PTR-MS Mass Spectrometer Detection of Buried Oil

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Can we use mass spectrometry to detect buried or submerged oil?

- Very powerful analytical tool for molecular identification
- High sensitivity

- Production of ions
- Separation and selection of ions
- Detection of ions

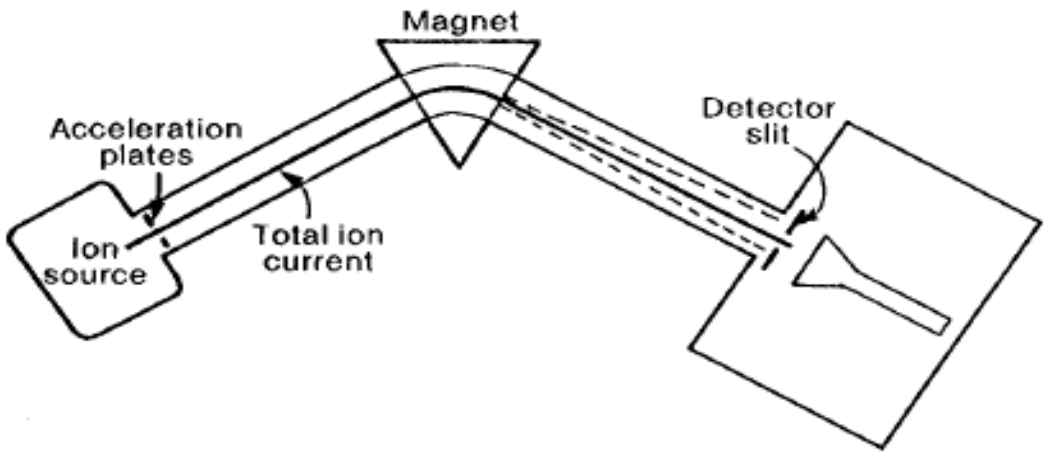
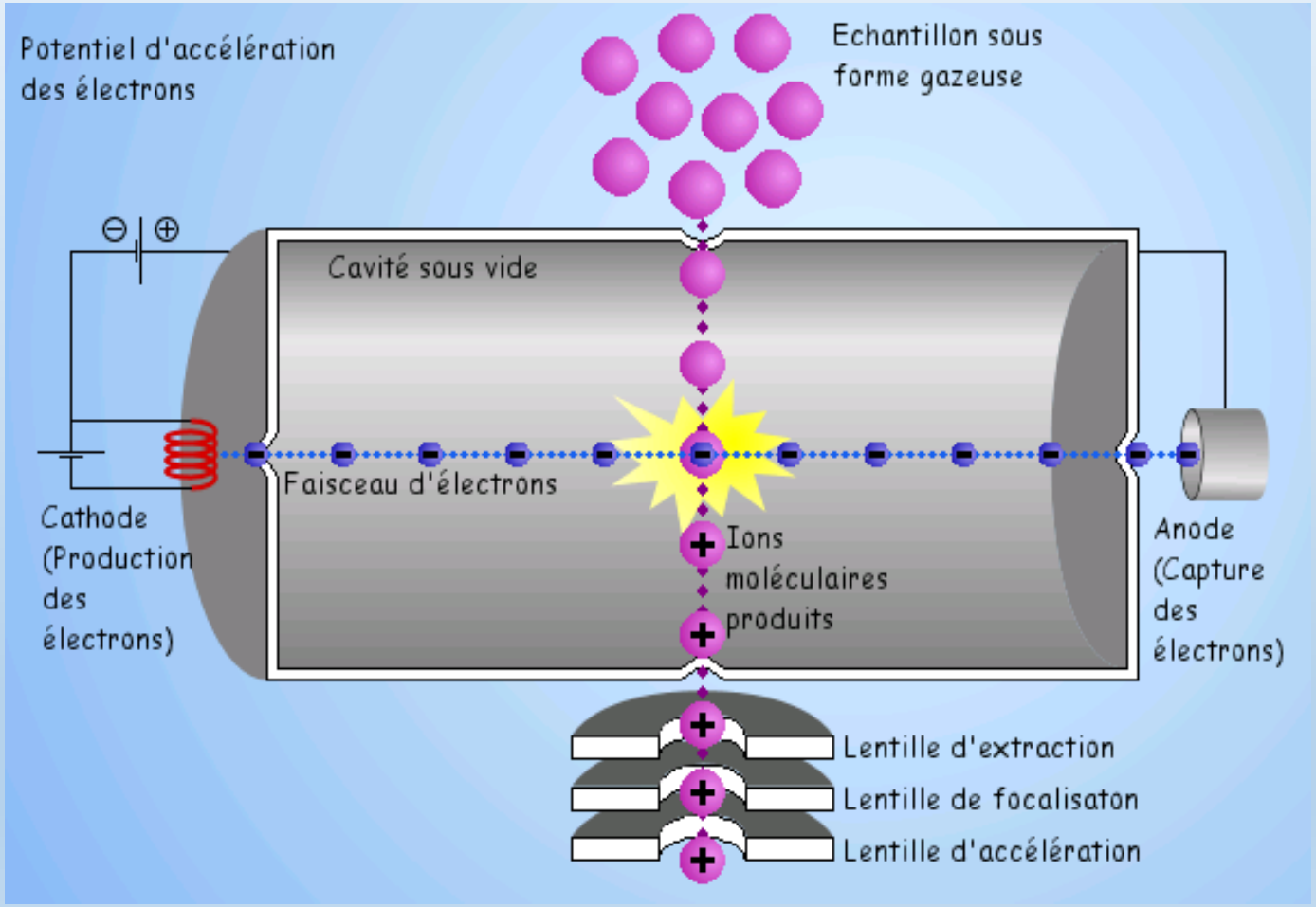


