

Laser Time-of-Flight Mass Spectrometry for Future *In Situ* Planetary Missions. S. A. Getty,¹ W. B. Brinckerhoff,¹ T. Cornish,² S. A. Ecelberger,² X. Li,³ M. A. Merrill Floyd,¹ N. Chanover,⁴ K. Uckert,⁴ D. Voelz,⁴ X. Xiao,⁴ R. Tawalbeh,⁴ D. Glenar,⁴ J. E. Elsila,¹ and M. Callahan¹ ¹NASA Goddard Space Flight Center (Mailstop 699.0, Greenbelt, MD 20771; Stephanie.A.Getty@nasa.gov), ²C&E Research, Inc., Columbia, MD 21045, ³University of Maryland, Baltimore County, Baltimore, MD 21250, ⁴New Mexico State University, Las Cruces, NM 88003.

Introduction: Laser desorption/ionization time-of-flight mass spectrometry (LD-TOF-MS) is a versatile, low-complexity instrument class that holds significant promise for future landed *in situ* planetary missions that emphasize compositional analysis of surface materials. Here we describe a 5kg-class instrument that is capable of detecting and analyzing a variety of analytes directly from rock or ice samples. Through laboratory studies of a suite of representative samples, we show that detection and analysis of key mineral composition, small organics, and particularly, higher molecular weight organics are well suited to this instrument design. A mass range exceeding 100,000 Da has recently been demonstrated. We describe recent efforts in instrument prototype development and future directions that will enhance our analytical capabilities targeting organic mixtures on primitive and icy bodies. We present results on a series of standards, simulated mixtures, and meteoritic samples.

Current Instrument Design: The core instrument is housed in a high vacuum chamber, as shown in Figure 1, and includes an ultraviolet (UV) laser to desorb and ionize analytes from a solid surface, an electrostatic ion extraction lens assembly, a curved field ion reflectron, and back-to-back linear- and reflected-mode microchannel plate detectors [1-3]. A pulsed (4-7 ns), frequency tripled (355 nm) or quadrupled (266 nm) Nd:YAG laser is focused at the sample to generate ions from a ~ 100 micron diameter spot. The ions then separate according to their masses based on the TOF technique.

Complementary data can be acquired through the close integration of other *in situ* sample interrogation techniques, such as infrared (IR) point spectroscopy. This is illustrated by the recent integration of an acousto-optic tunable filter (AOTF) spectrometer developed at New Mexico State University [4] with a LD-TOF-MS prototype. The illumination source of the IR spectrometer is wavelength-tunable in the near-IR using an AOTF module, and the sample reflectance is recorded using an HgCdTe detector (Teledyne Judson Technologies Company). The resulting miniature AOTF spectrometer measures approximately 4.5" x 5" x 1.6" and was designed to fit into a 8" Kimball Physics vacuum chamber. To truly integrate the two instruments, the focal planes are designed with a common boresight, such that the same region on the sample surface can be

analyzed simultaneously by both techniques. This required that the LD-TOF-MS ion inlet be made narrow enough to penetrate a bore-hole in the AOTF mirror assembly, as shown in Figure 2. The sample focal plane is located ~ 5 mm below the LD-TOF inlet and AOTF housing.

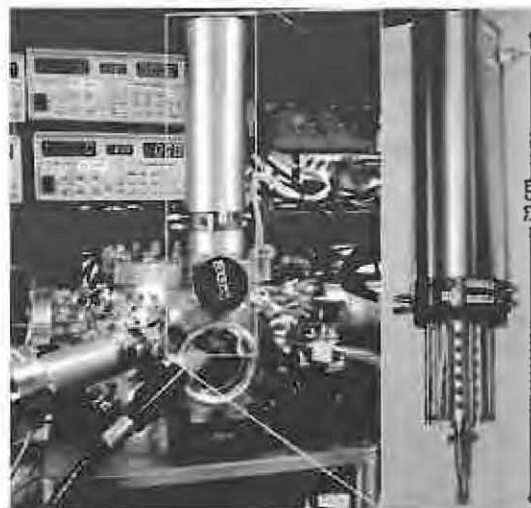


Figure 1. The LD-TOF-MS is a 5 kg-class instrument measuring ~ 30 cm long. Capabilities include positive and negative ion modes, advanced MS techniques such as tandem MS and L2MS, and demonstrated complementarity to other *in situ* analytical instruments, such as IR point spectroscopy.

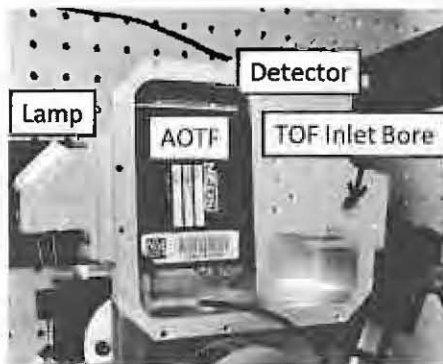


Figure 2. The AOTF IR point spectrometer is housed in a volume of ~ 4.5" x 5" x 1.6". Integration with the LD-TOF-MS will enable coordinated, coincident sample analyses.

