GC/µECD Analysis of Chlorinated Plaguicides Using Agilent J&W HP-1ms Ultra Inert and Agilent J&W DB-1301 Capillary GC Columns

Application Note

Environmental

Authors

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Abstract

This application demonstrates a dual column GC method with microelectron capture detection (µECD) for the determination of low level chlorinated plaguicides. This analysis was performed using an Agilent J&W HP-1ms Ultra Inert capillary column for primary detection. The proven inertness of Agilent's Ultra Inert line of columns yields more reliable detection and quantitation at trace levels of active analytes. The HP-1ms Ultra Inert column yielded symmetrical peaks with minimal to no tailing for all of the plaguicides analyzed. Confirmatory analysis was accomplished using a DB-1301 capillary column. Excellent signal-to-noise ratios were achieved at trace levels along with R^2 values of 0.998 and higher for all of the plaguicides in this study.

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Introduction

Plaguicides are a broad class of agrochemicals that are used to control and prevent harmful agricultural pests and diseases, and include a wide variety of herbicides and pesticides. The prevalent use of chlorinated plaguicides worldwide has led to concern about water pollution of both surface and deep water sources. Contamination of surface and underground water occurs through runoff and soil permeation of the plaguicides. Because of the potential environmental and toxicological impact, many governments have passed regulations regarding plaguicides levels in water, such as the European Union Water Framework Directive [1] which sets limits for various pesticides in surface waters.

Degradation and adsorption of analytes by chemically active sites in the sample flow path yields a loss in signal resulting in decreased sensitivity. This makes reliable quantitation difficult and can generate false 'not detected' results at trace levels by lowering an analytes' response below the level of detection. The Agilent J&W HP-1ms Ultra Inert capillary column is used for primary analysis of chlorinated plaguicides due to its high level of inertness [2]. Column inertness, or conversely lack of activity, is vital in achieving sharp, symmetrical peaks especially at trace levels. This property coupled with exceptional low bleed, translates into better signal-to-noise ratios allowing lower detection limits.

This analysis is typically done in dual column mode for simultaneous primary and confirmation analysis using a quartz y-splitter to connect the columns and retention gap. In this application note, an Agilent capillary flow technology (CFT) 2-way splitter without makeup gas [3] (Agilent p/n G3181B) was employed. A diagram of the splitter and column setup is shown in Figure 1. The reusable CFT splitter uses column connections which are individually connected into the splitter. This feature allows inlet and column maintenance to be done independent of the other flow path connections. Maintenance of a dual column analytical setup is simplified and instrument downtime significantly reduced. Other application notes have demonstrated the ease of use of the CFT splitter [4,5].

Experimental

An Agilent 7890A GC system equipped with dual µECDs and with an Agilent 7683B automatic liquid 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 Chlorinated Plaguicides Calibration Standards

GC:	Agilent 7890A GC system equipped with dual µECDs
Sampler:	Agilent 7683B automatic liquid sampler, 5.0 µL syringe (Agilent p/n 5181-1273) 0.5 µL splitless injection
Carrier:	Hydrogen 47.8 cm/s, Ramped flow 1.5 mL/min hold 8 min; 5 mL/min^2 to 1.8 mL/min
Inlet:	Pulsed splitless; 250 °C, Pulse pressure 40 psi until 0.25 min. Purge flow 35 mL/min at 0.75 min
Inlet Liner:	Deactivated dual taper direct connect (Agilent p/n G1544-80700)
Retention Gap: tubing	1 m of 0.32 mm id Hi-Temp Deactivated fused silica (Agilent p/n 160-2855-5) Alternative: 1 m of 0.32 mm id Deactivated fused silica tubing (Agilent p/n 160-2325-5)
Column 1:	Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm, 1.0 µm (Agilent p/n 19091-733UI)
Column 2:	Agilent J &W DB-1301 30 m × 0.25 mm, 1.0 µm (Agilent p/n 122-1333)
Oven:	125 °C (1 min) to 215 °C (35 °C/min), hold 5.5 min, 3 °C/min to 235 °C, 15 °C/min to 280 °C, hold 9 min
Detection:	µECD; 300 °C, N_2 makeup; constant column + makeup = 30 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 5188-5367)
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 organochlorine 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 40, 20, 10, 5, 2.5, and 1 ng/mL. All solutions were prepared in 2,2,4-trimethylpentane using class A volumetric pipettes and flasks. The 2,2,4-Trimethylpentane used was JT Baker Ultra Resi grade purchased thorough VWR International, West Chester, PA 19380-USA. 2,2,4-Trimethylpentane was used as a reagent blank and syringe wash solvent.

