ABSTRACT

Originally intended for the European Space Agency’s BepiColombo mission to Mercury, we have built a series of highly miniaturised laser ablation time–of–flight mass spectrometers (LMS), suitable for in situ measurements of the elemental and isotopic composition of the surface of airless planetary bodies. The instruments will determine major, minor, and trace element abundances in minerals on a spatial scale of 10 µm, and will have sufficient dynamic range and mass resolution to perform useful isotopic measurements in favourable cases. Solid material is simultaneously evaporated and ionised by means of laser ablation, requiring intense pulsed laser radiation. Laser ablation was chosen as the sample introduction technique principally because of its high spatial resolution and the lack of any need for sample preparation. Advantages of the technique include simplicity of the resulting design, speed of measurement, and the ability for depth profiling (potentially important for a regolith in which mineral grains are coated with impact produced glass). Time–of–flight mass spectrometers are simple, robust devices that couple well to a pulsed ion source and we have previous experience of their construction for space flight, e.g. the ROSINA instrument suite for the ROSETTA mission. For BepiColombo, we have built two prototype instruments, one with a design mass of 500 g and a volume comparable to a beer can intended to be deployed on a static lander, and a smaller cigarette-box sized version with a design mass of 250 g, small enough to be integrated in a rover or robotic arm.

Key words: LMS, Mercury, time–of–flight, laser, ablation, mass–spectrometer.

1. MOTIVATION: BEPICOLOMBO

As already mentioned, the primary motivation of our work was the proposed BepiColombo mission with its scientific goals, which are given in [1].

As is known from other observations, Mercury has a very high density which suggests an interior structure and chemistry with a large concentration of iron, about 70 weight-percent [2], where the iron is most likely concentrated in a large core. The core/planet radius ratio of Mercury is in this case about 80%, in comparison of approx. 50% for Earth, Venus, Mars, Io, Ganymede and approx. 30% for the Moon. The Core/Planet mass ratios are therefore 70% (Mercury), 30% (Earth, Venus, Mars) and 5% (Moon).

To understand the formation of Mercury, there are (at least) three basic models to explain Mercury’s unusual high density:

- A chemical gradient in the early proto–solar nebula
- The young hot sun sublimated the outer silicate layer
- A giant impact blew off the outer silicate shell
The more complex models introduce a “differentiated” nebula instead of a chemically homogeneous nebula. Another possibility is the formation of planets in our solar system out of different major planetesimals and therefore a more or less stochastic “mixing” of primordial material. For all models are different trace elements respectively different isotopic and elemental ratios of trace elements expected in the surface composition. With the LMS (lander and rover version), we want to measure this elemental and isotopic ratios.

Simulations [3] and observations of other atmosphere-less planets and moons suggest a highly processed surface on Mercury consisting mostly of regolith with particle sizes in the range 10–100 µm, where perhaps 50% of the particles are agglutinates. The filling factor of the top few meters is estimated to be about 50%.

2. LANDER PROTOTYPE (LMS1)

For the originally foreseen BepiColombo Mercury Surface Element (MSE), we built the laboratory prototype laser ablation time–of–flight mass spectrometer LMS1 (Laser Mass Spectrometer), see Figure 1. The spectrometer was foreseen to be deployed with a robotic arm onto the surface. The instrument is described in detail in [4].

3. ROVER PROTOTYPE (LMS3.2)

To measure the surface composition of Mercury on more sample points on a larger area, we substantially reduced the size of the laser mass spectrometer (see Figure 2 and [5]), so that it would fit in the largest compartment of the foreseen micro-rover [1]. Figure 3 shows the micro-rover prototype with the payload cabin articulated to perform a measurement on a stone with one of its payload instruments. Figure 4 shows the LMS accommodation in one payload compartment.

4. LMS OPERATION

Both LMS laboratory prototypes operate in the same way. The differences are only in the configuration of the mass analyser and the size. The spectrometers would be placed adjacent to the sample (regolith, a stone, ice,...). A laser pulse will desorb and ionise a small volume of the sample. While running the pulsed laser at a repetition rate of approximately 10 kHz, each laser pulse results in a mass spectrum; we can obtain 5–6 decades of dynamic range by accumulating the spectra over 1–4 seconds.

A correlation of the measurement of single grains with the LMS with camera images would benefit the scientific interpretation. By measuring with LMS at the same position, depth profiling with knowledge of which grain is measured, would be possible.

