GC-APCI-QTOF MS for Detection of PCBs and PCDDs: Classic innovation to meet today's trace detection and target quantitation requirements

The reliable detection and quantitation of low-to-medium polarity persistent organic pollutants in food or environmental samples as required by governmental regulations can be readily made via GC-APCI-QTOF MS. High sensitivity is supported by the soft ionization characteristics of the APCI source, preserving molecular ions. Using QTOF MS for the detection and subsequent fragmentation of these ions provides high resolution, high value data for broad screening workflows. The analytical performance of this workflow is demonstrated to meet specific US EPA criteria both in standard solutions and in a complex fish tissue matrix.

Introduction

The development of analytical instrumentation to detect and confidently identify compounds of interest has progressively evolved along with the wide array of technological advances over the last decades. Certain "classic" techniques have more recently been recognized as high value elements to modern analytical workflows. Gas chromatography (GC) has been utilized as a means of sample separation since the late 1950s. Its applicability in analytical schemes is well established,

Keywords:
APCI, GC, QTOF MS, dioxins, persistent organic pollutants (POPs), pesticide detection, food and feed safety, environmental screening

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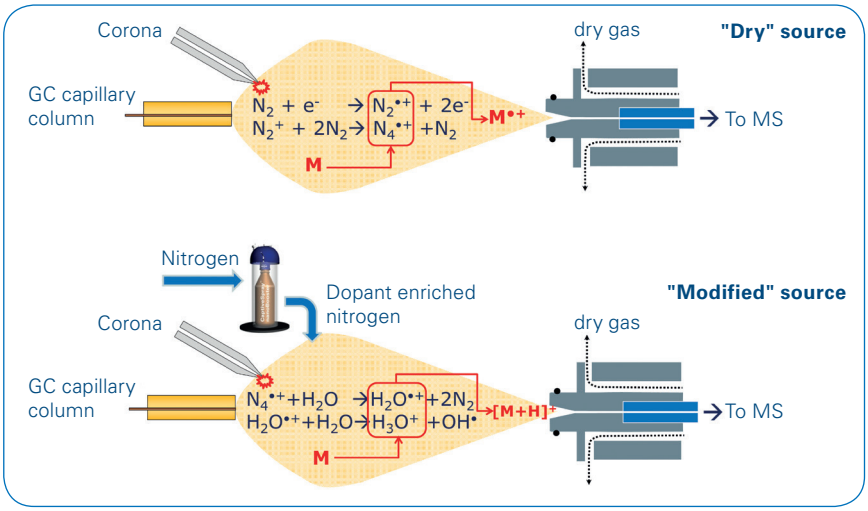


Figure 1: Principle of APCI. Ionization is made via charge transfer when using a "dry" source (top) and via protonation when using a "modified" source (bottom). APCI using a dry source is more suitable for non-polar compounds, while the modified source is more suitable for polar compounds.

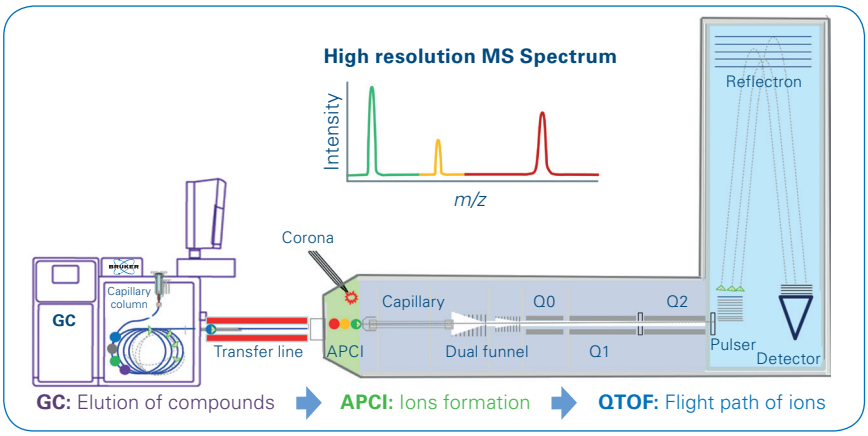


Figure 2: GC-APCI-QTOF schematics

benefiting from versatility of column chemistries and precision control of separatory temperature gradient programming, to support efficient and reproducible chromatographic resolution. Following compound separation, the identification and/or quantitation of target compounds typically relies on mass spectrometry (MS), along with some means of effluent ionization, traditionally under vacuum, to permit direct connection between the two instruments.

In recent years, the utility of GC coupled with atmospheric pressure chemical ionization (APCI) has been reintroduced. GC-APCI was developed in the mid-1970s by Dr. Evan Horning and his coworkers at The Institute for Lipid Research of the Baylor College of Medicine [1,2]. Via a transfer line, GC effluent is introduced into the APCI source chamber, where ionization is initiated (most typically) by a corona discharge. The APCI source chamber (Figure 1) may be used "dry," simply with N_2 carrier gas, forming highly reactive $N_2^{\bullet+}$ or $N_4^{\bullet+}$ species which predominantly result in the generation of $M^{\bullet+}$ molecular ions. The use of a dopant enriched nitrogen favors the formation of protonated molecular ions $[M+H]^+$. The dry approach is more suitable to non-polar target compounds, while the doped source can provide improved sensitivity for more polar compounds. Negative ions may also be generated in the APCI source by electron transfer or ion clustering processes.

