



# Orbitrap mass analyser for *in situ* characterisation of planetary environments: Performance evaluation of a laboratory prototype

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## ABSTRACT

For decades of space exploration, mass spectrometry has proven to be a reliable instrumentation for the characterisation of the nature and energy of ionic and neutral, atomic and molecular species in the interplanetary medium and upper planetary atmospheres. It has been used as well to analyse the chemical composition of planetary and small bodies environments. The chemical complexity of these environments calls for the need to develop a new generation of mass spectrometers with significantly increased mass resolving power. The recently developed Orbitrap<sup>TM</sup> mass analyser at ultra-high resolution shows promising adaptability to space instrumentation, offering improved performances for *in situ* measurements. In this article, we report on our project named “Cosmorbitrap” aiming at demonstrating the adaptability of the Orbitrap technology for *in situ* space exploration. We present the prototype that was developed in the laboratory for demonstration of both technical feasibility and analytical capabilities. A set of samples containing elements with masses ranging from 9 to 208 u has been used to evaluate the performance of the analyser, in terms of mass resolving power (reaching 474,000 at  $m/z$  9) and ability to discriminate between isobaric interferences, accuracy of mass measurement (below 15 ppm) and determination of relative isotopic abundances (below 5%) of various samples. We observe a good agreement between the results obtained with the prototype and those of a commercial instrument. As the background pressure is a key parameter for *in situ* exploration of atmosphere planetary bodies, we study the effect of background gas on the performances of the Cosmorbitrap prototype, showing an upper limit for N<sub>2</sub> in our set-up at  $10^{-8}$  mbar. The results demonstrate the strong potential to adapt this technology to space exploration.

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## 1. Introduction

It is a major goal of space exploration to decipher the origin and evolution of Solar System bodies in relation to the primordial conditions of the solar nebula, the chemical fingerprints of the formation of the Solar System, the evolutionary processing of minerals, volatiles and organic compounds, as well as to elucidate

the source and evolution of organic matter, its relevance for the origin of life, and to explore other possible modern habitats with suitable conditions to sustain life. The knowledge of the molecular, elemental and isotopic composition of Solar System bodies and of their environments is therefore central in space research. For instance, to understand the evolutionary processes, planetary sciences require *in situ* measurements of noble gas concentrations, their isotopic abundances, and the distribution of volatiles species such as H<sub>2</sub>O, HCN... Recently, in the frame of *in situ* measurements at bodies with potential relevance for astrobiology (Titan, Europa, Enceladus, comets, and asteroids), the need to develop a new

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generation of *in situ* space instruments able to handle and analyse the diversity and complexity of organics, their isotopic composition, and their potential interaction with inorganic material has emerged. This fosters the continuous effort to develop *in situ* analytical tools that are up to the analytical challenges of space exploration.

Mass spectrometry is arguably among the most desirable tool for *in situ* space exploration given its ability to analyse the composition of gaseous, liquid or solid samples, and its extreme sensitivity, versatility, and by the potential of extensive miniaturisation. Common mass spectrometers (MS) are made of independent units: (i) the ion source for generating charged (and optionally deliberately fragmented) species representative of the analysed sample, (ii) the mass analyser for sorting the ions by their mass to charge ratios ( $m/z$ ), and (iii) the detector, which produces electronic signals related to the abundances of each ionic species. The availability of several types of mass analysers, as well as different samples preparation apparatus and data processing software, yields a wide diversity of MS instruments.

Mass spectrometers have been employed in space for two applications (Palmer and Limero, 2001): air monitoring in inhabited spacecraft and space stations like Apollo, Mir and the International Space Station, and the *in situ* characterisation of the chemical composition of Solar System environments (Niemann and Kasprzak, 1983). To date, almost all the classical technologies of mass analysers have been adapted and used for space exploration: magnetic or electromagnetic sector deflectors (Biemann et al., 1976; Niemann et al., 1980; Balsiger et al., 2007), radio frequency quadrupole mass filters (Istomin et al., 1979, 1982; Niemann et al., 1992, 1998; Waite et al., 2004; Mahaffy et al., 2012, 2014) or radio frequency ion traps (Wright et al., 2007), and time-of-flight (TOF) (Gloeckler et al., 1992; Kissel and Krueger, 1987; Kissel et al., 2007; Srama et al., 2004; Scherer et al., 2006; Balsiger et al., 2007; Goesmann et al., 2007).

Interplanetary dust particles have been analysed *in situ* by mass spectrometry in previous space missions by two methods, depending upon the relative dust velocity with respect to the spacecraft. In the case of low relative velocity, *i.e.* up to  $0.2 \text{ km s}^{-1}$ , the dust particles can be non-destructively collected and analysed with a dedicated ionisation method such as an ion gun in the case of COSIMA (Cometary Secondary Ion Mass Analyzer) on-board the Rosetta orbiter (Kissel et al., 2007; Schulz et al., 2015; Hilchenbach et al., 2016). At impacts at velocities above  $1.5 \text{ km s}^{-1}$  direct mass spectrometry of the plasma cloud created by the impact of dust has been successfully used on Giotto, Vega, Stardust and Cassini (Krüger et al., 1999; Koschny and Grün, 2001; Krivov et al., 2003; Kempf et al., 2012). This technique even permits the study of planetary surface or sub-surface micrometric fragments (Postberg et al., 2009, 2011).

Requirements for *in situ* characterisation of extra-terrestrial surfaces and atmospheres (essentially in the context of the exploration of bodies with expected chemical complexity) led to the development of new instruments. These instruments aim to characterise bulk materials (Briois et al., 2008, 2013; Cottin et al., 2010; Tulej et al., 2014) (potentially containing organic matter), and to this end their main figure of merit is their mass resolving power.

The mass resolving power of an analyser refers to its ability to separate ions that have similar  $m/z$  ratios. It is measured by the ratio  $m/\Delta m$ , where  $m$  is the mass of a measured ion, and  $\Delta m$  is the full width at half maximum of the peak. Depending on the analyser concept, the resolving power varies with  $m/z$ . To be fully descriptive, it is therefore necessary to quote the mass to charge ratio at which the mass resolving power is determined.

The chemical composition of comet 67P/Churyumov–Gerasimenko has recently been analysed by dedicated instruments on

orbiter and lander (Philae) of the Rosetta mission that brought a wealth of information on the comet's composition (*e.g.* Capaccioni et al., 2015; Le Roy et al., 2015; Altwegg et al., 2015; Wright et al., 2015; Goesmann et al., 2015; Hilchenbach et al., 2016), but it is anticipated that the results can only partially assess the diversity of chemical species. Recently, tantalizing results on primitive meteorites and cometary organic matter analogues have been reported by high-resolution mass spectrometry (resolving power  $> 200,000$  at  $m/z$  200) (Schmitt-Kopplin et al., 2010; Danger et al., 2013). In the near future, pristine samples are expected from small carbonaceous bodies of the Solar System (*e.g.* Hayabusa 2 and OSIRIS-REx) and will be analysed with high performance instruments in the laboratory. Questions of contamination or volatile loss during Earth atmospheric entry are however an issue. Combining a sample return mission with a new generation of *in situ* analytical tools is therefore at the scale of the expected analytical challenge.

Mars is the most thoroughly explored extra-terrestrial body with currently six orbiters and two rovers collecting information about its atmosphere and surface. In particular, the Curiosity rover (Grotzinger et al., 2012) exploring the surface with solid sampling and Gas Chromatograph–MS (Vasavada et al., 2014; Mahaffy et al., 2012). However, although the presence of organic molecules at the Mars surface (Freissinet et al., 2015) and the past habitability of Gale crater have definitely been proven with the Curiosity rover, several key questions remain about the assessment of a prebiotic-like chemistry, which could have occurred in the past. Although the mass analysers allowed great advances, their limited mass resolving power did not prevent ambiguities in the attribution of ionic species, such as disambiguation between inorganic and organic material.

