Routine Analysis of Trace Level Carbamate Pesticides in Food Using LC/MSD

Application

Food, Environmental

Author

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Abstract

System linearity, sensitivity, and repeatability were evaluated on nine carbamates using positive electrospray ionization. Instrument detection limits were determined to be about 3 to 10 ppb for all the analytes in broccoli extract. The results demonstrate that the liquid chromatography with mass selective detection method is a viable technique to replace the nonspecific post-column derivatization process using fluorescence detection.

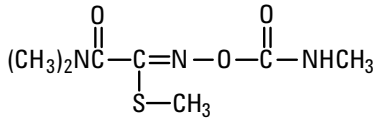
Introduction

Pesticides in food are a significant route to human exposure. Besides toxicity, many of the pesticides, including N-methyl carbamates, are also suspected endocrine disrupters. The most often used method for carbamate determination is the post-column derivatization technique using fluorescence detection. Drawbacks of the fluorescence method include false positives due to lack of specificity, required additional hardware and plumbing, and insufficient limits of detection. False positives were confirmed in samples having a positive carbaryl identification by a liquid chromatograph (LC) with a fluorescence detector [1].

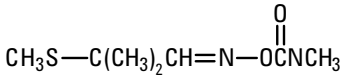
The goal of this study is to develop a routine liquid chromatograph/mass selective detector (LC/MSD) assay to detect carbamates in foods at low ppb levels without the derivatization step.

Experimental

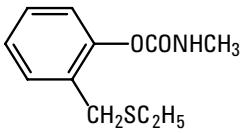
A mixture of nine analytes (see Figure 1) in methanol was used to evaluate system linearity, sensitivity, and repeatability. A spiked broccoli extract was used to study the matrix effect on system performances. The LC/MSD system used was the Agilent 1100 MSD SL Quad system.



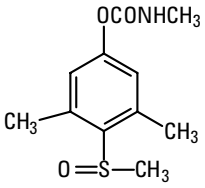
Oxamyl



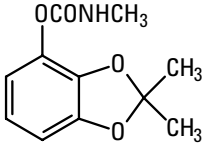
Aldicarb



Ethiofencarb



Methiocabsulfoxide



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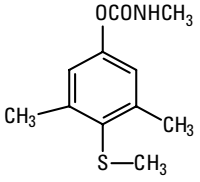
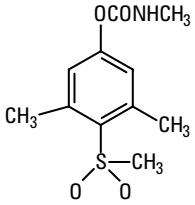
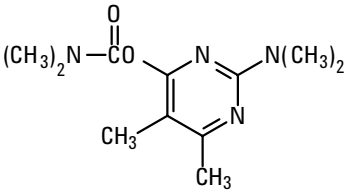


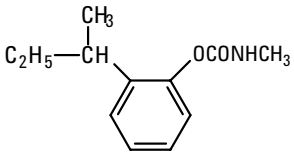
Methiocarb



Methiocabsulfone



Pirimicarb



Fenobcarb

Figure 1. Structures of the analytes used in this study.

Table 1. LC and MS Conditions

LC Conditions	
Columns	Inertsil ODS3 (150 mm × 2.1 mm × 5 µm) Zorbax Eclips XDB C18 (150 mm × 2.1 mm × 5 µm)
Mobile phase	A: MeCN B: 10 mM CH_3COONH_4 in H_2O 20% A/B to 100% A in 30 min
Flow rate	0.2 mL/min
Column temp	40 °C
Sample volume	10 µL
MS Conditions	
Ionization	Positive electrospray
Scan range	100 to 500
SIM ion	Base peak
Drying gas	10 L/min at 350 °C
Nebulizer gas	50 psi
Fragmentor	60 V
EM gain	7

Results and Discussion

TIC and SIM

Figure 2 shows the total ion chromatogram (TIC) of all nine analytes at 1 ppm. The base peaks for the analytes were either MH^+ or MNH_4^+, except Aldicarb, which was a fragment from the breakage of the N-O bond. Table 2, later in this note, lists the base peaks.

Figures 3 and 4 are the selected ion monitoring (SIM) chromatograms of all nine carbamate standards at 0.2 ppb. The signal-to-noise (S/N) ratios of these peaks range from 7 to 56.

