# Atmospheric Pressure Photo Ionisation in Environmental Chemistry

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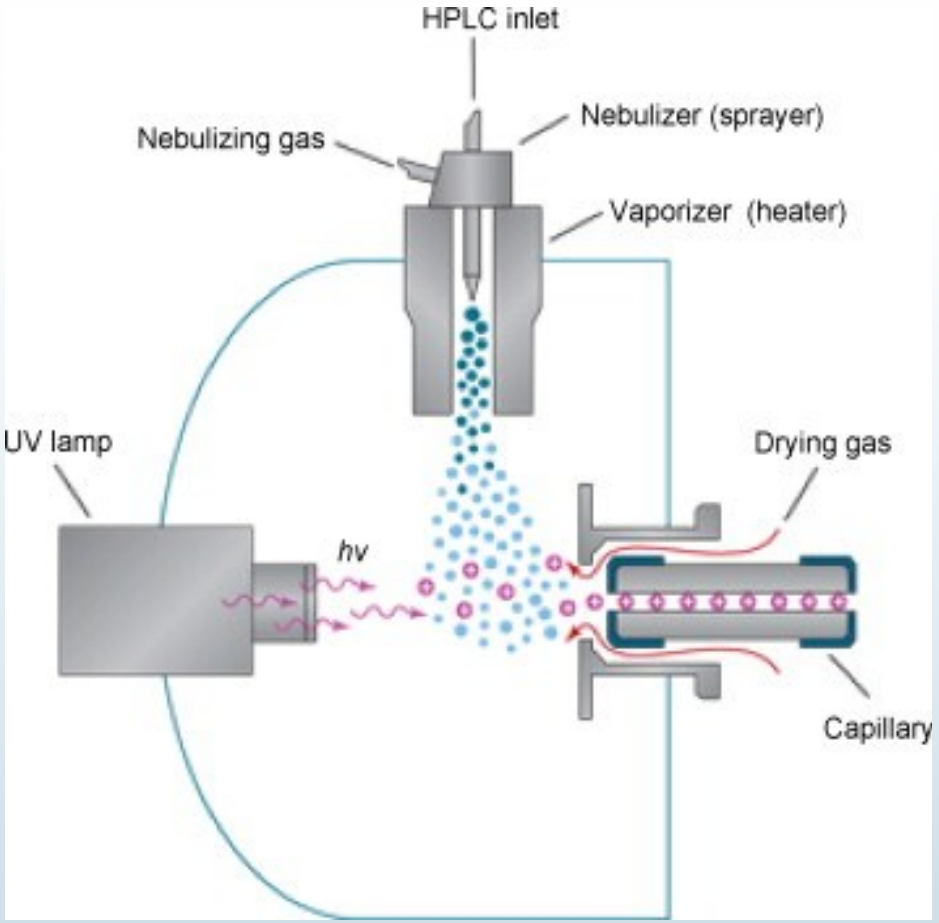
# Outline

- Principles APPI
- Experimental observations
- Environmental chemistry: Applications
  - Positive ionisation
  - Negative ionisation

# APPI principle

- Published in 2000 by Bruins and co-workers
- First application of photo ionisation in combination with LCMS
- Ionisation energy lamp < LC eluent



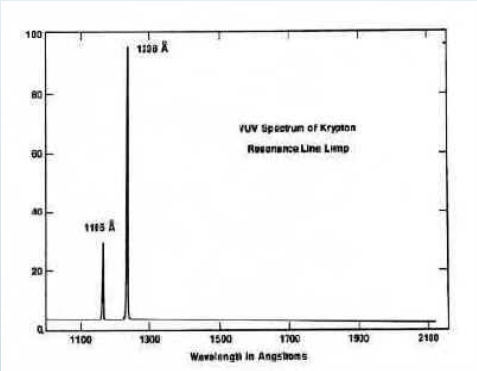
# Krypton Lamp

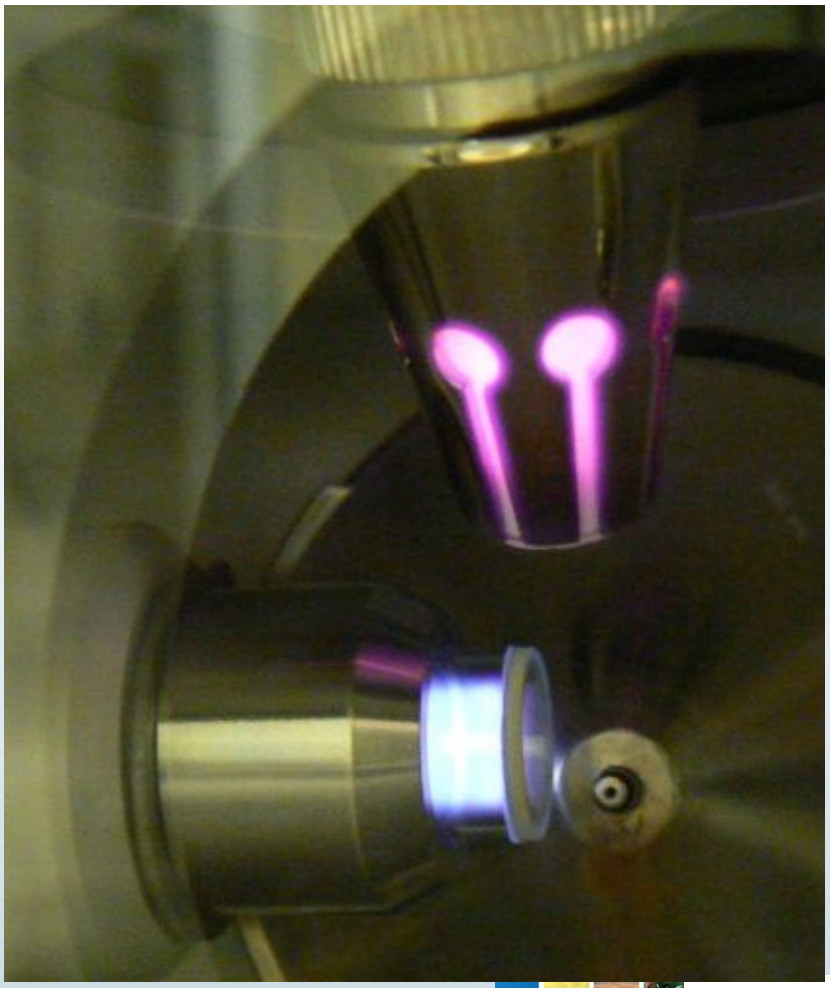
## V.U.V. (Vacuum Ultra Violet)

- Most common lamp used for photo ionisation
- Two emission wavelengths

$$E = h \cdot \nu$$

- Two ionisation energies
- 10.03eV and 10.64eV (4:1)



# Ionisation energy

Components with IE < lamp

Don't use solvent modifiers:

- Ammonium has a high proton affinity
- Acids may lead to signal suppression due to competition with positively and negatively charged particles

Use "Dopant" liquid (5-10% of solvent flow) with an I.E. < lamp

| Component | Ionisation energy (eV) |
|---|---|
| Nitrogen | 15.58 |
| Water | 12.62 |
| Acetonitrile | 12.20 |
| Oxygen | 12.07 |
| Krypton lamp | 10.03/10.64 |
| Methanol dimer | 8.74 |
| Acetone | 9.70 |
| Benzene | 9.24 |
| Toluene | 8.83 |