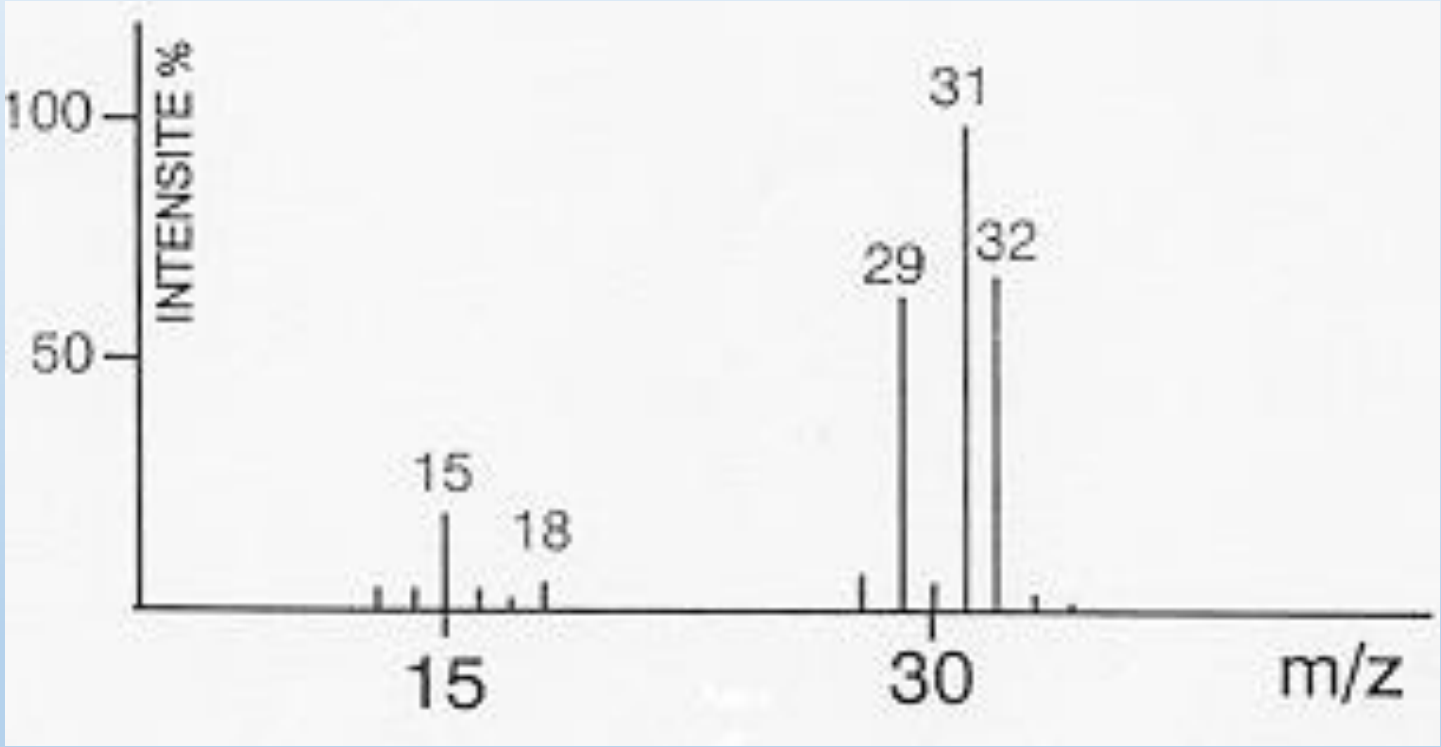
Figure 3-18 Magnetic Sector Mass Spectrometer (on - axis geometry)

