

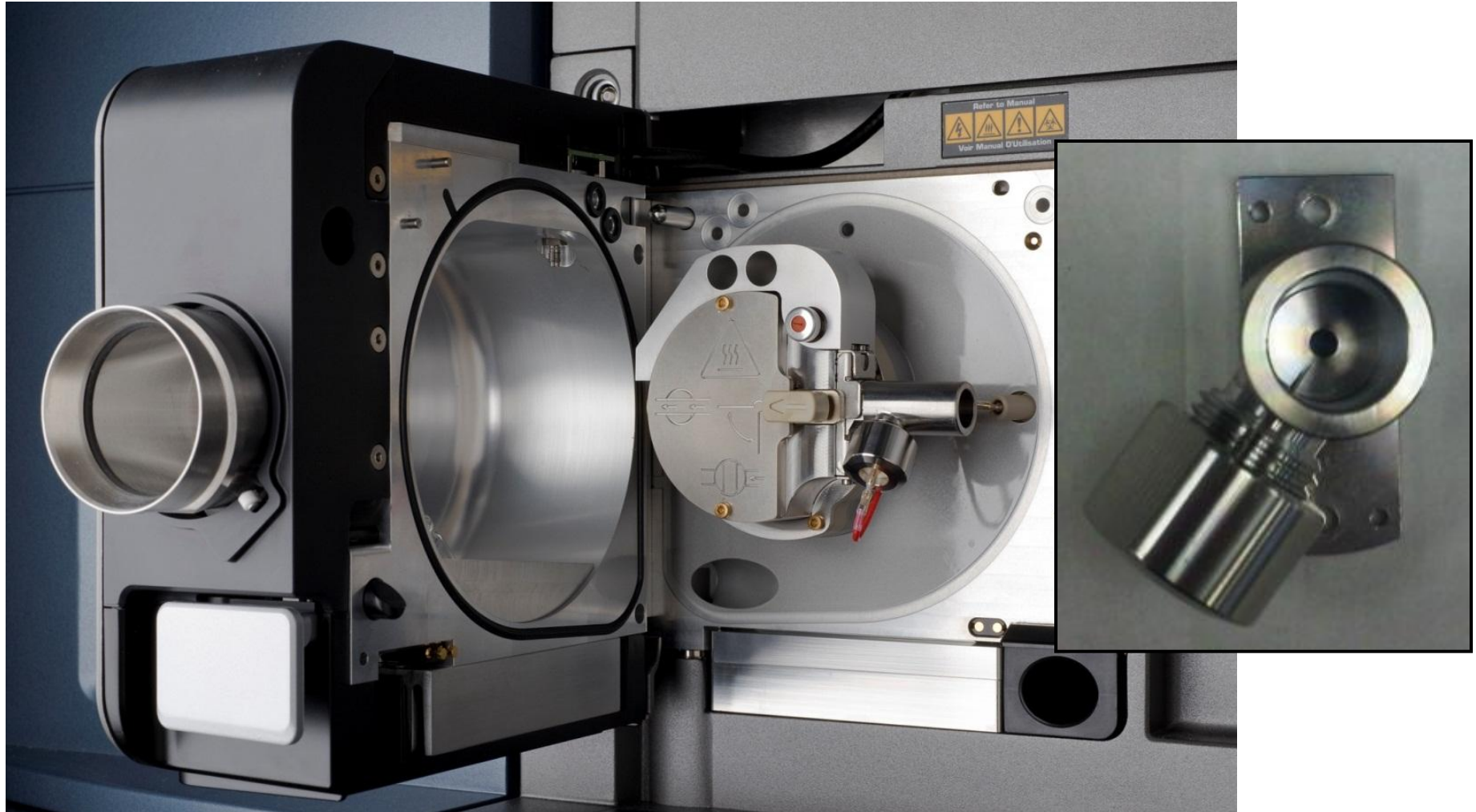
Sub-Femtogram Detection of Dioxins and Furans using Tandem Quadrupole Mass Spectrometer

Douglas Stevens
Waters Corporation

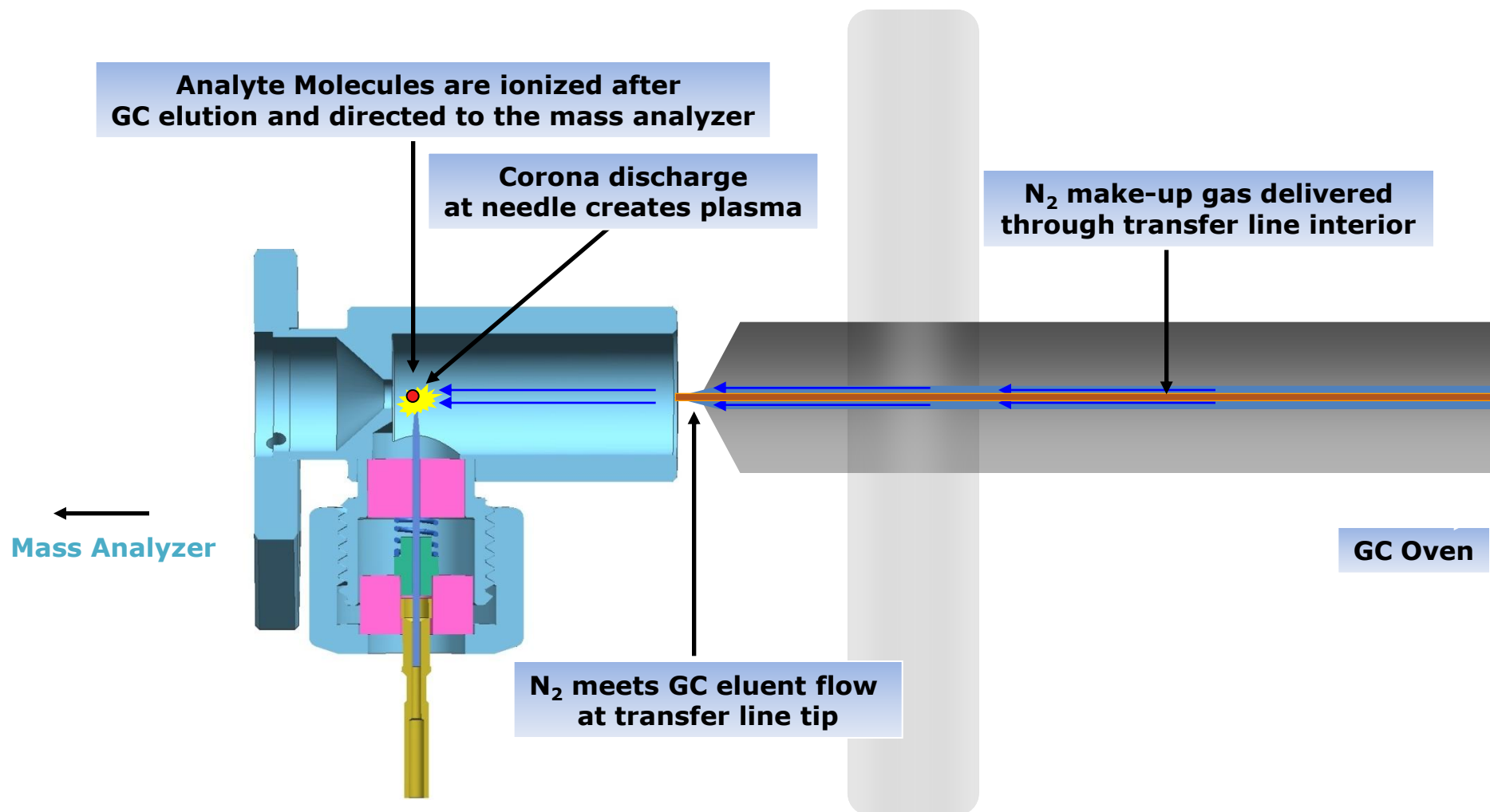
GC APCI Tandem Quadrupole System APGC Xevo TQ-XS



