AlyXan
INNOVATIVE ANALYSIS

# Real time monitoring of Volatile Organic Compounds (VOCs) in submarine air by Chemical Ionization Mass Spectrometry

**Julien Leprovost**
**Applications Engineer**

# Analytical strategies to measure VOCs into a French submarine

SSBN (nuclear powered, ballistic missile submersible ships)

Indoor air

In order to refresh air supply

Oxygen production plant

$VOCs/CO_2$ removal plant

**Current method: off-line analysis**

**A new approach: on-line analysis**

Off-line analysis are made by TD-GC/MS according to the standard ISO 16000-Part 6

**The French DGA propose to use an embedded analyzer for direct on-line VOCs analysis!**

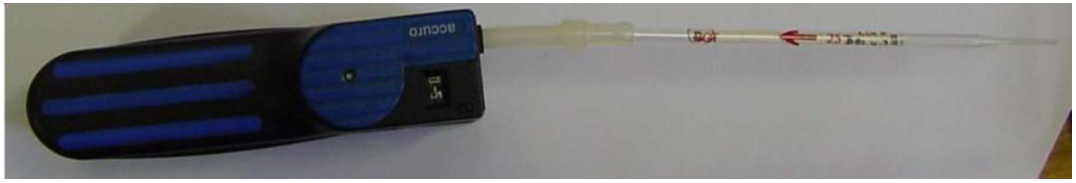
# The current analytical method: off-line analysis

Indoor air

according to the standard ISO « 16000-Part 6 »

## Sampling: on Tenax tubes

- In a place representative of atmosphere average board (every 2 days), or in case of incidents.



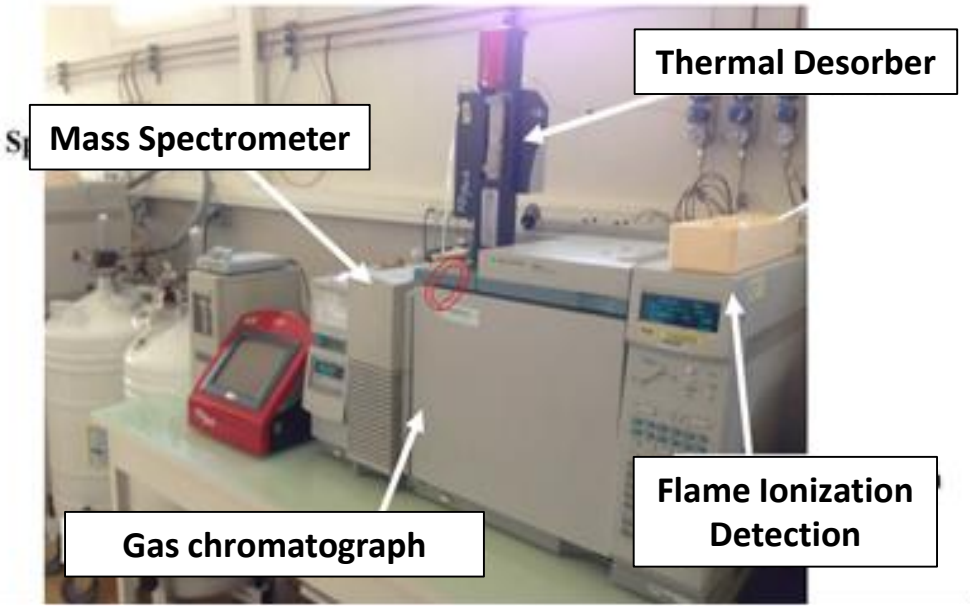
- In order to store properly the samples during the patrol, ends of the Tenax tubes are closed using a glass welding device.

# The current analytical method: off-line analysis

Indoor air

according to the standard ISO « 16000-Part 6 »

**Analysis : by Thermal Desorption – Gas Chromatography / Mass Spectrometry (identification) or FID (quantification)**




- VOCs are measured discontinuously
- All organic compounds cannot be monitored (e.g. formaldehyde)
- Results are known only after the patrol

