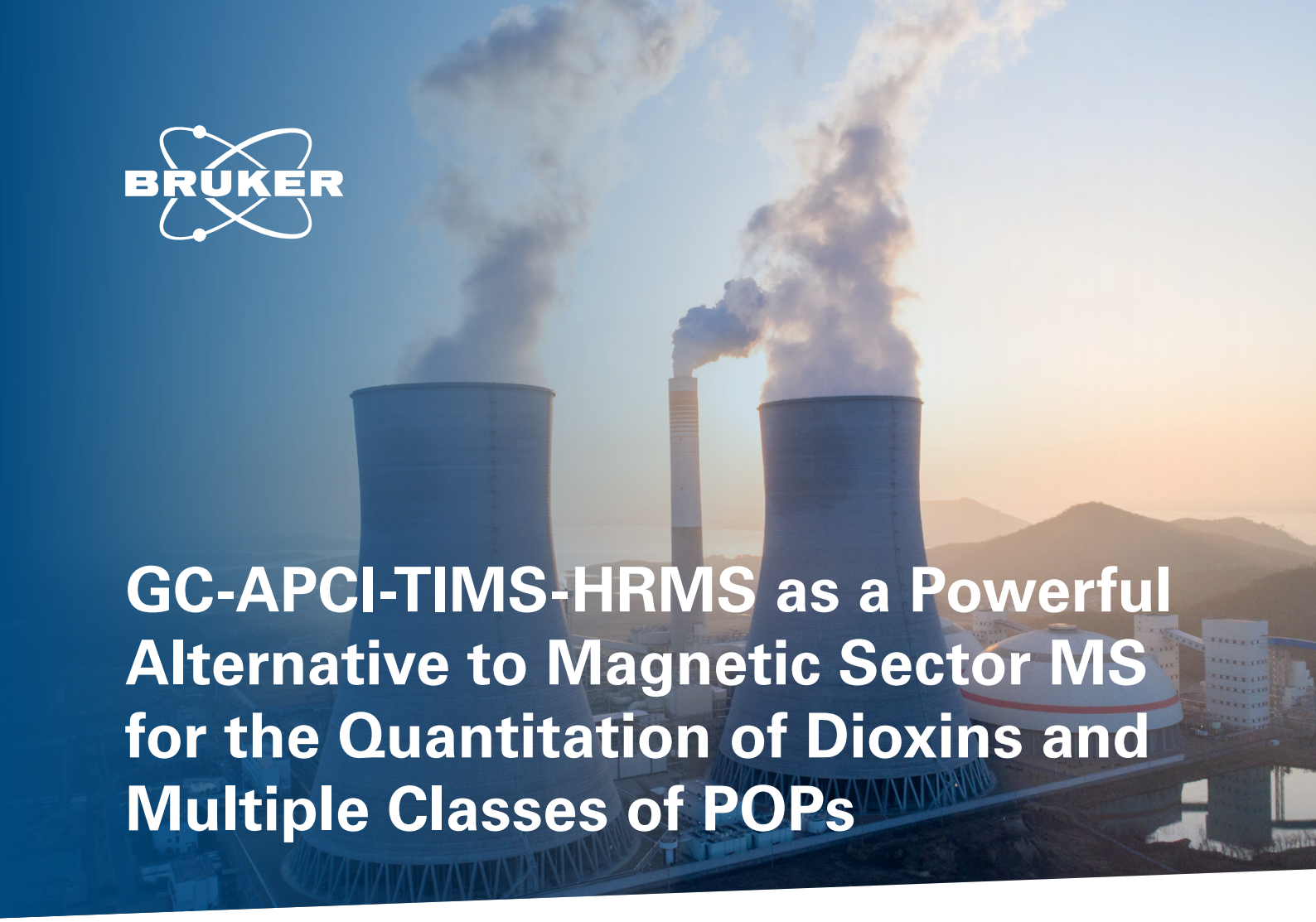


GC-APCI-TIMS-HRMS as a Powerful Alternative to Magnetic Sector MS for the Quantitation of Dioxins and Multiple Classes of POPs

Abstract

For the past decades, GC-HRMS based on magnetic sector instruments has been the main technique for dioxin quantitation in food and environmental samples. It is approved by most of the analytical regulatory bodies around the world due to its high selectivity and sensitivity.

However, magnetic sector instruments are expensive, costly to maintain, and require highly skilled personnel for operation. Consequently, the obligation for applying GC-HRMS for dioxin analysis is a limiting factor for the monitoring programs of these toxic pollutants in many countries.

Proposed here is a novel workflow which combines (1) a GC-Atmospheric pressure chemical ionization (APCI) source for high sensitivity, (2) trapped ion mobility spectrometry (TIMS) as an orthogonal criterion for the dioxin quantitation, and (3) a high-resolution, ultra-sensitive QTOF. A main benefit of this approach is the quantification of various classes of POP jointly with dioxins in a single GC run.

The objectives of this work are:

- To demonstrate the capabilities of GC-APCI-TIMS-HRMS for the confident and sensitive quantitation of POP matching the performance criteria of the worldwide standard methods (EPA 1613B, EN 1948) for environmental and food samples.
- To prove that GC-APCI-TIMS-HRMS is a superior alternative to traditional magnetic sector MS with the benefit of a higher analytical flexibility for more POP classes and the separation of isomers and isobars.
- To develop a method with a broad scope for POP screening and quantitation for future regulation compliance.

Keywords:
GC-APCI-TIMS-HRMS; POPs; dioxins; TASQ

Juan Gómez, Elena Bueno, Miguel Ángel Pérez
Bruker Applications Development Laboratory, Madrid, Spain

Introduction

Health risks of POPs

Persistent Organic Pollutants (POPs) are a group of heterocyclic chemical compounds that do not occur in nature but are formed as by-products of various industrial processes, particularly the combustion of organic material. They are bio-accumulative in the environment and the human body. POPs are known for their high toxicity and can have serious health effects, including cancer, reproduction and growth issues, immune system diseases and endocrine effects, even at low exposure concentration.

The role of the Stockholm Convention in POP regulation

The Stockholm Convention [1] aims to control the anthropogenic release of these contaminants and regulates 34 harmful substances with three additional compounds under review. These include (poly) halogenated, chlorinated (e.g., PCBs, Dioxins etc..), brominated (e.g., PBDEs, brominated flame retardants) compounds and PFAS. It is of great importance to monitor the POP level in food, environmental samples and biological material.
The GC-APCI-timsTOF technology allows for high-sensitivity detection and quantitation of POPs, even at femtogram levels, using advanced ion mobility separation. High sensitivity is supported by the soft ionization characteristics of the APCI source, preserving molecular ions. Using trapped ion mobility spectrometry (TIMS) for the detection and subsequent fragmentation of these ions provides high-resolution, high-value data for broad screening workflows and the capability to separate isomeric/isobaric compounds. TIMS separates ions by their collisional cross sections (CCS) which are a function of shape and size. Initially the ions are 'trapped', i.e., held stationary by the two opposing forces of a pushing gas pressure and a repelling electrical field. The electrical potential is then progressively reduced resulting in controlled and separated release of each ion species, with those of larger cross-sectional area eluting ahead of more compact analogues.