# Mechanisms I

## Direct APPI

*Direct APPI*

$M + h\nu \rightarrow M^*$

If Ionisation energy < E = $h\ ^*\nu$

$M^* \rightarrow M^{*+} + e^-$

*"solvent" APPI (S)*

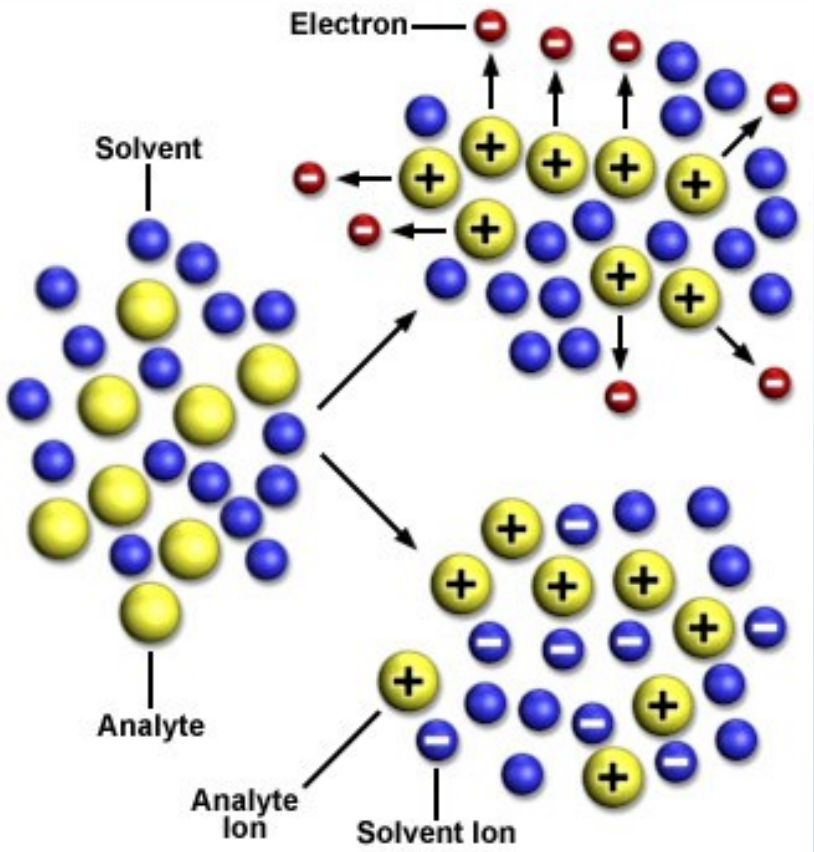
$M + S + h\nu \Rightarrow [M + H]^+ + [S - H]^-$

*'Electron capture', charge transfer*

$M + e^- \Rightarrow M^-$

$M + S + e^- \Rightarrow [M + S]^-$

$O + e^- \Rightarrow O^- ; M + O^- \Rightarrow [M+O]^-$



# Mechanisms II

## Dopant APPI

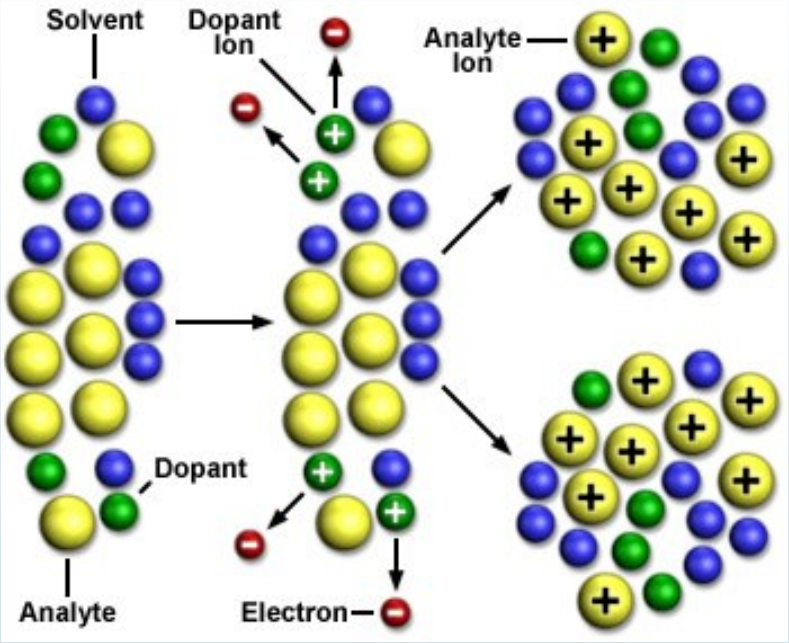
$$D + h\nu \rightarrow D^{\bullet+} + e^-$$

(1) charge transfer

$D^{\bullet+} + M \rightarrow D + M^{\bullet+}$ $(EA_D > EA_M)$

(2) Proton transfer

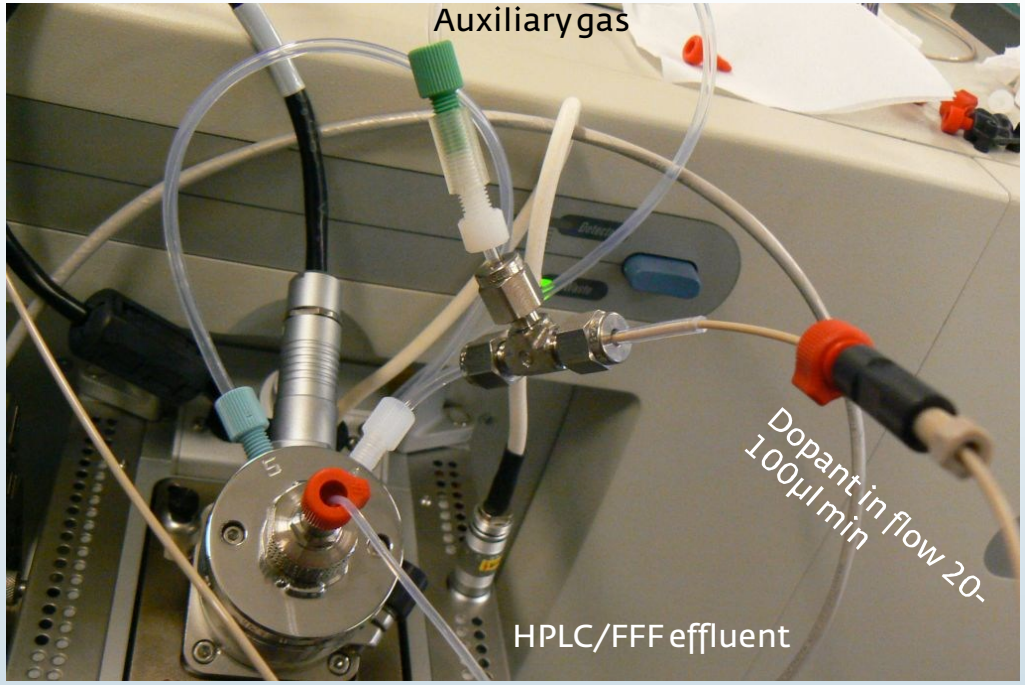
$D^{\bullet+} + M \rightarrow [D-H]^{\bullet} + [M+H]^+$ $(PA_M > PA_{[D-H]\cdot})$

