LASER ABLATION-ELECTRODYNAMIC ION FUNNEL FOR *IN SITU* MASS SPECTROMETRY ON MARS.
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NASA has invested a great deal of resources into the development of various instruments for *in situ* analysis of extraterrestrial bodies. As a result, there currently exists a wealth of instrumentation suitable for detailed *in situ* analytical investigation. One common characteristic among many of these instruments is that they require extensive sample handling in order to extract and ionize atoms and/or molecules, before interrogation by the instrument in question can take place. Instruments falling within this class of analytical technique include time-of-flight and quadrupole ion trap mass spectrometers, quadrupole mass filters, and ion mobility spectrometers. Despite the relative maturity of the fundamental analytical techniques and instrumentation, there exists a conspicuous lack of investigation into the details surrounding the sample manipulation and preparation required by such instruments. This situation is particularly troubling given that applicable practices, used commonly in terrestrial laboratories, do not readily lend themselves to robotic execution. We will address this issue by developing a front-end instrument to extract, ionize and inject samples into a mass spectrometer with no prior sample preparation.

A promising means of reducing the complexity of the sample handling required by instruments such as those discussed above is to employ laser ablation ionization. Laser ablation is a very attractive technique for *in situ* ionization of rock and soil samples since a laser is able to sample the surface of a rock or soil with minimal manipulation of the sample and no sample preparation. As such, the utility of laser ablation ionization for space applications has been considered previously [1,2]. However, despite the potential benefits of laser ablation ionization, there are major issues with the two scenarios for its implementation in an *in situ* Martian experiment that are possible with existing instrumentation. One possible scenario is to perform the ablation on a sample in Martian atmosphere and then transport the ions into the high vacuum of a mass spectrometer. The problem with this scenario is that traditional ion transportation and focusing devices do not function in this pressure regime (~ 5 Torr) due to collisions between the ions and the ambient gas. As a case in point, terrestrial instruments using atmospheric ionization techniques typically suffer ion losses as high as three orders of magnitude over the 0.1-10 Torr region of a primary pumping stage. The second scenario is to bring the sample within the high vacuum chamber, and evacuate the chamber before ablation and analysis. When investigating rock samples, this would either restrict the size of samples that could be interrogated or would require rocks to be crushed into sufficiently small fragments before being placed in the vacuum chamber. Additionally, the out-gassing of the porous and/or rough sample surfaces would make for extended pumping times especially given the pumping capacity of the miniature pumps that could realistically be included on a flight instrument. Beyond the added mass of the pump, this would drastically increase the power consumption of the instrumentation.

We are developing a front-end instrument that will exploit the advantages of laser ablation ionization while avoiding the pitfalls discussed above. This instrument, namely the laser ablation-ion funnel (LAIF), will ionize rock/soil samples in the ambient Martian environment with no sample preparation. The LAIF will then efficiently capture, transport and inject the product ions into a mass spectrometer for *in situ* analysis. Previous work with ion funnels in conjunction with electrospray ionization sources have shown their ability to trap and transport ions through the appropriate 1-10 Torr pressure regime with near 100% efficiency [3]. It is this ability that will turn laser ablation ionization into a truly tractable solution to the *in situ* sample handling and ionization problem. Finally, we note that the LAIF would have no restrictions in terms of the size of rock that could be analyzed. Since rock samples would not have to be contained within a vacuum chamber, the instrument could simply be positioned close to the surface of a rock, of arbitrary size, to perform the ionization and transport.

The electrodynamic ion funnel design, shown schematically in Figure 1, is based on the stacked ring rf ion guide described by Gerlich and co-workers [4]. Essentially, the ion funnel consists of a stack of concentric ring shape electrodes whose inner diameters (IDs) decrease over the length of the funnel. DC potentials are applied to each electrode to produce a smooth potential slope along the axial direction such that ions drift toward the ‘small’ ID or ‘exit’ end. As with the Gerlich ion guide, two radio frequency AC potentials, which are equal in amplitude and exactly 180° out of phase, are applied alternately to the ring electrodes by means of decoupling capacitors. The application of the rf potentials in this manner creates a local rf gradient field along the inner surface of the

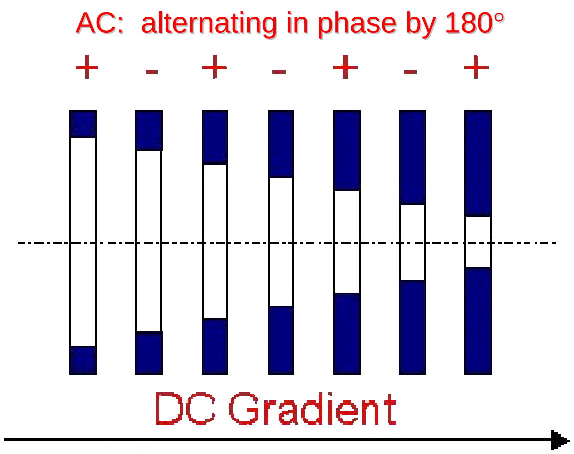

Figure 1: Schematic of an electrodynamic ion funnel electrode stack.

