AlyXan
INNOVATIVE ANALYSIS

Real time measurements of VOCs by transportable mass spectrometry using chemical ionization methods

air quality and industrial emissions assessment

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Why are VOCs so Important?

VOCs are produced by metabolic processes and by a wide range of industrial and domestic processes.

VOCs participate in the formation of tropospheric ozone

Formaldehyde, benzene, acetaldehyde… are toxic air contaminants

How to measure VOCs

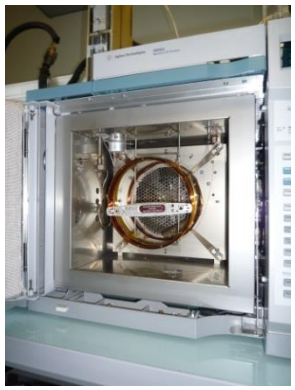
2 major challenges:

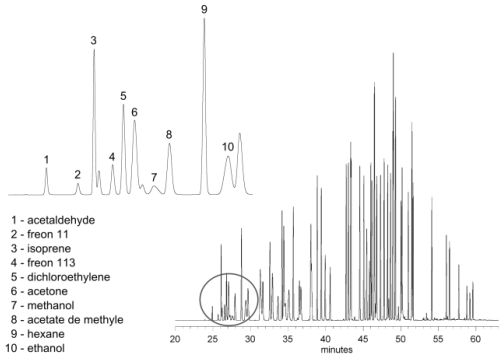
- A large variety of compounds
- Low concentration sub ppm, ppb, ppt level

Gas Chromatography

Adsorption on TENAX™ or equivalent

GC-FID for quantification
GC-MS for identification





Normalized laboratory technique (ISO 16000-6) for indoor air quality assessment
Slow: 2 minutes → 40 minutes

Need for « real time/online measurements »

Complex mixture analysis

How to analyze a complex mixture without a Gas Chromatography separation?

BTrap

Selective Chemical Ionization
+
High Resolution Mass Spectrometry (FTICR)

= well-suited analytical solution for a fast and accurate quantitative measurement of several VOCs, simultaneously and continuously.

Chemical Ionization

Based on Ion-molecule reaction:

-Positive or negative ions

-Proton Transfer, Charge Transfer, H Transfer, other reactions

Key points:

- **Selectivity :** *no reaction with the matrix*
- **Little or no fragmentation:** *mass spectra easier to interpret*
- **Quantitative methods :** *chemical ionization reactions follow first order kinetic laws - absolute measurements (without any calibration) is then possible* by knowing the rate constant.

PTRMS (Proton Transfer Reaction Mass Spectrometry)

$H_3O^+ + N_2, O_2, Ar \ldots \rightarrow$ no reaction

$H_3O^+ + VOC \rightarrow HVOC^+ + H_2O$

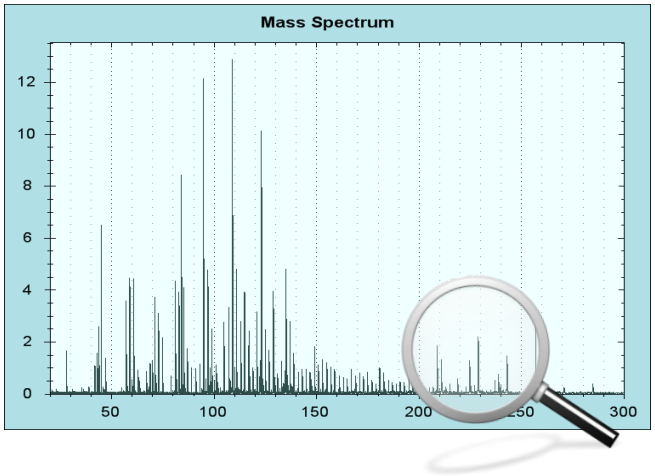
Which compounds can be measured?

H_3O^+	O_2^+	O^-
Alkenes	NO	Freon R134a
Aromatics	NO_2	….
Alcohols		
Acids	Alkenes	Fluorinated compounds
Aldehydes	Aromatics	Chlorinated compounds
Amines	Alcohols	
….	Acids	
	Aldehydes	

Possibility to work sequentially with several precursor ions (chemical ionization methods) : O_2^+, CF_3^+, O^-, NO^+...