Recent Instrument Improvements: Traditionally, mass spectrometers for planetary missions have focused on positive ion detection, but because both positive and negative ions are produced by the laser, the LD-TOF-MS is also naturally suited to negative ion analyses [5]. The laser pulse produces photoelectrons through interactions with the solid surface, and negative ions are formed through electron attachment to the desorbed neutrals. In negative mode, the detector voltage bias is held constant, but the other instrument voltages are adjusted to reverse polarity, to be optimized for the transmission of negatively charged species to the detector plane.

The ability to acquire both positive and negative mass spectra point-by-point represents a significant enhancement in our analytical capabilities. In positive mode, the mass spectra are often dominated by the omnipresent signatures of Na and K cations. Because the ionization potential of these species is relatively low, these ions and molecular adducts are formed easily from most sample surfaces. The dominant peaks that appear at m/z of 23 and 39 are often much higher intensity than the analytes of interest. Na and K are not seen in negative mode and the obscuring effects are therefore avoided.

Some classes of molecule are especially well suited to negative ion formation. For example, we have recently observed that negative ions are preferentially formed for carboxylic acids that are mixed with clays and other mineral matrices in laboratory simulants. The intact negative molecular ion is readily observed, whereas positive mode shows little evidence of the parent molecule. Negative ion mode is also particularly useful for detecting electronegative atomic and molecular species that may be present in planetary surface samples, such as described for the case of chlorine and perchlorate below.

Future Directions: Time-of-flight mass analysis is well suited to high molecular weight mass identification. In principle, the time-of-flight technique is unlimited in mass range, i.e., the heavier ions simply take longer to reach the detector, without additional requirements on the power supplies. For this reason, the LD-TOF-MS is a promising instrument technology for advanced *in situ* organics analysis from solid samples. New proof-of-concept modifications to the core prototype have demonstrated advanced spectrometric capabilities that will allow, not only the mass assignment from a complex mixture of organics, but also the possibility of molecular structure assignments.

Tandem mass spectrometry. In commercial instruments, tandem mass spectrometry, or MS/MS is used to isolate a particular mass of interest and intentionally

induce fragmentation of that species to produce a type of molecular fingerprint. The resulting fragmentation pattern can then be compared to published product ion data to assign a molecular structure to the mass peak. In practice, the parent molecular ion must be first selected by ion gating before the fragmentation step. Ion gating has recently been demonstrated in the miniature prototype shown in Figure 1. The fragmentation pattern is shown in Figure 3 for two peptide species that fragment spontaneously: angiotensin II and polyproline ($P_{14}R$). The ability to focus both the parent ion and the fragments simultaneously relies on our unique curved-field reflectron. Although this technique is widely used in commercial MALDI mass spectrometers, to our knowledge, this is the first report of pseudotandem MS on a miniature instrument.

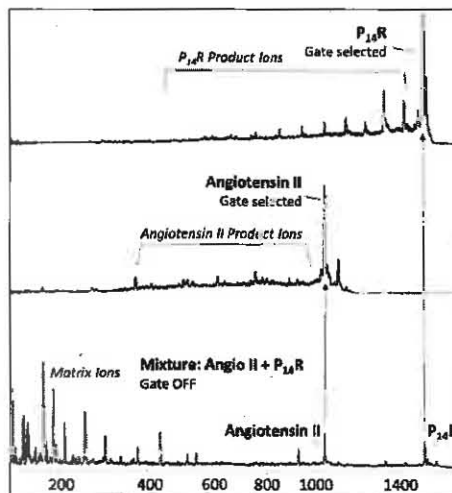


Figure 3. A critical first step towards tandem MS capabilities in a miniature LD-TOF-MS is this demonstration of ion gating. For a mixture of angiotensin II and polyproline ($P_{14}R$), a pulsed ion gate allows the isolation of each parent ion and its post-source decay product ions.

In the near term, we will be integrating an induced fragmentation functionality to the miniature instrument. In addition to species that spontaneously decay, as shown in Figure 3, this induced fragmentation will enable generalized fragmentation analysis of a wide range of parent molecules.

