

**ELEMENTAL AND ISOTOPIC PLANETARY SURFACE ANALYSIS AT STAND-OFF DISTANCES USING LASER-INDUCED BREAKDOWN SPECTROSCOPY AND LASER-INDUCED PLASMA ION MASS SPECTROMETRY.** R.C. Wiens, D.A. Cremers, J.D. Blacic, S.M. Ritzau, H.O. Funsten, and J.E. Nordholt, NIS-1, CST-1, EES-4, Los Alamos National Laboratory (Los Alamos, NM, 87545; rwiens@lanl.gov).

**Introduction.** Planetary analyses have traditionally relied on both *remote* and *in-situ* observations. Although *remote* observations from orbiting spacecraft provide spatially wide coverage, they do not, by themselves, provide sufficient information to understand geologic processes. On the other hand, rover-based *in-situ* analyses can provide detailed geological information but can be time-consuming and limited in scope. The optimum configuration for detailed analysis with wide spatial coverage may be a *stand-off* technique.

Stand-off techniques are being tested which utilize laser interrogation of a solid surface for elemental and isotopic analyses. We are simultaneously testing both laser-initiated emission spectroscopy to measure characteristic wavelengths in the laser-induced spark, and a mass spectrometer to measure the mass of ions generated and accelerated by the spark. Material can be analyzed from within a radius of several tens of meters from the instrument platform. A relatively large area can thus be sampled from a simple lander without requiring a rover or sampling arms. On a rover, such an instrument would allow sampling of locations not otherwise accessible, such as on a steep ledge, and its versatility would reduce rover travel requirements.

**Emission spectroscopy** of the laser-initiated spark can provide quantitative elemental abundances [1]. This method, commonly termed *laser-induced breakdown spectroscopy* (LIBS), has been studied for years at Los Alamos and has recently been adapted for several practical applications. In the LIBS method, laser pulses are focused on a material to form laser plasmas, or sparks. These sparks are the result of emission from excited atoms ablated from the surface. Collection of the light followed by spectral analysis permits identification of the elements via their unique spectral signatures. When calibrated, concentrations can be determined. Because the laser plasma is formed by focused optical radiation, the method has several advantages over conventional elemental analysis methods. These include 1) rapid analysis, i.e. one spectrum per laser pulse, 2) simultaneous multi-element detection, 3) ability to detect nearly all elements (high or low Z), and 4) stand-off analysis capability [2]. Stand-off analysis is possible because the laser pulses can be focused at a distance to generate the plasma on a solid. The distances that can be achieved depend on the quality of the laser beam, the power density of the laser pulse, and the method used to focus the laser pulses on the target. Using pulses of 300 mJ having a 10 ns duration and a very simple

four lens focusing system, the recording of spectra from geological samples has been demonstrated at distances up to 24 m. [3]. Measurements can be carried out with the sample in atmosphere or in a vacuum.

**Mass spectrometry** of the ionized plume from a laser is possible on airless bodies. Previous work in this area included a laser-mass spectrometer package on the ill-fated Soviet Phobos missions. This instrument used the time-of-flight (TOF) from sample to spectrometer to determine the mass of the constituent ions, and was huge by today's standards—close to 1 m<sup>3</sup> and 80 kg [4]. Others have proposed similar instruments [e.g., 5]. However, this basic design has several drawbacks in addition to size. First, it is difficult to achieve high mass resolution due to a spread in initial ion energies from the laser spot. Second, multiply-charged ions are produced in abundance, and can cause significant interference, such as <sup>56</sup>Fe<sup>++</sup> with <sup>28</sup>Si<sup>+</sup>, etc. An additional disadvantage common to most mass spectrometers is interference from isobaric species. For example, no spacecraft mass spectrometer has yet been able to determine high precision <sup>18</sup>O/<sup>16</sup>O ratios on extraterrestrial material due to the ubiquitous presence of H<sub>2</sub>O at mass 18.

These difficulties are overcome with a mass spectrometer design patented for space plasma physics applications [6,7] and flying on Cassini and DS-1. This design separates molecules into their atomic constituents and analyzes the resulting singly-charged ions. The linear electric field segment of this instrument yields high resolution mass spectra based on time of flight, independent of initial ion energy. This design thus holds great potential for both elemental and high precision isotopic planetary materials analyses. Preliminary estimates [8] indicate that major and some trace element detection is easily feasible at a stand-off distance of 25 m.

**Emission Spectroscopy Experiments** are presently underway for quantitative LIBS elemental determinations at stand-off distances in a vacuum and at low pressures (e.g., 10 Torr) to simulate lunar and martian environments. Initial experiments carried out at a distance of 8 m on samples in 10 Torr CO<sub>2</sub> yield the detection limits in Table 1. Other measurements have shown that the emission signal is dependent on the pressure of the surrounding gas with maximum signals occurring at pressures in the range 40-100 Torr. Measurements of the mass ablated also show a pressure dependence with the mass ablated increasing as the pressure is reduced

from atmospheric to ~10 Torr. Below 10 Torr the ablated mass remains constant as the pressure is further reduced. These results indicate that at the higher pressures the plasma partially shields the surface from the laser pulse reducing the mass ablated. As pressure is reduced, shielding decreases through a reduction in the plasma density thereby producing more ablated material and increased emission signals. As the pressure is reduced below the 40-100 Torr regime, however, the number of collisions in the plasma decreases linearly with pressure producing the observed decrease in the element signals. Other experiments planned to benchmark LIBS for measurements at reduced pressures include time- and spectrally-resolved imaging of the evolution of the plasma and the use of a double-spark method to decrease detection limits. Detection limits for other elements will also be determined along with measurements of precision and accuracy.

**Mass Spectrometry Experiments.** Spares of the IMS (Cassini) and PEPE (DS-1) plasma mass spectrometers are in preparation for testing to determine ion yields of various materials and from that, reasonable stand-off distance capabilities. A key parameter will be isotopic precision [9]. Mass spectrometry and LIBS are very complementary, as energy and mass information gleaned from the mass spectrometer can aid in calibrating matrix effects for optical spectroscopy, while elemental information from optical spectroscopy can aid interpretation of mass spectra. Work is progressing towards an eventual flight prototype.

**Instrument Size and Mass.** The present PEPE mass spectrometer is 5 W and 5 kg, including electronics. A flight-integrated optical detection system is estimated at < 1 kg, while a Nd-YAG laser system suitable for the above-mentioned distances is estimated at < 1 kg and < 1 W average power [3]. With these parameters, the detection limits in Table 1 would be achieved in 1 minute.

**Table 1 Mars Simulation LIBS Detection Limits**  
for selected minor elements

<u>Element</u>	<u>Det. Lim.</u>
Be	13 ppm
Ti	120 ppm
Mn	365 ppm
Cr	50 ppm
Cu	65 ppm
Zr	50 ppm
Ba	600 ppm

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