

Mass spectrometry for the identification of toxic compounds in air.

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Abstract

When very fast response to the presence of toxic compounds in air even at very low level is necessary techniques based on the manipulation and detection of ions such as mass spectrometry or ion mobility can provide an answer.

Applications in the security domain are very demanding: a very wide range of potentially dangerous species has to be detected. Some of them, such as explosives, have a very low volatility and therefore are present at very low concentrations. The concentration levels for the different species present can go from the ppb level to %.

The toxic species must be distinguished unambiguously from harmful species. This was not the case with first generation detectors based on ion mobility, because of their limited resolution, leading to false alarms.

Within the DIRECT project (CSOSG 2009-2011) we have developed a high resolution detector, based on Fourier Transform Mass Spectrometry coupled to an ambient ionization source. We will show results obtained on low volatility species with this instrument.

1. Introduction

Mass spectrometry is more and more going outside the laboratory for real time in situ measurements. Instruments are evolving very rapidly toward the goal of a universal detector that would be able to replace the use of many specialized detectors, each able to detect only a single species.

For many applications, not only in the security domain, a fast response (in the second range) is necessary. This will be the case for instance for industrial process monitoring where many compounds must be followed simultaneously and the feedback is used for the process control.

The required fast response exclude the use of separation techniques such as gas chromatography for which the time for a single analysis will be more than a quarter of an hour.

For the same reason most concentration techniques cannot be employed.

Techniques based on ion manipulation are very well positioned for the realization of a broadband detector. New ionization techniques allow sampling in ambient conditions, at atmospheric pressure, before transfer into the spectrometer. Ionization has to be soft, without extensive fragmentation of the molecule that would lead to a loss of information and to confusion in the interpretation of the spectra.

Ions are separated either by their different speed when drawn by an electric field in a buffer gas (in ion mobility spectrometers) or by the use of electromagnetic field (in mass spectrometers).

Ion mobility devices are cheaper, smaller and most of the first generation devices were based on this technique. However their limited resolution (<100) can result in a lack of discrimination between dangerous and not dangerous compounds.

Mass spectrometry allows for a much higher resolution. Among the available techniques for high resolution are the time of flight and Fourier Transform Mass Spectrometry (FTMS) either in magnetic traps or electrostatic traps.

In the DIRECT project, carried in collaboration between a public research laboratory (Laboratoire de Chimie Physique, UMR8000 CNRS Université Paris Sud) and a SME commercializing mass spectrometers for real time air analysis (ALYXAN) we developed an instrument based on FTICR (Fourier Transform Ion Cyclotron Resonance) mass spectrometry and coupled with an external discharge ion source.

2. High resolution mass spectrometry

Several types of high resolution mass spectrometers exist:

-Time of flight instruments in which ions are all accelerated up to the same kinetic energy before flying through a field free zone. They will be separated in time, the lightest ions arriving to the detector before the heaviest ones. An electrostatic mirror can help in reaching high resolutions in so called reflectron instruments. However a high mass resolving power always means using a long flight tube. They are well suited for coupling with laser sources [1].

-Electrostatic traps in which the trapping motion is harmonic (such as the Orbitrap). The oscillation frequency will depend on the ion mass. Detection of the ion motion is by the image current induced on the trap electrodes. High vacuum is necessary to keep the coherent motion of ions during detection. The temporal signal is then Fourier transformed to get the frequencies and the amplitudes (related to the number of ions for each mass).

-Magnetic trap in which the ions rotate in the magnetic field with a frequency characteristic of their mass. In order to trap the ions in the 3 spatial directions an electrostatic potential is superimposed to the magnetic field. An excitation radiofrequency signal is used to induce a coherent motion of the ions before detection of the ion motion using the image current induced by the ions on two electrodes connected to a broadband preamplifier. Analysis of the signal is here again by Fourier transform in order to get the frequency of the cyclotron motion (and thus the mass) together with the amplitude (giving the number of ions for each mass).

During the DIRECT project we have used this last technique: Fourier Transform Ion Cyclotron Resonance (FTICR). FTICR is mostly known for instruments using very high magnetic fields (the higher the magnetic the higher the mass resolving power) produced by superconducting magnets. 15 Tesla instruments are commercially available, with mass resolving power above one million for mass to charge ratio around 1000. They give access to high mass range and are mostly applied in the proteomics and petroleomics fields. But these instruments are very expensive and cannot be moved

outside the laboratory: their weight exceeds several tons and the cryostats keeping the superconducting wires at liquid helium temperature must not be subjected to vibrations.

The instrument developed for the DIRECT project aims at a lower mass range (volatile molecules are mostly in the range 2-500 u) and is based on a permanent magnet assembly to produce a nominal magnetic field of one Tesla in the detection cell. The magnet has a cylindrical shape; with an inside bore 50mm in diameter. The magnetic field is highest in the magnet center and this is where is placed the cell. Previous instruments developed by us used a cylindrical magnet producing a transverse magnetic field [1-3]. The configuration used in the DIRECT project produces a field coaxial with the cylinder main axis and therefore the ions can be moved from a source placed outside the magnetic field toward the analysis cell.

The quality of the electrostatic field is also important in order to have a good mass resolving power. For this reason the cylindrical cell is divided in seven segments and the potential are adjusted in order to have a quadrupolar potential inside the cell [3].

The quality of the detection with the analysis cell has been tested using Xenon ionized by electron impact inside the cell. The spectrum shown reflects the natural abundance of the Xenon isotopes and the resolving power obtained is above 10000.

