Class-Specific Determination of Carbamate Pesticides by Gas Chromatography

Tae Hyo Kim, Won Chul Park, Jung Hag Park,[†] Taeowan Chung, and Yong Tae Lee[*]

*Department of Biochemistry and Institute of Natural Sciences, Yeungnam University, Gyongsan 712-749, Korea*
[†]Department of Chemistry and Institute of Natural Sciences, Yeungnam University, Gyongsan 712-749, Korea
Received April 1, 2002

Class-specific determination of pesticides prior to chromatographic determination is an attractive approach for broader pesticide monitoring. If the total quantity of a class of pesticides in a sample can be determined and the quantity is less than the maximum residue limits of certain pesticides in the class, the sample can be eliminated from further inspection for those pesticides. Since it is usual that a vast majority of food and environmental samples turns out to be under maximum residue limits of pesticides, the time and cost saved by this approach may be enormous. There have been many studies aimed at developing such a class-specific determination method based on enzyme inhibition[1-5] or immunoassay,[6-8] but they were all very far from being quantitative. This paper describes development of a new quantitative class-specific determination method for carbamate pesticides.

Most of carbamate insecticides currently in use have the *N*-methyl carbamate group (-OCONHCH$_3$). Carbofuran and methomyl are examples.
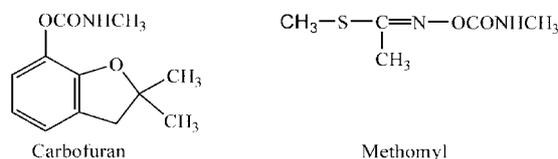
We found that amines react with *N*-methyl carbamate pesticides to give a common urea derivative (-NHCONHCH$_3$). Thus, derivatization of carbamate pesticides with an amine reagent followed by the determination of their common urea derivative allows their quantitative class-determination. We developed such a class-specific analytical method for carbamates using gas chromatography-electron capture detector (GC-ECD). In order to determine the urea derivative with high sensitivity, the derivatization was carried out with *p*-(trifluoromethyl)benzylamine (TFBA), an electrophoric reagent, and the primary derivative (Derivative I in Scheme 1) was converted to less polar secondary derivatives (Derivative II and III in Scheme 1).

The derivatizing reaction of each carbamate pesticide with TFBA was carried out by combining 0.1 mL of a 0.01 M pesticide solution in acetonitrile, 0.1 mL of a 0.05 M TFBA solution in acetonitrile and 0.1 g of K$_2$CO$_3$ in a vial and stirring at 80 °C for 1 h. The yields of the urea derivative[9] in the reactions were determined by analyzing the reaction mixtures by HPLC using an internal standard. The yields of the derivative based on the relative peak area compared to that of the standard are presented in Table 1.

The urea derivative was transformed to less polar secondary derivatives (Scheme 1) by acetylation (acetic anhydride/pyridine, 100 °C, 1 h). ^{1}H NMR spectrum[10] of the product revealed that the product consists of two isomers (Derivative II and III in 2.71 : 1 molar ratio) that resulted from acetylation of only one of the two NH groups (Scheme 1). Attempts to resolve the two isomers ended in failure, however, the peak encompassing the two isomers was fairly sharp.

A calibration curve for the secondary derivatives was obtained from the chromatograms of the standard solutions of the derivatives in acetonitrile (10^{-2}-10^{-10} M). The chromatograms for each standard solution were obtained using an HP-5 capillary column and an autoinjector. Typical chromatograms of the standard solutions are shown in Figure 1 and the calibration graph is presented in Figure 2. The curve was linear over the concentration range 10^{-7}-10^{-2} M. The

Table 1. The yields of the primary derivative in the derivatization of carbamate pesticides with TFBA

