TRAJAN

TECHNICAL ARTICLE

Pyrethroid analysis made easy

Introduction

There is increasing pressure in agricultural industries around the world to produce bigger and better quality crops in a cost-effective manner. The pressure to control pests that can potentially cause large-scale economic damage to crops has also increased. As a result, pesticide use is usually a major component of integrated pest control programs. One such class of compounds used to control pests is pyrethroids. Pyrethroids are also used in nearly every household fly spray and act by interfering with the insect's nervous system.

Pyrethroids may have a range of toxic effects on humans and as a result, careful control on maximum residue limits (MRL) in foodstuffs is required. Pyrethroids affect the nervous system by interacting with sodium channels in the neuronal cell membranes, leading to seizures if exposure is severe. Long term exposure to pyrethroids, which are part of a class of compounds known as endocrine disruptors, can cause damage to the liver by disrupting many of the vital metabolic processes performed by the liver. Other effects include causing asthmatic attacks, and some of the synthetic pyrethroids have been found to be potential carcinogens by the USEPA.

The analysis

Pyrethroids are based on the chemical structure of pyrethrum, which is a mixture of pyrethrin I (figure 1) and pyrethrin II, extracted from the Chrysanthemum plant.

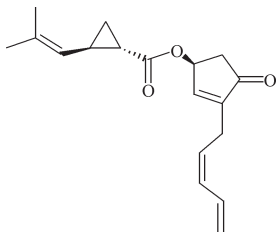

Figure 1. Structure of Pyrethrin I.

The number of chiral isomers of each synthetic pyrethroid as well as the degree of thermal stability complicates pyrethroid analysis by gas chromatography. For example three chiral centres in Cypermethrin result in the presence of 8 possible stereoisomers. The chromatogram shown in figure 2 displays 4 peaks which are the 4 diastereoisomers of cypermethrin. These isomers can also overlap with other pyrethroid components and cause considerable confusion when analyzing complex mixtures of pyrethroids.

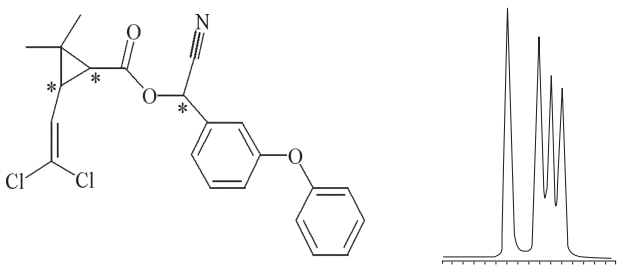

Figure 2 shows a chromatogram of the synthetic pyrethroid cypermethrin. Note the 4 peaks here representing the 4 diastereoisomers of cypermethrin. The structure of cypermethrin shows the 3 chiral centers (*).

Figure 2

Complicating the analysis of pyrethroids is the thermal instability of some of the components. Some synthetic pyrethroids act as precursors that breakdown to other active pyrethroids or are active constituents in their own right. Tralomethrin, which breaks down to deltamethrin during analysis, is one such synthetic pyrethroid. Esfenvalerate also breaks down to fenvalerate during analysis making quantitation of the various individual synthetic pyrethroids difficult.

Choice of capillary column

There is a wide choice of capillary columns available for the analysis of pyrethroids. The standard column used for this analysis is the non-polar 5% phenyl column, BPX5. The BPX5 capillary column is a low-bleed mass spectrum grade column that can be used with any GC detector. The use of a 5% phenyl column for the analysis of pyrethroids is often used in conjunction with a confirmation column of different polarity. The BPX35, 35% phenyl capillary column is an excellent alternative for the analysis of pyrethroids in its own right. The BPX35 capillary column is also a low bleed MS grade capillary column that has sufficient difference in polarity to the 5% phenyl to elute the pyrethroids in a different order, thereby making it the perfect confirmation column. Both the BPX5 and BPX35 phases show excellent inertness and robustness and do not show any peak tailing of the difficult-to-analyze pyrethroids (Figure 3a and 3b).

Conditions

Column part number	054101 (BPX5), 054701 (BPX35)
Phase	BPX5, BPX35
Column	30 m x 0.25 mm x 0.25 µm
Initial temperature	50°C, 1 min
Rate 1	30°C/min to 200°C
Rate 2	4°C/min to 300°C
Final temperature	300°C for 5 min
Detector	MS
Carrier gas	He, 6.5 psi
Carrier gas flow	0.9 mL/min
Constant flow	On
Average linear velocity	35 cm/sec at 50°C
Injection mode	Splitless
Purge on time	0.5 min
Purge on (split) vent	60 mL/min
Injection volume	1 µL
Injection temperature	250°C
Liner type	4mm ID Double taper liner

Components

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

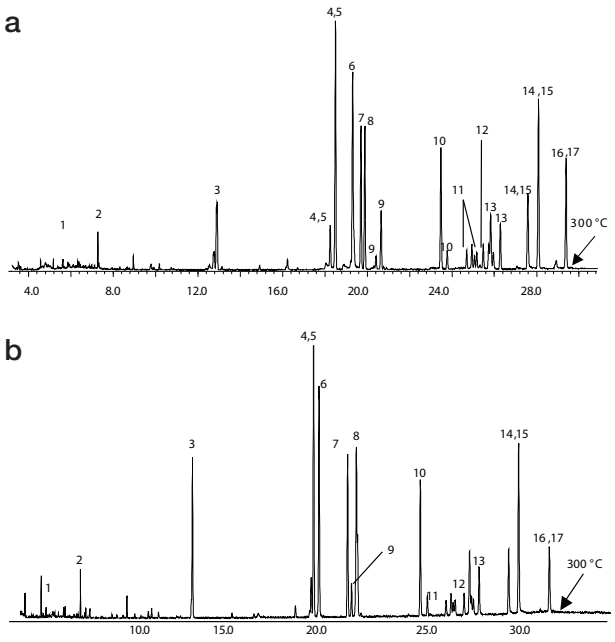

Figure 3. Chromatograms of synthetic pyrethroids analysed on a BPX5 (a) and a BPX35 (b) capillary column.

Advantages of thermal stability

The BPX5 and BPX35 capillary columns have a high thermal stability with a maximum temperature limit of 370°C. The high thermal stability of the capillary column is an essential requirement when analysing environmental samples. The composition of the samples in environmental laboratories can be quite variable, ranging from relatively clean water samples to extremely dirty extracted soil samples.

It is often useful to use a capillary column with a high maximum operating temperature. The column can then be 'baked out' following deposition of semi and non-volatile residue material on the front end of the column. Once peak shape deteriorates, it is common practice to condition the column to its upper maximum temperature recommended for at least 60 minutes to remove this residue. If this fails to re-establish good chromatography then the front 0.5 meters of the column can be cut and discarded.

The second advantage of a column with a high maximum operating temperature is the lower bleed level at the upper method temperature. Thus, if the upper maximum temperature of the column is 370°C, the bleed level at 300°C will be lower compared with a column with an upper maximum level of 320°C. This leads to better sensitivity for the higher maximum temperature column.

Conclusion

The BPX5 and BPX35 capillary columns are the ideal choice for the analysis of pyrethroids either on their own, or in combination as a confirmation column. The robust nature of the phase and the high level of inertness and thermal stability make the BPX5 and BPX35 columns the most suitable choice for the analysis of synthetic pyrethroids.

Information and support

Visit www.trajanscimed.com or contact techsupport@trajanscimed.com

Specifications are subject to change without notice.