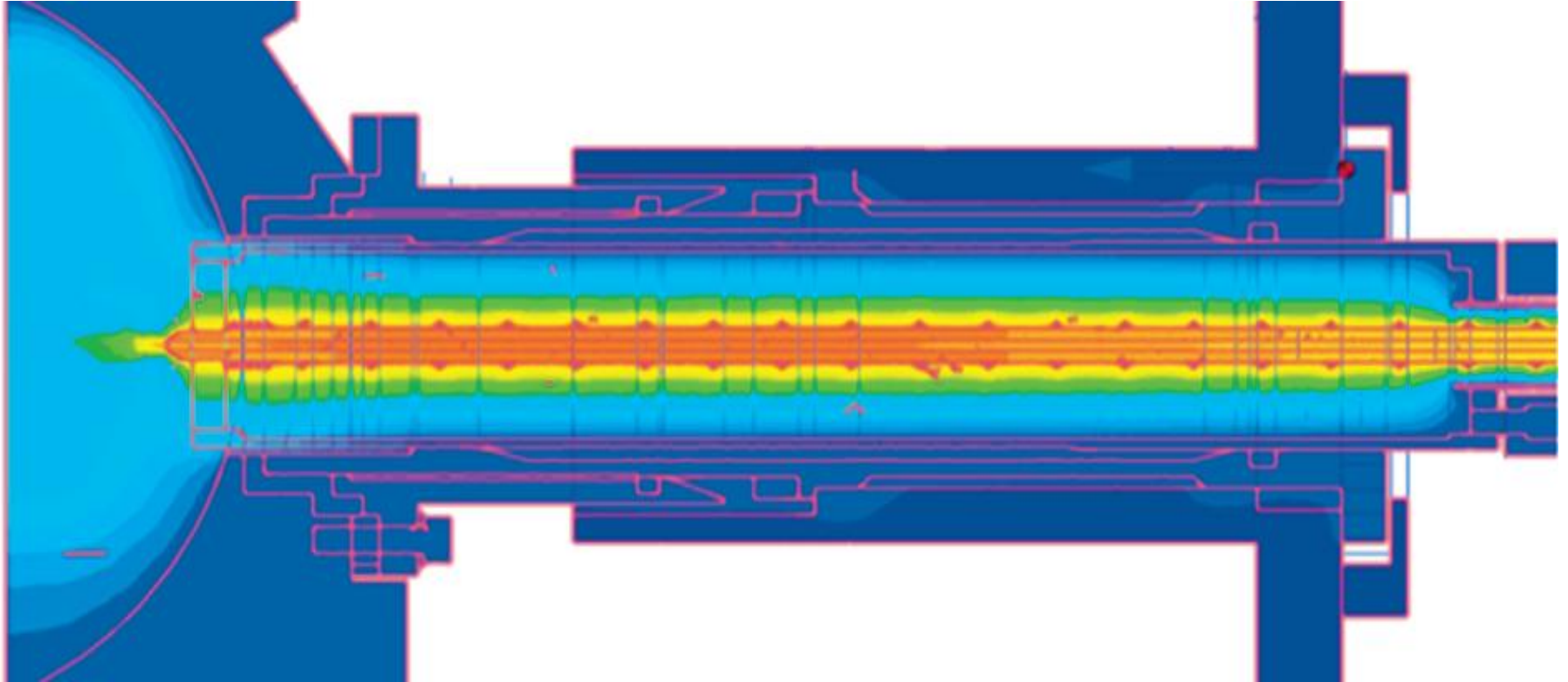
Source and Ion Chamber



How GC-APCI works

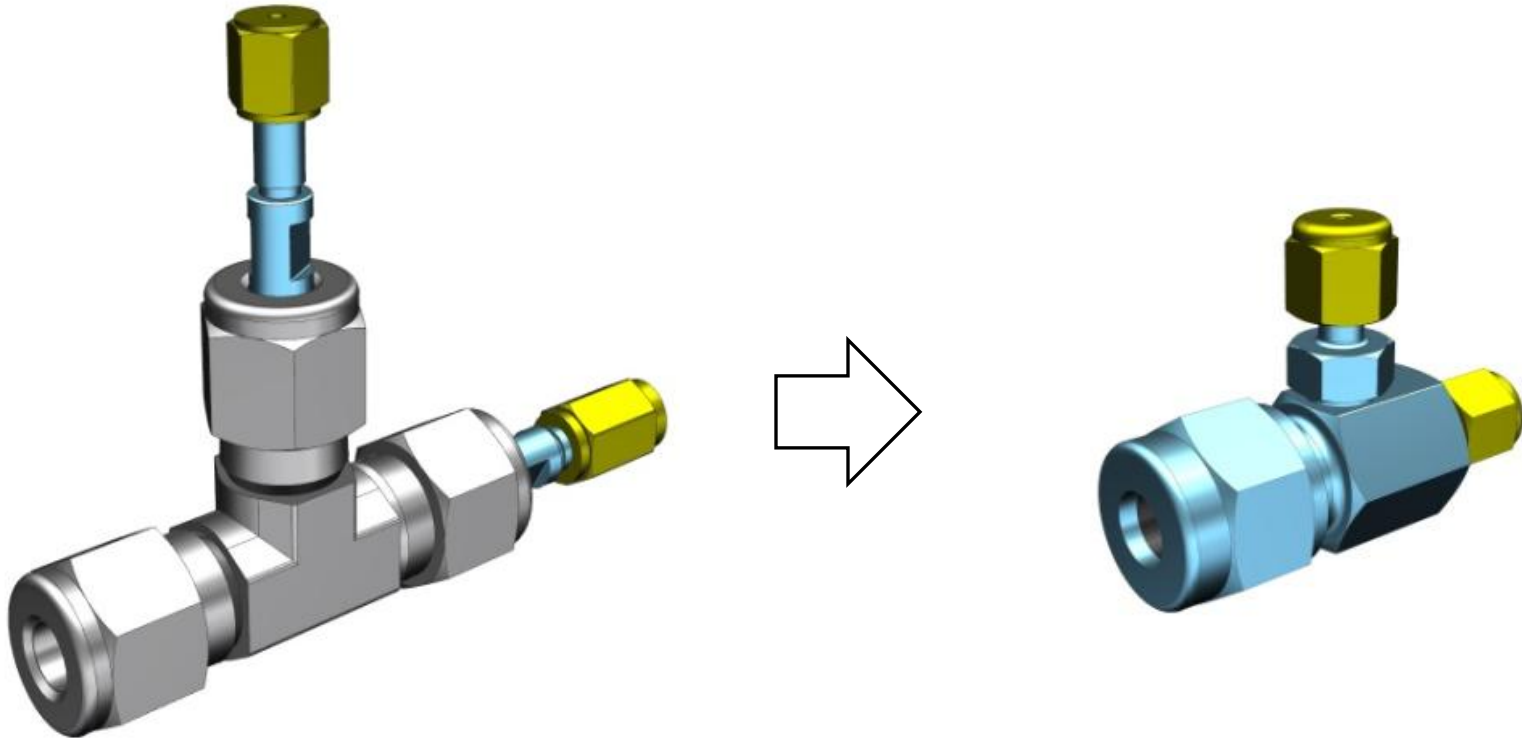


v2.0 GC-APCI Interface

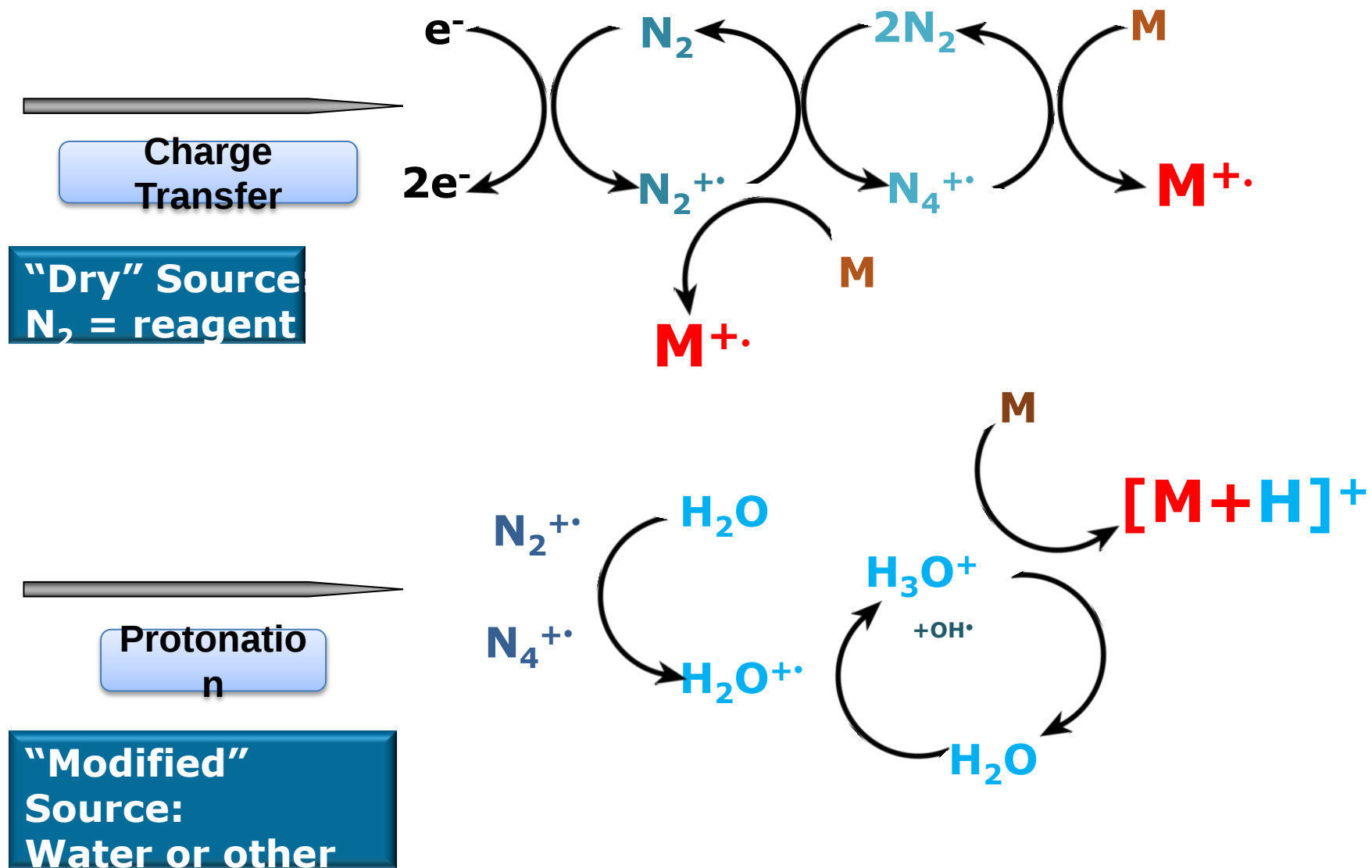


v2.0 GC-APCI Interface

- Also changed the tee piece design

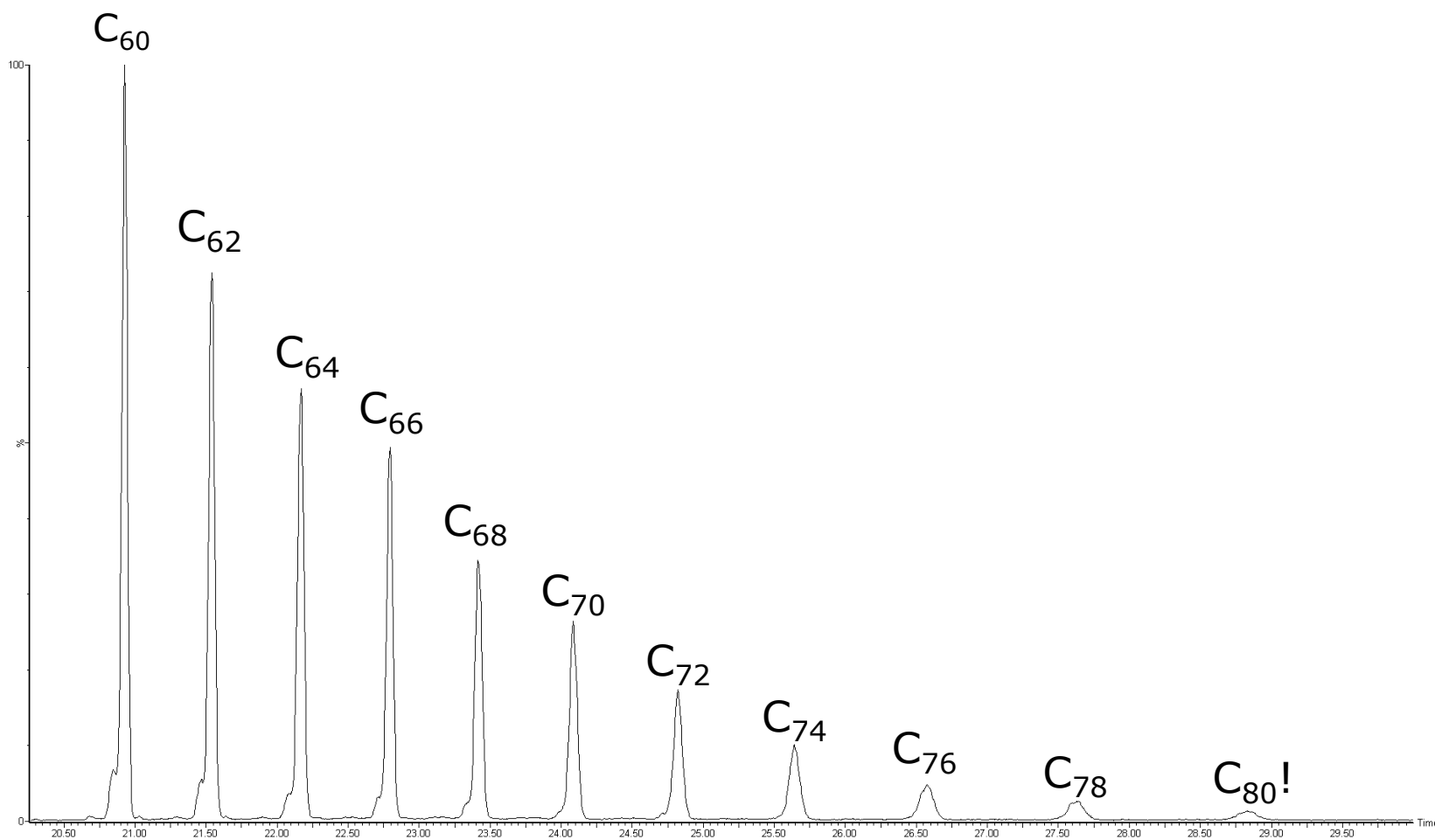


Ionization Mechanisms



