A transportable FTICR/MS for direct and real-time analysis of VOC contaminants in air and water

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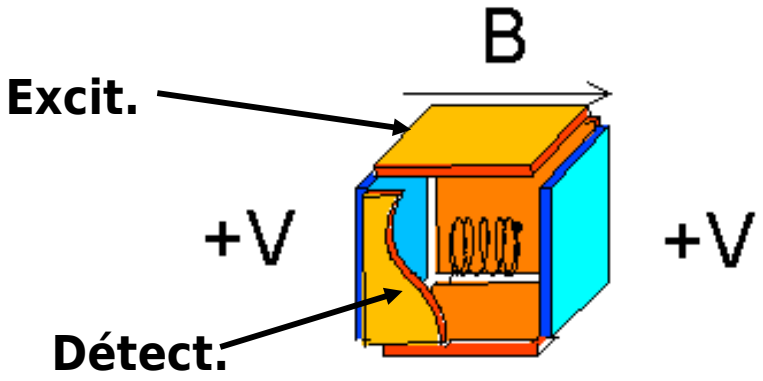
Outline

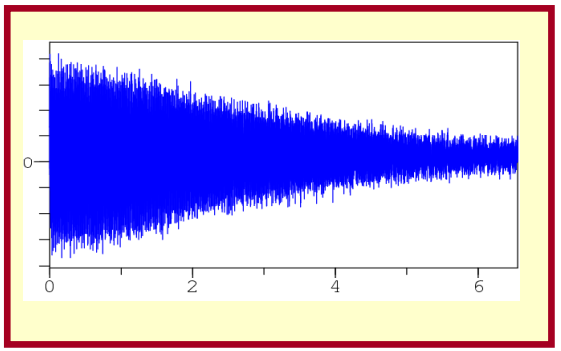
- FTICR mass spectrometry : a brief introduction
- Transportable FTICR : Micra and B Trap
- Traces analysis : chemical ionization
- A few applications
- Specific instruments
- Summary

FTICR spectrometry

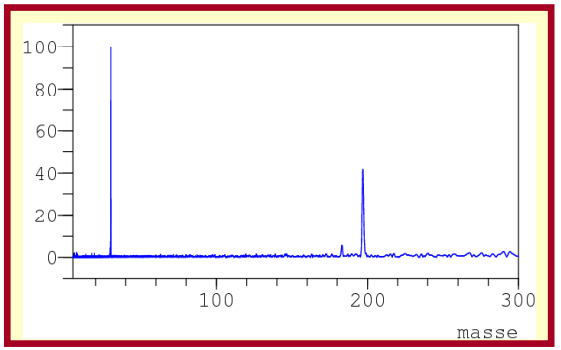


Frequency measurment in a magnetic trap

$$\nu_c = \frac{qB}{2\pi m}$$



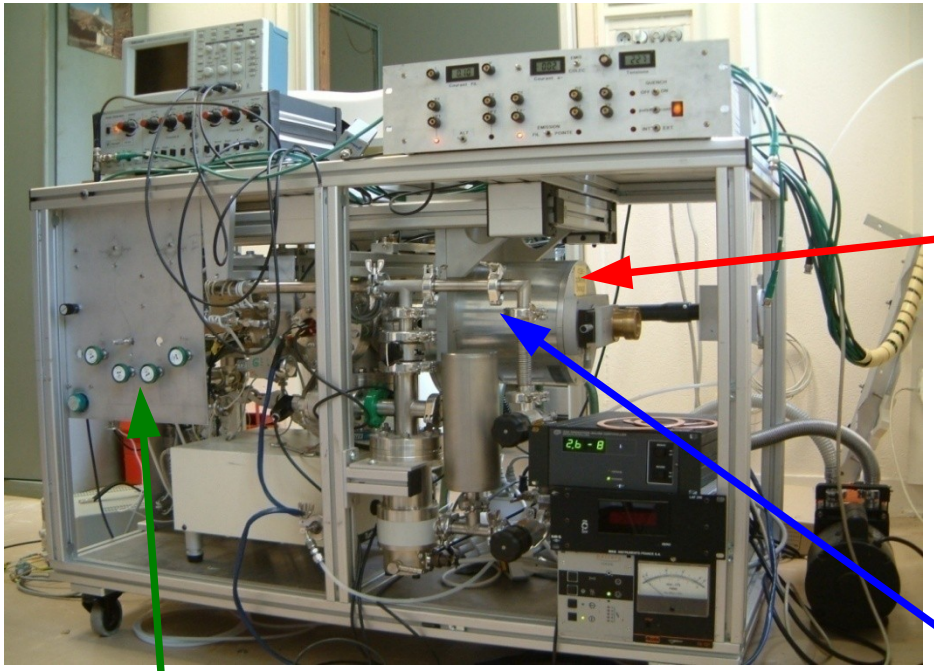
FT

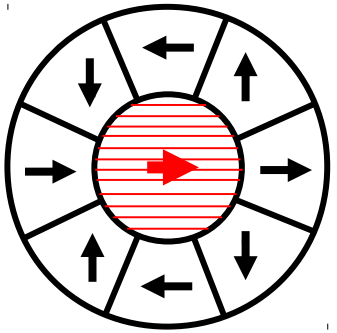


- mass resolution => formula
- trapping => controlled time sequence
- mass selection => precursor formation
- time control => controlled reaction kinetic

MICRA : Mobile ICR Analyzer (2004)

G. Mauclaire *et al.*, Eur. J. Mass Spectrom. 2004, *10*, 155-162

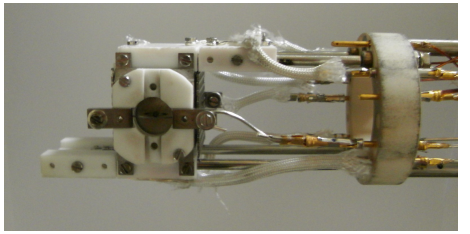




permanent magnet
Halbach structure
1,24 T, radial field

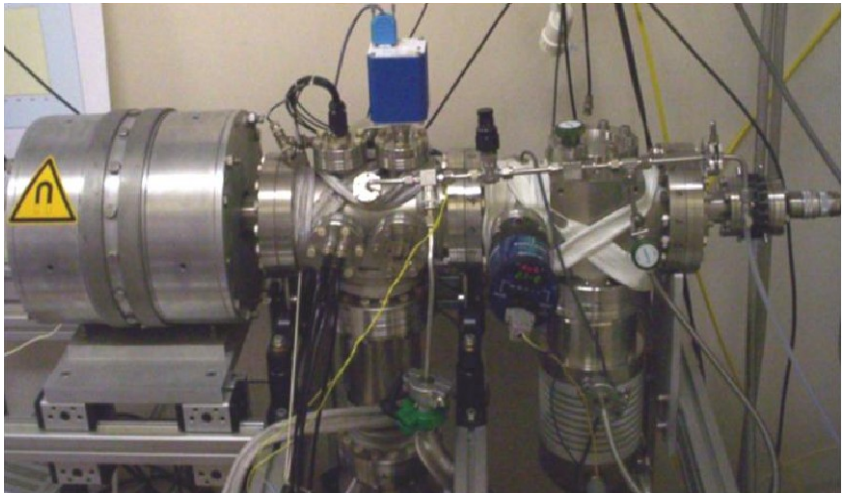
gas inlets :
4 + membrane inlet
(3-way pulsed valves)

