Application Note

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Instrument: Pegasus® BTX 4D

Determination of OCPs and PCBs in Sediments Using SPE-GCxGC-TOFMS

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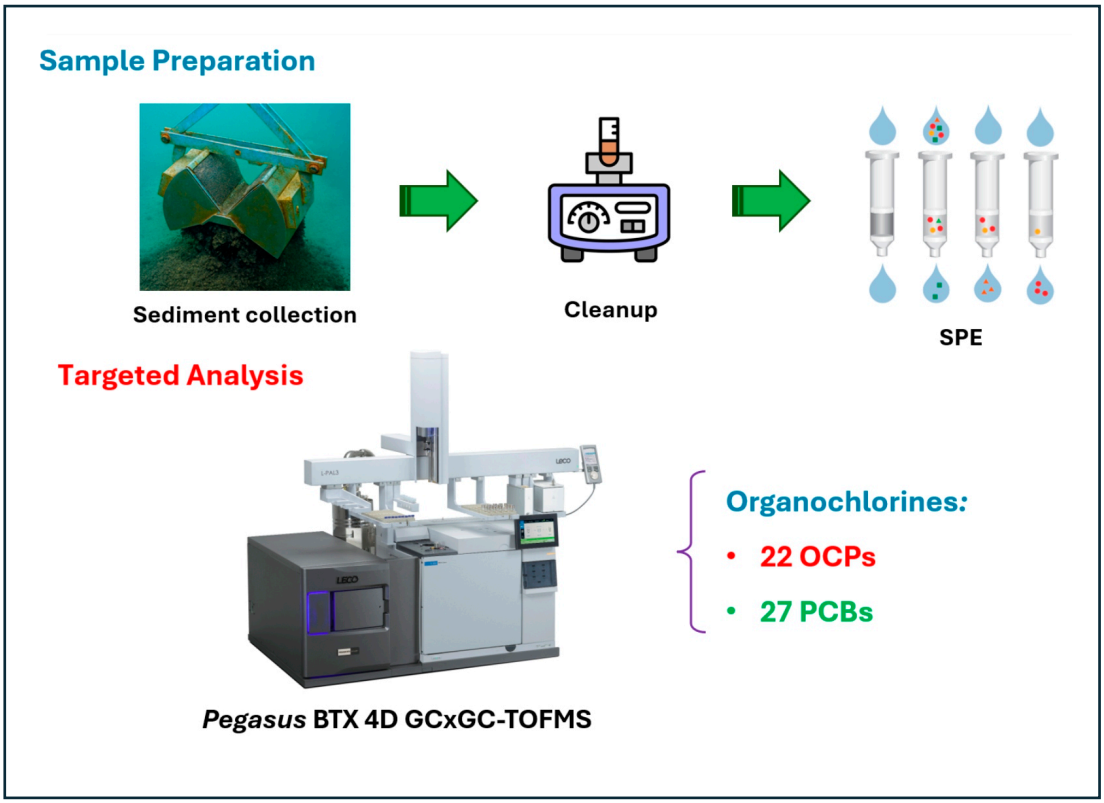
Introduction

Persistent organic pollutants (POPs), including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), represent significant environmental and public health concerns due to their persistent nature, potential for bioaccumulation, and toxicological effects. Despite regulatory controls, these contaminants remain detectable in environmental compartments—including sediments and soils—which serve as long-term reservoirs and secondary sources of pollution. Consequently, reliable analytical monitoring of these compounds at ultra-trace concentrations in complex matrices is necessary for environmental assessment and regulatory compliance.[1]

Conventional analytical approaches employing traditional gas chromatography (GC) techniques, often coupled with first-order detection methods (e.g., flame ionization detector, electron capture detector, thermal conductivity detector), may be insufficient to resolve highly complex mixtures typically encountered in environmental samples, especially when targeting numerous structurally similar analytes. To overcome these analytical limitations, comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GCxGC-TOFMS) has emerged as a robust alternative. This technology offers significantly enhanced separation capability, improved sensitivity, and greater peak resolution compared to conventional methods, thereby facilitating the simultaneous identification and quantification of multiple analytes.[2]

This application note describes an analytical workflow that utilizes solid-phase extraction (SPE) for the cleanup and enrichment of sediment samples prior to analysis by GCxGC-TOFMS using the LECO *Pegasus* BTX 4D system. The protocol focuses on the simultaneous determination of multiple target OCPs and PCBs, addressing the analytical requirements associated with complex environmental matrices and regulatory criteria.



