

IN-SITU LASER DESORPTION MASS SPECTROMETER DEVELOPMENT GUIDED BY PLANETARY ANALOG SAMPLE ANALYSIS. C. M. Corrigan, W. B. Brinckerhoff, T. Cornish, A. Ganesan, and S. Ecelberger, Johns Hopkins University Applied Physics Lab, 11100 Johns Hopkins Road, Laurel MD 20723 (cari.corrigan@jhuapl.edu).

Introduction: In the near future a number of planetary missions will call for high fidelity geochemical sample analysis, including landed missions to Mars, asteroids, comets, and planetary satellites. While emphasizing distinct science goals, all share certain categories of high-priority *in situ* measurement objectives. These include analyses of the elemental, mineralogical, and organic composition of solid samples from a variety of source regions, in order to learn more about the origin, evolution, and current state of the body. Looking to the next generation of *in situ* missions, there is a strong need to develop methods to improve analytical accuracy, to extend the range of species detected, to significantly lower the detection limits to trace levels, and to provide compositional data on a local, mineral-grain spatial scale. One technique that may contribute to the realization of such ambitious capabilities, within a low mass and power profile, is laser desorption mass spectrometry (LDMS).

The development of LDMS instruments has been an ongoing project at JHU/APL for a number of years [1-6], in an effort to construct instruments geared toward planetary missions and astrobiology research. Here we discuss progress made on our newest prototype and the program we have undertaken to ensure that the analyses performed by this new instrument are consistent with measurements obtained in proven commercial mass spectrometers.

Instrument Prototype: A previously-developed prototype demonstrated the potential of LDMS for broad and sensitive chemical analyses (from elements and isotopes through high molecular weight organics) [5,6]. The ability to vary the laser pulse energy as well as the time-of-flight (TOF) mass analyzer parameters “online” enables the composition to be obtained without any complex sample preparation. A

capability afforded by focused laser sampling is microscopic (point-by-point) analysis. The previous prototype was not optimized for chemical imaging; as such it has been prioritized in our new “Tower TOF” LDMS.

The coaxial Tower TOF mass analyzer consists of a nonlinear ion reflectron, a set of ion optical lenses, and a two-sided center-hole detector assembly. It is at the size scale of a likely flight model (~15 cm long) and is compatible with *in situ* operation (e.g., on Mars). For example, the sample is held at electrical ground. The flight tube is therefore biased to a high

voltage, typically -3 kV for positive ions. Some uncertainty in the sample position and roughness, relative to the LDMS entrance, has been assumed and accommodated. Grids have been eliminated from the ion flight path, improving transmission. The chamber (Fig. 1) is vertical to allow analyses of loose fines and to provide a stable bellows-coupled x-y-z motion stage, with 5 micron precision. In the prototype, samples are loaded on a standard puck through a door (near top of Fig. 1), such that the top of the sample is several mm below the instrument inlet. The imager and laser couple to a common optical path that passes through the top of the chamber and the entire LDMS sensor, normal to the sample surface. The laser spot diameter is ~50 microns; the analysis point is selected from a 2-3 mm diameter long focal length imager field of view.

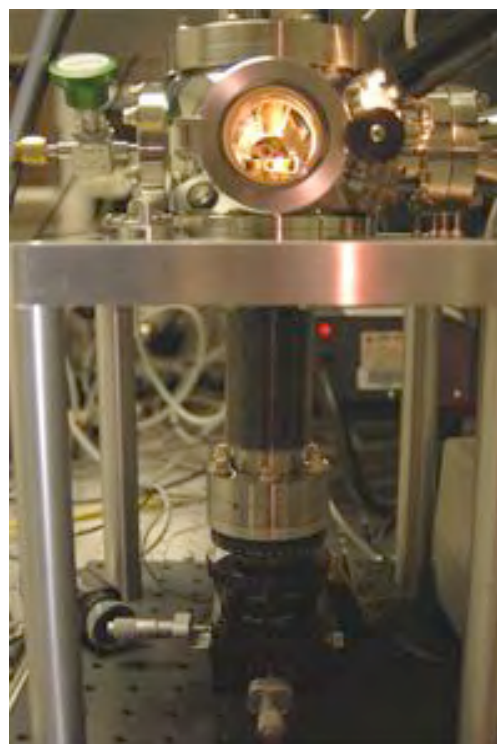


Figure 1. Tower TOF LDMS chamber, showing sample holder and detector inlet, and x-y-z sample motion stage.

Even such a highly miniaturized mass spectrometer has a large number of variable parameters, both in final design and in operation, that will affect its ability to analyze various unknown samples. Such parameters

may include the laser energy, wavelength, pulse duration, and spot size; the extraction voltage bias, profile, and tunability; and sample-dependent factors such as handling/preparation, the number of laser pulses needed, and the sample surface coverage. Therefore, it has been vital to examine a range of simple standards as well as “realistic” complex planetary analog samples with both miniature and more established facility instruments. By comparing data from common samples between these instruments under similar conditions, we may hope to establish a robust *in situ* approach.

