A 0.32 mm ID Capillary Column Approach to Contract Laboratory Program (CLP) Pesticides Analysis

Application Note

Environmental

Authors

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Abstract

Trace level organochlorine pesticide testing is a high volume critical analysis in the competitive contract laboratory marketplace. This application note demonstrates a robust gas chromatographic method using 0.32 mm id Agilent J&W DB-17ms and DB-XLB GC columns with hydrogen carrier coupled with dual electron capture detection for trace level CLP pesticides analysis. This information is useful for those who prefer the higher sample loading capacity of the 0.32 mm id versus the 0.18 mm id format. Agilent's Capillary Flow Technology (CFT) 2-way splitter without makeup device is used to transfer the sample onto the dual columns. The reusable CFT device simplifies maintenance by isolating the inlet from the analytical columns, which reduces instrument downtime.

Agilent Technologies

Introduction

This application note is for laboratories that prefer using 30-meter 0.32 mm id medium bore capillary columns for pesticide determination and are trying to increase speed of analysis versus a megabore approach while maintaining sample capacity. Analysis time and instrument maintenance are often a limiting factor in sample turnaround for some laboratories. In order to be competitive, a contract laboratory must have the ability to analyze a large number of samples quickly and efficiently, while providing high quality results. The use of a reusable two-way splitter simplifies maintenance and troubleshooting, which can lead to more billable instrument hours.

This analysis is typically done in dual column mode for simultaneous primary and confirmation analysis using a retention gap and quartz y-splitter to connect the columns. The analysis for this application note employed an Agilent Capillary Flow Technology (CFT) 2-way splitter without makeup gas [1] (p/n G3181B). A diagram of the splitter and column setup is shown in Figure 1. The retention gap and columns were installed into the CFT splitter module using ferrules and internal nuts similar to a typical column installation. The Agilent CFT splitter uses SilTite metal ferrules that minimize the likelihood of leaks or detachment even with thermal cycling as high as 350 °C.

With a traditional quartz y-splitter, replacement of the retention gap or analytical column involves replacing the y-splitter and reestablishing all column connections. The reusable CFT splitter uses column connections which are individually connected to the splitter. This feature allows inlet and column maintenance independent of the other analytical column connection. Maintenance of a dual column analytical setup is simplified and instrument downtime is significantly reduced.

Experimental

An Agilent 7890A GC equipped with dual µECDs and a 7683B auto-sampler was used for this series of experiments. Table 1 lists the chromatographic conditions used for these analyses. Table 2 lists flow path consumable supplies used in these experiments.

Table 1. Chromatographic Conditions for CLP Pesticide Calibration Standards

GC:	Agilent 7890A equipped with dual µECDs
Sampler:	Agilent 7683B, 5.0 µL syringe (Agilent p/n 5181-1273) 0.5 µL splitless injection
Carrier:	Hydrogen 79.7 cm/s, Ramped flow 3.76 mL/min hold 5.3 min; 3.76 mL/min to 5.77 mL/min at 100 mL/min^2; hold 4 min
Inlet:	Pulsed splitless; 250 °C, Pulse pressure 40 psi until 0.2 min Purge flow 15 mL/min at 1 min
Inlet Liner:	Deactivated dual taper direct connect (Agilent p/n G1544-80700)
Retention Gap:	1 m 0.32 mm id Hi-Temp Deactivated fused silica tubing (Agilent p/n 160-2855-5)
Column 1:	Agilent J&W DB-17ms 30 m × 0.32 mm × 0.25 µm (Agilent p/n 123-4732)
Column 2:	Agilent J&W DB-XLB 30 m × 0.32 mm × 0.5 µm (Agilent p/n 123-1236)
Oven:	180 °C (0.5 min) to 240 °C (20 °C/min); hold 1.3 min; 20 °C/min to 265 °C; 120 °C/min to 320 °C; hold 3 min.
Detection:	µECD 325 °C, N_2 makeup; constant column + makeup = 62.01 mL/min

Table 2 Flow Path Supplies

CFT device:	2-way splitter accessory without makeup gas (Agilent p/n G3181B)
	Alternative: Deactivated quartz y-splitter (Agilent p/n 5181-3398)
CFT fittings:	Internal nut (Agilent p/n G2855-20530)
	Swaging nut (Agilent p/n G2855-20555)
CFT ferrules:	SilTite ferrules, 0.32 mm id (Agilent p/n 5188-5362)
	SilTite ferrules, 0.25 mm id (Agilent p/n 5188-5361)
Vials:	Amber crimp cap glass vials (Agilent p/n 5183-4496)
Vial caps:	Crimp caps (Agilent p/n 5282-1210)
Vial inserts:	100 µL glass/polymer feet (Agilent p/n 5181-8872)
Syringe:	5 µL (Agilent p/n 5181-1273)
Septum:	Advanced Green (Agilent p/n 5183-4759)
Inlet seal:	Gold plated inlet seal (Agilent p/n 5188-5376)
Inlet liners:	Deactivated dual taper direct connect (Agilent p/n G1544-80700)
Ferrules:	0.5 mm id short; 85/15 Vespel/graphite (Agilent p/n 5062-3514)
20x magnifier:	20x Magnifier loop (Agilent p/n 430-1020)