In order to fully capitalize on the advantages of this separatory and ionization approach, a high resolution, high mass accuracy MS platform is required to anchor the analytical system (Figure 2). Quadrupole time-of-flight (QTOF) mass spectrometry meets this demand, while also enabling the detection of an unlimited number of compounds with high sensitivity across a broad dynamic range. Whether for targeted or discovery workflows, an extremely rich data set can be collected in minutes using alternating full scan and MS/MS acquisition modes.

In many GC-MS analyses, the more commonly used electron (impact) ionization (EI) results in significant target fragmentation within the ion source. Although extensive fragmentation can be valuable in the creation of pattern-based spectral libraries, lower resolution MS systems or co-eluting compounds may restrict confident identification. In contrast, APCI is a lower energy, "soft" ionization technique that maintains the parent molecular ion(s) and limits target fragmentation. This provides several key analytical advantages, including the high sensitivity necessary to detect lower abundant components (as mass accurate $M^{\bullet+}$ or $[M+H]^+$ species) within complex samples, and relatively simple fragmentation patterns (Figure 3). APCI-generated ions may then be subjected to controlled fragmentation within the QTOF MS to confirm target identity or characterize novel compounds. APCI is amenable to compounds of low to moderate polarity, up to ~1 kDa, including a much lower polarity range than that of traditional EI (Figure 4). These features support its use for the detection of broad classes of drugs, pesticides, and other environmental pollutants in toxicology, environmental, and food safety screening workflows.

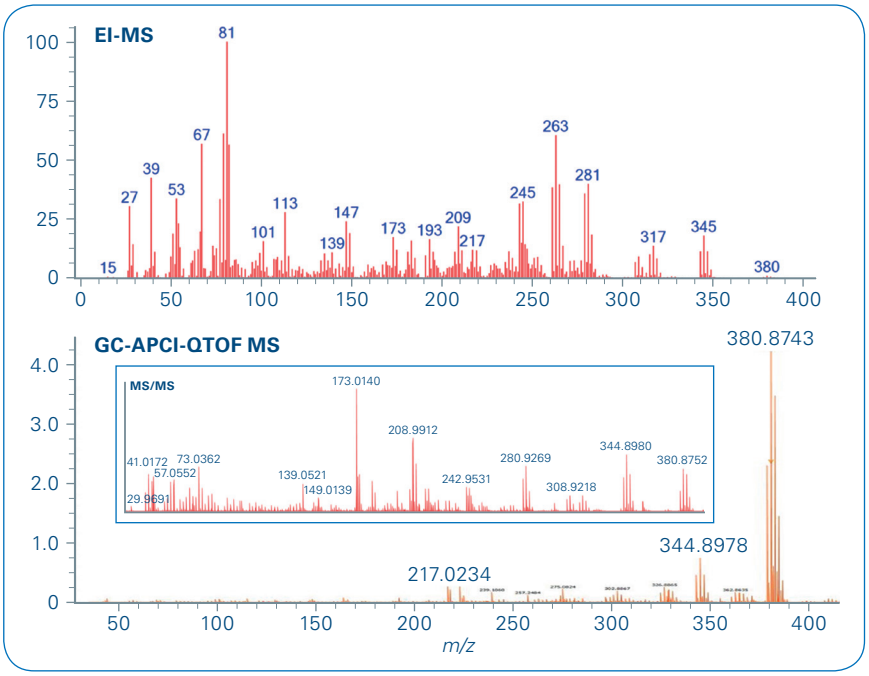
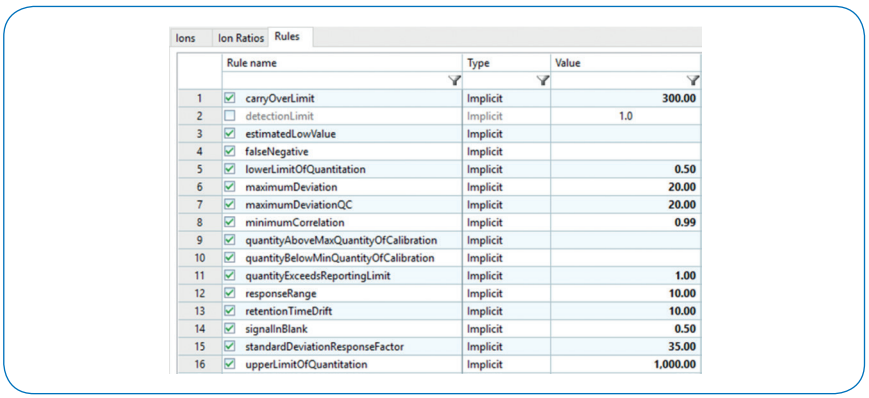


Figure 3: EI-MS and GC-APCI-QTOF MS spectra of endrin ($C_{12}H_8Cl_6O$), a banned herbicide. Using EI (top), the molecule is highly fragmented, such that no molecular ion is detected, and nominal masses are reported. Using GC-APCI-QTOF (bottom), the $M^{\bullet+}$ ion is prominent, the MS/MS fragmentation pattern (inset, collected simultaneously) is simplified, and all peaks are detected with high mass resolution.



