Analytical Protocols for the Analysis of Polybrominated Flame Retardants in Complex Matrix Samples

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Inspiring Excellence

Background

- PBDEs are a major environmental concern.
- They are often referred to as the new PCBs or Dioxins.
- Unlike PCBs and Dioxins they are not present by accident.
- Analytical progress means more labs are looking which means more PBDEs are being found in more samples

3 Stages of Analysis

1. Collection and Extraction

- Reasonably straight forward
- Similar to Organochlorine and PCBs

3 Stages of Analysis

2. Chromatographic Profile

- Very high molecular weights
- Potential of thermal degradation of many of the compounds
- Short run times required

3 Stages of Analysis

3. Mass Spectrometry

- Very high molecular weights
- Very high matrix levels
- Very low concentration
- High degree of certainty required
- Cost effectiveness

Analytical Approach

Combine two techniques that may not have been thought of as routine in a “standard, high throughput, laboratory”:

- Rapid-MS column technology
- Benchtop MS-MS detection

Rapid-MS

Rapid -MS columns make use of the separation conditions that are generated by doing the separation process under reduced pressure:

Low Pressure - Gas Chromatography

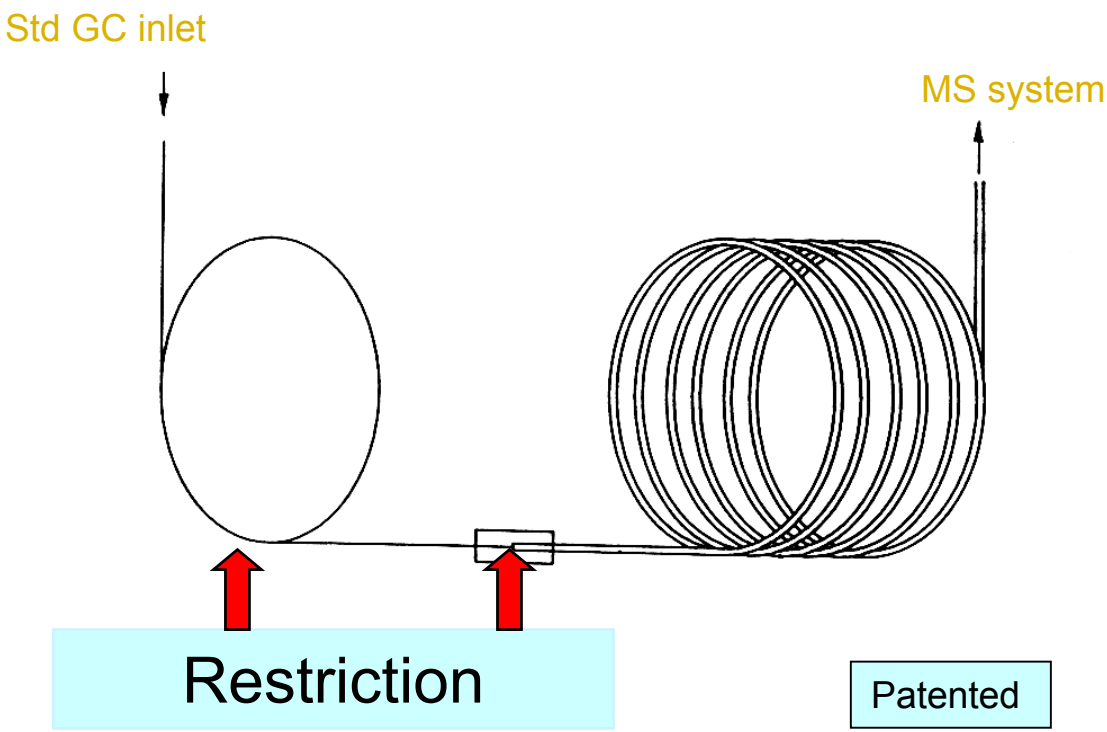
LP-GC

Don’t push when you can pull!

Rapid-MS

The Rapid-MS concept:

Make use of advantages of vacuum separation by applying a restriction at the injection side of the system



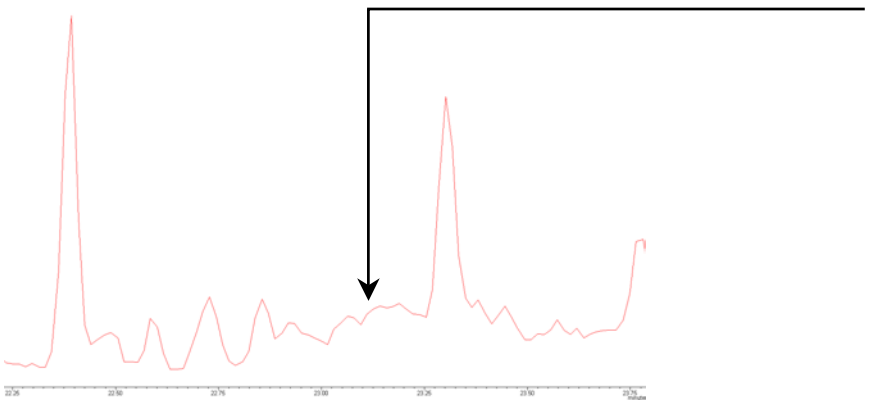
MS-MS Detection

Environmental Forensic Mass Spectrometry has three principles:

