Application Note: 10067

Improved Detection of Organophosphate Pesticides in EI GC/MS/MS with Higher Damping Gas Pressure

Thermo Fisher Scientific, Austin, TX, USA

Key Words

- Polaris*Q* ion trap
- GC-MS/MS
- Pesticides
- Variable Damping Gas

Overview

Purpose: Experiments were conducted to measure the improvement of product ion yield in GC/MS/MS analysis of pesticides in vegetable matrix using variable damping gas control in an external ion source ion trap.

Methods: Damping gas was varied in the Thermo Scientific PolarisQ™ ion trap to test the improvement in the trapping efficiency of the precursor ion. The required Collision Induced Dissociation (CID) energy at the default damping gas of 0.3 mL/min helium was compared to the energy at the optimum damping gas flow for each pesticide. The product ion yield was then compared to verify an improvement in response. A temperature programmable inlet was used to make a 5 µL large volume injection into a pre-column connected to a tee fitting and solenoid valve, so that the heavier components in the vegetable matrix could be backflushed before entering the analytical column.

Results: The detection of the target pesticides was improved by 4-5x using higher damping gas flows from 1.0 to 5.0 mL/min. The amplitude of CID voltage required was directly proportional to the flow rate used. The backflush of the pre-column eliminated heavier components in the vegetable matrix from the analysis. Over 30 extracts were run with <18 % loss in sensitivity for the internal standard.

Introduction

The EPA published a schedule for completion of tolerance reassessment in the Federal Register on August 4, 1997. In this document some of the pesticides studied in this paper are listed in the Tolerance Reassessment Priority Group One, which contains organophosphates and carbamates. The organophosphate pesticides will be reassessed first. GC/MS/MS is a very selective method for analysis of organophosphate pesticide residues in vegetable matrix. In the ion trap, the sensitivity is limited by the trapping efficiency of the precursor ion. Increasing the pressure of the helium damping gas in the quadrupole ion trap has been shown to increase sensitivity.[1,2]

The overall GC/MS/MS sensitivity for pesticides studied was improved by incorporation of a variable damping gas controller, enhancing the trapping efficiency of the precursor ion; which increased the product ion yield. Extracts were analyzed by making a 5 µL temperature programmed injection into a pre-column with backflush capability. This allowed the heavier matrix components to be eliminated, thus shortening the run time and minimizing instrument maintenance.

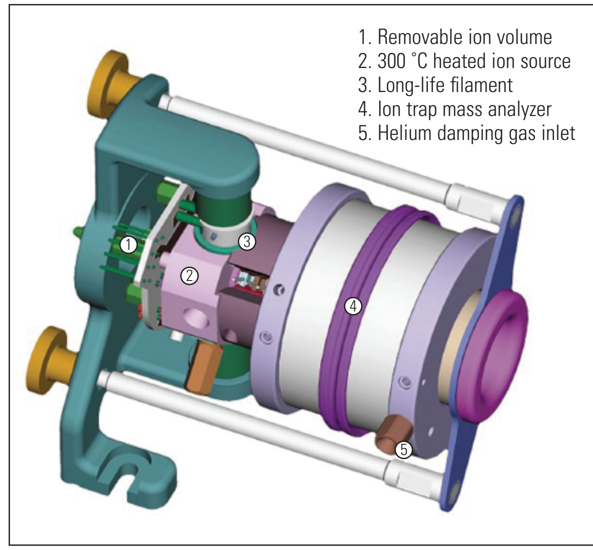

Figure 1: Polaris*Q* external source ion trap with variable damping gas.

Methods

A Thermo Scientific PolarisQ ion trap mass spectrometer (Figure 1) and a TRACE GC Ultra equipped with a Programmable Temperature Vaporizing Injector (PTV) were used.

A pre-column was installed with the effluent end connected to a tee to provide transfer to the analytical column or additional flow for backflushing the pre-column (Figure 2). The PolarisQ was equipped with the variable damping gas option which provides computer control of helium damping gas pressure in the ion trap.

