Fast Gas Chromatography Analysis of *N*-Carbamates with Cold On-Column Injection

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Abstract

Direct gas chromatographic (GC) analysis of thermally labile *N*-carbamates is studied by using fast GC with cold on-column injection. With the greatly reduced injection temperature, short column lengths, high flow rate, and fast temperature-programming rate, the exposure of carbamates to high temperature is reduced and degradation can be avoided. Nine *N*-carbamates in EPA Method 531 are eluted without thermal decomposition. The relative standard deviation percentage for peak areas average 1.9% for all of the carbamates analyzed. A conventional GC instrument is employed to simplify the experiments. GC–mass spectrometry is used to monitor the decomposition peaks.

Introduction

Capillary gas chromatography (GC) is a well-established technique for the analysis of pesticides in food, soils, water, and beverages. The high resolving power of capillary columns enables the screening of a wide range of pesticides in one run, even in the presence of a complex matrix.

N-Carbamates are widely used pesticides in agricultural production; however, until recently they have not been quantitated by general multiresidue methods using GC. The primary reason is their thermolability. Their chemical structures lead to degradation when applying conventional GC with hot split/splitless injectors. Therefore, almost all methods for *N*-carbamates employ high-performance liquid chromatography (1).

Fishbein and Zielinski (2) established the mechanism responsible for the thermal degradation of *N*-methylcarbamates. Phenylcarbamates are thermally decomposed into the corresponding phenol and methylisocyanate (as shown in Figure 1).

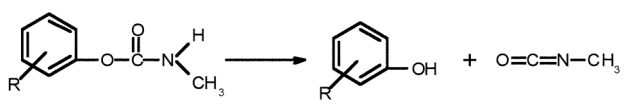

Figure 1. Thermal decomposition of *N*-methylcarbamates.

Some work has been done to analyze *N*-carbamates by GC after derivatization (3) or on carefully deactivated capillary columns (4). Dagan and Amirav (5) reported to have analyzed carbamates by very fast and ultrafast GC coupled with supersonic mass spectrometry (MS). Special instruments were needed.

The work reported in this study employs fast GC and cold on-column injection to minimize the exposure of carbamates at high temperature, thus minimizing thermal degradation. The effects of several factors (column length, flow rate, temperature-programming rate, as well as injector parameters) are examined and optimized.

The definition of fast GC used in this study is "high-speed GC" (which refers to those analyses accomplished in several minutes compared with tens of minutes of "normal GC") using commercially available GC instrumentation. Thus, most workers could repeat this work in their laboratory. A shorter column length, faster temperature-programming rate, and higher flow rate are commonly employed.

In this study, the *N*-carbamate pesticides studied were propoxur, carbaryl, carbofuran, methiocarb, aldicarb, aldicarb sulfone, aldicarb sulfoxide, methomyl, and oxmyl.

Experimental

Instrumentation

Equipment used included a Hewlett-Packard (Little Falls, DE) GC–MS Model 6890/5973 equipped with a hot split/splitless injector and an HP GC Model 6890 equipped with a cold on-column injector. Hot split/splitless injection and cold on-column injection were both studied.

Experimental conditions

HP-5 fused-silica columns were used in all analyses. Three column lengths (30, 10, and 7 m) were employed, all of which had the same internal diameter (0.25 mm) and film thickness (0.25 µm). The flow rate, temperature-programming rate, and other

parameters varied with different column parameter and injection techniques.

Materials

Propoxur (98%) was purchased from Ultra Scientific (North Kingstown, RI). Carbaryl (1000 µg/mL), carbofuran (1000 µg/mL), methiocarb (1000 µg/mL), aldicarb (100 µg/mL), aldicarb sulfone (100 µg/mL), aldicarb sulfoxide (100 µg/mL), methomyl (100 µg/mL), and oxmyl (100 µg/mL) were purchased from Absolute Standards, Inc. (Hamden, CT). Propoxur was dissolved in methanol to be 100 µg/mL; carbaryl, carbofuran, and methiocarb were diluted by methanol to 100 µg/mL. In order to further confirm the daughter peaks, the phenols resulting from the thermal degradation of the carbamates were purchased from ACROS Organics (Suwanee, GA).