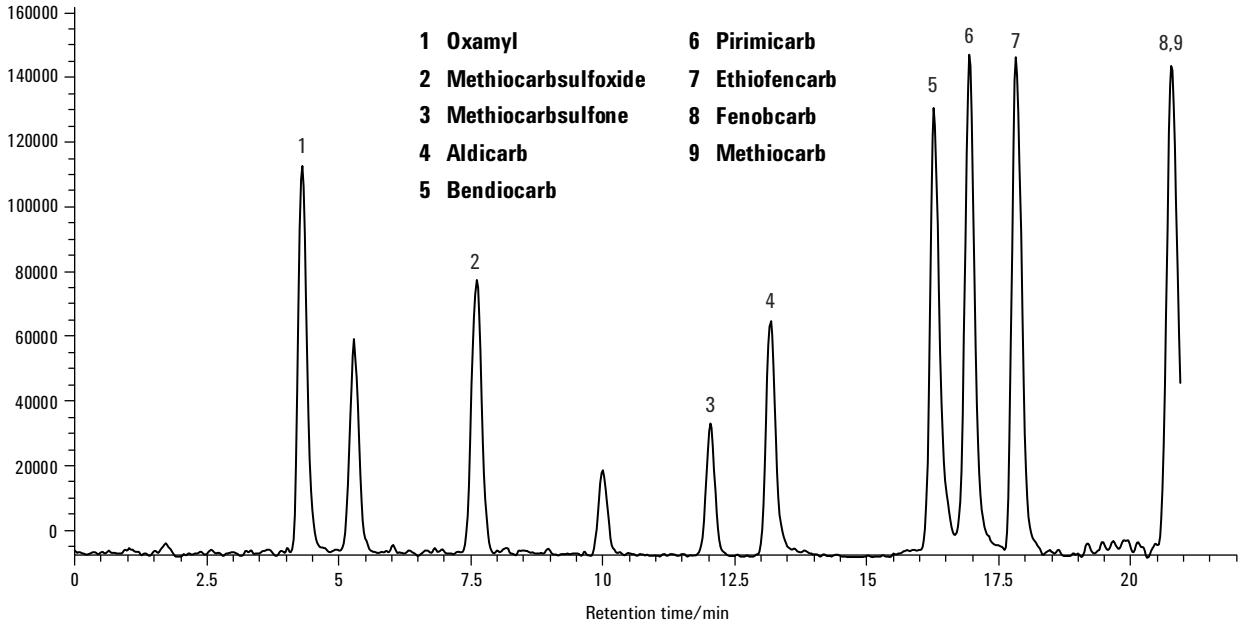


Figure 2. TIC of carbamate standards at 1 ppm.

