

New Developments in Reversible-Polarity Laser Time-of-Flight Mass Spectrometry for Future In Situ Planetary Missions. X. Li,¹ S. A. Getty,² A. Grubisic,³ W. B. Brinckerhoff,² T. Cornish,⁴ and S. A. Ecelberger,⁴
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Introduction: Laser desorption/ionization time-of-flight mass spectrometry (LD-TOF-MS) is a powerful analytical technique that can provide compositional information about both the inorganic and organic species present in a solid material. This conceptually simple technique has the advantage of relatively little need for sample preparation. Given the wide molecular mass range intrinsic to the TOF technique, the instrument is especially well suited to the analysis of high molecular weight organic compounds, a compelling capability for planetary science missions that continue to emphasize habitability and the origin and evolution of organics on planetary bodies, such as Mars, icy satellites of the Outer Planets, and small bodies, i.e. comets and asteroids. An *in situ* investigation of the surface composition of one of these targets of interest is expected to yield a diverse range from the inorganic elements (help to determine the mineralogy) to the important groups of organics like carboxylic acids, amino acids, and polycyclic aromatic hydrocarbons (PAHs). Over the past several years, we have developed a prototype reversible-polarity time-of-flight mass spectrometer (RP-TOF-MS) that is focused on enhancing the ability of the core LD-TOF-MS instrument to detect and resolve the structure of organics[1,2]. We describe our recent efforts in the instrument development that focus on the analog samples study in the negative ion mode, as well as enhance the sensitivity in the relatively high mass range in the positive ion mode by novel pin ion gating technique.

Instrument description. The RP-TOF-MS, detail as shown in Figure 1, is a 5 kg-class instrument measuring ~ 30 cm long. A curved field reflectron (CFR) is a distinguishing feature of the instrument[3]. The RP-TOF-MS is capable of measuring positive and negative ions, both of which are created in the process of laser desorption/ionization (LDI) from sample surface with a single UV laser pulse. In its present configuration, a UV laser (Nitrogen 337nm or Nd:YAG 266 nm) is focused onto the surface to generate ions within a few nanosecond pulse width, leading to unit mass resolution at several hundred Da. The RP-TOF-MS has also been upgraded with a

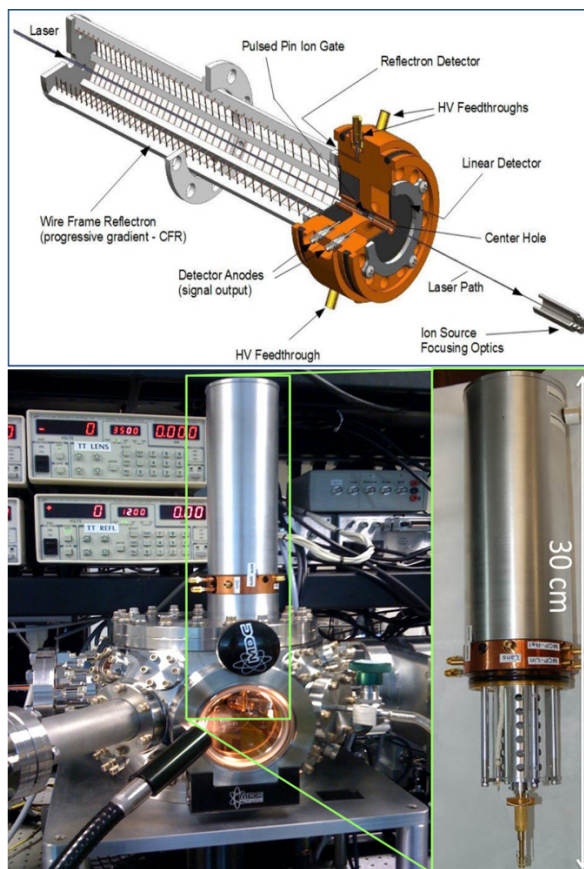


Figure 1. (TOP) The detailed wire frame reflectron and integrated detector body. (Bottom) The current RP-TOF-MS instrument, which is a 5 kg-class instrument measuring ~ 30 cm long.

prototype pulsed pin ion gate housed just prior to the entry to the reflectron.

