Application Note

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Reduction of Endrin and DDT Breakdown Using a PTV Injector

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INTRODUCTION

Current injection techniques consist of split, splitless, and on-column injection. The best technique for eliminating degradation is on-column injection, but industry standards mandate the use of a split/splitless injection port. With on-column injection, the analytes are placed directly into the GC column, eliminating residence time in the injection port. This is an advantage as well as a disadvantage. Since the sample is placed directly on column, everything in the sample including nonvolatile material enters the column, reducing the lifetime of the column. A new way to reduce degradation is to use a Programmed Temperature Vaporizing (PTV) injector in which the sample is injected into a cold injection port and ramped to the upper temperature required for vaporization.

EPA Method 8080 (Organochlorine Pesticides and PCBs) states that the degradation of either endrin or 4,4'-DDT must not exceed 20% [i]. This can often be a problem when running highly contaminated soil samples containing these compounds [1]. DDT and endrin are easily degraded if the injection port is dirty. This is a result of buildup of high boiling residue from sample injection.

Endrin tends to breakdown into endrin aldehyde (EA) and endrin ketone (EK), while 4,4'-DDT breaks down into 4,4'-DDE and 4,4'-DDD. A continuing calibration should be run daily to check the percentage of breakdown for each of these compounds. If the breakdown is greater than 20%, it is recommended that the analyst change the liner.

This study shows how to eliminate those tedious steps by simply using a Tekmar Optic PTV injector in the cold splitless mode with an Electron Capture Detector. Percent breakdown for these compounds are illustrated using both hot splitless and cold splitless injection.

EXPERIMENTAL

Isothermal

The degradation was examined initially using the OPTIC in a traditional isothermal splitless mode. A brand new silanized liner was placed in the OPTIC injector. A 1µl injection (0.5ng) of endrin and DDT was made to check for initial breakdown. The OPTIC and GC parameters are as follows:

Tekmar OPTIC (Hot Splitless) Parameters:

Start Temp	275°C
Ramp Rate	0°C/sec
Pause Temp	275°C 0
Pause Time	min.
Final Temp	275°C
Final Time	Extended

GC Parameter Conditions

GC	Carlo Erba HRGC Mega 2 Series
Detector	Electron Capture Detector
Column	XTI-5 30m x .53mm x 0.25µm (Restek Corp. Bellefonte, PA)
Carrier Gas	Helium @ 8mL/min.
Makeup Gas	Air
Oven Temp Program	
Initial Temp	150°C
Ramp 1	8°C/min to 275°C
Final Temp	275°C (Hold 5 min.)
Detector Temp	300°C

In order to induce breakdown in the injection port, a series of 1µL injections of hexane extracted soil were used. These injections were made daily into the liner for one week. This caused enough residue build up in the injection port to cause the endrin and DDT to breakdown (see Results and Discussion).

Temperature Programming

The second parameter consisted of running the OPTIC in the cold splitless or temperature programming mode. The same pyrex liner was used throughout the entire study. The GC parameters are the same but the OPTIC injector parameters were changed as follows:

Tekmar OPTIC (Cold Splitless) Parameters:

Start Temp	95°C
Ramp Rate	4°C/sec
Pause Temp	95°C
Pause Time	0 min.
Final Temp	275°C
Final Time	10 min.

RESULTS AND DISCUSSION

According to EPA Method 8080, the percentage breakdown for either endrin or DDT must not exceed 20%. The way to check for this breakdown is to run a medium level calibration standard of endrin and DDT and calculate as follows:

%DDT= peak area (DDE + DDD)

Breakdown peak area (DDT + DDE + DDD)

%endrin = peak area (EA + EK)

Breakdown peak area (endrin + EA + EK)

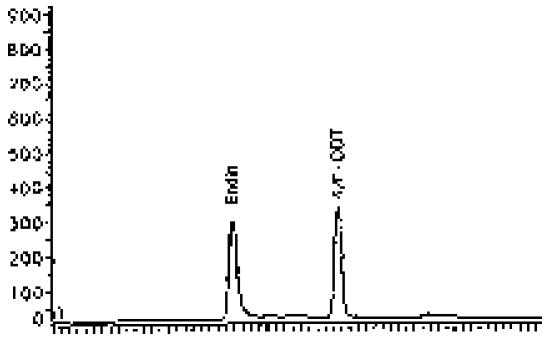

Figure 1 New Liner-0/5ng Endrin & DDT Std

Figure 1 shows 1µL (0.5ng) of endrin and DDT injected into a new liner. The injection port was run at 275°C isothermal (hot splitless). There is no indication of breakdown for either compound in this chromatogram.