With this resolving power we can make exact mass measurements and distinguish molecule having the same nominal mass but different atomic composition (differing by their chemical formula). For instance xylene and benzaldehyde, both having a nominal mass of 107u will be differentiated by their exact masses (107,086 u and 107,050 u respectively)

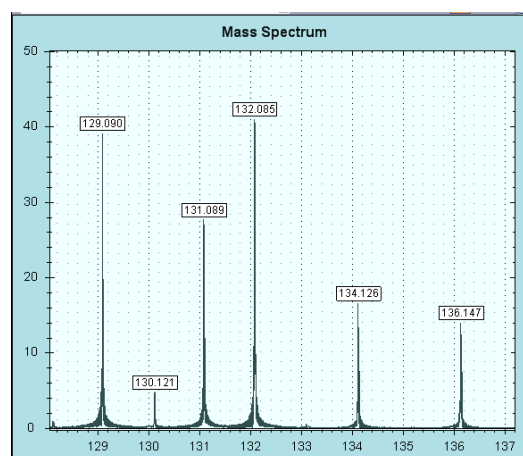


Figure 1 – Mass spectrum for xenon obtained by electron impact ionization in the analysis cell.

3. Ambient ionization source

Sampling is one of the crucial steps, especially when looking for the detection of low volatility species. When the air to be analyzed is transferred through sampling lines compounds can be lost due to deposition on surfaces and could never reach the analyzer. With ambient ionization techniques ionization takes place before the transfer [4]. The higher pressure is favorable for getting a good sensitivity.

A wide variety of sources for ambient sampling have appeared in the recent years. Many are desorption/ionization sources useful for detecting low volatility samples deposited on surfaces. Among them Desorption Electrospray Ionisation (DESI) [7], Direct Analysis in Real Time (DART [8], making use of a discharge in helium), Low Temperature Plasma (LTP [9], making use of a Dielectric barrier Discharge, generally in helium), Easy Ambient Sonic Spray Ionisation (EASI [10]),...

Other techniques allow for the direct ionization of species in gases, either using an electrospray, for instance with the Extractive Electrospray Ionisation (EESI) or using plasma discharge: Glow discharge in Helium, LTP or DART sources.

Among the different possible plasma sources we have opted for the Atmospheric Pressure Glow Discharge (APGD) because it generates high density of excited species (helium excited in metastables electronic states, helium or helium dimer ions). These primary species will react with air and in many cases volatile organic compounds will appear as protonated species. The ionization resulting from reaction with air is expected to be soft, with little fragmentation of the molecules, which is essential to identify them from their mass.

4. Results on low volatility species

First results on low volatility species have been obtained on air containing traces of polyaromatic hydrogenated compounds. These are not easy in air using chemical ionization techniques such as APCI (Atmospheric Pressure Chemical Ionization), but can be detected using laser photoionisation to specifically ionize this class of compounds.

The result is shown for acenaphthylene. A flux of air is flown above a little amount of acenaphthylene powder and is then directed to a small reaction chamber placed in front of the glow discharge source. The resulting ions are sent inside the mass spectrometer through a capillary in a 10 to 25 ms air pulse. Ions are intercepted in a hexapole radiofrequency trap in which collisions with air molecule bring the ions in the center of the trap. After a 3 to 5 seconds delay, when the air neutral molecules have been pumped away the ion packet is sent to the analysis cell located in a differentially pumped vacuum chamber for mass analysis.

As seen on the spectrum the parent ion mass peak is small and appears as a radical cation (at m/z 152). It is

probably formed by Penning ionization from Helium metastables or charge transfer from precursors such as He^+ , H_2^+ or N_2^+ . The peaks observed at higher masses correspond to singly oxygenated species (m/z 169) and doubly oxygenated species (m/z 185).

This pattern is characteristic of the ionization of PAHs in a discharge in air [12]. When comparing the results obtained with different PAHs the spectrum for each one was very specific and could be used for identification.

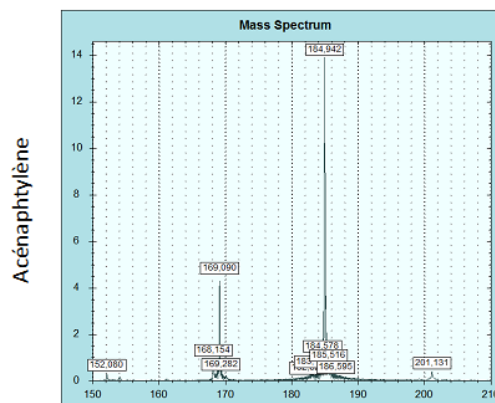


Figure 2 – Mass spectrum for acenaphthylene at trace concentration in air.

5. Conclusion

The results obtained clearly show the advantages of a high resolution mass spectrometer for a precise identification of the molecules present and the interest of ambient ionization sources in order to make the ionization of the molecules where they are, before any transfer. Then the fast transfer in a gas pulse through a capillary will affect most ions in the same way. The main difficulty is to go through 11 orders in magnitude in pressure (from atmosphere to 10⁻⁸ mbar in the analysis cell) using only two turbo pumps.

Further developments could involve the use of multi MS steps (to gain more information when necessary from the dissociation of selected ions), the combination of different separation techniques (in that way even isomeric molecules could be distinguished) and progress toward a much more miniaturized instrument.

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