Endrin and DDT Breakdown Evaluation Using an Agilent Inert Flow Path Solution

Application Note

Environmental

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Abstract

Flow path inertness plays a critical role in pesticide analysis for accuracy and precision, especially for analytes subject to degradation in a hot inlet such as endrin and DDT. Catalytic endrin and DDT breakdown products were tracked as part of an inert flow path performance evaluation. The results indicate that the Agilent Inert Flow Path Solution provides superior inertness and lower breakdown than standard flow path split/splitless inlets.

Introduction

The analysis of active compounds by gas chromatography (GC) continues to be challenging in areas such as pesticides, foods, environmental, and drug analysis. To achieve reliable and solid results for active compounds, it is critical to minimize the interaction of active analytes along the GC flow path, starting from the injector, to the column, and finally to the detector. All parts in this flow path play a key role in influencing the inertness of the flow path. Active sites in the flow path can lead to the degradation or adsorption of active analytes, resulting in poor linearity of calibration curves and loss of sensitivity. Therefore, it is critical to deactivate the entire sample flow path to make it fully inert. Minimizing surface activity throughout the flow path is essential to achieve consistent results.

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Many pesticide compounds are intentionally designed to decompose easily so that accumulation in the environment is minimized. However, this labile feature makes instrument analysis more difficult, especially when using GC and GC/MS as detectors, because the unwanted degradation or adsorption of labile compounds during analysis can result in inaccurate quantitative or qualitative results, or both.

Endrin and DDT are two well known compounds that can degrade excessively in gas chromatographic analysis, especially at the inlet. When the inertness of the GC flow path is not well controlled, active sites can initiate degradation so that endrin decomposes to endrin aldehyde (EA) and endrin ketone (EK), and DDT degrades to DDE and DDD. According to the US EPA Method 8081B, the percentage breakdown acceptance criteria for endrin and DDT are <15% individually and <30% combined [1].

Most breakdown reactions occur on Hot inlet surfaces. The degradation increases when the component's surface deactivation degrades with continuous use. The creation of additional active sites causes the breakdown reactions of endrin, and DDT to increase. Therefore, endrin and DDT breakdown is a very useful probe to evaluate not only the efficiency of deactivated flow path parts, but also the stability of surface deactivation over time for multiple injections.

Equations 1 and 2 show the calculation of endrin and DDT breakdown.

Equation 1

$$\%\ \text{Endrin breakdown} = \frac{(\text{Peak area}_{EA} + \text{Peak area}_{EK})}{(\text{Peak area}_{EA} + \text{Peak area}_{EK} + \text{Peak area}_{Endrin})} \times 100$$

Equation 2

$$\%\ \text{DDT breakdown} = \frac{(\text{Peak area}_{DDE} + \text{Peak area}_{DDD})}{(\text{Peak area}_{DDE} + \text{Peak area}_{DDD} + \text{Peak area}_{DDT})} \times 100$$

Experimental

Endrin and DDT stock standards were purchased from AccuStandard, Inc., New Haven, CT, USA. ULTRA RESI-ANALYZED iso-octane was purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. The 100/200 µg/mL endrin/DDT stock solution was diluted 2,000 times with iso-octane to 50/100 ng/mL endrin/DDT testing solution. This testing solution was stored at 4 °C in the refrigerator and used for no more than five days. Iso-octane was also used for solvent blank injections and syringe rinse solvent.

The endrin/DDT breakdown test was done on an Agilent 7890A GC equipped with an Agilent 7683B Automatic Liquid Sampler and a µECD.

Conditions

Columns:	Agilent J&W HP-5ms UI, 15 m × 0.25 mm, 0.25 µm, (p/n 19091S-431UI) Agilent J&W HP-5, 15 m × 0.25 mm, 0.25 µm, (p/n 19091J-431) non-Agilent 5ms column, 15 m × 0.25 mm, 0.25 µm
Carrier:	Helium at 1.0 mL/min (33 cm/s), constant flow
Oven:	For sample run 120 °C (1 min), 30 °C/min to 220 °C (0 min), 8 °C/min to 280 °C (1 min), for solvent run 250 °C (5 min)
Injection:	1 µL
Inlet:	Splitless 250 °C, 50 mL/min purge flow at 0.75 min
Detector:	µECD, 280 °C, constant column + makeup flow with combined flow of 60 mL/min
Autosampler:	Agilent G4513A, 10 µL syringe (p/n 5181-1267) solvent A wash, 3 pre-injection, 0 postinjection solvent B wash, 0 pre-injection, 3 postinjection sample wash, 1 sample pumps, 3

