

A miniature laser ablation time-of-flight mass spectrometer for *in situ* planetary exploration

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Abstract

We report the development and testing of a miniature mass spectrometer and ion source intended to be deployed on an airless planetary surface to measure the elemental and isotopic composition of rocks and soils. Our design concentrates at this stage on the proposed BepiColombo mission to the planet Mercury. The mass analyser is an axially symmetric reflectron time-of-flight design. The ion source utilizes a laser induced plasma, which is directly coupled into the mass analyser. Laser ablation gives high spatial resolution, and avoids the need for sample preparation.

Our prototype instrument has a demonstrated mass resolution $m/\Delta m$ (FWHM) in excess of 600 and a predicted dynamic range of better than four orders of magnitude. Isotopic fractionation effects are found to be minor. We estimate that a flight instrument would have a mass of 500 g (including all electronics), a volume of 650 cm³ and could operate on 3 W power.

Keywords: elemental and isotopic composition, laser ablation, mass spectrometry, planetary exploration

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The European Space Agency's (ESA) BepiColombo mission to Mercury is planned to include a lander that will investigate the composition and properties of the surface [1]. The instruments on this lander will both provide 'ground-truth' for the composition instruments on the orbiting spacecraft, and allow a higher resolution and more detailed analysis of the Hermean regolith at the landing site. Knowledge of the composition of the crust of Mercury will allow us to estimate the composition of the planet's interior, important to distinguish between models of formation, and to develop an understanding of internal geochemical differentiation processes.

We have developed a laboratory prototype of a mass spectrometer appropriate for this mission which will allow the measurement of both elemental and isotopic compositions with a spatial resolution (lateral and vertical) better than the expected regolith grain size, thus allowing an accurate picture of the modal mineralogy to be built up. The high spatial

resolution is of key importance as it will permit a detailed assessment of the individual constitution of the regolith and the significance of particular analyses to the global picture. It has been suggested, for example, that Mercury's surface may contain a significant component of meteoritic origin [2] and that, as on the Moon, agglutinates and glass will form a significant fraction of the surface material.

The mass and power constraints for a Mercury lander are severe (7 kg for scientific payload, 400 W h total energy budget) [1], necessitating an instrument that is very economical in its use of these resources. Also the environmental conditions on Mercury, with a temperature of up to +470 °C on the day side and –180 °C on the night side, are extremely severe. So the preferred landing place is on its cold side with the possibility of heating up the instruments using the dissipated heat of the electronics. Because of these challenging conditions, we expect that an instrument designed for Mercury could be used on other (airless) planetary surfaces with little or no modification.

2. Design

Most techniques for introducing solid samples to a mass spectrometer require processing and preparation of the material to be analysed (e.g. acid dissolution for ICP-MS, embedding in a conducting material for glow-discharge or spark-source mass spectrometry). For mechanical simplicity we have chosen to use direct laser ablation of the surface, producing a plasma plume which can be coupled directly to a mass analyser. Although this technique can produce large elemental and isotopic fractionation, these undesirable effects can be minimized by careful control of operating parameters, and by the calibration of matrix effects. A natural choice for a mass analyser to use with a laser ablation ion source is a time-of-flight (TOF) instrument. TOFs are robust, allow ion-optical correction of the large kinetic energy spread of ablated ions, make optimum use of a pulsed source with a low duty cycle, and are fast in acquiring spectra (typically a few microseconds for one spectrum and a few seconds for one measurement consisting of several thousand averaged spectra). Furthermore, we are able to capitalize upon our experience of building the RTOF instrument on the ROSETTA comet rendezvous mission [3] by essentially miniaturizing the existing mass analyser.

