



Application Note GCMS-01

Comparison of Ionization Techniques for the Analysis of Trace-Level Pyrethroid Insecticides by GC-MS/MS

Abstract

A study was carried out using the Bruker EVOQ GC-TQ to screen a group of pyrethroid insecticides at low concentrations in complex matrices including sewage outfall and ocean sediments. A comparison between electron impact and negative chemical ionization techniques in terms of the calibration range, method detection limits and precision was also conducted.

The GC-MS/MS approach with MRM demonstrated excellent specificity and sensitivity overall, with negative chemical ionization demonstrating the best results for most of the pyrethroids studied.

Introduction

Pyrethroids are synthetic insecticides based on the structure of pyrethrins, derived from chrysanthemum flowers. The compounds are used in a range of household insecticides and repellents as they are stable, toxic and effective against a wide range of pests. Pyrethroids make their way into the environment through agricultural use and domestic control of mosquitos, and tend to persist in soils and sediments. The compounds are lethal to mayflies, gadflies and other invertebrates at extremely low levels, as well as being toxic to fish and other aquatic organisms.

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Pyrethroids have been found to be unaffected by secondary treatment systems at municipal wastewater treatment facilities, often appearing in the effluent. State agencies in the USA such as the California Department of Food and Agriculture have implemented monitoring programs requiring low to sub-part-per-billion reporting limits in soil and water samples.

In pesticide monitoring, discrimination against matrix components arising from waste water outfall (sewage) and sediment extracts is critical to the success of any method. Tandem GC-MS/MS is an ideal technique to analyze for synthetic pyrethroids, because it can discriminate effectively against matrix interferences and provide trace level detection.

In this application note, a group of pyrethroids are analyzed with the EVOQ GC-TQ system. Electron impact (EI) and negative chemical ionization (NCI) techniques are optimized and compared in terms of calibration range, method detection limits and precision.

Experimental

Instrumental

EVOQ GC-TQ™ triple quadrupole mass spectrometer coupled to a Bruker 436 GC and CP-8400 liquid Autosampler.

A standard hot splitless injection is used which reduces instrument matrix load as compared to the commonly used large volume programmed temperature vaporization (PTV).



Figure 1: EVOQ GC-TQ with 436 GC and CP-8400 autosampler.

GC-MS/MS Parameters

Column: BR-5ms, 15 M x 0.25 mm id x 0.25 μm; Carrier gas: Helium at 1.0 mL/min; Oven: 60°C (2min), at 50°C /min to 150°C (1 min), at 5°C /min to 320°C (hold 3 min); Injection: 2 μL pulsed splitless @ 28°C with 4.0 mm ID fritted liner; Ion Source: EI @ 250°C; NCI @ 150°C; NCI Reagent Gas: Ammonia @ 20psi; (details see Table 1)

Results and Discussion

Calibration and instrument detection limits were determined for both NCI and EI modes. The calibration standards were prepared in dichloromethane with concentration range of 0.1 to 50 ppb. For EI, the average relative standard deviation (%RSD) and r^2 for all compounds was 8.7% and 0.9995 respectively. For NCI the average %RSD was 9.8% and r^2 was 0.9990. The added sensitivity observed for NCI allowed several compounds to have an extended lower calibration range, from 1 ppt to 5000 ppt.

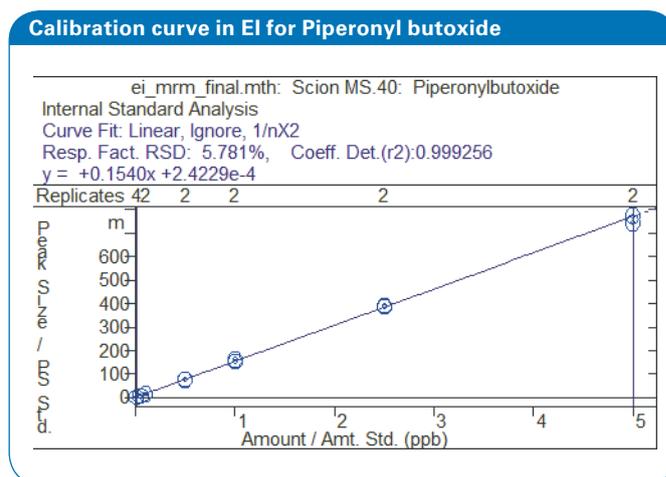


Figure 2: Example calibration curve in EI for Piperonyl butoxide, a synergist compound commonly added to pyrethroid formulations (0.1 to 50 ppb).

