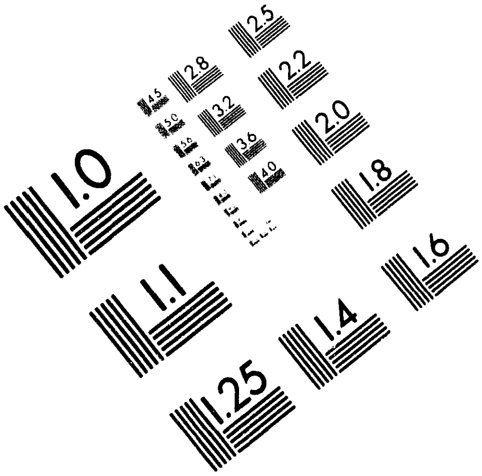

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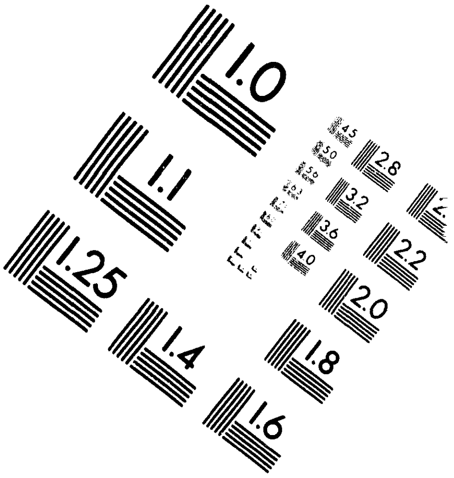

