Fast, Accurate Chlorinated Compounds by GC/ECD Using One Zebron™ ZB-CLPesticides Column Set

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Chlorinated pesticides, herbicides, and related compounds are regulated and routinely monitored in the environmental testing industry using dual-column GC/ECD. This technical note presents a specialized dual-column pair that provides fast, accurate separations of multiple halogenated compound classes, enables significant cost savings, and increases in throughput.

Introduction

Chemical pesticides, herbicides, and related substances are commonly used for pest control across the globe. Though useful and heavily relied upon for mitigating disease-causing or destructive organisms, pesticides inherently pose a variety of environmental and health risks. Chlorinated compounds in particular have proven hazardous and many are required to be eliminated, restricted, or prevented from unintentional release; the Stockholm Convention recognizes many chlorinated pesticides and related compounds on its list of Persistent Organic Pollutants (POPs)[1].

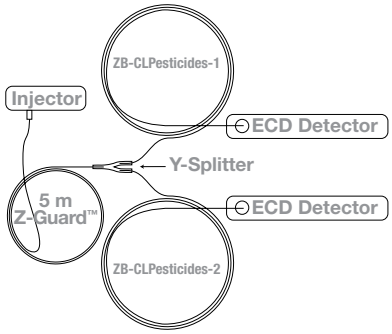
Specific testing for chlorinated pesticides and herbicides, organohalides, polychlorinated biphenyls (PCBs), haloacetic acids (HAAs), and EDB/DBCP/TCP is commonly regulated around the world; in the United States for example the Environmental Protection Agency (EPA) regulates many of these halogenated compounds under 7 methods (8081, 8082, 8151, 504, 505, 508, and 552). Resolution and linearity are frequently chromatographic struggles for analysis of these compounds; limited instrumentation resources and the need for increasingly higher throughput also pose significant challenges. Many laboratories therefore run multiple chlorinated compound methods on the same instrument, though separation needs for those methods often necessitate time-consuming switches between multiple column sets.

The following applications utilize a single specialized column set as an option for analyzing chlorinated pesticides, PCBs, and herbicides by dual-column GC/ECD. Accurate separations of all analytes are performed while providing fast run times for each application, with a single dual-column setup requiring no column changes. Labs are therefore able to increase throughput from significant time savings, while reducing downtime and cost.

Methods

For dual-column methods, compounds are identified using a primary column and confirmed by a secondary column of orthogonal selectivity. Identification and verification can be performed in parallel using setup as shown in **Figure 1**. Each application shown utilizes a dual-column setup with Zebron ZB-CLPesticides-1 (primary) and ZB-CLPesticides-2 (confirmation) columns. Experimental conditions and analytes for each application are shown with the chromatogram.

Figure 1. Example of a dual-column configuration.



Results and Discussions

Chlorinated Pesticides

Figure 2 shows a dual-column separation of chlorinated pesticides using specialized Zebron ZB-CLPesticides-1 and ZB-CLPesticides-2 GC columns. Each chromatogram shows complete resolution of 22 commonly analyzed compounds, with run times of less than 8 minutes. This ensures short cycle times and represents a 73 % improvement in throughput compared to traditional methods; methods using standard GC phases have resulted in long run times up to 30 minutes[2] (e.g. U.S. EPA Method 8081).

In calibration curves ranging from 5 to 250 ng/mL, the columns also provide good results for linearity (% Relative Standard Deviation, RSD). Many chlorinated pesticide methods specify strict RSD requirements; all compounds display RSD values less than 20 % with near-linear performance as shown in **Figure 3**.

Polychlorinated Biphenyls (PCBs) as Aroclors

PCBs are commonly tested in addition to chlorinated pesticides, and are analyzed either as individual congeners or as Aroclor mixtures. Aroclor mixtures are first qualitatively identified by their unique fingerprint in comparison to a standard. Any contaminants present in the run may interfere with Aroclor fingerprints, making data analysis difficult.