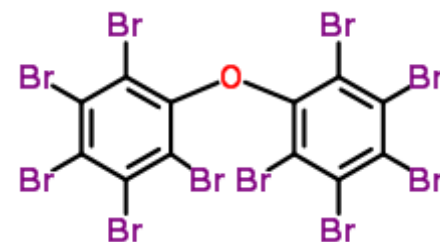
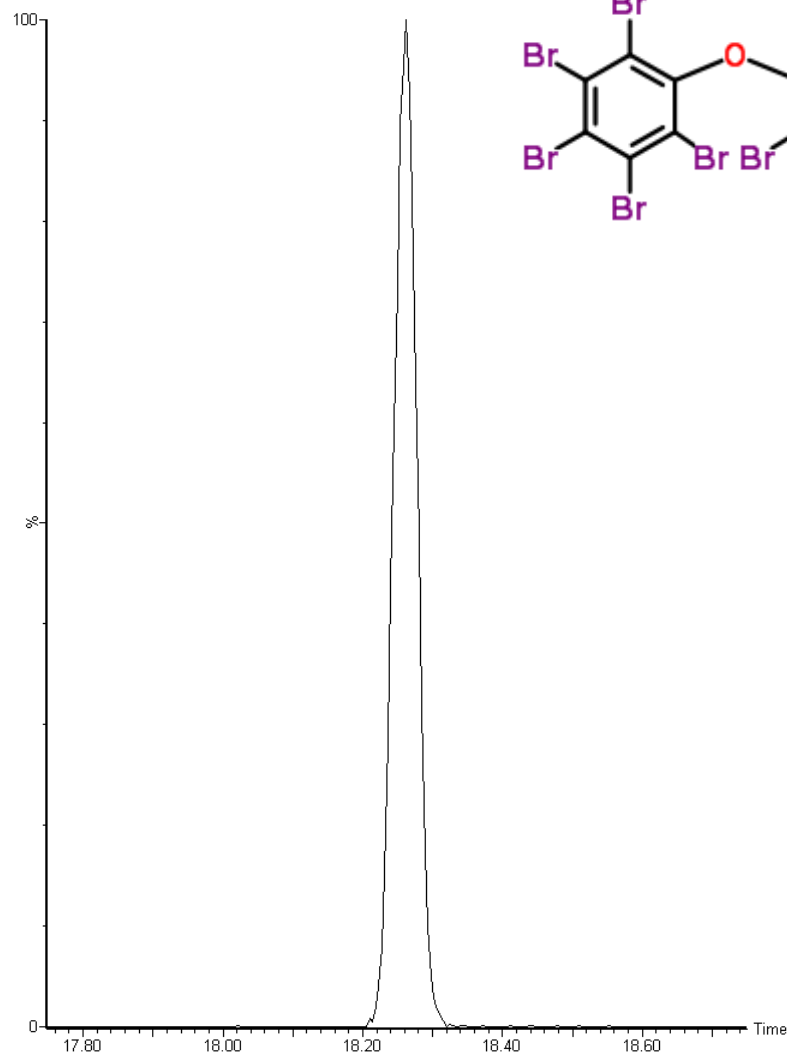
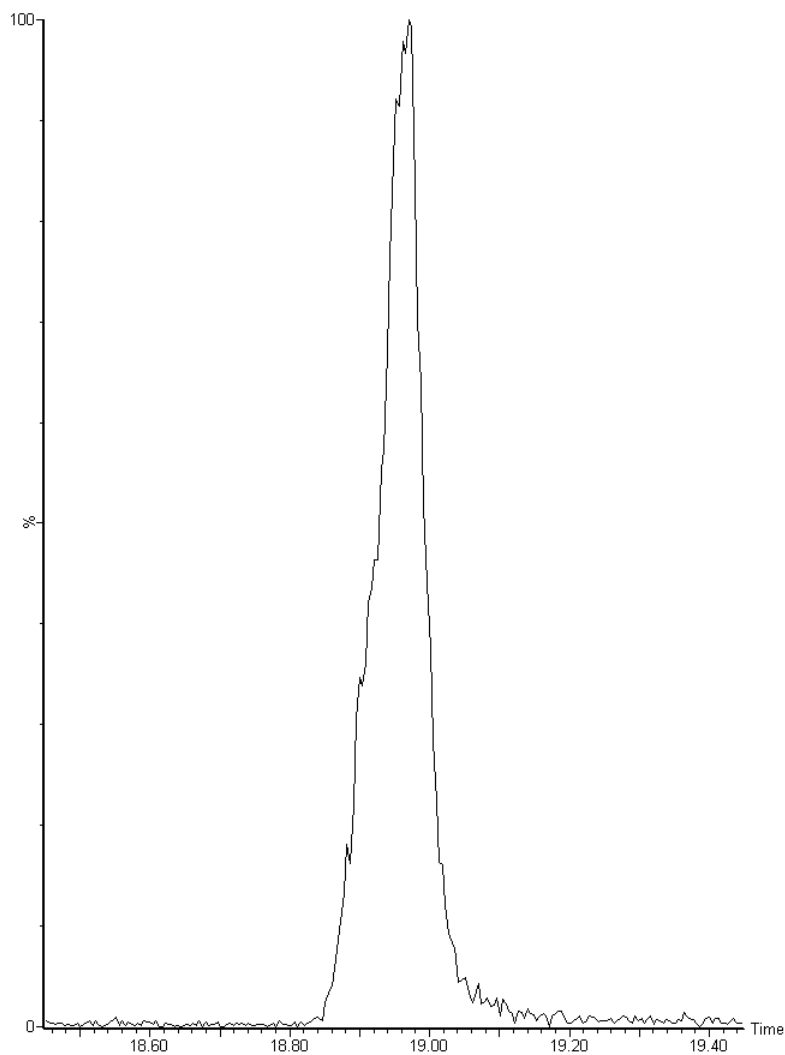
v2.0 GC-APCI Interface Performance

- With HTL at 380°C and GC carrier gas ramped up to 15mL/min



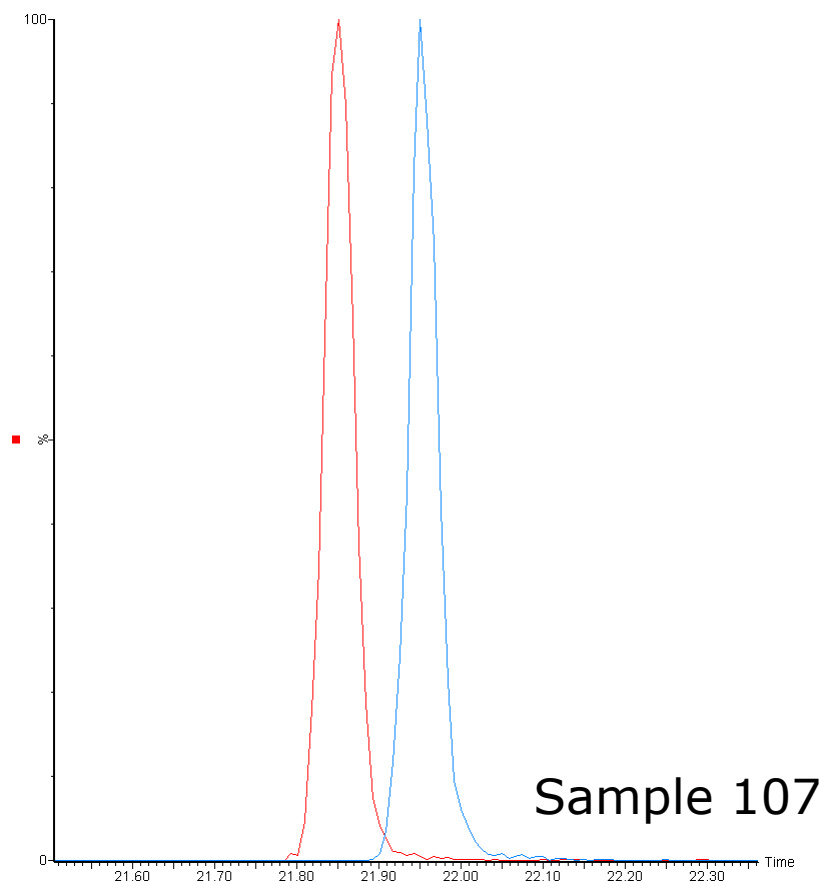
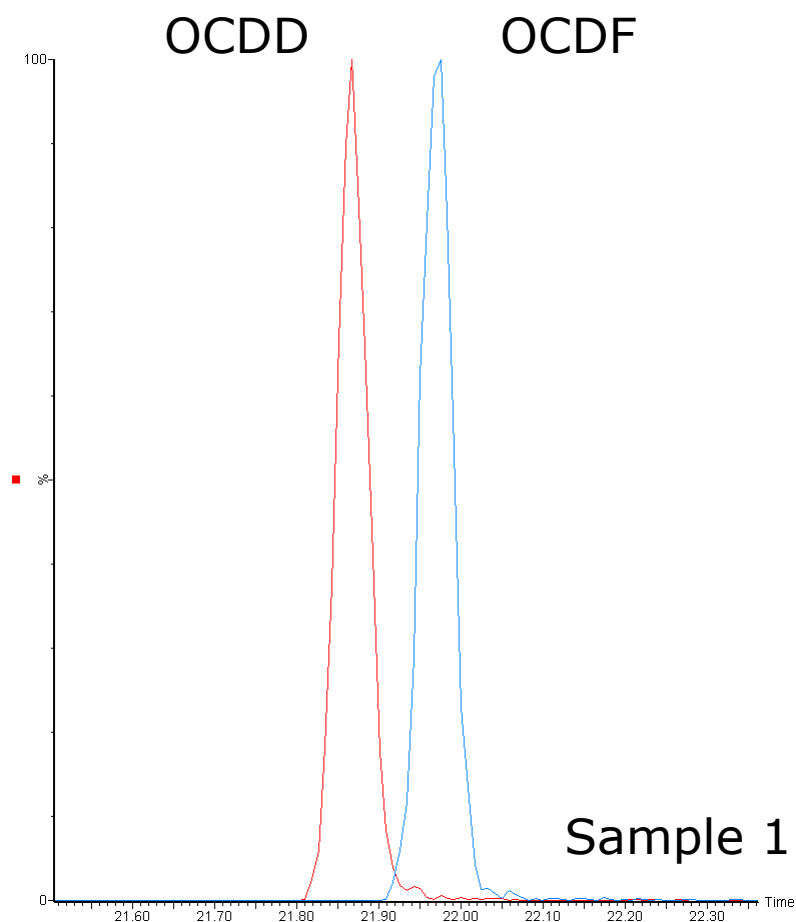
v2.0 GC-APCI Interface Performance