Sample Preparation

Two CLP pesticide standard mixes were purchased from Accustandard (New Haven, CT). CLP-023R-160X and CLP-024R-160X concentrates were first diluted in 2,2,4-trimethylpentane to yield a stock standard solution and then serially diluted.

The calibration standards were prepared with low level target component concentrations of 80, 40, 32, 16, 6.4, and 3.2 ng/mL. All solutions were prepared in 2,2,4-trimethylpentane using class A volumetric pipettes and flasks. JT Baker Ultra Resi grade 2,2,4-trimethylpentane was purchased thorough VWR International, West Chester, PA 19380 USA. The 2,2,4-trimethyl-pentane was used as a reagent blank and syringe wash solvent.

Results and Discussion

Simultaneous primary and confirmation analysis from a single injection source was accomplished using a dual µECD GC system. An Agilent Capillary Flow Technology 2-way splitter without makeup device was used in place of a traditional quartz y-splitter to connect the two columns to the retention gap. Figure 1 shows a schematic for the instrument setup. The fitting seal design provided extremely low dead volume column connections optimizing performance. The CFT splitter was deactivated, which yielded an inert sample path that minimized loss of signal from active sites.

Hydrogen was used as the carrier gas for this analysis, for shorter retention times with minimal or no loss in resolution. Agilent's GC Method Translation software [2] can be used to convert the chromatographic conditions for helium carrier to hydrogen carrier gas. This software is available for free download from the internet. The analysis was further improved with flow programming to help elute highly retained peaks faster. Flow programming is controlled by an electronic pneumatic control (EPC) to eliminate pressure reproducibility problems.

In this application note, a six-level pesticide calibration curve set was evaluated over the concentration range of 3.2–80 ng/mL using an Agilent J&W DB-17ms 30 m × 0.32 mm × 0.25 µm (p/n 123-4732) for primary analysis and an Agilent DB-XLB 0.32 mm id column (p/n 123-1236) for confirmatory analysis. The 0.5-µL injections were split between two columns yielding an on column loading down to 0.8 pg for low level pesticides. An example chromatogram of the dual column analysis for a 10 pg on column loading for low level target CLP pesticides is shown in Figure 2. Chromatographic conditions used are listed in Table 1.

Using hydrogen carrier gas and flow programming, separation for all 22 organochlorine analytes was achieved in less than 8 minutes. Sharp, symmetrical peaks were obtained under the chromatographic conditions listed in Table 1. Example chromatograms of the 0.8 pg on column loading for the low level target CLP pesticides on each column is shown in Figures 3 and 4. Resolution (R_s) between α-chlordane and endosulfan I was 1.4 on the primary column with excellent linearity (>0.999) and % RSD values below 5% across the concentration range studied.

Figure 5 lists the correlation coefficient for each of the pesticides on both the DB-17ms and DB-XLB columns. Linearity across the range studied gave R^2 values of 0.9993 or greater for all 22 organochlorine compounds on both capillary columns.