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

Figure 5: TASQ software facilitates the definition of target evaluation criteria according to any regulatory directive requirements. Evaluation criteria for US EPA 1613B are shown.

This note describes the use of GC-APCI-QTOF MS for the determination of dioxin-like polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) according to analytical performance criteria of method EPA 1613B [3] in solution and in prepared fish tissue. These dioxin/dioxin-like compounds are considered Persistent Organic Pollutants (POPs), with detrimental and long-lasting effects on human and animal health [4]. Many are highly toxic and are subject to numerous governmental regulations across the globe. Unambiguous detection, method sensitivity, and quantitation capabilities are required for accurate monitoring, and these demands may be met via GC-APCI-QTOF mass spectrometry.

Materials and Methods

Targeted congeners of dioxin-like PCBs and PCDDs/PCDFs are shown in Table 1, along with their relative toxicities. Native and ^{13}C labelled targets in n-nonane (Wellington

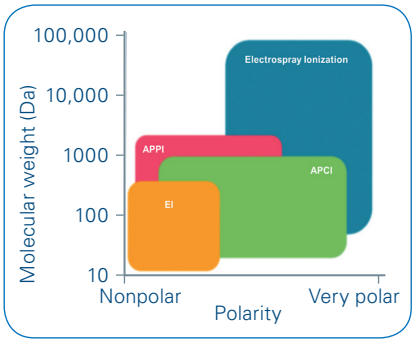


Figure 4: Ionization ability of different ion sources, indicating typical compound amenability and molecular weight ranges.

Laboratories) were analyzed by GC-APCI-QTOF MS at concentrations ranging from 0.5 - 2000 ng/mL. Fish tissue samples were spiked with a subset of the targeted compounds and prepared according to US EPA guidelines using Pressurized Fluids Extraction (PFE). Instrument conditions are detailed in Table 2.

Data screening and quantitation was made within TASQ (Target Analysis for Screening and Quantitation) software (Bruker Daltonics). All analytical performance criteria described in EPA 1613B were included within a custom method (Figure 5). Automatic mass filtering based on the expected molecular formulae was used (+/- 3 mDa). Within the TASQ software, MRSQ scores were automatically determined for each target compound, including values for mass accuracy, retention time, isotopic pattern fidelity, and the detection of (additional) diagnostic ions (Figure 6).

Results

Calibration Characteristics

The calibration curves had excellent linearity, with $R^2 > 0.998$ for all PCBs and $R^2 > 0.997$ for all PCDDs/PCDFs. The response factor (RF) RSD was <13.7% for the PCBs and <13.3% for the PCDDs/PCDFs (Figure 7). The EPA S/N criteria for the lowest calibration point (S/N ≥ 10) was achieved for all targets (Figure 8). A larger

mass deviation resulted in a lower MRSQ score for one targeted PCDD (1,2,3,6,7,8-HxCDD), although still falling within the wider limits established in the method and within the EPA method requirements.

% RSD and Recovery

Precision was calculated by the TASQ software for each isotopically labeled compound within the calibration batch, with each batch including five calibration levels. The RSD was <12.8% for all PCDD/PCDF compounds and <7.3% for all the PCB compounds (Figure 9). Using the median calibration concentration for each target, recoveries ranged from 98-115%. The RRT native/^{13}C ratios were from 1.00-1.01, and peak resolution was greater than 18,000 for all targets, easily meeting EPA method requirements (Figure 10).

LOD and LOQ

To experimentally calculate the signal-to-noise ratio (S/N), the lowest calibration level for PCDDs/PCDFs and PCBs was diluted 10-fold with n-nonane. As in previous analyses, 1μL was injected. As required within the referenced EPA criteria, two exact mass ions were detected for each target. As examples, the LOD/LOQ calculation for two target compounds are shown in Figure 11. The LOD for these targets was determined to be 50 fg on-column, with an LOQ of 150 fg on-column.

Carry-over evaluation

According to the EPA criteria, the analytical system used must be free from sample carry-over as demonstrated though the injection of an appropriate sample blank following sequential analyses. Immediately following the analysis of the calibration verification QC of PCDDs/PCDFs targets (median concentrations), an n-nonane blank was injected.

Table 1: Studied PCDD/PCDF and dioxin-like PCB congeners and their relative toxicities. Toxic Equivalency Factors (TEF) have been established by the WHO [5] to compare toxicity of dioxins relative to the most toxic TCDD (TEF=1).