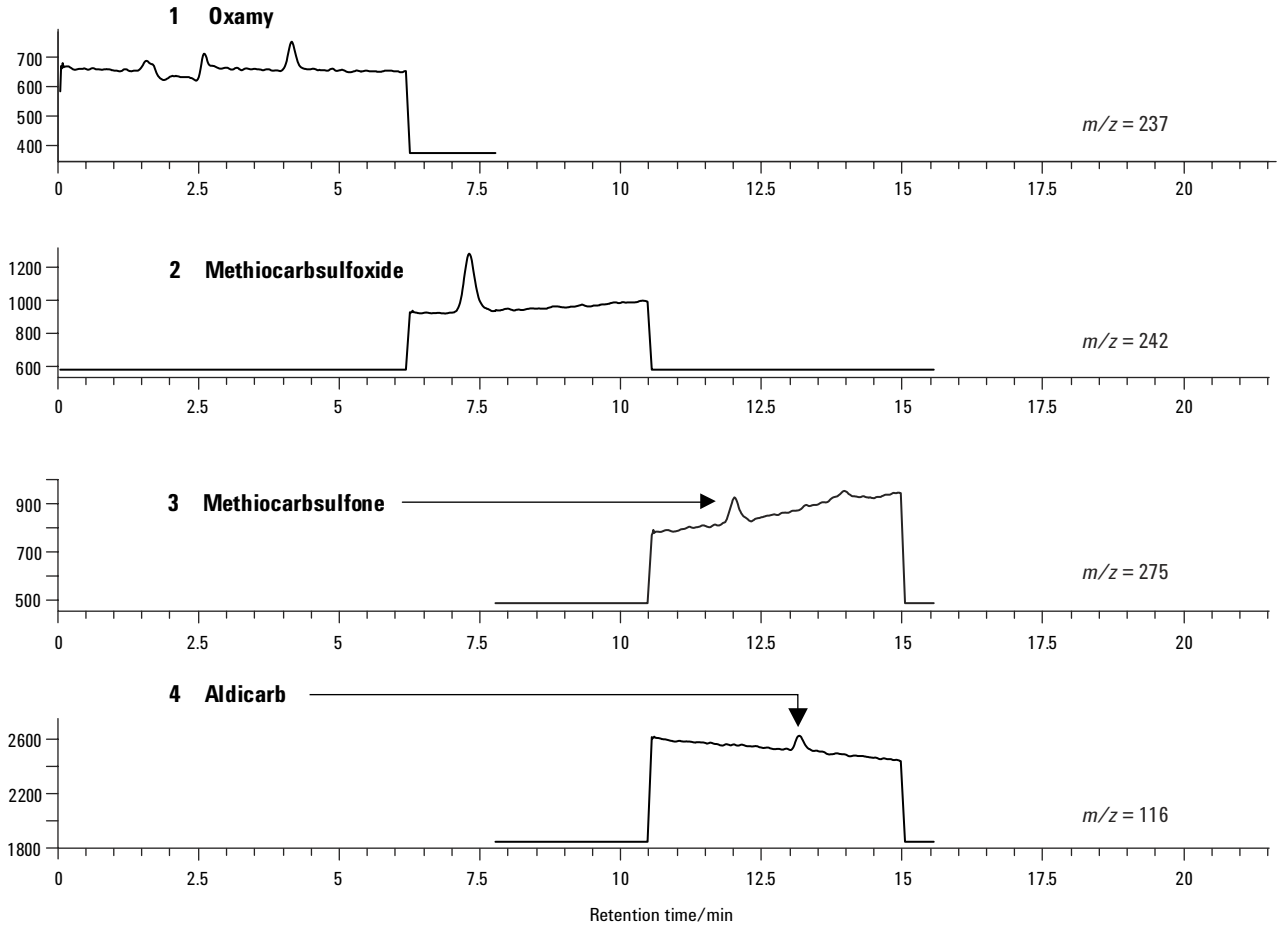


Figure 3. SIM chromatograms of four carbamate standards at 0.2 ppb. The base peak is labeled in each chromatogram.

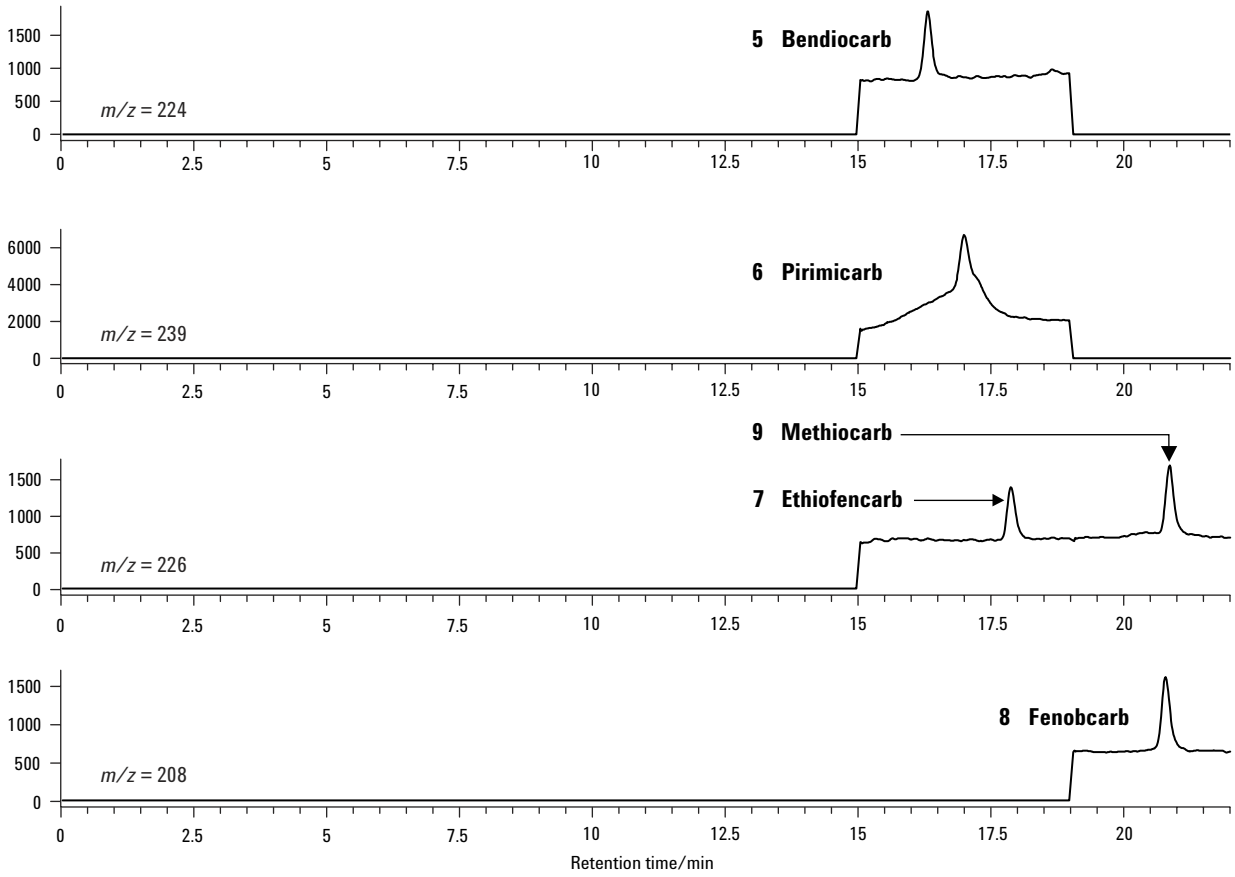


Figure 4. SIM chromatograms of five carbamate standards at 0.2 ppb. The base peak is labeled in each chromatogram.

Ionization

Electrospray is a soft ionization technique that produces a large number of molecular-related ions. These ions are typically protonated molecular ions $[M+H]^+$. In this study, both $[M+H]^+$ and $[M+NH4]^+$ are dominant adduct ions. The fragmentor voltage is applied to the exit of the capillary and affects the transmission and fragmentation of sample ions by the in-source collision-induced dissociation in this region. By changing the voltage of the fragmentor, various degrees of fragmentation may be achieved. With a low voltage, there is little fragmentation; with higher voltages, a molecular-related ion is fragmented to a larger degree.

