ASMS 2024,MP 174

A Novel Approach in Addressing the Challenges of Monitoring Multi-classes of POPs in a Single Run by GC-Ion Mobility-HRMS

Arnd Ingendoh, Carsten Baessmann, Javier Lopez*, Miguel Angel Perez*, Hugo Mueller#, Gauthier Eppe#

Bruker Daltonik GmbH, Bremen, Germany;
*Bruker Espanola, Madrid, Spain;
Mass Spectrometry Laboratory, MolSys Research Unit, Chemistry Department, University of Liège, Belgium

Introduction

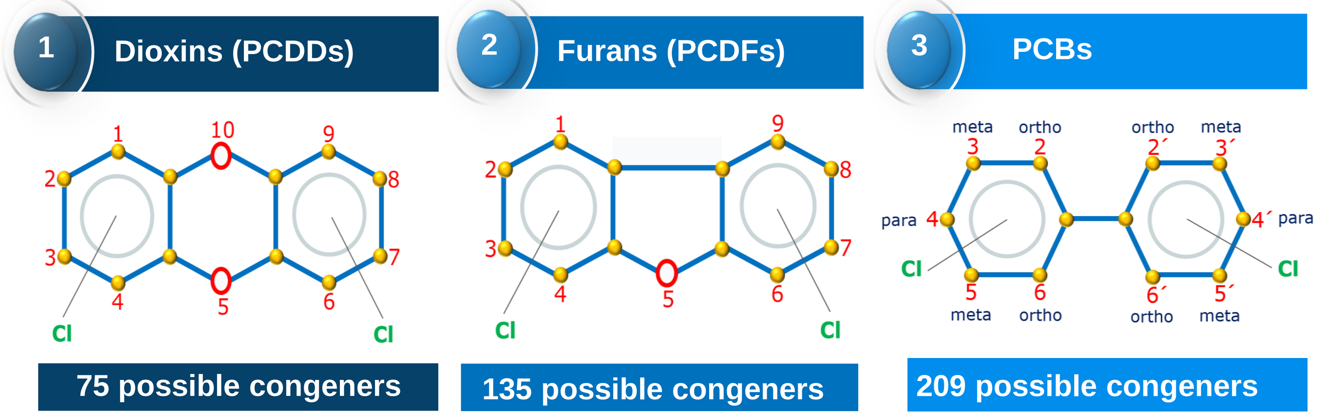
Polychlorinated dioxins and furans are bio-accumulative molecules formed during combustion and industrial manufacturing processes. Their analysis is complex due to low regulatory exposure limits and difficult sample matrices. They are persistent organic pollutants (POP), widely found in environmental samples. Severe consequences, even at low exposure concentration, include cancer, reproduction and growth issues, immune system diseases and endocrine effects. Dioxins and furans are mainly quantified in natural matrices by high-resolution sector field MS.

Objectives

1. Demonstrate the capabilities of the GC-APCI-timsTOF for dioxin determination matching the performance criteria of the worldwide standard methods (EPA 1613B, EN 1948) for environmental and food samples.
2. Proof GC-APCI-timsTOF technology as a superior alternative to traditional magnetic sector MS with the benefits of higher analytical flexibility for other POPs and the separation of isomers/isobars for ultra-trace analysis in complex matrices.
3. Develop a broad scope method for POPs screening and quantification for future regulation compliance.

Analytical performance criteria: EPA 1613B

MS Resolution	>10,000 for HRMS systems
m/z ions	Two exact mass ions to be monitored for each congener
Identification	By retention times and ion ratios. Check RRT native/[13]C
Quantitation	By isotope dilution technique
Calibration	Calibration curve with 5 levels: CS1-CS5
Linearity	Response factor (RF) RSD < 35% coefficient of variation
Ion ratios QC	Tolerance: +/- 15%
Precision	Verification with CS3 level: recoveries RSD
Sensitivity	Minimum level: first calibration point CS1, S/N>10
Carry-over	Analyze a blank after a sample or after CS3



