

A TWO-STEP TANDEM LASER TIME-OF-FLIGHT MASS SPECTROMETER FOR THE *IN SITU* STUDY OF THE SURFACES OF PRIMITIVE AND ICY SOLAR SYSTEM BODIES. S. A. Getty¹, X. Li², T. Cornish³, A. Grubisic⁴, K. Uckert⁵, J. Elsila¹, W. B. Brinckerhoff¹, Q. Wu⁶, R. N. Zare⁶, ¹NASA Goddard Space Flight Center (8800 Greenbelt Road, Mailstop 699, Greenbelt, MD 20771; Stephanie.A.Getty@nasa.gov), ²University of Maryland, Baltimore County (1000 Hilltop Cir, Baltimore, MD 21250), ³C & E Research, Inc. (9194 Red Branch Rd., Suite L, Columbia, MD 21045), ⁴University of Maryland (Dept. of Astronomy, College Park, MD 20742), ⁵New Mexico State University (Department of Astronomy, Las Cruces, New Mexico 88003), ⁶Stanford University (Department of Chemistry, Stanford, CA 94305)

Introduction: Laser desorption/ionization time-of-flight mass spectrometry (LD-TOF-MS) offers detailed compositional analysis of solid samples using an instrument that can be made compact, low power, and lightweight. Mission applications emphasizing in situ compositional analyses of surface astrobiology and astrochemistry in primitive bodies and icy moons are the focus of this instrument development. Recent advances in prototype instrumentation have enhanced our ability to distinguish between classes of organic species, identify and assign structures to mass peaks of interest, and detect organic species in a mineral matrix with enhanced sensitivity. The result is a two-step tandem laser time-of-flight mass spectrometer (L2MS) that has most recently been used to characterize a suite of synthetic analog powders intended to simulate the surface composition of small bodies and icy moons.

Primitive small bodies. The surfaces of small, primitive bodies feature a mixture of inorganic and organic materials that can provide insight into the formation and processing of the body since (and even prior to) solar system formation. Given the importance of the delivery of volatiles via impacts to the evolution of and chemical inventory available to early Earth, the study of small bodies, such as comets and asteroids, is an active area of planetary research. The arrival of the ROSETTA spacecraft at 67P Churyumov-Gerasimenko and near-future landed science investigation of the Philae lander, will provide further insight into the surface composition of an active comet. This mission promises to conjure new lines of inquiry into the detailed inorganic and organic composition of small bodies and the compositional variations that may exist between populations.

Icy moons. A landed mission to Europa, Enceladus, or other icy moons in the outer solar system would reveal unprecedented detail about the surface materials characteristic of these potentially habitable worlds. Detection of organic species entrained in the surface ices would offer profound implications for the habitability of the subsurface oceans, the mass transport dynamics between the surface and subsurface, and the radiolytic processes and lifetimes in these energetic environments. An orbiter or multiple flyby mission to

Europa would lay the foundation for the safe landing of a future payload. The mass and power constraints – as well as the science objectives – of such a mission would be well addressed by the L2MS instrument.

Instrument Description: The laser desorption/ionization mass spectrometer at this core of the L2MS instrument prototype has been described in detail elsewhere [1,2]. Briefly, an electrostatic Einzel lens is positioned at the entrance of the instrument to accelerate laser-ionized molecular ions to the ~5kV operating voltage of the time-of-flight analyzer. A curved-field reflectron is used to effectively lengthen the ion flight tube and focus the ions at a microchannel plate detector. In the simplest configuration, the 266 nm or 355 nm harmonic of a 7-ns pulsed Nd:YAG laser, focused down to 50 μm , is used to desorb and ionize the solid analyte. In this configuration, the system operates in laser desorption mass spectrometry (LDMS) mode.