The Titan atmosphere hosts naturally occurring chemical processes leading to the synthesis of complex organic molecules, potentially prebiotic (Hörst et al., 2012). The Cassini–Huygens mission revealed an extraordinarily complex ionospheric composition. At an altitude of 1000 km, the Ion Neutral Mass Spectrometer (INMS) detected roughly 50 positive ions in the mass range 1–99 u (Cravens et al., 2006) while the Cassini Plasma Spectrometer (CAPS) provided evidence for positive ions reaching up to  $m/z \sim 350$  (Waite et al., 2007) as well as negative ions with  $m/z$  up to  $\sim 10,000$  (Coates et al., 2007). These complex ions are the precursors of the aerosols visible at lower altitude (Lavvas et al., 2013). Mass spectrometry is the best tool to analyse Titan's upper atmosphere, but the chemical identification is hampered by the limited mass-resolving power ( $m/\Delta m \leq 500$  at best) of the instruments (Waite et al., 2004; Young et al., 2004). It is clear that Instruments with a far better mass resolving power are to be developed. For example, the model payload for the Titan and Saturn System Mission included a polymer mass spectrometer to measure the densities of gases and aerosols ( $10\text{--}10,000 \text{ u}$ ), with a resolving power of  $\sim 10,000$  (Coustenis et al., 2009).

Among all the mass spectrometers flown so far, the Rosetta mission hosts two MS instruments with the best resolving power achieved in space: the ROSINA (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis) and COSIMA instruments, respectively dedicated to the chemical analysis of gaseous and to dust samples from the comet 67P/Churyumov–Gerasimenko. ROSINA includes a mass analyser based on an electromagnetic sector deflector called the Double-Focussing Mass Spectrometer (DFMS) with a mass resolving power better than 9000 at  $m/z$  28 (Balsiger et al., 2007; Jäckel et al., 2011). COSIMA is a Time Of Flight – Secondary Ion Mass Spectrometer (TOF-SIMS) with a mass resolving power of 1400 at  $m/z$  100 (Kissel et al., 2007).

Compared to state-of-the-art MS instruments on Earth, space borne *in situ* MS offers limited performance due to technical constraints related to the launch and journey of the space probes

and their instrument in space, as well as the space operating conditions that can be sometimes far from those used on Earth. These constraints require *in situ* space instruments to be miniaturised to limit their weight, size, power consumption and data volume. They also need to be designed to survive harsh environmental conditions such as solar and cosmic radiation, pressure, temperature, to withstand mechanical stress related to the probe launch, the journey in space, and sometimes descent and landing on a Solar System body. All these constraints on space borne MS instruments challenge the mass resolving power, and the mass measurement accuracy.

“High-resolution mass spectrometry” denotes the ability to resolve the isobaric interferences by measuring the accurate mass to charge ratios of ions. This ability is related to the sum of the nuclear mass defects of all the constituting atoms. It implies to resolve better than the second decimal in the measurement of the ionic mass. Hence, increasing the mass resolving power gives access to plateaus of chemical information in the following manner:

- i)  $m/\Delta m < 2500$  allows separation of peaks with different nominal masses (e.g., 28 u versus 29 u), or with small mass differences at small masses (e.g. discriminating  $^{25}\text{Mg}$  from  $^{24}\text{MgH}$  already requires a  $m/\Delta m$  of  $\sim 2000$ ).
- ii)  $2500 < m/\Delta m < 10,000$  allows separation of peaks for isobaric molecular species (e.g.,  $\text{N}_2$  versus CO at 28 u) but only with  $m/z$  below 50, e.g., major molecular entities in the Solar System, which could be identified by other spectroscopic methods.
- iii)  $10,000 < m/\Delta m < 100,000$  provides separation of isobaric species with masses up to  $m/z$  500, i.e., it allows unequivocal identification and quantification of the building blocks of life, and discriminates against their potential interaction with inorganic material.

Significant efforts to develop further high-resolution mass spectrometers (HRMS) for space exploration are currently ongoing under Research and Technology (R&T) programs, but no HRMS instrument has flown yet on a space exploration probe. One can cite two different concepts based on extending the time-of-flight of the ions by multiple reflections. The first concept is the ion and neutral mass spectrometer MASPEX (MASS Spectrometer for Planetary EXploration), which is a Multi-Bounce high-resolution time-of-flight mass spectrometer. Its principle is based on the concept described by Wollnik and Przewłoka (1990). It has achieved NASA Technology Readiness Level (TRL) 5 and has been recently selected for the future NASA discovery mission to Europa ([www.jpl.nasa.gov/missions/europa-mission](http://www.jpl.nasa.gov/missions/europa-mission)). At current best estimate, its length, average power consumption and mass are 48 cm, 36 W and 6.7 kg respectively, without harness and radiation shielding (Hässig et al., 2015a). It has proven a mass resolution of  $m/\Delta m = 13,500$  at  $m/z$  28 after 12 cycles, that can be increased up to 59,000 in bunch mode (Libardoni and Synovec, 2013), but with a reduced mass range. The second concept is the MULTi-TURN time-of-flight Mass spectrometer, MULTUM (Shimma and Toyoda, 2012), which was the first laboratory model studied for the COSAC (COmetary SAMpling and Composition) experiment of the Rosetta mission (Matsuo et al., 1999). Its operation principle is described in Sakurai and Baril (1995). It consists of 4 cylindrical electrostatic sectors and 28 electric quadrupole lenses. The mass resolution increases according to the number of ion cycles. A resolving power up to 350,000 at  $m/z$  28 has been reported after 1200 cycles (Toyoda et al., 2003). A portable version “MULTUM-S II” (70 dm<sup>3</sup>; 35 kg (including vacuum pump and electric circuits)), dedicated to greenhouse gases or polychlorobiphenyl analysis, reached a resolving power of  $\sim 30,000$  at  $m/z$  44 after 50 cycles (Shimma et al., 2010).

Laboratory mass spectrometry has been revolutionized by

access to Ultra High-Resolution Mass Spectrometers (UHRMS) ( $m/\Delta m$  better than  $10^5$ ). They are based on ion trapping and on Fourier Transform (FT) of the signal induced by their oscillations in the analyser. Initially, the trapping was achieved by a strong magnetic field and the ion cyclotron frequency was the signature of mass to charge ratio (so-called FT-ICR for Fourier Transform-Ion Cyclotron Resonance). Although very powerful, this concept requires high field magnets, which are heavy and thus not suitable for space exploration. In 2000, a new type of Fourier Transform Mass Spectrometry analyser based on a purely electrostatic field was demonstrated by Makarov (2000). This mass analyser, which has been marketed by Thermo Fisher Scientific as the Orbitrap™ analyser, confines ions in a compact volume, with all dimensions of the analyser electrodes smaller than 5 cm. Sophisticated mass spectrometers based on the Orbitrap mass analyser allow for UHRMS up to  $m/\Delta m \sim 10^6$  at  $m/z$  200 as achieved in the laboratory (Denisov et al., 2012). Several laboratory studies performed with commercially available LTQ Orbitrap mass spectrometers (which incorporate both the Orbitrap and quadrupole ion trap mass analysers) on planetary materials give a good illustration of the potential of this technique for space applications (Pernot et al., 2010; Vuitton et al., 2010; Hörst et al., 2012; Somogyi et al., 2012; Danger et al., 2013; Gautier et al., 2014).

Our team is conducting an R&T effort – called Cosmorbitrap – to bring the Orbitrap technology to spaceflight conditions, with the driving motivation to operate in space the first Fourier Transform Mass Spectrometry (FTMS) analyser.

The aim of this paper is to present the performance and capability tests conducted on a prototype set-up used as a first stage of the R&T Cosmorbitrap development, and the promising perspectives in the context of future Solar System exploration. In the following, a brief discussion of the Orbitrap mass analyser is provided followed by a description of the prototype set up, and evaluation of its performances.

