade the quality of the plasma and obscure analytical results by reducing sputtering rates and affecting excitation conditions [3,4]. Internal standardization has been carried out in both atomic absorption and emission dc-GD analyses in order to improve precision and accuracy which are affected by these problems [3,5-7].

Radio frequency glow discharge (rf-GD) sources have been shown to be effective, sensitive and efficient means of analyzing both conductive and nonconductive powders and bulk materials directly in the solid state, without matrix modification [1]. The ability to directly sputter-atomize and excite
nonconducting materials with an rf-GD has been demonstrated by Winchester, Lazik and Marcus [8,9]. This approach easily permits the qualitative elemental analysis of the sample. Figure 1 shows the spectrum of Macor™, a machinable ceramic comprised of approximately 46% SiO₂ and 17% MgO, which is very difficult to analyze by solution-based techniques.

The elemental analysis of vitrified nuclear waste involves many complexities that arise from both the physical and chemical nature of these samples. Significant matrix modification is required for analysis by arc/spark vaporization (involving compaction in a conductive host matrix) and labor intensive sample dissolution for solution analysis by ICP emission or mass spectrometries. The analysis of ²³⁸Pu oxides pose further difficulties in terms of high levels of radioactivity in the sample and waste solutions. Direct solids analysis would therefore be advantageous for such samples, allowing a greater ease of sampling and a decrease in the amount of chemical waste produced and possible contamination. More specifically, rf-GD atomic emission spectrometry (AES) has the advantages of rapid plasma stabilization times, simple and compact construction, and a relatively lower cost of operation compared with mass spectrometry systems. These benefits contribute to the potential for miniaturization of the rf-GD source which can be housed within a glove box and remotely sampled by an optical spectrometer via an optical fiber.

This study focused on the applicability of rf-GD-AES for the direct analysis of nonconducting materials. Particular targets included plutonium oxides and defense waste glasses. There were several goals in this study, including the parametric evaluation of plasma operating conditions, an assessment of limits of detection for trace analysis in simulated vitrified waste samples and the quantification of these types of samples. The final goal was to
design a contained rf-GD-AES system for remote sampling of radioactive materials at the Savannah River Site in Aiken, SC, in the most efficient, safe and cost-productive manner.

EXPERIMENTAL

Figure 2 shows the experimental set-up for this study. The rf-GD source and collection optics have previously been described in detail [1]. The spectrometer system employed is a JY-38, 1.0 meter scanning monochromator with a 3600g/mm holographic grating (Jobin-Yvon, Division of Instruments, SA, Edison, NJ). Entrance and exit slits were 14 and 25 microns, respectively. Data acquisition is achieved with the use of the "IMAGE" fast scanning electronics and software (Jobin-Yvon, Division of Instruments, SA, Edison, NJ). This allows a full wavelength spectrum (200-550 nm) to be acquired in two minutes. Thus, rapid data acquisition for radioactive materials would be possible, while still maintaining sufficient resolution (<0.1 nm) needed for properly evaluating spectra. This system incorporates an automatic gain between 1 and $10^6$ by high voltage control of the PMT, therefore yielding a dynamic range that is sufficient for analyzing trace to major constituents of a sample in one complete spectrum.

Sample preparation for direct solids analysis was minimal, involving only cutting the sample with a diamond cutter (Raytech Industries Inc., Stafford Springs, Conn.) and grinding with 120 and 400 grit SiC paper, respectively, to yield a sample of 1-3mm thickness. To avoid errors in data acquisition, the sample is pre-sputtered for several minutes before an analysis in order to remove any SiC residue on the surface. The diameter of the sample must be large enough to fit over the teflon or viton o-ring (5mm diameter) in order to achieve an adequate vacuum seal. High-purity argon gas
(99.999%) fills the discharge chamber and the rf power (generally 20-40W) is applied to the back of the sample.

