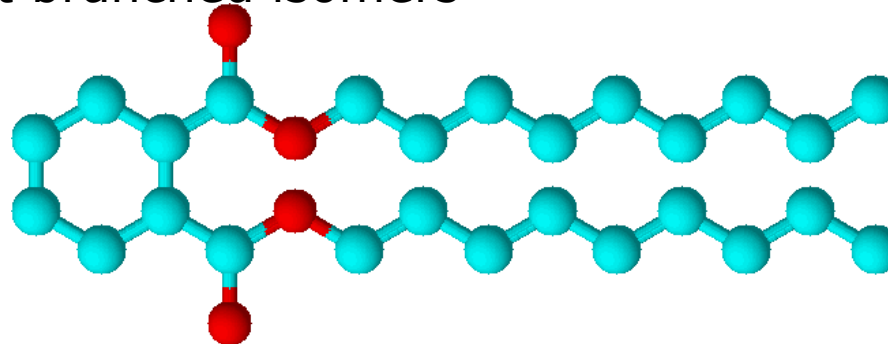


# Determining High-Molecular Weight Phthalates in Sediments using Atmospheric Pressure Gas Chromatography (APGC)

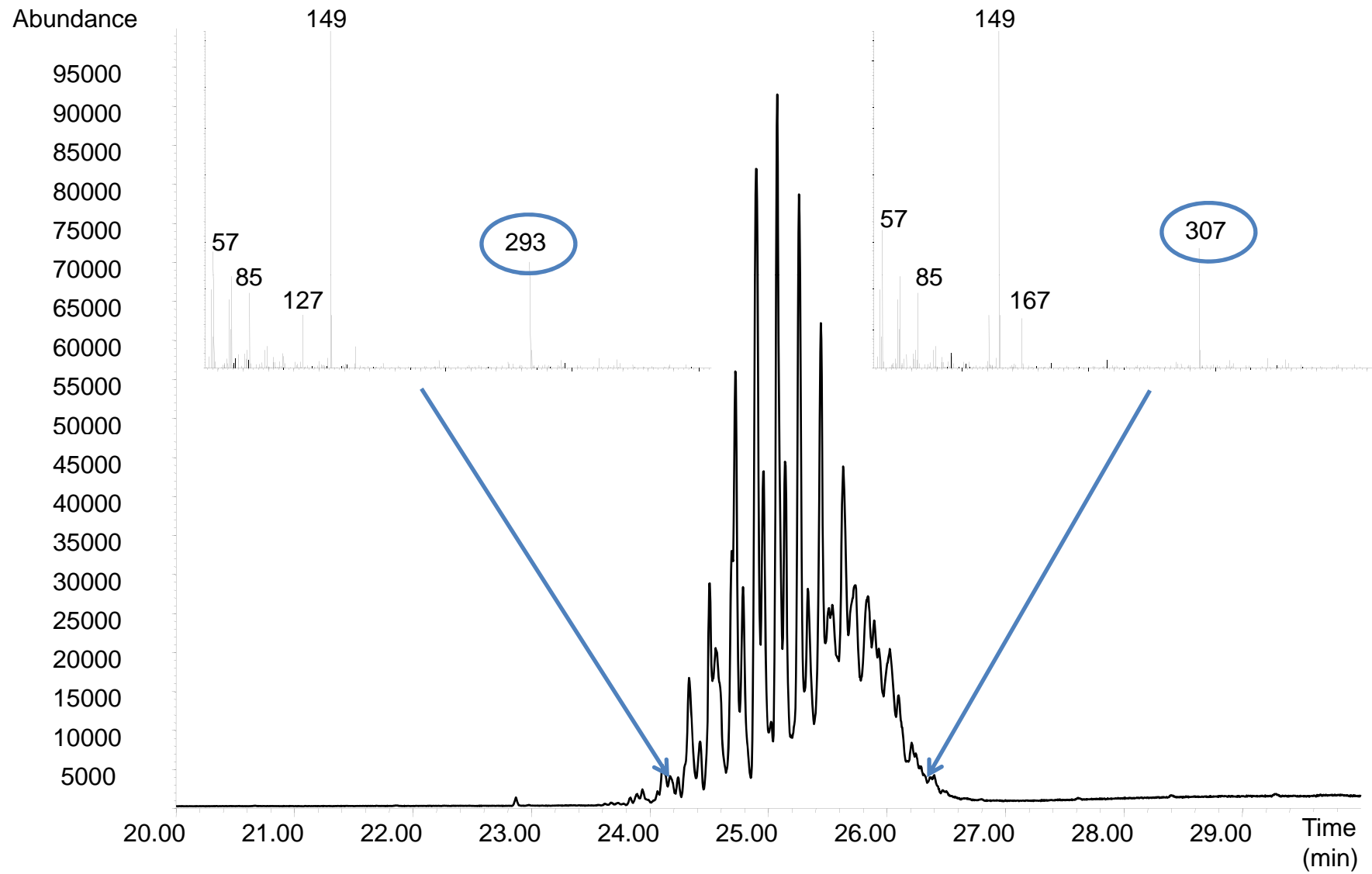
Chemical Analysis Business Operations  
Waters Corporation  
Milford MA  
Email: [ken\\_rosnack@waters.com](mailto:ken_rosnack@waters.com)

# High-Molecular Weight Phthalates

- Phthalates are considered to be potential EDCs
- Classical environmental methods focus on the analysis of dialkyl esters of phthalic acid by GC/MS
  - Dimethyl phthalate (DMP) to dioctyl phthalate (DOP)
  - Dibutyl (DBP), Di-isobutyl (DiBP) and 2-ethylhexyl (DEHP) phthalates are the most important found in environmental samples
- More recently attention has switched to di-isononyl phthalate (DiNP) and di-isodecyl phthalate (DiDP) from C<sub>9</sub>- and C<sub>10</sub>-alcohols
  - GC analysis results in a cluster of unresolved peaks corresponding to different branched isomers