Congener	WHO TEF
Dioxins (PCDDs)	
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0003
Furans (PCDFs)	
2,3,4,7,8-PeCDF	0.3
2,3,7,8-TCDF	0.1
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,7,8-PeCDF	0.03
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.0003

IUPAC N°	Congener	WHO TEF
Dioxin-like PCBs		
126	3,3',4,4',5-PeCB	0.1
169	3,3',4,4',5,5'-HxCB	0.03
81	3,4,4',5-TeCB	0.0003
77	3,3',4,4'-TeCB	0.0001
105	2,3,3',4,4'-PeCB	0.00003
114	2,3,4,4',5-PeCB	0.00003
118	2,3',4,4',5-PeCB	0.00003
123	2',3,4,4',5-PeCB	0.00003
156	2,3,3',4,4',5-HxCB	0.00003
157	2,3,3',4,4',5'-HxCB	0.00003
167	2,3',4,4',5,5'-HxCB	0.00003
189	2,3,3',4,4',5,5'-HpCB	0.00003

Table 2: Instrument conditions

Gas Chromatography	
Instrument	Bruker 436 GC
Carrier gas	Helium, 1.5 mL/min constant flow
Injector	1177 split/spitless, 280°C
Injection volume	1 μL, splitless
Insert	2 mm ID straight liner
Column	BR-Dioxin2, 60 m x 0.25 mm, 0.25 μm film thickness
Column temp. (PCBs)	120°C, hold 0.4 min; 190°C at 50°C min; 300°C at 2.75°C/min hold 0 min; 320°C at 20°C/min, hold 2.20 min
Column temp. (PCDDs/PCDFs)	120°C, hold 5 min; 250°C at 25°C min; 300°C at 3°C/min hold 15 min
Mass Spectrometry	
Instrument	Bruker impact II UHR QTOF
Source	GC-APCI
Head temp.	300°C
X-line temp.	280°C
Capillary	4,500 V
Corona	8000 nA
Drying gas	1.5 at 175°C
Nebulization pressure	2.4 bar
MS mode	Full Scan

No peaks were detected, meeting the analytical performance criteria established in the method. False positive identifications are highly improbable due to the method's automated data processing and multi-faceted detection criteria, and the sensitivity of the system eliminates false negative identifications.

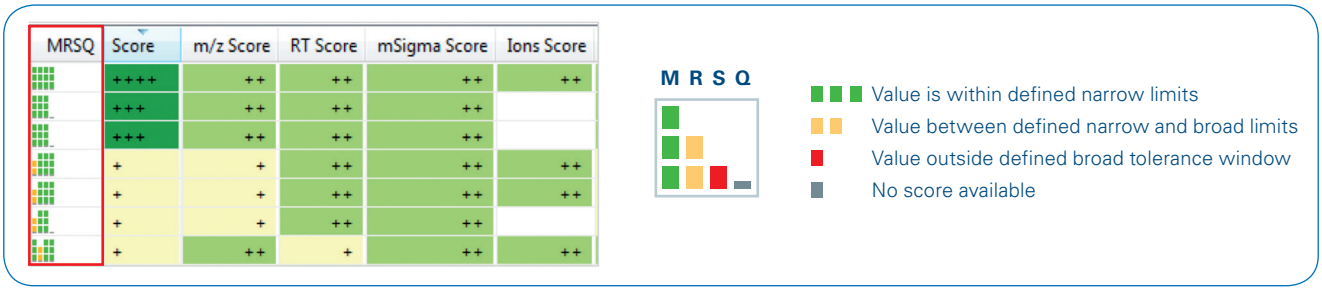


Figure 6: Pictorial, color coded depiction of analysis results within TASQ software. MRSQ scoring depends on key parameters of mass accuracy (M), retention time (R), mSigma scores of isotopic fidelity (S), and the presence of qualifier diagnostic ions (Q). This multi-feature scoring eliminates false positive and false negative results.*

**mSigma scores use a scale of 0-1000, where lower values indicate a better fit to theoretical isotopic patterns.*

Fish tissue analysis

Three PCDDs/PCDFs were simultaneously identified and quantitated by GC-APCI-QTOF MS in the fish tissue extract. Using alternate GC column temperature gradient conditions (Table 2), twelve PCBs were likewise simultaneously identified and quantitated. All identification criteria were met according to the referenced EPA guidelines (Figures 12 and 13). The high resolution and mass accuracy of this instrument configuration enables high selectivity in complex sample matrices, such as animal tissue.

Discussion

The detection and quantitation of the PCDDs/PCDFs and dioxin-like PCBs demonstrated within this study supports the use of GC-APCI-QTOF MS in regulated environmental screening workflows. This technique has also been shown to be effective in the analysis of food packaging contaminants [6,7], other classes of pesticides [8], and drugs of abuse [9]. Although only a small, specific group of toxic pollutants were targeted in this study, other known compounds of interest may be retrospectively sought within the simultaneously collected MS and MS/MS data pool.

