Analysis of Cypermethrin in Blueberries by Agilent 240 Ion Trap GC/MS^3

Application Note

Food Safety

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Abstract

A rugged method has been developed on the Agilent 240 Ion Trap GC/MS using GC EI/MS^3 in blueberry matrix for cypermethrin. The method easily meets the requirements of fruit growers in the Pacific Northwest responsible for importing and exporting blueberry/caneberry.

Cypermethrin is a synthetic pyrethroid used as an insecticide in large-scale commercial agricultural applications as well as in consumer products for domestic purposes. It behaves as a fast-acting neurotoxin in insects. Cypermethrin is an often used pesticide in the war against the Spotted Wing Drosophila for blueberry/caneberry growers/exporters. Though effective and widely accepted at a relatively manageable level for importers, cypermethrin has its challenges analytically. Cypermethrin was analyzed using the benefits of gas chromatography coupled to Ion Trap Mass Spectrometry (MS^3) or (GC/MS/MS/MS) as one solution to the growing problem experienced by testing laboratories around the world. MS^n is has been used as a research tool and not applied to the routine testing environment until now.

Low detection levels along with excellent linearity and precision were afforded by the selectivity, sensitivity and simplicity of MS^3 detection of the 240 Ion Trap GC/MS.

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Introduction

In contrast to multisector instruments, ion traps do not have transmission losses that limit tandem-in-space analyses or linear quadrupole systems. Because of this tandem-in-time approach, sensitivity is maintained even for multiple MS stages.

Ion trap users can use MS^n to probe fragmentation pathways as well as enhance selectivity in sample matrix interferences. Every stage of MS reduces background interferences further when high matrix samples are being analyzed. Every stage in MS^n requires a unique choice of precursor ion and collision energy to produce a unique set of product ions. Thus, confidence in identity is increased significantly. Because the ions are stored in the ion trap, they can be manipulated repeatedly.

MS/MS

Isolate a parent ion, dissociate, scan out the mass spectrum.

MS/MS/MS

Isolate Parent Ion 1, dissociate to product ions, isolate Parent Ion 2, dissociate to new product ions, scan mass spectrum.

Cypermethrin elutes off the column as a group of isomer peaks, therefore there is a need for group summing of the ions in a large time window.

Cypermethrin is a late eluter (late retention time), and this is where the matrix from the sample extract elutes as well. The sample prep uses QUECHERS extractions, which are not the cleanest. This means there is a high possibility of interference in full scan acquisition and quantitation, as well as SIS Selected Ion Storage (SIS) and MS/MS modes, especially when using group summing.

There are two easy options:

MS/MS or MS^2, AMD experiments yield an optimal excitation voltage for our initial quantitation ion (181.3) of 2.20 V in resonant mode, the challenge is that the fragmentation yields a small range of product ions (150–154). These might also be matrix generated ions. The result is a hump instead of a real fingerprint.

The second option is MS^3. We take our initial precursor Ion 181.3, dissociate it using a 2.20 V resonant excitation energy, store the most abundant product Ion, 152.2, dissociate that with an excitation voltage of 3.40 V, then store its major product ions 99 and 123, using 123 as the quantitation ion. This process yields a resultant chromatographic fingerprint.

There is some chromatographic resolution between the isomer peaks (which can be a useful way of confirming presence of the different isomers), but now there are several steps removed from any matrix interference that could have given false positive or negative results.

MS^n has normally been seen as a research tool for qualitative work, but this application shows its real world (production lab) use in a quantitative environment.

Experimental

GC/MS ion trap analysis

Cypermethrin analysis was performed on a 240 Ion Trap GC/MS system. The GC was operated in constant flow mode. The 240 Ion Trap GC/MS was operated in External Electron Impact (EI) MS^3 mode.