Improved sensitivity and identification with CCS values and TIMS technique

The information about the CCS as an additional, orthogonal parameter to the MS information significantly enhances the identification confidence. Additionally, TIMS enhances sensitivity and reduces detection limits by minimizing background interference. Finally, complex POP samples usually contain many isomeric and isobaric analytes and interferences which can be separated by TIMS (Figure 1).

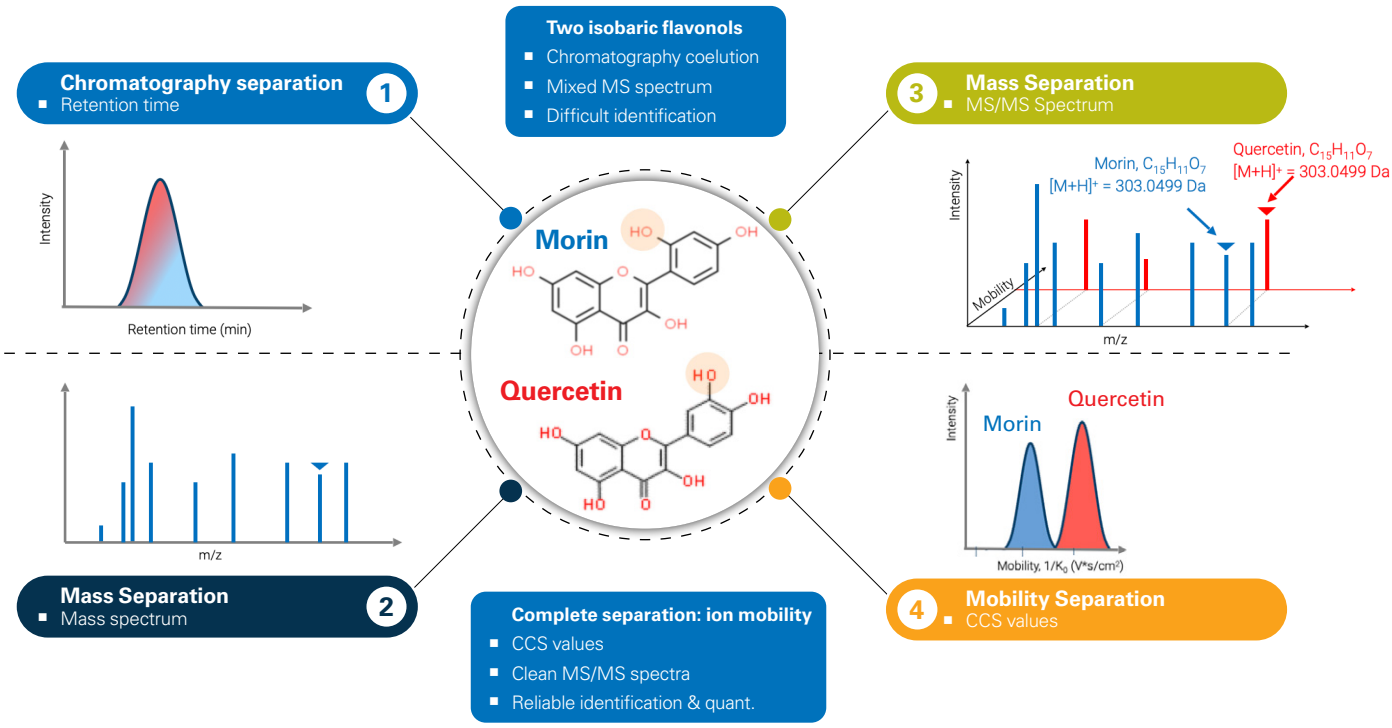


Figure 1. Trapped ion mobility spectrometry (TIMS): the power of the 4th dimension to separate isomeric/isobaric compounds.

APCI for soft ionization in POP detection

In conventional GC-MS, the commonly used electron impact (EI) ionization results in significant fragmentation within the ion source. In contrast, APCI is a low-energy, "soft" ionization technique that maintains the parent molecular ion and limits target fragmentation. This provides several key analytical advantages, including the high sensitivity necessary to detect lower abundant components as accurate molecular masses of $M^{\bullet+}$ or $[M+H]^+$ species within complex samples from MS/MS spectra. APCI-generated ions may then be subjected to controlled MS/MS fragmentation within the timsTOF system to confirm identity (target workflow) or characterize novel compounds (non-target workflow).

Materials and methods

The targeted congeners of PCDDs/PCDFs and dioxin-like PCBs analyzed are listed in Table 1.

Native and 13C-labeled targets diluted in n-Nonane were provided by Wellington Laboratories, Ontario, CA (EPA 1613 standard mixture, ref: EPA-1613CVS) and analyzed by GC-APCI-timsTOF.

Sample preparation

Food and environmental samples were prepared according to US EPA guidelines.

Instrumentation

Sample injections (1 µL) were performed into a PTV injector in splitless, solvent vent mode, using the 8500 GC with a Bruker 8400 Pro autosampler coupled to a GC-APCI II source and the timsTOF Pro 2 high resolution QTOF system (all Bruker Daltonics). Hydrogen was used as carrier gas for a total run time of 35 min. Advantages are shorter run times (i.e., cost savings) and a significantly increased sensitivity in GC-APCI by promoting the formation of protonated species. The GC effluent is introduced into the APCI source chamber, where ionization is initiated by a corona discharge producing an intense $M^{\bullet+}$ or $(M+H)^+$ molecular ion. More relevant instrument conditions are summarized in Table 2.

Table 1. List of the 29 target congeners of PCDDs/PCDFs and dioxin-like PCBs analyzed as well as their corresponding 13C-labeled compounds used as internal standards according to the isotopic dilution method workflow.

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

Table 2. Instrument parameters.

