ADVANCEMENT OF A COMPACT REFLECTRON TOF-MS FOR PLANETARY SAMPLE ANALYSIS.

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Introduction: Future landed missions to Mars, gas giant moons, comets, asteroids, and other bodies will require increasingly sensitive and flexible chemical sample analysis capabilities to address detailed questions about planetary evolution and astrobiology. However, payload mass and power limitations will generally remain extremely tight. These limitations are particularly challenging for solid sample mass spectrometry, which is a powerful approach to the broad analysis of unknowns, but typically has sample introduction, gas handling, and control electronics requirements that can tax resources. We are developing a miniature laser time-of-flight mass spectrometer (TOF-MS) that requires little or no sample contact, yet remains a powerful tool for both elemental and nonvolatile organic analysis of complex planetary samples.

Instrument Design: The basic design of our laser TOF-MS uses single pulsed laser desorption and ionization point-by-point from a sample surface *in vacuo*. A number of features under development comprise the core sensor, as depicted in **Fig. 1**:

Reflectron. A short (<10 cm), gridless nonlinear reflectron [1] provides high-order temporal focusing of ions with a distribution of energies. This component accommodates the wide distribution of laser-induced ion energies that result from the analysis of samples with widely-varying mineral and analyte absorptivities. The reflectron also allows the simultaneous focusing of unimolecular decay fragments of organic molecules, which helps distinguish peak patterns associated with different classes of compounds. Lower-energy fragment ions remain in focus because temporal compression of ion packets occurs over a significant fraction of the reflectron length.

Reversible Polarity. The instrument is now capable of analyzing both positive and negative prompt ions from the same sample. Complementary composition information from positive and negative polarity ions can significant improve the ability to identify particular elements and classes of organics. Laser desorption/ionization (LDI) data for biomolecular analysis are most commonly collected in positive ion mode, owing primarily to the development of matrix assisted LDI (or MALDI), in which protonation of an analyte M gives the positive ion MH^+. Negative ions are also used in MALDI; these can form less ambiguous parent and fragment peaks. Negative ions form by electron attachment to desorbed neutrals, during which the supply of electrons is reduced. At lower laser intensities, negative ionization is electron-supply limited; the ionization probability is strongly correlated to electron affinity. Organics with more electronegative functional groups and/or complex pi orbitals are more likely to ionize [2]. Anion fragmentation patterns often differ significantly from those of cations, providing additional information on parent molecular structure. In addition, negative mode spectra lack the intense Na and K peaks that can dominate baseline noise when analyzing complex geological samples (**Fig. 2**).

Reversible polarity is implemented in the present design by floating the mass analyzer and detector assembly to an adjustable negative voltage, and by eliminating the detector entry grid. This grid is normally used to provide post-acceleration of ions just prior to impacting the microchannel plate detector, however it is less critical in this application. The detector bias is clamped to the flight tube at the base of the reflectron.

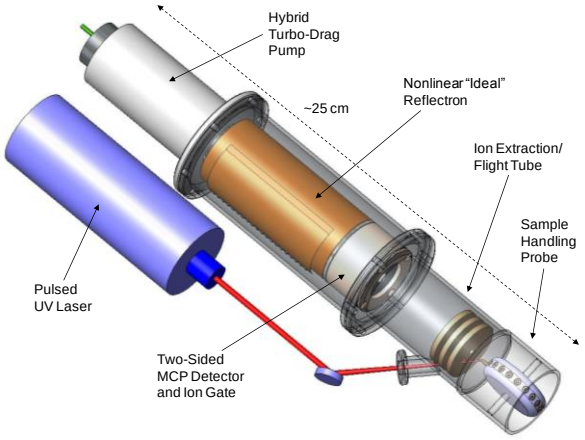

Fig. 1 Schematic arrangement of reflectron TOF-MS (center section) with turbo-drag pump and pulsed laser systems. Notional sample handling probe seals small solid samples at vacuum interface.