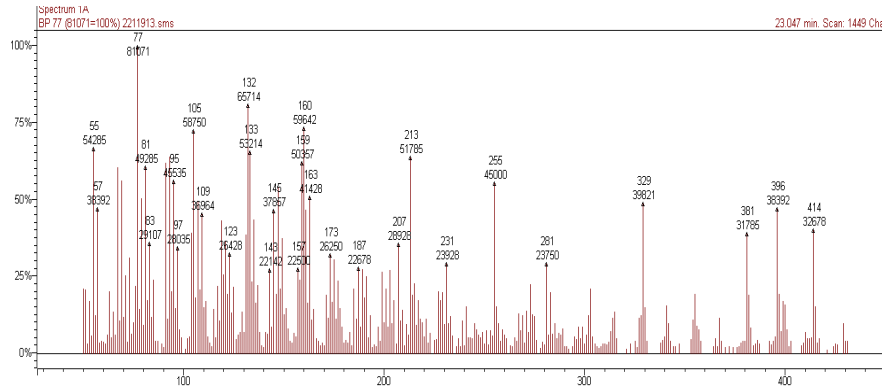
- The truth, (SIM)
- The whole truth, (scan)
- Nothing but the truth, (MS/MS or High Res)

Cost effectiveness becomes a dominant factor here.
High Res means we mimic the Dioxin program.
MS/MS means we have simple, routine analysis

Matrix Problems- a generic example

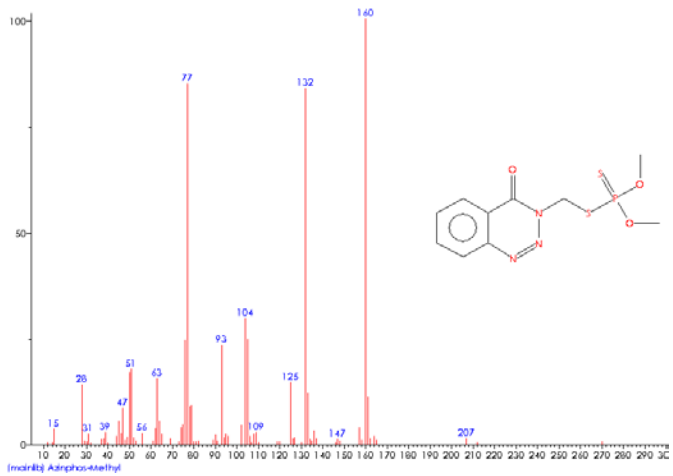


Chromatographic Separation profile



Mass spectrum at the expected time

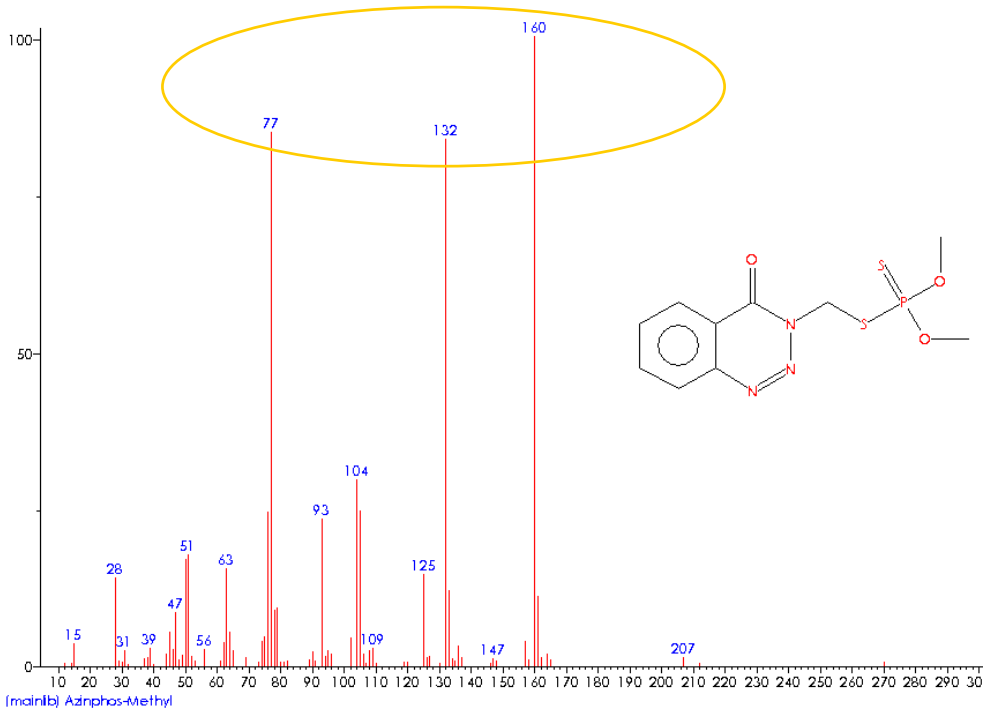
This is due to the analysis being non-selective with significant matrix inclusion