■ Comparison of Deca-BDE (209)



v2.0 GC-APCI Interface Performance

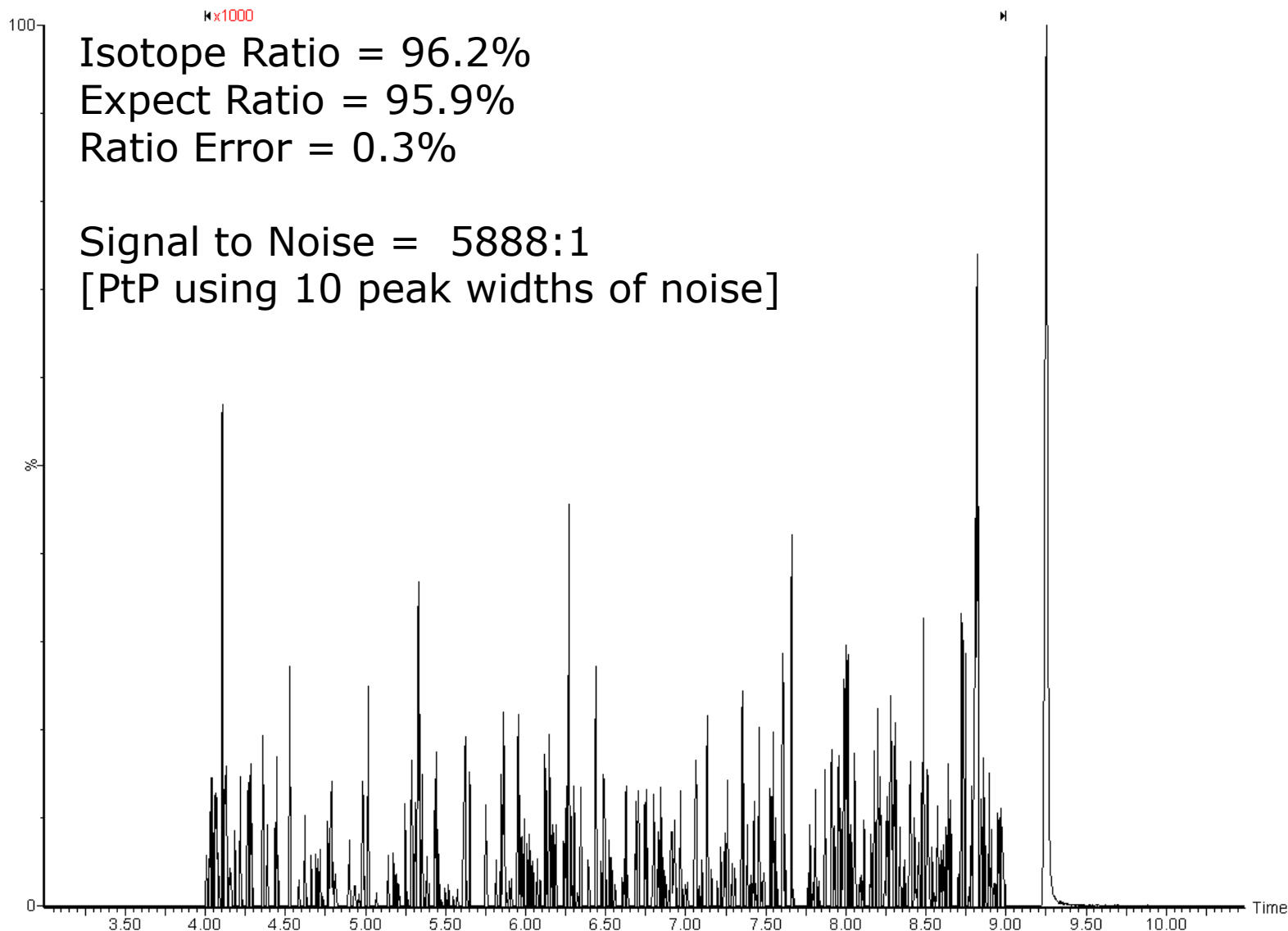
- Evaluated dioxins and furans (EPA1613 CS3 standard) with a 107 repeat acquisition (62 hour long) experiment



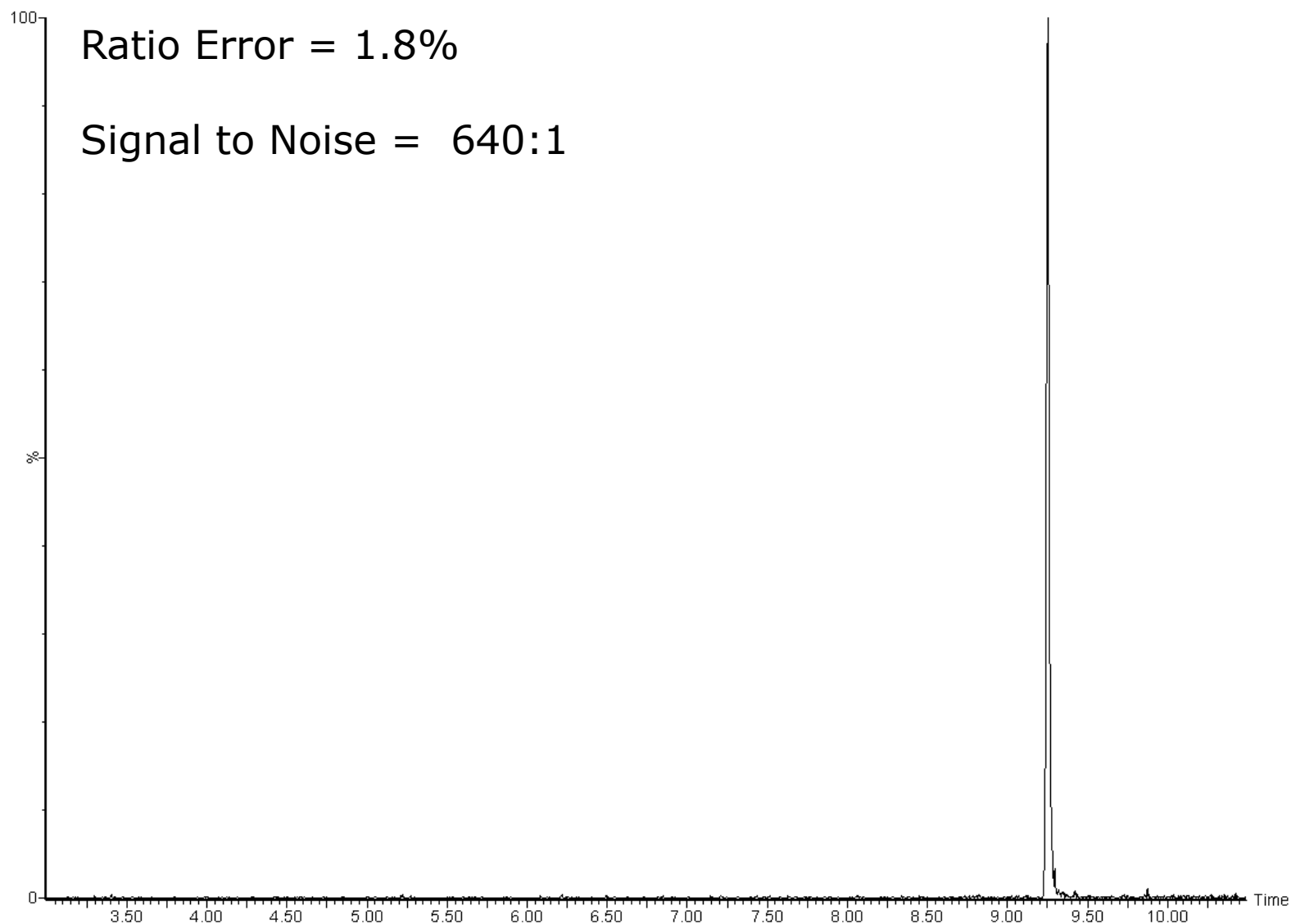
Performance Evaluation

- Started evaluation using a single component 2,3,7,8 TCDD sample (Supelco) diluted to various concentrations
- Used to evaluate linearity of response and establish limit of detection and point of saturation
- 1.0 μ L injections on an 7890A GC, split/splitless injector operating in pulsed splitless mode
- GC column was an DB-5MS 30m x 0.25mm x 0.25 μ m
- Monitored the two primary isotope MRM transitions
 - 319.9 -> 256.9
 - 321.9 -> 258.9

