

A MINIATURE LASER DESORPTION/IONIZATION TIME-OF-FLIGHT MASS SPECTROMETER FOR IN SITU ANALYSIS OF MARS SURFACE COMPOSITION AND IDENTIFICATION OF HAZARDS IN ADVANCE OF FUTURE MANNED EXPLORATION. S. A. Getty¹, W. B. Brinckerhoff¹, R. D. Arevalo, Jr.¹, M. M. Floyd¹, X. Li², T. Cornish³, and S. A. Ecelberger³, ¹NASA Goddard Space Flight Center (Stephanie.A.Getty@nasa.gov), ²University of Maryland, Baltimore County, ³C&E Research, Inc.

Introduction: Future landed missions to Mars will be guided by two strategic directions: (1) sample return to Earth, for comprehensive compositional analyses, as recommended by the 2011 NRC Planetary Decadal Survey [1]; and (2) preparation for human exploration in the 2030s and beyond, as laid out by US space policy. The resultant mission architecture will likely require high-fidelity *in situ* chemical/organic sample analyses within an extremely constrained resource envelope. Both science goals (e.g., MEPAG Goal 1, return sample selection, etc.) as well as identification of any potential toxic and biological hazards to humans, must be addressed [2]. Over the past several years of instrument development, we have found that the adaptable, compact, and highly capable technique of laser desorption/ionization time-of-flight mass spectrometry (LD-TOF-MS) has significant potential to contribute substantially to these dual objectives. This concept thus addresses *Challenge Area 1: Instrumentation and Investigation Approaches*.

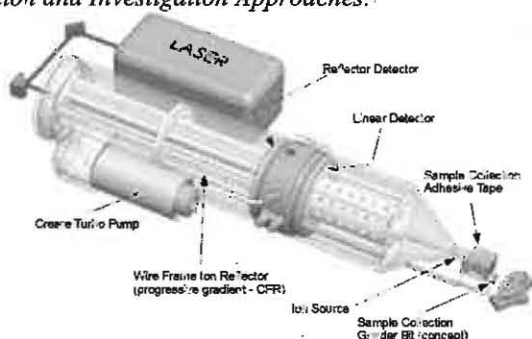


Figure 1. The reversible polarity (RP) TOF-MS is a 5 kg-class instrument optimized for *in situ* analysis of inorganic and high mass organics in Mars surface materials.

LD-TOF-MS is a conceptually simple technique that can provide exquisitely-detailed information about the inorganic and organic species present in a solid material without the need for complex sample preparation steps. As shown in Fig. 1, our core LD-TOF-MS prototype [3] measures as few as 20 cm long and features a UV harmonic (266 nm or 355 nm) of a pulsed Nd:YAG laser focused to a 50-200 μm spot for localized desorption and ionization of nonvolatile species from a solid surface. Ions are accelerated into the instrument, reflected in a curved field ion reflector [4], and detected as mass-to-charge (m/z) peaks as a function of time (TOF). The instrument is evacuated to μtorr pressures with a miniature turbomolecular pump

developed by Creare, Inc., and can be interfaced to a variety of sample acquisition mechanisms. One example is the Precision Subsampling System [5], which extracts fines from mm-scale spot on a rock or core and positions them at the laser focus. A separate highly-compact, dedicated sampler is depicted in Fig. 1.

Owing to the low (< 7 kV) DC voltages, and the simplicity of construction, a flight-ready LD-TOF-MS would be a 5 kg-class instrument, well suited to a prospecting and caching instrument suite, or a portable analyzer for future human exploration missions. Furthermore, the generality of the technique would be adaptable to a broad range of lander, rover, and habitat operations, including sample analysis and screening, targeted astrobiology-themed investigations, and toxin and biohazard detection in support of astronaut safety.

Near-Term Instrument Opportunities: We have developed a reversible-polarity (RP-) TOF-MS that is focused on enhancing the ability of our core LD-TOF-MS instrument to detect certain inorganic species, such as Cl and S, and to resolve the structure of organics. The RP-TOF-MS is capable of measuring positive and negative ions, both of which are created in the process of laser desorption/ionization (LDI) from a solid sample surface with a single UV laser pulse. A straightforward reconfiguration of instrument voltages allows for measurements in either polarity.

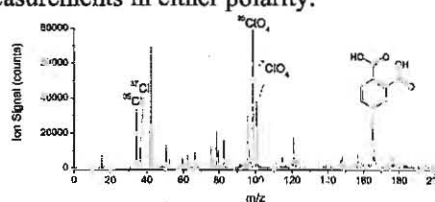


Figure 2. Negative ion mass spectrum of kaolinite clay spiked with phthalic acid and sodium perchlorate as a Mars regolith simulant. The RP-TOF-MS can preserve organic structure, even in the presence of perchlorate.

Using positive mode, we have previously reported compositional studies of various inorganic and organic standards, minerals, complex analogs, laboratory simulants, and meteoritic materials [6,7]. Negative ion mode is well suited to electronegative moieties typically incorporating S and Cl, and certain organics such as carboxylic acids and amino acids. An example negative ion mass spectrum (Fig. 2) was obtained for a mixture of a phthalic acid organic standard and sodium perchlorate salt spiked onto an inorganic clay matrix

(Clay Mineral Society KGa-1b; kaolinite) using a commercial LD-TOF-MS (Bruker Autoflex Speed) to demonstrate proof-of-principle.

