Large Volume Injection of Organochlorine Pesticide Extracts Using a Programmable Temperature Vaporizer in the Solvent Split Mode

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Abstract

Programmed Temperature Vaporizers (PTVs) provide new sample introduction techniques for gas chromatographs such as solvent split injection and cold split injection. Solvent split injection allows injection of larger sample volumes than the standard injection techniques. 1 µl cold splitless injection and 100 µl solvent split injection using the OPTIC PTV are evaluated for linearity, thermal degradation and sensitivity.

Introduction

Traditionally, organochlorine pesticides are analyzed by capillary gas chromatography using an electron capture detector and either direct injection or splitless injection. These techniques are used for trace pesticide analysis because they allow the maximum amount of sample to reach the GC column. Injecting more sample into the GC is a simple way to improve method sensitivity. However, injector overflow limits the injection volumes of standard techniques to only a few microliters. Injector overflow occurs when the volume of solvent vapor exceeds the volume of the liner.[1]

Currently there are 3 techniques that allow more sample to be introduced into the GC: on-column injection with a retention gap, pressure pulsing using splitless injection with electronic pressure control, and solvent split mode using a PTV. On-column injection with a retention gap allows large volumes to be injected but cannot accommodate dirty samples because the head of the column becomes contaminated with non-volatile components. Pressure pulsing is limited to sample volumes of only 5 µl.[2] Solvent split mode allows injections of up to 150 µl and dirty samples are not a problem because non-volatile compounds remain in the packed liner.[3]

This work shows that 100 µl of extract can be injected "at-once" without the need for a complex autosampler using the OPTIC PTV and solvent split injection. Linearity compares with cold splitless injection and sensitivity is increased 100 fold. Also, breakdown of Endrin and DDT is lower than hot splitless injection.

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Experimental

Instrumentation and Equipment

All experiments were performed on a Carlo Erba 8560 GC (Fisons Instruments) with an electron capture detector, an Optic PTV injector (Tekmar-Dohrmann, Cincinnati, Ohio) and a DB-35 30 m x 0.53 mm ID column with a 0.5 µm film (J&W Scientific, Folsum, CA). The carrier gas was helium with a linear velocity of 30 cm/sec.

Conditions:

1) Cold Splitless Injection

For cold splitless injections, a straight pyrex liner without packing was used. The Optic PTV initial temperature was 50°C, final temperature 275°C, ramp rate 4°C/sec, split flow 170 ml/min, and a splitless time of 2.0 min. The gas chromatograph column program initial temperature was 150°C, ramp rate 4°C/min and final temperature 275°C. 1 ul injections were done manually.

2) Solvent Split Mode

For solvent split mode, a straight pyrex liner packed with 24 mg of silanized pesticide grade glass wool (Altech, Deerfield, II) was used. The liner dimensions are 80mm x 3.4 mm ID x 5.1 mm OD. The Optic PTV initial temperature was 30°C, final temperature 275°C, ramp rate 16°C/sec, split flow 50 ml/min, split time 113 seconds, and a splitless time of 37 seconds. The gas chromatograph column program initial temperature was 40°C, ramp rate 4°C/min and final temperature 275°C. 100 µl injections were done by hand.

The USEPA method 8080 analytes (AccuStandard, New Haven, CT) were diluted to the appropriate concentrations in high purity pesticide quality hexane (Burdick & Jackson GC2, Muskegon, MI).

Optimization: Solvent Split Mode

The main steps that describe solvent split injections are outlined in Procedure 1. The first step in optimizing solvent split injections is to determine the split time. The technique used in this work was to inject 100 µl of hexane into the cold liner with the split vent open and ignite the hexane vapors at the split vent outlet. The time from inject until the yellow flame extinguishes is the split time. This time should be very reproducible as long as there is enough packing to hold the volume of solvent injected.