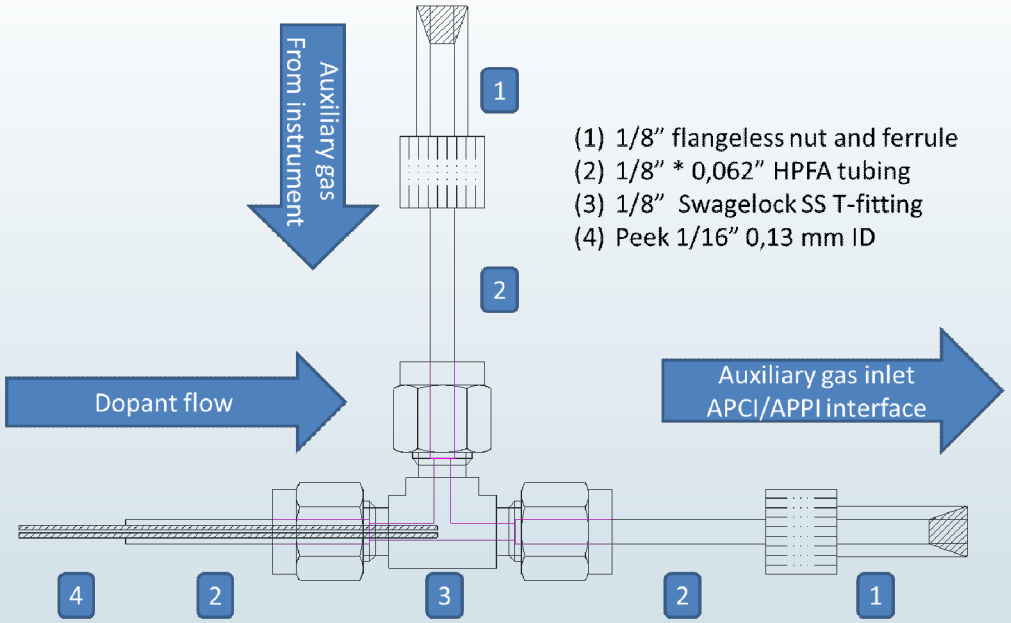


Experimental

# Practical experiences

## Reversed phase system



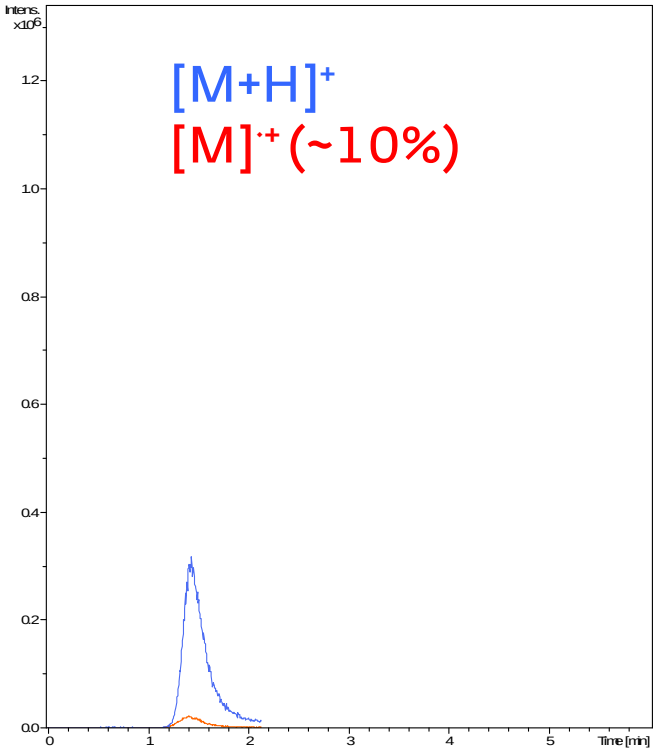

Herrero et al. J.Chrom.A 2014

# APPI dopants

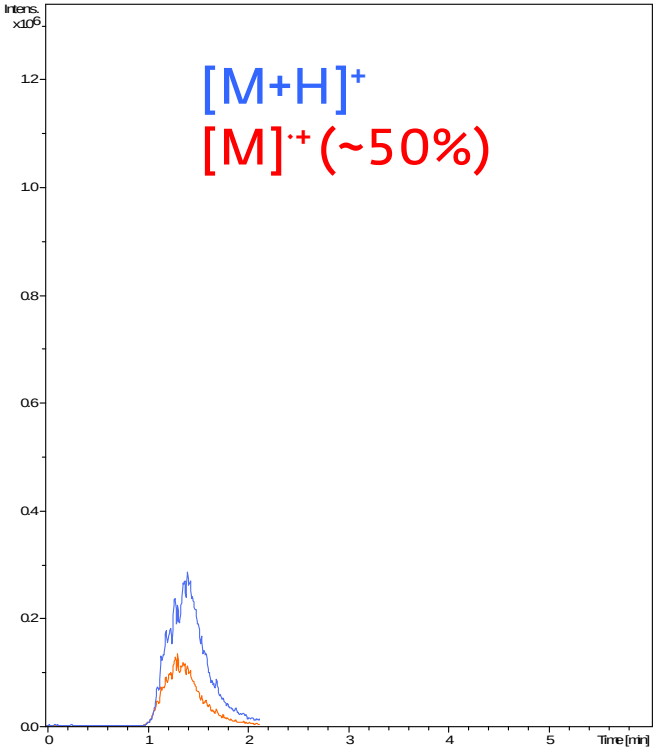
Experimental

## Injections of anthracene standard solution, FIA in QTOF

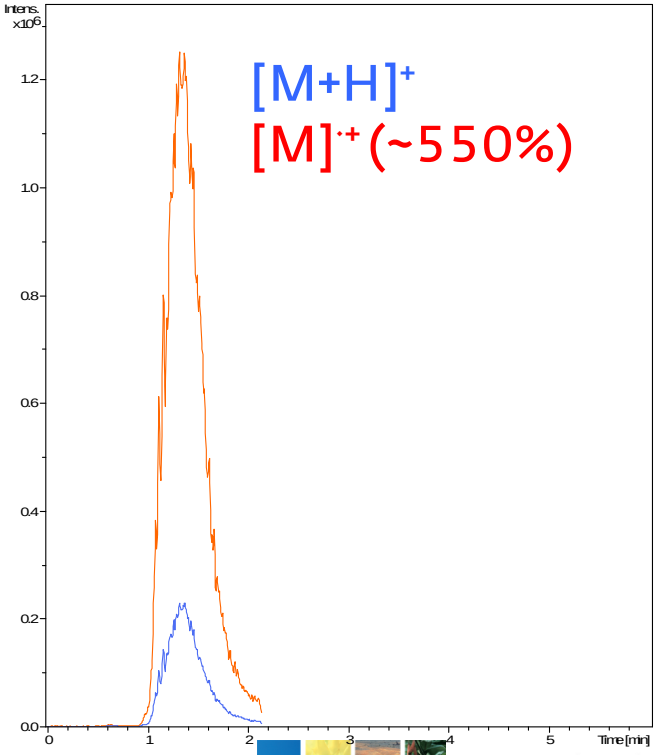
### No dopant




### 10% toluene




### 10% toluene + 0.05% anisole

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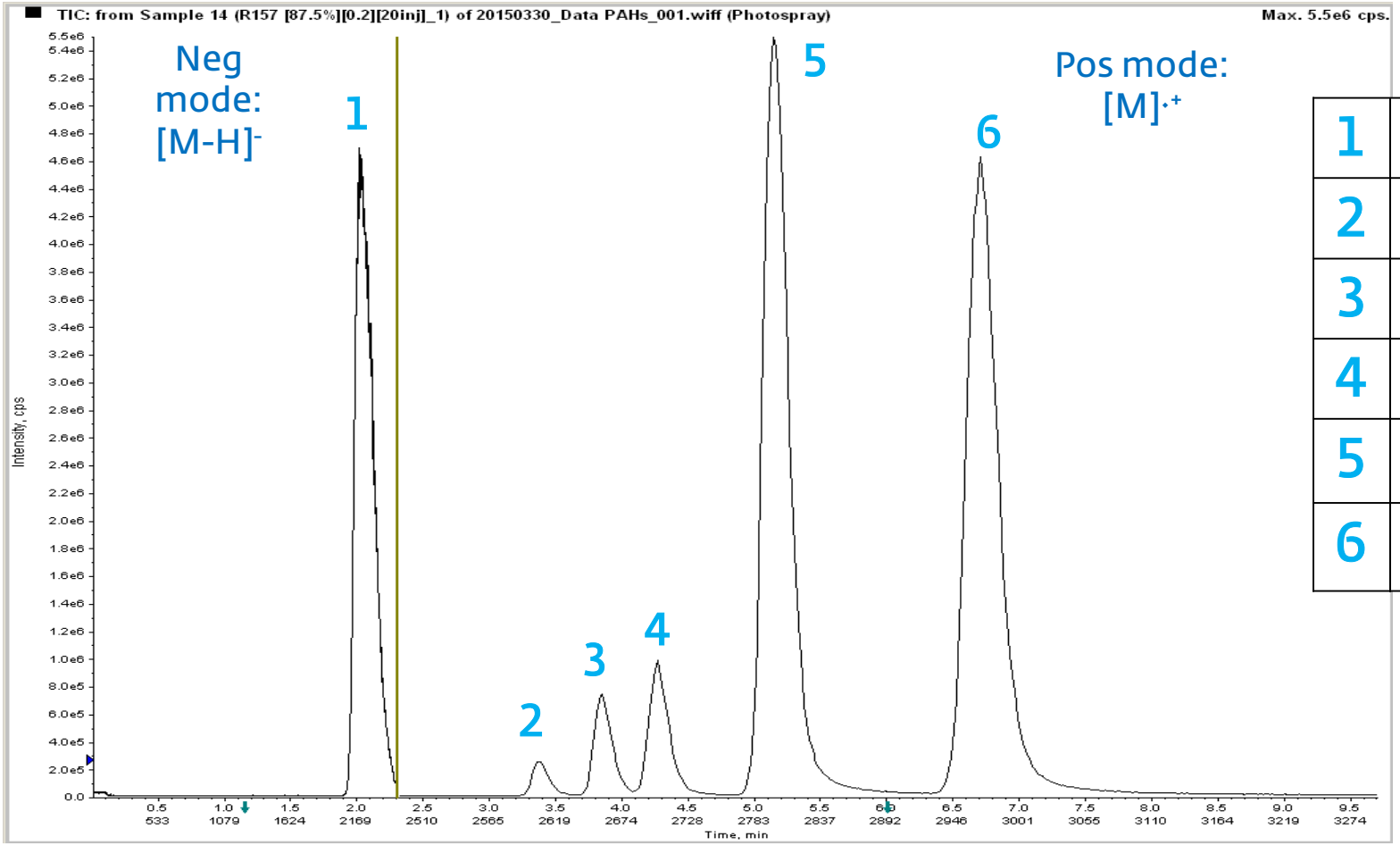
# Applications APPI

| | | Detection |
|---|---|---|
| Pharmaceuticals | Cai et al.2005/Wang et al. 2012 | MS/MS |
| Hormones | Yamamoto et al.2006/Wang et al.2012 | MS/MS |