Results and Discussion

The 30-m-long capillary column was installed in the GC–MS system with a heated split/splitless injector. Propoxur, carbaryl,

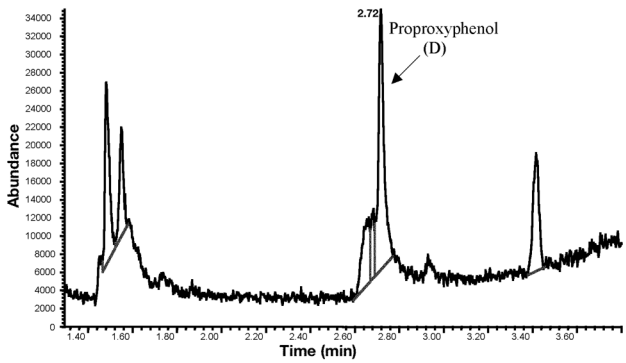

Figure 2. Chromatogram of propoxur analyzed by conventional GC–MS with a high-temperature-programming rate of 100°C/min.

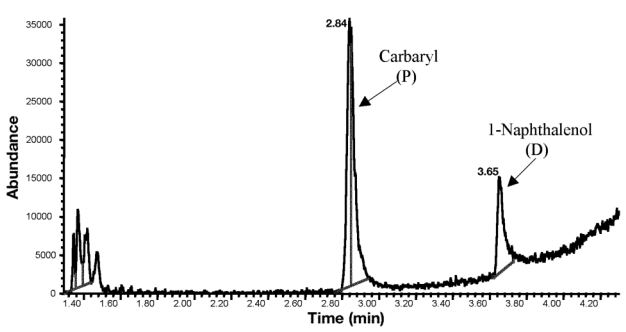

Figure 3. Chromatogram of carbaryl analyzed by conventional GC–MS with a high-temperature-programming rate of 100°C/min.

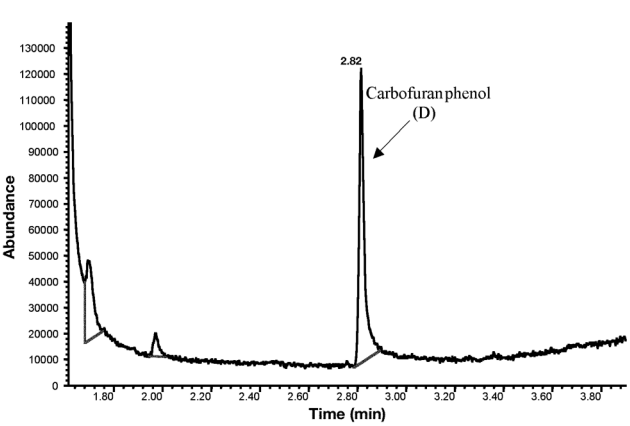

Figure 4. Chromatogram of carbofuran analyzed by conventional GC–MS with a high-temperature-programming rate of 100°C/min.

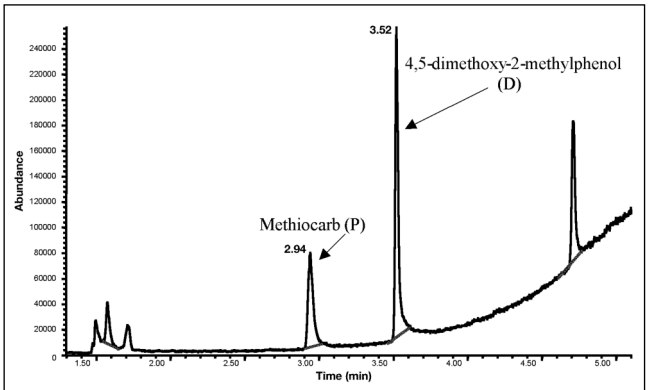

Figure 5. Chromatogram of methiocarb analyzed by conventional GC–MS with a high-temperature-programming rate of 100°C/min.

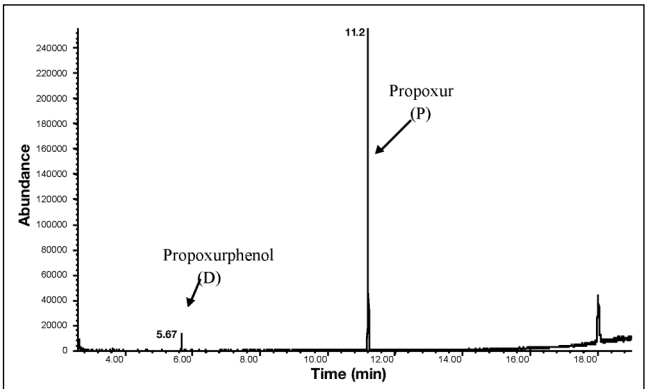

Figure 6. Chromatogram of propoxur analyzed by conventional GC–MS with a temperature-programming rate of 10°C/min.

