

Evaluating CLP and EPA Methods for Pesticides in Water Using Agilent J&W DB-CLP1/DB-CLP2 GC Columns

Application Note

Environmental

Authors

Doris Smith and Ken Lynam
Agilent Technologies, Inc.

Abstract

The Agilent J&W DB-CLP1 and DB-CLP2 column pair has the selectivity to separate many different halogenated compounds by GC/ECD. Chlorinated pesticides, herbicides, organohalides, and PCBs in drinking and ground water are well resolved by these columns with multiple Contract Laboratory Program (CLP) and United States Environmental Protection Agency (US EPA) methods. Some manufacturers offer different column sets for the different methods. However, the Agilent CLP single column set avoids the downtime of switching between different columns and analyzes multiple methods. This productivity increase can lead to more billable instrument-hours. Compared to other vendors' columns, the J&W DB-CLP1/DB-CLP2 provides better combinations of faster analysis times and fewer coelutions, for analysis of a wider range of pesticides and pollutants covered by US EPA methods, all in a single operation.



Agilent Technologies

Introduction

GC column manufacturers design columns specifically for pesticide residue analysis, with differing capability and efficacy. This type of measurement is typically done on 2 columns for simultaneous primary and confirmation analysis, using a retention gap and γ -splitter to connect the columns. In this application note, we analyzed pesticides and other potential water contaminants according to 9 United States Environmental Protection Agency (US EPA) and Contract Laboratory Program (CLP) methods. We used Agilent J&W DB-CLP1 and DB-CLP2 columns, a pair of arylene phases that handle high oven temperatures for rapid analysis of CLP chlorinated pesticides in drinking and ground water. We demonstrated the columns' suitability for phenoxy acids, haloacetic acids, polychlorinated biphenyls, and other pollutants, according to EPA methods for the analysis of water samples.

Nine CLP and EPA methods were investigated.

- CLP Pesticides -19 targeted organohalides
- EPA 504 -1 1,2-dibromoethane (EDB), 1,2-dibromo-3-chloropropane (DBCP), and 1,2,3-trichloropropane (123TCP)
- EPA 505 - organohalides
- EPA 508.1 - chlorinated pesticides, herbicides, and organohalides
- EPA 551 - chlorinated solvents, trihalomethanes (THMs), and disinfection byproducts (DBPs)
- EPA 552.3 - haloacetic acids and dalapon
- EPA 8081B (extended analyte list) - organochlorine pesticides
- EPA 8082A - polychlorinated biphenyls (PCBs) and aroclors
- EPA 8151A - chlorophenoxyacid herbicides

Materials and Methods

The same column pair was used for every analysis. Other conditions varied and are shown with their respective results. Traditionally, replacement of the retention gap or analytical column involved replacing the quartz γ -splitter and re-establishing all column connections. To avoid the downtime and extra maintenance associated with γ -splitters, we also used an Agilent Capillary Flow Technology (CFT) reusable splitter. The CFT splitter uses column connections that are individually connected to the splitter, allowing inlet and column maintenance independent of the other analytical column connection.

Column 1:	Agilent J&W DB-CLP1, 30 m x 0.32 mm, 0.25 μ m (p/n 123-8232)
Column 2:	Agilent J&W DB-CLP2, 30 m x 0.32 mm, 0.5 μ m (p/n 123-8336)
Guard column:	5 m x 0.32 mm, deactivated
CFT device:	Inert tee (p/n G3184-60065), split ratio 1:1
Inlet liner:	Agilent Ultra Inert, single taper splitless (p/n 5190-2292)
Inlet liner (EPA Method 505):	Agilent Ultra Inert, double taper splitless (p/n 5190-3983)
Instrument:	Agilent 7890 GC with dual μ ECD
Sampler:	Agilent 7693 Automatic Liquid Sampler
Sampler (EPA Method 505 and 508.1):	Agilent 7873B Automatic Liquid Sampler

Results and Discussion

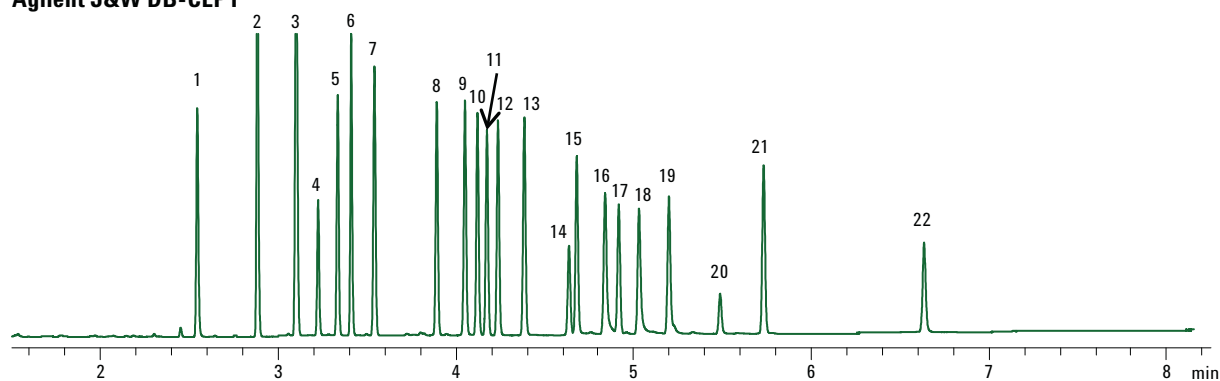
Figures 1 to 10 show the analytical results obtained on the DB-CLP1 and DB-CLP2 columns.