# A new approach for on-line analysis: SMHR analyzer

Indoor air | VOCs/$CO_2$ removal plant

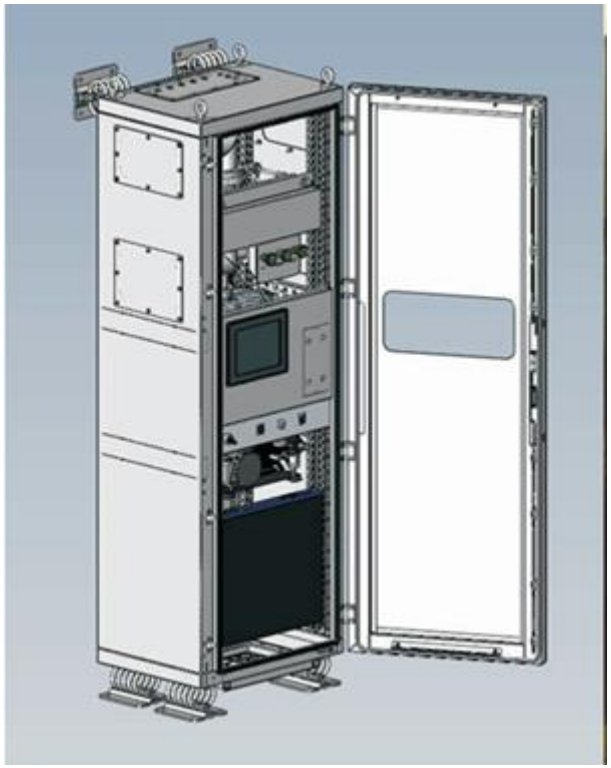
R&D project

**On board analyzer to:**

- Know the air quality (VOCs) on board.
- Broaden the data on submariner exposure.

**2 major challenges:**

- A large variety of compounds to detect simultaneously at trace levels (ppb to ppm).
- Automation of the measurements.

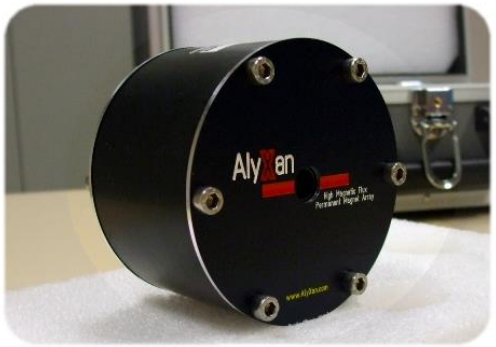


SMHR (high resolution mass spectrometer) conception and development - a BTrap analyzer adapted to submarine environment

# How to measure a complex mixture of VOCs in real-time?

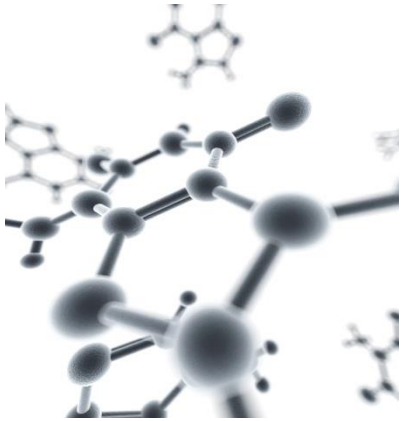
**High Resolution Mass Spectrometry associated to Chemical Ionization can play a key role in this field!**

## Fourier Transform Ion Cyclotron Resonance (FTICR)




- A magnetic trap analyzer, using a permanent magnet.
- Ions rotation frequencies are measured in the analytical cell for mass attribution.

## Chemical Ionization (CI)



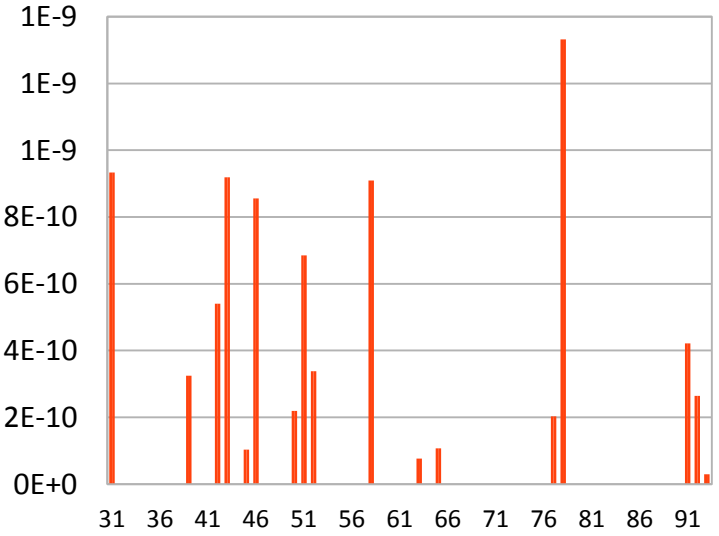
- Several "ion-molecule" reactions are available for a versatile, sensitive and quantitative measurements.