The splitless time determination is less straightforward. It is the minimum time that gives quantitative transfer of analytes, yet not so long as to contribute interferences. If the splitless time is too short then loss of the less volatile analytes occurs because they vaporize at higher temperatures. The splitless time was determined in two trials.

Two mechanisms of solute retention take place in the glass wool packed liner: cold trapping and solvation. In cold trapping, the liner cools during solvent evaporation causing the analytes to retain in the glass wool packed liner during solvent elimination. The liner stays cool because the heat capacity of glass wool is low, thus heat transfer from the liner wall to the evaporation site is low. In the solvation mechanism solutes will remain in the solvent rather than exit the split vent. Organochlorine pesticides are of intermediate volatility so cold trapping is sufficient to keep them in the liner during solvent elimination. This fact makes it easy to optimize the split time for organochlorine. Analytes of high volatility requires solvation to keep them in the liner during solvent elimination. This requires that the split valve close just before all the solvent is evaporated, thus optimization of the split time is more critical.

Procedure 1: Main steps in solvent split injections
A Liquid sample is injected into a cool liner with the split vent open.
B Solvent is eliminated via the split vent.
C The split vent is closed and the liner is heated to transfer the analytes to the column.
D The split vent is opened to remove excess solvent and interferences from the liner.

Results and Discussion

5 point standard curves were run using cold splitless injection with a concentration range of 5 to 80 ng/ml for 17 organochlorine pesticides using pentachloronitrobenzene as an internal standard. Relative standard deviations of the relative response factors for the curve of each analyte are shown in Table 1. The relative standard deviations average 7%. Figure 1 shows a 10 ng/ml chromatogram using cold splitless injection.
After optimizing the solvent split mode for 100 µl injections, a 100 µl injection was made using the same 10 ng/ml standard. The chromatogram is shown in Figure 2. Comparison of the millivolt scale for Figures 1 & 2 show that a 100 fold gain in sensitivity for the solvent split mode has been achieved. Next, a 5 point curve was run from 0.1 to 1.6 ng/ml. Figure 3 shows the chromatogram for the low point of the curve at 0.1 ng/ml. Table 2 shows the relative standard deviations of the relative response factors for this curve. The relative standard deviations average 8%.

Up to 100 µl can be injected manually "at-once" because the liner internal volume is large and can accommodate enough glass wool to suspend 100 µl of solvent during the solvent elimination step. This allows a large increase in sensitivity without using expensive autosamplers to do speed controlled injections or timed injections which require complicated optimization.
Because it is believed that glass wool can contribute active sites for the thermal breakdown of compounds like Endrin and DDT, the quantity of glass wool is always minimized when performing hot injections. But for solvent split injections, a large amount of glass wool is required as a support for the large volume of solvent. Three 100 µl solvent split injections of a Endrin and DDT standard were made and breakdown products were used to calculate percent breakdown. Average breakdown was 0.5% for Endrin and 4.4% for DDT. A breakdown study was also carried out for hot splitless injection. 1 µl of an Endrin and DDT standard was injected into a 275°C injection port without packing. Endrin breakdown was 11 % and DDT breakdown was 3.6%. This indicates that the most important factor in the degradation of Endrin and DDT is temperature.

Conclusions

Large volume injections using the Optic PTV in the solvent split mode is easy to use and allows significant gains in capillary GC sensitivity. 100 ul injections using the solvent split mode increase organochlorine pesticide sensitivity 100 fold. Linearity for large volume injections in the solvent split mode measured as average RSD is 8% and compares well with cold splitless injections at 7% RSD. Breakdown of the thermally labile compounds, Endrin and DDT, is lower than hot injection techniques.