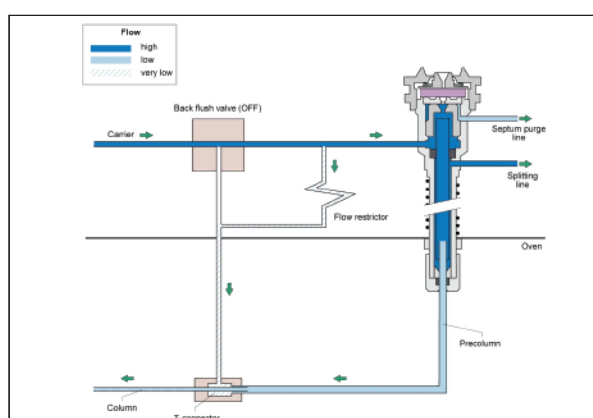

Figure 2: PTV with backflush of pre-column.

Higher Damping Gas Flows

The pesticides were analyzed in EI Full Scan to determine their retention times. Segments were defined during the run to isolate the precursor ion for each pesticide. To measure the trapping efficiency of the precursor ion, the CID energy was set to zero volts. Duplicate injections of the standard at 500 pg/µL in acetone were made at damping gas flows of 0.3, 1.0, 2.0, 3.0, 4.0, and 5.0 mL/min helium. The response at least doubled at the optimum flow for each pesticide studied versus that of the default flow of 0.3 mL/min (Figure 3).

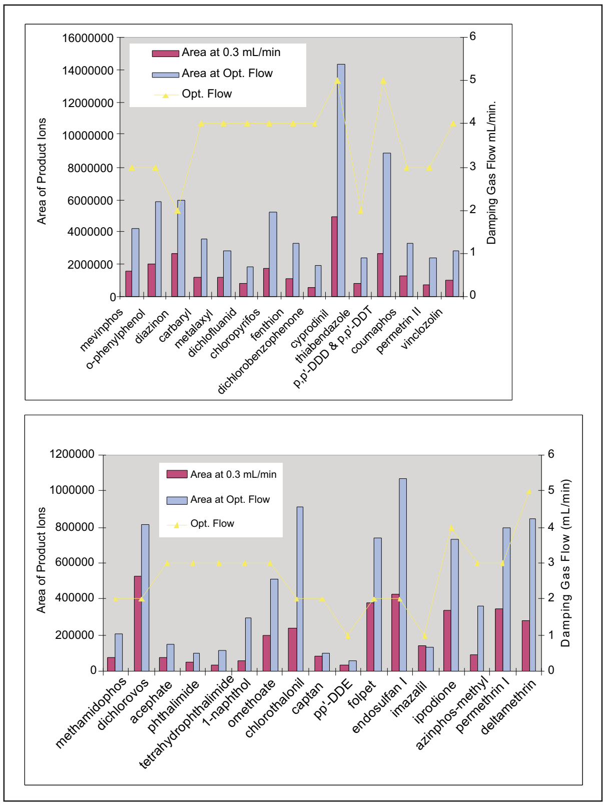

Figure 3: Increasing damping gas flow to the optimum doubled the response for the precursor ion. (CID=0V)

Results: CID Voltage Was Directly Proportional to the Damping Gas Flow

To test the effect of the higher damping gas flows on the generation of the product ions, the 500 pg/µL standard of pesticides was run at multiple CID voltages at the default flow of 0.3 mL/min and then at the optimum damping flow for each pesticide as defined in the individual MS/MS segments. The required CID energy for each pesticide at the default flow of 0.3 mL/min is plotted in Figure 4 in pink and the CID for the optimum damping gas flow is plotted in blue. The third plot line is the optimum damping gas flow for each pesticide plotted in yellow.

