Laser Mass Spectrometry in Planetary Science

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ABSTRACT

Knowing the chemical, elemental, and isotopic composition of planetary objects allows the study of their origin and evolution within the context of our solar system. Exploration plans in planetary research of several space agencies consider landing spacecraft for future missions. Although there have been successful landers in the past, more landers are foreseen for Mars and its moons, Venus, the jovian moons, and asteroids. Furthermore, a mass spectrometer on a landed spacecraft can assist in the sample selection in a sample-return mission and provide mineralogical context, or identify possible toxic soils on Mars for manned Mars exploration. Given the resources available on landed spacecraft mass spectrometers, as well as any other instrument, have to be highly miniaturised.

INTRODUCTION

In this paper we will review the present status of mass spectrometry in planetary science with emphasis on solid surfaces and the near-surface soil/regolith. We will not discuss mass spectrometric research of atmospheres (e.g. gas-chromatographic mass spectrometers). The motivation to perform mass spectrometric measurements of the surface is to learn the elemental composition of the rocks and the soil on the surface of a planetary body. From the elemental composition one can derive a normative modal mineralogy of the surface. If the sampled spot is commensurate with the grain size of the soil or mineral then a more direct determination of the modal mineralogy may be possible. The use of complementary measurement techniques may be necessary for an unambiguous identification of the mineralogical composition. Mass spectrometry also gives the isotopic composition of elements (if the instrument has sufficient mass resolution) that allows the study of the origin and evolution of the material investigated. If there is sufficient dynamic range in the mass spectra then the abundance of trace elements can be determined to provide further information on the nature of planetary differentiation and the geological origin of surface materials (e.g. from rare-earth fractionation patterns). Of relevance to the search for life, or for manned missions, mass spectrometric investigations can identify potentially toxic elements in the soil.

In addition, mass spectrometric compositional analysis also provides context science for the other investigations performed on the landing site. The use of a mass spectrometer with sufficiently high spatial resolution allows one to infer the modal mineralogy of a surface far more directly and with more confidence than from bulk measurements. Furthermore, the spatial resolution allows confident identification of secondary alteration products, e.g. due to weathering by aqueous solutions, such as seen for many Martian surface materials. Thus, the underlying mineralogy allows one to identify the rock type (e.g. basalt, granite, sandstone), and therefore the process responsible for its origin (igneous, plutonic, sedimentary). The nature of any alteration products provides information and constraints on the history of the environment in which these rocks have been e.g. the presence of liquid water, the pH, the nature of trace elements in solution etc. This is particularly important when assessing the significance of any possible biomarkers.

For compositional analysis of solid surfaces Laser Mass Spectrometers (LMS) are very well suited. Laser ablation was chosen as a sample introduction technique principally because of its high spatial resolution and the lack of any need for sample preparation [Becker and Dietze, 2003]. Ions for analysis are generated directly from the surface under investigation by short, intense laser pulses. Advantages of laser ablation/ionisation include simplicity of the resulting instrument design, speed of measurement, and the ability to do depth profiling (potentially important for a regolith in which mineral grains are coated with impact produced glass). Time-of-Flight mass spectrometers (TOF-MS) are a natural match to the pulsed laser ablation/ionisation because they couple well to a pulsed ion source such as that produced by laser ablation. The produced ions are accelerated into the ion optical system of the

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TOF-MS, which consists of the ion acceleration, a drift tube, an ion mirror, another drift tube and an ion detector (e.g. Cotter, 1994). TOF-MS are simple, robust instruments that are used more and more frequently in space research.

Laser ablation and ionisation is a common analytical method in the laboratory for mass spectrometric analysis of surfaces (Vertes et al., 1993). The formation of a laser-induced plasma out of nearly every solid material can be used to bring material from the solid into the ion phase, which then can be easily analysed by mass spectrometric means to measure the surface composition itself. For laboratory applications this technique is known as Laser Induced Mass Spectrometry, LIMS, and early applications date back to the 1960's. Once a critical power density of approximately 10^9 W/cm^2 is exceeded during the laser pulse the ionisation of released surface material is more or less independent of the element, i.e., minimal inter-element fractionation in the ionization process occurs (Managadze, 1992; Managadze and Shutyaev, 1993; Vertes et al., 1993; Brinckerhoff et al., 2000). In laboratory instrumentation the detection limit for LIMS is normally between 10 ppb and 1 ppm depending on element, and fractionation is less than in the often used spark source mass spectrometry (Dietze and Becker, 1993).