Conventional Mass Spectrometer

Ionisation by electron impact

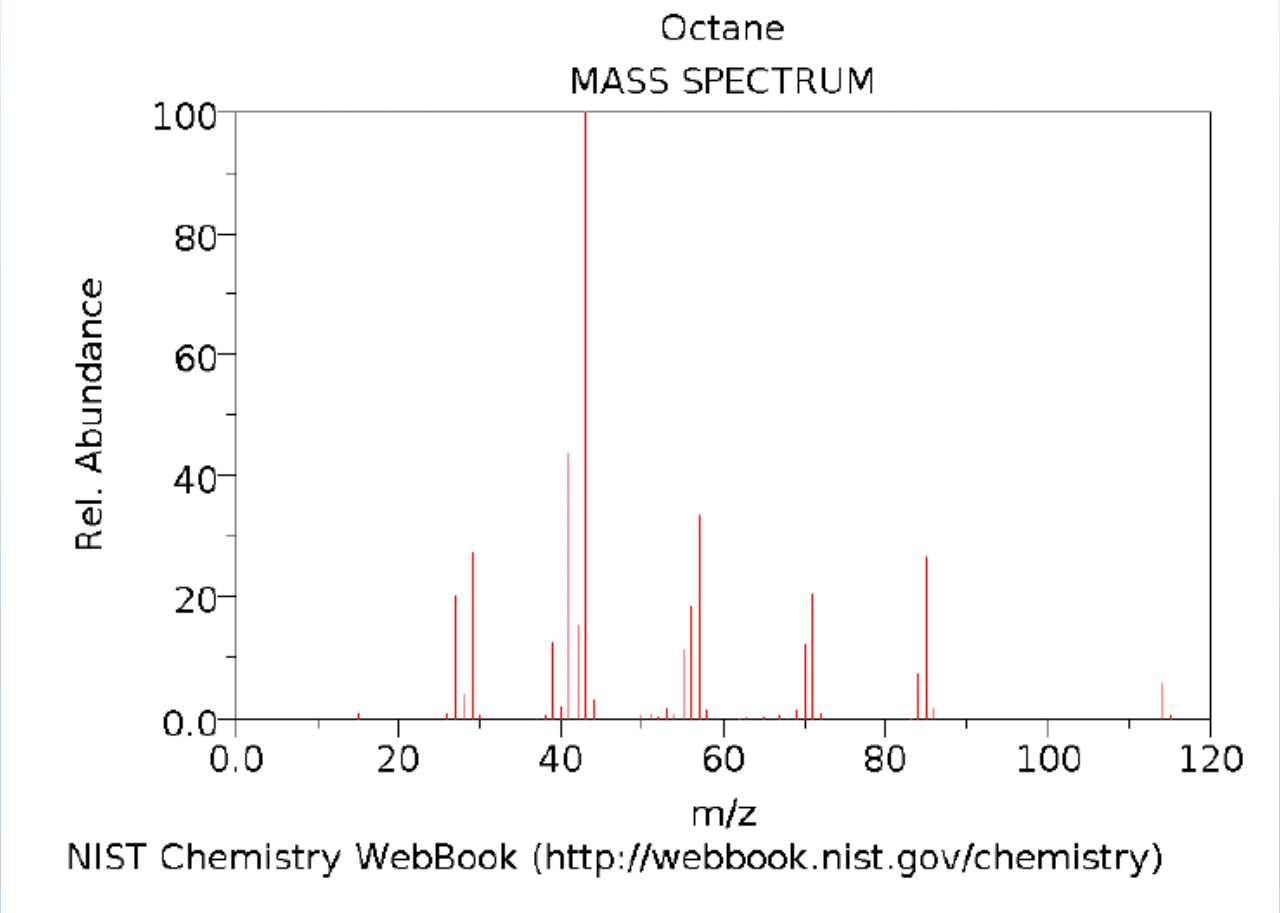


Spectrum of Methanol (CH3OH – Mass 32)

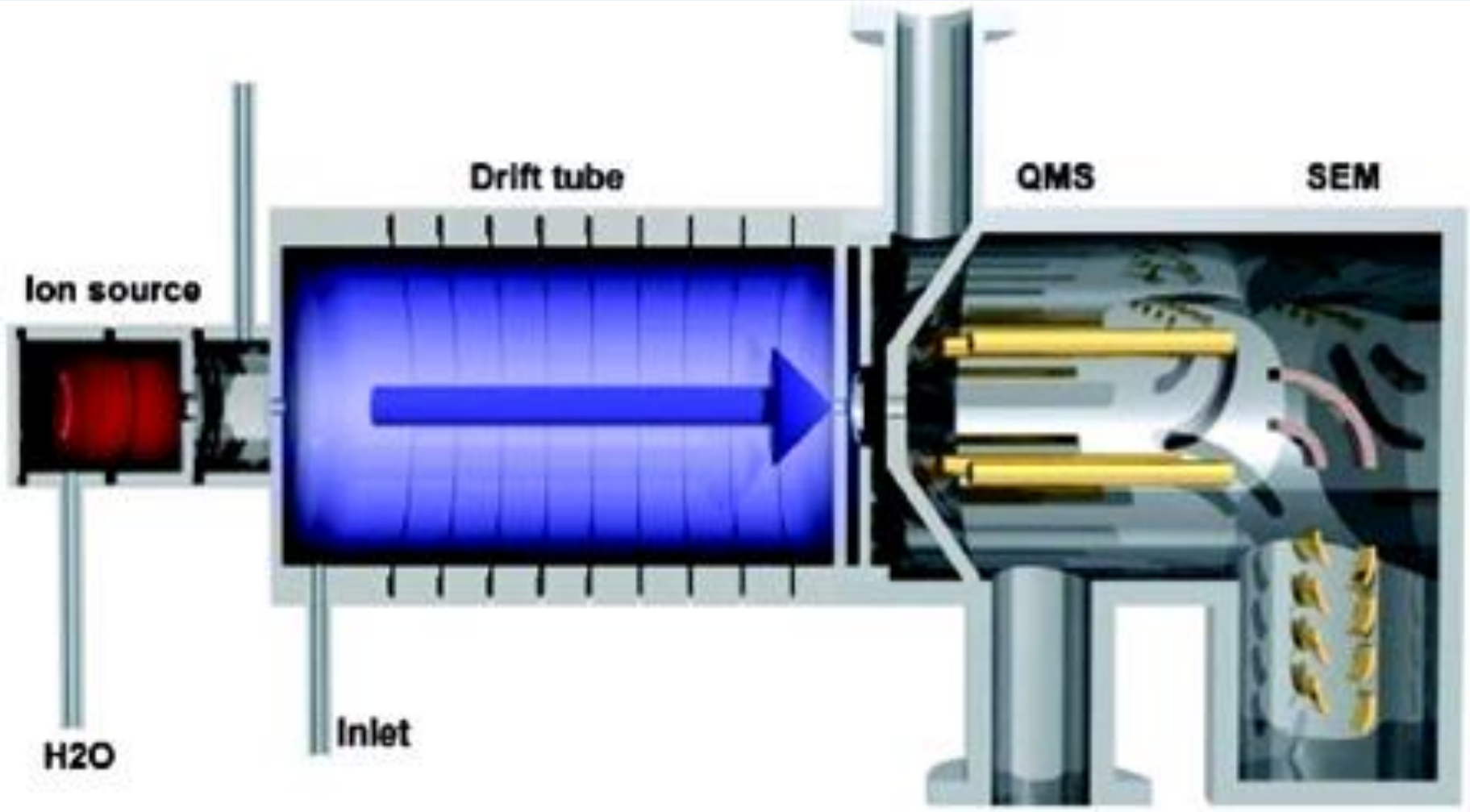


Octane

C_8H_{18}
Masse 114.23



Proton-Transfer Mass Spectrometer



Precursor Ion Formation

Source Drift region

- Ion molecule reactions yield H_3O^+

$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$

But, $H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$

Why H_3O^+?

Advantages of using H_3O^+ as a reagent ion

- On-line analysis of VOCs
  - H_3O^+ does not react with the major components of air.

$$H_3O^+ + N_2 \rightarrow$$
$$H_3O^+ + O_2 \rightarrow$$
$$H_3O^+ + Ar \rightarrow$$
$$H_3O^+ + CO_2 \rightarrow$$

