

## Ultra high resolution Fourier Transform mass analyzer for space exploration: Orbitrap

R. Thissen (1), L. Thirkell (2), A. Makarov (3), P. Puget (1), C. Briois, C. Szopa (4), N. Carrasco (4), J.J. Berthelier (4) H. Henkel (5) A. Koch (5) and A. Glassmachers (6)

- (1) Laboratoire de Planétologie de Grenoble, UMR 5109 CNRS - UJF, 38000 Grenoble, France ([roland.thissen@obs.ujf-grenoble.fr](mailto:roland.thissen@obs.ujf-grenoble.fr))
- (2) Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E) - UMR-CNRS 6115 3A, av de la recherche scientifique, 45071 Orléans, France
- (3) Thermo Fisher Scientific, Hanna-Kunath Str 11, 28199 Bremen, Germany
- (4) Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), CNRS, UVSQ, UPMC, Route des Gâtines, 91371 Verrières le Buisson Cedex, France
- (5) Von Hoerner & Sulger GmbH, Schlossplatz 8, 68723 Schwetzingen, Germany
- (6) Bergische Universität Wuppertal, FB-E Messtechnik Rainer Gruenter Strasse 21, 42119 Wuppertal Germany

### Abstract

We describe a new concept of mass analyzer that is lightweight, uses DC voltages, and provides ultra high resolving power capabilities ( $m/\Delta m = 100,000$  at mass 400). Such resolving power allows ascribing exact mass to each detected species and therefore opens new opportunity for molecular characterization, isotopic abundance evaluation, and more generally environmental characterization.

### Introduction

Space exploration is dealing more and more with astrobiology or prebiotic environment, requesting for optimized methods of analysis. One of the best methods to evaluate those media is mass spectrometry due to its ability to reveal quantitatively almost any material.

Over the past decade, mass spectrometry has been revolutionized by access to instruments of ultra high mass-resolving power, based on Fourier transform of a image current induced by ion oscillations in the analyzer. As mass-resolving power ( $m/\Delta m$ ) increases, several new plateaus of chemical information become accessible:

1.  $m/\Delta m > 500$  (Quadrupole mass filters) allows separation of peaks of different nominal mass (e.g., 325 Da versus 326 Da);

2.  $m/\Delta m > 3,000$  (Rosina's DFMS on Board Rosetta) allows separation of peaks for nominally isobaric species ( $N_2$  / CO at 28 Da).

3.  $m/\Delta m > 10,000$  (proposed resolution for the TSSM polymer analyser) ensures separation of isobaric species up to 100 Da (toluene  $C_7H_8$  / methyl pyrimidine  $C_5N_2H_4$  / dicyanocetene  $C_4N_2O$  at 92 Da).

4.  $m/\Delta m > 100,000$  (FT mass spectrometry resolution) provides separation of isobaric species up to 500 Da. (Estradiol dibenzoate  $C_{34}H_{36}O_4$  / Glycerol - pentapropylene glycol  $C_{24}H_{44}O_{11}$ ).

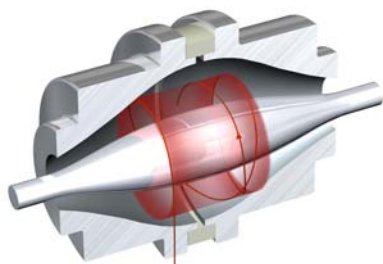
FT MS offers (i) the multiplex advantage of yielding the entire mass spectrum at once, rather than requiring that each peak be scanned through separately and (ii) in the zero-collision limit, mass-resolving power increases directly with data acquisition period.

FT mass analyzers are based on measurements of frequency rather than on ion deflection (electric/magnetic sectors), ion stability (quadrupole mass analyzer, quadrupole ion trap), or time of flight (TOF). Up to now, FT MS was available only through recording of the Ion Cyclotron frequency (ICR) in an intense magnetic field (beyond 1 Tesla). As magnets are heavy, this method was unavailable for space exploration. In the year 2000, a new concept avoiding any

magnetic or RF field was demonstrated to be feasible for FT MS: orbitrap (1, 2).

### Principle

The orbitrap confines ions in an electrostatic quadro-logarithmic potential created between carefully shaped coaxial central and outer electrodes (Figure 1). Ions are pulsed into the device so that they rotate around the central electrode and oscillate along it with axial frequencies of 200–2000 kHz for  $m/z$  of 10–1000. The outer electrode is split into two halves to allow differential image-current detection. Unlike ICR, coherent motion of ion packets is provided during the injection process and detection occurs immediately after all ions have been injected into the trap and after voltage on the central electrode has stabilized.



**Figure 1:** Schematic diagram of an orbitrap, showing ion injection (*lower left*) and subsequent ion trajectory. Detection is based on splitting the outer ring electrode at the trap middle and detecting the difference in charge induced on the two halves.

The orbitrap axial oscillation frequency is independent of ion energy and amplitude and is thus ideal for  $m/z$  analysis. The axial frequency  $\nu_z$  depends only upon the ion  $m/z$  and the field curvature  $k$ .

$$\nu_z = (ek/m)^{1/2}/2\pi. \quad (1)$$

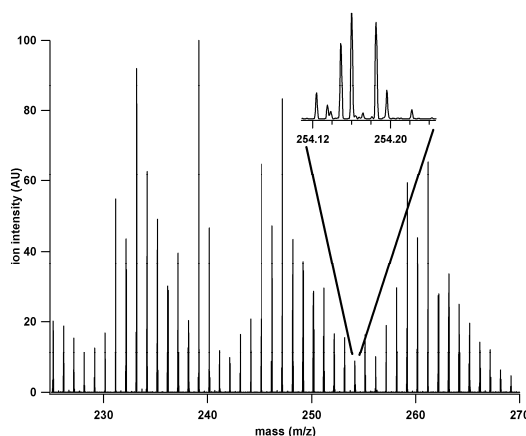
From equation 1, it can be shown that mass-resolving power is one-half the frequency resolving power and is proportional to  $1/(m/z)^{1/2}$ . The consequence is that mass-resolving power decreases slowly with  $m/z$ .

The orbitrap typically achieves a mass-resolving power of 100,000 at  $m/z$  of 400 in a 760-ms detection period. Resolving power is limited by the observation period duration, the collisions with

residual gas molecules, and the imperfections in the electric field (caused, for example, by the ion injection slot and/or inaccuracy of machining), and instability of the high-voltage power supply.

Accurate exact mass measurement (<2 ppm) is maintained for dynamic ranges greater than 5000, which is at least an order of magnitude higher than that for TOF.

Figure 2 shows an excerpt from complex mixture mass spectra recorded on the commercial LTQ-orbitrap XL instrument.



**Figure 2:** Mass spectrum of complex mixtures illustrating the exceptional resolution at mass 254.

Since January 2009, the CNES has funded a R&D program to develop a space instrument based on the new concept. The analyzer has since been chosen as a candidate analyzer in two instruments: The Ion Laser Mass Analyzer (ILMA) Instrument, proposed on the Mascot lander of the Marco Polo NEO sample return mission, and on the Dust Detector proposed on the future Jupiter orbiter mission of ESA.

### References

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- [2] Hu, Q. et al. *J. Mass Spectrom.* (2005) 40, 430.