In recent years highly miniaturised laser mass spectrometers for planetary research have been developed by two groups for various planetary missions. A compact LMS prototype based on an earlier Russian design (Managadze and Shutyaev, 1993) has been demonstrated for mineralogical studies of meteorites (Brinkerhoff et al., 2000). An adapted version of this instrument, the LASMA instrument will be discussed below, which will be part of the lander payload of the Russian Phobos-Grunt mission. The major scientific goal of the Phobos-Grunt mission is to return a sample of Phobos' soil to the Earth. In addition, there will be in situ investigations of the regolith to learn about Phobos' origin and evolution to which the LASMA instrument will contribute (Zakharov and Zelenyi, 2007). One the scientific goals of the BepiColombo mission of ESA to Mercury is the formation and evolution of the planet (Balogh et al., 2000). To address this scientific goal two miniature and highly miniaturised laser ablation time-of-flight mass spectrometers (LMS) were developed and built, suitable for in situ measurements of the elemental and isotopic composition of the surface of airless planetary bodies (Rohner et al., 2003, 2004). These instruments were designed to determine major, minor, and trace element abundances in minerals on a spatial scale of 10 μm, and have sufficient dynamic range and mass resolution to perform useful isotopic measurements in favourable cases, i.e., no isobaric interferences and isotope ratios larger than about 10^{-3} (e.g. the iron isotopes).

If one wants to go deeper than the top-most surface, let's say a few meters, then one needs a drill to bring up material to be analysed. Drilling below the surface is planned for the Exo Mars mission of ESA and the Mars Science Laboratory mission of NASA. For the Russian Phobos-Grunt mission it is planned to take samples from the very surface and from not deep (up to 1 cm) surface layer with the help of manipulator. Again, a LMS instrument is a good choice for the analysis of samples brought up by a drill. Having a LMS inside the drill bit is currently not feasible because mass spectrometers cannot be accommodated within the small volumes available inside a drill. Typical drill designs for planetary exploration have an outer diameter of about 30 mm, which would need a miniaturisation of our smallest LMS, the rover LMS (see below), by roughly a factor of two.

Investigating the sub-surface has also been discussed for icy planetary surfaces, like the Martian polar caps or for the surface of Europa. In the case of an icy surface, access to the interior can be accomplished via a melting probe (Zimmerman et al., 2001), rather than a mechanical drill. The realistic goal is to penetrate at least below the radiation altered layer of Europa's surface (a few meters) but more ambitious investigations aim at going through Europa's entire ice shell into the putative ocean. In any case, a mass spectrometer for a payload of a melting probe needs a special design. The Membrane Inlet Mass Spectrometer discussed below is a possible design for such an application.

INSTRUMENTATION

LMS systems have previously been proposed as spacecraft instrumentation (Sagdeev et al., 1985; Sagdeev et al., 1993; Managadze and Shutyaev, 1993; DeYoung and Situ, 1994; Meyer et al., 1995; Brinckerhoff et al., 2000), and one such instrument, LIMA-D (Managadze et al., 1987), was included in the previous Phobos missions (Sagdeev and Zakharov, 1990). LIMA-D was a time-of-flight mass spectrometer (TOF-MS) designed to study the surface composition of Phobos from a hovering distance of 30–80 m. However, these instruments are rather heavy, due largely to the mass of the laser system.

In the following we will discuss the LMS instrument for the Phobos-Grunt mission, the two LMS instruments developed for BepiColombo mission, and the membrane inlet mass spectrometer.