Results and Discussion

In this application note a six level plaguicides calibration curve set was evaluated over the concentration range of 1-40 ng/mL using an Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm, 1.0 µm column (p/n 19091S-733UI) for primary analysis and confirmatory analysis on the Agilent J&W DB-1301 column (p/n 122-1333). The 0.5-µL injections were split between two columns yielding an on-column loading down to 0.25 pg for the low level plaguicides. An example chromatogram of the dual column analysis for a 1.25 pg on column loading for the low level target plaguicides is shown in Figure 2. Chromatographic conditions used are listed in Table 1.

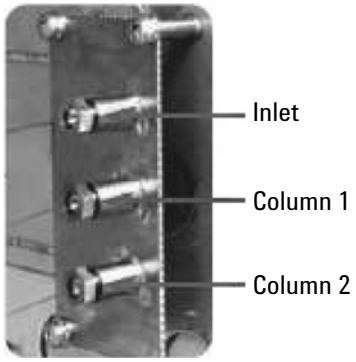
Chemically active sites in a GC column can result in adsorption of target analytes. This can be seen chromatographically in poor peak shape and peak tailing. Unsymmetrical and tailing peaks make reliable quantitation difficult. Figure 3 shows sharp symmetrical peaks for the chlorinated plaguicides using the HP-1ms Ultra Inert. Excellent USP tailing factors (T_f) were noted even for the later eluting plaguicides. This factor is calculated using the following formula [6]:

$$T_f = W_{5.0}/(T_w \times 2)$$

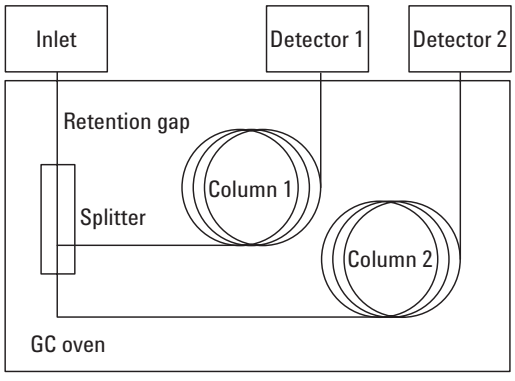
Where T_w = distance between peak front and retention time of peak (T_r) at 5% of peak height, units are the same as used for $W_{5.0}$
$W_{5.0}$ = width at 5% of height

Column inertness and low bleed are essential to sensitivity and accurate detection of trace level analytes. The exceptional inertness of the HP-1ms Ultra Inert column gives excellent detection at trace levels as shown in Figure 4. An on column loading of 0.25 pg β-BHC on the HP-1ms Ultra Inert had a signal-to-noise ratio greater than 11. This allows more precise quantitation at trace levels extending the lower linear range of the analysis. Linearity across the range studied gave R^2 values of 0.998 or greater for all of the organochlorine plaguicides. Figure 5 lists the correlation coefficient for each of the pesticides on both the HP-1ms Ultra Inert and DB-1301 columns.

Simple assembly offers quick and easy maintenance maximizing instrument uptime



Two-way splitter without makeup gas connections



Plumbing diagram for the two-way splitter without makeup gas

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.

