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

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 R² values of 0.998 and higher for all of the plaguicides in this study.

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Application Note

Environmental
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) |
| Carrier:                        | Hydrogen 47.8 cm/s, Ramped flow 1.5 mL/min hold 8 min; 5 mL/min2 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:                  | 1 m of 0.32 mm id Hi-Temp Deactivated fused silica tubing (Agilent p/n 160-2855-5) |
| 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, N2 makeup; constant column + makeup = 30 mL/min |

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<th>Table 2. Flow Path Supplies</th>
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<td>CFT device:</td>
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<td>Alternative:</td>
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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 (Tf) were noted even for the later eluting plaguicides. This factor is calculated using the following formula [6]:

\[ T_f = \frac{W_{5.0}}{T_w \times 2} \]

Where \( T_w \) = distance between peak front and retention time of peak \( (T_f) \) 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.
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.
1. Tetrachloro-m-xylene (SS)
2. α-BHC
3. β-BHC
4. γ-BHC
5. δ-BHC
6. Heptachlor
7. Aldrin
8. Heptachlor epoxide
9. γ-Chlordane
10. Endosulfan I
11. α-Chlordane
12. 4,4'-DDE
13. Dieldrin
14. Endrin
15. Endosulfan II
16. 4,4'-DDD
17. Endrin aldehyde
18. Endosulfan sulfate
19. 4,4'-DDT
20. Endrin ketone
21. Methoxychlor
22. Decachlorobiphenyl (SS)

SS - Surrogate Standard

**USP Tailing Factor (T_f)**

\[ T_f = \frac{W_{5.0}}{2(T_w \times 2)} \]

- \( T_w \): 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

**Peak shape on the J&W HP-1ms Ultra Inert Column is Symmetrical with Minimal Tailing**

**Excellent signal-to-noise Yields Better Detection at Trace Levels**

**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.
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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