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GAS CHROMATOGRAPHIC ANALYSIS OF HEPTAFLUOROBUTYRYL DERIVATIVES OF SOME CARBAMATE INSECTICIDES

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SUMMARY

The gas chromatography (GC) of a number of carbamate insecticides as their heptafluorobutyryl derivatives has been studied. The reaction makes use of heptafluorobutyric anhydride with trimethylamine in benzene as a catalyst. Conversion of the insecticides to their products is complete in 15–20 min at room temperature. The same reaction proved satisfactory for trifluoroacetylation. The excess reagent and trimethylamine are removed by partitioning with water in the reaction test tube. An aliquot of the organic phase is used for analysis. The heptafluorobutyryl derivatives are stable for several days on the lab bench without removal of the aqueous phase from the test tube. GC detection was carried out with a Coulson conductivity detector in the halogen (reductive) mode. About 1.0 ng produced a 50% full-scale response for most of the carbamates (3 min retention time) on 3% OV-1. This method was applied to the analysis of several carbamates spiked in corn, mustard greens, turnip greens, lettuce and cabbage.

INTRODUCTION

The routine screening of food for carbamate insecticide residues by gas chromatography (GC) has been hampered by the fact that these compounds are not completely stable at normal column temperatures. Methods utilizing the direct chromatography of carbamates have appeared in the literature[1,2] but many workers prefer to analyse them as GC suitable derivatives[3–5]. The direct trifluoroacetylation of N-methylcarbamate insecticides has been reported[6–9]. The reactions produce a single product sensitive to electron capture detection. However, the conditions used were rigorous and required a minimum of 2–16 h for complete reaction depending upon solvent and temperature. The use of trimethylamine as a catalyst for amides and non-insecticidal carbamates which are difficult to trifluoroacetylate directly has been reported[10,11].

The present author has found a dramatic increase in rate of trifluoroacetylation and heptafluorobutyrylation of carbamate insecticides by the addition of tri-

methylamine. The heptafluoro derivatives were studied in detail because of their good response to electrolytic conductivity detection after GC.

MATERIALS AND METHODS

Apparatus

An HYFI Model 600 C gas chromatograph (Varian Aerograph) equipped with a Coulson electrolytic conductivity detector in the halogen mode and a 2 m × 6 mm O.D. glass column packed with 3% OV-1 on Chromosorb W HP (80–100 mesh) was employed. Operating conditions were: transfer unit temperature, 210°; pyrolysis furnace temperature, 800°; helium carrier flow-rate and sweep, 50 ml/min; hydrogen flow-rate, 50 ml/min; d.c. bridge potential, 30 V. A 0.004-in. diameter stainless-steel wire was inserted into the capillary water entrance to the mixing chamber[10]. This improved sensitivity 3-fold.

Reagents

Table I lists the chemical names of the insecticides used in this work. Stock solutions were prepared at 1 mg/ml in acetone. Working solutions were prepared by appropriate dilution with acetone. All organic solvents were glass-distilled residue-free materials. The heptafluorobutyric (HFB) and trifluoroacetic (TFA) anhydrides were used as received from the supplier (Pierce, Rockford, Ill., U.S.A.). The trimethylamine (TMA) solution was prepared by adding cooled (0°) ampoules of anhydrous trimethylamine (Eastman-Kodak, Rochester, N.Y., U.S.A.) to cool tared benzene to produce a molarity of 1.0. The solution was then diluted to 0.1 *M* in a 100-ml volumetric flask. The solution is stable for longer than 6 months.

The foods studied were corn, lettuce, cabbage, mustard greens and turnip greens.

