

**COMBINED MEASUREMENTS BY LASER INDUCED BREAKDOWN SPECTROSCOPY AND LASER ABLATION MOLECULAR ISOTOPIC SPECTROMETRY FOR PLANETARY EXPLORATION.** E. A. Lalla<sup>1</sup>, M. G. Daly<sup>1</sup>, A. Quaglia<sup>2</sup>, S. Walker<sup>2</sup>, G. Flynn<sup>2</sup>, G. Levy<sup>2</sup>, and M. Konstantinidis<sup>1</sup>. <sup>1</sup>Department of Earth & Space Science & Engineering, Lassonde School of Engineering, York University, Toronto, Ontario, Canada, ([elalla@yorku.ca](mailto:elalla@yorku.ca)). <sup>2</sup>Sciencetech Inc, 1450 Global Drive, London, Ontario, Canada. <sup>3</sup>Dalla Lana School of Public Health, University of Toronto, 155 College St. Toronto, Canada.

**Introduction:** The Canadian Space Agency (CSA) is providing financial support, as part of the effort from the Government of Canada, to Canadian Companies to for increasing their competitiveness in space technologies [1]

The STPD Program from the CSA supports basic research and development (R&D) in new space technologies that encourage innovation and increase Canadian industrial capabilities [1]. These efforts are paramount to increase the role of the Canadian Space industry as key collaborators in planetary missions and further industrial applications.

**Laser Induced Breakdown Spectroscopy (LIBS):** The progress and development of new portable analytical techniques for planetary exploration have facilitated the development of autonomous planetary rovers by various Space agencies such as NASA, ESA, and CNSA. Laser-Induced breakdown spectroscopy (LIBS) has become one of the most efficient and reliable techniques onboard different rovers such as ChemCam and the most recently evolved system – SuperCam onboard on NASA Mars2020 Perseverance [2, 3]. Indeed, LIBS is a rapid methodology for obtaining analytical results of major and minor elements in geological samples, soil samples, and surface cleaning (with repetitive laser ablation). Furthermore, LIBS can obtain quantitative and qualitative information on the sample’s composition for different planetary surfaces. Also, the LIBS technique is aligned with CSA research priorities for future planetary exploration that includes: Planetary Science, Astrobiology, Planetary Geology, Geophysics and Prospecting, Planetary Space Environment, and Space Health [4].

**Laser Ablation Molecular Isotopic Spectrometry (LAMIS):** LIBS, like many other methods (e.g., Raman Spectroscopy or X-Ray Diffraction) present some limitation in their ability to characterize the geological origin of a sample and several features can be lost (e.g., geochronology, isotopic features and possible origin of organic matter). To address these limitations, LAMIS has emerged as a promising complementary technique to cover some of the limitations of LIBS. LAMIS is based on isotopic shift (so-called isotopologues) from the molecular emission at a time delay defined in terms of when the plasma and atoms associate during the laser ablation [5].

**LIBS and LAMIS for Planetary Exploration:** LIBS and LAMIS are two techniques that could be combined in a concept instrument for space exploration and further improve the capabilities of future space missions (i.e., to Mars or the Moon). Moreover, the proposed system will benefit from both techniques and hence have the capability of elemental composition analysis, isotopic measurements without sample preparation, rapid surface mapping and depth profiling [5].

**Laser Ablation Elemental Isotopic Spectrometer (LABEISS):** This project is being undertaken and lead by Sciencetech Inc. (SCI) and the Planetary Exploration Instrumentation Laboratory (PIL) at York University. The LABEISS project is focused on providing new insight into a putative instrument that combines the LIBS and LAMIS technologies mentioned above. Moreover, the project is aligned to provide Basic R&D of space technology to be used in future missions while exploring extraterrestrial environments. It will provide isotopic analyses with a precision that can help our understanding of how these bodies came to be, their continuing dynamics, and even give clues to biologically related processes. The current status of the LABEISS system is being undertaken via two parallel and interrelated tasks: “Science” and “Engineering.”