Gas chromatograph: Bruker 8500 GC	
Carrier gas	Hydrogen, 1.5 mL/min, constant flow
Injector	1079 PTV, temp. program up to 300 °C
Injection mode	1 µL splitless, solvent vent mode
Insert	3.4 mm Siltek fritted
Column	BR-Dioxin2, 60 m, 0.25 mm, 0.25 micron film thickness
Oven temperature	140 °C (1′) –> 230 °C at 50 °C/min (1′) –> 320 °C at 5 °C/min (13.20′)
Total run time	35 min
Mass spectrometer: Bruker timsTOF Pro 2	
Source	GC-APCI II
Transfer line	300 °C
End plate offset	300 V
Capillary	5000 V
Corona current	8000 nA
Nebulizer	3,5 bar
Dry gas	1,5 L/min
Dry temperature	250 °C
MS mode	tims-bbCID (Full scan & MS/MS)

Software

Data screening and quantitation was performed using TASQ® (Target Analysis for Screening and Quantitation) software (Bruker Daltonics). All analytical performance criteria described in EPA 1613B were included within a custom TASQ method (Table 3) for automated validation.

Table 3. Validation rules included in the automated TASQ processing according to US EPA 1613B analytical performance criteria.

Ions | Ion Ratios | Rules

	Rule name	Type	Value
1	☑ carryOverLimit	Implicit	300.00
2	☐ detectionLimit	Implicit	1.0
3	☑ estimatedLowValue	Implicit	
4	☑ falseNegative	Implicit	
5	☑ lowerLimitOfQuantitation	Implicit	0.50
6	☑ maximumDeviation	Implicit	20.00
7	☑ maximumDeviationQC	Implicit	20.00
8	☑ minimumCorrelation	Implicit	0.99
9	☑ quantityAboveMaxQuantityOfCalibration	Implicit	
10	☑ quantityBelowMinQuantityOfCalibration	Implicit	
11	☑ quantityExceedsReportingLimit	Implicit	1.00
12	☑ responseRange	Implicit	10.00
13	☑ retentionTimeDrift	Implicit	10.00
14	☑ signalInBlank	Implicit	0.50
15	☑ standardDeviationResponseFactor	Implicit	35.00
16	☑ upperLimitOfQuantitation	Implicit	1,000.00

Automated mass filtering based on the expected molecular formulae was used with an allowed mass error window of ±3 mDa. TASQ provides a fast and easy overview of the results, and users can set an extensive number of evaluation rules to meet any stringent analytical regulation. These rules and threshold values are applicable and customizable for each target compound in the method. Within TASQ, MRSQC scores were automatically determined for each target compound, for the mass accuracy (M), the retention time (R), isotopic pattern fidelity (mSigma S), detection of (additional) diagnostic ions (Q) and CCS values (C) for the ion mobility separation (Figure 2). This multi-feature scoring efficiently eliminates false positive and false negative results.

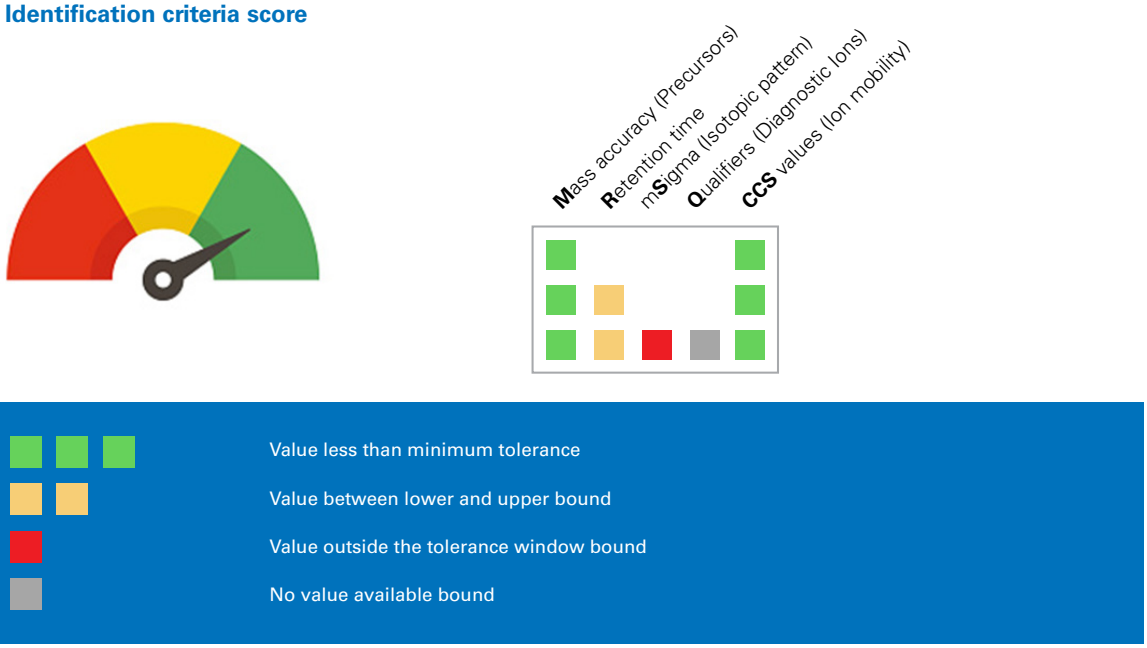


Figure 2. Color coded schematics of analysis results within the TASQ® software. The MRSQC scoring reflects the key parameters mass accuracy (M), retention time (R), mSigma* scores of isotopic fidelity (S), qualifier diagnostic ions (Q) and the collisional cross section or CCS values (C) for the ion mobility separation. This multi-feature scoring eliminates false positive and false negative results.
**mSigma scores use a scale of 0-1000, where lower values indicate a better fit to theoretical isotopic patterns.*

The Bruker TargetScreener 4D and TASQ software modules were used as post-processing tools for the automated POP quantitation. A TargetScreener 4D method "ready-to-use" was developed for the simultaneous analysis of multiple compound classes in the very same GC-HRMS run. Criteria for the quantitation were two ions associated to each analyte (principal ion $[M]^+$ in full scan MS and MS/MS product ions $[M\text{-}CClO]^+$ for dioxins and $[M\text{-}Cl_2]^+$ for dioxin-like PCBs) with an ion ratio tolerance of ±30% for both ions and expected CCS tolerance of ±2%.

Results

Excellent linearity in calibration curves

Due to the exceptional sensitivity of the GC-APCI-timsTOF Pro 2 system, all calibration levels were diluted 10x in Nonane and analyzed at concentrations ranging from 0.025 to 40 ng/mL for PCDDs/PCDFs and 0.01 to 5 ng/mL for dioxin-like PCBs. This approach offers several advantages, including reduced matrix effects from the dilution, cost savings on expensive standards, improved reproducibility, and a longer instrument maintenance cycle.
Representative calibration curves for selected dioxins and dioxin-like PCBs are shown in Figure 3, both the chromatograms and the mobilograms can be used to generate these.

