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Ultra high mass-resolution for space exploration: the Orbitrap mass analyser

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Abstract

We describe a new concept of space mass analyser that is lightweight, uses pulsed DC voltages, and provides ultra-high mass-resolving power capabilities ($m/\Delta m$ = 100,000 up to m/z 400). Such mass-resolving power allows ascribing exact mass to each detected species and therefore opens new opportunities for molecular characterisation, isotopic abundance evaluation, and more generally environmental characterization of the atmospheres and surfaces of planetary bodies.

Introduction

Space exploration is dealing more and more with astrobiology, with a particular interest for environments that could bring information about prebiotic chemistry. In this context, the characterisation of organic materials is a primary objective requiring significant improvements of techniques for *in situ* chemical analysis. The method of choice in this context is mass spectrometry, due to its ability to reveal quantitatively the composition of almost any material.

Over the past decade, laboratory mass spectrometry has been revolutionized by the emergence of ultra-high mass-resolving power instruments. This technique is envisaged for developing new-generation space instruments.

As mass-resolving power ($m/\Delta m$) increases, several new plateaus of chemical information become accessible:

1) $m/\Delta m \leq 500$ (Quadrupole mass filters) allows separation of peaks of different nominal mass (e.g., 28 Da versus 29 Da) but without giving the ability to ascribe a formula to those masses (i.e. 28 could be N_2^+, CO^+ or Si^+), only models and other inputs can differentiate between the candidates;

2) $m/\Delta m \approx 3,000$ (Rosina's DFMS on Board Rosetta[1]) allows separation of peaks for nominally isobaric species (N_2^+, CO^+ or Si^+ now appear as different peaks).

3) $m/\Delta m \approx 10,000$ (proposed mass-resolving power for the polymer analyser of the ESA-NASA TSSM study[2]) ensures separation of isobaric species up to 100 Da (e. g. toluene C_7H_8 / methyl pyrimidine $C_5N_2H_6$ at 92 Da).

4) $m/\Delta m \geq 100,000$ up to 400 Da (FT-Orbitrap mass spectrometry) provides separation of isobaric species up to 500 Da. Estradiol dibenzoate $C_{34}H_{36}O_4$ (509.269 Da) and pentapropylene glycol $C_{24}H_{44}O_{11}$ (509.296 Da) are then resolved in two different peaks.

Beyond mass-resolving power, FT Mass Spectrometry (FT-MS) has two advantages: (i) it yields the mass spectrum of an extended mixture of ions at once, rather than scanning through peaks separately and (ii) in the zero-collision limit, mass-resolving power increases linearly with the data acquisition period, allowing for adjustable mass-resolving power during the course of a mission.

FT-MS is based on the non-destructive measurement of the frequency of the harmonic oscillation of ions in a trap. Up to a decade ago, FT-MS was available only through recording the frequency of the Ion Cyclotron Resonance (ICR) in intense magnetic fields (beyond 1 Tesla). As magnets are heavy, this method has not been considered for space usage. In 2000, a new concept avoiding any magnetic or RF field was demonstrated to be feasible for FT-MS: the FT Orbitrap MS[3, 4].

Principle of the orbitrap

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 are captured by switching the potential of the central electrode. They then have a coherent motion in which they rotate around the central electrode and oscillate along it with axial frequencies in the range 200–2000 kHz for m/z 1000–10 Da. The outer electrode is split into two halves for the detection of the electromagnetic signal induced by the oscillating ions. Unlike ICR, harmonic motion of ion packets is achieved through the pulsed injection and detection starts after ions have been captured.
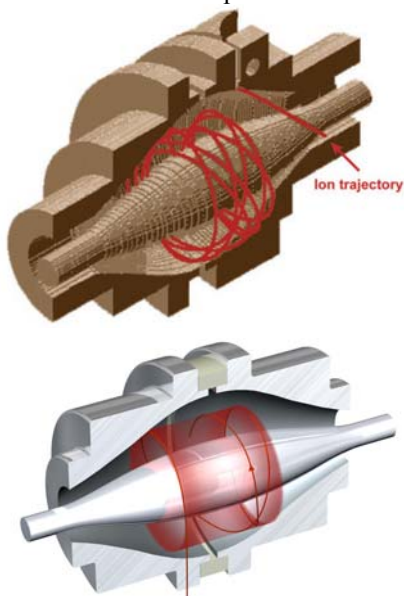
Figure 1: Schematic diagram of an orbitrap, showing ion injection (upper figure) and subsequent ion trajectory (bottom figure). The splitting the outer electrode allows the detection of the electromagnetic signal induced by the harmonic motion of ions.

The orbitrap axial oscillation frequency is independent of ion energy, ion density and ion source aberrations. It is thus ideal for high quality m/z analysis. The harmonic potential implies that the axial frequency v_z depends only upon the ion m/z and a geometric parameter describing the field curvature k.

$$v_z = (ezk/m)^{1/2}/2\pi \quad \text{where } k \approx 50.10^{12} \, Da.Hz^2 \quad (1)$$

From this equation, mass-resolving power decreases slowly with increasing m/z.

The orbitrap typically achieves a mass-resolving power better than 100,000 up to m/z 400 Da by recording the ion transient signal during 800 ms. Mass-resolving power is limited by the transient signal duration, itself limited by the collisions with residual gas in the trap, and deviations of the electric field from the theoretical solution. It requires a proper calibration to achieve the full mass-resolving capability of the instrument.

Accurate mass measurement (for species in concentration <2 ppm) can be obtained with S/N greater than 5000 per spectrum.

The capability of such an instrument is illustrated in Figure 2. It shows an example of a complex mixture mass spectrum recorded on a commercial LTQ-Orbitrap XL instrument: Titan's tholin, a $C_xH_yN_z$ solid material simulating the photochemical smog surrounding Titan[5] has been ionized by Electro Spray Ionization through proton attachment. Peaks in this spectrum can be zoomed in (as shown for m/z 254 Da) to provide unique formula $C_xH_yN_z$ for each individual peak corresponding to unfragmented molecular ion present in the mixture.
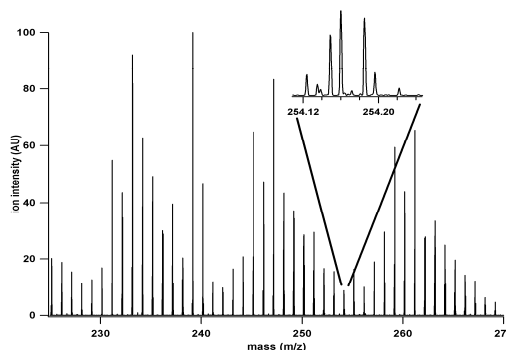
Figure 2: FT-orbitrap mass spectrum of a Titan's tholin sample, here shown in mass range m/z 222-270 Da and zoomed-in for m/z 254 Da.

Since January 2009, an intensive R&D program to develop a space version of an orbitrap analyser is funded by CNES. It is since considered as a candidate analyser for a Dust Detector to be proposed on the recently selected ESA JUpiter Icy moon Explorer (JUICE) mission[6]. It is also part of the Ion Laser Mass Analyser (ILMA)[7] under study as a potential instrument for the Marco Polo - R asteroid sample return mission currently under study by ESA.

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