Laser Ablation – Ion Storage Time of Flight Mass Spectrometry

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Abstract

A new mass spectrometer system was developed for studying laser ablation and performing analytical chemistry. The system is based on an ion trap used in an ion-storage (IS) mode, coupled with a reflectron time of flight mass spectrometer (TOFMS). The LA-IS/TOF-MS can be used for MALDI or direct ionization of samples on a probe tip. This paper will describe the system configuration and related operating principles for measuring sensitive and accurate isotopic ratios. Preliminary measurements identified ultra-trace contaminants of Ag, Sn, and Sb in a Pb target with single laser-shot experiments. Survey analyses of uranyl acetate, hair samples, and mushrooms demonstrated that this technology can be applied to a wide range of sample materials.

Introduction

Direct analysis of solid and particle compositions is an important component of environmental and proliferation-signature monitoring. For single particle analysis, excellent detection sensitivity must be available because of the limited absolute mass and concentration from a micron-sized particle. An efficient and sensitive approach would be to perform direct analysis of the suspect particle once it was identified. This scenario is the basis for our instrument using laser ablation inside an ion-storage time-of-flight mass spectrometer (IS/TOF-MS) with an imaging system to observe, select, vaporize, ionize and analyze individual particles or spatial locations on a solid surface.

Laser ablation inside the cavity of an ion trap was used to provide direct atomic mass spectrometric analysis of particulate samples (1). However, this work did not include an imaging system to selectively control where the laser beam ablated the sample, and a TOF was not used. Ramsey developed a novel technology for injecting single droplets (or particles) into an ion-trap

and then subsequently timed the firing of a laser beam to ablate the injected droplet (2). Freiser used FTICR MS coupled with laser sampling for laser ablation and ionization inside the trap of the spectrometer (3,4). Our CCD based microscope camera system allows us to view inside the ion-trap and position the laser beam before acquiring the mass spectrum. In this way, we select the particle (s) or section of a bulk solid to be analyzed and ignore the majority of the mass, the background. The system also is suited for MALDI; the analyte is embedded in a matrix that absorbs the laser light and energy transfer mechanisms are responsible for ionization (5). In our LA-ISTOF-MS, the particles are directly ionized by the short pulsed, high-fluence laser beam. Descriptions of the system and preliminary data are presented in this manuscript.

Experimental System

The laser ablation ion-trap mass spectrometer system with imaging capabilities was developed in house using a combination of commercial components. Figure 1 shows a diagram of the overall system. The ion-storage time-of-flight is a modified system developed by Chambers, et. al. using a conventional ion trap electrode and a reflectron TOF MS (6). The ion trap ring electrode was drilled with three small holes, two placed at 180 degrees apart and the third placed above one of the on-axis holes. The sample chamber is generally at 10^{-4} torr and the reflectron TOF MS is at 10^{-5} – 10^{-6} torr. Air is used to back-fill the sample chamber. A probe containing the sample is directly inserted into the center ring of the ion trap. The laser beam enters the trap on the probe axis, at 180^{o} to the probe. The system contains a CCD imaging camera/microscope for viewing the sample inside the ion trap; the CCD is slightly off axis from the laser beam and views the probe tip. The CCD microscope allows observation of samples on the probe tip down to approximately 30 μm in diameter. The laser-beam spot size at the target plane is approximately 10 microns in diameter and remains uniform in its spatial extent across the 3 mm diameter probe tip. The photos in figure 2 demonstrate the imaging and laser focusing capabilities of the system.

The laser used for ablation (ionization) was a Quanta-Ray GCR-130 Nd:YAG with the third harmonic (λ = 354 nm). The pulse duration was approximately 6 ns. A Newport 935-10 variable attenuator was used to control the laser energy. One of the critical issues was that of timing between firing of the laser and the rf cycle of the mass spectrometer. The laser can be fired into the trap at a controlled and variable phase of the rf-trapping cycle (figure 3). By

varying the phase, the ions are trapped at different spatial positions in the trap, which has an effect on the mass resolution and space charge.

The imaging system was a HiScope compact microvision system, model KH 2200 MD2 with a MX 400 lens and L-8X extender (8cm). This microscope system contains an on-axis CCD camera.

Discussion

The initial certification of the system was to verify its mass spectrometric performance when using an ion-trap ring-electrode with holes. We did not experience any limitations or distortions for trapping ions because of these holes, based on spectra acquired using the conventional electron impact ionization and organic and inorganic reference samples. The same mass resolution and sensitivity was measured by using ring electrodes with and without the three holes.