RESULTS AND DISCUSSION

This work demonstrates the ability of rf-GD-AES to analyze nonconductive simulated waste glasses with various trace inorganic components. Figure 3 shows the full wavelength spectrum of a glass frequently made during the waste vitrification process (DWPF). This glass is comprised of the following elements, some of which are easily identifiable in the spectrum: Al 4.6%, B 7.6%, Ca 1.1%, Fe 12%, Mg 1.5%, Mn 2.5%, Na 8.6%, Ni 1.1% and Si 52.3%.

An optimization of operating parameters is essential before beginning an analysis, and previous work in this laboratory has been carried out in order to parametrically evaluate experimental conditions for nonconducting materials. The diameter of the orifice plate, which limits the amount of sample to be sputtered, was determined to be 3mm. Because of the fragile nature of the nonconducting samples, powers lower than those normally used for conductive ones were used, typically 20-40W. Discharge pressure is also a very important parameter in that it effects the amount of sputtering which may take place, as well as the plasma excitation conditions. Figures 4 and 5 show the optimization of discharge pressure at 30W for two transitions that are characteristic of elements that are typically found in NIST standard reference materials and in the simulated waste glasses. Silicon is a major component of NIST 1412 standard reference glass, present at 19.8%, while magnesium is at a minor level of 2.8%. Transitions for both of these elements, as shown in Figures 4 and 5, yield optimum signal intensities at a discharge pressure of 4 torr. It is often more informative to examine the signal-to-background (S/B) ratio, since background levels can often be high
due to spectral interferences or high noise levels (photon and electronic). Upon plotting S/B as a function of pressure, it is observed for both transitions that 6 torr is optimum. Since S/B has been deemed to be a more thorough estimate of spectroscopic information, the working pressure chosen for these studies was 6 torr.

The time required to establish a stable emission signal is very important in determining the overall time for an analysis. This is a vital concern for analyses of radioactive glasses for which the time required to handle the sample should be minimal. Figure 6 shows overlaid stabilization curves for both a trace and a major component of a multicomponent NIST 610 standard reference glass. Despite the difference in concentration levels, the emission intensities reach a steady count level approximately 30 seconds after initiation of the plasma. This level of stability (<1% RSD) exists for a time suitable for conducting a rapid analysis, even with a sequential spectrometer. Table 1 lists the precision values for acquiring an emission signal repetitively for > 1 minute at 0.5 second integration times. Emission intensities maintain levels of <1 %RSD for acquisition times of 2 minutes, for total plasma operation times as high as 20 minutes should extended integration or signal processing be required.

An important aspect in the quantitative analyses of glasses and ceramics that must be considered is how the oxide-rich nature of these types of samples affects the quality of the plasma. The majority of glasses and ceramics, including the nuclear waste glasses, contain 40-60% oxygen which can be released into the plasma through the sputtering process. Although rf-GD-AES direct solids analysis eliminates the process of pressing powders which can trap atmospheric gases, these gases can be trapped within the pores of the sample itself. Often the fragile nature of the sample dictates that the
amount of pressure applied to hold the sample in place be decreased, which may subsequently introduce a leak in the discharge vacuum system. The upper portion of Figure 7 illustrates the negative effect on the plasma of air introduced via an inadequate seal between the sample and vacuum o-ring. Strong band emission in the region between 300-400 nm is observed (as shown in Figure 8) arising from molecular N2, NH, NO and other components of air. In order to improve the plasma quality, an argon bath accessory, shown in Figure 9, was utilized in which a brass cup was placed around the sample, external to the source chamber. Argon gas flowed inside the cup so that in the case of an inadequate seal or porous sample, the argon bath gas was introduced into the plasma (which is supported by argon) instead of air. This arrangement improves the spectral quality by enhancing the analyte emission that was previously suppressed by the presence of air in the plasma as shown in Figure 10.

Many factors may influence the level of sample-to-sample precision obtained in an analysis, including the variation in pressure applied to the back of the sample, small changes in vacuum conditions and/or discharge gas pressure and the physical nature of the sample itself. The latter factor is exemplified in the large %RSD values of 3 separate analyses of the same sample listed on the right side of Table 2. Since glass samples may be porous in nature, air may be introduced into the plasma under vacuum conditions. The use of the argon bath has been shown to also greatly improve sample-to-sample reproducibilities as well as internal precision values, as shown on the left portion of Table 2.

