Uranium analysis by Resonance Ionization Mass Spectrometry: High Useful Yield and Rapid Isotopic Analysis

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We describe a new Resonance Ionization Mass Spectrometer and demonstrate a useful yield for uranium analysis of 24% for sputter-cleaned metallic samples, and 0.4% for oxides, which rises to 2% after ion-beam reduction. We measured the $^{235}$U/$^{238}$U ratio in two different uranium oxide materials with RSD <0.5% in less than four hours.

I. Introduction

Characterizing the isotopic compositions of nuclear materials is important in determining origins, histories, and intended uses. Resonance Ionization Mass Spectrometry (RIMS) uses laser spectroscopy to selectively ionize elements for isotopic analysis, and is attractive for actinide analysis in part because sample preparation requirements are minimal. RIMS can achieve very high useful yield (atoms detected per atom consumed) for most elements, but this is difficult to achieve for U because of the propensity for U to form strongly bound gas-phase oxides. We describe the first results from a new RIMS instrument called LION (Laser Ionization of Neutrals) and demonstrate a useful yield for U from metal and UO$_2$, and discuss factors that control useful yield. We also report rapid isotope measurements on uranium oxide powders.

II. Methods

RIMS has been described in detail elsewhere.$^{1,2}$ In brief, a solid is sputtered with an energetic ion pulse and the neutral atoms are allowed to fly away from the surface for a few hundred ns. Laser beams with wavelengths tuned to electronic transitions in the element of interest are then pulsed just above the surface to intersect the cloud of neutrals and ionize only that element. The photoions are then accelerated into a time-of-flight mass spectrometer. The LION mass spectrometer is a modified version of an instrument called SPIRIT.$^3$ LION has a fine-focus ion gun (15 keV Ga$^+$) and six tunable Ti:Sapphire lasers for resonance ionization. A three-color resonance ionization scheme for U was used, i.e. excitation through two resonance transitions followed by an autoionizing step.

III. Results

Figure 1a shows a maximum 24% useful yield for analysis of U metal for primary ion pulses of 100-200 ns. RIMS useful yield is determined by 1) the efficiency of sputtering ground state neutral atoms, 2) the fraction of sputtered material that is irradiated by the lasers, 3) the ionization efficiency of neutral atoms, 4) the efficiency of ion transport to the detector, and 5) the efficiency of the detector. Factors 2-5 are maximized by judicious choice of the laser ionization scheme and good instrument design. Models of the LION instrument suggest a maximum useful yield of ~36% for uranium if 100% ionization efficiency is achieved. The actual efficiency is less than 100% due to the population of low-lying electronic states by the sputtering process, and loss of neutral atoms to secondary ions and especially uranium oxide molecules. In order to achieve 23% useful yield it was necessary to sputter the oxide layer from the surface to expose metallic U, otherwise the mass spectrum is dominated by UO$^+$ and UO$_2^+$, which are inefficiently ionized (and which we ignore in calculating useful yield).

Sputtering a clean UO$_2$ sample gives a useful yield of 0.4%. Both UO$^+$ and UO$_2^+$ are greatly enhanced in the mass spectrum of UO$_2$ compared to U metal, indicating a much lower fraction of neutral atoms in the sputtered flux. Fig. 1b shows that sputtering the UO$_2$ surface with a dose of $2 \times 10^{16}$ ions (sufficient to remove ~50 nm of material) increases the useful yield to 2% due to the reduction of the material by preferential sputtering of oxygen.

To put our RIMS measurements in context, we compare our results with Secondary ion Mass Spectrometry (SIMS) measurements made on oxide samples. Unlike RIMS, SIMS useful yields are higher on oxidized materials than on metals due to higher secondary ion formation efficiency, therefore these measurements represent the best available for the two
techniques. Ranebo et al.\(^4\) obtained a useful yield of 1.27% from UO\(_2\) on a large-geometry magnetic sector SIMS instrument, and Hervig et al.\(^3\) obtained 0.67% from NIST 610 glass on a small-geometry SIMS instrument. The RIMS result on UO\(_2\) is thus comparable to SIMS, while the U metal useful yield is much higher.

Isotope ratios were measured in U oxides of two different \(^{235}\)U enrichments (4% and 63%), using a third oxide (50%) as a standard. One of the goals was to determine isotope ratios quickly, therefore sample preparation was minimal (powders were pressed as-is into indium) and counting times were kept short. The total counting time for all measurements in Table 1 was 217 minutes. All measurements agree with the certified values at the 95% confidence level. The larger RSDs for \(^{234}\)U/\(^{238}\)U reflect the low abundance of \(^{234}\)U and short analysis times, which limited the ion counts.

**IV. CONCLUSIONS**

A new RIMS instrument has demonstrated a 24% useful yield for uranium metal, and 2% for uranium oxide when reduced by pre-sputtering. The oxide result is comparable to state-of-the-art SIMS, while the metal result is higher. Rapid isotopic analysis of solid UO\(_2\) can be done quickly with only a bare minimum of sample preparation. Isotopic analysis of uranium at the level of <0.5% RSD for \(^{234}\)U/\(^{238}\)U for two different samples is achievable in less than four hours.

**TABLE I.** Isotope ratios measured on uranium oxide powders. Uncertainties are 95% confidence intervals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio</th>
<th>Certified</th>
<th>Measured</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRM 125A</td>
<td>(^{235})U/(^{238})U</td>
<td>0.00039130(38)</td>
<td>0.000402(24)</td>
<td>2.9%</td>
</tr>
<tr>
<td>CRM 125A</td>
<td>(^{234})U/(^{238})U</td>
<td>0.042301(25)</td>
<td>0.0423(3)</td>
<td>0.3%</td>
</tr>
<tr>
<td>CRM U630</td>
<td>(^{234})U/(^{238})U</td>
<td>0.01765(49)</td>
<td>0.0174(7)</td>
<td>2.2%</td>
</tr>
<tr>
<td>CRM U630</td>
<td>(^{235})U/(^{238})U</td>
<td>1.8067(16)</td>
<td>1.8049(115)</td>
<td>0.4%</td>
</tr>
</tbody>
</table>

**ACKNOWLEDGMENTS**

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**REFERENCES**