GC conditions

Column	Agilent VF-XMS 30 m × 250, 0.25 + 10 m easy guard CP9019
Injection mode	Split/Splitless inlet, splitless mode Pulse pressure 40 psi for 0.8 minutes Injector purge flow of 100 mL/min at 0.75 minutes
Inlet temperature	250 °C single taper glass wool insert
Carrier gas	Helium, constant flow mode, 1.0 mL/min
Oven Program	80 °C for 0 minutes, 15 °C/min to 250 °C hold for 0 minutes, 5 °C/min to 300 °C hold for 2 minutes
Total run time	23 minutes

Agilent 240 Quadrupole Ion Trap MS conditions

Tune	Auto-tune, +300 V multiplier, 45 µA filament current	
Acquisition	External electron ionization (EI) MS^3 (MS/MS/MS) mode	
Damping gas	3.0 mL/min	
Solvent delay	17.0 minutes	
MS temperatures	Source	270 °C
	Trap	150 °C
	Manifold	60 °C
	Transfer line	300 °C

MS conditions

Precursor	Excitation voltage	Product ion range	Emission current
MS1-181.3	2.2 V	151–153	45
MS2-152.2	3.4 V	74–124	45

Compounds were initially identified using full-scan acquisition of reference standards.

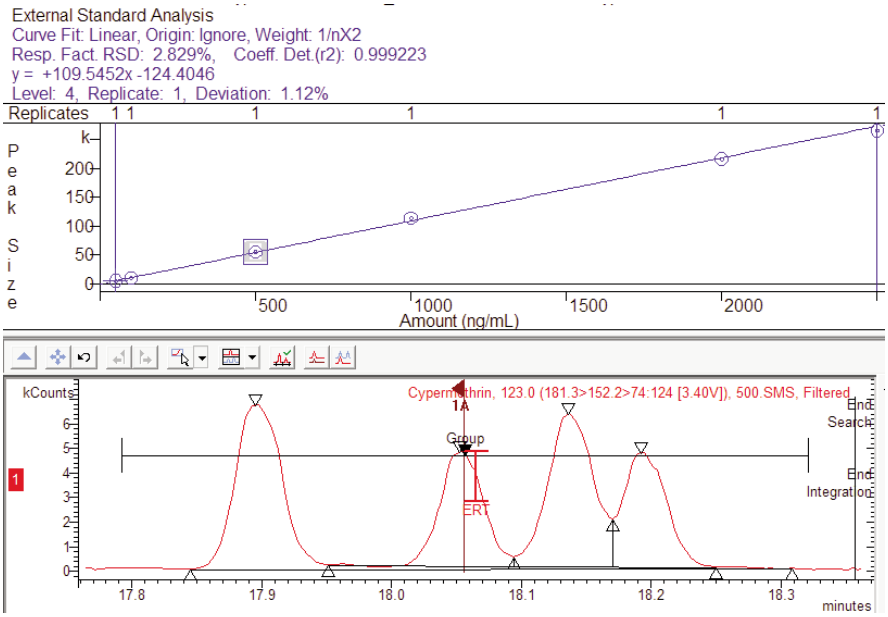


Figure 1. Cypermethrin calibration was done in blueberry matrix, 50 ng/mL to 2,500 ng/mL.

