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# Direct Laser Ablation and Ionization of Solids for Chemical Analysis by Mass Spectrometry

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**Abstract.** A laser ablation/ionization mass spectrometer system is described for the direct chemical analysis of solids. An Nd:YAG laser is used for ablation and ionization of the sample in a quadrupole ion trap operated in an ion-storage (IS) mode that is coupled with a reflectron time-of-flight mass spectrometer (TOF-MS). Single pulse experiments have demonstrated simultaneous detection of up to 14 elements present in glasses in the ppm range. However, detection of the components has produced non-stoichiometric results due to difference in ionization potentials and fractionation effects. Time-of-flight secondary ionization mass spectrometry (TOF-SIMS) was used to spatially map elemental species on the surface and provide further evidence of fractionation effects. Resolution ( $m/\Delta m$ ) of 1500 and detection limits of approximately 10 pg have been achieved with a single laser pulse. The system configuration and related operating principles for accurately measuring low concentrations of isotopes are described.

## 1. Introduction

Laser ablation is one of the leading areas being investigated for direct solid sample analysis. Direct chemical analysis of solids without chemical pretreatment can offer many advantages for the analytical chemist. Elimination of chemical solvents and wastes, reduced sample handling, and faster analysis times are some of the motivations for developing such techniques. Focusing a short pulse laser beam onto a sample will create an explosion that produces atoms, ions, clusters and particles<sup>1-3</sup> for direct analysis by mass or optical spectrometry, or introduction into an ICP-MS. The spatial resolution of the laser beam makes this an excellent technique for chemical mapping, however, excellent detection sensitivity is required due to the limited absolute mass and concentration from small spot sizes.

Laser ablation ionization for direct introduction into a mass spectrometer has been reviewed in several excellent references.<sup>4,5</sup> Numerous types of mass spectrometers have been used for detection, including time-of-flight, Mattauch – Herzog, magnetic sector, FT-MS, quadrupoles, and ion traps. Most of these systems have used external ablation/ionization followed by aerosol introduction into the mass spectrometer. Laser ablation has also been performed inside the cavity of an ion trap for direct mass spectrometric analysis of bulk and particulate samples. Gill and Blades investigated the ablation of metals, ceramics and polymers inside the ion trap, demonstrating the capability to perform atomic and molecular mass spectrometry.<sup>6,7</sup> Gill et al. followed by demonstrating the power of resonant laser ablation for selective ablation/ionization of metals in the ion trap.<sup>8</sup> Ramsey et al. demonstrated the capability of ablating single droplets (or particles) injected into an ion trap.<sup>9,10</sup> Song et al. applied laser

ablation inside an ion trap mass spectrometer for the analysis of rare-earth elements in soil samples with scans averaged 100 times.<sup>11</sup>

Although the ion trap functions as a scanning mass spectrometer, it can also be used as a storage device for preconcentration of ions as a front end for injection into a time-of-flight mass spectrometer.<sup>12</sup> The ion trap can store a large range of masses or be used to selectively store narrow mass regions, thus reducing background interferences from sample matrices. However, the ion trap is limited by the number of ions that can be stored and by space-charge effects. When high resolution over a large mass range is required, the scan times can be lengthy and may be a limiting factor for some applications. TOF spectrometers provide excellent resolution of short pulse injected ions over extended mass ranges. These instruments can use gated sample introduction but are incapable of ion storage and accumulation. Lubman et al. developed the hybrid ion-storage time-of-flight mass spectrometer (IS-TOF-MS) which takes advantage of the storage capabilities of the ion trap and the speed and resolution of the time-of-flight.<sup>13,14</sup>

The goal of our research is to develop a system capable of achieving good sensitivity for detection of laser generated ions.

## 2. Experimental

The IS-TOF-MS system in our laboratory has been previously described.<sup>15,16,17</sup> A brief description is presented here. The Nd:YAG laser used for ablation/ionization is introduced radially into the ring electrode of a quadrupole ion trap. A sample is introduced into the ring electrode from the opposite direction and the laser beam generates ions directly inside the ion trap. Ions are stored and then ejected axially through one of the end cap electrodes into a reflectron TOF mass spectrometer.

A PHI TRIFT III time-of-flight secondary ion mass spectrometer was used to collect the TOF-SIMS spectra. A beam of 25 keV Ga<sup>+</sup> ions was incident upon the surface, and ejected positive secondary ions were mass analyzed by their time of flight through a three bending magnet trajectory. The analysis was performed under static conditions (ion dose  $\sim 10^{10}$  ions/cm<sup>2</sup>) using a pulsed beam. Images are 30  $\mu\text{m}$  x 30  $\mu\text{m}$ , with 400 nm spatial resolution. The mass resolution of the peak for Ba<sup>+</sup> ions is  $\Delta m/m > 1000$  on the barium silicate glasses.