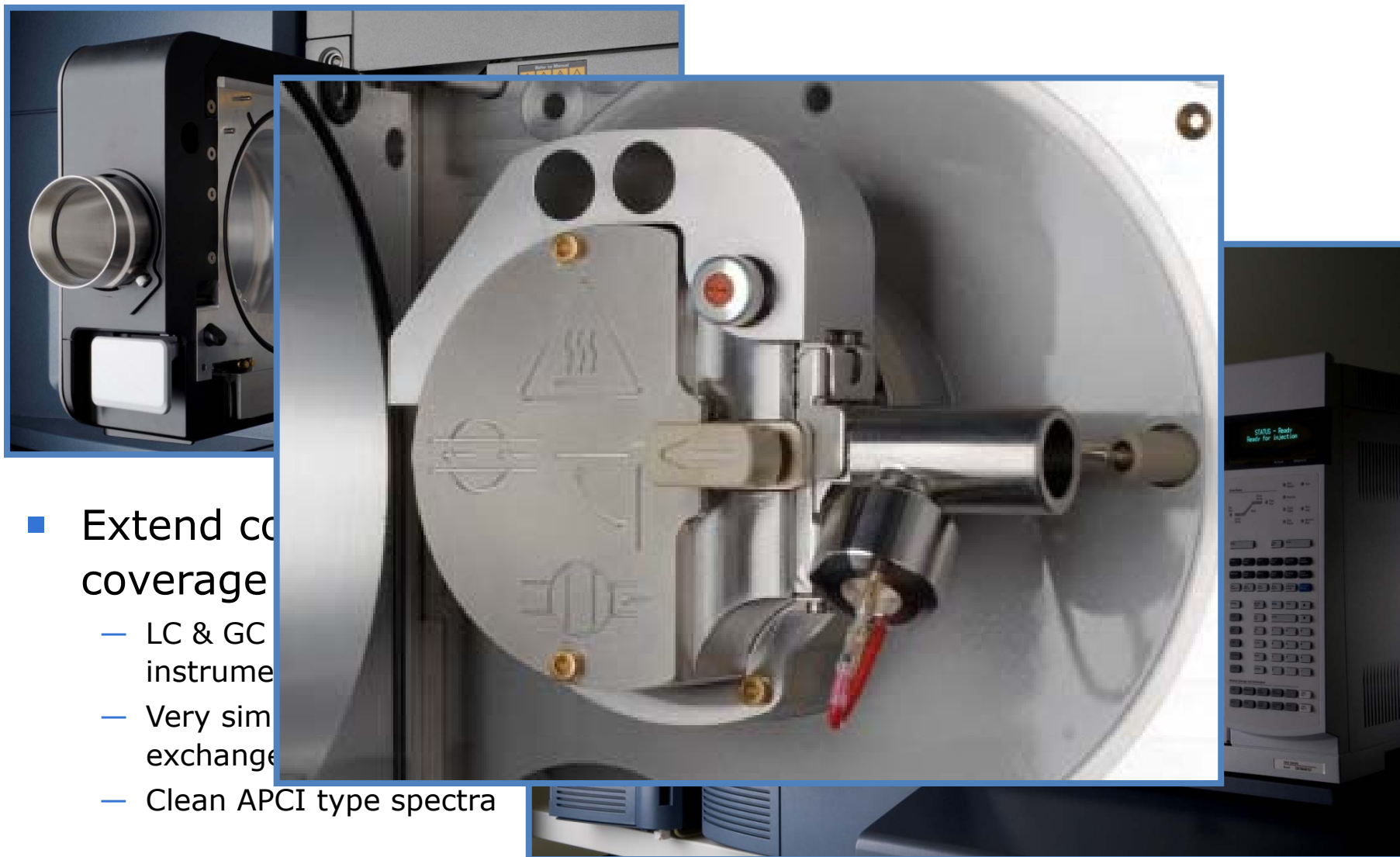


# GC-EI-MS DiNP/DiDP



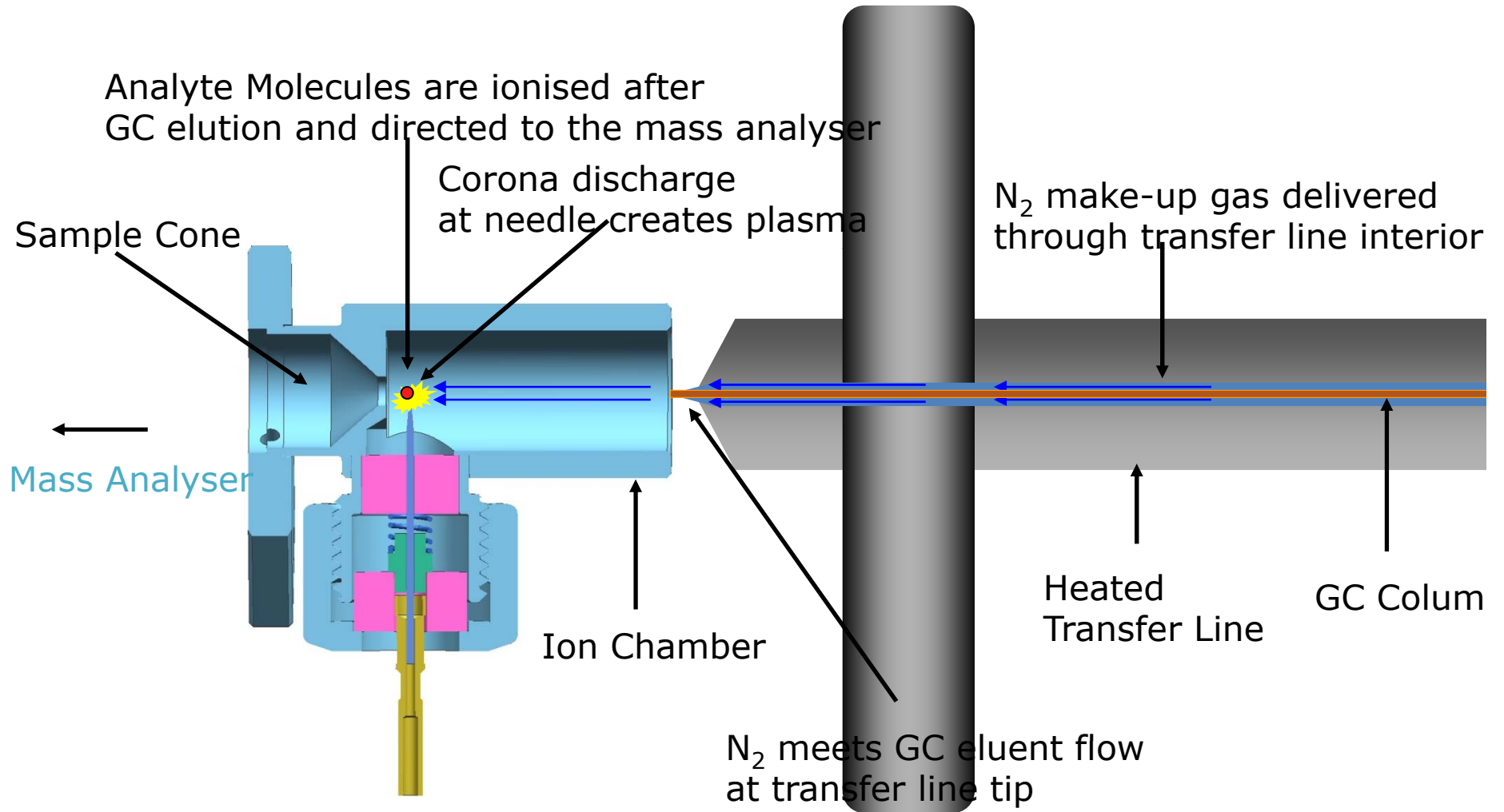
# Atmospheric Pressure GC

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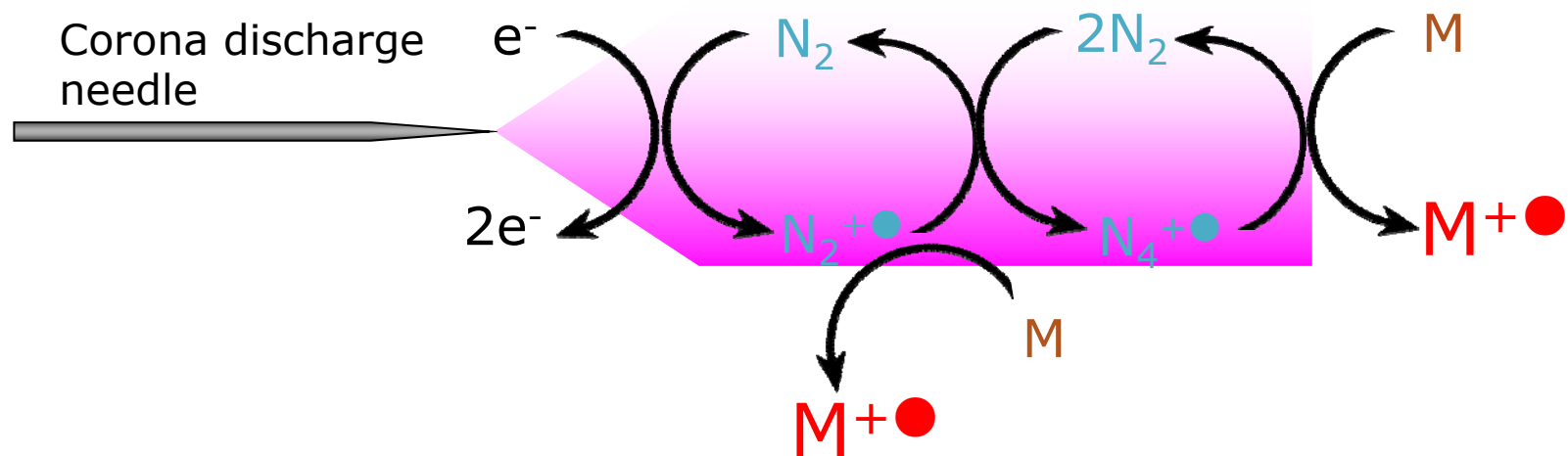


- Extend coverage  
coverage
  - LC & GC  
instruments
  - Very simple  
exchange
  - Clean APCI type spectra