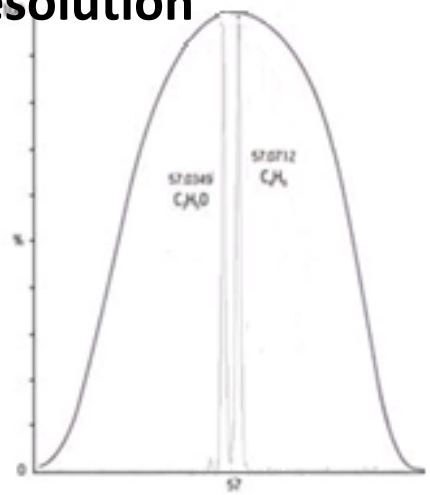
FTICRMS: High resolution solution for VOCs analysis

Broadband detection: monitoring/screening…



Pre-defined and unexpected components

High resolution



Isobaric separation

Identification

Measured mass

Difference with exact mass (10^{-3})

Mass 59

Protonated acetone

Technical data

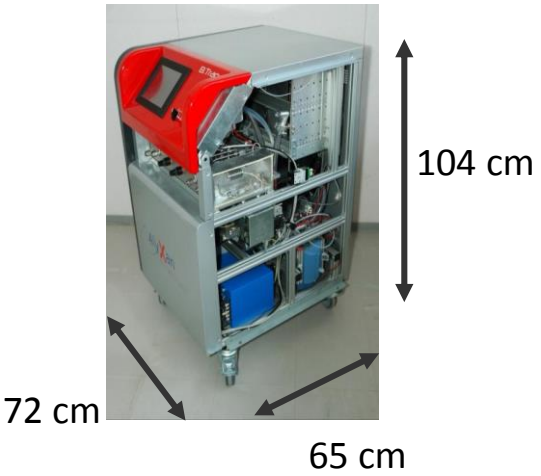
Low magnetic field: 1T to 1,5T (Two patents)

- Permanent magnet: Halbach cylinder
- Cubic cell: edge between 1.8 cm to 3 cm

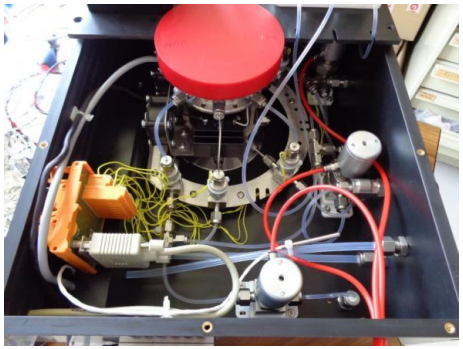
Turbomolecular pumps
Pulsed Valves
Electron Impact and Chemical Ionization

Mass range: 4-300 u
Mass resolution power: 10 000

Weight: ~ 150 kg.
Mobile, no fluid needed .

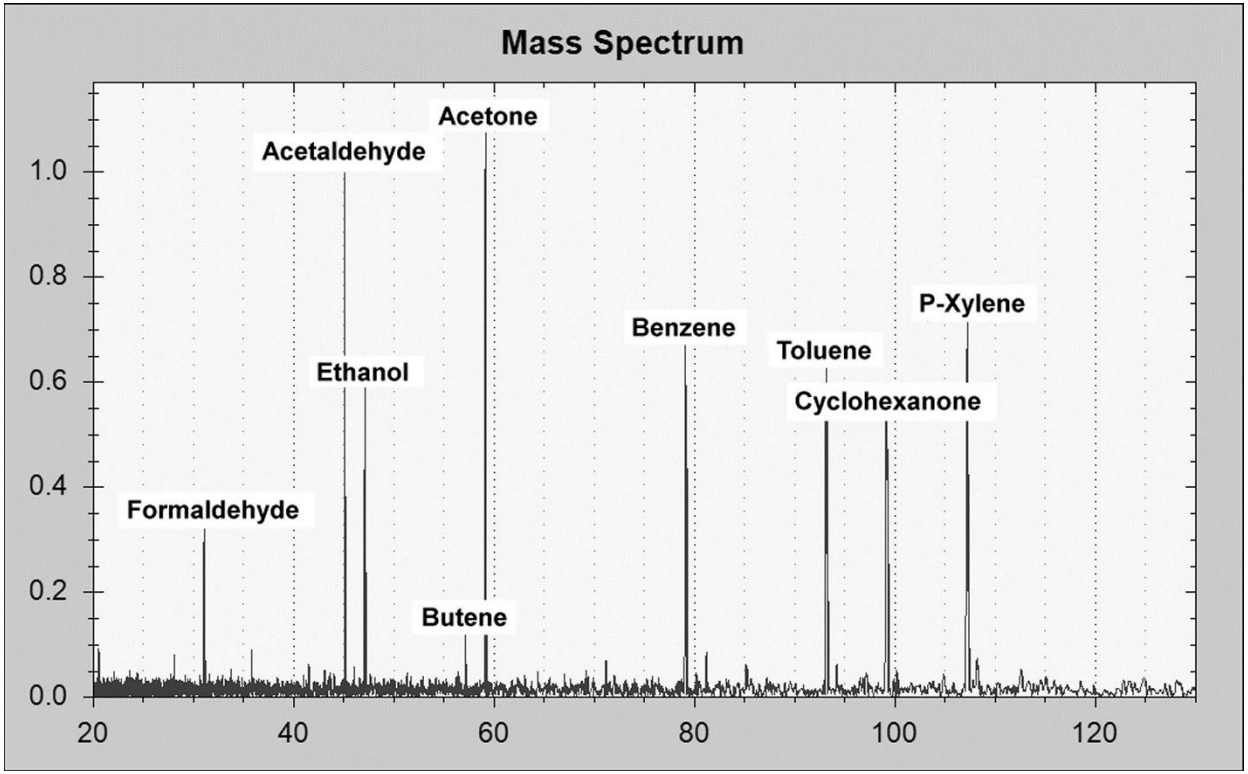


Sensitivity: LOD 200 ppb (1s).
Few ppb (min) with MIMS preconcentration
No limitation for high concentrations (%).



