ULTRA-SENSITIVE ISOTOPIC ANALYSIS BY RESONANCE IONIZATION MASS SPECTROMETRY

Analytical Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Abstract

A high-powered pulsed dye laser has been interfaced to a commercial ion microprobe mass analyzer. This combination should provide ultra-high sensitivity for isotope ratio measurements of selected elements in environmental samples. The technique is an outgrowth of resonance ionization mass spectrometry which has demonstrated high precision for isotope ratio determinations of uranium and plutonium using thermal filament atomization. Sputter atomization using a pulsed argon ion beam represents a significant improvement in efficiency because the temporal overlap between the atom cloud and the laser pulse can approach 100%. This, coupled with the high ionization efficiency of laser induced resonance ionization methods, promises an analytical sensitivity which is significantly better than other microprobe techniques. A description of the experimental set-up is given along with the modifications to the ion microprobe instrument which were necessary to obtain acceptable ion extraction efficiency. Also shown are results for samarium and uranium demonstrating the optical and mass spectra obtained.

Introduction

The technique of resonance ionization mass spectrometry (RIMS) has recently been developed for isotope ratio measurements. Studies performed in our laboratory^1-^5 and elsewhere6-13 have been reported for a number of elements using thermal vaporization sources to produce the atom reservoir for laser-induced resonance ionization. Other methods of atomization such as a glow discharge,^1^4 laser ablation,^1^5 and ion beam sputtering^1^6-1^7 have been reported.

Ion beam sputtering is an efficient atomization process for coupling with pulsed laser ionization because the rate of atom formation can be highly controlled. Sputter rates for pure metals have been measured under differing conditions of incident ion beam composition, energy, angle, and current density. Knowledge of the energy and angular distribution of the sputtered atoms allows one to calculate the geometrical overlap between a sputter "plume" and a laser beam of given cross-section. In addition, when pulsed sputtering is utilized, the temporal overlap between the atomization and ionization can approach 100%. Provided the laser beam is sufficiently powerful to saturate the ionization process, the overall efficiency will allow one ion to be formed for every 10 or fewer atoms removed from the sample. It then becomes a matter of extracting these atoms into a suitable mass spectrometer, followed by pulse counting or pulse height detection.

A commercial ion microprobe mass analyzer (IMMA) has been interfaced with a tunable pulsed laser for carrying out resonance ionization mass spectrometry of sputtered atoms. The IMMA instrument has many advantages for this work, including a micro-focused primary ion beam (2 μm in diameter) of selected mass, complete sample manipulation and viewing capability, and a double-focusing mass spectrometer for separation and detection of the secondary or laser-generated ions. This paper will describe the changes necessary to adapt the IMMA instrument for resonance ionization, along with preliminary results for the elements Sm and U. Data are presented demonstrating the number and type of ions formed along with optical spectral information showing the wavelengths at which resonance ionization occurs.

Experimental

IMMA

The secondary ion mass spectrometer used in this work was manufactured by Applied Research Laboratories (Sunland, CA) and is based on the design of Liebl.18 In essence, the instrument is two mass spectrometers. In the primary spectrometer, a beam of ions is generated via a Duoplasmatron ion source, mass analyzed, and focused onto the surface of interest. Ions sputtered from the sample surface are directed into a double focusing mass spectrometer where mass analysis is accomplished. Modifications to the ion extraction lens system, which allow discrimination against sputtered ions while allowing collection of resonance ions, are described in a following section. For this work, the secondary mass...
The analyzer was operated at mass resolutions (M/ΔM) on the order of 200. Primary ions were generated by using a mixed gas consisting of approximately 2 atom % Ar, 34 atom % N₂ and 64 atom % O₂ in the duoplasmatron ion source. This allowed the sputter targets to be bombarded with operator-selected mass analyzed ion beams of Ar⁺, N₂⁺ or O₂⁺. As expected, it was found that high current density (micro-focused) Ar⁺ sputtering beams are more effective than reactive beams such as O₂⁺ and N₂⁺ in producing a large sputtered neutral atom population from reactive targets such as U and Sm.

Laser Source and Light Optics

The laser source used in this study was a Chromatix CMX-4 flashlamp-pumped dye laser with a bandwidth of approximately 3 cm⁻¹ and an optical pulse width of about 1 µsec. A useful wavelength range of approximately 580-610 nm was generated with the Rhodamine-6G dye used in all the experiments. The pulse energy measured directly at the laser output was about 5 mJ with the available energy above the sample surface estimated to be from 10-50 times less. A stepping motor was attached to the micrometer-driven wavelength selection mechanism to permit reproducible spectral scans to be made under computer control. The wavelength calibration was performed by directing the laser beam into the bore of a Ne-filled U hollow cathode lamp and recording its optogalvanic spectrum. Least-squares regression analysis of the data for known Ne and U wavelengths produced a calibration slope of $5.49 \pm 0.02 \times 10^{-4}$ nm-step⁻¹ and a standard deviation of the residuals of 0.04 nm.

