
Lunar and Planetary Science XXX
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Introduction

The restricted mass and power budgets of landed science missions present a challenge to obtaining detailed analyses of planetary bodies. In-situ studies, whether alone or as reconnaissance for sample return, must rely on highly miniaturized and autonomous instrumentation, producing less comprehensive data sets. Nevertheless, the great desire to deepen our knowledge of the surfaces and interiors of planets, moons, and small bodies has driven the development of small, robotic techniques with ever-increasing capabilities.

One of the most important goals on a surface mission is to obtain composition data from many geological contexts. The mineralogical, molecular, elemental, and isotopic content of near-surface materials (regolith, rocks, soils, dust, etc.) at a variety of sites can complement broader imaging to describe the makeup and formative history of the body in question. Instruments that perform this site-to-site analysis must be highly transportable and work as a suite. For instance, a camera, microscope, spectrophotometer, and mass spectrometer can share several components and operate under a parallel command structure. Efficient use of multiple systems on a small rover has been demonstrated on the Mars Pathfinder mission.

The best instrument type for composition at the elemental and isotopic level is the ion mass spectrometer. A single peak is obtained for each isotope and detection limits and sensitivity can be excellent, even for miniature instruments. The ion mass spectrometer extracts and ionizes molecules and atoms from an analyte, which are separated and detected according to their mass-to-charge (m/z) ratios. (On bodies with significant atmospheres, the use of ions, rather than photons, requires sample acquisition and evacuation steps.) Several methods are available for sampling, including bombardment by atoms, ions, neutrons, or electrons, laser desorption/ablation, and thermal evaporation. For the direct analysis of unprepared solids, the laser has several advantages: it can desorb and ionize in one step, it can be small and low-power, it avoids target charging, and it can be used by other instruments in the suite. In addition, a pulsed laser provides the ideal "start pulse" when coupled with a time-of-flight (TOF) mass spectrometer. The TOF technique does not require magnets (which are heavy) or mass-scaning (which is data-intensive), making it very desirable for the types of surface missions described above [2].

The Laser Ablation Mass Spectrometer (LAMS), under development in our laboratory, combines such a laser-TOF technique with a microscopic imager into a single instrument. As previously reported [1], the LAMS instrument (Fig. 1) uses a miniature pulsed Nd:YAG laser to ablate and ionize a sample volume of approximately \(2 \times 10^3 \mu m^3\) (1 ng at 2 g cm\(^{-3}\)). Ions are detected at times proportional to the square-root of their mass-to-charge ratios. Each laser pulse produces a full mass spectrum, typically 60 \(\mu s\) in duration for total elemental coverage.

There is no high-voltage source extraction in LAMS, meaning that ions are not accelerated away from the target surface to reduce their energy spread, unlike most TOF-MS instruments. This permits LAMS to be used in a totally contactless, or standoff, mode, minimizing the risk of contamination. This mode is especially desirable on missions to airless bodies, such as asteroids and moons, because it does not require sample acquisition. The ion kinetic energy distribution is instead focused with a two-stage reflectron (Fig. 1). The reflectron temporally focuses ions of the same mass sufficiently to distinguish all elements and isotopes.

The laser and micro-imager systems in LAMS share the main focus objective, and the instrument is coaxial with the optical path. That is, the laser passes through the back of the reflectron and hits the target at normal incidence. This design provides highly reproducible spectra, maximal imaging and laser spatial resolution, and a highly compact instrument. The imager is used to select a region of interest, and the laser then probes that region with 30-50 \(\mu m\) lateral and \(0.2 \mu m\) depth resolution. Due to this geometry, a flight version of LAMS is potentially only 15-20 cm total length and 2 kg total mass.

Analysis of NIST SRM C1154a

The relative sensitivity of LAMS to different elements under varying experimental conditions has been studied with a series of reference materials such as those from NIST (SRM). Initial results for the 19Cr-13Ni steel SRM C1154a are presented here. The major tunable experimental parameter was the kinetic energy range. As the kinetic energies of the emitted ions have been observed to range from a few eV up to several hundred eV, the electrostatic grid assembly was set to act as a band-pass filter for improved resolution. Fifty laser shots from each of seven windows were sampled, denoted by the lower and upper bounds \((V_o, V_R) = (35,45), (45,55), (55,65), (65,80), (80,110), (110,150), \) and \((150,200) \ V\). A single-shot spectrum showing the major constituents of SRM C1154a is shown in Fig. 2. Within the sequences recorded, LAMS detected the elements C, N, Si, P, S, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, and Ta, which are all the known elements in the target except Ti, W, and Pb. In addition, the elements H, B, O, K, Ca, Cl, Sc, and As were also easily identified. H and O are likely surface contaminants adsorbed from the vacuum environment. The other uncertified elements were detected in clusters and at various depths (taken as shot counts from unablated surfaces). These impurities accounted for as much as 4% of the total detected ion yield (TDY) depending on energy window.
The target was found to be quite heterogeneous on length scales larger than the sampled volume, but the number of acquired spectra was sufficient to give initial statistical measures of the bulk elemental abundances of major elements. Fig. 3 compares atomic abundances of some of the detected elements with values provided by NIST. The relative sensitivity coefficient (RSC) is the ratio of measured to given atomic percentage. Most major elements are accurate within one standard deviation, with mainly ranging from 5% to 20% of the measured abundance. No explicit correction was made for the impurity elements in each spectrum.

The performance of LAMS on measuring minor isotopic abundance ratios in this target was very good. Ratios of $^{10}$B, $^{13}$C, $^{35}$Cl, $^{53}$Cr, $^{54}$Ni, $^{56}$Ni, and $^{65}$Cu to their total elemental yields had an uncorrected average accuracy of less than 7%. It is noted that isotopic accuracy improved with separation from the dominant $^{56}$Fe peak, implying baseline and peak shape sensitivity introduced systematic errors.

The detection limit in SRM C1154a was estimated as 18 ppm-atoms by the detection of $^{34}$S with a signal-to-noise of 2.

**Layer-by-Layer Analysis of Basalt** A terrestrial desert basalt was provided as a test specimen for analysis. As demonstrated with a blind meteorite sample [1], the subclassification of unknown rocks with only elemental data and imaging is a complex, inferential process. Nevertheless, the ability of LAMS to detect small changes of abundance ratios between shot sequences opens the possibility for a very powerful joint mineralogical analysis between LAMS and a cofocused spectrophotometer in one landed package.

The quantitative work with the basalt is ongoing, however, a very clear demonstration of the depth capability of LAMS has been completed with this sample. The laser was focused onto a fresh surface region on the basalt chip, as chosen by visual inspection through the imager. In a sequence of 150 shots, the Mn/Fe ratio was calculated and plotted in Fig. 4. The absolute Fe abundance remained relatively constant over the sequence, but the Mn/Fe ratio began at an anomalously high value (> 1) and then dropped after about 70 shots to a value more reasonable for bulk basalts. This behavior is interpreted as the removal of the desert-varnished exterior of this sample, with a thickness of about 20 µm. Such varnish, which has been occasionally termed Burnessite, is primarily characterized by just such an excess of Mn, though its origin has been a matter of debate [3].

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**References:**

