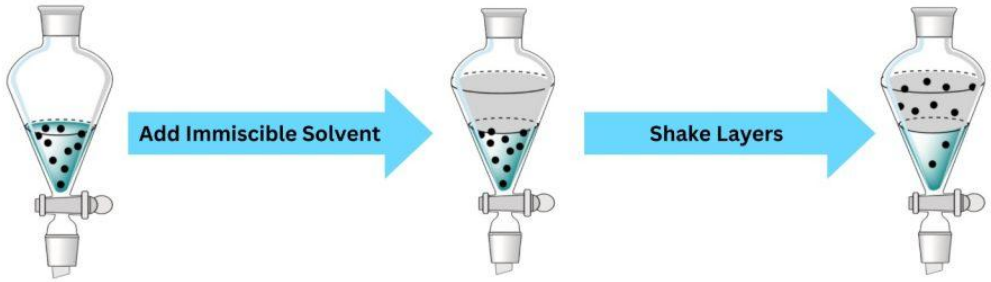
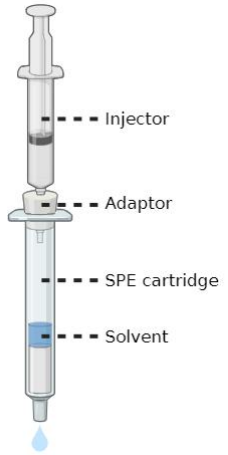
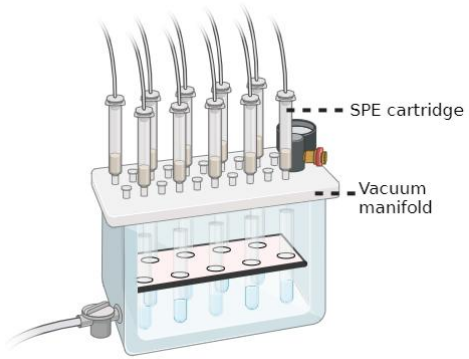
MODES D'INTRODUCTION DE L'ÉCHANTILLON

- Analyse directe
- Couplage GC-MS
- Couplage LC-MS
- Couplage CE-MS
- Couplage SFC-MS

Extraire (LLE, SLE, SPE)







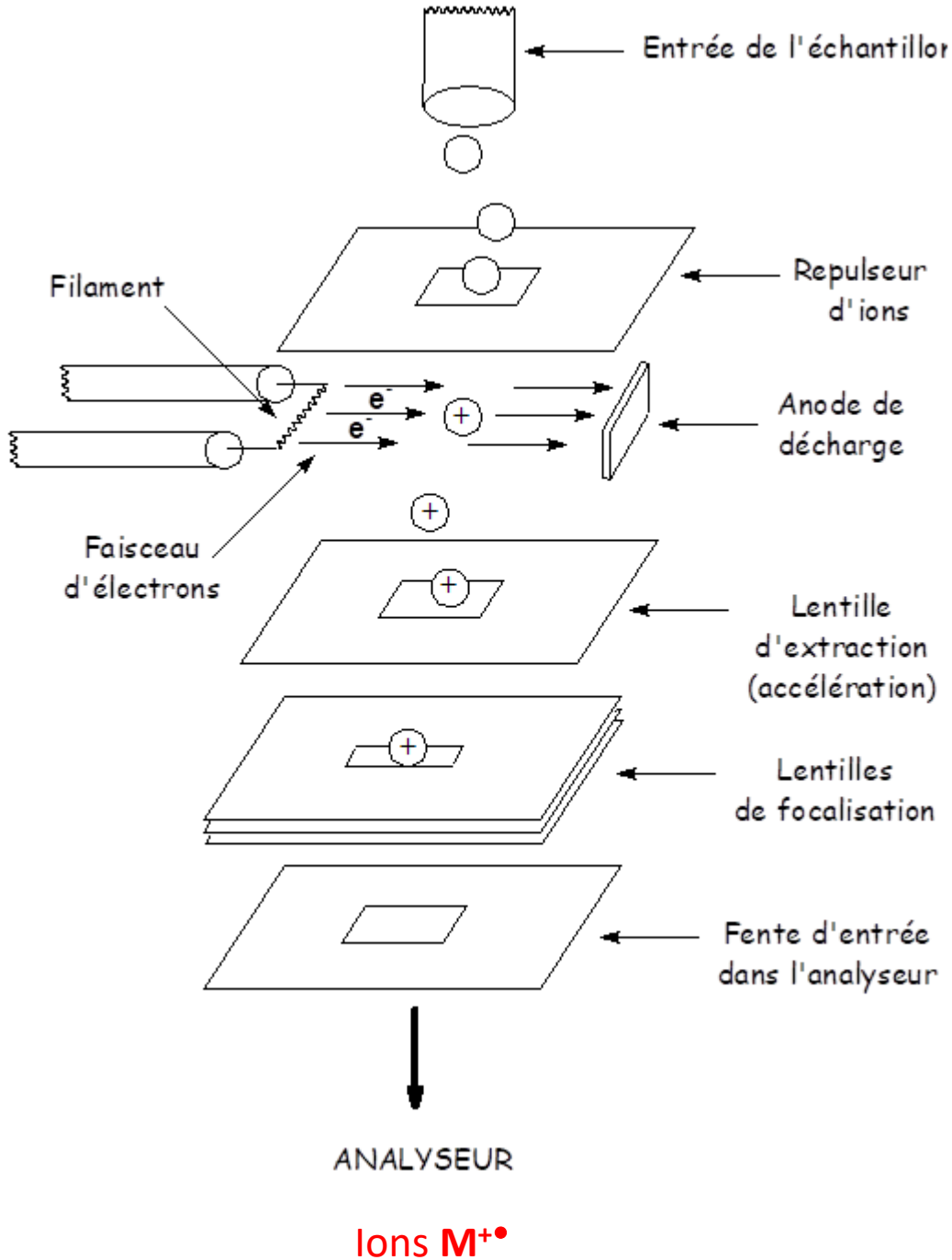
Resolubiliser si nécessaire

Dériver si nécessaire

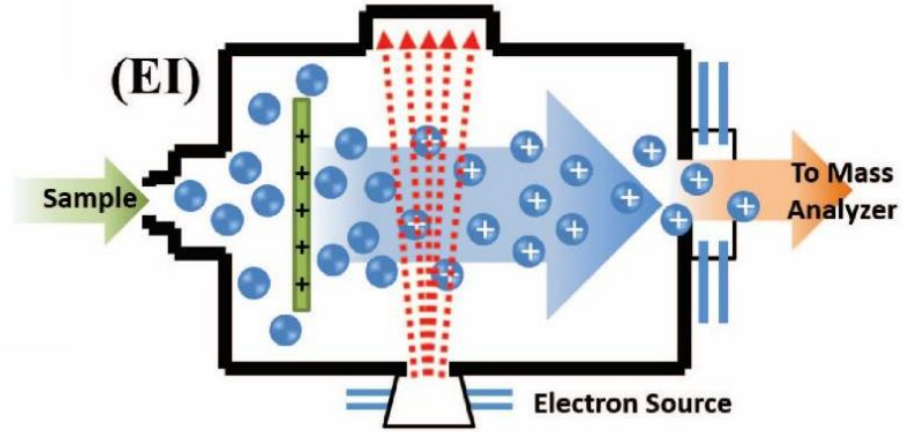
COUPLAGES GC-MS

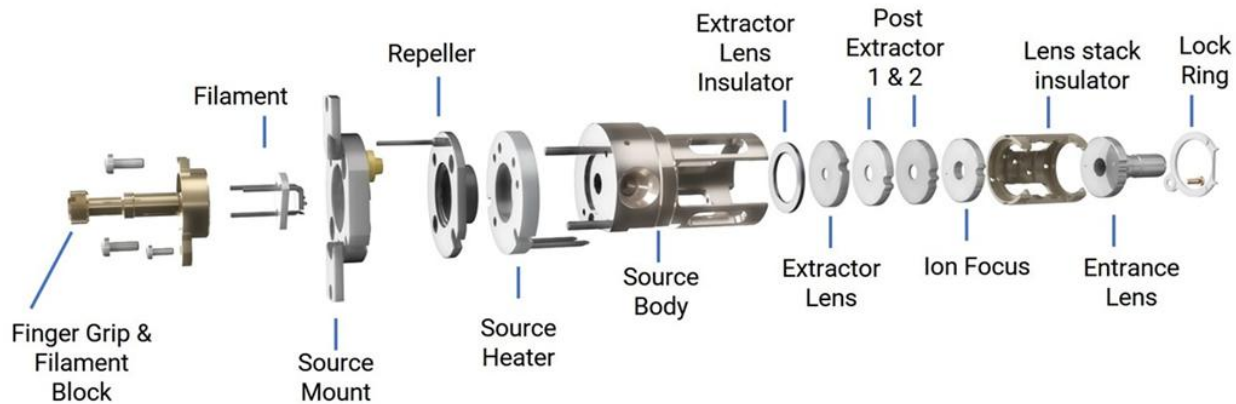
ANALYSE DES PETITES MOLÉCULES VOLATILES

Impact électronique
(EI)