Correct mass spectrum

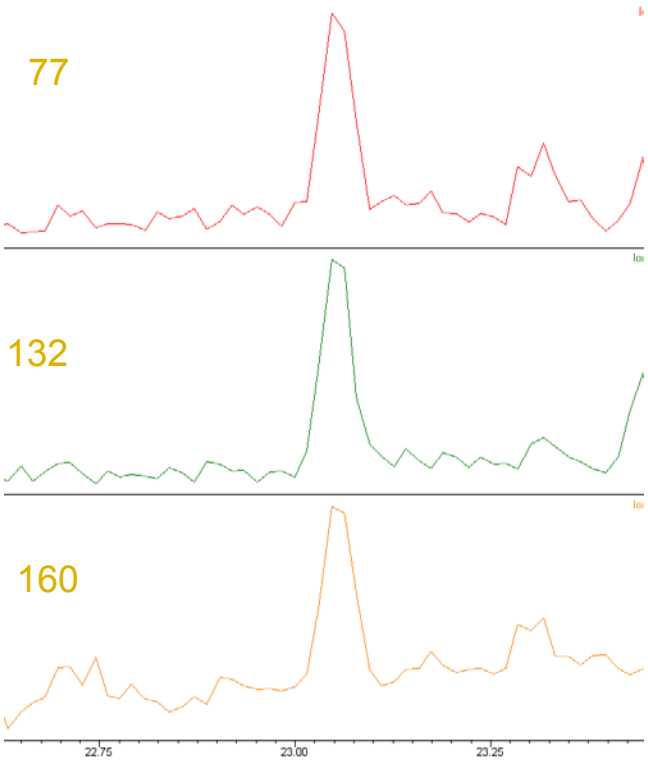
Attempt at Selectivity

Rather than look at all the ions we set the instrument to look at 3 ions which will be there if azinphos methyl is present.



This is referred to as 3 ion Selected Ion Monitoring, SIM

Attempt at Selectivity



The lack of spectral data means that the confirmation levels are reduced.

The ratio of the three ions are critical

Ion	True Compound	Residue Analysis
77	847	855
132	836	1000
160	1000	535

False positives / false negatives will be reported due to matrix

Mass Spectrometry-Mass Spectrometry

Selectivity can be introduced by using another stage of mass spectrometry

- Technique is known as MS/MS.
- MS/MS is an instrument based matrix elimination tool.
- MS/MS provides highly defensible data.
- It is accepted by UK, European and US regulatory bodies
- By introducing selectivity we also introduce better sensitivity and faster analysis.
- It can be explained by a simple “chain of custody” sequence.

MS/MS Logic

There are a few fundamental criteria which we consider with respect to the MS-MS process.

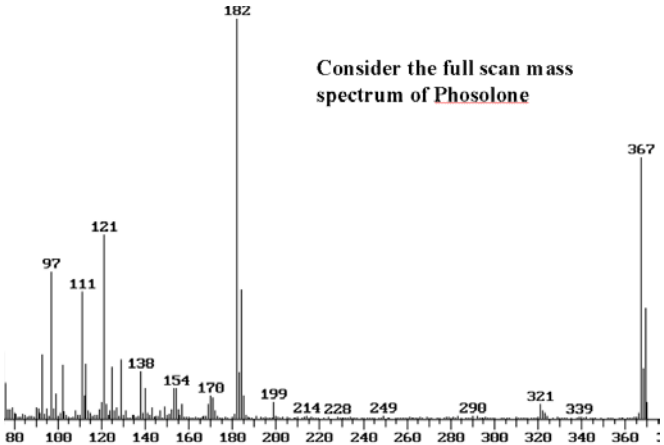
e know that the mass spectrum obtained for a gi
alyte is a “fingerprint” of that compound.

