Volatile organic compounds analysis by MIMS-FTICR

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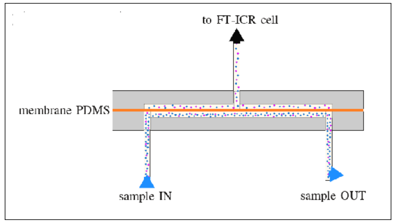
Introduction

The detection and quantification of Volatile Organic Compounds (VOC) in complex mixture is a growing concern for environmental analysis. The water quality monitoring involves a constant analysis of the ever growing number of VOC. It is then a necessity to develop efficient analytical method for environmental analysis. The Fourier Transform Ion Cyclotron Resonance mass spectrometer (FT-ICR) is able to discriminate many different molecules thanks to its high mass resolution. The association of FT-ICR, chemical ionization (CI) and membrane inlet mass spectrometry (MIMS) techniques is then a mean to discriminate rapidly a complex mixture, allowing thus real-time.

Membrane Introduction

MIMS is based on the **preferential permeation** of the non-polar VOC compared to the matrice i.e. water, leading to an **enrichment** of the permeat in VOC [1]. The membrane is a silicone (PDMS) membrane that separates the sample from the FT-ICR reaction cell.



Permeation theory

Steady-state flux through the membrane I_{ss} :

$$I_{ss} = ADS\frac{P_m}{l}$$

Response time (10% to 90%) t_{1090} :

$$t_{10-90} = 0{,}237\left(\frac{l}{D}\right)^2$$

where :
A = membrane surface
D = diffusion coefficient
S = solubility (in PDMS)
P_m = pressure
l = membrane thickness

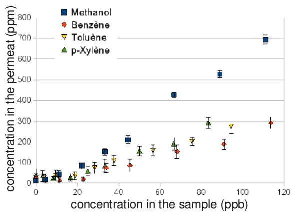
Enrichment coefficient

Enrichment calculation from the sample (spl) to the permeat (perm) :

$$\beta = \frac{C^{perm}_{COV}}{C^{spl}_{COV}}$$

C^{perm}_{COV} : concentration in the permeat (ppm)
C^{spl}_{COV} : concentration in the sample (ppm)

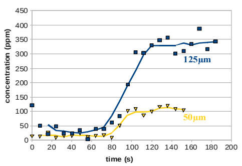
	FB	β	
methanol	CH_4O	6,5	miscible in water
benzene	C_6H_6	2700	low solubility in water
toluene	C_7H_8	3000	
p-xylene	C_8H_{10}	3800	



Enrichment coefficient evolution

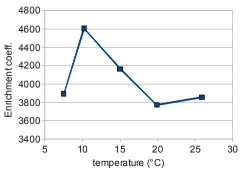
Membrane thickness influence :

On a water-low solubility compound (toluene)



thickness ↗ ⇒ β ↘

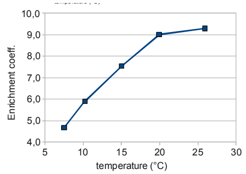
On a water-low solubility compound (p-xylene)



T ↗ ⇒ β ↘

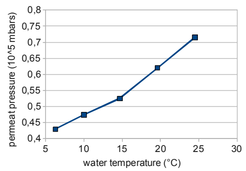
Temperature influence :

On a water-miscible compound (methanol)



T ↗ ⇒ β ↗

On water

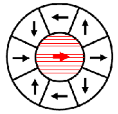


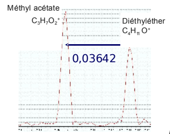
T ↗ ⇒ P (or water I_{ss}) ↗

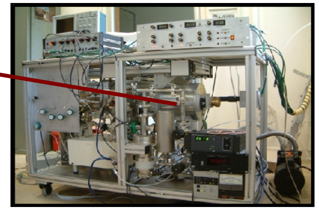
Portable FTICR

MICRA (Mobile ICR Analyzer) Charactericties [2]:

- 1,2T permanent Magnet (Homogeneity 10^{-2})
- Mass Range : 2-200 amu
- Resolving Power : m/Δm > 70000 @ 131 Dalton
- Separation @ mass 75 = 0,03642







more info poster : « Broadband gas analysis at high resolution with a small FTICR », Lemaire et al. Session: MP31, Instrumentation: FTMS, Time Slot/Poster Number: 663, Monday, Poster Hall

Chemical Ionisation (CI)

CI advantages :

- soft ionization : low fragmentation
- specific : no matrice ionization
- quantification [3]

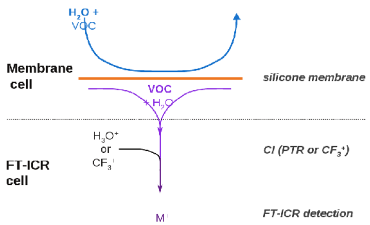
$$X_m = \frac{1}{RTP}\,\frac{-\ln(H_3O^+)(MH^+)}{k_M t_R (1-(H_3O^+))}$$

relative amount of the precursor and ion product
temp. and pressure of the analyte
reaction time (s)
ion-molecule rate coefficient ($cm^3.molecule^{-1}.s^{-1}$)

	Precursor Formation :	Ion Formation (principal way):	C_6H_6	CH_2FCF_3 (R134a)	$CHCl_3$	C_3H_6O (acetone)
H_3O^+	$H_2O + e^-_{70eV} \rightarrow H_2O^{\bullet+} + 2e^-$ $H_2O^{\bullet+} + H_2O \rightarrow \mathbf{H_3O^+} + HO^{\bullet}$	$H_3O^+ + M \rightarrow H_2O + [\mathbf{M+H}]^+$	$C_6H_7^+$ 1,9[1,9]			$C_3H_7O^+$ 4,1[3,9]
CF_3^+	$CF_4 + e^-_{70eV} \rightarrow CF_4^{\bullet+} + 2e^-$ $CF_4^{\bullet+} \rightarrow \mathbf{CF_3^+} + F^{\bullet}$	$CF_3^+ + RX \rightarrow CF_3X + \mathbf{R^+}$	not tested	$C_2H_2F_3^+$ 1,1[1,8]	$CHCl_2^+$ 0,2	n.t.
HO^-	$H_2O + e^-_{7eV} \rightarrow H^{\bullet} + \mathbf{HO^-}$	$HO^- + M \rightarrow H_2O + [\mathbf{M-H}]^-$		n.t.	CCl_3^- [2,3]*	$C_3H_5O^-$ [4,0]*

TAB 1 : Comparison of formation, principal ion-molecule reaction and ion products (of benzene, HFC-134a, chloroform and acetone) for three precursors. The number situated under the ion products X[X] correspond respectively to the experimental rate coefficient k_M and to the collisional rate coefficient k_c both in 10^{-9} $cm^3.molecule^{-1}.s^{-1}$. * ref[4]

Conclusion



Membrane inlet is an **efficient technique** for trace analysis in aqueous sample for :

- it is direct (into MS cell)
- it enriches the analytes (DL : down to 10ppb for BTX)

Though, many parameters have **to be optimized** (depending on compounds solubillity in water) : temperature, thickness, feed speed,...

The use of a few precursor for chemical ionization allows to consider a **complex mixture** with a global view.

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