Because Aroclors are often run on the same instrument as chlorinated pesticides or other halogenated compounds, it is important to minimize carryover between injections by baking off contaminants or residual sample. A high level of thermal stability is therefore necessary. **Figure 4** shows a dual-column example of individual Aroclor 1260 on the ZB-CLPesticides-1 and -2 column set, which provides the temperature stability for the analysis.

For a full technical note on PCB congeners and Aroclors, please visit www.phenomenex.com/GC.

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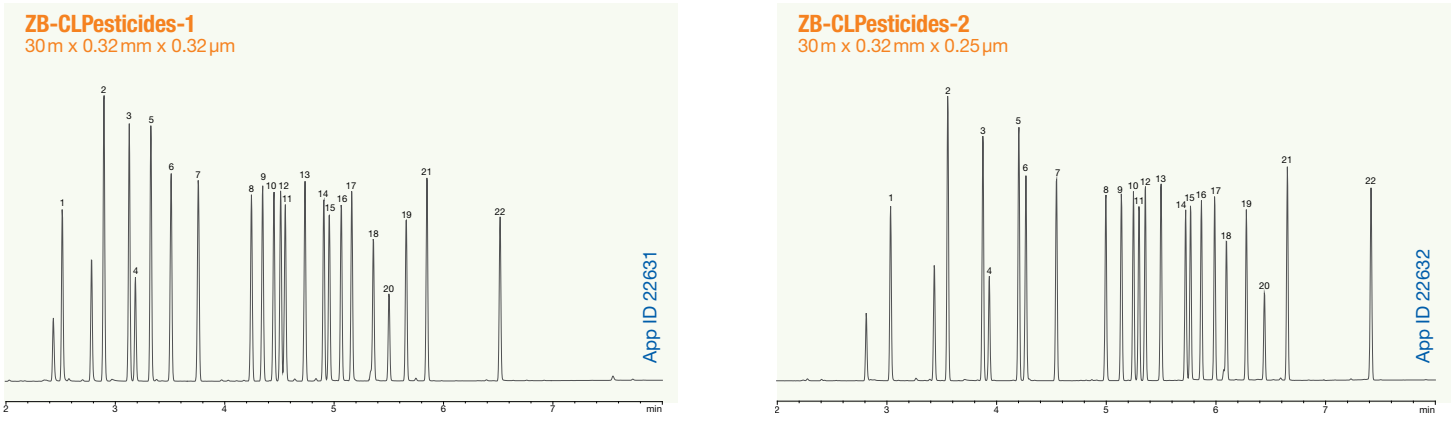
Figure 2. Dual-column GC/ECD analysis of chlorinated pesticides using Zebron™ ZB-CLPesticides-1 and -2.



Conditions for all columns:
Columns: As listed
Dimensions: As listed
Part Number: 7HM-G028-51 (ZB-CLPesticides-1)
7HM-G029-11 (ZB-CLPesticides-2)
Injection: Splitless (hold 0.3 min) @ 250 °C, 1 µL
Carrier Gas: Helium @ 3.9 mL/min (constant flow)
Oven Program: 120 °C to 200 °C @ 45 °C/min to 230 °C @ 15 °C/min to 330 °C @ 30 °C/min for 2 min
Detector: ECD @ 330 °C
Y-Connector: AG0-4717
Guard Column: 7AM-G000-00-GZ0 (5 m Z-Guard™)
Liner: AG0-8499 (Single Taper with Wool at Bottom)
Septum: AG0-4696 (PhenoRed™-400)
Inlet Seal: AG0-8620 (Gold-Plated Easy Seals™)
Sample: Analytes are 250 ng/mL in hexane.

Figure 3. Five-point calibration curve at 5, 15, 25, 100, and 250 ng/mL.