## 3. Results and Discussion

A series of NIST standard reference material glasses (SRM 1873: K-963, and SRM 611) containing trace impurities (0.003% up to 1% by weight) have been analyzed with laser ablation ion-storage time-of-flight mass spectrometry (LAISTOFMS) and time-of-flight secondary ion time-of-flight mass spectrometry (TOFSIMS). The two materials differ primarily in their matrix composition, with K-963 being a barium-silicate, while SRM 611 is predominately a silicate.

Figure 1 shows a mass spectrum acquired with the LAISTOFMS on K-963. The spectrum is dominated by barium, with none of the trace species (present at 0.06-0.95 wt%) detectable. Electron microprobe analysis was performed which confirmed that indeed these trace species were present in the material. By contrast, the mass spectrum acquired on SRM 611 in Figure 2 shows a wealth of the trace species, predominately Rb and Sr (present at  $\sim 0.05$  wt%), with the Si matrix undetectable. These species are observed, despite their much lower abundance in SRM 611. Several factors may contribute to the difference in these two spectra. The Ba present in K-963 is both easily ionized (IE = 5.2 eV) and in high abundance, and may have saturated the ion trap, screening out the trace species. The proximity of its mass to that of the other trace species in the material that were of interest precluded the possibility of tuning the ion trap RF voltage to screen it out. By contrast, Si has both a higher ionization energy (IE = 8.2 eV) and due to its lower mass, could effectively be screened out of the ion trap by increasing the RF voltage.

Scanning electron microscopy (SEM) images of craters in the two different glasses were quite different. In the case of the K-963 glass, significant melting and splattering near the vicinity of the ablation crater was observed. These melting/splattering effects are often believed to be the source of elemental fractionation during laser ablation sampling. By contrast, SRM 611 revealed less

melting/splattering in the crater vicinity and appeared to show more fracturing of the glass. These results cannot be explained simply on the basis of the relative melting points of the two glasses. The weighted average melting points determined for these two glasses were actually quite comparable to one another, differing by less than 100°C.

To gain further insight into processes occurring on the surface of these glass samples during ablation, samples were examined by and elemental surface mapping was carried out using TOFSIMS. This analysis focused on barium-silicate glasses (SRM 1873: K-458, K-489, and K-963), given the significant melting observed in these samples. Figure 3 shows elemental maps of Ba and Si near the ablation crater in K-489 glass. These images have been normalized by the total ion count, so as to eliminate topological effects associated with crater profile from the apparent elemental abundance. An apparent local enrichment in Ba concentration was seen near the ablation crater, with a corresponding depletion in Si. There was also a more subtle depletion of Pb in this region. These effects may reflect surface segregation that occurs upon melting and subsequent recrystallization within the crater region. Similar effects were seen in the other two glasses examined – K-458 and K-963.

To further explore the role of matrix effects on elemental sensitivity, another NIST standard reference material was examined. Figure 4 shows a mass spectrum of this coal fly ash sample (SRM 1633b) obtained with the LAISTOFMS. Several trace species were detectable here, including the easily ionized Sr and Ba (5.7 eV, 5.2 eV), as well as U/ $\text{UO}_x$ , with U present at levels of only ~ 10 ppm (nominally). The observation of other trace species in the spectrum rules out the notion that the sample examined was inhomogeneous and that the ablated spot was anomalously rich in U. The observation of uranium and its oxides may relate to its composition within the powder source material, as well as storage time effects within the ion trap. We have previously observed a shift in the mass spectrum towards oxide species as the storage time increases from the 10s of  $\mu\text{s}$  time range to 10s of ms. This result again illustrates the importance of screening out the matrix element (predominately carbon in this case) to achieve high trace element sensitivity.

#### 4. Conclusions

Trace impurities (< 0.05 wt%) were detected in a silicate glass reference material, while similar impurities were undetectable in a barium-silicate glass, in which the matrix species dominated. Significant melting and splattering was observed in the barium-silicate glasses, perhaps reflecting their stronger optical absorption in the 266 nm regime. TOFSIMS analysis revealed an apparent local enrichment in barium concentration near the ablation crater, with a corresponding depletion of silicon, perhaps indicative of surface segregation effects in the melt region. Trace quantities of U/ $\text{UO}_x$  (~10 ppm) were detected along with other trace species (Sr, Ba) in a coal fly ash sample (SRM 1633b), demonstrating the sensitivity of the LAISTOFMS technique. The key to achieving high sensitivity with the LAISTOFMS appears to be screening out the matrix elements. This result, coupled with the high sensitivity observed for U detection, suggests that with proper tuning, the technique could be used for isotopic distribution measurements in enriched U samples.