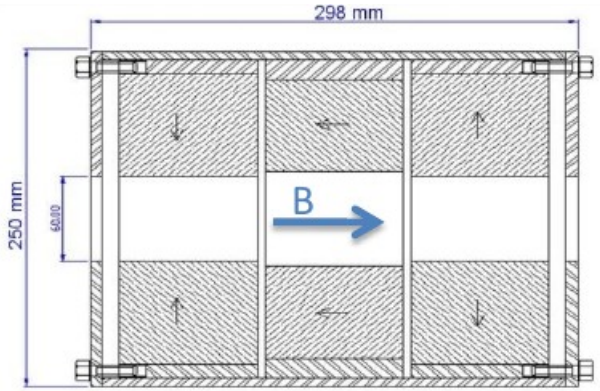
cubic cell
2x2x2 cm



Transportable FTICR

Axial field instrument

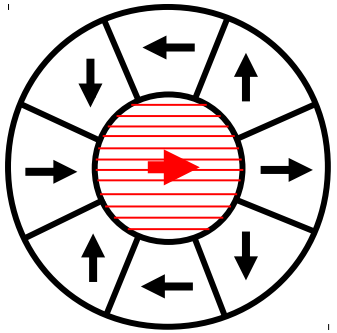




B Trap
radial (1 to 1,5 T) or axial
@1,5 T : DL = 200 ppb

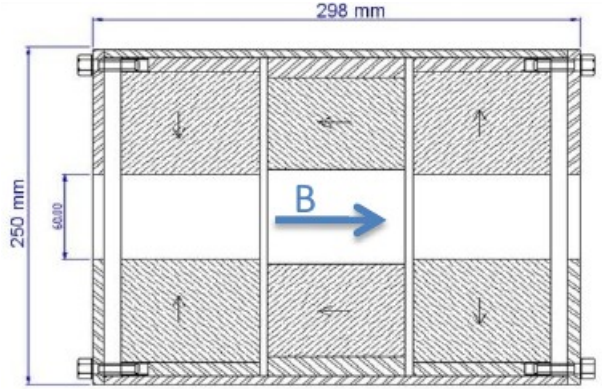
Permanent magnet

Halbach structure : cylinder, radial field



B = 0.8-1.5 T
weight ~12 kg
NdFeB

Axial field



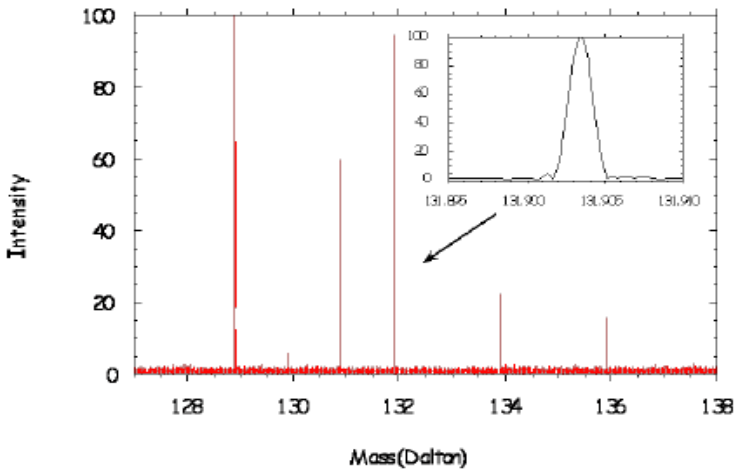
Standard Halbach homogeneity : 10^{-2}
Association of two cylinders : 10^{-3}

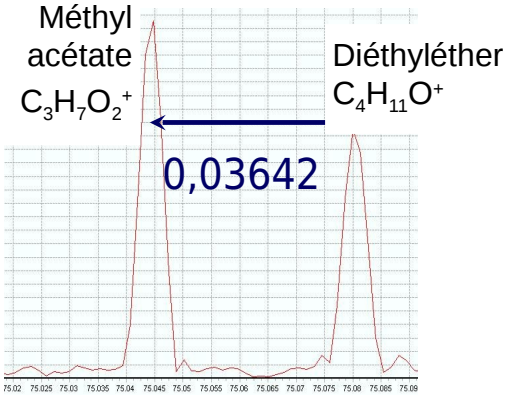
B = 1.1 T (less than radial)

MICRA : performance

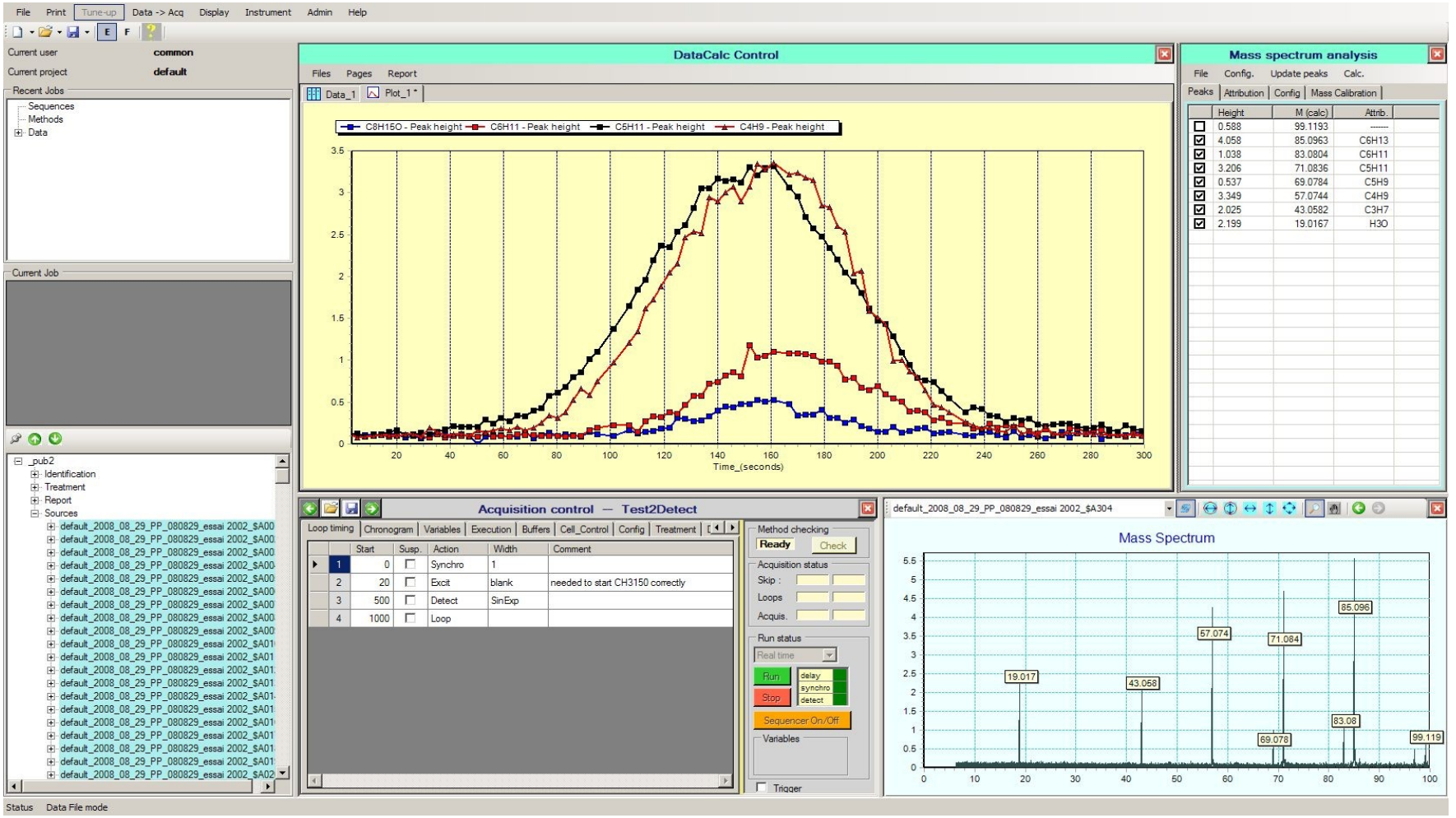
G. Mauclaire *et al.*, Eur. J. Mass Spectrom. 2004, ***10***, 155-162