Instrument detection limits (IDLs) were performed by analyzing seven replicates at 0.1 ppb prepared in dichloromethane and using the following equation:

$$IDL = S t_{(n-1, 1-\alpha = 0.99)}$$

Where $t_{(n-1, 1-\alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom.

For EI/MS/MS IDLs ranged from 0.01 to 0.28 ppb with mean of 0.1 ppb and average %RSD of 10.6%. For NCI/MS/MS IDLs were from 0.01 to 0.3 ppb with mean of 0.04 ppb and average %RSD of 6.1%. Analysis with NCI demonstrated excellent sensitivity for Fipronil, Fipronil sulfide, Fipronil sulfone, Esfenvalerate, Bifenthrin, Danitol and Deltramethrin and IDLs were determined at 10 ppt with mean at 2.6 ppt and %RSD of 9.2%.

Table 1: MRM transitions for both NCI and EI modes for the compounds studied.

Compound Name	EI Q1	EI Q3	EI (CE)	NCI Q1	NCI Q3	NCI (CE)
cis/trans-Permethrin	183	128	-20	207.2	35.2	10
	183	152	-20	209.2	37.2	10
	183	168	-18			
Fipronil sulfide	351	255	-20	384	314.9	20
				384	248	25
				384	244	25
Esfenvalerate-A/B	225	91	-25	211.2	35.2	20
	225	119	-18	211.2	167.2	10
	225	147	-10			
Allethrin/Prallethrin	123	81	-15	167.4	167.4	1
	123	95	-10			
Fipronil sulfone	383	255	-20	415.9	282.9	25
	383	335	-10	415.9	243.9	30
Danitol	181	152	-25	141.4	141.4	1
	181	127	-30			
Bifenthrin	181	115	-40	386	205	5
	181	165	-18	386	161	15
	181	166	-10			
Cyfluthrin isomers	206	151	-15	207.2	35.2	20
	206	179	-20	171.2	35.2	20
	226	206	-10			
Cypermethrin isomers	181	127	-30	207.2	35.2	20
	181	152	-20	171.2	35.2	20
Deltamethrin	253	172	-10	296.9	79	2
	253	199	-25	296.9	81	2
	253	174	-10			
Fipronil	367	178	-40	397.9	303.8	30
	367	213	-30	397.9	281.9	30
	367	255	-15	397.9	271.9	30
Piperonyl butoxide	176	131	-10	ND	ND	ND
	176	117	-18			
	176	103	-25			
Cyhalothrin	208	181	-10	241	205	20
	181	152	-20	241	35	10

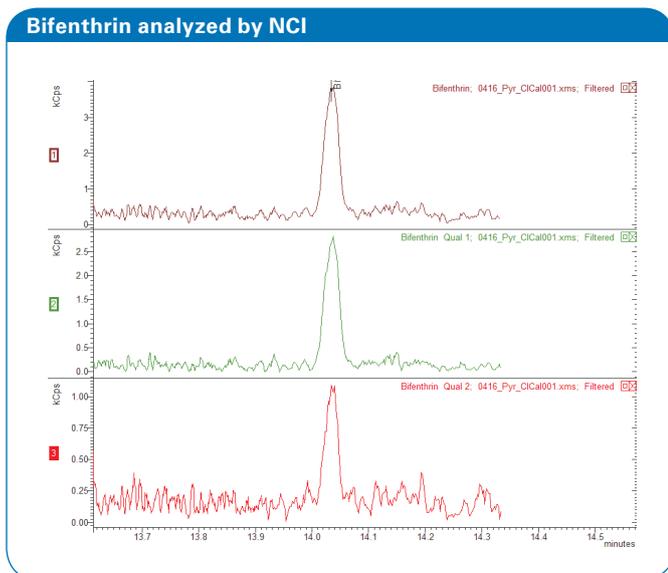


Figure 3: 10 ppt of Bifenthrin analyzed by NCI.

