

**TWO-STEP RESONANCE-ENHANCED DESORPTION LASER MASS SPECTROMETRY FOR IN SITU ANALYSIS OF ORGANIC-RICH ENVIRONMENTS.** S. A. Getty<sup>1</sup>, A. Grubisic<sup>2</sup>, K. Uckert<sup>3</sup>, X. Li<sup>4</sup>, T. Cornish<sup>5</sup>, J. E. Elsila<sup>1</sup>, and W. B. Brinckerhoff<sup>1</sup>, NASA/GSFC, 8800 Greenbelt Rd., Greenbelt, MD 20771 (Stephanie.A.Getty@nasa.gov), <sup>2</sup>University of Maryland, College Park, MD, <sup>3</sup>New Mexico State University, Las Cruces, NM, <sup>4</sup>University of Maryland, Baltimore County, <sup>5</sup>C&E Research, Inc., Catonsville, MD.

**Introduction:** A wide diversity of planetary surfaces in the solar system represent high priority targets for *in situ* compositional and contextual analysis as part of future missions. The planned mission portfolio will inform our knowledge of the chemistry at play on Mars, icy moons, comets, and primitive asteroids, which can lead to advances in our understanding of the interplay between inorganic and organic building blocks that led to the evolution of habitable environments on Earth and beyond. In many of these environments, the presence of water or aqueously altered mineralogy is an important indicator of habitable environments that are present or may have been present in the past. As a result, the search for complex organic chemistry that may imply the presence of a feedstock, if not an inventory of biosignatures, is naturally aligned with targeted analyses of water-rich surface materials.

Here we describe the two-step laser mass spectrometry (L2MS) analytical technique that has seen broad application in the study of organics in meteoritic samples [1,2], now demonstrated to be compatible with an *in situ* investigation with technique improvements to target high priority planetary environments as part of a future scientific payload.

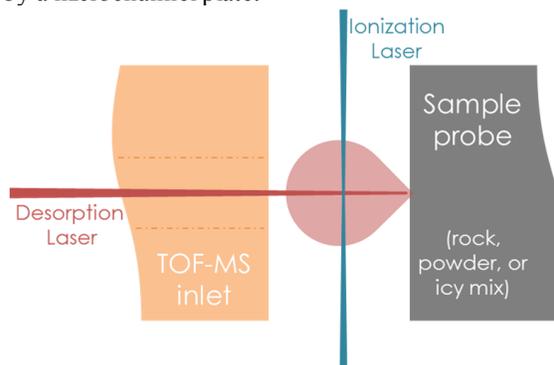
An ultraviolet (UV) pulsed laser is used in previous and current embodiments of laser desorption/ionization mass spectrometry (LDMS) to produce ionized species traceable to the mineral and organic composition of a planetary surface sample. L2MS, an advanced technique in laser mass spectrometry, is selective to the aromatic organic fraction of a complex sample, which can provide additional sensitivity and confidence in the detection of specific compound structures. Use of a compact two-step laser mass spectrometer prototype has been previously reported to provide specificity to key aromatic species, such as PAHs, nucleobases, and certain amino acids [3,4]. Recent improvements in this technique have focused on the interaction between the mineral matrix and the organic analyte.

The majority of planetary targets of astrobiological interest are characterized by the presence of water or hydrated mineral phases. Water signatures can indicate a history of available liquid water that may have played an important role in the chemical environment of these planetary surfaces and subsurfaces. The studies we report here investigate the influence of water content

on the detectability of organics by L2MS in planetary analog samples.

**Instrument and Methodology:** The core mass analyzer has been described in detail previously [5,6]. Briefly, the mass analyzer measures 30 cm in length and 5 cm in diameter, and the sample is held at the focal plane of the instrument, approximately 2-3 mm from the ion inlet. Whereas in conventional LDMS ions are generated by the use of a single UV pulsed laser focused at the laser surface, L2MS employs a crossed-beam configuration to desorb neutrals from the surface with a pulsed infrared (IR) laser and forms ions above the surface with a delayed, orthogonal UV pulse, as shown in Figure 1.