## 2. Orbitrap mass analyser

The Orbitrap cell consists of four main electrodes: a central inner spindle-shaped electrode, two external outer electrodes and a deflection electrode (Fig. 1). The measurement principle is based on the pulsed injection of ions inside the cell, in which an electrostatic field is produced by polarising the central electrode at a high-voltage with respect to the outer electrodes, which are at floating ground, and act as the detector. A two-level high-voltage is applied on the central electrode. The shapes of the central and the outer electrodes are such that a quadro-logarithmic electrostatic field is generated inside the cell. The deflection electrode, which can be polarised between 0 and 350 V, optimises the injection of the ions and compensates the internal field aberration caused by the injection aperture. The field strength is changed during the injection process by a transient increase of the absolute voltage applied on the central electrode. Ion capture over the broadest possible mass range requires that the low level of the high-voltage (typically  $-2500$  V for positive ions) is applied on the central electrode prior to ion injection (Hu et al., 2005). During ions injection, the high-voltage is ramped up to its high-level (typically  $-3500$  V for positive ions), with a rise time between 20 and 100  $\mu\text{s}$ , which allows trapping the ions inside the cell; the process is termed electrodynamic squeezing (Makarov, 2000). Pulsed ions injected into the cell are trapped in orbits around the central electrode. The trapped orbiting ions oscillate harmonically along the axial electrode with frequencies proportional to  $(m/z)^{-1/2}$ . Thanks to the splitting of the outer electrode into two halves, the axial oscillation of the trapped ions generates an image current that produces a transient signal, which can be amplified,

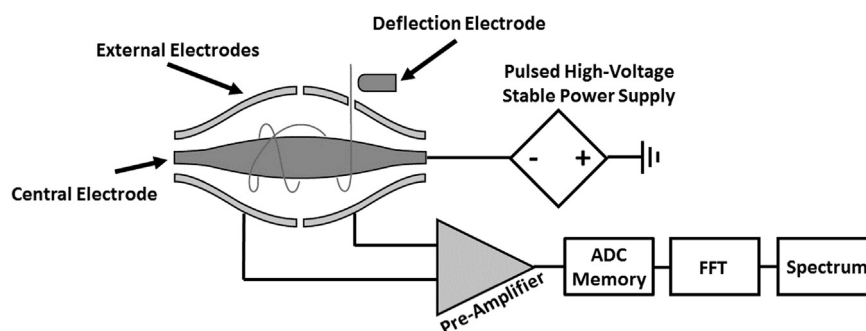


Fig. 1. Schematic diagram of an Orbitrap analyser (Adapted with permission from Makarov, 2006).

digitised and converted into a frequency spectrum by Fourier Transform (FT) techniques. The typical frequency range of trapped ions in a standard Orbitrap mass analyser<sup>1</sup> is 0.1–7 MHz for  $m/z$  in the range 1–4000 (Zubarev and Makarov, 2013) (Fig. 2).

A large frequency (corresponding to mass) range can be covered simultaneously. The ion capture is optimised for a mass range defined by a minimum to maximum mass ratio of 30. The signal obtained in the frequency domain after FT processing is converted into a mass spectrum with resolving power better than  $10^5$  up to  $m/z=400$ .

Orbitrap technology has several salient characteristics which make it very attractive for a space instrument: (i) the multiplexed detection yields a broad mass spectrum at once, rather than requiring that each peak be scanned through separately, (ii) the mass resolving power is adjustable, and increases proportionally with the transient length in the zero-collision limit, (iii) the size and weight of the analyser are reduced (typically 40 mm in diameter, over 60 mm long and 250 g for a D30 cell), and (iv) only two electrical voltages are needed to operate the analyser, facilitating measurement of positive and negative ions by switching the polarity of the electrode potentials.

### 3. Laboratory prototype

Since 2009, a series of R&T programs has been undertaken by a consortium of five French laboratories (LPC2E, Orléans; LISA, Créteil; LATMOS, Guyancourt; IPAG, Grenoble; CSNSM, Orsay) in order to evaluate the potential of the Orbitrap ultra high-resolution mass analyser as a viable key subsystem for the future generation of *in situ* space mass spectrometers (Thissen et al., 2011; Carrasco et al., 2012; Briois et al., 2012, 2014; Vuitton et al., 2014). The aim of the project is twofold:

- To increase the technology readiness level (TRL) of five key elements that are necessary to build up the Cosmorbitrap mass analyser subsystem: these five elements are (i) the Orbitrap cell, (ii) the pulsed high-voltage (HV) power supply, (iii) the transient signal pre-amplifier (PA), (iv) the data acquisition and FT processing, and (v) the control/command board and primary power supplies.
- To develop joint collaborations with international partners, in order to integrate the Cosmorbitrap mass analyser into a complete instrument, including sample handling, ionisation stage, pumping if required, heating and decontamination devices, and interfaces with a satellite (see Fig. 3).

Initially, a simplified laboratory prototype was built with elements provided under a specific cooperation agreement with Thermo Fisher Scientific (Bremen, Germany), in order to define and measure the characteristic instrument parameters and test their influence on the mass analyser performances. The laboratory prototype used in the framework of instrument development for spaceflight purpose (Fig. 4) is a Laser Ablation and ionisation (Lab) mass spectrometer including an Orbitrap mass analyser, called hereafter Lab-Cosmorbitrap. It is the simplest configuration foreseen in space for chemical analysis of solid samples by mass spectrometry. Laser ablation and ionisation is a very attractive technique for the *in situ* analysis of the composition of rocks and soils since a laser is able to sample the surface with minimal manipulation and preparation. As such, laser ablation ionisation for space applications has been considered previously and was even incorporated into the missions to Phobos (Managadze and Shutyaev, 1993; Tulej et al., 2014). Another advantage of laser ablation ionisation is the intrinsically pulsed character of the ion bunch that is created, which is ideal to implement a simple interface (like an electrostatic lens) between the source and the Orbitrap cell. Furthermore, the TRL status of existing lasers is already compatible with the requirement of a Cosmorbitrap analyser (e.g., TRL 6 with MOMA/Exomars 2018 (Brinckerhoff et al., 2012).

A vacuum chamber maintained at a  $10^{-8}$  mbar was designed to host the sample holder and the ion optics. This chamber is combined with a Thermo Fisher Scientific chamber hosting the Orbitrap mass analyser at  $10^{-10}$  mbar. Two turbo pumps (with 0.2 and  $0.5 \text{ m}^3 \text{ s}^{-1}$  pumping speed) and three Pfeiffer diaphragm pumps ( $3 \text{ m}^3 \text{ h}^{-1}$ ) are used to reach the required vacuum pressures. The pressure inside the Orbitrap cell cannot be measured directly, but is estimated on the basis of the vacuum chamber pressure measured by the Pfeiffer pressure gauge (IKR 270, calibrated by the manufacturer).

The ablation/ionisation laser is a UV Nitrogen laser (VSL-337ND-S from Laser Science Inc.) at a wavelength of 337 nm with 4 ns pulse duration and 300  $\mu\text{J}$  energy per pulse. The laser beam is focused at the target through a lens (focal distance of 30 cm) and aligned with two mirrors. A camera combined with a small telescope allows imaging of the sample spark during desorption process and therefore the alignment of the laser beam with the optical axis of the ion optics. The laser beam reaches the target with an incident angle of  $50^\circ$ . It enters the chamber through a  $\text{MgF}_2$  window. The laser energy delivered to the target is adjusted through a mechanical slit. The laser spot size at the target plane is about 50  $\mu\text{m}$  in diameter, as measured by image analysis of the holes produced by a single laser shot on the target. The energy deposited on the target is measured through an Ophir PE9-SH power meter.

A 17 cm long ion optics, supplied by Thermo Fisher Scientific, focuses the ions emerging from the ionised sample into the mass analyser through a conductivity restrictor and an electrostatic deflector. The high voltages applied to the target and the ion optics

<sup>1</sup> Standard Orbitrap mass analyser such as the version incorporated into the LTQ Orbitrap or Q Exactive instruments, which is referred to as the D30 to reflect the fact that its largest inner diameter is 30 mm.