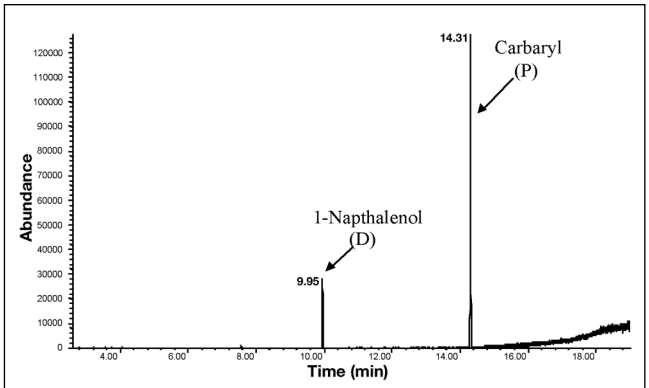

Figure 7. Chromatogram of carbaryl analyzed by conventional GC–MS with a temperature-programming rate of 10°C/min.

carbofuran, and methiocarb were employed first to investigate the direct GC method. They were chromatographed separately under both a high-temperature programming rate of 100°C/min and a normal rate of 10°C/min. Other experimental conditions were kept the same: the injector was set at 250°C, the initial oven temperature was 70°C, an MS was used in scan mode, the carrier gas was helium at 28 cm/s, and the injection volume was 1 µL. These conditions were used to monitor the thermal decomposition products of carbamates.

Figures 2, 3, 4, and 5 are the chromatograms of the four *N*-carbamates analyzed by the conventional GC–MS with a high-temperature programming rate of 100°C/min. In the chromatograms, D ("daughter") indicates the decomposed compound and P ("parent") indicates the original carbamate.

All four carbamates showed thermal decomposition under the conditions used. Propoxur and carbofuran were totally decomposed. Most of methiocarb was decomposed, and carbaryl was eluted as a major parent peak.

By changing the temperature-programming rate from 100°C/min to 10°C/min, the thermal decomposition of all four carbamates was minimized (although they were still partially decomposed). Figures 6, 7, 8, and 9 show these chromatograms. The high temperature of both the injector and column oven led to the thermal decomposition of the carbamates, and the higher temperature-programming rate made the decomposition even worse. The elution order of the carbaryl parent and daughter peak was reversed at different temperature-programming rates (Figures 3 and 7). The same change happened to methiocarb (Figures 5 and 9), which may result from the large programming rate change.

When we reduced the temperature of the injector to 200°C, thermal decomposition still occurred. A 10-m column with cold on-column injection was then used to study the four carbamate standards under increasing temperature-programming rates (50°C/min, 80°C/min, and 100°C/min in order to study this parameter). Other experimental conditions were kept the same: the initial oven temperature was 60°C and then programmed to 230°C, the injector was in track oven mode, a flame ionization detector was used at 280°C, the time constant was at 50 Hz, the

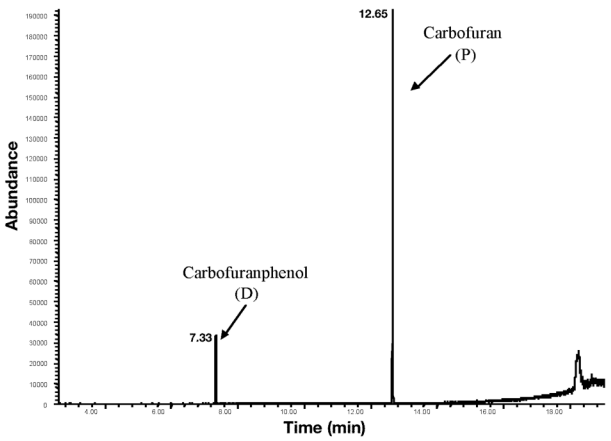

Figure 8. Chromatogram of carbofuran analyzed by conventional GC–MS with a temperature-programming rate of 10°C/min.

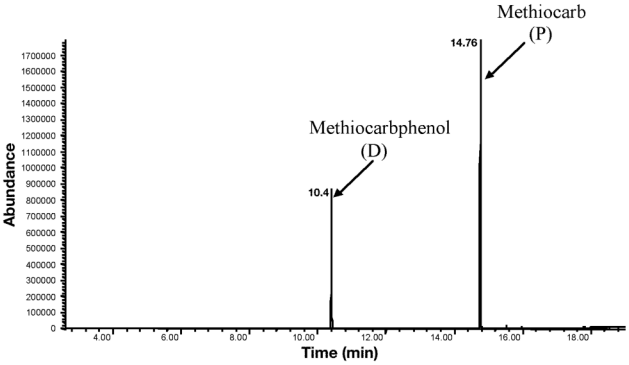

Figure 9. Chromatogram of methiocarb analyzed by conventional GC–MS with a temperature-programming rate of 10°C/min.