The average force on an ion due to such a local gradient field is repulsive; thereby creating an effective potential barrier. The effective potential barrier (in the radial direction) created in this arrangement is flat throughout the majority of the funnel volume with a sharp rise near the inner ring surfaces [4]. This effective potential contains ions within the inner volume while having virtually no effect on any axial motion within the funnel volume.

When ions are introduced into the 'mouth' of the funnel, the DC potential drives them toward the exit while the effective rf barrier prevents the ions from hitting the electrodes. The net effect is to capture the entire expanding ion cloud and then to focus the ions towards the axis of the ionizer. At the same time, collisions with the ambient gas damp the motion of the ions resulting in a narrow kinetic energy distribution at the end of the funnel. After reduction of both their radial and kinetic energy distributions within the funnel, the ions are perfectly suited for injection into the high vacuum stage of a mass spectrometer, where they can be mass analyzed (see Figure 2).

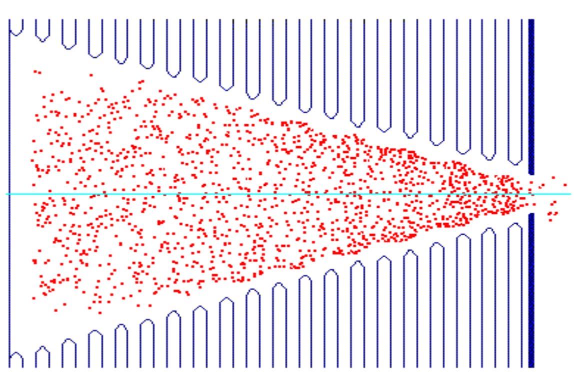

Figure 2: Ion focusing simulation for m/z 1000 ions at a pressure of 10 Torr.

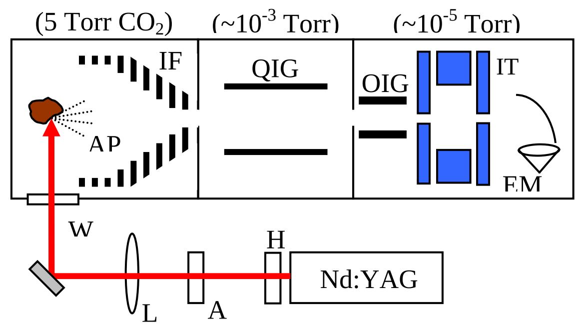

Figure 3: Schematic of the LDIF test bed; harmonic generator (HG) for 266, 355, or 532 nm emission (omitted for 1064 nm emission), attenuator (A), lens (L), mirror (M), window (W), sample (S), ablation plume (DP), ion funnel (IF), quadrupole ion guide (QIG), octopole ion guide (OIG), ion trap (IT), electron multiplier (EM).

We are currently working to demonstrate the utility of the LAIF concept, with rock samples contained in a chamber backfilled to ~5 Torr CO_2 in conjunction with a Thermo-Finnigan LCQ ion trap mass spectrometer. A schematic of the test-bed instrument is given in Figure 3.

References: [1] Managadze G. G. and Shutyaev I. Y. (1993) in Laser Ionization Mass Analysis; Vertes A., Gijbels R. and Adams F. eds.; John Wiley and Sons Inc.: New York, 505-549. [2] Brinckerhoff W. B., et al. (2000) *Rev. Sci. Instr.*, 71, 536-545. [3] Shaffer S. A. et al. (1998) *Anal. Chem.*, 70, 4111-4119. [4] Gerlich D. (1992) in State-Selected and State-to-State Ion-Molecule Reaction Dynamics, Part 1: Experiment, Vol. LXXXII; Ng C.Y. and Baer M. eds.; Wiley and Sons Inc.: New York, 1-176. [5] Shaffer S.A. et al. (1997) *Rapid Comm. Mass Spec.*, 11, 1813-1817.

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