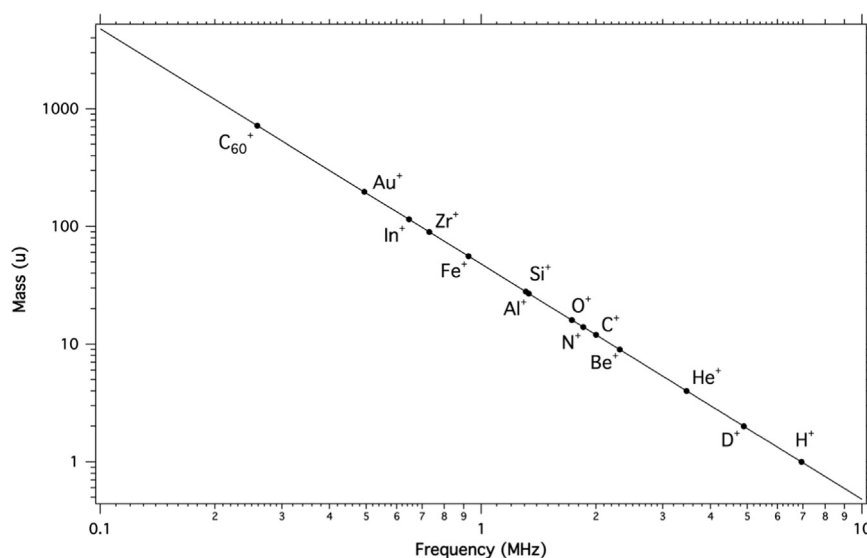


Fig. 2. Calculated frequency range versus mass for a standard Orbitrap mass analyser.

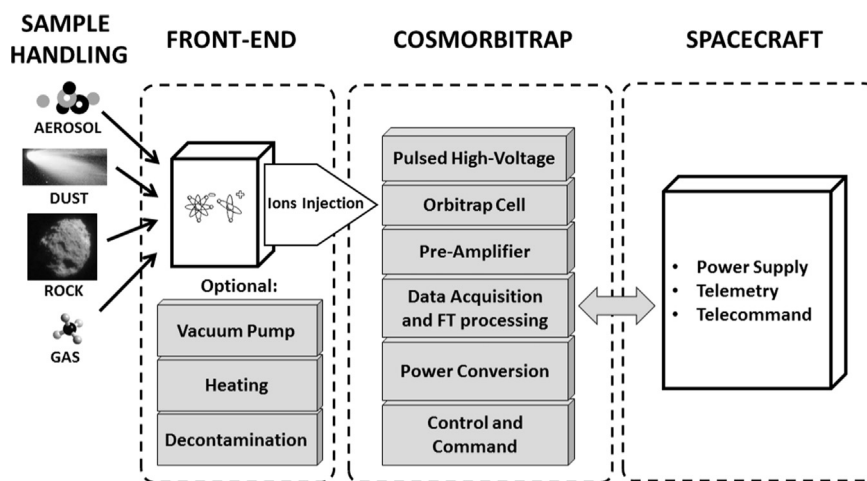


Fig. 3. Elements of a Cosmorbitrap-based UHRMS instrument. The Cosmorbitrap subsystem is under R&T development by the consortium.

are delivered by Thermo Fisher Scientific power supplies. The requirement to apply a high voltage to the target is a consequence of the virtual ground applied to the external electrodes (Fig. 1) due to the fact that the pre-amplifier is operated at a low voltage. To have a stable trajectory, an injected ion should have a high tangential velocity to compensate for the radial electrical force. The ion velocity is provided by the applied high voltage. The Orbitrap central electrode potential is powered by a power supply that delivers the voltage ramp needed for capturing the ions, as well as the high stability voltage (better than 100 ppm) needed during the measurements. A Wavetek waveform generator delivers trigger signals to synchronise the laser pulse with the pulsed high-voltage board, the pre-amplifier and the acquisition board. A standard pre-amplifier from Thermo Fisher Scientific amplifies the current induced by the ions oscillations into the cell. The signal processing of the LAB-Cosmorbitrap prototype is then performed by a data acquisition system supplied by the Alyxan Company (Orsay, France). It is digitised by a data acquisition board (Acquitek CH-3160, 40 MS/s, 12 bits) and the stored transient signal, contains up to  $4 \cdot 10^6$  data points recorded over 0.8 s. It can be evaluated in real time after Hanning apodisation and Fast Fourier Transform (FFT) into a frequency/mass spectrum, without zero filling.

For specific spectra shown in this article, further data treatment and evaluation were undertaken with the in-house Attributor

software of UHRMS tools developed in the Igor Pro environment. Optional zero filling and apodisation were carried out before FFT. Mass calibration was performed on a single peak in mass spectra, usually corresponding to the most intense ion detected in the 7–800  $m/z$  range. If not specifically stated, the pressure in the vacuum chamber containing the Orbitrap analyser was lower than  $5 \cdot 10^{-9}$  mbar for all measurements.

#### 4. Results and performance of the prototype

Experiments presented in this section were conducted using the LAB-Cosmorbitrap depicted in Fig. 4. Samples were inserted using a stainless steel sample holder rod (30 cm long and 1 cm diameter) through a primary vacuum (at about  $10^{-2}$  mbar) injection airlock directly into the ion optic vacuum chamber. The testbed is based on a direct injection probe, allowing sample repositioning or exchange within few minutes. In order to characterise the ultimate mass resolution of the present prototype, tests were mostly performed on a set of metallic samples, but an example organic molecule, Adenine was also studied. The list of samples used in this study is given in Table 1.

Sample holder removable tips of different types have been produced and analysed: pure metal tips of stainless steel and of

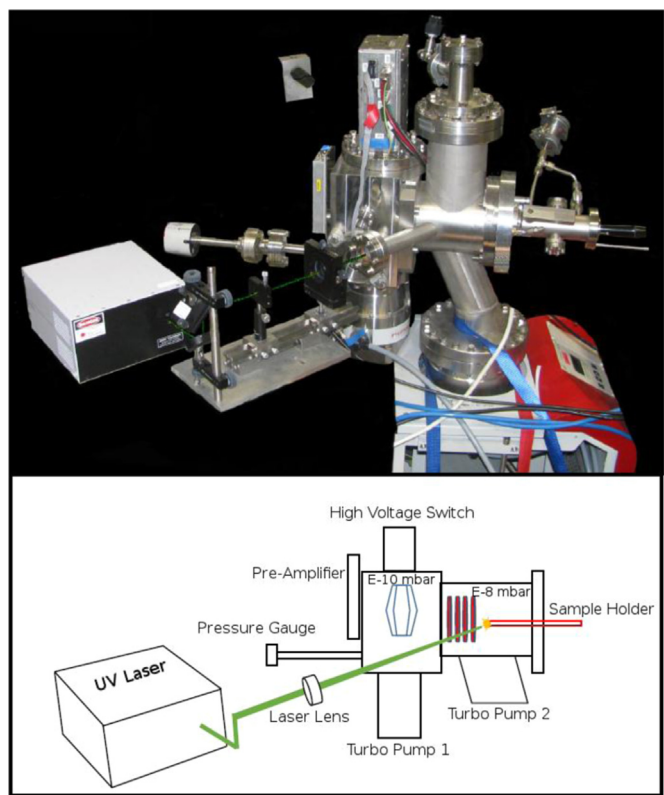


Fig. 4. Lab-Cosmorbitrap: prototype testbed used in the framework of instrument developments for spaceflight purpose.

aluminium, and three casted metal tablets (indium, lead, and Indalloy) inside circular brass tips. Most of the foil samples have been glued to a pure metal tip. Platinum samples and adenine powder were pressed on casted indium tips. Zirconium and molybdenum foils have been milled using a band saw; their powders were then mixed and pressed on casted indium tips.

4.1. Evolution of the mass resolving power with the mass to charge ratio

The first advantage of the Orbitrap mass analyser is its high mass resolving power capability. Therefore, to characterise our testbed, this capability was tested and optimised first.