- Resolving power : m/Δm > 70000 @ m/z 131
- Mass Domain : 2-500
- Separation @72
- Ionization : electronic and chemical

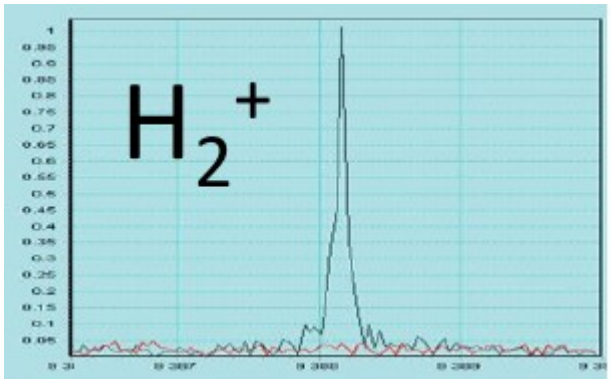


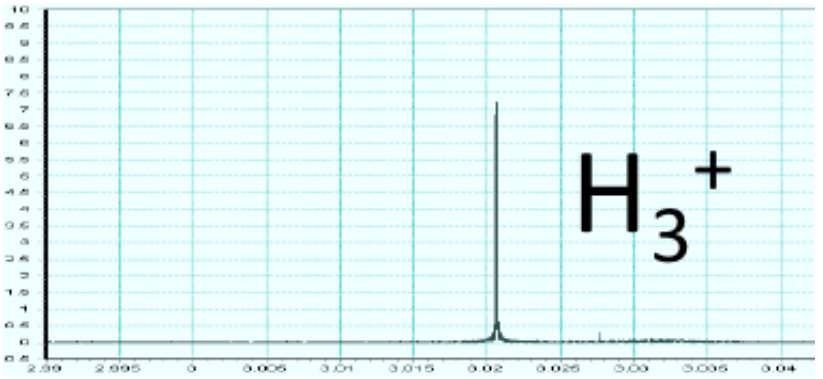


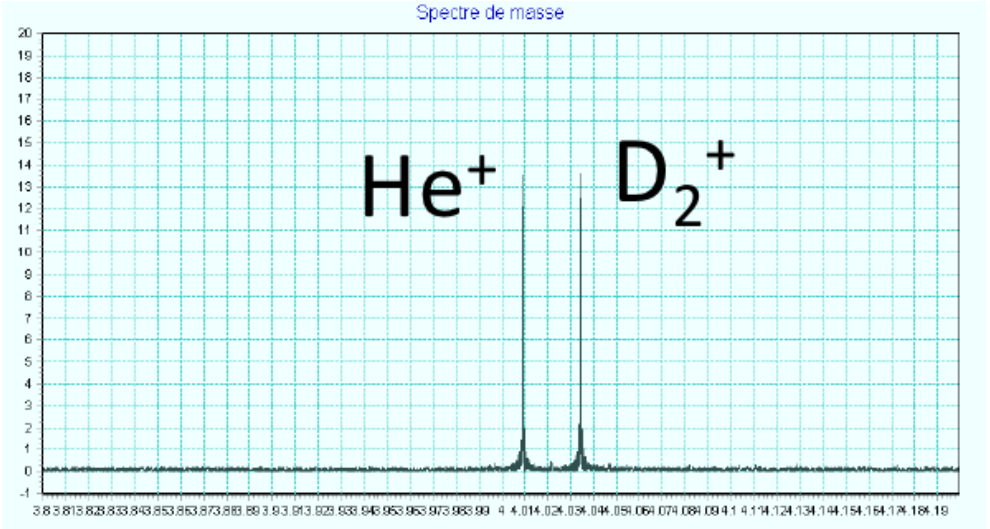
Software


File Print Tune-up Data -> Acq Display Instrument Admin Help
Current user common
Current project default
Recent Jobs
Sequences
Methods
Data
Current Job
_pub2
Identification
Treatment
Report
Sources
DataCalc Control
Files Pages Report
Data_1 Plot_1
C8H15O - Peak height C6H11 - Peak height C5H11 - Peak height C4H9 - Peak height
Time_(seconds)
Mass spectrum analysis
File Config. Update peaks Calc.
Peaks Attribution Config Mass Calibration
Height M (calc) Attrib.
0.588 99.1193
4.058 85.0963 C6H13
1.038 83.0804 C6H11
3.206 71.0836 C5H11
0.537 69.0784 C5H9
3.349 57.0744 C4H9
2.025 43.0582 C3H7
2.199 19.0167 H3O
Acquisition control — Test2Detect
Loop timing Chronogram Variables Execution Buffers Cell_Control Config Treatment
Start Susp. Action Width Comment
1 0 Synchro 1
2 20 Excit blank needed to start CH3150 correctly
3 500 Detect SinExp
4 1000 Loop
Method checking
Ready Check
Acquisition status
Skip :
Loops
Acquis.
Run status
Real time
Run
Stop
delay
synchro
detect
Sequencer On/Off
Variables
Trigger
default_2008_08_29_PP_080829_essai 2002_$A304
Mass Spectrum
19.017
43.058
57.074
71.084
85.096
69.078
83.08
99.119
Status Data File mode

Low mass domain





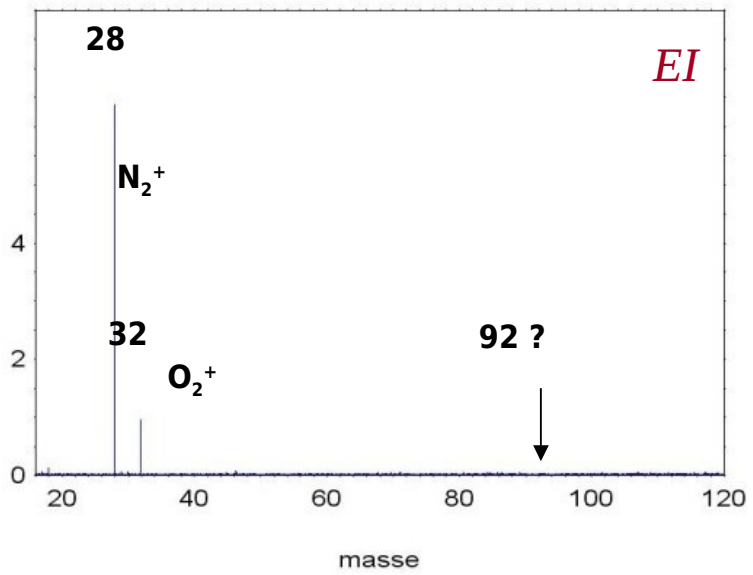


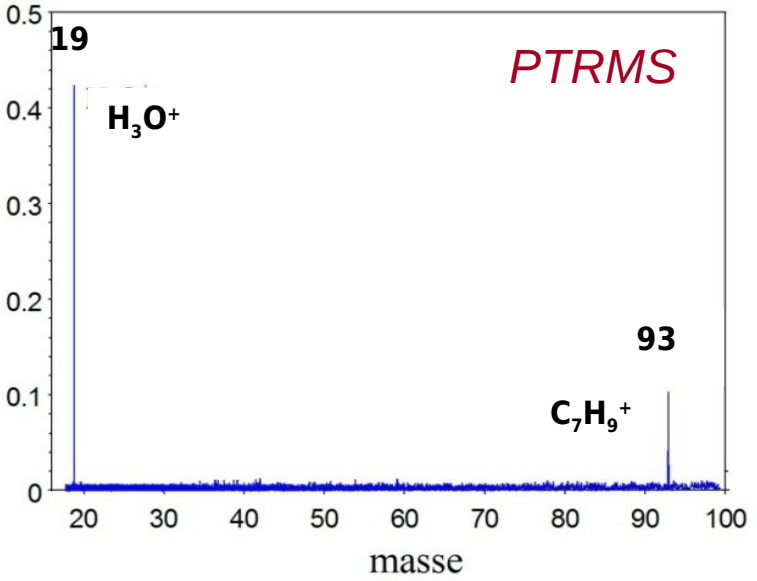
He^+ 4.00260 dalton
D_2^+ 4.02800 dalton