| Toxines | Capriotti et al. 2012 | MS/MS |
| Pesticides | Itoh et al. 2009/Yamamoto et al. 2012 | MS/MS |
| PAHs | Hollosi 2012 | MS/MS |
| Azareenes | Brulik et al. 2013 | MS/MS |
| Fullerenes | Li et al. 2012 /Nunez et al. 2013; Emke et al.2015 | Ion trap / Orbitrap and FTICR |
| Screening | Chiaia-Hernandez | Orbitrap |

Modified from Vughs and Kolkman , BTO 2013.236 (s), KWR

# LC Retention experiments (courtesy: Jort Hammer, UvA)




| | |
|---|---|
| 1 | Uracil ($t_0$) |
| 2 | Anthracene |
| 3 | Pyrene |
| 4 | Chrysene |
| 5 | Benzo[k]fluoranthene |
| 6 | Benzo[ghi]perylene |

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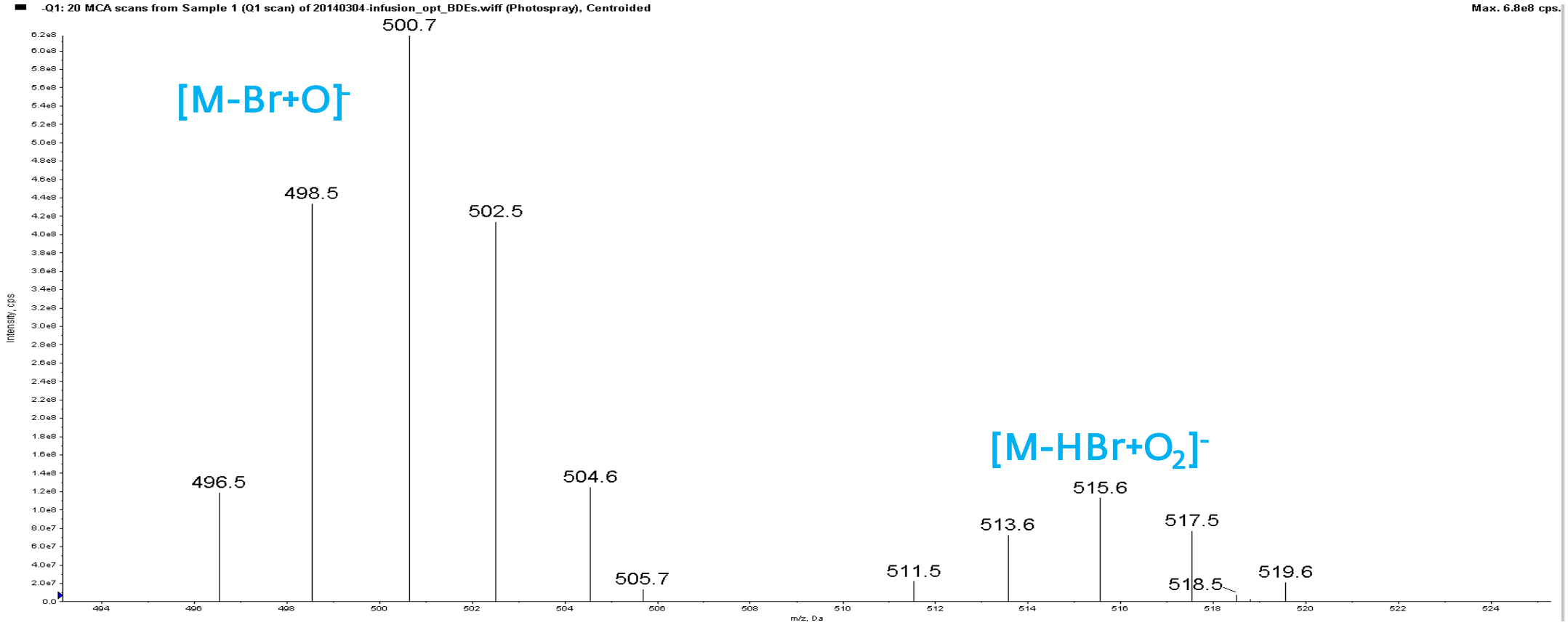
# Penta BDE MS

