

PROGRESS IN LASER DESORPTION MASS SPECTROMETRY FOR *IN SITU* ANALYSIS.

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Introduction: Understanding the connections between chemical compounds observed in the interstellar medium, those preserved in comets and asteroids, and those found on planets is a central goal of planetary science. To make these connections our inventory of such species must be as complete as possible. Analyses of samples, whether on Earth or *in situ*, should include a breadth of measurements including atomic, isotopic, mineralogical, and organic/molecular compositions, preferably species-by-species and on a fine spatial scale. While this kind of analytical power comes naturally in terrestrial labs applied to meteorites and returned samples, *in situ* investigations must be highly selective of scope. Ideally, only the most important *combined* capabilities of complementary techniques, relative to mission science goals, should determine the performance criteria of any one instrument. Mass spectrometry plays an important role in this balance because (i) it is, in principle, sensitive to any chemical; (ii) it can be adapted to wide range of sample types and sampling conditions; and (iii) mass spectra are often diagnostic of data from other methods. We are developing miniature laser desorption mass spectrometers (LDMS) that may contribute significantly toward these benefits. The latest LDMS, a time-of-flight (TOF) instrument prototype built at a “flight-like” scale, has the potential to realize a powerful elemental and organic chemical mapping capability that could be implemented on a variety of planetary surface missions.

Background: LDMS instruments geared toward planetary missions and astrobiology research have been under development at JHU/APL for several years. The basic technique shared by all prototypes is pulsed laser desorption and ionization of solid samples, followed by mass analysis in a reflectron TOF-MS. A small, commercial Nd:YAG or N₂ laser with ns-class pulse duration is focused onto the surface of an unprepared geological sample through a long-focal-length objective system. The 30–100 μm diameter laser spot is selected from a larger (few mm diameter) field of view using a co-focused imager. This combination permits visible mineral phases or other inclusions to be selected for exclusive analysis. The position of the sample in LDMS depends on the implementation, but we have generally found that the most compact and effective geometry is that due to G. Managadze [1,2]: the laser is focused through the reflectron and the center hole of a microchannel plate detector, to

a point external to the TOF-MS flight tube, normal to the sample surface. At high intensities, $\epsilon > 1 \text{ GW cm}^{-2}$, the laser ablates a few ng of sample. This step is the same as that used in laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS), a mainstream laboratory technique for elemental and isotopic analysis. LDMS differs in that it detects the prompt (laser-induced) ions rather than those formed from laser ablated neutral particles. At lower intensities, some molecular ions survive desorption and are detected out to high mass-to-charge (m/z) ratios in the same MS. In practice, the maximum observed m/z of a singly-charged organic ion in direct desorption from an unprepared geological surface is limited to a few thousand Da by absorptivity and ionization effects related to molecular structure, host mineral matrix, and absolute abundance. This range can be extended with various sample preparation steps.

Following the development of a high- ϵ instrument exclusively for elemental and isotopic analysis on airless bodies [2,3], we have increasingly focused on designs that add the ability to detect non-volatile organics through online tuning of instrument parameters. These include ultraviolet (UV) laser desorption, a monolithic “ideal” nonlinear reflectron, and various other ion optical features to obtain high mass resolution in a miniature, flight-compatible package [4,5].

Laser Analyses: We are attempting to characterize the sensitivity of lower- ϵ UV-LDMS instruments to atomic and molecular species in realistic samples. Studies of carbonaceous chondrites such as Allende, Murchison, and ALH 83100, and of synthetic standards, indicate that UV-LDMS is sensitive to more-refractory aromatics within fine-grained matrix, such as the free polycyclic aromatic hydrocarbons (PAHs) in soluble organic matter and corresponding fragments of kerogen-like material in the insoluble phases [5]. Particularly when spatially resolved with the “chemical imaging” implementation of LDMS, detection of these compounds is of interest for their relevance to the early organic inventory in the solar system and to the delivery and survival of organics on Mars or elsewhere.

Laser analyses of complex terrestrial samples such as organic-bearing standards (Green River and other shales; urban pollutants) and Mars analogs (Mauna Kea tephra, courtesy D. Ming and R. Morris, JSC; some basalts and minerals) are underway to understand the effects of laser wavelength, host mineralogy, and

sample preparation (crushing) on the sensitivity to organics and elements. This is needed to plan for the analysis of unknown samples *in situ* using “fixed” hardware. For example, we have previously noted the very high relative signals from the alkali metals Li, Na, K, Rb, and Cs in meteorites and silicate rocks, near the threshold laser fluence at 355 nm. This is primarily due to their low enthalpies of vaporization and first ionization potentials (for cationization). Limits of detection for these elements are typically in the sub-ppmw range, and the Li isotope ratio is consequently quite precise ($\sigma \sim 1\%$) due to the widths and reproducibilities of the peak shapes of ^6Li and ^7Li at low ϵ .