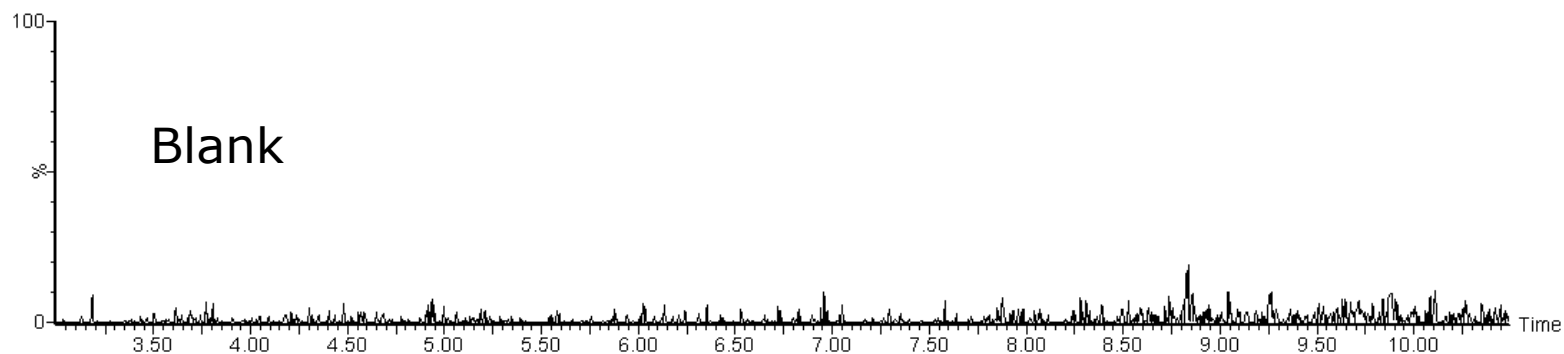
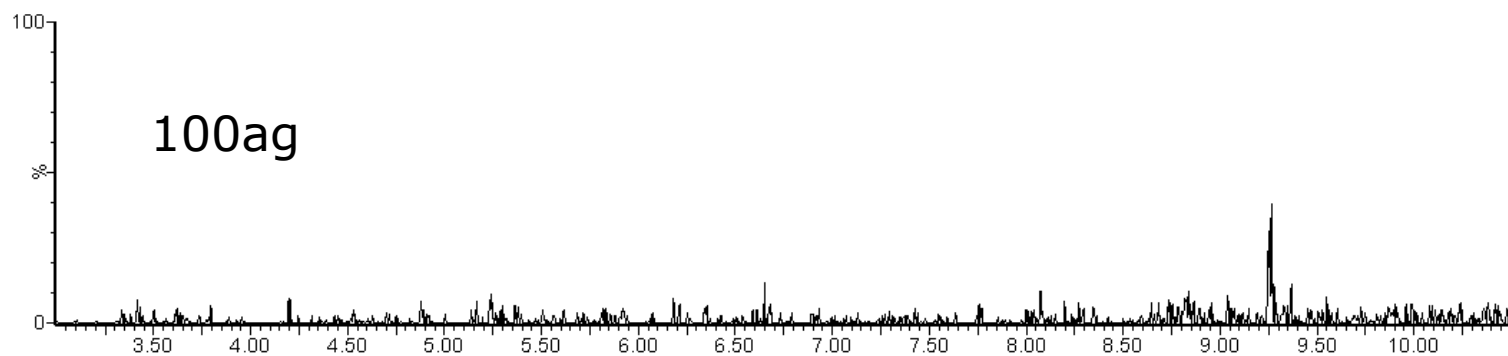
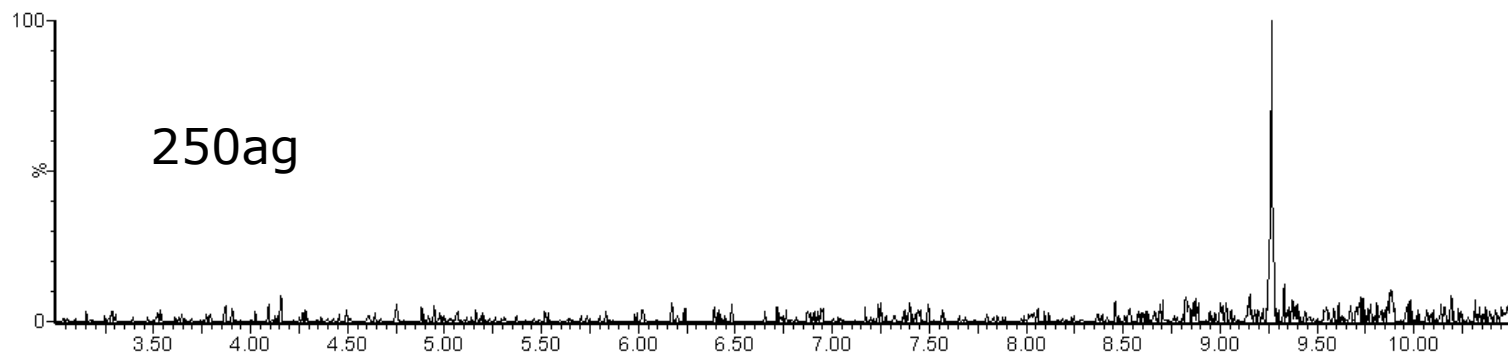
2,3,7,8 TCDD – 100fg injection



2,3,7,8 TCDD – 10fg injection



2,3,7,8 TCDD

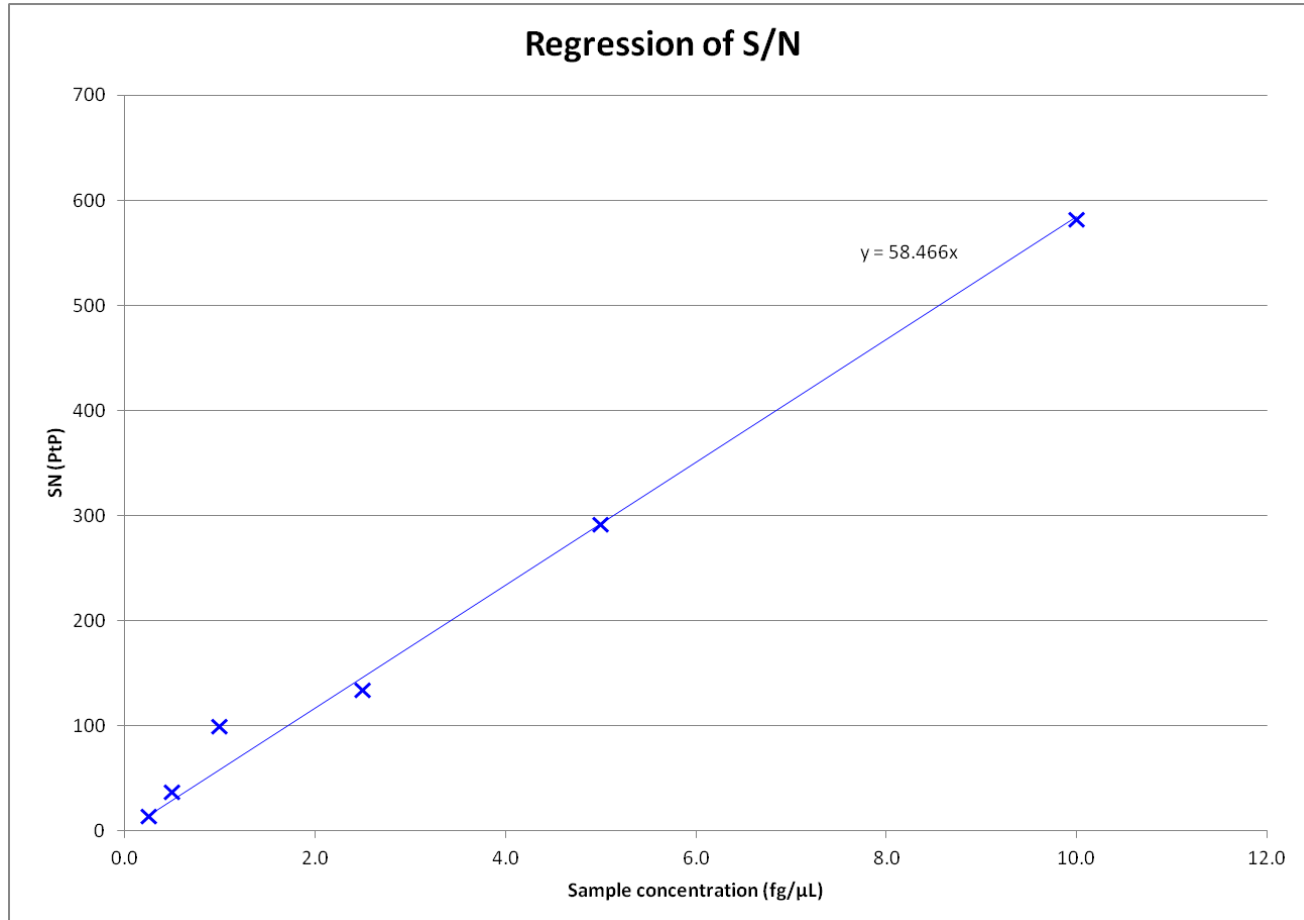


Limit of Detection

- First method for evaluating LoD is by regression of the relationship between signal to noise and sample amount
- Define the LoD as a signal to noise ratio of 3:1
 - Peak to peak noise
 - Over 10 peak widths
 - As defined in European dioxin and furan legislation*
- Using n between 3 and 12 for injection amounts of 250ag, 500ag, 1fg, 2.5fg, 5fg and 10fg

*Commission Regulation (EU) 589/2014, laying down methods of sampling and analysis for the control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs.