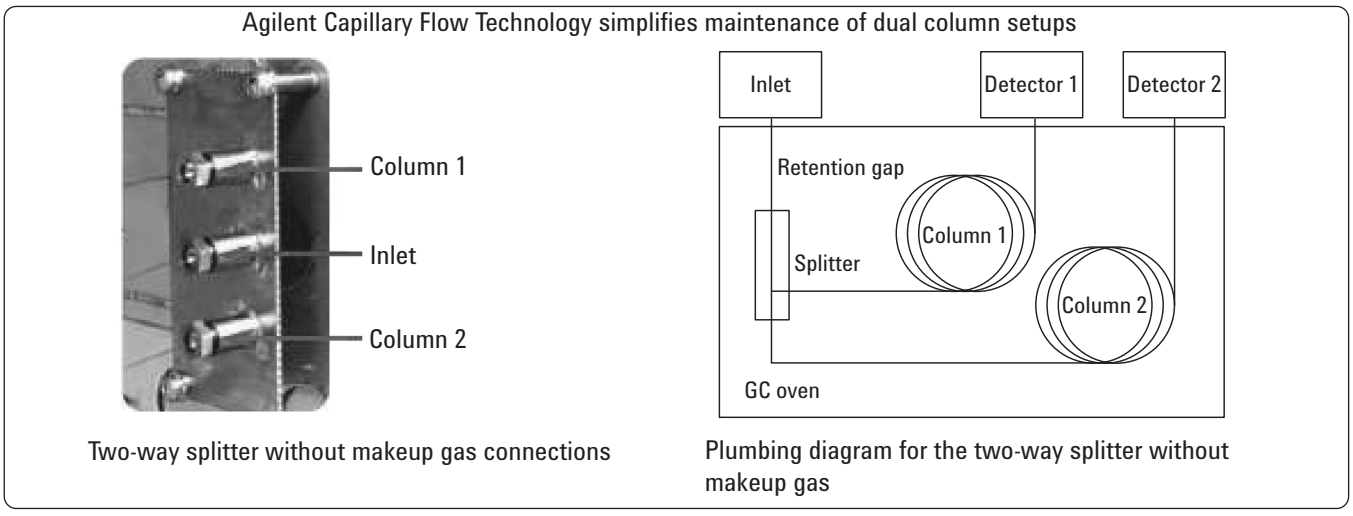

Figure 1. Agilent Capillary Flow Technology 2-way splitter without makeup gas (p/n G3181B) and diagram of instrument setup of simultaneous confirmation from a single injection onto both the primary and confirmation columns.

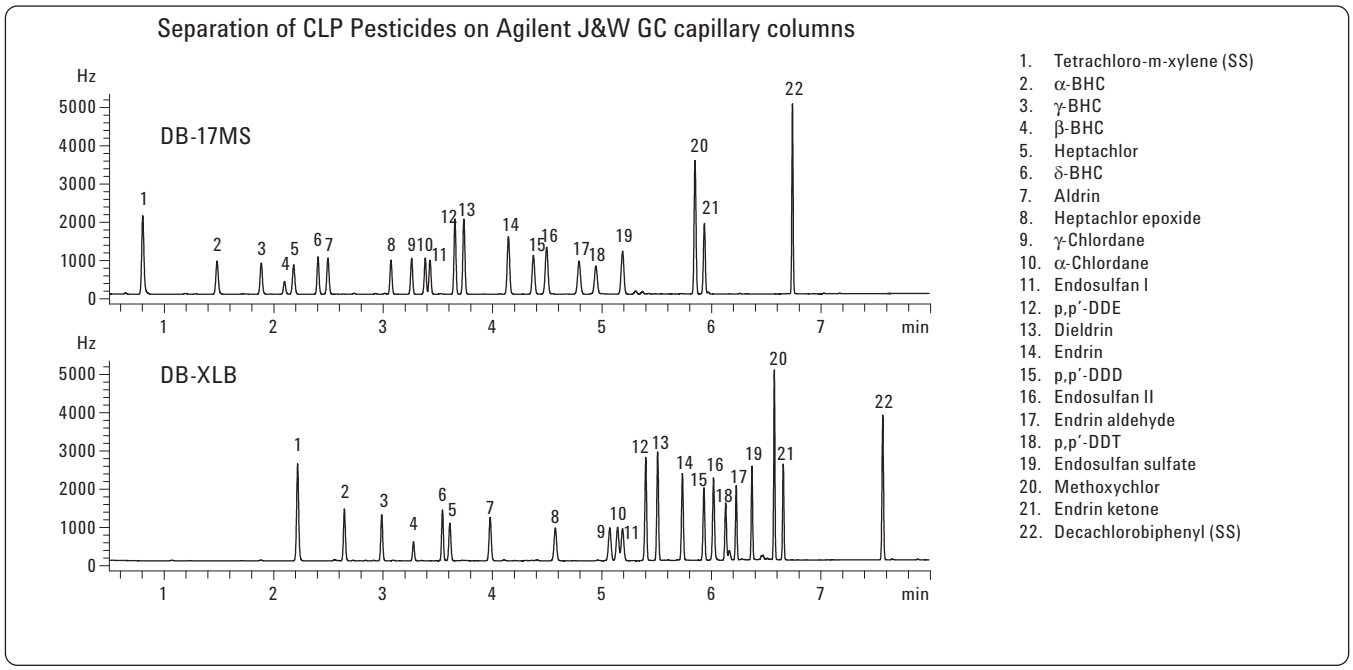

Figure 2. Chromatogram of the 10 pg on column loading of low level target CLP pesticide standard solution on a dual column analysis using an Agilent J&W DB-17ms and DB-XLB capillary GC columns.