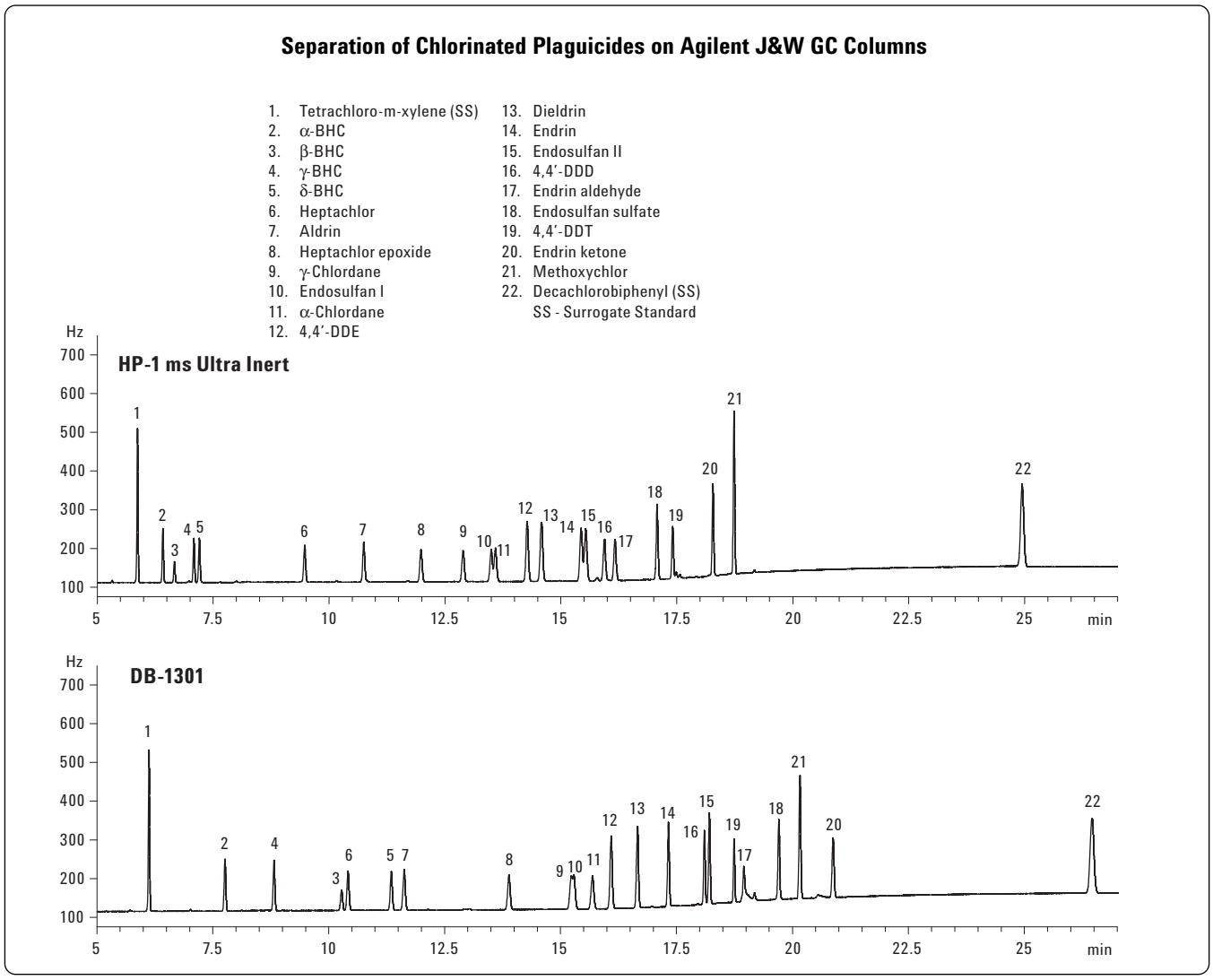


Figure 2. Chromatogram of the 1.25 pg on column loading of chlorinated plaguicides standard solution on a dual column analysis using Agilent J&W HP-1ms Ultra Inert and DB-1301 capillary GC columns.