Laser ablation TOF mass spectrometers of similar conceptual design have previously been developed for space science. LIMA-D, flown on the Russian Phobos mission, was a stand-off instrument intended to operate tens of meters from the surface and had a mass of about 80 kg [4]. Trials of another proposed stand-off instrument with both ion trap and reflectron TOF mass analysers were also carried out [5, 6]. Laboratory prototypes for *in situ* measurements in the 2 kg range (suitable for deployment on a planetary rover) have been developed more recently [7–9] and precisions of better than 10% for elemental abundances, and 30‰ for isotopic compositions have been demonstrated with detection limits of better than 10 ppm. The instrument reported here promises similar performance in a significantly less massive and smaller package. Advantages of a laser ablation mass spectrometer over other analytical instruments include sensitivity to almost all elements, a high dynamic range allowing the detection of trace elements, spatially resolved measurements and the determination of isotopic compositions. The measurement of isotopic compositions can in principle allow the determination of radiometric ages, test models which suggest a relationship between isotopic composition and heliocentric distance (e.g. for oxygen), and determine the extent of volatile element loss (from kinetic fractionation effects during evaporation).

2.1. Laser ablation ion source

Several publications have shown that the laser irradiance on the target must be of the order of 1 GW cm^{-2} in order to produce an ion plume with minimal elemental fractionation relative to the true composition of the surface [7, 10, 11]. To produce this high irradiance from a compact solid state laser requires a short-pulse *Q*-switched system, which is also advantageous for coupling with a TOF mass analyser. (For a miniature mass analyser with flight times of about 10 μs , a temporal ion pulse

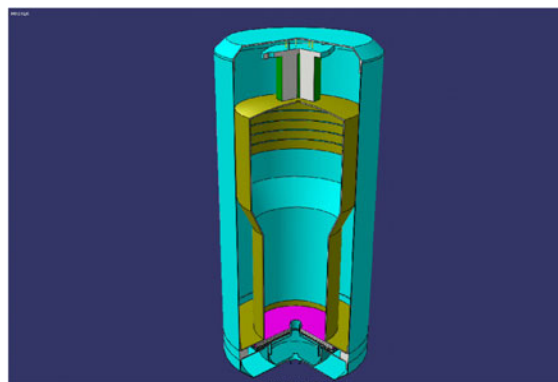


Figure 1. A detailed engineering study corresponding in its physical properties to our laboratory prototype (see figure 4). Electronics will fill the empty volumes at the top and around the TOF tube.

width at the detector of 10 ns is required for a mass resolution of 500. Therefore the laser pulse width at the start should be of the order of 1 ns.) The laser wavelength is expected to be less important, although studies of laser-ablation inductively coupled mass spectrometry, in which particles produced by the laser pulse are swept by a carrier gas into a plasma at atmospheric pressure for ionization, suggest that for some mineral targets shorter-wavelength lasers result in reduced elemental fractionation during the ablation process [12].

The low mass and power budgets of an interplanetary mission, and the severe shock loads associated with launch and landing, lead naturally to the choice of a diode-pumped passively *Q*-switched microchip laser; these devices have been described in detail elsewhere [13, 14]. Their suitability for this application stems principally from their small size, the monolithic nature of the laser cavity (in this case mirrors are coated onto the ends of a Nd:YAG gain-medium and Cr:YAG *Q*-switch which together form a single crystal), and the simplicity of passive *Q*-switching (no extra components or control circuitry). Additional advantages include good beam quality (allowing the laser beam to be focused to a small spot, or readily frequency doubled), and the fact that output pulse energy is approximately independent of the pump power. In this work we report results obtained using a 1064 nm laser system from Poly-Scientific (see figure 2). The 1064 nm MegaChip device (ML-00040) produces 12 μJ pulses at 7 kHz with a pulse width of 0.66 ns. The laser was focused obliquely onto the target using a 25.4 mm focal length doublet lens (Newport PAC016) after 20 cm of free propagation to produce slightly elliptical spots of approximately 15 μm diameter (see figures 3, 5).