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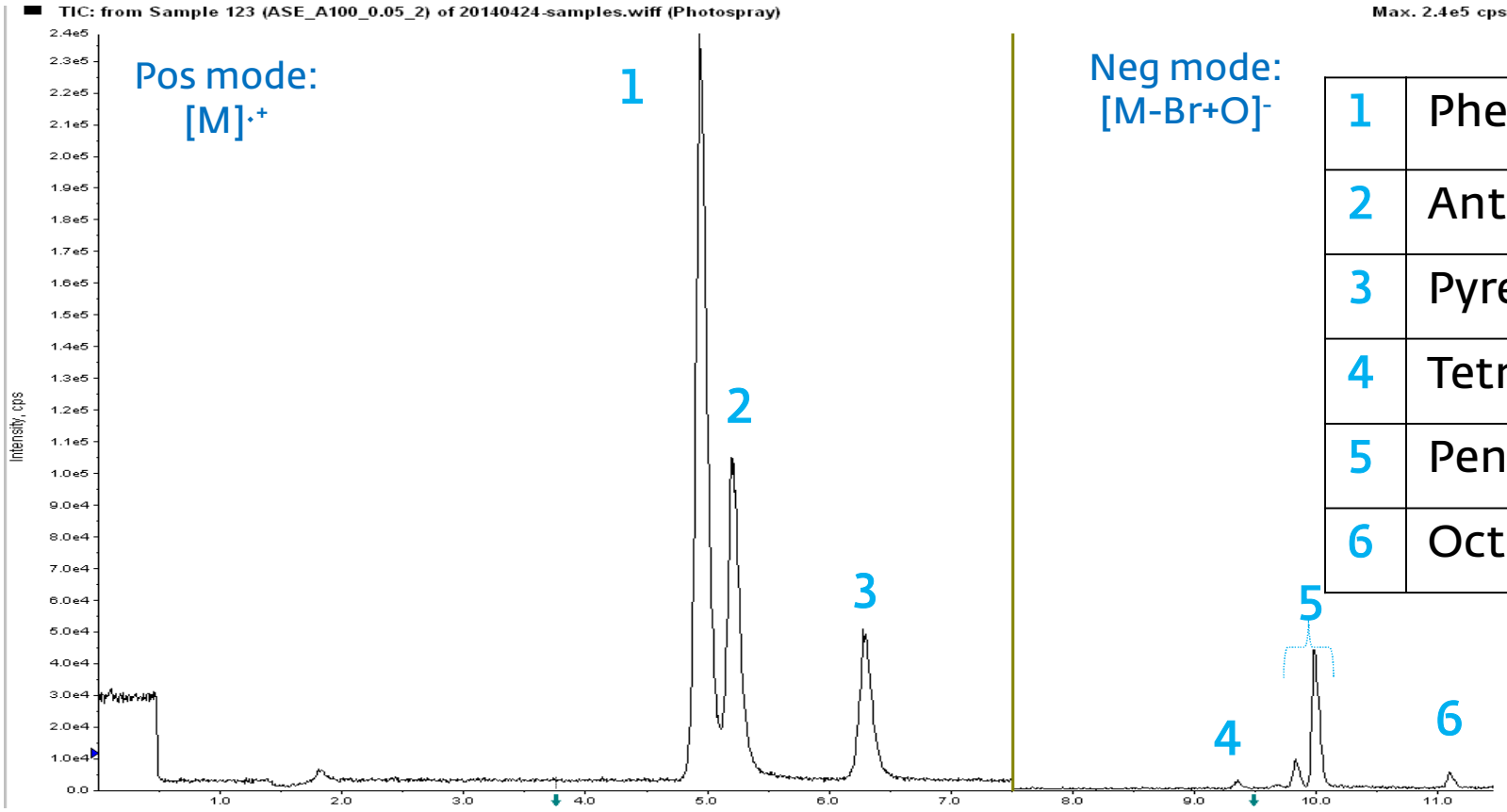
# Sorption to micro/nano plastics (courtesy Eugenie Troia, UvA)




| | |
|---|---|
| 1 | Phenanthrene |
| 2 | Anthracene |
| 3 | Pyrene |
| 4 | Tetra BDE |
| 5 | Penta BDE |
| 6 | Octa BDE |