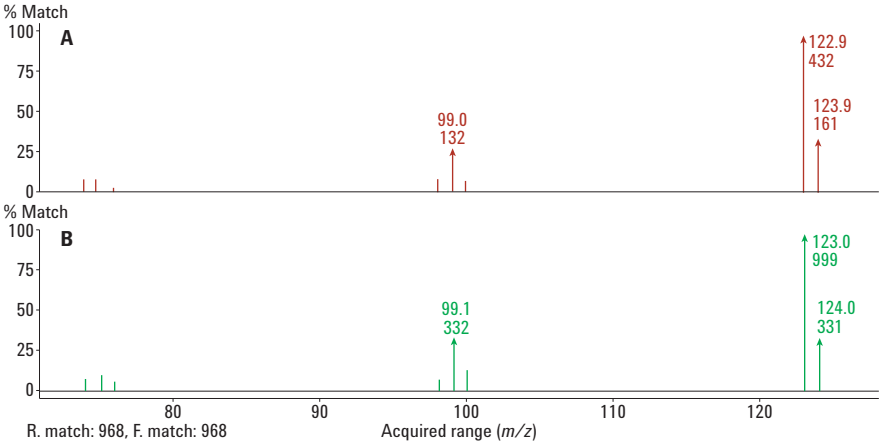
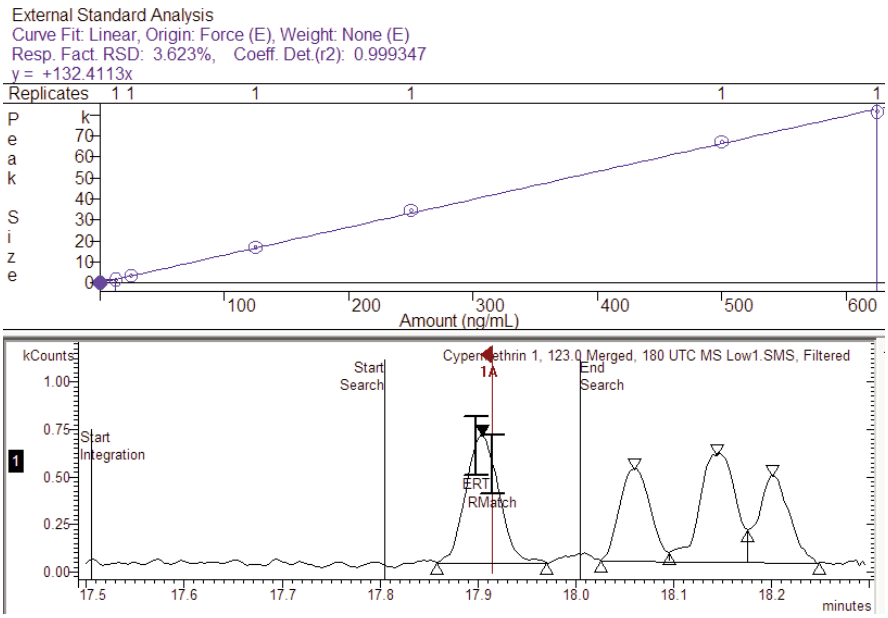


Figure 2. Spectrum of the 50 ng/mL (A) and 2,500 ng/mL (B) blueberry matrix.

