Development of the Molecular Analyzer for Complex Refractory Organic-rich Surfaces (MACROS). Xiang Li[1], S . A. Getty[2], A. Grubisic[3], T. Cornish[4], J. E. Elsila[2], J. Ferrance[5], A. Southard[6], M. Balvin[2], and W. B. Brinckerhoff[2]. [1]University of Maryland, Baltimore County, Baltimore, MD (xiang.li@nasa.gov); [2]NASA/GSFC, Greenbelt, MD; [3]University of Maryland, College Park, College Park, MD; [4]C&E Research, Inc., Columbia, MD; [5]J[2]F Engineering, Charlottesville, VA; [6]Universities Space Research Association, Greenbelt, MD.

Introduction: The Molecular Analyzer for Complex Refractory Organic-rich Surfaces, MACROS, is a novel analytical instrument package we have been developing for the surface composition analysis of targeted bodies (Figure 1). MACROS couples two powerful techniques into one compact instrument package: (1) laser desorption/ionization time-of-flight mass spectrometry (LDMS) for broad detection of inorganic mineral composition and non-volatile organics, and (2) liquid-phase extraction methods to gently isolate the soluble organic and inorganic fraction of a planetary powder for enrichment and detailed analysis by liquid chromatographic separation coupled to LDMS. The LDMS includes two modes of operations: single laser LDMS and two step laser mass spectrometry (L2MS). LDMS is capable of positive and negative ion detection, precision mass selection, and fragment analysis providing structural analysis. The liquid-phase extraction is done in a newly designed extraction module (EM) prototype, providing selectivity in the detailed analysis of a complex sample. MACROS enables the *in situ* characterization of a sample's composition for a mission targeting an icy moon, carbonaceous asteroid, or comet.

Instrument and Methodology:

LDMS and L2MS: MACROS relies on a reversible-polarity time-of-flight mass spectrometer (RP-TOF-MS) as the main composition analyzer, which we have been develoing [1,2] over the past several years. The core of the mass analyzer is a curved field reflectron (CFR). A UV laser (Nitrogen 337 nm, Nd:YAG 355 nm, or Nd:YAG 266 nm) is focused onto the sample surface to generate ions, and both positive- and negative-ion mass spectra can be achieved.[3] On this analyzer, a novel pin ion gating technique has also been employed, enabling precision mass selection.[4] Benefit of it includes improved sensitivity to mid- and high-molecular weight species, and detection of product ion spectra (MS/MS) providing more structural information to the measurement.

In addition to the single laser configuration, the two step laser mode, L2MS, employs a crossed-beam configuration to desorb neutrals from the surface with a pulsed infrared (IR) laser and forms ions above the surface with a delayed, orthogonal UV pulse. The wavelength of the IR desorption pulse can be tuned from 2700 nm to 3100 nm (generated by a Opotek IR Opolette 2731 laser), and focused at the plane of the sample

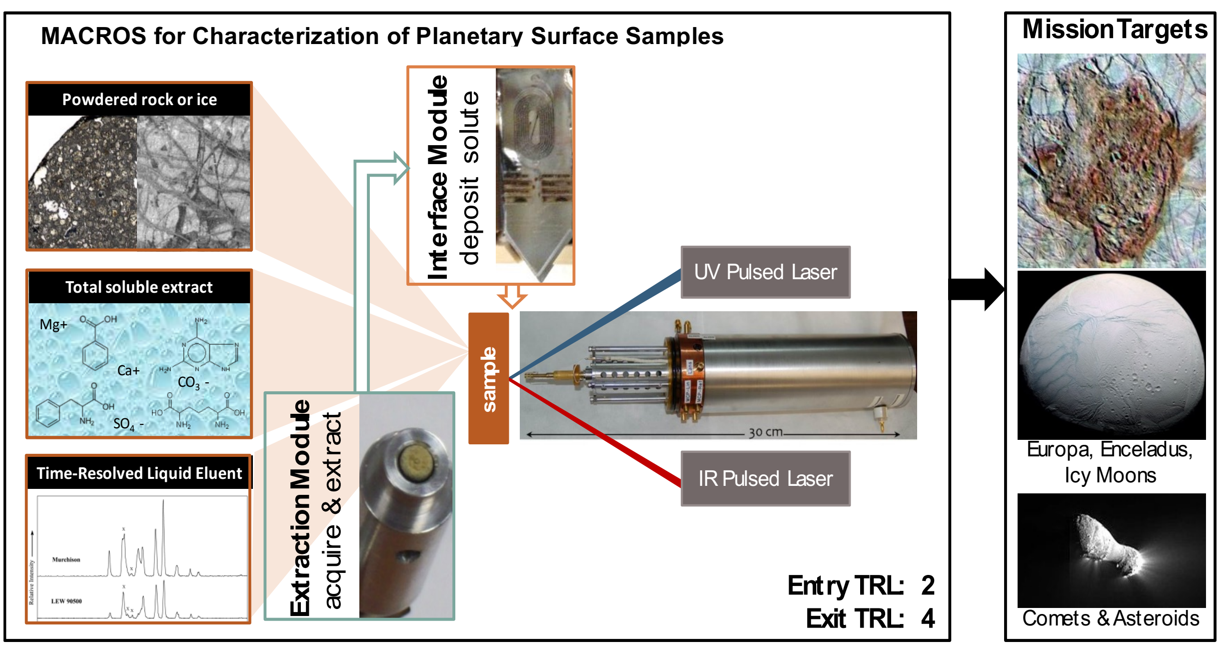

Figure 1. MACROS is capable of acquiring sample from rock or ice, acquiring a broad survey mass spectrum of major inorganic and organic composition, isolating key soluble sample constituents for detailed liquid analysis, and presenting solute or eluent for high-sensitivity and high-confidence analysis of sample composition, including structural assignments.