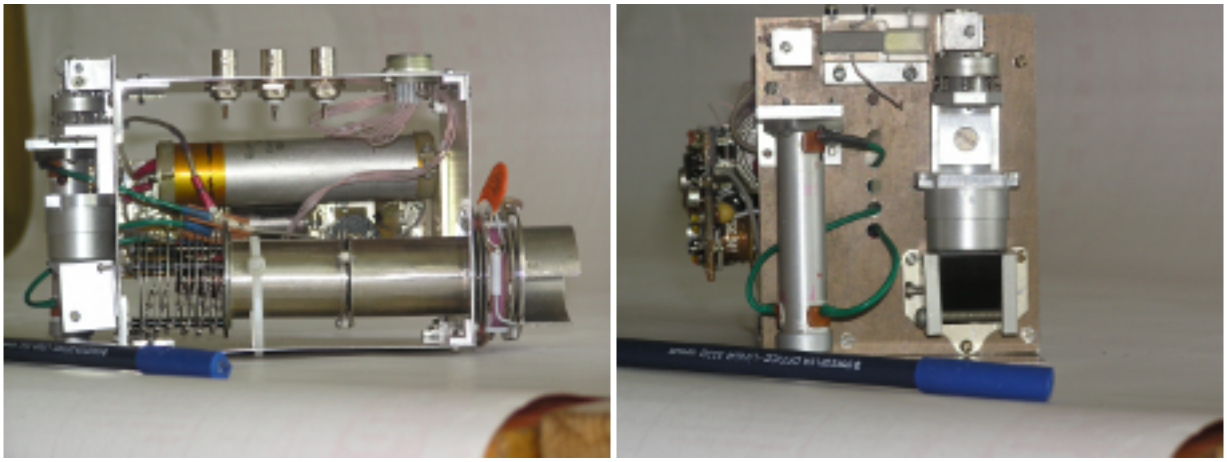

Figure 1: Left: LASMA ion-optical system with ion reflector on the left, the ion detector on the right, and the field-free drift tube in between these two. The charging capacitor for the laser is the smaller tube further in the back. Sample is to be placed at right, in front of the thick cylinder. Right: Laser-optical system with laser tube on the left, folding mirror, lenses, and the prism (black unit) to deflect the laser beam through the ion-optical system.

Lander LMS

The LMS for the landing spacecraft (the lander LMS) is intended to be installed on a spacecraft landing on a planetary surface, either mounted on a fixed position or on an articulated arm. Samples are taken directly from the landing site, or brought to the instrument by an arm from places in the immediate vicinity. The advantage of being on a lander are the larger resources available on a lander compared to a rover; the disadvantage is that the choice of samples might be limited depending on landing location.

The lander LMS is a simple time-of-flight instrument using a grid-less reflectron as ion mirror. For the laser, commercially available Nd:YAG microchip lasers were used operating either at λ=1064 nm or at λ=532 nm. These microchip lasers provided sub-nanosecond pulses of about 10 µJ at a repetition rate of 10 kHz, which can be focused to spot sizes of less than 20 µm diameter. Each laser pulse results in a mass spectrum, but typically 10^3 to 10^4 spectra are accumulated for good dynamic range. The ions removed from the target surface by the laser pulse are accelerated into the mass spectrometer through a small hole by an electric field and are focussed through a narrow tunnel in the centre of the detector toward the reflectron. The ions pass through the time-of-flight tube and are reflected by the ion mirror back onto the MCP detector. Mass resolution is typically $m/\Delta m$ = 600 FWHM. With this instrument Cr and Fe isotope ratios were measured at the ‰ level for a NBS stainless steel sample [Rohner et al., 2003]. The mass resolution can be adjusted ion-optically; a higher mass resolution can be set at the expense of ion-optical transmission and vice-versa. The total dimension of the instrument, is 120 mm x Ø60 mm. A flight instrument would be somewhat taller since the laser electronics would be accommodated in a compartment above the ion mirror. The anticipated weight of the flight unit would be about 500 g including all electronics [Rohner et al., 2003].

The LASMA Instrument

The LASMA instrument to be used for the Phobos-Grunt mission is a typical lander LMS and is based on an earlier development (Managadze, 1992; Managadze and Managadze, 1999; Brinckerhoff et al., 2000). In this instrument a 7 ns laser pulse with 16 mJ power from a flash-lamp pumped Nd:YAG laser (wavelength 1064 nm) is used, which is focussed to a spot of Ø 50 µm on the sample surface. Since the laser repetition rate has to be kept very low to stay within the power limits of the spacecraft, spectra are recorded with a high-dynamic range detector and signal acquisition system, and all spectra are transmitted individually to Earth. The flight instrument will be 220 x 110 x 260 mm^3, will weigh about 1.5 kg, and will be mounted on the

Element	LASMA analysis	Reference
Au	84.68	84.5
Pt	7.12	6.9
Pd	4.30	5.0
In	1.22	1.75
Ag	1.10	1.0
C	$2.5\text{x}10^{-3}$	$2\text{x}10^{-3}$
Fe	0.49	0.7
H	0.31	N/I
Zn	0.13	0.15
Re	0.65 Max	0.1

Table 1: Concentration in % weight derived from LASMA measurements in comparison to the reference values.

outside wall of the lander. Two pictures of the LASMA prototype unit are shown in Figure 1. An articulated arm will collect surface soil samples from the vicinity of the landing site and deliver these to the sample carousel of LASMA, which can accommodate up to 14 samples.