A) Cypermethrin I - Calibration from 12.5 to 625 ng/mL



B) Cypermethrin II - Calibration from 12.5 to 625 ng/mL

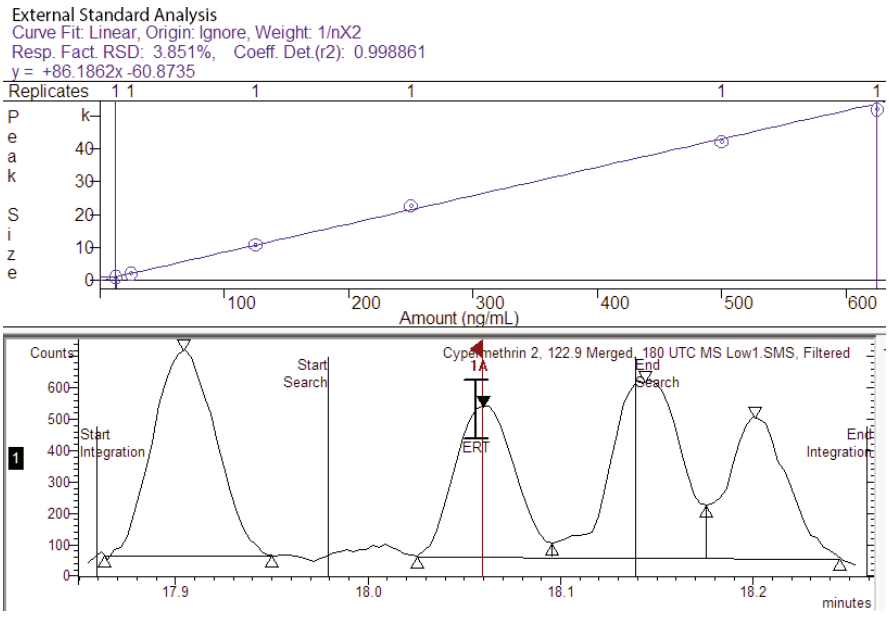
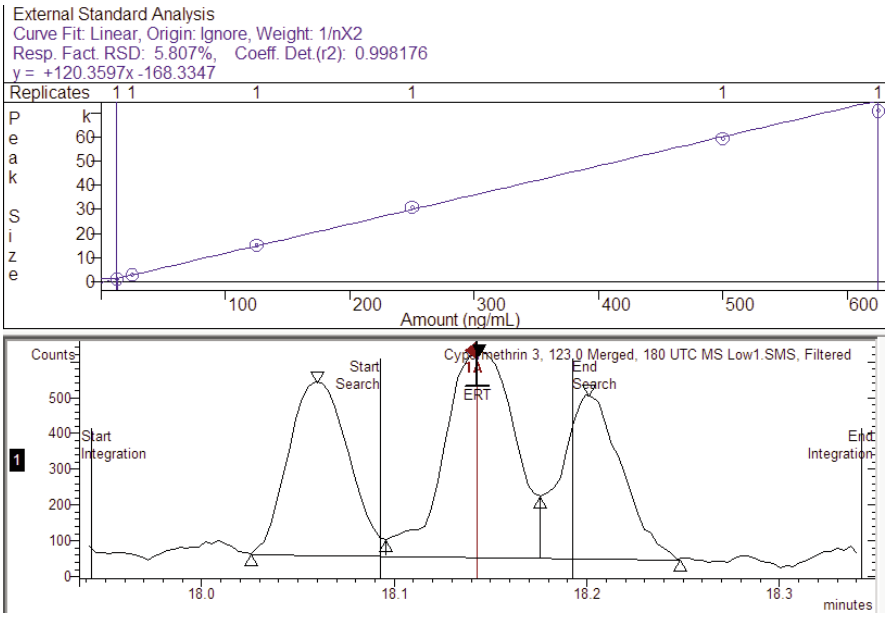


Figure 3. A,B) Individual stereoisomer concentrations.