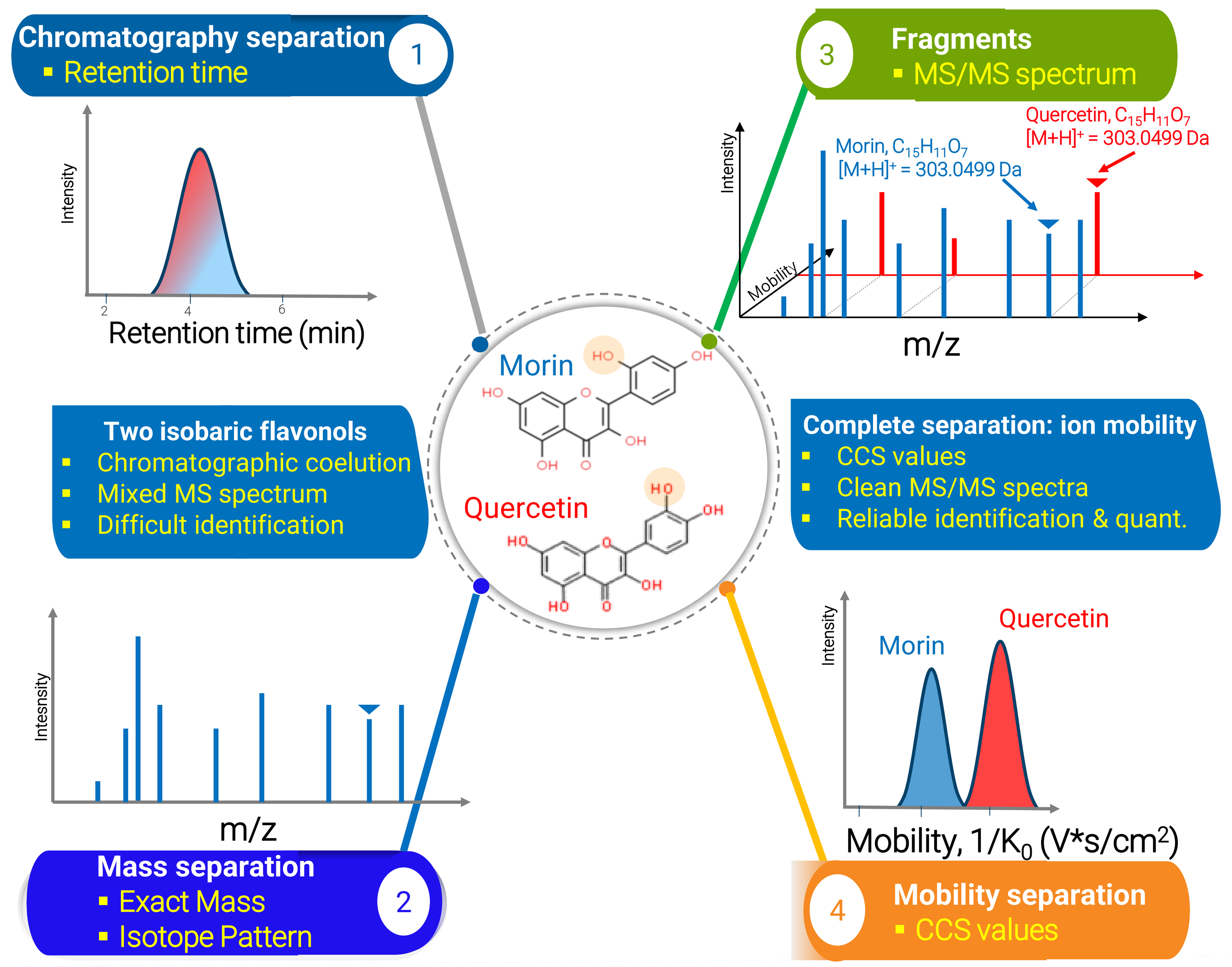
Total of 419 possible congeners. 17 congeners are classified as toxic (due to 2,3,7,8-chlorine substitution).