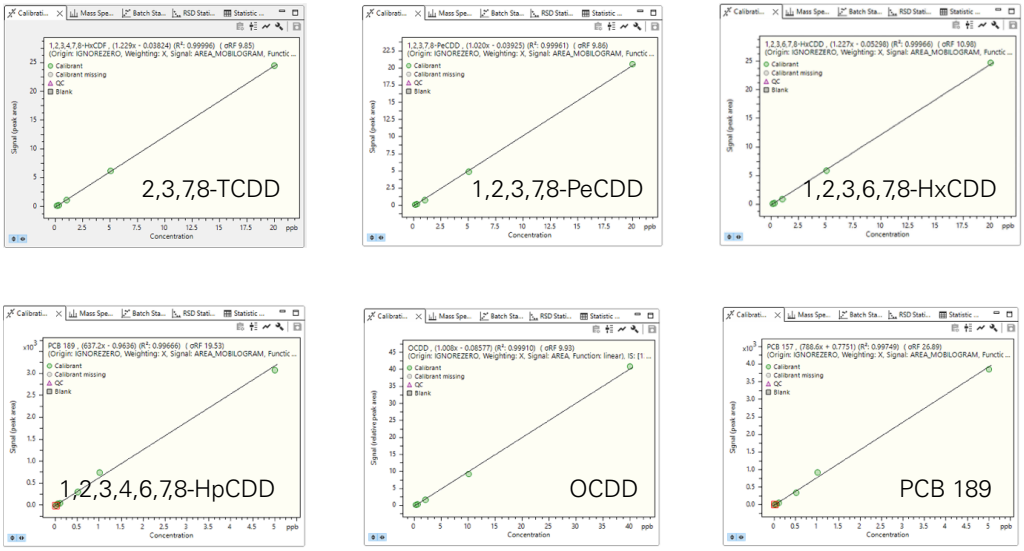


Figure 3. Calibration curves for representative dioxins and dioxin-like PCBs. Concentration ranges for tetras (0.025-4 ng/mL), pentas, hexas and heptas (0.125- 20 ng/mL), octas (0.250-40 ng/mL) and PCBs (0.01- 5 ng/mL)

The calibration curves had excellent linearities of $R^2 > 0.996$ for all PCDDs/PCDFs. The average response factor (RF) was RSD < 15%. This average and all individual values are in accordance with the EPA 1613B request of RSD < 35% (Table 4). The US EPA S/N criteria for the lowest calibration point of S/N ≥ 10 was achieved by far for all targets.

Table 4. Summary of the calibration and linearity results for all 17 PCDDs/PCDFs with $R^2 > 0,996$ and response factor RSD % < 33%.

Analyte name	Function term	Function type	Origin	Weighting	R^2	RSD RF %
2,3,7,8-TCDF	y=1.022x - 0.00405	Linear	Ignore	1/x	0.99979	9.19
2,3,7,8-TCDD	y= 0.7742x + 0.00358	Linear	Ignore	1/x	0.99924	19.07
1,2,3,7,8-PeCDF	y= 1.010x - 0.02963	Linear	Ignore	1/x	0.99795	7.47
2,3,4,7,8-PeCDF	y= 0.9934x - 0.04537	Linear	Ignore	1/x	0.99863	10.49
1,2,3,7,8-PeCDD	y= 1.020x - 0.03925	Linear	Ignore	1/x	0.99961	9.86
1,2,3,4,7,8-HxCDF	y= 1.229x - 0.03824	Linear	Ignore	1/x	0.99996	9.85
1,2,3,6,7,8-HxCDF	y=1.142x - 0.04023	Linear	Ignore	1/x	0.99920	15.91
1,2,3,7,8,9-HxCDF	y= 1.0581x - 0.05018	Linear	Ignore	1/x	0.99942	10.32
1,2,3,4,7,8-HxCDD	y= 1.084x - 0.04158	Linear	Ignore	1/x	0.99913	9.09
1,2,3,6,7,8-HXCDD	y= 1.227x - 0.05298	Linear	Ignore	1/x	0.99966	10.98
1,2,3,7,8,9-HxCDD	y= 12.65x - 0.3952	Linear	Ignore	1/x	0.99640	9.41
2,3,4,6,7,8-HxCDF	y= 1.045x - 0.02576	Linear	Ignore	1/x	0.99583	20.95
1,2,3,4,6,7,8-HpCDF	y= 0.5322x - 0.00484	Linear	Ignore	1/x	0.99752	33.01
1,2,3,4,6,7,8-HpCDD	y= 0.7736x - 0.05756	Linear	Ignore	1/x	0.99598	20.56
1,2,3,4,7,8,9-HpCDF	y= 0.5939x - 0.01803	Linear	Ignore	1/x	0.99673	32.96
OCDD	y= 1.008x - 0.08577	Linear	Ignore	1/x	0.99910	9.93
OCDF	y= 0.8921x - 0.1037	Linear	Ignore	1/x	0.99815	14.08

System performance: Precision and recovery analysis using TASQ

Precision and recovery were calculated by TASQ software using the verification level (CS3 standard level diluted by 10x) for each target within a complete batch of calibration and real samples. Recoveries are within the range of 91 - 122%. The RRT native/^{13}C ratios were 1.00 - 1.01, for all targets, easily meeting US EPA method requirements (Table 5).

Table 5. Target recoveries of the 17 PCDDs/PCDFs compounds using the verification level (CS3 standard level diluted by 10x) meeting the US EPA accuracy request and relative retention time native/^{13}C ratios. Shown is a screenshot from Analysis Results in TASQ.

Analyte Name	Quantity [ppb]	Quantity expe...	Accuracy [%]	Area of PI	Δm/z [mDa]	Rel. RT
2,3,7,8-TCDF	0.906	1.000 ppb	90.61	1677373	-0.36	1.00
2,3,7,8-TCDD	1.219	1.000 ppb	121.94	2005489	-0.37	1.00
1,2,3,7,8-PeCDF	4.835	5.000 ppb	96.71	7536136	-0.28	1.00
2,3,4,7,8-PeCDF	4.995	5.000 ppb	99.89	8447787	-0.17	1.00
1,2,3,7,8-PeCDD	4.889	5.000 ppb	97.77	6914768	-0.57	1.00
1,2,3,4,7,8-HxCDF	4.805	5.000 ppb	96.10	6559200	-0.15	1.00
1,2,3,6,7,8-HxCDF	5.049	5.000 ppb	100.99	7285652	-0.25	1.00
1,2,3,7,8,9-HxCDF	4.747	5.000 ppb	94.93	6689728	-0.01	1.00
1,2,3,4,7,8-HxCDD	4.399	5.000 ppb	87.98	5995342	0.12	1.00
1,2,3,6,7,8-HxCDD	4.781	5.000 ppb	95.62	5688915	0.09	1.00
1,2,3,7,8,9-HxCDD	4.735	5.000 ppb	94.69	5050143	0.50	1.00
2,3,4,6,7,8-HxCDF	4.840	5.000 ppb	96.81	4697613	-0.06	1.00
1,2,3,4,6,7,8-HpCDF	4.709	5.000 ppb	94.18	3540364	-0.05	1.00
1,2,3,4,6,7,8-HpCDD	5.032	5.000 ppb	100.64	3623252	0.05	1.00
1,2,3,4,7,8,9-HpCDF	4.858	5.000 ppb	97.17	3569561	0.02	1.00
OCDD	8.872	10.000 ppb	88.72	3042525	-0.35	1.00
OCDF	9.185	10.000 ppb	91.85	2755323	-0.13	1.01