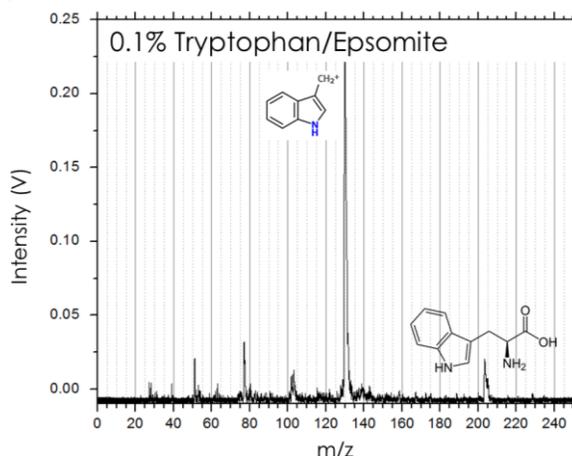
In the work reported here, the IR desorption pulse is generated from a commercially available Opotek 2731, focused at the plane of the sample to a sub-mm spot. Its wavelength can be tuned (via an optical parametric oscillator) between 2.7  $\mu\text{m}$  and 3.1  $\mu\text{m}$ , and its output is pulsed with repetition rate up to 20 Hz and pulse width as short as 4 ns. The UV ionization laser (Nd:YAG at 266 nm, pulse width 4-7 ns) is oriented parallel to the sample plane and focused at an adjustable distance above the sample. The UV pulse is triggered at a tunable delay after the IR laser pulse to intersect and ionize the neutral plume. The resulting ions are accelerated into a time-of-flight mass analyzer with curved-field reflectron. The time-resolved ion packets are detected by a microchannel plate.



**Figure 1.** Two-step laser mass spectrometry can elucidate trace organic composition in planetary analog and meteorite samples. A crossed-laser beam configuration lends sensitivity and specificity to an LDMS prototype instrument.

The L2MS instrument prototype is flexible to sample preparation. Solid rock chips, powders, and icy mixtures are compatible with our experimental design. To demonstrate the performance of L2MS on a hydrated analog sample in particular, we have prepared a mixture of a model amino acid with a hydrated mineral powder. The sample was prepared by adding a solution of tryptophan dissolved in a nonaqueous solvent (methanol in this case) to epsomite powdered to a  $<150\mu\text{m}$  grain size. In this study, we measured a quantity of the tryptophan solution to achieve a 1000ppm tryptophan in epsomite concentration. The powdered mixture was pressed onto a stainless steel stub and mounted into the vacuum chamber of the instrument.

**Results:** L2MS results are shown for a synthetic mixture of epsomite powder and the amino acid tryptophan. This chemistry was selected for its relevance to Europa and small bodies that have been aqueously processed.

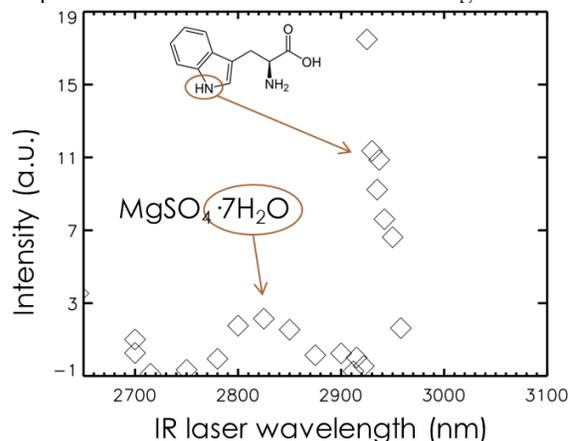


**Figure 2.** A mixture of 0.1% tryptophan and powdered epsomite shows clear signatures of the tryptophan structure.

L2MS is particularly sensitive to the aromatic organic content of a mixed sample, as illustrated by the mass spectrum shown in Figure 2. The molecular ion is detected at  $m/z$  204 and a major fragment at  $m/z$  130. L2MS is insensitive to the mineral matrix, but the presence of waters of hydration, as in the case of epsomite, can be inferred through resonance features in the IR wavelength dependence of the signal intensity, as shown in Figure 3.

The peak intensity of the major fragment ion at  $m/z$  130 is given as a function of IR laser wavelength in Figure 3, showing evidence of two local maxima in ion signal. The highest maximum in ion signal is observed at approximately 2935 nm, which strongly correlates with a vibrational stretching mode of the the trypto-

phan molecule at the characteristic aromatic N-H stretching mode. A second resonance is seen in the IR dependence at a wavelength centered at approximately 2830 nm. We interpret this resonance in tryptophan signal to derive from a desorption enhancement of the organic molecule through interactions with the waters of hydration in epsomite. We therefore conclude that the detection of key organic species can be promoted by judicious selection of the IR desorption wavelength to exploit vibrational resonances characteristic of the compounds and/or substrates under investigation.



**Figure 3.** L2MS signal intensity is seen to be maximized at two IR wavelengths, centered at 2830 nm and 2935 nm, corresponding to characteristic vibrational resonances of the tryptophan/epsomite mixture.

The measurements here demonstrate enhanced detection of organics in a planetary analog mixture. Dependence of signal intensity with IR wavelength is strongly suggestive of enhanced desorption efficiency due to coupling to characteristic vibrational resonances. This technique provides enhanced specificity to the aromatic organic fraction in complex planetary samples by coupling into molecule-specific or mineral-specific vibrational features. Now shown to be compatible with future *in situ* payloads, L2MS is a promising advanced mass spectrometric technique for the analysis of organic composition in complex samples.

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