Ionization and traces

C. Dehon *et al.*, IJMS, 2008, *272*, 29-37

- soft ionization : little fragmentation
- specific : based on ion-molécule reaction (no matrix ionisation)





Quantitation

C. Dehon *et al.*, IJMS, 2008, *272*, 29-37

$$H_3O^+ + M \rightarrow MH^+ + H_2O \qquad k_M$$

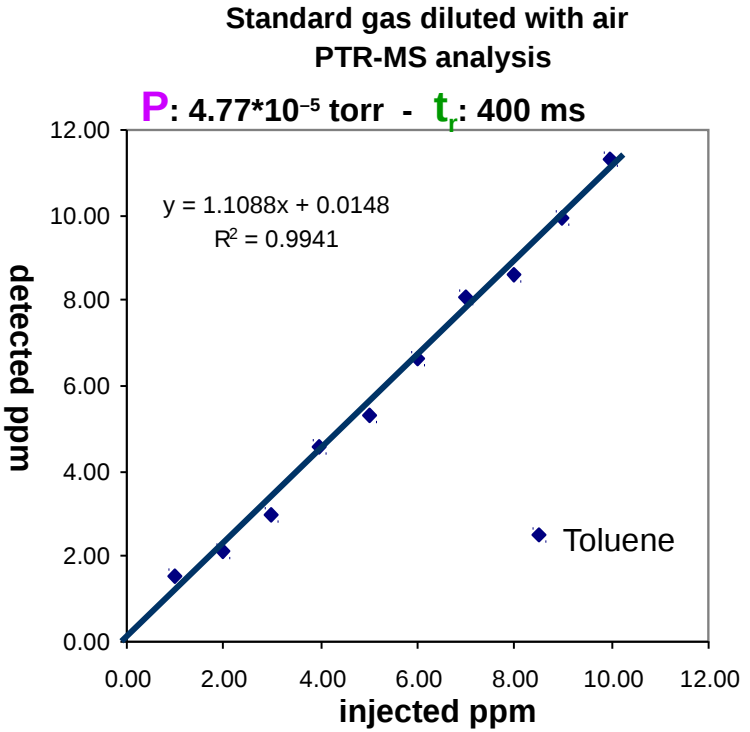
Rate constant

$$d(MH^+) / dt = k_M [M] t$$

$$[M] = \frac{-\ln(H_3O^+) \times (MH^+)}{k_M t_r \ (1-(H_3O^+))}$$

Relative abundance
Reaction time
Pressure

$$\text{At } 300 \text{ K}: \ X_M \text{ (ppm)} = \frac{10^6 [M]}{P(\text{torr}) \times 3.21 \times 10^{16}}$$