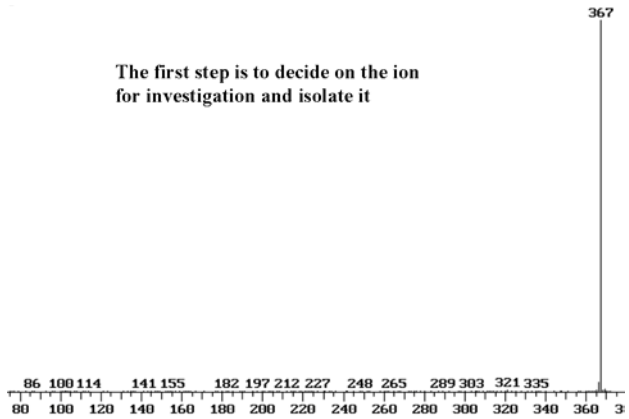
t this can mean is that all the spe
ed back to the original molecular struc

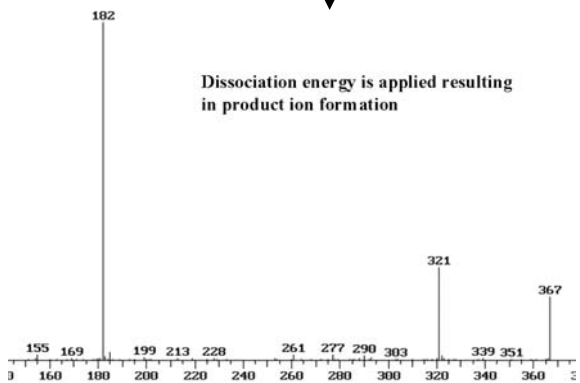
ok at a single ion in a mass spec f
related to the original molecul

