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Tandem Quadrupole MS/MS v. Magnetic Sector HRMS in the Analysis of Mixed-Halogenated Dioxins and Furans: Firefighter Occupational Exposure

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Waters Corporation

Overview

- Atmospheric Pressure Chemical Ionisation Gas Chromatography (APGC aka GC-APCI) source on HP TQ can achieve extremely low limits of detection, e.g. <100ag for 2,3,7,8 TCDD

- Comparisons with magnetic sector and 2D GC EI TOF was performed and will be discussed

100fg 2,3,7,8 TCDD on Magnetic Sector

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Signal to Noise = 125:1
[PtP using 10 peak widths of noise]

APGC on Xevo TQ-XS

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100fg 2,3,7,8 TCDD on TQ-XS

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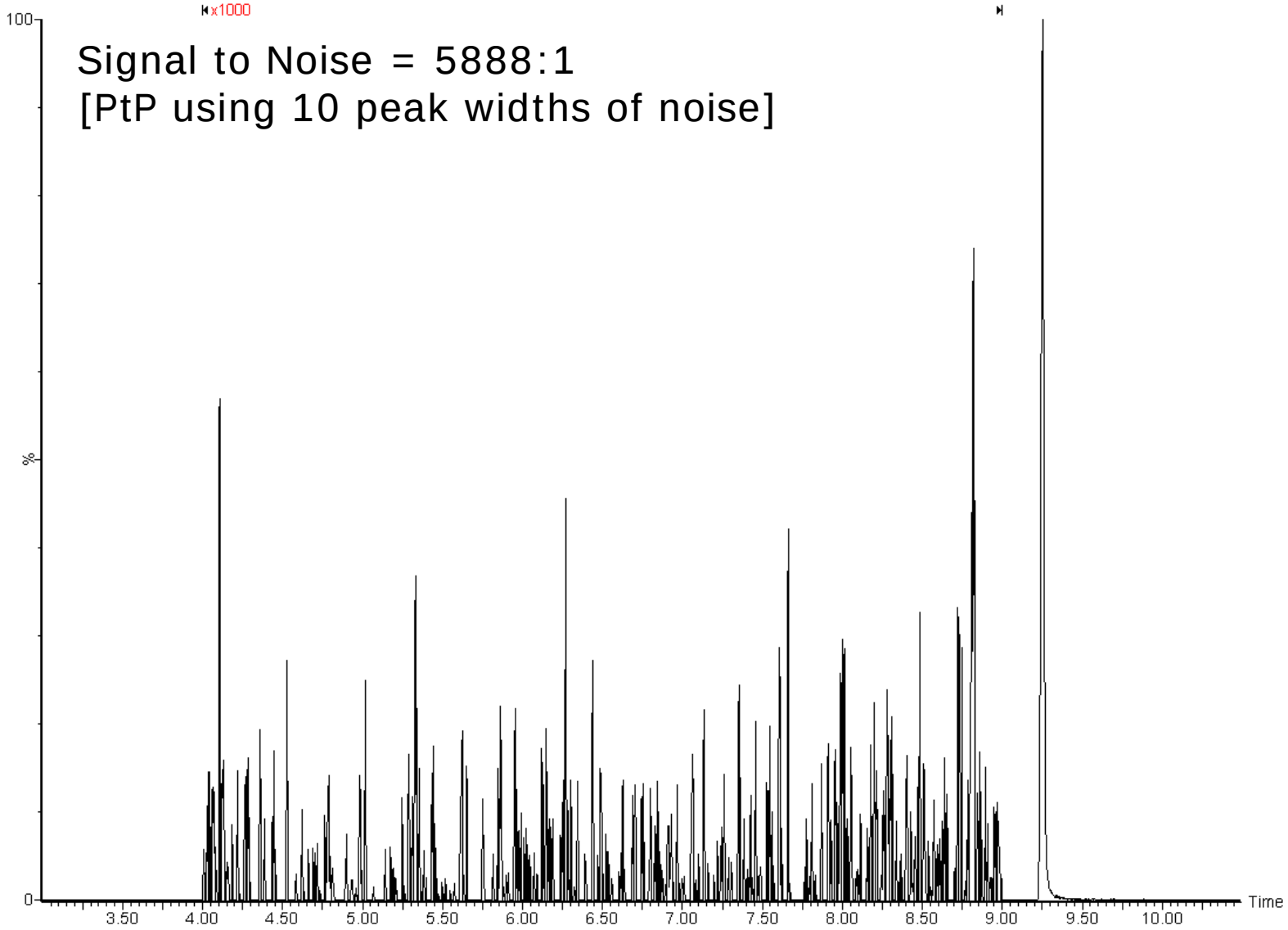

Wellington Labs TCDD-MXB Standard

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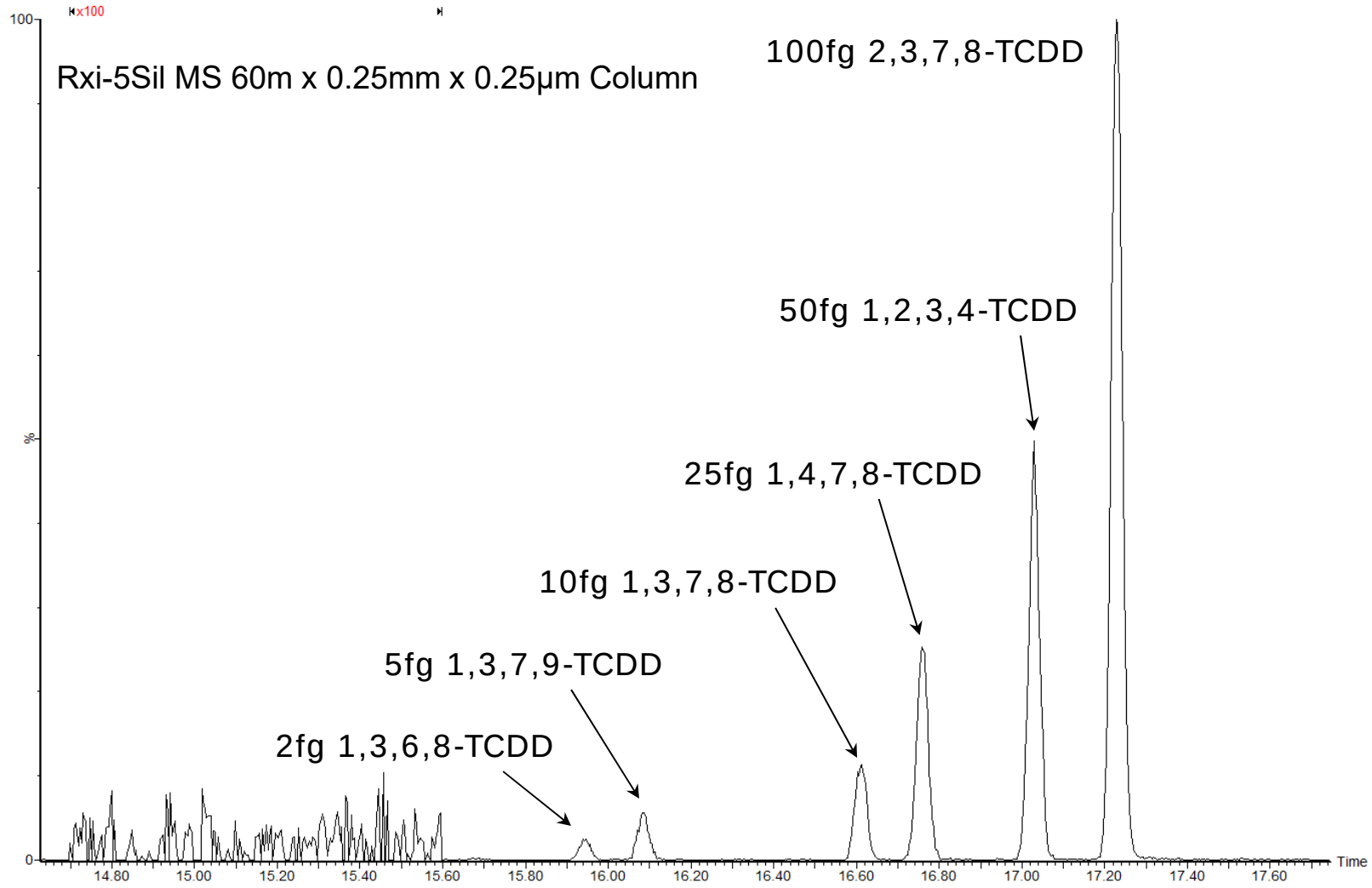