2.2. Mass analyser

The TOF mass analyser is an axially symmetric reflectron instrument constructed from stainless steel. Positive ions are accelerated and focused from the laser plasma above the target surface through a hole in the centre of the detector, they then traverse the field-free and reflectron regions, and are detected by a pair of microchannel plates with five concentric ring anodes. Figure 4 shows a picture of the instrument. During the design phase, attention was paid to keeping the number of independent voltages low (to reduce the complexity and mass



Figure 2. Microchip laser system, installed into a standard TO-3 package. This is a commercially available passively *Q*-switched Nd:YAG laser operating at 1064 nm (Poly-Scientific ML-00040).

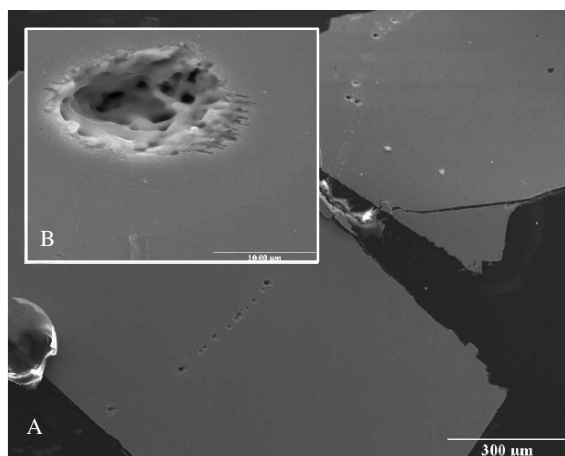


Figure 3. Laser shots in a flat reference sample of synthetic cadmium sulfide. The holes have a diameter of about 15 μm . B: magnified hole from sample A.

of the flight electronics) whilst maximizing the transmission (to increase efficiency, and reduce instrumental fractionation effects). To reduce the complexity of the power supplies, ion-optic voltages were kept below 500 V, except at the detector.

As ions enter the mass analyser through the hole in the conical nose-piece, they pass through four potentials which accelerate and focus them into the field-free region (between the detector assembly and the reflectron, see figure 5). The reflectron is a gridless ion mirror, and consists of five metal rings at individual potentials and the backplate. The backplate has a black and conducting copper sulfide coating to reduce back-scattered laser light to the detector. Since this surface treatment has micrometre sized tips, ions or neutral adsorptions would not produce any significant insulation layer which could give a wrong effective potential to the plate. The voltage gradient in the reflectron is approximately linear in two stages, but was optimized numerically (see table 1). (A linear reflectron with no field free regions would allow perfect energy focusing [15, 16].) The detector consists of two chevron-mounted microchannel plates with a 6.4 mm central hole and



Figure 4. Laboratory prototype mass analyser v1.0. At the top of the image are the plates defining the reflectron. The flight tube is visible in the centre of the picture, and at the bottom are shown the ion optics that would be adjacent to the surface to be sampled. The dimensions are 150 mm in height, and 60 mm in diameter, i.e., about the size of a soda can.

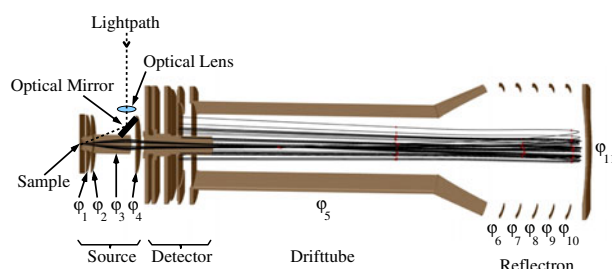


Figure 5. Schematic drawing of the spectrometer with some calculated ion trajectories. The system is composed of an ion source, a detector and a grid-free reflectron. The detector and the ion source are integrated into one unit, together with a simple ion lens.