The Orbitrap mass resolving power is known to decrease with the square root of  $m/z$  (Makarov, 2000; Perry et al., 2008). The ultimate mass resolution of the present prototype has been

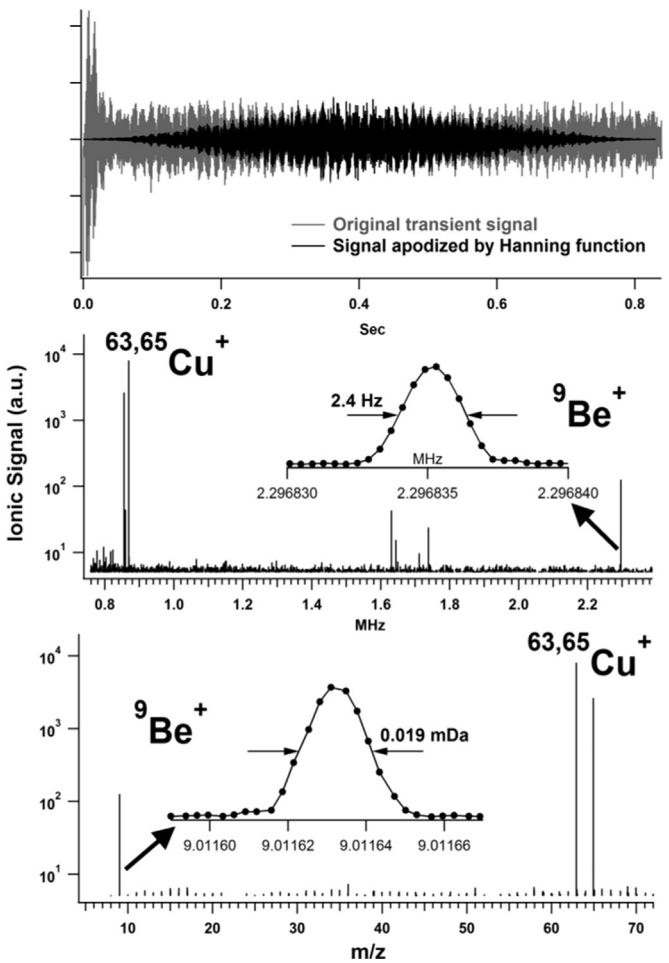
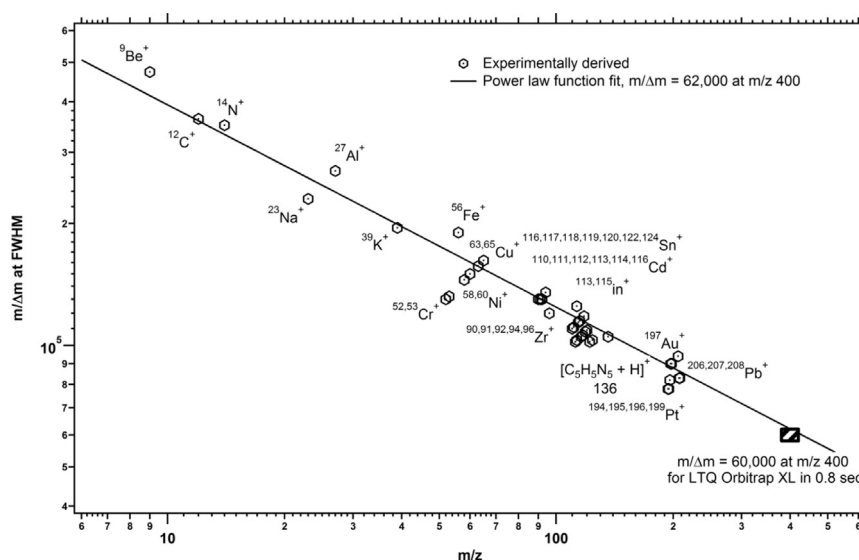


Fig. 5. Single laser shot spectrum of a copper/beryllium foil recorded with the LAB-Cosmorbitrap. Top panel: in grey, transient signal recorded between 10 and 830 ms; in black, transient signal apodised by Hanning function. Middle panel: zoom of the frequency spectrum obtained by Fourier Transform (FT) and zoom on the  $^9\text{Be}^+$  peak (peak centroid of  $^9\text{Be}^+$  is at 2296.835 kHz). Bottom panel: mass spectrum and zoom on  $^9\text{Be}^+$  peak.

characterised by recording a transient signal of 830 ms duration to provide optimal balance between spectral resolution and signal intensity. Fig. 5 represents the typical transient signal (top panel) and zooms of the subsequent frequency (middle panel) and mass (bottom panel) spectra for a single laser shot on a copper/beryllium foil. Beryllium  $^9\text{Be}^+$ , and copper isotopes  $^{63}\text{Cu}^+$ ,  $^{65}\text{Cu}^+$  are clearly detected. A Full Width at Half Maximum (FWHM) of 2.4 Hz

Table 1  
List of analysed compounds.

Sample	Composition	Analysis status	Supplier
Stainless steel 304	Fe <sub>71.98</sub> C <sub>0.02</sub> Cr <sub>18</sub> Ni <sub>10</sub>	Sample-holder	Germond SA
Stainless steel 316L	Fe <sub>68.98</sub> C <sub>0.02</sub> Cr <sub>17</sub> Ni <sub>12</sub> Mo <sub>2</sub>	Tip of sample-holder	Germond SA
Aluminium 2017	Al	Tip of sample-holder	Euralliage
Indalloy 181	Sn <sub>51.2</sub> Pb <sub>30.6</sub> Cd <sub>18.2</sub>	Casted foil on brass tip	LucasMillaut
Indium	In	Casted foil on brass tip	Goodfellow
Lead	Pb	Casted wire on brass tip	Goodfellow
Copper–Beryllium CW101C	Cu <sub>98.1</sub> Be <sub>1.9</sub>	Foil, glued on pure metal tip	Euralliage
Gold	Au	Foil, glued on pure metal tip	Goodfellow
Iron–Chromium–Molybdenum	Fe <sub>90</sub> Cr <sub>9</sub> Mo <sub>1</sub>	Foil, glued on pure metal tip	Goodfellow
Platinum	Pt	Foil piece pressed on casted-In tip	Goodfellow
Molybdenum	Mo	Powder pressed on casted-In tip	Goodfellow
Zirconium	Zr	Foil glued on casted-In tip	Goodfellow
Adenine	C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>	Powder pressed on casted-In tip	Aldrich



**Fig. 6.** Mass resolving power of the LAB-Cosmorbitrap as a function of  $m/z$  for each sample analysed ( $9 \leq m/z \leq 208$ ). The data from single laser shots have been generated by a FT of the transient signal recorded for 830 ms. The power function has been fitted according to (Makarov, 2000; Perry et al., 2008) and results in a resolving power of 62,000 at  $m/z$  400, similar to the commercial value delivered by a LTQ Orbitrap XL instrument for a 0.8 s transient.

at a frequency of about 2.3 MHz for the  $^9\text{Be}^+$  is highlighted in Fig. 5, which corresponds to a FWHM frequency resolution close to  $10^6$  and a mass resolution of about 474,000. It is the highest resolution obtained to date with the laboratory LAB-Cosmorbitrap.

In Fig. 6, the mass resolving power for a single laser shot of each sample is plotted, obtained at a total pressure lower than  $10^{-9}$  mbar and a transient acquisition time of 830 ms duration. In order to get more points on the curve in the low mass range, sodium and potassium ions have been added (they are present as usual surface pollutants). Evolution of  $m/\Delta m$  as a function of  $m/z$  can be fitted by a power law,  $m/\Delta m = k \cdot (m/z)^{-1/2}$ , in agreement with the Orbitrap resolving power law (Makarov, 2000; Perry et al., 2008). The mass resolving power performance of the prototype varies from 474,000 to 90,000 for a 9 to 208  $m/z$  range, and the fit of the power law extrapolates at 62,000 at  $m/z$  400. The mass resolving power of the LAB-Cosmorbitrap fits well with that of commercial LTQ-Orbitrap instruments for similar transient time though our set-up is much more simplified. Indeed intrinsic parameters are optimised in a commercial Orbitrap instrument, while in our laboratory testbed prototype:

- The energy absorbed by the target is not stable due to the instability of the laser itself and it has been observed that the dimension of the hole produced into the target are different at each laser shot. The number of ions injected in the analyser is therefore different for each laser shot;
- The number of ions injected in the Orbitrap cell is not controlled, whereas on a commercial instrument the use of active gain control by the ion trap enables careful control of ion population.