TCDD-MXB Standard diluted 10:1

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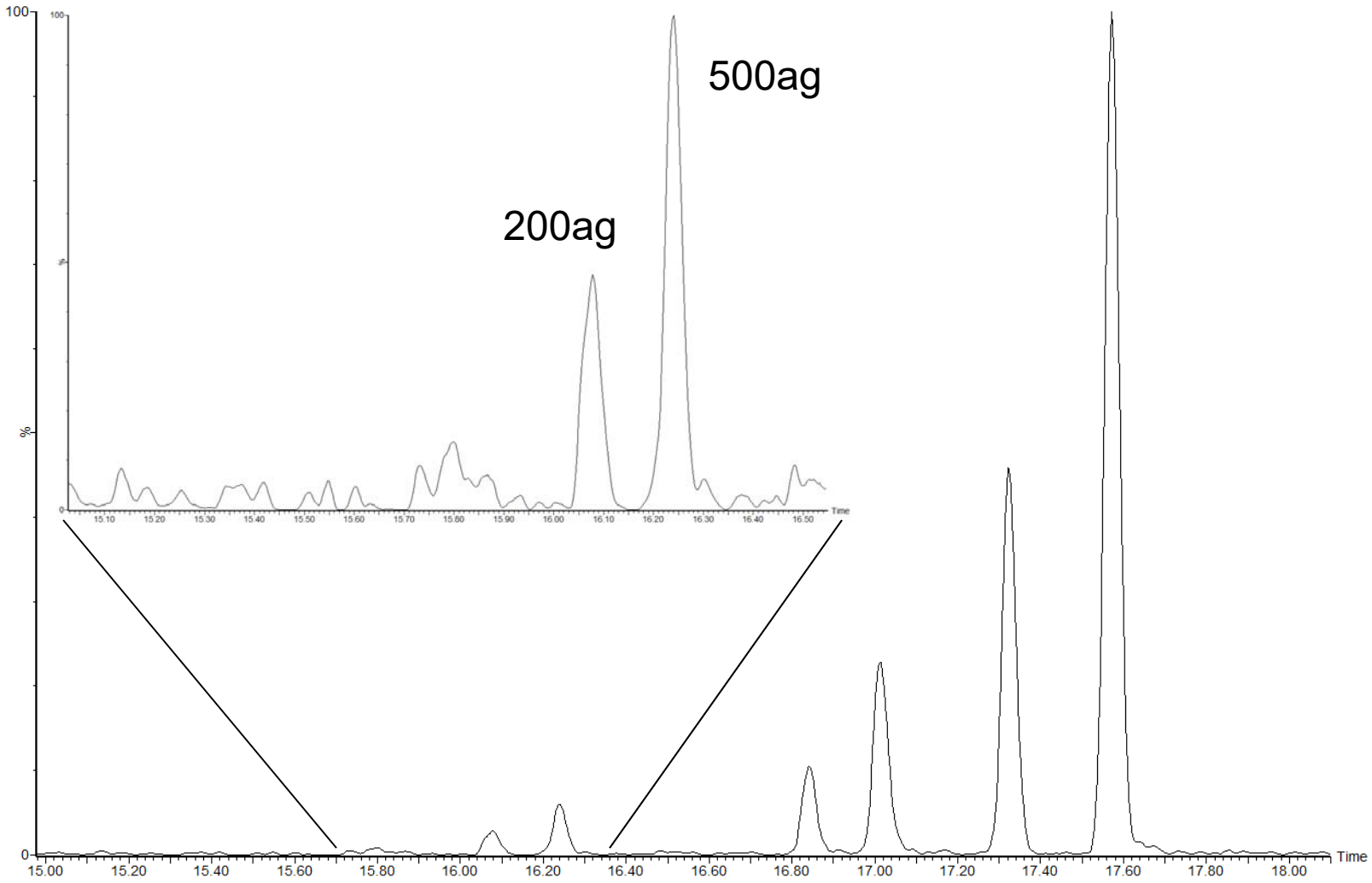
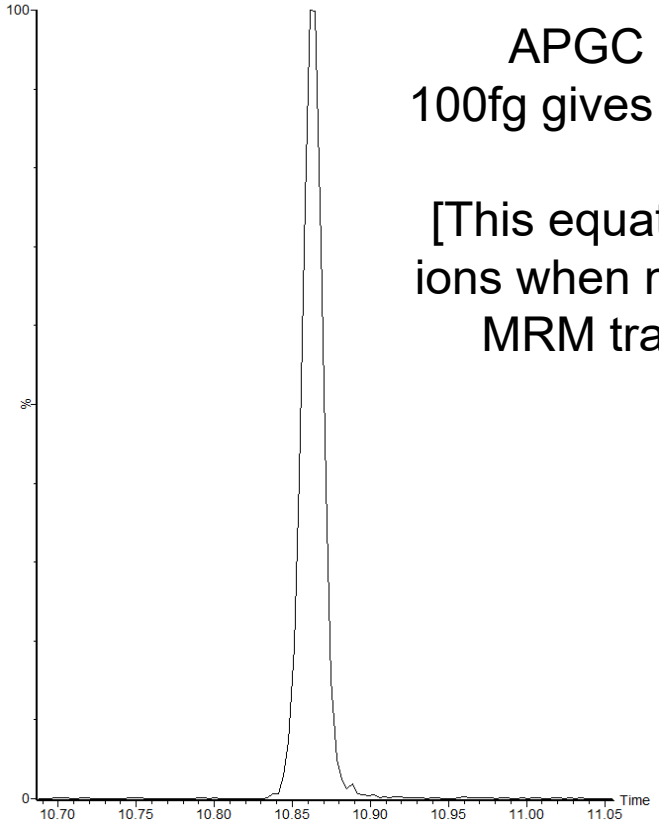


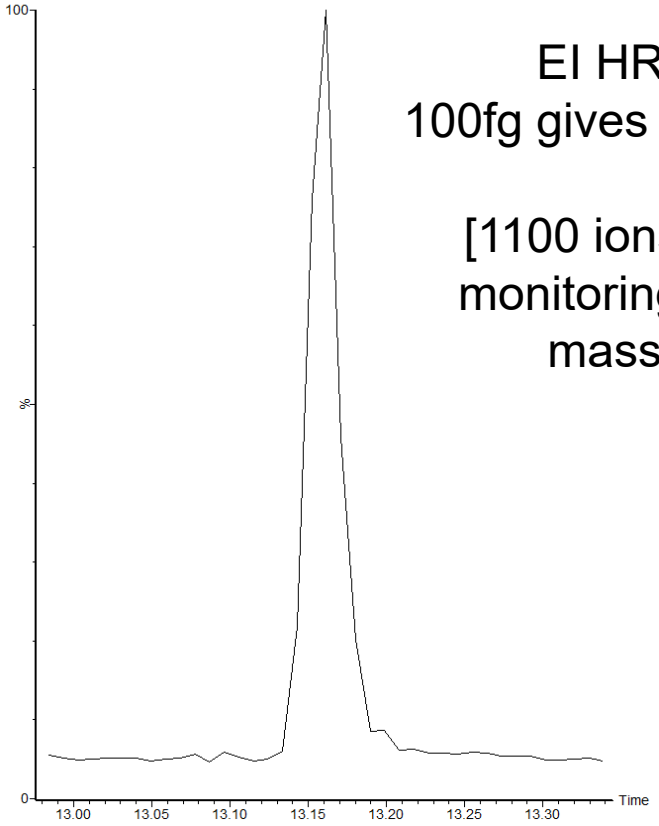
TCDD sensitivity GC APCI MS/MS v EI HRMS

- Quantification of peak areas in terms of number of ions detected



APGC MS/MS
100fg gives 63,500 ions

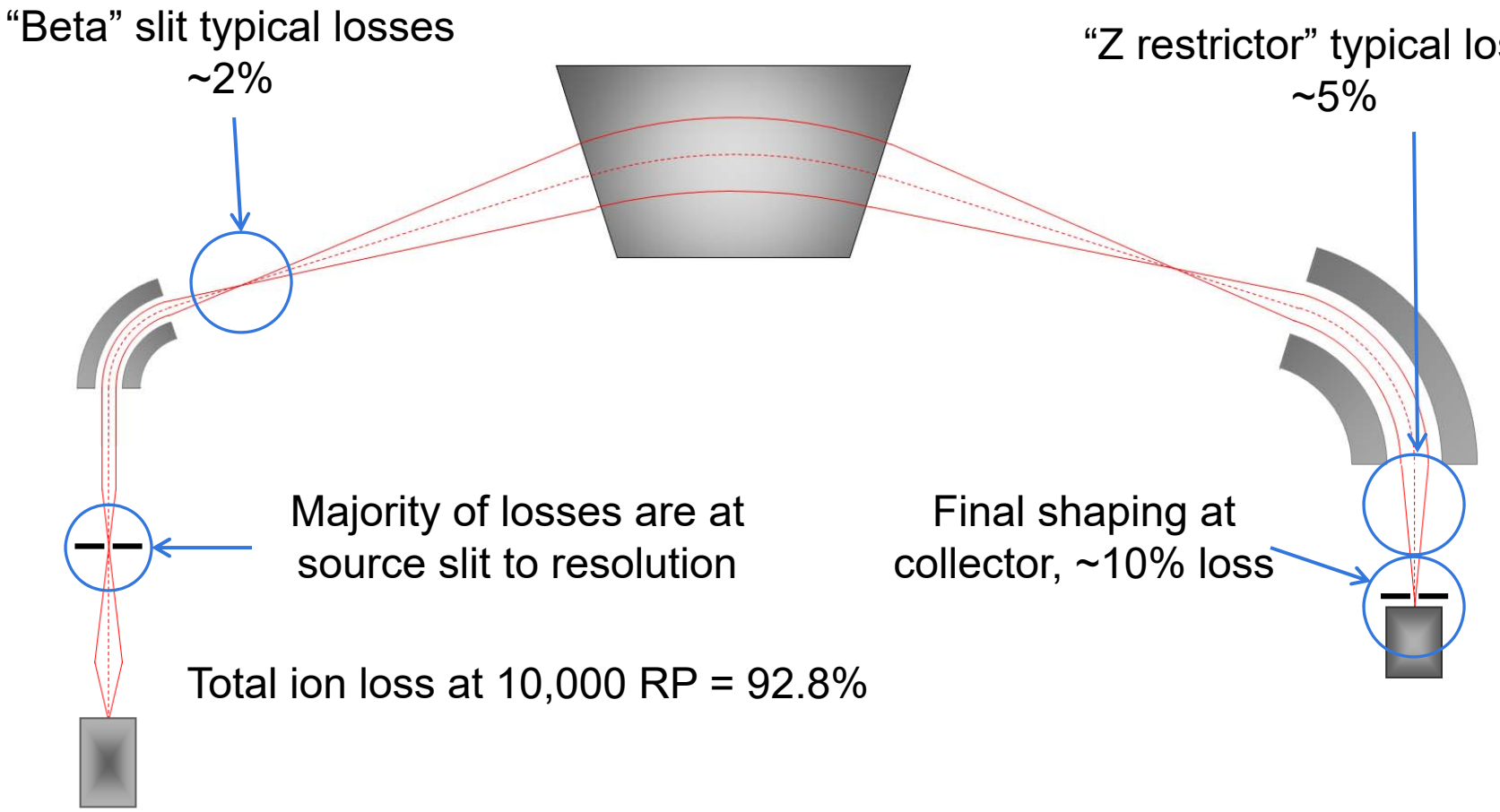
[This equates to 7060 ions when monitoring 9 MRM transitions]