Recovery: 91-122%

RRT native/13C 1.00-1.01

LOD and LOQ

The sensitivity of the method has been experimentally determined by two parameters: Limit of Quantitation (LOQ) resp. Minimum Value (ML) and Limit of Detection (LOD) resp. Method Detection Limit (MDL) for an injection volume of 1 µL.
The LOQ for dioxins corresponds to the first calibration point and represents the lowest concentration that can be reliably quantified under the FDA criteria of precision and accuracy. As required within the referenced US EPA regulation, two exact mass ions were detected for each target. The chromatographic peaks of the first calibration level for all PCDDs/PCDFs are shown in Figure 4. As LOQ were achieved: tetras (25 fg), pentas, hexas, heptas (125fg) and octas (250 fg).

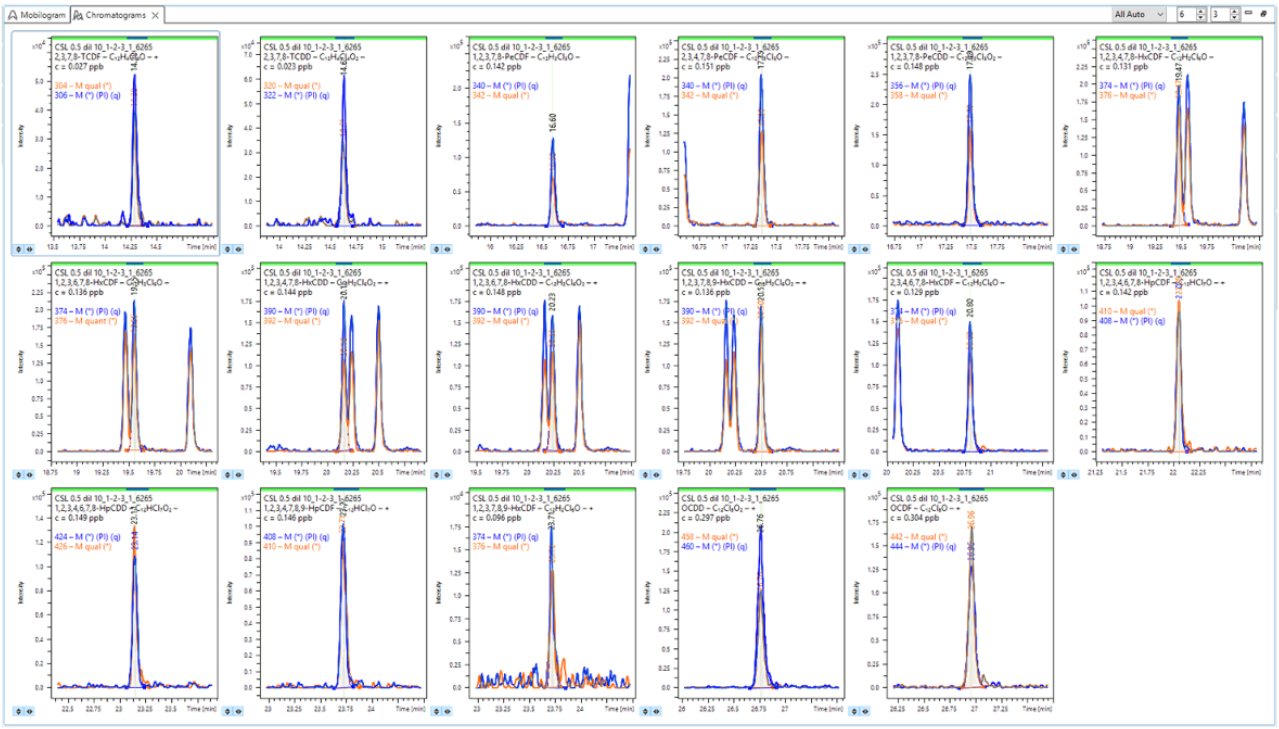


Figure 4. Limit of Quantitation (LOQ): Chromatographic peaks of the first calibration level for all PCDDs/PCDFs that are set as LOQ. Tetras (25 fg), pentas, hexas, heptas (125 fg) and octas (250 fg). 1 µL of sample has been injected.

The LOD (or MDL) was calculated following the US EPA guidelines (40 CFR part 136 appendix B, revision 2, July 1, 2023) based on the standard deviation calculated on replicate analyses [2]. For this purpose, 10 injections (1µL each) of 10 fg of 2,3,7,8-TCDD (CSL standard level diluted by 10x) have been performed (Figure 5). Following this procedure, the LOD (or MDL) for 2,3,7,8-TCDD is calculated to be as low as 3 fg on-column.