Experimental

Certified standards used for calibration included 49 organochlorine compounds (22 OCPs and 27 PCBs). An external standard calibration method was developed and validated for each target compound. Calibration solutions at concentrations ranging from 0.10 to 1.96 ng kg^{-1} were prepared from certified standards (Ultra PPM-5090-1 and Ultra RPCM-240-1) along with the internal standard (decachlorobiphenyl, 0.98 ng kg^{-1}). The solutions were analyzed by GCxGC-TOFMS, and calibration curves were constructed by normalizing each analyte's peak area to that of the internal standard and plotting the resulting ratios against concentration. The analyte concentrations in the sediment extracts were subsequently determined by interpolation from these calibration curves.

Sediment samples were prepared using SPE for cleanup and pre-concentration, following modified protocols based on EPA Methods 3550B, 3660B, and 3620C.[3–5] Briefly, sediment samples (5 g, lyophilized) underwent sequential ultrasonic extraction (3 x 10 min) using 20 mL of an acetone:hexane mixture (1:1, v/v). Extracts were pooled, concentrated under a nitrogen stream to a final volume of approximately 1 mL, and subjected to sulfur cleanup via TBA sulfite treatment. The extracts were further purified using Florisil SPE cartridges, eluted with 9 mL of an acetone:hexane (10:90, v/v) mixture, concentrated, reconstituted to 1.0 mL with hexane, and spiked with 20 µL of internal standard (decachlorobiphenyl, 1000 µg mL^{-1} in hexane) prior to GCxGC-TOFMS analysis.

The analyses were conducted on a *Pegasus* BTX 4D GCxGC-TOFMS equipped with a QuadJet™ dual-stage cryogenic modulator. Data were acquired and processed using ChromaTOF® software. Table 1 summarizes the GCxGC-TOFMS analytical conditions employed in this study.

Table 1. Instrumental parameters for GCxGC-TOFMS analysis.

Gas Chromatograph	**LECO GCxGC with QuadJet™ Thermal Modulator**
Inlet (MMI)	2 µL Cold Splitless (1.25 min), 40 °C (0.05 min) 720 °C/min to 300 °C
Carrier Gas	Helium 1.4 mL/min
Columns	^{1}D: HP-5ms Ultra Inert (30 m x 0.25 mm x 0.25 µm) ^{2}D: Rxi-17SilMS (1.3 m x 0.25 mm x 0.25 µm)
Oven Program	45 °C (1.25 min), ramp 5 °C/min to 330 °C (5 min)
Secondary Oven Temp	+10 °C (relative to the GC oven temperature)
Modulator Temp	+15 °C (relative to the secondary oven temperature)
Modulation Period	2.8 s
Transferline Temperature	330 °C
TOFMS	**LECO *Pegasus* BTX 4D**
Ion Source Temperature	250 °C
Mass Range (*m/z*)	29–600
Acquisition Rate	150 Hz

Results and Discussion

The analytical method combining SPE with GCxGC-TOFMS provided effective separation and quantification of the 49 targeted analytes (22 organochlorine pesticides and 27 PCBs).[6] Figure 1 illustrates the high-resolution chromatographic separation achieved with the LECO *Pegasus* BTX 4D system for a standard calibration mixture.