#### 4.2. Accurate mass measurement

As accurate mass spectrometry can unambiguously determine a chemical composition, it was essential to evaluate the mass measurement error (or mass accuracy) of our testbed. With a commercial LTQ Orbitrap instrument, Xu et al. (2010) reported a mass measurement error of less than 5 ppm without external calibration over a 75–810  $m/z$  range, consistent with data obtained by Makarov et al. (2006). To estimate the capability of the LAB-Cosmorbitrap testbed to obtain accurate mass measurements with a single shot experiment, the mass measurement error expressed

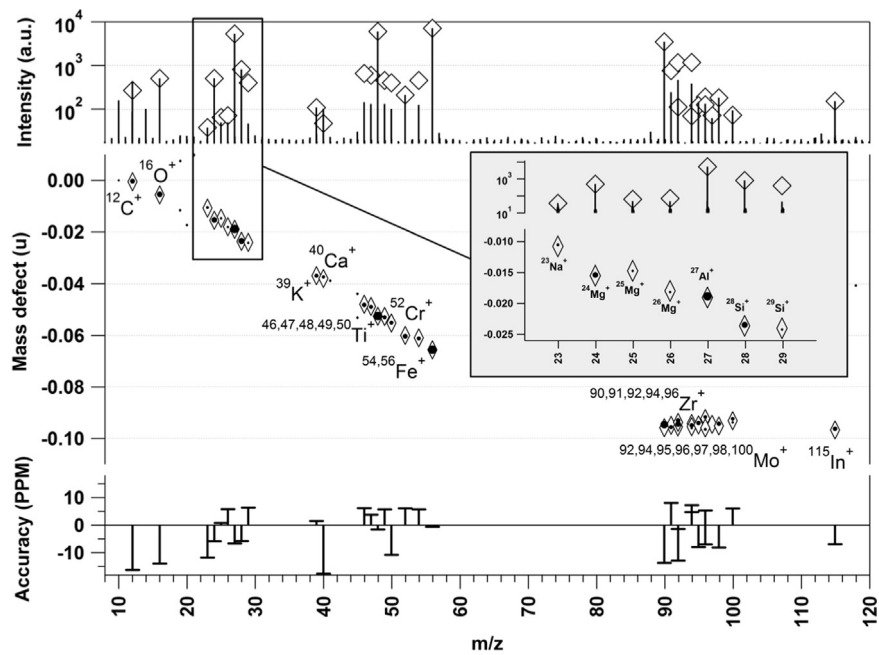
in ppm was calculated as shown in Eq. (1):

$$\text{Mass measurement error (ppm)} = \left[ \frac{(m/z)_{\text{theo}} - (m/z)_{\text{exp}}}{(m/z)_{\text{theo}}} \right] \cdot 10^6 \quad (1)$$

Fig. 7 illustrates the ability of the LAB-Cosmorbitrap laboratory testbed to identify in a single shot, a very large variety of ionic species originating from the sample, owing to the very good accuracy on the exact mass measurement. The data correspond to a single laser shot on mixed powders of zirconium and molybdenum pressed over an indium target. These Zr/Mo powders were produced by milling machines and this preparation protocol added contamination species on the target, which can readily be identified: constituents of stainless steel (Fe, Cr, Ti, Mn, C and O), alkali metals (Na, and K) as well as alkaline earth metals (Mg, and Ca) and some silicon (Si), probably originating from previous use of the mill and contact with operator's hands. As these elements exhibit abundant isotopes, some of these are also detected and confirm the detection of Mg, K, Ti, Cr and Fe. The dataset has been internally calibrated on the  $^{56}\text{Fe}^+$  peak.

The peak intensity over the 12–115  $m/z$  range is plotted on the upper part of Fig. 7, in which diamonds cross-refer the sample peaks. In the middle of Fig. 7, the diagram presented is a so-called mass defect versus exact mass diagram (Danger et al., 2013). Measured data are the small dots, and highlighted by a diamond is the matching with exact mass of an atomic ion within 15 ppm. On the bottom of Fig. 7, the mass accuracies expressed in ppm are plotted for ions in the 12–115  $m/z$  range. For the reasons invoked previously about instability of the energy absorbed by the target and the absence of automatic gain control of our setup, the mass accuracy of the LAB-Cosmorbitrap, with absolute values of the mass measurement errors up to 15 ppm, is a bit reduced compared to the 5 ppm of commercial Orbitrap instrument.

To evaluate the Mass Measurement Accuracy (MMA) of the testbed, i.e. the average of the mass measurements errors, repeatability of the measurement has been examined over 13 subsequent laser shots. The sample studied was a foil of zirconium pressed on a casted indium tip. As seen in Table 2, for the zirconium foil analysed, the measured  $m/z$  values show a good repeatability between laser shots, and are in good agreement with the literature (Audi et al., 2012a, b).



**Fig. 7.** Single shot laser data of a Zr/Mo milled powder mixture deposit on an indium target, recorded with the LAB-Cosmorbitrap and FT of a transient signal between 1 and 830 ms. Top panel: peaks intensity versus mass range 12–115 u (contamination of elements other than Zr, Mo and In results from sample preparation). Middle panel: measured Mass defect versus mass diagram. Bottom panel: measured mass accuracy in ppm.

#### 4.3. Relative isotopic abundances (RIA)

In planetary and cosmochemistry sciences, the isotopic study of extra-terrestrial materials is of particular importance, as isotopic data provide valuable information on the origin and evolution of organic and inorganic materials in the Solar System [e.g., [Valley and Cole, 2001](#); [Johnson et al., 2004](#)]. The required accuracy on relative isotopic abundances (RIA) to answer such questions is however demanding and depends on the sample nature and ionisation method. It therefore suggests that further evaluation is required in a future development of a fully integrated instrument containing the Cosmorbitrap mass analyser.

[Kind and Fiehn \(2006\)](#) showed that mass spectrometers, with 5% accuracy on RIA measurement in addition to MMA and resolving power performances, give more reliable chemical identification. The isotope pattern is therefore a useful tool to discriminate possible elemental candidates.

As a first investigation of the capability of the LAB-Cosmorbitrap testbed to obtain accurate RIA, the isotope pattern of a zirconium sample pressed on a casted indium tip has been investigated. Top panel of [Fig. 8](#) presents a zoom over the  $m/z$  90–96 range for a single laser shot mass spectrum. The abundance of the zirconium isotopes of the sample analysed is in agreement with the literature standard relative isotopic abundances  $\text{RIA}_{\text{theo}}$  (see [Table 3](#)) ([Audi et al., 2012a, b](#)). The RIA errors (%) were calculated as shown in Eq. (2) ([Xu et al., 2010](#); [Knolhoff et al., 2014](#)):

$$\text{RIA errors}(\%) = \left[ \text{RIA}_{\text{theo}} - \text{RIA}_{\text{exp}} \right] * 100 / \text{RIA}_{\text{theo}} \quad (2)$$

For this preparation with a single laser shot and with all the previously discussed limitations of the laboratory set up, RIA errors obtained were below 4%, which lies within the 5% threshold stated by [Kind and Fiehn \(2006\)](#).

Repeatability of the isotope abundances (IA) has also been explored over 13 subsequent laser shots on zirconium sample (see [Table 2](#)). This result shows how much the IA measured are compatible with the literature data within standard error bars. The difference between the isotopic abundance average of each isotope of the 13 subsequent measurements to their standard literature value is plotted in the bottom panel of [Fig. 8](#). The bars highlight the deviation in percent (the IA errors) and are calculated as shown in Eq. (3):

$$\text{IA errors}(\%) = 100 \times (\text{IA}_{\text{exp}} - \text{IA}_{\text{theo}}) / \text{IA}_{\text{theo}} \quad (3)$$

The higher IA error is found for the zirconium isotope with the lowest abundance,  $^{96}\text{Zr}^+$ , but remains lower than 3% of the theoretical Isotope abundance for this ion.