EI HRMS
100fg gives 9900 ions

[1100 ions when monitoring 9 SIR masses]

Ion losses in HRMS



Total Losses = 94.0%

Ion losses in TQ MS/MS

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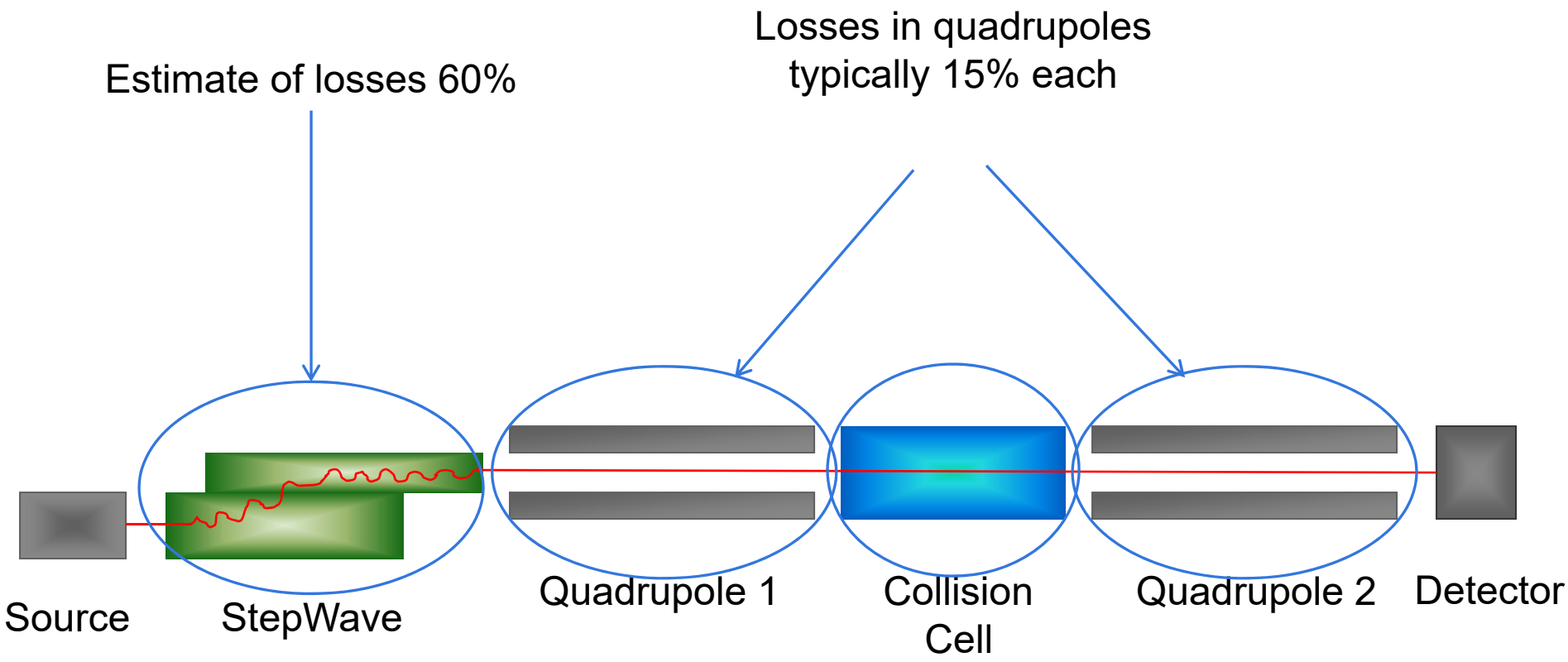

Losses in collision cell are ~5%

MRM fragmentation loss = 52% [for TCDD]

Total Losses = 86.8%

TCDD sensitivity APGC MS/MS v EI HRMS

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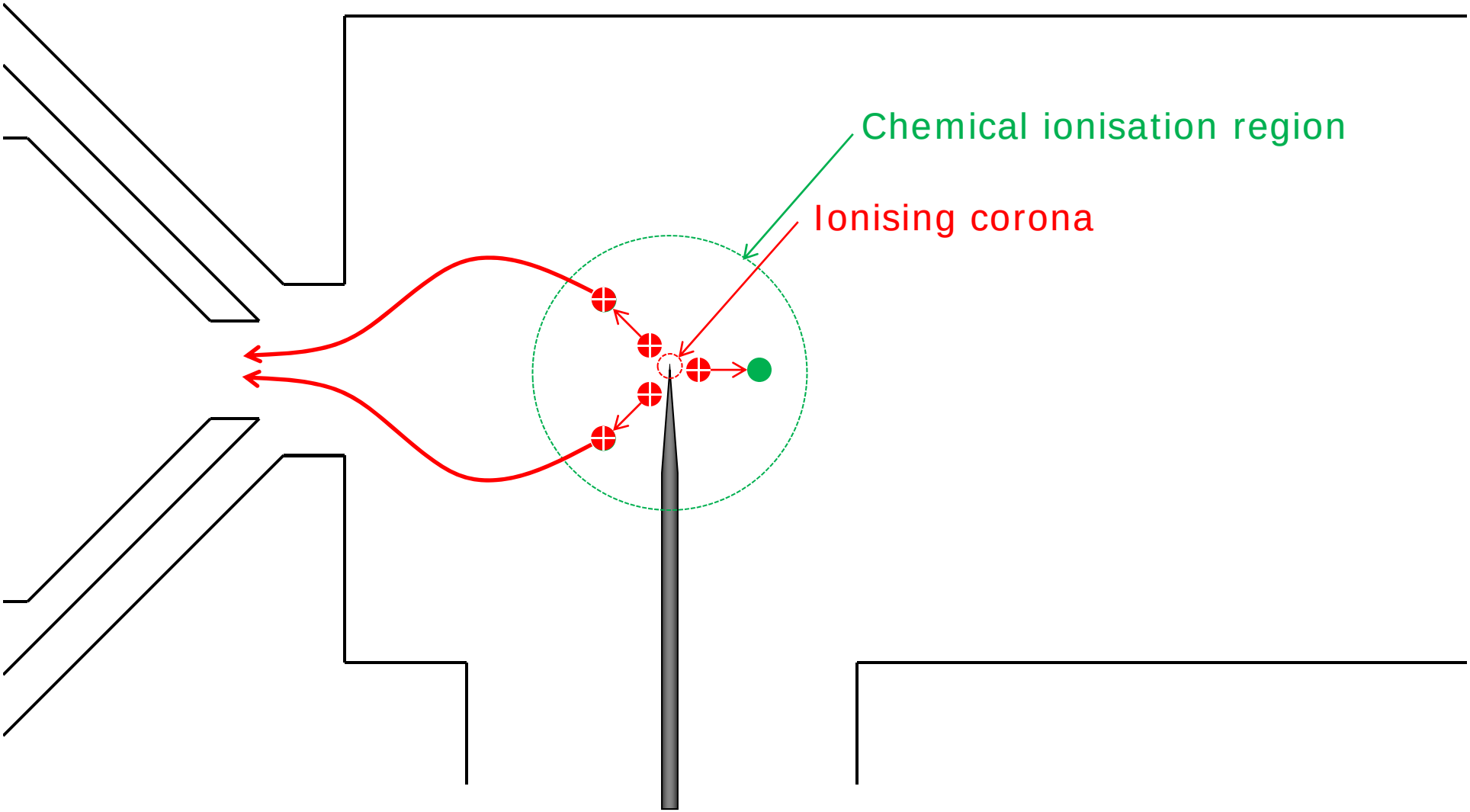
	HRMS	**APGC MS/MS**
Analyser Ion Loss	**94.0%**	**86.8%**
System Efficiency	0.018%	0.117%
Ionisation Efficiency	**0.30%**	**0.89%**