Ions $M^{+\bullet}$



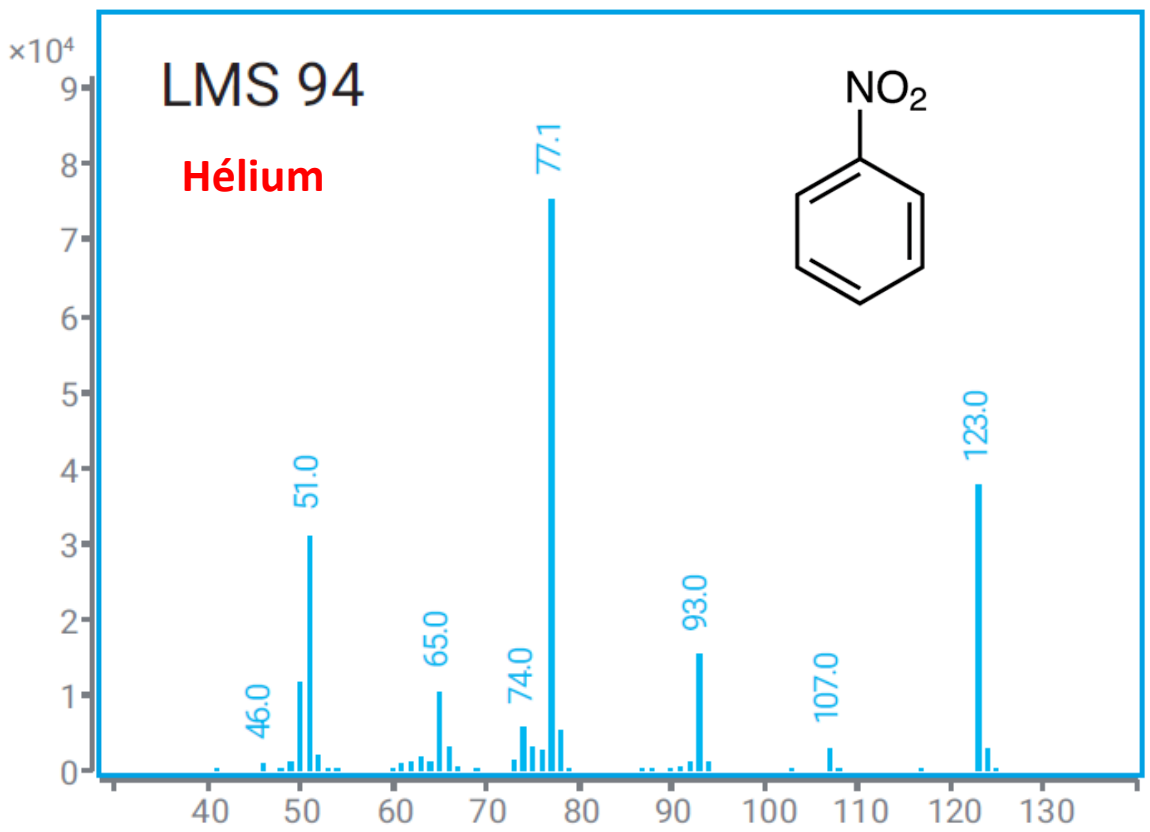


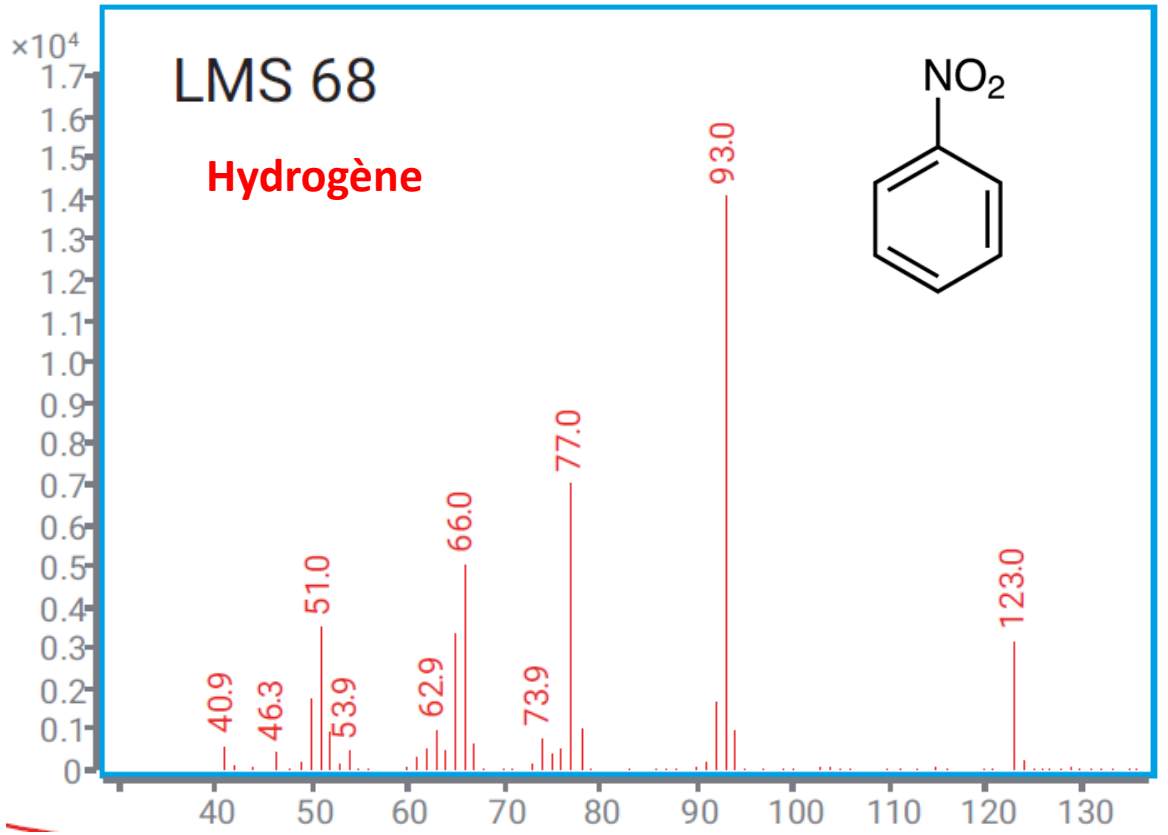
Principaux ions:

Type d'analyte	Ionisation positive Principal // occasionnel	Ionisation négative
apolaire	**$M^{+\bullet}$** // M^{2+}	-
polarité moyenne	**$M^{+\bullet}$** // $[M+H]^+$, M^{2+}	-
polaire	**$M^{+\bullet}$** // $[M+H]^+$, M^{2+}	-

Intérêts et limitations:

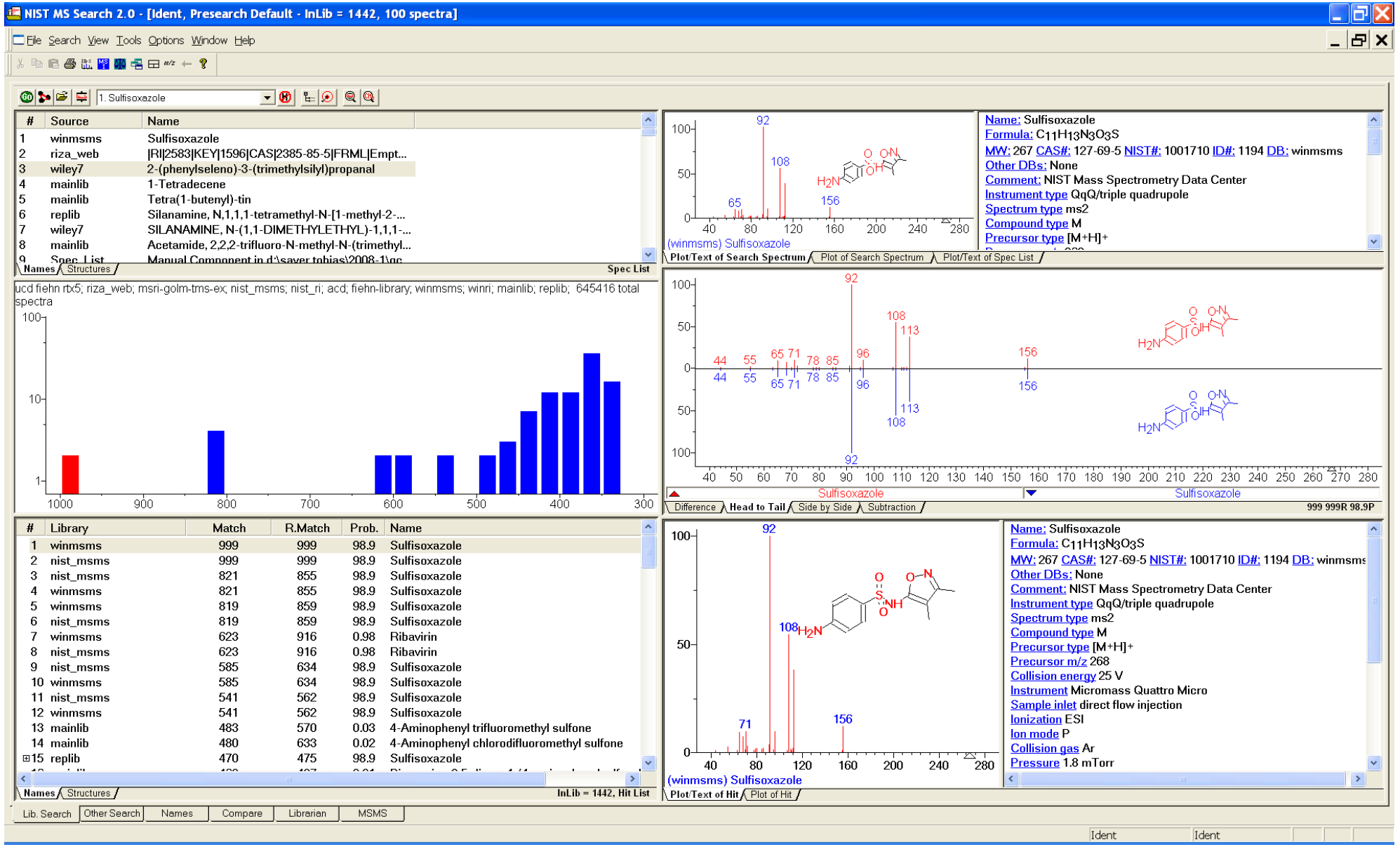
- le composé doit être volatil (T_{eb}< 500°C; limite de masse ≈10^3)
- ion moléculaire $M^{+\bullet}$ (mais pas toujours) => **masse?**
- ions fragments => **informations structurales**
- source sous vide => **contraintes sur GC (dc, débits, gaz vecteur…)**





Confirmation?

Il existe des bases de données intégrant des outils recherché performants



- NIST NIST/EPA/NIH Mass Spectral Library 2023: 394.000 spectres EI / 341,000 composés => **2500€**
- WILEY Registry of Mass Spectral Data 12th Edition 860.000 spectres EI / 700. 000 composés => **8500€**

Ionisation Chimique (CI)

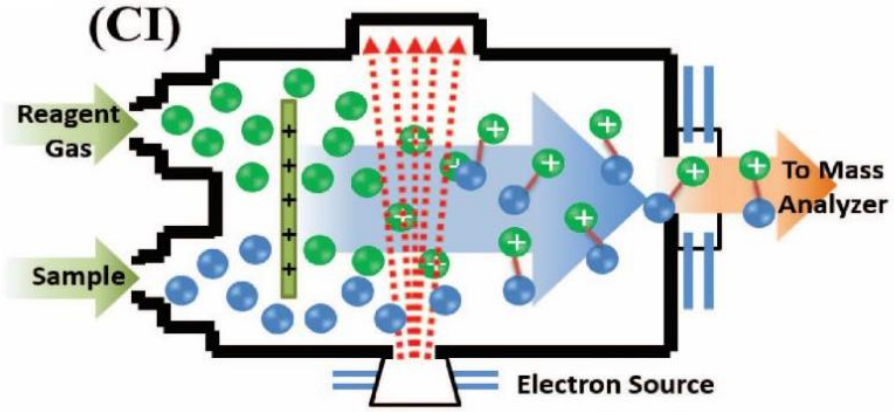
Principe:

Qté de Gaz Réactif >>> Qté de Produit Étudié

10^3 -> 10^4

ionisation préférentielle du gaz réactif (méthane, isobutane ou ammoniac)

Collision avec d'autres molécules du même gaz => **plasma** d'ionisation



Gaz réactif	AP (kcal.mol^{-1})	Ions réactifs	m/z	Abondance (%)
Méthane	127	CH_5^+ $C_2H_5^+$ $C_3H_5^+$	M+17 M+29 M+41	47 41 6
Isobutane	195	$C_4H_9^+$ $C_3H_7^+$ $C_3H_3^+$	M+57 M+43 M+39	93 4 3
Ammoniac	207	NH_4^+ NH_3+NH_4^+	M+18 M+35	97 3

molécules organiques AP ≈ 200 Kcal.mol^{-1}

=> ammoniac + sélectif que isobutane et méthane

- énergétique que EI => **favorise l'obtention de l'ion moléculaire**
(peu de fragmentation car énergie interne + faible que pour EI).

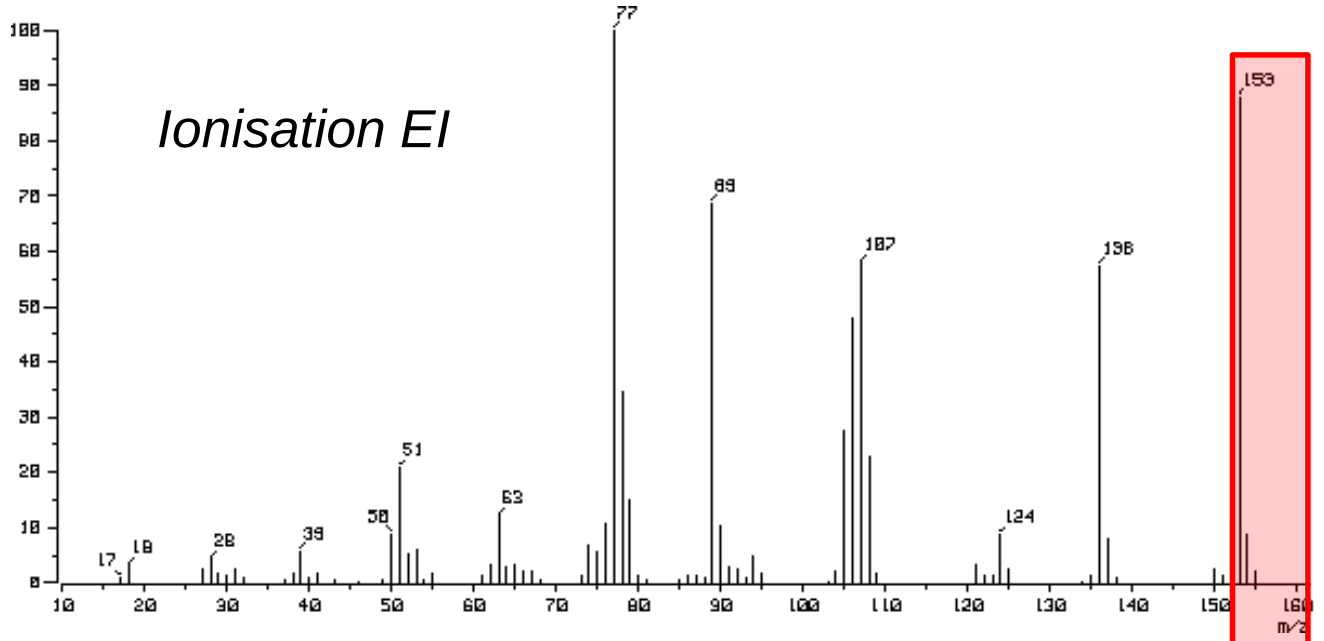
Principaux ions:

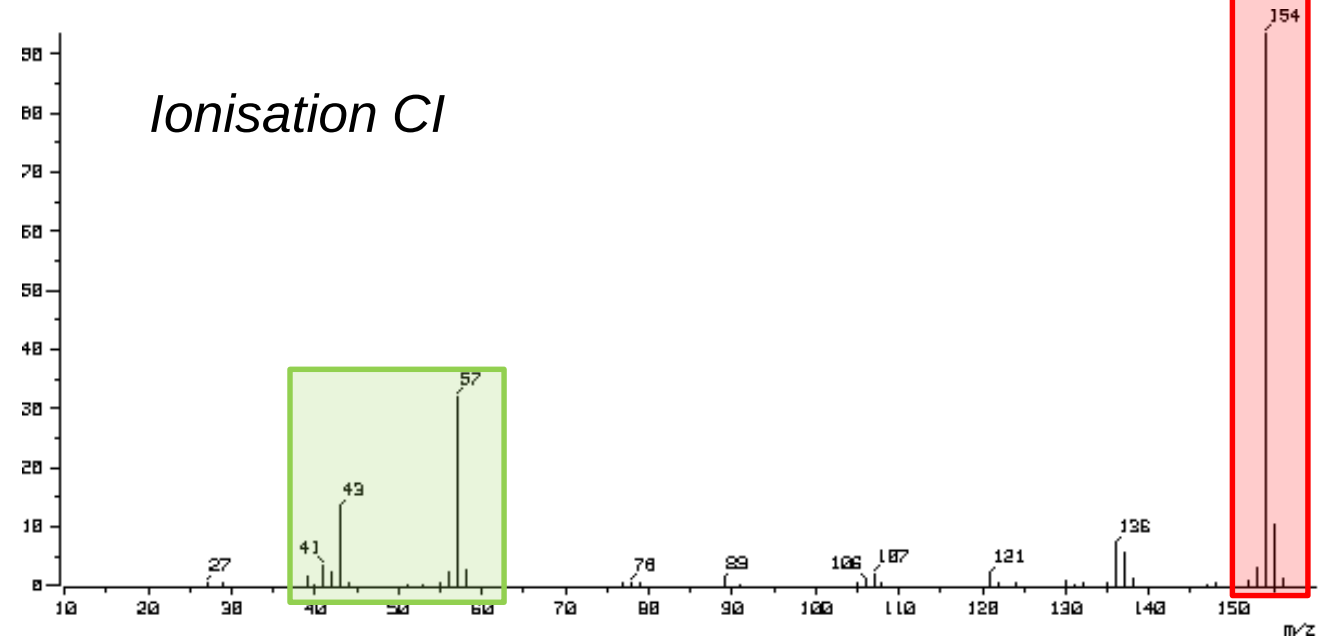
Type d'analyte	Ionisation positive principal // occasionnel	Ionisation négative principal // occasionnel
apolaire	**$[M+H]^+$**	**$M^{-\bullet}$** // $[M-H]^-$
polarité moyenne	**$[M+H]^+$** // $[M+X]^+$, $[2M+H]^+$	**$M^{-\bullet}$, $[M-H]^-$**
polaire	**$[M+H]^+$, $[M+X]^+$** // $[2M+H]^+$	**$[M-H]^-$** // $[M+R]^-$, M^-

X => selon les gaz (ex: $[M+NH_4]^+$):

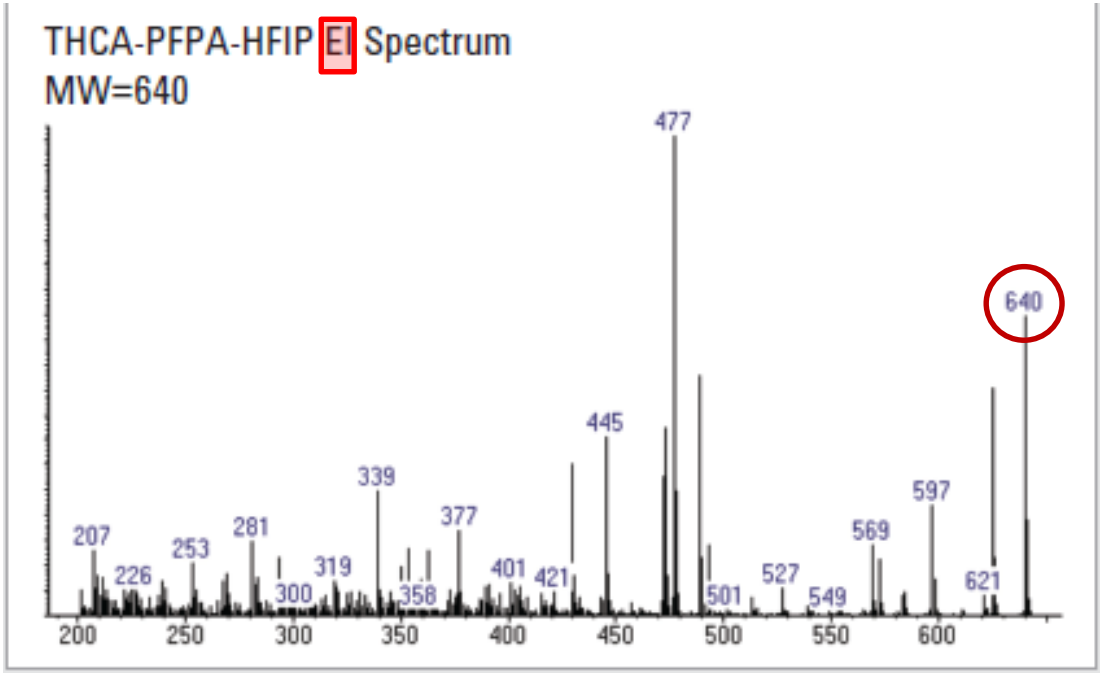
$M^{-\bullet}$: capture d'électron $M+e^-$

