Screening Sediment for Pyrethroid Insecticides Using GC-MS/MS

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A simple screening method for pyrethroid insecticides in sediment samples is described. Electron impact ionisation (EI) with tandem MS/MS in combination with programmed temperature vaporisation injection (PTV) were used to obtain excellent selectivity and low limits of detection (LOD). Pyrethroids are synthetic chemical insecticides whose chemical structures were adapted from the chemical structures of the pyrethrins. Pyrethroids have been modified to increase their stability in sunlight. They are toxic to aquatic organisms at extremely low concentrations, especially to invertebrates that are at the bottom of the food chain.

The increased use of pyrethroids in urban areas for mosquito control has led to unintended contamination of local streams and reservoirs due to urban runoff. As a result, state and federal agencies have initiated monitoring programs to characterise the extent of contamination in water supplies and their potential impact on aquatic life. In general, there are no set requirements for minimum detection or reporting levels. However, the lowest reporting level that can be achieved by a given technique is desired.

The SCION TQ triple quadrupole mass spectrometer in EI mode with PTV injection is ideal for screening sediment extracts at low to sub-parts-per-billion concentrations. PTV injection combined with the sensitivity and selectivity of MS/MS result in excellent low-level screening of pyrethroids in river and lake sediments. The SCION TQ with Compound-Based Scanning (CBS) allows easy set-up and management of the pyrethroid MRM parameters. Compound MRM information is loaded directly into the method by choosing them from the on-board or user created library. It links the mass spectrometer acquisition table directly with data handling parameters, streamlining the data process.

Pyrethroids are a class of synthetic agricultural insecticide commonly used in mosquito control and to optimise production of both food crops and cotton. As such, they are an important component in the routine environmental toxicology screening used to measure, manage and minimise potential hazards of pesticides to aquatic organisms and the wider ecology. Pyrethroids have a particular affinity for sediments, and recent research has moved away from the more traditional water toxicity test methods to focus on sediment testing techniques.

In this article a simple screening method for pyrethroid insecticides in sediment samples is described. A case study demonstrates how electron impact ionisation (EI) with tandem mass spectrometry (MS/MS), in combination with programmed temperature vaporisation injection (PTV), can be used to obtain excellent selectivity and low limits of detection (LOD).

Integrated Pesticide Testing

Uncontrolled and illegal application of pesticides represents a significant risk to human health and the environment. As a result, most countries have adopted strict regulations governing their use and laboratories are under pressure to implement diagnostic screening protocols for efficient and effective pesticide monitoring and control.

While there is currently no set requirement for minimum detection or reporting levels, government agencies such as the United States' Environmental Protection Agency (EPA) are in the process of formulating an integrated approach to testing and assessment. The drive is towards an improved ability to predict chemical toxicity and exposure through the application of more efficient and effective screening tools, including diagnostic biomonitoring and surveillance methods [1].

In addition to water quality testing, sediment analysis is a key aspect of an integrated test program. Sediment tests do not require prior knowledge of specific interaction pathways between sediment and test organisms. Additionally, when spiked with known contaminants, sediment data can be used to establish interactions between chemicals and the response within biological organisms. This means they can be used to uncover relationships between toxic effects and bioavailability. They can also be employed to investigate interactions among contaminants and determine both spatial and temporal distribution of that contamination. Results and analysis can also be used to evaluate dredged materials, prioritise areas requiring clean-up and estimate the potential effectiveness of remedial measures and hazard control.

Why Pyrethroid Screening is Important

Pyrethroids are chemically adapted from pyrethrins, which are naturally occurring chemicals produced by chrysanthemum flowers (pyrethrums) as protection against certain insects. They are synthetically modified to have increased stability in sunlight. In addition to agricultural applications, they are also used increasingly for both residential and commercial pest control to replace organophosphate insecticides, which are being increasingly phased out. Adding to the hazard risks posed by this increased usage, there is also a shift from using first generation pyrethroids, such as permethrin, to newer compounds that can be a great deal more toxic.

Due to their stability, pyrethroids can enter waterways from run-off during storms before they can breakdown. Their high hydrophobicity in aquatic environments allows them to adhere to particulate matter making them easier to detect in sediments.

Even in extremely low concentrations, pyrethroids are highly toxic to aquatic organisms and researchers are still working to understand their impact on the environment. They are, however, known to be especially harmful to invertebrates at the bottom of the food chain [2]. As a consequence, it is extremely important to have robust methods that are sensitive enough to detect and quantify these compounds at environmentally relevant concentrations.

Triple Quadrupoles for Efficient Screening

Triple quadrupole mass spectrometers (TQ MS) provide the necessary high speed scanning in full scan mode to provide faster run times, greater sensitivity, with the overall benefit of processing more samples, resolving more compounds and improving identification of compounds. As a consequence they are ideal for use in a more efficient, integrated screening program.

