

INTEGRATED PORTABLE, RUGGED OPTICAL AND MASS INSTRUMENT SUITE (PROMIS) FOR GEOLOGIC, BIOLOGIC, AND ORGANIC SIGNATURE CHARACTERIZATION FOR SPACE EXPLORATION. J. R. Scott¹, B. Beardsley², G. S. Groenewald¹, S. Lammert³, E. Lee³, T. R. McJunkin¹, G. Ritchie², J. Almirall⁴, L. Becker⁵, ¹Idaho National Laboratories, Chemical Sciences, 1765 North Yellowstone Highway, Idaho Falls, ID 83415-2208; jill.scott@inl.gov, ²Catalina Scientific Instruments, 1870 West Prince Rd., Suite 21 Tucson, AZ 85705, ³Torion Technologies INC, 796 E. Utah Valley Dr., Suite 200, American Fork, UT 84003, ⁴Florida International University, Department of Chemistry & Biochemistry, University Park Campus Miami, FL 33199, and ⁵Caerus Science and Engineering, 1700 Union Ave., Suite C, Baltimore, MD 21211.

Introduction: The portable, rugged optical and mass instrument suite (PROMIS) concept is a fully integrated, multi-functional, miniature laboratory that incorporates laser-induced fluorescence (LIF), Raman, laser-induced breakdown spectroscopy (LIBS), and mass spectrometry for both solids (i.e., laser desorption (LD)) and gases (i.e., gas chromatography (GC)). The complete PROMIS configuration as illustrated in Figure 1 has optical detection capabilities (i.e., LIBS, LIF and Raman) in the lower section of the instrument referred to as Sample and Optical Spectroscopy (SOS) chamber coupled to a laser desorption LD/GC toroidal ion trap mass spectrometer (TMS) module. The TMS will be based on the mature TRIDION™-9 [1] design (Torion Technologies LLC) that is commercially available, while the scanning system and the optical detection system for Raman, LIF, and LIBS housed in the SOS chamber are based on a design currently used for a laboratory instrument at the Idaho National Laboratory (INL) [2] that also incorporates an imaging mass spectrometer [3]. The five analytical techniques may be used alone or be invoked sequentially to obtain correlated spectroscopic and spectrometric analyses at the same micron-scale spot. LIF and Raman utilize low laser power for nondestructive (i.e., non-ablative) sample interrogation, which allows for signal averaging. Higher laser power is used to desorb or ablate a small portion (<1 µg) of the sample into the gas phase for LIBS and LD-TMS. Optical spectra from desorption plumes provide LIBS data for primarily elemental and potential isotope ratio analyses, depending on the spectrograph/sensor employed. The same desorption plume used for LIBS also provides ions that are swept efficiently into the TMS for mass spectrometric analysis, which is possible primarily because of the INL's Total Ion Control (TIC) technology [4]. Because hundreds to thousands of spectra can be acquired from a heterogeneous sample, PROMIS would be automated and equipped with the INL's Spectral Identification Inference Engine (SIDIE)[®] software to assist and/or automate interpretation of spectra [5,6].

PROMIS is an ideal candidate for near-term Mars exploration because it is a lightweight, inexpensive, and low power *in situ* instrument suite for identifying and prioritizing high-interest samples for analysis. In

addition, it will detect trace-level organic compounds in rock and dust without sample preparation. Because PROMIS can function in either vacuum or viscous atmospheres, it can also meet the science requirements for a variety of other NASA missions ranging from small bodies (e.g., asteroids or comets) to the outer planets. Moreover, PROMIS addresses several astrobiology missions related to the detection of extant or extinct life on Earth including goals 2, 3, 4 and 7 of the Astrobiology Roadmap. The multi-mode imaging analysis for solid samples combined with addition of

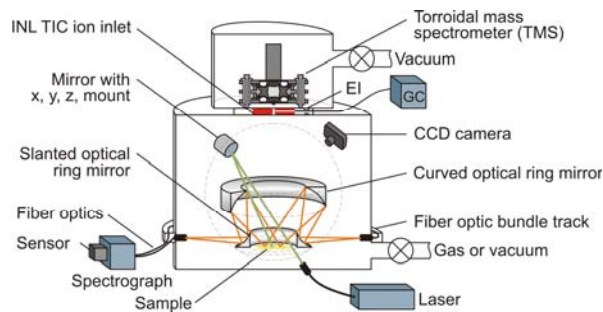


Fig. 1. Schematic of PROMIS concept showing the arrangement of the SOS chamber, TIC ion inlet, TMS module, laser, laser beam manipulator, light collection system, GC with electron ionization source (EI), and sample.

GC capability for gas analysis will enable collection of complimentary data (i.e., PROMIS is in essence a 'quinta-corder' as opposed to the proverbial 'tri-corder') for characterizing geochemistry, detecting and identifying organic compounds as well as biological signatures for seeking signs of life. PROMIS takes a giant step by providing both optical spectroscopy and mass spectrometry in an integrated architecture, as opposed to using separate instruments to acquire the various measurements, which can complicate sample manipulation. The compact, integrated design better utilizes space, resources (i.e., power), reduces mass, and minimizes sample handling.