For ablation studies, Pb, Cu or Au foil was used as test samples to establish optimum MS properties and laser conditions. Laser irradiance was found to be a critical parameter effecting the entire process; ablating a controlled and reproducible level of ions. Because of non-linear, threshold ionization mechanisms, small changes in the laser irradiance led to a large difference in the MS signal intensity. For these foil samples, we found that only a few μJ's of energy was sufficient in most cases for generating reproducible signal levels. The laser-beam spot size was approximately 12 μm, which provides an irradiance of approximately 1 GW/cm^2. The mass spectra in figure 4a show the reproducibility of the primary Pb isotopes, for five separate laser pulses at five locations on the Pb foil. The reproducibility of ion generation by laser ablation was improved considerably by running the laser flashlamps at their specified rate, and using the sync-out from the MS to trigger the laser Q-switch. The improvement in the pulse-to-pulse stability of the YAG laser when fired using this approach significantly benefits the reproducibility when averaging successive mass spectrometric scans. The relative standard deviation for the Pb ions in figure 4a spectra was 4 – 5%. Figure 4b shows the impurities in the Pb sample; trace contaminants of Ag, Sn, and Sb were identified in the Pb foil with a single laser-shot experiment.

A primary advantage of this system for sensitivity is that the ions are generated directly inside the ion trap. However, in this case, the ion trap can not used as the mass spectrometer because of space charging effects. When we originally ablated inside an ion-trap mass

spectrometer (ITMS), space charging was a critical issue. Instead, the ion-trap is only used as a storage device and the TOF performs the mass spectrometry. In this case, space charging has been found to be almost eliminated, except in cases of using extremely high laser fluence, which was not necessary for sensitivity. A preliminary demonstration of sensitivity was conducted by measuring the volume from a crater created by a single laser pulse with 10 μJ of energy and 12 μm spot size. The crater volume correlated to approximately 800 pg of mass ablated for each laser pulse on the copper target. Based on the signal level recorded, and the background sensitivity of the instrument, the theoretical limit of detection would be 5 pg. This is a worst case scenario, it assumes that all of the ablated mass was ionized and trapped.

Finally, we were successful in using the laser to vaporize sample into the gaseous state, and use electron impact as the ionization scheme. Several organic samples (benzophenome, cholesterol,) were analyzed in this manner and characteristic spectra matching library data were recorded. This approach would be similar to a MALDI experiment, with imaging capability.

Conclusion

Preliminary studies have demonstrated the capabilities of this new LA-IS/TOF-MS. Reproducible spectra were measured with only approximately 10 μJ of laser energy. The imaging system provides a spatial resolution of approximately 12 μm with the ability to guide the laser beam to a specific location on a target sample, including a single particle. Improved reproducibility was obtained by controlling the timing between the laser pulse and the rf-cycle of the ion-trap. In terms of fundamental laser ablation studies, the system provides excellent sensitivity which should be suitable for measuring ionization thresholds and ion-energy distributions from complex targets, as a function of laser parameters. Ionization yields can be determined by varying the laser energy and wavelength. In addition, the pressure and ambient gas environment in the differentially-pumped ion trap region can be varied to study ion quenching and ion-ion plasma interactions. Such studies are currently underway.

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References

1. Gill, C.G.; Daigle, B.; Blades, M.W. Spectrochimica Acta 1991, **46B**, 1227-1235.
2. Yang, M.; Dale, J.M.; Whitten, W.B.; Ramsey, J.M. Analytical Chemistry 1995, **67,** 4330-4334.
3. Freiser, B.S. Talanta 1985, **8B**, 697.
4. Cody, R.B.; Burnier, R.C.; Reents, W.D.; Carlin, T.J.; McCrery, D.A.; Lengel, R.K.; Freiser, B.S. Int. J. Mass Spectrom. Ion. Phys. 1980, **33**, 37.
5. Qian, M.G. and Lubman, D.M., Analytical Chemistry1995 **67**, , 234A- 242A.
6. Chambers, D.M.; Grace, L.I.; Andresen, B.D. Analytical Chemistry 1997, **69**, 3780-3790.

Figure Captions:

1) Schematic diagram of ion-trap portion of mass spectrometer showing probe port for sample, port for laser input and CCD camera port for imaging.

2) Examples of images showing laser ablation craters in hair and alloy samples.

3) Timing diagram for laser firing versus rf cycle of the ion-trap.

4) A) Mass spectra showing the reproducibility of the primary Pb isotopes, for five separate laser pulses at five locations on the Pb foil. The relative standard deviation for the Pb ions was 4 – 5%. B) impurities in the Pb sample; trace contaminants of Ag, Sn, and Sb were identified in the Pb foil with a single laser-shot experiment. The laser-beam spot size was approximately 12 μm, which provides an irradiance of approximately 1 GW/cm^2.