Fast CLP pesticides - chlorinated pesticides

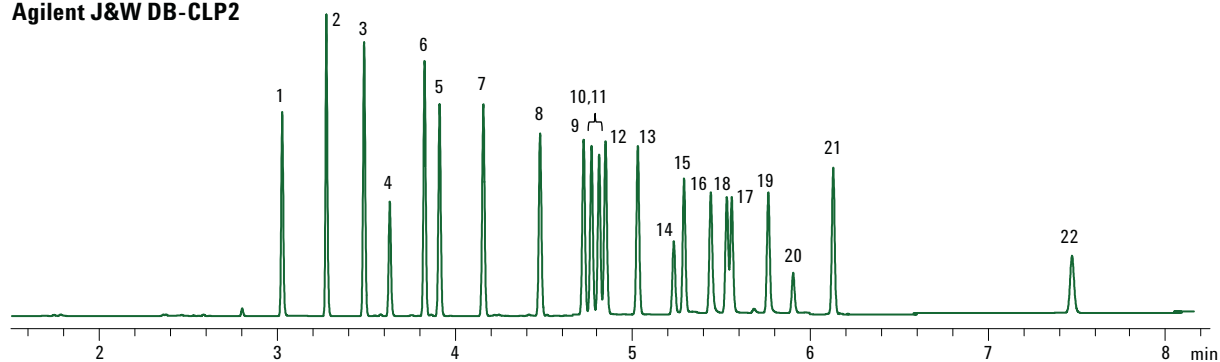
Conditions

Carrier: Helium, constant flow, 3.5 mL/min
 Injection temperature: 250 °C
 Injection: 1 µL, splitless
 Oven: 150 °C, hold 0.2 min, 45 °C/min to 250 °C,
 18 °C/min to 300 °C, 30 °C/min to 330 °C,
 hold 2.5 min
 Detector: µECD, 340 °C
 Sample: 50 ng/mL CLP Pesticides

Agilent J&W DB-CLP1



Agilent J&W DB-CLP2



Peak ID

1. Tetrachloro-m-xylene (surrogate standard)	8. Heptachlor epoxide	16. Endosulfan II
2. α -BHC	9. γ -Chlordane	17. 4,4'-DDT
3. γ -BHC	10. α -Chlordane	18. Endrin aldehyde
4. β -BHC	11. Endosulfan I	19. Endosulfan sulphate
5. Heptachlor	12. 4,4'-DDE	20. Methoxychlor
6. δ -BHC	13. Dieldrin	21. Endrin ketone
7. Aldrin	14. Endrin	22. Decachlorobiphenyl (surrogate standard)
	15. 4,4'-DDD	

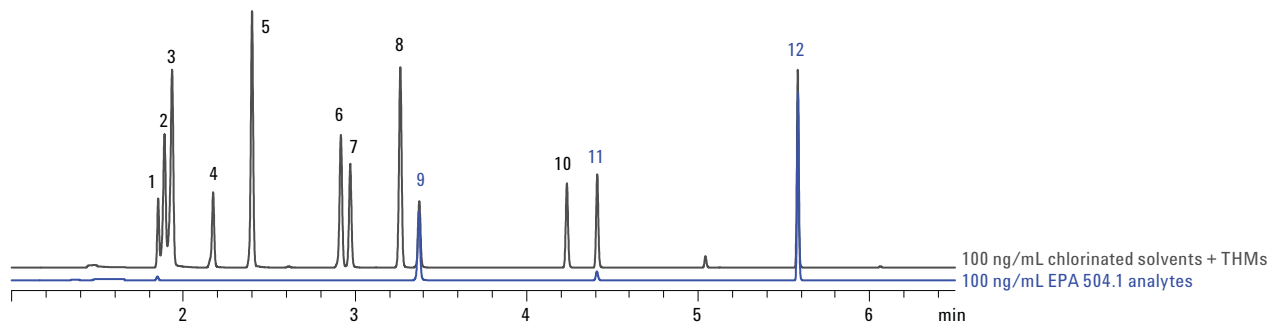
Figure 1. Agilent J&W CLP1/CLP2 columns analyze chlorinated pesticides according to the CLP Pesticides method in 7.5 minutes.

EPA Method 504.1 - 1,2-dibromoethane (EDB), 1,2-dibromo-3-chloropropane (DBCP), and 1,2,3-trichloropropane (123TCP)

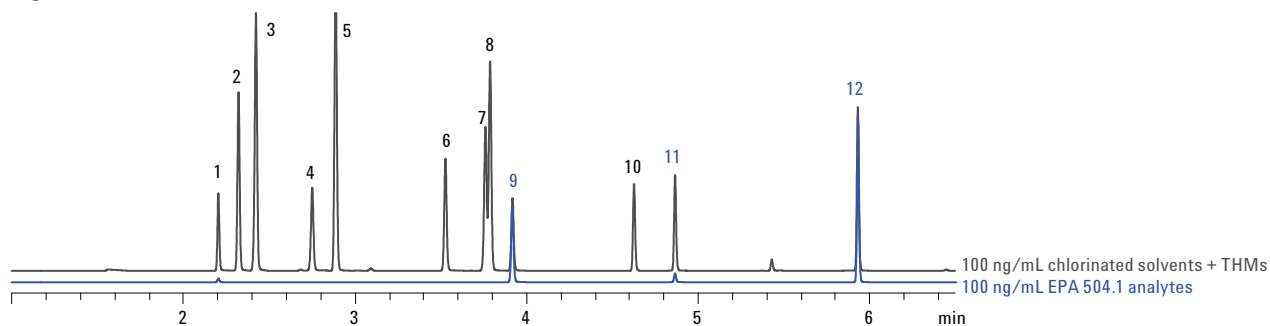
Conditions

Carrier: Helium, constant flow, 3.75 mL/min
 Injection temperature: 200 °C
 Injection: 2 µL, splitless
 Oven: 50 °C, hold 1.5 min, 20 °C/min to 95 °C,
 40 °C/min to 175 °C, hold 1.25 min
 Detector: µECD, 300 °C
 Sample: 100 ng/mL EPA 504.1 analytes, 100 ng/mL
 chlorinated solvents + trihalomethanes

