Recent Advances in the Analysis of Pyrethroid Insecticides in Surface Water and Sediments by Tandem GC/MS

Tim Conjelko and Stephan Baumann: Agilent Technologies, Santa Clara, CA

ASMS 2011
WP 319

Agilent Technologies

Introduction

Pyrethroid insecticides are of increasing environmental concern because of their widespread use and high aquatic toxicity. Pyrethroids are frequently detected in California in both agricultural and urban areas and more recently pyrethroids have become a concern in other parts of the United States. Recent advances in analytical instrumentation have allowed the development of new analysis methods to detect pyrethroid insecticides in surface water and sediments. The analytes target list includes seven pyrethroid insecticides most used in agriculture and structural pest control in California.

Experimental

Sample Preparation Procedure

The sediment samples are prepared by pressurized fluid extraction, gel permeation chromatography, and florisil SPE. The water samples undergo a liquid-liquid extraction and florisil SPE. A GC is equipped with a large-volume inlet (LVI) in order to allow large volume injections. Two 15-m DB-XLB (0.25mm id x0.25um) columns joined by a purged union are used for the separation. The purged union permits back flushing of the first column to eliminate the very close eluting high boilers while the analytes of interest continue on the second analytical column. Water and sediment sample extracts are analyzed using negative chemical ionization tandem GC mass spectrometry.

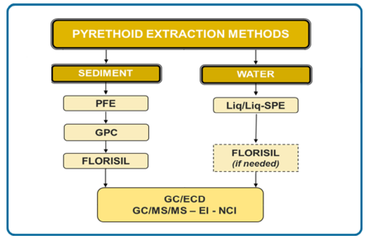

Figure1: A flow diagram of the sample preparative procedure shows the differences between water and sediment. PFE is an abbreviation for Pressurized Fluid Extraction and GPC is an abbreviation for Gel Permeation Chromatography.

Experimental

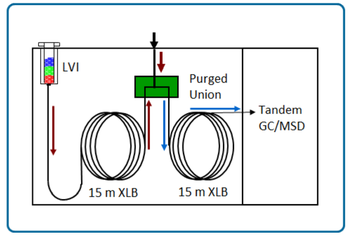

Figure 2: Tandem GC/MS system configuration with mid-column back flushing.

The inlet program events

A 2 µL pulsed splitless injection is made with a 240°C inlet temperature. A pressure pulse of 25 psi is used for 0.5 min. At 1.6 min, the split vent is opened to flush out the inlet.

GC oven program

The GC oven is 150°C at injection. The oven is ramped to 220°C at 30°C/min with a 1 minute hold. It is then ramped to 300°C at 5°C/min with a 2 minute hold. The post-run temperature is 300°C for 0.5 min – long enough to flush the columns with 10 volumes of helium carrier gas.

GC flow program

The front 15 m XLB column has a flow of 1.2 mL/min and the secondary XLB column flow is slightly higher at 1.25 mL/min. The flow is constant until the end of the run when the GC column is back flushed. The front column flow is reversed and increased to 19.7 mL/min while the back column flow is increased to 20.2 mL/min. This is typically four times as efficient as a post column bake out because both the distance and the back pressure have been cut in half.

Tandem GC/MSD parameters

The source and quad temperatures are 150°C. The instrument is auto tuned in Negative Chemical Ion (NCI) mode with ammonia as reagent gas at 35% flow. Helium quench gas flow is 2.25 mL/min and the helium collision gas flow is 0.75 mL/min.

Results and Discussion

Negative Chemical Ionization

e^- (10s eV) ----(buffer gas)---> e^- (.1 eV) + M -------> M^-

NCI Attributes

- Only electrophilic molecules are capable of capturing thermal electrons.
- Electron capture is extremely efficient for halogenated compounds. This leads to high sensitivity.
- Matrix interferences typically do not capture electrons. Detection limits are generally very low due to lack of response by contaminants or matrix.

Figure3: Description of the Negative Chemical Ionization process.

Negative Chemical Ionization

Negative Chemical Ionization (NCI) provides a less energetic and highly selective method for detecting and quantifying electrophilic compounds in complex matrices than electron impact ionization mass spectrometry. It exploits the electrophilic nature of halogenated compounds in the same way that electron capture detectors have in the past. We are fortunate that the more critical type II pyrethroids such as Cyfluthrin and Permethrin are electronegative for NCI. However, there are at least two type I pyrethroids (resmethrin and fenpropathrin) that are not detected by traditional NCI techniques. Ammonia is used as the reagent gas over methane because it has approximately seven times the thermalizing power of methane[1]. The advantage of a tandem quadrupole mass spectrometer is that very selective precursor to product ion transition data is generated. This lends an additional degree of selectivity and certainty to the analysis.

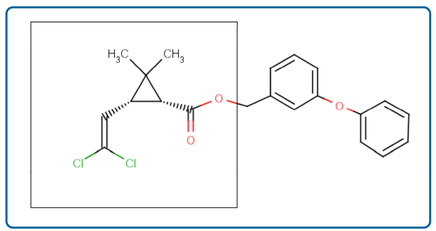

Figure 4: The cyclopropane portion of synthetic pyrethroids is detected by NCI Tandem GC/MS. Most NCI work has been done with methane as the reagent gas but greater sensitivity is achieved with ammonia reagent gases.

Tandem MS Fragmentation

In NCI mode, fragmentation often occurs at the ester bond with the oxygen carrying the negative charge. Alternatively, if the pyrethroid is not able to stabilize the negative charge, the charge goes with the chlorine ion and there is a characteristic 35 or 37 *m/z* product ion.

Results and Discussion

Synthetic pyrethroid	std conc µg/L	MS/MS-NCI-Signal to Noise S/N		Estimated Limit of Detection (ELOD)	
		Methane	Ammonia	(A)-Water ng/L	(B)-Sediment ng/g
Bifenthrin	0.050	973	2345	0.10	0.08
Cyhalothrin	0.050	683	1890	0.20	0.1
Permethrin	0.050	25	150	1.00	1.5
Cyfluthrin	0.050	277	1217	0.20	0.2
Cypermethrin	0.050	336	1410	0.20	0.18
Es-fenvalerate	0.050	2757	6450	0.05	0.05
Deltamethrin	0.050	190	463	0.15	0.3

Figure 5: The water estimated limit of detection calculations are based on 500 mL water to 1mL (500 fold concentration) while the sediment estimated LODs are based on 10g sediment to 1mL with 50% moisture.

Discussion

Synthetic pyrethroids are extremely toxic to aquatic organisms with a median lethal concentration (LC_{50}) values < 1 ppb. Water and sediment sample extracts were analyzed using ammonia NCI tandem GC/MS. Method detection limits have been established for water and sediment that are well below the toxicity of type II pyrethroids such as Cyfluthrin and Permethrin. Analysis of pyrethroids by this technique yields the sub- ppb detection limits that are required to ensure the safety of aquatic organisms. Prior techniques were unable to reproducibly reach these low detection limits in water and sediment matrix.

Conclusions

A back-flushed LVI ammonia negative chemical ionization tandem mass spectroscopy enables the sensitive detection of toxic pyrethroids in sediment.

References

[1]Modern Practice of Gas Chromatography, R. L. Grob, E. F. Barry, pp 382 (2004).