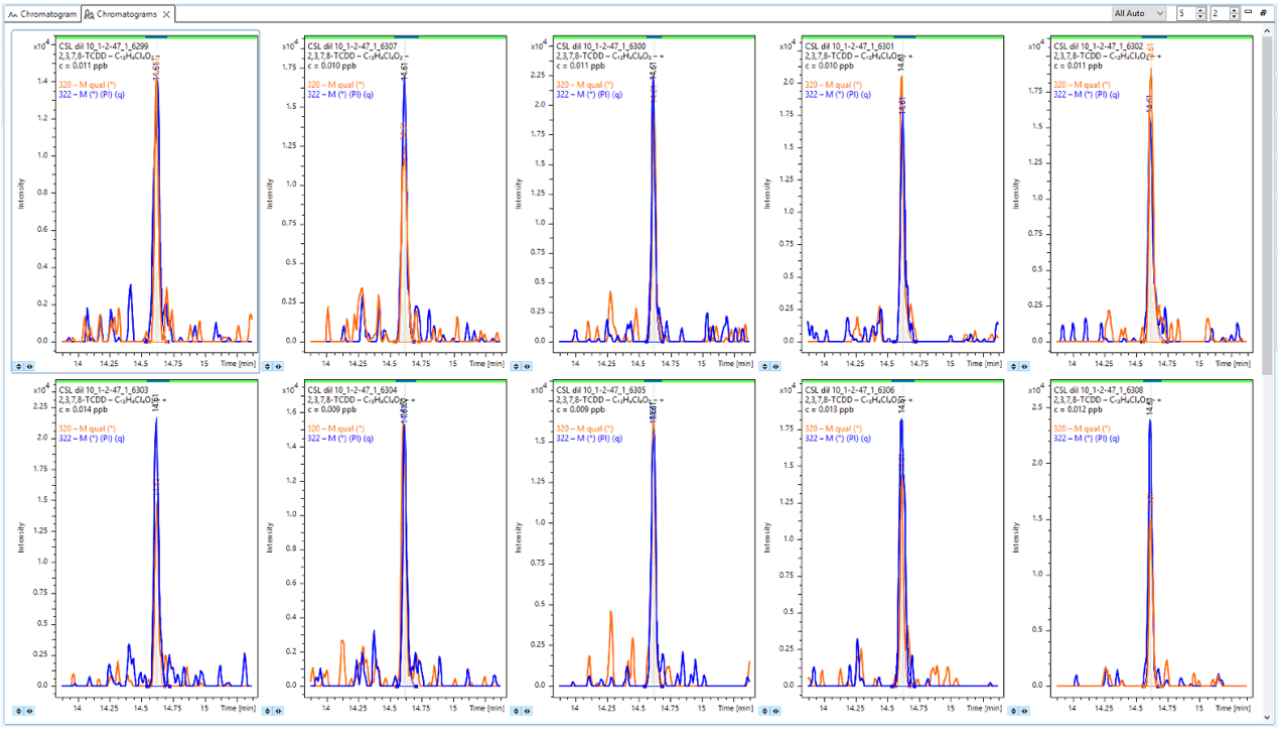


Figure 5. Ten replicates (1 µL) of 10 fg of 2,3,7,8-TCDD used to calculate the LOD.

Carry-over evaluation

According to the US EPA criteria, the analytical system must be free from sample carry-over as demonstrated through the injection of an appropriate sample blank following the sequential analyses. Immediately after the analysis of the verification QC of PCDDs/PCDFs and PCBs targets (CS3 standard level), a n-Nonane blank was injected. No peaks were detected. False positive identifications are highly improbable due to the method's automated data processing and multi-faceted detection criteria (MRSQC score). The high sensitivity of the system eliminates false negative identifications.

Analysis of food and environmental samples

Real food samples (rapeseed oil, palm fatty acid) as well as environmental extracts (fly ash and sewage sludge) spiked with several dioxin congeners have been analyzed to evaluate the method performance (sensitivity and selectivity) as well as the extraction procedure (recoveries of 13C internal standards).

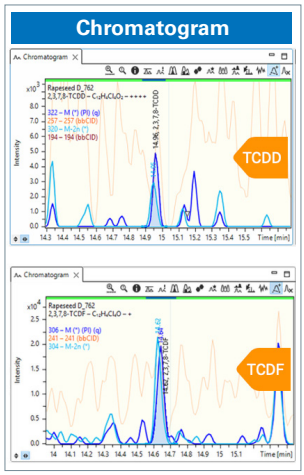
Because of the high sensitivity of the workflow, an extract of 4.66 g of rapeseed oil was diluted 3x with n-Nonane. 1 µL of this sample was injected into the GC-APCI-timsTOF system. Chromatograms and mobilograms of the detected amounts of 2,3,7,8-TCDD and 2,3,7,8-TCDF can be seen at values as low as 0.8 pg and 0.1 pg, respectively.

Example Rapeseed oil: High sensitivity

As an example, Figure 6 shows the results of the dioxin content in a rapeseed oil sample (recoveries of 13C internal standards).

Rapeseed oil

MRSQC	Analyte Name	Quantity [ppb]	Area of PI	Δm/z [mDa]	RT expected [min]	ΔRT [min]	Rel. RT
	2,3,7,8-TCDF	0.857	58,094	-0.55	14.70	-0.06	1.00
	2,3,7,8-TCDD	0.166	11,200	1.18	15.03	-0.07	1.00
	1,2,3,7,8-PeCDF	0.609	34,084	-0.66	17.01	-0.06	1.00
	2,3,4,7,8-PeCDF	0.679	46,981	-0.57	17.76	-0.06	1.00
	1,2,3,7,8-PeCDD	0.464	27,121	-0.44	17.89	-0.05	1.00
	1,2,3,4,7,8-HxCDF	0.759	33,851	-0.69	19.88	0.02	1.00
	1,2,3,6,7,8-HxCDF	1.645	53,822	-0.69	19.97	-0.06	1.00
	1,2,3,7,8,9-HxCDF	0.427	22,636	0.30	20.51	-0.06	1.00
	1,2,3,4,7,8-HxCDD	0.290	17,596	-1.19	20.57	0.02	1.00
	1,2,3,6,7,8-HxCDD	0.545	35,415	-1.19	20.64	-0.05	1.00
	1,2,3,7,8,9-HxCDD	0.268	10,146	-1.19	20.91	-0.31	0.99
	2,3,4,6,7,8-HxCDF	0.932	46,652	0.94	21.22	-0.25	0.99
	1,2,3,4,6,7,8-HpCDF	1.150	42,752	-1.19	22.48	-0.06	1.00
	1,2,3,4,6,7,8-HpCDD	3.099	79,862	1.25	23.60	-0.06	1.00
	1,2,3,4,7,8,9-HpCDF	0.139	6,377	-3.54	24.19	-0.06	1.00
	OCDD	6.857	108,076	0.82	27.30	-0.06	1.00
	OCDF	1.484	11,372	-1.92	27.53	-0.11	1.01



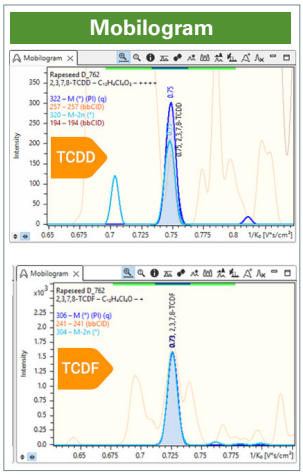


Figure 6. Results for dioxin contents in a rapeseed oil sample diluted 3x with n-Nonane (left). Chromatogram and mobilogram for the TCDD (0.1 pg) and TCDF (0.8 pg) detected (right). 4.66g of rapeseed oil sample was extracted and diluted 3 times with nonane before injection (1µL)

To report the results in Toxic Equivalent (TEQ), these values must be multiplied by their respective Toxic Equivalency Factors (TEF): TCDD=1 and TCDF= 0.07 [3].