Spectres de masse du 3-nitrobenzyl alcool

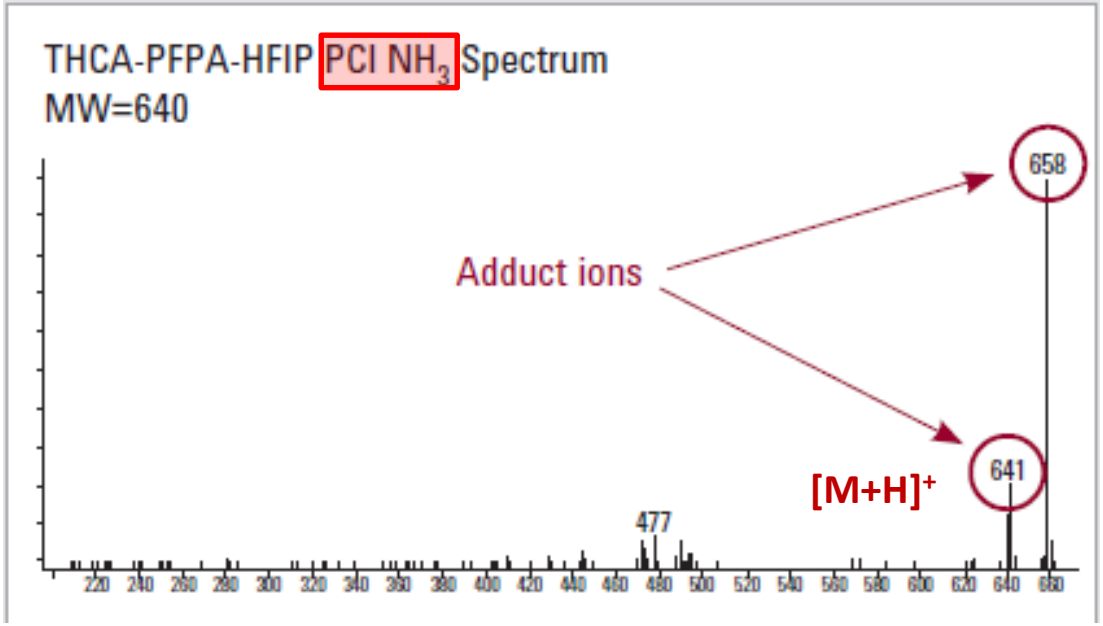




Isobutane

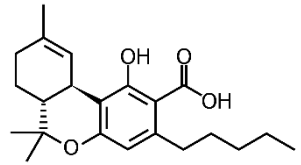


$M^{+\cdot}$



$[M+NH_4]^+$

***Comparison of Δ1-Tetrahydrocannabinolic acid (THCA)**. The EI spectra show many fragments, but PCI and NCI show fewer. CI spectra enable easier identification of compounds by GC/MSD.*



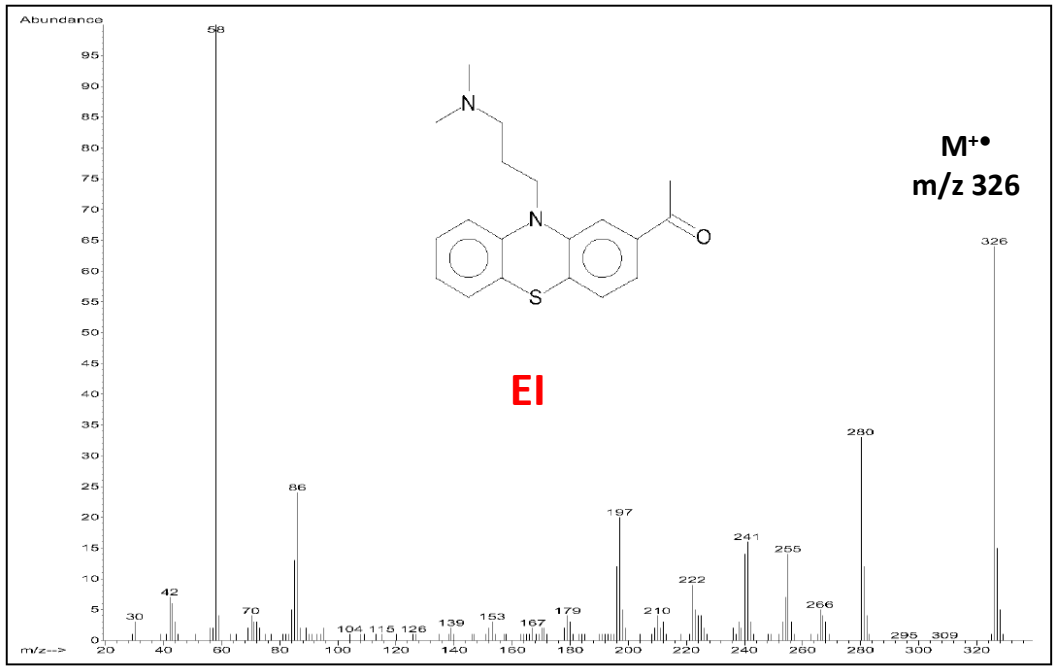
Intérêts et limitations:

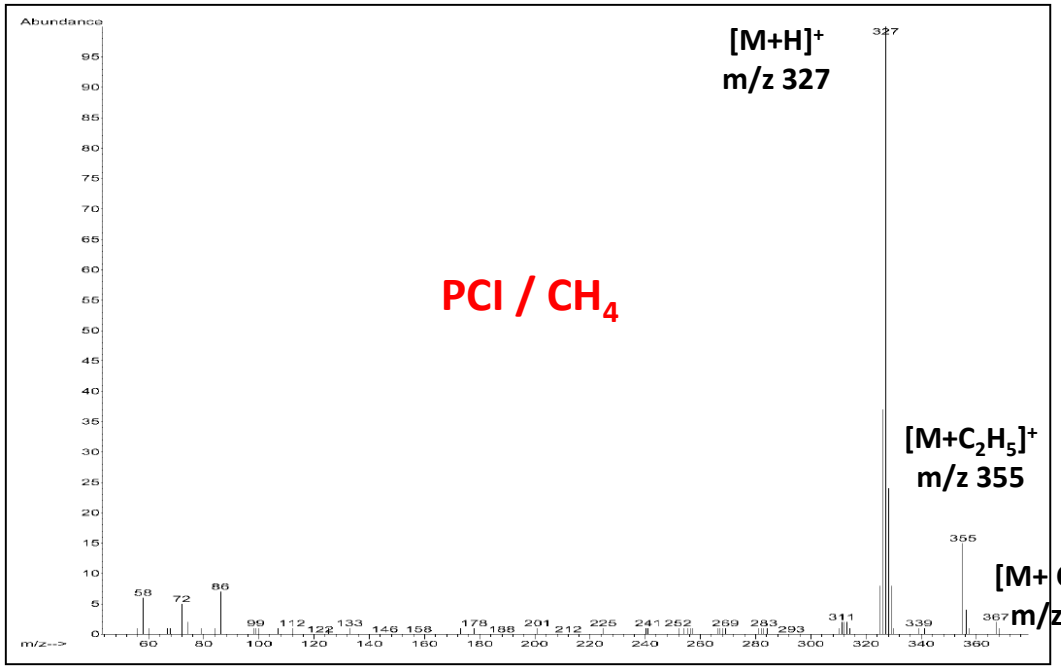
- on peut observer l'ion pseudo-moléculaire => **masse OK**
- c'est une technique **douce** :on obtient des ions fragments mais moins que pour EI
=> **peu d'informations structurales**
- le composé doit être volatil (T_{eb}< 500°C; limite de masse 10^3)
- source sous vide => **contraintes sur GC (dc, débits,…)**