that ion to identify str ion using a
spectral proce

MS/MS Logic - a generic example





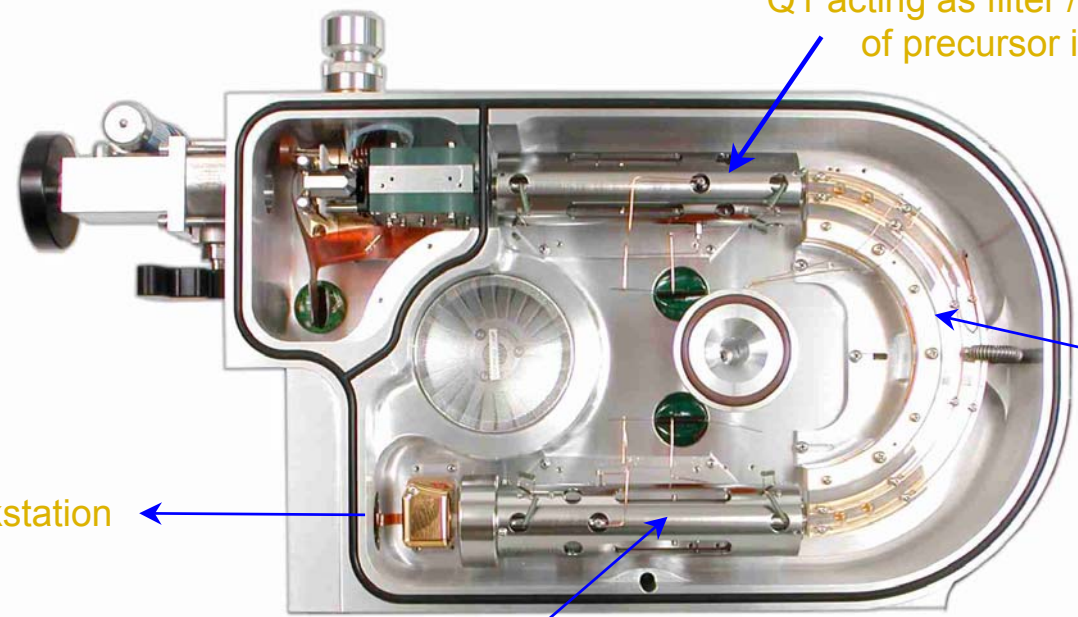


We would monitor the 367 > 182 transition

and/or the 367 > 321 transition

MS/MS Instrumentation

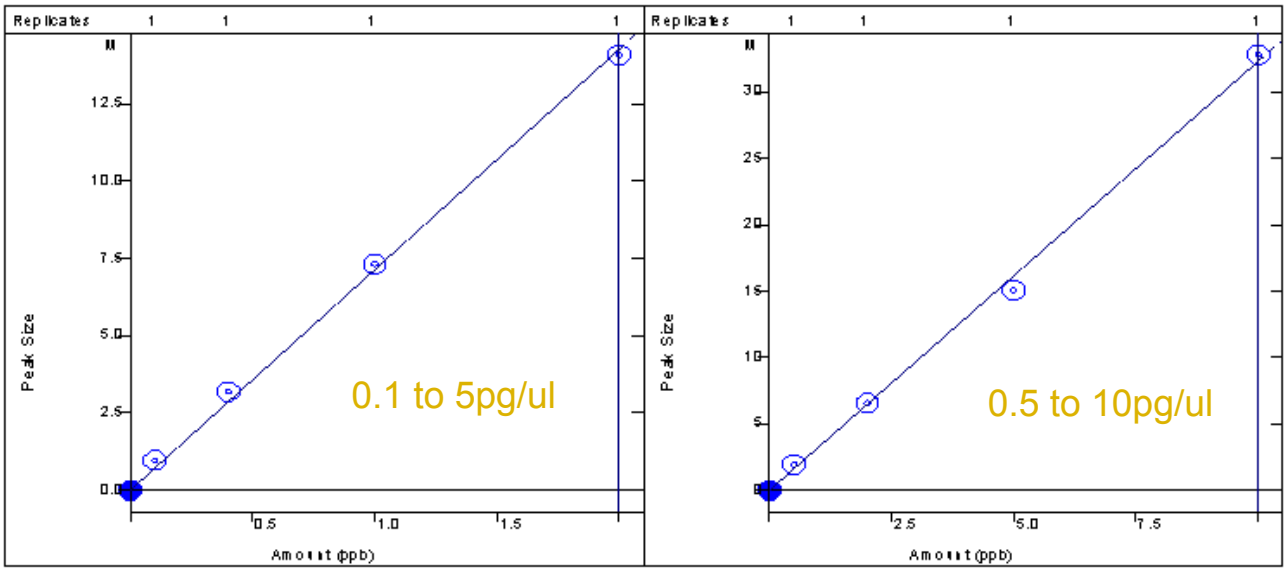
System suited to MS/MS of PBDEs, 1200 triple quadrupole
1500 amu range
excellent sensitivity
routine operation



Initial Calibration

Penta BDE
Curve Fit: Linear, Origin: Force, Weight: None
Coeff. Det.(r2): 0.999227
y = +7.1336e+6x

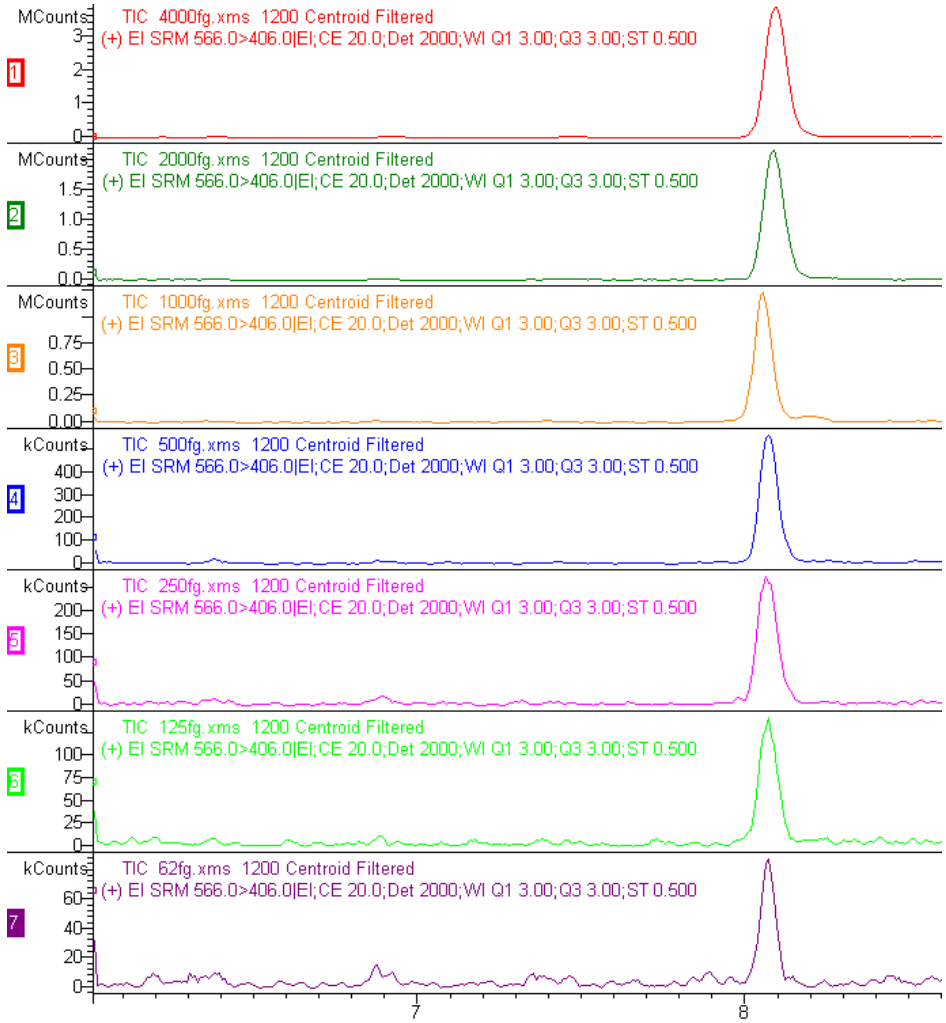
Deca BDE
Curve Fit: Linear, Origin: Force, Weight: None
Coeff. Det.(r2): 0.997821
y = +3.2341e+6x