Dioxins and Furans	Quantitation ion	Confirmation ion	Internal standards
2,3,7,8-TCDF	305.8982	303.9011	[13C12] 2,3,7,8-TCDF
2,3,7,8-TCDD	321.8931	319.8660	[13C12] 2,3,7,8-TCDD
1,2,3,7,8-PeCDF	339.8592	341.8563	[13C12] 1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	339.8592	341.8563	[13C12] 2,3,4,7,8-PeCDF
1,2,3,7,8-PeCDD	355.8541	357.8513	[13C12] 1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDF	373.8202	375.8173	[13C12] 1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF	373.8202	375.8173	[13C12] 1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	373.8202	375.8173	[13C12] 1,2,3,7,8,9-HxCDF
2,3,4,6,7,8-HxCDF	373.8202	375.8173	[13C12] 2,3,4,6,7,8-HxCDF
1,2,3,4,7,8-HxCDD	389.8152	391.8123	[13C12] 1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD	389.8152	391.8123	[13C12] 1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	389.8152	391.8123	[13C12] 1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDF	407.8712	409.7784	[13C12] 1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	407.8712	409.7784	[13C12] 1,2,3,4,7,8,9-HpCDF
1,2,3,4,6,7,8-HpCDD	423.7762	425.7733	[13C12] 1,2,3,4,6,7,8-HpCDD
OCDF	443.7394	441.7423	[13C12] OCDD
OCDD	459.7343	547.7372	[13C12] OCDD

PCBs	Quantitation ion	Confirmation ion	Internal standards
PCB 77	291.8189	289.9218	[13C12] PCB 77
PCB 81	291.8189	289.9218	[13C12] PCB 81
PCB 105	325.8799	327.8771	[13C12] PCB 105
PCB 114	325.8799	327.8771	[13C12] PCB 114
PCB 118	325.8799	327.8771	[13C12] PCB 118
PCB 123	325.8799	327.8771	[13C12] PCB 123
PCB 126	325.8799	327.8771	[13C12] PCB 126
PCB 156	359.8410	361.8381	[13C12] PCB 156
PCB 157	359.8410	361.8381	[13C12] PCB 157
PCB 167	359.8410	361.8381	[13C12] PCB 167
PCB 169	359.8410	361.8381	[13C12] PCB 169
PCB 189	393.8020	395.7991	[13C12] PCB 189

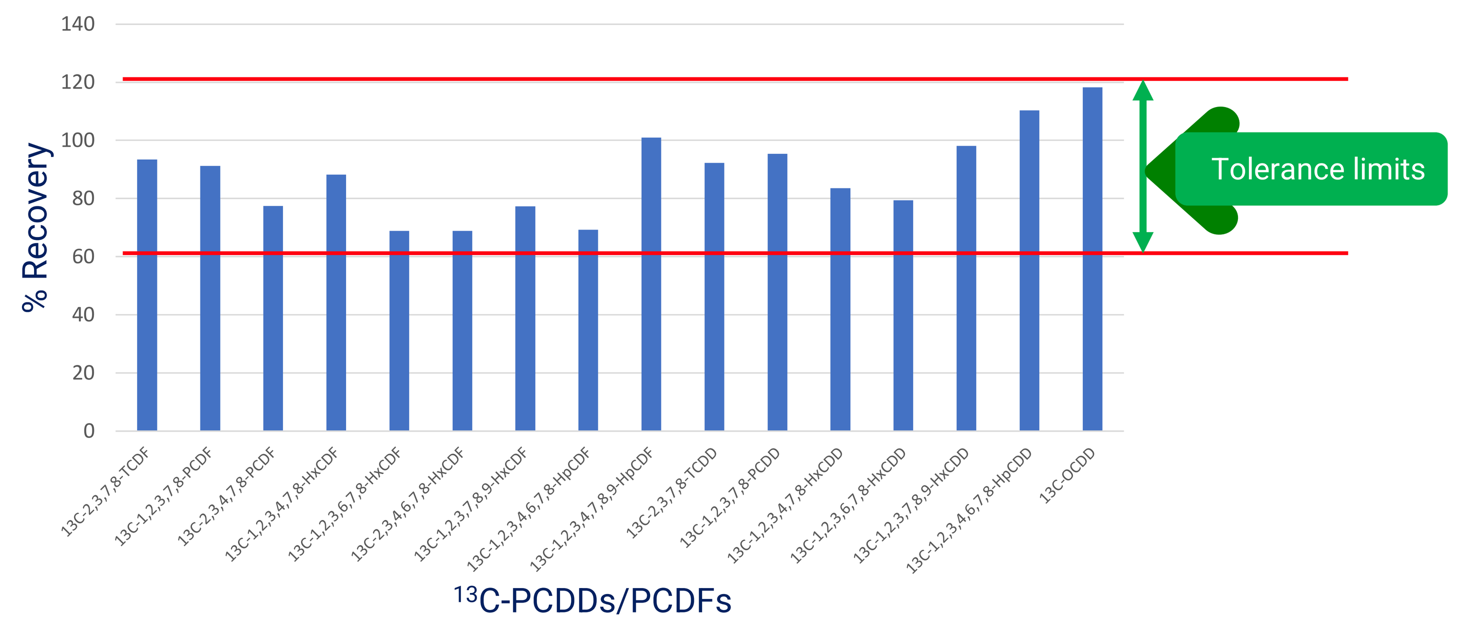
List of analyzed compounds: dioxins, furans and dioxin-like PCBs.