# Chemical Ionization

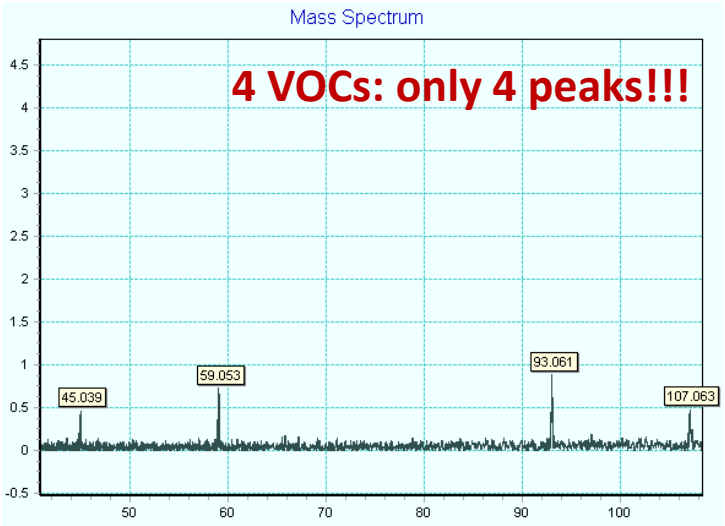
## Key points:

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

**IE 70 eV**




**PTRMS**




**Sample: (acetaldehyde, acetone, toluene, xylene) – A few ppm in air (matrix)**

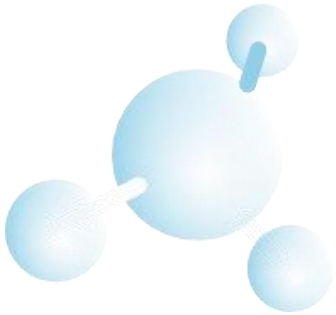
## Our standard chemical ionization method for the most exhaustive analysis:

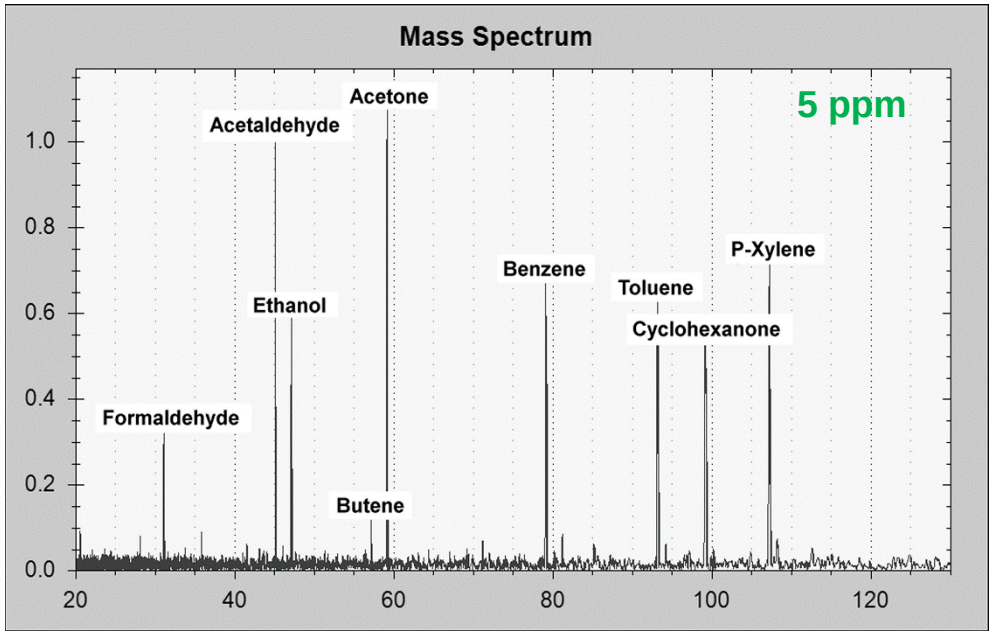
**PTRMS**

(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?