Using Bruker's impact II QTOF MS, there is no practical limit to the number of targets that may be sought and identified. This detection capability, with demonstrated high resolution and high sensitivity, has established QTOF MS as a highly valuable analytical tool for both targeted and untargeted screening approaches. Integrated quality control elements within Bruker's TASQ software avoid false positive and false negatives and demonstrate compliance to

Analysis Results | Batch Results | Calibration Data Point | Calibration Functions

Row	Analyte Name	Formula	Function T...	Origin	Weighting	R^2	No. of data points	RSD RF
1	1,2,3,4,6,7,8-HpCDD	$C_{12}HCl_7O_2$	Linear	Ignore	1/x	0.99941	5	7.63
2	1,2,3,4,6,7,8-HpCDF	$C_{12}HCl_7O$	Linear	Ignore	1/x	0.99980	5	6.86
3	1,2,3,4,7,8,9-HpCDF	$C_{12}HCl_7O$	Linear	Ignore	1/x	0.99828	5	8.70
4	1,2,3,4,7,8-HxCDD	$C_{12}H_2Cl_6O_2$	Linear	Ignore	1/x	0.99996	5	9.68
5	1,2,3,4,7,8-HxCDF	$C_{12}H_2Cl_6O$	Linear	Ignore	1/x	0.99940	5	9.60
6	1,2,3,6,7,8-HxCDD	$C_{12}H_2Cl_6O_2$	Linear	Ignore	1/x	0.99967	5	8.61
7	1,2,3,6,7,8-HxCDF	$C_{12}H_2Cl_6O$	Linear	Ignore	1/x	0.99862	5	13.3
8	1,2,3,7,8,9-HxCDD	$C_{12}H_2Cl_6O_2$	Linear	Ignore	1/x	0.99948	5	11.1
9	1,2,3,7,8,9-HxCDF	$C_{12}H_2Cl_6O$	Linear	Ignore	1/x	0.99911	5	8.34
10	1,2,3,7,8-PeCDD	$C_{12}H_3Cl_5O_2$	Linear	Ignore	1/x	0.99797	5	12.1
11	1,2,3,7,8-PeCDF	$C_{12}H_3Cl_5O$	Linear	Ignore	1/x	0.99983	5	7.39
12	2,3,4,6,7,8-HxCDF	$C_{12}H_2Cl_6O$	Linear	Ignore	1/x	0.99885	5	12.6
13	2,3,4,7,8-PeCDF	$C_{12}H_3Cl_5O$	Linear	Ignore	1/x	0.99934	5	7.40
14	2,3,7,8-TCDD	$C_{12}H_4Cl_4O_2$	Linear	Ignore	1/x	0.99950	5	4.09
15	2,3,7,8-TCDF	$C_{12}H_4Cl_4O$	Linear	Ignore	1/x	0.99925	5	5.42
16	OCDD	$C_{12}Cl_8O_2$	Linear	Ignore	1/x	0.99863	5	5.37
17	OCDF	$C_{12}Cl_8O$	Linear	Ignore	1/x	0.99933	5	5.70

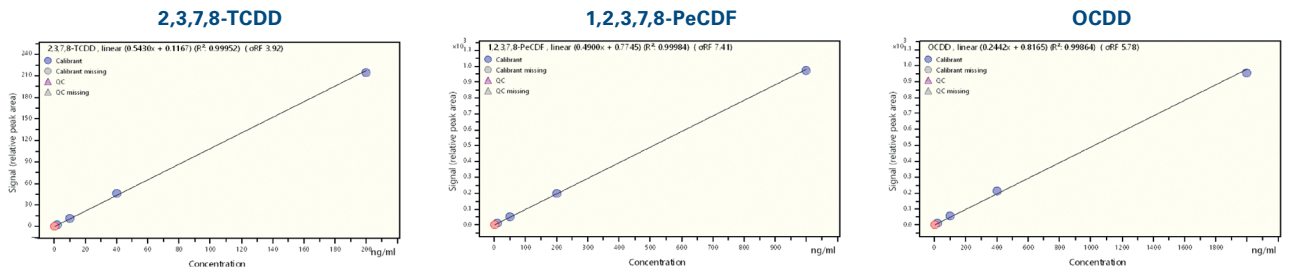


Figure 7: Automated generation of individual PCDD/PCDF calibration curves, demonstrating excellent R^2 values and low RSDs for all compounds