Limit of Detection

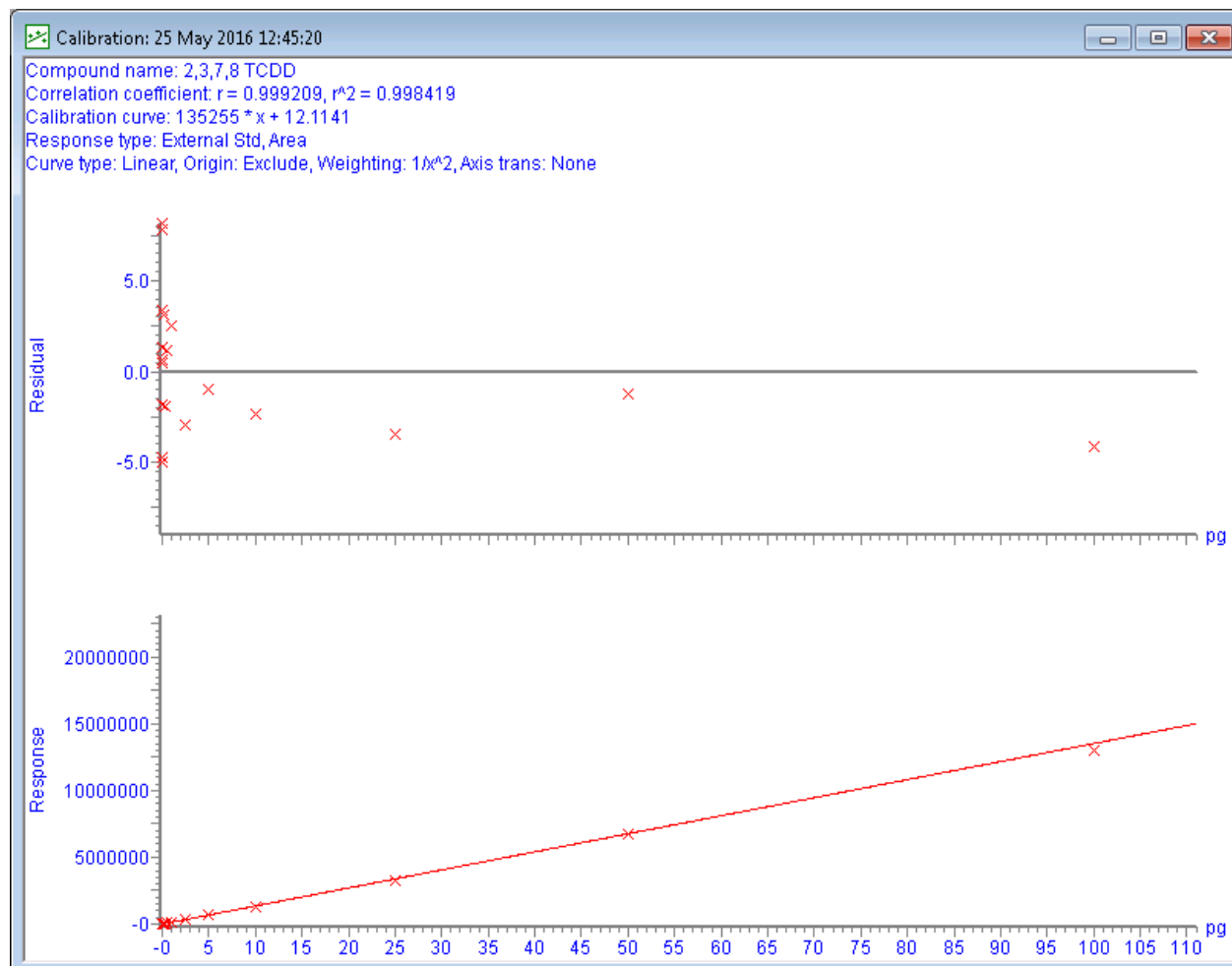


LoD = 51 attograms

2,3,7,8 TCDD – 500ag Reproducibility

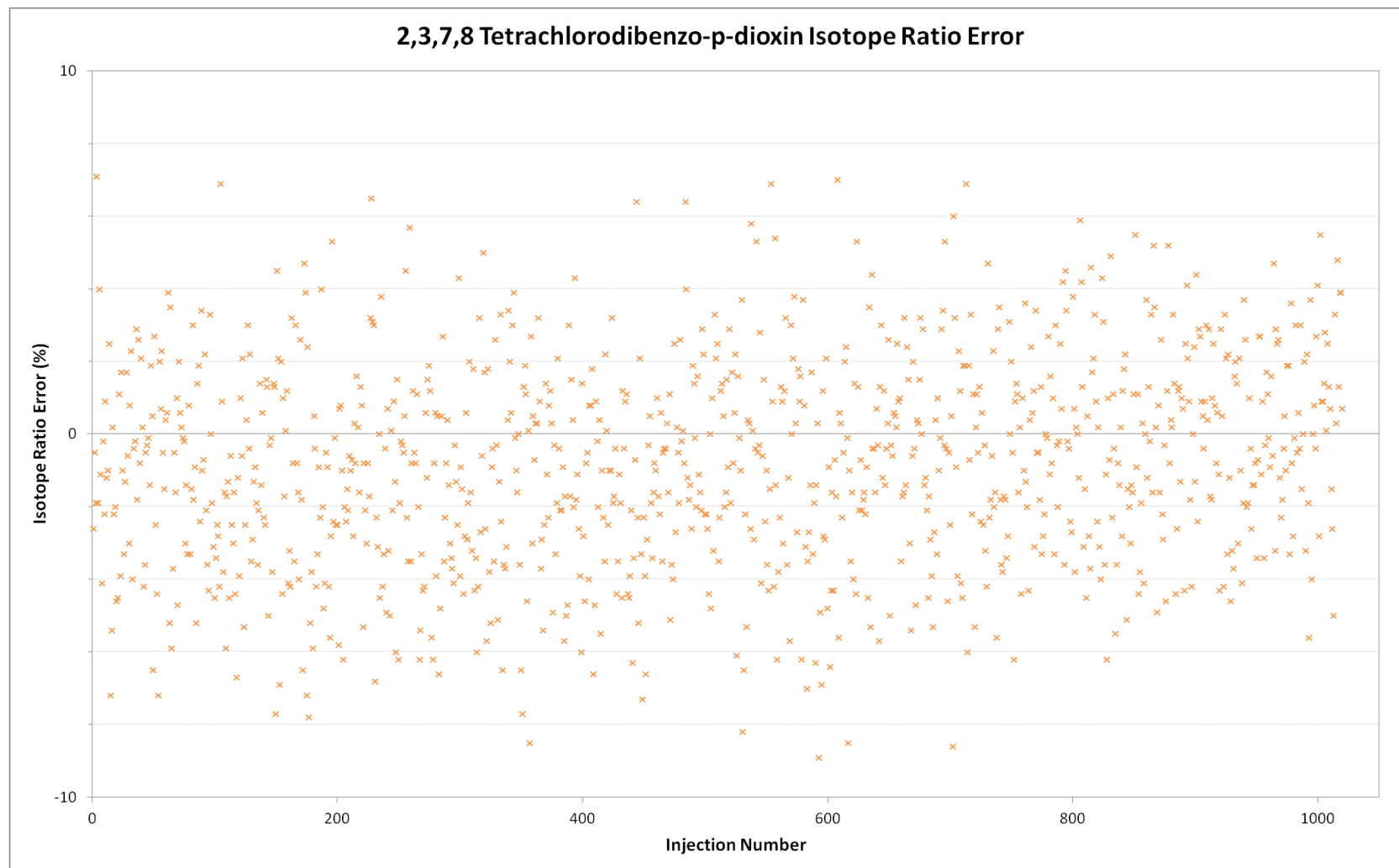
Injection number	Peak Area	Ion Ratio Error (%)	Signal to Noise
1	73	-6.2	13
2	85	-2.1	41
3	84	-3.2	56
4	82	-4.3	43
5	79	2.3	27
6	83	-0.7	43
7	74	2.9	27
8	81	-2.2	53
9	74	2.7	35
10	75	6.3	32
11	71	-7.2	44
12	82	-4.7	37
Mean	78.5		
%RSD	6.2		

Linearity and dynamic range



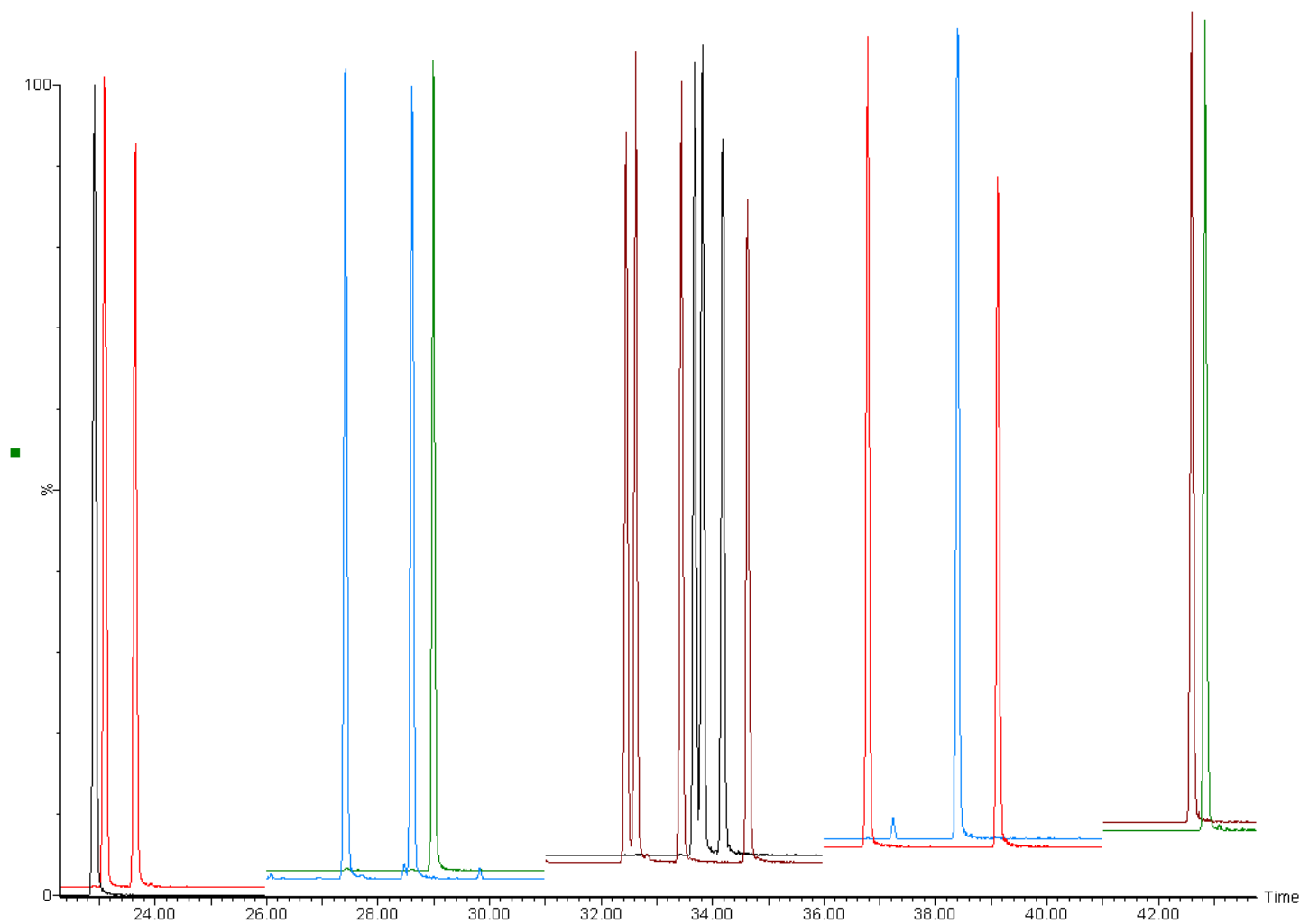
linearity within $\pm 8\%$ over the range of 100ag to 100pg