The SCION gas chromatography mass spectrometer triple quad (GC-MS TQ) (Bruker Chemical and Applied Markets, US) in EI mode with tandem MS/MS in combination with programmed temperature vaporisation injection (PTV) is capable of obtaining excellent selectivity and low LODs, with the additional design elements, that provide zero cross-talk and reduced signal to noise ratio (S/N).

Able to efficiently measure sediment extracts at low to sub-part-per-billion concentrations, this triple quad system provides an excellent tool for pyrethroid screening in river and lake sediments.

Compound-Based Scanning Software

A unique software feature known as Compound-Based Scanning (CBS) is incorporated into the SCION TQ enabling easy multiple reaction monitoring (MRM) assays to be set-up. Rather than focus on individual MRM, the CBS workflow is designed to focus on compounds *(Figure 1)*. Using CBS, MRMs are grouped under each individual target compound and automatically linked across both acquisition method and data handling.

A built-in reference library containing more than 2,500 MRM transitions for more than 900 common contaminants, including pyrethroids, supports the method editor. Target compounds can be rapidly matched, selected and uploaded, leaving the operator free to carry out other tasks.

Optimal scan time is quickly calculated based on the average peak width following a few initial runs to locate the retention time window for each compound. The CBS software then optimises the duty cycle by removing excess segments from all the overlapped retention windows.

Additional operation time is saved by the automatic creation of the data handling table. This is also linked to the scan acquisition method. Each entry in the compound library is supported by relevant retention time, primary and secondary MRM transitions and their collision energies.

This information is imported to the method editor, allowing the software to automatically build-up the method by populating the acquisition MRM table that is then synchronised with the data processing.

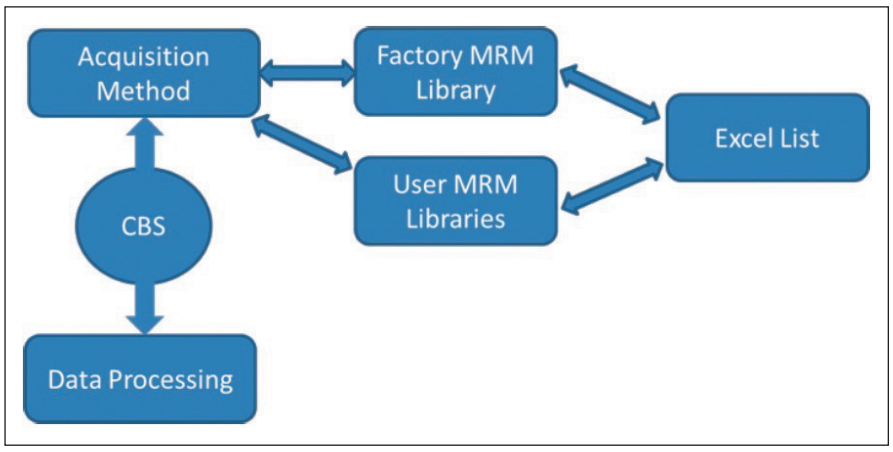

Figure 1. The SCION TQ Compound-Based Scanning workflow.

Simple Pyrethroid Screening: A Case Study

To demonstrate simple pyrethroids screening using the SCION TQ [3] in EI mode in combination with PTV injection, a sample was prepared by adding 5g copper powder/magnesium sulphate to 20g wet sediment. The mixture was then extracted and concentrated to a final volume of 2mL before being cleaned up on Florisil® Sep Pak.

Calibration standards in hexane were also prepared and a blank sediment matrix was spiked at various concentrations *(Table 1)*.

The equipment was set-up using the experimental conditions outlined in *Tables 2 and 3*.

Table 1: MS/MS Parameters for Pyretroids Insecticides

Compound Name	RT (min)	RT Window	Precursor	Product	Collision Energy
Lambda Cyhalothrin_Ep1+2	19.150	1.000	208	181	-10
	19.150	1.000	181	152	-20
Fenvalerate+Esfenvalerate	24.230	1.000	167	125	-15
	24.230	1.000	225	91	-25
	24.230	1.000	225	119	-10
Bifenthrin	17.560	0.500	181	165	-18
	17.560	0.500	181	166	-10
	17.560	0.500	181	115	-40
trans+cis-Permethrin	20.880	1.000	183	168	-18
	20.880	1.000	183	128	-20
	20.880	1.000	183	152	-20
Cypermethrin-Isomers	22.580	1.200	181	152	-20
	22.580	1.200	181	127	-30
Cyfluthrin-Isomers	21.980	1.200	226	206	-15
	21.980	1.200	206	151	-15
Resmethrin_1+2	16.690	1.000	171	128	-12
	16.690	1.000	171	143	-12
Fenpropathrin	17.860	0.500	265	181	-20
	17.860	0.500	265	210	-10
Deltamethrin-1+2	25.200	1.000	253	174	-10
	25.200	1.000	253	172	-10