LASMA can record mass spectra in the mass range from 1 to 250 amu, with mass resolutions m/Δm between 200 and 600 (FWHM). Figure 2 shows a section of a mass spectrum with the major lead isotopes resolved, recorded with the laboratory prototype. The accuracy of the isotope measurement is about 1%. The detection efficiency for the elements is reasonably constant allowing for quantitative elemental analysis of solid surfaces. Table 1 shows a comparison between measurements with the LASMA prototype and the reference values from the glass standard NBS-610 sample.

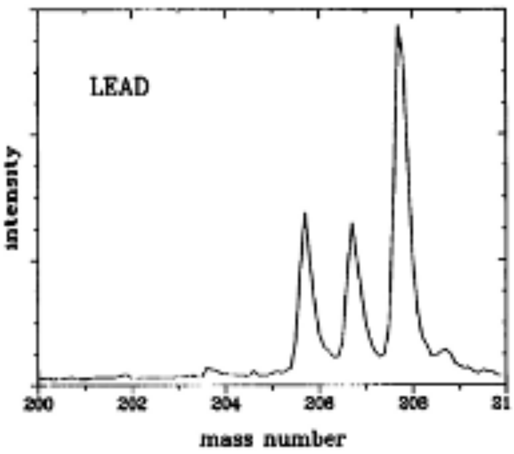

Figure 2: Mass spectrum recorded with the LASMA prototype showing the major lead isotopes.

Rover LMS

The instrument for the rover (the rover LMS) has the advantage that the mobility of the rover possibly gives access to a larger variety of samples. Since resources are typically much smaller on a rover compared to a lander, a rover LMS needs to be much more economic in using resources.

The rover LMS is also of the time-of-flight type, but of substantially smaller size, and also used a microchip laser system. Because of the limited space, a novel combination of an electrostatic analyser and grid-less reflectron was used to fold the time-of-flight path two times to make it sufficiently long for decent mass analysis [Rohner et al., 2004]. The prototype instrument has a demonstrated mass resolution m/Δm in excess of 180 (FWHM) and a predicted dynamic range of better than five orders of magnitude. The ion-optical system itself has a measured mass resolution of 400, as seen from single shot spectra, which is in good agreement with the ion-optical design. Again, the major Cr and Fe isotope ratios were measured with this instrument and accuracies at the % level were achieved [Rohner et al., 2004]. As with all time-of-flight instruments, covering a large mass range is not a problem here and elements from hydrogen up uranium have been detected with this instrument. When aiming for the detection of chemical compounds of higher mass we have to improve the mass resolution during routine operations to the single-shot value, which is about the theoretical limit of an instrument of that size.

Figure 3 shows the prototype of the rover LMS consisting of three printed circuit boards (PCB). The top board contains the actual mass spectrometer and laser system. The entrance to the LMS is the small hole in the vertical plate of the ion optics, which is also where the laser comes out. The sample is placed directly in front of this hole. The middle PCB contains the laser electronics, and the bottom board the high voltage power supplies. We estimate that a flight instrument would have a mass of 280 g (including laser and all electronics) and a total volume of 7 x 4 x 3 cm^3 including all electronics. For full operation only 3 W power will be needed making use of local energy storage to accommodate the short-term power needs of the laser system.

