Application Note: 10039

Determination of Derivatized Carbamate Insecticides by GC-MS/MS

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Key Words

- GC-MS/MS
- Carbamates
- Ion Trap
- Method 622
- Pesticides
- Wastewater

Introduction

The determination of carbamate pesticides, insecticides, and herbicides has long been relegated to liquid chromatography. Liquid chromatography was chosen due to the thermally labile nature of the various carbamates. Of the three EPA LC methods referenced, two of these methods (531.1 and 8318A) utilize post column derivatization fluorescence detection while Method 632 monitors the native components. Two of these methods stipulate "...analyte identifications should be confirmed by at least one additional qualitative technique.[1,2,3] One proposition is to use LC/MS for detection but electrospray ionization generally only produces a single protonated ion and very little fragmentation. While this is good for sensitivity, it does not address the need for confirmation.

This report details a methodology utilizing a GC-MS/MS system that provides both the sensitivity and confirmation for this application in a single injection without the need for extensive sample preparation.

The Thermo Scientific PolarisQ external source GC-ITMS operated in EI-MS/MS was used to develop a sensitive and robust methodology for the analysis of EPA Method 632 carbamates. This was accomplished by coupling the split injection technique with flash methylation of the analytes in the injection port. By utilizing MS/MS for the N-aryl-carbamates and MS/MS/MS for the O-aryl-carbamates both sensitivity and confirmation can be achieved in standards as well as matrix.

Instrument Conditions

PolarisQ Ion Trap

Ion source temperature: 250°C
Ionization mode: +EI; 70 eV
AGC: 50
Injection waveforms: ON (default)
Buffer gas flow: ~1.7/mL/min
MS/MS parameters: See Table 1

TRACE GC Ultra

Column: SGE BPX-50 0.25 mm ID x 60 meter, 0.25 micron film thickness
Oven: 70 °C (1 min); 10°C / min 300°C (6 min) : 30 min run time
Split/Splitless injector: Split mode
Injector temperature: 250 °C
Column flow: 1.2 mL/min
Split flow: 12 mL/min
Injection port liner: 5 mm straight; packed with 1 cm glass wool

Autosampler

Injection volume: 2 microliters

Objective

To develop a robust, simple, and sensitive method for the determination of the 19 carbamates by GC-MS/MS. After some literature searches it was determined that many experiments were performed to develop gas chromatographic methodology for the analysis of the carbamates.[4] Of all the techniques that were attempted for this study, methylation by flash alkylation in the injector was best suited for these 19 compounds. With this technique, all 19 compounds could be chromatographed and confirmed in a single injection by using the conditions described here.

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Sample Preparation

100 mL of pond water was extracted with 30 mL of methylene chloride. The methylene chloride was dried with sodium sulfate and the resulting extract was evaporated to dryness. The "blanks" were reconstituted with 100 µL 50:50 MethElute (Pierce Chemical Company) : methanol. The "spiked" samples were prepared with 100 µL of 500 pg/µL solution of method 632 standards (Accustandard) and evaporated to dryness. The "spiked" samples were then also reconstituted with 50:50 MethElute and methanol. All standards were evaporated to dryness and reconstituted with 50:50 MethElute and methanol.

Results and Discussion

Each of the compounds listed in Table 1 was injected as a single component with the methylating agent to determine the resulting spectrum and retention time. The O-aryl carbamates yielded a methyl aryl ether (Figure 1), whereas the N-aryl carbamates were methylated at the amine(Figure 2). Each individual standard was then injected to optimize collision energies to determine the correct value (the MS/MS experiment was performed as a single injection by alternating scans with varying collision energy). For most of the methyl-aryl-carbamates the MS/MS experiments produced a loss of a methyl group (15 *m/z*). This loss is not very diagnostic for confirmation. For each of the compounds that exhibited loss of a methyl group, another stage of MS was performed.

After each compound was optimized, the entire mixture was analyzed for interferences. A 6-point (10, 5, 2, 1, 0.5, 0.1 ng/µL) calibration curve was injected five times. All extracts were quantified by the external standard technique. See Table 2 for linearity data and Figure 3 and 4 for calibration curves of methylated Carbofuran and methylated Neburon.

A pond water sample was extracted and spiked at 500 pg/µL (500 ppt in the water) and injected 20 times to determine analytical reproducibility. These data can be seen in Table 3. The ability to detect and confirm these components can be seen in Figures 5 and 6 for methylated Carbofuran and methylated Neburon respectively. From the spectra obtained, one can easily identify and confirm the presence of these compounds.