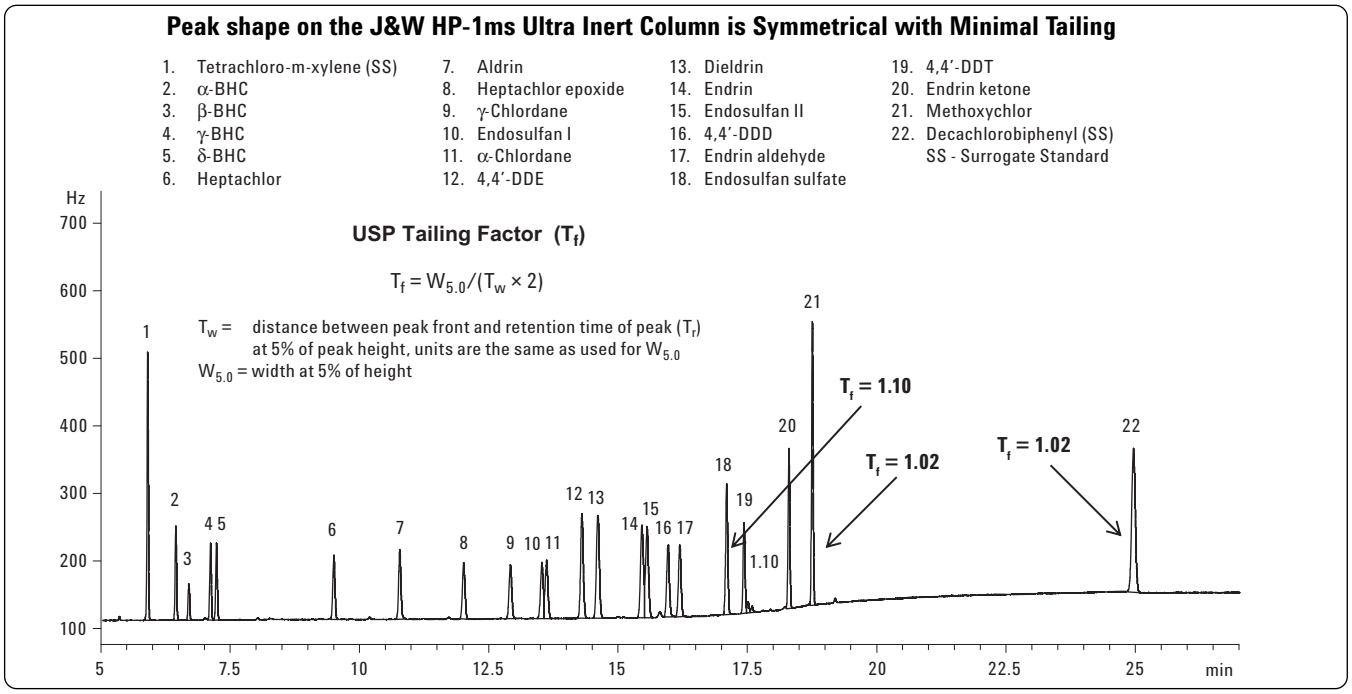


Figure 3. Chromatogram of the 1.25 pg on column loading of chlorinated plaguicides standard solution on an Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm, 1.0 µm capillary GC column.