The light optics used to position and focus the laser beam above the sample are diagrammed in Figure 1. The beam was spatially filtered and focused to approximately a 0.01 cm diameter spot directly above the sample with a beam expander assembly housing a 10 µm pinhole. The horizontal and vertical positions relative to the sample surface were varied by an adjustable mirror mount. The elevation of the laser beam was lowered to a plane parallel and just above the sample surface by a periscope assembly mounted in the sample chamber.

Signal Processing. Photomultiplier anode pulses produced by individual ions reaching the Daly detector were processed by a preamplifier/discriminator. The collection of pulses produced by a single laser shot was integrated into a single pulse approximately 10 usec wide by a variable gain, pulse-shaping amplifier as shown in Figure 2. The amplitude of this pulse is proportional to the number of ions produced by the laser shot. The output pulse was sampled by a gated integrator triggered by the sync pulse from the laser; the gate delay was adjusted to coincide with the output pulse which occurs approximately 25 usec after the laser sync pulse. The resultant DC output signal from the gated integrator was further processed by the data system.

Data System

Data acquisition and control for the experiments were performed by an LSI-11/2 microcomputer housing an analog-to-digital converter (ADC), two digital-to-analog converters (DAC), and a 16-bit parallel I/O interface. The ADC samples the DC output of the gated integrator and converts it into a digital value. The parallel interface controls the direction and speed of the stepping motor attached to the wavelength micrometer drive of the laser. The DAC outputs drive an x-y scope for real-time display of spectra or an x-y plotter for post-acquisition recording of spectra.

Spectral Acquisition

Optical data were collected as the average of 15 laser shots per datum, with a 50-step (0.027 nm) interval between data points. One thousand such data points, corresponding to a wavelength range of 27 nm, were collected for each optical spectrum.

Mass spectral data were obtained by scanning the secondary magnet via front panel controls while leaving the laser fixed at the resonant wavelength of the desired element. Data were acquired at 0.2 amu intervals with each datum representing the average of 15 laser shots.

Ion Optics

The existing ion extraction optics of the IMMA instrument were designed to efficiently extract secondary ions produced at the sample surface. The sample is held at a potential of +1500V relative to the extraction electrode which is at ground potential. However, these conditions were found to be inefficient for extracting ions formed above the sample surface by the laser interaction with a sputter 'plume'. Therefore, new ion optics systems were studied using the SIMION computer program. One of the most successful designs is shown in Figure 3. The objective was to create a flat extraction field in the volume directly above the sample surface, with the field equipotential surfaces inclined at the desired 45° angle relative to the sample surface. To achieve this, a "pusher" electrode was added.
(shown to the right in the figure) and the pick-up electrode itself was significantly changed. As can be seen, the equipotential surfaces are relatively flat in the region between the two electrodes, although they are less so directly above the sample surface. Ions formed in the volume element shown follow a nearly perfect trajectory through the pick-up electrode.

Electrodes using this design were fabricated and installed in the IMMA instrument. Surprisingly, the performance of the system for sputtered secondary ions was acceptable, with little loss of sensitivity, and an improvement in mass spectral resolution.

**Samples**

Samples consisting of natural U and Sm metal embedded in low vapor pressure epoxy were polished until a smooth metallographic finish was obtained. The cross-sectional area of each metal sample was approximately 0.1 cm².

**Results and Discussion**

**Sensitivity**

The ion bundle produced in a single laser pulse (nominally 1 usec long) was found to be 3 ± 1 usec wide at the detector following a delay of 23 usec (for Sm) or 30 usec (for U) due to time-of-flight through the secondary mass spectrometer. The number of ions in each bundle could be counted using a fast oscilloscope to monitor the output of the ion multiplier preamplifier. Individual ions produced a signal of approximately 1 V amplitude, with a nsec width. The largest signals obtained for 238U were found to have >100 ions per pulse while those for 152Sm were found to have 40 ions per pulse.

Without more information about the sputter yields for U and Sm under Ar⁺ bombardment, it is not possible to obtain a reliable measurement of the number of resonance ions collected per sputtered atom. However, under the conditions which gave >100 U⁺ ions per laser pulse, with a primary Ar⁺ current of 21 nA, the number of U⁺ ions detected per incident Ar⁺ and l in 1300. This reveals that a factor of 10² improvement is necessary before reaching the goal of 1 ion per 10 atoms sputtered. Improvements in the laser system and ion optics should increase the overall efficiency.

**Optical Spectra**

Figure 4 shows the optical ionization spectra of Sm over the wavelength range 580-607 nm. The top spectrum was obtained using sputter atomization, while the lower spectrum resulted from heated thermal filament atomization (at 1500°C) taken under conditions similar to Ref. 2. The peaks observed for sputter atomization match quite closely with those from thermal atomization with the exception of the line at 580.16 nm. This line is absent from the upper spectrum because of reduced bandwidth in the dye output spectrum due to lower power. The remainder of the spectral range was adequately covered, as can be seen by the close match in relative intensity of the lines.