TABLE I

NAMES OF CARBAMATE INSECTICIDES USED IN THIS WORK

Carbamate	*Chemical name*
Aldicarb	2-Methyl-2-(methylthio)proprionaldehyde-O-(methylcarbamoyl)oxime
Aminocarb	4-Dimethylamino-3-methylphenyl-N-methylcarbamate
Banol	2-Chloro-4,5-dimethylphenyl-N-methylcarbamate
Benomyl	Methyl-N-(1-(butylcarbamoyl)-2-benzimidazole) carbamate
Butacarb	3,5-Di-*tert.*-butylphenyl-N-methylcarbamate
Bux	Mixture of *m*-(1-methylbutyl)-phenyl-N-methylcarbamate, *m*-(1-ethylpropyl)-phenyl-N-methylcarbamate and their isomers
Carbaryl	1-Naphthyl-N-methylcarbamate
Carbofuran	2,3-Dihydro-2,2-dimethylbenzofuran-7-yl-N-methylcarbamate
Carbofuran-3-OH	2,3-Dihydro-3-hydroxy-2,2-dimethylbenzofuran-7-yl-N-methylcarbamate
Landrin	3,4,5-Trimethylphenyl-N-methylcarbamate
Meobal	3,4-Dimethylphenyl-N-methylcarbamate
Methiocarb	4-Methylthio-3,5-xylyl-N-methylcarbamate
Methomyl	1-(Methylthio)ethylideneamino-N-methylcarbamate
Mobam	4-Benzothienyl-N-methylcarbamate
Propoxur	2-Isopropoxyphenyl-N-methylcarbamate
Zectran	4-Dimethylamino-3,5-xylyl-N-methylcarbamate

Analytical procedure

Derivatization. A 15-μl volume of HFB anhydride was added to a 20-ml test tube with a PTFE-lined screw cap containing the insecticide. Following this, 0.4 ml of 0.1 *M* TMA in benzene was added. The test tube was capped, gently shaken and allowed to stand at room temperature for 30 min. The cap was removed and 4.5 ml hexane was added and the contents shaken. Then, 10 ml of distilled water were added, the cap replaced and the contents vigorously shaken. An aliquot of the hexane layer was used for GC.

Sample extraction. Spiked food (50 g) were blended for 4 min in a Sorval homogenizer with 100 ml of ethanol. The homogenate was suction-filtered through a 150-ml medium-porosity sintered glass funnel. One-half of the filtrate (equivalent to 25 g of sample) was transferred to a 500-ml separatory funnel containing 300 ml of distilled water. The mixture was extracted with 3 × 50 ml of chloroform. The combined organic extracts were dried by the addition of about 5 g anhydrous sodium sulphate and were carefully decanted into a 500-ml round-bottom flask. The sodium sulphate was rinsed twice with 3 ml of chloroform which were added to the round-bottom flask. The solution was reduced just to dryness at 30° by rotary vacuum evaporation. The residue was transferred with hexane to the top of a 15 × 2 cm 2% deactivated Florisil column and eluted with 250 ml of 20% ethyl acetate in hexane. This fraction was evaporated just to dryness by rotary vacuum evaporation at 30°.

The residue was transferred with a small volume of acetone to a 20-ml screw-capped test tube. The acetone was evaporated under a gentle stream of nitrogen. The remaining contents were treated as described in the derivatization procedure.

RESULTS AND DISCUSSION

Fig. 1 shows two composite chromatograms of the HFB-carbamates. Only aldicarb and benomyl (fungicide) did not give a response by GC.