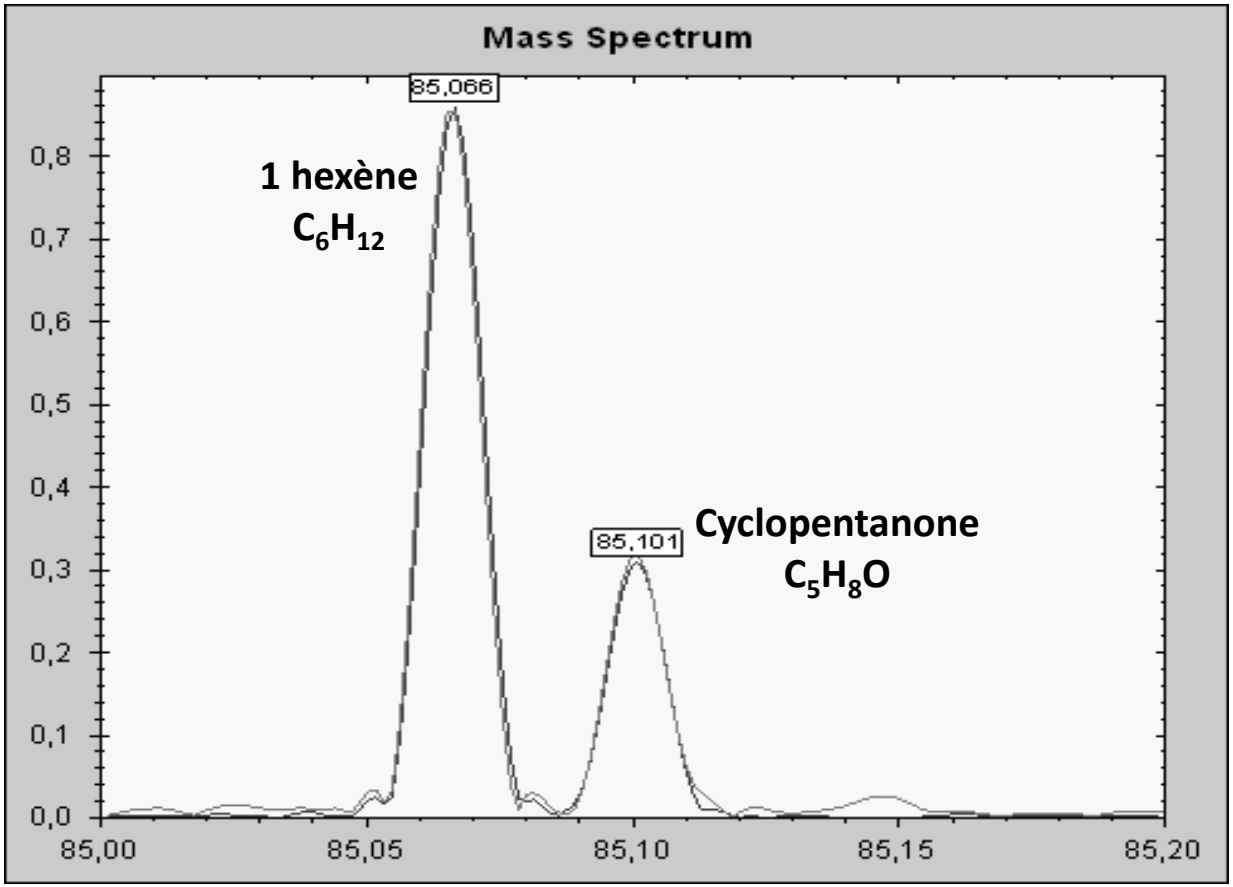
BTrap sampling system

BTrap performances – on site applications



Air analysis of 9 pollutants at ppm level

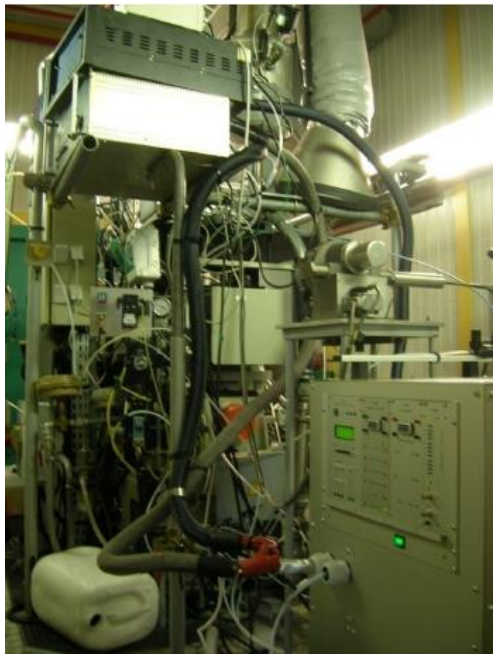
BTrap performances – on site applications