Analysis of Complex Matrices

10 g ocean sediment was extracted in 50:50 DCM: Acetone with an accelerated solvent extraction technique (ASE) at 2000 psi and 125 oC, and the extracts were dried with sodium sulfate, evaporated to 1 mL without any further clean-up. 1 L of sewage outfall was prepared by continuous liquid-liquid extraction (CLLE) with DCM, dried and concentrated to 1 mL. A glass fritted 4 mm liner was used for the injections.

Severe matrix interferences were noticed for several compounds in the EI method and resulted in very highly biased results. As can be seen on the right hand side of Figure 5, there are interferences in the EI/MS/MS analysis for the ocean sediment samples for Allethrin/Pallethrin, Cypermethrin isomers, and Deltamethrin at the transitions studied. Elevated baselines and distorted peaks encumber quantitation, even though the ion ratios are in range. The NCI/MS/MS analyses for the same sediment extract shown on the left hand side of Figure 5 demonstrate comparable results to the pure standard and give acceptable percent recoveries.

The sewage samples exhibited similar interferences in EI/MS/MS but to a lesser extent. Deltamethrin spiked sewage for example showed some elevation in baseline but gave a similar response compared to the calibration standard (Figure 6).

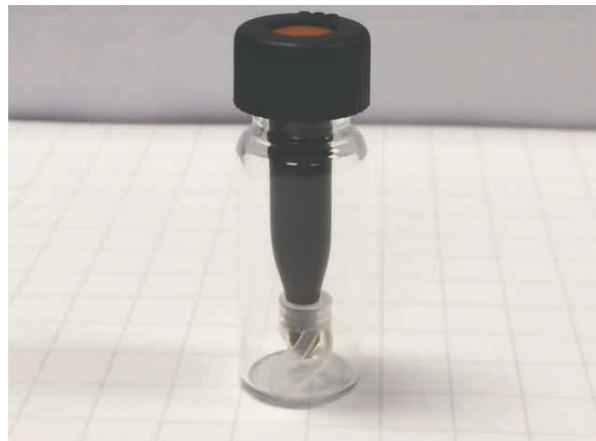


Figure 4: Ocean extract (top) and sewage extract (bottom) used for matrix studies.

Comparison of NCI and EI extracted ion chromatograms



Figure 5: Comparison of NCI (left) and EI (right) extracted ion chromatograms for (top to bottom) Allethrin/Pallethrin, Cypermethrin isomers, Deltamethrin.

EI/MS/MS

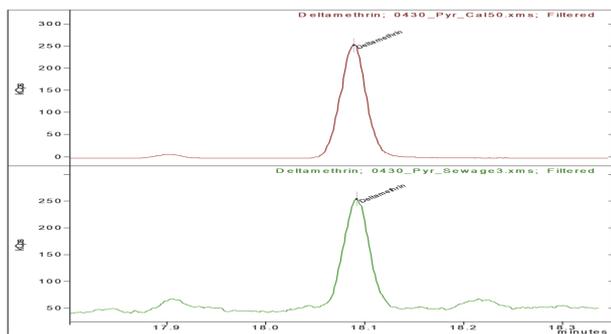


Figure 6: Deltamethrin in Cal standard (top) and sewage extract (bottom) by EI/MS/MS.

Conclusion

This method demonstrates the benefits of using GC-MS/MS with multiple reaction monitoring for low level pyrethroids analysis. In particular, excellent specificity and selectivity can be achieved in extremely complex matrices.

The importance of evaluating the ionization technique alongside matrix to deliver improved performance is also demonstrated. In this case, NCI combined with MS/MS clearly provides the best results for most pyrethroids in the matrices studied.

References

- [1] 'Pyrethroid pesticides in municipal wastewater: A baseline survey of publicly owned treatment works facilities in California in 2013', James C. Markle et al., January 22 2014.

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