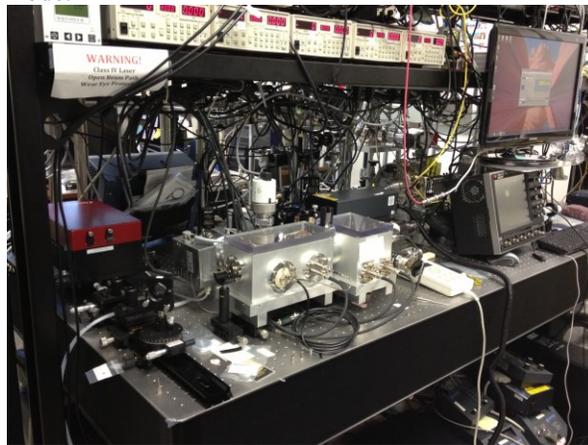


Figure 1. The L2MS analyzer prototype is in operation at NASA GSFC.

Recently, the two-step laser ionization approach has been demonstrated in a compact prototype [1,2], as shown in Figure 1, following the instrument and technique development efforts of co-author Zare. L2MS has been shown to be important to the analysis of aromatic organics in various planetary materials (such as meteorites and cometary samples [3-6]) and complex terrestrial materials (such as asphaltenes), and it is

compatible with a future 5 kg-class *in situ* analytical instrument.

Two-step laser desorption/ionization. The L2MS technique decouples the desorption and ionization steps of laser mass spectrometry. This allows the energy imparted at each step to be carefully controlled. In practice, an infrared laser is used to couple to the vibrational modes of a solid sample to desorb the analyte below the threshold for ionization. IR wavelengths between 1064 nm and 10 μm have been demonstrated for desorption; here, a tunable 2.7-3.1 μm OPO laser is used. For ionization, a ultraviolet laser (266 nm or 157 nm for this work) is best matched to the range of ionization energies of elemental and molecular sample constituents. Through direct resonant ionization or resonance-enhanced multi-photon ionization, aromatic organic species are preferentially ionized. As a result, fragmentation is minimized, and the parent organic species can be more readily assigned in the baseline mass spectrum.

The specificity offered by two-step laser desorption/ionization (LDI) can serve inherently as a separation technique to identify aromatic species in a mass spectrum that would be otherwise heavily populated and perhaps dominated by inorganic species and metastable clusters.

Fragment analysis. The L2MS analyzer also features an advanced fragment analysis mode that provides clues to enable the structural assignment of particular mass peaks of interest. Using the pulsed pin gate, time-resolved mass packets can be either transmitted into the reflectron or deflected for rejection from the mass spectrum. This allows for the strategic rejection of low mass elements and clusters that can compromise the sensitivity of the detector in this time-of-flight instrument. That is, high-intensity peaks that arrive at the detector first can degrade the response and sensitivity of the detector to later, lower-intensity mass packets.

Certain molecular ions fragment spontaneously through a post-source decay mechanism. Because the molecular ion and product masses have the same speed, as determined by the electric field within the ion source, they can be selected by a single, well timed gate pulse. A unique feature of the curved-field reflectron is its ability to focus both the molecular ion and its fragmentation products at the detector plane for a pseudo-tandem MS capability.

For those molecular ions that do not fragment spontaneously, we have developed a collision-induced dissociation cell (shown schematically in Figure 2 (top)) that is compatible with the compact dimensions of the analyzer, without inducing arcs or stresses to the chamber pump. Because diffusion time scales are much

longer than typical flight times to the dissociation region, a single laser pulse can be used to ionize the sample neutrals and generate the collision gas simultaneously. The laser-induced burst of neutrals that promotes fragmentation of the molecular ion is localized to the flight path of the ions, and the global pressure is maintained at high vacuum. The LA-CID fragmentation pattern of pyrene is shown as an example in Figure 2.

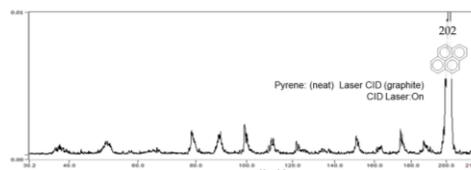


Figure 2. Laser-assisted collision-induced dissociation (LA-CID) is used to promote fragmentation in gate-selected mass peaks of interest. An example LA-CID fragmentation pattern is shown for pyrene.