References

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2. Stafford. "Electronic Pressure Control in Gas Chromatography", Hewlett-Packard Company (1993)
3. Mol, H.-G. Janssen, and C. Cramers, J. High Res. Chromatogr. 18 (1995) 19-27

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Table 1: Cold splitless injection linearity[a]

Analyte	RSD of Relative Response
Factors	
alpha-bhc	14
gamma-bhc	13
beta-bhc	5 6
Heptachlor	10
delta-bhc	9 5
Aldrin	3 3
Heptachlor Epoxide	5 3
Endosulfan I	3 3
DDE	5
Dieldrin	14
Endrin	8
DDD	9
Endosulfan II	7
DDT	5 to 80 ng/mL
Endrin Aldehyde	
Endosulfan Sulfate	
Methoxychlor	
Average	

[a] five 1 µl injections from

Table 2: Solvent split mode linearity[b]

Analyte	**RSD of Relative Response**
Factors	
alpha-bhc	14
gamma-bhc	14
beta-bhc	7 3
Heptachlor	11
delta-bhc	8 3
Aldrin	1
Heptachlor Epoxide	10
Endosulfan I	5 4
DDE	8
Dieldrin	13
Endrin	5 4
DDD	4
Endosulfan II	13
DDT	8
Endrin Aldehyde	
Endosulfan Sulfate	
Methoxychlor	
Average	

[b] five 100 µl injections from 0.1 to 1.6 ng/ml

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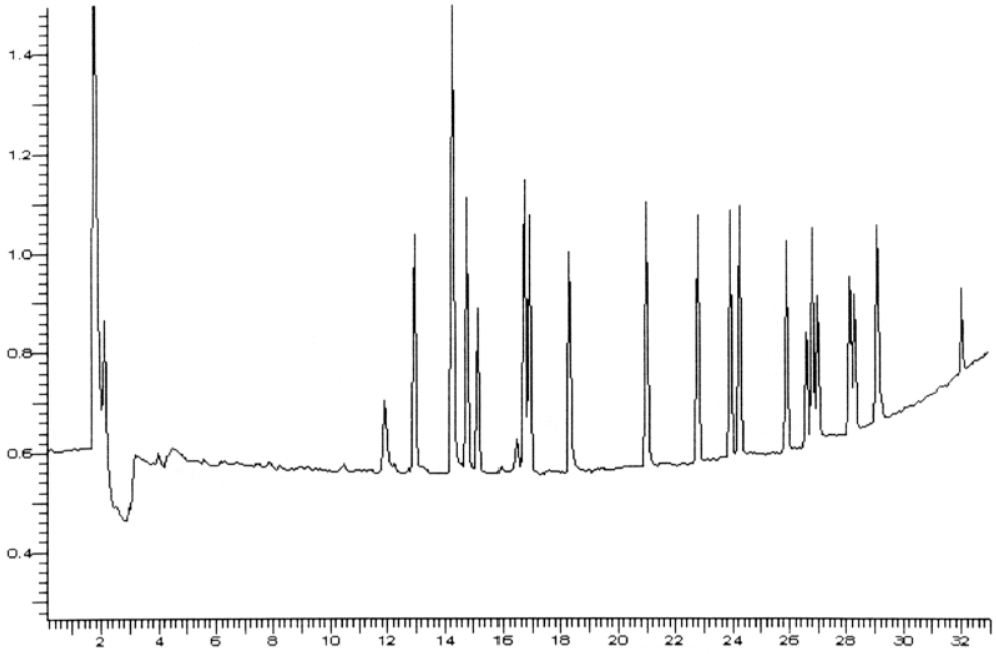

Figure 1: 1 uL injection using cold splitless mode (10 ng/ul)

