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S C I E N T I F I C

# Overcoming Analytical Challenges in PBDEs Quantification in Environmental Samples using GC-Orbitrap MS

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# Synopsis

## Introduction

- Background
- Current analytical methods
- Challenges of PBDE analysis

## Objectives

## Technology and Configurations

## Experimental

## Software

## Standards

## Samples

- Sample preparation

## Results

- Chromatography
- Sensitivity, selectivity, and linearity
- Instrument Detection Limit (IDL)
- Mass Accuracy / repeatability
- Samples analysis

## Conclusions / Acknowledgments

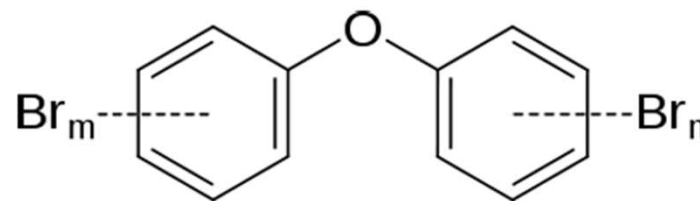
## Introduction

### Polybrominated diphenyl ethers (PBDEs):

- A group of organobromine chemicals



- Many PBDEs are toxic:
  - with links to cancer and endocrine disruption
- Certain PBDEs (including penta, tetra and deca BDE) have been prohibited in many countries
  - listed in the Stockholm Convention inventory of persistent organic pollutants

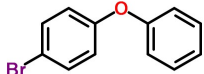


where  $m + n = 1$  to  $10$



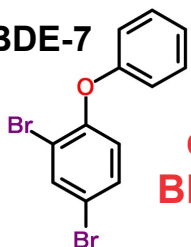
# Polybrominated diphenyl ethers (PBDEs)

mono-BDE

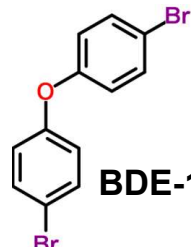


BDE-3

BDE-7

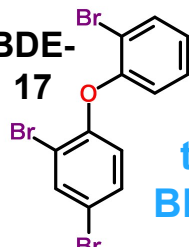


di-BDEs

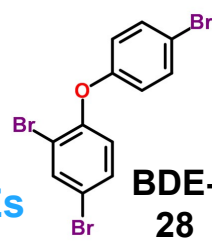


BDE-15

BDE-17

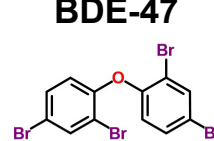


tri-BDEs

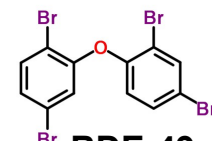


BDE-28

BDE-47

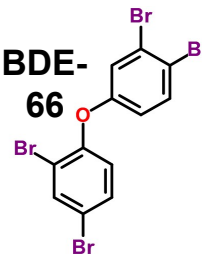


tetra-BDEs

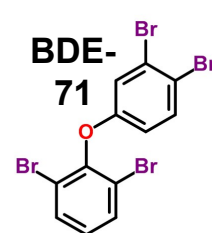


BDE-49

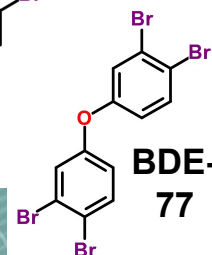
BDE-66



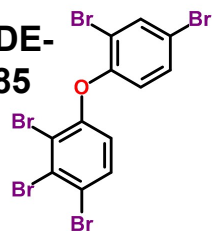
BDE-71



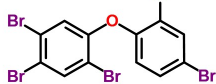
BDE-77



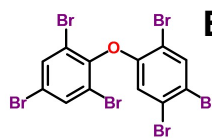
BDE-85



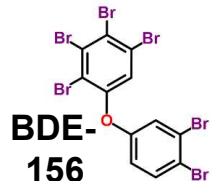
BDE-99



BDE-154

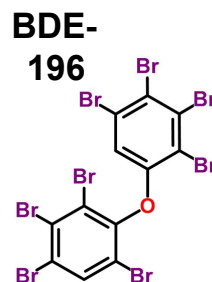


hexa-BDEs

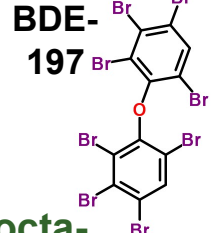


BDE-156

BDE-196

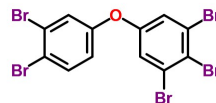


BDE-197



octa-BDEs

penta-BDEs



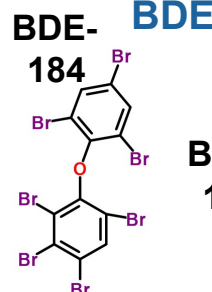
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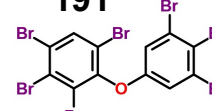
BDE-138

hepta-BDEs

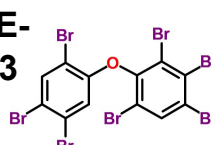
BDE-184



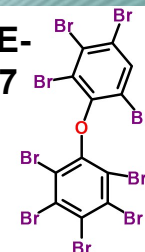
BDE-191



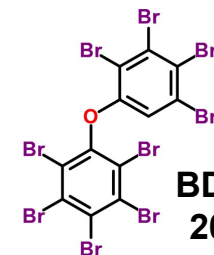
BDE-183



BDE-207

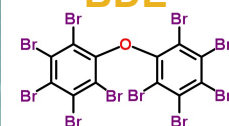


nona-BDEs



BDE-206

deca-BDE



BDE-209

## Polybrominated diphenyl ethers (PBDEs)

- Inhibit or suppress combustion in organic material
- Used as flame retardants in a wide range of commercial and household products:
  - textiles, building materials, electronics, furnishings, motor vehicles, and plastics



## Polybrominated diphenyl ethers (PBDEs)

- Persistent Organic Pollutants (POPs)
- Resist degradation, persist and bioaccumulate in both the environment and food chains
- Can be transported through air and water over long distances
- They have been identified, in some cases far from their place of use, in a wide range of samples including air, water, sediment, fish, birds, marine mammals, and humans

## Polybrominated diphenyl ethers (PBDEs)

- Current Routine Analytical Methods:

- Gas Chromatography (GC)

- electron capture detector (ECD)

- mass spectrometer (MS) - EI/CI

- Challenges:

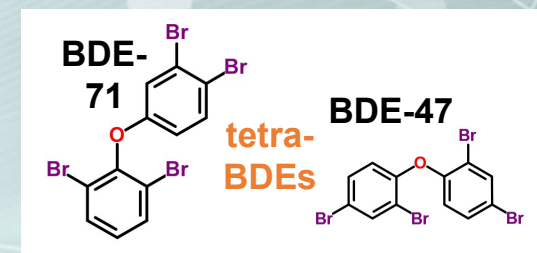
- Compound degradation

- BDE-209

- Matrix interferences

- chromatographic separation of BDE-49 and BDE-71

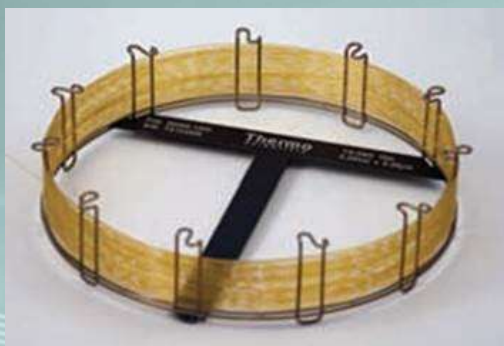
- Long run times



## Aims of the study



- To evaluate quantitative performance of the Thermo Scientific™ Exactive™ GC Orbitrap™ GC-MS mass spectrometer for the routine analysis of PBDEs in environmental samples



- To assess the performance of Thermo Scientific™ TG-PBDE™ 15 m capillary column (15 m x 0.25 mm I.D. x 0.10  $\mu$ m film) for this application





## Aims of the study

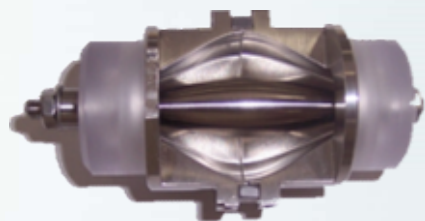
Answer the following questions:

- Can compound degradation be minimized?
  - BDE-209
- Do matrix interferences effect chromatographic separation?
  - BDE-49 and BDE-71
- What sensitivity / selectivity and linearity can be achieved?
- What is the Instrument Detection Limit (IDL)?
- What is the repeatability/mass accuracy?
- Are the demands of routine sample analysis achieved?