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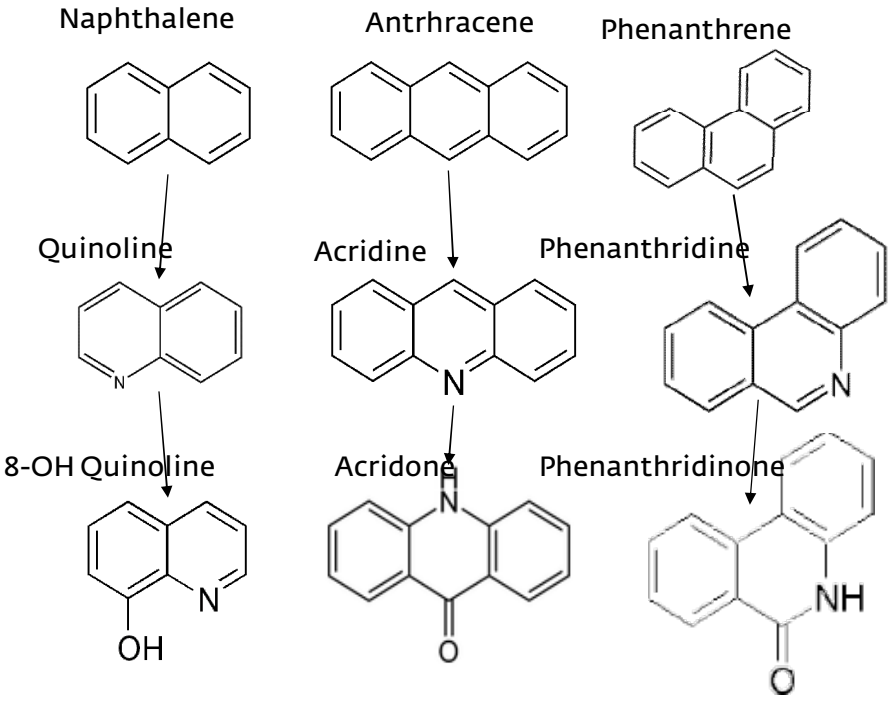
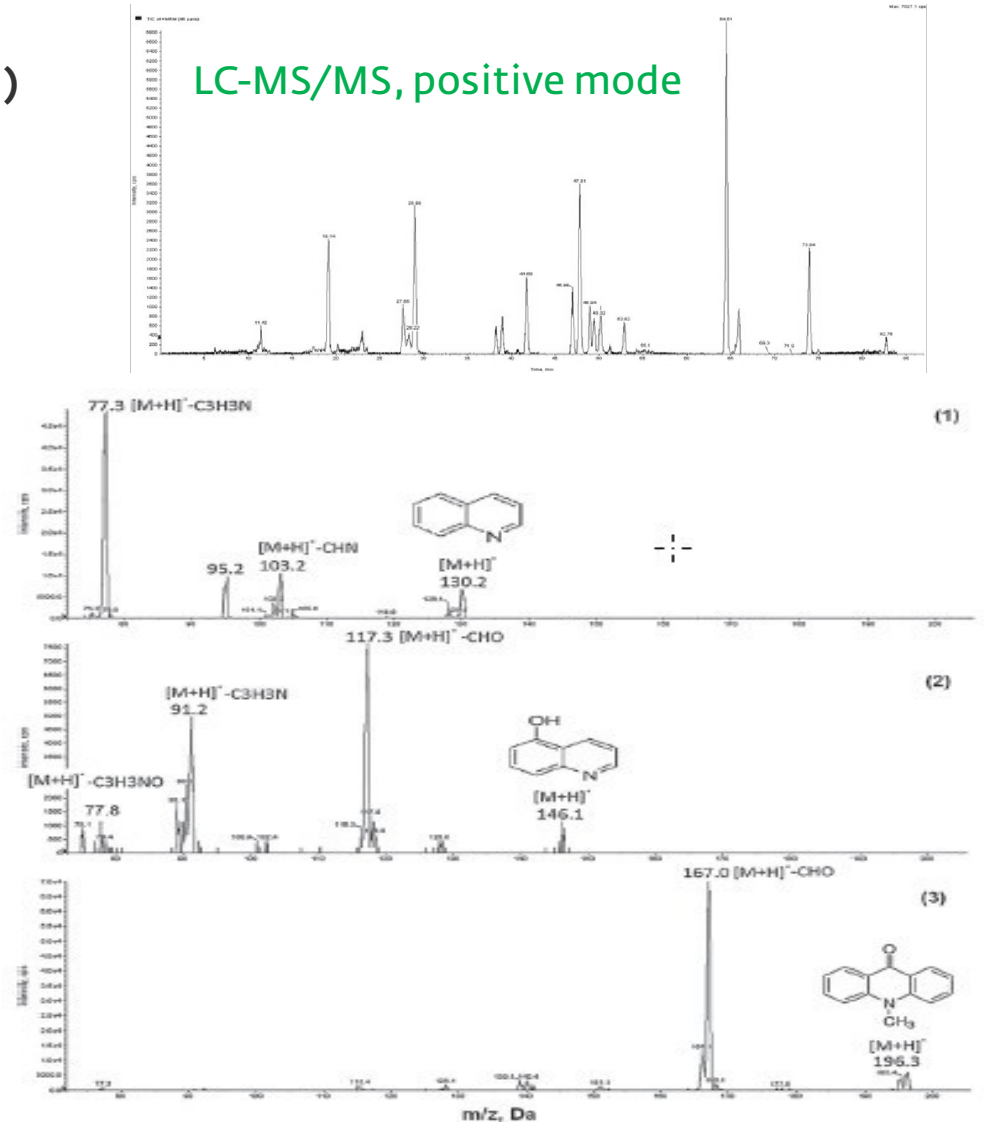
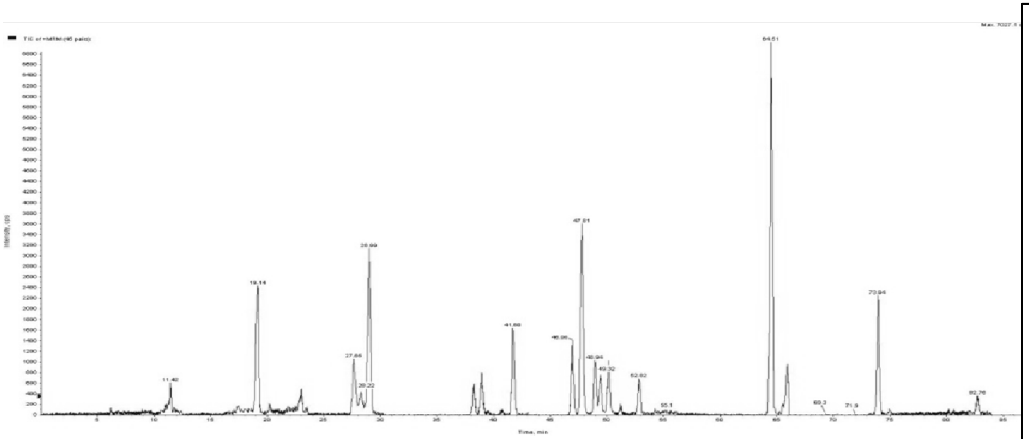
# Azaarenes (Brulik et al. J.Chrom.A,2013)



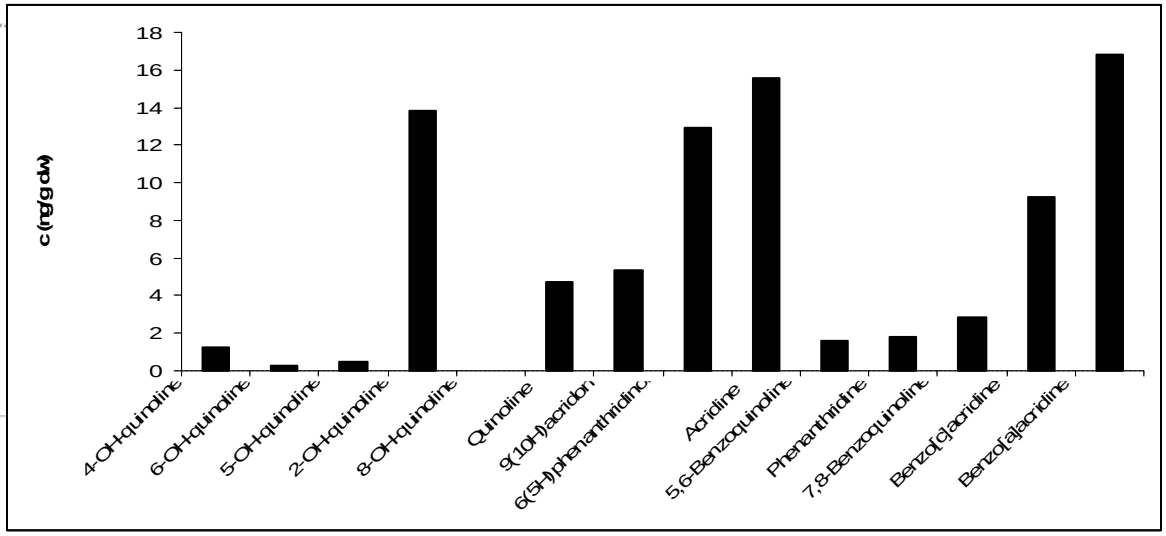

LC-MS/MS, positive mode



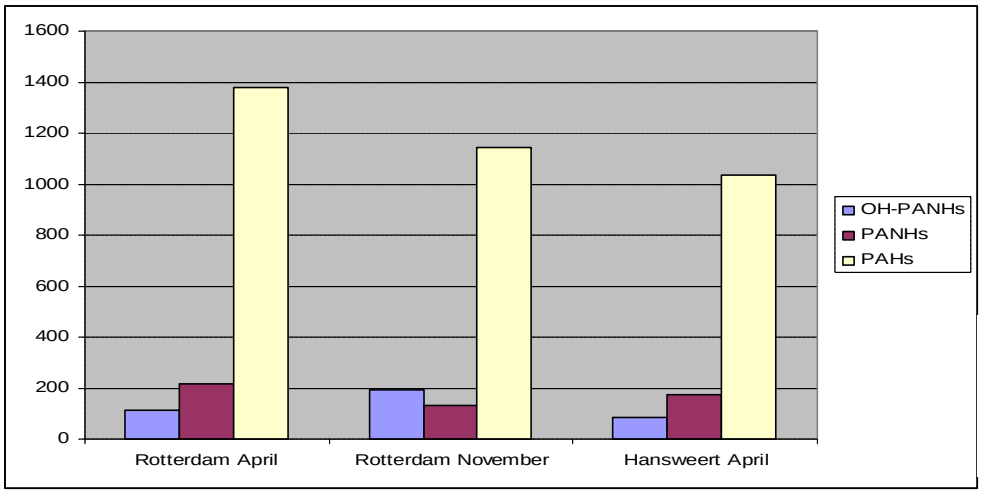
# Results Azaarenes (Brulik et al. J.Chrom.A 2013)