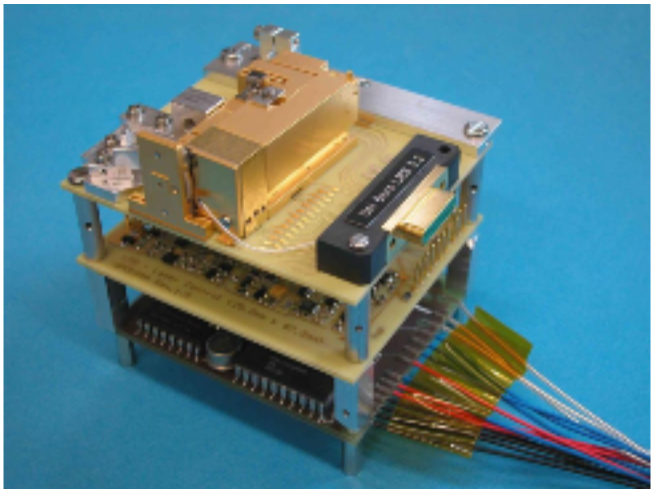

Figure 3: Rover-LMS prototype instrument (Rohner et al., 2004) built onto a printed circuit board (top board), together with laser and temperature control board (middle board) and the high-voltage supply board (bottom board). The sample inlet is the small hole on the left of the TOF structure. The ion drift path is folded two times, using an electrostatic analyser and an ion mirror, to attain the required TOF path length.

Membrane-Inlet Mass Spectrometer

As part of the scientific payload of a melting probe, e.g. for an Europa lander or Mars polar lander, we propose to use a Membrane-Inlet Mass Spectrometer (MIMS). Since melting probes melt their way through water ice, the probe is always immersed in liquid water, at ambient pressures depending on depth. Therefore, a mass spectrometer on a melting probe has to be contained in a sealed vacuum system. The problem then is how to bring in a sample from the outside, perhaps at a few bars outside pressure, to the inside of the mass spectrometer that is operated at 10^{-6} mbar. A simple solution is to use membranes for sample inlet, which have permeability for certain chemical substances, but cannot be penetrated by water. Such membrane inlet (or introduction) systems have been used in a variety of applications (Johnson et al., 2000) in water depths up to 250 m (Wenner et al., 2004). An instrument intended for use on Europa would make measurements similar to an environmental monitoring instrument in a terrestrial ocean: the abundances of dissolved gases (oxygen, nitrogen, carbon dioxide and others) allow to determine the geochemical environment and the abundances of volatile organic compounds that might suggest the presence of life.

Figure 4 shows a design study of a MIMS instrument for an outside pressure up to 120 bars. The inside volume is pumped by an ion pump. The mass spectrometer itself is based on the Rover LMS. There are three membranes with different chemical selectivity for the transmitted species, and each has a reservoir for sample gas collection. With electrical actuated gas valves a sample reservoir can be opened to the ion source of the mass spectrometer and the collected gas is analysed. The three reservoirs will be analysed in sequence. Since the melting probe moves slowly through the ice there is ample time for sample collection and its analysis.

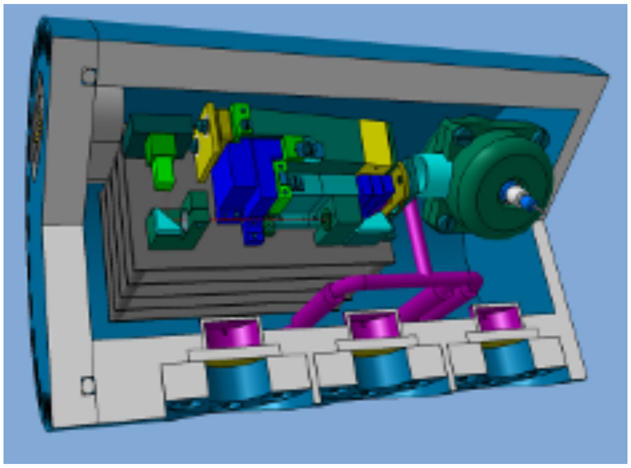

Figure 4: Cut-away drawing of the design of a MIMS for a high-pressure application. The green disks are the membranes, each having a reservoir for gas collection behind. The valves are inside the thicker tubes connecting the reservoirs to the ion source. The TOF-MS design is the similar to the Rover LMS. The green unit in the upper right corner is the ion pump. The outside dimensions are 17 x Ø 10 cm.

CONCLUSIONS

Miniaturised mass spectrometers for planetary research have been developed to a high level of technical maturity and they are ready for use on spacecraft. The LASMA instrument on the Phobos-Grunt spacecraft will be the first application of such an instrument on the surface of a planetary body. Unfortunately, the original intention of ESA to have a lander as part of the BepiColombo mission was dropped because of high costs. However, we can expect more missions in the future with landing spacecraft (e.g. as evaluated by ESA within the Cosmic Vision programme), and thus there will be opportunities for mass spectrometric measurements of soils and rock.

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