

Two-step Laser Time-of-Flight Mass Spectrometry to Elucidate Organic Diversity in Planetary Surface Materials.

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Introduction: Laser desorption/ionization time-of-flight mass spectrometry (LD-TOF-MS) holds promise to be a low-mass, compact *in situ* analytical capability for future landed missions to planetary surfaces. The ability to analyze a solid sample for both mineralogical and preserved organic content with laser ionization could be compelling as part of a scientific mission payload that must be prepared for unanticipated discoveries. Targeted missions for this instrument capability include Mars, Europa, Enceladus, and small icy bodies, such as asteroids and comets.

Some of these planetary surfaces could be expected to be host to endogenous organic materials. Exogenous delivery of meteoritic materials are an additional important source of organic material on planetary surfaces. Studies of meteorites, their parent bodies, and simulants strongly indicate that an *in situ* analytical investigation would be likely to encounter a diversity of organic species across classes, including (but not limited to) polycyclic aromatic hydrocarbons (PAHs), carboxylic acids, amino acids, nucleobases, and high molecular-weight kerogen-like material. For a broadband detection technique such as LD-TOF-MS, this complexity can pose a challenge: how can we confidently interpret individual peaks within a populated mass spectrum? Recent efforts to explore new LD-TOF-MS operational features has improved our ability to interpret diverse mass spectra that are complicated by the presence of isomolecular interferences.

The instrument has been described in detail previously [1,2]. In the simplest configuration, a pulsed ultraviolet (UV) laser (at 266 nm, 337 nm, or 355 nm) is focused at the surface of a solid sample to desorb analyte into the gas phase and produce ionization through a multi-photon process. The ions are accelerated into the TOF-MS analyzer, and separate according to mass-to-charge ratio before reaching the microchannel plate detector. A curved field reflectron [3] is used to achieve longer path lengths and mass resolution exceeding $m/\Delta m$ of several hundred in a compact instrument envelope measuring only 6.5 cm in diameter and \leq 30 cm in length. We estimate that a flight instrument of only 5-6 kg is possible.

LD-TOF-MS is a technique by which sample composition can be analyzed directly from a solid surface. In a mixed sample, the resulting mass spectrum contains mass signatures of inorganic and organic content, and assigning peaks to specific species with high con-

fidence can be challenging without additional elucidating spectrometric techniques. Towards the development of advanced spectrometric methods compatible with an *in situ* investigation, we have demonstrated [4] the implementation of two-step laser desorption/ionization mass spectrometry (L2MS) as a means of introducing compound class-specific detection of aromatic species in the presence of inorganic constituents, such as salts.

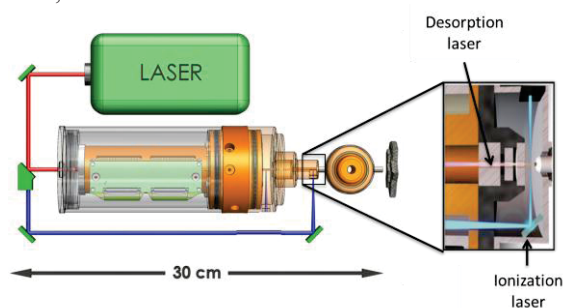


Figure 1. Our LD-TOF-MS prototype has been recently shown to be compatible with advanced mass spectrometric techniques, such as two-step laser desorption/ionization or L2MS.

The L2MS technique employs two laser pulses to sequentially desorb and ionize surface species prior to their extraction and analysis as described above. In a testbed instrument, we have used the fundamental frequency of a pulsed Nd:YAG laser (1064 nm, pulse width \sim 5 ns) to generate a plume of desorbed species from a solid sample surface. After a delay of 100 ns to 3 μ s, an ionization laser pulse is directed orthogonally to the desorption pulse, intersecting the plume with ultraviolet photons at the fourth harmonic of a Nd:YAG laser (266 nm). This process is selective to species, such as aromatic organics, that can be ionized through resonance-enhanced multi-photon ionization (REMPI).

As has been reported in previous work [5,6], the use of postionization techniques can offer some clarification of the sample composition. In particular, L2MS using a pulsed infrared desorption laser and pulsed ultraviolet ionization laser offers two advantages, compared to UV LD-TOF-MS: (1) fragmentation can be minimized, as this is a resonance-enhanced ionization process, and (2) the technique is selective to those species that have excited states that are resonant with the UV photon energy, namely aromatic compounds. Recently, we have implemented L2MS on a compact

prototype and demonstrated selectivity and minimal fragmentation in an instrument package that is compatible with future *in situ* science [4].

Demonstration of L2MS : We have modified an existing LD-TOF-MS testbed (of the same scale as shown in Figure 1) to demonstrate L2MS using a series of chemical standards. One such standard is pyrene, a commonly detected polycyclic aromatic hydrocarbon (PAH) found in primitive solar system materials and likely to be a measurable component of the organic contribution to differentiated planetary surfaces by meteoritic infall.