Negative Ion Mode. Taken with the conventional positive ion spectrum, mass analysis of the negative ions provides additional structural information to the measurement, with particular specificity to species bearing electronegative elements (such as S, Cl, and N). An example mass spectrum of the perchlorate salt (Figure 2) has clearly showed the perchlorate related peaks are detected in the negative mode which is absent in the positive mode. In similar cases, we demonstrate here the laser desorption mass spectra of representative clay minerals, eg. nontronite, kaolinite,

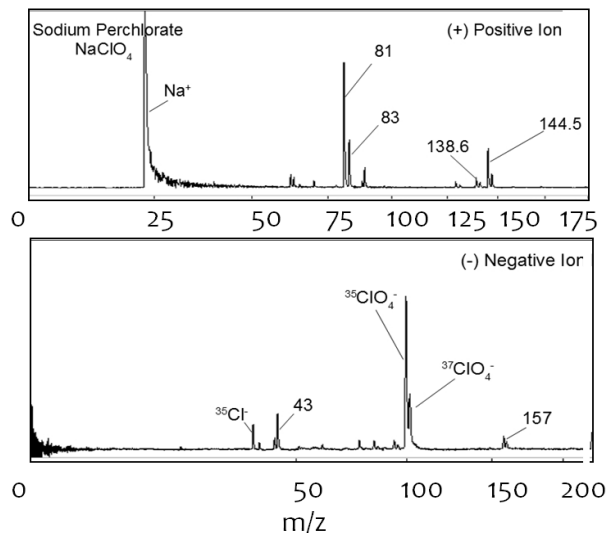


Figure 2. Mass spectra of Sodium perchlorate in both positive and negative ion modes. The negative mode clearly provide more critical information in identifying the species.

montmorillonite, butterfinger clay, etc., can provide important additional information in the negative ion mode. The mass spectra of nontronite in both positive and negative modes are shown in Figure 3 as an example.

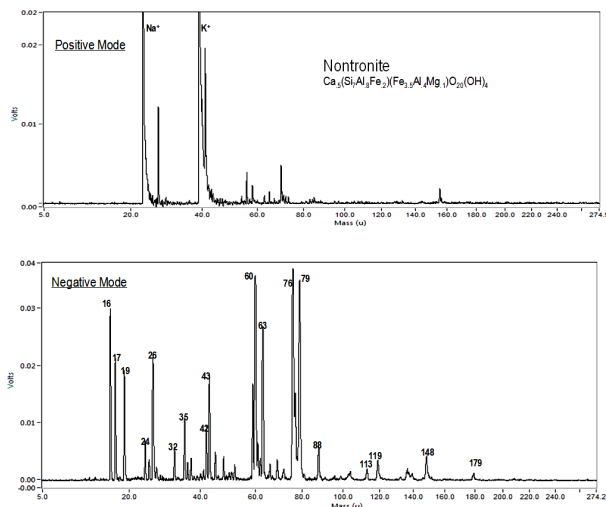


Figure 3. Mass spectra of nontronite in both positive and negative ion modes.

Ion Gating. The benefits of the pulsed pin ion gate are two-fold: (1) it enables improved sensitivity by eliminating detector saturation due to intense salt peaks that appear at low mass (and therefore early in the time-of-flight spectrum). As an example shown in Figure 3, the signal sensitivity of high mass (organic) species in the positive mode got significantly enhanced

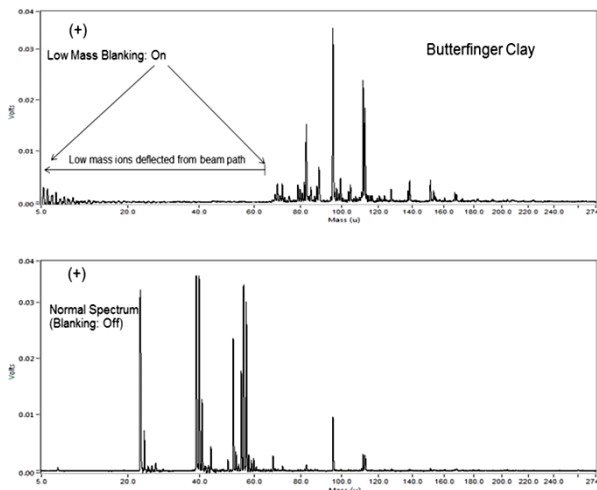


Figure 4. Demonstration of pin-gate "low mass blanking" mode in the positive mode to enhance sensitivity of higher mass ions embedded within a sample (Butterfinger clay) containing high salt content.

once the ion gating is on and the low mass (salt) species got filtered out. (2) It enables selectivity by isolating a single species of interest with its affiliated fragment ions. Fragmentation studies have been limited to those compounds that experience neutral loss spontaneously through collisions with background chamber gas. The CFR is crucial for this analysis of post-source fragmentation products as it allows simultaneous focusing of both parent and product ions at the detector.

Conclusion. An integrated, reversible polarity laser desorption/ionization time-of-flight mass spectrometer incorporating curved field reflectron, and pulsed pin ion gate has been developed. Data from this analyzer is shown to have advanced analytical capabilities in representative samples including clays and minerals for planetary studies and future *in situ* space missions.

References: [1] Getty S, et al., (2012) *International Workshop on Instrumentation for Planetary Missions*. 1100. [2] Getty S, et al., (2012) *Concepts and Approaches for Mars Exploration*. 4302. [3] Cornish T, Cotter R, (1994) *Rapid Commun. Mass Spectrom.* 8, 781.