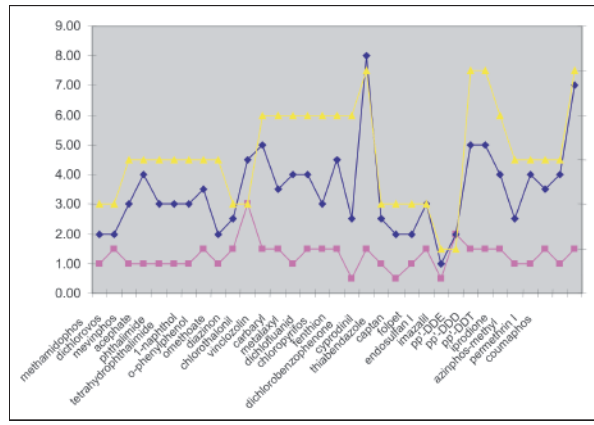

Figure 4: As the damping was increased, more cooling of the precursor ion occurred, which resulted in higher CID voltages being required.

Results: Product Ion Yield Enhanced at Higher Damping Gas Flows

The sensitivity was studied at a damping flow of 0.3 mL/min (default) and the optimum for each pesticide. At the optimum flow, all of the pesticides showed product ion yields of 4 to 5 times higher than at the default flow. The NIST library spectra for selected pesticides are shown below, along with the extracted ion profile of the precursor ion in Full Scan as compared to the summation of the product ions at the default damping gas flow and the optimum. The Full-Scan data was collected simultaneously with the MS/MS data as multiple scan events within each segment (Figure 5).