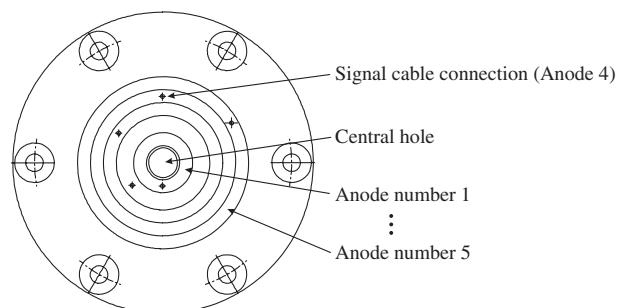


Figure 6. Top view of the five anode-rings used in the detector.

a concentrically segmented anode (see figure 6) to study the spatial variation of transmission and mass resolution. For the flight version of the spectrometer, only one anode would be used because of the limitations in the electronics budget, while the other anodes would be set to ground potential.

2.3. Ion-optical simulations

Following the initial selection of geometry and approximate dimensions, all voltages and positions of the ion-optical elements were optimized using the computer program SIMION v7 in conjunction with a set of macros and C-programs [17].

Table 1. Voltage settings for the spectrometer (see figure 5 for labelling and figure 7 for the calculated transmissions and resolutions). Column (a): voltage setting for a transmission optimized spectrum (simulated), column (b): voltages for a resolution optimized spectrum (simulated), column (c): voltage settings used for acquiring the CuBe spectrum shown in figure 10.

		Potential (V)		
Ion-optical element		(a)	(b)	(c)
Mercury	φ_1	0	0	0
Lens	φ_2	−300	−300	−320
Lens	φ_3	−80	−90	−93
Lens	φ_4	−290	−300	−320
Drift	φ_5	−500	−600	−500
Reflectron 1	φ_6	−300	−285	−315
Reflectron 2	φ_7	−100	−195	−93
Reflectron 3	φ_8	−65	−117	−55
Reflectron 4	φ_9	−30	−58	+10
Reflectron 5	φ_{10}	+10	−7	+12
Backplate	φ_{11}	+40	+40	+42

A merit function was constructed to optimize transmission and mass resolution within the constraints imposed on the voltages and overall dimensions. To estimate the transmission and mass resolution obtainable, we assumed that the laser-produced plasma consists of a plume of ions with an initial start-position distribution described by a three-dimensional Gaussian distribution with a width of $\sigma_w = 5 \mu\text{m}$ centred on the symmetry axis at the entrance of the spectrometer. The initial direction distribution of the ions was modelled as a Gaussian distribution normal to the target surface with an angular width of $\sigma_a = 20^\circ$. The energy distribution of the ions was assumed to be a half-Gaussian with cut-off at 0 eV and an energy width of $\sigma_E = 100 \text{ eV}$. The effects of plasma shielding were neglected entirely because with these parameters and a sub-nanosecond laser pulse, the plasma jet does not travel a significant distance in the time it takes for the plasma to cool, and thus the Debye length to become large and the plasma to become ‘transparent’ to electric fields. The choice of angular and energy dispersions was guided by theoretical and measured values [5, 11, 18] and is justified by our results (see section 3).

Figure 7 shows the calculated transmissions and mass resolutions for two different solutions to the optimization, in which more emphasis was placed either on transmission or mass resolution, respectively. The figures show values for both the whole detector area, and for each concentric anode separately. It can be seen that most ions are detected on the innermost regions of the channel plates, and that mass resolution can be significantly increased, but only over part of the detector (reducing effective transmission). This does present the possibility of using the same instrument in both high resolution and high transmission modes. A similar approach (using explicit energy windowing) has been suggested to improve accuracy in LA-TOF measurements [8]. The transmission of 9% at maximum using all five anodes together is limited by the large angular spread of the ions having energies up to several hundred electronvolts, which cannot be focused into a spectrometer of this size without losing significant resolution.