Isotope Ratio Accuracy



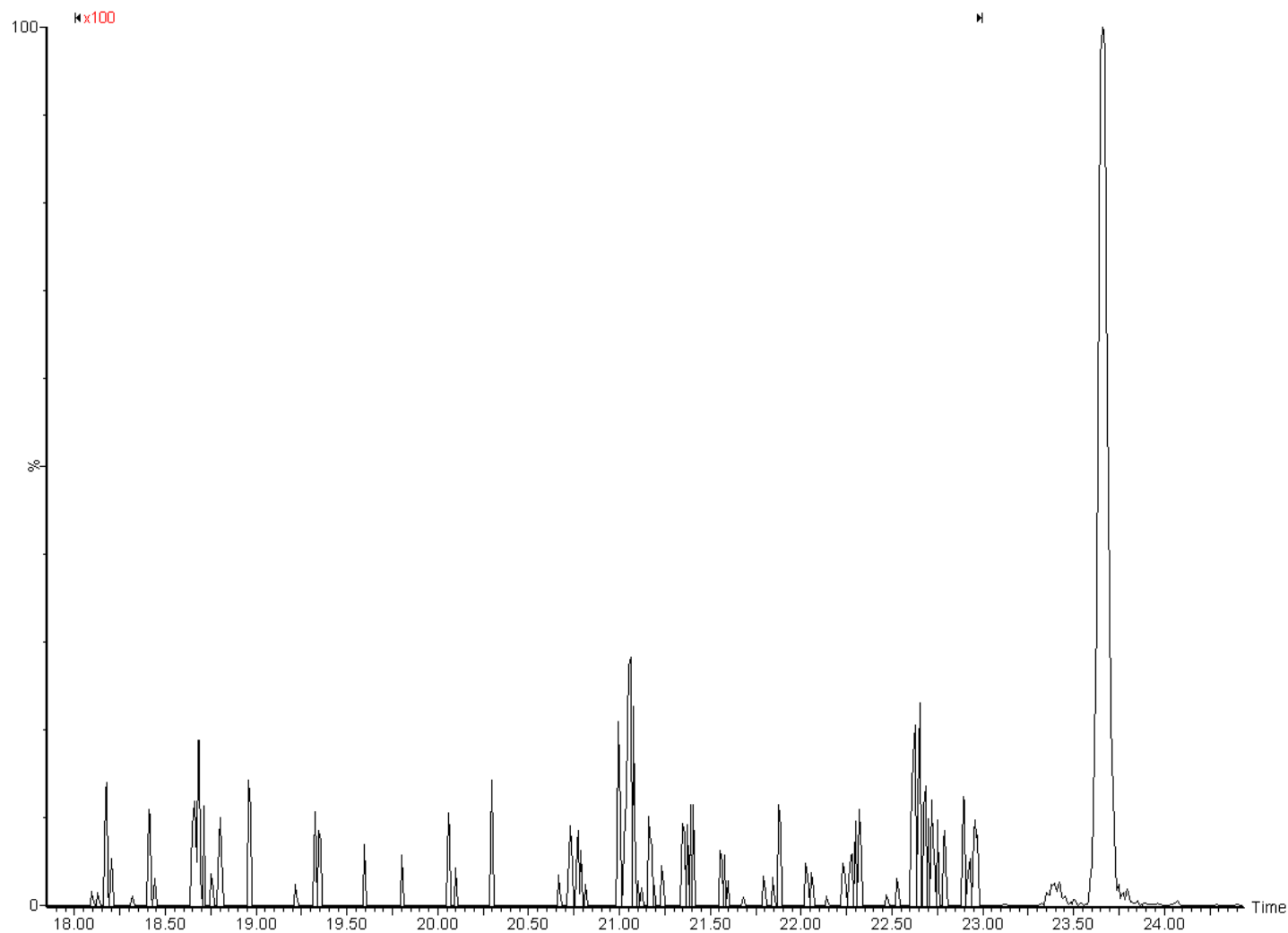
100fg TCDD, 1030 injections over 21 days

Performance with calibration standard

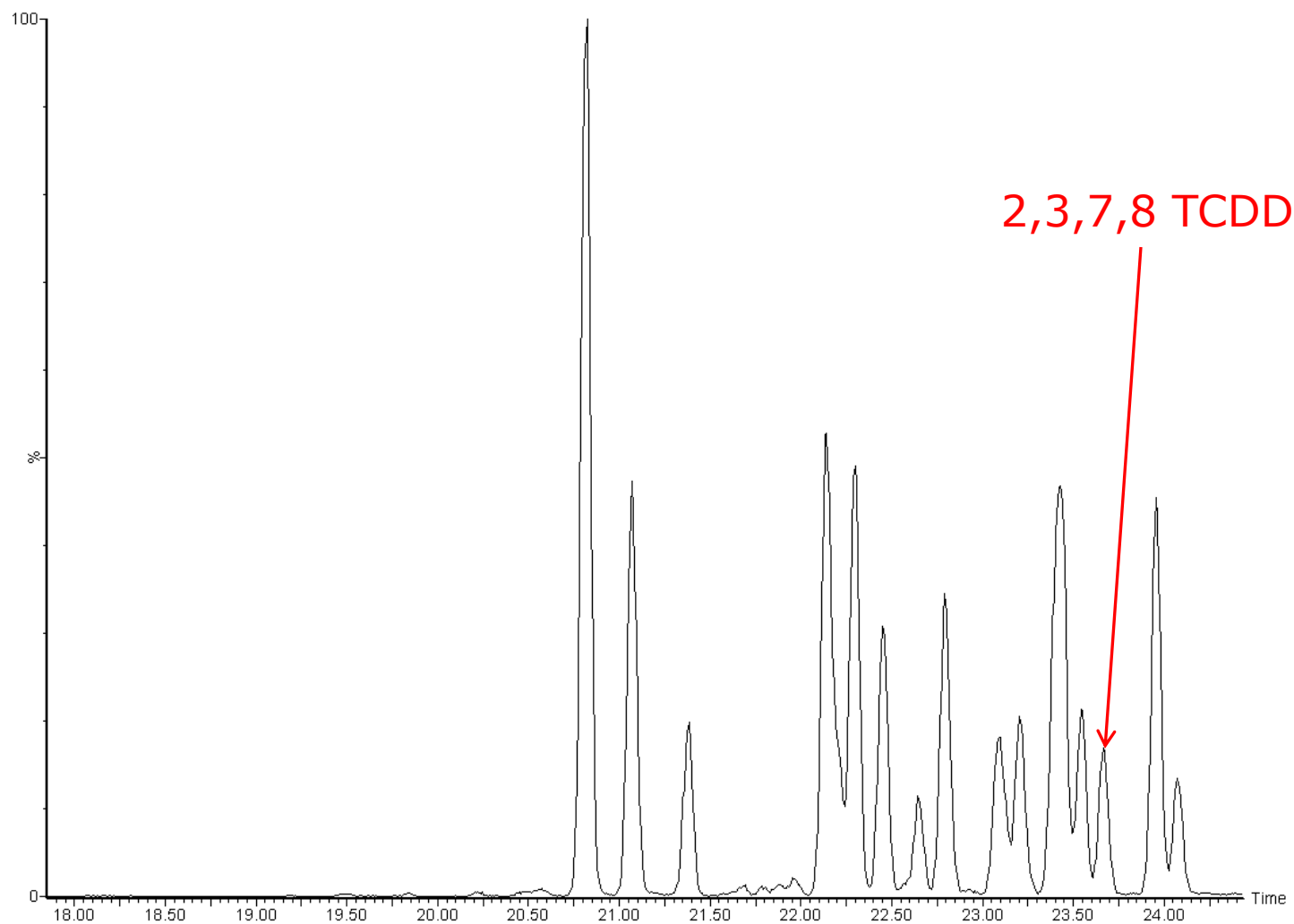


EPA1613 CS3 diluted 100:1 on 60m x 0.25mm x 0.25 μ m Zebron ZB-5MS

10fg 2,3,7,8 TCDD on 60m column

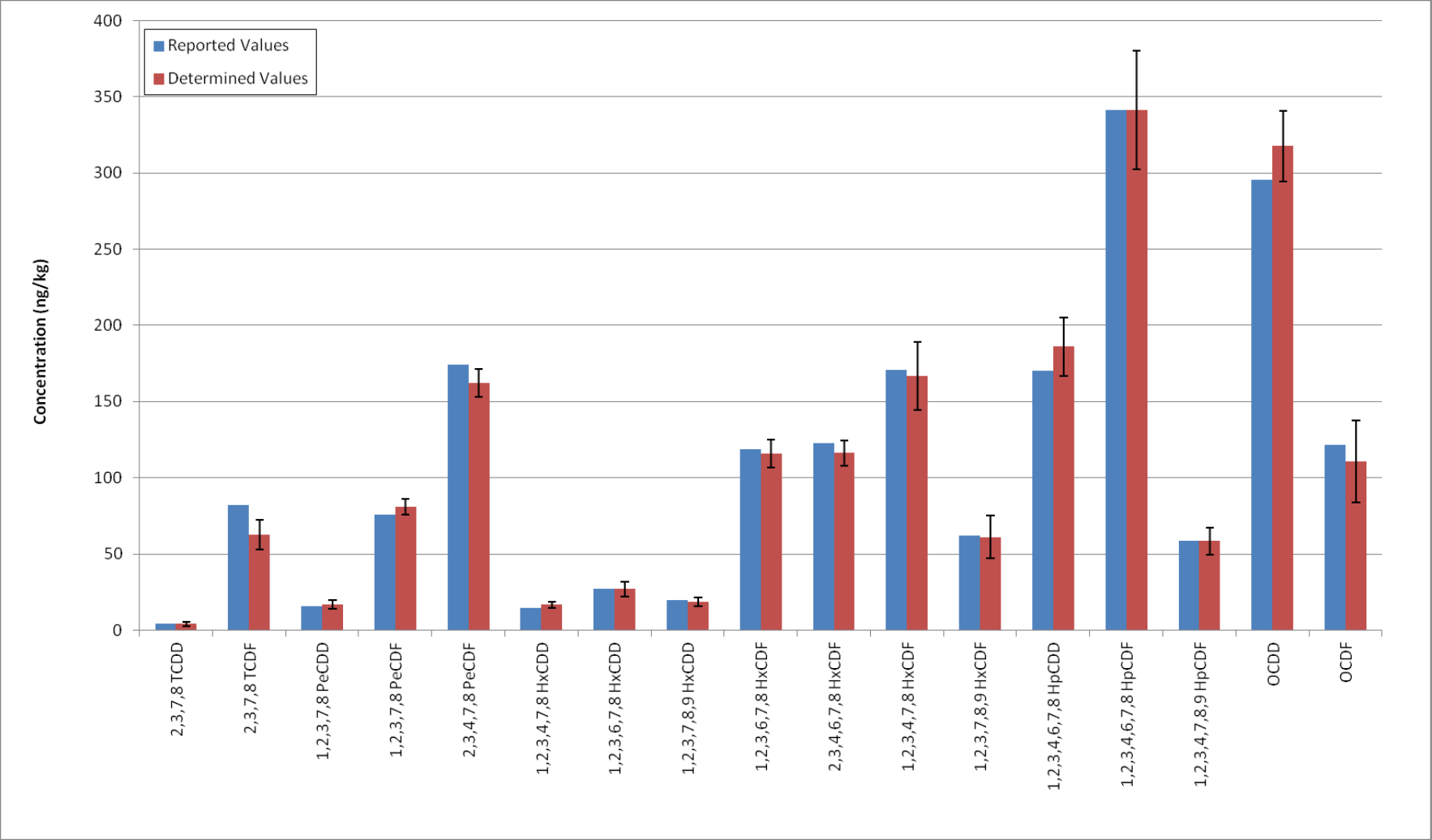


QA/QC ash extract - TCDD



Sample from Hall Analytical, Manchester, UK

QA/QC ash extract



Comparison of HRMS (Sector) with APGC Xevo TQ-S

Atmospheric pressure chemical ionization tandem mass spectrometry (APGC/MS/MS) an alternative to high resolution mass spectrometry (HRGC/HRMS) for the determination of dioxins.



