

MINIATURE TWO-STEP LASER TOF MASS SPECTROMETER WITH REVERSIBLE ION POLARITY.

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Introduction: Several recent developments have advanced the capabilities of miniature time-of-flight (TOF) mass spectrometers for planetary surface missions. A gridless analyzer configuration sensitive to both ion polarities has improved the ability to identify particular elements and classes of organics [1]. The incorporation of scanning optics and/or a precision subsampling system (PSS) has opened up the possibility of point-by-point laser microanalysis on intact heterogeneous rock samples [2]. In the interest of minimizing mass, power, and complexity, these instruments have typically used single Nd:YAG pulsed laser desorption/ionization (LDI). This approach is also common in laboratory instruments offering particular sensitivity to high molecular weight (several to hundreds of kDa) compounds through the matrix assisted LDI (MALDI) mechanism. However, the indiscriminate ionization and mineral matrix effects associated with single-laser LDI can limit the ability to identify individual or even classes of compounds, when dealing with complex natural samples. A new two-step laser mass spectrometer (L2MS) now under development uses two laser sources which permit the desorption and ionization steps to be separately optimized. The objective is to improve the selectivity and sensitivity of the instrument to key classes of organics such as aromatic hydrocarbons. At the same time, the benefits of such additional capability must be carefully weighed against the increased complexity of an eventual flight design.

Approach: Two-step laser techniques have proven extremely powerful in laboratory analysis of organics

in rocks, meteorites, and returned samples for a number of years [3]. The method can enhance the sensitivity and selectivity for key classes of organics, such as trace polycyclic aromatic hydrocarbons (PAHs), which can be distinguished from the many potentially-interfering fragments and clusters from the mineral matrix of a sample that appear in single-laser spectra. Such hydrocarbons comprise a fraction of the organic matter in carbonaceous asteroids and in comets, and may survive in the near surface of Mars and other planetary bodies. The resonance enhanced multiphoton ionization (REMPI) two-step laser method pioneered by R. Zare and co-workers at Stanford University was applied to the analysis of martian meteorite ALH 84001 [4] and to several carbonaceous chondrites. Nonvolatile compounds are also generally challenging to analyze with traditional methods such as pyrolysis MS.

The L2MS method (**Fig. 1a**) uses two laser pulses to introduce molecular ions into a time-of-flight (TOF) mass spectrometer. A first pulse desorbs molecular neutrals from the sample surface under vacuum conditions. Following an adjustable delay of up to several microseconds, a second laser pulse ionizes molecules in the volume just above the surface, allowing them to be accelerated into the TOF-MS for analysis. This approach offers analytical advantages over the simpler single-laser LDI technique. First, the laser intensity required for neutral desorption is generally lower (by at least an order of magnitude) than needed to generate prompt ions, resulting in less molecular fragmentation and surface modification. Second, the wavelength of

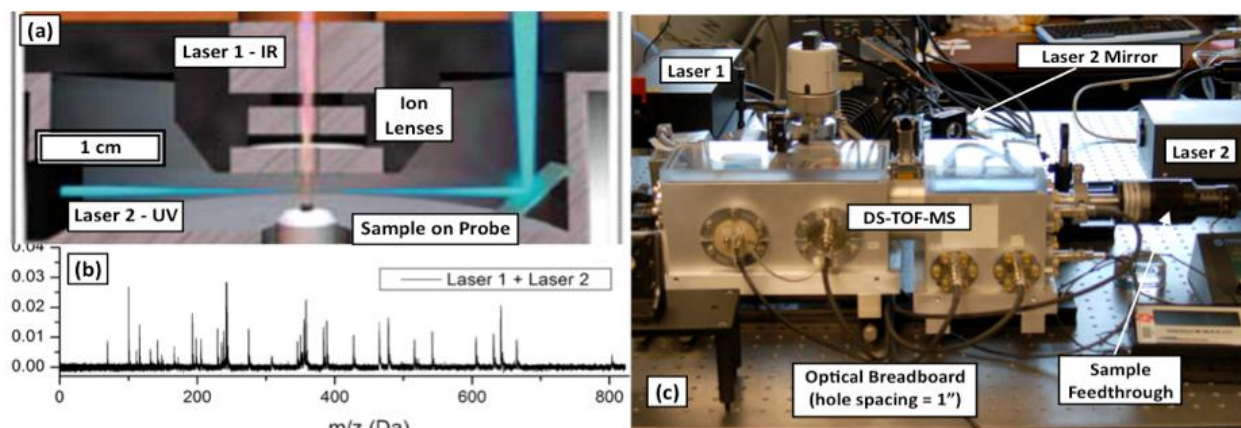


Fig. 1 L2MS (a) combines coaxial near IR desorption (laser 1) of neutral molecules and lateral UV ionization (laser 2) to enhance key relative sensitivities by more than an order of magnitude. With TOF-MS of simple analytes such as ink dye (b) we demonstrated that L2MS works in a miniature instrument (c) operating in the lab.

each laser pulse in L2MS can be selected for its distinct function. The traditional approach uses infrared wavelengths for neutral desorption and ultraviolet (e.g., 266 nm) for postionization of aromatics.