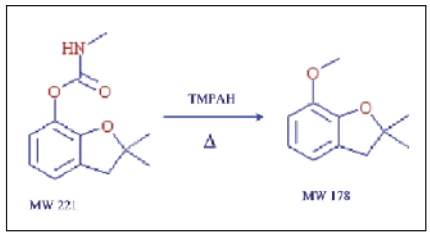

Figure 1: Flash methylation reaction of Carbofuran

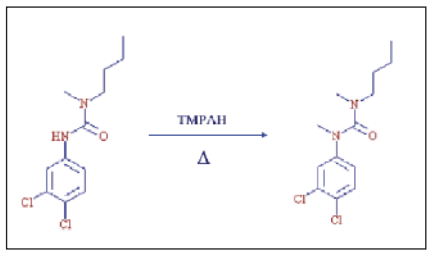

Figure 2: Flash methylation reaction of Neburon

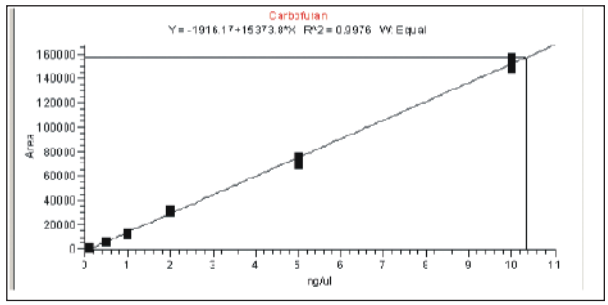

Figure 3: Linearity of MS/MS/MS of methylated Carbofuran from 0.1-10 ng/µL

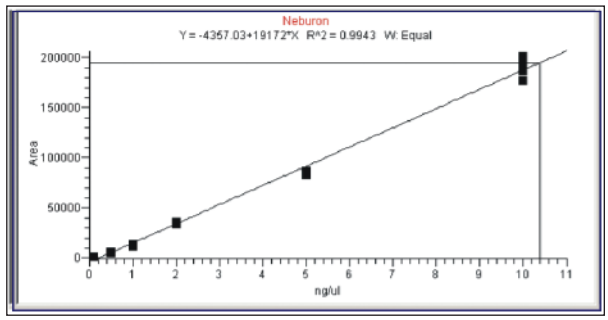

Figure 4: Linearity of MS/MS of methylated Neburon from 0.1-10 ng/µL

Carbofurans in Pond Water Extract

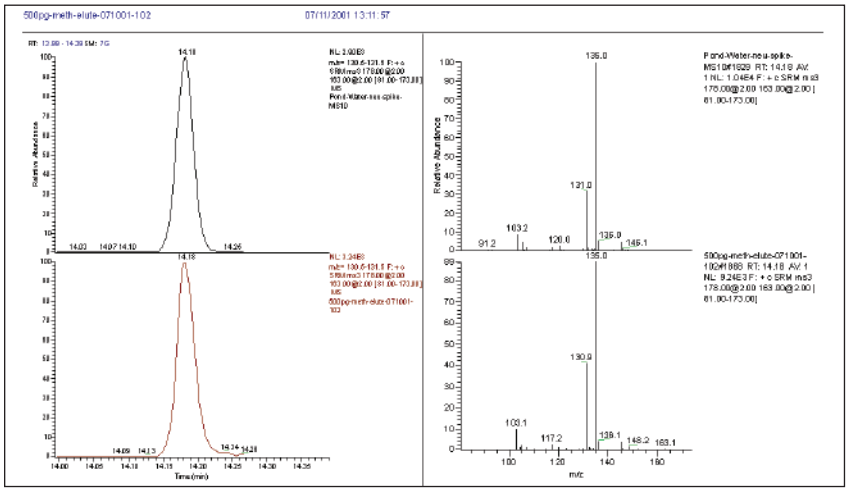

Figure 5: Showing the spectra and mass chromatograms for methylated Carbofuran at the 500 ppt level in both the standard and the pond water extract.