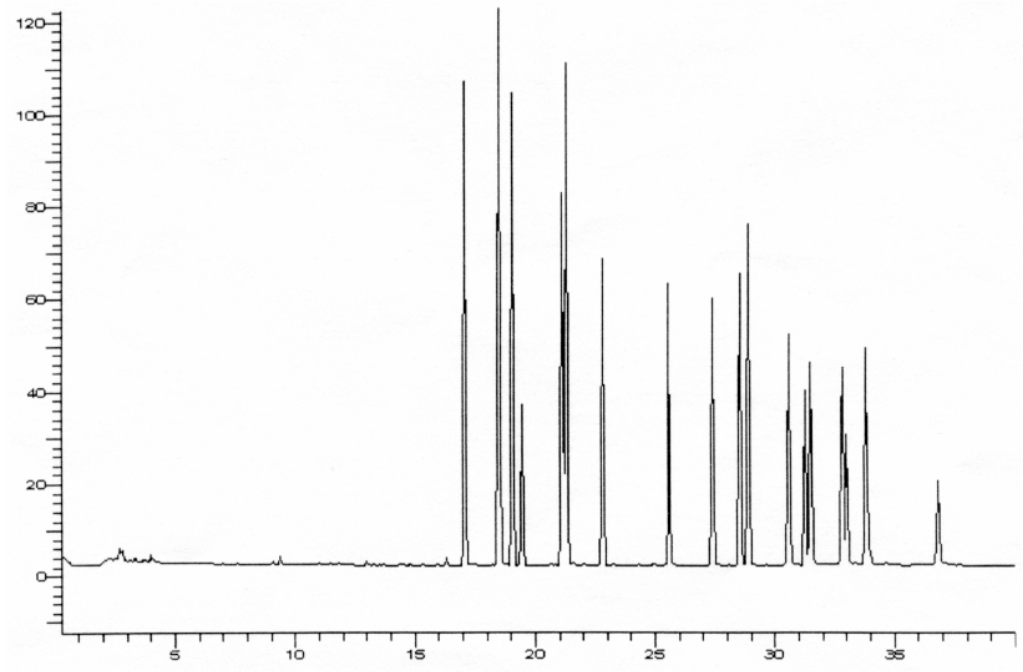

Figure 2: 100 µl injection using solvent split mode (10 ng/ml)

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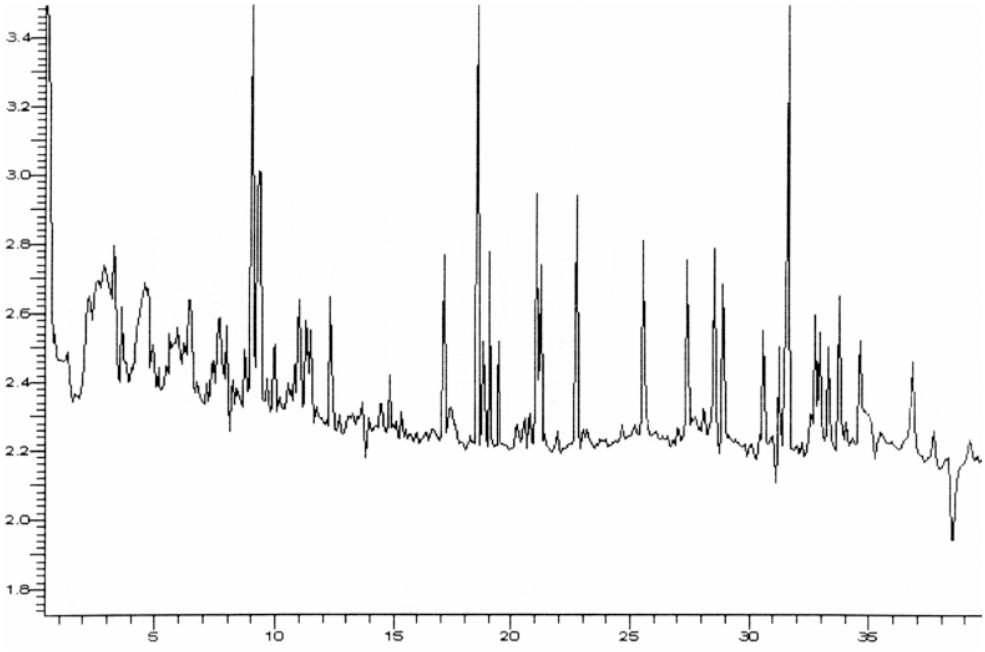

Figure 3: 100 µl injection using solvent split mode (0.1 ng/ml)

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