Isobaric separation in real time

Transportable, rugged

Air measurements in a wastewater treatment plant



Engine test

Air monitoring in a confined space

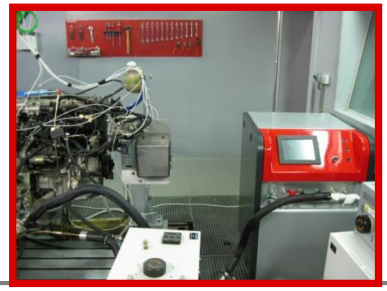
Applications

Air quality assessment

Industrial emissions

VOCs emissions from degradation of materials

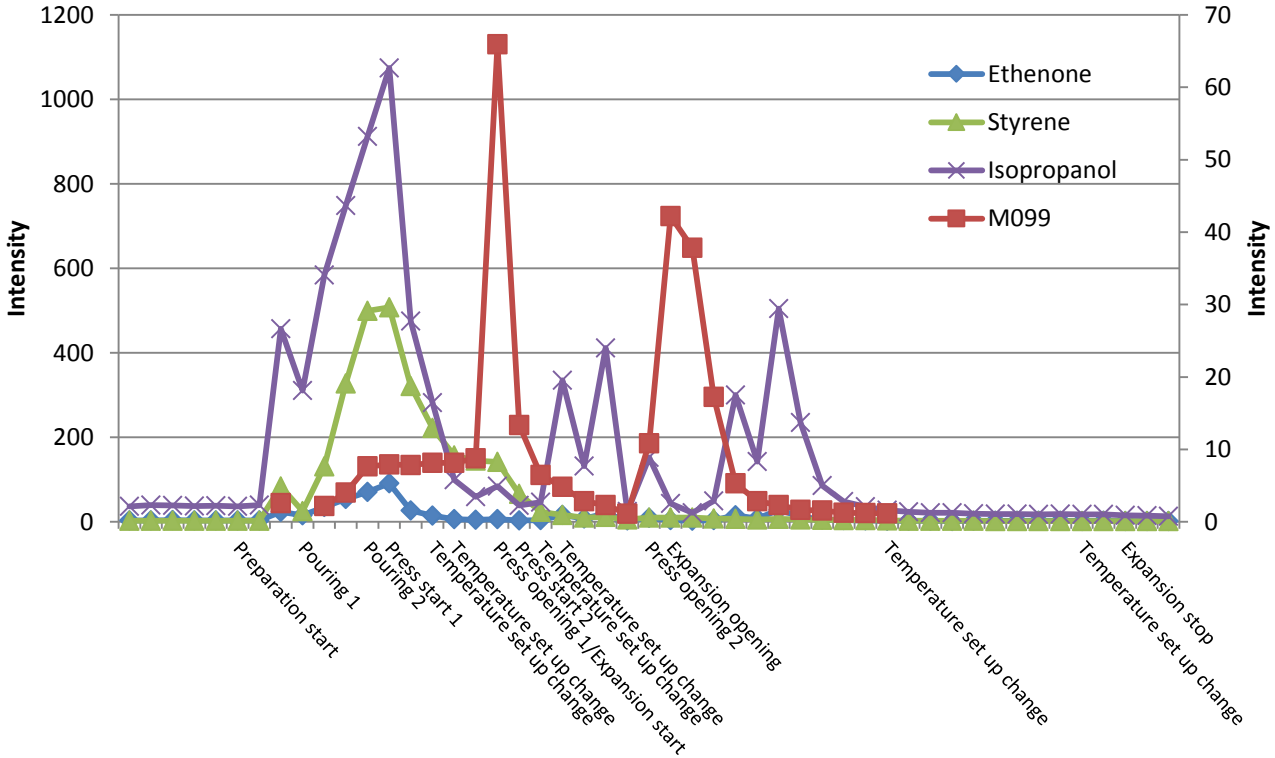
Car exhaust emissions

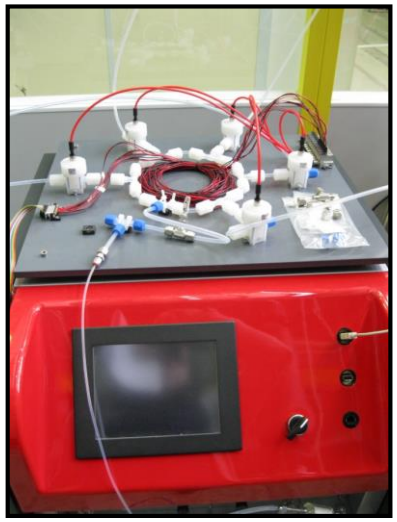


Indoor air pollution

Analysis of indoor workplace air: example of a polymer production line.