Optical Spectroscopy Suite: The optical spectroscopies would all share the same laser, light collecting optics, and detector (i.e., spectrograph/sensor), which would represent a major cost and mass savings. A feature of the light collecting optics is that they provide a large field of view, which is especially useful

for LIBS in reduced atmospheres where the plume tends to expand [7]. Using multiple fiber optics improves the ability to detect low light level signals. All of the fiber optics can be combined using a multiplexer, similar to that used in the communication industry, which was originally designed at the INL (US Patent 5,045,018). The ultimate resolution for optical spectroscopy on PROMIS will depend on the spectrograph/sensor and will take advantage of improved designs [8].

Ion-Trap vs. Time-of-Flight Mass Detectors:

The toroidal ion-trap mass spectrometer was chosen because it holds two significant advantages compared to a time-of-flight mass spectrometer (TOF-MS). (1) The TMS can operate at high pressures with a variety of buffer gases, making it compatible with non-standard atmospheres like the CO₂ found on Mars. (2) The TMS can accumulate ions from multiple laser pulses, which effectively composites signature ions from multiple experiments, which increases signal-to-noise ratios (S/N) because all of the trace ions from the productive laser shots can contribute to the signal when scanned out, improving detection limits and the odds of detecting signs of life or trace elements. TMS ion accumulation is a significant advantage compared to alternative mass analyzers, such as a TOF, which rely on signal averaging spectra from individual laser pulses. If the S/N is low (as expected), detection capability will be limited regardless of how many laser shots are averaged by mass analyzers that cannot accumulate ions.

Mass and Power for PROMIS: The complete PROMIS suite mass is estimated at ~12 kg at this time. The TRIDION™-9 electronics and analyzer kit is only 5.8 kg and includes all GC/TMS analyzer components except the GC injector interface assembly (to accommodate the SPME injector), computer display, battery, and helium cylinder. The two largest power-consuming systems are the GC and the vacuum pumps. A low thermal mass column (Agilent LTM column) with a custom low thermal mass injector minimizes the power consumption by the chromatographic inlet. The entire GC/MS analyzer system consumes approximately 60 W average power in steady-state mode and ~74 W during an average three minute GC/MS run. The power and mass specifications for the current GC and vacuum pump components are summarized in Table 1. The critical components (i.e., ion trap analyzer, continuous dynode electron multiplier (CDEM) detector, detection/integrator circuitry, and rf supply) only add up to a total of 640 g.

Table 1. Select TRIDION™-9 system components weight and power estimates.

Subsystem	Weight (grams)	Average power (Watt) assuming 10 minute run cycle, default GC temperature program
Turbomolecular Pump	1564 g	7.9 W
Backing Pump	717 g	5.3 W
GC Subsystem (including all below)	636 g	25 W
GC Injector		11 W
GC Column		3 W
GC Transfer line		8 W

State of Planetary Science Missions Program:

At the moment, the future of Planetary Science missions going forward is tenuous at best. However, the excitement generated by upcoming missions such as Mars Science Laboratory (MSL) will no doubt rejuvenate public interest in exploring the Solar System as well as generate new interest in the question of how life evolved on Earth. Could the same set of chemical precursors and conditions have existed or exist today on other planetary bodies? Unraveling the mystery of biogenesis remains a major theme for the future of planetary science and encourages NASA to continue to search for organic signatures indicative of earth-based life forms, as well as signatures of alternative life forms that may have developed in very different planetary environments. The need for flexibility to extreme environments that may harbor life with a completely different set of building blocks (NRC Weird Life report) will also be important to determining whether or not life ever evolved in the Solar System.

References: [1] Lammert S. A., Rockwood A. A., Wang, M., Lee, M. L., Tolley, S. E., Oliphant, J. R., Jones, J. L., Waite, R. W. (2006) *J. Am. Soc. Mass Spectrom.* 17, 916–922. [2] Gresham, G. L., Scott, J. R., Groenewold, G. S., Tremblay, P. L., Mincher, B. J. (2002) 50th ASMS Conference on Mass Spectrometry and Allied Topics, Orlando, FL, June 2–6. [3] Scott, J. R., Yan, B., Stoner, D. L. (2006) *J. Microbiol. Meth.* 67, 381–384. [4] Scott, J. R., Tremblay, P. L., McJunkin, T. R. (2010) US Patent Pending. [5] Yan, B.; McJunkin, T. R.; Stoner, D. L., Scott, J. R. (2006). *Appl. Surf. Sci.* 253, 2011–2017. [6] Hatch, J. J., McJunkin, T. R., Hanson, C., Scott, J. R. (2012) *Appl. Opt.* 51, B155–B164. [7] Effenberger Jr., A. J. and Scott J. R. (2011) *Anal. Bioanal. Chem.* 400, 3217–3227. [8] Effenberger Jr, A. J., and Scott, J. R. (2012) *Appl. Opt.* 51, B165–B170.