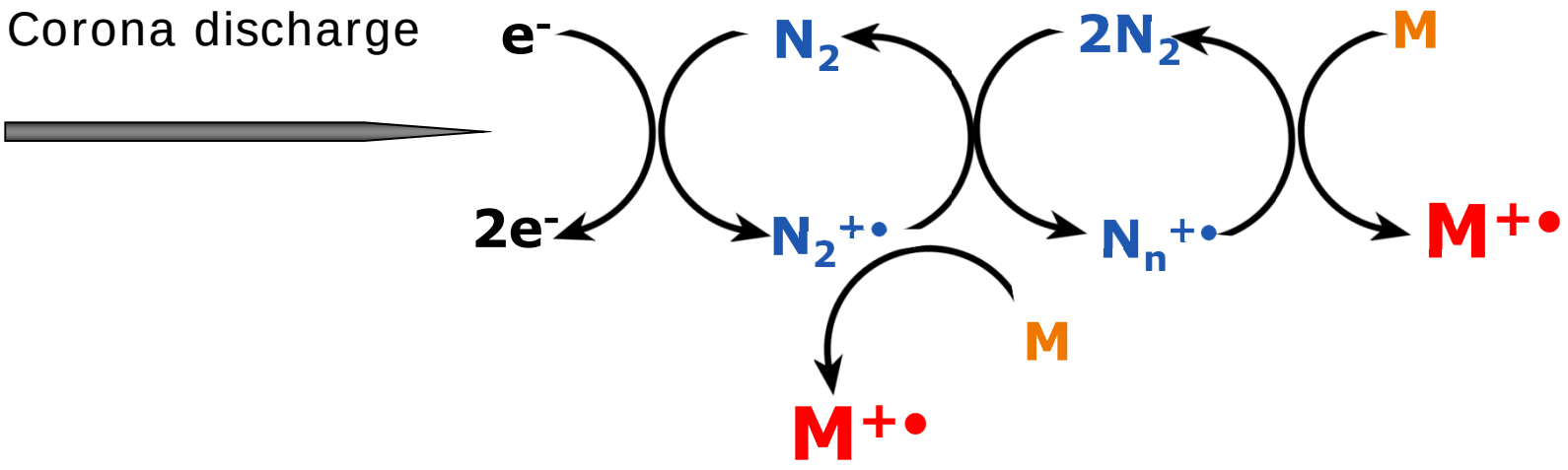
APGC source producing ~ **+3X** more ions for TCDD

Further ~ **+2X** sensitivity from **MS/MS** v HRMS

Atmospheric Pressure Chemical Ionisation



Atmospheric Pressure Chemical Ionisation



Charge Exchange is driven by Ionisation Energy

$$A^{+\cdot} + B \longrightarrow A + B^{+\cdot}$$

ONLY IF $IE_A > IE_B$

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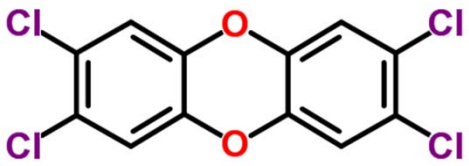
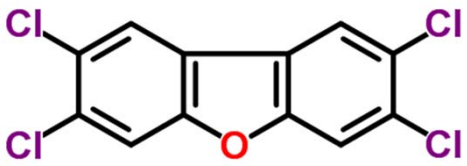
Dioxins and Furans
Spectral Comparisons





PeCDD Spectra

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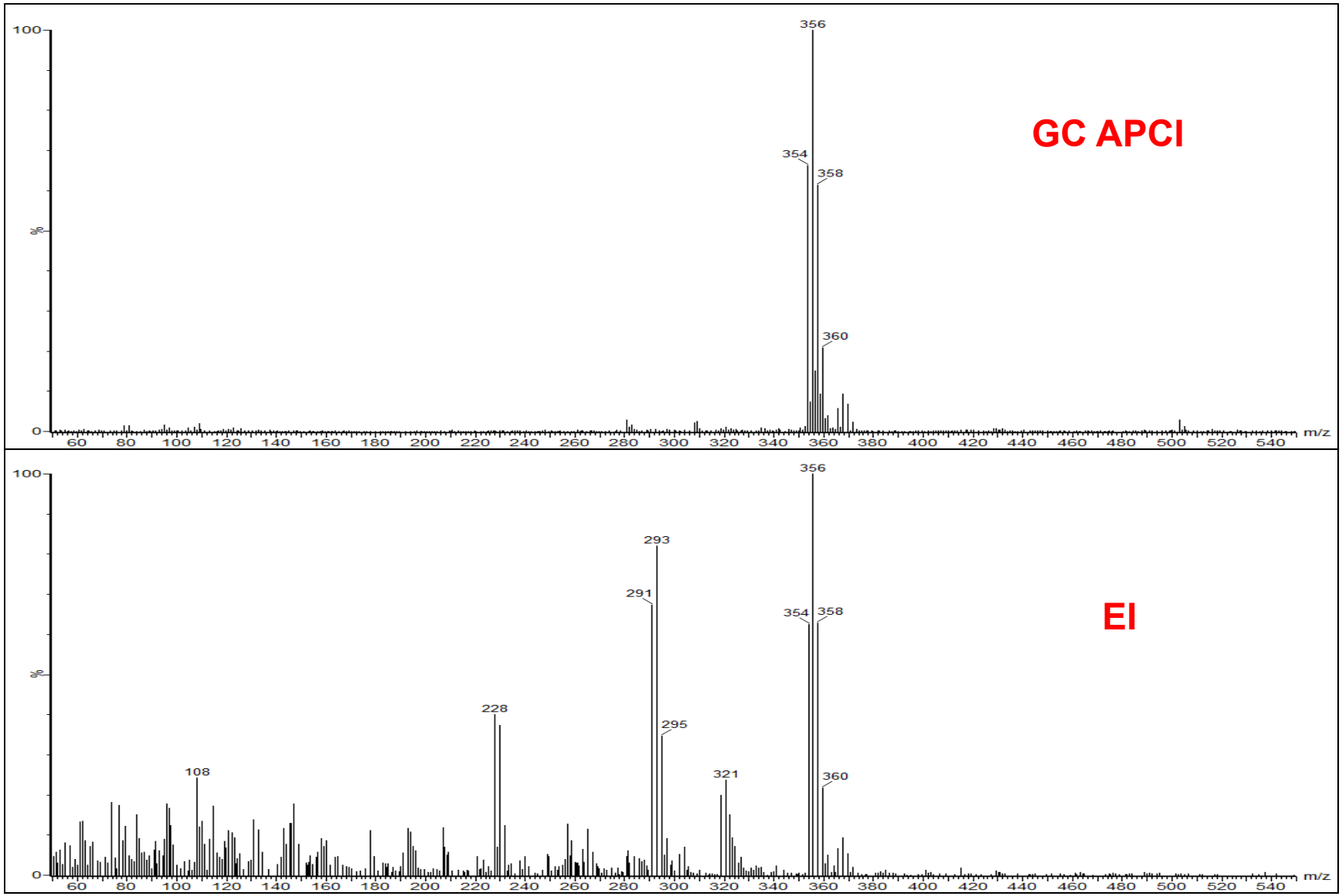

