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Detection of Arsenic by Resonance Ionization Mass Spectrometry

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Abstract

This is the final report of a two-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The development of sensitive analytical techniques for environmental analysis is a problem of immediate interest. Waste residues containing heavy metals such as chromium, lead and arsenic are particular problems due to their widespread usage and sometime incomplete recovery or inadequate storage. The objective of this project was to apply resonance ionization mass spectrometry (RIMS) to the detection of trace levels of arsenic.

1. Background and Research Objectives

Detection of As in environmental matrices is important because of the toxicity of arsenical compounds and their widespread presence in all phases of the ecosystem - soil, water, and air. Commercial production and use of inorganic and organic arsenic compounds have raised local concentrations of this element well above the natural backgrounds levels, particularly in soils and ground water. Common methods of arsenic determination generally require extensive extraction, separation, derivatization, and pre-concentration steps prior to actual analysis. Resonance-ionization mass spectrometry (RIMS) offers the possibility of reducing the amount of sample pretreatment required because of its selectivity and sensitivity. The RIMS technique is a selective ionization method that is particularly well suited to the analysis of heavy metals in a variety of samples.

The intent of this work was to develop methods for the quantitation of trace metals in the environment. Initial effort was directed toward the detection of arsenic and arsenic compounds by laser mass spectrometry. Laser mass spectrometry provides a method for the selective ionization (laser photoionization) followed by mass spectral sorting and detection for isotopic and elemental analysis of trace components in complex mixtures. Since the first report of laser action, it has been recognized that laser ablation (evaporation/volatilization) may

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provide a useful sampling mechanism for chemical analysis [1-4]. In particular, laser ablation is rapidly gaining popularity as a method of sample introduction for mass spectrometry [5-9].

2. Importance to LANL's Science and Technology Base and National R&D Needs

The development of sensitive analytical techniques for environmental analysis is a problem of immediate interest to both LANL and nationally across the DOE complex. This project supports the Laboratory's core competency in Earth and Environmental Systems and enhances the ability of the Los Alamos to respond to initiatives requiring environmental analyses.

3. Scientific Approach and Results to Date

Since its original description, numerous research papers and review articles have appeared on various aspects of laser mass spectrometry. Several attributes are characteristic of laser mass spectrometry. No background is introduced due to bulk heating of the sample, though depth profiling can certainly be accomplished. Spatial resolution can be very good, limited only by diffraction of the incident beam (typically on the order of 1 μm in diameter) and, at high fluxes, cratering of the surface (typically on the order of 10 μm). This capability can be very important for small samples and for samples containing inhomogeneously distributed components. Little sample preparation is needed. Conventional wet analytical samples can be dried on a sample introduction device and non-conventional samples can also be introduced directly into the source region of the mass spectrometer. Sensitivity is excellent, and the detection limit frequently falls in the femtogram to attogram (absolute) or sub-parts-per-billion range. The possibility also exists for absolute measurements without recourse to standard samples.

While most laser ablation/mass spectrometry has been performed with fixed frequency lasers operating at relatively high intensities/fluences (greater than 10^8 W/cm^2 greater than one J/cm^2), we have chosen to implement the use of tunable lasers to enhance the ionization yield of selected components in an analytical sample. This process has been termed resonant laser ablation (RLA) [10-14], and typically relies on irradiation of a sample in a mass spectrometer with modest intensity laser pulses tuned to a one- or two-photon resonant transition in the analyte of interest. In one early study, a tunable dye laser was interfaced to a commercial laser microprobe apparatus to examine resonant excitation effects in metal-doped polymers [14]. At intensities in the range 10^9 - 10^{11} W/cm^2 , a two-order-of-magnitude improvement in detection

limit was observed with significant selectivity (preferential ionization of the targeted metal atom). In another early experiment, a 70-fold enhancement in ionization yield was observed for resonant laser ablation of sodium and copper at intensities greater than 10^8 W/cm^2 [15]. In this latter work, indirect spectroscopic evidence (no mass spectrometer was used) suggested that sodium dimer was also being preferentially ionized. In both of these studies, the use of one-photon resonances and relatively high intensities resulted in substantial power broadening of the observed resonant transitions and modest selectivity. More recently, Ledingham's group has begun a systematic study of the process on a variety of materials [10,12,13,16,17]. Potential advantages of RLA include: (1) simplification of the mass spectrum, by enhancement of signal from the analyte of interest; (2) improvement of the absolute detection limits by improving the ionization efficiency; and (3) improvement in relative sensitivity. The sensitivity enhancement results from reduction of spurious signal, and accompanying noise, in the detection channel. This spurious signal may be due to bleed through from adjacent mass channels, or from isobaric interferences. The RLA technique tends to produce higher mass resolution because of minimal spatial spread in the ion source and small space charge effects.

We initially implemented RLA for the detection of As in multilayer GaAs/AlGaAs samples. Arsenic could easily be detected in this work, but was difficult to quantitate. In order to quantitate and understand the process better, we began an exploration of a simpler system, i.e., single-crystal silicon (1, 1, 0) wafers overcoated with 20 Å of copper. We had previously demonstrated the facile detection of copper via a "2+1" (photons to resonance + photons to ionize) resonance-ionization process. Initial results (Figure 1) showed the detection of both silicon and copper when the sample was irradiated with low-energy laser pulses (8 μJ) tuned to the two-photon copper resonance at 465 nm. We observe both the resonant copper transition, as well as non-resonant contributions from silicon, sodium and potassium. These are impurities present in the sample and their presence was perhaps enhanced by excessive manual manipulation. These components are observed because of their high volatility, low ionization potential, preferential segregation at the surface, and presence on the surface as ionic compounds. They are thus easily vaporized, and ionized, by low-order non-resonant multiphoton processes. Figure 2 shows the temporal evolution of the copper signal obtained from the same sample, i.e., a single crystal overcoated with approximately 20 Å of copper. The laser pulse energy was also monitored, with a photodiode viewing a beam split fraction of the beam, as was the potassium (nonresonant) signal. The copper signal rises with the laser pulse energy (at approximately point number 75), decreases slowly for a period, and then is reduced to near zero (at approximately point number 500). The dip observed in the copper signal (at approximately point number 125) was due to insertion of the laser power meter into the beam in order to obtain an absolute pulse energy measurement. The reduction at point

number 500 is due to erosion of the copper coating by the incident laser beam. Based on this data, we obtain a removal rate from copper of 0.005 mL/shot. The slight increase in the potassium signal concomitant with the reduction of the copper signal suggests that potassium is segregated at the copper/silicon interface.

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Fig. 1 Mass spectrum obtained from interrogation of a copper-coated silicon-wafer surface irradiated with $8\mu\text{J}$ laser pulses tuned to the two-photon copper resonance at 465 nm.

Fig. 2 Time dependence of the copper-ion signal obtained from a copper-coated silicon-wafer surface irradiated with 8 μJ laser pulses tuned to the two-photon copper resonance at 465 nm.