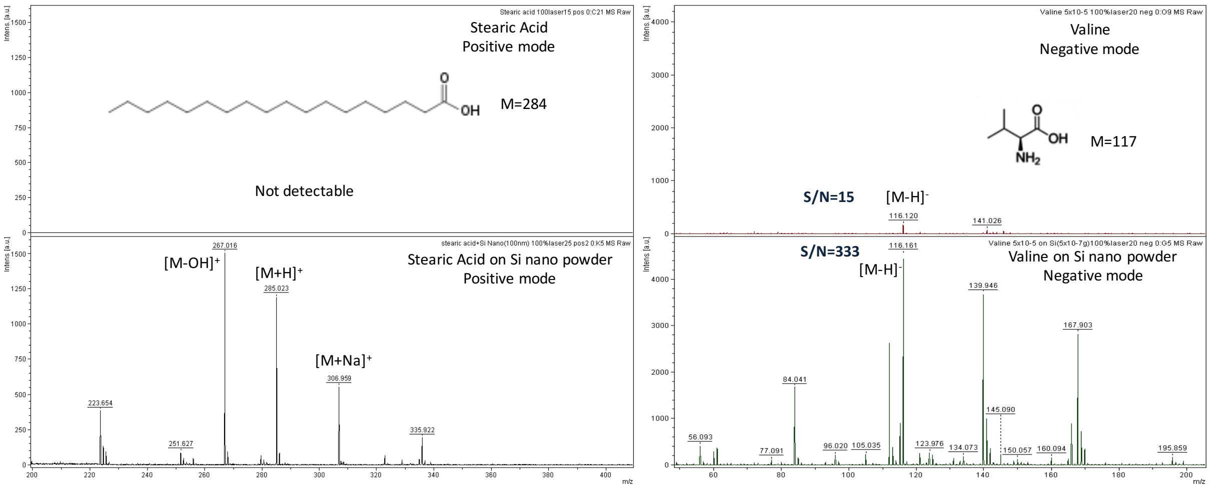

Figure 2. iMALDI enhanced detection of stearic acid (in positive mode) and valine (in negative mode) is seen for a silicon nanoparticle thin underlayer. This substrate offers better resistance to radiation damage and improved shelf stability during a mission cruise than the traditional organic matrix.

to a sub-mm spot. The UV pulse (generated by a Nd:YAG laser at 266 nm, pulse width 4-7 ns) is triggered at a tunable delay after the IR laser pulse to intersect and optimally ionize the neutral plume. The resulting ions are accelerated into a time-of-flight mass analyzer.

To further enhance the detection sensitivity of the soluble organics, the substrate features an inorganic matrix; iMALDI (inorganic matrix-assisted laser desorption/ionization) which has been shown to promote laser desorption and ionization process. [5]

Liquid Handling and Delivery to LDMS Interface: MACROS utilizes an indirect ionization method. The liquid eluent from the extraction module is first spotted on a surface from the end of a fluidic outlet; the small spotting area (< 1 mm^2) is well matched to a typical laser spot size. The spotted surface is then transfered into the high vacuum (<10^{-5} torr) region necessary for laser ionization and MS analysis. We built a test system to optimize the solute deposition conditions. The system, under reduced pressures, consists of a syringe pump that pushes solution through a 20 um ID capillary tube positioned above a stainless steel tape, where solution is deposited.

Results: As the MACROS development is ongoing, the preliminary results here demonstrated several initial key fundermentals to the instrument operation. We quantified the limits of detection for a series of model compounds (e.g, Rhodamine 6G, coronene etc.) by using our prototype TOF mass spectrometer to understand the fundamental behavior of laser desorption/ionization. In addition, we have investigated several kinds of iMALDI particles for use as an inorganic matrix, and selected the silicon nanoparticles for pursuant sample analyses based on the trade between sensitivity and background signal. Two example enhancements are shown in Figure 2 for pure stearic acid and valine.

We also tested deposition on a conveyor tape. Figure 3 shows an experiment to evaluate the size of drops, where we compared two 5-minute depositions of gentian violet solution onto (a) a silicon nanopowder iMALDI-coated and (b) an uncoated stainless steel substrate at <50 mTorr pressure and 0.5 uL/min solution flow. The iMALDI-coated surface consistently showed a more evenly spread droplet across all deposition times and pressures tested. These results suggested that the iMALDI coated surface an additional benefit, in addition to the LDI signal enhancement, in that it helps to homogenize the deposited droplet.

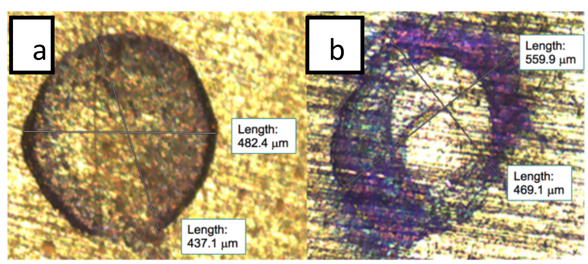

Figure 3. 5 minute depositions of gentian violet solution onto a) iMALDI (silicon nanopowder) coated, and b) uncoated stainless steel substrates.

References: [1] S. A. Getty, et al. (2012) *Rapid Commun. Mass Spectrom.* 26, 2786-2790. [2]S. A. Getty, et al. (2014) *2014 IEEE Aerospace Conference*, pp. 1-6. [3]X. Li, et al. (2012) *2015 IEEE Aerospace Conference*, 2015, pp. 1-10. [4] X. Li, et al. (2016) *2016 IEEE Aerospace Conference*, 1-8. [5] K. Tanaka, et al. (1988) *Rapid Commun. Mass Spectrom.,* 2, 151-153.