The use of a **multiplexing** inlet system is needed for a sequential analysis of the pollutants emissions from the different parts of an industrial process.



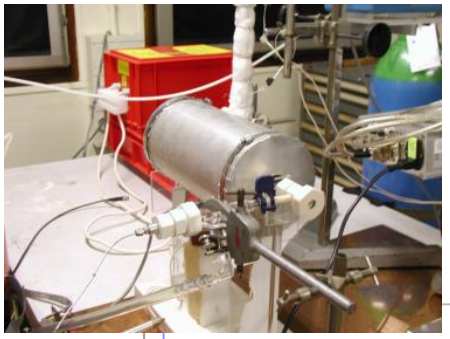


Multiplexing inlet system

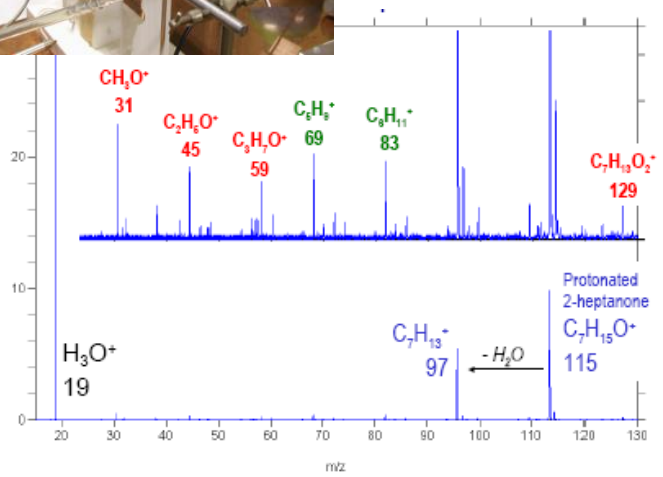
Pollution control system

Cold plasma pollution control system : study of 2-heptanone degradation (200 ppm in air).

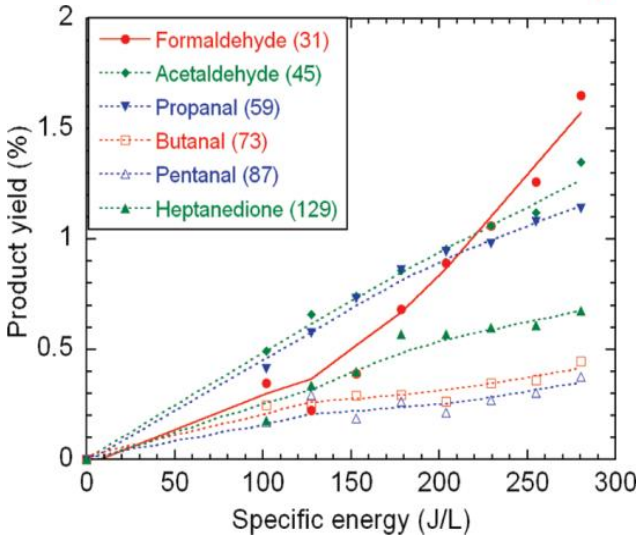
The use of a real time analyzer is needed for the characterization of the discharge which removes VOCs in the air.



Dielectric Barrier Discharge (DBD)



Identification of by-products generated by a 20 kV discharge applied on air containing 200 ppm of 2-heptanone.



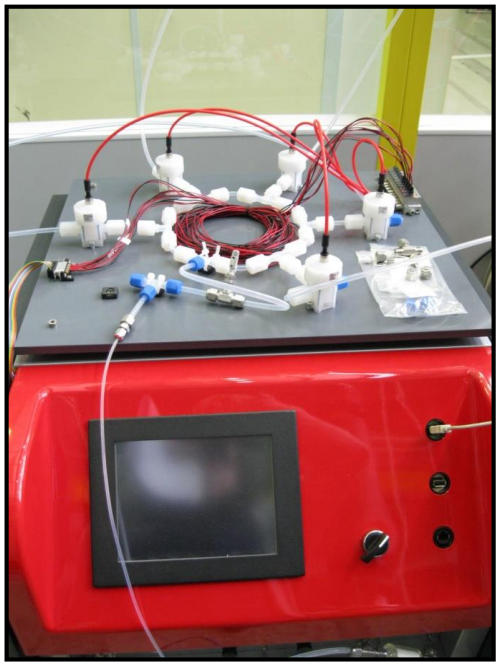
Quantification of by-products generated according to the plasma energy used

VOCs removal efficiency on an industrial process

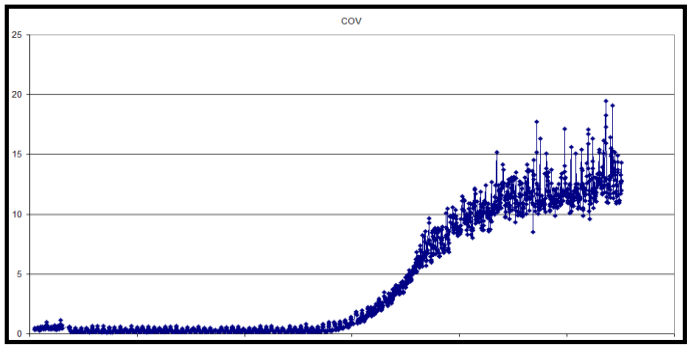
Continuous measurements over 35 days on an air pollution control unit.