Laser ablation/ionisation as ion source was chosen because of its advantages to traditional solid sample ionisation methods, e.g. dissolution and inductively coupled plasma (ICP), glow-discharge, spark source or particle bombardment. All these ionisation processes require sample preparation and a controlled gas pressure. Laser ablation/ionisation, in contrast, couples well with time–of–flight mass spectrometers (TOF-MS) with a direct interface to the mass analyser without any preparation. Due to the simplicity of this method, also the mass, size and power requirements are very small compared to the above mentioned ion-sources. Also power savings using duty-cycles can be easily introduced by just turning off the laser and its driver electronics.

Laser ablation is widely used to introduce material to ICP-MS instruments and direct laser ionisation is already used widely in chemical analysis [7] and commercial instruments are available. For space missions, laser ablation/ionisation and TOF-MS instruments have been previously developed for the LIMA-D instrument flown on the Russian Phobos mission [8] and the LAMS instrument from APL, John Hopkins University (still at prototype stage).

4.1. How does laser ablation/ionisation work?

With a powerful laser pulse, we shoot at a sample from which particles (neutrals and ions) will then...
be removed (desorbed or ablated) and the resulting neutral atoms will be ionised in the gas phase by the laser or the produced plasma. The positive (or negative) ions are introduced directly into the mass analyser. At low to medium irradiance of the laser (< \(10^8\) Wcm\(^{-2}\)), the sample will be desorbed, heated and vaporised, which results in complicated physics and therefore difficult interpretations of the resulting mass spectra, because of elemental fractionation. By using photo-ionisation with a second laser, this problem could be eliminated at the cost of a second laser. At high irradiance (> \(10^9\) Wcm\(^{-2}\)), a plasma is formed above the surface, which absorbs and reflects laser radiation. This will redistribute the incident energy. The plasma pressure is typically 10 kbar, with an electron temperature of approximately \(5 \times 10^4\) K, where the properties depend on the mass number and charge state (and also the power and wavelength of the laser pulse). The advantages of working at this high irradiance are a nearly uniform ionisation efficiency and a relatively high ion yield of \(\approx 0.1\%\), which is almost independent of the target chemistry.

4.2. Laser Requirements

To meet the requirements imposed by the optimal plasma parameters and the BepiColombo mission constraints, a high peak output power laser is needed that must nevertheless have a low average power consumption. Laser pulses shorter than 1 ns are desirable because such short pulses couple well with TOF mass-spectrometers, which need short pulses for a good mass resolution. To obtain the necessary high irradiance on the target probably requires a small spot size and therefore good beam quality is needed to allow diffraction-limited focusing. To reach the optimal parameters of 1–4 GWcm\(^{-2}\) at
focus [9] with a depth of focus of at least 100 \( \mu m \) 
(\( \pm 10\% \) irradiance points) and an irradiance ideally constant across the focus, the laser source needs to fulfill very high requirements. A possible laser is a passively Q-switched diode pumped microchip laser (Nd:YAG, \( \lambda = 1064 \) nm) with pulse energies of typically 10 \( \mu J \), a 0.5–1 ns wide pulse resulting in a peak power of 10 kW at a repetition rate of 10 kHz. When this light is focused to a spot of 10 \( \mu m \) diameter, it results in an energy density of approx. 10 GW cm\(^{-2}\). Each laser pulse is expected to remove 0.1 \( \mu m \) material per pulse and produce around \( 10^{11}–10^{18} \) ions.

These microchip lasers (see Figure 5) are small, cheap, robust and efficient devices and can be obtained commercially (although not yet flight qualified). The use of a passive Cr:YAG Q-switch generates short pulses and high peak powers without the need for additional electrical or optical components. (The Q-switch material is fabricated with the gain medium and cavity to produce a monolithic device [10]). In Figure 6, one can see holes from single and multiple laser shots in a cadmium sulfide sample, which was moved under the focus of the laser (1064 nm).

4.3. Present Work

At the moment, we are mounting the laser system with an improved optical design into the rover laboratory prototype. This design uses a “diffraction optical element” (DOE) in the light path to increase the depth of field of the laser focus. Also the high voltage and laser driver electronics with an appropriate size are being tested and will be integrated soon.