Agilent J&W DB-CLP1



Agilent J&W DB-CLP2



Peak ID

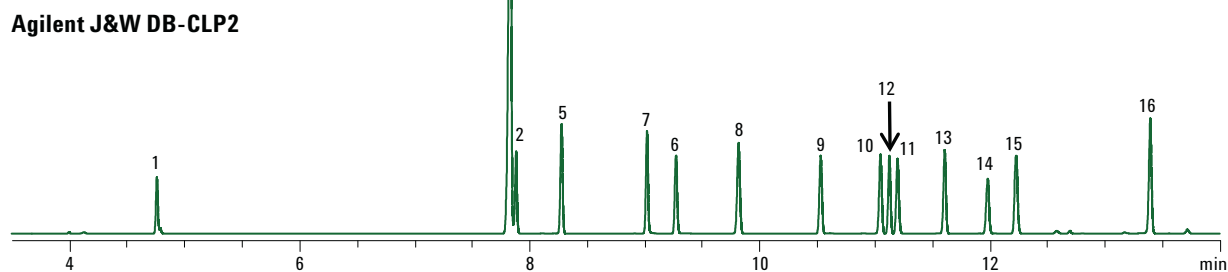
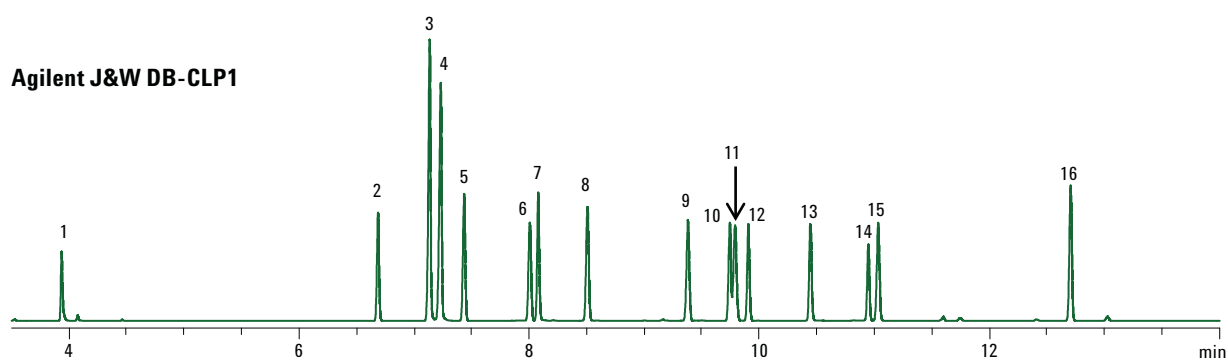
1. Chloroform	7. 1,1,2-Trichloroethane
2. 1,1,1-Trichloroethane	8. Dibromochloromethane
3. Carbon tetrachloride	9. 1,2-Dibromoethane (EDB)
4. Trichloroethene	10. Bromoform
5. Bromodichloromethane	11. 1,2,3-Trichloropropane (123TCP)
6. Tetrachloroethene	12. 1,2-Dibromo-3-chloropropane (DBCP)

Figure 2. Agilent J&W CLP1/CLP2 columns analyze 1,2-dibromoethane (EDB), 1,2-dibromo-3-chloropropane (DBCP), and 1,2,3-trichloropropane (123TCP) according to EPA Method 504.1, with cooler analysis temperatures allowing a faster GC cycle time.

EPA Method 505 - organohalide pesticides

Conditions

Carrier: Helium, constant flow, 2.5 mL/min
Injection temperature: 250 °C
Injection: 2 µL, splitless
Oven: 90 °C, hold 0.5 min, 35 °C/min to 175 °C,
12 °C/min to 300 °C, hold 1.75 min
Detector: µECD, 325 °C
Sample: 100 ng/mL EPA 505 analytes



Peak ID

1. Hexachlorocyclopentadiene	7. Alachlor (1 µg/mL)	13. Dieldrin
2. Hexachlorobenzene	8. Aldrin	14. Endrin
3. Atrazine (25 µg/mL)	9. Heptachlor epoxide	15. <i>cis</i> -Nonachlor
4. Simazine (25 µg/mL)	10. γ -Chlordane	16. Methoxychlor (0.5 µg/mL)
5. γ -BHC	11. <i>trans</i> -Nonachlor	
6. Heptachlor	12. α -Chlordane	

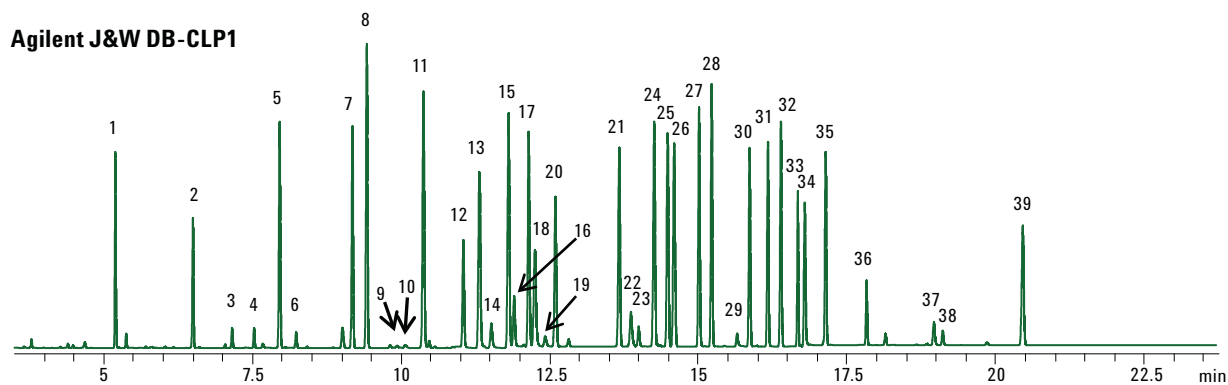
Figure 3. Agilent J&W CLP1/CLP2 columns analyze organohalide pesticides in under 24 minutes according to EPA Method 505.

EPA Method 508.1 – chlorinated pesticides and herbicides

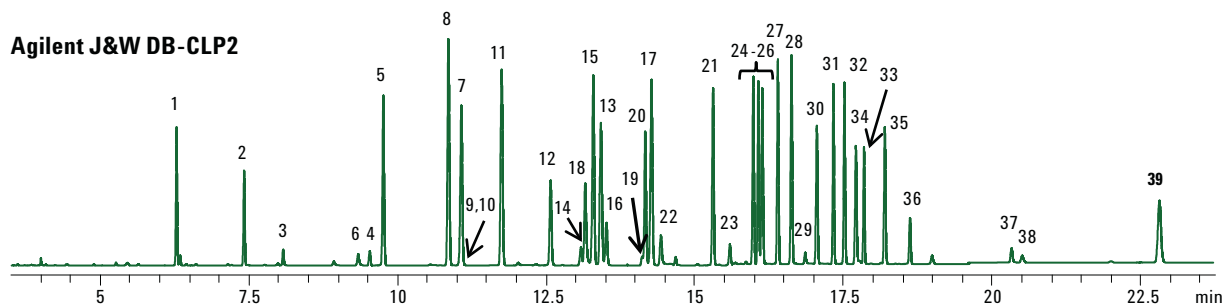
Conditions

Carrier: Helium, constant flow, 35 cm/s
 Injection temperature: 250 °C
 Injection: 2 µL, splitless
 Oven: 80 °C, hold 0.5 min, 26 °C/min to 175 °C,
 6.5 °C/min to 235 °C, 15 °C/min to 300 °C,
 hold 6 min
 Detector: µECD, 340 °C
 Sample: 100 ng/mL EPA 508.1 analytes,
 100 ng/mL pesticide surrogate mix