Table 1 shows the interpretation of the lines found with sputter atomization. In all cases, the lines originate in the ground state 7F₁₇ manifold of Sm, with a distribution of states resembling that of the thermal atomization process at 1500°C. The apparent ground state originating line at 599.11 nm is enhanced in the sputtering case relative to two lines originating from the 7F₃ level at 587.69 nm and 602.81 nm. This indicates a lower "temperature" of the atoms produced by sputtering, although in the absence of local thermal equilibrium, the ground state may be enhanced by decay of highly excited species a short time after the sputtering event but before the ionizing laser is turned on.

The lines observed for Sm at these wavelengths can only result from a single-color three photon process. The ionization energy of Sm is 45519 cm⁻¹ compared to the energy range of the photons used (16500 - 17200 cm⁻¹). Provided that the interpretation in Table 1 is correct, the absorption of two photons would result in states which are 7000 - 12000 cm⁻¹ below the ionization energy. A third photon absorption is therefore required before ionization would result. The sharp line nature of the peaks observed strongly suggests that resonant absorption occurs for the first two photons, proceeding through allowed upper energy levels about which nothing has been published. This also resembles the case for the actinide elements described in another report.21

Figure 5 shows the spectra of U taken under conditions similar to those for Sm. The agreement between sputter atomization and thermal atomization is excellent. The interpretation of the lines in the thermal spectrum can be found elsewhere.21 The two largest lines at 591.54 nm and 596.92 nm are believed to arise from the 5Lo₆ ground state and...
the $5\text{d}^7$ (5620 cm$^{-1}$) state, respectively. Again, a three-photon resonant process is invoked using single-color excitation (within the bandwidth of the laser, 3 cm$^{-1}$). The ratios of the two strongest lines in each case are not significantly different, thus the "temperature" of the sputtered atoms can be compared to that of thermally produced atoms at 1800°C.

Mass Spectra

It was of interest to know what other ionic species are produced by the laser beam. Therefore, mass spectra were scanned over the mass range 0-300 amu near the resonant wavelengths for U and Sm. Figure 6 shows the results for Sm over a smaller mass region since no other peaks were found outside of this range. At the resonant wavelength of 602.72 nm, the Sm$^+$ peaks are observed in the expected isotopic abundances between masses 144 and 154. At higher mass, the SmO$^+$ peaks appear with almost equal intensity in spite of the fact that Ar$^+$ was the bombarding species. In fact, the SmO$^+$ peaks occur at all wavelengths produced by the dye laser, indicating a non-resonant ionization process. As an example, the top spectrum in Fig. 6 shows the effect of detuning the laser 0.2 nm, resulting in the disappearance of the Sm$^+$ signal with no change in the SmO$^+$ intensity.

Figure 7 shows similar results for U at 591.54 and 591.30 nm. The U$^+$ signal is sharply tunable, while what of UO$^+$ and UO$_2^+$ is not. These results suggest that residual oxygen is interacting with the sample to produce metal oxide species which are sputtered and ionized by the laser in a non-resonant process. The SIMS spectra of these metals under Ar$^+$ bombardment also show strong MO$^+$ and MO$_2^+$ peaks.

Future Studies

Future work will involve refinements of the ion optical system to obtain higher extraction and transmission efficiency of the laser generated ions. In addition, a more powerful laser system is being acquired to produce saturated resonance ionization over a larger volume. Investigations of different sample types will involve use of resin beads and small particles of Sm or U oxides, to test the capability of the technique for measuring real-life samples.

Acknowledgment


References


**Table 1. Optical Ionization Spectrum of Sm**

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Intensity</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>586.67</td>
<td>W</td>
<td>7F6 - H05</td>
</tr>
<tr>
<td>587.46</td>
<td>M</td>
<td>7F2 - 7F03</td>
</tr>
<tr>
<td>587.69</td>
<td>M</td>
<td>7F3 - 5G4</td>
</tr>
<tr>
<td>589.69</td>
<td>M</td>
<td>7F2 - ( )1</td>
</tr>
<tr>
<td>590.53</td>
<td>M</td>
<td>9D4 - 5H5</td>
</tr>
<tr>
<td>593.71</td>
<td>W</td>
<td>7F3 - ( )2</td>
</tr>
<tr>
<td>599.11</td>
<td>S</td>
<td>7F0 - 7D1</td>
</tr>
<tr>
<td>602.81</td>
<td>S</td>
<td>7F3 - 7H2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7F5 - 5G6</td>
</tr>
</tbody>
</table>
Fig. 1. Laser optics for resonance ionization of sputtered atoms.

Fig. 2. Electronics for data acquisition and laser control.

Fig. 3. Modified ion optics to extract and focus ions produced in a volume above the sample surface.

Fig. 4. Optical ionization spectra of $^{157}$Sm atoms produced by ion beam sputtering (top) and thermal filament atomization (bottom).