Application Note

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Endrin/DDT Stability for Fritted and Wool Liners

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Abstract

This application note demonstrates the lifetime of Agilent Ultra Inert fritted liners for environmental applications with complex, nonvolatile matrix in comparison to wool packed liners. Endrin and 4,4'-DDT breakdowns were used to determine deactivation consistency and liner lifetime when exposed to real-world samples, such as soil extracts. The Ultra Inert deactivation, with the new fritted liner design, allows liners to remain chemically inert throughout more injections of complex matrix and have consistently longer lifetimes.

Introduction

Endrin and 4,4'-DDT are organochlorine pesticides that, according to various methods dictated by the United States Environmental Protection Agency (U.S. EPA),[1,2,3] can be used to assess the inertness of a gas chromatograph. The breakdown of 4,4'-DDT into 4,4'-DDE and 4,4'-DDD (called DDT, DDE, and DDD from here on) and the isomerization of endrin into endrin aldehyde and endrin ketone can be caused by various factors. Examples are active sites in the flow path and high temperatures, where matrix, septum, nondeactivated metal particles, or open silanol groups can be responsible for the active sites.

Methods, such as U.S. EPA 8081B and U.S. EPA 525, set limits on the levels of the breakdown components of endrin and DDT, both individually and in total.[1,2,3] Liner lifetime is important in the context of these methods, because once breakdown limits are reached, maintenance must be performed on the GC to return it to the specifications. This can introduce significant downtime into analyses. Combining some of the strictest guidelines for these two compounds yields a limit of 15% breakdown for each individual compound, or 20% in total (whichever is reached first). In U.S. EPA 8081B, various matrices are listed for testing purposes, including soil. Soil extracts were used in this application note to test the inertness and robustness of different inlet liners.

Experimental

Two standards, an endrin and DDT mixture (which will be referred to as the performance mixture), and a degradation product mixture, were procured for performance testing. The endrin and DDT standard contained endrin at 250 µg/mL and DDT at 500 µg/mL. The degradation product standard contained endrin aldehyde and endrin ketone (endrin breakdown products) at 250 µg/mL and DDD and DDE (DDT breakdown products) at 500 µg/mL.

Both standards were diluted separately with hexane to concentrations of 25 ng/mL for endrin and endrin-related breakdown products, and 50 ng/mL for DDT and DDT-related breakdown products. A stock solution of β-BHC was procured and added at a concentration of 20 ng/mL as an internal standard in both mixtures. The breakdown product mixture was used to identify the retention times of breakdown products relative to the β-BHC, endrin, and DDT retention times.

A composite mixture of soils extracted with dichloromethane was procured from Pace Analytical (Mt. Juliet, TN). This soil extract was also diluted 1:1 in hexane to serve as the matrix.

Instrumentation

An Agilent 7890B gas chromatograph (GC) with dual electron capture detectors (ECDs) was configured for dual simultaneous injections with two Agilent 7693A automatic liquid samplers and two identical flow paths. The instrument and consumables chosen for testing are listed in Table 1. The front split/splitless inlet was connected to the front ECD with an Agilent Ultra Inert DB-8270D column. The rear split/splitless inlet was connected to the rear ECD with an identical Agilent Ultra Inert DB-8270D column. Nitrogen was used as the make-up gas for the ECDs. Fritted liners and wool packed liners with different locations for the frit or wool in the liner were tested and are specified in Table 2. The GC method parameters are listed in Table 3.

Table 1. The instrument and consumables used in testing.

Parameter	Value
GC	Agilent 7890 gas chromatograph
Autosampler	Agilent 7693A automatic liquid sampler
Sample Tray	G4514A 150 vial autosampler tray
Syringe	Agilent ALS syringe, Blue Line, 10 µL, PTFE-tip plunger (p/n G4513-80203)
Column	Agilent DB-8270D Ultra Inert GC column, 30 m × 0.25 mm, 0.25 µm (p/n 122-9732)
Inlet Septum	Agilent Advanced Green septum, nonstick, 11 mm (p/n 5183-4759, 50/pk)
Vials	Agilent A-Line certified vial, screw top, amber, 100/pk (p/n 5190-9590)
Vial Inserts	Agilent deactivated vial inserts; 100/pk (p/n 5181-8872)
Vial Screw Caps	Agilent screw cap, PTFE/silicone/PTFE septa, cap size: 12 mm, 500/pk (p/n 5185-5861)

Results and discussion

A chromatogram of the performance mixture, shown in blue in Figure 1, was overlaid with a chromatogram of the respective degradation products (red trace), showing acceptable separation between the degradation products, endrin, and DDT.