Agilent J&W DB-CLP1



Agilent J&W DB-CLP2



Peak ID

1. Hexachlorocyclopentadiene	11. γ -BHC	22. Cyanazine	33. 4,4'-DDT
2. Etr Diazole	12. β -BHC	23. Butachlor	34. Endrin aldehyde
3. Chloroneb	13. Heptachlor	24. γ -Chlordane	35. Endosulfan sulfate
4. Trifluralin	14. Alachlor	25. α -Chlordane	36. Methoxychlor
5. Tetrachloro-m-xylene (surrogate standard)	15. δ -BHC	26. Endosulfan I	37. <i>cis</i> -Permethrin
6. Propachlor	16. Chlorothalonil	27. 4,4'-DDE	38. <i>trans</i> -Permethrin
7. Hexachlorobenzene	17. Aldrin	28. Dieldrin	39. Decachlorobiphenyl (surrogate standard)
8. α -BHC	18. Metribuzin	29. Chlorobenzilate	
9. Atrazine	19. Metolachlor	30. Endrin	
10. Simazine	20. DCPA	31. 4,4'-DDD	
	21. Heptachlor epoxide	32. Endosulfan II	

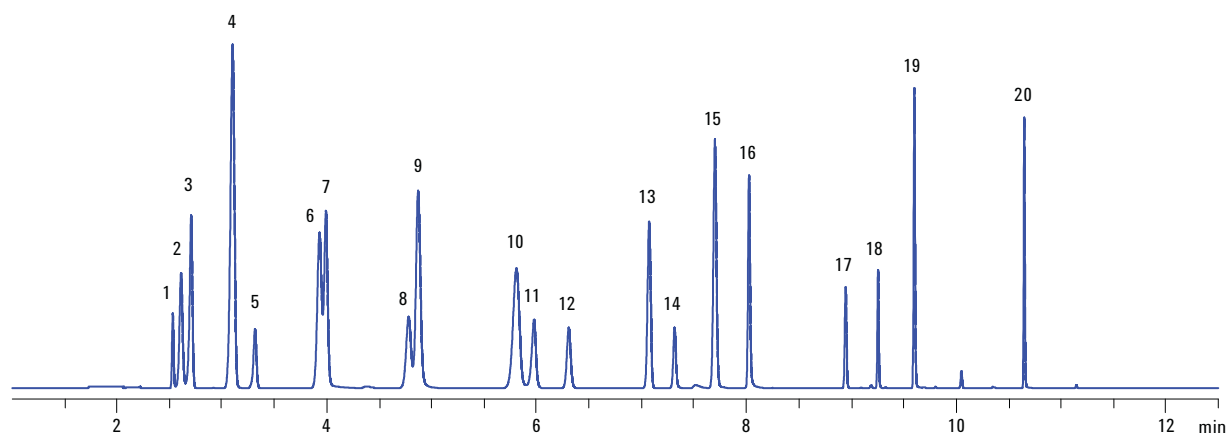
Figure 4. The Agilent J&W CLP1 column separates all chlorinated pesticide and herbicide analytes according to EPA Method 505.

EPA Method 551 - chlorinated solvents, trihalomethanes (THMs), and disinfection byproducts (DBPs)

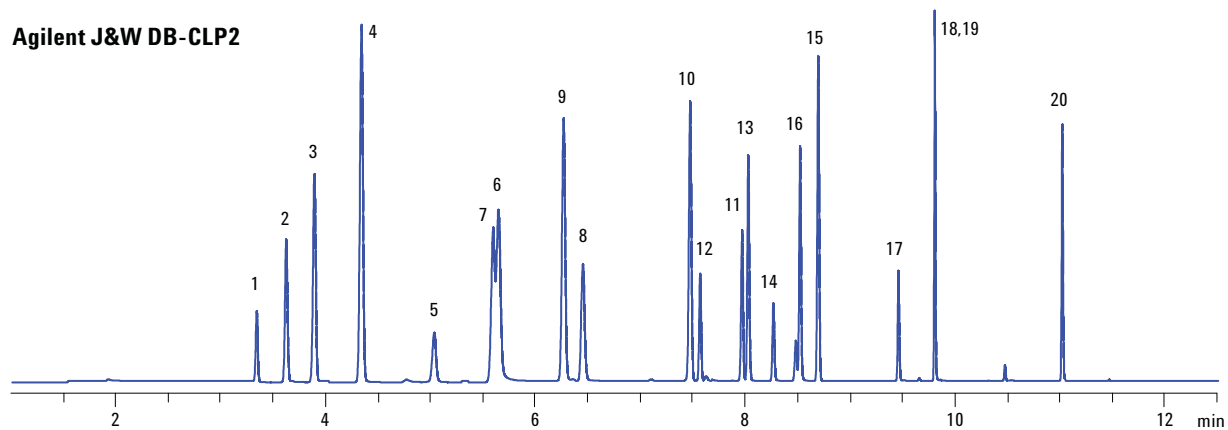
Conditions

Carrier: Helium, constant flow, 45 cm/s
 Injection temperature: 200 °C
 Injection: 2 µL, splitless
 Oven: 35 °C, hold 5.75 min, 20 °C/min to 95 °C,
 40 °C/min to 200 °C, hold 1.25 min
 Detector: µECD, 300 °C
 Sample: 100 ng/mL chlorinated solvents, THMs and DBPs

Agilent J&W DB-CLP1



Agilent J&W DB-CLP2



Peak ID

1. Chloroform	8. 1,1-Dichloro-2-propanone	15. 1,1,1-Trichloro-2-propanone
2. 1,1,1-Trichloroethane	9. Dichloroacetonitrile	16. Bromochloroacetonitrile
3. Carbon tetrachloride	10. Chloropicrin	17. Bromoform
4. Trichloroacetonitrile	11. Tetrachloroethene	18. 1,2,3-Trichloropropane
5. Trichloroethene	12. 1,1,2-Trichloroethane	19. Dibromoacetonitrile
6. Chloral hydrate	13. Dibromochloromethane	20. 1,2-Dibromo-3-chloropropane
7. Bromodichloromethane	14. 1,2-Dibromoethane	