Flow path supplies

All Agilent unless otherwise stated

Vials:	Amber, screw cap (p/n 5182-0716)
Vial caps:	Blue, screw cap (p/n 5182-0717)
Vial inserts:	Glass, 150 µL, with polymer feet (p/n 5183-2088)
Septum:	Advanced Green non-stick, 11 mm (p/n 5183-4759)
Ferrules:	Graphite, 0.4 mm id (p/n 500-2114)
O-rings:	Nonstick liner O-ring (p/n 5188-5365)
Inlet liners:	Agilent Ultra Inert single taper splitless liner (p/n 5190-2292) Agilent original deactivated single taper splitless liner (p/n 5181-3316) non-Agilent splitless single taper gooseneck
Inlet weldments:	(split/splitless inlet): Agilent standard (untreated), cap inlet shell weldment assembly (p/n G3452-80570) and insert weldment (p/n G3452-60585) Siltek (SilcoNert 2000), cap inlet shell weldment assembly and insert weldment; Agilent UltiMetal Plus, cap inlet shell weldment assembly, inert (p/n G3452-60570) and insert weldment, inert (p/n G3452-60586)
Inlet seals:	Gold plated inlet seal with washer (p/n 5190-2209), Ultra Inert gold-plated inlet seal with washer (p/n 5190-6144), non-Agilent stainless steel Siltek-treated inlet seal, 0.8 mm id

Results and Discussion

These tests evaluated the Agilent inert flow path, and compared it with Agilent and non-Agilent standard flow path components.

Possible contributors to the degradation or adsorption of active compounds include: injector inlet weldments (body and insert), liner, inlet seal, analytical column, column coupling material, and detector. Therefore, it is critical to minimize the impact of all of these parts on flow path activity and also keep the test conditions consistent for accurate comparison.

We selected µECD for detection to eliminate any activity contributed from the mass spectrometer. Different liner configurations have different effects on liner activity. This application note used the hot splitless mode and single taper splitless liner because of their wide application in pesticide analysis [2].

Endrin/DDT breakdown test

As described above, an endrin/DDT breakdown test was used for flow path evaluations.

A 50/100 ppb endrin/DDT solution made in iso-octane was used for a multiple injection test.

An iso-octane blank was normally injected as the very first run in the sequence. A standard sample was run afterwards to collect the initial breakdown data for endrin/DDT breakdown. Nine solvent injections were run after the standard run. This cycle was repeated 19 more times until 200 injections were made. One more standard was then injected to determine the final breakdown data. A fast solvent run method was used for solvent runs to save time. The endrin/DDT standard run data were collected; and these data were used to calculate the breakdown results and generate the breakdown profile. In addition to the Agilent inert flow path, the Agilent standard flow path and Siltek-deactivated components with equivalent liner and column configuration were tested for comparison (Table 1).

Table 1. Flow path components for the different test configurations.

Flow path component	Inlet weldment (split/splitless)	Inlet seal	Liner (single taper/splitless)	GC column (15 m × 0.25 mm, 0.25 µm)
Agilent standard flow path	Untreated, cap inlet shell weldment assembly, insert weldment	Standard gold seal (10/pk)	Agilent original deactivation	HP-5
Agilent inert flow path	UltiMetal Plus, cap inlet shell weldment, insert weldment	Ultra Inert gold seal	Ultra Inert deactivation	HP-5ms UI
non-Agilent flow path	Siltek (SilcoNert 2000), cap inlet shell weldment assembly, insert weldment	Stainless steel Siltek seal	non-Agilent	non-Agilent 5ms

Figure 1 shows the sample chromatograms of endrin/DDT standards run on the Agilent inert flow path.

The first injection delivered 2.1% endrin breakdown and 2.6% DDT breakdown, the 201st injection had 9.2% endrin breakdown and 4.4% DDT breakdown. These data indicated that endrin/DDT breakdown was well controlled by all individual inert-deactivated flow path components.

Figure 2 shows the comparison of % endrin/DDT combined breakdown results over 200 injections for the Agilent standard flow path, Agilent inert flow path, and non-Agilent deactivated components. The endrin/DDT breakdown on the Agilent inert flow path was well under control with less than 15% combined breakdown even after 200 injections. This result clearly met the acceptance criteria for endrin/DDT breakdown[1].