# APGC – How it Works

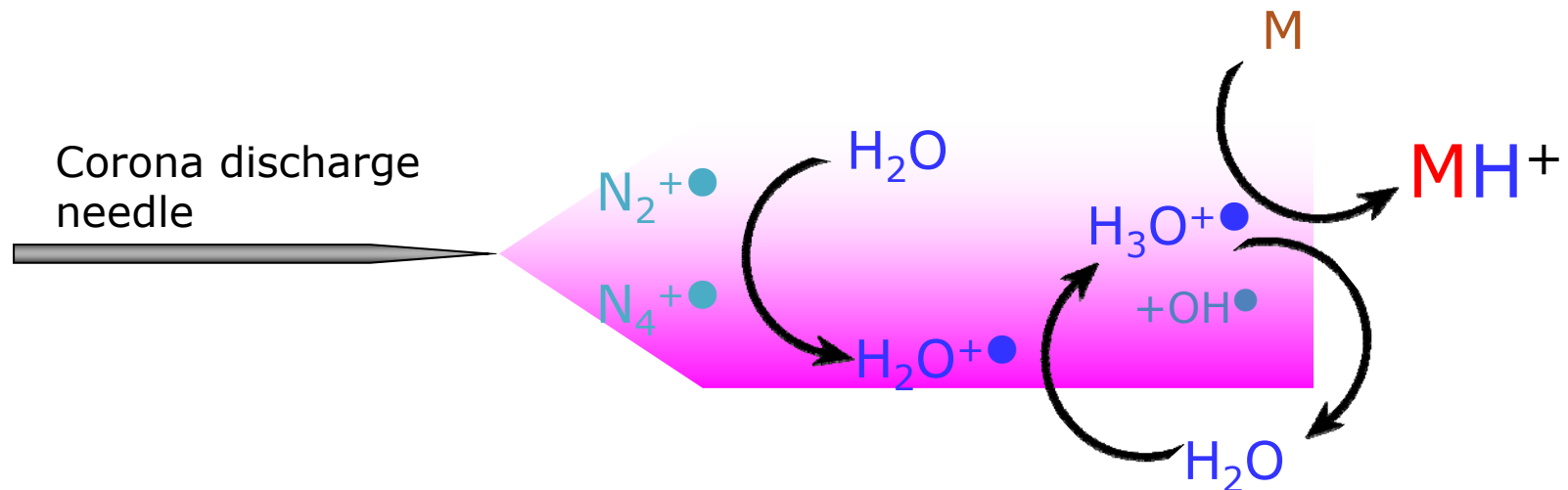


## Charge Transfer



- "Dry" source conditions
- Favoured by relatively non-polar compounds

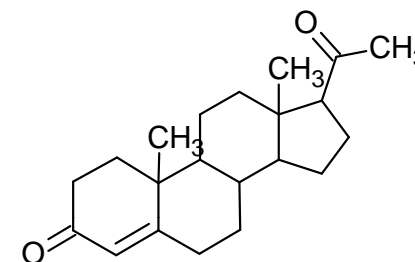
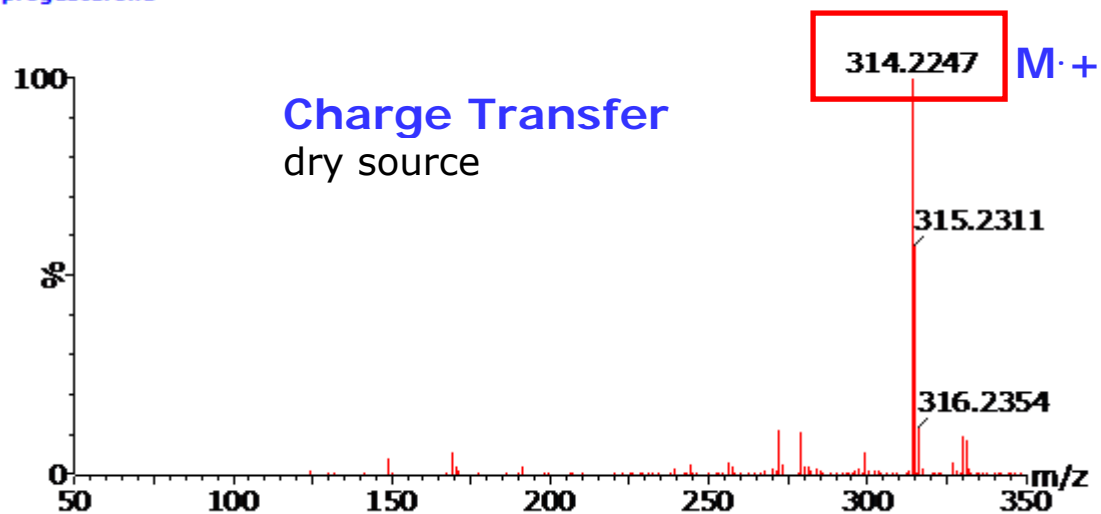
## Proton Transfer



- Modified source conditions, e.g. with water or methanol
- Favoured by relatively polar compounds