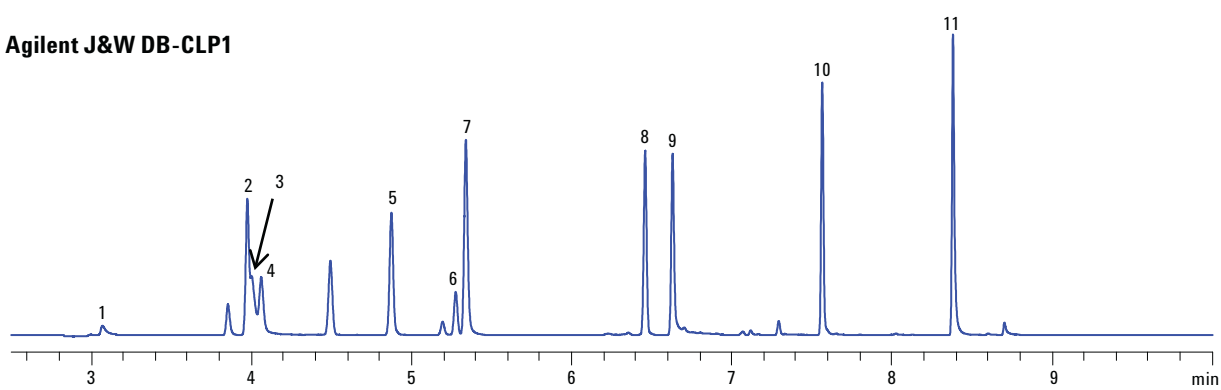
Figure 5. The Agilent J&W CLP1 column separates all 20 analytes in 11 minutes according to EPA Method 551.

EPA Method 552.3 - haloacetic acids and dalapon

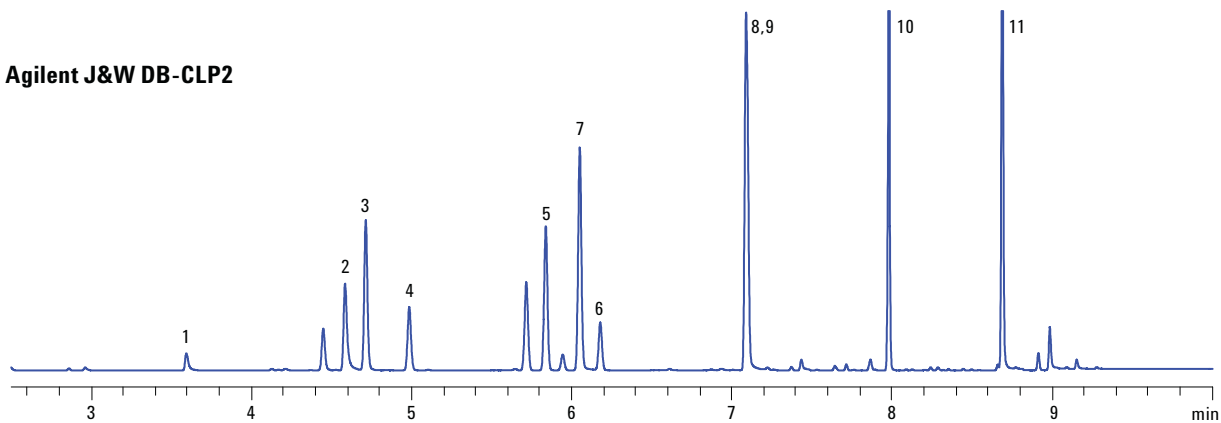
Conditions

Carrier: Helium, constant flow, 54.79 cm/s
Injection temperature: 180 °C
Injection: 1 µL, splitless
Oven: 40 °C, hold 0.5 min, 10 °C/min to 95 °C,
30 °C/min to 200 °C, hold 1 min
Detector: µECD, 340 °C
Sample: 10 to 100 ng/mL haloacetic acids and dalapon
(methyl esters)

Agilent J&W DB-CLP1



Agilent J&W DB-CLP2



Peak ID

1. Methyl chloroacetate (30 ng/mL)	7. Methyl bromochloroacetate (20 ng/mL)
2. Methyl bromoacetate (20 ng/mL)	8. Methyl bromodichloroacetate (20 ng/mL)
3. Methyl dichloroacetate (30 ng/mL)	9. Methyl dibromoacetate (10 ng/mL)
4. Dalapon methyl ester (20 ng/mL)	10. Methyl dibromochloroacetate (50 ng/mL)
5. Methyl trichloroacetate (10 ng/mL)	11. Methyl tribromoacetate (100 ng/mL)
6. 1,2,3-Trichloropropane (IS) (50 ng/mL)	

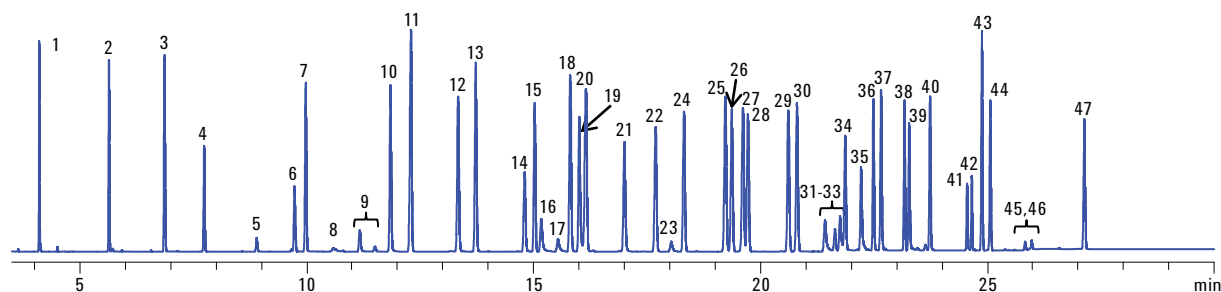
Figure 6. The Agilent J&W CLP1/CLP2 column pair separates 13 haloacetic acids and dalapon in 9 minutes according to EPA Method 552.3.