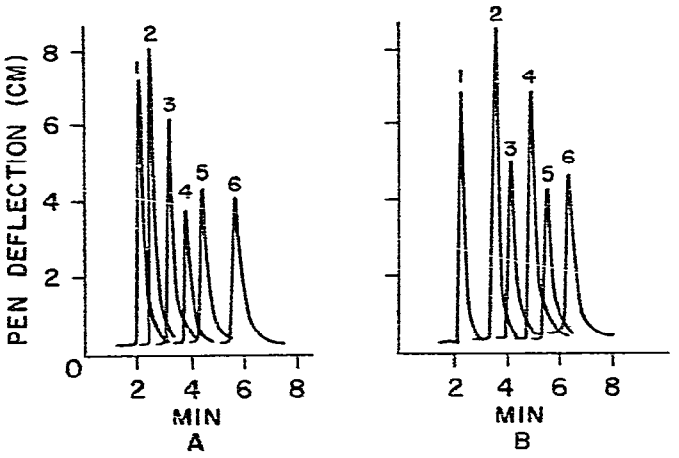

Fig. 1. Chromatogram A: 1 = methomyl, 2 = propoxur, 3 = carbofuran, 4 = aminocarb, 5 = zectran, 6 = mobam. Chromatogram B: 1 = landrin and meobal, 2 = banol and bux, 3 = 3-OH carbofuran, 4 = butacarb, 5 = carbaryl, 6 = methiocarb. About 50 ng each injected; attenuation, 64×; potential, 30 V.

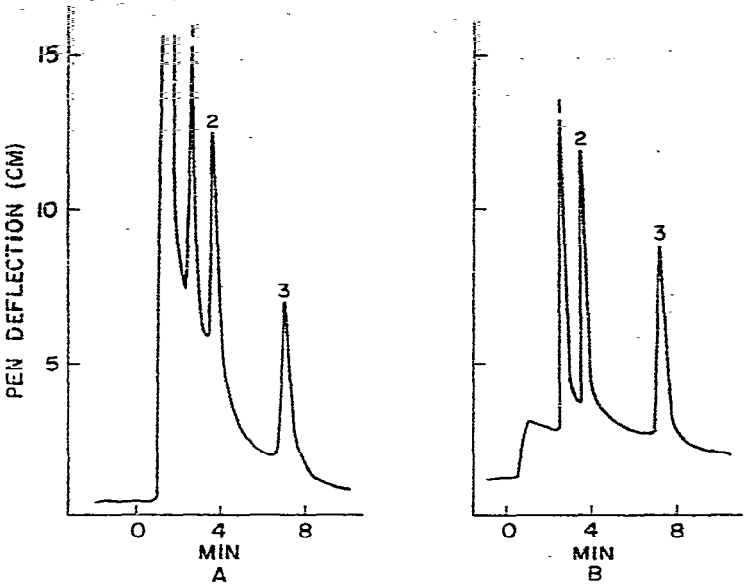

Fig. 2. Comparison of corn analysis for propoxur (1), carbofuran (2) and methiocarb (3) spiked at 1.0 ppm (B) with florisil cleanup and (A) without. 5 ng of equivalent carbamates were injected (5 mg sample); attenuation, 4×; potential, 30 V.

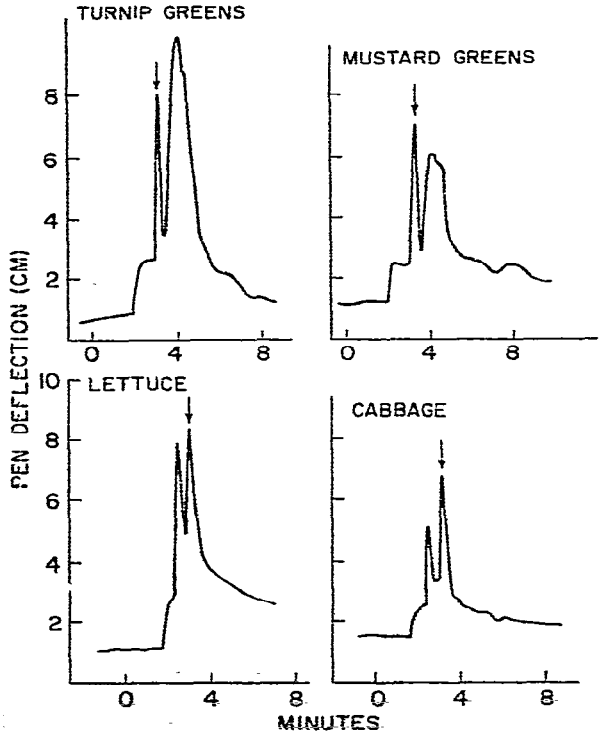

Fig. 3. Leafy vegetable analysis for propoxur spiked at 1.0 ppm in each food (Florisil cleanup). 2 mg equivalent sample were injected; attenuation, 4×; potential, 30 V; a 2-min vent time was used. Arrow indicates propoxur peak.