A sequence of 106 injections was run to determine the working lifetime of the different liner styles. This sequence includes a repeating section which consists of the following, and was repeated 10 times:

- One blank injection of hexane
- One injection of the performance mixture
- Six injections of matrix
- One injection of the performance mixture
- One injection of the degradation products (to reverify retention times)

Table 2. Liners tested in the GC-ECD analysis.

Liner	Name Used in Text
Low-Frit/Wool Liners	
Agilent Ultra Inert inlet liner, splitless low fritted (p/n 5190-5112)	Agilent low frit liner
Agilent Ultra Inert inlet liner, splitless, single taper with wool (p/n 5190-2293)	Agilent low wool liner
Splitless single taper liner with wool A	Low wool liner A
Splitless single taper liner with wool B	Low wool liner B
Splitless single taper liner with carbon frit A	Low carbon frit liner A
Mid-Frit/Wool	
Agilent Ultra Inert inlet liner, universal, mid-frit (p/n 5190-5105)	Agilent mid-frit liner
Agilent Ultra Inert inlet liner, split low pressure drop, with glass wool (p/n 5190-2295)	Agilent mid-wool liner
Mid-frit liner A	Mid-frit liner A
Liner, low pressure drop, with glass wool A	Mid-wool liner A

Table 3. Method parameters.

Parameter	Value
Injection Volume	1 µL
Inlet Temperature	200 °C
Inlet Mode	Pulsed splitless
Pulse Pressure	60 psi until 0.3 min
Purge Flow To Split Vent	75 mL/min at 0.5 min
Column Flow	3 mL/min, constant flow of helium
Oven Temperature Ramp	120 °C (hold 1 min); 30 °C/min to 220 °C; 8 °C/min to 280 (1 min) Run time: 12.83 min
Detector (ECD) Temperature	280 °C
Make-Up Flow	N_2, 30 mL/min

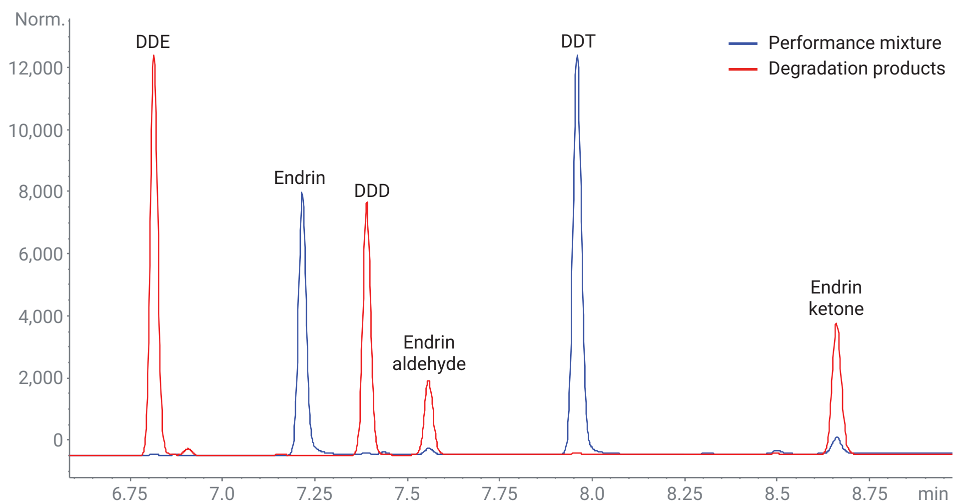

Figure 1. Overlaid chromatograms of the performance mixture (blue trace) and degradation products (red trace). The concentration of endrin and related breakdown products was 25 ng/mL; DDT and related breakdown products were concentrated at 50 ng/mL.