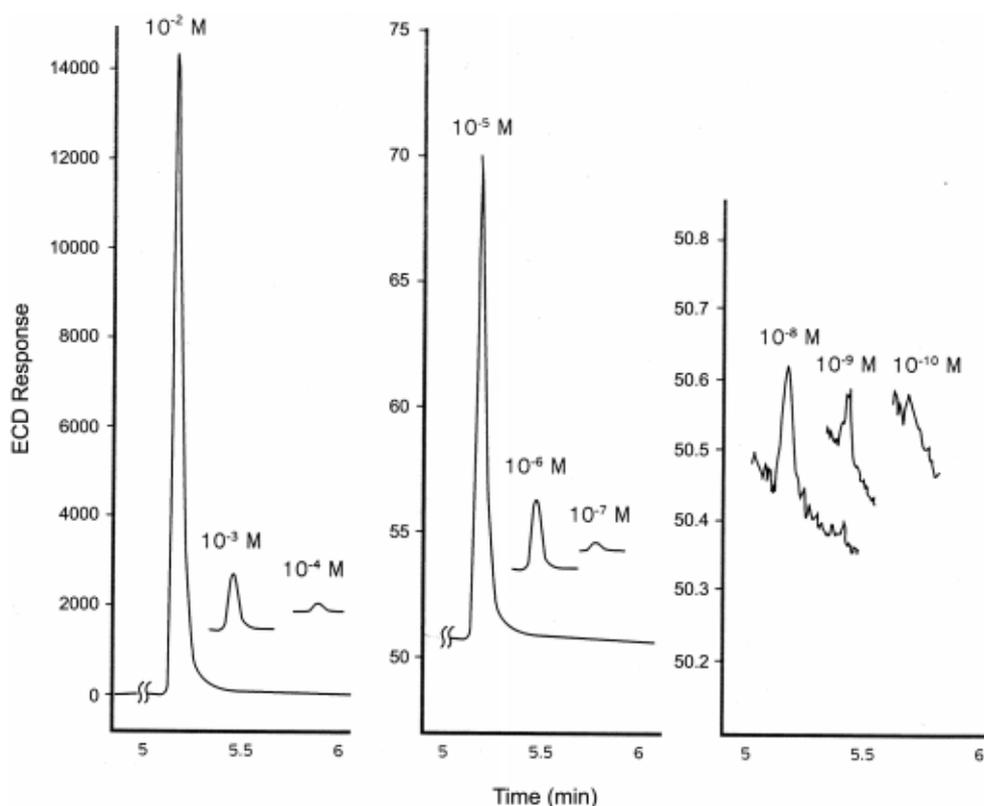| Carbamate pesticides	Yields (%)
Carbofuran	94
Carbaryl	90
Isoprocarb	78
Bendiocarb	83
Methiocarb	84
Methomyl	72
Aldicarb	67
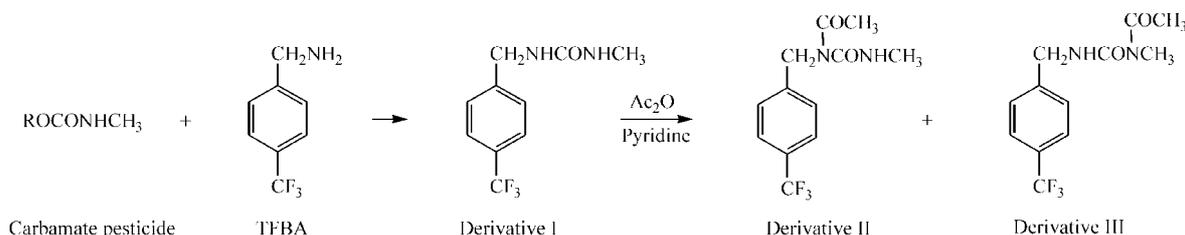
Scheme 1