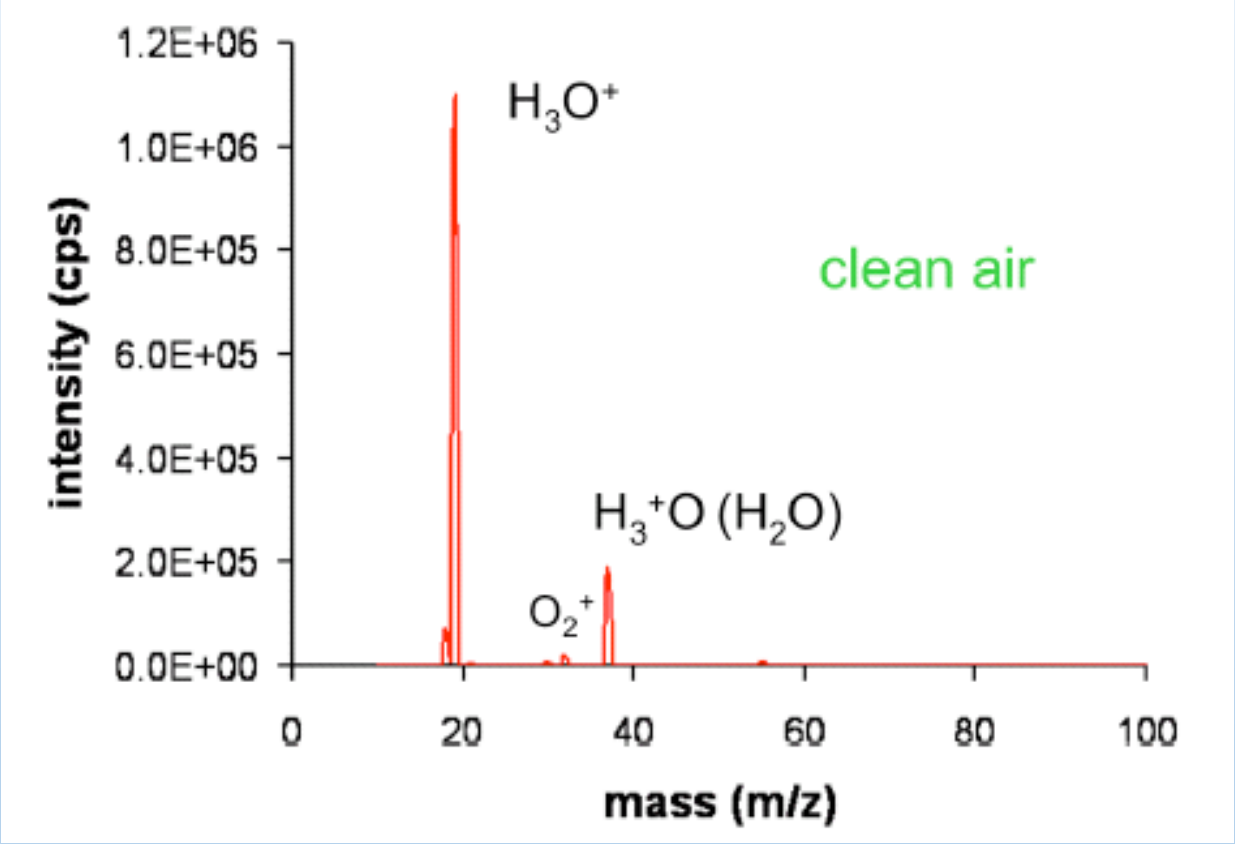
No Reaction

Proton Affinity

Type of compound	Proton affinity (kcal/mole)
Permanent gases Ar, O_2, N_2, CO_2	< 130
Alkanes C_nH_{2n+2}	< 167
Water H_2O	167
>C2-olefins and aromatics	>167
Alcohols and ethers	>167
Aldehydes and ketones except formaldehyde	>167