In comparison to conductors, the quantitative analysis of dielectric materials is not as straightforward. In a previous parametric evaluation of rf-GD for the analysis of glass and ceramic samples, it was found that rf applied
potentials and dc bias potentials are appreciably lower in these types of materials in comparison with conductors [9]. The measured decrease in dc bias potentials is related to the reduction in sputtering rates and emission intensities as well. The dependence of emission intensity on sample thickness indicates that the thicker samples, which have higher capacitance, result in substantial power losses and decreased intensities. Therefore, another goal of this study was to develop a suitable method for calibration which normalizes emission intensities for variations in sample thickness. This dependence can be measured quantitatively by the dc bias potential established on the sample surface. A near-linear response relating bias potential with emission intensity is observed for the measured intensity of Mg 285.1 nm emission (a major component in Macor™) as shown in Figure 11, which is inversely related to sample thickness. As in the case observed for atomic absorbance intensities in rf-GD, this relationship between emission and dc bias voltage allows for a corrected intensity (I_c) based on the slope of the line and the observed bias potential of the analytical sample:

\[ I_c = I_m + (m \times u) \]  \hspace{1cm} (1)

where \( I_m \) is the measured intensity, \( m \) is the calculated slope using two standards and \( u \) is the voltage deficit between the measured dc bias of each sample and that of the thinner sample. The product \( (m \times u) \) provides a correction factor for power losses experienced. Figure 11 also shows the corrected intensities of the DWPF glass at four different thicknesses. Intensities of a DWPF waste glass ranging from 1-4 mm thickness were measured with the RSD of the corrected intensities being 8.3%, which is well within normal sample-to-sample precision values. Using the corrected intensities, it is possible to generate a calibration curve using the DWPF waste
glass along with NIST standard reference glasses, as shown for Ca II 393.4 nm in Figure 12.

Limits of detection for elements present in the DWPF waste glass were evaluated in order to determine if the sensitivity of the rf-GD-AES approach was sufficient for in-house WSRTC analyses. The method of calculating detection limits employed here is based on the relationship between the analyte signal-to-background ratio and the relative standard deviation of the spectral background, termed by Boumans as the RSDB approach. As can be seen in Table 3, the values for a 3 mm thick simulated DWPF glass range from 1-20 ppm. Note that the values are a function of the specific analyte concentration, which amplifies contributions from flicker noise. As a result, lower calculated limits would be expected from analytes of lower concentration; i.e., approaching the detection limit. Even so, these values are sufficient for the target cases at hand. In fact, given the inverse relationship between sample thickness and analyte intensity, one would expect detection limits to be approximately a factor of 10 lower simply by analyzing a 1 mm thick sample.

In order to meet the requirements of radioactive sample assaying, an isolated glove box was designed to house the rf-GD source. As illustrated in Figure 13, a 3 m long of optical fiber serves as a conduit to transport light from the source to the monochromator. Sampling of the source remotely via optical fiber can be implemented. A commercial optical fiber adapter is being implemented to connected one end of optical fiber with the monochromator slit mount. Focusing light from rf-GD source into the optical fiber is a tedious operation, we are planning to use a fixed lens to do this. This device will allow the ready disposal of the spectrochemical source at the end of its practical lifetime, while isolating the spectrometer from radioactive
contamination. Pneumatic valves will be used to carry out the sample mounting and to control the source vacuum and discharge gas introduction.

CONCLUSIONS

Although much work is still needed in the quantification of nonconducting materials, the studies to date have demonstrated the incredible potential of rf-GD-AES for these applications. Despite the unique factors that must be considered in the analysis of glasses and ceramics, the ease of direct sampling for these types of samples in rf-GD has attracted much interest in the technique.

Establishing the relationship between thickness and intensity enables corrections to be made in analyses. Despite the reduction in emission intensities, sensitivities in glasses have been shown to be comparable to those of other techniques (in the single ppm range) [9,10]. Figure 12 illustrates the calibration method using corrected emission intensities as shown in Figure 11. The fact that DWPF glass can be quantified with NIST standard glasses is very promising for future calibration. Limits of detection listed in Table 3 are shown to be sufficient for trace elemental analyses. Finally, the glove box design shown in Figure 13 appears to be a practical, safe and cost effective means of sampling radioactive waste glasses.