Analog Measurements: An important aspect of any instrument development effort is the demonstration of the instrument performance when applied to realistic planetary analog samples. Initial instrument characterization efforts focused on simple organic standards, such as polycyclic aromatic hydrocarbons (PAHs), including pyrene, coronene, and a commercially available calibration mixture; amino acids, such as tryptophan; and nucleobases, such as 2,6-diaminopurine [2].

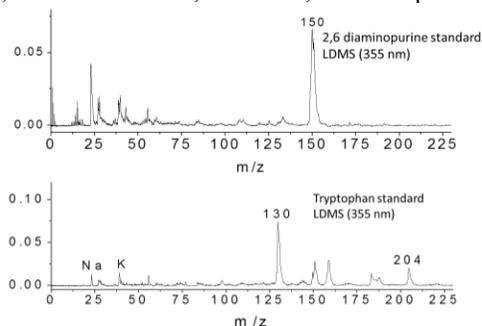


Figure 3. Single-laser UV LDMS spectra of 2,6-diaminopurine (top) and tryptophan (bottom) show both inorganic salt composition of the sample, as well as fragments and the parent molecular ions for both species.

Example spectra are shown for tryptophan and 2,6-diaminopurine. A comparison between single-laser LDMS (Figure 3) and L2MS (Figure 4) is shown, illustrating the advantages of each. In the LDMS spectrum, the salt content of the sample can be seen at low masses for Na (m/z 23) and K (major isotope at m/z 39). The L2MS spectrum largely neglects these inorganic signatures, thereby producing a mass spectrum that is predominantly specific to the organic constituent. Such

specificity can simplify the data interpretation in more complex mixtures.

A mixture of minerals and organics can represent an intermediate step in the continuum of sample complexity, moving closer to the full complexity of a primitive or icy planetary surface material. A set of representative minerals and organics have been selected for the preparation of a suite of synthetic mixtures, as shown in Table 1. The minerals were chosen to reflect relevant mineralogy that could be expected on primitive and icy bodies, including olivine ($(\text{Mg}^{+2}, \text{Fe}^{+2})_2\text{SiO}_4$), enstatite (MgSiO_3), and epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). The organic standards coronene and tryptophan were the focus of this particular suite. Samples with a range of concentrations have been prepared, ranging from 0.01% to 10%.

Table 1. A suite of mineral-organic mixtures focusing on small and icy body composition were prepared for characterization by L2MS and single-laser LDMS.

Organic	Mineral	Epsomite	Enstatite	Olivine
PAH				
Coronene				
1%		X	X	X
0.10%		X		X
0.01%		X		X
Amino Acid				
Tryptophan				
10%		X	X	X
1%		X		X
0.1%		X		X

These mixtures were prepared in a solvent slurry and dried down while ultrasonicated the sample to promote an even distribution of the organic dopant. Uniformity was confirmed by optical microscopy in a test mixture of beta carotene and calcite, in which the color contrast could be easily evaluated.

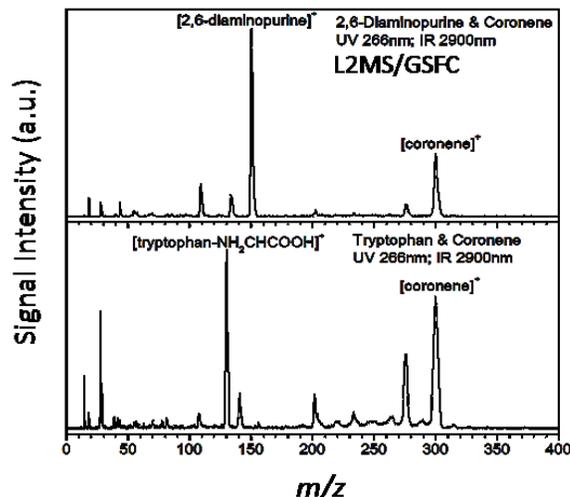


Figure 4. L2MS spectra of 2,6-diaminopurine (top) and tryptophan (bottom), with coronene as an internal mass calibrant.