Two-step laser mass spectrometry. Another advanced MS technique that represents a new advance for these prototypes is post-ionization, or two-step laser mass spectrometry (L2MS). In some cases, use of a single laser to desorb and ionize in one step leads to an excess of energy in the resulting molecular ion, which can produce undesirable fragmentation. By decoupling the desorption and ionization processes, we are better

able to tune the laser energies to operate below the fragmentation threshold. This is accomplished by using a lower-intensity infrared laser pulse to first desorb neutrals "intact" from the sample surface, followed by an orthogonal UV laser pulse to intersect the neutral plume to produce ionization. L2MS offers the advantage of selectivity to aromatic compounds, as has been thoroughly demonstrated on laboratory-scale L2MS instrumentation [e.g., 6-9]. In the miniature prototype, we have conducted L2MS studies of a model PAH, pyrene, to show that fragmentation can be minimized by operating the IR laser *below* the ionization threshold and the UV laser *just above* the ionization threshold [10].

Terrestrial Planets: The mineralogy of solid planetary bodies is of primary interest as part of a landed investigation. Understanding the mineralogy of a sampling site gives valuable geologic and petrologic context for any compositional analyses that are undertaken. The insights enabled by spatially correlated LD-TOF-MS and AOTF analyses produces clues to mineralogy by revealing the vibrational signatures of key functional groups, *as well as* the overall inorganic composition. As a low-power screening tool, the AOTF capability offers information that supports sample composition, mineralogy, and organic content. Detailed analyses can then be conducted on a sample of interest using the LD-TOF-MS to produce in-depth compositional data from a solid or powdered sample.

Prior to integration of the AOTF spectrometer with the LD-TOF-MS prototype, a suite of mineral samples were analyzed in parallel by each instrument. The sample suite was selected to span major classes of mineral that would have implications for an aqueous geologic history: sulfates, carbonates, iron oxides, and clays. A carbonate series is shown in Figure 4, as measured in LD-TOF-MS positive ion mode.

As can be seen for siderite, magnesite, calcite, and dolomite, the cation is readily detected using LD-TOF-MS. With corroborative AOTF measurements, as shown in Figure 5, the $-\text{CO}_3$ group is identified by a series of characteristic features in the IR spectrum, as indicated. Taken together with LD-TOF measurements, the two data sets strongly suggest source mineralogy and can reveal mass peaks originating from organic content. Although not shown here, we have found that the population of higher order oxides in the LD-TOF spectra is found to correlate with degree of hydration of the particular mineral, as verified by AOTF hydration signatures and the known source mineral [4].

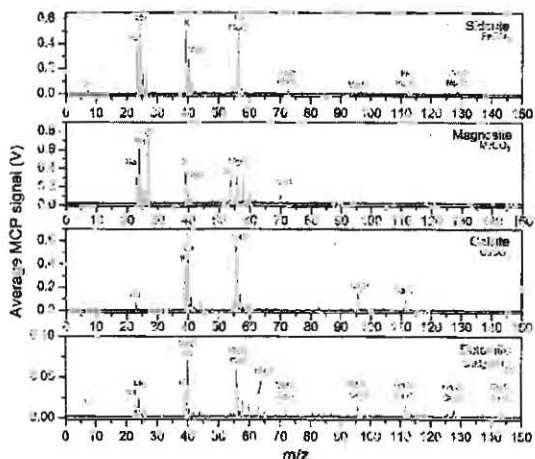


Figure 4. LD-TOF-MS analyses of a suite of carbonate minerals allows identification of the cation composition in positive ion mode.

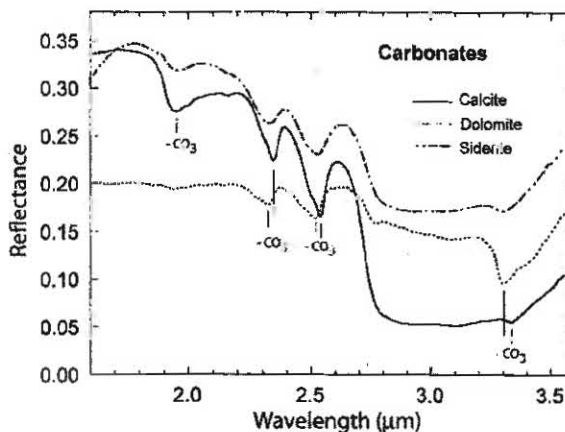


Figure 5. AOTF point spectrometer analysis reveals vibrational signatures at IR wavelengths that identify carbonate groups in calcite, dolomite, and siderite.

Perchlorate salt is an important species known to be present at the Martian surface. We have conducted negative ion mode studies of perchlorate salt as a standard and in the presence of a clay mineral matrix with organic species added. An example of this laboratory simulant sample is shown in negative mode in Figure 6. With kaolinite clay as the mineral matrix, a 1% NaClO_4 solution was added to the clay and allowed to dry. Finely ground phthalic acid powder was also added to the clay sample and mixed thoroughly. In negative ion mode, the Cl isotopes are seen at m/z 35 and 37, and the perchlorate anion is a dominant feature in the spectrum at m/z 99 and 101. Even in the presence of perchlorate salts, the parent molecular ion of phthalic acid is observed at m/z 166. This distinguishes LD-TOF-MS from other regolith analyzers, such as pyrolysis-mass spectrometry, which evolves

sample volatiles and decomposition products using prolonged application of heat. This thermal decomposition process may promote the degradation of organics that are co-located with perchlorate salts, thereby destroying the structural information of the parent organic compound. In contrast, LD-TOF-MS does not impart appreciable heat into the mixed sample and therefore preserves the organic parent ion.

