CLP and EPA methods for Pesticides in Water using Agilent J&W DB-CLP1 / DB-CLP2 Columns

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PittConn 2013
Poster # 1480-10P

Agilent Technologies

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 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 can analyze 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.

Introduction

GC column manufacturers design columns specifically for pesticide residue analysis, with differing capability and efficiency. This type of measurement is typically done on 2 columns for simultaneous primary and confirmation analysis, using a retention gap and a y-splitter to connect the columns. In this poster, 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 backbone 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.

The Nine CLP and EPA methods investigated were:

- CLP Pesticides – 19 targeted organohalides
- EPA 504 – 1 (EDB), (DBCP), and(123TCP)
- EPA 505 - organohalides
- EPA 508.1 – chlorinated series
- EPA 551 – solvents, (THMs), and (DBPs)
- EPA 552.3 – haloacetic acids and dalapon
- EPA 8081B – (extended analyte list)
- EPA 8082A – (PCBs) and arochlors
- EPA 8151A – chlorophenoxyacid herbicides

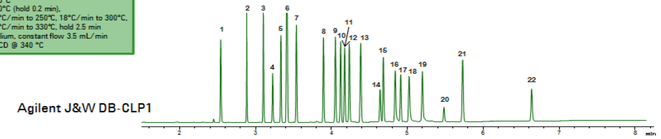
Results of Dual Column Confirmation

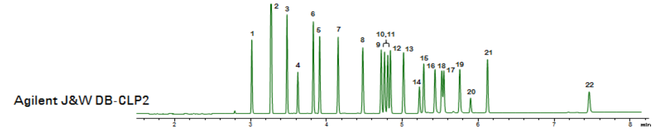
CLP Pesticides

DB-CLP1 30m 0.32mm ID 0.25µm (cat.# 123-8232)
DB-CLP2 30m 0.32mm ID 0.5µm (cat.# 123-8336)
5m x 0.32mm ID deact. guard column
Inert Tee CFT device (cat.# G3184-60065) 1:1 Split

Instrument: Agilent 7890 GC with dual µECD
Sampler: Agilent 7693
Sample: 50 ng/mL CLP Pesticides
Ini. Vol.: 1 µL splitless
Liner: Ultra Inert liner, single taper splitless (cat.#5190-2292)
Ini. Temp.: 250°C
Oven Temp: 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
Carrier Gas: Helium, constant flow 3.5 mL/min
Detector: µECD @ 340 °C

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

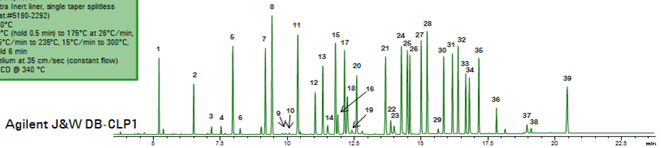


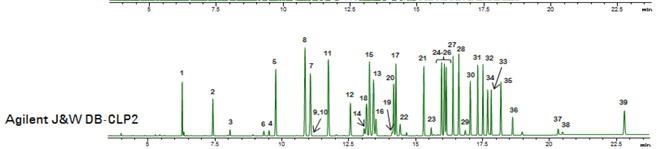


EPA 508.1

DB-CLP1 30m 0.32mm ID 0.25µm (cat.# 123-8232)
DB-CLP2 30m 0.32mm ID 0.5µm (cat.# 123-8336)
5m x 0.32mm ID deact. guard column
Inert Tee CFT device (cat.# G3184-60065) 1:1 Split

Instrument: Agilent 7890 GC with dual µECD
Sampler: Agilent 7673B
Sample: 100 ng/mL 508.1 analytes
100 ng/mL Pesticide Surrogate Mix
Ini. Vol.: 2 µL splitless
Liner: Ultra Inert liner, single taper splitless (cat.#5190-2292)
Ini. Temp.: 250°C
Oven Temp: 80°C (hold 0.5 min) to 175°C at 26°C/min, 6.5°C/min to 235°C, 15°C/min to 300°C, hold 6 min
Carrier Gas: Helium at 35 cm/sec (constant flow)
Detector: µECD @ 340 °C