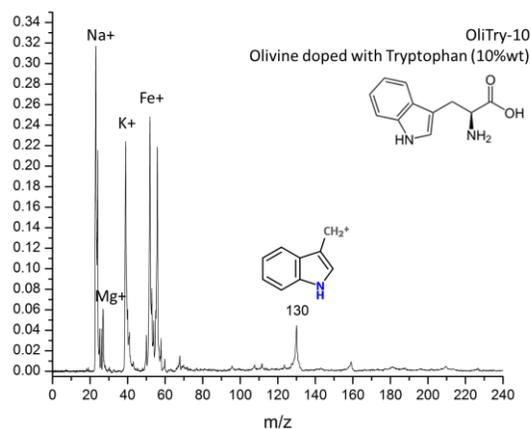


Figure 5. Single-UV laser mass spectra of an example synthetic analog mixture: olivine with 10 wt% tryptophan.

LD-TOF-MS measurements on two mixtures out of the sample matrix are shown in Figure 5. A compact prototype of the scale shown in Figure 1 was used. A major fragment of tryptophan at m/z 130 is detected in the mass spectrum of the olivine mixture. In addition, signatures of the Fe- and Mn-bearing mineralogy can be seen at lower masses.

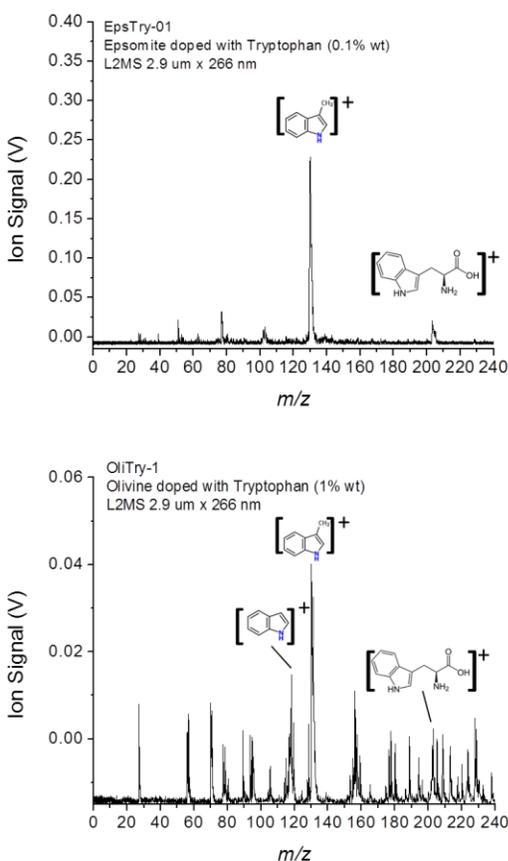


Figure 6. L2MS spectra of two example synthetic analog mixtures: epsomite with 0.1 wt% tryptophan (top) and olivine with 1 wt% tryptophan (bottom).

In comparison, an L2MS spectrum for 0.1 wt% tryptophan in epsomite is shown in Figure 6. The salt peaks and those reflecting inorganic cationic composition are not the predominant mass features in this spectrum. Instead, the dominant masses are the tryptophan molecular ion at m/z 204 and the fragment at m/z 130. In an olivine/tryptophan mixture with 1 wt% organic doping, a second tryptophan fragment is seen at m/z 117. A number of additional peaks in the olivine sample likely reflect a small amount of residual high vapor-pressure pyrene and coronene from a previous sample. In comparison to the LDMS spectrum of olivine/tryptophan (10 wt%) shown in Figure 5, the L2MS spectra indicate a lower limit of detection of organics present in a host mineral. These results illustrate the specificity and sensitivity to aromatic organics offered by the L2MS technique.

Conclusions: LD-TOF-MS is a low-mass, low-power instrument capability that is well suited to compositional analyses of planetary surface materials with-

out extensive sample preparation. An advanced L2MS prototype is currently being developed to allow specificity of the LDI method to key classes of organic molecules, such as PAHs, aromatic amino acids, nucleobases, and small peptides. MS/MS analysis has been demonstrated to be compatible with this compact instrument design using a laser-assisted collision-induced dissociation approach, coupled with a pulsed ion gate. The L2MS instrument provides a compelling instrument capability that could provide the core science of a future *in situ* landed mission to a primitive or icy body.

References:

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