Analog Analyses: A set of crushed Mars analogs was obtained courtesy of R. Morris and D. Ming, NASA/JSC. Samples were loaded into holders compatible with the miniature LDMS as well as a Bruker Autoflex TOF/TOF LDMS available at JHU/APL. The Bruker instrument uses a 337 nm N₂ laser and features high voltage extraction, positive and negative ion detection, and tandem capabilities for fragment analysis.

Example Bruker spectral data for two analogs, Mauna Kea jarositic tephra and Columbia River basalt, are shown in Figs. 2 and 3, respectively. In both cases, the first few low-energy laser pulses on a fresh surface desorbed a large quantity of organics, with characteristic CH₂ repeat units and molecular weights as high as 1 kDa. It could not be determined whether these compounds were present in the field or were subsequently introduced during handling. The data shown here are averages recorded after this initial transient had disappeared. The “bulk” material contained very low organic concentrations. The salt-containing tephra tended to yield higher-mass positive ions through potassium ionization, as K has a low ionization potential. These peaks are likely associated with potassium sulfite clusters with varying O atom number. By contrast, this route is not available for negative ions, and as such these data include some oxide clusters as well as small organic compounds. Negative ionization may be the best approach for such samples.

The basalt sample proved a good absorber of the near-UV laser light and did not require high pulse energy or long averages to obtain both elemental and small-organic composition within one scan. The inset of Fig. 3 shows the complete major and minor cation composition between *m/z* 20 and *m/z* 70. At higher masses a few oxide peaks are evident, along with several small organics such as PAHs and alkyl-PAHs.

Other analogs, such as the albite 1481 BANAB1, included mainly individual mm-scale mineral grains. These typically exhibited a sharp laser intensity desorption threshold. In the Bruker LDMS, specific points on each grain were targeted for analysis. While most of each grain’s surface did not yield organics beyond the first few shots, some albite grains had inclu-

sions or other features that appeared to incorporate extensive organics at depth. As mineral grains might be capable of preserving water-borne organics in such features over long timescales (e.g., on Mars), the need for micro-analysis of intact sample surfaces *in situ* warrants further attention and investigation.

Comparison of these data with those from the previous and new prototype LDMS instruments is ongoing. These analogs are also being used at NASA/GSFC to calibrate the Sample Analysis at Mars (SAM) suite in development for the 2009 Mars Science Laboratory (MSL) mission. LDMS data may support SAM by providing an independent check of the composition as measured by the SAM pyrolysis/electron ionization GCMS technique.

References: [1] Brinckerhoff W. B. et al. (2000) *Rev. Sci. Instr.* 71, 536. [2] Cornish T. et al. (2000) *Rapid Comm. Mass Spec.* 14, 2408. [3] Brinckerhoff W. B. (2004) *Appl. Phys. A* 79, 953. [4] Brinckerhoff W. B. et al. (2005) *Planet. Space Sci.* 53, 817. [5] Brinckerhoff W. B. et al. (2005) *Proc. 6th IAA Conf. Low Cost Plan. Missions*. [6] Brinckerhoff W. B. et al. (2006) *LPS XXXVII*, #2015.

Acknowledgments: We appreciate the collaboration and assistance of E. Vicenzi, T. McCoy, P. Mahaffy, D. Stepp, N. Hagen, and P. Demirev. Funding provided by NASA PIDD and MSL programs.

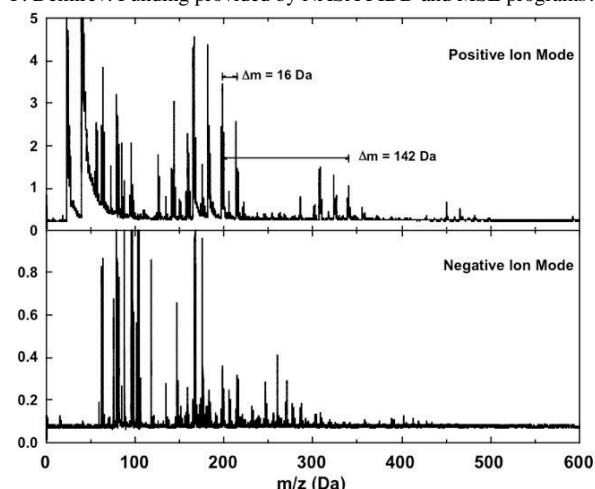


Figure 2. LDMS spectra at 337 nm from analog sample HWMK501, a jarosite-bearing tephra.

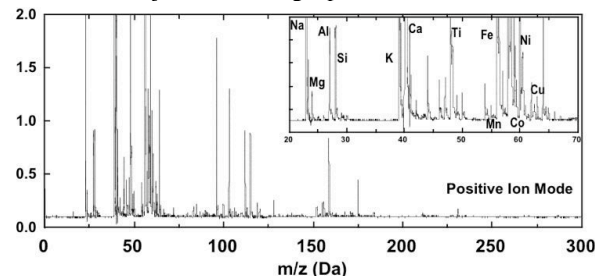


Figure 3. LDMS spectra at 337 nm from ground Columbia River Basalt CRBSW1. Inset shows low mass range.