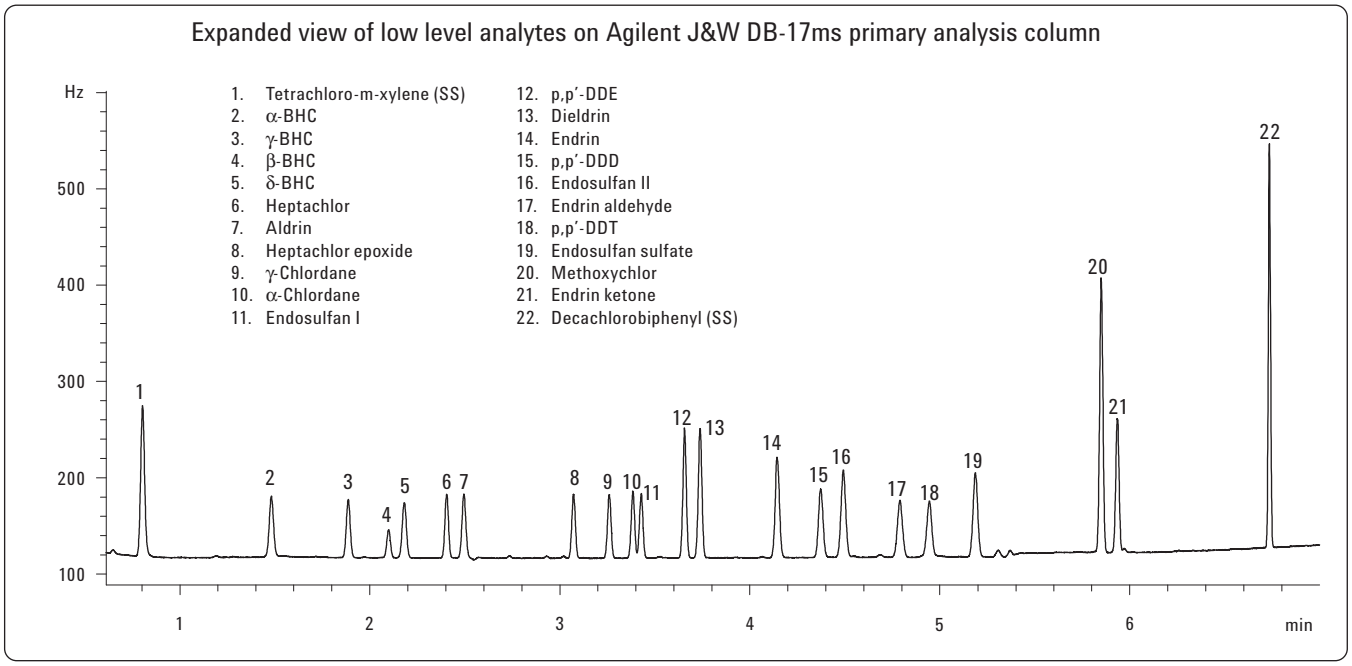

Figure 3. Chromatogram of the 0.8 pg on column loading of low level target CLP pesticide standard solution on an Agilent J&W DB-17ms 30 m × 0.32 mm × 0.25 µm capillary GC column (p/n 123-4732).