PCDDs/PCDFs

	Score	Flag	Analyte	RT Score	ΔRT [min]	m/z Score	Δm/z [mDa]	Ions Score	Exp.Diag.Ions	Area	S/N
1	++++		1,2,3,4,6,7,8-HpCDD	++	-0.00	++	0.87	++	1	43030	71
2	++++		1,2,3,4,6,7,8-HpCDF	++	-0.00	++	0.02	++	1	58733	111
3	++++		1,2,3,4,7,8,9-HpCDF	++	0.00	++	-0.14	++	1	40167	58
4	++++		1,2,3,4,7,8-HxCDD	++	0.00	++	0.61	++	1	66725	62
5	++++		1,2,3,4,7,8-HxCDF	++	-0.00	++	-1.03	++	1	90327	18
6	+		1,2,3,6,7,8-HxCDD	++	-0.00	+	2.16	++	1	65919	16
7	++++		1,2,3,6,7,8-HxCDF	++	-0.00	++	1.05	++	1	93942	17
8	++++		1,2,3,7,8,9-HxCDD	++	0.00	++	0.32	++	1	71964	38
9	++++		1,2,3,7,8,9-HxCDF	++	0.00	++	1.04	++	1	86630	22
10	++++		1,2,3,7,8-PeCDD	++	0.00	++	0.05	++	1	104771	57
11	++++		1,2,3,7,8-PeCDF	++	-0.00	++	0.23	++	1	108558	168
12	++++		2,3,4,6,7,8-HxCDF	++	0.00	++	1.04	++	1	103516	16
13	++++		2,3,4,7,8-PeCDF	++	0.07	++	0.71	++	1	101456	96
14	++++		2,3,7,8-TCDD	++	0.00	++	0.32	++	1	22506	40
15	++++		2,3,7,8-TCDF	++	0.01	++	-0.21	++	1	26338	53
16	++++		OCDD	++	-0.01	++	0.92	++	1	37778	17
17	++++		OCDF	++	-0.00	++	-1.18	++	1	39762	13

PCBs

	Score	Analyte	RT Score	ΔRT [min]	m/z Score	Δm/z [mDa]	Ions Score	Exp.Diag.Ions	Area	S/N
1	++++	PCB189	++	0.00	++	1.67	++	1	21159	475
2	++++	PCB 81	++	0.00	++	0.59	++	1	33108	262
3	++++	PCB 167	++	0.03	++	0.51	++	1	32547	441
4	++++	PCB 77	++	0.00	++	0.34	++	1	39201	306
5	++++	PCB 123	++	0.00	++	0.25	++	1	35311	222
6	++++	PCB 105	++	0.00	++	0.09	++	1	34645	263
7	++++	PCB 126	++	0.00	++	-0.02	++	1	22851	262
8	++++	PCB 157	++	0.00	++	-0.43	++	1	17617	86
9	++++	PCB 156	++	-0.00	++	-0.44	++	1	21790	166
10	++++	PCB 114	++	0.00	++	-0.69	++	1	34406	68
11	++++	PCB 118	++	0.00	++	-0.72	++	1	33016	77
12	++++	PCB 169	++	0.00	++	-1.11	++	1	19069	100

Figure 8: Summary of PCB and PCDD/PCDF compounds at lowest calibration level. All S/N values are greater than 10, meeting EPA method requirements.

PCDDs/PCDFs

Row	Analytes	%RSD	Mean	Median	Std.Dev.	Minimum	Maximum	No. of Datapoints
1	[13C12] OCDD	12.76	100.0	95.79	12.763	85.50	119.1	5
2	[13C12] 2,3,7,8-TCDF	5.79	100.0	100.0	5.7895	92.66	106.8	5
3	[13C12] 2,3,7,8-TCDD	6.54	100.0	100.8	6.5435	91.59	109.3	5
4	[13C12] 2,3,4,7,8-PeCDF	3.55	100.0	99.26	3.5487	95.89	105.2	5
5	[13C12] 2,3,4,6,7,8-HxCDF	6.14	100.0	99.53	6.1354	93.70	108.3	5
6	[13C12] 1,2,3,7,8-PeCDF	2.95	100.0	100.8	2.9506	95.97	103.4	5
7	[13C12] 1,2,3,7,8-PeCDD	6.06	100.0	100.8	6.0616	91.08	108.0	5
8	[13C12] 1,2,3,7,8,9-HxCDF	7.85	100.0	97.40	7.8476	90.86	110.4	5
9	[13C12] 1,2,3,7,8,9-HxCDD	7.15	100.0	102.6	7.1465	89.93	107.8	5
10	[13C12] 1,2,3,6,7,8-HxCDD	3.89	100.0	99.18	3.8939	94.57	104.6	5
11	[13C12] 1,2,3,6,7,8-HxCDF	6.95	100.0	100.6	6.9480	88.92	105.9	5
12	[13C12] 1,2,3,4,7,8-HxCDF	4.22	100.00	99.28	4.2223	93.86	104.6	5
13	[13C12] 1,2,3,4,7,8-HxCDD	8.59	100.0	104.2	8.5925	87.05	107.2	5
14	[13C12] 1,2,3,4,7,8,9-HpCDF	9.92	100.0	99.64	9.9191	88.18	114.4	5
15	[13C12] 1,2,3,4,6,7,8-HpCDF	7.90	100.0	98.61	7.8986	89.21	109.3	5
16	[13C12] 1,2,3,4,6,7,8-HpCDD	10.44	100.00	104.0	10.440	84.48	111.0	5