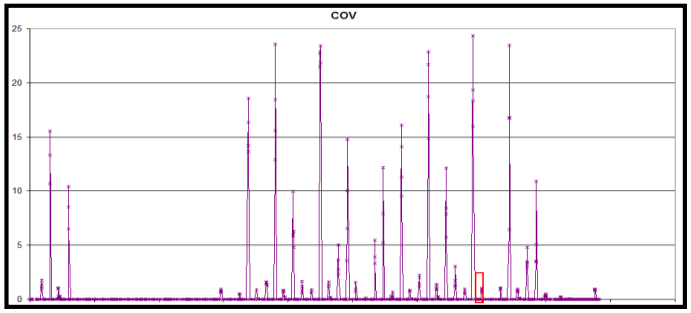
Analysis were made sequentially on 6 sample points of a process in which VOCs are filtrated.

Multiplexing inlet system



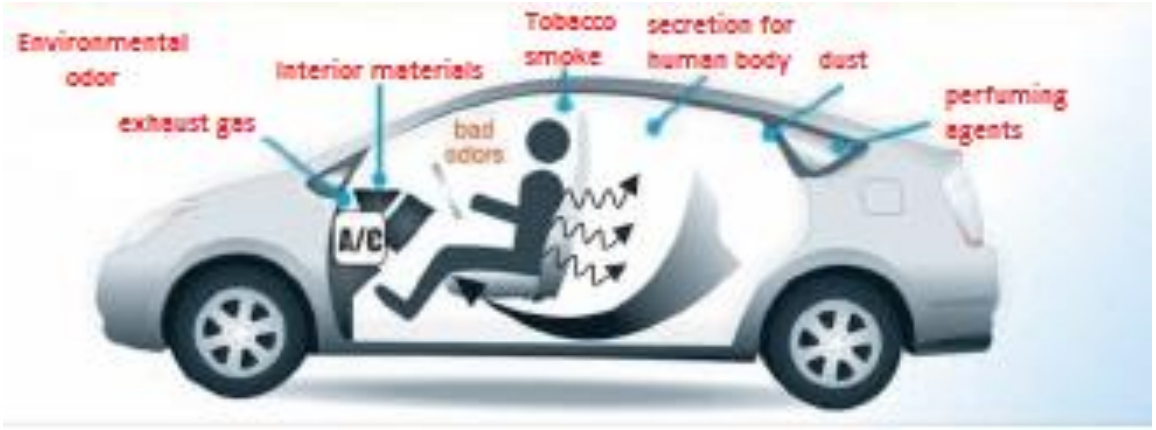
Time to breakthrough volume monitoring of filters in the process





Emission and degradation of materials

Thermo-degradation of material: kinetic recording of VOCs emissions is necessary to understand mechanisms of their degradation or to estimate the associated health risks.



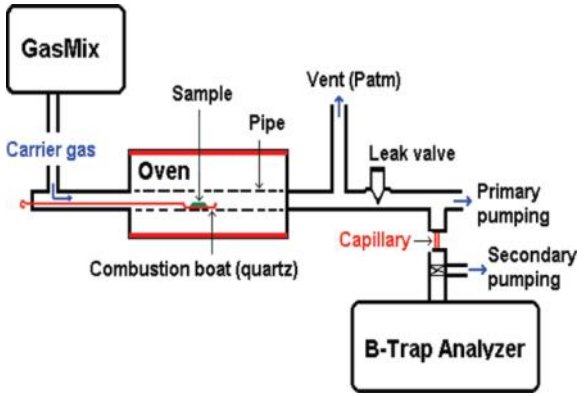
Car's passenger compartment material degassing

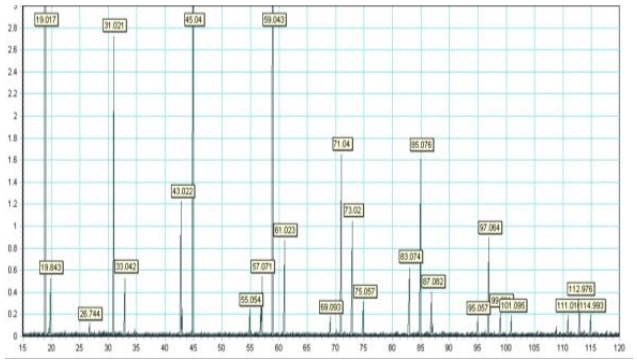
Material degassing in housing environment
(aldehydes, nitrogen oxides, carbon monoxide, BTX, PFC, phthalates, allergens, moistures…)