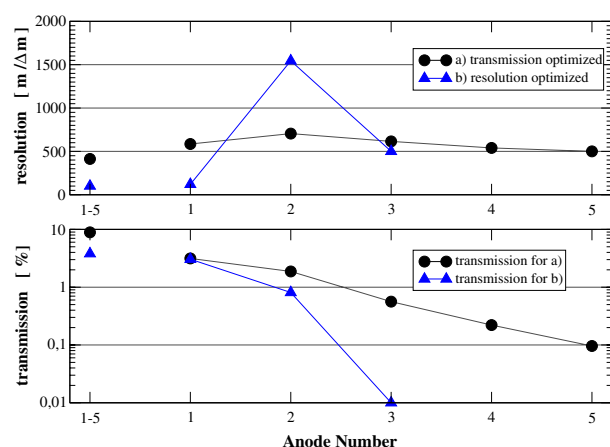


Figure 7. In the upper panel, the calculated mass resolutions for mass 16 are shown, depending on which anode the spectrum is taken. In the lower panel, the corresponding overall transmissions are plotted. The values are shown for each single anode, and also for the sum of all five anodes (i.e. total detector response).

3. Measurements

To make measurements, the entire mass analyser was placed within a large UHV chamber that could be pumped down to 10^{-8} mbar. All connections were made via electrical feedthroughs but the laser system was placed outside the vacuum chamber and the laser beam was passed through a fused silica window. No adjustment of laser focus was possible from outside the chamber, so samples were positioned manually to give the strongest laser-induced ‘spark’ in air, before closing and evacuating the chamber. TOF mass spectra were acquired using an 8 bit digital oscilloscope (Tektronix TDS 7404, 4 GHz, 20 Gs s^{-1}) connected directly to one of the five concentric, 50Ω matched anodes of the channel plate detector. A Hamamatsu high-speed photodiode (G8376) was used for recording the laser pulse and triggering the data acquisition.

To confirm the performance of the prototype, measurements were first made using a conventional electron impact ion source operated in pulsed-mode. Figure 8 shows a mass spectrum of argon obtained in this way. Subsequent spectra were obtained using the infrared microchip laser described in section 2, with the pulse repetition rate reduced by modulating the pump diode current. This was necessary because the oscilloscope could not trigger at the frequency of the free-running laser. The limited depth of the oscilloscope’s memory restricted the dynamic range of the data acquired.

Only very minor adjustments to the potentials predicted by the computer modelling were found necessary to obtain mass spectra in good agreement with the simulations. Figure 9 shows averaged data for part of the mass range from an austenitic steel. The mass resolution is 280 confirming that the reflectron does a good job of compensating for the range of ion energies produced in the plasma. The dynamic range is as good as can be expected for averaging performed within the 8-bit memory of the oscilloscope. Figure 10 shows data from a copper–beryllium alloy (98 wt% Cu, 2 wt% Be). In addition to the expected peaks for ^9Be , ^{63}Cu and ^{65}Cu , and Na and K from surface contamination, there are many peaks due to cluster ions of the form CuBe, Cu_2 and Cu_3 .

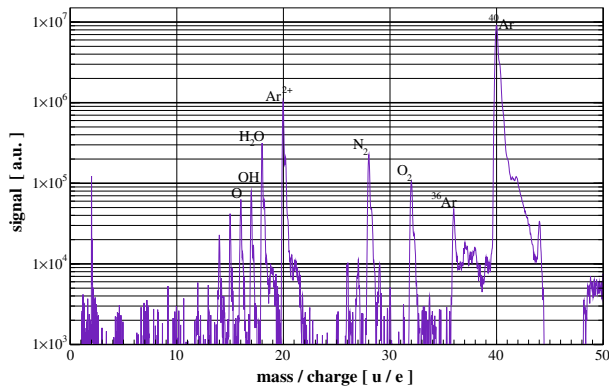


Figure 8. Mass spectrum of argon obtained with a conventional electron impact source to check operation of the prototype.