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^d EU Reference Laboratory(EU-RL) for Dioxins and PCBs in Feed and Food, State Institute for Chemical and Veterinary Analysis of Food, Freiburg, Germany.

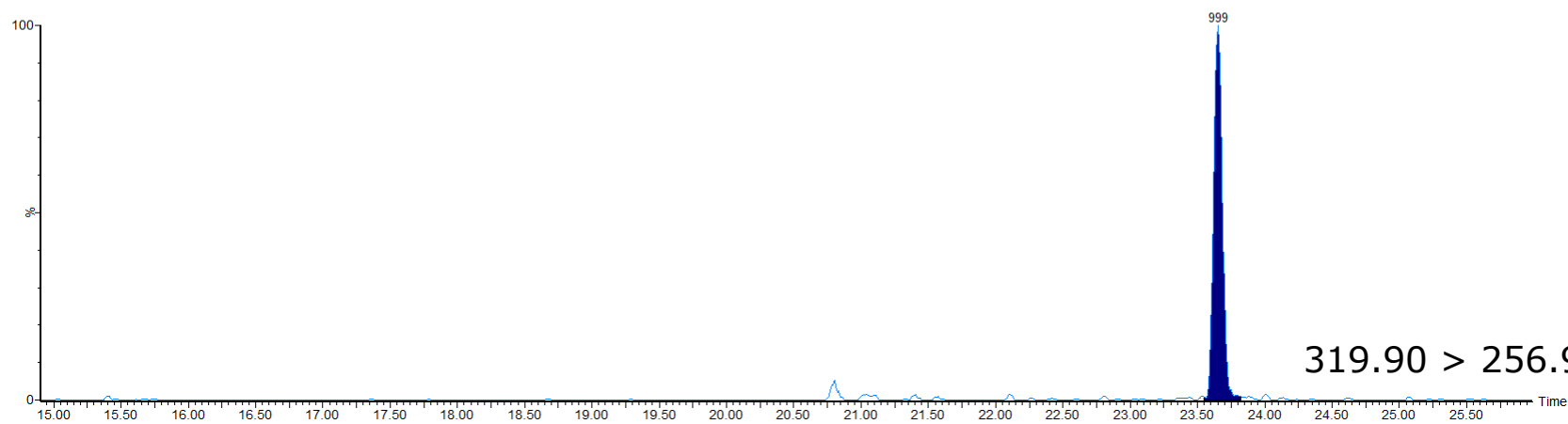
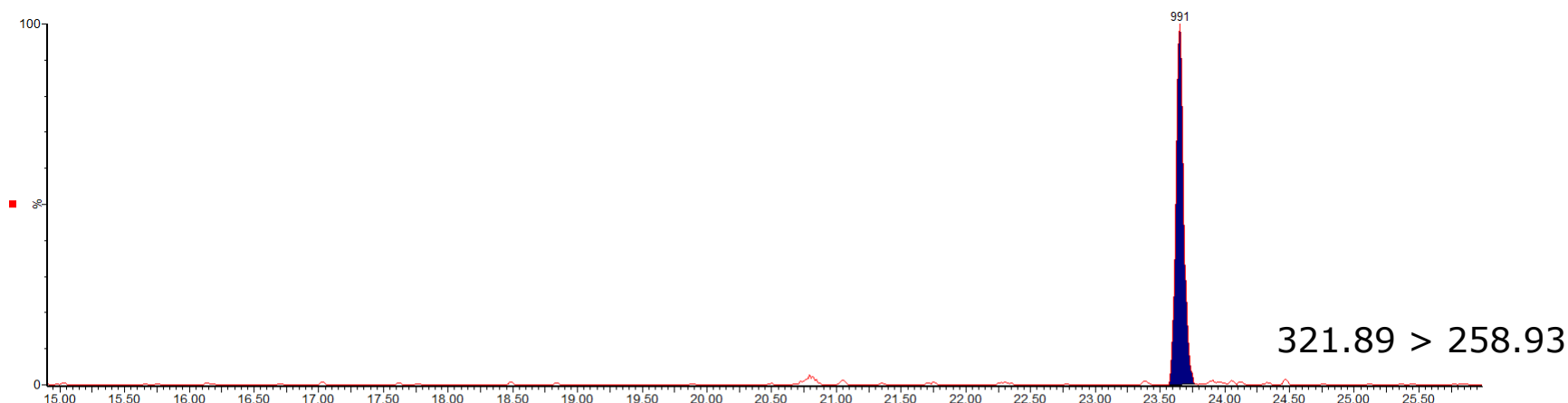
^e Waters Corporation, Manchester, UK.

^f RIKILT, Institute of Food Safety, PO Box 230, NL-6700 AE Wageningen, The Netherlands.



Soil Extracts

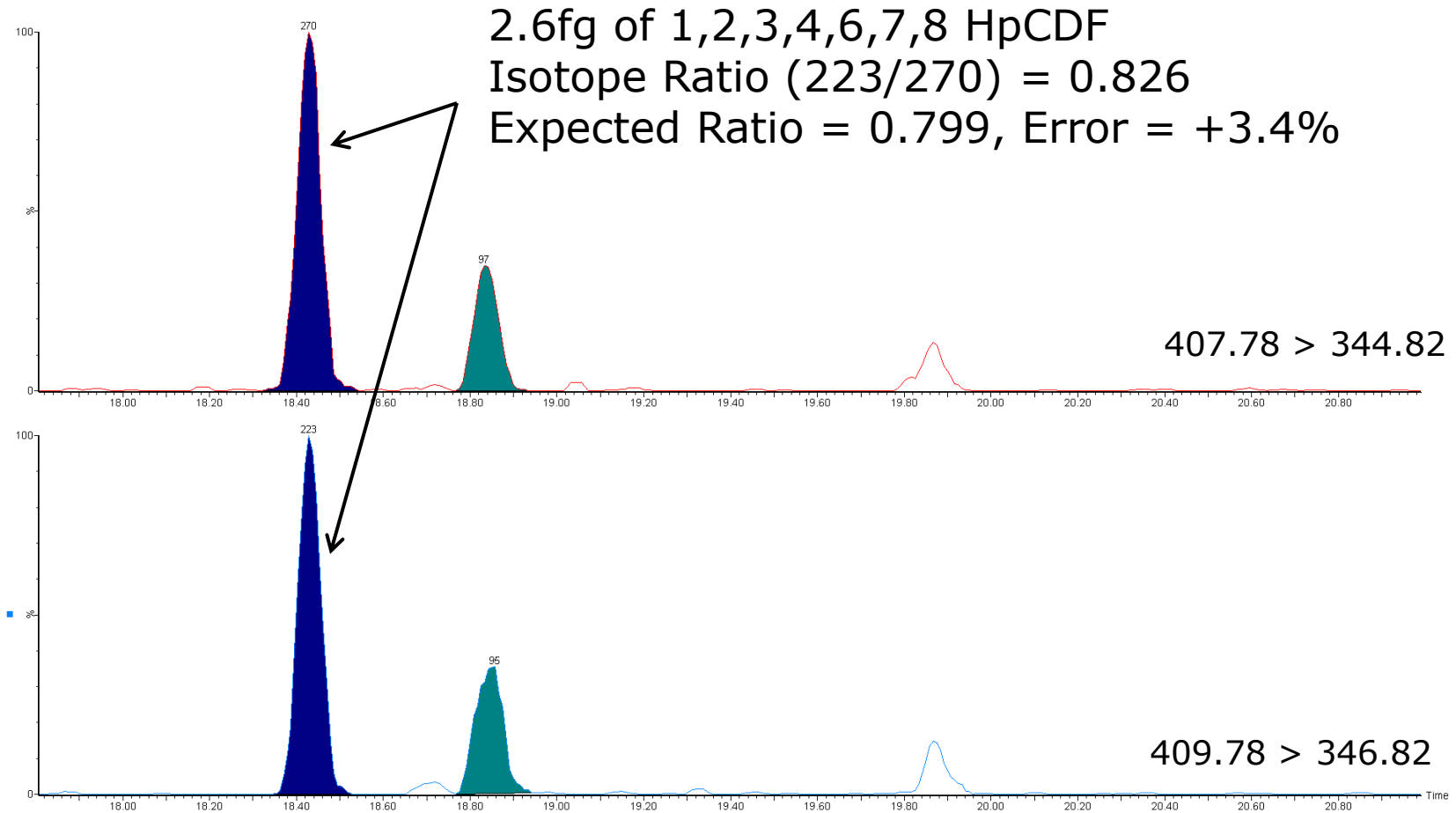
- 9.2fg 2,3,7,8 TCDD, isotope error +3.5%



Sample from Penn State University, USA

Pork Fat Extract

■ HpCDF trace of pork fat extract

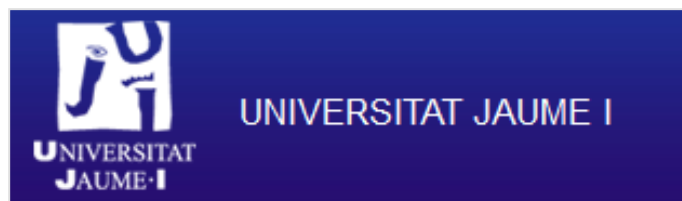


Sample from LABERCA, France

Conclusions

- Xevo TQ-XS (tandem quadrupole) with APGC (GC-APCI) meets or exceeds performance requirements for analysis of dioxins in environmental matrices
- Single instrument can be used for high sensitivity GC and LC MS/MS for coverage of a broader range of environmental matrices and analytes – dioxins/BFRs to PFAS's/microcystins

Acknowledgements



Acknowledgements

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- Keith Hall, Hall Analytical, UK

Thank you for your time

■ **Questions?**