The mass range in LD-TOF-MS is primarily a function of data acquisition time and largely independent of systems-level constraints (such as RF amplitude or frequency); the technique has particular promise for *in situ* structural characterization of high molecular weight species. To this end, we have recently integrated a precision ion gate into the RP-TOF-MS. In commercial TOF instruments, ion gating is used to isolate particular mass peaks, usually a large molecule, from a complex mass spectrum, by passing only that ion into the reflector. Subsequent fragment analysis is thus possible, for example, following spontaneous decay of easily fragmented peptides. An example of two peptides that undergo such post-source decay are P14R and Angiotensin II (gated spectra in Fig. 3). For parent species needing additional stimulation to decay, we are exploring fragmentation through photoinduced and collision-induced dissociation.

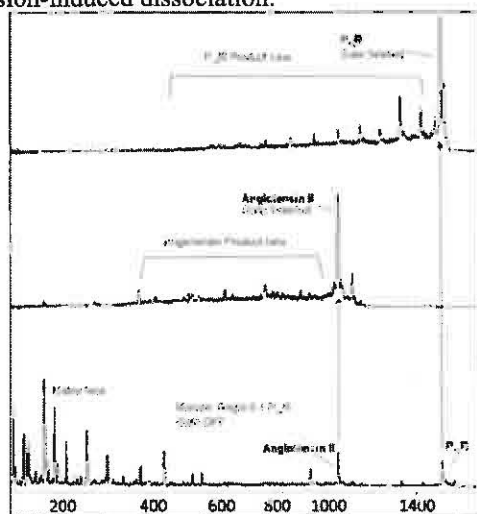


Figure 3. A precision ion gate enables product ion analysis of selected organic parent peaks for structural analysis and identification of high-m.w. species in a complex mixture.

Key Measurements:

Perchlorates. Perchlorate salts were detected by the Phoenix lander and in fact may play an important role in the preservation of organics near the surface of Mars in general. Perchlorates however may impact the ability of bulk heating techniques, such as pyrolysis, to detect organics mixed with oxidants in regolith, ice, or bedrock. The RP-TOF-MS is able to detect the ClO_4^- anion in negative mode, while preserving the signature of admixed organics. The ~ 5 ns laser desorption event and subsequent extraction are far too brief for effective organic oxidation, even in the presence of 1% perchlorate salt intimately mixed into the analog sample.

High Molecular Weight Organics. The detection and identification of high molecular weight, complex organic molecules is of singular importance to both future astrobiology investigations of Mars and the determination of biological activity in advance of landed astronauts. When coupled to a TOF analyzer, matrix-assisted LDI (MALDI) is well suited to analyses of large biomolecules. MALDI is widely used in the health and medical fields to detect and analyze peptides and proteins, up to 100,000 Da. In MALDI, an organic acid “matrix” is added to the sample to promote LDI of large analytes. With the addition of a MALDI matrix, compounds up to 25,000 Da have been detected with our RP-TOF-MS; as such developing such a capability for *in situ* investigations is compelling. Typically, MALDI matrix is mixed with sample in solution, but we are investigating approaches that are compatible with a robotic platform, such as vacuum sublimation of MALDI matrix onto a sample surface, thin film front-end mechanical application, and liquid handling and spray systems leveraging parallel developments for spaceflight applications.

Crocoite. On Earth, crocoite (PbCrO_4) is the only natural source of hexavalent chromium, a form that is highly toxic to humans. Based on analysis of martian meteorites, the level of hexavalent chromium is not expected to exceed levels that can be otherwise mitigated by engineering controls, but weathering and oxidizing conditions at the Martian surface introduce uncertainty to these estimates. Consequently, *in situ* measurements of hexavalent chromium are a high priority prior to astronaut surface exploration [2]. The RP-TOF-MS could play a role in the detection of crocoite on Mars; our instrument has been shown to be effective in detecting trace levels of Cr and Pb in positive ion mode. Because the LDI process is localized to as small as a ~ 50 micron spot, the coincident detection of both Pb and Cr in a single spectrum could provide evidence for naturally occurring Martian crocoite. Careful calibration would be needed to estimate abundances and determine limits of detection of such mineral phases; such studies are ongoing in our lab.

References: [1] National Research Council. *Vision and Voyages for Planetary Science in the Decade 2013-2022*. Wash, DC: The National Academies Press, 2011. [2] National Research Council. *Safe on Mars: Precursor Measurements Necessary to Support Human Operations on the Martian Surface*. Wash, DC: The National Academies Press, 2002. [3] Brinckerhoff W. B. et al. (2000) *Rev. Sci. Instr.* **71**, 536. [4] Cornish T. et al. (2000) *Rapid Comm. Mass Spec.* **14**, 2408. [5] Brinckerhoff W. B. et al. (2010) *Am. Soc. Civil Eng. Conf. Proc.* **366**, 123-140. [6] Corrigan, C. M., W. B. Brinckerhoff, et al. (2007). *Met. & Plan. Science* **42**:

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