ANALYSIS OF SYNTHETIC PYRETHROIDS USING CAPILLARY COLUMNS OF VARIOUS POLARITIES

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Introduction

Analysis of synthetic pyrethroids by gas chromatography is often a difficult and confusing task for environmental laboratories. Difficult because synthetic pyrethroids are based upon the natural pyrethrin structure extracted from chrysanthemum flowers, namely the chrysanthemic acid (**Figure 1**) where the R group can be any type of substituent. Some pyrethroids may act as a precursor to other active pyrethroids. The analysis may be confusing because some synthetic pyrethroids such as Cypermethrin (**Figure 2a**) can have anywhere up to 8 isomers in some instances due to the presence of chiral centers. This makes analysis of synthetic pyrethroids by gas chromatography confusing when multiple peaks represent a single pyrethroid (**Figure 2b**) with some of these signals are overlapping. Also of concern is the ability of environmental labs to meet the performance criteria while analyzing extracts that contain high boiling contaminants. There are several choices of columns for these types of analyses. Phases such as BPX5, BPX35 and BPX50 where the percentage phenyl content is progressively increased and as the names suggest, BPX5 has a 5% phenyl content, BPX35 – 35% phenyl and BPX50 – 50% phenyl, are excellent for this type of analysis. All of these columns meet these criteria when analyzing synthetic pyrethroids. BPX5, 35 and 50 give excellent resolution of the 16 synthetic pyrethroids in less than 32 minutes.

Pyrethroids are extremely potent insecticides that are widely used in agriculture, disease control and in household products. For instance all fly sprays use pyrethroids as their insecticides whether they are surface or airborne sprays. Pyrethroids act by interfering with the insect's nervous system and in high concentrations affect humans in a similar way. They can also bring on asthma attacks, cause liver damage and allergic reactions and many of the pyrethroids are also carcinogenic. Their persistence in the environment can be anywhere between 1-16 days in soil and as such can reach natural water ways for which they are especially toxic to fish and other aquatic organisms. For these reasons, the levels of synthetic pyrethroids in foods and the environment are always under close scrutiny.

Figure 1. Chrysanthemic acid.

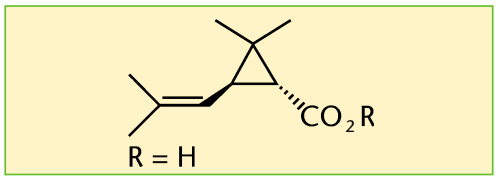
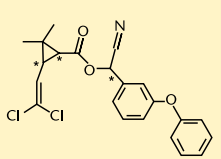


Figure 2. Chromatogram of the synthetic pyrethroid cypermethrin. Note the 4 peaks seen here representing the 4 diastereoisomers of cypermethrin. The structure of cypermethrin shown here shows the 3 chiral centers (*) of cypermethrin.

2a. Cypermethrin



2b. Cypermethrin chromatographic peaks

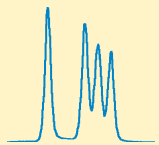


Figure 3. Separation of 16 pyrethroids on BPX5. Note the superb bleed profile at 300°C. BPX5 gives excellent separation of synthetic pyrethroids.
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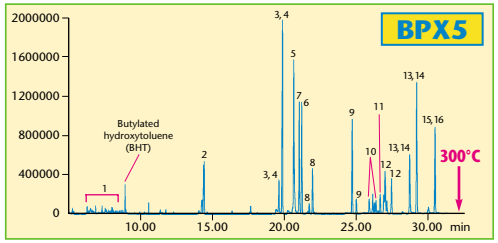
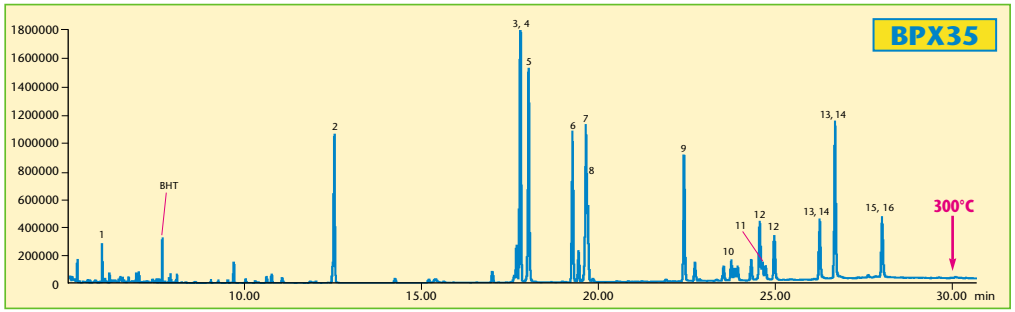


Figure 4. Unparalleled separation of the 16 synthetic pyrethroids on BPX35. The bleed at 300°C is also excellent.

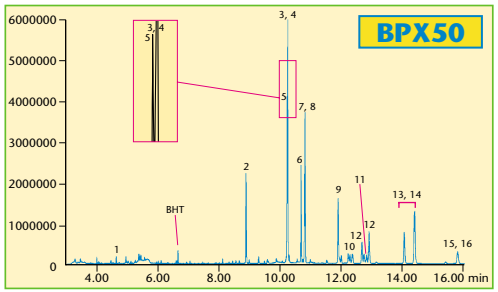


Most laboratories will use a relatively non-polar column such as a 5% phenyl as the quantitation column (many laboratories still prefer a confirmation column to have a completely different selectivity). BPX35 and BPX50 are excellent confirmation columns for BPX5 giving different retention times, elution orders and degrees of overlap of the various isomers. These columns also have the added advantage of being thermally stable at 360°C allowing the baking out of any high boiling contaminants without damaging the phase. This bake out ensures that these contaminants do not interfere with the retention times and elevated baselines of target compounds for future analyses. All these columns show exceptional peak shape of each pyrethroid indicating the high degree of inertness of all 3 columns.

Summary

BPX5, BPX35 and BPX50 columns show unparalleled performance for the separation of the 16 synthetic pyrethroids. They can be conditioned at the end of each analysis to remove any high boiling point contaminants without any degradation to the stationary phase. The bleed levels are exceptionally low at 300°C and excellent peak shape indicating a high degree of inertness are all features of these three columns.

Figure 5. Separation of the synthetic pyrethroids on a BPX50. Note the run time on this chromatogram is 16 minutes for complete elution of the 16 pyrethroids. This allows analytical laboratories to have a higher sample throughput.



Components (for Figure 3, 4 & 5)

1. Natural Pyrethrums
2. Allethrin
3. Bioresmethrin
4. Resmethrin
5. Bifenthrin
6. Fenpropathrin
7. Tetramethrin
8. Sumithrin
9. Permethrin
10. Cyfluthrin
11. Cypermethrin
12. Flucythrinate
13. Fenvalerate
14. Esfenvalerate
15. Tralomethrin
16. Deltamethrin