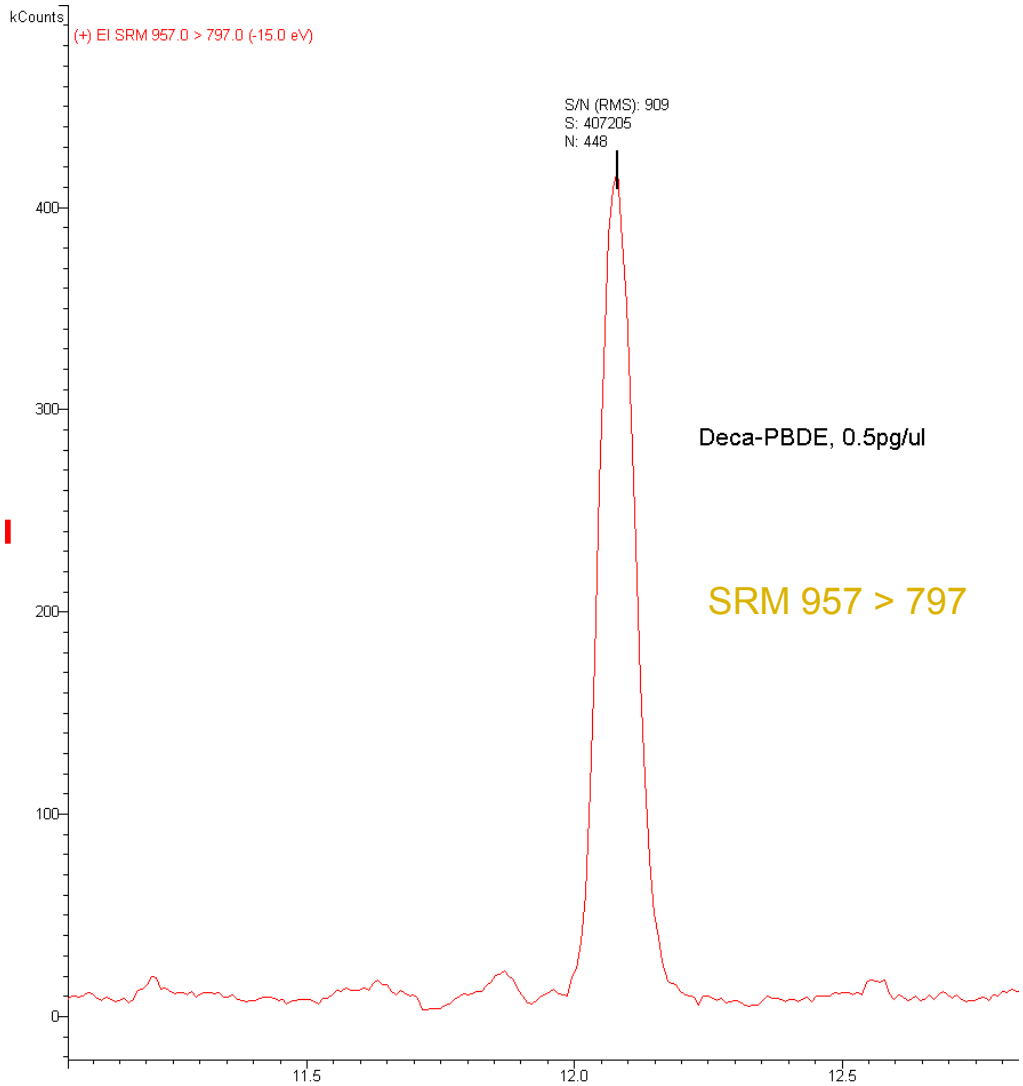
Penta-BDE chosen as they are very toxic.