# *Technology and Configurations*



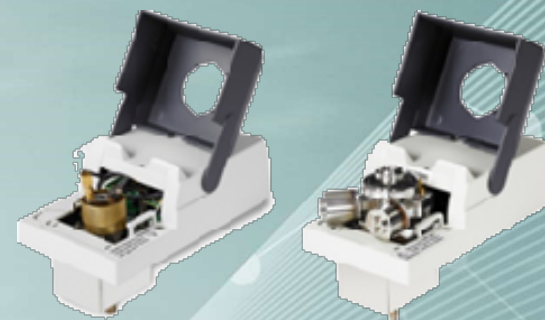
# Exactive GC Orbitrap GC-MS system



**Orbitrap mass analyzer**

**Incredible HRAM performance**

**Highly regarded Q Exactive GC system platform**



**Thermo Scientific™ TRACE™ 1310 GC System**

**Unique modular injector and detector design**

**Rapid heat cycling**

## Thermo Scientific™ Exactive™ GC Orbitrap™ GC-MS system

**Thermo Scientific™ ExtractaBrite™ Ion Source technology**

**Routine grade robustness**

**Patented RF lens**

**Removable without breaking vacuum**



# Exactive GC Orbitrap GC-MS system



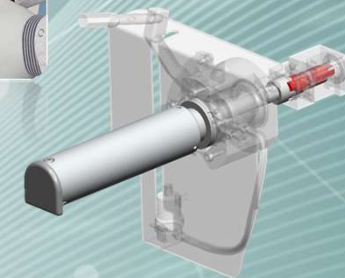
## V-Lock Source Plug

- Allows vent free GC column exchange
- No complicated fluidics / extra connections

## NeverVent™ Technology



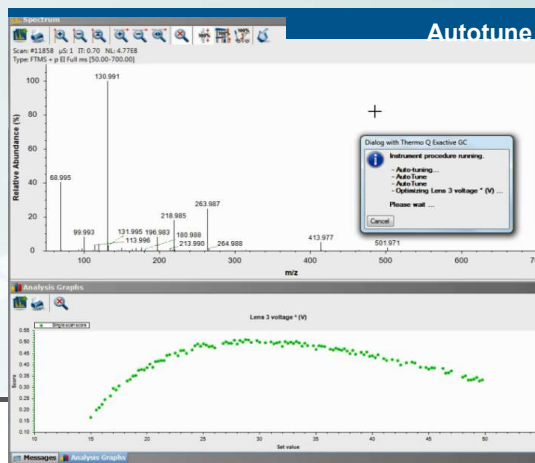
## Vacuum Probe Interlock (VPI)



## Thermo Scientific™ Exactive™ GC Orbitrap™ GC-MS system

## Tuning and Calibration

- Simple status
- Automated leak checking
- Automated tuning & calibration
- Source and lens tuning ~25 s
- Mass calibration ~30 s
- Ready to go < 1 min



## ExtractaBrite

- Vent free ion source exchange
- Operate with spare source and clean offline
- Switch from EI to CI and back without venting



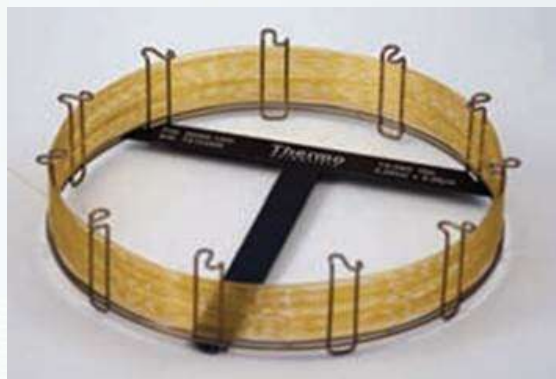
# *Experimental*



# GC and injector conditions

## TRACE 1310 GC Parameters

Injection Volume ( $\mu\text{L}$ ):	1.0
Liner	PTV baffled liner (Siltek) (P/N: 453T2120)
Inlet ( $^{\circ}\text{C}$ ):	40
Carrier Gas, (mL/min):	He, 1.5
Inlet Module and Mode:	PTV, Large Volume mode
Column:	Thermo Scientific™ TG-PBDE™ 15 m x 0.25 mm I.D. x 0.10 $\mu\text{m}$ film capillary column (P/N 26061-0350)
Transfer delay (min):	0.2
Injection time (min):	0.1



## GC and injector conditions

<b>PTV Parameters:</b>	Rate (°C/sec)	Temperature (°C)	Time (min)	Flow(mL/min)
Injection	-	40	0.10	-
Transfer	2.5	330	5.00	-
Cleaning	14.5	330	5.00	50

<b>Oven Temperature Program:</b>	RT(min)	Rate (°C/min )	Target Temperature (°C)	Hold Time (min)
Initial	0	-	100	2.00
Final	2.00	30	340	3.00
Run Time	13	-	-	-



## MS conditions



### Exactive GC Mass Spectrometer Parameters

Transfer line (°C):	300
Ionization type:	EI
Ion source(°C):	250
Electron energy (eV):	35
Acquisition Modes:	Targeted SIM / full scan
Mass range (Da):	68 - 1000
Mass resolution(FWHM):	60,000 (FWHM at $m/z$ 200)



# MS conditions



targeted-SIM inclusion list

Mass ( <i>m/z</i> )	Start time (min)	End time (min)	BDE number
260.02339	4.00	4.50	3L, 3
327.89164	4.50	5.60	7, 15
339.93186	4.50	5.60	15L
405.80214	5.60	6.60	17, 28
417.84237	5.60	6.60	28L
485.71063	6.60	7.30	47, 49, 66, 71, 77
497.75084	6.60	7.30	47L, 79L
563.62113	7.30	8.00	85, 99, 100, 119, 126
575.66135	7.30	8.00	99L, 100L, 126L
483.69498	7.80	8.62	138, 153, 154, 156
495.73518	7.80	8.62	153L, 154L, 138L
561.60525	8.58	9.20	183, 184, 191
573.64569	8.58	9.20	183L
641.51390	9.20	9.70	196, 197
653.55416	9.20	9.70	197L
719.42446	9.70	10.40	206, 207
731.46467	9.70	10.40	207L, 206L
799.30000	10.40	12.50	209
811.30000	10.40	12.50	209L

Isolation window = 25.0 *m/z*

# Software

Thermo Scientific™ Chromeleon™ 7.2 Chromatography Data System (CDS) software was used for instrument control, data acquisition, processing and reporting