Figure 5 has five SIM chromatograms collected at different fragmentor voltages ranging from 40 V to 120 V. Using the abundance of carbamates at 40 V as reference, Figure 6 shows the changes in relative abundances of carbamates at four fragmentor voltages. For compounds that do not fragment easily, ion transmission improves at the higher fragmentor voltage because the fragmentor voltage gives these ions a push that helps them travel through the relatively high pressure region between the exit of the capillary and the skimmer. For stable compounds, base peak abundance increases with fragmentor voltage up to about 100 V. Setting the fragmentor to either 60 or 80 V will have the best results.

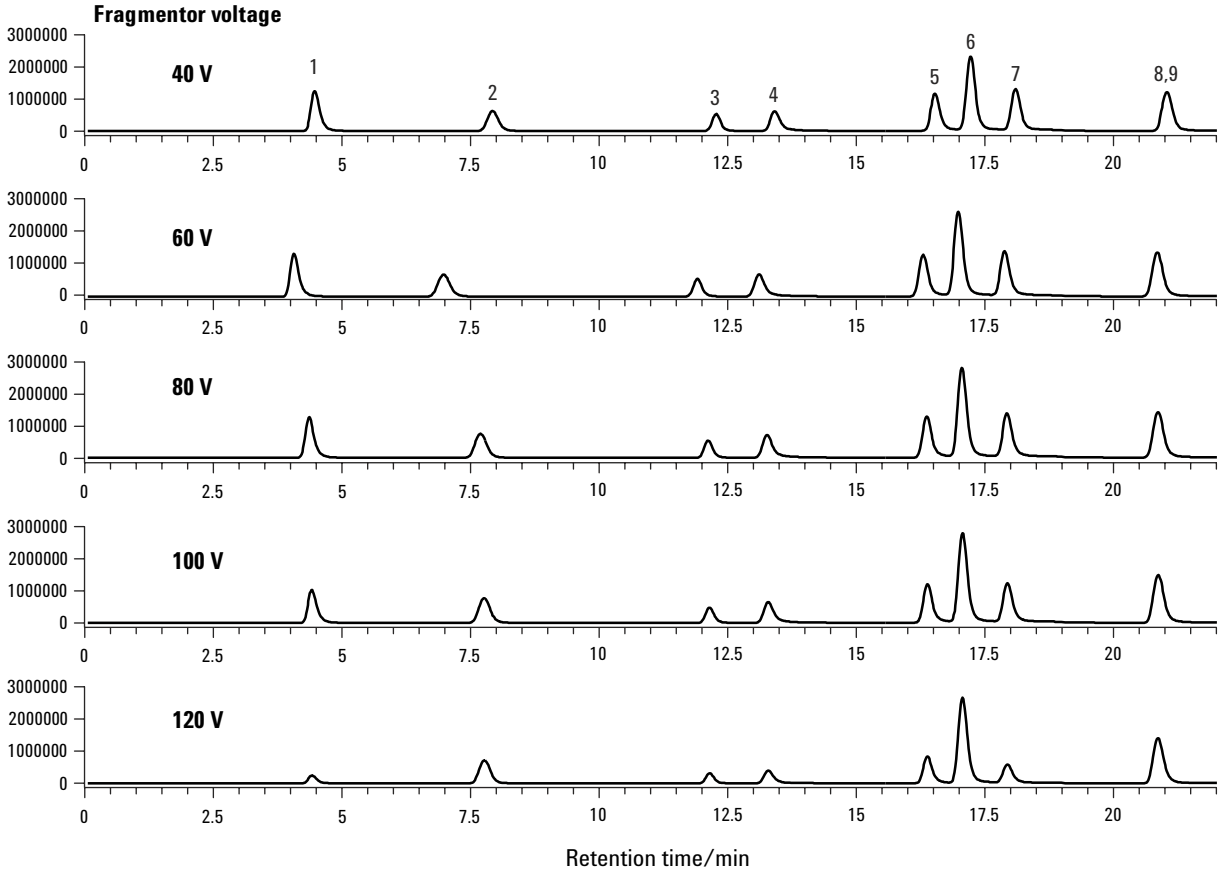


Figure 5 SIM chromatograms of carbamate standards at different fragmentor voltages.