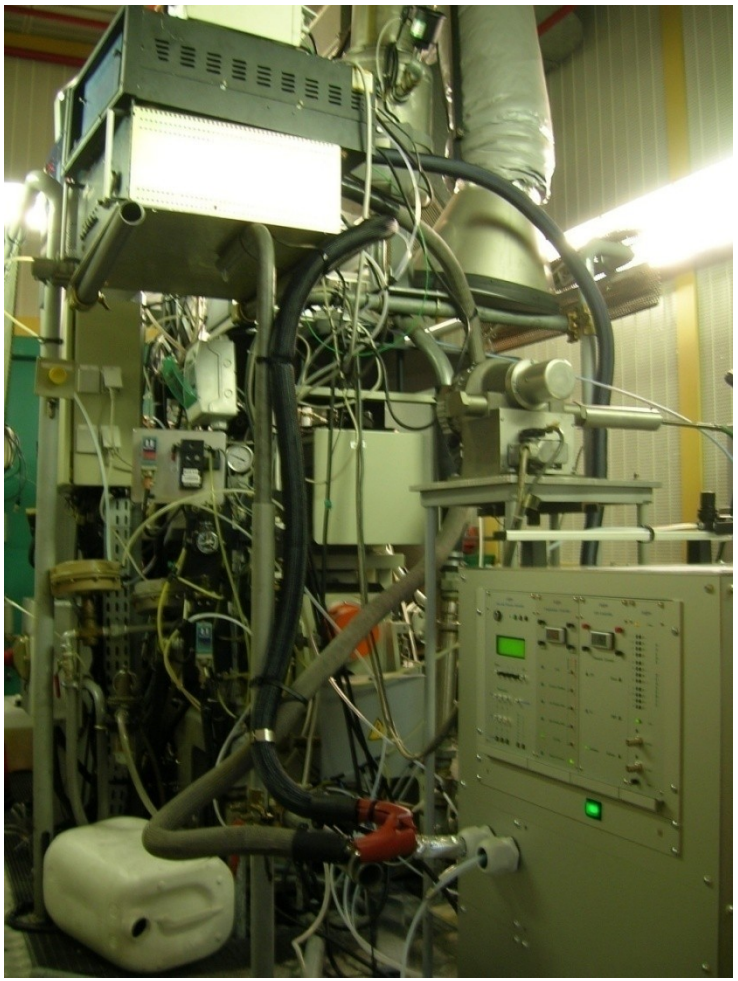


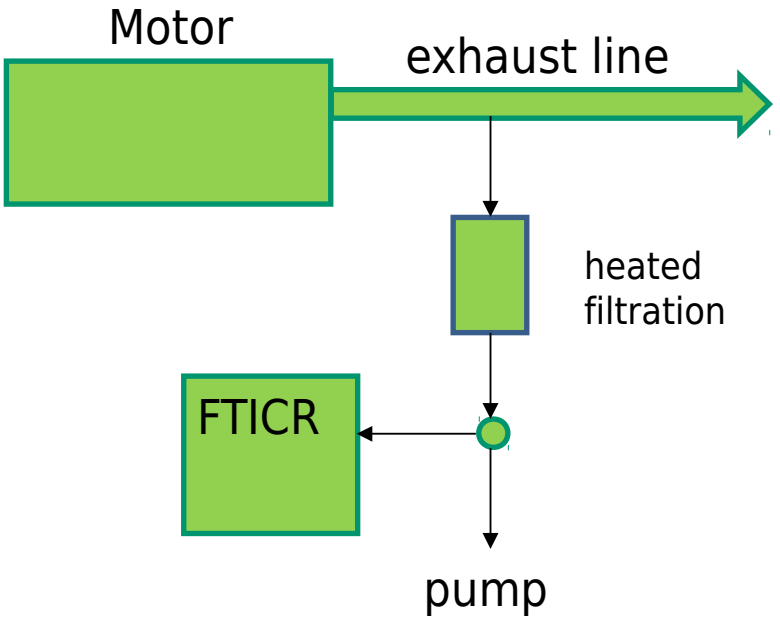
Chemical Ionization : precursors

C. Dehon *et al.*, IJMS, 2008, *272*, 29-37
C. Dehon *et al.*, IJMS, 2011, *299*, 113-119

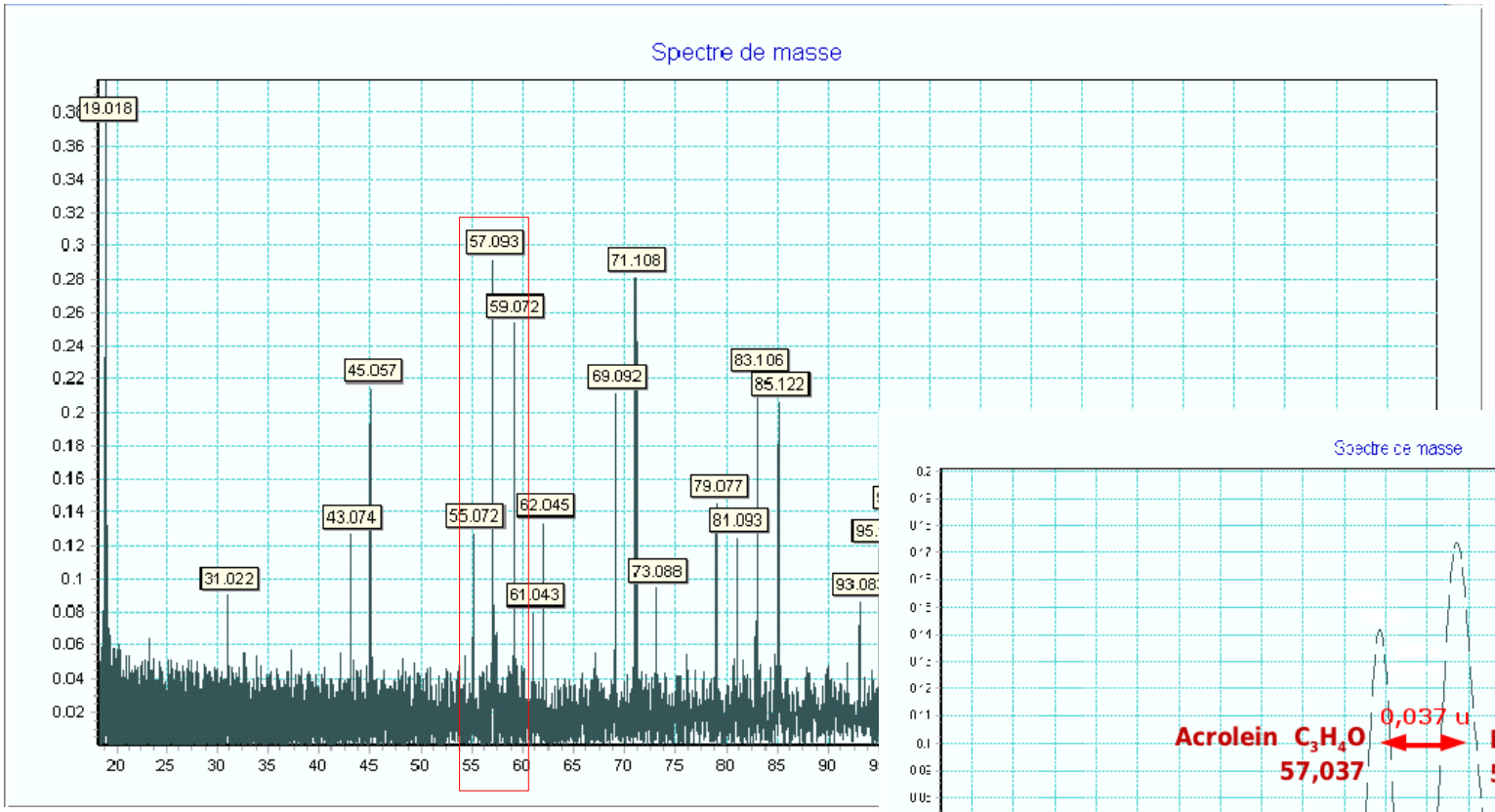
	precursor formation	ions formation	alkanes C_3H_8	CFC,… CH_2FCF_3 (R134a)	HCFC, THM,… $CHCl_3$	Oxygenated,… C_3H_6O
H_3O^+	$H_2O + e^-_{70eV} \rightarrow H_2O^{+\cdot} + 2e^-$ $H_2O^{+\cdot} + H_2O \rightarrow H_3O^+ + HO^\cdot$	$H_3O^+ + M \rightarrow H_2O + \mathbf{[M+H]^+}$				$C_3H_7O^+$ 4,1 [3,9]
CF_3^+	$CF_4 + e^-_{70eV} \rightarrow CF_4^{+\cdot} + 2e^-$ $CF_4^{+\cdot} \rightarrow CF_3^+ + F^\cdot$	Ex : $CF_3^+ + RX \rightarrow CF_3X + \mathbf{R^+}$	$C_3H_7^+$ 0,5 [1,1]	$C_2H_2F_3^+$ 1,1 [1,8]	$CHCl_2^+$ 0,2	$C_3H_6F^+$ 1,1 [2,6]
HO^-	$H_2O + e^-_{7eV} \rightarrow H^\cdot + HO^-$	$HO^- + M \rightarrow H_2O + \mathbf{[M-H]^-}$		not tested	Ccl_3^- 3,4 [2,3]	$C_3H_5O^-$ 5,0 [4,0]

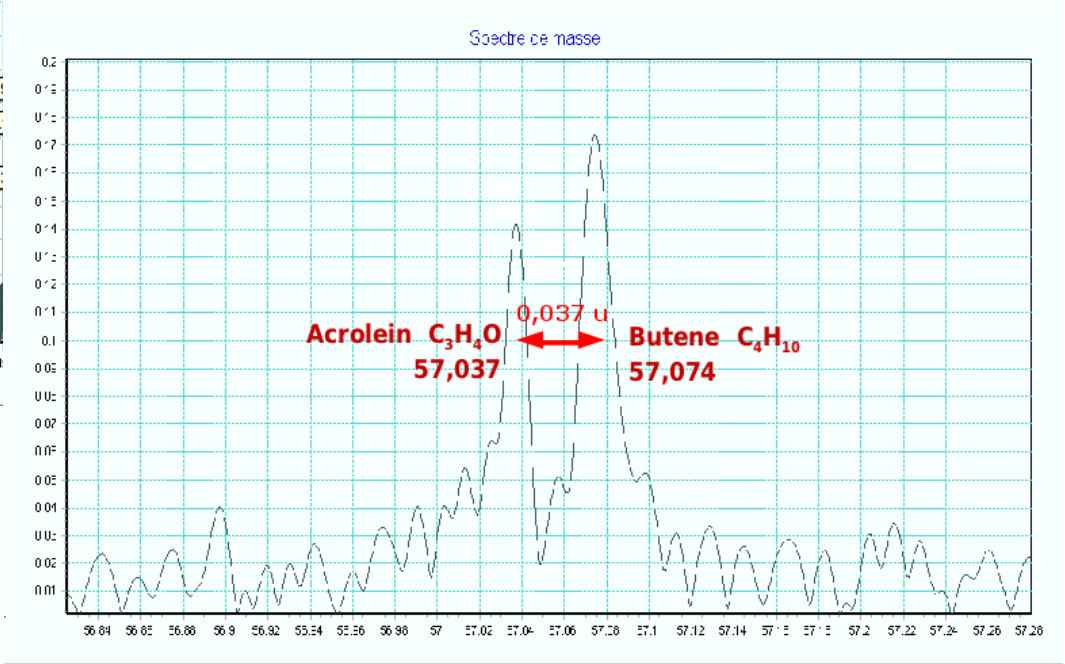
Exhaust fumes analysis (IFP)