## Standard CI method

**$H_3O^+$**

Alkenes
Aromatics
Alcohols
Acids
Aldehydes
Amines
….

## Specific CI methods

| **$O_2^+$** | **$O^-$** | **$CF_3^+$** |
|---|---|---|
| NO | Freon R134a | Cyclohexane |
| $NO_2$ | … | Alkanes (Tot.) |
| COS | | |
| Decane | | |
| … | | |

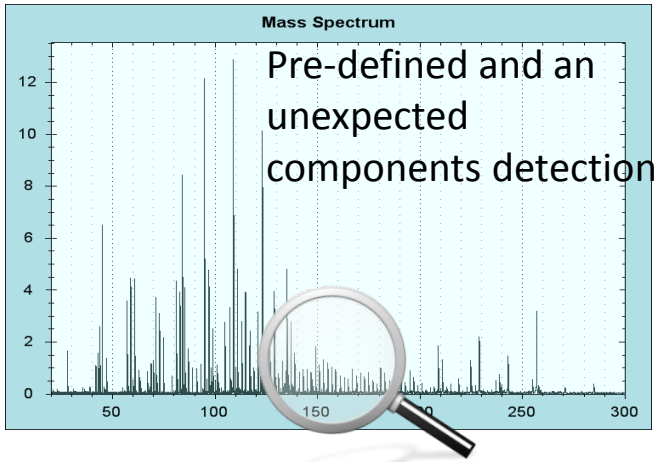
**Ex. R134a specific detection:**

$$O^- + C_2H_2F_4 \rightarrow C_2F_4^- + H_2O$$

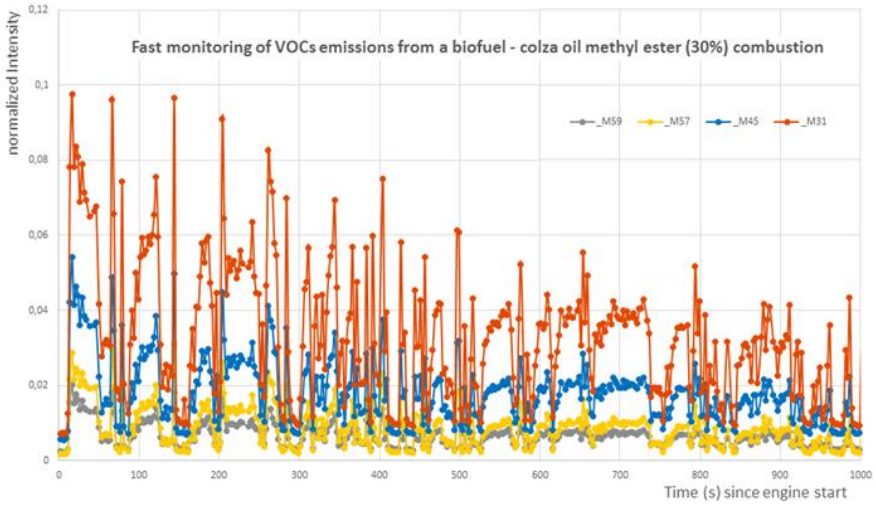
**Possibility to work sequentially with several precursor ions (chemical ionization methods): $O_2^+$, $CF_3^+$, $O^-$, $NO^+$ and so on.**

# FTICRMS: High resolution solution for VOCs analysis

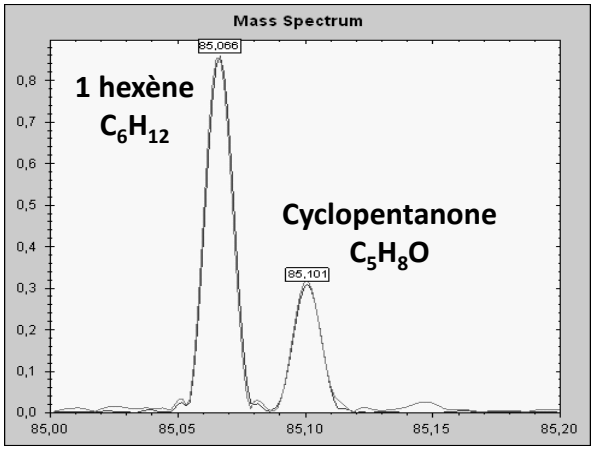
## Broadband detection: monitoring/screening…