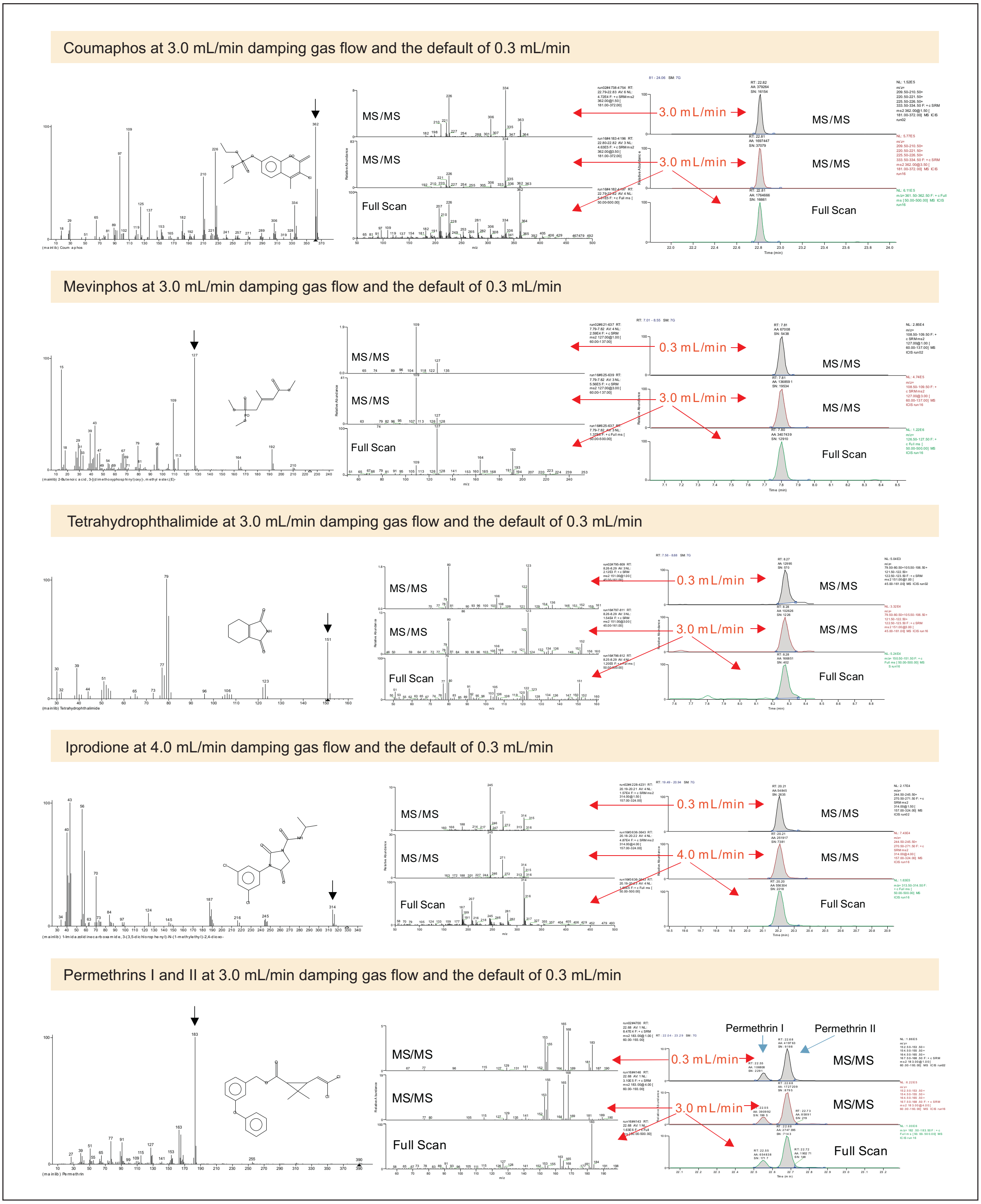

Figure 5: The sensitivity (product ion yield) at higher damping gas flows was 4-5 times greater than at the default damping gas flow.