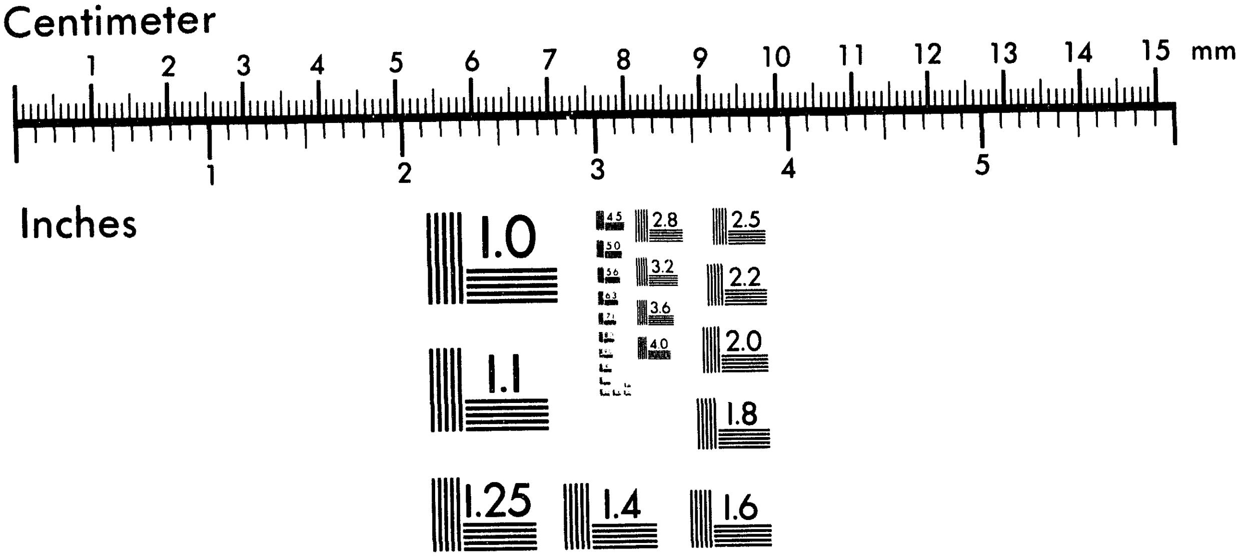

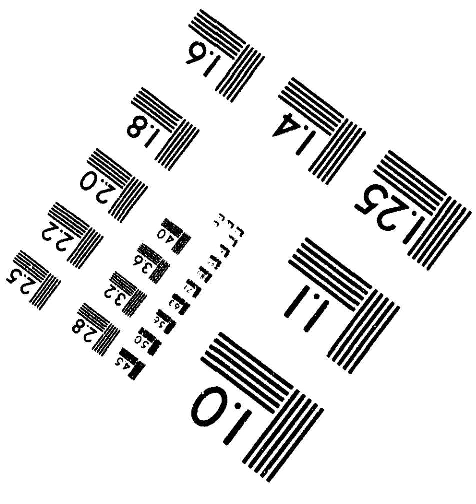

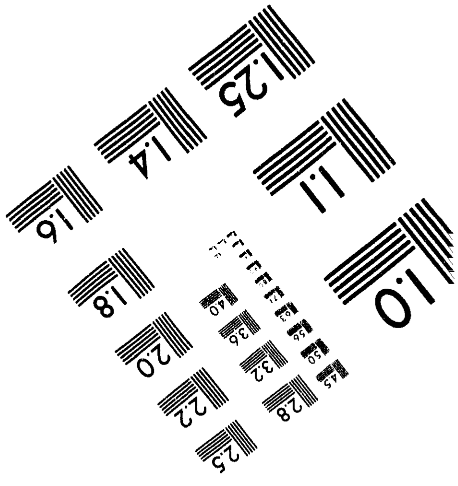

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Study of Laser Resonance Ionization Mass Spectrometry Using a Glow Discharge Source

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Abstract. The mass spectra of a metal alloy sample consisting of Al, Cu and Fe were studied using both glow discharge mass spectrometry (GDMS) and resonance ionization mass spectrometry (RIMS). Particular emphasis was placed on the reduction of isobaric interferences and discrimination between those ions formed by the discharge and those formed by the laser radiation.

INTRODUCTION

Previous applications of a glow discharge source as an atom reservoir for RIMS employed a system in which the laser interaction zone was contained within the negative glow region of the discharge plasma (1). As a natural extension, this study reports the first effort designed to couple a laser system, magnetic sector mass spectrometer, and glow discharge source in such a manner as to allow the resonance interaction of the sputtered atom population to be carried out external to the discharge source. A sample consisting of 63% Al, 25% Cu, and 12% Fe was examined using GDMS and RIMS, with particular emphasis on the reduction of isobaric interferences and discrimination between ions formed by the two processes.

INSTRUMENTATION

The experimental system used in this study was modified from a previously reported RIMS instrument (2). It included the laser system, the glow discharge source, the mass spectrometer, and the data collection electronics. An overview of this modified system is shown in Figure 1. Laser radiation from a tunable dye laser pumped by the second harmonic of a Nd:YAG laser was frequency doubled and tuned to the iron atomic transition at 302 nm. It had a pulse duration of 10 ns, a repetition rate of 10 Hz, and a bandwidth of 0.01 nm. The laser beam diameter was 3-4 mm with a pulse energy of 500 μJ. The unfocused laser ultraviolet (UV) radiation was directed in front of the glow discharge exit orifice, external to the source.

The mass spectrometer was a 90° 12-inch magnetic sector instrument with a nominal mass resolution of 600. The glow discharge device, operated with argon gas, was inserted into the source chamber, replacing the original thermal atomization source. The stainless steel housing served as the anode. The cathode was made of material under investigation in the form of an 8 mm pin. Discharge pressures from 0.1-1.2 torr were used, generating 1-6 mA currents with a voltage of 2.5 kV. The differential pumping system included two turbo pumps (110 l/s and 330 l/s) and an ion pump (140 l/s).