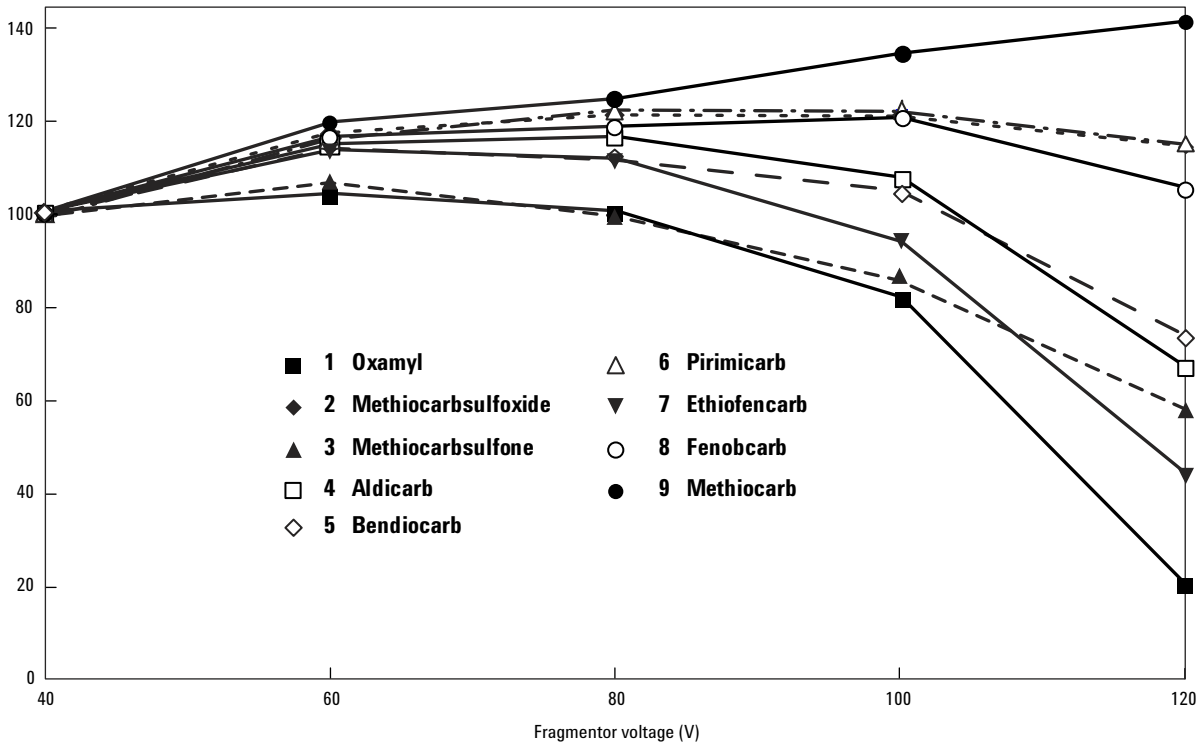


Figure 6 Relative abundance of carbamate standards at different fragmentor voltages. Abundances at 40 V were used as the reference values.

Repeatability and Linearity

Figure 7 shows five repeat injections of the carbamate standards at 5 ppb. The %RSD for each analyte ranges from 1.4% to 13% (Methiocarbsulfone). The 13% variation reflects the relatively weak response of the peak at this low concentration.

Figure 8 shows some of the calibration curves of carbamate standards. The responses are linear for all the analytes over a very wide concentration range. For the range from 0.2 to 1000 ppb, the correlation coefficients of all analytes are all greater than 0.998 (see Table 2).