**CHROMELEON 7.2**  
Simply Intelligent

# Standards



# Standards

BDE number	Native BDEs	Chemical formula	CAS number	Calibration range ng/mL
3	4-Bromodiphenyl ether	C <sub>12</sub> H <sub>9</sub> BrO	101-55-3	1.0 to 400
7	2,4-Dibromodiphenyl ether	C <sub>12</sub> H <sub>8</sub> Br <sub>2</sub> O	171977-44-9	1.0 to 400
15	4,4'-Dibromodiphenyl ether	C <sub>12</sub> H <sub>8</sub> Br <sub>2</sub> O	2050-47-7	1.0 to 400
17	2,2',4-Tribromodiphenyl ether	C <sub>12</sub> H <sub>7</sub> Br <sub>3</sub> O	147217-75-2	0.96 to 384
28	2,4,4'-Tribromodiphenyl ether	C <sub>12</sub> H <sub>7</sub> Br <sub>3</sub> O	41318-75-6	1.0 to 400
47	2,2',4,4'-Tetrabromodiphenyl ether	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	5436-43-1	1.0 to 400
49	2,2',4,5'-Tetrabromodiphenyl ether	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	243982-82-3	1.0 to 400
66	2,3',4,4'-Tetrabromodiphenyl ether	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	189084-61-5	1.0 to 400
71	2,3',4',6-Tetrabromodiphenyl ether	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	189084-62-6	1.0 to 400
77	3,3',4,4'-Tetrabromodiphenyl ether	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	93703-48-1	1.0 to 400
85	2,2',3,4,4'-Pentabromodiphenyl ether	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	182346-21-0	1.0 to 400
99	2,2',4,4',5-Pentabromodiphenyl ether	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	32534-81-9	1.0 to 400
100	2,2',4,4',6-Pentabromodiphenyl ether	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	189084-64-8	1.0 to 400
119	2,3',4,4',6-Pentabromodiphenyl ether	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	189084-66-0	1.0 to 400
126	3,3',4,4',5-Pentabromodiphenyl ether	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	366791-32-4	1.0 to 400
138	2,2',3,4,4',5-Hexabromodiphenyl ether	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	446254-95-1	2.0 to 800
153	2,2',4,4',5,5'-Hexabromodiphenyl ether	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	68631-49-2	2.0 to 800
154	2,2',4,4',5,6'-Hexabromodiphenyl ether	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	207122-15-4	2.0 to 800
156	2,3,3',4,4',5-Hexabromodiphenyl ether	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	405237-85-6	2.0 to 800
183	2,2',3,4,4',5',6-Heptabromodiphenyl ether	C <sub>12</sub> H <sub>3</sub> Br <sub>7</sub> O	207122-16-5	2.0 to 800
184	2,2',3,4,4',6,6'-Heptabromodiphenyl ether	C <sub>12</sub> H <sub>3</sub> Br <sub>7</sub> O	117948-63-7	2.0 to 800
191	2,3,3',4,4',5',6-Heptabromodiphenyl ether	C <sub>12</sub> H <sub>3</sub> Br <sub>7</sub> O	446255-30-7	2.0 to 800
196	2,2',3,3',4,4',5,6'-Octabromodiphenyl ether	C <sub>12</sub> H <sub>2</sub> Br <sub>8</sub> O	446255-39-6	2.0 to 800
197	2,2',3,3',4,4',6,6'-Octabromodiphenyl ether	C <sub>12</sub> H <sub>2</sub> Br <sub>8</sub> O	117964-21-3	2.0 to 800
206	2,2',3,3',4,4',5,5',6-Nonabromodiphenyl ether	C <sub>12</sub> HBr <sub>9</sub> O	63936-56-1	5.0 to 2000
207	2,2',3,3',4,4',5,6',6-Nonabromodiphenyl ether	C <sub>12</sub> HBr <sub>9</sub> O	437701-79-6	5.0 to 2000
209	Decabromodiphenyl ether	C <sub>12</sub> Br <sub>10</sub> O	1163-19-5	5.0 to 2000

Calibration standards containing 27 native PBDE congeners at five concentration levels



# Standards

BDE isomer number	<sup>13</sup> C labelled PBDEs	Chemical formula	Concentration (ng/mL)
3L	4-Bromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>9</sub> BrO	100
15L	4,4'-Dibromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>8</sub> Br <sub>2</sub> O	100
28L	2,4,4'-Tribromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>7</sub> Br <sub>3</sub> O	100
47L	2,2',4,4'-Tetrabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	100
79L	3,3',4,5'-Tetrabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	100
99L	2,2',4,4',5-Pentabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	100
100L	2,2',4,4',6-Pentabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	100
126L	3,3',4,4',5-Pentabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	100
138L	2,2',3,4,4',5-Hexabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	200
153L	2,2',4,4',5,5'-Hexabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	200
154L	2,2',4,4',5,6'-Hexabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	200
183L	2,2',3,4,4',5,6-Heptabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>3</sub> Br <sub>7</sub> O	200
197L	2,2',3,3',4,4',6,6'-Octabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> Br <sub>8</sub> O	200
206L	2,2',3,3',4,4',5,5',6-Nonabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> HBr <sub>9</sub> O	500
207L	2,2',3,3',4,4',5,6,6'-Nonabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> HBr <sub>9</sub> O	500
209L	Decabromo[ <sup>13</sup> C <sub>12</sub> ]diphenyl ether	<sup>13</sup> C <sub>12</sub> Br <sub>10</sub> O	500