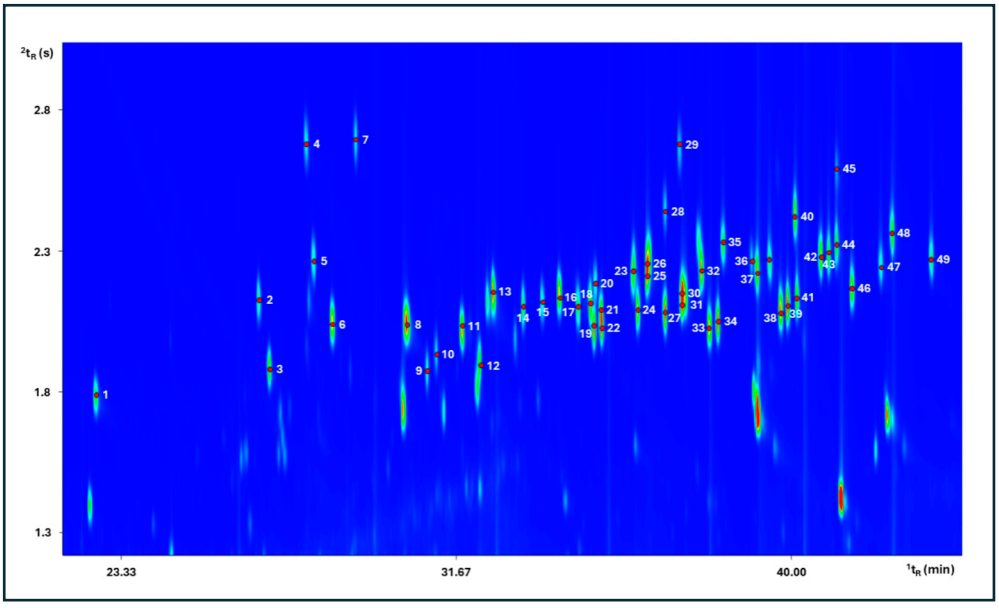


Figure 1. GCxGC-TOFMS 2D TIC plot of the calibration standard mixture. Target OCPs and PCBs are labeled by number.

The performance of the analytical method was evaluated by assessing linearity, limits of detection (LOD), limits of quantification (LOQ), accuracy, and precision (Table 2). Calibration curves demonstrated excellent linearity ($r^2 > 0.99$) across the investigated concentration range (0.10 to 1.96 ng kg-1). Exceptionally low detection and quantification limits were achieved, effectively addressing the analytical requirements outlined in international environmental guidelines and standards.

Table 2. Quantification values for target organochlorine compounds analyzed by GCxGC-TOFMS.