For the measurements in which only glow discharge ion signals were monitored, a Faraday cup was used as the collector. Signals from the Faraday cup were sent to a electrometer, and then through a digital voltmeter to the laboratory computer. When pulsed laser generated ions were monitored, an electron multiplier was used. Its signals were sent through a current preamplifier and a boxcar averager to the digital voltmeter.

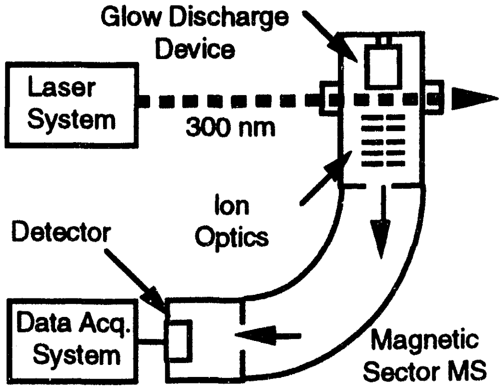
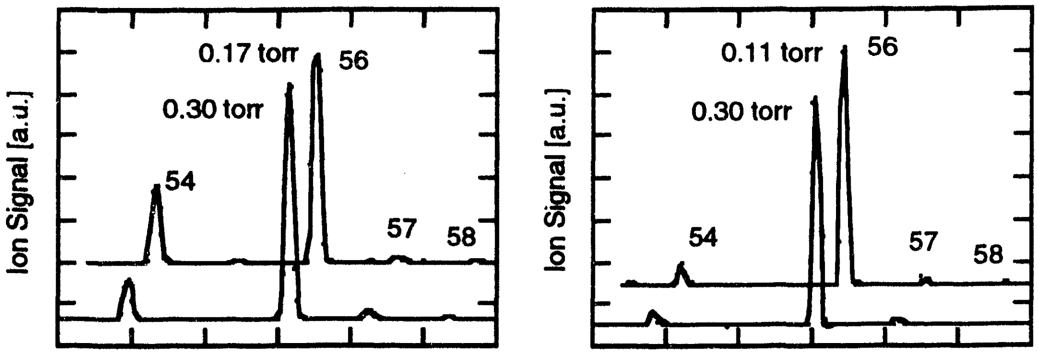


FIGURE 1. Experimental system of laser resonant ionization glow discharge mass spectrometry.

RESULTS AND DISCUSSION

Glow discharges provide sample atomization through sputtering of the cathode surface. Discharge pressures, currents, and voltages are closely related parameters, which play an important role in the study of GDMS. In this experimental system, the discharge voltage was held constant. This operation mode provides a direct relationship between the discharge pressures and currents, with higher currents resulting at higher pressures. Using the sample described above, the impact of different discharge conditions on the discharge mass spectra was investigated. Figure 2A illustrates the glow discharge mass spectra of iron isotopes without the laser. It is clear that the spectra are pressure dependent. The measured ^{56}Fe/^{54}Fe ratio, changing from 2.388 at 0.17 torr (~ 2 mA) to 6.127 at 0.3 torr (~ 3 mA), was much smaller than the 15.76 calculated from the relative natural abundance (5.82% ^{54}Fe, 91.7% ^{56}Fe, 2.19% ^{57}Fe, 0.33% ^{58}Fe). In the glow discharge, polyatomic and multiply charged species can cause isobaric interferences which limit the isotopic information available, especially when using mass spectrometer systems with limited resolution. The pressure dependent isobaric interferent present at nominal mass 54 would most likely come from



(A)

(B)

FIGURE 2. Mass Spectra of Fe isotopes by glow discharge ionization (A) and laser resonant ionization (B) at different pressures (currents) with a discharge voltage of 2.5 kV.