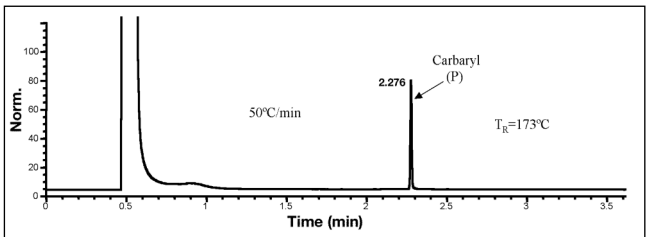

Figure 10. Chromatogram of carbaryl analyzed by GC with a cold on-column injector at a temperature-programming rate of 50°C/min.

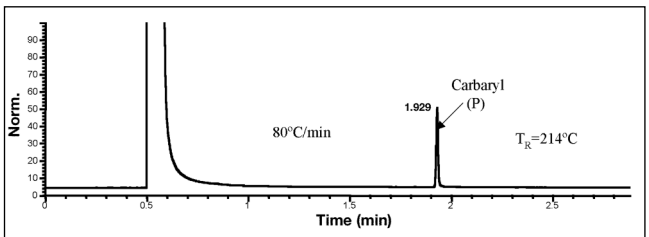

Figure 11. Chromatogram of carbaryl analyzed by GC with a cold on-column injector at a temperature-programming rate of 80°C/min.

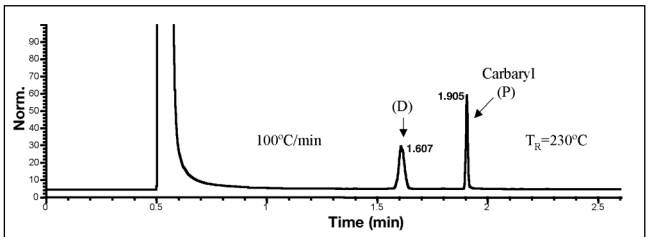

Figure 12. Chromatogram of carbaryl analyzed by GC with a cold on-column injector at a temperature-programming rate of 100°C/min.

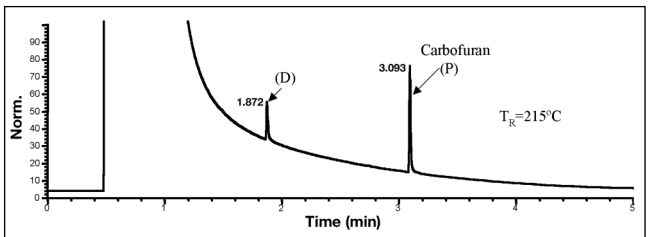

Figure 13. Chromatogram of a carbofuran analyzed by GC with a cold on-column injector at a temperature-programming rate of 50°C/min.

carrier gas was helium at 60 cm/s, and the injection volume was 1 µL.

Figures 10, 11, and 12 are the chromatograms of carbaryl analyzed by GC with a cold on-column injection. The initial oven temperature was 60°C and was then ramped at different temperature-programming rates to 230°C and then held for 1 min. The increasing elution temperature (T_R) with the faster programming rate should be noted. At 100°C/min, the first evidence of a daughter peak can be seen, indicating that a T_R of 230°C is too hot for carbaryl.

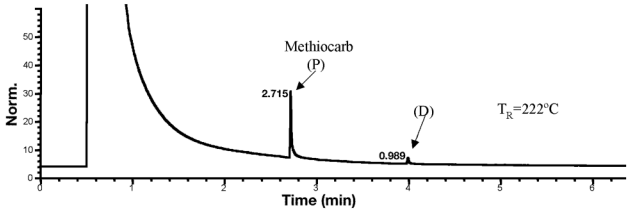

Figure 14. Chromatogram of methiocarb analyzed by GC with a cold on-column injector at a temperature-programming rate of 50°C/min.

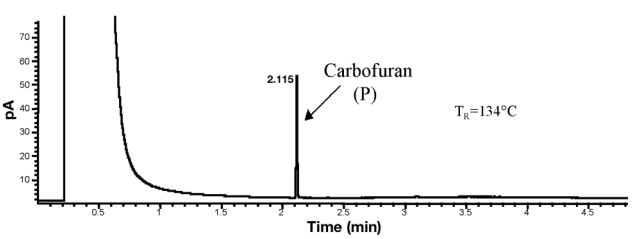

Figure 15. Chromatogram of carbofuran analyzed by GC with a cold on-column injector at a lower elution temperature.