#	Target	r^2	LOD (ng kg^{-1})	LOQ (ng kg^{-1})	Accuracy (%)[a]	Precision (%)[b]
1	Pentachlorobenzene (PeCB)	0.9999	4.0	12.0	97	2.7
2	α-BHC	0.9984	3.0	9.1	102	2.7
3	Hexachlorobenzene	0.9996	6.1	18.0	106	3.5
4	ß-BHC	0.9988	4.3	12.0	96	3.1
5	γ-BHC	0.9956	1.8	5.4	98	1.7
6	PCB-18	0.9997	3.0	9.0	99	1.9
7	δ-BHC	0.9982	2.3	6.8	114	1.7
8	PCB-28	0.9994	4.1	13.0	98	2.8
9	Heptachlor	0.9920	4.1	12.0	109	4.5
10	Alachlor	0.9986	0.9	2.6	99	1.8
11	PCB-52	0.9980	4.4	13.0	103	2.8
12	Aldrin	0.9998	1.0	3.2	102	0.6
13	PCB-44	0.9996	2.7	8.3	97	1.9
14	Isodrin	0.9998	2.3	7.0	107	1.4
15	Heptachlor epoxide	0.9947	3.7	11.0	110	3.1
16	PCB-95	0.9993	0.9	2.7	103	0.6
17	*trans*-Chlordane	0.9995	7.4	23.0	100	4.0
18	2,4'-DDE	0.9990	5.2	16.0	99	3.4
19	PCB-101	0.9929	4.1	12.0	114	3.3
20	Endosulfan I	0.9996	2.1	6.3	96	2.2
21	*cis*-Chlordane	0.9983	1.0	3.1	108	0.8
22	PCB-99	0.9994	3.2	9.8	99	1.9
23	Dieldrin	0.9997	0.4	1.2	98	0.2
24	4,4'-DDE	0.9991	4.9	15.0	100	3.4
25	PCB-110	0.9953	1.8	5.6	108	1.4
26	2,4'-DDD	0.9926	1.1	3.4	106	1.0
27	PCB-151	0.9994	3.1	9.3	102	2.2
28	Endrin	0.9995	7.2	22.0	95	2.9
29	Endosulfan II	0.9972	0.4	1.1	104	0.8
30	PCB-149	0.9998	3.5	11.0	100	2.1
31	PCB-118	0.9986	0.8	2.5	90	1.1
32	PCB-114	0.9989	2.2	6.7	106	3.2
33	PCB-146	0.9955	1.2	3.5	105	0.9
34	PCB-153	0.9992	2.3	6.8	104	1.7
35	PCB-105	0.9979	0.9	2.7	96	2.2
36	4,4'-DDT	0.9154	3.1	9.4	139	3.7
37	PCB-138	0.9977	2.5	7.5	102	1.8
38	PCB-187	0.9976	3.4	10.0	105	2.0
39	PCB-183	0.9995	2.5	7.6	102	1.7
40	PCB-128	0.9974	2.1	6.3	98	1.8
41	PCB-167	0.9994	2.3	6.9	102	2.0
42	PCB-177	0.9984	1.4	4.4	104	1.0
43	PCB-156	0.9902	1.7	5.1	107	1.7
44	PCB-157	0.9950	2.1	6.3	110	2.4
45	Methoxychlor	0.9063	14.0	41.0	136	24.0
46	PCB-180	0.9986	1.9	5.7	99	1.3
47	PCB-169	0.9997	3.3	9.8	100	3.9
48	PCB-170	0.9988	1.1	3.2	102	0.8
49	PCB-189	0.9974	4.3	13.0	95	2.7

a: 200 ng kg^{-1}, n = 3
b: 100 ng kg^{-1}, n = 3

The accuracy and reliability of the analytical workflow were validated through the analysis of a certified reference material (CNS391-50G, Sigma-Aldrich). Most analytes exhibited experimentally determined concentrations within certified tolerance intervals, confirming the method's efficient accuracy and recovery.

The validated protocol was subsequently applied to real sediment samples (S1, S2, and S3), in which PCBs and OCPs, including 4,4'-DDE and PCB-28, were detected at concentrations below internationally established guideline values (Table 3).[7–9] Representative GCxGC-TOFMS chromatograms of these samples are shown in Figure 2. The two-dimensional plots generated by the LECO *Pegasus* BTX 4D system underscore the chemical complexity of environmental matrices. The enhanced separation of GCxGC effectively resolved the target analytes from numerous co-extracted interferences, demonstrating the method's robustness for the reliable detection and quantitation of persistent pollutants at trace levels.

Table 3. Concentrations of detected target PCBs and OCPs in the three sediment samples analyzed.

Target	Concentration (ng kg^{-1}) [*mean ± standard deviation*]		
	S1	**S2**	**S3**
PeCB	< LOQ	< LOQ	ND
PCB-18	43.8 ± 0.8	68.0 ± 1.1	ND
PCB-28	131.4 ± 0.7	168.6 ± 2.2	129.1 ± 0.1
PCB-52	83.2 ± 0.6	98.7 ± 1.1	88.8 ± 1.2
PCB-44	95.2 ± 0.7	103.9 ± 0.6	107.2 ± 1.2
PCB-95	59.6 ± 0.9	65.7 ± 0.1	61.0 ± 0.2
PCB-101	121.8 ± 1.7	129.8 ± 1.5	133.4 ± 0.8
4,4'-DDE	45.7 ± 1.3	66.6 ± 0.9	55.7 ± 0.3
PCB-110	108.6 ± 0.5	153.7 ± 0.9	137.2 ± 0.3
PCB-153	56.4 ± 0.6	91.1 ± 0.1	75.6 ± 0.6
PCB-138	66.7 ± 0.3	114.6 ± 1.2	96.4 ± 0.1
PCB-187	26.5 ± 0.1	33.2 ± 0.2	30.8 ± 0.1
PCB-183	ND	10.1 ± 0.1	9.4 ± 0.1
PCB-157	38.0 ± 0.1	39.0 ± 0.1	ND
PCB-180	ND	50.6 ± 0.1	41.2 ± 0.1