EPA Method 8081B (extended) - organochlorine pesticides

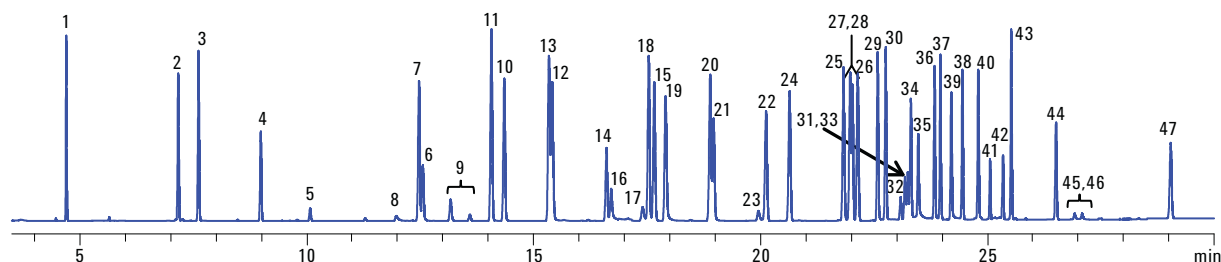
Conditions

Carrier: Helium, constant flow, 43.5 cm/s
 Injection temperature: 250 °C
 Injection: 2 µL, splitless
 Oven: 80 °C, hold 0.5 min, 20 °C/min to 150 °C,
 5 °C/min to 235 °C, 15 °C/min to 300 °C, hold 5 min
 Detector: µECD, 325 °C
 Sample: 50 ng/mL EPA 8081B analytes

Agilent J&W DB-CLP1



Agilent J&W DB-CLP2



Peak ID

1.	1,2-Dibromo-3-chloropropane	17.	Alachlor	33.	Chloropropylate (250 ng/mL)
2.	Hexachlorocyclopentadiene	18.	<i>o</i> -BHC	34.	Endrin
3.	1-Bromo-2-nitrobenzene	19.	Chlorothalonil	35.	Nitrofen
4.	Etr Diazole	20.	Aldrin	36.	4,4'-DDD
5.	Chloroneb	21.	DCPA	37.	Endosulfan II
6.	Trifluralin	22.	Isodrin	38.	4,4'-DDT
7.	Terachloro- <i>m</i> -xylene (surrogate standard)	23.	Kelthane	39.	Endrin aldehyde
8.	Propachlor	24.	Heptachlor epoxide	40.	Endosulfan sulphate
9.	Diallate isomers (250 ng/mL)	25.	<i>γ</i> -Chlordane	41.	Captafol
10.	Hexachlorobenzene	26.	<i>trans</i> -Nonachlor	42.	Methoxychlor
11.	<i>α</i> -BHC	27.	<i>α</i> -Chlordane	43.	Endrin ketone
12.	Pentachloronitrobenzene	28.	Endosulfan I	44.	Mirex
13.	<i>γ</i> -BHC	29.	4,4'-DDE	45.	<i>cis</i> -Permethrin
14.	<i>β</i> -BHC	30.	Dieldrin	46.	<i>trans</i> -Permethrin
15.	Heptachlor	31.	Chlorobenzilate (250 ng/mL)	47.	Decachlorobiphenyl (surrogate standard)
16.	Dichlone	32.	Perthane (250 ng/mL)		

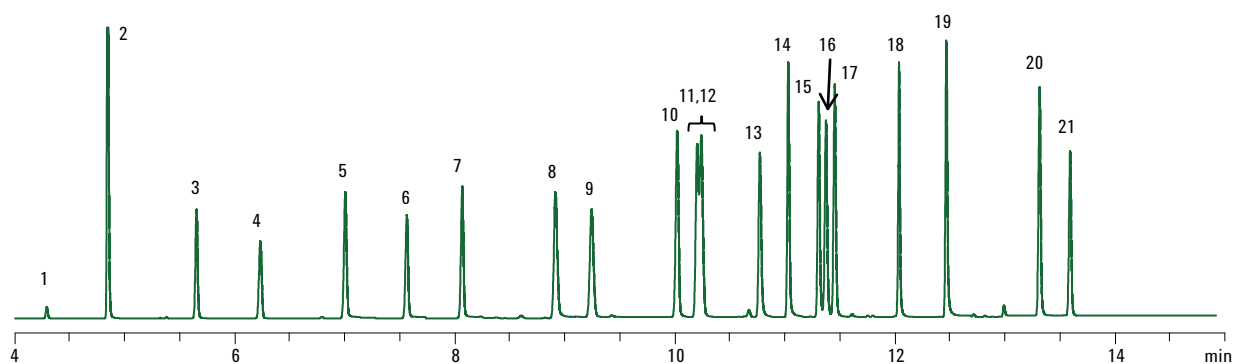
Figure 7. The Agilent J&W CLP1 and CLP2 column separate 47 organochlorine pesticides in less than 30 minutes according to EPA Method 8081B (extended).

EPA Method 8082A- PCBs and aroclors

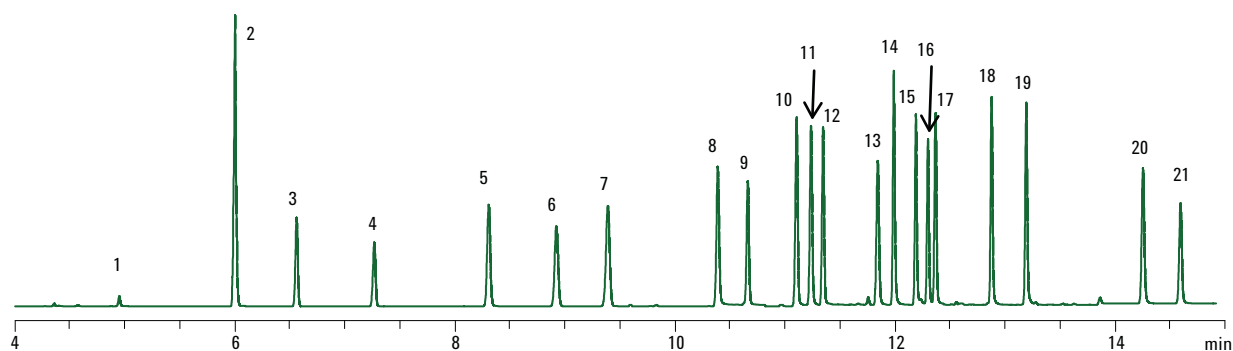
Conditions - PCBs

Carrier: Helium, constant flow, 3 mL/min
 Injection temperature: 250 °C
 Injection: 2 µL, splitless
 Oven: 125 °C, hold 0.25 min, 20 °C/min to 210 °C,
 hold 0.5 min, 7 °C/min to 235 °C, hold 0.75 min,
 25 °C/min to 325 °C, hold 2 min
 Detector: µECD, 340 °C
 Sample: 100 ng/mL PCB congeners,
 100 ng/mL pesticides surrogate mix