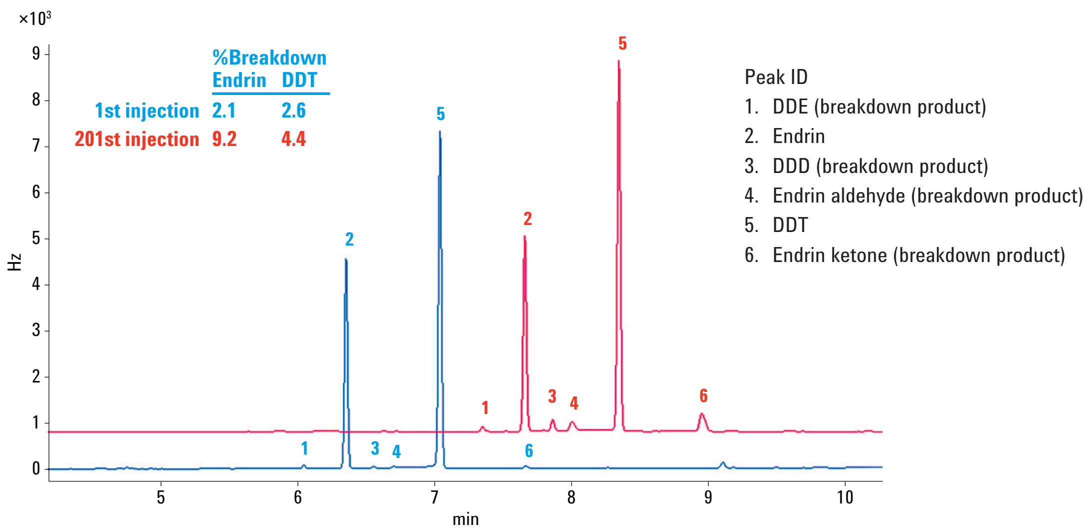

Figure 1. Endrin/DDT breakdown test chromatograms using the Agilent Inert Flow Path Solution; 50 ppb endrin/100 ppb DDT in iso-octane.

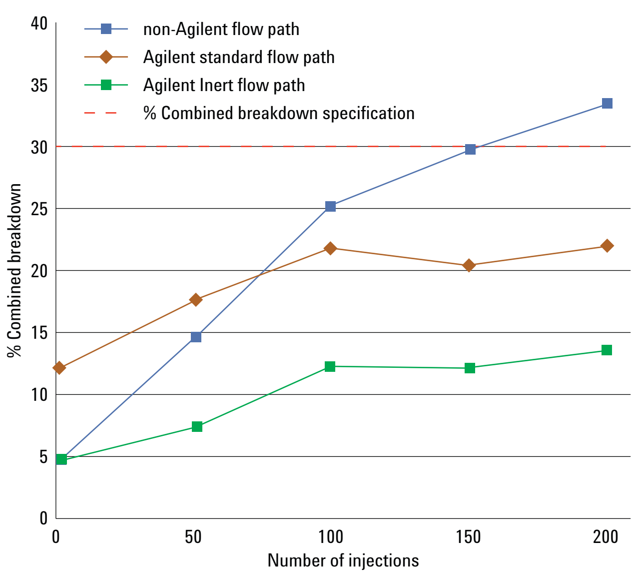

Figure 2. Endrin/DDT combined breakdown profile over 200 injections (iso-octane) for Agilent inert (green), Agilent standard (brown), and non-Agilent deactivated flow path (blue).

Figure 3 shows the comparison of % endrin breakdown contribution over 200 injections. After 75 injections, the non-Agilent flow path deactivation already exceeded the critical level of 15% endrin breakdown.

Figure 4 shows the comparison of % DDT breakdown contribution over 200 injections.

Figure 5 shows the repeatability for non-Agilent flow path components (n=2) and Agilent inert flow path (n=2). Repeatability of the Agilent inert flow was more consistent compared to that of the non-Agilent flow path components.

The results indicated that non-Agilent flow path parts provided similar initial inertness, but the Agilent inert flow path demonstrated much more consistency, stability and durability throughout the test sequence, up to 200 injections.

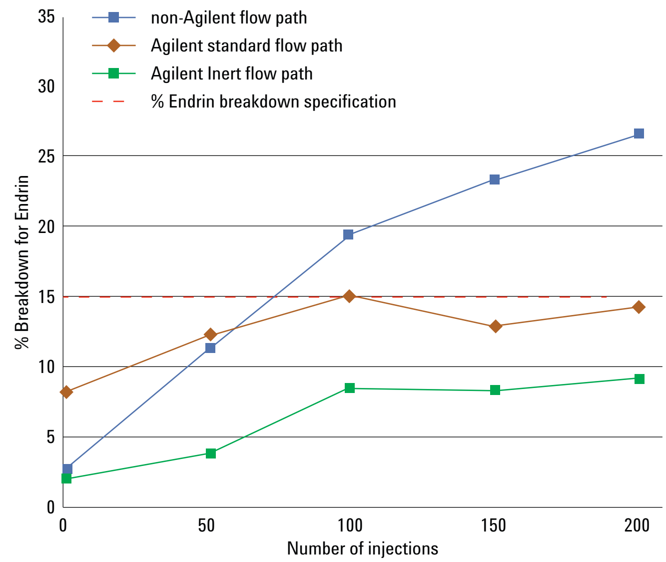

Figure 3. Endrin breakdown profile over 200 injections (iso-octane) for Agilent inert (green), Agilent standard (brown), and non-Agilent deactivated flow path (blue).