16 (<sup>13</sup>C labelled) PBDE internal standards

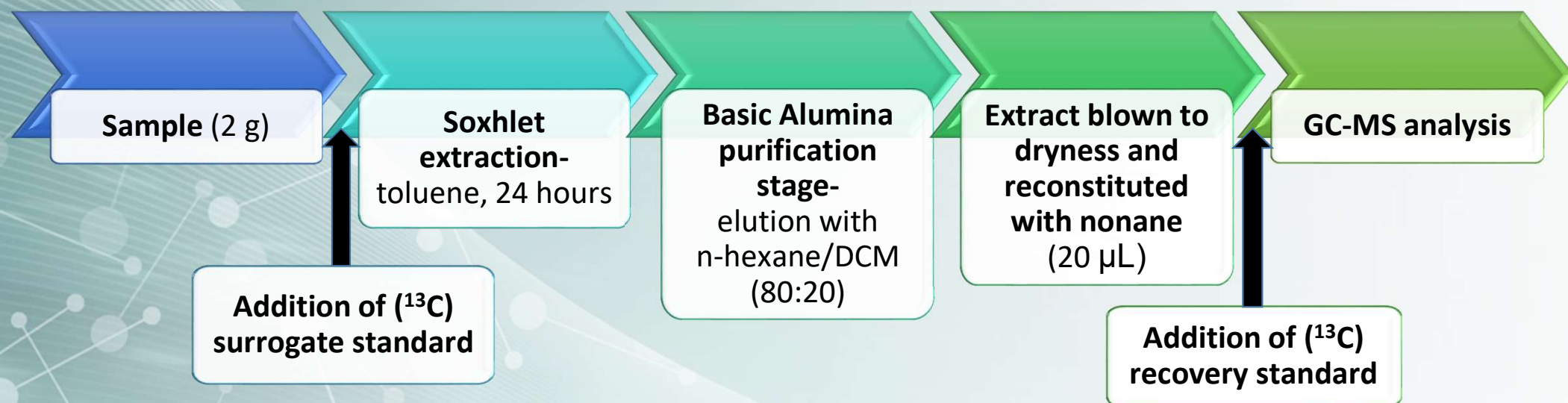
- suffix "L" indicates mass-labelled



# *Sample Preparation*



## Sample preparation