## Fast response time




## High resolution




Isobaric separation

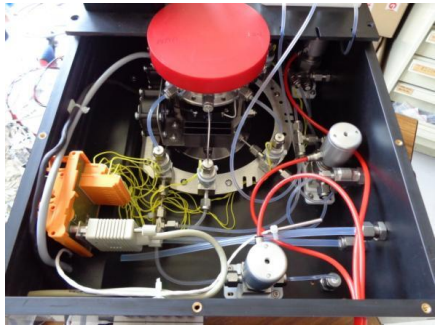
## Identification

Measured mass (M+1)

Difference with exact mass (< $5.10^{-3}$ u)


Chemical attribution:
$C_3H_6O$ (Acetone)

# SMHR analyzer: technical data



Turbomolecular pumps

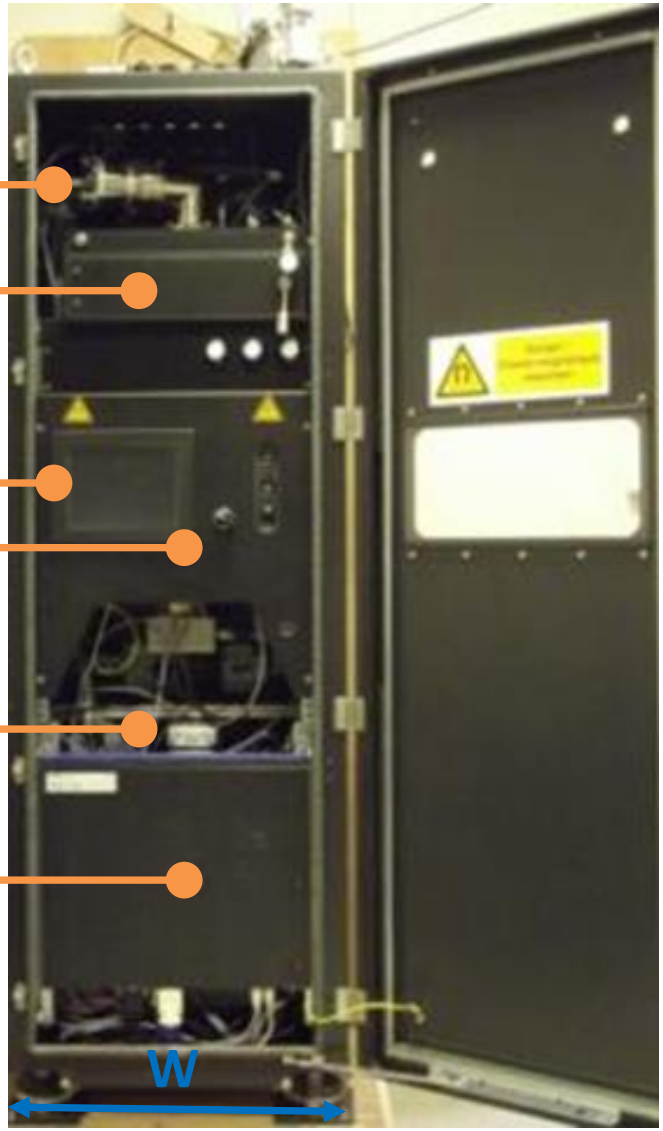
Sampling gas system

Touch-screen display

1,5 T permanent magnet
with analytical cell

Air compressor

Embedded computer




**width: 57 cm, height: 173cm, depth: 55cm**
**weight ~ 250 kg**
**No cryogenic fluid, no sample preparation**

# SMHR analyzer: technical data

## Sensitivity in direct injection

- ~ 200 ppb / Response time: a few seconds (regardless the number of analytes to detect).

## Sensitivity with a MS accumulation step

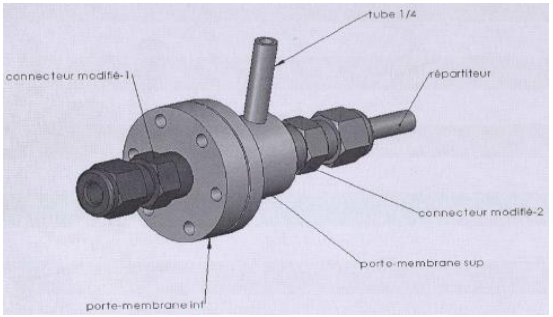
- ~ 10 ppb / Response time: a few minutes (regardless the number of analytes to detect).

