

TWO-STEP RESONANCE-ENHANCED DESORPTION LASER MASS SPECTROMETRY FOR IN SITU ANALYSIS OF ORGANIC-RICH ENVIRONMENTS. S. A. Getty¹, X. Li², A. Grubisic³, K. Uckert⁴, T. Cornish⁵, J. E. Elsila¹, M. P. Callahan¹, and W. B. Brinckerhoff¹, NASA/GSFC, 8800 Greenbelt Rd., Greenbelt, MD 20771 (Stephanie.A.Getty@nasa.gov), ²University of Maryland, Baltimore County, ³University of Maryland, College Park, MD, ⁴New Mexico State University, Las Cruces, NM, ⁵C&E Research, Inc., Columbia, MD.

Introduction: The interrogation of solid-phase samples by laser desorption/ionization mass spectrometry (LDMS) is a powerful analytical technique that can elucidate inorganic and organic composition from an unprepared planetary surface material. LDMS will be used as part of the Mars Organic Molecule Analyzer (MOMA) investigation on the 2018 ExoMars rover mission. Here we report efforts, using a time-of-flight mass spectrometer prototype, to advance laser desorption/ionization (LDI) beyond single-color, broadband analysis, to provide further confidence in the identification of sample constituents.

In two-step laser mass spectrometry (L2MS), one laser wavelength is dedicated to a desorption step, while a second laser wavelength is optimized for ionization of the resulting neutrals. With L2MS, the fragmentation of the resulting molecular ions can be minimized, and selectivity to certain organics in the presence of an inorganic matrix can be enhanced [1-3].

In a laboratory prototype, we have demonstrated the use of a tunable infrared (IR) laser to effect resonance-enhanced desorption for those species having a vibrational mode within the accessible range. We demonstrate the technique for the case of Murchison meteorite powder.

Instrument and Methodology: The L2MS is a compact prototype, as shown in Figure 1, with the mass analyzer measuring only 30 cm in length and 5 cm in diameter [3-5]. The sample is held at the focal plane of the instrument, approximately 2-3 mm from the ion inlet. The IR desorption laser (Opotek 2731) is focused at the plane of the sample. Its wavelength can be tuned (via an optical parametric oscillator) between 2.7 μm and 3.1 μm , and its output is pulsed with repetition rate up to 20 Hz and pulse width as short as 4 ns. The ultraviolet (UV) ionization laser is oriented parallel to the sample plane, and it is focused at some distance (< 1 mm) above the plane of the sample. The UV laser is operated at the 266 nm harmonic of a pulsed Nd:YAG with pulse duration as short as 4 ns. The UV pulse is triggered at a delay after the IR laser pulse to intersect and ionize the neutral plume generated by the desorption step. 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.

The sample preparation was minimal, consisting simply of affixing a layer of powdered meteorite onto a layer of double-sided tape that has been shown to impart negligible background signal to the mass spectrum at the energies used in this study.

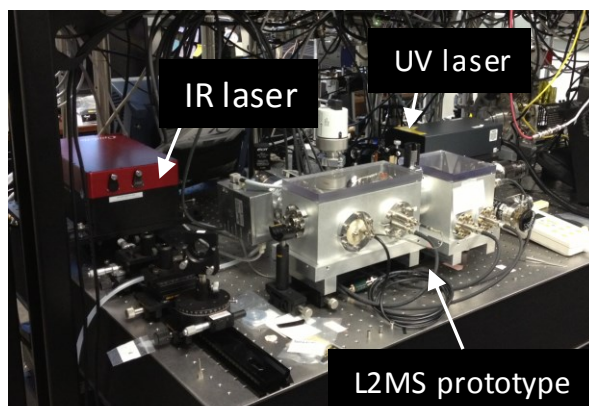


Figure 1. A compact prototype has been developed that enables two-step laser mass spectrometry on planetary analog and meteorite samples in an *in situ*-compatible instrument volume.