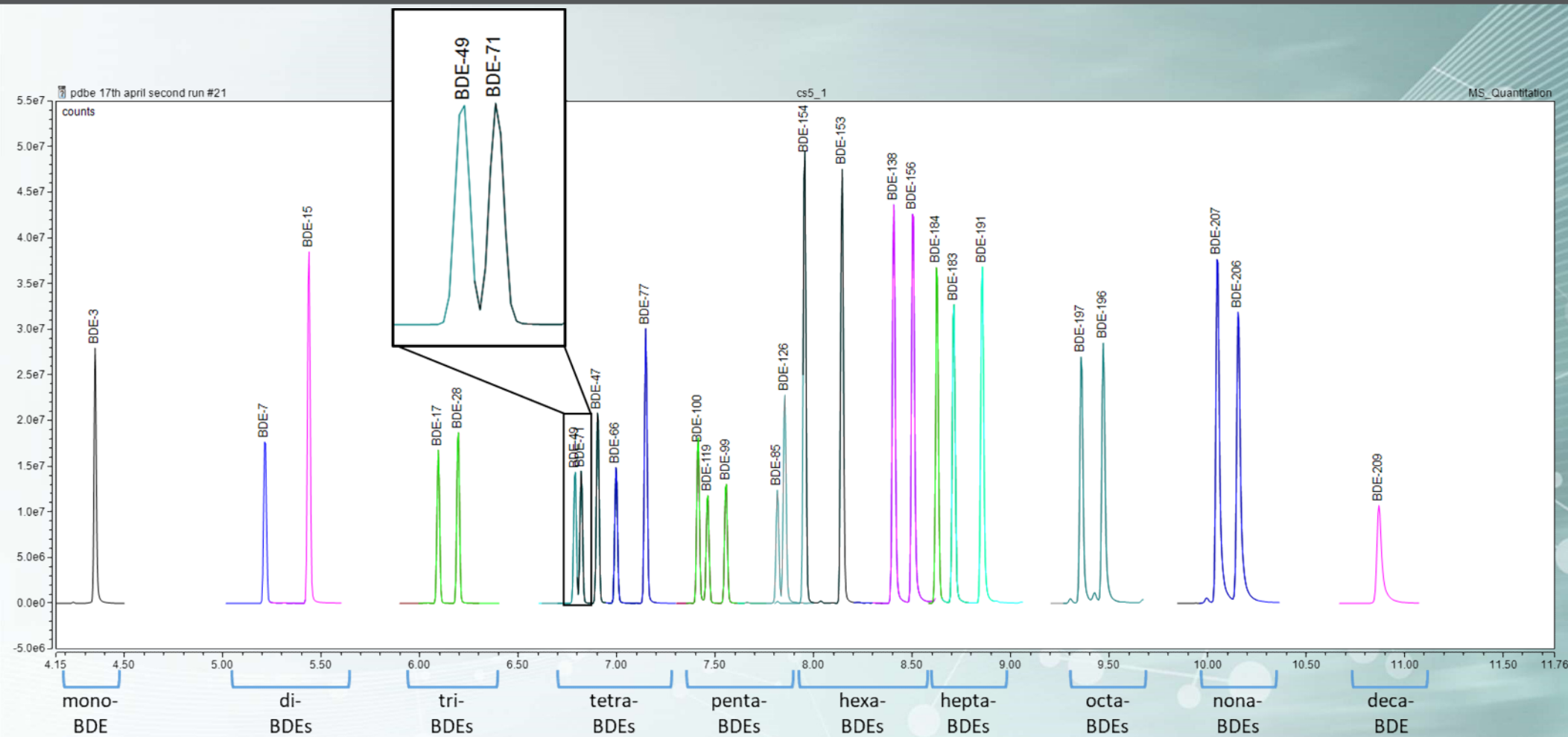


# Results

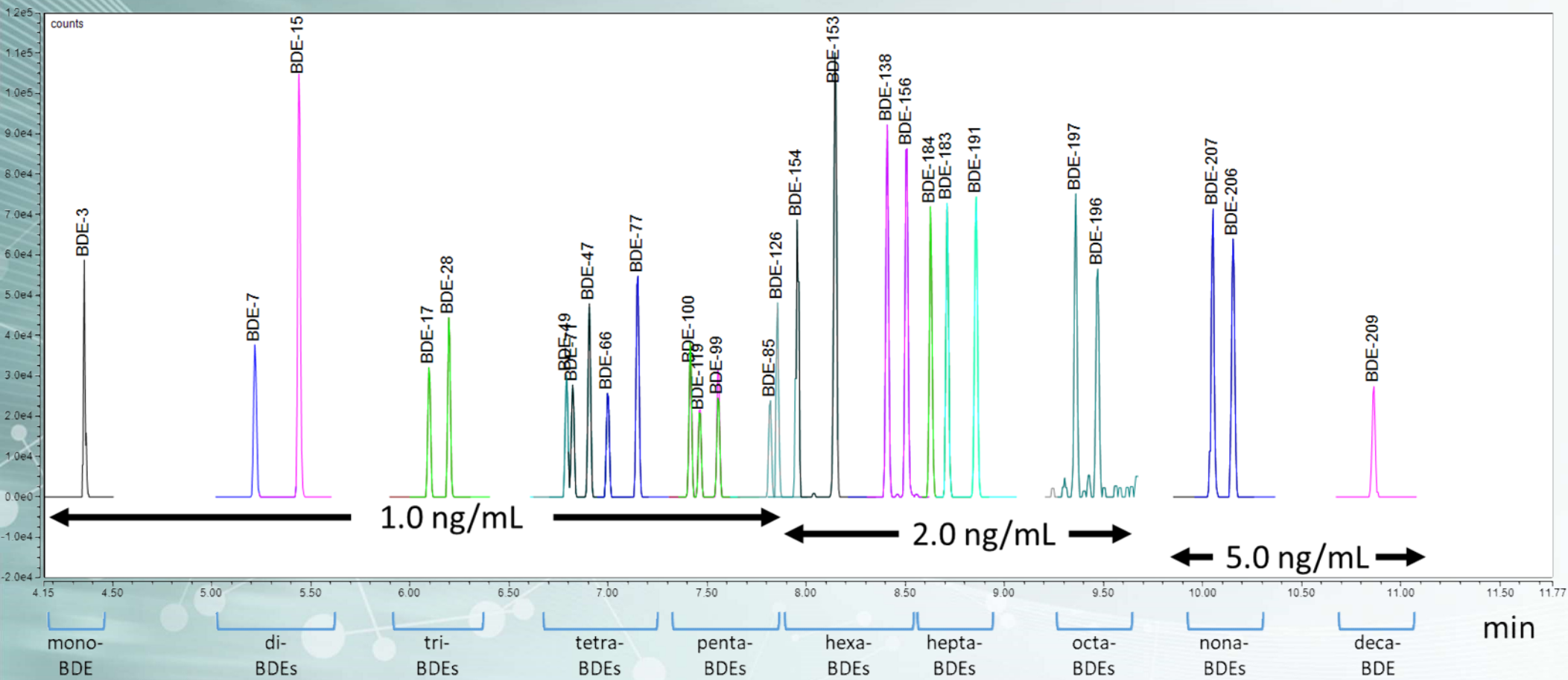




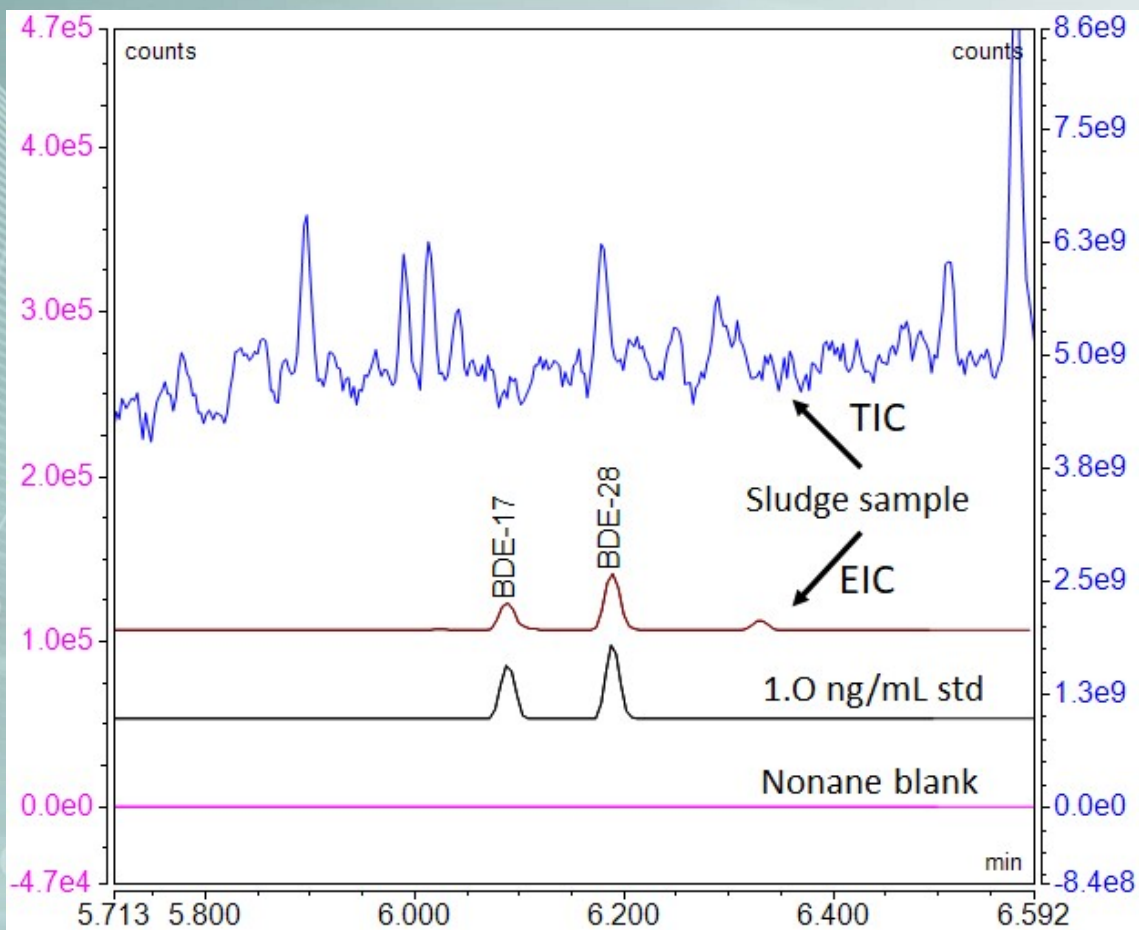
# Chromatography – Extracted Ion Chromatogram