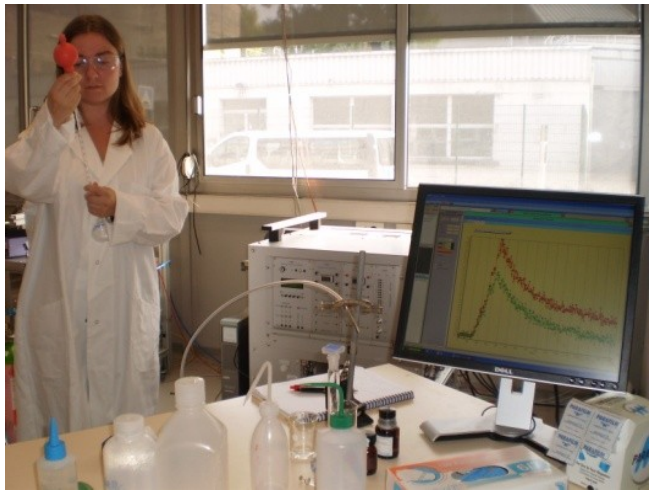


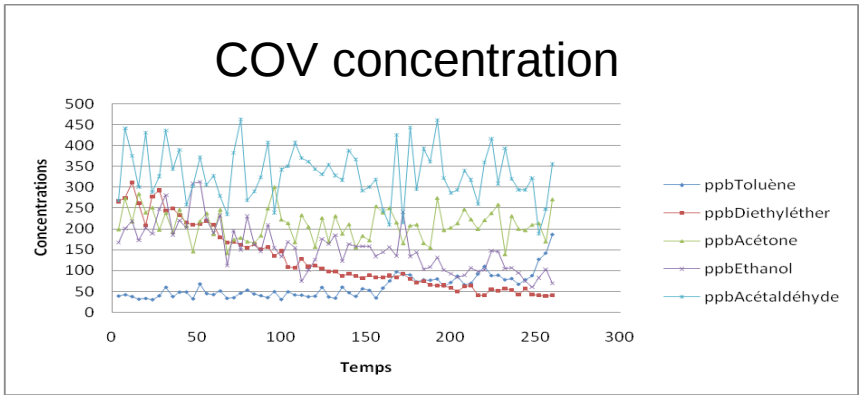
Exhaust fumes analysis

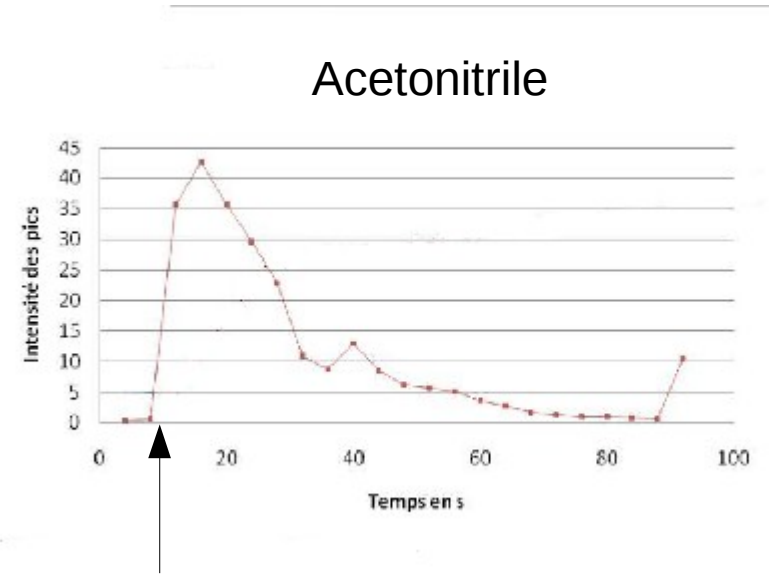




Air analysis : organic chemistry lab







Fridge door open

Water analysis : Membrane Introduction

PDMS

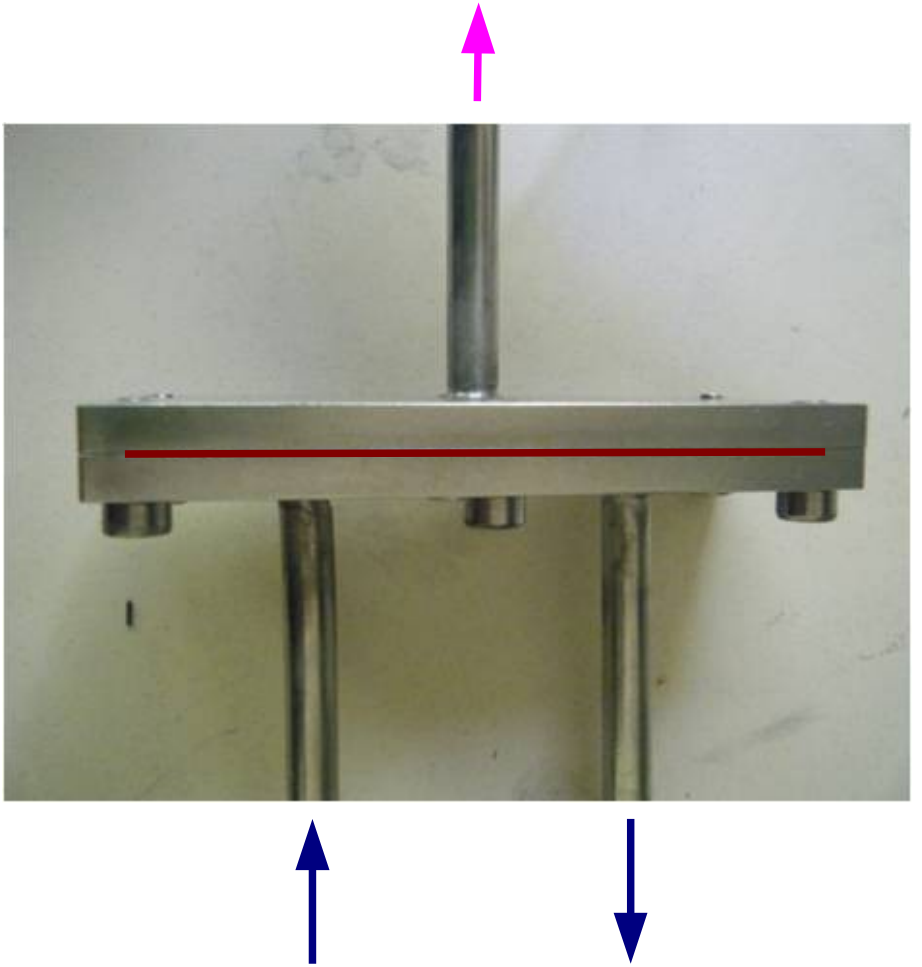
planar

50 or 125 µm

0,6 cm²