J/mole

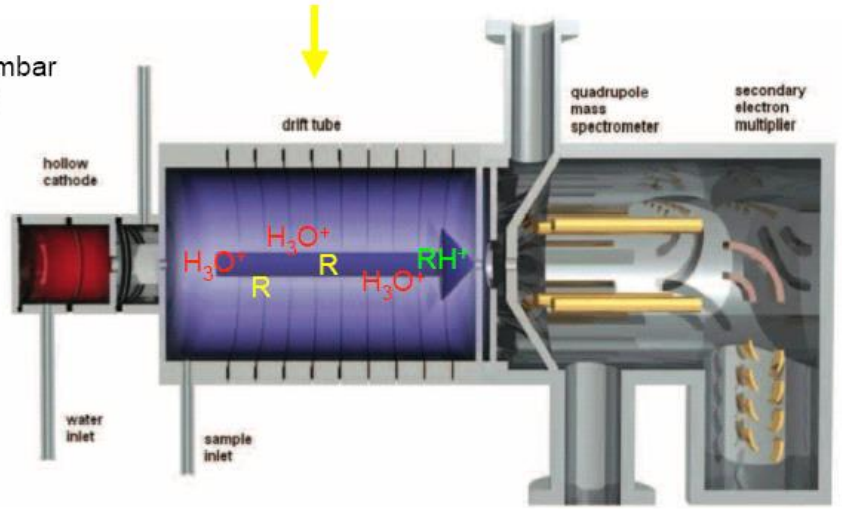
Precursor mass spectrum



Quantification

Drift Tube Reaction Region

Drift tube Pressure = 2mbar
Temperature - ambient



$$H_3O^+ + R \xrightarrow{k} RH^+ + H_2O$$

$$[RH^+]_t = [H_3O^+]_0 (1-e^{-(k[R]t)})$$

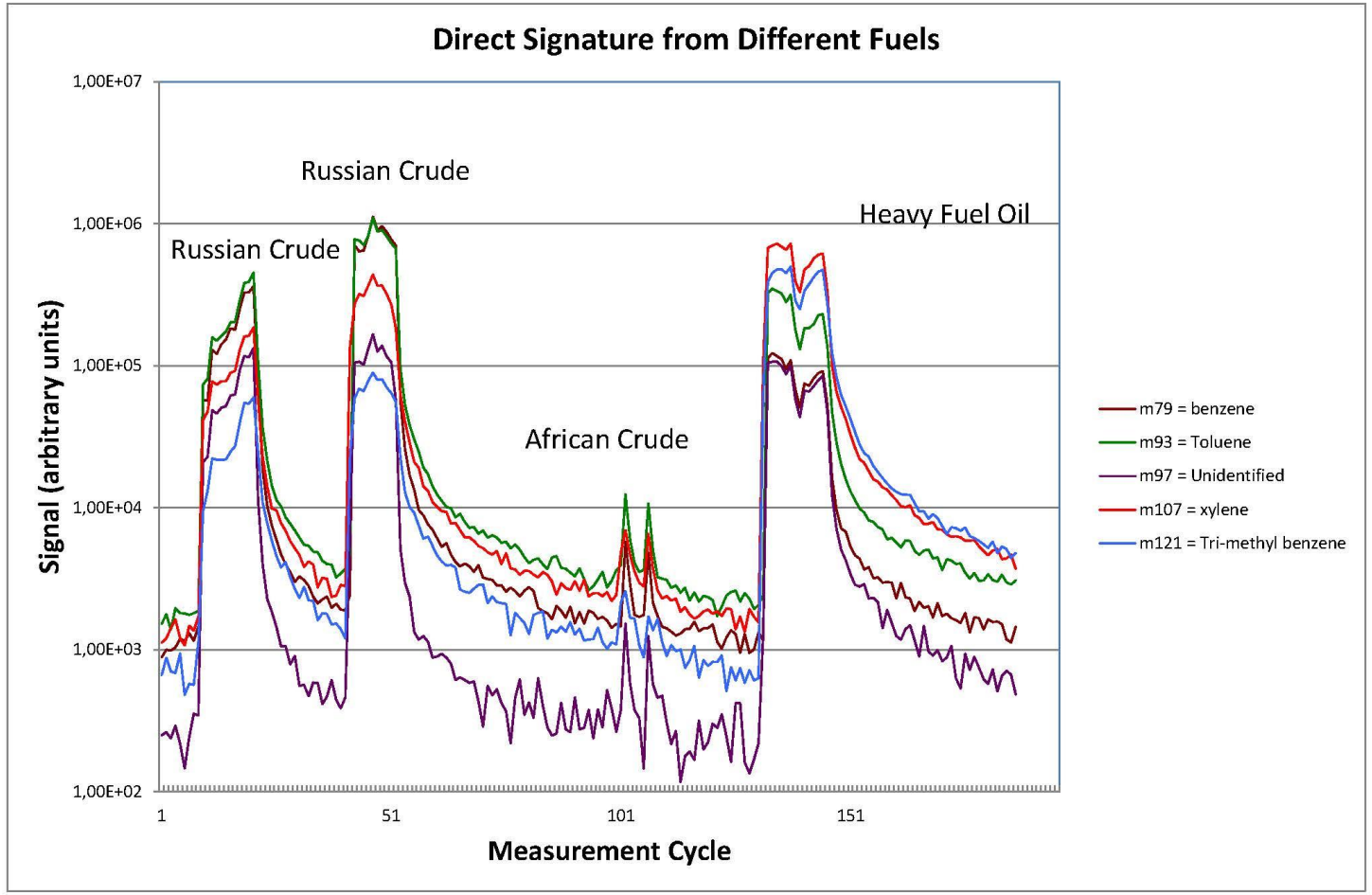
at low [R], $[RH^+]_t = [H_3O^+]_t (k[R]t)$

where $k = k_{collisional}$ can be calculated from theory and
t = drift time of H_3O^+ reactant ions (~ 0.1 ms)