# Sensitivity

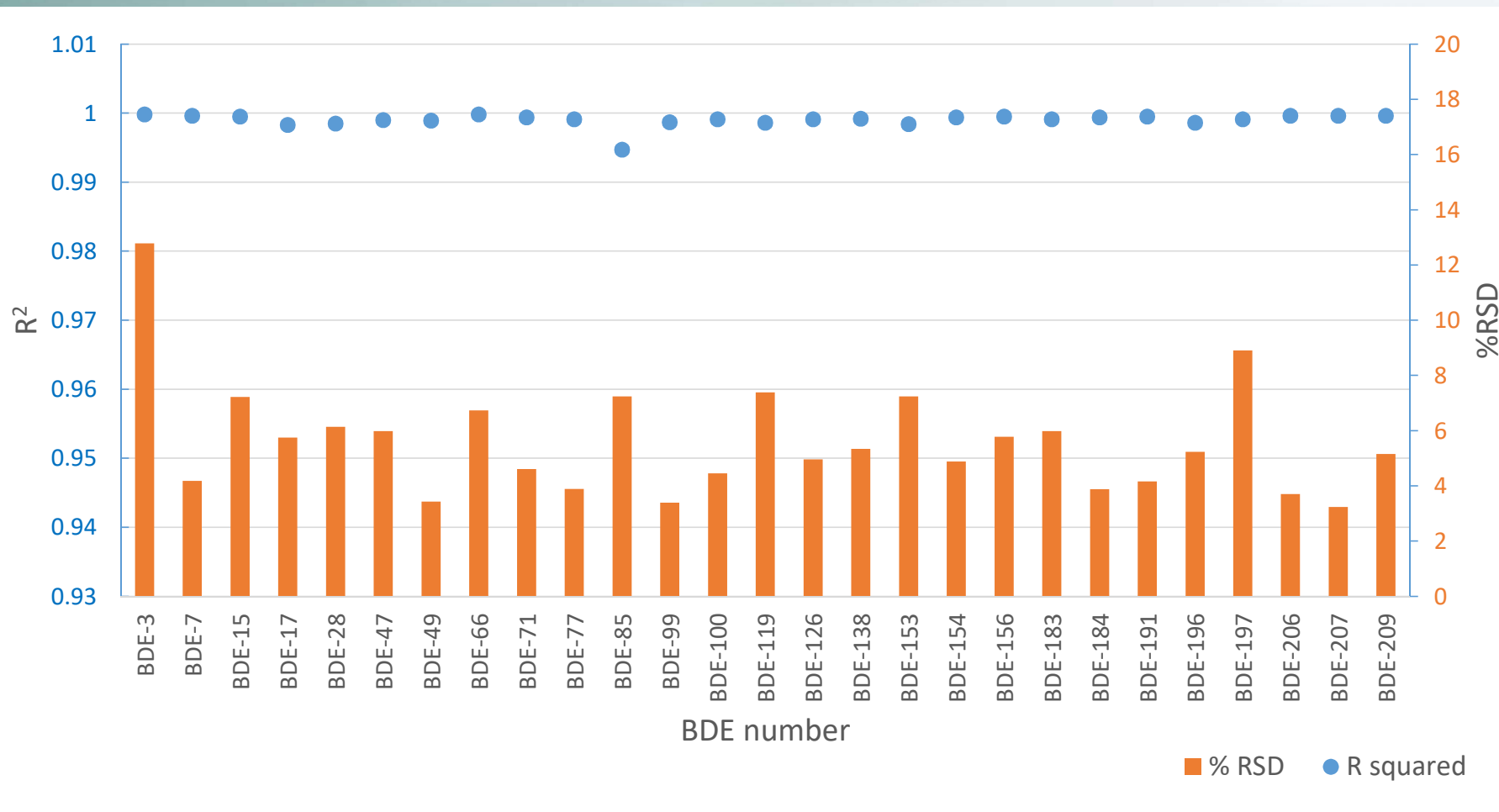


# Selectivity

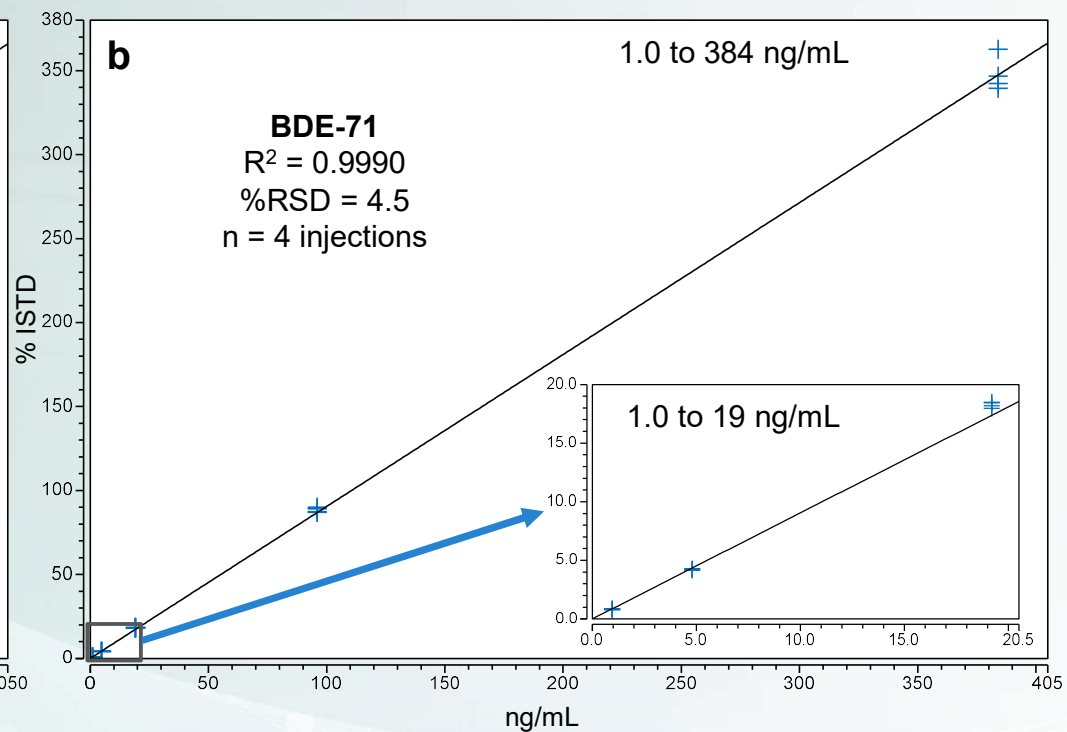
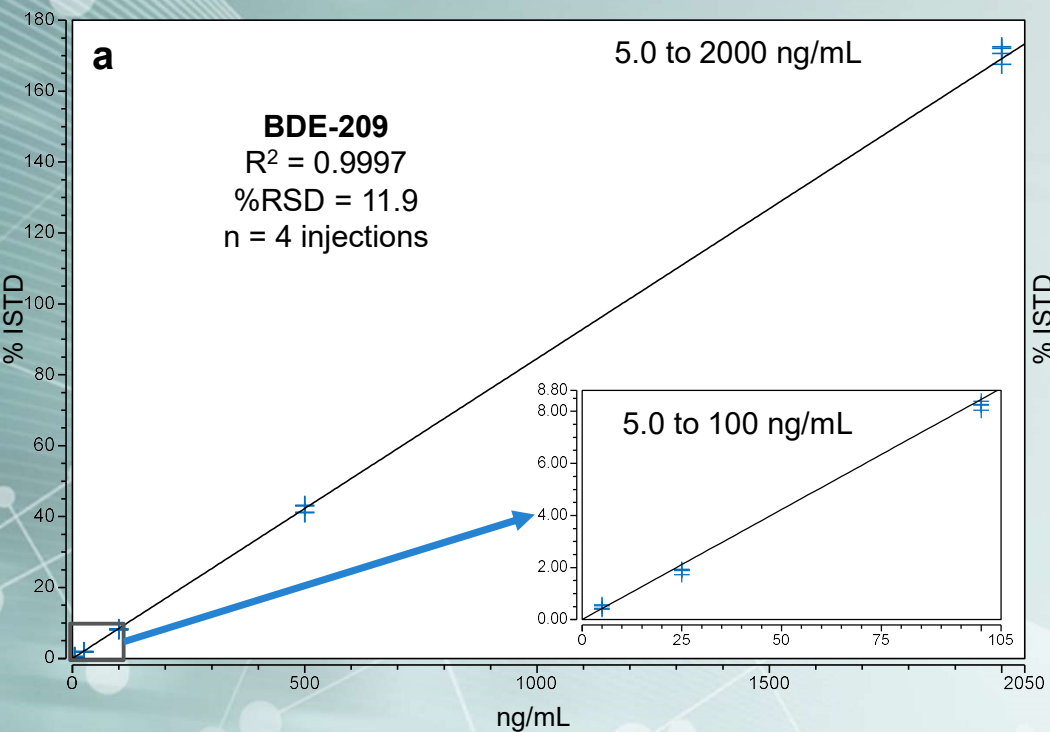


BDE-28 and 17  
(1 ng/mL, 1 pg on column),  
identified in a sludge sample  
at a similar level