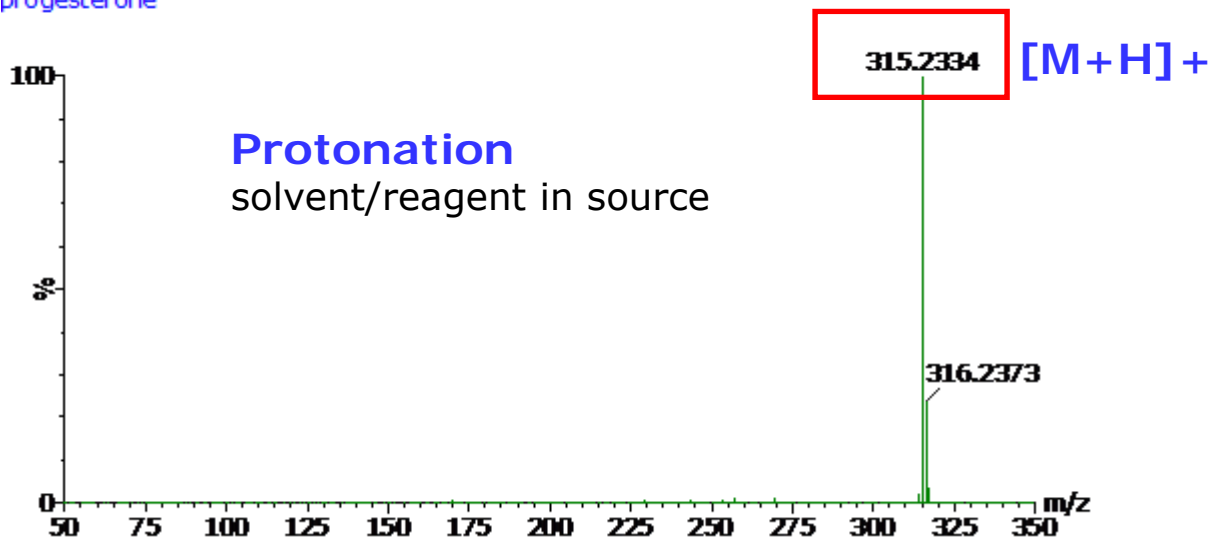
# Ionization Comparison

progesterone



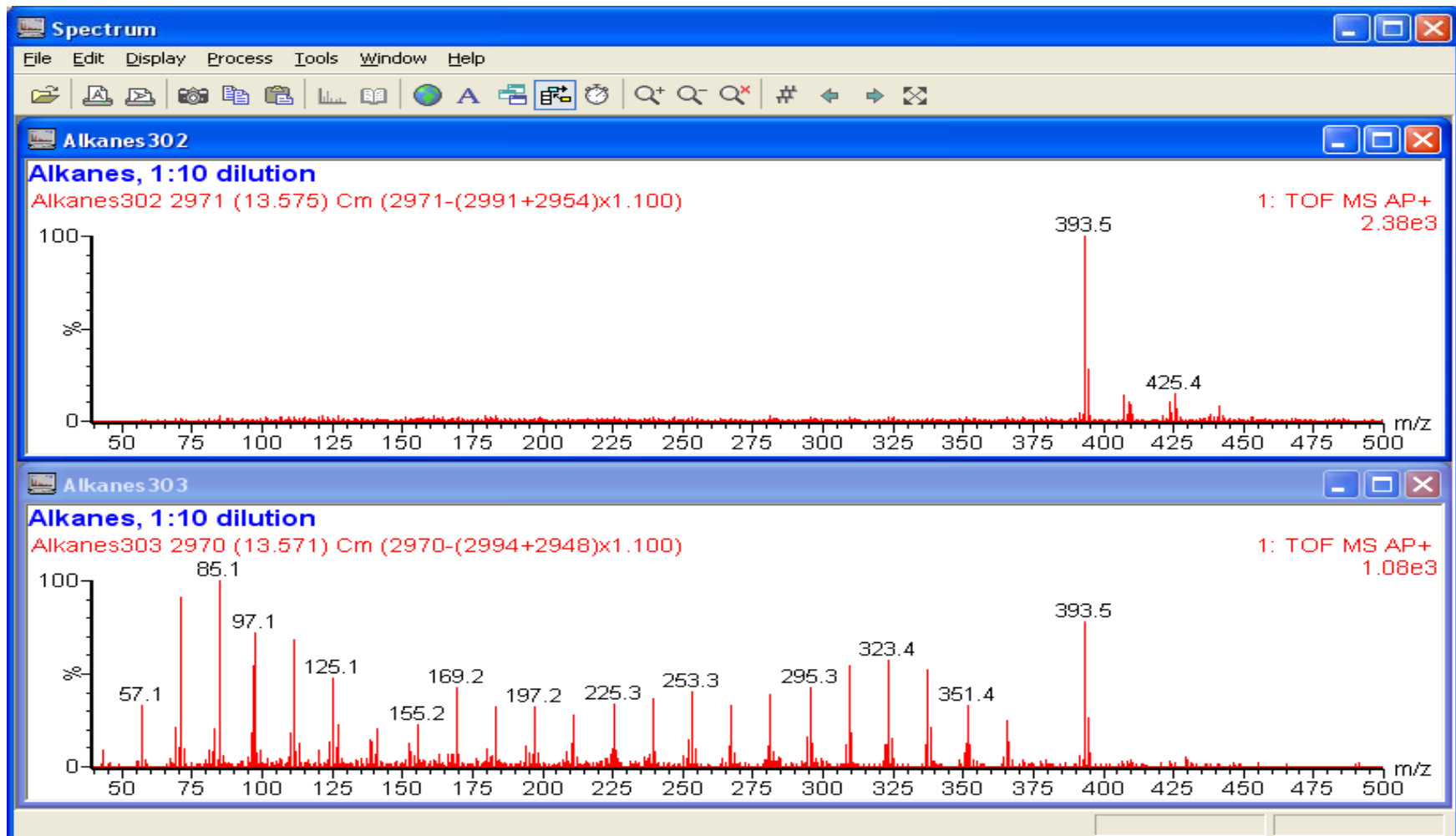
$C_{21}H_{30}O_2$   
Progesterone

progesterone

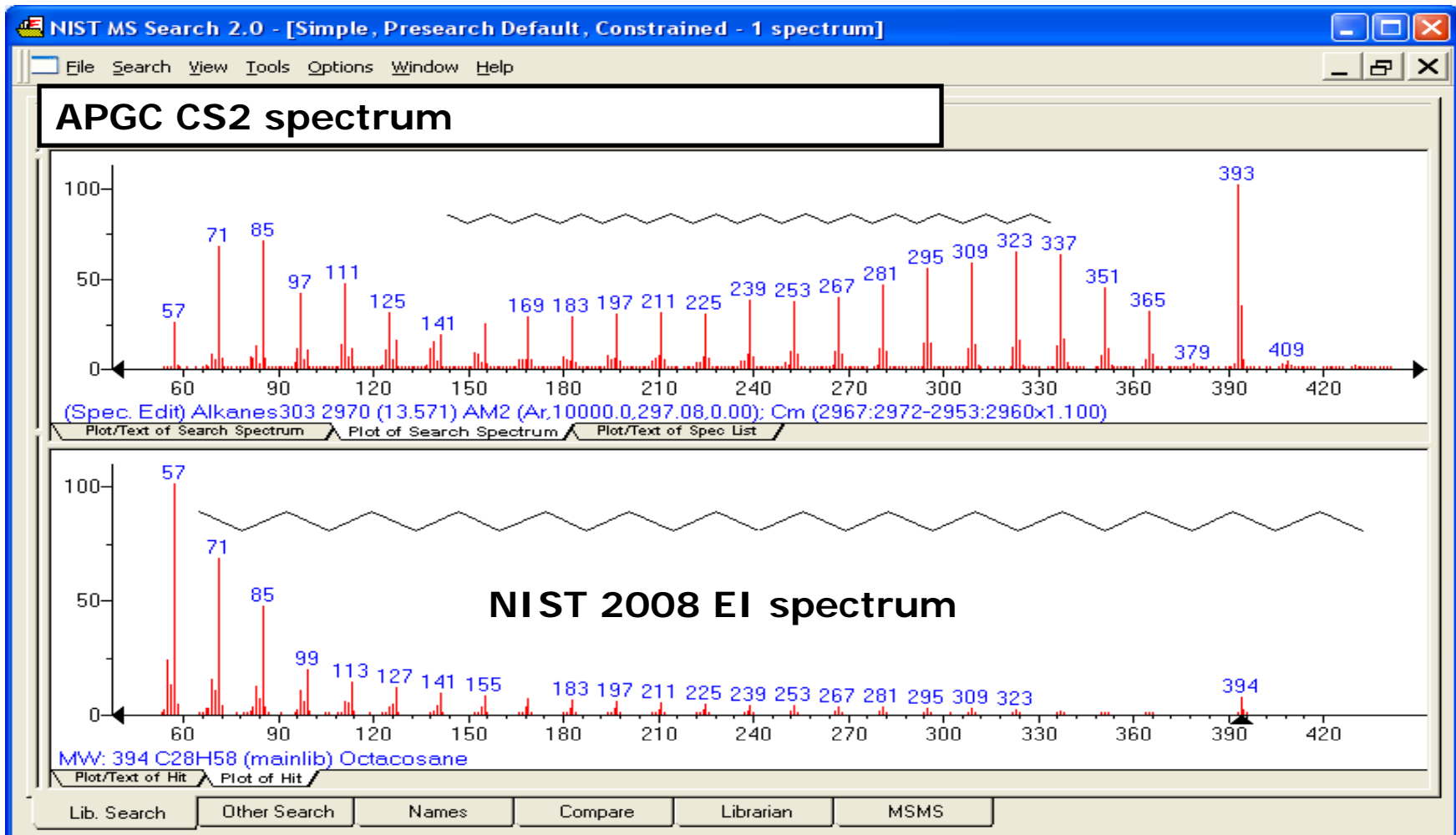




# APGC Spectral Quality/Content Water v. CS2

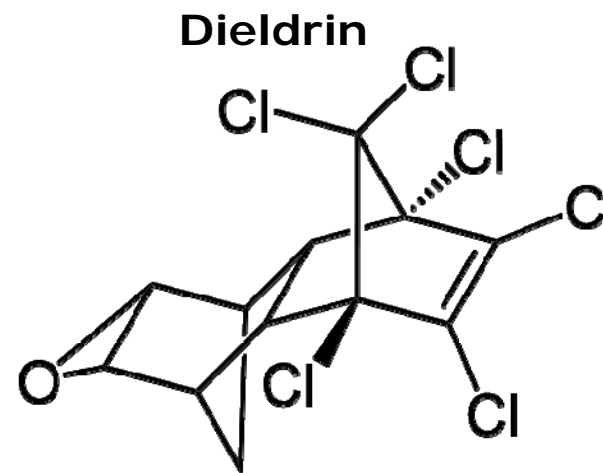
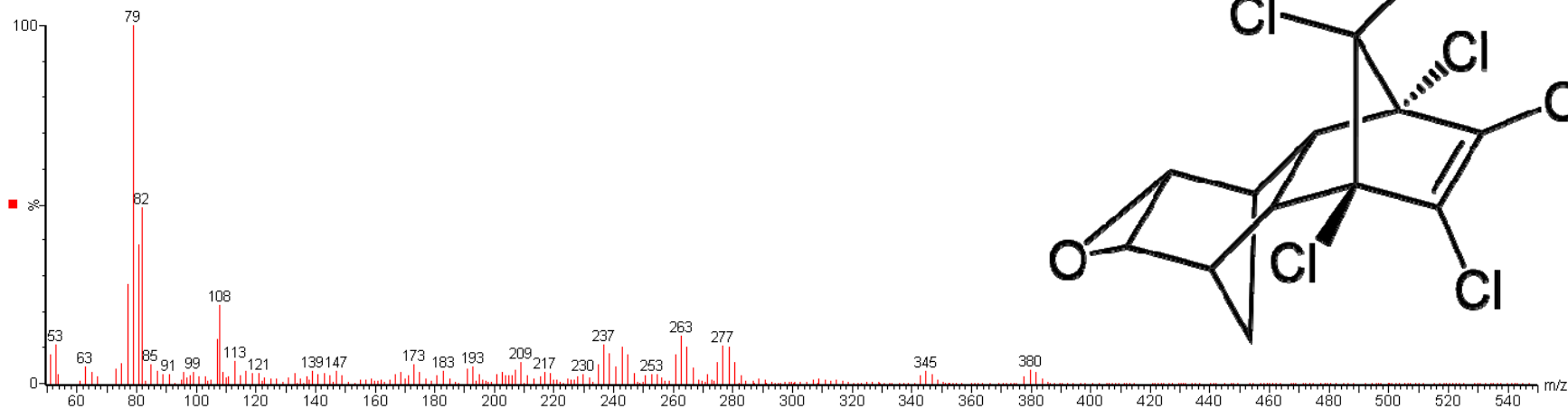