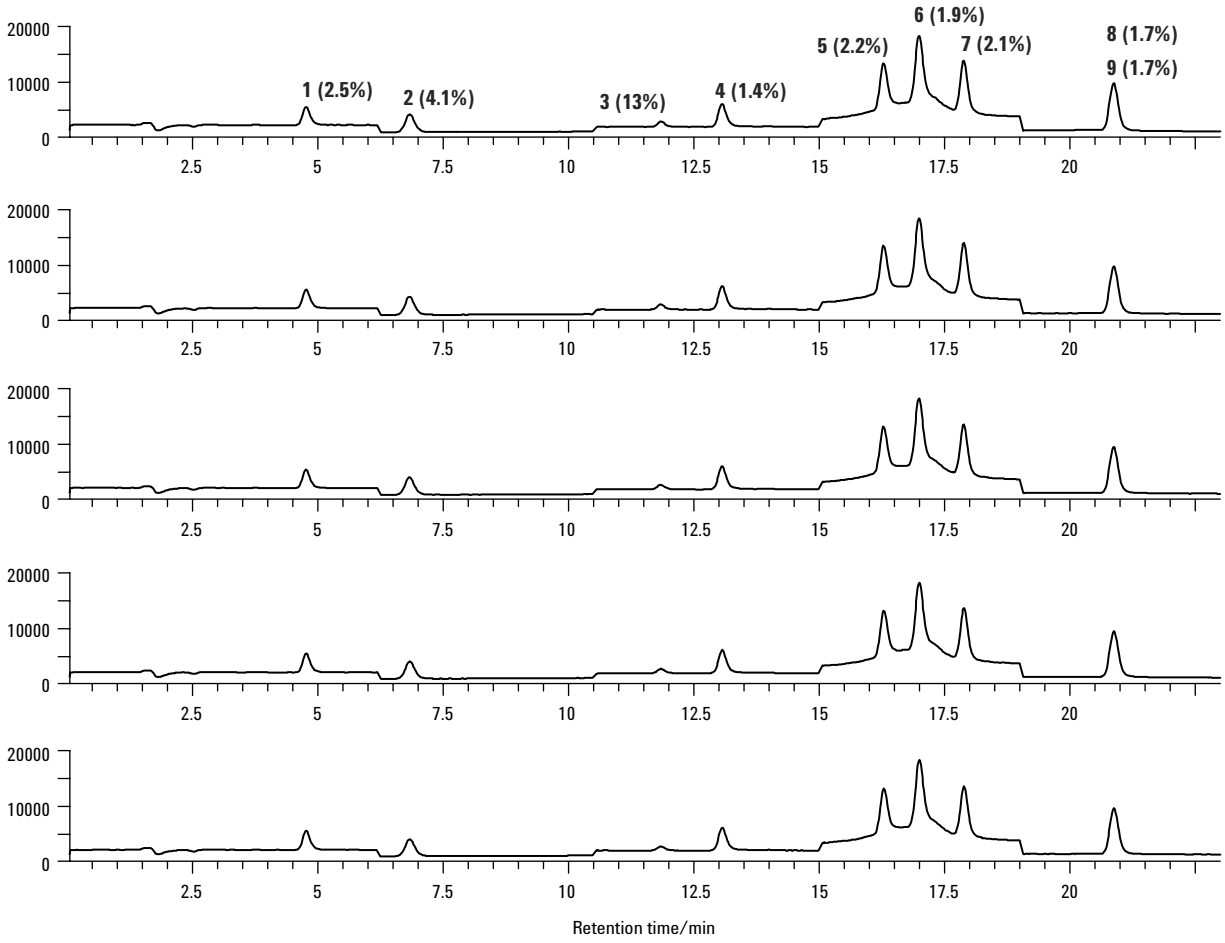


Figure 7. Repeatability of five repeat injections of the carbamate standards at 5 ppb. The percentage number in each parenthesis is the %RSD value for the peak.