Agilent J&W DB-CLP1



Agilent J&W DB-CLP2



Peak ID

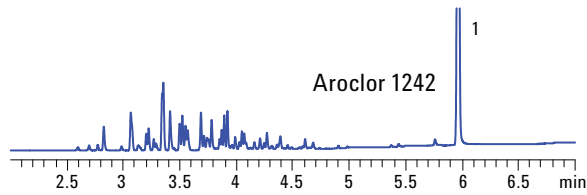
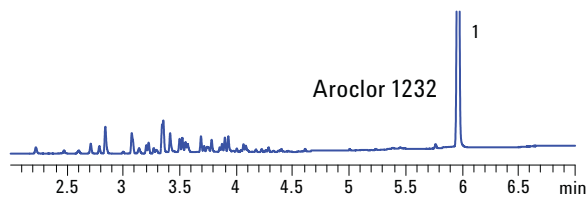
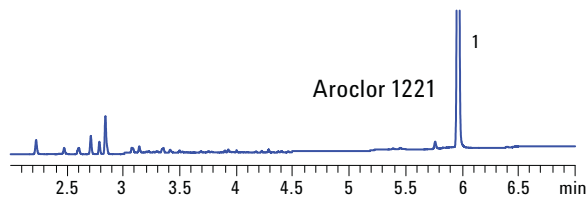
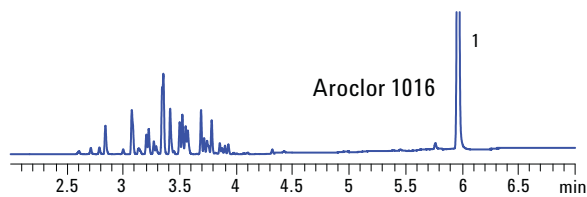
1. BZ #1	8. BZ #66	16. BZ #187
2. Tetrachloro-m-xylene (surrogate standard)	9. BZ #101	17. BZ #183
3. BZ #5	10. BZ #87	18. BZ #180
4. BZ #18	11. BZ #110	19. BZ #170
5. BZ #31	12. BZ #151	20. BZ #206
6. BZ #52	13. BZ #153	21. Decachlorobiphenyl (surrogate standard)
7. BZ #44	14. BZ #141	
	15. BZ #138	

Figure 8. The Agilent J&W CLP1/CLP2 column pair resolves 19 PCB congeners and surrogates in less than 15 minutes according to EPA Method 8082A.

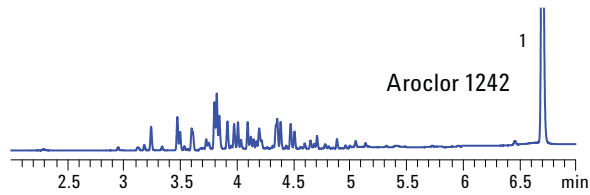
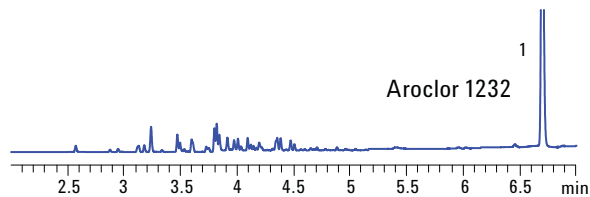
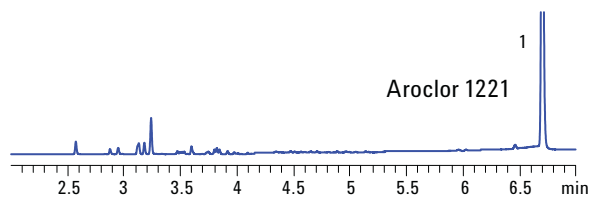
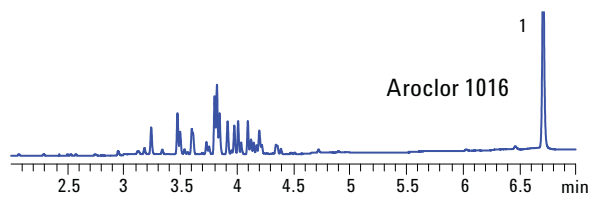
Conditions - aroclors

Inlet liner: Agilent Ultra Inert, single taper splitless
(p/n 5190-2292)
Carrier: Helium, constant flow, 3.75 mL/min
Injection temperature: 250 °C
Injection: 2 µL, splitless
Oven: 160 °C, hold 0.25 min,
35 °C/min to 330 °C, hold 3 min
Detector: µECD, 340 °C
Sample: 100 ng/mL individual aroclor,
100 ng/mL decachlorobiphenyl

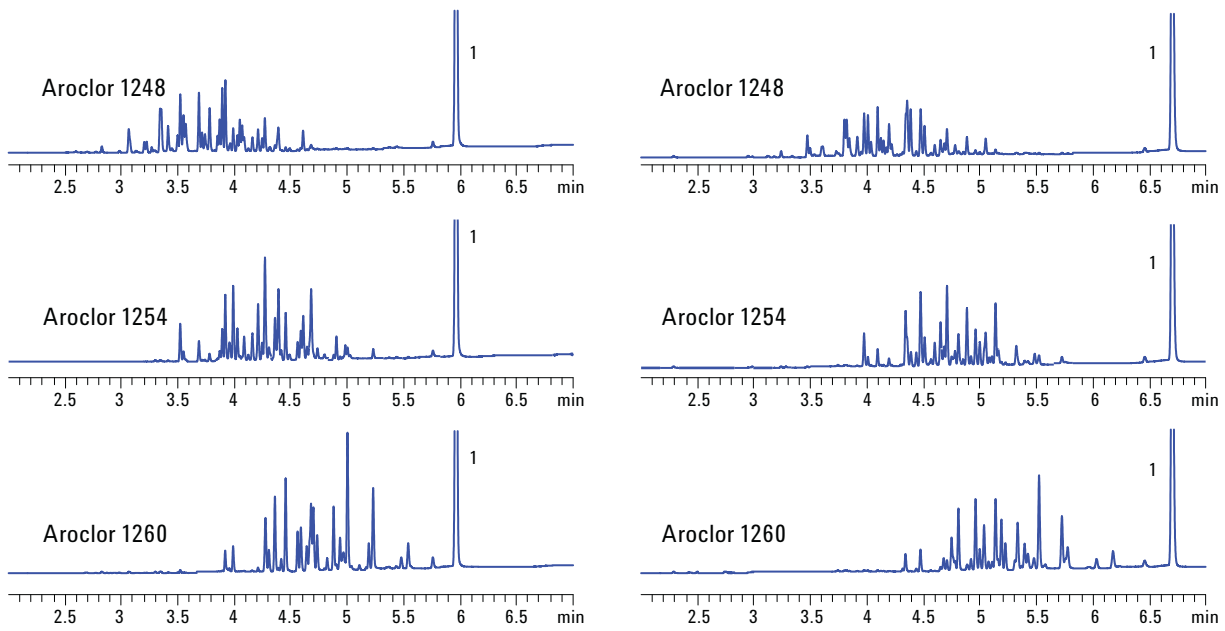
Agilent J&W DB-CLP1



Agilent J&W DB-CLP2



(Continued)