OCDD Spectra

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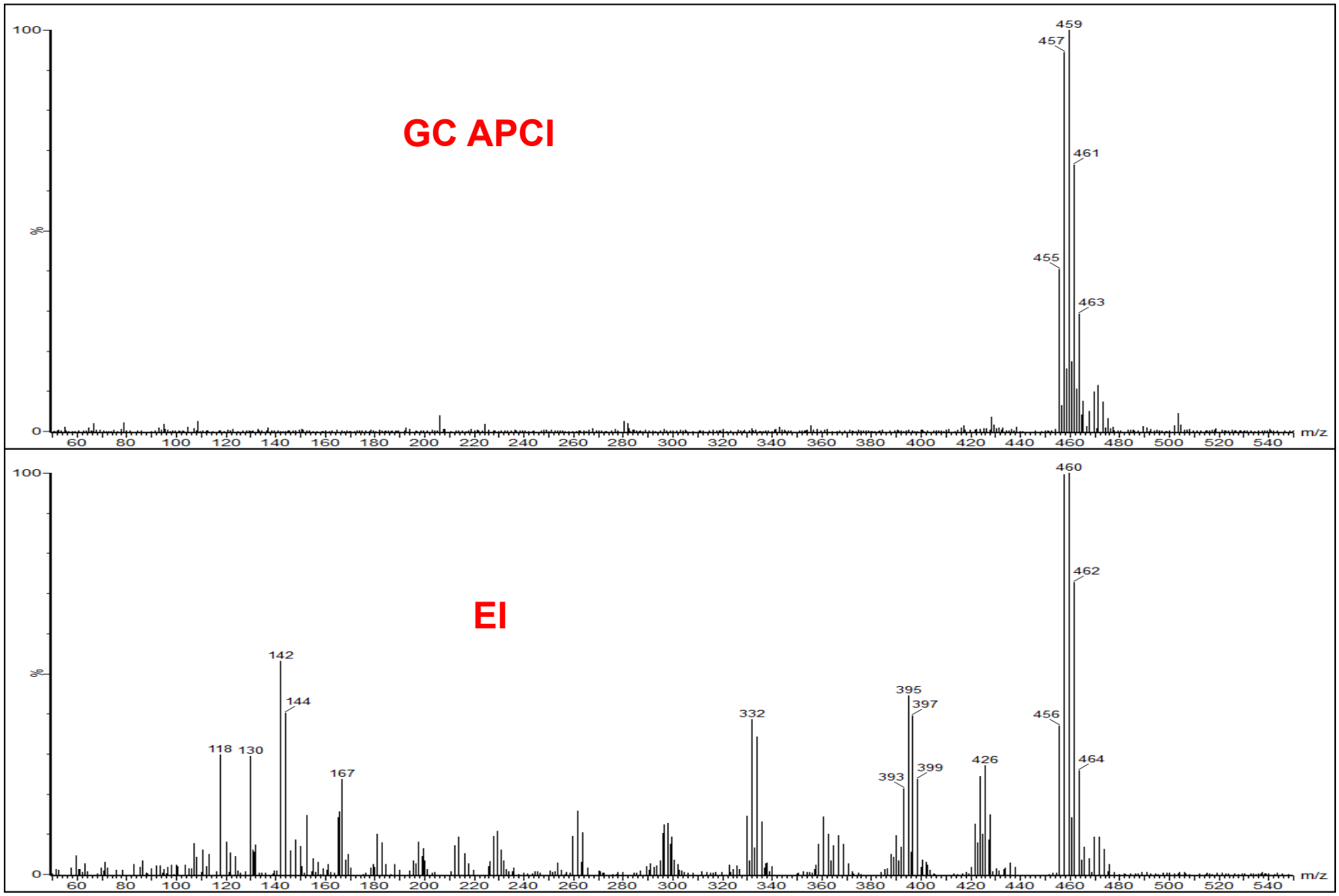
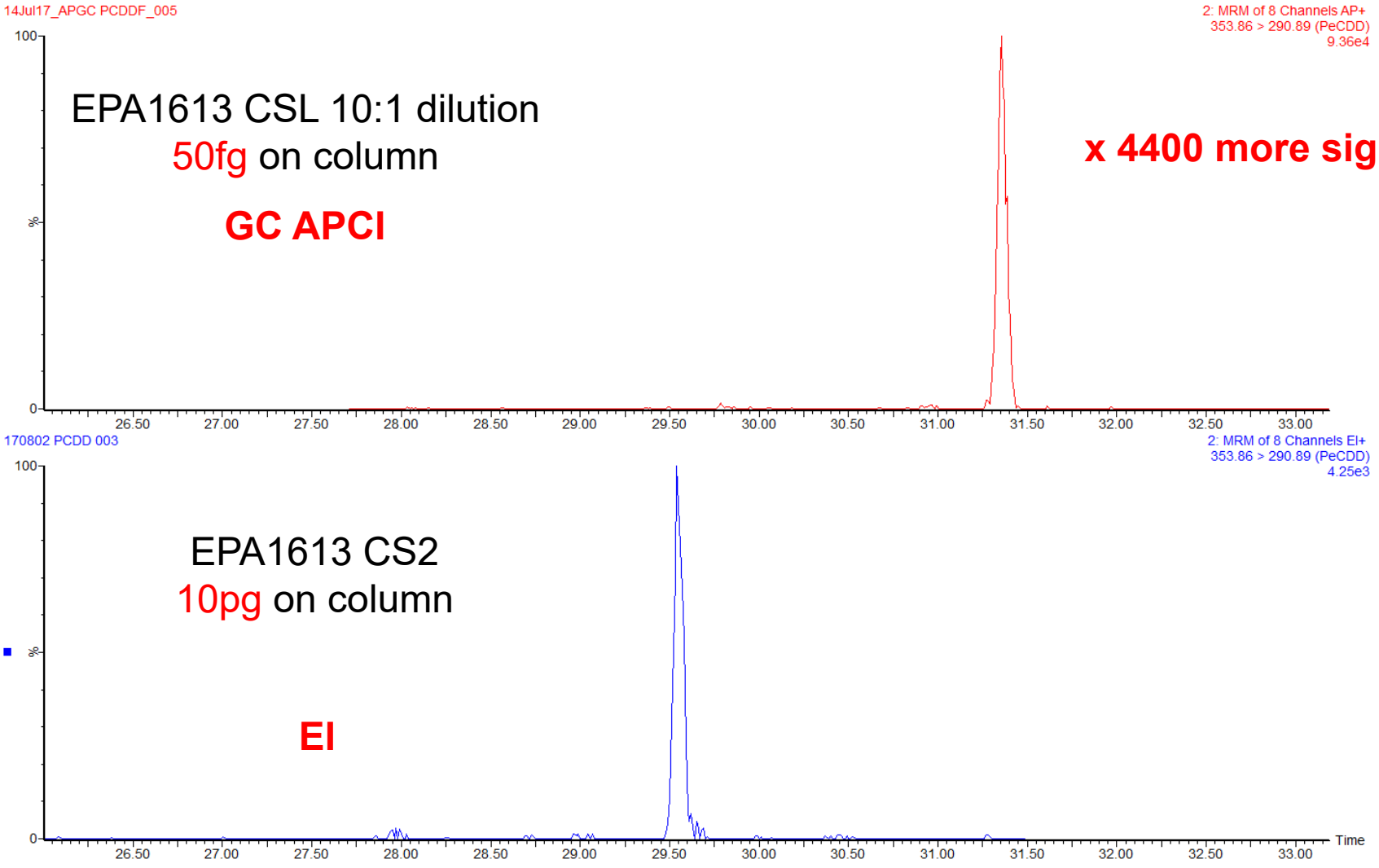
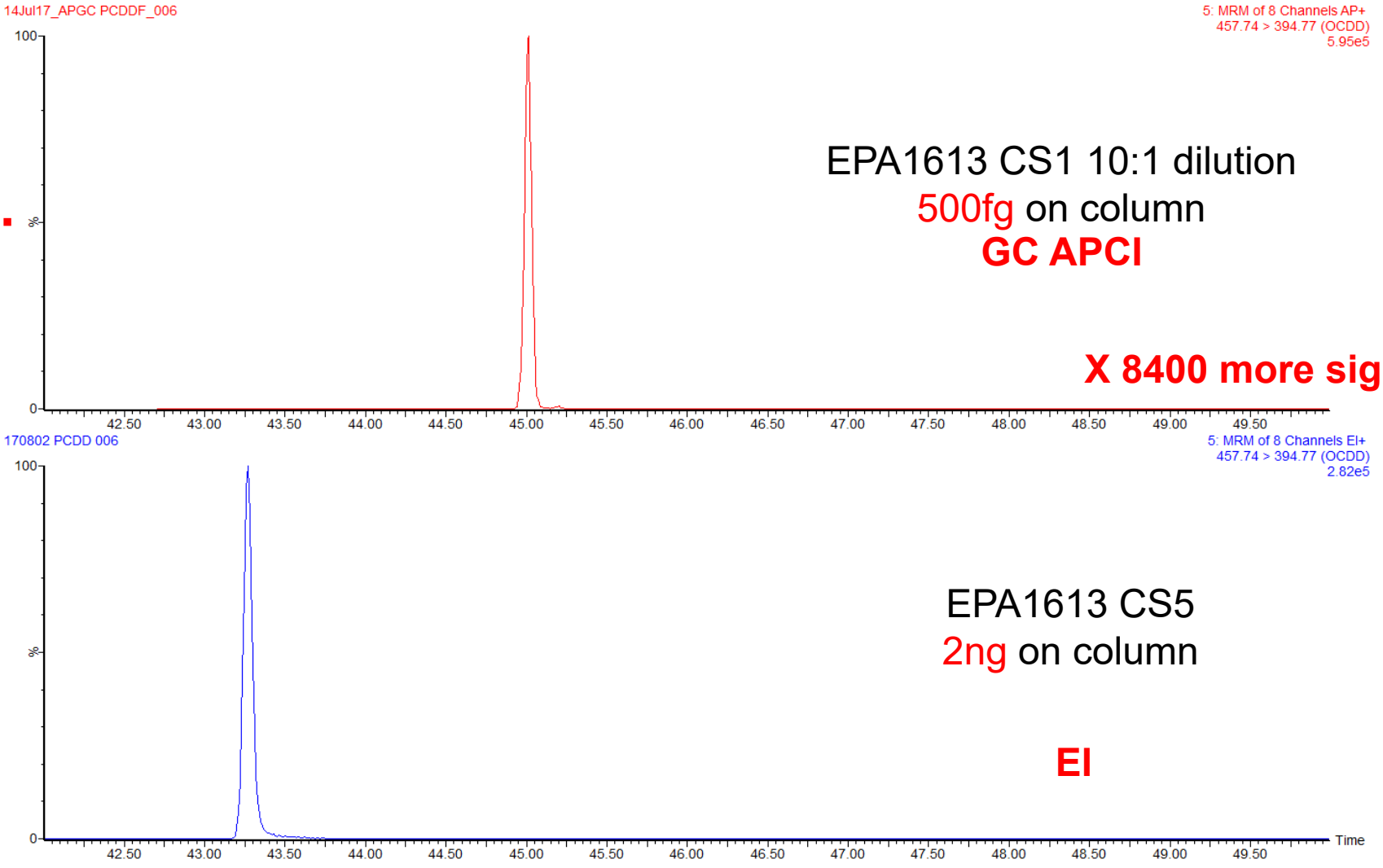


Detection Examples – 1,2,3,7,8 PeCDD



Detection Examples - OCDD



EPA1613 CS1 10:1 dilution

500fg on column

GC APCI

X 8400 more signal

EPA1613 CS5

2ng on column

EI

Background – Why fix what is not broken?