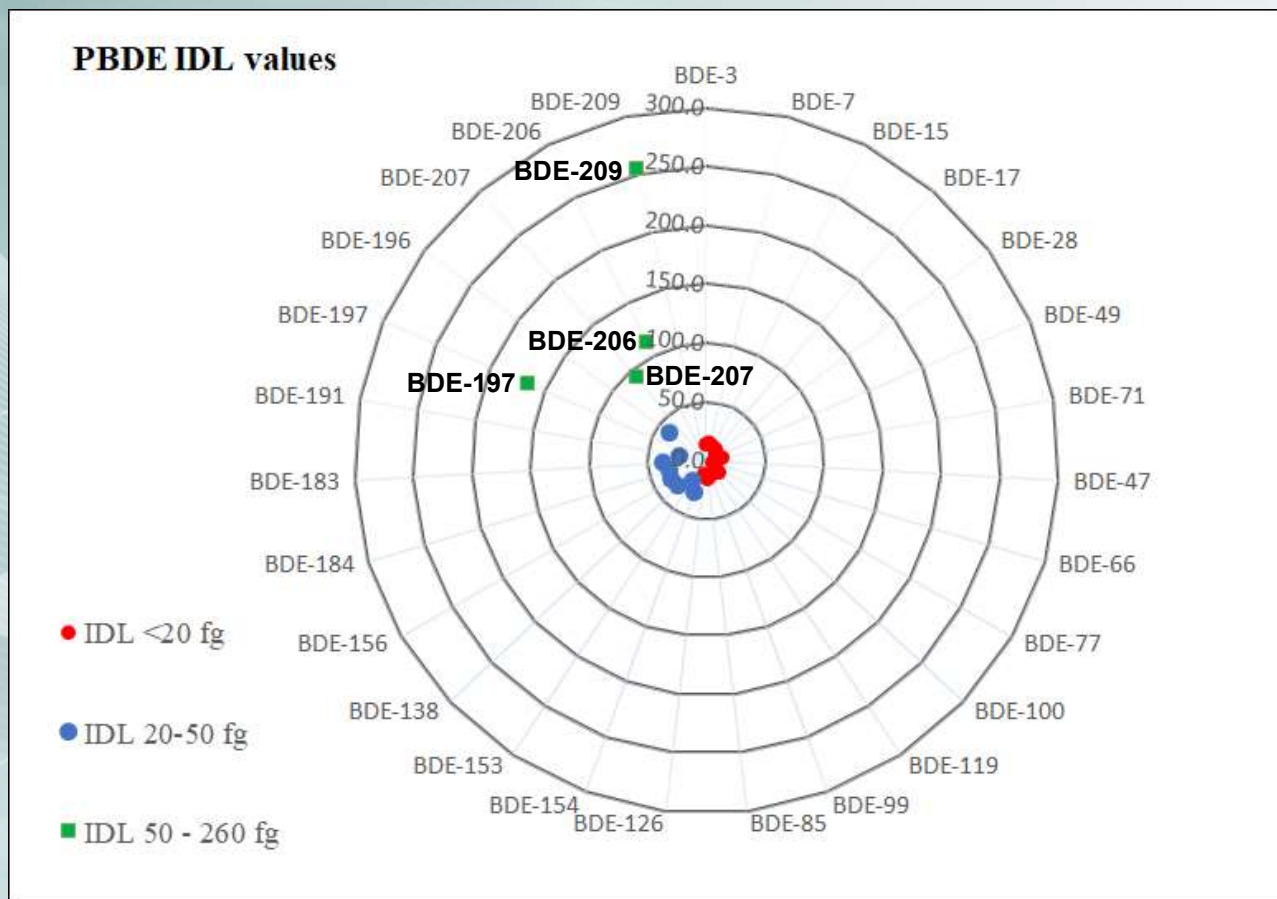
# Linearity



# Linearity

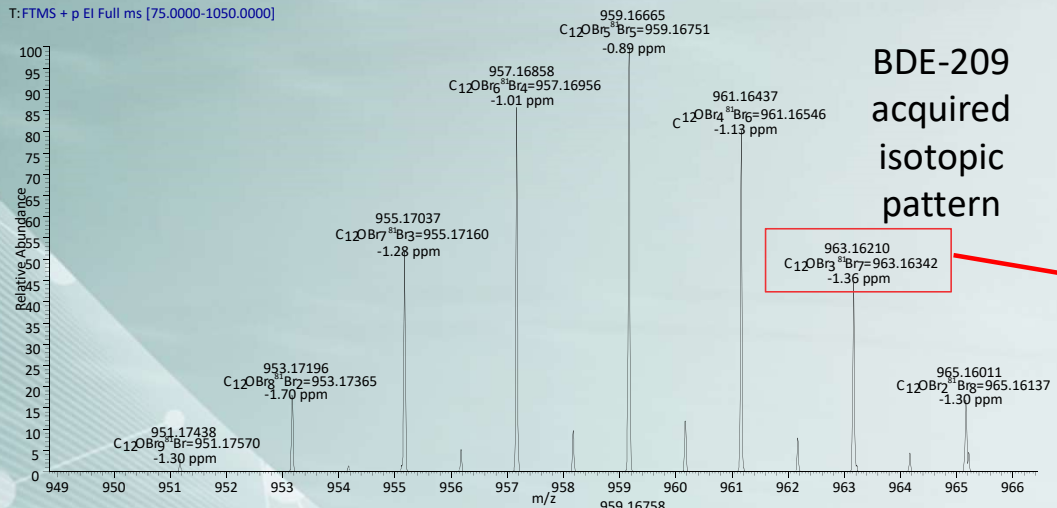


# Instrument Detection Limit



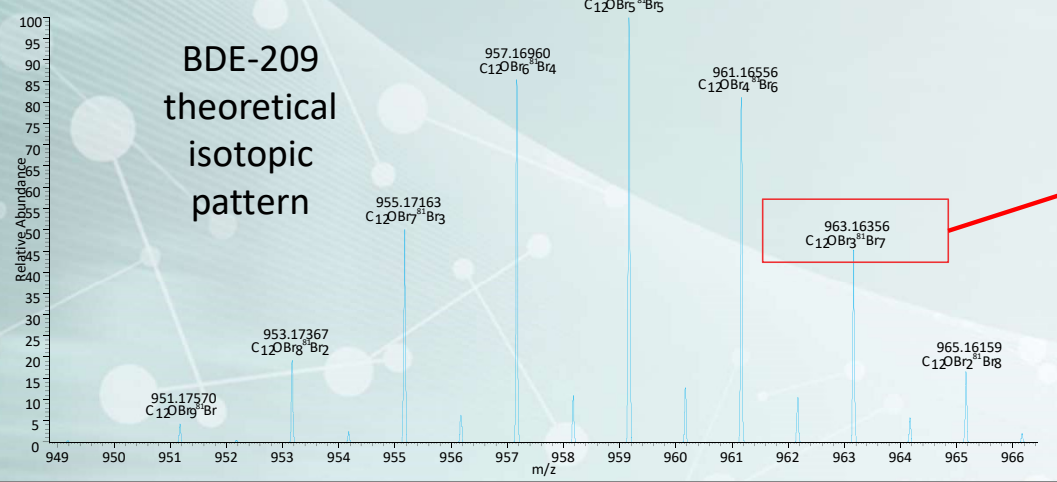
# Mass Accuracy

T: FTMS + p EI Full ms [75.0000-1050.0000]



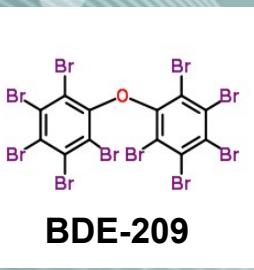
BDE-209  
acquired  
isotopic  
pattern

963.16210  
 $C_{12}OBr_3^{81}Br_7 = 963.16342$   
-1.36 ppm

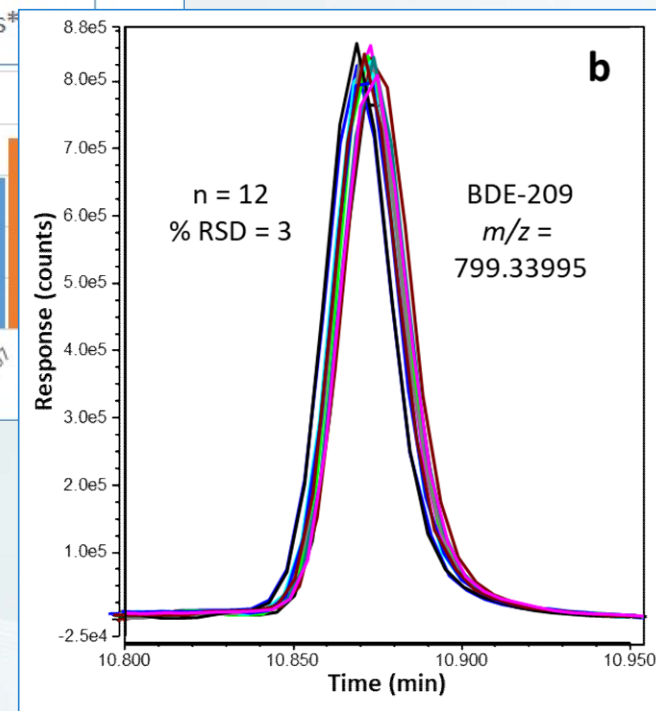
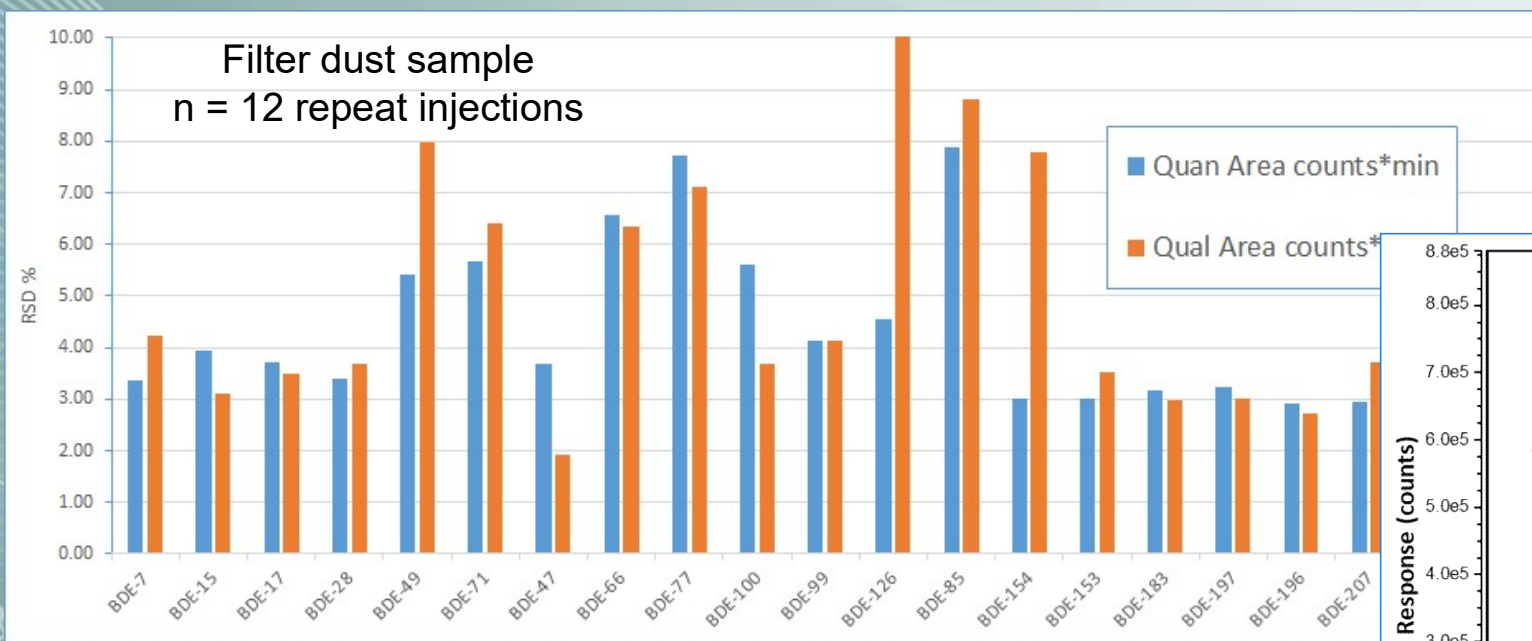