Pseudo Tandem MS. A tandem mass spectrum is one in which a limited range of mass-to-charge (m/z) values (possibly a single peak) is isolated and fragmented for mass analysis. This spectrum permits the

association of fragments with a known parent ion, which upon further analysis can dramatically reduce the ambiguity of structural assignment in complex mixtures. This capability is implemented to some extend in the laser TOF-MS by using a Bradbury-Nielsen gate (BNG). The function of the BNG is to pass selected segments of the ion beam into the reflectron for detailed analysis. The BNG has found increasing use in TOF-MS instruments due to its planar geometry [3]. The electric field of an interdigitated array of wires held at opposing voltages falls off very rapidly with distance normal to the plane. Any ion passing between the biased wires is efficiently scattered, but ions not in the immediate vicinity of the plane are unaffected. In our design the BNG can be used as a notch filter to select individual peaks for propagation into the reflectron. As selected molecules will continue to undergo metastable decay, the post-gate fragment spectra are directly linked to the parent molecule selected from previous spectra, generating a *de facto* tandem mass spectrum. However this is only practical in concert with the nonlinear reflectron, because ions of all energies (parent and fragments) must be simultaneously focused. Scanning the gate to isolate each precursor ion in a mixture yields a series of spectra which can help identify its individual components.

Sample Handling Probe. A robotic mechanism to entrap particulate sample on a probe tip and position it for laser analysis is included (**Fig. 1**) as one of several possible sample handling approaches under development. The probe enables reproducible positioning of small (sub-mg) sample masses, vacuum sealing (if required), tip change-out for multiple samples, as well as the sample pre-processing via microfluidic extraction or MALDI matrix application. The compact rotating wheel holds "spoke" probe tips that extend and retract along wheel radii. Tip actuation may occur via spring/catch-based motion (such as in retractable pens) using a shape memory alloy (SMA)-based spring.

Demonstration Spectra: As part of the standardization and planetary analog testing plan, we have analyzed a number of Mars analogs using both miniature and facility-class (Bruker Autoflex) laser TOF-MS instrumentation. Analyses of a Hawaiian jarositic tephra (HWMK501, provided courtesy R. Morris, NASA/JSC) have supported the potential use of laser TOF-MS in sulfate-rich environments on Mars [4]. An organic (hydrocarbon-rich) signal was mainly confined to the first few dozen laser pulses, likely indicating an exposed surface biomass, with only trace organics associated with mineral grain interiors seen in longer integrations. In positive mode (**Fig. 2**, left side), the salt-rich tephra yielded higher-mass positive ions through K^+ attachment, primarily associated with potassium sulfite clusters with varying O number. This route is not available for negative ions, and as such these data include some oxide clusters as well as organic compounds (**Fig. 2**, right side). The mass resolution and sensitivity of the miniature TOF-MS fare well in comparison with the Autoflex, considering its acceleration voltage is seven times higher and its flight tube is ten times longer. The high-fidelity match between data in both ion polarity modes is very encouraging for the effort to optimize the miniature laser TOF-MS for analysis of complex unknowns *in situ*.

References: [1] Cornish T.J. et al. (2000) *RCMS 14*, 2408. [2] Bezabeh D.Z. et al. (1997) *JASMS 8*, 630. [3] Yoon O.K. et al. (2007) *JASMS 18*, 1901. [4] Corrigan C.C. et al. (2007) *LPSC XXXVIII*.

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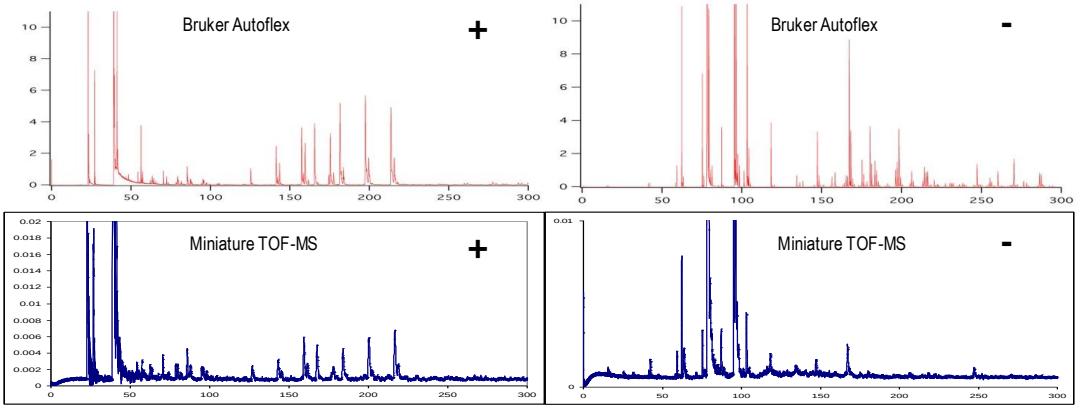

Fig. 2 Jarositic tephra Mars analog data from our modified miniature TOF-MS demonstrate resolution and sensitivity comparable to the commercial Bruker Autoflex as well as the complementary information available from alternate polarities.