Adding the 4th analytical dimension: CCS



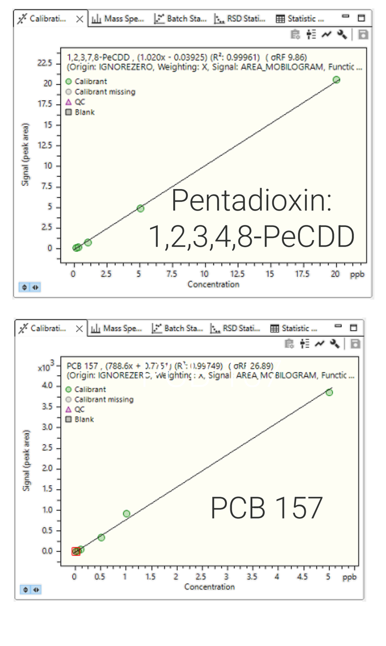
Methods

1 uL sample separated by GC (35 min run, Restek 60 mx0.25 um). GC-APCI source coupled to an ion mobility QTOF (timsTOF Pro 2, Bruker) enabling fast and sensitive quantitative analysis of the different classes of dioxins, furans and PCBs in a single GC/HRMS run. Criteria for validation and quantification of compounds: mass accuracy, retention time, isotope pattern matching, MS/MS qualifiers and collision cross sections (CCS) from ion mobility filtering. Kendrick mass defect plots filtered specific compounds containing Cl or Br from the complete GC/MS chromatogram. TargetScreener 4D software (Bruker) used as a post-processing tool for the automated quantification of the POP.



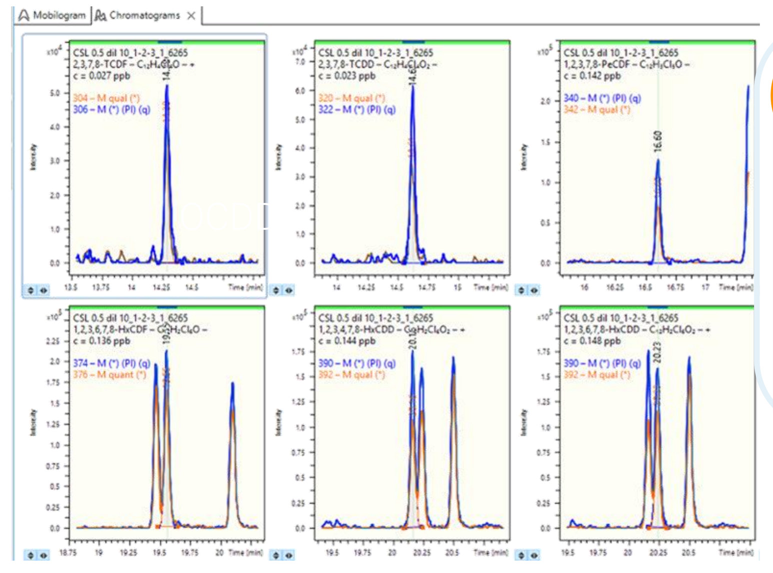
Recovery of [13]C internal standards in a real sample