BDE-209  
theoretical  
isotopic  
pattern

963.16356  
 $C_{12}OBr_3^{81}Br_7$



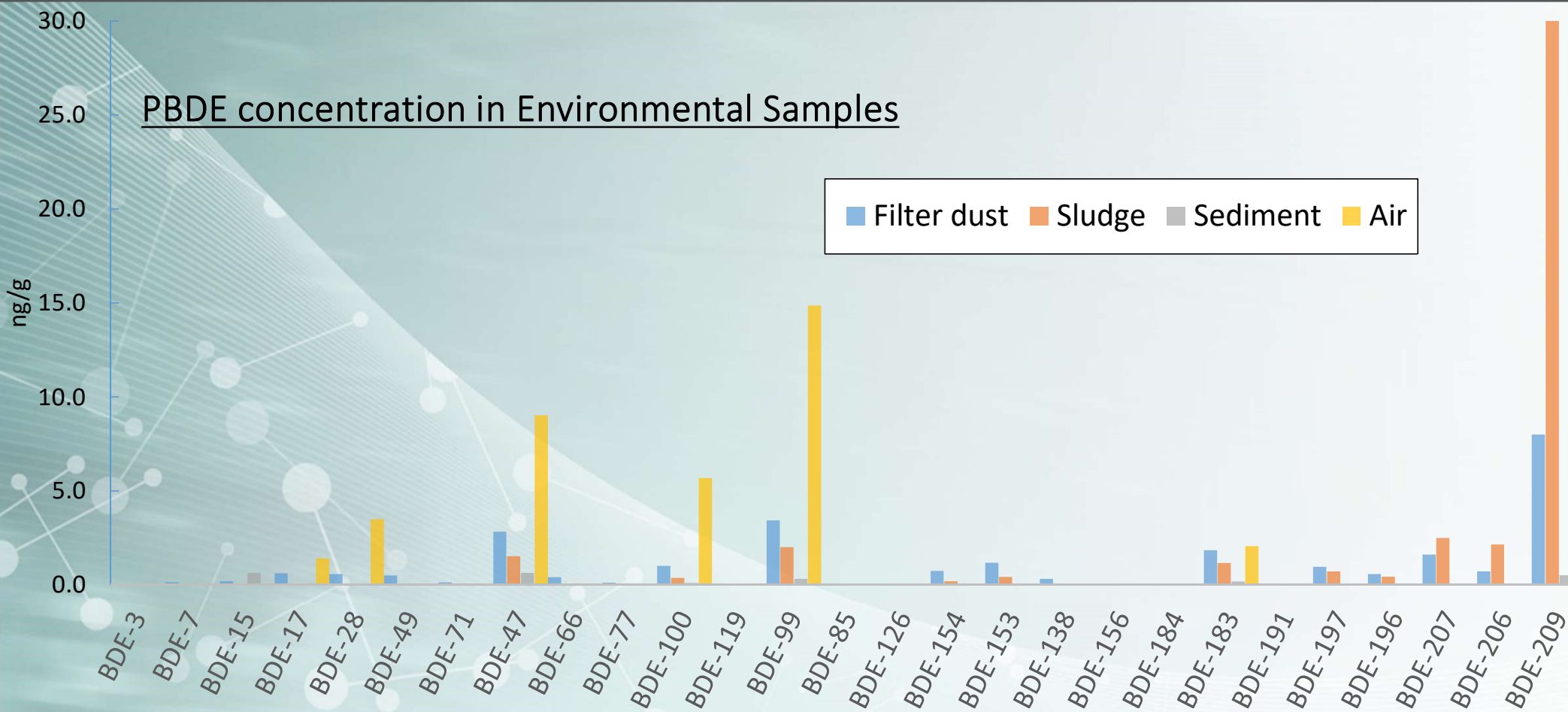
# Repeatability



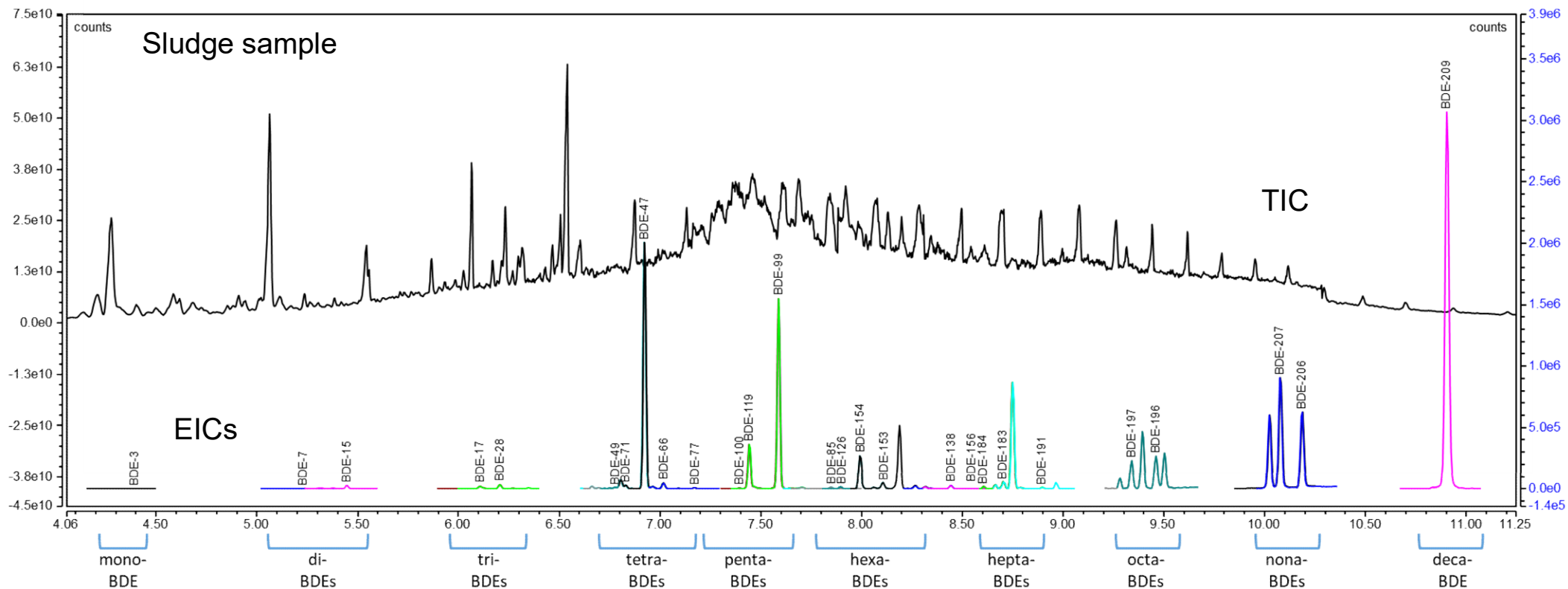


# Sample analysis

## PBDE concentration in Environmental Samples



# Sample analysis



# Conclusions



## Conclusions

- The results of this study demonstrate that using the simple set up of an Exactive GC Orbitrap GC-MS coupled with a TRACE 1310 GC system provides an excellent solution for the targeted quantification of PBDEs in complex environmental samples
- The predominant PBDE congeners identified in analyzed samples were BDE-209, 206, 207 and 99 in sludge, BDE-209, 47 and 99 in filter dust, BDE-99, 47 and 100 in air, and BDE-15, 47 and 99 in sediment
- Using Thermo Scientific TG-PBDE 15 m capillary column, good chromatographic separation in < 11 minutes for all the PBDE congeners considered was achieved, with excellent chromatographic resolution of the critical pair (BDE-49 and BDE-71)

## Conclusions (cont.)

- Excellent linearity was demonstrated with  $R^2 > 0.998$  and residual values  $RSD\% < 13\%$ , over five calibration levels
- All PBDEs were detected in the lowest calibration standard:
  - 1.0 ng/mL for mono- to penta-PBDEs, 2.0 ng/mL for hexa- to octa-PBDEs, and 5 ng/mL for nona- to deca-PBDEs.
- Instrument detection limits (IDLs) of between 6 and 250 fg on column were achieved for the PBDEs considered
- Thermo Scientific Chromeleon Chromatography Data System (CDS) software, offers an ideal solution for the targeted isotopic dilution quantification of PBDEs in environmental samples

## Acknowledgements

**Richard Law and Cristian Cojocariu**  
Thermo Fisher Scientific, Runcorn, UK

# Questions