PTR-MS Apparatus used at CEDRE laboratory, Brest, France

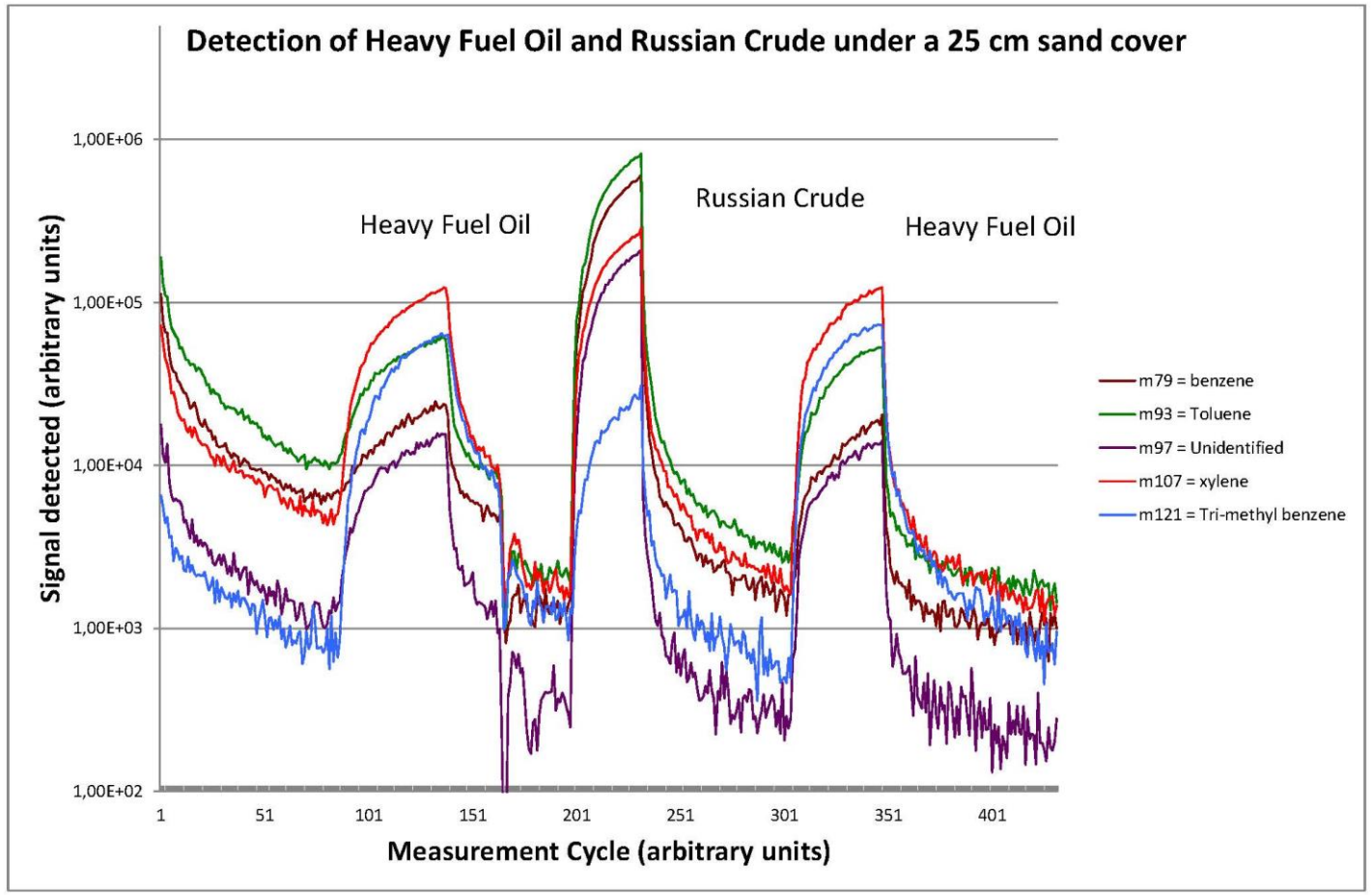
WARNING

Fuel Signatures



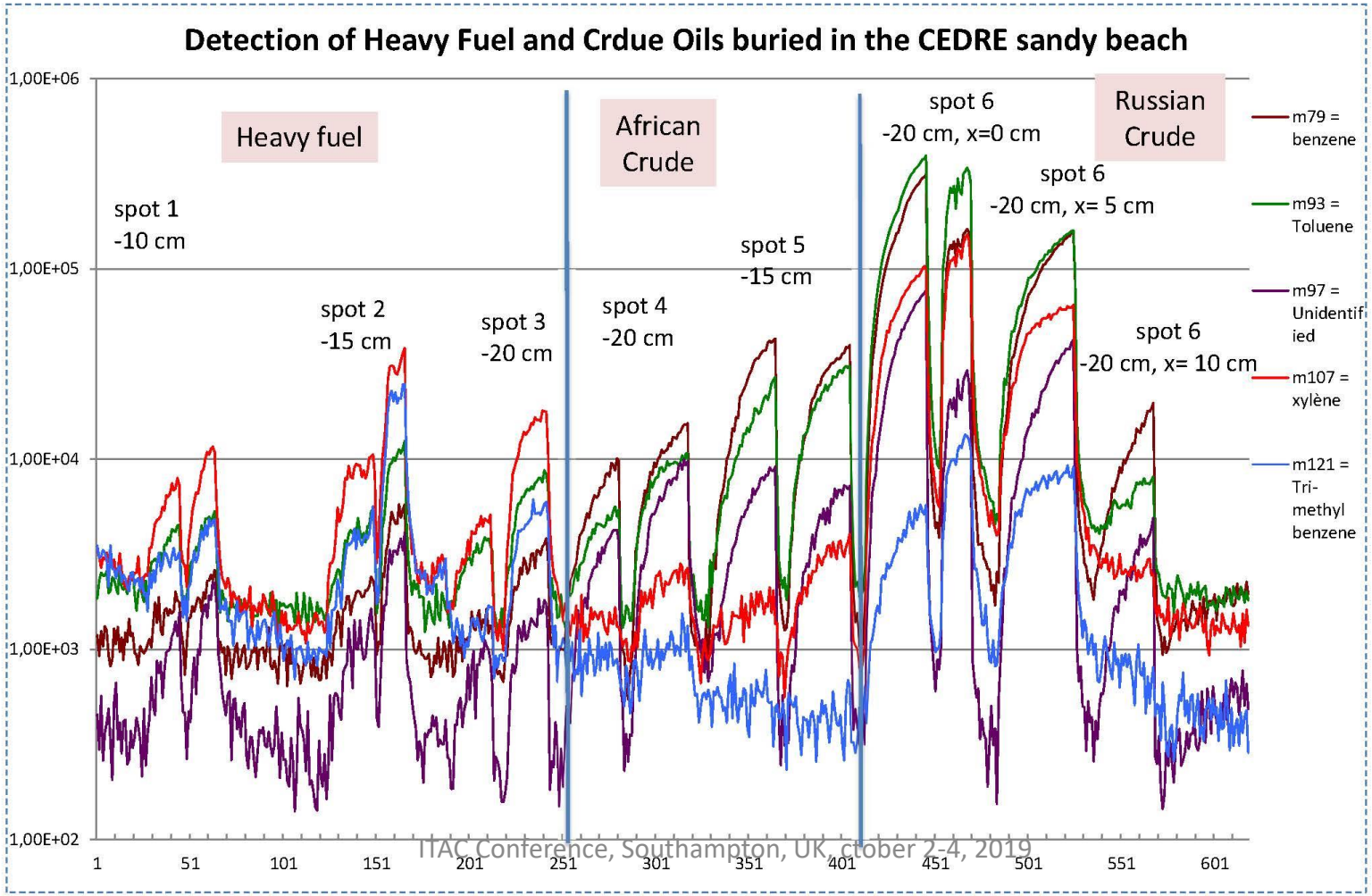
Beaker Test