A set of three performance mixture injections was performed before any matrix injections and at the end of the sequence, totaling 60 matrix injections, 24 performance mixture injections, 12 hexane blanks, and 10 degradation product injections. The peak areas of endrin and DDT and their degradation products were monitored throughout the sequence, and the percentage breakdown of each compound was calculated using Equations 1 and 2, as specified in U.S. EPA 8081B and 525.2.[1,2]

The number of injections before reaching the failure criteria were recorded and averaged for each liner type to estimate a working lifetime. With some liners, neither endrin nor DDT would reach 15% breakdown and the total would not reach 20% within the span of the 106-injection sequence. For these cases, a value of 105 (the number of the last performance mixture injection) was used to generate an approximate average. The results of these averages and their respective relative standard deviations are shown in Table 4. Graphic representations of these average liner lifetimes are shown in Figures 2 and 3 for the splitless (low frit and low wool) liners and the mid-wool and mid-frit liners, respectively.

For the comparison of low wool and low frit liners, the Agilent low frit liner had the longest average lifetime (87 runs) of the splitless (low wool or low frit) liners. Low wool liner A exhibited the second longest lifetime of 81 runs, compared to the Agilent low wool liner (74 runs), which could be explained by greater amount of wool in low wool liner A. More glass wool in the liner may trap matrix in the wool without causing significantly increased inlet activity, leading to a longer lifetime. Low wool liner B exhibited the shortest lifetime of 58 runs. This liner was packed with a similar amount of wool as low wool A, but more wool than the Agilent low wool liner. As noted in the Table 4 footnote, low carbon frit A liners failed

Equation 1.

$$\%\ \text{breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDE + DDD)}}{\text{sum of all peak areas (DDT + DDE + DDD)}} \times 100$$

Equation 2.

$$\%\ \text{breakdown of endrin} = \frac{\text{sum of degradation peak areas (aldehyde + ketone)}}{\text{sum of all peak areas (endrin + aldehyde + ketone)}} \times 100$$

Table 4. Average lifetime and relative standard deviation for each liner type.

Liner	Average Lifetime (Number of Runs)	%RSD
Low Frit/Wool		
Agilent Low Frit	87	17%
Agilent Low Wool	74	34%
Low Wool A	81	27%
Low Wool B	58	40%
Low Carbon Frit A	–*	–
Mid-Frit/Wool		
Agilent Mid-Frit	96	14%
Agilent Mid-Wool	100	27%
Mid-Frit A	89	14%
Mid-Wool A	86	29%

* Low carbon frit A liners were tested, but immediately failed the required breakdown specifications and could not be evaluated.

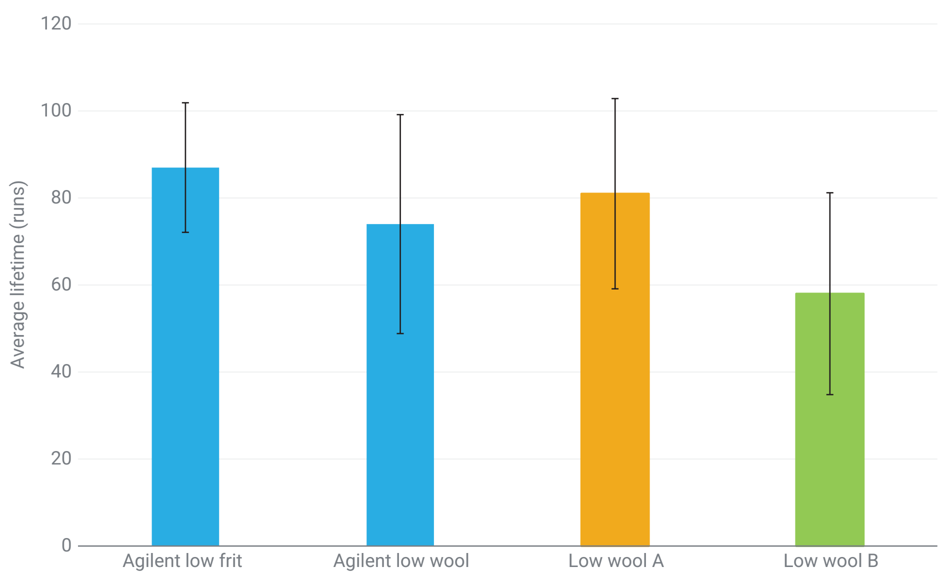

Figure 2. Comparison of the lifetimes of the low wool and low frit liner styles with error bars of ±1 standard deviation.