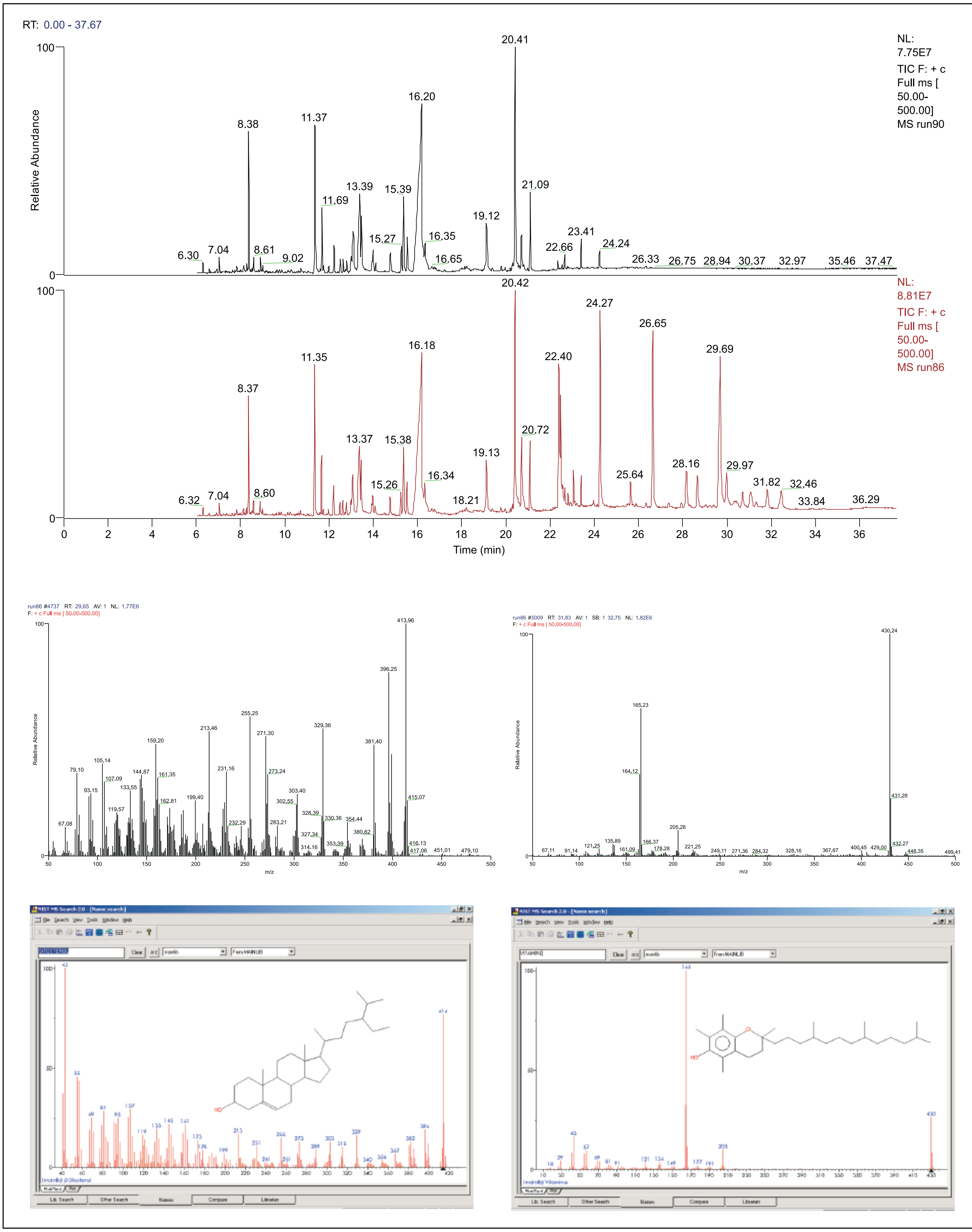

Figure 6: The effect of backflushing the pre-column on GC run time.

Results: Analysis Time Reduced by Backflush of Pre-column

Analysis of spiked samples of a prepared matrix of 1.0 g/mL of equal portions of spinach, strawberries, peppers, tomatoes, and peaches in methylene chloride by GC/MS/MS were made. Some heavy matrix components were prevented from entering the analytical column by back-flushing the pre-column prior to elution of these components, shortening the run time from 35 to 26 minutes (Figure 6).

Results: Tabulation of GC/MS/MS Parameters

Table 1 shows the GC/MS/MS parameters at the default damping gas flow of 0.3 mL/min and at the optimum damping gas flow for each pesticide. More studies will be performed in the future on other pesticides.