Figure 1. Chromatograms of the standard solutions of the secondary derivatives. The GC operating conditions: splitless injection using an autoinjector (1 μL), 250 °C; carrier gas, helium; oven temperature, from 120 °C to 200 °C at 20 °C/min; detector (ECD) temperature, 320 °C.
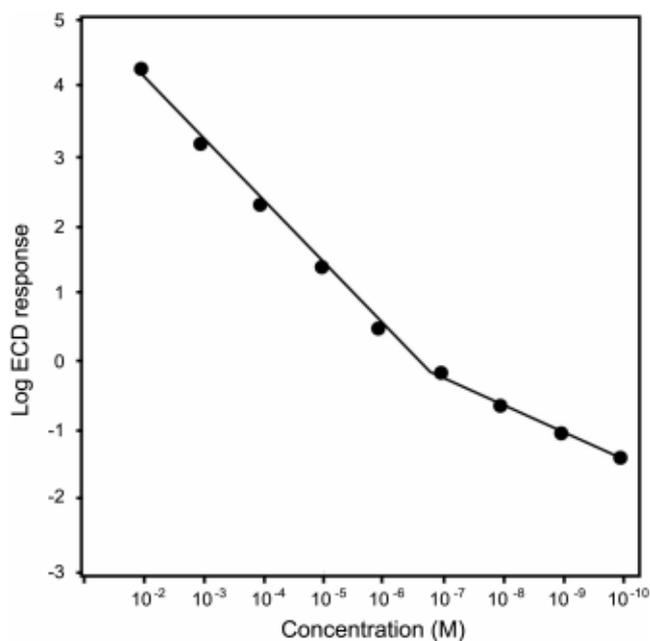

Figure 2. Calibration graph of the secondary derivatives.

minimum detectable concentration of the derivative was 10^{-10} M (S/N = 5). Recovery of carbofuran spiked into tap water (1 ppm) was 56%.

In conclusion, the analytical method developed in this study is useful for the quantitative class-specific determination of carbamate pesticides, and may be utilized for preliminary screening of food and environmental samples to evaluate the necessity of further inspection for individual carbamate pesticides. Therefore, this method may be useful for broadening the current scope of pesticide monitoring.

References and Notes

1. Tran-Minh, C.; Pandey, P. C.; Kumaran, S. *Biosens. Bioelectron.* **1990**, *5*, 461.
2. Trojanowitz, M.; Hitchman, M. *Trends Anal. Chem.* **1996**, *15*, 38.
3. Chung, M. S.; Lee, Y. T.; Lee, H. S. *J. Biochem. Mol. Biol.* **1998**, *31*, 296.
4. Lee, H. S.; Kim, Y. A.; Lee, Y. T. *Chemosphere* **2002**, *46*, 571.
5. Cho, Y. A.; Lee, H. S.; Cha, G. S.; Lee, Y. T. *Biosens. Bioelectron.* **1999**, *14*, 435.
6. Johnson, J. C.; Van Emon, J. M.; Pullman, D. R.; Keeper, K. R. *J. Agric. Food Chem.* **1998**, *46*, 3116.
7. Banks, J. N.; Chaudhry, M. Q.; Mattews, W. A.; Harvely, M.; Watkins, T.; Northway, B. *J. Food Agric. Immunol.* **1998**, *10*, 349.
8. Alcocer, M. J. C.; Dillon, P. P.; Manning, B. M.; Doyen, C.; Lee, H. A.; Daly, S. J.; OKennedy, R.; Morgan, M. R. A. *J. Agric. Food Chem.* **2000**, *48*, 2228.
9. ^{1}H NMR (300 MHz, CDCl$_3$)(ar: aromatic, *J* in Hz): δ 7.58 (2H, d, *J* = 8.1, ar), 7.42 (2H, d, *J* = 8.0, ar), 4.45 (2H, d, *J* = 5.9, CH$_2$), 2.80 (3H, d, *J* = 4.9, CH$_3$).
10. ^{1}H NMR (300 MHz, CDCl$_3$)(ar: aromatic, *J* in Hz), higher yield product: δ 7.58 (2H, d, *J* = 8.5, ar), 7.42 (2H, d, *J* = 8.0, ar), 4.54 (2H, d, *J* = 5.9, CH$_2$), 3.32 (3H, s, NCH$_3$), 2.32 (3H, s, COCH$_3$); lower yield product: δ 7.61 (2H, d, ar), 7.32 (2H, d, *J* = 8.2, ar), 5.10 (2H, s, CH$_2$), 2.93 (3H, d, *J* = 4.7, NCH$_3$), 2.21 (3H, s, COCH$_3$).