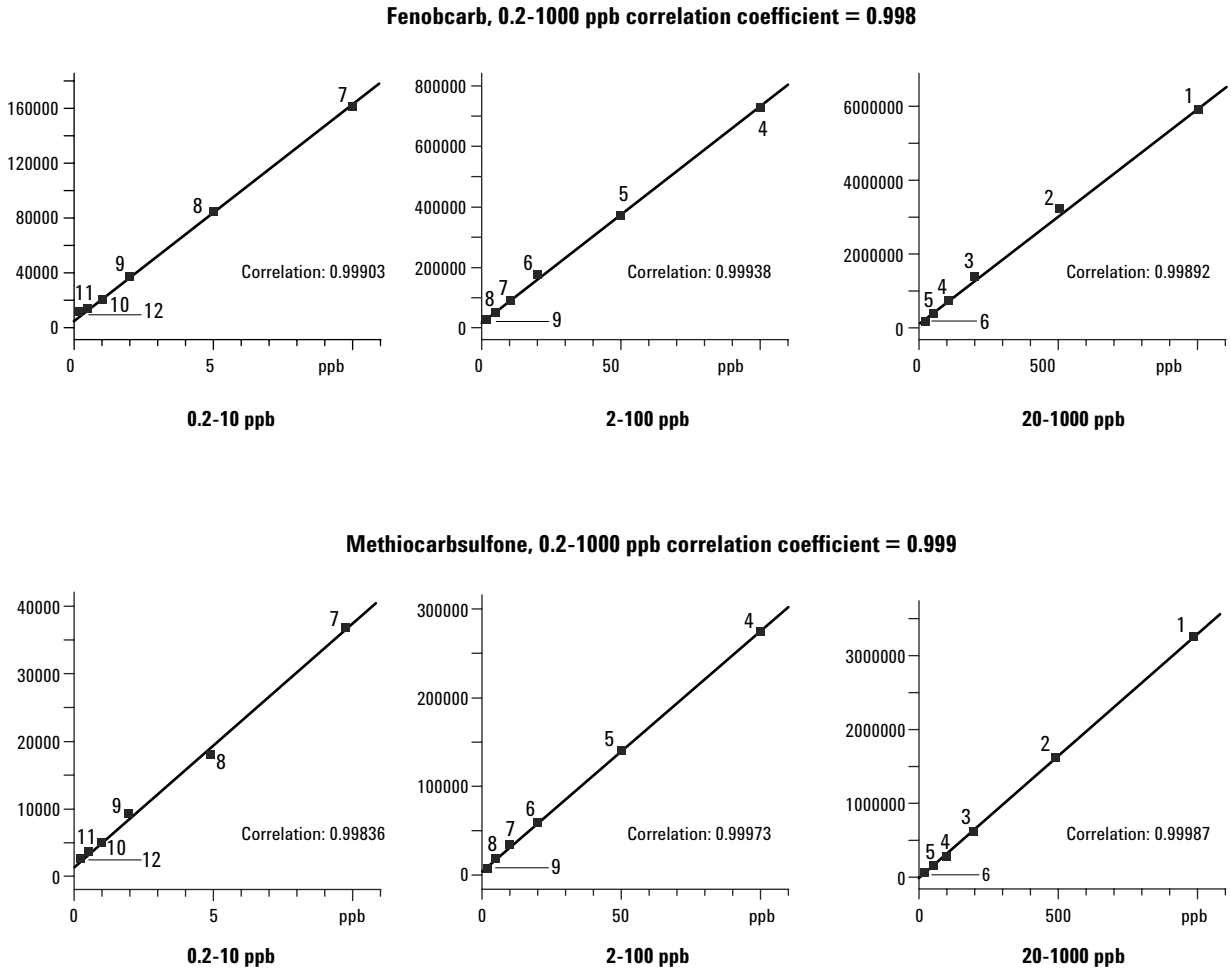


Figure 8. Calibration curves of carbamate standards.

Column Size

Figure 9 is a comparison of 10-ppb chromatograms on a 2.1-mm column and a 4.6-mm column. The column length and particle size are the same. The responses from the 4.6-mm column are about 40% of the responses from the 2.1-mm column even though the flow rate is five times higher on the 4.6-mm column.

Matrix Effect and LOD

In many cases, the sample matrix interferes with the analyte responses. A SIM method collects less background signal. See Figure 10 for the SIM chromatograms of 10-ppb carbamates in broccoli extract. The injection was 5 µL on a 2.1-mm column. The percentage number in each parenthesis is the relative response of the analyte from the broccoli extract to the peak intensity from the analyte standard in methanol. Most of the analytes showed responses very similar (98 to 115%) to the standards, except Methiocarbsulfoxide, which had 71% of the response of the standard in methanol.

The Limit of Detection (LOD) is defined as the sample concentration that produces a signal-to-noise (S/N) ratio of three in the broccoli extract. The LOD values of the nine carbamates are listed in Table 2.

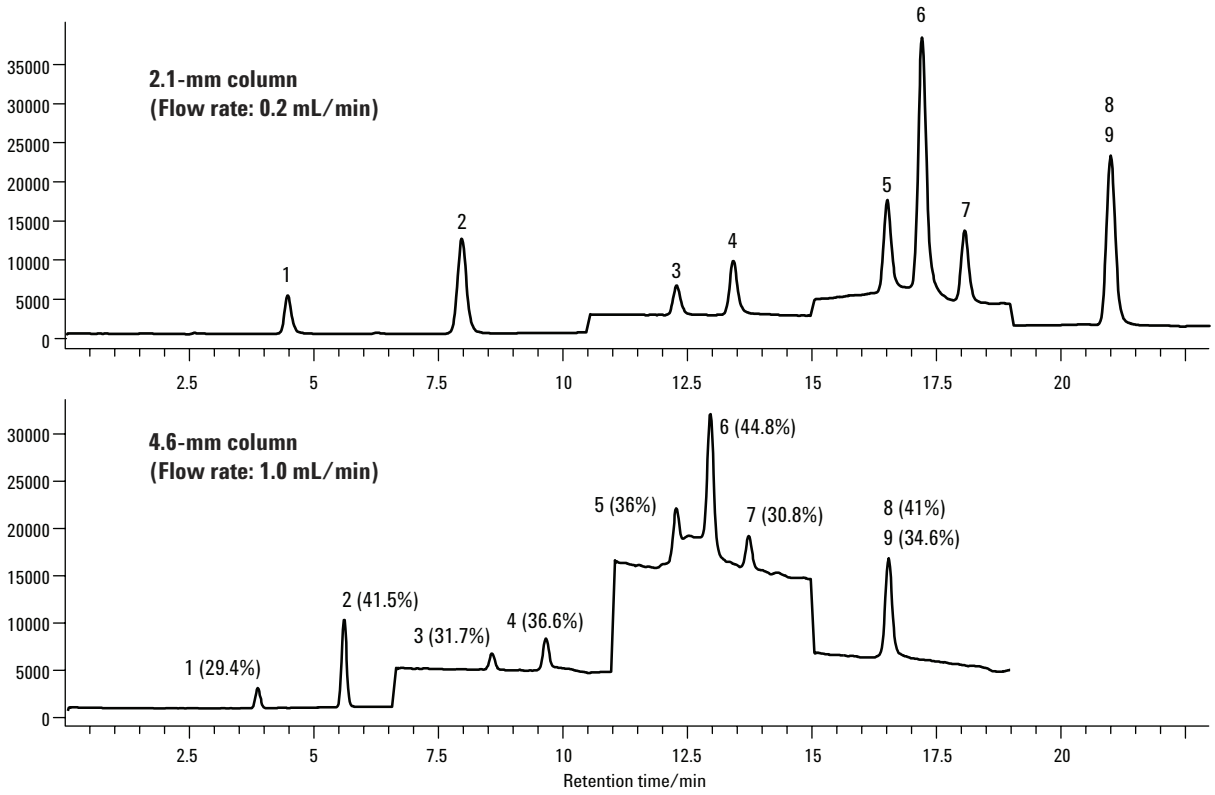


Figure 9. Comparison of 10-ppb chromatograms on a 2.1-mm column and a 4.6-mm column. The percentage number in each parenthesis is the relative response of the analyte from the 4.6-mm column to the peak intensity from the 2.1-mm column.