PCBs

Row	Analytes	%RSD	Mean	Median	Std.Dev.	Minimum	Maximum	No. of Datapoints
1	[13C12] PCB 81	7.29	100.0	99.21	7.2867	92.46	108.8	5
2	[13C12] PCB 77	3.83	100.0	98.79	3.8299	96.36	105.2	5
3	[13C12] PCB 189	3.46	100.0	100.2	3.4572	95.28	105.0	5
4	[13C12] PCB 169	4.58	100.0	101.0	4.5819	93.40	104.8	5
5	[13C12] PCB 167	2.88	100.0	100.3	2.8785	95.26	102.9	5
6	[13C12] PCB 157	6.07	100.0	98.12	6.0742	93.24	107.8	5
7	[13C12] PCB 156	4.82	100.0	101.5	4.8170	91.77	103.6	5
8	[13C12] PCB 126	2.99	100.0	99.79	2.9907	96.65	104.0	5
9	[13C12] PCB 123	1.77	100.0	99.44	1.7680	98.29	102.1	5
10	[13C12] PCB 118	1.57	100.0	99.51	1.5702	98.50	102.5	5
11	[13C12] PCB 114	1.81	100.0	101.1	1.8125	97.63	101.5	5
12	[13C12] PCB 105	2.33	100.0	99.91	2.3316	97.04	102.6	5

Figure 9: % RSD values for ^{13}C labelled analogs of targeted compounds using GC-APCI-QTOF MS.

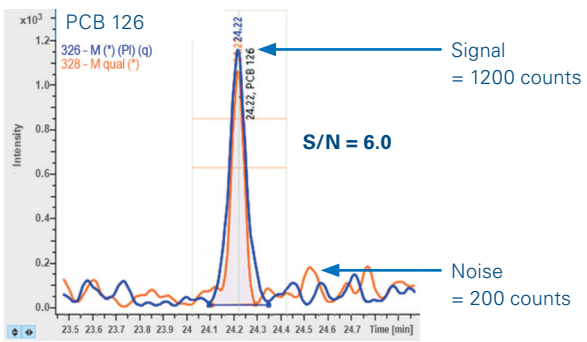
PCDDs/PCDFs

Analysis Results

	MRSQ	Analyte Name	ΔRT [min]	Area of PI	Quantity [ng/ml]	Accuracy [%]	Δm/z [mDa]	Resolution	Rel. RT	mSigma
1		1,2,3,4,6,7,8-HpCDD	-0.00	1072610	56.0	112.04	0.01	29089	1.00	66.7
2		1,2,3,4,6,7,8-HpCDF	-0.00	1247843	55.8	111.56	0.86	28487	1.00	79.8
3		1,2,3,4,7,8,9-HpCDF	0.02	913244	55.2	110.32	0.56	46903	1.00	64.3
4		1,2,3,4,7,8-HxCDD	-0.00	1354556	49.1	98.13	0.68	25709	1.00	33.5
5		1,2,3,4,7,8-HxCDF	-0.00	1618187	56.2	112.32	0.63	18124	1.00	32.6
6		1,2,3,6,7,8-HxCDD	-0.00	1457162	52.3	104.59	0.53	28928	1.00	33.8
7		1,2,3,6,7,8-HxCDF	-0.00	1717513	57.5	114.92	0.68	28832	1.00	32.4
8		1,2,3,7,8,9-HxCDD	-0.01	1505842	54.2	108.37	0.53	24455	1.00	33.5
9		1,2,3,7,8,9-HxCDF	-0.00	1654419	59.0	118.00	0.34	28497	1.00	32.4
10		1,2,3,7,8-PeCDD	-0.00	1904543	55.0	109.99	0.81	28432	1.00	18.7
11		1,2,3,7,8-PeCDF	-0.01	2298951	54.7	109.30	0.70	28432	1.00	6.5
12		2,3,4,6,7,8-HxCDF	-0.00	1719257	57.7	115.45	0.76	22772	1.00	32.9
13		2,3,4,7,8-PeCDF	0.07	2079077	55.7	111.31	0.79	28077	1.00	6.5
14		2,3,7,8-TCDD	-0.00	504481	10.8	107.77	0.37	23935	1.00	165.2
15		2,3,7,8-TCDF	-0.00	535202	9.9	99.44	0.21	26462	1.00	13.3
16		OCDD	0.01	837197	109.6	109.55	0.22	23500	1.00	98.4
17		OCDF	0.01	917310	113.1	113.07	0.19	21207	1.01	98.1

Figure 10: Target recovery analysis of PCDD/PCDF compounds using the median calibration level standard (CS3). MRSQ results indicate high confidence matches to targets compounds, and characteristics meet EPA method requirements.