# Charge Exchange v. EI

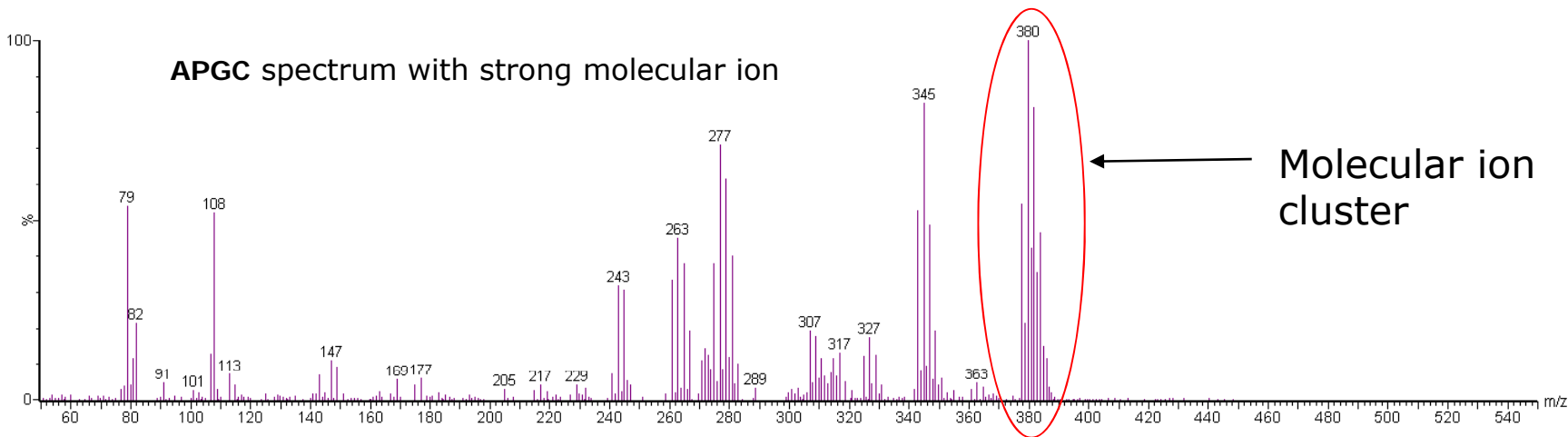


# Comparison of APGC to EI

Typical EI GC/MS spectrum with extensive fragmentation

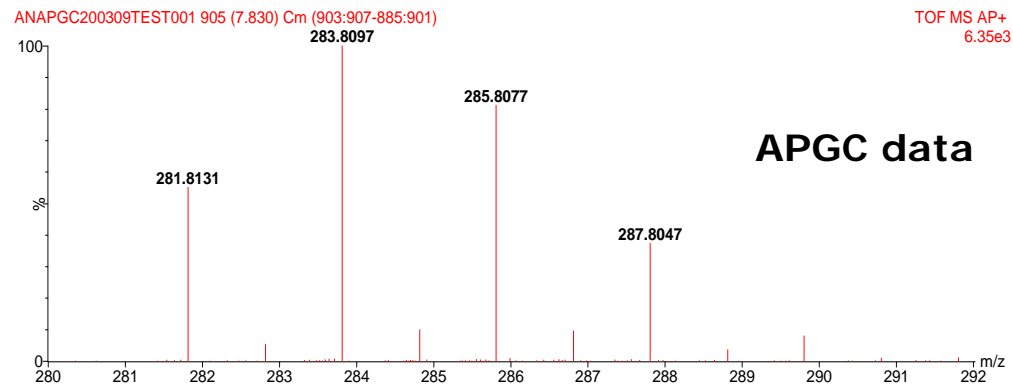
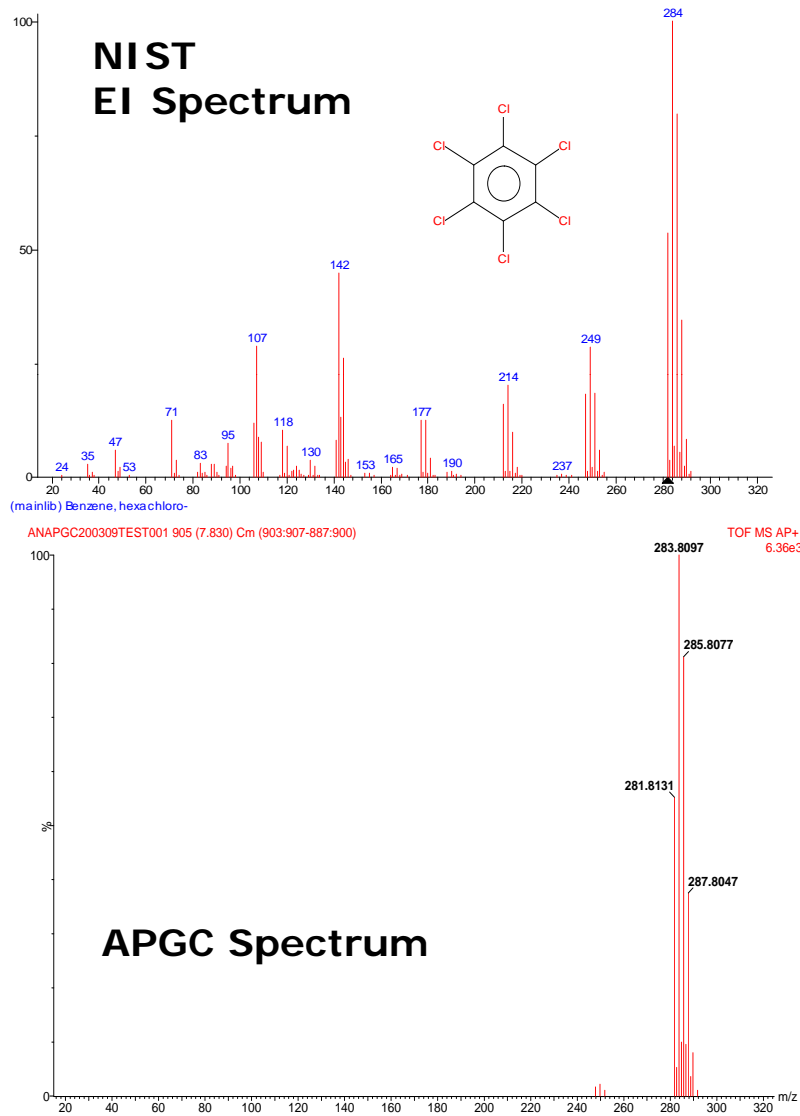


APGC spectrum with strong molecular ion



# APGC: Spectral Characteristics

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Monoisotopic Mass, Odd and Even Electron Ions  
600 formula(e) evaluated with 64 results within limits (all results (up to 1000) for each m  
Elements Used:

C: 0-20 H: 0-30 N: 0-4 O: 0-10 Cl: 0-6

Minimum:

-1.5

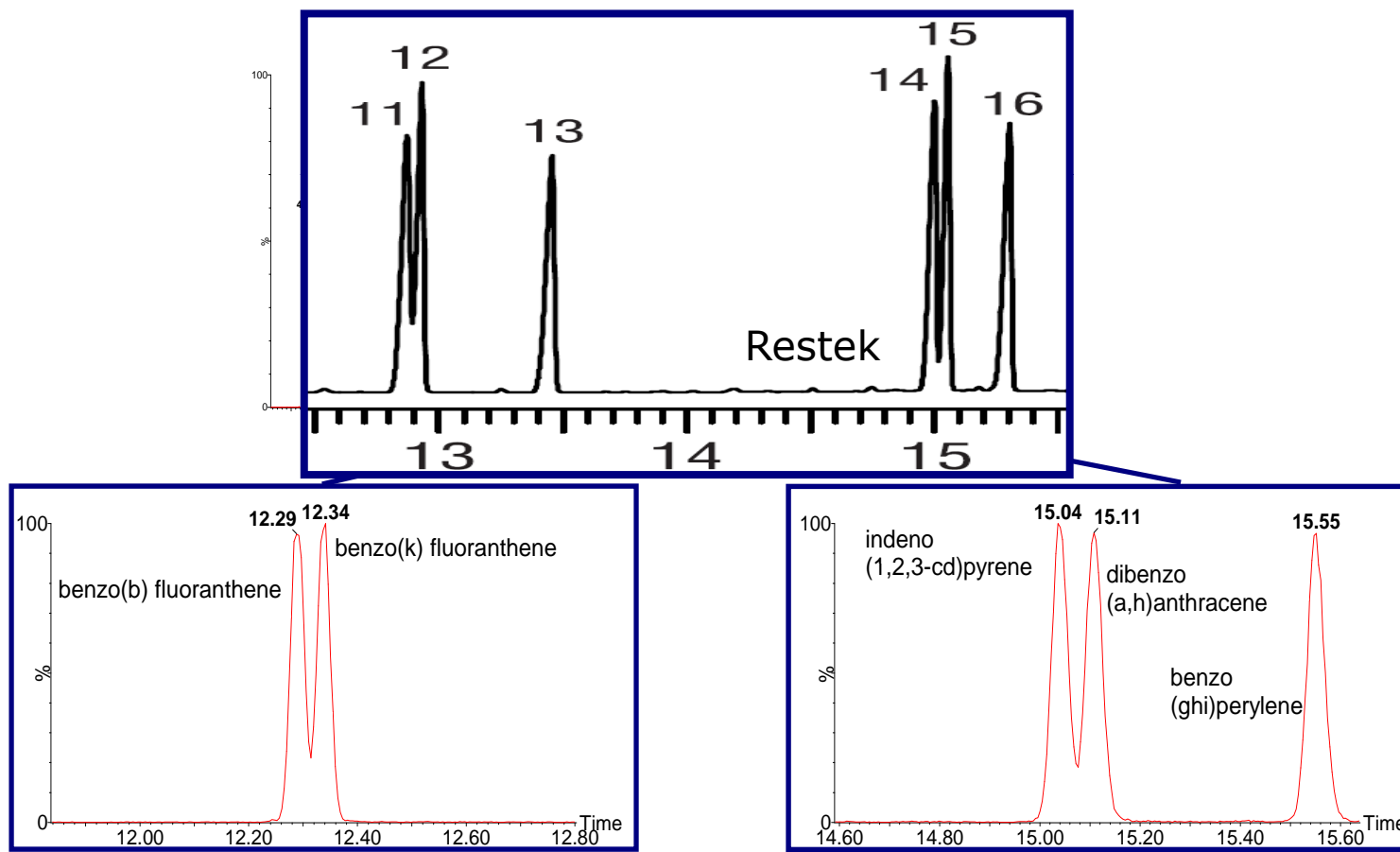
Maximum:

100 10 50

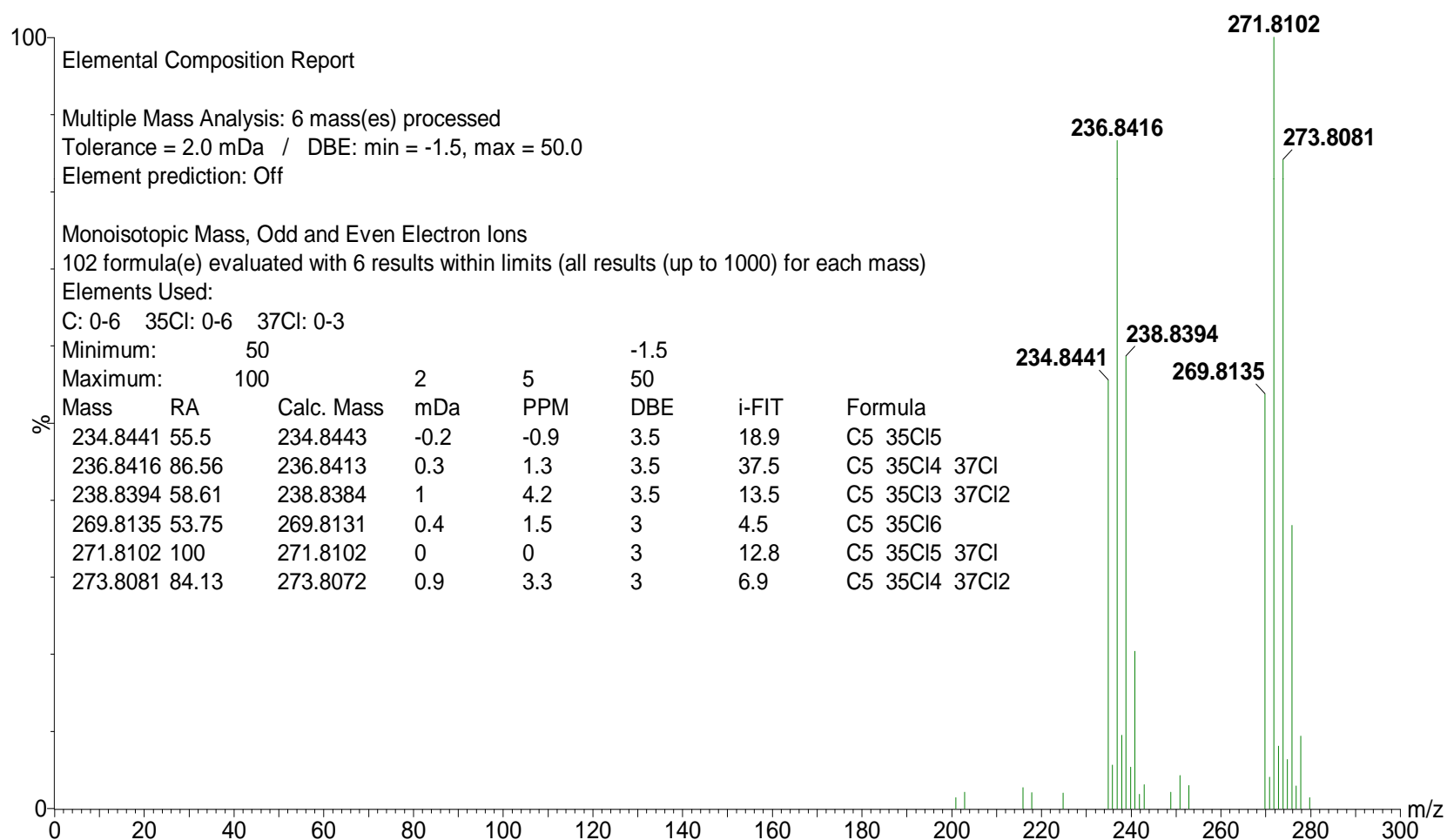
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
281.8131	281.8131	0	0	4	14	C6 Cl6
281.8217	281.8217	-8.6	-30.5	-0.5	93.9	C2 H2 N O2 Cl
281.8091	281.8091	4	14.2	0	108.4	C N2 O2 Cl6
281.8203	281.8203	-7.2	-25.5	0	124	N4 O Cl6
281.8342	281.8342	-21.1	-74.9	-1	125.1	C3 H4 O2 Cl6
281.7979	281.7979	15.2	53.9	0	126.2	C2 O3 Cl6

# APGC Performance: Chromatographic

- Chromatographic resolution and integrity maintained for compounds eluting at 310C.



## Exact mass measurements on hexachloropentadiene



## Experimental: Samples

- Reference Samples of DiNP & DiDP were obtained from BASF, Ludwigshafen, Germany.
- Stock solutions prepared in cyclohexane at 1000 ppm.
- Calibration solutions prepared by dilution in cyclohexane at 1-10ppm.
- Sediment sample obtained during an environmental study and was dried by lyophilization.
- A 10 g sample was extracted with 50 mL of cyclohexane and concentrated to 10mL.