< LOQ: below the limit of quantification.
ND: Not detected

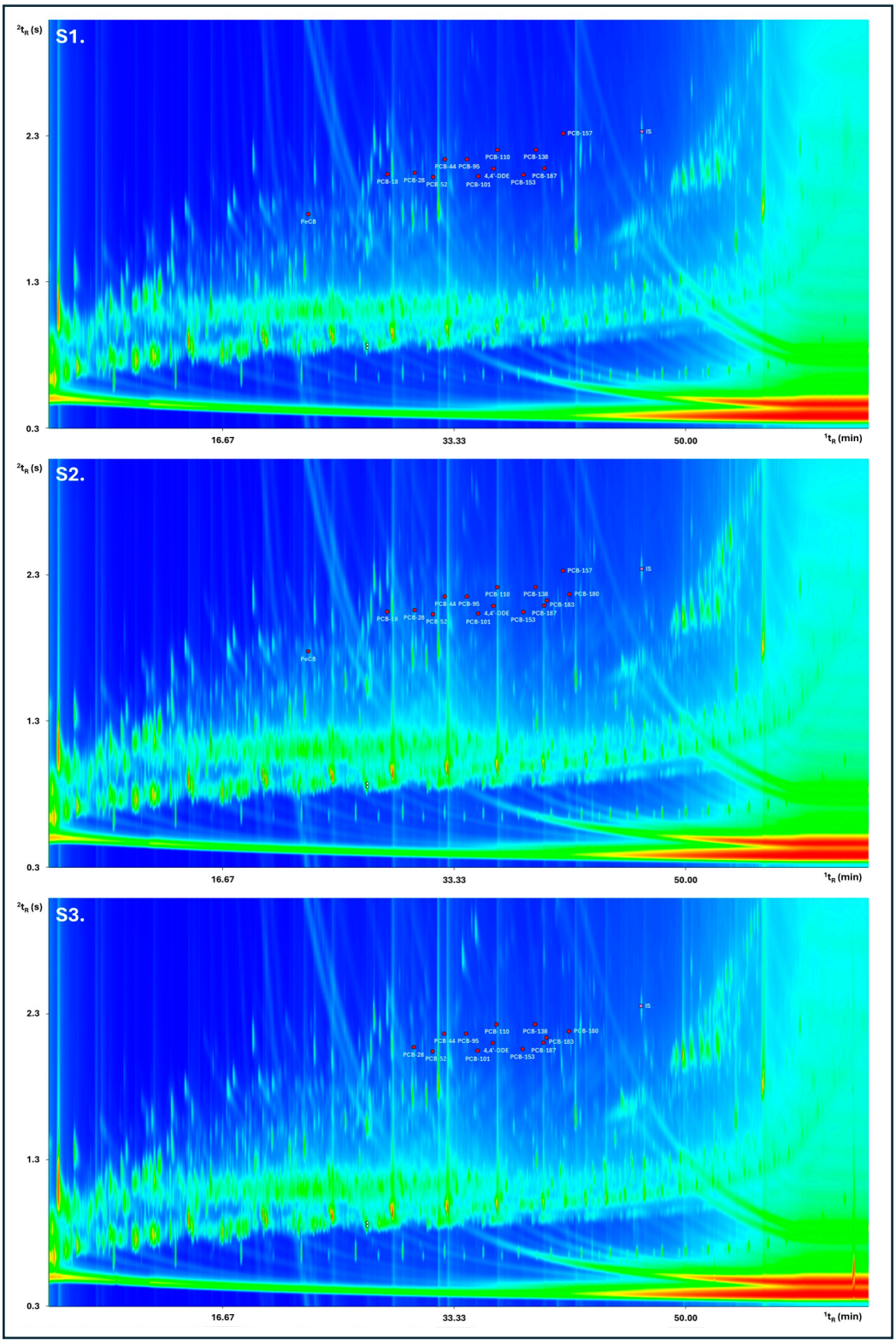


Figure 2. GCxGC-TOFMS chromatograms of the three sediment samples analyzed (S1, S2, and S3).