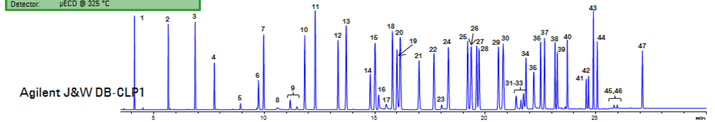
Results of Dual Column Confirmation

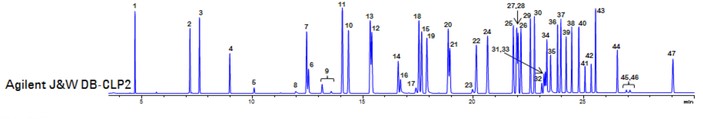
EPA 8081B

DB-CLP1 30m 0.32mm ID 0.25µm (cat.# 123-8232)
DB-CLP2 30m 0.32mm ID 0.5µm (cat.# 123-8336)
5m x 0.32mm ID deact. guard column
Inert Tee CFT device (cat.# G3184-60065) 1:1 Split

Instrument: Agilent 7890 GC with dual µECD
Sampler: Agilent 7693
Sample: 50 ng/mL 8081B analytes
Ini. Vol.: 2 µL splitless
Liner: Ultra Inert liner, single taper splitless (cat.#5190-2292)
Ini. Temp.: 250°C
Oven Temp: 80°C (hold 0.5 min) to 150°C at 20°C/min, 5°C/min to 235°C, 15°C/min to 300°C, hold 5 min
Carrier Gas: Helium at 43.5 cm/sec (constant flow)
Detector: µECD @ 325 °C

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



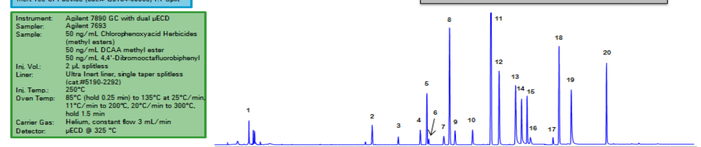


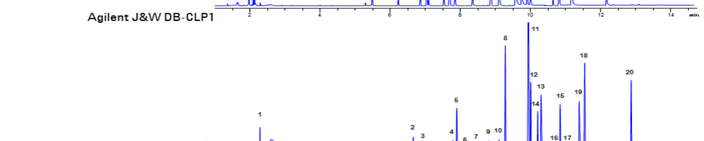
EPA 8151A

DB-CLP1 30m 0.32mm ID 0.25µm (cat.# 123-8232)
DB-CLP2 30m 0.32mm ID 0.5µm (cat.# 123-8336)
5m x 0.32mm ID deact. guard column
Inert Tee CFT device (cat.# G3184-60065) 1:1 Split

Instrument: Agilent 7890 GC with dual µECD
Sampler: Agilent 7693
Sample: 50 ng/mL Chlorophenoxyacid Herbicides (methyl esters)
50 ng/mL DCAA methyl ester
50 ng/mL 4,4'-Dibromooctafluorobiphenyl
Ini. Vol.: 2 µL splitless
Liner: Ultra Inert liner, single taper splitless (cat.#5190-2292)
Ini. Temp.: 250°C
Oven Temp: 85°C (hold 0.25 min) to 135°C at 25°C/min, 11°C/min to 200°C, 20°C/min to 300°C, hold 1.5 min
Carrier Gas: Helium, constant flow 3 mL/min
Detector: µECD @ 325 °C

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





Materials and Methods

The same column pair was used throughout these analyses. Other conditions varied and are shown with their respective chromatograms. Traditionally, replacement of the retention gap or analytical column involved replacing a quartz y-splitter and re-establishing all column connections. To avoid the downtime and extra maintenance associated with y-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.

Column1:Agilent J&W DB-CLP1 30m x 0.32mm, 0.25µm(p/n 123-8232)
Column 2: Agilent J&W DB-CLP2 30m x 0.32mm, 0.25µm (p/n 123-8336)
Gap: 5m x 0.32 mm, deactivated fused silica tubing
CFT Device: Inert-tee (p/nG3184-60065), split1:1
Inlet liner: Agilent UI, single taper splitless (p/n 5190-2292)
(Method 505 liner was dual taper (p/n 5190-3983)
Instrument: Agilent 7890 GC w/ dual µECD
Auto-sampler: Agilent 7693 Automated Liquid Sampler
(Method 505 and 508.1 : 7873B Liquid Sampler)
Magnifier: 20x Coddington magnifier (p/n 430-1020)

References

Please see the application notes listed below additional details at;
http://www.chem.agilent.com/chem
Agilent Application Notes: 5991-0207EN, 5991-0541EN, 5991-0615EN

Conclusions

Agilent J&W DB-CLP1 and DB-CLP2 columns 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.