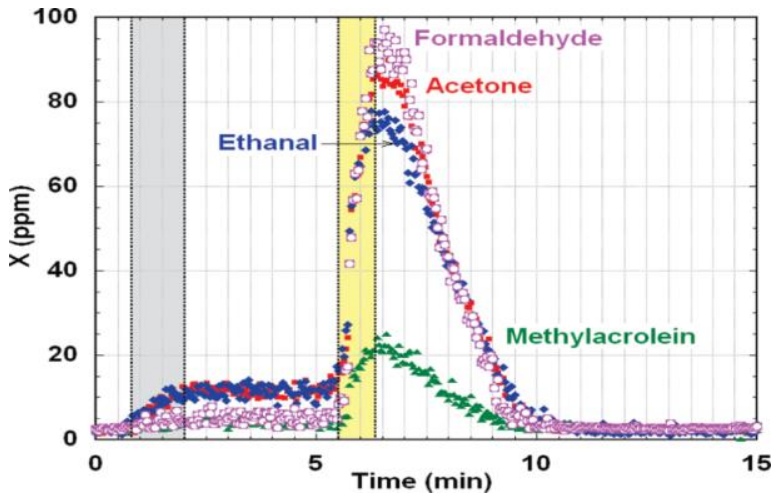
Thermo-oxidation of Polypropylene (PP)

Thermo-degradation of PP in ambient air at 256°C (isotherm study) : kinetic VOCs emissions of a PP sample under operating conditions (T°, matrix) in a process.

Experimentation set-up for thermal oxidation of PP under ambient air at 256°C.

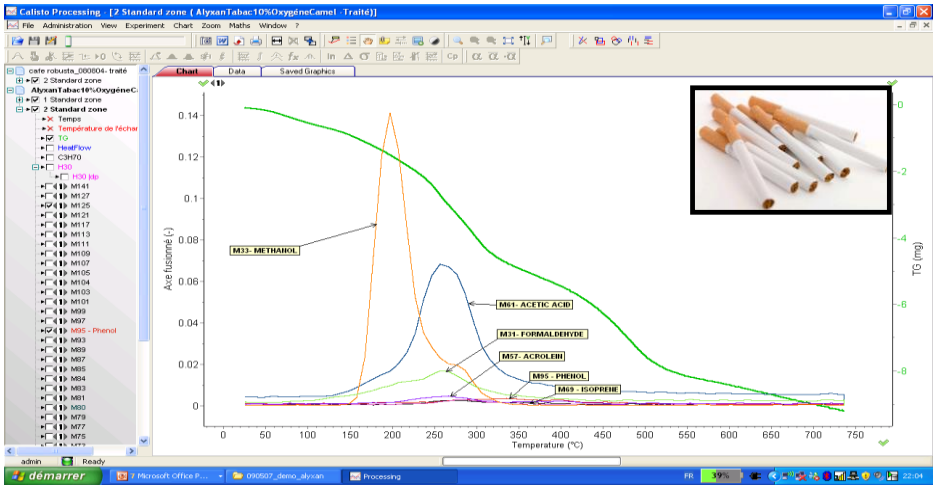




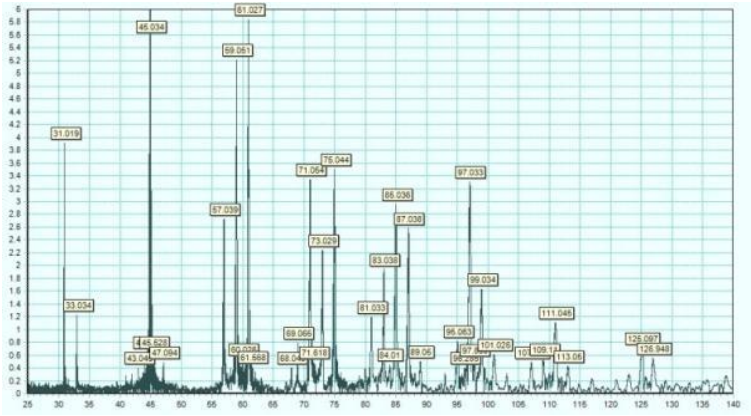


Main VOCs emitted monitoring

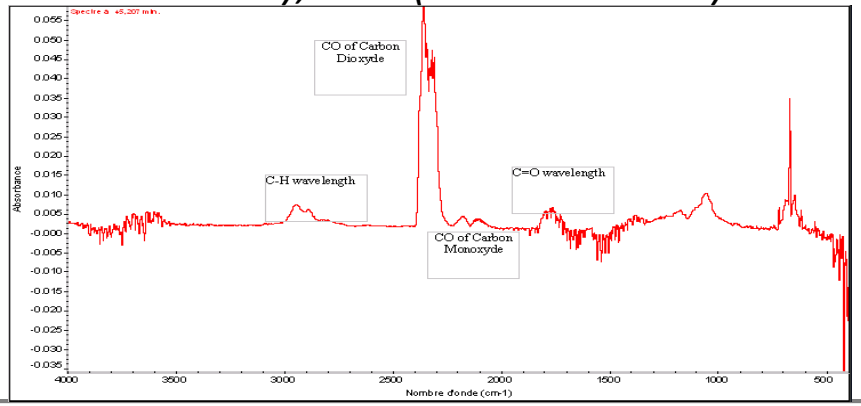
Tobacco combustion: analysis by TGA/MS & TGA/IR



Direct attribution of the molecular formula of each compound present in the gas.