- GC-HRMS (sector) has been the “gold standard” for decades
- Existing systems are robust (relatively) and integrated systems
- Reference data all based on HRMS data
- Small range of target compounds allows for simple descriptors (17-TEF compounds)
- Robust prep method removes most (?) interferences

Is anything “broken”

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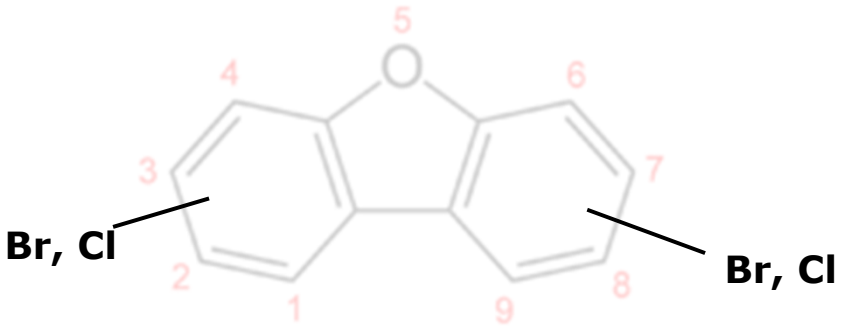
- 17 TEF’s may not be enough for a true TEQ determination
- The current targets are certainly not enough to truly characterize a source or environmental impact
- There is the potential to have increasing levels of mixed halo and poly-Br compound formation in more modern samples

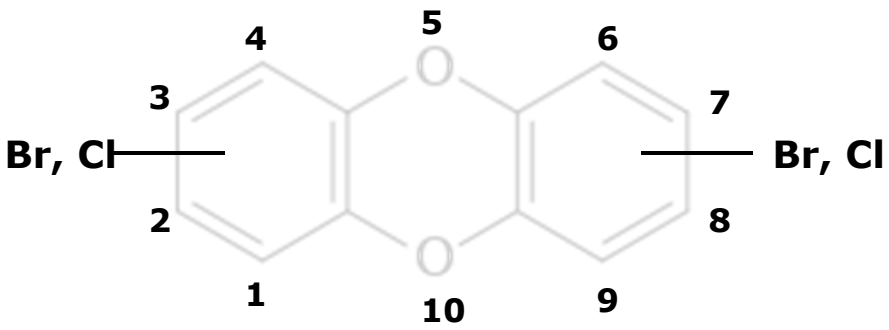
What is something they all have in common?

Δ
+ source of chlorine

Δ
+ source of chlorine



Dibenzofuran



Dibenzo-p-dioxin

Do we care about other compounds?

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- Very few studies of the mixed halo congeners
  - Analytical
  - Biochemical
- Do they follow similar chemistry as the polychloro analogs?

To Investigate Further

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- Analytical Approach?
  - What technique/s
- Reference Materials?
  - Very few are available
- Sample Accessibility?
  - How do we obtain “real” samples