REFERENCES


Figure 1  Emission Spectrum of Macor™
Figure 2 Experimental Set-up for RF-GD-AES
Figure 3  Emission Spectrum of Simulated Waste Glass (DWPF)

30W, 3mm thick
6 Torr
Figure 4: Effect of Pressure on Si 288.2 nm at 30W
Figure 5  Mg 285.2 nm Intensity and S/B as a Function of Discharge Pressure at 30W
Figure 6: Stabilization Times for Elements in Glass

- Co intensity (390 ppm)
- Si intensity (>80%)
Figure 7  Comparison of Plasma Emission with and without the Presence of Air
Figure 8: Plasma Emission in the Presence of Air
Figure 9 Argon Bath for Improved Sample-to-Sample Precision
Figure 10  Enhancement of Mg Signal with the Use of an Ar Bath
Figure 11 Correction of Mg 285.1 nm Emission Intensity in DWPF Glass Using dc bias Voltage
Figure 12 Generation of Calibration Curve using NIST Standards and DWPF Simulated Waste Glass

\[ R^2 = 0.999 \]
Figure 13 Glove Box Design for rf-GD-AES Analysis of Radioactive Waste Glasses
**Table 1**  
Short-Term Precision for Various Elements in NIST 610 Glass

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Concentration (ppm)</th>
<th>Internal Prec. (%RSD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag 328.07</td>
<td>254 ±10</td>
<td>0.943</td>
</tr>
<tr>
<td>Au 267.59</td>
<td>(25)*</td>
<td>0.73</td>
</tr>
<tr>
<td>Co 346.58</td>
<td>(390)</td>
<td>1.05</td>
</tr>
<tr>
<td>Cu 324.75</td>
<td>(444)</td>
<td>0.899</td>
</tr>
<tr>
<td>Fe 385.99</td>
<td>458 ±9</td>
<td>0.252</td>
</tr>
<tr>
<td>Ni 352.45</td>
<td>458.7 ±4</td>
<td>0.742</td>
</tr>
</tbody>
</table>

* concentrations in ( ) are uncertified
Table 2  Comparison of External Precision in NIST 610 Glass with and without Ar bath

<table>
<thead>
<tr>
<th>Element (nm)</th>
<th>with Ar bath</th>
<th></th>
<th></th>
<th>without Ar bath</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ave. S/B</td>
<td>%RSD</td>
<td>Ave. S/B</td>
<td>%RSD</td>
<td></td>
</tr>
<tr>
<td>Co 346.48</td>
<td>14.3</td>
<td>3.87</td>
<td>9.88</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>Cu 324.75</td>
<td>48.8</td>
<td>7.45</td>
<td>24.7</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>Ag 328.07</td>
<td>17.4</td>
<td>5.14</td>
<td>5.56</td>
<td>26.7</td>
<td></td>
</tr>
<tr>
<td>Fe 371.99</td>
<td>2.39</td>
<td>4.35</td>
<td>2.75</td>
<td>32.1</td>
<td></td>
</tr>
</tbody>
</table>
Table 3 Limits of Detection for Minor Components in DWPF Simulated Waste Glass (3mm)

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>Concentration (wt %)</th>
<th>L.O.D. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>394.4</td>
<td>4.6</td>
<td>7.3</td>
</tr>
<tr>
<td>Cr</td>
<td>425.4</td>
<td>0.39</td>
<td>1.2</td>
</tr>
<tr>
<td>Cu</td>
<td>324.7</td>
<td>0.41</td>
<td>3.8</td>
</tr>
<tr>
<td>Fe</td>
<td>385.9</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>Mg</td>
<td>285.2</td>
<td>1.5</td>
<td>5.3</td>
</tr>
<tr>
<td>Ni</td>
<td>352.4</td>
<td>1.1</td>
<td>8.4</td>
</tr>
</tbody>
</table>