Real sediment sample chromatogram




Mean concentrations in ng/g dw (n=9) in the sediments from Dutch rivers (Rhine at NWW and W-Scheldt)



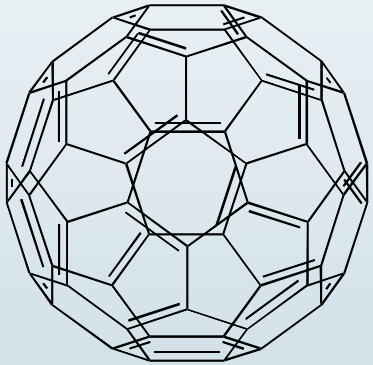

Average concentrations (ng/g dw) of sum of OH-PANHs, PANHs and PAHs. (Rotterdam April n=5, Rotterdam November n=2, Hansweert n=3)

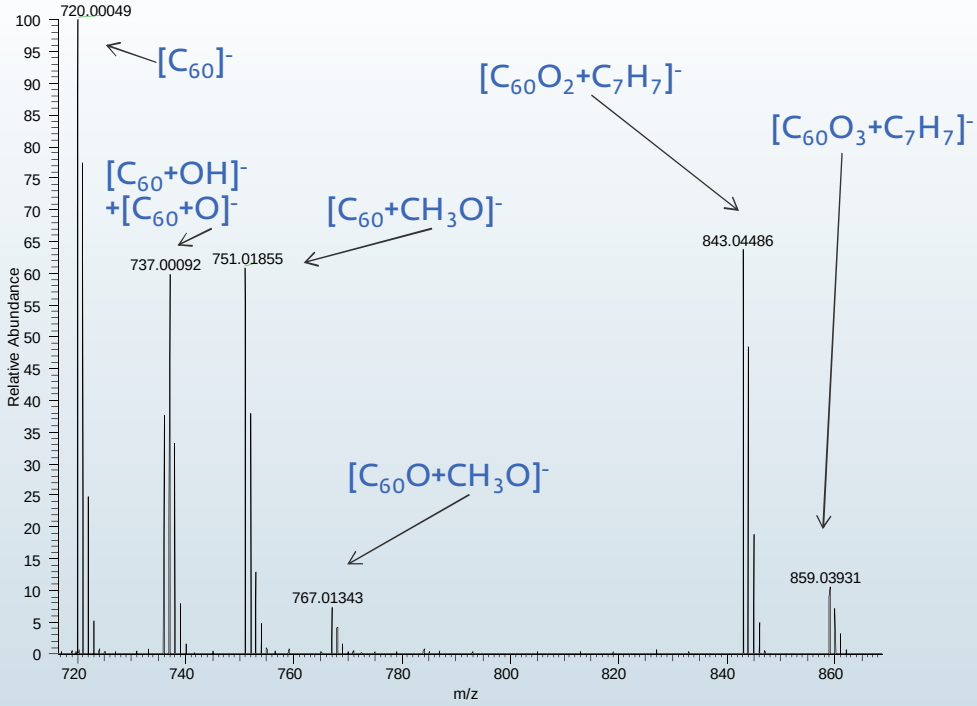
Applications

# Fullerenes

## Fullerene analysis with HPLC-HESI-Orbitrap, negative mode

- Buckyprep column (normal phase)
- Eluent: toluene/acetonitrile
- Electron donor methanol post column infusion
- Interface HESI
- Tube lens 200 V

