

On Site Generation Of Low Level Odorous Standards For Validation Of FTICR-MS Gas Detector In Ambient Air.

Hélène Mestdagh¹, Joël Lemaire¹, Michel Heninger², Julien Leprovost², Carine Cardella³, Laurent Courthaudon³,
Nicolas Bouton³

1. Laboratoire de Chimie Physique, Bât. 350, Université Paris-Sud, 91405 Orsay, France

2. AlyXan, Bat 207B, Université Paris-Sud, 91405 Orsay, France, contact@alyxan.fr

3. Alytech, Centre Hoche, 3, rue Condorcet, 91260 Juvisy-sur-Orge, France, gasmix@alytech.fr

Abstract

Gas sensors and analyzers can be externally calibrated with standard gases. These gas cylinders are usually difficult to obtain when it comes to low concentration standards, and their lifetime may be questionable. Starting from high concentration and diluting on site to desired concentration allows to set up multi-point calibrations of the analytical device, such as an electronic nose.

Volatile Organic Compounds (VOCs), including odorous chemicals, have been analyzed using, Gas Chromatography (GC) often coupled with Mass Spectrometry (GC-MS), or specific olfactometric sensors. Proton Transfer Reaction (PTR) coupled with Fourier Transform Ion Cyclotron Resonance (FTICR) MS is proposed to analyse low level of VOCs in air. FTICR MS is the most accurate and has the highest mass resolution of the MS techniques. B-Trap is a miniaturized FTICR instrument meant for VOCs analysis [1-4].

1. Introduction

According to ISO 6145, GasMix generates on site multi-point gas calibration standards.

The principle is based on the mixing and/or dilution of two to four gases by Mass Flow Controllers, which are controlled by software to deliver accurate flows of each gas. It is then possible to vary one gas concentration in a fixed matrix of other gases coming from different sources.

Added standard method and internal calibration are also possible.

More than just a gas standard preparation device, GasMix operates on its own from a single injection to a fully automated and pre-programmed sequence, and thus can run unattended 24/7. It turns automatically the gases on when purging to prepare a new standard concentration or mixture, and off during the time needed by the analyser to make the separation and detection, in case of long GC runs for example.

FTICR MS is a specific Mass Spectrometry widely spread in life sciences for the analysis of peptides and other high molecular weight compounds. The use of a permanent magnet allows to offer this technique for smaller molecules, such as VOCs. Among its benefits:

- Simultaneous separation and detection for broadband and real time analysis of complex mixtures of gases (typically 1s analysis cycles).
- Accurate mass (± 0.01 uma) and high resolution (10,000 over the whole range) to assign accurately a molecular weight for each peak, and thus easy identification of unknown compounds.

- Soft Chemical Ionization for no fragmentation and ease of interpretation (1 peak/compound), and for specific ionization of VOCs compared to O₂ and N₂ (increased sensitivity), by Proton Transfer Reaction (PTR) : $AH^+ + M \rightarrow MH^+ + A$ [7].
- Absolute quantification based on the reaction kinetics of the odorous molecules and ionic precursor.

B-Trap has been proven to be an additional technique in automotive pipe exhaust, atmospheric and ambient air analysis [5], and polymer degradation studies [6].

2. Experimental and Methods

B-Trap (AlyXan, Orsay, France) is equipped with a sniffer line to sample ambient air containing the odorous VOCs. If the concentration of target analytes is lower than the detection limit of B-Trap (ppm), another sniffer sampling line is equipped with a membrane to preconcentrate the VOCs, and allow B-Trap to detect ppb levels.

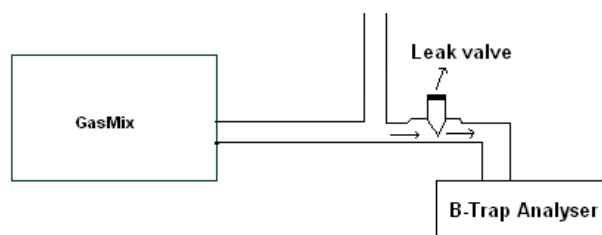
The sniffer is placed above widely encountered products : whiteboard markers, a white correction fluid, sprays for plant and garden treatment, or for solid wood pieces of furniture.