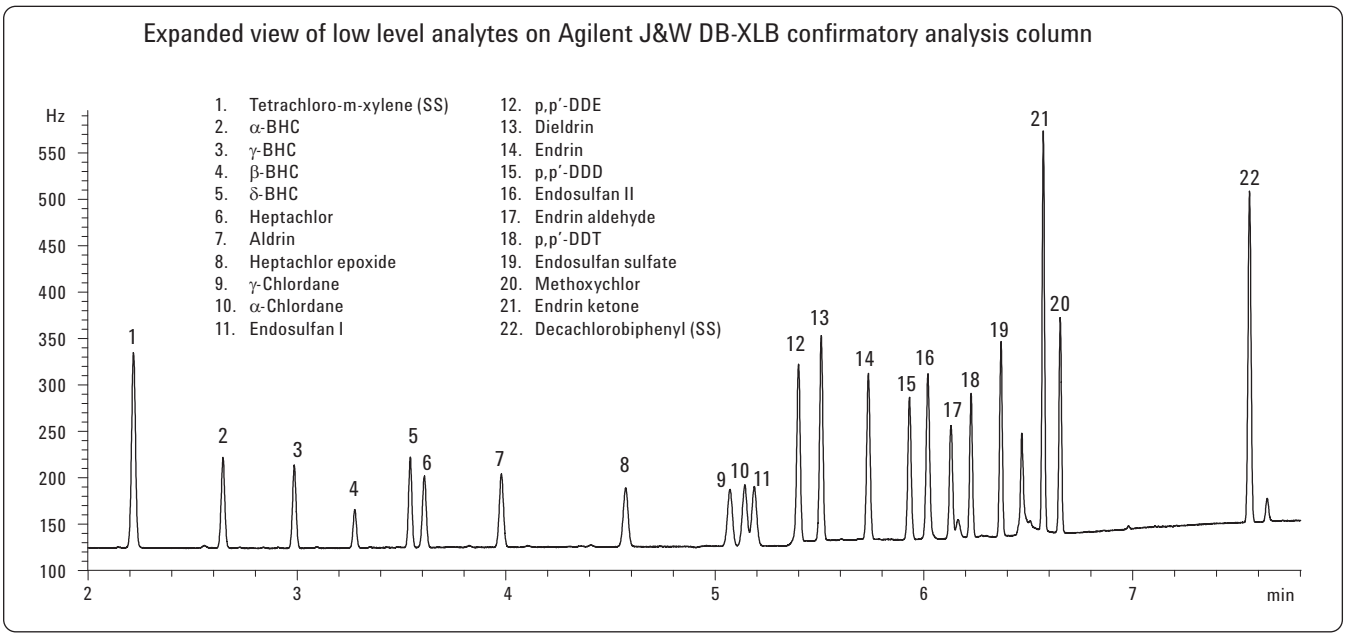

Figure 4. Chromatogram of the 0.8 pg on column loading of low level target CLP pesticide standard solution on an Agilent J&W DB-XLB 30 m × 0.32 mm × 0.5 µm capillary GC column (p/n 123-1236).

Linearity Table for CLP Pesticides on Agilent J&W Primary and Confirmatory analysis columns

DB-17MS

	R^2
TCMX(**SS**)	0.9998
α-BHC	0.9996
γ-BHC	0.9996
β-BHC	1.0000
δ-BHC	0.9996
Heptachlor	0.9998
Aldrin	0.9995
Heptachlor epoxide	0.9998
γ-Chlordane	0.9996
α-Chlordane	0.9997
Endosulfan I	0.9998
4,4'-DDE	0.9997
Dieldrin	0.9996
Endrin	0.9995
4,4'-DDD	0.9998
Endosulfan II	0.9998
4,4'-DDT	0.9995
Endrin aldehyde	0.9996
Endosulfan sulfate	0.9998
Methoxychlor	0.9998
Endrin ketone	1.0000
Decachlorobiphenyl(**SS**)	1.0000

DB-XLB

	R^2
TCMX(**SS**)	0.9998
α-BHC	0.9993
γ-BHC	0.9995
β-BHC	0.9998
δ-BHC	0.9995
Heptachlor	0.9996
Aldrin	0.9994
Heptachlor epoxide	0.9996
γ-Chlordane	0.9995
α-Chlordane	0.9995
Endosulfan I	0.9995
4,4'-DDE	0.9995
Dieldrin	0.9996
Endrin	0.9997
4,4'-DDD	0.9996
Endosulfan II	0.9996
4,4'-DDT	0.9995
Endrin aldehyde	0.9998
Endosulfan sulfate	0.9998
Methoxychlor	0.9997
Endrin ketone	0.9998
Decachlorobiphenyl(**SS**)	0.9998

Figure 5. R-squared values for the organochloropesticides in the CLP calibration standard over the 3.2 ng/mL to 80 ng/mL range of this study.

Conclusions

This study was performed using an Agilent 7890A Gas Chromatograph equipped with dual µECDs. The sharp, symmetrical peak shapes achieved on the Agilent J&W DB-17ms and DB-XLB columns allow for more reliable detection at trace levels. Linearity was excellent for all the pesticides analyzed yielding 0.9993 and higher R^2 values on both primary and confirmatory columns, down to 0.8 pg on column for the low level target compounds.

This application successfully demonstrates a CLP pesticides method using 0.32 mm id Agilent J&W DB-17ms and DB-XLB capillary columns. By using hydrogen as the carrier gas and employing flow programming, complete primary and confirmatory analysis of 22 organochlorine compounds was accomplished in less than eight minutes while maintaining resolution and analytical performance. The 8 minute analysis and confirmation, with an easily maintained, reusable CFT splitter can mean more billable samples per hour for each instrument.

References

1. Agilent G3181B Two-Way Splitter Kit Without Makeup Gas Installation and Operation Guide: http://www.chem.agilent.com/Library/usermanuals/Public/G3181-90120_045611.pdf
2. To download Agilent Method Translation software, please visit the link below: www.agilent.com/chem/gcmethodtranslation

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