Result for beaker test

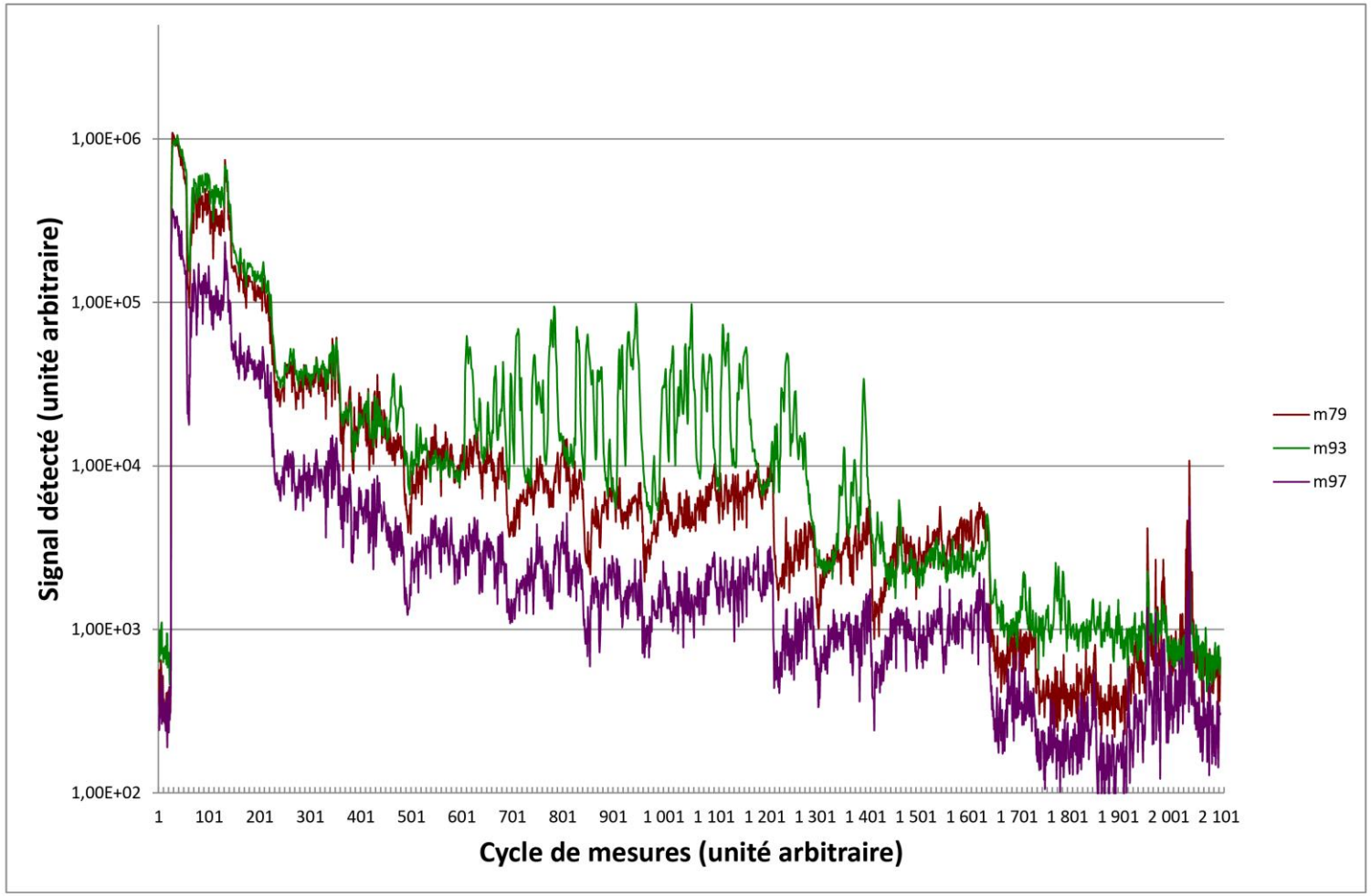


Beach Test

Sand Buried on Beach



Toluene phenomenon during beaker test



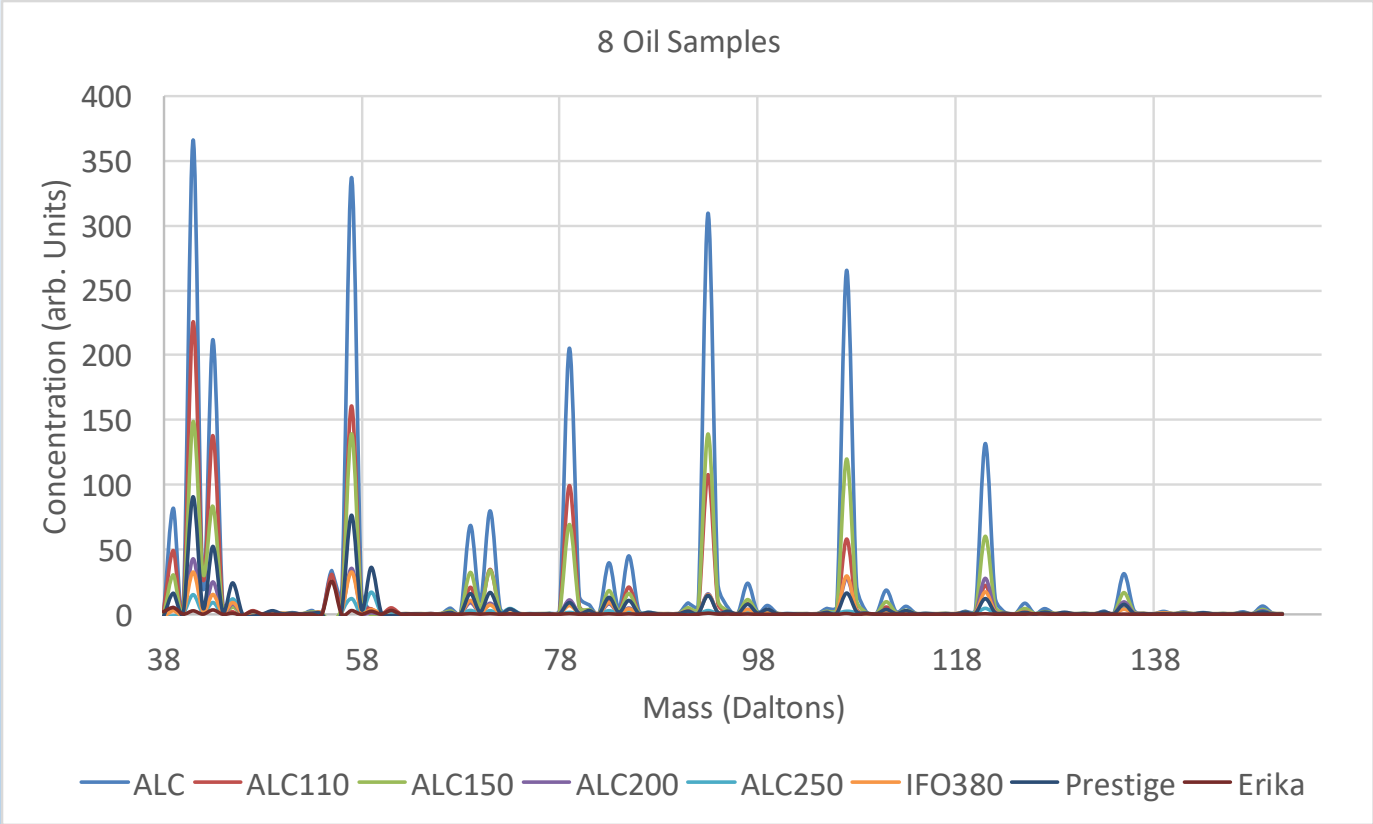
The Canadians!