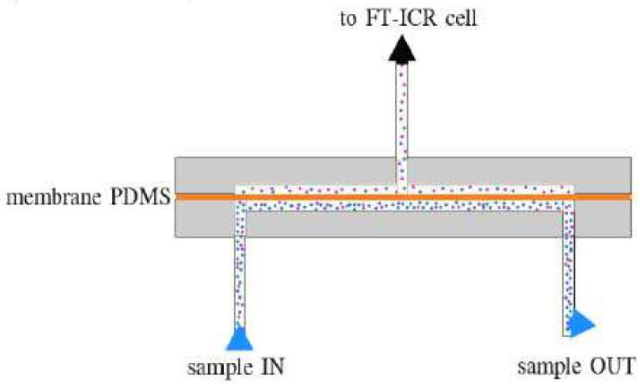
## Sensitivity with a preconcentration step: Membrane Inlet MS (MIMS)

- A few ppb / Response time: a few minutes (regardless the number of analytes to detect).

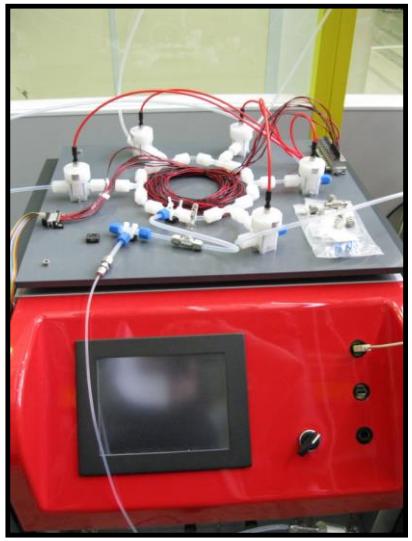
<u>On-line preconcentration</u>

Enrichment factor: 10-1000 (depending the analyte)

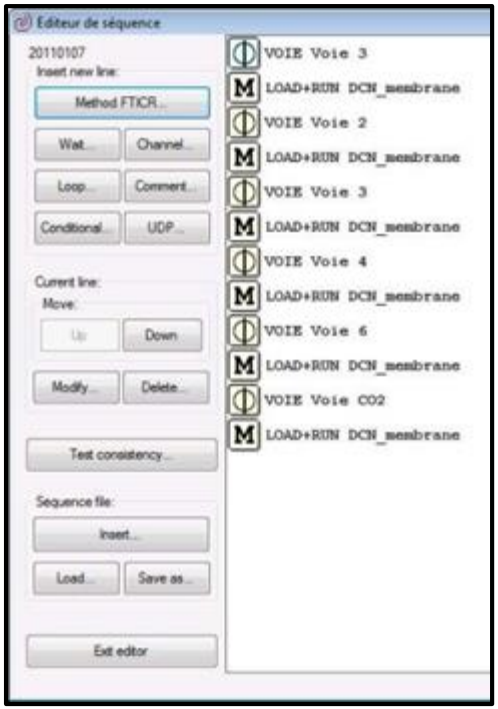


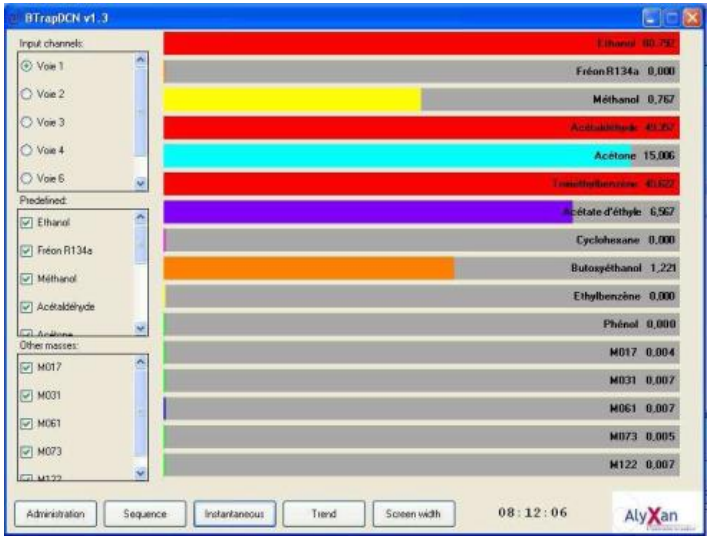
# Automation of the system for VOCs monitoring at several sampling point