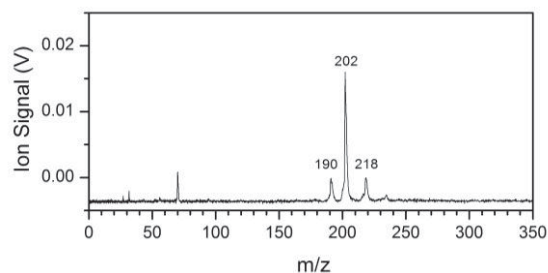


Figure 2. The pyrene spectrum in L2MS analysis is clearly dominated by the molecular ion at m/z 202.

The molecular weight of pyrene is 202 Da, and in L2MS analyses of pyrene standard, the dominant peak is that of the molecular ion. Single-laser LD-TOF-MS (not shown) captures the inorganic content of a given sample containing pyrene [4], and even the pyrene standard contains salt cations, such as sodium and potassium, which can dominate the mass spectrum in single-laser mode. L2MS, in contrast, clearly reveals the organic of interest with minimal fragmentation, and the inorganic species can be suppressed for ease of spectral interpretation in L2MS mode.

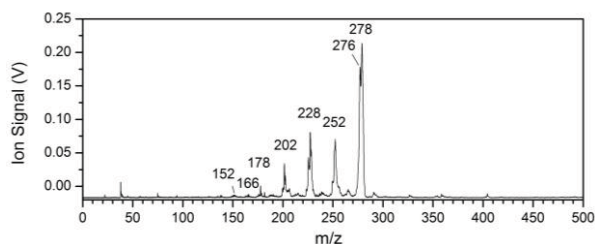


Figure 3. A sequence of PAHs can be detected by L2MS, as shown for this standard mixture.

Pyrene is one common PAH found in extraterrestrial materials, but a broad range of compounds in the PAH family are also likely to be encountered in an *in situ* landed investigation of a planetary surface material. A calibration mixture of PAH standards (product number 47940-U, Sigma-Aldrich Company) was also measured by L2MS to demonstrate the technique for a mixed sample. As shown in Figure 3, a series of mass peaks

in seen to correlate with the expected sequence of PAHs, from acenaphthylene at m/z 152 to dibenzo(a,h)anthracene at m/z 278.

Identifying Organics in a Complex Mixture:

Comparison of LD-TOF-MS and L2MS is shown for a Murchison meteorite extract in Figure 4. In LD-TOF-MS mode, a broad distribution of peaks is observed. Some structural ambiguity is contained in this spectrum owing to isobaric interferences of plausible molecular structures, the complicating effects of C isotope peaks accompanying each distinct species, and the presence of fragmentation products.

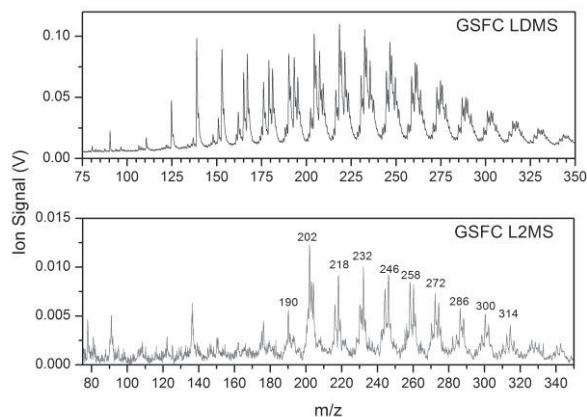


Figure 4. Compared to the single-laser LD-TOF mass spectrum of a Murchison meteorite extract (top), L2MS provides specificity to the aromatic content (bottom).

The L2MS spectrum shown in Figure 4 (bottom) preferentially reveals the aromatic hydrocarbon content of the sample. The familiar pattern of methylated PAHs is easily recognized in this instrument demonstration. All data presented here were acquired using a compact instrument prototype that could be compatible with a future mission to a planetary surface harboring a diversity of organic species.

References: [1] Getty S. A. *et al.* (2012) *Int. Workshop on Instr. for Planetary Missions*, #1100. [2] Brinckerhoff W. B. *et al.* (2000) *Rev. Sci. Instr.* **71**, 536. [3] Cornish T. *et al.* (2000) *Rapid Comm. Mass Spec.* **14**, 2408. [4] Getty, S. A. *et al.* (2012) *Rapid Communications in Mass Spectrometry* **26**, 1. [5] Zenobi R. *et al.* (1989) *Meteoritics* **24**, 344. [6] Chanover N. *et al.* (2012) *IEEE Aerospace Conf. Proc.*, DOI: 10.1109/AERO.2012.6187060. [7] Elsilá J. E. *et al.* (2005) *Geochim. Cosmochim. Acta* **69**, 1349.

Additional Information: We acknowledge support from the NASA Planetary Instrument Definition and Development Program, the Astrobiology Science and Technology Instrument Development Program, and the NASA Astrobiology Institute.