Results: The Murchison meteorite is well known to contain a wide variety of organic molecules and carbonaceous macromolecular material in its composition [6]. Here we examine spectra from a powdered sample of Murchison meteorite with the L2MS technique and with single-color LDMS for comparison. LDMS can be used to infer the broadband composition of the inorganic and organic constituents of the sample. Two-color L2MS mode with the use of 266 nm ionization wavelength lends specificity to the fraction of organic material that is aromatic in nature.

An LDMS spectrum of Murchison meteorite powder is shown in Figure 2. This single-color measurement used a 266 nm laser pulse to desorb and ionize the sampled species in a single step. No data processing was used here, for example, to amplify the higher molecular weight peaks to compensate for the dominant Na and K peaks (seen at m/z 23 and 39/41, respectively). Despite the low relative intensity of the organic species, a familiar envelope of mass peaks can be seen at higher m/z , corresponding to the masses of acenaphthylene, phenanthrene and/or anthracene, fluoranthene

and/or pyrene, and a series of their methylated derivatives.

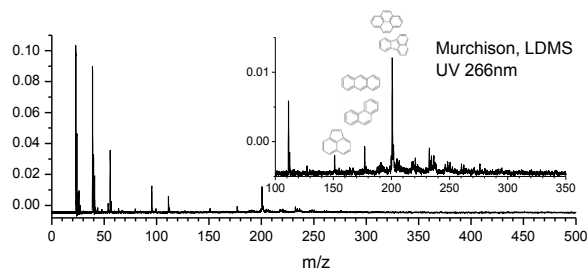


Figure 2. A single-color UV LDMS spectrum of the Murchison meteorite is dominated by the Na and K salt peaks and shows low-intensity mass signatures of organic composition at $m/z > 150$.

A series of L2MS spectra are shown in Figure 3 for the same Murchison meteorite powder, using varying IR wavelength to desorb neutrals from the sample. The IR and UV laser powers were held constant as the wavelength was varied. A maximum in signal strength is observed to occur at an intermediate wavelength, between 2.9 μm and 3.0 μm . The signal is significantly reduced at wavelengths outside of this range; lower wavelength of 2.8 μm and higher wavelength of 3.1 μm is shown in Figure 3.

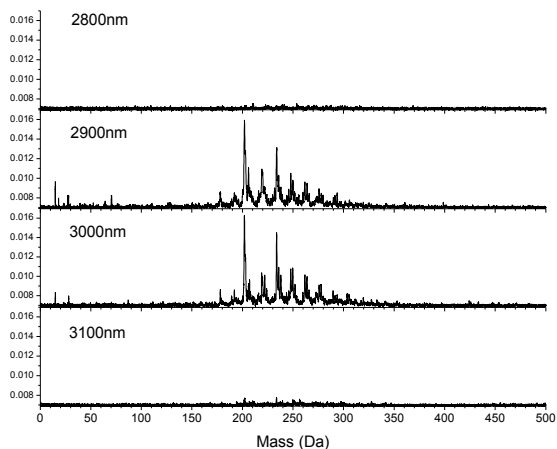


Figure 3. L2MS signal intensity is seen to be maximized at IR wavelength between 2.9 μm and 3.0 μm .

The wavelength at which these spectra exhibit a maximum coincides with a range of vibrational resonances of polycyclic aromatic hydrocarbons known to occur in the Murchison meteorite. The pattern of mass peaks is, specifically, consistent with contributions from phenanthrene and/or anthracene, fluoranthene and/or pyrene, and their corresponding methylation series. Anthracene and fluoranthene, in particular, ex-

hibit an absorption feature seen in the vibrational spectra in the range 2.9-3.1 μm [7]. This feature is smaller than the well-known C-H stretch mode at 3.2-3.3 μm . Taken together, these data suggest that the IR desorption laser at particular wavelengths can couple strongly to the vibrational resonances of specific sample analytes. For the Murchison meteorite, the dual specificity offered by the IR vibrational resonance and resonance-enhanced ionization at 266 nm provides high confidence in the peak assignments of methylated PAHs discussed here.

The measurements reported here illustrate the utility of exploiting the effects of resonance-enhanced desorption in two-step laser mass spectrometry. This technique enables enhanced specificity in analyses of complex samples and can improve confidence in the identification of mass peaks in L2MS spectra.

References:

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