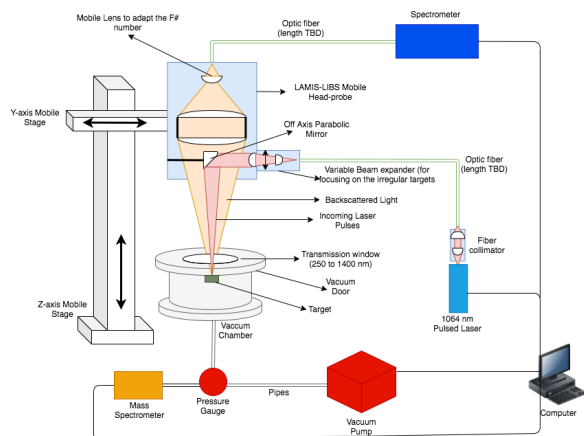
The primary challenge (Science) of LABEISS is to determine the best implementation by which to combine the LAMIS method with LIBS to determine isotopic elemental composition and quantification for different targets. This challenge includes scientific research and characterization of the selected targets of planetary interest (space simulant, meteorites and certified isotopic samples) such as: 1) understanding of the relationship between line intensity in the spectrum and the concerned isotopic mass fractions in the samples; 2) research of the electronically, vibrationally and rotationally excited “isotopologues” of dimers, oxides, nitrides or halides in plasma reactions of the ablated sample atomized matter.

The second engineering challenge of the proposal includes developing a robust system that can be applied in future planetary space exploration and other fields such as geology and archeology, among other emerging needs of the marketplace. Our engineering and design approach starts with a baseline Instrument. We are determining and selecting the spectroscopic

(Spectrometer + gated camera) system, laser system, and optics, according to the technical and scientific requirements of LIBS and LAMIS.

Subsequently, we plan to set up the LABEISS breadboard with the selected mechanical and optical configuration (Laser, Spectrometer, camera, optical configuration and sensing distances). Finally, we will characterize the breadboard with respect to key characteristics such as required laser power, sensing distance, spectrometer configuration (delay time, acquisition time, delay-width), and calibration methods (intensity and wavelengths). As such, the full characterization will help us establish the definition of single measurements vs tandem measurements (e.g. SNR versus number of shots), the limit of detection (LOD) and the limit of identification (LOI) in LIBS and LAMIS.

**LABEISS breadboard configuration:** The proposed configuration for the LABEISS Breadboard is shown in Figure 1. It will employ a 1064 nm pulsed laser (the output power, pulse duration and frequency TBD). The incoming beam will be delivered through fibre optics and expanded by using a variable beam expander. Subsequently, the ablation scattering will be focused onto the sample with an off-axis parabolic mirror coated for 1064 nm. The backscattered radiation from LIBS and LAMIS will be collected using the LIBS-LAMIS probe head and subsequently delivered to the spectrometer with optic fibres, as shown in Figure 1.



**Figure 1.** Sketched configuration of the LABEISS breadboard system.

To fulfill the scientific requirements and establish a better approach to emulate real, in-situ measurements under laboratory conditions, we will include several augmentations. We are thereby addressing the scientific and technical limitations of the LABEISS breadboard in advance, which will increase the chances of developing a successful future flight instrument. The first

augmentation will consist of a X-Y LIBS-LAMIS scanning mode. Furthermore, scanning capability would be particularly advantageous with 3D-mobile stages for mapping which would result in high-fidelity (to real missions) result. The second augmentation intended is to create a vacuum simulation chamber, as shown in Figure 1. Using a simulation chamber, we aim to demonstrate the performance of LIBS-LAMIS in a laboratory and different planetary environments such as Earth, Moon and Mars.

**Spectrometer Design:** The state of the art in LIBS and LAMIS spectroscopies involves designing a specific spectrometer with a suitable resolution and capabilities to carry out LAMIS and LIBS measurements. Therefore, we are performing experiments to understand the required resolution and signal-to-noise ratio to perform both LIBS and LAMIS measurements sequentially (or in parallel). These measurements will enable us to prototype the most suitable spectrometer for LIBS and LAMIS and be finally integrated into the LABEISS breadboard.

**Summary, current status and future activities:** Our Phase 0 study, until April 2021, is building the prototype the system for LAMIS. Subsequently we will determine the parameters and spectrometer requirements for a custom LAMIS instrument. These results will be used to roadmap a future instrument development and possible flight on a planetary mission in the near future. At this conference, we will report on the latest results of the current project.

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**References:** [1] <https://www.asc-csa.gc.ca/eng/funding-programs/funding-opportunities/ao/2019-stdp-ao-6-1.asp>. [2] Weins R. C. et al. (2013) *Spectrochim. Acta Part B* 82: 1–27. [3] Weins R. C. et al. (2021) *Space Sci Rev*: 217 (1): 4. [4] <https://www.asc-csa.gc.ca/eng/publications/rpp-2016.asp>. [5] Bol'shakov et al. (2016) *J. Anal. At. Spectrom* 31, 119-134.