Instrument: A miniature demonstration prototype of the L2MS has been implemented in approximately the configuration shown in **Fig. 1a**, where the desorption laser is focused on the sample at normal incidence from the back of the reflectron, through the center holes of a combination linear/reflected microchannel plate detector assembly, and finally through the apertures of the asymmetric Einzel extraction lens as shown. The postionization laser is triggered with the L1 output and a delay generator to pass laterally above the sample at an adjustable position (approximately halfway across the ~4-5 mm extraction gap). The example L2MS spectrum in **Fig. 1b** from a blue ink standard containing methyl violet (penta- and hexamethylated forms) was obtained in the dual-source (DS) TOF-MS prototype shown in **Fig. 1c** with an interpulse delay of approximately 2 μ s. This standard has a reproducible LDI signature with a sharp laser intensity threshold for ion formation and aromatic organics amenable to near-UV post-ionization. The pattern of peaks in the m/z range 200-400 Da is diagnostic of the methyl violet molecular ion with related neutral losses of multi-C ligand and CH_3 (15 Da) groups. Expected peak distributions are apparent at desorption intensities significantly lower than typical in direct LDI. The high-time tailing of intense peaks may be attributed to the prompt extraction (static voltage) of ions formed over a volume (rather than very near the surface as in LDI). This will be addressed through a combination of improved UV laser focusing and delayed extraction techniques. In larger instruments, such a finite size effect may be negligible however with the drift length of only a few cm here ion source dispersion is critical.

The production of exclusively post-ionized spectra has been demonstrated with a series of tests in which the desorption and ionization laser energies are individually varied across a signal threshold. For the ink spot spectra in **Fig. 2** the desorption laser wavelength was 1064 nm (fundamental frequency of a Nd:YAG laser), and the ionization laser wavelength was 266 nm (a separate frequency-quadrupled Nd:YAG). The resolution in these spectra is relatively low due to raw averaging over TOF jitter and a finite ionization volume. However reproducible energy thresholds for each individual laser were clearly demonstrated, lending confidence in the plan to optimize the technique and apply it to complex samples.

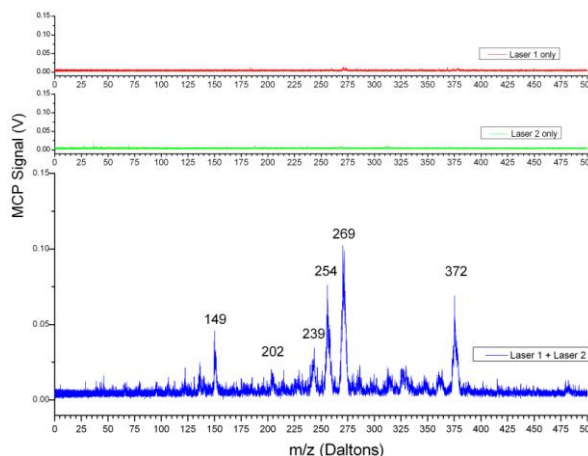


Fig. 2 DS-TOF spectra of a methyl violet dye demonstrated that L2MS works on a miniature instrument. The top two spectrum show absence of signal with low (sub-threshold) laser 1 or laser 2 energies, respectively. The bottom L2MS spectrum occurred only with sufficient laser 2 energy.

Development Plan: Ongoing improvements to the existing prototype include addressing the mass resolution limitations as mentioned above and to quantify the sensitivity and selectivity for a range of standards including PAHs and other aromatic species. This will be completed for both positive and negative ion modes, and in each case where possible compared with interleaved direct LDI spectra. Subsequently, a small number of previously well-studied natural and synthetic planetary analog samples, as well as meteorites such as Murchison and other C-chondrites, will be subjected to comparative L2MS analysis to understand how well the miniature analyzer can capture (or re-capture) documented results for detection of particular species such as PAHs, substituted PAHs, and carboxylic acids.

References: [1] Brinckerhoff W. et al. (2010) *LPS 41*, 2358. [2] Brinckerhoff W. B. et al. (2010) *Proc. Earth and Space 2010*, Honolulu, HI. [3] see e.g., Kovalenko L. J. et al. (1992) *Anal. Chem.* 64, 682-290; Mahajan T. B. et al. (2001) *J. Am. Soc. Mass Spectrom.* 12, 989-1001; Elsila J. E. et al. (2004) *Anal. Chem.* 76, 2430-2437; Davis A. M. et al. (2009) *LPS 40*, 2404. [4] see e.g., Clemett S. J. et al. (1998) *Faraday Disc.* 109, 417-436.

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