Relative abundances, local mineralogy, and sample preparation appear to have significant effects on UV-LDMS detection of higher-mass organics. Compared to C-chondrites in both intact and powdered forms, the organics observed at low- ϵ in finely powdered Green River shale show less evidence of large refractory aromatic units (indicated by distinct C_NH_M envelopes with maxima at stable PAH and alkyl-PAH parent masses). Results appear to be more consistent with the expected higher relative *n*-alkane abundance associated with an algal source. The higher-mass peaks in **Fig. 1** are likely related to the electron-ionization-stable $\text{C}_8\text{-C}_{29}$ hydrocarbons and to certain biomarker fragments previously observed in laser microprobe GC-MS [6]. The larger peaks emerge from an oscillating signal from aromatic and aliphatic species, with periodicity $\Delta m \sim 12$ or 14 amu, superposed on a significant unresolved background of organic fragments. We are presently working to lower vacuum pressure and limit the ion formation volume (e.g., by minimizing sample roughness and increasing the extraction lens ion optical focal depth), which should reduce chemical noise and bring the mass resolution up to the required range.

New Prototype: In addition to performing extensive sample analyses, we are also developing a new LDMS (**Fig. 2**) at the size scale of a flight model and in a mode closer to how it would be used on a long-term robotic mission (e.g., to Mars). The sample is held at electrical ground, which is most compatible

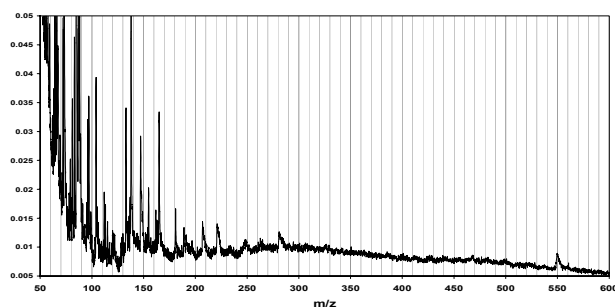


Fig. 1. Low- ϵ near UV (355 nm) laser desorption/ ionization mass spectrum of Green River oil shale sample.

with *in situ* operation. The flight tube is therefore biased to a high voltage, typically -3 kV for positive ions. Negative ions, quite useful in the analysis of small organics, can also be obtained with a new bipolar detector design that maintains the sample at ground. All intermediate and detector entry grids have been removed, reducing transmission losses and memory effects, which can affect trace detection. The vertical orientation permits examination of unconsolidated fines (e.g., soil and dust), and is compatible with a range of sample manipulation systems being studied at JHU/APL and elsewhere. In the current setup, a custom x-y-z sample stage assembly permits up to 12.5 mm lateral travel and 25 mm vertical travel using an edge-welded bellows. The reflectron length is reduced from 15 to 7.5 cm, as is the drift length. The shorter flight tube length (~ 15 cm) permits improved coaxial imaging and a smaller laser spot due to the larger relative aperture.

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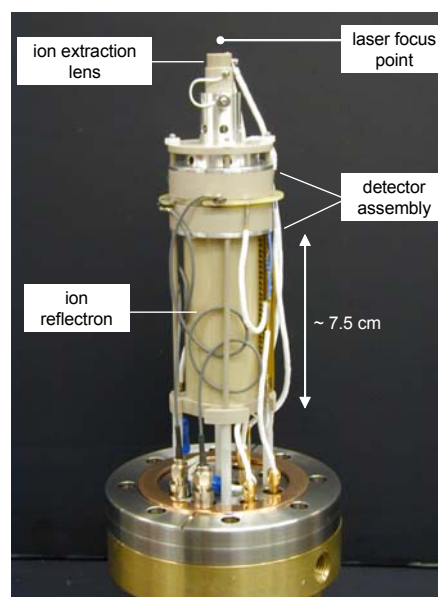


Fig. 2. The interior components of the $\sim 1:1$ scale LDMS prototype, shown inverted relative to the intended geometry. Flange ID is ~ 5 cm.