#### 5. Acknowledgments

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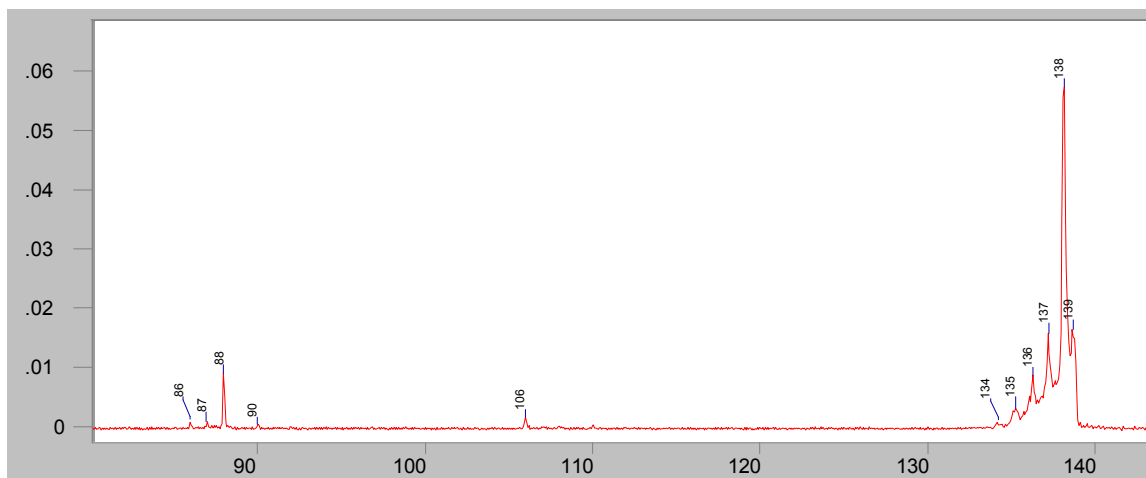


Figure 1. LAISTOFMS spectrum of barium-silicate glass K-963.

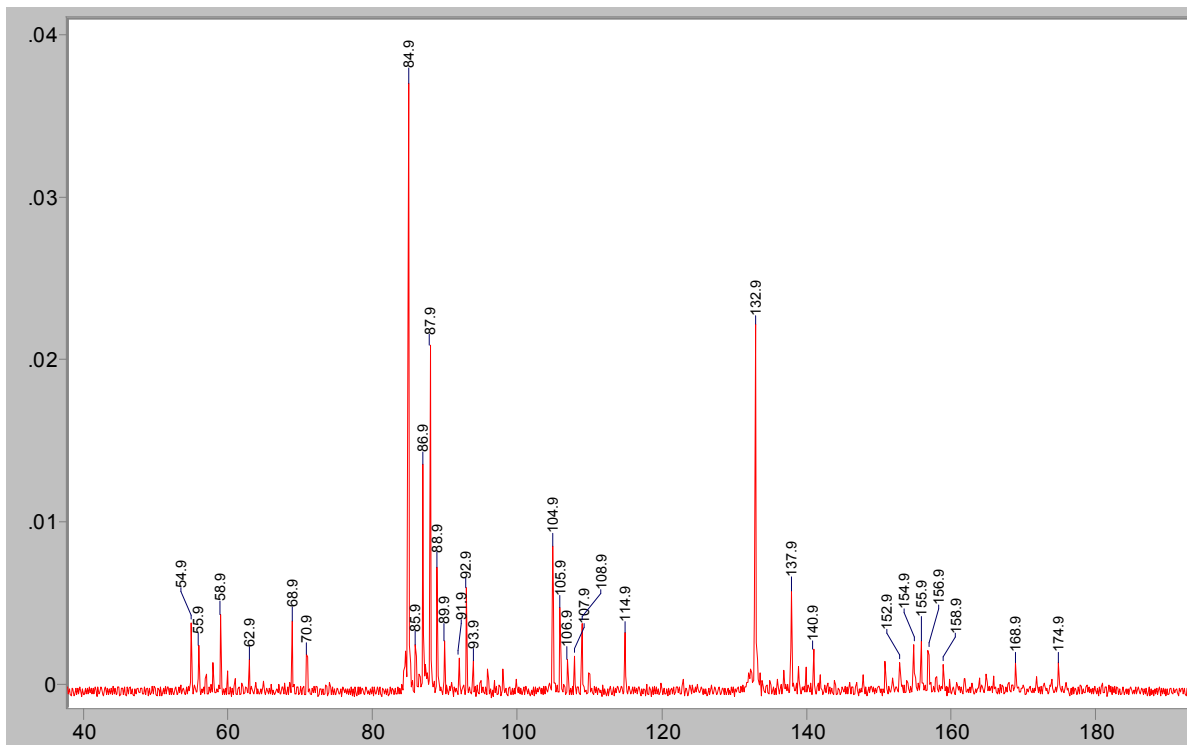


Figure 2. LAISTOFMS spectrum of silica glass NIST SRM 611.

