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Laser Desorption Mass Spectrometry (LDMS) with an Orbitrap mass analyzer: a historical perspective and future projection

Ricardo Arevalo¹, Ashley Hanna¹, Ziqin Ni¹, Soumya Ray¹, Adrian Southard², Ryan Danell³, Andrej Grubisic⁴, Jacob Graham⁴, Anthony Yu⁴, Molly Fahey⁴, Cynthia Gundersen⁵, Niko Minasola⁵, Julie Llano⁵, Christelle Briois⁶, Laurent Thirkell⁶, Fabrice Colin⁶, and Alexander Makarov⁷

¹University of Maryland, College Park, MD, USA

²UMD/CRESST II, College Park, MD, USA

³Danell Consulting, Inc., Winterville, NC, USA

⁴NASA GSFC, Greenbelt, MD, USA

⁵AMU Engineering, Miami, FL, USA

⁶LPC2E, Orléans, FR

⁷Thermo Fisher Scientific, GmbH, Bremen, DE

Critical Need for LDMS Techniques: Laser desorption mass spectrometry (LDMS) enables 2D and/or 3D chemical imaging of organic and inorganic analytes, supporting focused research objectives as well as discovery-based science. Many minerals and (aromatic) organics effectively absorb UV radiation, and photon energies of UV light approximate the first ionization energies of many elements in the Periodic Table. Consequently, UV laser sources, particularly those with controllable output attenuation, serve as effective ionization sources for many materials. In the realm of *in situ* planetary science, LDMS techniques are valued to detect refractory organic molecules, including prospective biosignatures, and identify the host phases that harbor said compounds. The short pulse widths offered by many solid-state laser systems, such as the 266 nm laser system developed for the Mars Organic Molecule Analyzer (MOMA) onboard the ExoMars rover, have been shown to circumvent the challenges associated with pyrolyzing organic-rich samples in the presence of strong oxidants, like the perchlorates found across the Martian surface [1].

Critical Need for Ultrahigh Mass Resolution: Heritage mass spectrometers, such as that flown on the Sample Analysis at Mars (SAM) investigation onboard the Curiosity rover [2], are limited to mass resolving powers of $m/\Delta m < 1000$ (FWHM), leading to uncertainty in the identification of molecular signals. Peaks are often assigned based on known isotope abundances, diagnostic fragmentation patterns, and/or corroborative measurements provided by other payload instruments. Alternatively, hardware additions such as gas chromatographs, resonance lasers sources, and/or collision cells can increase the confidence of molecular assignments, albeit at the cost of additional mass, volume, and power requirements.

In contrast, the Orbitrap™ analyzer commercialized by Thermo Scientific [3], adapted for spaceflight by a consortium of French laboratories [4], and miniaturized and ruggedized through a collaboration with the University of Maryland and NASA GSFC [5], enables identification of molecular stoichiometry through mass resolving powers of $m/\Delta m > 100,000$ (FWHM) and ppm-level mass accuracies. Unrivaled disambiguation of isobaric interferences and isotopologues across a wide

intrascan mass range (e.g., 20 – 600 u) distinguishes the Orbitrap from other high-resolution analyzers.

LDMS with an Orbitrap mass analyzer: The analytical and scientific value of integrating a pulsed UV laser source with an Orbitrap mass analyzer for planetary applications was first recognized with the development of the Ion Laser Mass Analyzer (ILMA) for Marco Polo [6], a joint ESA-JAXA sample return mission targeting a primitive Near-Earth Object (NEO). In response to the Pre-Release of an Announcement of Opportunity for a NASA Europa Lander Mission, a laser-enabled Orbitrap was modified to analyze ice residues and seek out physicochemical signs of life in potentially habitable cryogenic environments [5]. More recently, a permutation of the instrument was adapted for operation on the lunar surface, facilitating investigations into the composition of the bulk silicate Moon, dynamics of the lunar interior, space weathering of the surface, rates of exogenous infall, and the alteration of organic materials due to exposure to cosmic rays [7].

Advanced analytical capabilities with a laser-enabled Orbitrap mass spectrometer: To support the evolving objectives of the planetary community, such as the prioritization of an Enceladus Orbilander in the most recent Decadal Survey [8], advanced LDMS techniques are currently being explored to maximize the science return for a spectrum of mission architectures. The characterization of complex organic materials simulating extraterrestrial matter (e.g., Titan-like tholins), and planetary analog samples doped with organic compounds commonly associated with living systems, such as proteinogenic amino acids and the nucleobase uracil found in RNA, demonstrates the detection of prospective biomarkers, classification of host mineralogy, and establishment of geological context/provenance [9-11]. In order to improve spectral reproducibility and enhance limits of detection, a variety of sample plate materials spanning a range of thermal diffusivities, electrical conductivities, and ionization potentials are being tested. Inorganic chemical matrices, such as Si nanoparticles, are being explored to promote ionization efficiency and the preservation of the molecular ion of a compelling suite of organic macromolecules, including short chain peptides [12] and simple, compound, and derived lipids [13].

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