# Experimental: GC Conditions

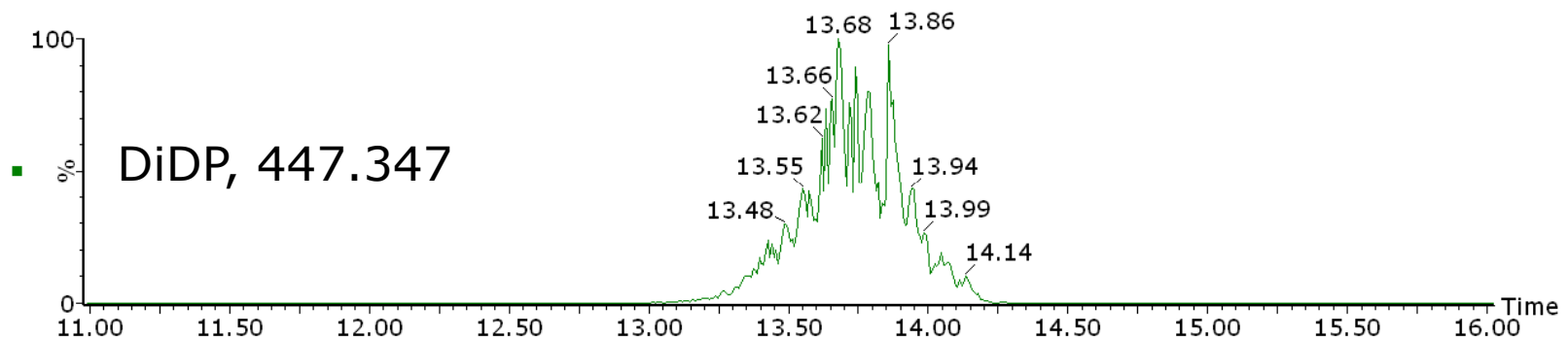
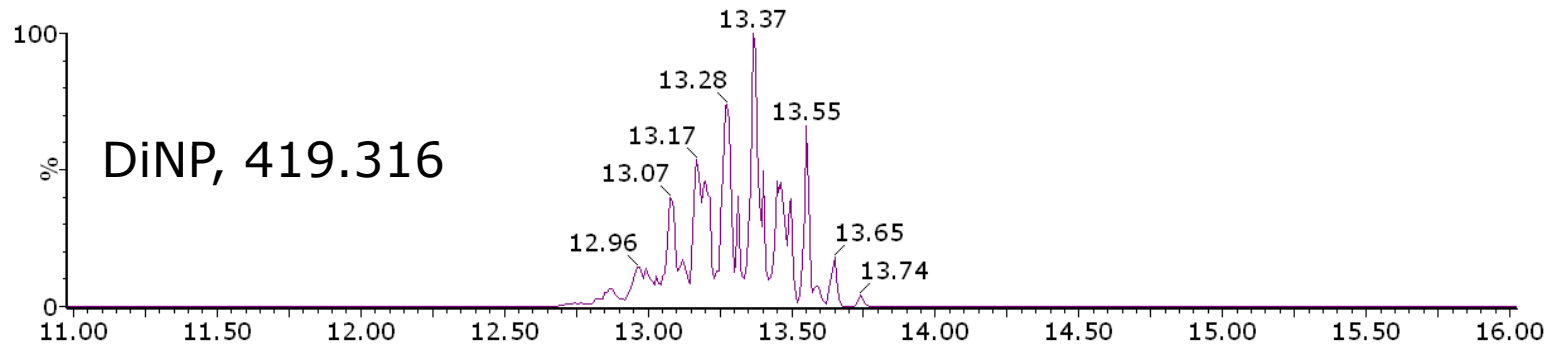
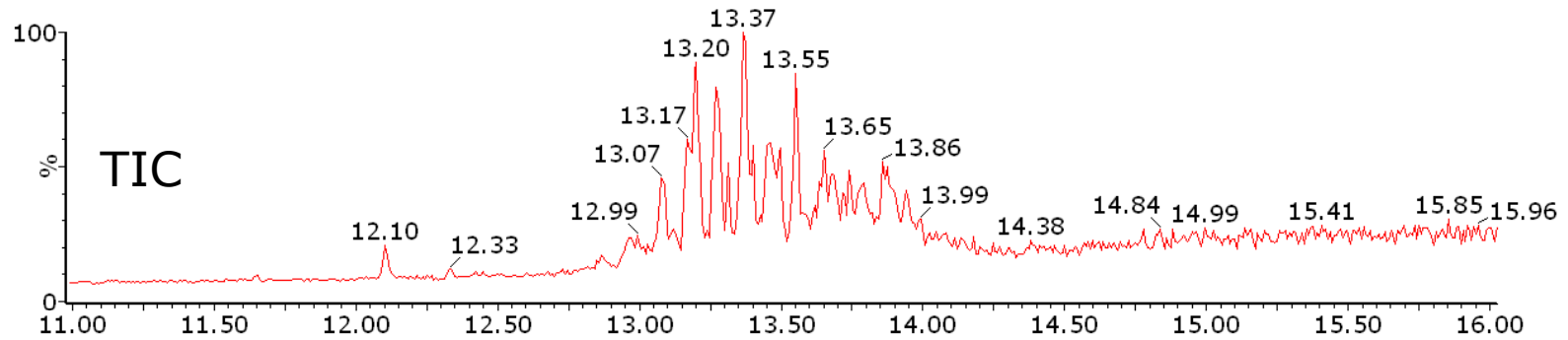
- GC Agilent 7890A
- Column DB5-MS 30m x .25mm x 0.25μm
- Carrier Gas He at 2.0mL/min
- Injection 1μL Splitless, 1.05min purge delay, 300°C
- Program 50°C for 1.0 min to 320°C at 20°C/min  
and hold 2.5min.
- N2 make-up gas at 300ml/min flows down the heated transfer line (310° C) and acts as a sheath gas