The Canadians!

Mass 97

- Mike Moir – Chevron Oil, San Francisco
- $C_6H_6 \cdot H_3O^+$ mass = 97
- Benzene hydronium adduct
- $(H_2O).\ H_3O^+ + C_6H_6 \rightarrow C_6H_6 \cdot H_3O^+ + H_2O$

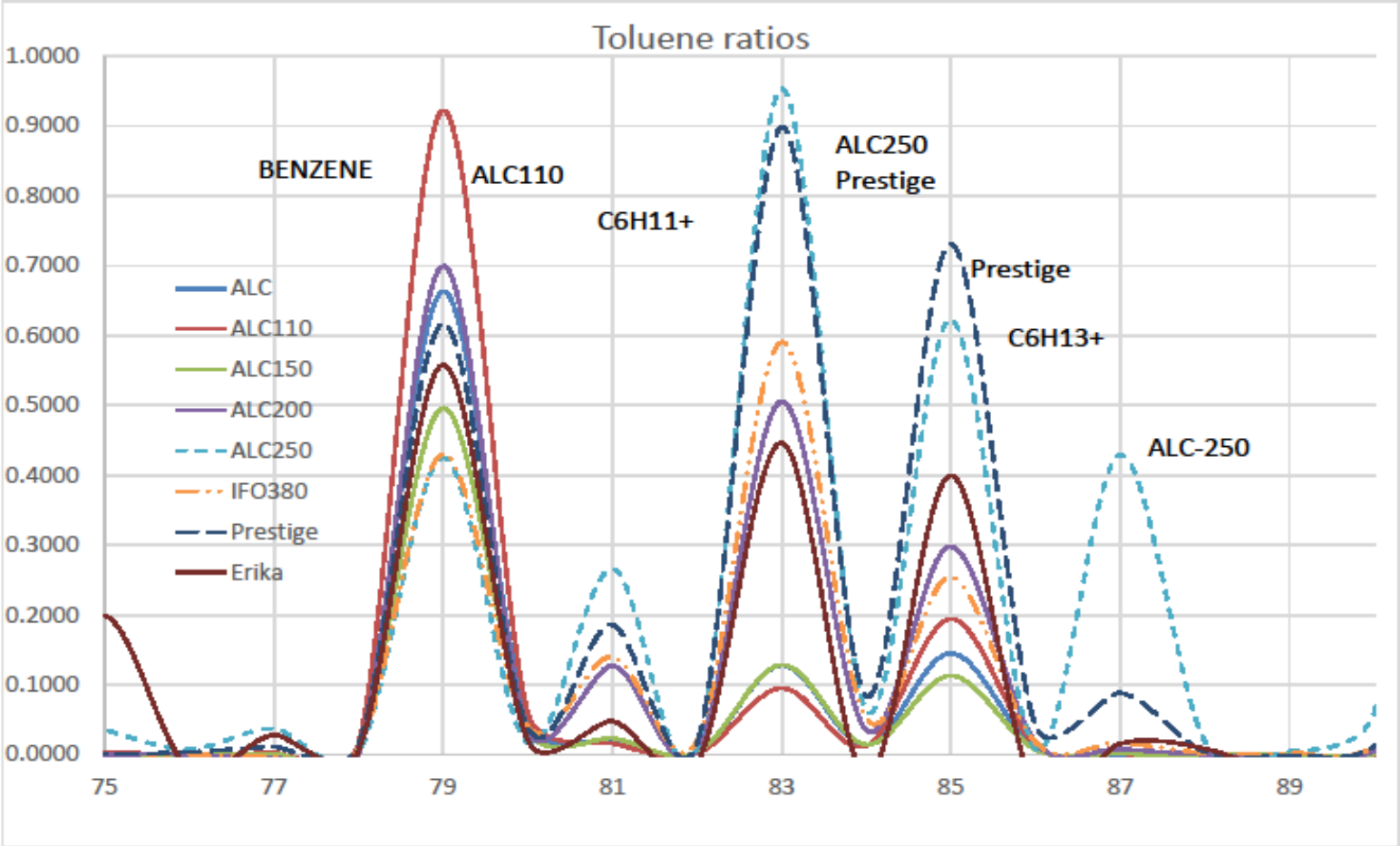
Basic mass spectrum for 8 oil samples



Oil
Arabian Light Crude Fresh
Arabian Light Crude topped at 110° C
Arabian Light Crude topped at 150° C
Arabian Light Crude topped at 200° C
Arabian Light Crude topped at 250° C
IFO 380
Prestige oil (HFO)
Erika oil (HFO)

Mass (Daltons)	Ion	Identity
39	$C_3H_3^+$	
41	$C_3H_5^+$	
43	$C_3H_7^+$	
55	$H_3O^+(H_2O)_2$	Water cluster
57	$C_4H_9^+$	
69	$C_5H_9^+$	
71	$C_5H_{11}^+$	
79	$C_6H_6.H^+$	Protonated benzene
83	$C_6H_{11}^+$	
85	$C_6H_{13}^+$	
91	$C_7H_7^+$	
93	$[C_6H_5CH_3+H]^+$	Protonated Toluene
97	$C_7H_{13}^+$	
99	$C_7H_{15}^+$	
107	$[C_6H_4(CH_3)_2+H]^+$	Protonated xylene
121	$[C_6H_3(CH_3)_3+H]^+$	Protonated Tri-methyl-benzene (TMB)
135	$[C_6H_2(CH_3)_{4.+}H]^+$	Protonated Tetra-methyl-benzene

Toluene peak normalization



Conclusions and Future Work

- Possible to detect fresh and weathered oil under 10 inches of sand.
- Identification of oil signatures possible
- Future Work*
- Field trials planned with RETIA (Total Subsidiary) of contaminated site surveying
  - More systematic study of detection with blind tests
  - Oil under ice test –possibilities of detection of oil trapped under ice?
  - Development of a protocol for detection – sampling array

  - Development of more portable apparatus*

  - *Depending upon funding

Lubrizol Plant Fire, Rouen 27, September 2019