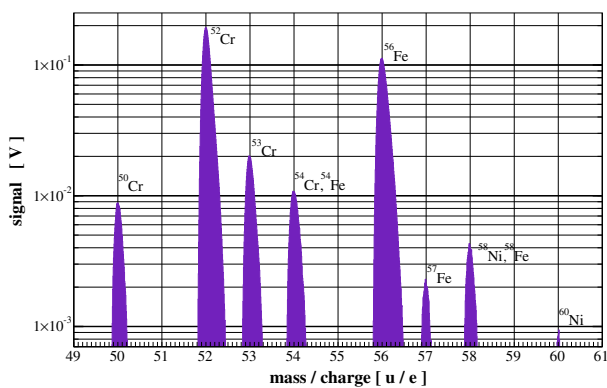


Figure 9. Sample spectrum of a standard reference stainless steel (NBS 479) showing the capability of measuring isotopic abundances with % errors. This spectrum was taken by averaging five thousand shots during a few seconds. For better visibility, the spectrum was cut at its noise level of 0.7 mV.

Not only metals, but also ferro-magnesian silicate minerals give good results with the infrared laser. Figure 11 shows an enlargement of the minor ^{58}Fe peak from a mass spectrum obtained from the Qingzhen meteorite. No special preparation of the surface of the sample was carried out—it was a rough surface from splitting the stone. Qingzhen was chosen because it belongs to a group of chemically reduced meteorites known as enstatite chondrites, which may have some geochemical similarity to the surface of Mercury [19, 20], although they do not have an igneous origin. These meteorites consist largely of the pyroxene mineral enstatite (nominally MgSiO_3) and iron–nickel metal and sulfides. The figure shows a mass resolution of 600, which is better than the resolution obtained with the austenitic steel sample, where we averaged five thousand spectra to get statistically good values for the rare isotopes in comparison to the 96 averages at the Qingzhen meteorite. This is caused by the slowing down of the laser repetition rate and therefore long acquisition time.

3.1. Accuracy of measurements

A comparison of the mass spectra in figures 9 and 10 with the known sample composition indicates that elemental fractionation is rather severe, favouring the more volatile

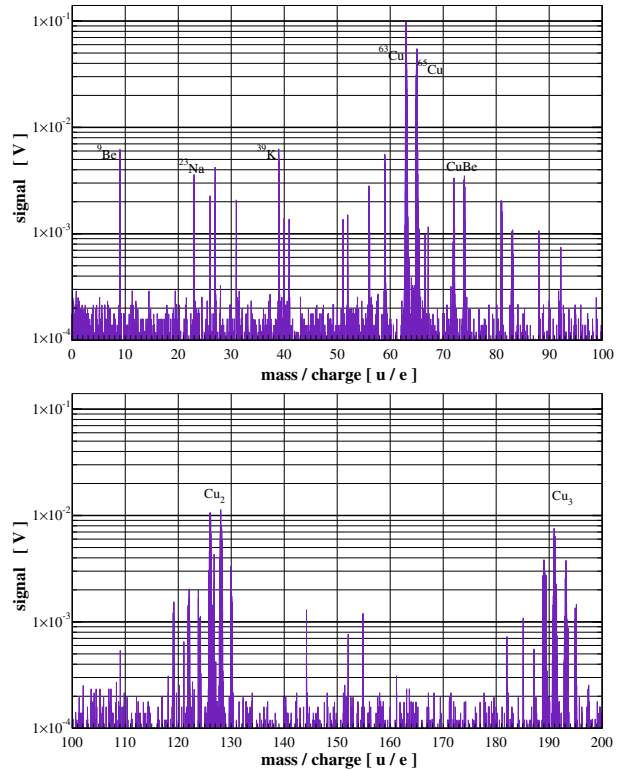


Figure 10. This typical spectrum of an uncleaned copper–beryllium foil is an average of 63 sequential laser shots, recorded on a regular digital oscilloscope (Tektronix TDS 7404) without further data processing. The presence of peaks attributed to both sodium and potassium indicates both the sensitivity of the technique to alkali metals (potentially useful in understanding the origin of Mercury's exosphere) and that ablation is only affecting the near-surface of the target. Spectra obtained later (and therefore at greater depth) do not show the alkali metal peaks.