Example Fly ash: Enhanced quantitation and identification

It is highly remarkable that adding the 4th dimension of ion mobility (mobilogram) as an additional filtering criterion removes most interferences and significantly improves the sensitivity and selectivity compared to traditional chromatographic separation. This can be observed even in a more significant way in Figure 7 showing the results of 2,3,7,8-TCDD and 2,3,7,8-TCDF in a fly ash sample. It is well known that environmental samples exhibit much more interferences than food samples in dioxin analyses. Here it is clearly visible that ion mobility can remove all interferences which are observed in the chromatogram. This allows for a more precise quantitation and more reliable identification of the target compounds.

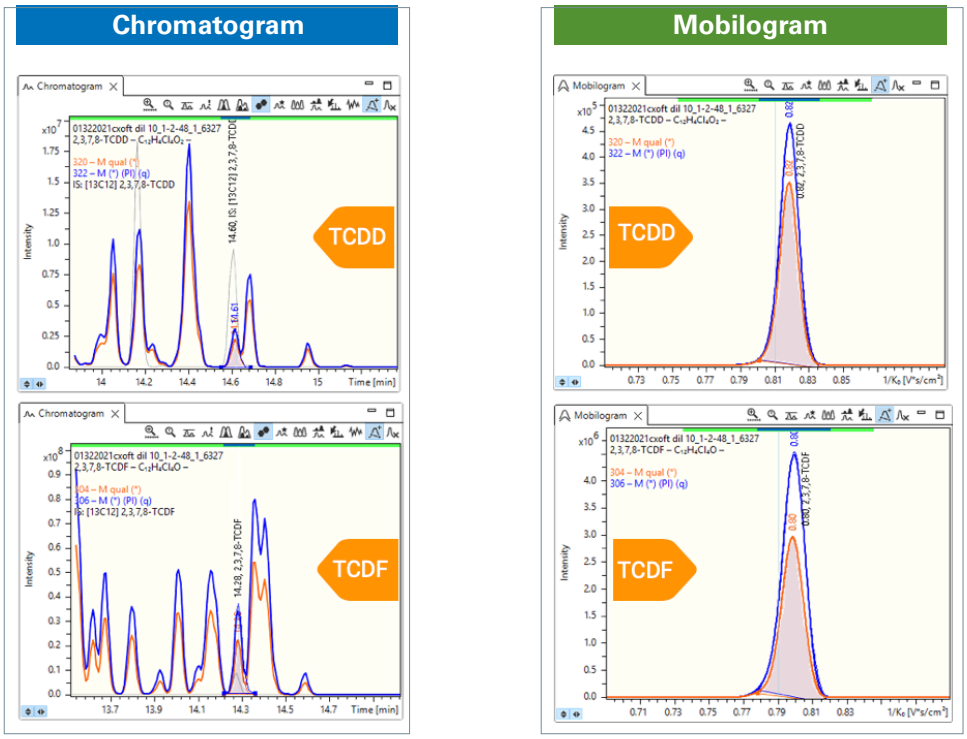


Figure 7. Analysis of dioxins content in a fly ash sample. Chromatograms (left) and mobilograms (right) for the 2,3,7,8-TCDD (top) and 2,3,7,8-TCDF (bottom). All interferences shown in the chromatogram are removed by adding the ion mobility filter (mobilogram).

Example Palm fatty acid: 13C Internal standard recovery meets European regulation

By adding a known amount of a labeled compound to every sample prior to extraction, a correction for the recovery of the dioxins can be achieved. In the case of European regulation, the recoveries for individual internal standards shall be in the range of 60 - 120% [4]. Figure 8 shows that the results for the recovery of the 13C internal standards in the palm fatty acid sample are within the limits of the European regulation.

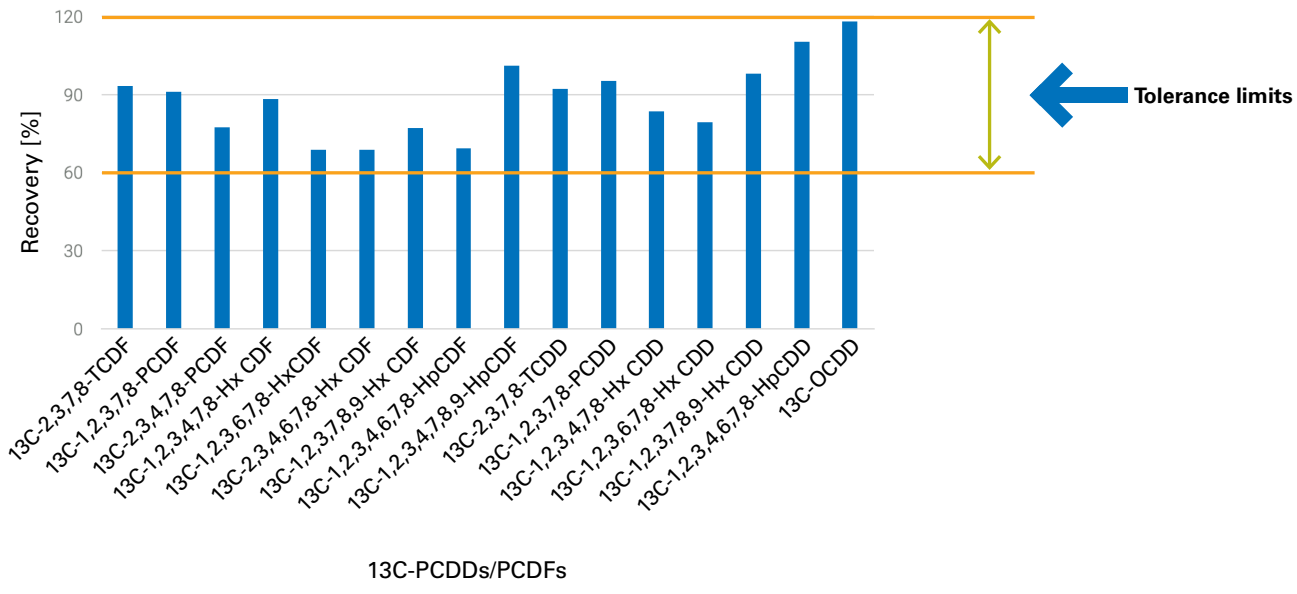


Figure 8. Recovery of 13C labeled analog PCDD/PCDF compounds in palm fatty acid are within 60-120% i.e. the limits of the EU regulation.