Simulated burn studies

Simulated burn studies

Household Fire

- Mattress
- Sofa Chair
- Vinyl / Wood Chair
- Carpet
- Pillows
- Television

Electronics Fire

- Televisions
- Microwave
- Printers
- Computer monitors
- Laptop
- Cables/Wires

Simulated burn studies

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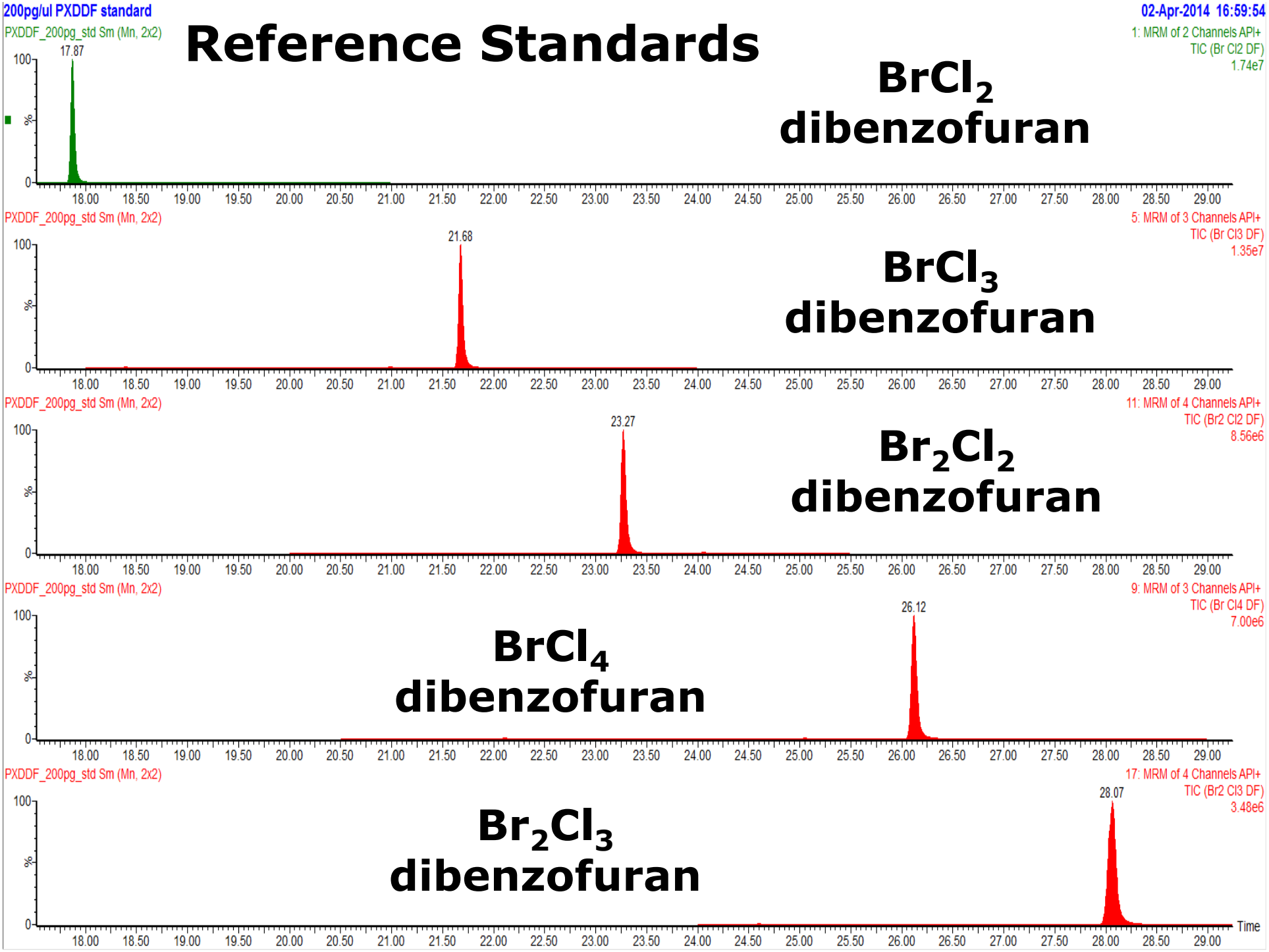
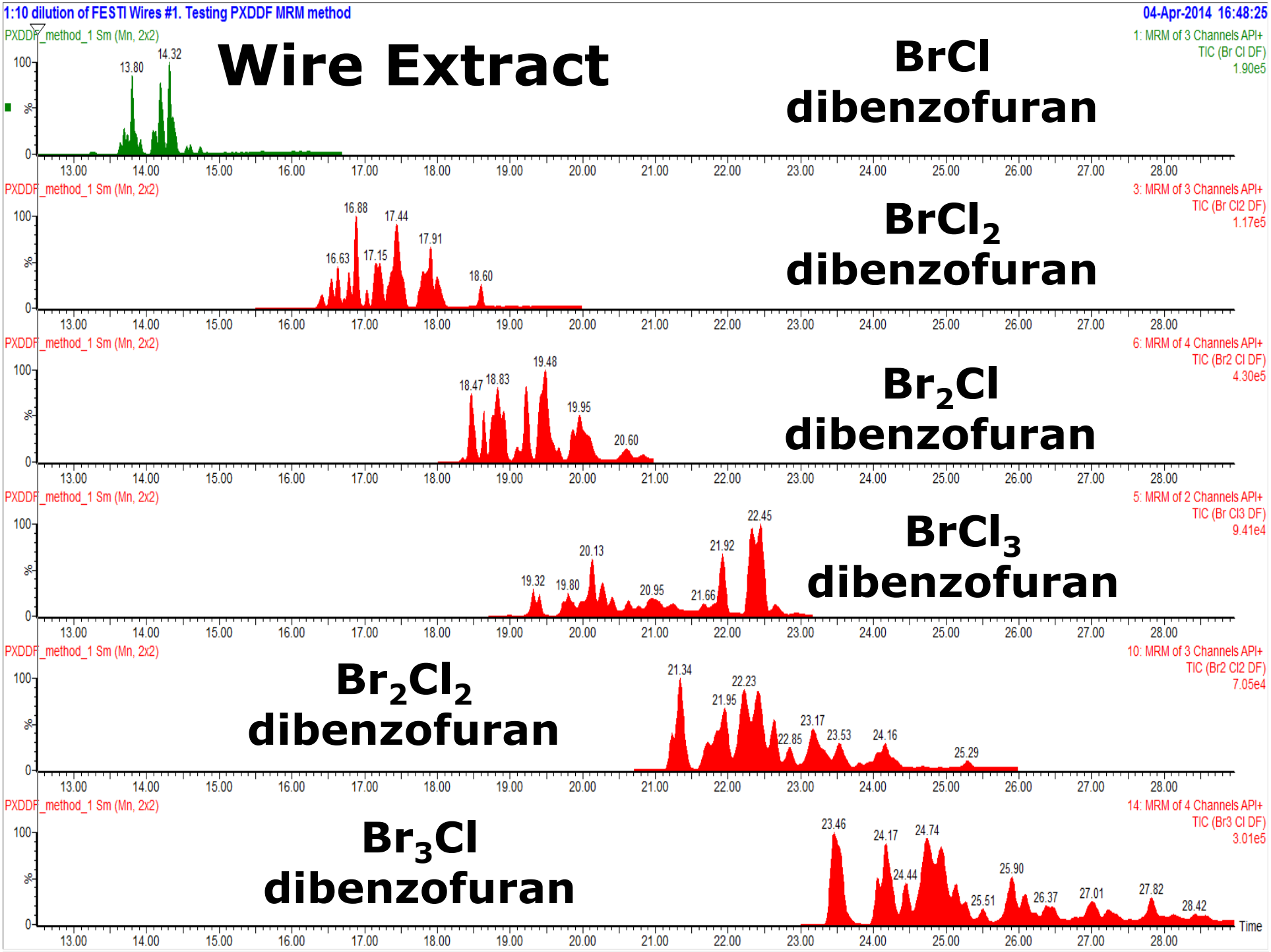
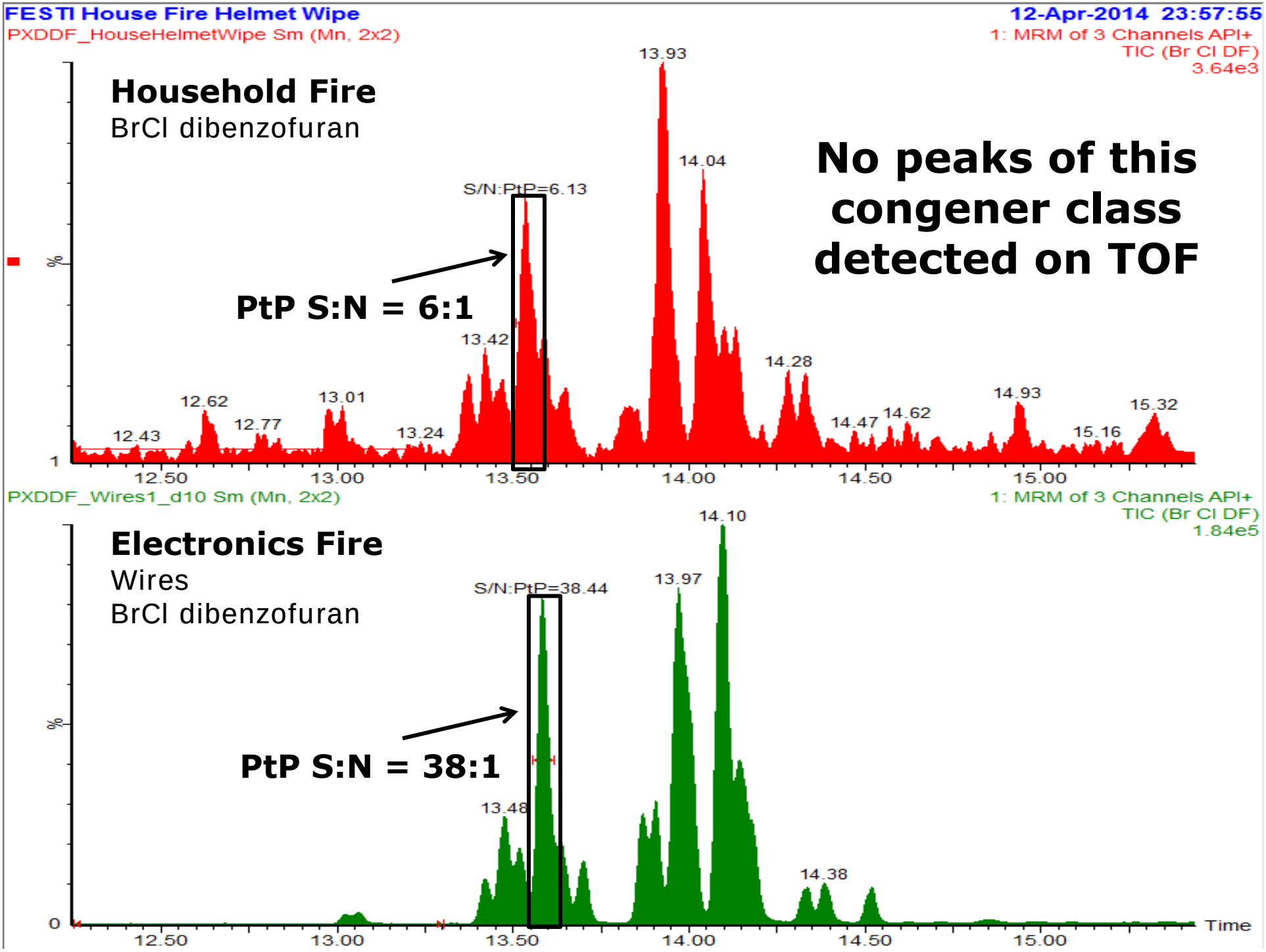
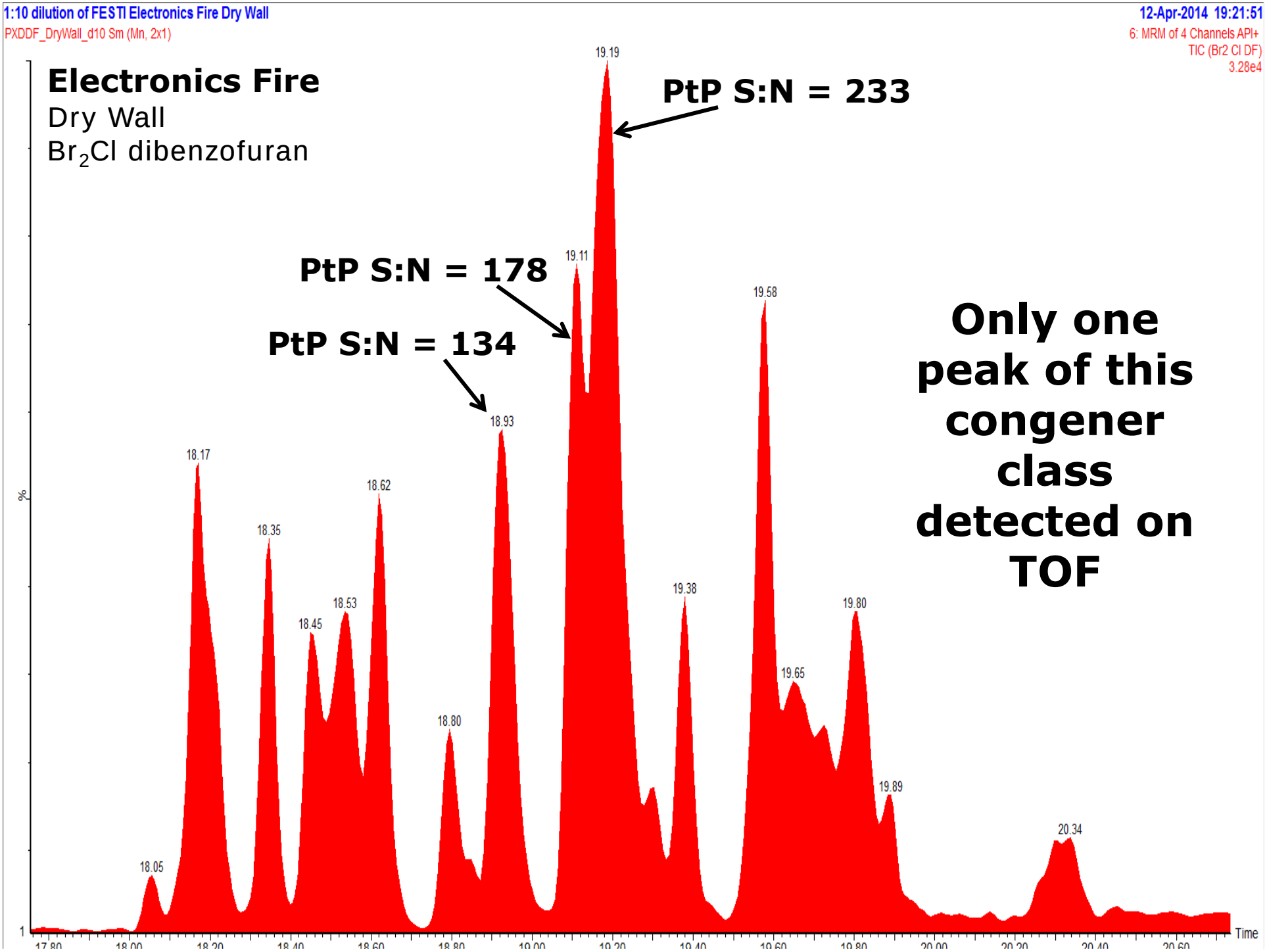
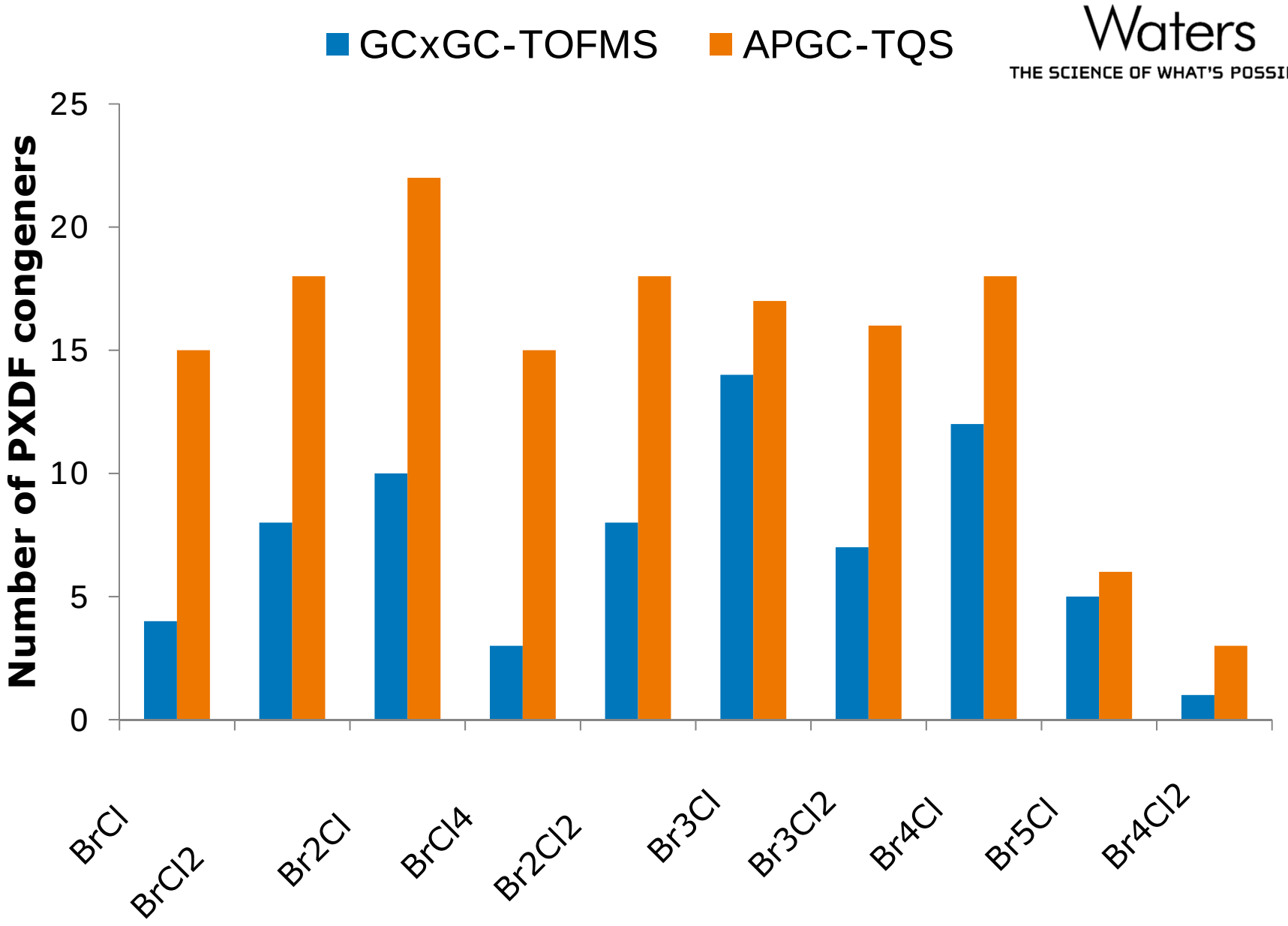
Characterizing Fire Debris Samples: Mixed Halogenated Dioxins