Peak ID

1. Decachlorobiphenyl

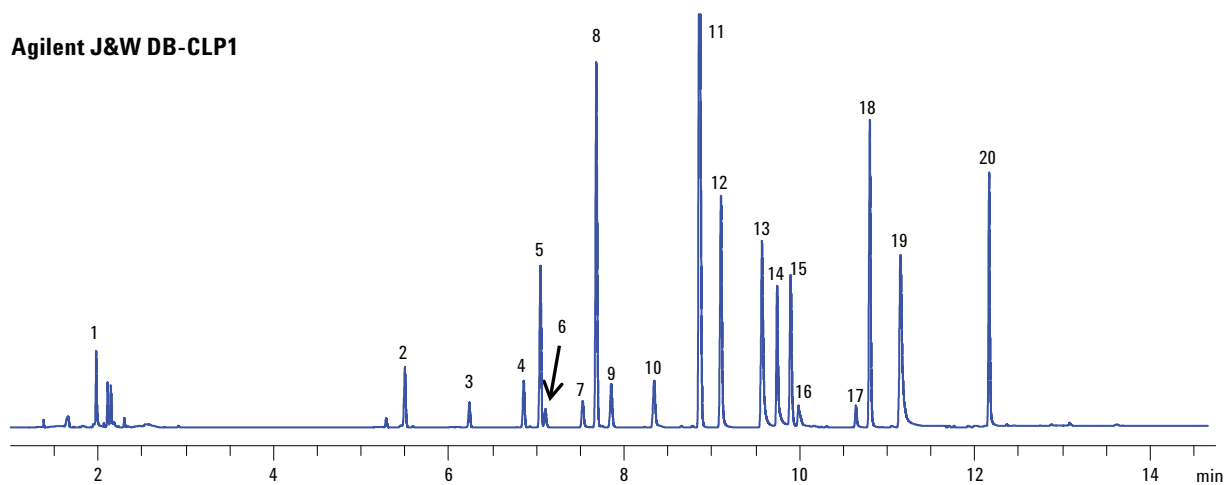
Figure 9. The Agilent J&W CLP1/CLP2 column pair resolves 14 aroclors in under 7 minutes according to EPA Method 8082A.

EPA Method 8151A - chlorophenoxyacid herbicides

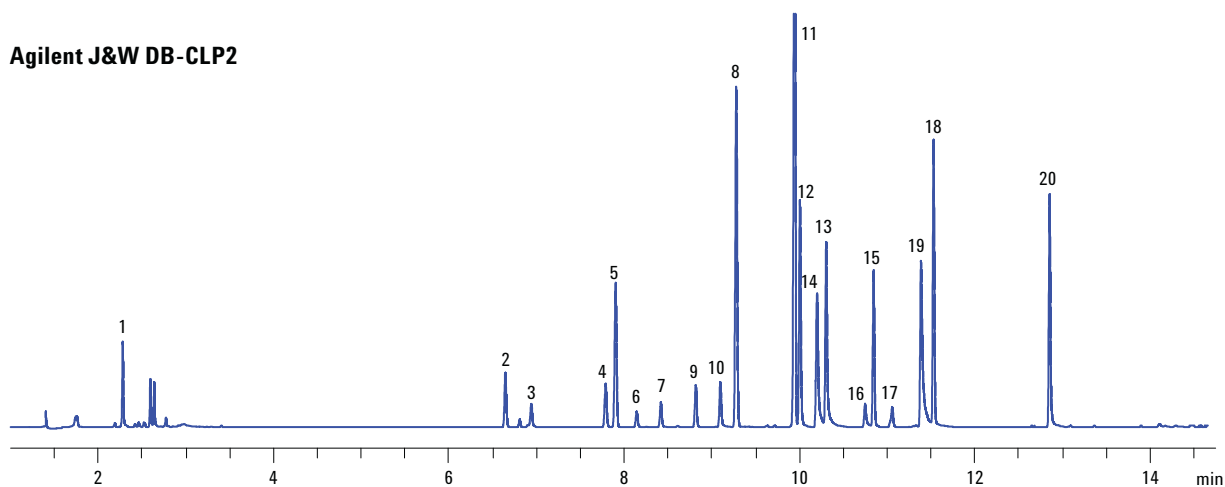
Conditions

Carrier: Helium, constant flow, 3 mL/min
 Injection temperature: 250 °C
 Injection: 2 µL, splitless
 Oven: 85 °C, hold 0.25 min, 25 °C/min to 135 °C,
 11 °C/min to 200 °C, 20 °C/min to 300 °C,
 hold 1.5 min
 Detector: µECD, 325 °C
 Sample: 50 ng/mL chlorophenoxyacid herbicides
 (methyl esters), 50 ng/mL DCAA methyl ester,
 50 ng/mL 4,4'-dibromooctafluorobiphenyl

Agilent J&W DB-CLP1



Agilent J&W DB-CLP2



Peak ID

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

Figure 10. The Agilent J&W CLP1/CLP2 column pair resolves chlorophenoxyacid herbicides in 13 minutes according to EPA Method 8151A.

Conclusions

Agilent J&W DB-CLP1 and DB-CLP2 columns successfully analyze 9 EPA methods along with CLP pesticides, without changing column sets. This capability increases sample throughput with faster analysis times for greater lab productivity. In addition, this column pair delivers fewer coelutions, allowing more accurate determination. This column pair is the pair of choice for your dual ECD methods.

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem. To learn more about the Agilent J&W CLP1 & CLP2 GC column pair please visit www.agilent.com/chem/clp.

www.agilent.com/chem

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