Comparison of results between GC-APCI-timsTOF and GC-HRMS magnetic sector instruments

An aliquot fraction of the rapeseed oil sample was sent to an external dioxin reference laboratory, where it was analyzed using a GC-HRMS magnetic sector system to compare the results with GC-APCI-timsTOF.

The results in Figure 9 demonstrate that both technologies yield entirely comparable data, even for a complex sample like rapeseed oil with low dioxin content.

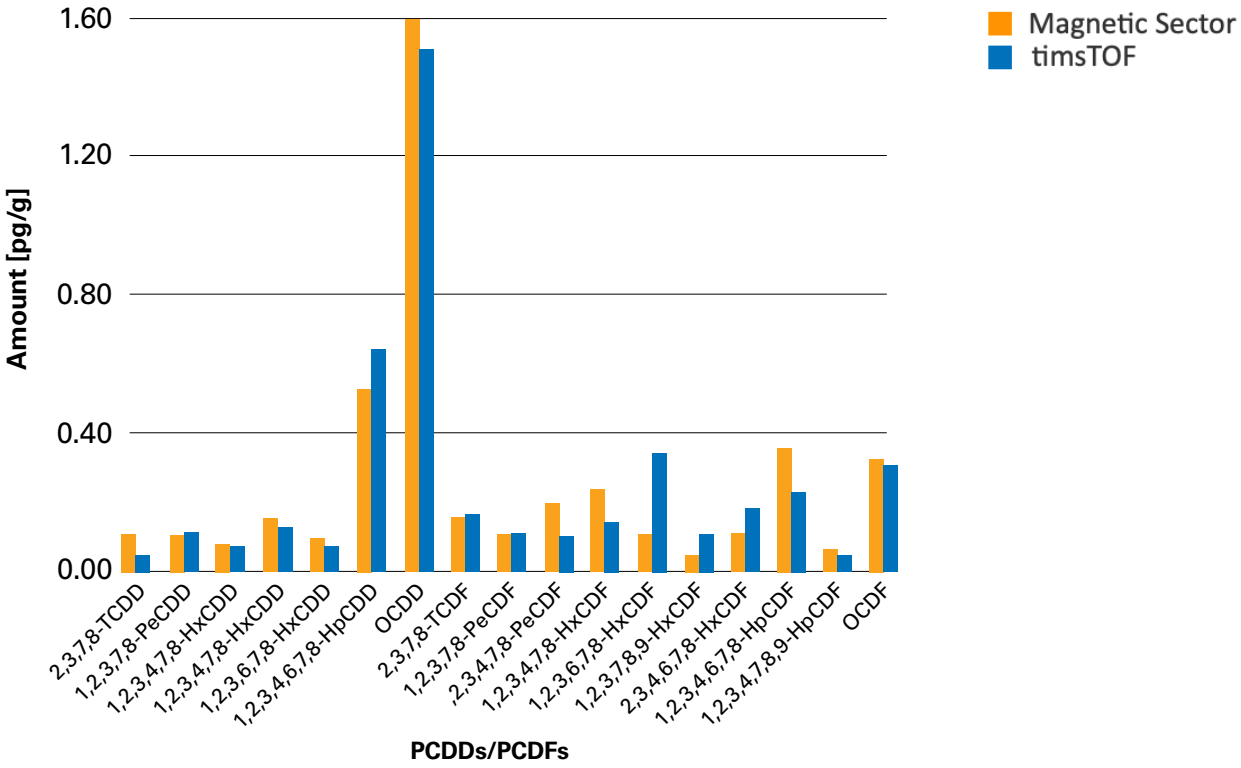


Figure 9. Comparison of PCDDs/PCDFs results [pg/g] in a rapeseed oil sample between GC-APCI-timsTOF and GC-HRMS magnetic sector.

Discussion

Adding the 4th dimension of ion mobility to GC-HRMS allows a precise quantitation and reliable identification of the PCDDs/PCDFs and dioxin-like PCBs in the low femtograms range for complex matrices and, as demonstrated within this study, supports the use of Bruker GC-APCI-timsTOF technology according to the globally important regulatory bodies.

Although this study has been focused on the analysis of dioxins, this technology can be expanded to the analysis of a wide range of legacy and new emerging halogenated persistent organic pollutants (POP) included in the Stockholm Convention list [1]. There is no practical limit to the number of compounds that can be accurately identified and quantified by GC-APCI-timsTOF.

This offers a unique flexibility for the Bruker GC-APCI-timsTOF compared to traditional instruments like the GC-HRMS magnetic sector. The demonstrated performance of the workflow with increased selectivity by ion mobility, a high resolution and high sensitivity has established the GC-APCI-timsTOF as a highly valuable analytical tool for both targeted and untargeted studies. Integrated quality control features within Bruker's TASQ software avoid false positive and false negatives and demonstrate the full compliance with governmental regulatory detection criteria.

As shown within this work, target screening requirements in environmental, food safety, occupational health, and toxicology settings can be confidently met via GC-APCI-timsTOF.

Conclusions

GC-APCI-timsTOF is well suited for the quantitative assessment of targeted PCDDs/PCDFs and dioxin-like PCBs in food and environmental samples:

- Exceeding all performance criteria of the to US EPA and EU regulations
- Reduction of potential isobaric interferences with matrix compounds in complex samples
- Outstanding LOD of low femtograms in real samples. Aside of a safe trace quantitation, the samples can be highly diluted for higher robustness and cost saving
- Less false positives/negatives with extensive QC parameters for each target compound, such as retention time, mass accuracy, diagnostic ions, isotopic pattern fidelity and collisional cross section (ion mobility) which are defined in the TASQ analysis software. Simple visualization of results using color-coded schemes.
- The preservation of molecular ions via APCI jointly with high resolution timsTOF analysis supports comprehensive suspect screening and unknown compound characterization in many sample types
- Analysis of a broad scope of POPs in complex matrices prepared for future regulation compliance and extensions

Acknowledgement

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References

[1] Stockholm Convention on Persistent Organic Pollutants (POPs): https://chm.pops.int

[2] US EPA Guidelines: 40 CFR Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit-Revision 2, July 1, 2023

[3] Regulatory Toxicology and Pharmacology 146 (2024) 105525

[4] EU 2017/771 of 3 May 2017 as regards the methods for the determination of the levels of dioxins and polychlorinated biphenyls.

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Bruker Switzerland AG

Fällanden · Switzerland
Phone +41 44 825 91 11

Bruker Scientific LLC

Billerica, MA · USA
Phone +1 (978) 663-3660

marketing.bams.emea@bruker.com - www.bruker.com

linkedin.com/company/brukerappliedmassspec