Additionally, the advantages of the GCxGC-TOFMS approach in resolving matrix interferences were demonstrated. As shown in Figure 3, hexachlorobenzene was effectively separated from co-extracted interferents in the second chromatographic dimension. Similarly, the benefit is evident in Figure 4, where PCB-52 was distinguished from a co-extracted compound with overlapping isobaric MS signals. Together, these examples highlight the role of multidimensional separation for reliable quantification and demonstrate the resolving power of the LECO *Pegasus* BTX 4D system.

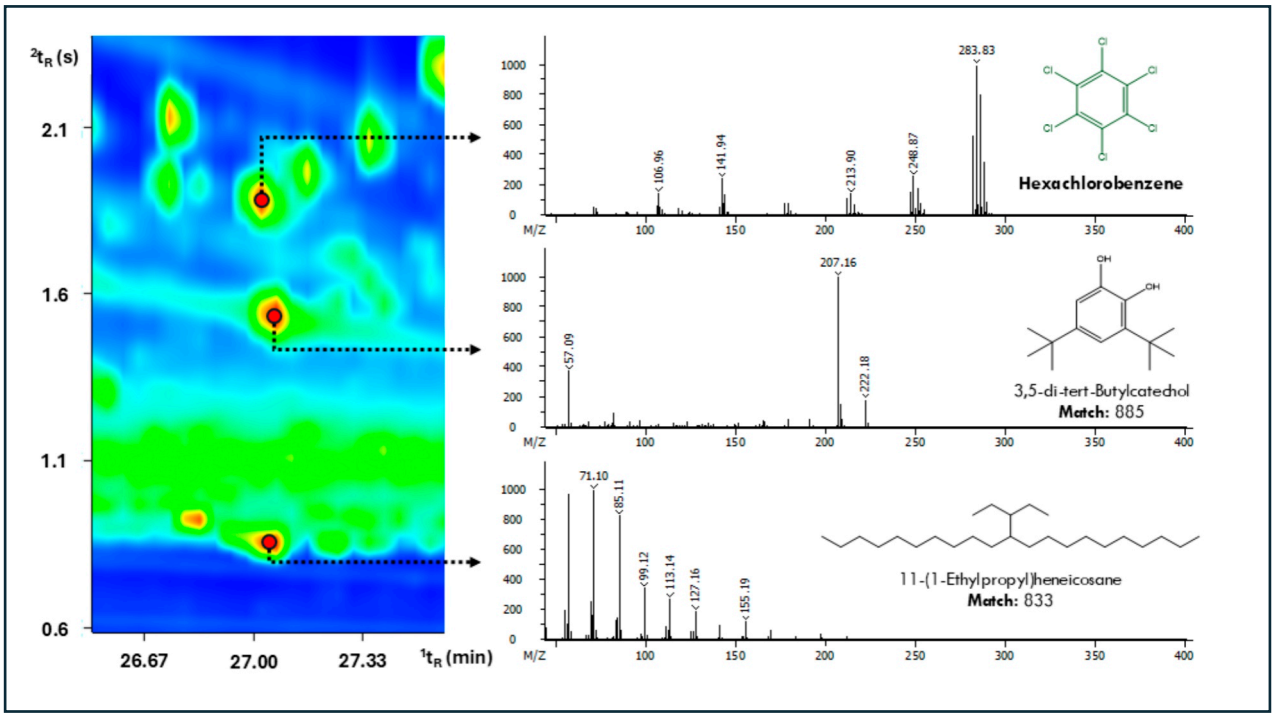


Figure 3. Section of a GCxGC-TOFMS chromatogram illustrating the efficient 2D separation of hexachlorobenzene (identified by the use of the analytical standard) from two interferences from the matrix.