200pg/ul PXDDF standard
02-Apr-2014 16:59:54
Reference Standards
PXDDF_200pg_std Sm (Mn, 2x2)
1: MRM of 2 Channels API+
TIC (Br Cl2 DF)
1.74e7
17.87
BrCl2
dibenzofuran
PXDDF_200pg_std Sm (Mn, 2x2)
5: MRM of 3 Channels API+
TIC (Br Cl3 DF)
1.35e7
21.68
BrCl3
dibenzofuran
PXDDF_200pg_std Sm (Mn, 2x2)
11: MRM of 4 Channels API+
TIC (Br2 Cl2 DF)
8.56e6
23.27
Br2Cl2
dibenzofuran
PXDDF_200pg_std Sm (Mn, 2x2)
9: MRM of 3 Channels API+
TIC (Br Cl4 DF)
7.00e6
26.12
BrCl4
dibenzofuran
PXDDF_200pg_std Sm (Mn, 2x2)
17: MRM of 4 Channels API+
TIC (Br2 Cl3 DF)
3.48e6
28.07
Br2Cl3
dibenzofuran
100
%
0
18.00 18.50 19.00 19.50 20.00 20.50 21.00 21.50 22.00 22.50 23.00 23.50 24.00 24.50 25.00 25.50 26.00 26.50 27.00 27.50 28.00 28.50 29.00
Time


1:10 dilution of FESTI Wires #1. Testing PXDDF MRM method
04-Apr-2014 16:48:25
Wire Extract
BrCl dibenzofuran
BrCl2 dibenzofuran
Br2Cl dibenzofuran
BrCl3 dibenzofuran
Br2Cl2 dibenzofuran
Br3Cl dibenzofuran
1: MRM of 3 Channels API+ TIC (Br Cl DF) 1.90e5
3: MRM of 3 Channels API+ TIC (Br Cl2 DF) 1.17e5
6: MRM of 4 Channels API+ TIC (Br2 Cl DF) 4.30e5
5: MRM of 2 Channels API+ TIC (Br Cl3 DF) 9.41e4
10: MRM of 3 Channels API+ TIC (Br2 Cl2 DF) 7.05e4
14: MRM of 4 Channels API+ TIC (Br3 Cl DF) 3.01e5
Time


FESTI House Fire Helmet Wipe
PXDDF_HouseHelmetWipe Sm (Mn, 2x2)
12-Apr-2014 23:57:55
1: MRM of 3 Channels API+
TIC (Br Cl DF)
3.64e3
Household Fire
BrCl dibenzofuran
No peaks of this congener class detected on TOF
S/N:PtP=6.13
PtP S:N = 6:1
13.93
14.04
13.42
14.28
12.62
13.01
14.93
15.32
12.77
14.47
14.62
12.43
13.24
15.16
%
1
12.50
13.00
13.50
14.00
14.50
15.00
PXDDF_Wires1_d10 Sm (Mn, 2x2)
1: MRM of 3 Channels API+
TIC (Br Cl DF)
1.84e5
Electronics Fire
Wires
BrCl dibenzofuran
14.10
S/N:PtP=38.44
13.97
PtP S:N = 38:1
13.48
14.38
%
0
Time
12.50
13.00
13.50
14.00
14.50
15.00


1:10 dilution of FESTI Electronics Fire Dry Wall
PXDDF_DryWall_d10 Sm (Mn, 2x1)
12-Apr-2014 19:21:51
6: MRM of 4 Channels API+
TIC (Br2 Cl DF)
3.28e4
Electronics Fire
Dry Wall
Br2Cl dibenzofuran
PtP S:N = 233
PtP S:N = 178
PtP S:N = 134
Only one peak of this congener class detected on TOF
19.19
19.11
19.58
18.93
18.17
18.62
18.35
18.53
18.45
19.38
19.80
19.65
18.80
19.89
20.34
18.05
%
1
Time



Conclusions

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- APGC-TQ-S allows for considerable improvement in sensitivity
  - 20-40 X versus Autospec
- Mixed-halo congeners can be quantified (though not identified)
- They are found in most all fire debris samples studied so far…

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Acknowledgements

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  - Frank L. Dorman
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  - David Douce, Murray Booth
  - Dave Gordon