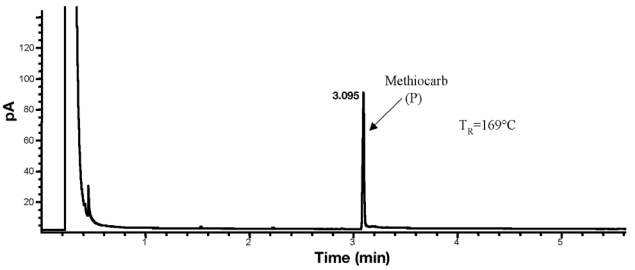

Figure 16. Chromatogram of methiocarb analyzed by GC with a cold on-column injector at a lower elution temperature.

Table I. %RSD* of Direct GC Injections for Nine Carbamates by Peak Area and Retention Time

	Retention time (min)	%RSD (peak area)	%RSD (retention time)
Propoxur	3.16	1.1	0.17
Carbaryl	2.48	1.8	0.19
Carbofuran	2.12	1.3	0.12
Methiocarb	3.33	1.2	0.13
Aldicarb	1.85	2.6	0.08
Aldicarb sulfone	1.95	2.9	0.04
Aldicarb sulfoxide	1.47	1.3	0.05
Methomyl	1.36	2.1	0.12
Oxmyl	1.49	2.7	0.13

* n = 5.

When analyzed by fast GC with a cold on-column injection technique at a temperature-programming rate of 50°C/min and 80°C/min, carbaryl eluted without thermal decomposition (Figures 10 and 11). When the temperature-programming rate increased to 100°C/min, a big daughter peak eluted (Figure 12). For propoxur, there was no decomposition at 50°C/min; however, the daughter appeared with a programming rate of 80°C/min and became bigger at 100°C/min. This result can be explained by the T_R, which is the temperature at which the peak elutes. Thus, the faster the temperature-programming rate is, then the higher the T_R and the worse the thermal decomposition will be. Therefore, carbaryl must be eluted at 214°C or even lower. The maximum T_R for propoxur is 225°C.

Carbofuran and methiocarb were studied under the same conditions, and daughter peaks were found at all temperature-programming rates (Figures 13 and 14).

It should be noted that the elution order of the carbaryl parent and daughter peak at 100°C/min was the same as that at 100°C/min when using a 30-m-long column (Figure 7). However, the methiocarb parent eluted before the daughter, which was the same as the elution order at 100°C/min using the 30-m-long column (Figure 5). The reason for the elution order change is not clear; the big change in temperature-programming rate and column length may play an important role.

Even fast GC with cold on-column injection could not prevent the thermal decomposition of carbofuran and methiocarb under the specified conditions. An even lower T_R is needed. In order to lower the T_R, a shorter, 7-m-long column, a slower temperature-programming rate (35°C/min), and a faster linear velocity (75 cm/s) were employed. The initial oven temperature was set at 60°C then ramped at 35°C/min to 200°C and held for 2 min.

Both carbofuran and methiocarb were swept quickly out of the column at lower T_R values (134°C and 169°C, respectively). No thermal decomposition occurred (Figures 15 and 16).

The four carbamates together with other *N*-carbamates (aldicarb, aldicarb sulfone, aldicarb sulfoxide, oxmyl, and methomyl) were studied separately for the precision of the peak area and retention time under the same experimental conditions developed for the 7-m column. The relative standard deviation percentage (%RSD) (n = 5) for the peak area and retention time were calculated and are listed in Table I.

All nine carbamates were eluted without undergoing degradation by using fast GC with cold on-column injection. The %RSD for the peak area was between 1% and 3% for all nine carbamates. The linearity was demonstrated by solutions of 0.5 µg/mL, 10 µg/mL, 50 µg/mL, 80 µg/mL, and 100 µg/mL, and the correlation coefficients to straight lines were > 0.98. The detection limit was calculated statistically as three times the noise level, which was < 100 ppb. Both linearity and limit of detection studies were performed on four carbamates: propoxur, carbaryl, carbofuran, and methiocarb.

The results presented in this study are acceptable and suggest the possibility of the quantitative analysis of thermolabile carba-

mates by fast GC with cold on-column injection, and it also would be a good choice for other thermolabile pesticides or pharmaceutical products.

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