#### 4.4. Isobaric interferences separation

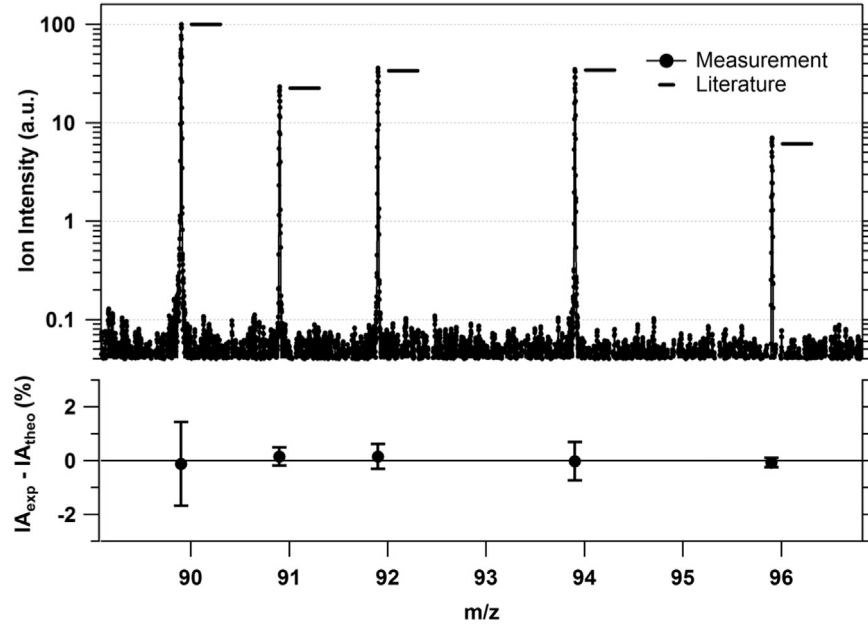
In a second stage of this study, the ability of the prototype to distinguish between isotopes of different elements occurring at the same nominal mass has been investigated by employing mixed powders of zirconium and molybdenum samples. [Fig. 9](#) shows on

**Table 2**

Comparison of average of measured (LAB-Cosmorbitrap) and literature mass to charge value and isotope abundances of 13 laser shot mass peaks of zirconium.

Species	Literature ( $m/z$ ) <sub>theo</sub>	Average of 13 measurements ( $m/z$ ) <sub>exp-aver</sub> ( $\pm 1\sigma$ )	Mass measurement accuracy (ppm) ( $\pm 1\sigma$ )	Literature abundance (%)	Average of 13 measured abundances (%) ( $\pm 1\sigma$ )
$^{90}\text{Zr}^+$	89.9041558	89.90525 $\pm$ 0.00020	–12.2 $\pm$ 2.2	51.45	51.57 $\pm$ 1.56
$^{91}\text{Zr}^+$	90.9050972	90.90577 $\pm$ 0.00019	–7.4 $\pm$ 2.1	11.22	11.07 $\pm$ 0.33
$^{92}\text{Zr}^+$	91.9044922	91.90520 $\pm$ 0.00015	–7.7 $\pm$ 1.6	17.15	17.00 $\pm$ 0.46
$^{94}\text{Zr}^+$	93.9057666	93.90649 $\pm$ 0.00015	–7.7 $\pm$ 1.6	17.38	17.40 $\pm$ 0.71
$^{96}\text{Zr}^+$	95.9077248	95.90662 $\pm$ 0.00018	11.5 $\pm$ 1.9	2.80	2.87 $\pm$ 0.18





**Fig. 8.** Zirconium sample data recorded with the LAB-Cosmorbitrap and FT signal between 1 and 100 ms. Top panel: a single laser shot mass spectrum of zirconium; horizontal bars represent the literature relative abundance of the 5 zirconium isotopes. Bottom panel: deviation between the average of the 13 consecutive laser shots mass spectra and the literature isotopic abundances of zirconium, normalised to the literature values; the squares are the difference value and the bars the deviation.

**Table 3**

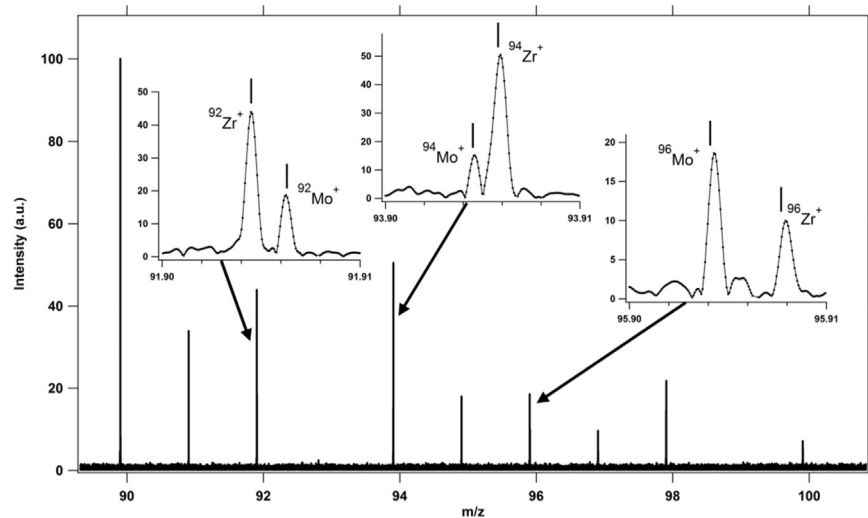
Comparison of measured (LAB-Cosmorbitrap) and literature isotopic ratios of zirconium for a single shot measurement.

Ratio	RIA <sub>theo</sub> Literature (standard)	RIA <sub>exp</sub> of one single shot	RIA error (%)
<sup>91</sup> Zr/ <sup>90</sup> Zr	0.2181	0.2214	1.53
<sup>92</sup> Zr/ <sup>90</sup> Zr	0.3333	0.3348	0.43
<sup>94</sup> Zr/ <sup>90</sup> Zr	0.3378	0.3479	3.01
<sup>96</sup> Zr/ <sup>90</sup> Zr	0.0544	0.0565	3.75

separated sections a single shot mass spectrum acquired on this sample. The three isotopic isomers are clearly well separated. The mass resolution reached for isotopes 94 (115,000 for <sup>94</sup>Zr) is larger than that needed to resolve these elements (72,000 to resolve <sup>94</sup>Zr and <sup>94</sup>Mo).

#### 4.5. Evolution of the mass resolving power with the background pressure

To obtain the maximum achievable resolving power, a low vacuum pressure is required in the vicinity of the analyser. This is an important parameter in planetary exploration, which depends on the environment of future space missions, and on the complete mass spectrometer instrument configuration. For *in situ* airless bodies exploration (i.e. asteroids, comets), the background pressure is usually very low but could approach  $10^{-8}$  mbar. However, *in situ* investigations of bodies like Titan and Mars would require advanced pumping systems. The impact of the internal pressure on the performances of the Cosmorbitrap needs to be assessed. Therefore, an adjustable leak valve (Rotarex M6S-8ML SS) linked to a N<sub>2</sub> gas tank (Alphagaz with less than 3 ppm H<sub>2</sub>O, AirLiquide) was connected to the Orbitrap cell vacuum chamber (see Fig. 4) to adjust the vacuum level. The leak valve was first opened to reach a



**Fig. 9.** Zooms of a single laser shot mass spectrum from a zirconium and molybdenum mixed powder sample acquired with the LAB-Cosmorbitrap and FT of a transient signal between 1 and 800 ms. Sections presented here focus on the shared isotopes of the two elements at  $m/z$  92, 94 and 96. The vertical lines above the peaks in the insets give the exact mass of each ion, to be compared with the experimental position of the peaks, which have been internally calibrated on <sup>90</sup>Zr<sup>+</sup>.