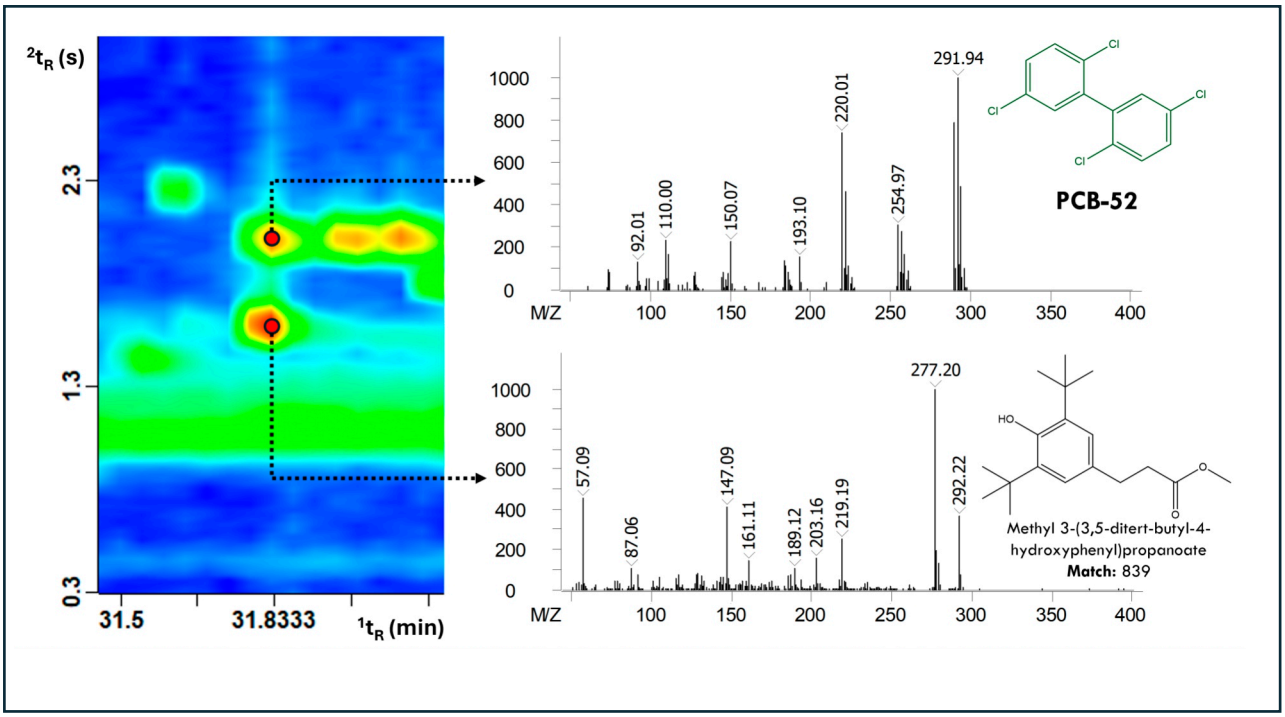


Figure 4. Expanded GCxGC-TOFMS chromatogram illustrating the 2D separation of PCB-52 (identified by the use of the analytical standard) from a matrix interferent displaying isobaric mass spectral signals.

Conclusions

The combination of SPE and GCxGC-TOFMS using the LECO *Pegasus* BTX 4D system enabled the simultaneous determination of OCPs and PCBs in complex sediment matrices. The method demonstrated excellent chromatographic resolution, selectivity, and sensitivity, allowing reliable quantification of 49 target analytes.

The enhanced separation capability of GCxGC was particularly beneficial for resolving co-eluting compounds and matrix interferences, thereby improving analytical confidence in the identification and quantification of trace-level contaminants. The analytical performance achieved meets the requirements for environmental monitoring and regulatory compliance. This workflow provides a reliable solution for laboratories conducting routine trace analysis of legacy persistent organic pollutants in sediments.

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Acknowledgment

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