Development of the Switchable Ion Polarity on Linear Ion Trap Mass Spectrometry (LITMS). Xiang Li¹, Andrej Grubisic², Stephanie A. Getty³, William B. Brinckerhoff³, Friso van Amerom⁴, Ryan M. Danell⁵, Veronica T. Pinnick¹, Ricardo D. Arevalo Jr.¹, ¹Center for Space Science & Technology, University of Maryland, Baltimore County, Baltimore, MD, ²Center for Space Science & Technology, University of Maryland, College Park, College Park, MD, ³NASA Goddard Space Flight Center, Greenbelt, MD, ⁴Mini-Mass Consulting, Inc., Hyattsville, MD, ⁵Danell Consulting, Inc., Winterville, NC.

Introduction: A new, highly compact linear ion trap mass spectrometer (LITMS) has been under development building upon the design of the Mars Organic Molecule Analyzer (MOMA) mass spectrometer (MS) onboard the 2018 ExoMars rover. LITMS combines two powerful approaches to organics analysis, pyrolysis gas-chromatography/mass spectrometry (GCMS) and Mars-ambient laser desorption mass spectrometry (LDMS), linked through a single, highly-miniaturized mass analyzer. The instrument thus enables analysis of (i) volatile/semivolatile organic compounds via electron impact (EI) ionization and (ii) non-volatile/refractory organic and inorganic content under Mars-ambient conditions via laser desorption ionization (LDI). Compared to MOMA, LITMS features further miniaturization and substantial analytical enhancements identified during the MOMA-MS development but not realized due to schedule or mission architecture limitations. Specifically, the additional analysis capabilities on LITMS include dual RF power supplies to increase mass range compared to MOMA, both positive and negative ion detection, precision subsampling of drill cores at fine (< 1 mm) spatial scales, and pyrolysis of powdered sample for evolved gas analysis (EGA) of minerals and organics. The envisioned operational sequence of LITMS would employ dual-polarity LDMS to screen the length of a planetary core sample. Features or layers of interest may then be subsampled using a Precision Subsampling System [1] to deliver fines from a targeted core region to a high temperature pyrolysis oven for evolved gas analysis. Here, we present results on two LITMS subsystems to demonstrate the advanced capabilities enabled by (i) positive and negative ion detection and (ii) EGA of synthetic mineral/mixtures using a prototype high temperature pyrolysis oven coupled to a LITMS breadboard mass spectrometer.

Negative ion mode: Complementary information from negative ion LDI spectra significantly increases the probability of identifying electronegative moieties that incorporate elements such as S and Cl, as well as classes of organic compounds (including several carboxylic and amino acids) that favor anion formation. To achieve the switchable polarity capability, we modified the MOMA ion detector setup, which is limited to cation detection. With the addition of a small “buffer” electrode (Figure 1), the LITMS dynode voltage polarity can be switched enabling negative ions detection.

Mass spectra of representative organic compounds in standards and Mars analog samples can be obtained in both positive and negative ion modes, as well as both EI and LDI modes. For certain samples, negative mode can be critical for composition analysis. An example is given in Figure 2 showing the negative ion mode detection of mellitic acid in the LDI mode.

![Figure 1: Modified ion detection system thus enable the mass spectra measurement in both positive and negative ion mode.](image1)

![Figure 2: Representative positive and negative ion mass spectra of mellitic acid collected in the LDI mode, showing the importance of the negative mode in detecting the molecule.](image2)
Evolved gas analysis (EGA): Precisely selected sub-samples, with masses up to several mg, can be captured in LITMS for high temperature evolved gas analysis (EGA) and gas chromatography. The pyrolysis oven is derived from the high-temperature Volatile Analysis by Pyrolysis of Regolith (VAPoR) design. LITMS also inherits maturity from the flight-proven analysis protocols of the Sample Analysis at Mars (SAM) investigation now operating on Mars [2]. The LITMS pyrolysis system is able to heat samples from ambient to a maximum temperature of 1300°C, providing more broad coverage and separation of both mineral and organic volatile decomposition products (H₂O, CO₂, SO₂, HCl, O₂, alkane and aromatic hydrocarbons) from phases including phyllosilicates, sulfates, and carbonates [3].

Preliminary data have been obtained by coupling the VAPoR pyrolysis oven system to the LITMS breadboard ion trap mass spectrometer to enable EGA on representative Mars related minerals. For this demonstration, 5-10 µg of powdered mineral mixture were added manually to the oven. An EGA thermogram is shown in Figure 3 for melanterite, a hydrated iron sulfate. The production of evolved gases SO, SO₂ and SO₃ is shown in the yellow, blue, and red traces, respectively. These characteristic sulfate peaks are shown to be centered around 575°C, in excellent agreement with laboratory scale instrumentation. The characteristic temperature is diagnostic of the cationic composition of the mineral and can allow the differentiation between candidate sulfates.

![EGA spectrum of melanterite (FeSO₄·7H₂O) using VAPoR oven and LITMS ion trap.](image)

**Summary:** Advanced techniques of dual polarity ion mode and evolved gas analysis have been integrated with an ion trap mass spectrometer, towards the development of the LITMS instrument. The hardware addition enabling negative ion mode requires only a minimal increase in instrument mass and power, and no detrimental impact to sensitivity of positive ion mode has been seen. Evolved gas analysis has been integrated with an ion trap mass spectrometer breadboard, demonstrating the EGA capability of LITMS. Future efforts will demonstrate the operation of a LITMS brassboard instrument under Mars pressures toward flight readiness of this advanced instrument for future in situ investigations at Mars and other potential planetary environments.

**References:**