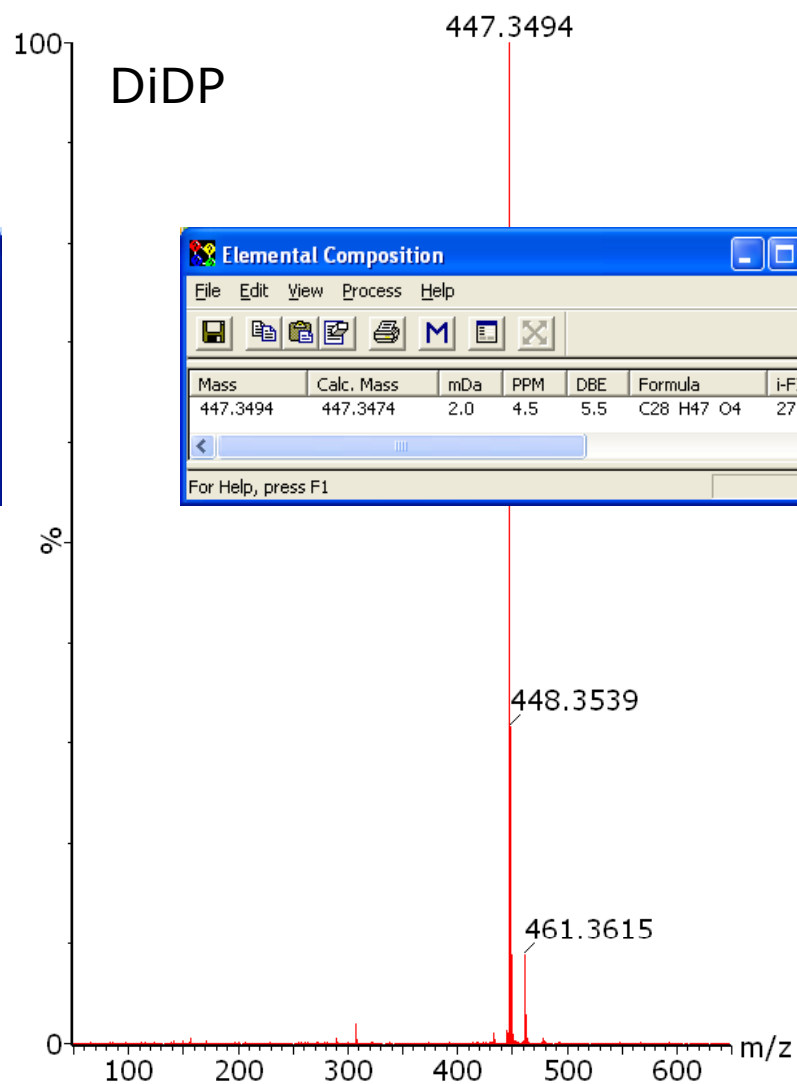
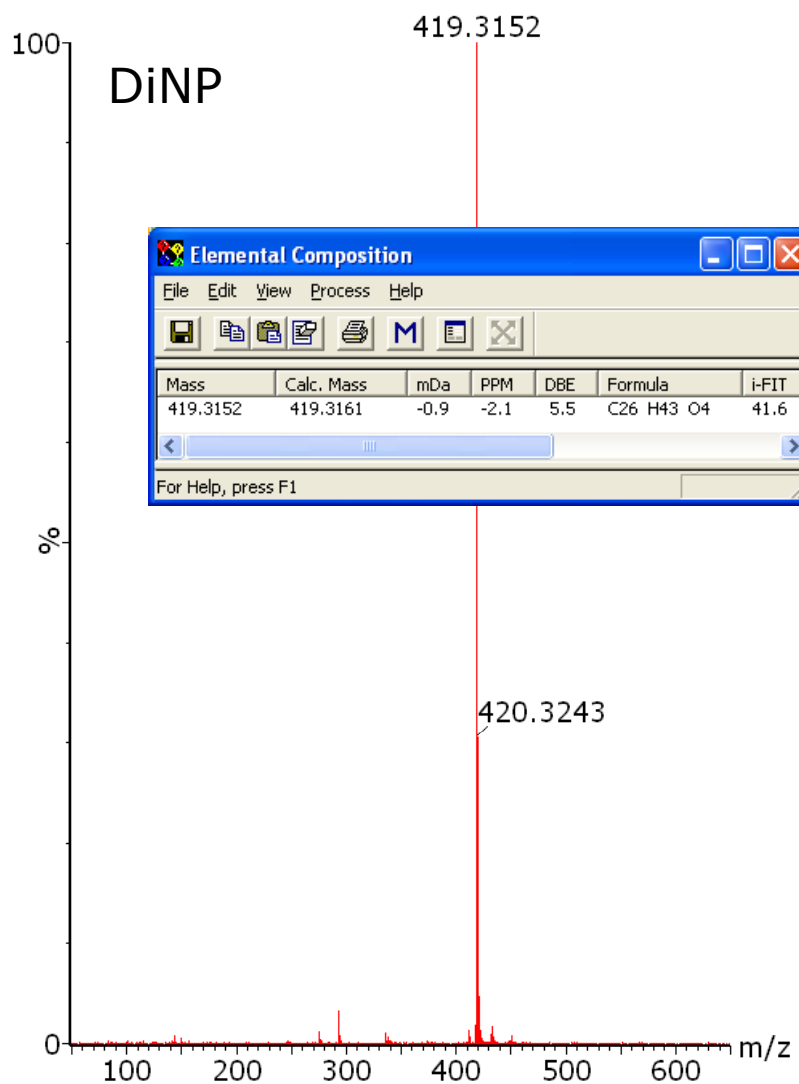
# Experimental: MS Conditions

- MS Xevo QTof™
- Source 140 °C
- Corona 4.0 μA
- Sample Cone 10V
- Cone Gas 30L/hr N2
- Source auxiliary Gas 300L/hr N2
- Source Modifier Water

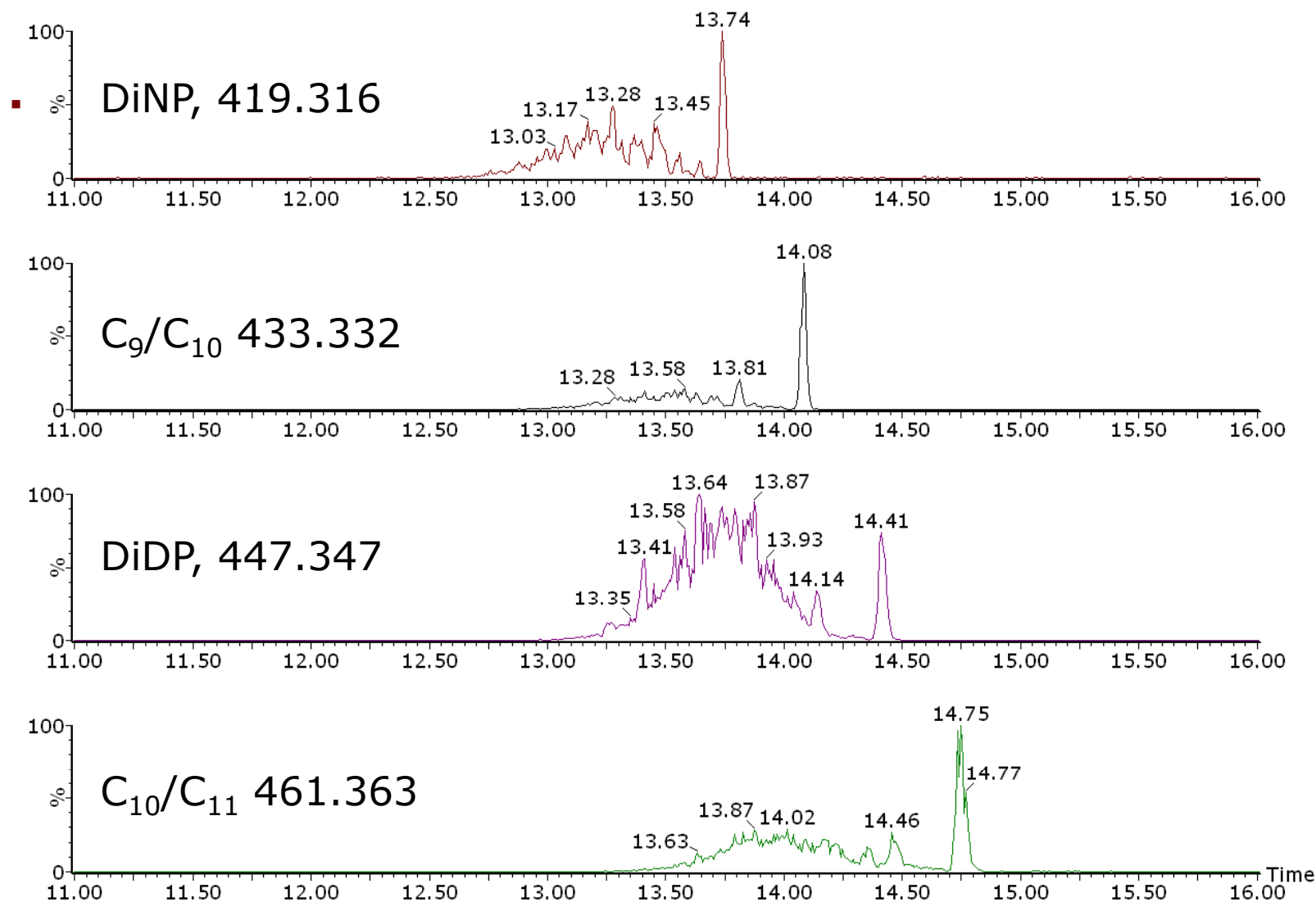
# GC-APGC-TOF DiNP/DiDP



# Proton transfer APGC spectra



# Detection of High-MW Phthalates in Sediment by GC-APGC-TOF



# Summary & Conclusions

- DiNP and DiDP were successfully ionized in proton transfer APGC, yielding spectra that contained the molecular ion as the base peak with mass errors less than 5 ppm
- High-molecular-weight phthalates could be detected below 1 ppm in sediment using APGC by extracting exact mass chromatograms
- At least two additional phthalate moieties were also identified in the extracted sediment sample using exact mass chromatograms
  - Calculated formulae suggest mixed C9/C10 and C10/C11 phthalates
- APGC offers an interesting perspective for detailed characterization of high-molecular weight phthalates and for their sensitive and selective detection in environmental samples

- J. Romano & D. Stevens  
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- P. Hancock  
Waters Corporation, Manchester, UK
- \*\*\*F. David & P. Sandra\*\*\*  
Research Institute for Chromatography,  
Kortrijk, Belgium

# Thank You!

# Questions?

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