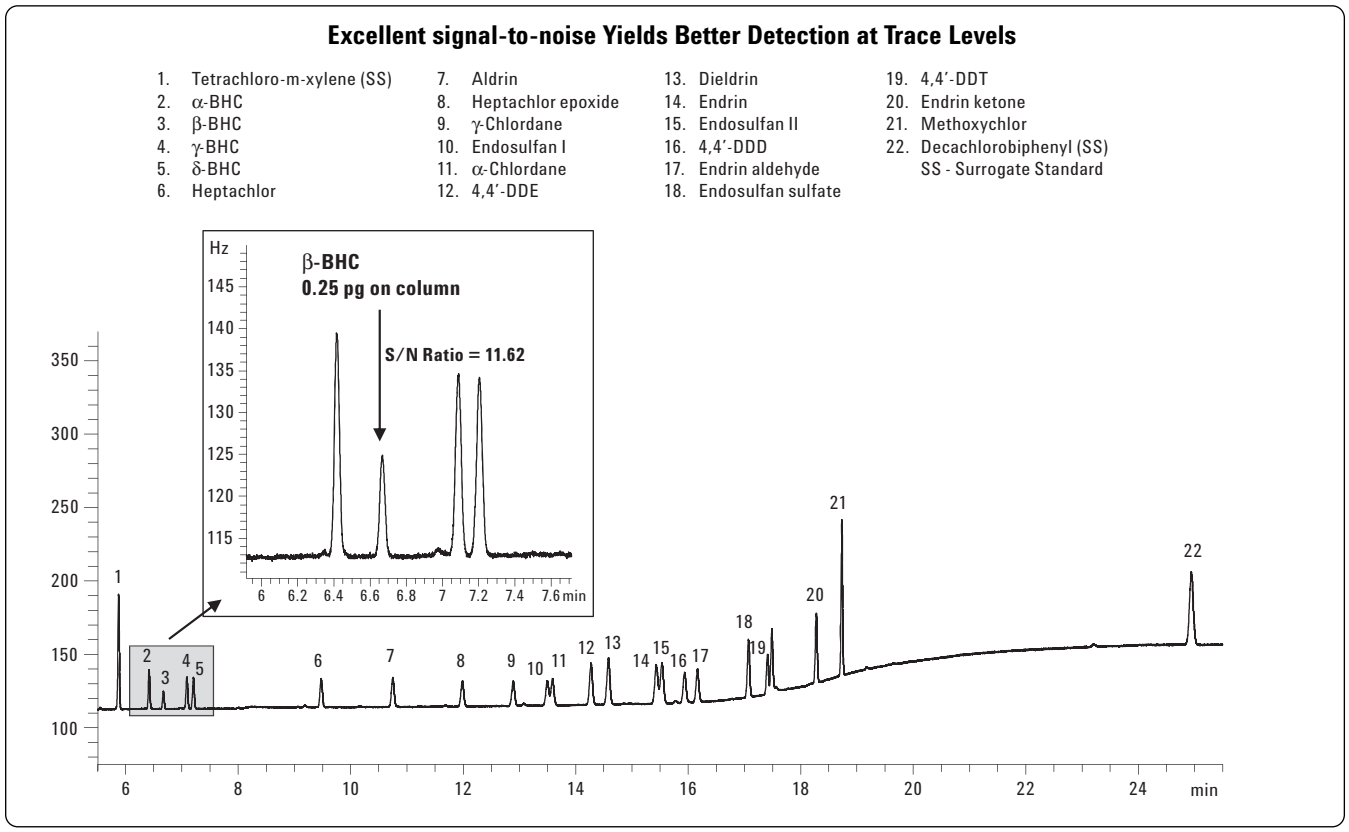


Figure 4. Chromatogram of the 0.25 pg on column loading of trace chlorinated plaguicides standard solution on an Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm, 1.0 µm capillary GC column.

Linearity Results on Agilent J&W Primary and Confirmation Columns

HP-1MS UI		DB-1301	
	R^2		R^2
Tetrachloro-m-xylene (SS)	0.9994	Tetrachloro-m-xylene (SS)	0.9995
α-BHC	0.9982	α-BHC	0.9977
β-BHC	0.9999	β-BHC	0.9998
γ-BHC	0.9989	γ-BHC	0.9985
δ-BHC	0.9984	δ-BHC	0.9982
Heptachlor	0.9989	Heptachlor	0.9990
Aldrin	0.9987	Aldrin	0.9984
Heptachlor epoxide	0.9994	Heptachlor epoxide	0.9992
γ-Chlordane	0.9993	γ-Chlordane	0.9988
Endosulfan I	0.9994	Endosulfan I	0.9994
α-Chlordane	0.9994	α-Chlordane	0.9993
4,4′-DDE	0.9986	4,4′-DDE	0.9983
Dieldrin	0.9989	Dieldrin	0.9987
Endrin	0.9990	Endrin	0.9987
Endosulfan II	0.9995	Endosulfan II	0.9994
4,4′-DDD	0.9991	4,4′-DDD	0.9993
Endrin aldehyde	0.9996	Endrin aldehyde	0.9997
Endosulfan sulfate	0.9998	Endosulfan sulfate	0.9996
4,4′-DDT	0.9996	4,4′-DDT	0.9991
Endrin ketone	0.9999	Endrin ketone	0.9997
Methoxychlor	0.9996	Methoxychlor	0.9992
Decachlorobiphenyl (SS)	0.9997	Decachlorobiphenyl (SS)	0.9997

Figure 5. R-squared values for the organochloropesticides and surrogate standards (SS) in the plaguicides calibration standard over the 1 ng/mL to 40 ng/mL range of this study.

Conclusions

This application successfully demonstrates the use of an Agilent J&W HP-1ms Ultra Inert Capillary GC column for the analysis of trace level chlorinated plaguicides. Linearity was excellent for the plaguicides analyzed yielding 0.998 and higher R^2 values on both primary and confirmatory columns down to 0.25 pg on column for the low level target compounds. The symmetrical peak shapes and excellent signal-to-noise ratios at trace levels emphasize the value of column inertness, making the HP-1ms Ultra Inert a quality choice for consistent and reliable trace analysis of chlorinated plaguicides.

References

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