Peak No.	Analyte	ZB-CLPesticides-1 % RSD*	ZB-CLPesticides-2 % RSD*	US EPA Specifications
1	2,4,5,6-TCMX (Surr)	3.8	3.0	< 20
2	α-BHC	8.3	3.8	< 20
3	γ-BHC	5.9	5.6	< 20
4	β-BHC	6.9	6.9	< 20
5	δ-BHC	4.9	5.7	< 20
6	Heptachlor	8.0	6.5	< 20
7	Aldrin	4.2	2.3	< 20
8	Heptachlor epoxide	3.8	2.3	< 20
9	trans-Chlordane	4.1	3.8	< 20
10	cis-Chlordane	4.0	3.3	< 20
11	4,4'-DDE	4.8	2.9	< 20
12	Endosulfan I	6.0	2.5	< 20
13	Dieldrin	7.7	4.9	< 20
14	Endrin	9.4	6.6	< 20
15	4,4'-DDD	9.2	3.6	< 20
16	Endosulfan II	6.6	4.1	< 20
17	4,4'-DDT	11.6	6.9	< 20
18	Endrin aldehyde	8.3	7.3	< 20
19	Endosulfan sulfate	8.0	7.1	< 20
20	Methoxychlor	6.7	6.1	< 20
21	Endrin ketone	6.5	7.2	< 20
22	Decachlorobiphenyl (Surr)	6.7	6.6	< 20
	Average	6.6 %	4.9 %	< 20

*Calculated using response factors as per EPA guidelines.

Chlorinated Herbicides

Additional compound classes are commonly run on the same instrument used for chlorinated pesticide and PCB testing due to resource constraints. **Figure 5** shows separation of chlorinated herbicides using the same dual-column setup and dimensions as the chlorinated pesticides and PCB runs. The ZB-CLPesticides column pair provides good resolution of 17 commonly monitored chlorinated herbicides, as well as surrogates and internal standards, in less than 14 minutes.

Conclusion

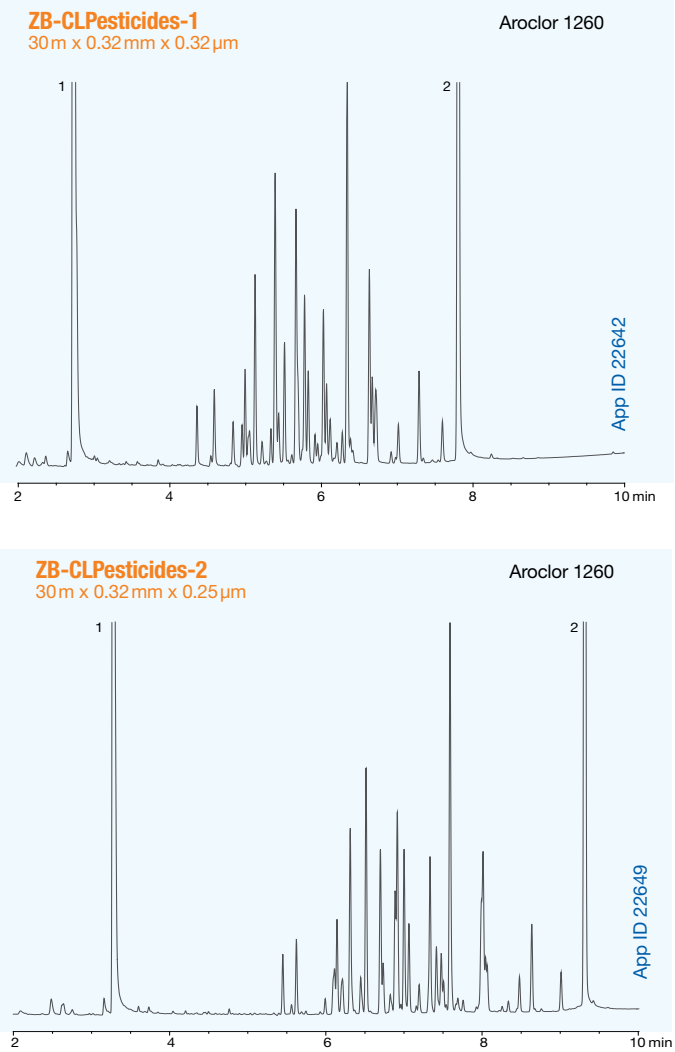
Test methods using specialized Zebron ZB-CLPesticides-1 and -2 GC columns were performed by dual-column GC/ECD for chlorinated pesticides, PCBs, and chlorinated herbicides. Short run times for all methods were observed and no column switches were required as all methods utilized the same setup and columns.