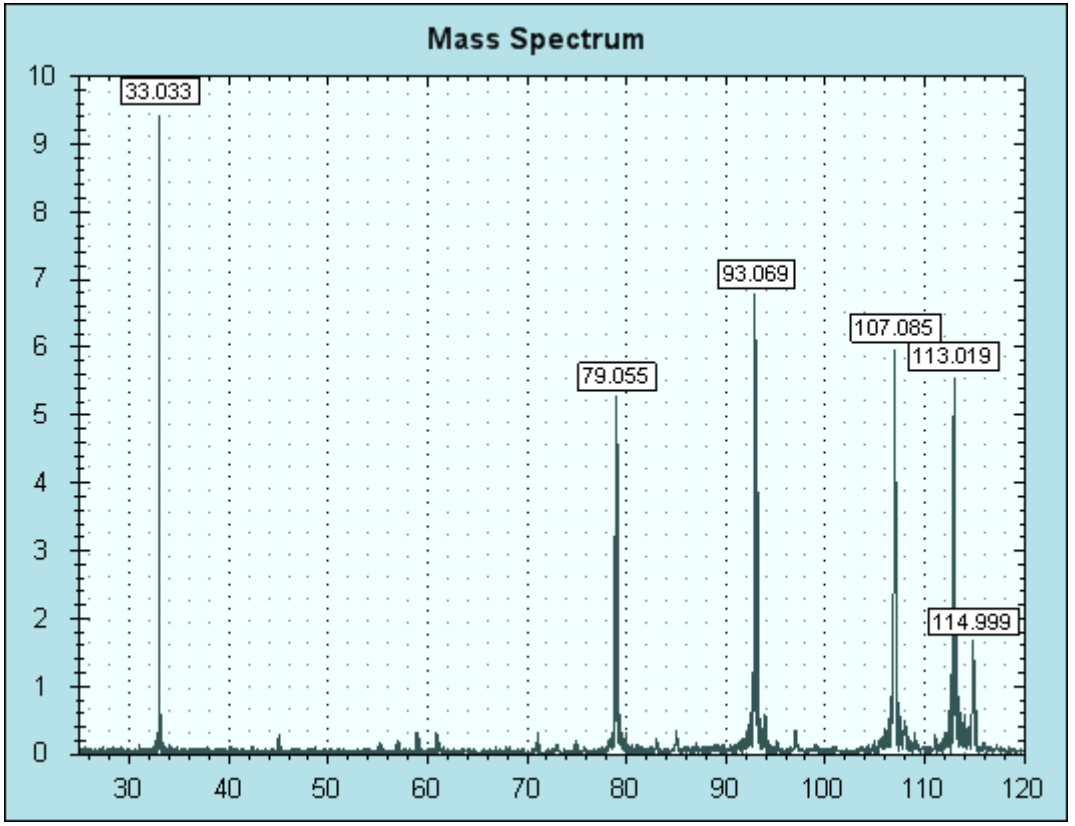
controlled flow temperature

controlled sample flow



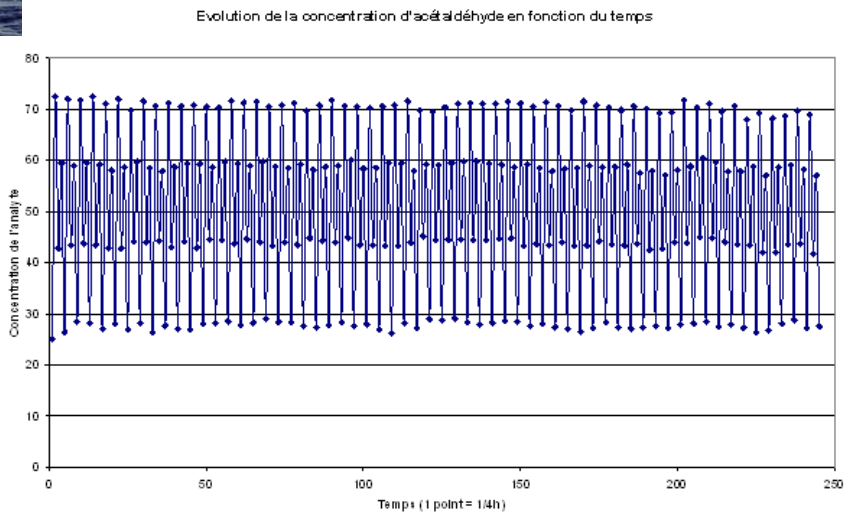
Time response < 1 min

Water analysis : Membrane Introduction



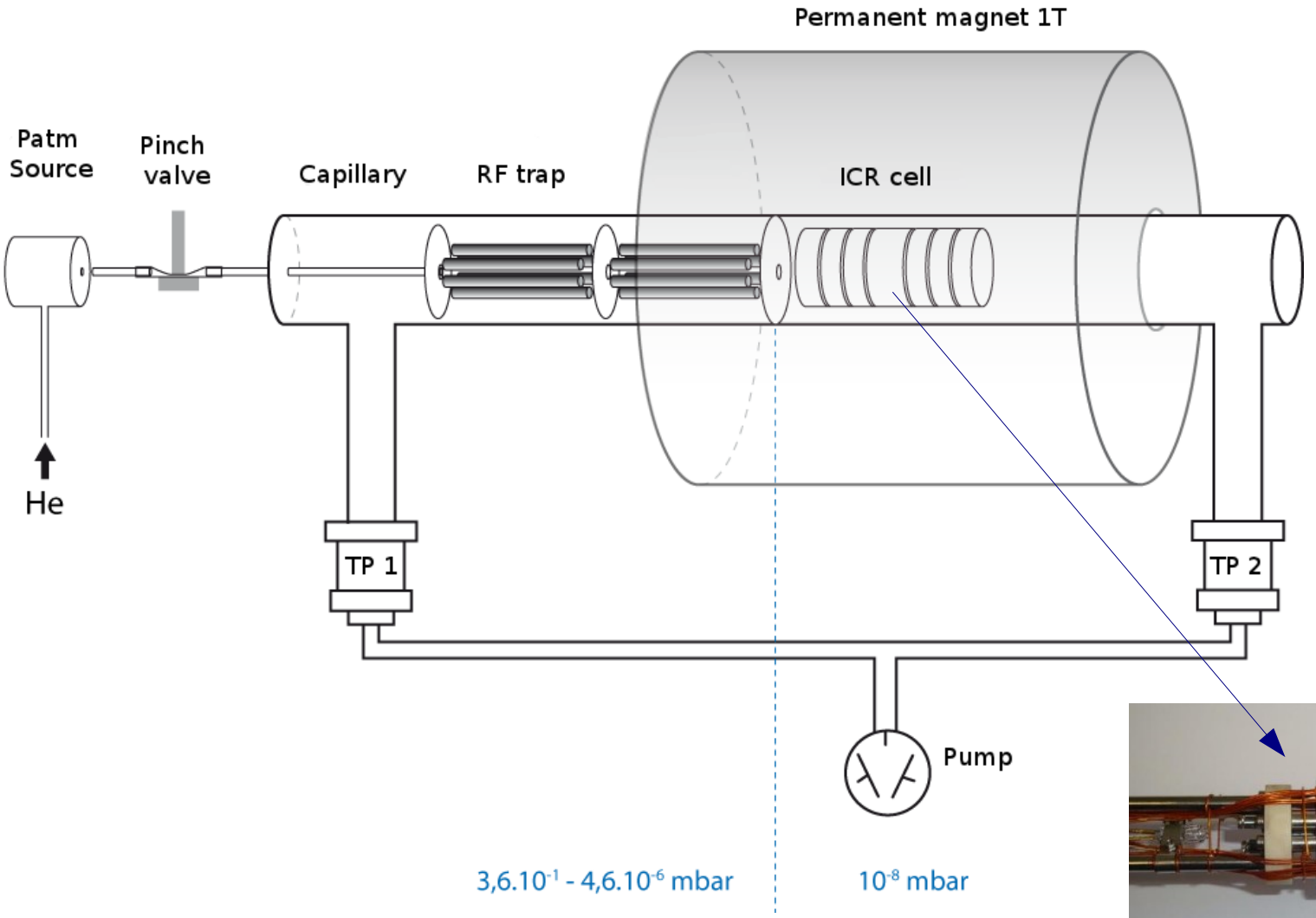
Compounds	Enrichment
BTX	~ 2000
THM	~ 10 000
CHBr3	~ 70 000
chloramines	20-80
Alcool	~ 10
phenol	~ 4