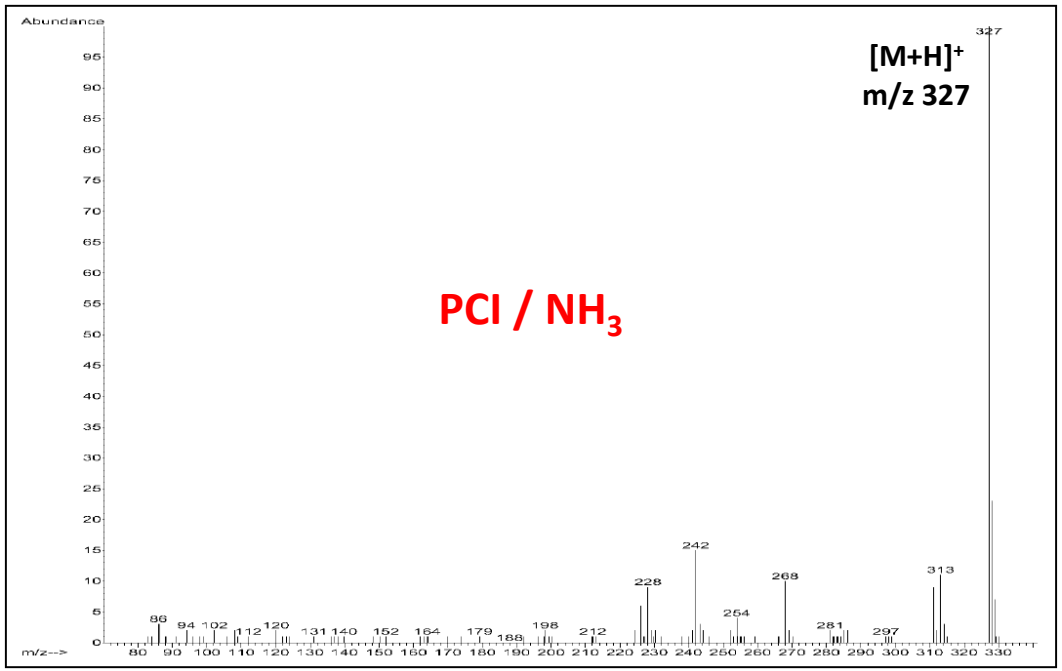
Acepromazine

CAS-Nr. 61-00-7

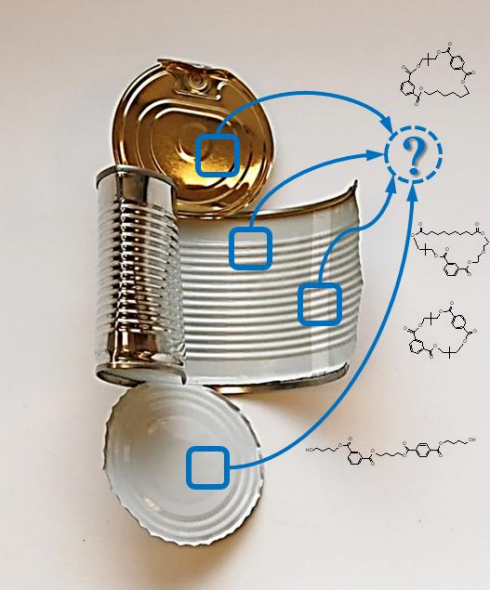
Molecular formula: $C_{19}H_{22}N_2OS$

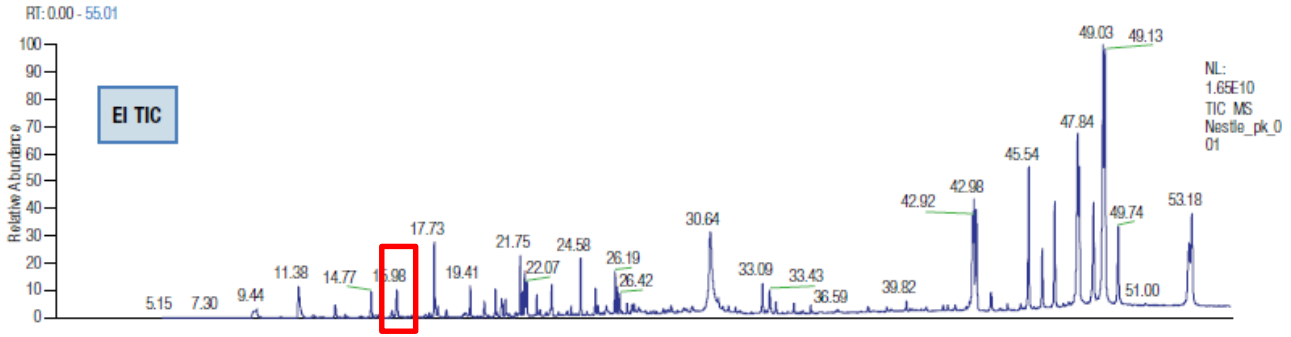


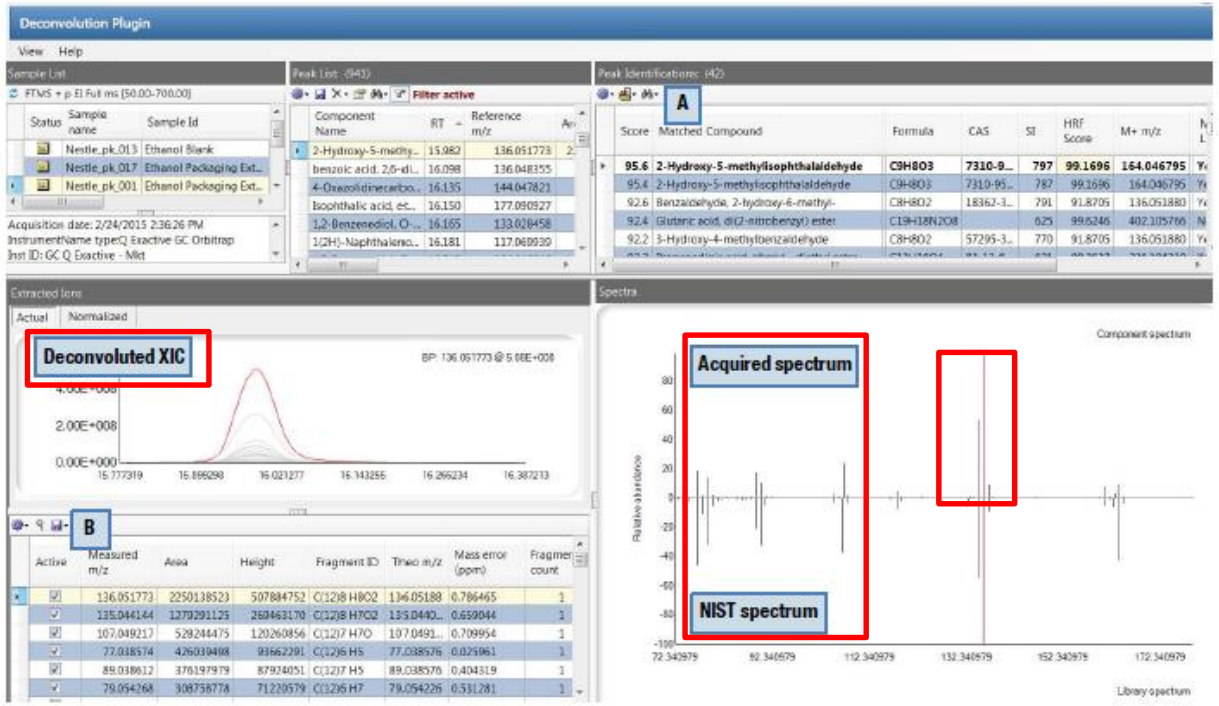




Applications GC-MS



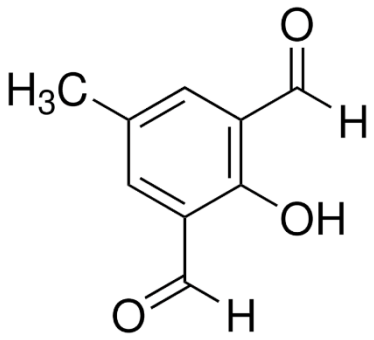




TRACE 1310 GC System Parameters	
Injection Volume (µL)	1
Liner	Single gooseneck P/N 453A0344-UI
Inlet (°C)	SSL 280
Carrier Gas, (mL/min)	He, 1.3
Oven Temperature Program	
Temperature 1 (°C)	40
Hold Time (min)	0.5
Temperature 2 (°C)	325
Rate (°C/min)	5.5
Hold Time (min)	12

Table 2. Mass spectrometer conditions.

Q Exactive GC Mass Spectrometer Parameters	
Transfer line (°C)	280
Ionization type	EI/PCI
Ion source (°C)	230 EI / 190 CI
Electron energy (eV)	70
Acquisition mode	Full-scan
Mass range (Da)	50–700
Resolving power (FWHM at *m/z* 200)	120,000
Lockmass, column bleed *(m/z)*	207.03235