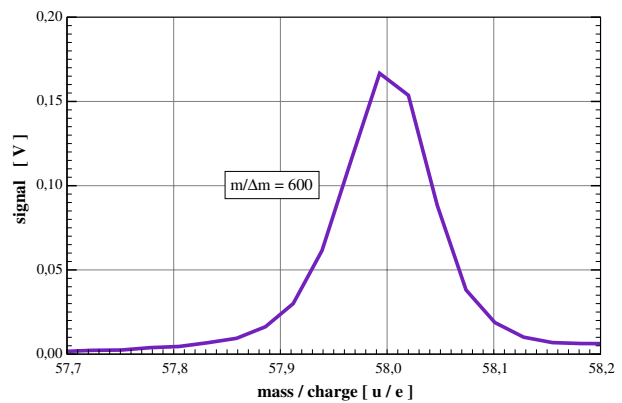


Figure 11. Averaging over 96 shots resulted in this spectrum, showing the mass resolution $m/\Delta m$ at FWHM of 600. This spectrum was taken from a meteoritic sample, the enstatite chondrite Qingzhen (EH3).

elements. This suggests that the laser irradiance on the sample is too low and this interpretation is supported by the existence of cluster ions, and the lack of any doubly charged ions. The laser irradiance at full power is calculated to be 3.3 GW cm^{-2} based on the measured pulse energy of $7 \mu\text{J}$ at the target, the manufacturer's given pulse width of 0.66 ns, and the observed crater size (not necessarily the same as the Gaussian beam

Table 2. Measured isotopic composition of the NBS 479 austenitic steel sample and the CuBe sample. The error is given as relative error (meas. – std)/std $\times$ 100. In the last column, the number of spectra which were averaged is given.

	Std%	Meas.%	Error%	No of spectra
⁵⁰ Cr	4.345	4.43	+2.01	5000
⁵² Cr	83.789	83.90	+0.14	5000
⁵³ Cr	9.501	9.30	–2.12	5000
⁵⁶ Fe	91.754	91.76	+0.01	5000
⁵⁷ Fe	2.119	2.11	–0.25	5000
⁶⁰ Ni	26.2231	26.23	+0.04	5000
⁶² Ni	3.6345	3.62	–0.31	5000
⁶³ Cu	69.17	66.82	–3.5	63
⁶⁵ Cu	30.83	33.18	+7.1	63

width). However, when using the full pulse energy we find that the detector is heavily saturated, and in order to obtain linear signals (and prolong the life of the microchannel plates) the laser beam is attenuated with a neutral density filter, so the irradiance is not high enough to avoid thermal effects at the surface. This situation could be improved if the laser could be focused to a smaller spot, thus giving the same irradiance with a reduced pulse energy and so fewer ions. However, the geometry of the prototype does not allow us to readily obtain a smaller spot. An alternative approach would be to reduce the ion flux using an aperture or a grid within the mass analyser or an energy filter. The few spectra we have taken at full laser power appear to show much reduced fractionation effects, and support the literature observations that the ionization efficiency of laser ablation is relatively constant across the periodic table when optimal conditions are achieved. On the other hand, isotopic fractionation effects are found to be minor (as expected). The measurements of iron and chromium isotope ratios in steel, and copper isotopes in copper–beryllium foil are within 4% (mostly much better) of the accepted values (see table 2). These isotopic compositions were calculated from the raw data of the recorded spectrum without any correction for instrumental fractionation effects.

4. Conclusions

Early results from a prototype mass spectrometer, with dimensions, mass and laser source similar to those envisaged for a flight model deployed from a lander to Mercury's surface, are very promising. We have achieved a mass resolution and transmission in good agreement with our ion-optical simulations, and the mass resolution is sufficient to clearly resolve adjacent isotopes when used with laboratory data acquisition hardware. This performance is more than adequate to answer major questions concerning the origin of Mercury.

We estimate that a flight version of this instrument would have a mass of 500 g (mechanics 220 g, laser control and interface electronics 50 g, high voltage power supply 100 g, data acquisition electronics 80 g, margin 50 g), consume 3 W average power (with local energy storage) and have a volume of 650 cm³ including all electronics (see figure 1).

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