

Environmental

Determination of Carbamates by UHPLC/SQ MS



Carbamates are organic compounds derived from carbamic acid (NH_2COOH). They are generally highly poisonous chemicals when ingested at high concentrations. They're not considered carcinogenic but there are some studies about the possible formation of cancerous chemicals when they mix with other elements in the stomach.

Carbamate insecticides have been used in agricultural pest control since the 1960's.

In this application brief, we describe a UHPLC/SQ MS method for the determination of carbamates and carbamate-based insecticides that could be used – after the proper sample preparation – on different sample matrices.

Experimental Conditions

Target Analytes: Aldicarb sulfone, aldicarb sulfoxide, oxamyl, methomyl, carbofuran-3-hydroxy, aldicarb, proprosur, carbofuran, 1-naphthyl-n-methylcarbamate, mercaptodimethur (methiocarb)

Standard Concentrations

A 100 $\mu\text{g/mL}$ carbamates standard in methanol purchased from Sigma was diluted 1:100 in acetonitrile to 1 $\mu\text{g/mL}$ (1 ppm). A calibration curve for the carbamates was prepared with a concentration ranging from 0.05 ppb to 19.53 ppm.

Liquid Chromatography Conditions

Pump Type:	PerkinElmer® Flexar™ FX-15		
Column:	Restek Ultra II® (2.1 mm x 100 mm, 3 μm)		
Mobile Phase:	A: water containing 10 mM ammonium acetate B: methanol containing 10 mM ammonium acetate		
Flow Rate:	0.5 mL/min		
Cooling Temp:	35 °C		
Injection Volume:	2 μL		
Gradient:	Time (min)	%A	%B
	6	90	10
	9	10	90
	1	90	10

Mass Spectrometer Conditions

Ionization:	Ultraspray™ ESI – Positive mode
Scan Range:	50-300 m/z
Scan Rate:	2500 u/sec
Selected Ion Monitoring (SIM) Mode:	Reported in Figure 1; dwell time of 150 ms each
Capillary Exit Voltage:	45 V for Scan data; reported in Figure 1 for SIM data

Figure 1. [M+H]⁺ of each carbamate in SIM mode.

Peak	Pesticide	SIM Ion	Time Period	Capillary Exit Voltage
1	Aldicarb sulfone	223.1	0-4.5 min	80 V
2	Aldicarb sulfoxide	207.1	0-4.5 min	60 V
3	Oxamyl	237.1	0-4.5 min	35 V
4	Methomyl	163	0-4.5 min	40 V
5	Carbofuran-3-hydroxy	238.1	4.5-5.1 min	70 V
6	Aldicarb	208.1	4.5-5.1 min	30 V
7	Proproxur	210.1	5.1-5.8 min	40 V
8	Carbofuran	222.1	5.8-6.8 min	65 V
9	1-Naphthyl-n-methyl-carbamate	202.1	5.8-6.8 min	40 V
10	Mercaptodimethur (methiocarb)	226.1	6.8-11.0 min	75 V

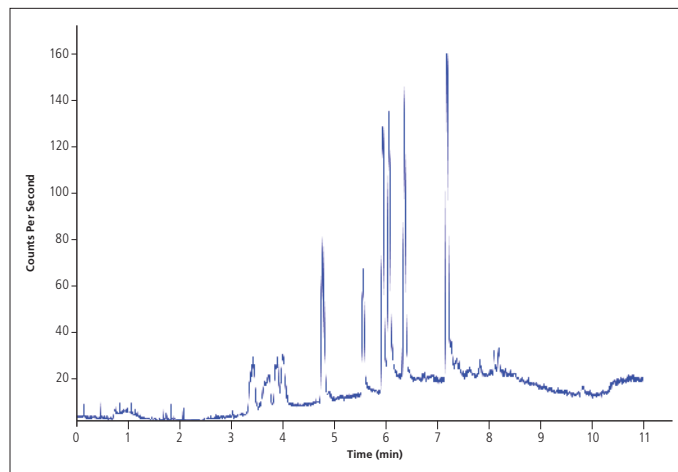


Figure 2. Full Scan separation of the carbamates mixture at 5 ppm.

Results

The mass spectrum of each target analyte has been identified by initial experiments in Full Scan UHPLC/SQ MS (Figure 2). Selected Ion Monitoring (SIM) was used to achieve optimal separation and sensitivity (Figures 3 and 4). In each case, the molecular ion is the only one used for quantitation because of its high abundance in each carbamate mass spectrum.

Conclusions

In this application brief, carbamates separated by UHPLC are detected with MS achieving sensitivity similar to conventional post-column derivatization methods followed by Fluorescence detection.

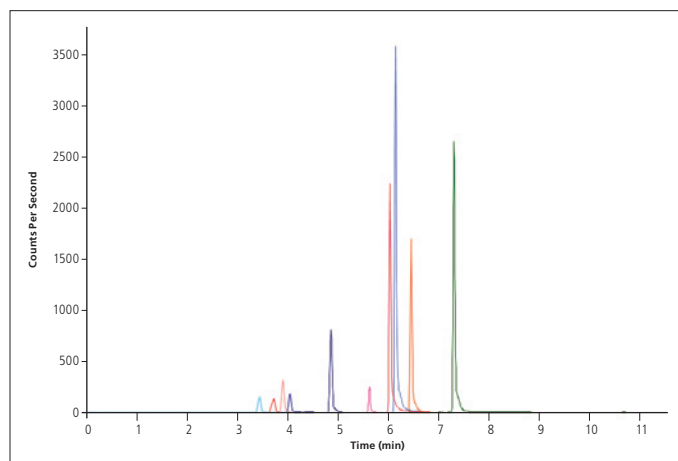


Figure 3. Overlaid chromatograms of [M+H]⁺ ions for each of the carbamates in SIM mode.

The calculated detection limits for each of the carbamates are:

0.05 ppb for proproxur, carbofuran, 1-Naphthyl-N-methylcarbamate, Mercaptodimethur

1.25 ppb for Aldicarb sulfoxide, methomyl, carbofuran-3-hydroxy, aldicarb

6.25 ppb for aldicarb sulfone, oxamyl

When compared to these methodologies, the Flexar SQ 300 MS provides additional flexibility and applicability to multiple applications, thus representing a better return on investment.

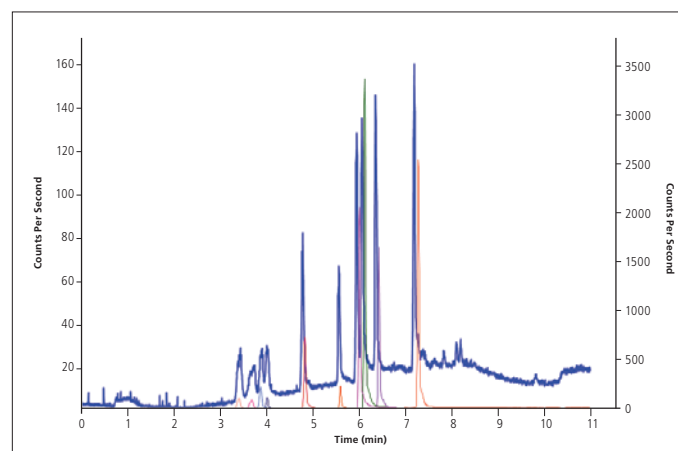


Figure 4. Full Scan mode versus SIM mode.

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