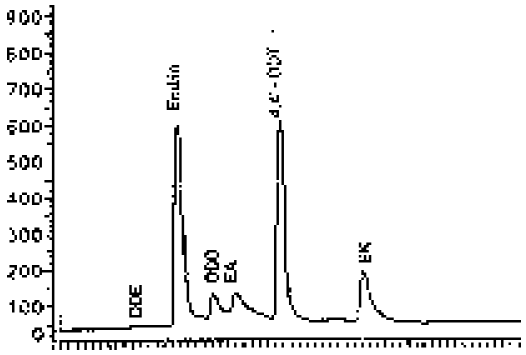

Figure 2 Injector: 275°C Isothermal

After inducing breakdown through the use of hexane extracted soil injections, the endrin and DDT begin to breakdown in Figure 2. Over several injections, the percent breakdown for endrin and DDT ranged from 7.9% to 40.2% (see Table 1).

Table 1 Percent Breakdown-Hot Splitless

DDT	Endrin
11.5%	20.9%
7.9	22.5
16.8	40.2
8.1	43.5

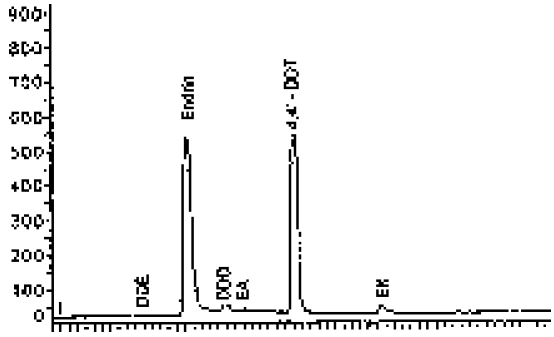

Figure 3 Injector 95°C to 275°C @ 4°C/sec

Figure 3 is the same standard and liner but the injection port was run at a starting temperature of 95°C and ramped to 275°C at 4°C/sec (cold splitless). The breakdown percentage for both compounds was well below 10% (see Table 2).

Table 2 Percent Breakdown-Cold Splitless

DDT	Endrin
9.6%	6.6%
5.6	4.3
4.6	7.8
3.9	7.3

Breakdown of endrin and DDT results from the combination of residue buildup and heat. Upon injection, vaporization of the solvent and solutes occurs immediately. The solute molecules interact with active sites in the liner resulting in breakdown.

In a cold splitless injection, the breakdown still occurs but is minimized. The vaporization of the solvent and solute occurs in a more controlled manner. The solute remains solvated as it travels through the injection port liner. Due to the high concentration of the solvent, the active sites are masked and breakdown is minimized.

CONCLUSION

In summary, there are several steps that can be taken to reduce the amount of endrin and DDT breakdown. The first is proper silanization of injection port liners. This will aid in the removal of any active sites present in the liner.

The second recommendation is to eliminate the use of glass wool where possible. Several internal studies have indicated greater than 50% breakdown of 4,4'-DDT consistently every run when glass wool was used in the liner. Even though glass wool is also silanized, it still acts as reservoir of active sites and causes an increase in breakdown.

The last suggestion is to use a PTV injector. This allows for introduction of the sample into a cold injector minimizing the exposure time to heat and active sites. This reduces the amount of endrin and DDT breakdown.

REFERENCES

[i] U.S. Environmental Protection Agency, Method for the Determination of Organochlorine Pesticides and PCBs, EPA-8080 1986.