B-Trap (AlyTech, Juvisy-sur-Orge, France) allows to inject gas standards into B-Trap for accurate mass calibration and quantification validation.

3. Results

3.1 Sampling

GasMix is placed before the sniffer introduction line of B-Trap and the flow is forced in front of the vacuum chamber of the MS:



The vent line allows to stabilize the inlet pressure at atmospheric conditions and vent the excess amount of gas coming from GasMix, the MS intake being 10^{-5} torr only during a fraction of a second. When analysing ambient air, GasMix flows are turned off, and the vent line becomes the sniffer inlet line.

A PDMS membrane (polydimethylsiloxane) can be installed before B-Trap which works as an in-line

preconcentrator of VOCs compared to N₂ and O₂ [8]. Membrane Inlet Mass Spectrometry (MIMS) is a real time preconcentrator where analytes pass through the membrane continuously whereas the rest of the matrix flows along the membrane and is less injected into the instrument. The membrane is then also the physical barrier between the ambient air pressure and the MS vacuum chamber.

3.2 Mass calibration

After Fourier Transform, the instruments provides frequencies, which have to be transformed into masses. Before analysing unknown samples, a standard gas is injected and obtained frequencies are adjusted to calibrate in mass. When recalculating, found masses are very close to exact masses.

Molecules	Exact masses (Da)	Measured masses (Da)	ΔM (mDa)
Water	19,0184	19,0171	-1,3
Acetonitrile	42,0344	42,0368	+2,4
Ethanol	47,0497	47,0525	+2,8
Acetone	59,0497	59,0502	+0,5
THF	73,0653	73,0635	-1,8
Benzene	79,0548	79,0529	-1,9
Dioxane	89,0602	89,0573	-2,9
Toluene	93,0704	93,0724	+2,0

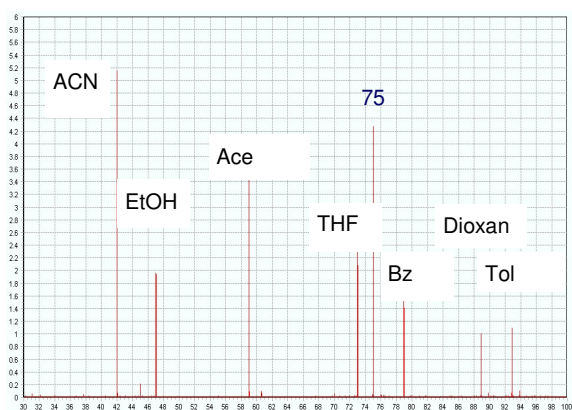


Figure 1: obtained spectrum by PTR-FTICR of the calibrant.

If zooming in the $m/z=75$ region, the high resolving power of FTICR allows to separate two compounds of $\Delta M=0.0364$ Da:

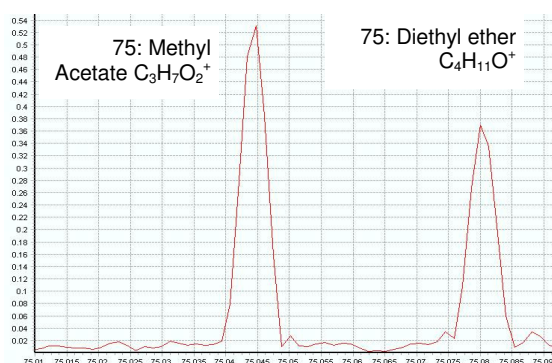


Figure 2: zooming of figure 1 for $m/z=75$.