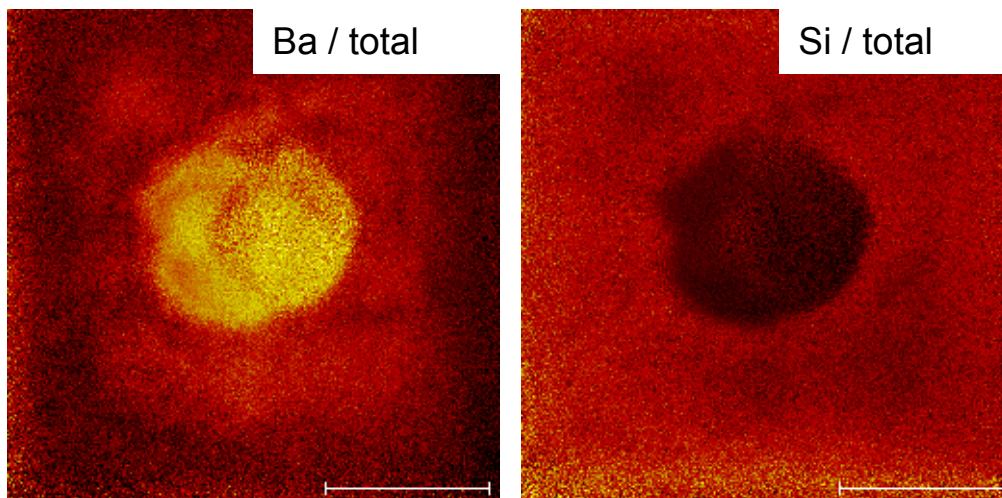


Figure 3. TOFSIMS elemental maps near craters in K-489 glass. Image dimensions are 30x30 $\mu$ m and are total ion count normalized.

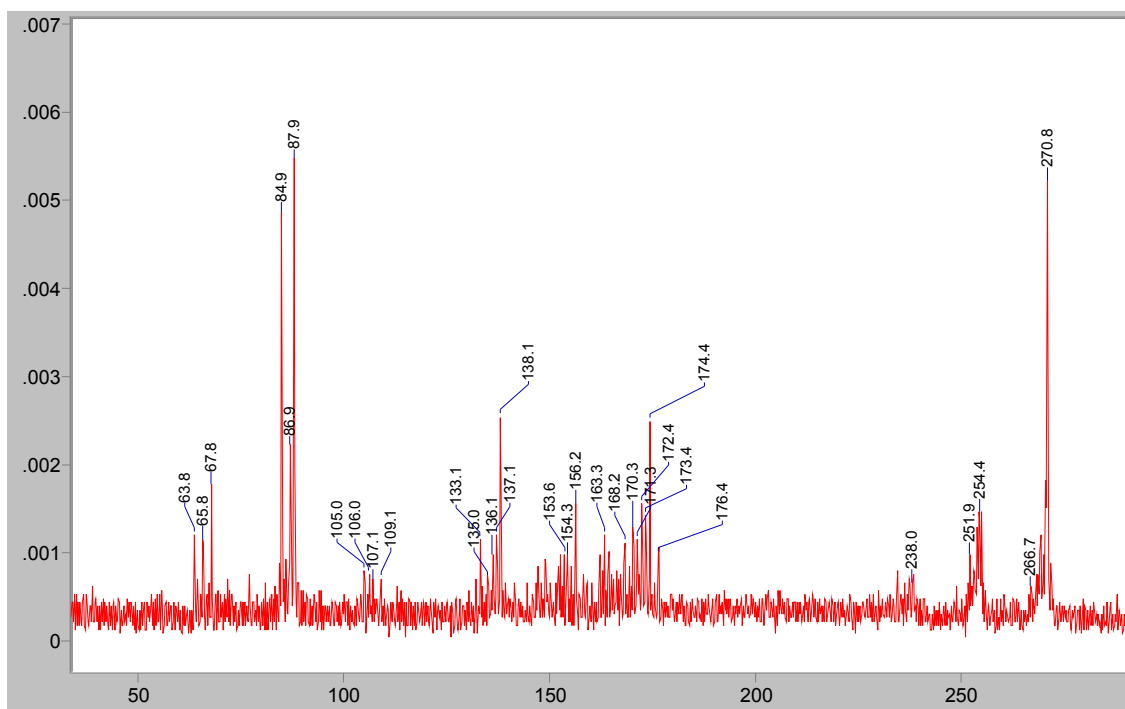


Figure 4. LAISTOFMS spectrum of coal fly ash NIST SRM 1633.