the breakdown requirements in the initial three performance mixture injections, indicating the style of liner is not designed for this analysis.

When reviewing the mid-wool and mid-frit liner lifetimes, the Agilent mid-frit liner provided a longer lifetime of 96 runs compared to both mid-frit A and mid-wool A. The Agilent mid-wool liner lasted the longest number of injections (100) for the middle barrier liner style. There is a large amount of wool in the Agilent mid-wool liner compared to the size of the frit, which may account for the longer lifetime.

Across the board, the low frit and mid-frit liners have more consistent lifetimes than the wool liners, evidenced by lower relative standard deviations (Table 4). This can be attributed to the fact that physical characteristics of the frit, such as overall size and porosity, can be controlled more precisely than those of the glass wool, which can be more irregular. Both Agilent low frit and mid-frit liner styles yielded relatively long lifetimes and had low %RSDs, demonstrating the excellent performance of the Ultra Inert deactivation with the fritted liner design.

Conclusion

Agilent Ultra Inert deactivation of inlet liners provides an inert environment for sample vaporization. Agilent low frit, mid-frit, and mid-wool liners tend to have longer lifetimes, and the fritted liners perform more consistently than other tested liners with a complex matrix. These two characteristics make the Agilent Ultra Inert splitless low fritted liner and Agilent Ultra Inert universal mid-frit liner ideal choices for minimizing downtime when routinely analyzing sensitive compounds, such as endrin and DDT.

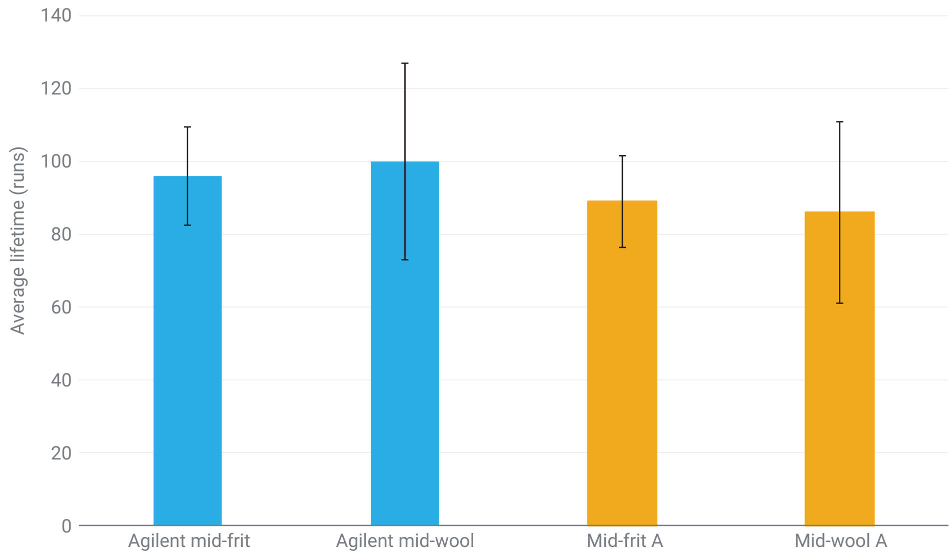

Figure 3. Comparison of the lifetimes of the mid-wool and mid-frit liner styles with error bars of ±1 standard deviation.

References

1. Method 8081B: Organochlorine Pesticides by Gas Chromatography. *United States Environmental Protection Agency*, **2007**.
2. Munch, J. W. Method 525.2: Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/ Mass Spectrometry. *United States Environmental Protection Agency*, *Department of Water,* **1995**.
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