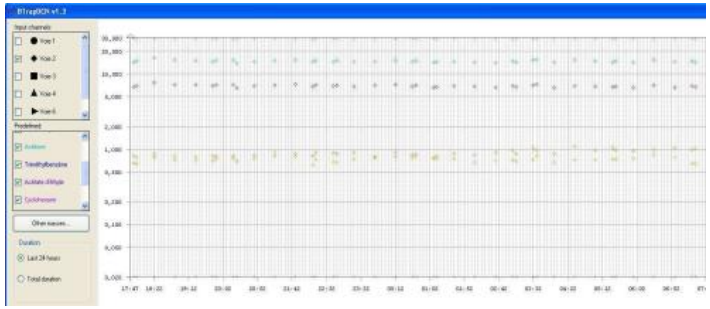
**Sequential analysis of sampling points from VOCs/$CO_2$ removal plant**




**Sequence of analysis**




**Instantaneous quantification**

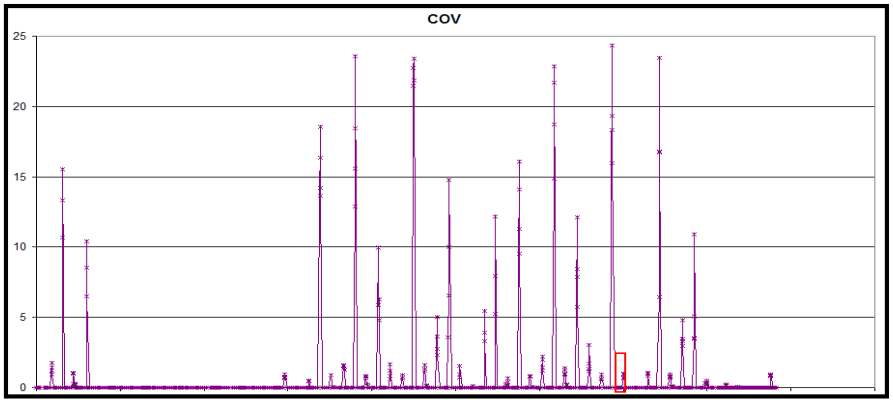


**VOCs monitoring in real time**

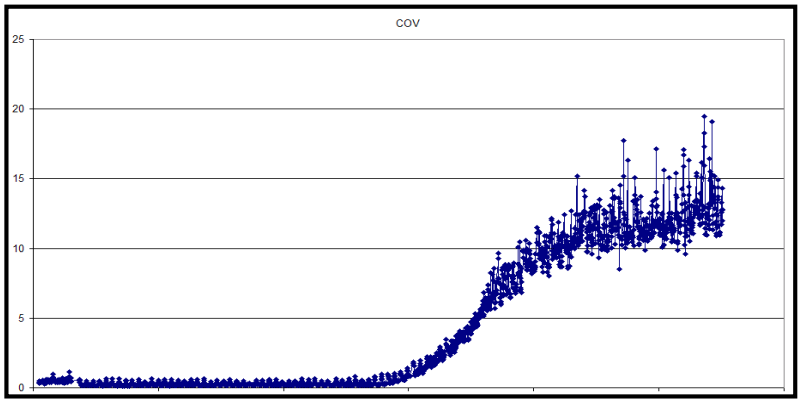
# Measurements on a VOC/$CO_2$ removal plant

## Air purification unit efficiency tests

- VOCs removal is made by successive filtration step: a cooling unit, activated charcoal unit, catalyst and so on.
- 7 sampling points from the plant, to characterize the filter units, have been sequentially monitored in real-time.
- Measurements during 35 days (24h/day) without any assistance, with a measurement every 10 min per sampling point.