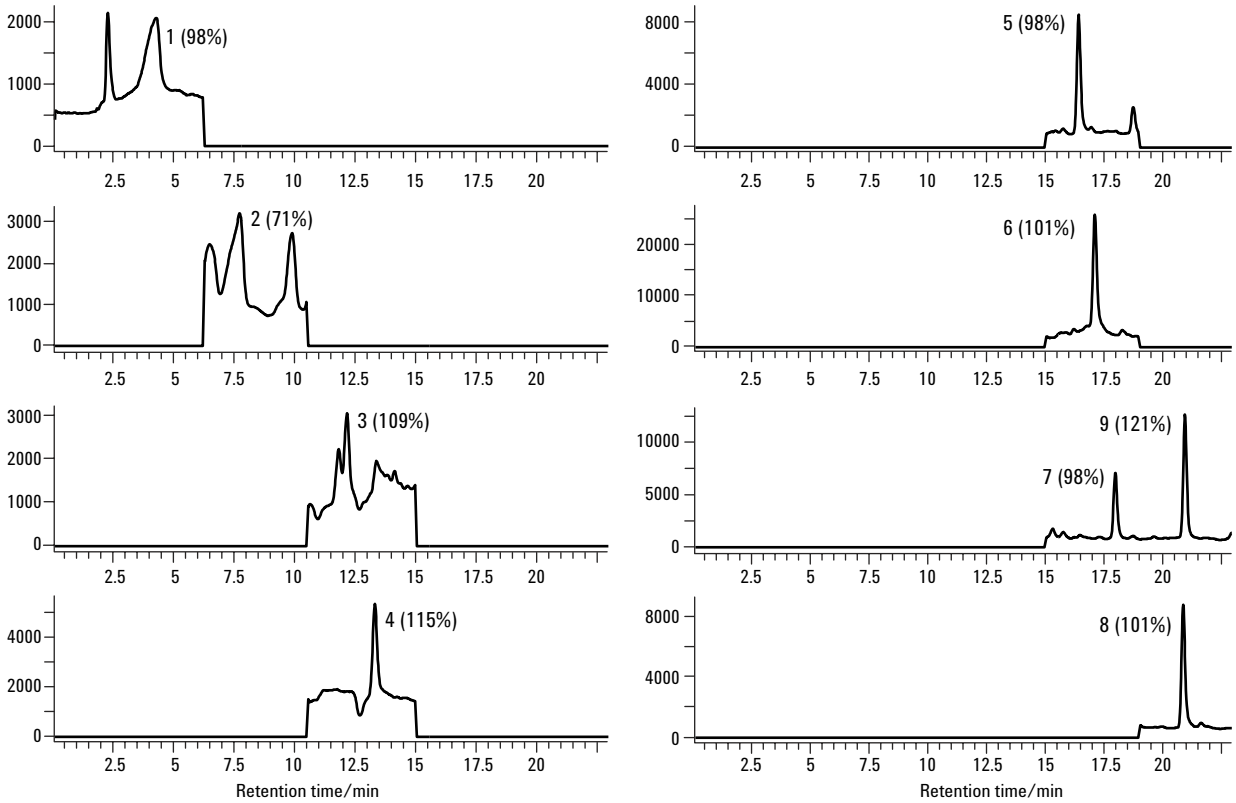


Figure 10. SIM chromatograms of 10-ppb carbamates in broccoli extract.

Table 2. Carbamates with the Base Peak, Correlation Coefficient and LOD in Broccoli Extract

#	Compound	Base peak	Correlation coefficient (0.2—1000 ppb)	LOD (S/N = 3 in broccoli extract)
1	Oxamyl	237 $[M+NH4]^+$	0.999	3 ppb
2	Methiocarbsulfoxide	242 $[M+H]^+$	0.999	10
3	Methiocarbsulfone	275 $[M+NH4]^+$	0.999	10
4	Aldicarb	116 (fragment)	0.999	2
5	Bendiocarb	224 $[M+H]^+$	0.999	1
6	Pirimicarb	239 $[M+H]^+$	0.999	3
7	Ethiofencarb	226 $[M+H]^+$	0.999	2
8	Fenobcarb	208 $[M+H]^+$	0.998	1
9	Methiocarb	226 $[M+H]^+$	0.998	2

Conclusions

Several carbamates can be analyzed routinely using LC/MSD with low ppb detection limits and excellent linearity in broccoli extract. The results demonstrate that the LC/MSD method is a viable technique to replace the non-specific post-column derivatization process using fluorescence detection.

References

1. *Detection of Low Levels of Carbaryl in Food Using Agilent LC/MSD Trap System*, Agilent Application Note, 5980-0332, April, 2000.

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