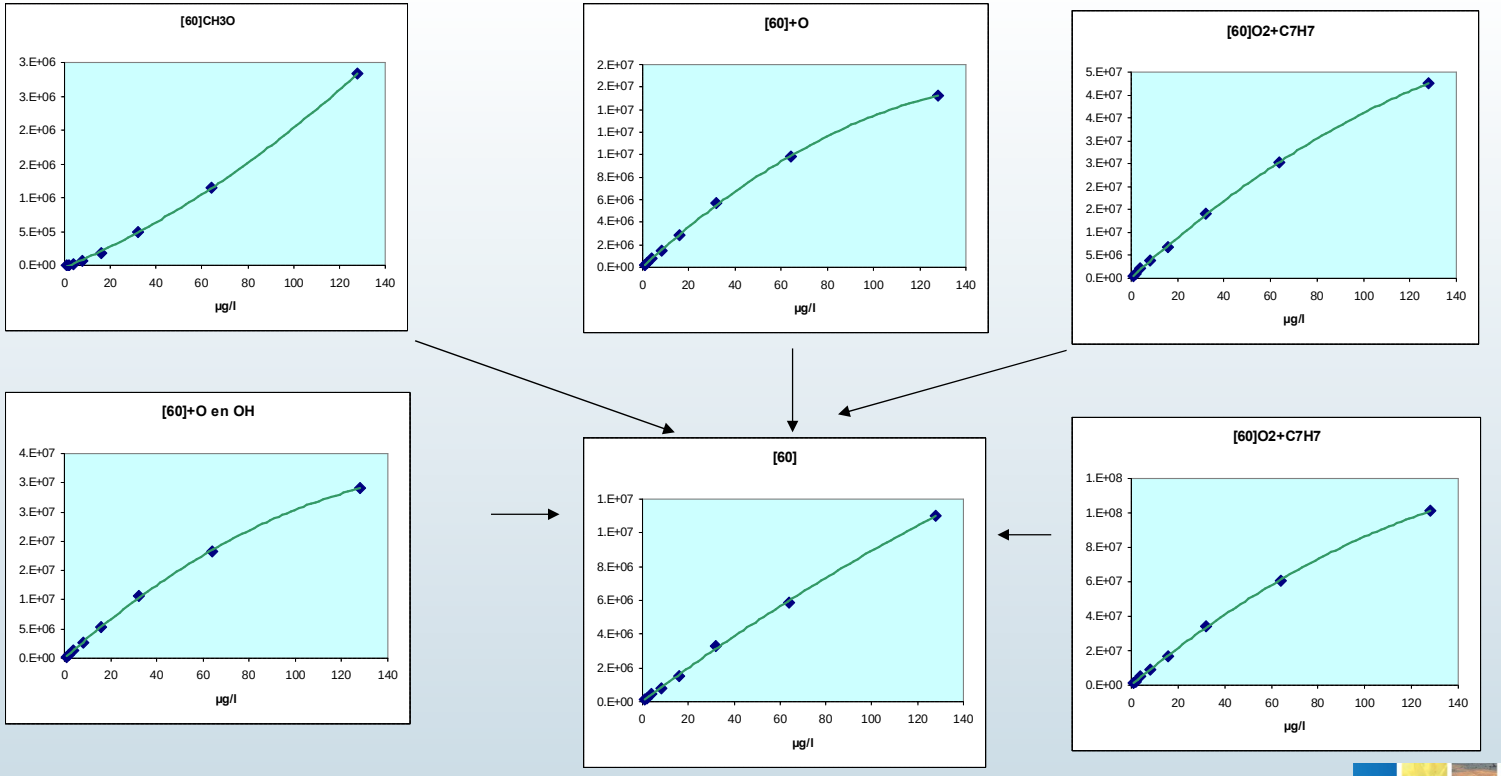





Emke et al, Environ.Sci. Nano 2015

# Calibration

## HPLC-HESI-Orbitrap: different calibration curves for every adduct



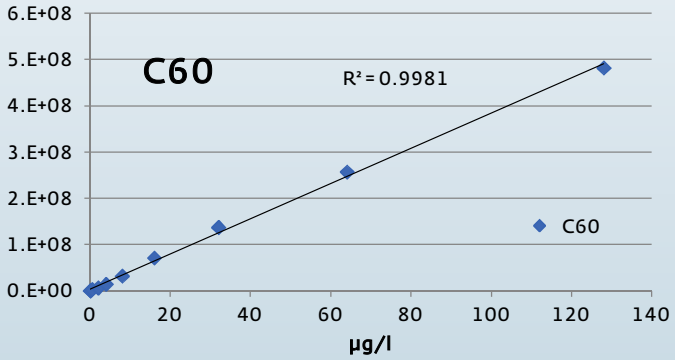
Applications

# Fullerenes

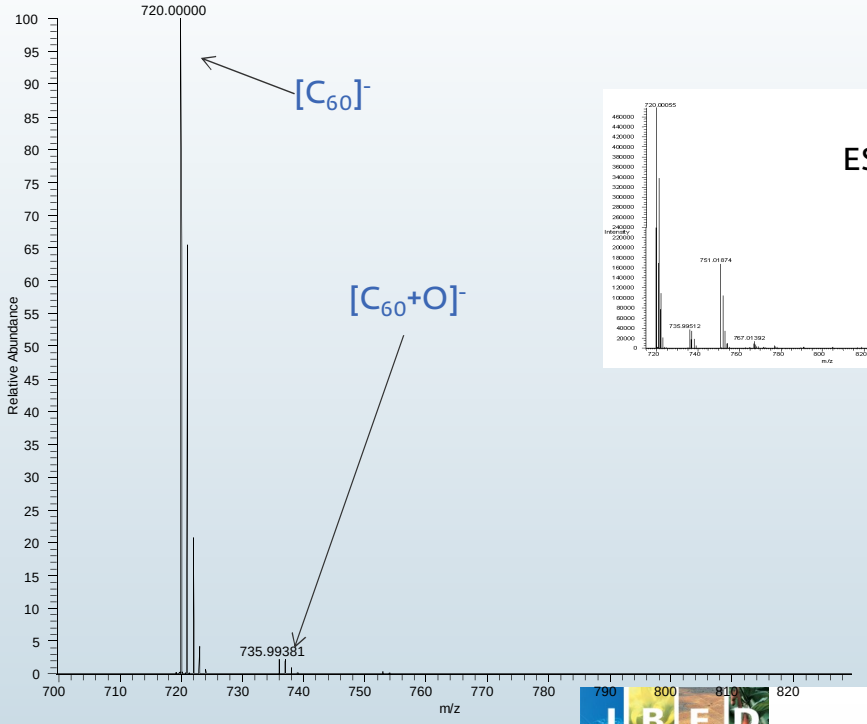
## Fullerene analysis with HPLC-APPI-Orbitrap, negative mode

- Buckyprep column (normal phase)
- Eluent: toluene
- Interface APPI (no dopant necessary)
- Tube lens 200 V

- Linear 0.025µg/l – 128 µg/l




HPLC (toluene) -APPI-Orbitrap

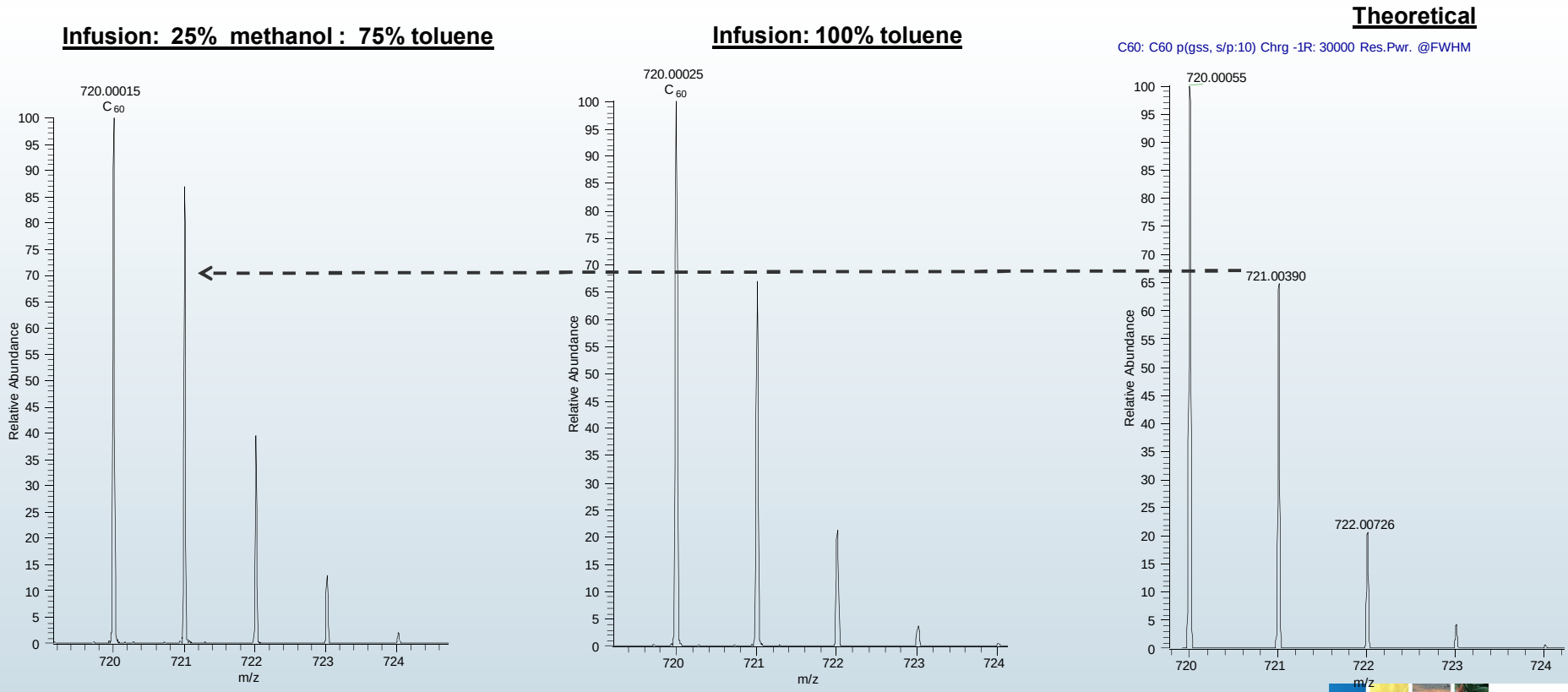



Emke et al, Environ.Sci. Nano 2015

Applications

# APPI of Fullerenes, identification

## Influence of presence of methanol in toluene on the isotopic pattern




Emke et al, Environ.Sci. Nano 2015

# Conclusions

- **APPI is a promising technique for identification and quantification of apolar emerging compounds**
- **Apolar compounds including Fullerenes can be very well analysed in negative mode by APPI/MS**
  - Low LODs, wide linear response ranges , little adduct formation
  - Potential for widening non target screening scope
- **In positive mode many components can be ionised, but**
  - Background problems from atmospheric contamination
- **APPI in positive mode combined with Orbitrap : applications far from simple. May be solved by using**

  **APPI unit in $N_2$-pressurised/flushed box**
- **Target screening: use APPI-QqQ.**

# Acknowledgements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