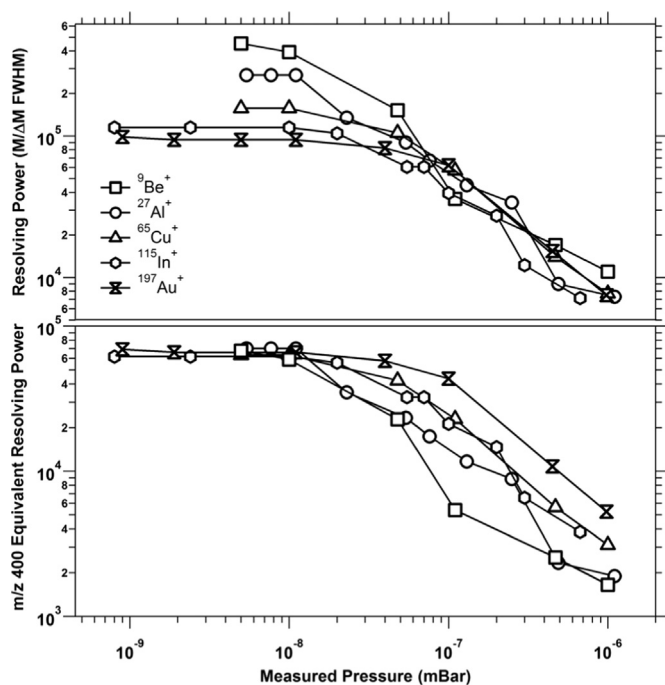


Fig. 10. The effect of the background pressure on the resolving power of the LAB-Cosmorbitrap.

stabilised pressure of  $10^{-6}$  mbar in the Orbitrap cell vacuum chamber. The valve was then gradually closed to achieve lower pressures. Measurements of the pressure in the vacuum chamber were performed with a Pfeiffer pressure gauge (IKR 270), calibrated by the manufacturer, after one minute of stabilisation. Two experiments were performed to measure the influence of this parameter using two samples: a piece of gold foil on an indium tip, and a piece of copper–beryllium glued on an aluminium tip.

Fig. 10 presents the resolving power performance of the current testbed. In the top panel the values obtained directly from the gauge are plotted. The resolving power is constant and optimal for pressures below  $10^{-8}$  mbar in the Orbitrap vacuum chamber. Note that as this plateau was observed with the first sample (Au glued on In), experiments performed with the second sample (Cu–Be

glued on Al) were stopped at pressure around  $10^{-8}$  mbar. Beryllium at  $m/z$  9 and gold at  $m/z$  197 reach resolving powers of, respectively, 474,000 and 94,000. Above this pressure threshold, the resolving power decreases with the pressure. The  $m/\Delta m$  remains better than 7000 for pressures below  $10^{-6}$  mbar. Taking into account locally elevated pressure at the entrance to the analyser and limited conductance from its interior, the pressure inside the Orbitrap cell is estimated to be higher by a factor 1/4 because of the pumping speed of the gauge. The lower panel shows equivalent resolving power values for a hypothetical equivalent ion of  $m/z$  400 using the law established in Section 4.1. Below a pressure of  $10^{-8}$  mbar, the different ions exhibit the same trend, and behave accordingly to the power law describing the resolution as a function of mass. For higher pressures, the curves depart from the same trend, and it is the lighter ions that show the most sensitivity, while gold ion at  $m/z$  197 is the less perturbed. As HRMS is particularly needed for heavier species, the lower sensitivity to pressure for heavier ions is a positive aspect highlighted by this result.

#### 4.6. Current status of the Cosmorbitrap development

To be highly performing and integrated in a space mission, instrumentation has to reach a very high standard of technological readiness level, usually TRL 5–6. Instruments with heritage from previous space missions are favoured by such selection criteria, and little room is left for highly innovative instruments that allow significant performance jumps. The Cosmorbitrap team R&T efforts to bring the Orbitrap technology into space are concentrated on the core elements of a space UHRMS instrument that would be based on the Cosmorbitrap subsystem as illustrated in Fig. 3. Our R&T efforts are primarily focussed on the Orbitrap cell itself, the high-stability pulsed high-voltage power supply and the highly sensitive pre-amplifier. In addition, work is being pursued in collaboration between the Cosmorbitrap team and international partners. For instruments to be flown in interplanetary space or to airless bodies, such as for a dust spectrometer (Kempf et al., 2012; Briois et al., 2013), the core elements will be coupled with the open vacuum to guarantee the high vacuum required within Orbitrap itself. However for other *in situ* planetary instruments, such as the Planetary Organic Detector (Beauchamp et al., 2014) or the Advanced Resolution Organic Molecule Analyzer (Arevalo et al.,

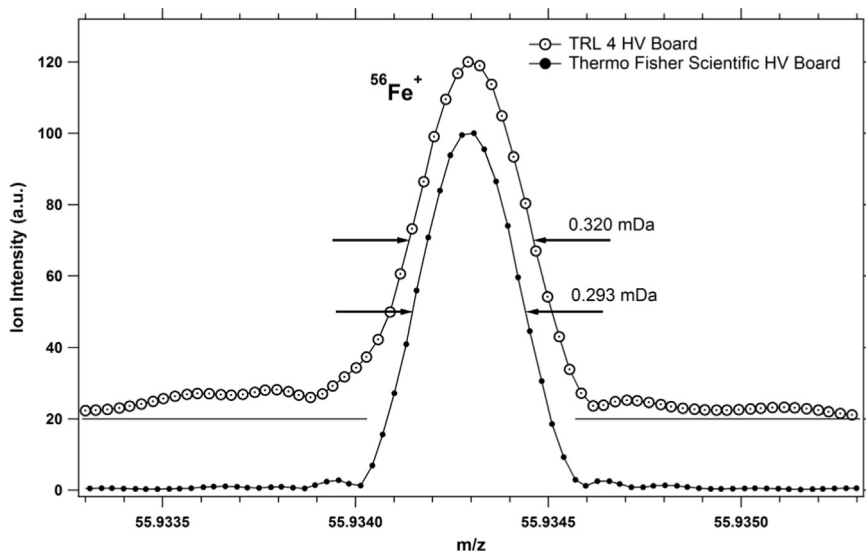


Fig. 11. Single laser shot mass spectra of a stainless steel target performed with the LAB-Cosmorbitrap implemented with the TRL 4 HV prototype power supply, compared with the one obtained with the Thermo Fisher Scientific (TFS) HV power supply. For the sake of clarity the baseline of data obtained with the TRL4 HV prototype power supply has been shifted.

2015), a pumping subsystem is needed for maintaining the ultra-high vacuum required within the Orbitrap itself.

One of the key performance targets reached at the time of writing this paper relates to the pulsed high voltage power supply, as illustrated in Fig. 11. It shows a mass spectrum recorded with the TRL 4 high voltage (HV) power supply unit in comparison with the commercial power supply. These encouraging test results give us confidence that the TRL 5 high voltage power supply unit will meet the Cosmorbitrap performance requirements.

## 5. Conclusions

This paper presents the current performance of the prototype of the Cosmorbitrap subsystem mass analyser coupled with a laser ablation ionisation source. These reported tests demonstrate the capabilities of such subsystem. The LAB-Cosmorbitrap testbed is capable of providing mass resolving power as a function of  $m/z$  similar to the commercial instrument using the same type of Orbitrap cell, reaching 474,000 at  $m/z$  9, with mass accuracy below 15 ppm, which is very unusual for space instrumentation that can have large limitations due to mass and power constraints. Repeatability of the measurements is well preserved, and the relative isotopic abundances are found below 5%. A specific study of the effect of background gas on performances reveals an upper limit at  $10^{-8}$  mbar, measured in our set-up for  $N_2$ .

The unprecedented capabilities of the Cosmorbitrap would make it a key mass analyser to measure molecular, elemental and isotopic compositions, and to search for complex organic molecules in various extra-terrestrial environments. The Orbitrap technology is therefore effective for space, and is suitable for planetary exploration missions. Complete instrument configurations alternative to the LAB-Cosmorbitrap are explored. Future instruments based on the Cosmorbitrap concept will be essential for the future space exploration of the Solar System. Depending on the science objectives of a mission, a Cosmorbitrap-based mass spectrometer could be adapted on-board an orbiter or a lander. As Cosmorbitrap operation requires reduced pressures, its extended operation inside an atmosphere will require the addition of a pumping device to the instrument. The work toward a space borne Cosmorbitrap analyser paves the way for the development of new analytical high-resolution instruments.

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