Results



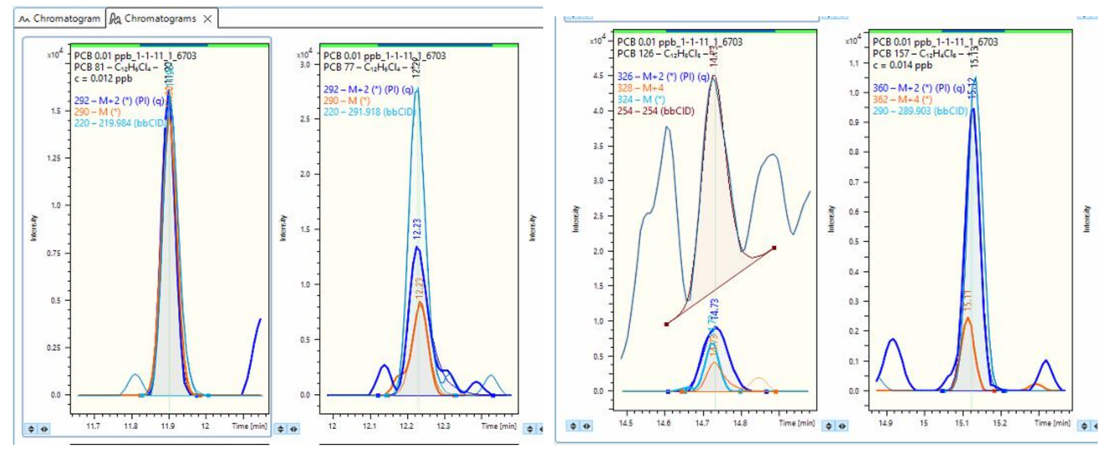
Analyte name	R^2	RSD_{RF} %
2,3,7,8-TCDF	0.99979	9.19
2,3,7,8-TCDD	0.99924	19.07
1,2,3,7,8-PeCDF	0.99795	7.47
2,3,4,7,8-PeCDF	0.99863	10.49
1,2,3,7,8-PeCDD	0.99961	9.86
1,2,3,4,7,8-HxCDF	0.99996	9.85
1,2,3,6,7,8-HxCDF	0.99920	15.91
1,2,3,7,8,9-HxCDF	0.99942	10.32
1,2,3,4,7,8-HxCDD	0.99913	9.09
1,2,3,6,7,8-HxCDD	0.99966	10.98
1,2,3,7,8,9-HxCDD	0.99640	9.41
2,3,4,6,7,8-HxCDF	0.99583	20.95
1,2,3,4,6,7,8-HpCDF	0.99752	33.01
1,2,3,4,6,7,8-HpCDD	0.99598	20.56
1,2,3,4,7,8,9-HpCDF	0.99673	32.96
OCDD	0.99910	9.93
OCDF	0.99815	14.08

Dioxins and dioxin-like PCB: linearity and RSD.



LOQ: Dioxins	
Tetras	25 fg/µL (ppt)
Pentas	125 fg/µL (ppt)
Hexas	125 fg/µL (ppt)
Heptas	125 fg/µL (ppt)
Octas	250 fg/µL (ppt)

Dioxins: Limit of Quantitation (LOQ)