Labs under production deadlines can improve resolution, cycle time, and therefore throughput while maintaining data quality and accuracy, as observed in the below quote by Shealy Environmental Services, Inc.:

"Overall, the Zebron columns are fairly impressive. ZB-CLPesticides columns are comparable to our current columns, with the added benefit of no co-eluting peaks. There is also the potential to optimize our method parameters using these columns to run a slightly faster analysis."

Labs can additionally run multiple methods on a single instrument without changing columns, for the added flexibility to respond dynamically to fluctuating sample demands.

Figure 4. Polychlorinated biphenyl (PCB) Aroclor 1260 by GC/ECD on Zebron™ ZB-CLPesticides-1 and -2.



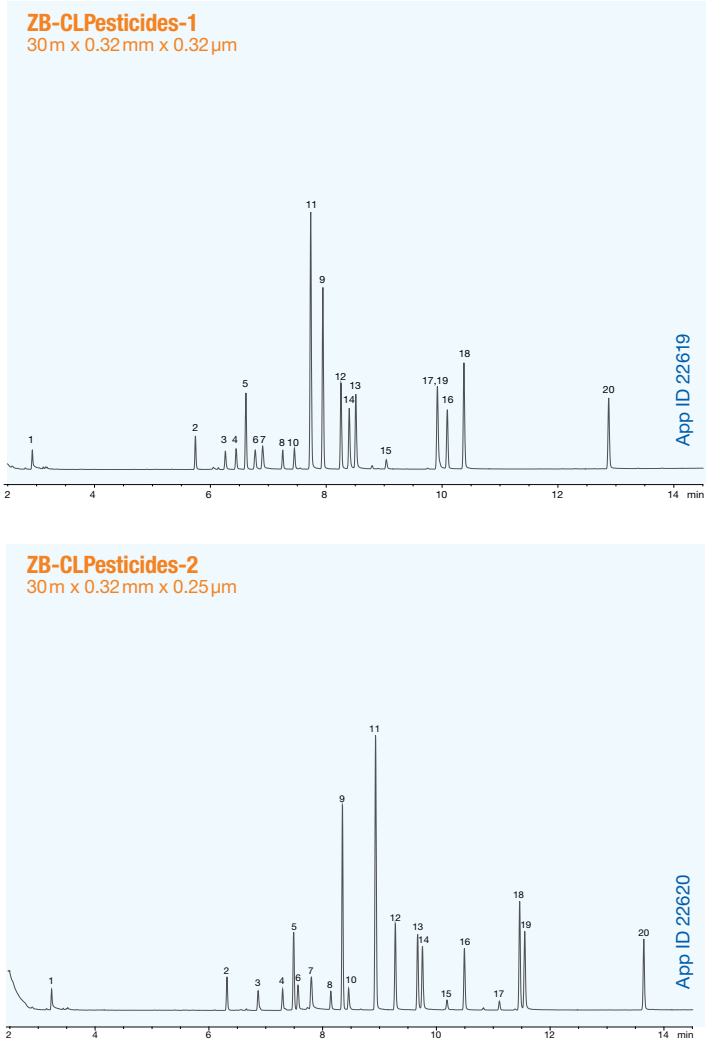
Conditions for all columns:

Columns: As listed
Dimensions: As listed
Part Number: 7HM-G028-51 (ZB-CLPesticides-1)
7HM-G029-11 (ZB-CLPesticides-2)
Injection: Pulsed Splitless @ 30 psi (hold 20 sec) @ 250 °C, 1 µL
Carrier Gas: Helium @ 60 cm/sec (constant flow)
Oven Program: 120 °C to 200 °C @ 45 °C/min to 330 °C @ 15 °C/min for 2 min
Detector: ECD @ 330 °C
Y-Connector: AG0-4717
Guard Column: 7AM-G000-00-GZ0 (5 m Z-Guard™)
Liner: AG0-8499 (Single Taper with Wool at Bottom)
Septum: AG0-4696 (PhenoRed™-400)
Inlet Seal: AG0-8620 (Gold-Plated Easy Seals™)
Sample: Aroclor is 1000 ng/mL and SS and IS are 100 ng/mL in hexane.

1. Tetrachloro-meta-xylene (TCMX)*
2. Decachlorobiphenyl**

* surrogate standard
** internal standard

Figure 5. Chlorinated herbicides by GC/ECD on Zebron ZB-CLPesticides-1 and -2.



Conditions for all columns:

Columns: As listed
Dimensions: As listed
Part Number: 7HM-G028-51 (ZB-CLPesticides-1)
7HM-G029-11 (ZB-CLPesticides-2)
Injection: Splitless (hold 0.75 min) @ 250 °C, 1 µL
Carrier Gas: Helium @ 36 cm/sec (constant flow)
Oven Program: 70 °C for 0.5 min to 190 °C @ 25 °C/min for 1 min to 300 °C @ 11 °C/min for 5 min
Detector: ECD @ 325 °C
Y-Connector: AG0-4717
Guard Column: 7AM-G000-00-GZ0 (5 m Z-Guard)
Liner: AG0-8499 (Single Taper with Wool at Bottom)
Septum: AG0-4696 (PhenoRed-400)
Inlet Seal: AG0-8620 (Gold-Plated Easy Seals™)
Sample: Analytes are 100 ng/mL in hexane.

1. Dalapon methyl ester
2. 3,5-Dichlorobenzoic acid methyl ester*
3. 4-Nitroanisole
4. DCAA methyl ester*
5. Dicamba methyl ester
6. MCPP methyl ester
7. MCPA methyl ester
8. Dichlorprop, methyl ester
9. 4,4'-DBOB**
10. 2,4-D methyl ester
11. Pentachloroanisole
12. 2,4,5-TP methyl ester
13. 2,4,5-T methyl ester
14. Chloramben methyl ester
15. 2,4-DB methyl ester
16. Dinoseb methyl ester
17. Bentazon methyl ester
18. DCPA methyl ester (Chlorthal-dimethyl)
19. Pichloram methyl ester
20. Acifluorfen methyl ester

* surrogate standard
** internal standard

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Zebron™ ZB-CLPesticides GC Columns

ZB-CLPesticides-1 GC Columns

Length (m)	ID (mm)	df (µm)	Temperature Limits (°C)	Part No.
30	0.25	0.25	40 to 320/340	7HG-G028-11
	0.32	0.32	40 to 320/340	7HM-G028-51
	0.32	0.50	40 to 320/340	7HM-G028-17
	0.53	0.50	40 to 320/340	7HK-G028-17

ZB-CLPesticides-2 GC Columns

Length (m)	ID (mm)	df (µm)	Temperature Limits (°C)	Part No.
30	0.25	0.20	40 to 320/340	7HG-G029-10
	0.32	0.25	40 to 320/340	7HM-G029-11
	0.32	0.50	40 to 320/340	7HM-G029-17
	0.53	0.42	40 to 320/340	7HK-G029-16

References

1. Listing of POPs in the Stockholm Convention.
2. Run time as listed in EPA Method 8081B: Organochlorine Pesticides By Gas Chromatography.

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guarantee

If Zebron GC columns do not provide you with equivalent separations as compared to any other GC column of the same phase and dimensions, return the column with comparative data within 45 days for a FULL REFUND.

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