C) Cypermethrin III - Calibration from 12.5 to 625 ng/mL



D) Cypermethrin IV - Calibration from 12.5 to 625 ng/mL

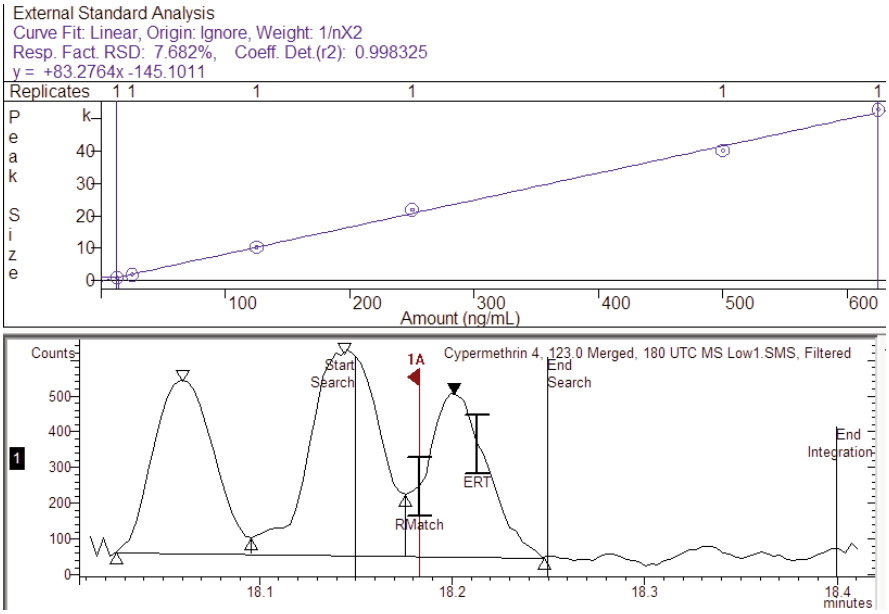
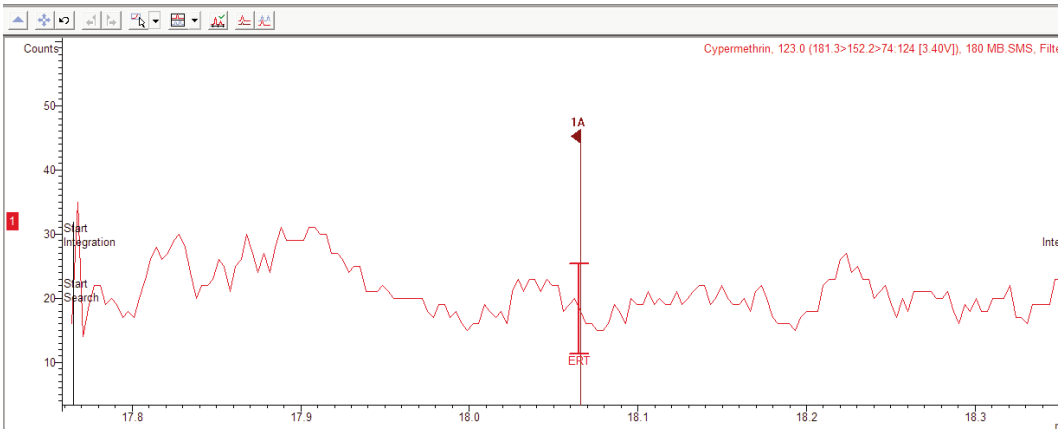


Figure 3. C,D) Individual stereoisomer concentrations.

Table 1. Reproducibility

50.SMS	18.057	Cypermethrin	4,577	45.50
50001.SMS	18.057	Cypermethrin	4,928	48.73
180 UTC MS Low1.SMS	18.057	Cypermethrin	5,280	51.96
180 UTC MS Low2.SMS	18.057	Cypermethrin	5,320	52.33
180 UTC MS Low3.SMS	18.057	Cypermethrin	4,953	48.96
180 UTC MS Low4.SMS	18.057	Cypermethrin	4,701	46.64
Average concentration	49.018			
RSD	5.6%			
CCV	1,000			
Area	85,810			
Recovery	80%			



180 MB.SMS	18.065	Cypermethrin	0	–
180 UTC.SMS	18.065	Cypermethrin	0	–
Blank.SMS	18.065	Cypermethrin	0	–
Blank001.SMS	18.065	Cypermethrin	0	–

Figure 4. Blank runs.

Results and Discussion

Results are reported as total concentration for the analyte and as individual stereoisomer concentrations. External standard calibration was used to quantify the cypermethrin.

Conclusion

For the analysis of cypermethrin, the benefits of GC Ion Trap MS^3 cannot be underestimated, in terms of reducing sample matrix interference, improving signal to noise and coupling its high selectivity and sensitivity. GC/MS^3 Ion Trap acquisition provides a more confidence driven solution for cypermethrin quantitation. GC/MS^3 Ion Trap analysis will reduce false positive and negatives and will provide an additional degree of confidence in the results obtained. Using the optimized method listed above a fast, targeted GC/MS^3 method can be used to resolve the analytical difficulties of quantitating cypermethrin in challenging matrixes.

References

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2. R. Carpenado, V. Carla, G. Moneti, A. Chiarugi, and F. Moroni "Identification and Measurement of Oxindole (2-Indolinone) in the Mammalian Brain and Other Rat Organs" *Analytical Biochemistry*, **244**, 1997, 74-79.

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