3.3 Linearity check

Further dilution by GasMix of the standard allows to validate linearity of the detector:

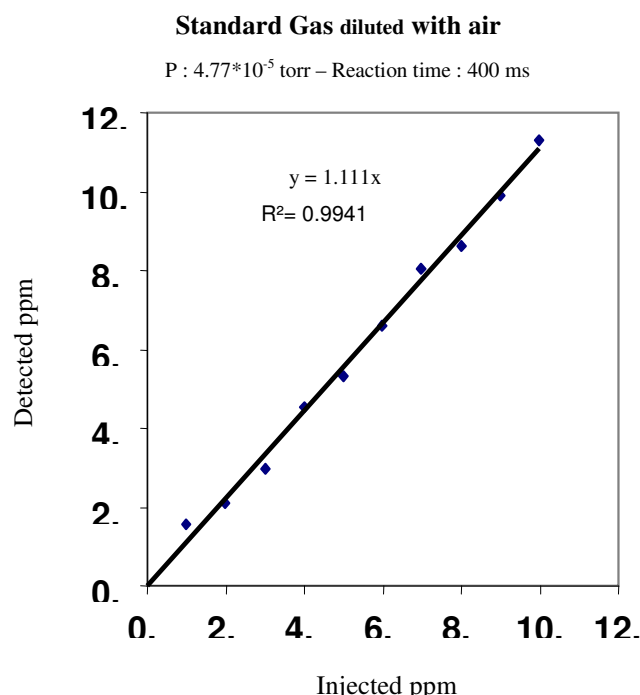


Figure 3: gas multi-point calibration of B-Trap using GasMix

3.4 Head Space analysis of commercial products

In the air above a white correction fluid, butene, pentene, heptene and octene were found at the ppm level (C₈H₁₁⁺ being an internal calibrant), while heptene only is found in a similar product of another brand:

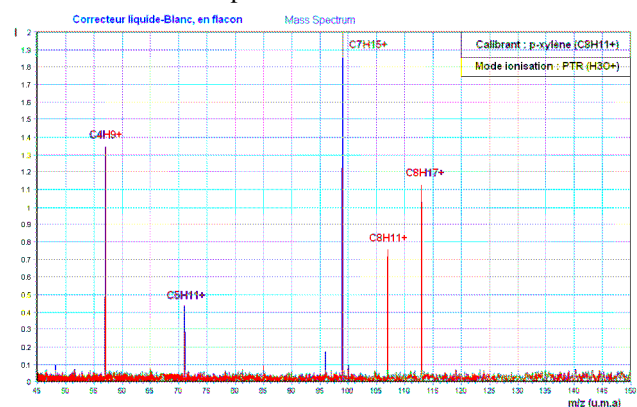


Figure 4: mass spectrum of the head space of a white correction fluid.

Above an anti-oxdyant for metals, a higher number of components have been detected (see figure 5): butene, cyclopentene, pentene, benzene, cyclohexene and cyclohexadiene, hexene, toluene, 2-norbornene, heptyne, heptene, octyne (C₈H₁₄, or C₈H₁₅⁺ in figure 5), octene, trimethyl-benzene, nonyne, nonene, and even decyne and decene.

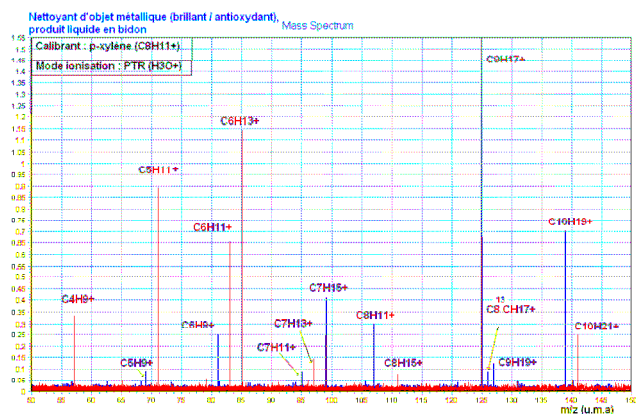


Figure 5: head space above a commercial anti-oxydant for metals.

4. Conclusions

PTR-FTICR MS allows to detect, without prior separation by Gas Chromatography, VOCs present at trace levels in air. B-Trap is a miniaturized instrument that can be transported for on-site analysis. Applications for olfactometry have been developed with the introduction of a sniffer sampling line, equipped with an on-line membrane for preconcentration if necessary. MIMS is also possible in case of aqueous matrices, for solubilised organic compounds.

GasMix has been used for both mass calibration and linearity check of B-Trap. GasMix is the appropriate companion for all gas analysers or detectors for validation purposes.

References

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