These classes of mineral samples are relevant analogs for the surface of Mars and perhaps Venus. It is worth noting that $MgSO_4$ is also suspected of contributing to the salty deposits on the surface of Jupiter's icy moon Europa. Direct measurements of epsomite are planned for the near future.

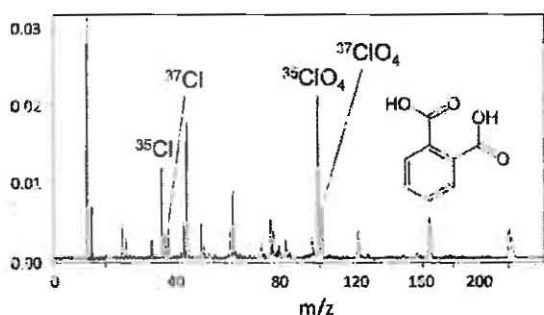


Figure 6. LD-TOF-MS mass spectrum of kaolinite clay spiked with $NaClO_4$ and phthalic acid shows clear signatures of Cl isotopes, the perchlorate anion, and the phthalic acid parent ion.

Primitive and Icy Bodies: In a complex mixture, such as that seen for carbonaceous chondrite meteorites, a mixture of organic compounds is present, which can lead to challenges in peak identification and the ability to resolve isomolecular interferences. The selectivity of L2MS to aromatics effectively separates the aromatic composition from the mixture *without* the need for front-end chromatography. This is shown in Figure 7 for a Murchison meteorite extract. The total organic extract (top) was first analyzed by LD-TOF-MS (data from a commercial Bruker Autoflex Speed is shown here) to reveal the complexity of the mixture. Using GSFC liquid chromatography facilities, the non-polar fraction was isolated and analyzed by the commercial Bruker LD-TOF-MS (center). The bottom spectrum shows the total organic extract, as measured by L2MS. The mass spectrum shows striking similarities with the LC-separated non-polar extract, suggesting that L2MS effectively accomplishes this separation through the specificity of the two-laser pulse technique.

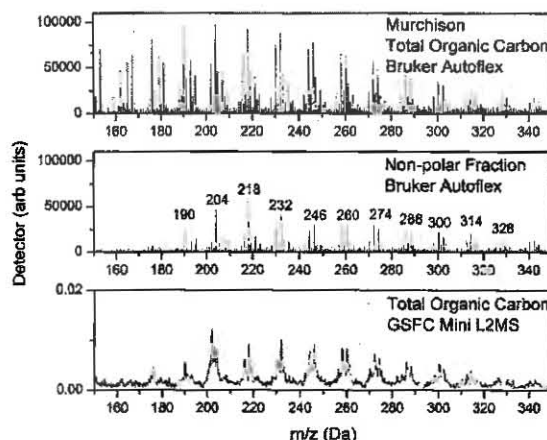


Figure 7. L2MS offers enhanced specificity to aromatic species within a complex mixture, such as is shown here for a Murchison meteorite total organic extract (LD-TOF-MS, top). The L2MS spectrum (bottom) produces comparable information to that seen in a single-laser LD-TOF-MS analysis of an LC-separated non-polar fraction (center).

The Murchison meteorite is a representative sample, but only the beginning of analyses, relevant to primitive and icy bodies. In future work, we plan to incorporate the capability to analyze icy surfaces towards future mission opportunities to the icy satellites and primitive, icy bodies.

References: [1] Brinckerhoff W. B. et al. (2000) *Rev. Sci. Instr.* **71**, 536. [2] Cornish T. et al. (2000) *Rapid Comm. Mass Spec.* **14**, 2408. [3] Getty et al. (2012) *Concepts and Approaches for Mars Exploration*, Abstract #4302. [4] Chanover et al. (2011) *IEEE Aerospace Conf.* DOI: 10.1109/AERO.2011.5747295. [5] Getty et al. (2011) *Lunar Plan. Sci. Conf.* Abstract #2490. [6] Zenobi et al. (1989) *Science* **246**, 1026-1029. [7] Pizzarello et al. (2001) *Science* **293**, 2236-2239. [8] Clemett et al. (2003) *Science* **262**, 721-725. [9] Elsila et al. (2005) *Geochim. Cosmochim. Acta* **69**, 1349-1357. [10] Getty et al. (2012) *Rapid Commun. Mass Spec.* in review.