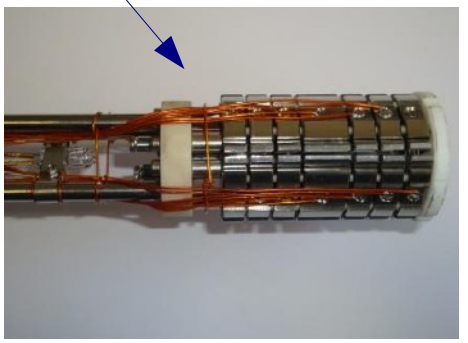
Indoor measurments (DGA)



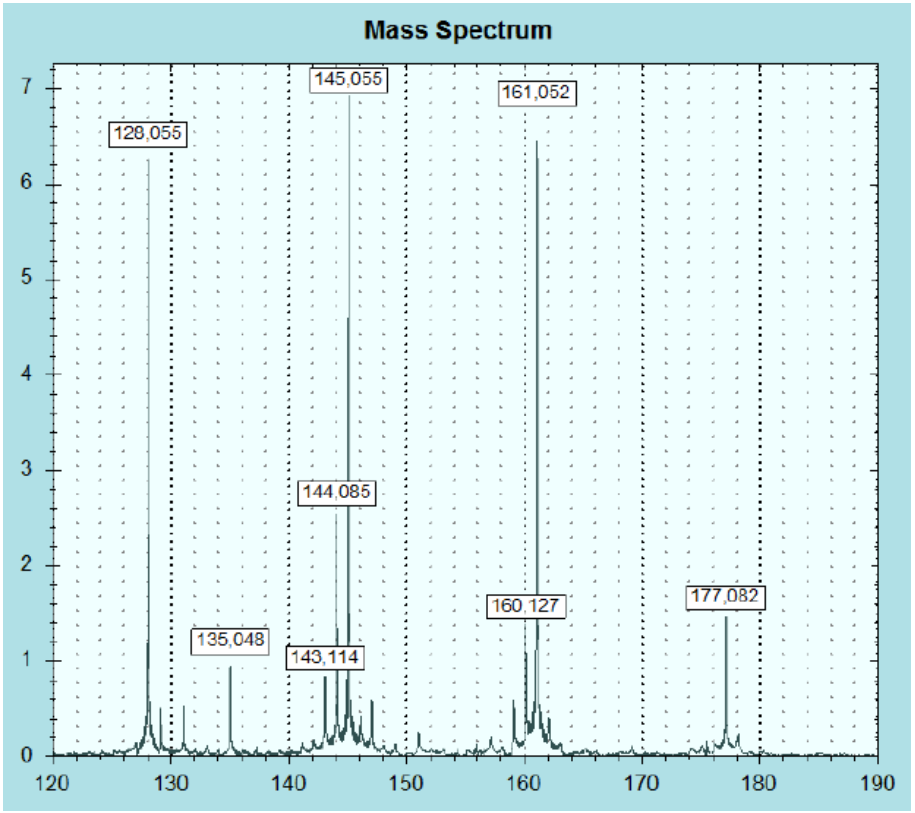
PTRMS,
Acetaldehyde 100 ppm: 220, 800, 400, 600 ppb
Measurement every 15 minutes for 60 h

Ambient ionization

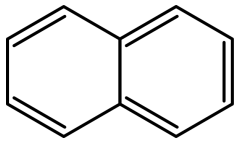




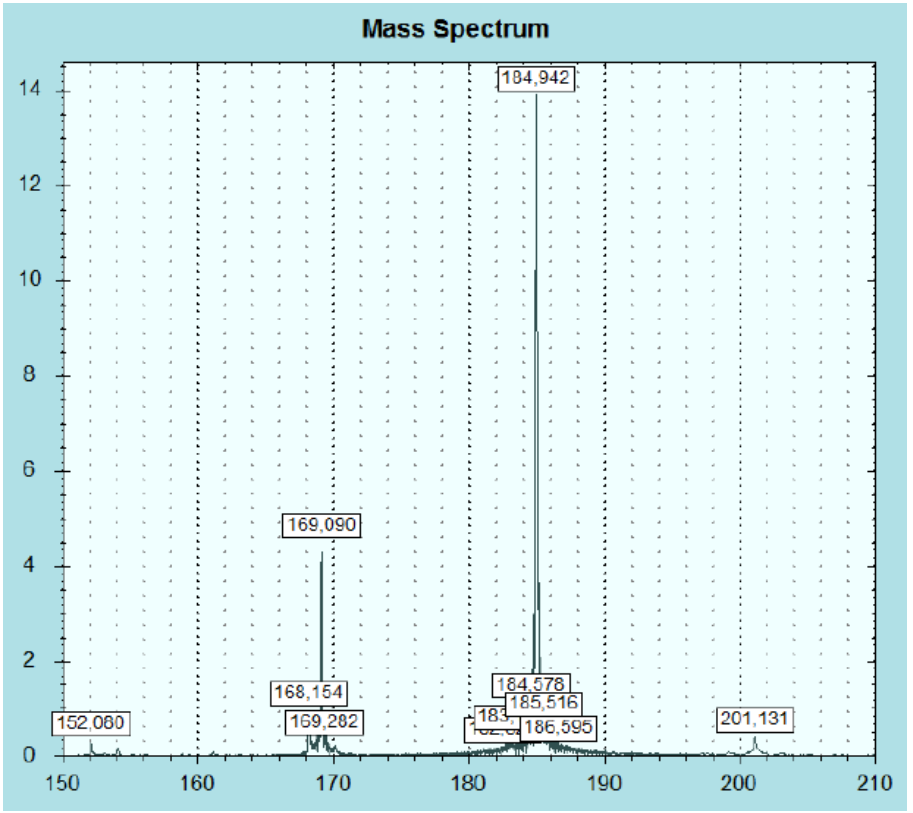
Ambient ionization : HAP identification



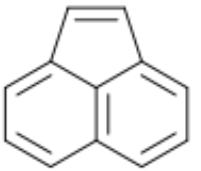
naphtalene



128 u



acenaphtylene



152 u

Conclusions

- Complexe mixture analysis in a few seconds (1s to 4s)
- Identification
- Broadband analysis
- Direct quantification

And Next ?

- Working on size and power consumption :
  - Introduction system
  - Pumping system
- Developing other precursors (negative ionization especially)

Thanks for your attention !

Prof. Hélène Mestdagh

Joël Lemaire

Clotilde Le Vot

Essyllt Louarn

Previous Students :

- Christophe Dehon (PhD 2009)
- Mounem Masri Idlibi (2011)
- Romain Janssoone (2011)
- Mouhamadou Diagne (2010)
- Céline Puig (2010)
- Thibault Navarro (2009)

AlyXan

Michel Héninger (CEO)

Julien Leprovost (applications)

Cyril Messager (development)

Pierre Boissel (soft and physics)

Gérard Mauclaire (electronic and physics)

Philippe Gremillet (software)

David Robin (design)

Hubert Latappy (young padawan)