**Regeneration step of a filter**

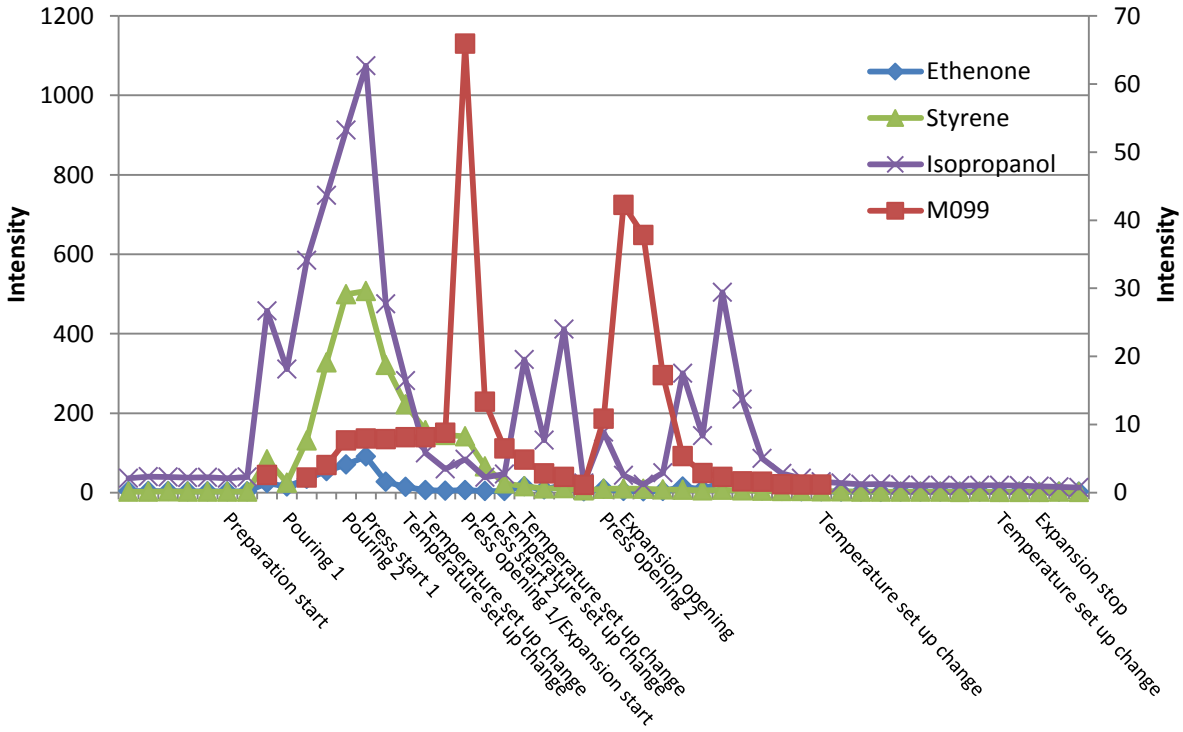


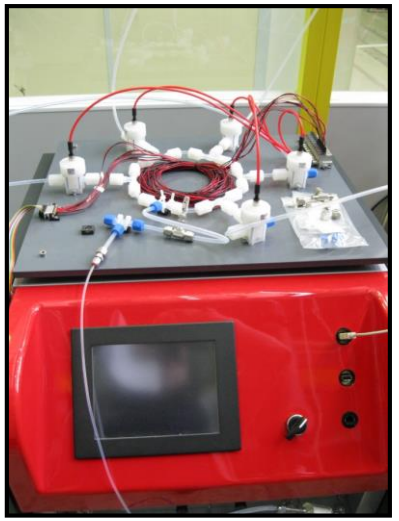

**Breakthrough time of the activated charcoal filter**

# Indoor pollution

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

The use of a multiplexing system is needed for a sequential analysis of the pollutants emission from the different parts of the industrial process.



# Conclusions/Perspectives

**High Resolution Mass Spectrometry coupling with Chemical Ionization is well suited for real time exhaustive analysis of volatile organic compounds.**

- SMHR analyzer is a prototype.
- About six measurement campaigns on air purification units has been realized with such analyzer:
  - With bench tests in order to evaluate the analyzer.
  - With new plants in order to characterize them in operation.
- Sea trials, with the SMHR analyzer, are planned to begin next year on SSBN.
- Developments for an analyzer more compact are possible.

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M. Colombier

E. Rabillard
E. Coat
J. Salaun
K. De Cadenet
F. Mesnage
H. Quéré



**Contact:**

**julien.leprovost@alyxan.fr**

Phone : +33 1 69 96 95 19