5. FUTURE APPLICATIONS

We have described the use of miniature time–of–flight mass spectrometers with laser ablation ion sources to make measurements of solid surfaces e.g. rocks or regolith. Scientific applications of these sorts of measurements are primarily in the fields of geochemistry and mineralogy, and to provide “ground truth” for orbiting instruments. However, the technology is also highly suitable for measurements of atmospheres and molecular species of interest to exobiologists. Time–of–flight mass analysers have very large mass ranges (easily up to 10000) and so can be used to detect large complex molecules such as proteins, or poly-cyclic aromatic hydrocarbons (PAHs) and other types of molecule regarded as “biomarkers” [11].

Lasers may also be applied in a more subtle fashion than ablation at high irradiances by making use of wavelength dependent resonances or particular substrates in order to obtain molecular mass spectra rather than elemental ions.

5.1. Gas Mode

Any of our miniature mass analysers described here can be used not only for the measurement of solids, but also, with a suitable ionisation source, of gases. A laser at sufficiently high irradiances will ionise any gas through dielectric breakdown [12], and would be appropriate for the elemental and isotopic measurement of, e.g., the martian atmosphere either directly or following pyrolysis or combustion of soil samples. Alternatively an ultra-violet laser might be used for the relatively “soft” ionisation of volatile molecular species. Ultra-miniature solid-state UV lasers similar to the infra-red and visible passively Q-switched systems described earlier are under development. Where sufficient mass and power are available, one might consider the use of tunable lasers to take advantage of resonance ionisation effects [13] for greater efficiency or selectivity of detection for either elements or molecules. Electron impact ion sources with a suitably short pulse length (obtained either by pulsing the electron source or by rapidly sweeping out ions from a continuous source) would also be suitable for use with the time–of–flight mass analyser, and would in some cases allow a higher transmission or mass resolution [14] than a laser ion source because of the relatively narrow range of resultant ion-energies.

5.2. Combination of LMS with gas-chromatography or ion-mobility

Given the ability of LMS to measure a gas stream at a high repetition rate, it is natural to consider the mass spectrometer as the detector for a chemically sensitive separation technique such as gas-chromatography or ion-mobility spectrometry. The advantages of a mass spectrometer over, e.g., thermal conductivity or ion-current detectors are the extra information gained about the analyte (molecular mass and fragmentation pattern) and the potential for isotopic measurements, e.g. of carbon dioxide derived from combustion of a soil sample.

Both gas-chromatography and ion-mobility spectrometers can be built on a scale similar to that of LMS, and we are investigating appropriate interfaces (and any required vacuum pumps) between the gas stream and the mass spectrometer. Another very compact form of chemically selective filter is the use of a semi-permeable membrane inlet to a mass spectrometer (Membrane Introduction Mass Spectrometry or MIMS) [15]. MIMS has been applied to both gaseous and liquid media, thus a version of the mass analysers described here with a MIMS interface could be lowered into a sub-surface brine. The dimensions of such a system would allow the entire instrument to be suspended inside a drill string allowing real-time monitoring of the composition of any fluids encountered.
5.3. LMS with MALDI

Matrix Assisted Laser Desorption/Ionisation (MALDI) is a means of ionising large molecules from a surface without excessive fragmentation, and so the identity of the parent molecule can be more readily determined [16]. Many applications of MALDI use an ice as the matrix, and thus the surface of icy planets may well need no additional preparation to measure trace abundances of complex molecules that may be present in the ice [17]. This technique would be particularly useful for exo-biology investigations as it has been shown that amino acids and proteins are readily detected [18].

A laser source for MALDI could have much lower irradiances than those required by LMS for elemental measurements, but it is likely that best results would be obtained from an ultra-violet source.

6. CONCLUSIONS

Results of measurements on planetary surface analogues obtained with both our lander and rover laboratory prototypes, with their dimensions of a few centimetres and total mass and laser sources similar to those envisaged for a flight model, are very promising. We have achieved a mass resolution and transmission in good agreement with our simulations, and the mass resolution is sufficient to clearly resolve adjacent isotopes when used with laboratory data acquisition hardware. Encouraged by this, we are working on further improvements of the hardware, i.e., final miniaturisation of the electronics and the development of additional measurement modes such as gas analysis which would also allow us to use our instrument as the detector for e.g. a gas chromatograph. However, a great deal of work still needs to be done to fully characterise all the chemical and isotopic fractionation effects that occur in the laser induced plasma at the surface, and to assess how appropriate the choice of laser wavelength, pulse duration and irradiance may reduce analytical artefacts.

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REFERENCES