aluminum dimer, $^{27}Al_2^+$, which would also appear at nominal mass 54. To separate ^{54}Fe (53.9396 amu) and the aluminum dimer (53.9631 amu), the required instrument resolution would be on the order of 2-3000. Higher discharge pressures would produce a more collisionally active environment for the dimer, resulting in a greater probability of collisional dissociation of the dimer and a reduction in the mass 54 interferent, as is observed experimentally. Under the same experimental conditions, the mass spectra of copper showed no such pressure dependence as appeared in the iron spectra, indicating that the Cu ion signal is relatively free from isobaric interferences in the aluminum sample matrix. The measured $^{63}Cu/^{65}Cu$ ratios of 2.20 at a discharge pressure of 0.35 torr (~ 3.5 mA), and 2.21 at 0.15 torr (~ 1.5 mA) were consistent with the natural abundance ratio of 2.24 (69.2% ^{63}Cu, 30.8% ^{65}Cu).

To overcome the above interferent problem, the dye laser radiation was tuned to 302 nm for a specific atomic transition of iron (Fe $3d^64s^2\ ^5D_4$ -> $3d^74p\ ^5D_4$), thereby selectively ionizing this element and reducing the isobaric interferences. The spectra of the same mass range as Figure 2A using laser resonant ionization with the same aluminum matrix cathode sample are shown in Figure 2B. Although the pulsed laser shot to shot fluctuations are reflected in the spectra, they showed no pressure dependence, evidence that the interferent at mass 54 has been eliminated. Using laser resonance ionization, the measured $^{56}Fe/^{54}Fe$ ratios of 16.39 at 0.18 torr (~ 2 mA) and 16.27 at 0.3 torr (~ 3 mA) are in good agreement with the calculated natural abundance ratio within the experimental uncertainty.

When employing laser resonance ionization coupled with the glow discharge plasma, the laser generated ions must be identified and collected while discriminating against the background ions formed in the glow discharge. In the current experimental system, two types of discrimination methods were employed. The first method is to use discharge conditions for enhancing laser produced ions while reducing glow discharge ions. Signal dependence on pressure is shown in Figure 3 for both types of ions. The RIMS signal peak is observed at a pressure of about 0.2 torr, while the peak signal for glow discharge ions is approximately at 0.8 torr. Using lower pressures appears favorable for both enhancing the laser resonant ionization signal and discriminating against the glow discharge ions.

The second discrimination method is to use differences in ion energy between the glow discharge ions and laser ions. In this experimental system, the interaction of the laser radiation with the sputtered atom population was carried out external to the glow discharge source. Therefore, the laser generated ions would be in a different spatial volume and acquire different energy than the glow discharge ions. The discrimination between the two types of ions is achieved by changing ion focusing. A more elaborate method would prevent the discharge ions from entering the extraction region of the mass spectrometer by placing a grid with proper potential between the discharge source and the laser interaction region.

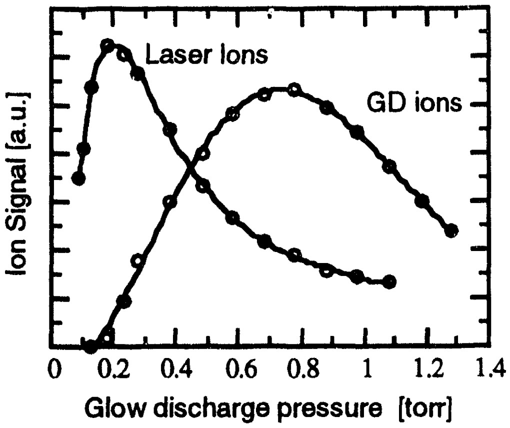


FIGURE 3. Pressure dependence of glow discharge and laser ion signals at fixed discharge voltage.

CONCLUSION

Resonance ionization of material sputtered from the cathode surface of a glow discharge with laser ionization external to the discharge cell has been demonstrated for the first time. This technique has illustrated the ability to reduce isobaric interferences present in GDMS by selective laser ionization, and to provide a detectable RIMS signal of ^{58}Fe at 400ppm. Although the potential for analytical utility is present in the technique, the method requires further investigation and refinement before this utility may be realized.

ACKNOWLEDGMENTS

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