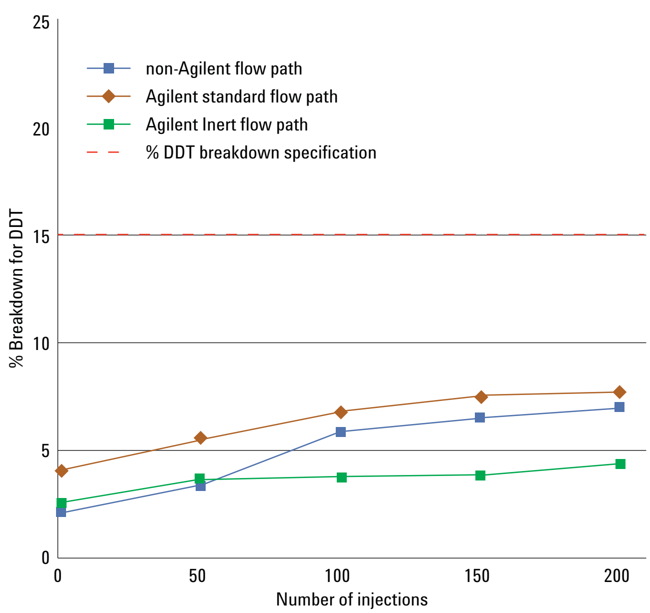

Figure 4. DDT breakdown profile over 200 injections (iso-octane) for Agilent inert (green), Agilent standard (brown), and non-Agilent deactivated flow path (blue).

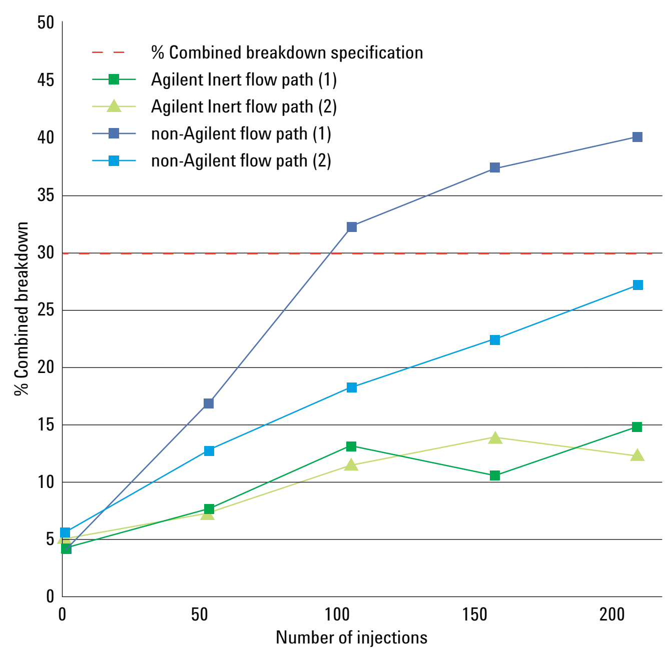

Figure 5. Two replicates of a repeatability trial of the Agilent inert flow path and non-Agilent flow path.

Conclusions

The Agilent Inert Flow Path Solution was evaluated and compared with equivalent-configured Agilent standard and non-Agilent deactivated flow path components, using an endrin/DDT (catalytic) breakdown test as a probe.

The Agilent inert flow path had <15% combined breakdown over 200 injections at 50 ppb endrin and 100 ppb DDT standard level. The non-Agilent flow path components exceeded the acceptance criterion of <15% endrin breakdown level after 75 injections.

These results of flow path deactivation evaluation and comparison demonstrate that, given the equivalent flow path configuration, the Agilent Inert Flow Path Solution is well suited for high sensitivity (chlorinated) pesticide analysis.

The Agilent inert flow path, including Ultra Inert column, Ultra Inert liner, Ultra Inert gold seal, and UltiMetal Plus split/splitless inlet, provide excellent surface inertness through the entire flow path, prevent analyte catalytic breakdown, response loss, and peak shape distortion, and thus support reliable qualitative and quantitative analysis for sensitive pesticide analysis. Additionally, the Agilent inert flow path provides excellent consistency, stability, and durability over multiple injections, which firmly support reliable and accurate analysis results over time, and reduce instrument downtime.

References

1. US EPA. Organochlorine Pesticides by Gas Chromatography. Environmental Protection Agency, Washington, DC, USA (2007). http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8081b.pdf

2. L. Zhao, A. D. Broske. Evaluation of Ultra Inert Liner Deactivation for Active Compound Analysis by GC. Application note, Agilent Technologies, Inc., Publication number 5990-7380EN (2011).

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