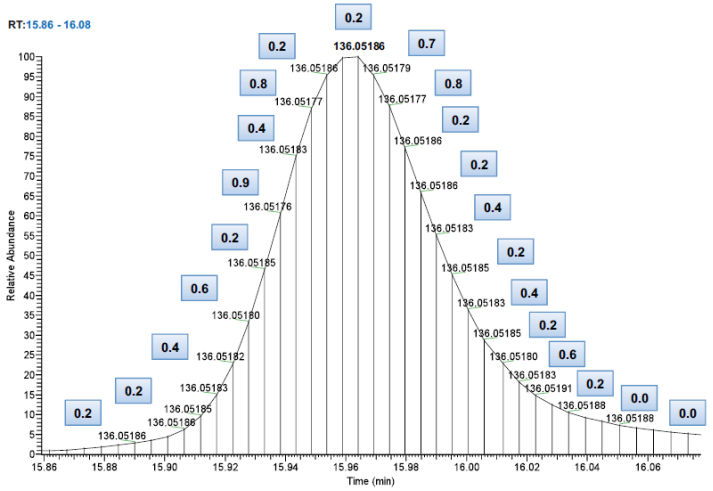


Monoisotopic mass: 164.047344

2-Hydroxy-5-methyl-1,3-benzenedicarboxaldehyde

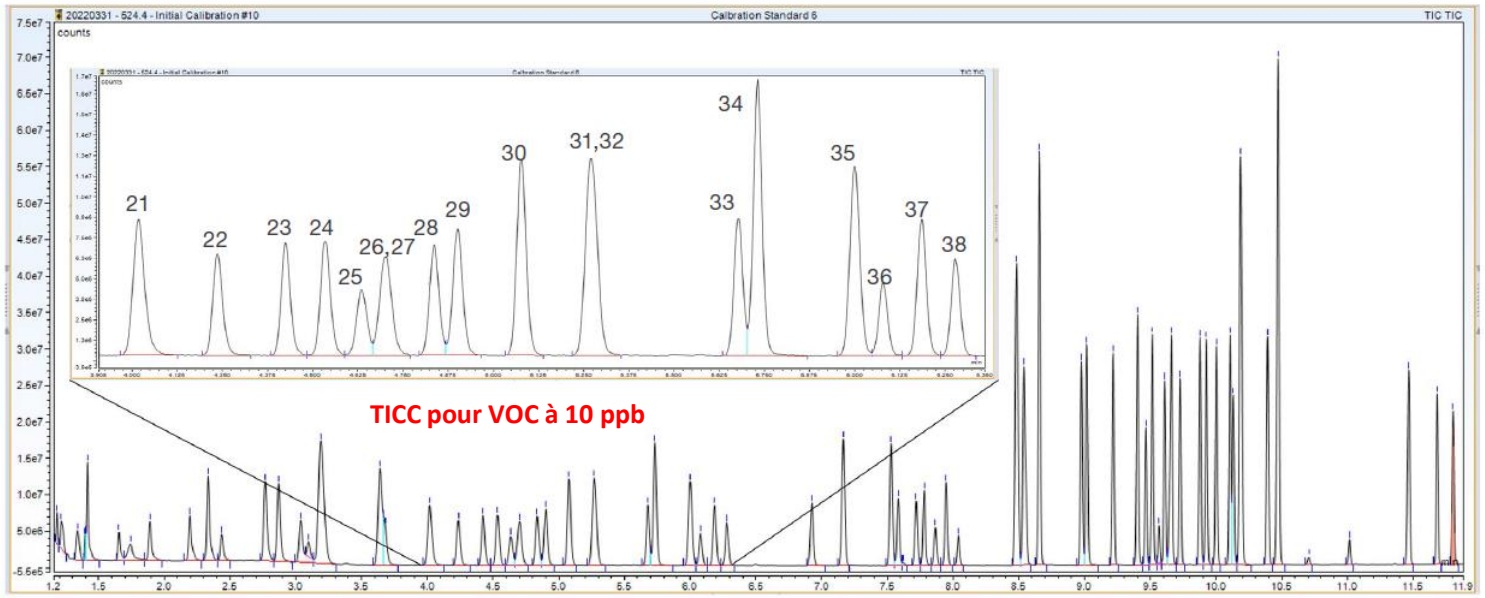
Active	Measured m/z	Area	Height	Fragment ID	Theo m/z	Mass error (ppm)
☑	136.051773	2250138523	507884752	C(12)8 H8O2	136.05188	0.786465

GC-HRMS



EIC 136.05188 ± 5 ppm

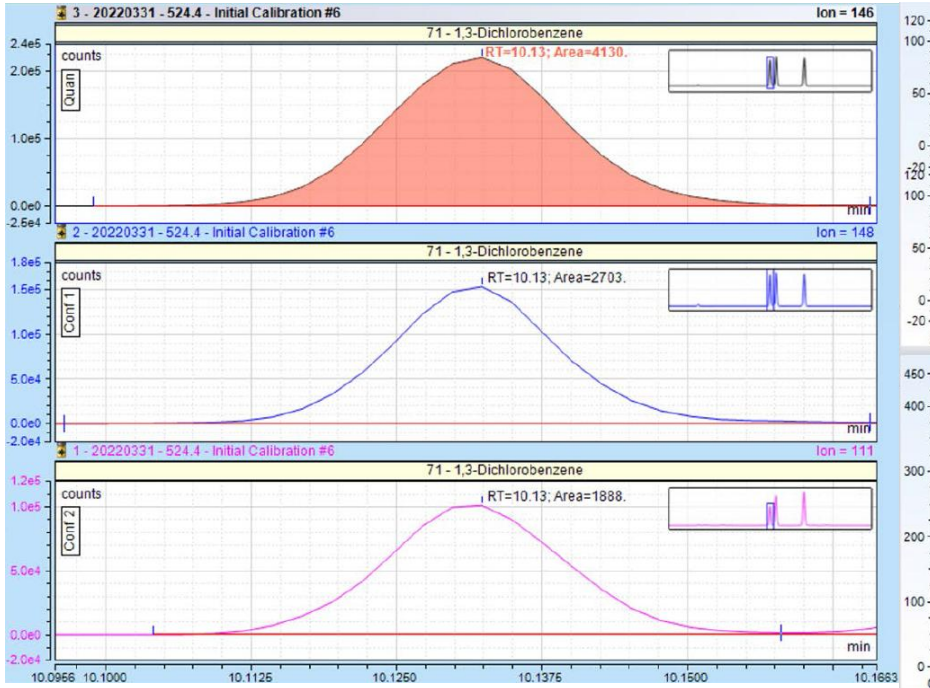
Characterizing unknowns in food packaging using GC Orbitrap Mass Spectrometry
Dominic Roberts, Jesus Varela, Yves-Alexis Hammel and Paul Silcock
Thermo AN 10527 (2016)

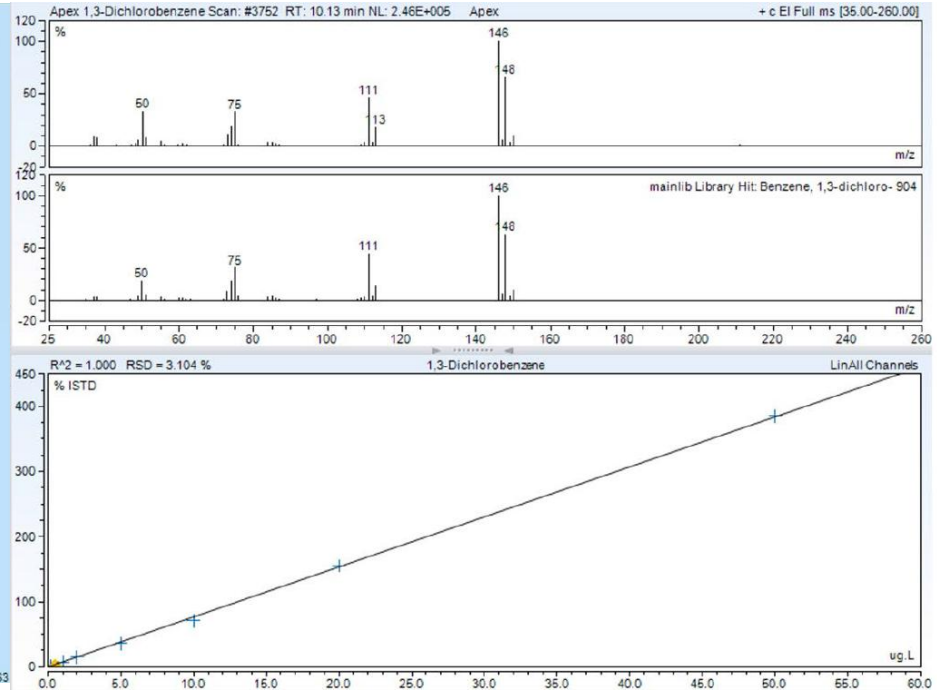


TICC pour VOC à 10 ppb

21. *t*-butyl ethyl ether
22. *cis*-1,2-dichloroethene
23. Bromochloromethane
24. Chloroform
25. Carbon tetrachloride
26. Tetrahydrofuran
27. 1,1,1-trichloroethane
28. 1,1-dichloropropene
29. 1-chlorobutane
30. Benzene
31. *t*-amyl methyl ether
32. 1,2-dichloroethane
33. Trichloroethylene
34. 1,4-dichluorobenzene (IS)
35. *t*-amyl ethyl ether
36. Dibromomethane
37. 1,2-dichloropropane
38. Bromodichloromethane