The reaction conditions described in the experimental section were determined for propoxur, carbofuran and methiocarb. Propoxur reacted completely in 15 min while the other two took 5–10 min longer. Allowing the reaction to proceed for up to 90 min had no effect on the yield. Thirty minutes was chosen to ensure acetylation was complete. The remaining carbamates were carried through this reaction procedure. Sensitivities of the derivatives were similar. From 1–2 ng produced a 50% full-scale deflection at 3.00 min retention time. Fluorine was found to respond with similar sensitivity as chlorine in the halogen mode of the Coulson. The sensitivity was proportional to the number of fluorine atoms present. The TFA derivatives of the same carbamates produced slightly less than half the sensitivity of the HFB derivatives.

Fig. 2 shows results before and after Florisil column cleanup of the corn samples spiked with propoxur, carbofuran and methiocarb at 1.0 ppm. The Florisil removed the large tailing solvent front and made analyses at the lower levels possible. The Florisil however, did not provide as good a cleanup of the leafy green crops studied. Fig. 3 shows the analyses at 1.0 ppm for propoxur in these samples. Background interference (high baseline) was much greater than for the corn and only 2 mg of sample material could be injected on the 4× attenuation. Also a 2 min vent time was used to avoid as much interference as possible at the solvent front. Fig. 4 shows a chromatogram of 2 ng of propoxur and methiocarb injected with 20 mg of mustard

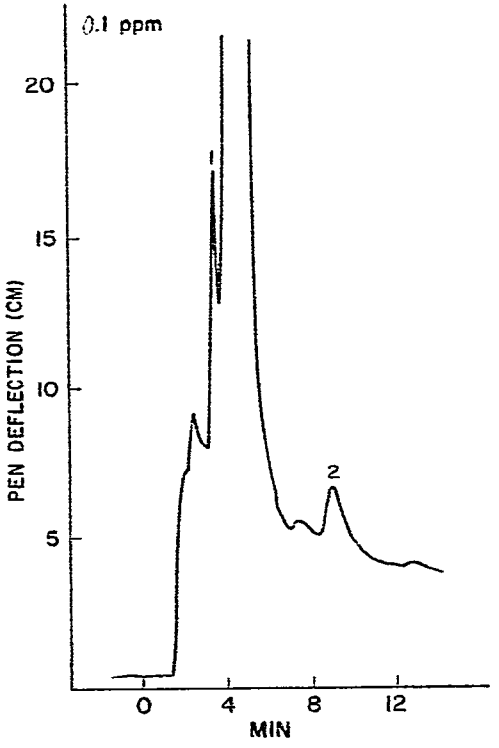

Fig. 4. Chromatograms obtained for 2 ng each of propoxur (1) and methiocarb (2) injected with 20 mg equivalent of mustard greens. Attenuation, 4×; potential, 30 V; column temperature, 170°.

greens to simulate a 0.1-ppm sample. The results show that 0.1 ppm can readily be detected for these two insecticides assuming high recovery through the extraction procedure. Recoveries at the 1.0-ppm spiking level were >80 for propoxur and methiocarb in all samples studied. Carbofuran gave similar results in the corn sample.

CONCLUSIONS

The use of heptafluorobutyryl derivatives of carbamate insecticides for GC electrolytic conductivity detection shows much potential for screening samples. The reaction used is much faster and simpler than previously reported for these compounds. The use of perfluorooctanoic anhydride (15 fluorine atoms) should increase the sensitivity of the derivatives more than two-fold compared to HFB anhydride.

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