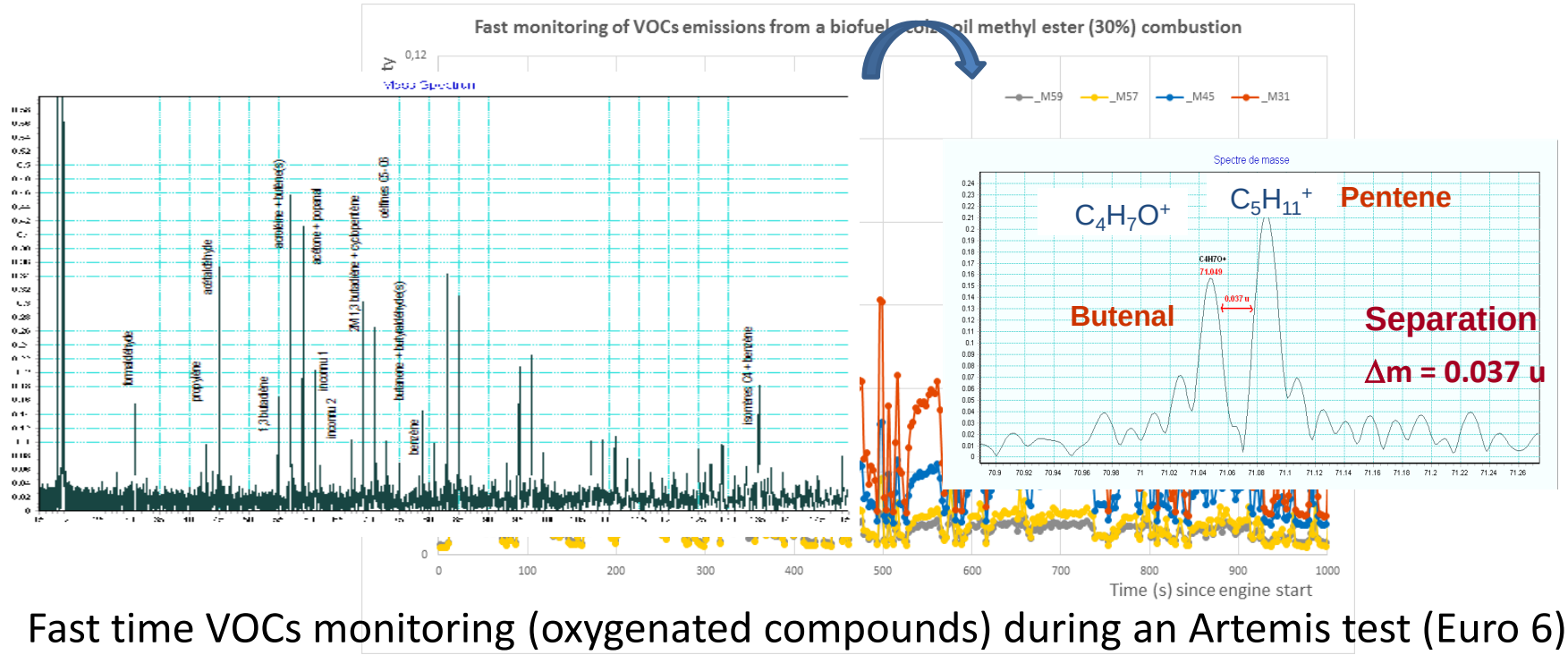
Specific wavelength response: C-H (alkanes, aromatics); O-H (alcohols, water); C=O (carbonyl compounds); C=O (carbon monoxide); C=O (carbon dioxide)



Car exhaust emissions

Test of engines using biofuels : On-line measurements of regulated compounds (NH_3, NO) or unregulated compounds (VOCs).

High resolution is important to separate oxygenated compounds; O (15.9949 u); from hydrocarbons; CH4 (16.0313 u); in car exhaust emissions from a biofuel combustion



Fast time VOCs monitoring (oxygenated compounds) during an Artemis test (Euro 6)

Conclusion/Key points

High resolution MS coupled with Chemical Ionization is well suited for real time exhaustive analysis of volatile organic compounds !

- Broadband detection: full spectrum in one second.
- High resolution and mass precision: determination of molecular formula.
- No water cluster $H_3O^+(H_2O)$,… → detection of VOCs in water.
- Quantitative measurements with or without calibration


Engine emissions


Indoor air pollution


Materials degradation


Environmental analysis


Industrial process

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