GC-MS

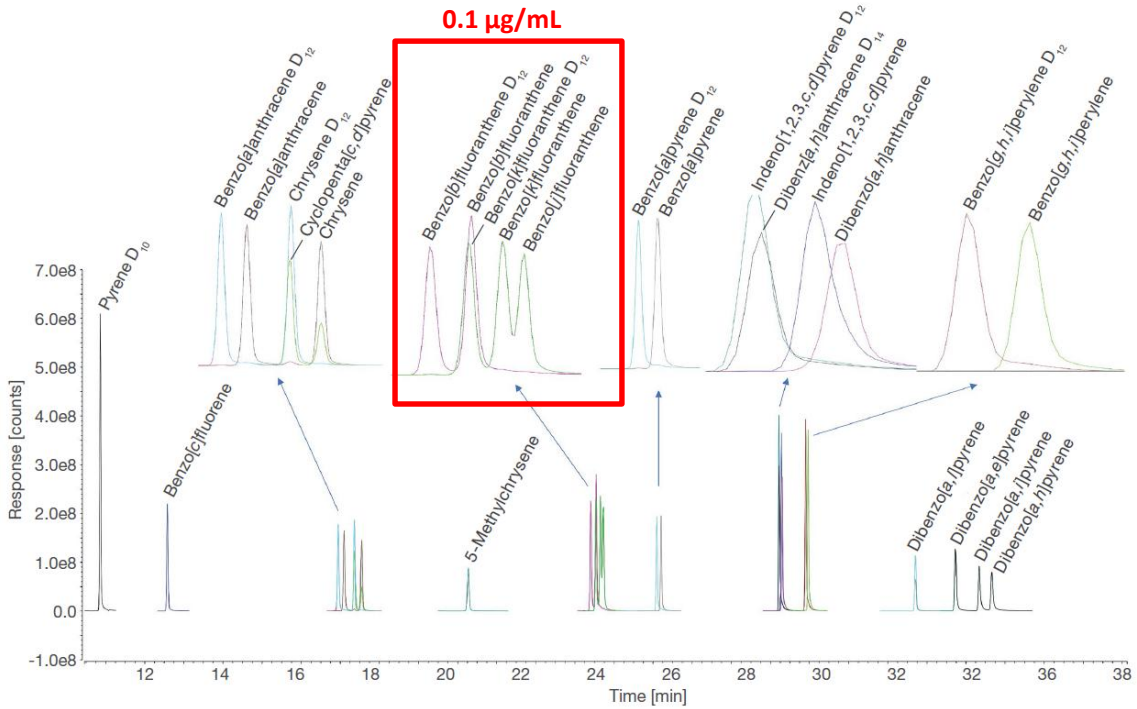


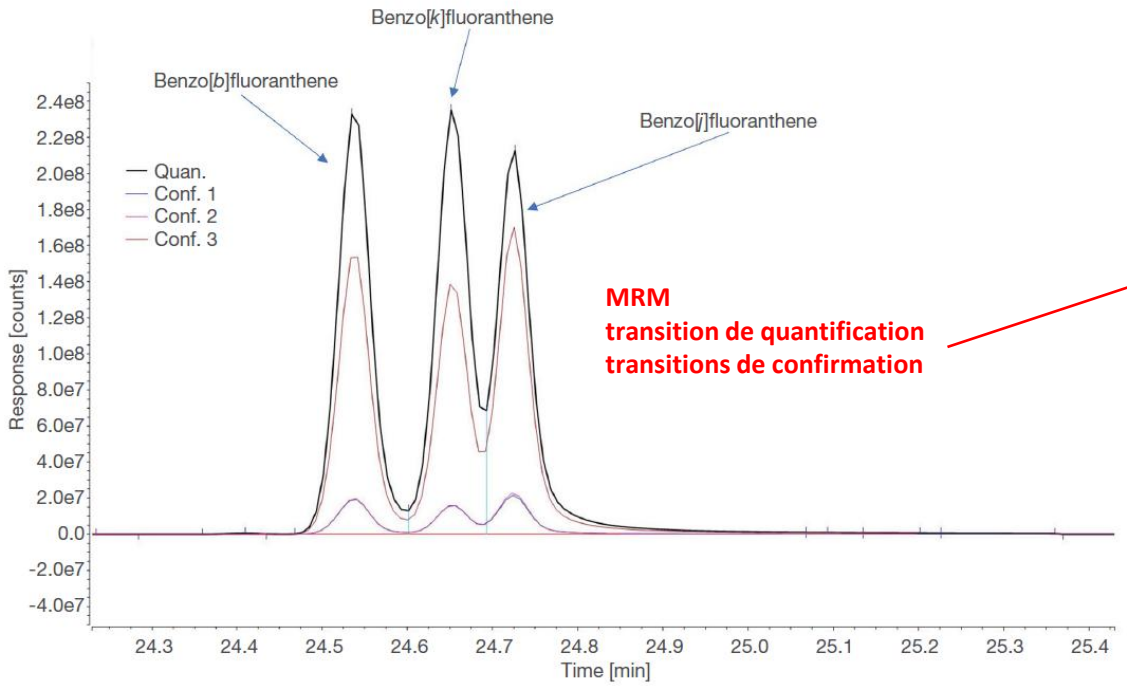


EIC pour 1,3-dichlorobenzene à 0.5ppb
Ion de quantification m/z 146
Ions de confirmation m/z 148 et 111

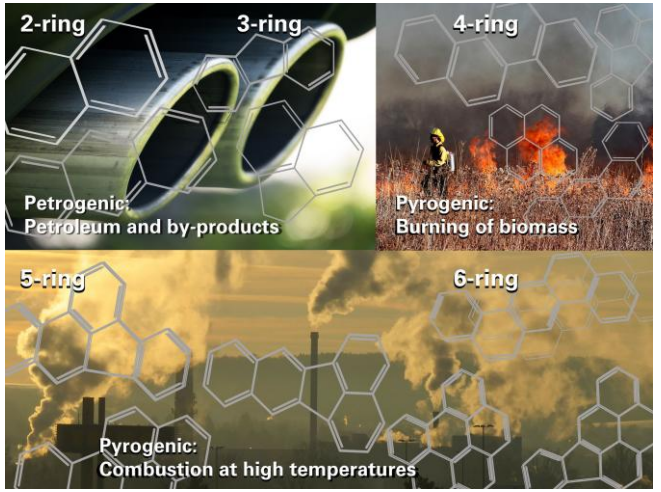
gamme : 0.2 à 50 ppb

Analysis of volatile organic compounds in drinking water according to U.S. EPA Method 524.4
Thermo AN 001236 (2022)





MRM
transition de quantification
transitions de confirmation



GC-MS/MS

sub ppb

Compound	R^2	Range [µg/mL]	IDL [µg/mL]
Benzo[*b*]fluoranthene	0.9995	0.0005–1.0000	0.0001
Benzo[c]fluorene	0.9992	0.0005–1.0000	0.0002
Benzo[*g,h,i*]perylene	0.9996	0.0005–1.0000	0.0002
Benzo[*j*]fluoranthene	0.9996	0.0005–1.0000	0.0001
Benzo[*k*]fluoranthene	0.9996	0.0005–1.0000	0.0001

Compound	Retention time (min)	Precursor ion (*m/z*)	Product ion (*m/z*)	Collision energy (V)
Benzo[*b*] fluoranthene	24.69	252	226	30
	24.69	252	250	30
	24.69	252	252	20
Benzo[*k*] fluoranthene	24.83	252	226	30
	24.83	252	226	20
	24.83	252	250	30
	24.83	252	252	20
Benzo[*j*] fluoranthene	24.87	252	226	30
	24.87	252	250	30
	24.87	252	252	20

Sensitive and reproducible analysis of 16 polyaromatic hydrocarbons (PAHs) using gas chromatography – triple quadrupole mass spectrometry (GC-MS/MS). Thermo AN 10566 (2022)