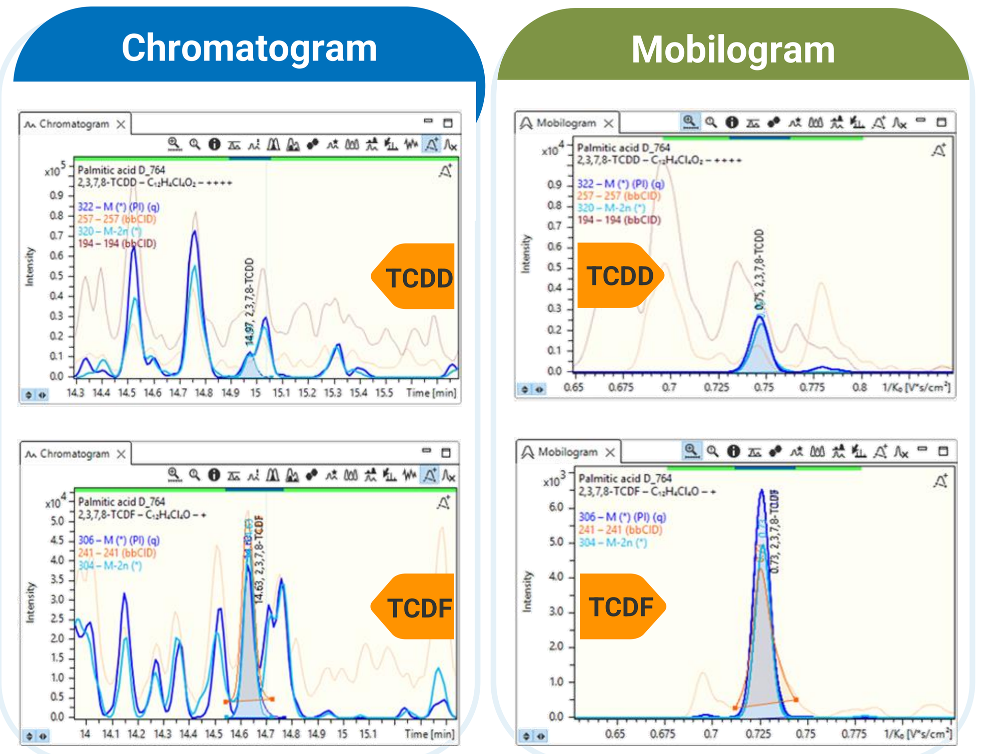
Limit of Quantitation (LOQ) for dioxin-like PCBs: 10 ppt

Analysis of dioxins in palm fatty acid

Palm fatty acid

4.52 g of rapeseed oil sample extracted and diluted 3 x with nonane before injection (1µL)

MRSQC	Analyte Name	Quantity [ppb]	Area of PI	Δm/z [mDa]	RT expected [min]	ΔRT [min]	Rel. RT
	2,3,7,8-TCDF	4.123	131792	0.04	14.70	-0.07	1.00
	2,3,7,8-TCDD	1.938	39163	-0.27	15.03	-0.06	1.00
	1,2,3,7,8-PeCDF	1.504	58022	0.46	17.01	-0.06	1.00
	2,3,4,7,8-PeCDF	1.244	58045	-0.90	17.76	-0.06	1.00
	1,2,3,7,8-PeCDD	2.057	95851	0.25	17.89	-0.06	1.00
	1,2,3,4,7,8-HxCDF	n.a.			19.88		
	1,2,3,6,7,8-HxCDF	n.a.			19.97		
	1,2,3,7,8,9-HxCDF	0.331	13851	-0.85	20.51	-0.05	1.00
	1,2,3,4,7,8-HxCDD	0.873	11112	0.33	20.57	-0.05	1.00
	1,2,3,6,7,8-HxCDD	0.656	28371	0.65	20.64	-0.04	1.00
	1,2,3,7,8,9-HxCDD	3.093	90878	0.73	20.91	-0.05	1.00
	2,3,4,6,7,8-HxCDF	n.a.			21.22		
	1,2,3,4,6,7,8-HpCDF	1.750	36215	-0.77	22.48	-0.05	1.00
	1,2,3,4,6,7,8-HpCDD	20.797	703710	0.31	23.60	-0.06	1.00
	1,2,3,4,7,8,9-HpCDF	0.300	10335	-1.14	24.19	-0.03	1.00
	OCDD	1014.376	12098706	-0.42	27.30	-0.06	1.00
	OCDF	1.073	3201	-0.58	27.53	-0.12	1.01



The presence of dioxins is close to the action limit (table, left). Ion mobility (green, right) significantly improves the selectivity and sensitivity of single peaks compared to GC alone (blue, middle).

Conclusions

A new era adding the 4th dimension for Dioxins and POPs analysis in complex matrices

- Reduction of potential isobaric interferences in complex matrices
- Separation of isomers/isobaric compounds
- More precise quantitation
- Outstanding sensitivity: Low femtograms level in real samples
- Analyze not only Dioxins but a broad scope of POPs in complex matrices
- Prepared for future regulation compliance

timsTOF Pro 2