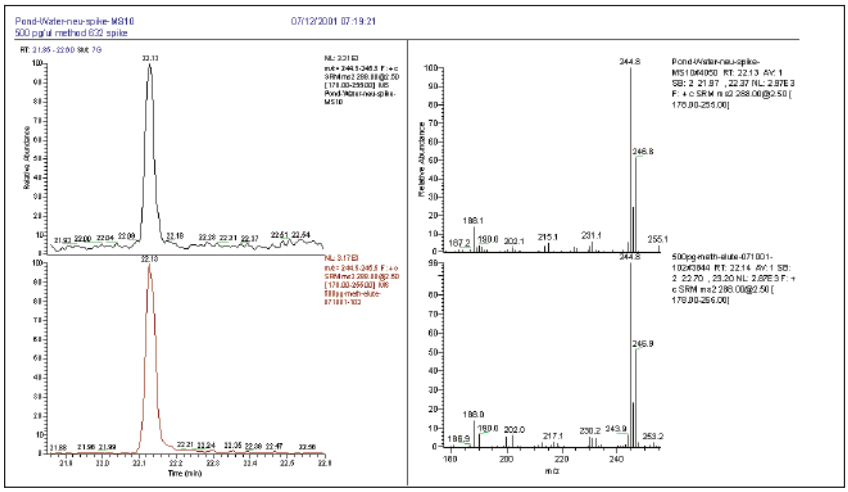

Figure 6: Showing the spectra and mass chromatograms for methylated Neburon at the 500 ppt level in both the standard and the pond water extract. Note the agreement of the chlorine isotope pattern.

COMPOUND	RETENTION-TIME (MIN)	PRECURSOR ION	MS/MS/MS	QUAN ION
Methomyl	8.90	119		88
Baygon	11.95	166	124	109
Aminocarb	13.21	165	150	122
Mexacarbate	13.68	179		148
Carbofuran	14.19	178	163	131
Propham	14.47	193		151
Fluometuron	14.57	246	231	174
Oxamyl	15.98	145		61 + 88 + 111
Fenuron	16.03	178	163	106
Methiocarb	16.07	182	167	152
Carbaryl	16.30	158	143	115
Chlorpropham	16.63	227		185
Monuron	18.45	212		146
Swep	18.80	233		176
Barban	19.49	222	193	166
Linuron	20.23	231		196
Karmex	20.51	246		174
Siduron	21.66	260		163
Neburon	22.16	288		245

Table 1: Ions used for the MS^n experiments.

COMPOUND	R^2
Methomyl	0.9824
Baygon	0.9962
Aminocarb	0.9948
Mexacarbate	0.9948
Carbofuran	0.9976
Propham	0.9963
Fluometuron	0.9957
Oxamyl	0.9966
Fenuron	0.9895
Methiocarb	0.9948
Carbaryl	0.9964
Chlorpropham	0.9953
Monuron	0.9917
Swep	0.9939
Barban	0.9922
Linuron	0.9890
Karmex	0.9939
Siduron	0.9917
Neburon	0.9943

Table 2: Showing the R^2 values obtained for the linear fit for 100 pg/µL to 10 ng/mL.

COMPOUND	CALC. AMOUNT (PPT)	% RSD (N = 20)
Methomyl	583	2.7
Baygon	470	2.9
Aminocarb	457	3.2
Mexacarbate	475	2.1
Carbofuran	446	6.0
Propham	536	2.3
Fluometuron	400	3.7
Oxamyl	452	3.5
Fenuron	517	6.8
Methiocarb	450	3.0
Carbaryl	412	4.9
Chlorpropham	490	2.3
Monuron	337	5.1
Swep	483	3.5
Barban	223	13
Linuron	554	3.6
Karmex	507	3.0
Siduron	414	17
Neburon	521	3.0

Table 3: The recovery and precision data for 20 replicate injections of a pond water extract spiked at 500 ppt

Conclusion

By utilizing flash alkylation in the injection port and GC-MS/MS/MS the PolarisQ is a viable alternative to LC and LC/MS for those laboratories who wish to have a sensitive, robust and simple methodology for the determination of carbamates. This methodology allows detection and confirmation of carbamates with comparable detection limits, reproducibility, and linearity as conventional EPA methods in a single injection.

References

1. Method 632, The Determination of Carbamate and Urea Pesticides in Municipal and Industrial Wastewater US EPA, November 1994.

2. Method 531.1 Rev. 3.1, Measurement of N-Methylcarbamoyloximes and N-Methylcarbamates by Direct Aqueous Injection HPLC with Post Column Derivatization, US EPA, 1995.

3. Method 8318A, N-Methylcarbamates by High Performance Liquid Chromatography (HPLC) Rev. 1, US EPA, 2000.

4. Knapp, D. R., Handbook of Analytical Derivatization Reactions; John Wiley and Sons: New York, 1979, 364

Acknowledgement

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In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

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AN10039_E 08/07C