ANALYTE	RETENTION TIME (MIN)	MOL. ION (m/z)	SEGMENT START TIME (MIN)	SEGMENT #	SCAN EVENT #	PRECURSOR ION (m/z)	WIDTH (AMU)	EXCITATION ENERGY (q)	CID AT DEFAULT DAMPING GAS FLOW	CID AT OPTIMAL DAMPING GAS FLOW	OPTIMAL DAMPING GAS FLOW (mL/min)	PRODUCT IONS
methamidophos	6.46	141	5.00	1	1	141	2	0.225	1.00	2.00	2.00	95,111,126
dichlorovos	6.55	220			2	185	2	0.225	1.50	2.00	2.00	93,109,131
mevinphos	7.81	224	7.00	2	1	127	2	0.225	1.00	3.00	3.00	109
acephate	7.94	183			2	136	2	0.225	1.00	4.00	3.00	94
phthalimide	8.16	147			3	104	2	0.225	1.00	3.00	3.00	76
tetrahydrophthalimide	8.29	151			4	151	2	0.225	1.00	3.00	3.00	80,106,122,123
acenaphthene-d10	8.37				5			Full Scan (50-500)				162,164
1-naphthol	8.6	144	8.45	3	1	144	2	0.225	1.00	3.00	3.00	116
o-phenylphenol	8.6	170			2	170	4	0.225	1.50	3.50	3.00	141
omethoate	9.4	213	9.00	4	1	156	2	0.225	1.00	2.00	3.00	110,126,141
diazinon	11.4	304	11.00	5	1	179	2	0.225	1.50	2.50	2.00	96,137,161,164
chlorothalonil	11.58	264			2	266	4	0.450	3.00	4.50	2.00	168,170,203,205,229,000
anthracene-d10	11.37				3			Full Scan (50-500)				188
vinclozolin	12.66	285	12.00	6	1	212	4	0.225	1.50	5.00	4.00	172,177
carbaryl	12.87	201			2	144	2	0.225	1.50	3.50	4.00	116
metalaxyl	13.02	279			3	160	2	0.225	1.00	4.00	4.00	119,130,145
dichlofluanid	13.68	332	13.30	7	1	123	2	0.225	1.50	4.00	4.00	77,96
chloropyrifos	13.98	330			2	314	4	0.450	1.50	3.00	4.00	258,286
fenthion	14.02	278			3	278	4	0.450	1.50	4.50	4.00	151,169,231,245,246,263
dichlorobenzophenone	14.14	250			4	250	4	0.225	0.50	2.50	4.00	139,215,250
cyprodinil	14.79	225	14.40	8	1	224	4	0.225	1.50	7.00	5.00	207,208,209,224
thiabendazole	15.24	201	15.00	9	1	201	2	0.225	1.00	2.50	2.00	174
captan	15.31	299			2	149	2	0.225	0.50	2.00	2.00	105,107,121
folpet	15.51	295			3	260	4	0.225	1.00	2.00	2.00	130,200,232
endosulfan I	16.17	397			4	241	6	0.225	1.50	3.00	2.00	170,204,205,206,207
imazalil	16.77	296	16.50	10	1	215	4	0.225	0.50	1.00	1.00	159,173
pp'-DDE	16.89	316			2	318	6	0.450	2.00	2.00	1.00	246,248,281,283
pp'-DDD	19.2	318		11	1	235	6	0.225	1.50	5.00	5.00	165,199,200
pp'-DDT	19.2	352				235	6	0.225	1.50	5.00	5.00	165,199,200
iprodione	20.23	329	20.00	12	1	314	4	0.450	1.50	4.00	4.00	245,271
chrysene-d10	20.46				2			Full Scan (50-500)				240
azinphos-methyl	21.35	317	21.00	13	1	132	2	0.225	1.00	2.50	3.00	77,104,132
permethrin I	22.57	390	2.00	14	1	183	2	0.225	1.00	4.00	3.00	153,155,165,168
coumaphos	22.7	362			2	362	4	0.450	1.50	3.50	3.00	221,226,334
permetrin II	22.84	390			3	183	2	0.225	1.00	4.00	3.00	153,155,165,168
perylene-d12	24.31				4			Full Scan (50-500)				264
deltamethrin	25.87	503	25.00	15	1	253	6	0.450	5.00	7.00	5.00	172,174

Table 1: Tabulation of GC/MS/MS parameters of pesticides studied.

Conclusion

The addition of higher damping gas pressure in the PolarisQ ion trap GC/MS gave better detectivity by 4-5x for the list of pesticides studied. The CID voltages required at the higher damping gas flows were proportional to the increase of flow from the default of 0.3 mL/min. The trapping efficiency of the precursor ion was enhanced at the higher flows. The backflush of the pre-column allowed the analysis run time to be shortened and the mass spectrometer and analytical column were kept cleaner, requiring less maintenance.

References

1. J.C. Schwartz, R.G. Cooks, M. Weber-Grabau, P.E. Kelley, "Quantitative Evaluation of Ion Injection Into a Quadrupole Ion Trap", Proceedings of the 36th ASMS Conference on Mass Spectrometry and Allied Topics, San Francisco, CA, June 5-10, 1988.

2. Y. Wang, M. Schubert, J. Franzen, "Enhancement of Ion Trapping Efficiency in an Ion Trap with a Pulsed Valve", Proceedings of the 43rd ASMS Conference on Mass Spectrometry and Allied Topics, Atlanta, GA, May 21-26, 1995.

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Authors: Jessie C. Butler, Scott T. Quarmby, John D. Ragsdale III, and Meredith Conoley

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Australia
+61 2 8844 9500
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