Table 2: 451-GC gas chromatographic conditions

Column	BR-5ms, 30m x 0.25mm x 0.25µm
Carrier	He 1.0mL/min
Injector	PTV with 3.4mm ID Siltek Fritted Liner, 8µL injection
Injector Conditions	60°C hold 0.4 min to 310°C at 200°C/min, hold 30 min
Column Temperature Program	55°C, hold 3 min, ramp to 200°C at 40°C/min, hold 1 min; ramp to 310°C at 5°C/min, hold 1 min

Table 3: SCION TQ MS conditions

Ion Source Temperature	250°C
Transfer Line Temperature	280°C
Filament Delay Time	12 min
Filament Emission Current	80µA
Dwell Time	100ms each transition

Each of the pyrethroids being studied was found in the Factory Library of the CBS software and quickly downloaded directly into the scan acquisition method.

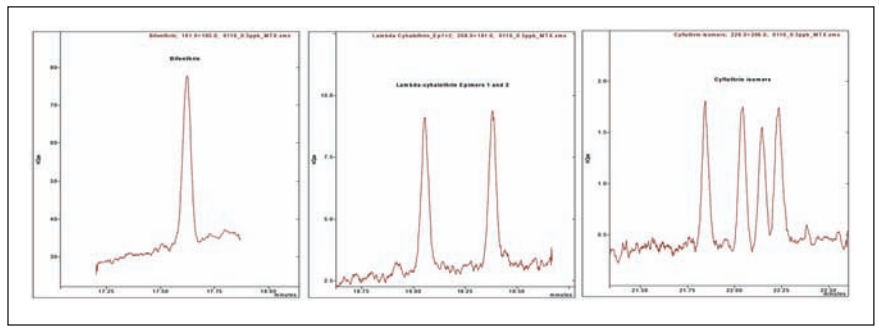

Figure 2. MS/MS for bifenthrin (left), two epimers of lamda-cyhalothrin (mid), and cyfluthrin isomers (right) in the sediment matrix.

The use of MS/MS provided excellent sensitivity and selectivity for the analysis. Compounds detected in the sediment sample spiked at 0.5 ppb are shown in *Figure 2*. Calibration curves prepared in pure solvent (hexane) and in blank sediment extracts were linear, indicating no matrix interference from the sediment extract. An example calibration curve is shown in *Figure 3*.

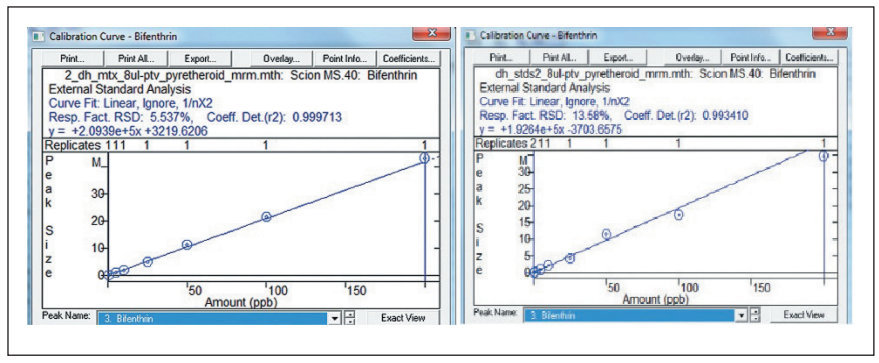

Figure 3. Calibration curves for Bifenthrin prepared in hexane from 0.1 to 200 ppb (left) and those prepared in a spiked sediment extract (right) calibrated from 0.5 ppb to 200 ppb.

Conclusion

Pyrethroid pollution represents an ongoing threat to the environment due to continued and increasing usage. Therefore, there is a growing need for robust and efficient screening methods, capable of supporting integrated methodology, across all environmental toxicology testing programs.

The sensitivity and selectivity of MS/MS combined with PTV injection is capable of delivering the low-level screening of pyrethroids in river and lake sediments. Offering the additional benefits of Compound-Based Scanning software, the SCION TQ is the ideal solution for integrated testing programs. Compound-Based Scanning allows easy set-up and management of the pyrethroid MRM parameters. Compound MRM information is loaded directly into the method by choosing them from a factory or user created library. It links the mass spectrometer acquisition table directly with data handling parameters, streamlining the data process and leaving the operator free.

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