CS0.1=0.1 pg/µL



CS0.1=0.05 pg/µL

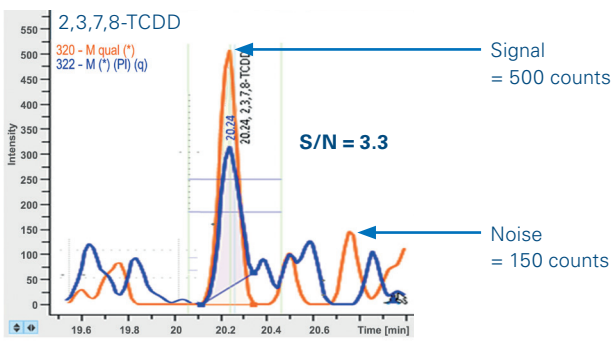


Figure 11: S/N calculation for target LOD determination. 1 µL sample injected.

governmental regulatory detection criteria. Although sample separation and introduction have been traditionally made via HPLC and sample ionization via electrospray, well-suited for more polar compounds, the utility of this MS platform to detect and quantitate a wider array of compound classes and sample types may be dramatically extended with the use of a GC-APCI interface. The exchange of ion sources can be made without system venting and with virtually no instrument downtime, supporting rapid turn-around times for result reporting. As shown within this study, target screening requirements in environmental, food safety, occupational health, and toxicology settings can be confidently met via GC-APCI-QTOF MS.

Further reading:

https://www.bruker.com/products/mass-spectrometry-and-separations/targetscreener-hr.html

https://www.bruker.com/products/mass-spectrometry-and-separations/lc-ms/ion-sources/captivespray-nanobooster/overview.html

PCDDs/PCDFs

Calibration Data Point | Batch Results | Analysis Results

	MRSQ	Analyte Name	RT Score	RT [min]	m/z Score	Δm/z [mDa]	Ions Score	Found.Diag.Ions	mSigma Score	Quantity
1		2,3,4,7,8-PeCDF	++	24.26	++	0.65	++	1	++	1.0 ng/ml
2		2,3,7,8-TCDD	++	20.24	++	0.12	++	1	++	1.1 ng/ml
3		2,3,7,8-TCDF	++	19.76	++	0.52	++	1	++	1.8 ng/ml

PCBs

Calibration Data Point | Batch Results | Analysis Results | Chromatograms

	MRSQ	Analyte Name	RT Score	RT [min]	m/z Score	Δm/z [mDa]	Ions Score	Found.Diag.Ions	mSigma Score	Quantity
1		PCB 105	++	22.97	++	0.25	++	1	++	1561.1 ng/ml
2		PCB 114	++	22.36	++	0.17	++	1	++	155.5 ng/ml
3		PCB 118	++	21.95	++	0.22	++	1	++	3411.3 ng/ml
4		PCB 123	++	21.73	++	0.24	++	1	++	578.4 ng/ml
5		PCB 126	++	24.23	++	0.06	++	1	++	26.2 ng/ml
6		PCB 156	++	24.52	++	0.20	++	1	++	1527.6 ng/ml
7		PCB 157	++	25.34	++	0.09	++	1	++	447.1 ng/ml
8		PCB 167	++	18.82	++	0.36	++	1	++	10.4 ng/ml
9		PCB 169	++	25.45	++	-0.03	++	1	++	145.4 ng/ml
10		PCB 77	++	21.22	++	0.20	++	1	++	72.7 ng/ml
11		PCB 81	++	20.81	++	0.33	++	1	++	12.8 ng/ml
12		PCB189	++	21.94	++	0.18	++	1	++	7.0 ng/ml

Figure 12: Analysis results for fish tissue extract screening by GC-APCI-QTOF MS. Three PCDDs/PCDFs and twelve PCBs were identified and quantitated within the sample. Color-coded MRSQ scoring indicates all targets are matched within the narrow limits defined in the analysis method.

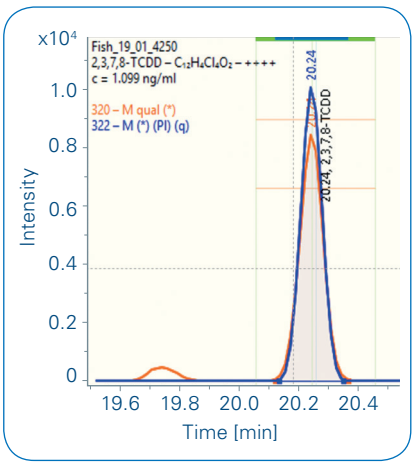


Figure 13: Example mass filtered (+/- 3mDa) EIC chromatogram of targeted analysis of fish tissue extract by GC-APCI-QTOF MS. The dioxin 2,3,7,8-TCDD was identified.

Conclusion

- GC-APCI-QTOF MS is well suited for the quantitative assessment of targeted PCDDs/PCDFs and dioxin-like PCBs in aqueous and animal tissue samples, exceeding all performance criteria according to EPA-1613B requirements.
- Extensive QC parameters for each target compound, including retention time, mass accuracy, ion ratios, and isotopic pattern fidelity, are defined within the TASQ analysis software, with results easily visualized using color-coded schematics.
- GC-APCI-QTOF MS is a robust and easy-to-use technology for the study of many compound classes, including persistent organic pollutants (POPs). In addition to enabling precise target quantitation, the preservation of molecular ions via APCI together with high resolution QTOF MS analysis supports comprehensive suspect screening and unknown compound characterization in many sample types.

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