Deca-BDE chosen due to chromatographic issues

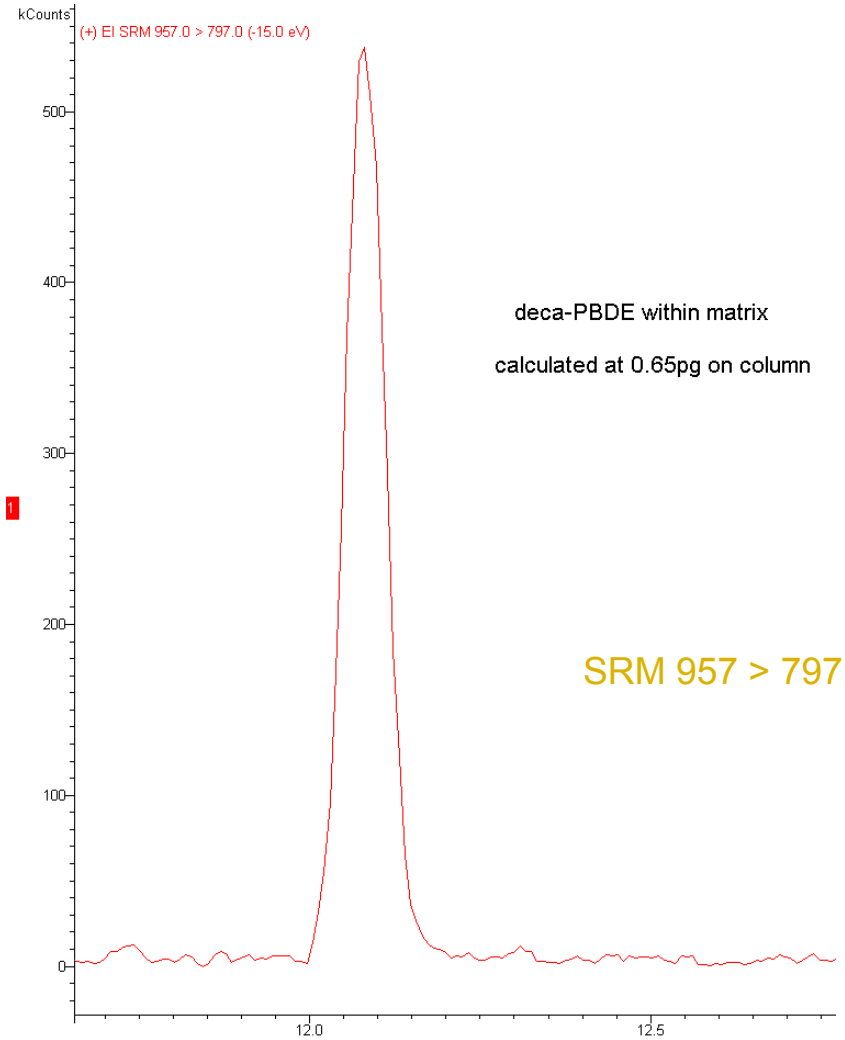
Penta BDE, real peaks at 62fg/ul



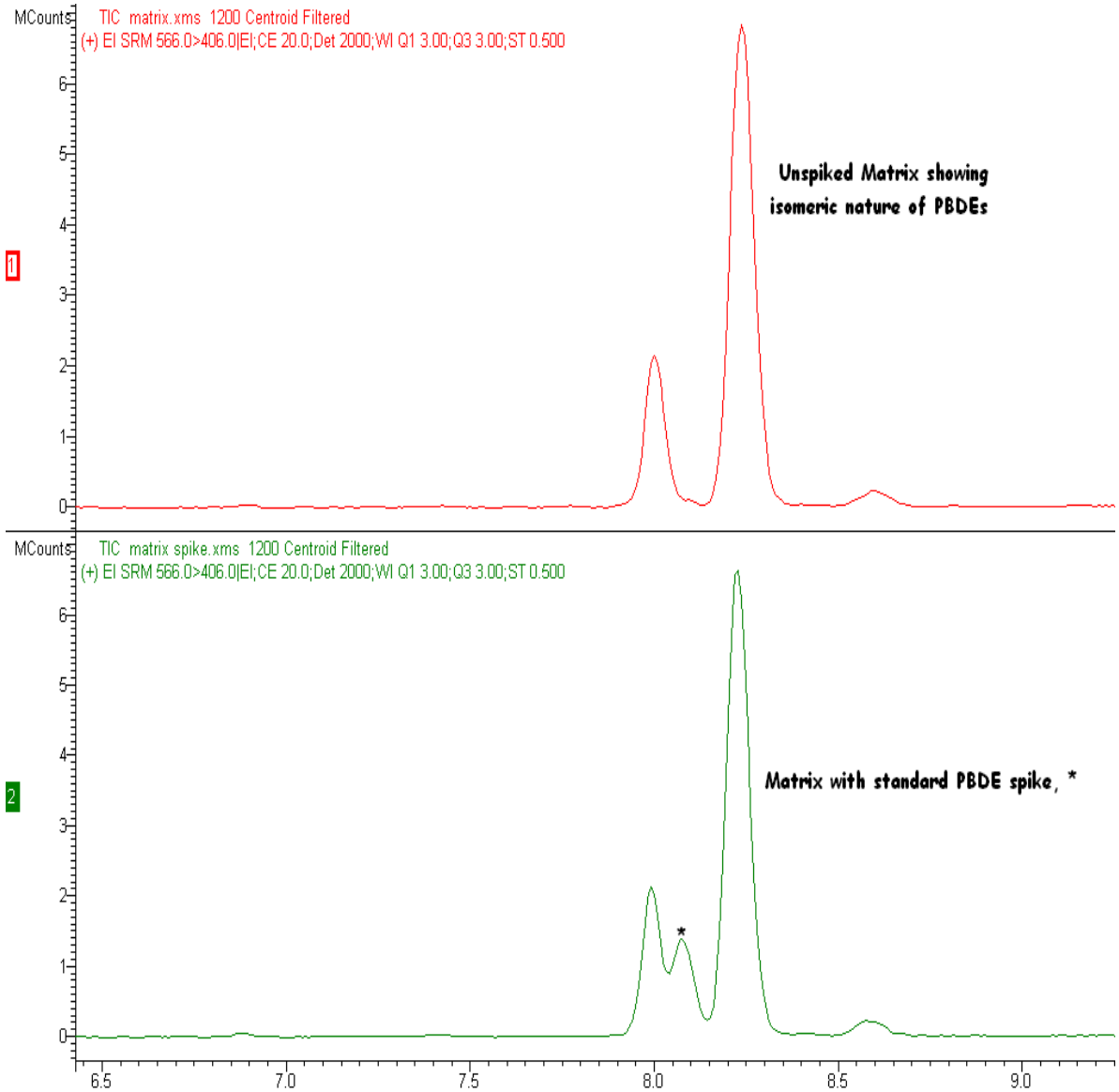
Rapid-MS Performance on Standard



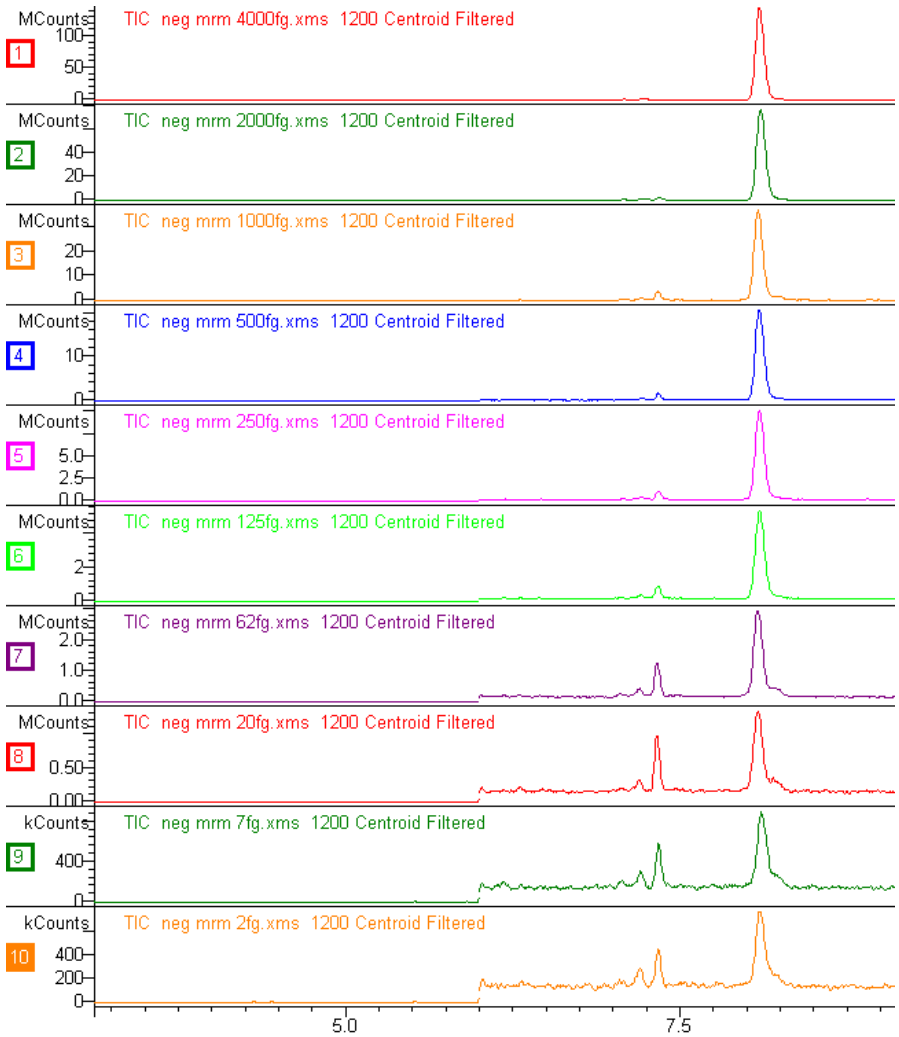
Rapid-MS Performance on Matrix Spike



If you look closely at matrix blanks…….



Negative ion MS/MS



Appears very sensitive as data shown goes from 4000fg/ul down to 2fg/ul

HOWEVER……

Background issues in relation to the analysis

And…….

Negative ion work does not give good molecular ions

- Gives mainly Br_2^-
- Which we take to Br^- by MS/MS
- Too generic for PBDEs but would highlight a problem with bromine in samples

Conclusions

Rapid-MS with MS/MS detection

- Good selectivity
- Good sensitivity
- Best in EI-MS/MS
- Method will go congenor specific not arochlor approach
- Cost Effective
- Suitable for routine laboratories