Gas Chromatographic Determination of Carbamate Pesticides after Flash-Heater Methylation with Trimethylsulfonium Hydroxide

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A simple and quick on-line derivatization method for the gas chromatographic trace analysis of 13 carbamate pesticides in water is described. Sample preparation consisted of solid-phase extraction with RP C18 cartridges. Trimethylsulfonium hydroxide solution was added to the concentrated eluate, and an aliquot of the mixture was injected in a programmed temperature vaporizer (PTV) at 60 °C. After solvent purging and a subsequent heating step, carbamate pesticides underwent methylation in the PTV, and the derivatives were separated, detected, and quantitated using high-resolution gas chromatography/mass spectrometry. The average recoveries at four concentration levels in water (25, 50, 100, and 200 ng/L) ranged from 46 to 104% with determination limits of 25 and 50 ng/L, depending on the compounds.

INTRODUCTION

Carbamate pesticides may have either insecticidal (*N*-methylcarbamates: fenobucarb, propoxur, promecarb, 3,4,5-trimethacarb, bendiocarb, carbofuran, methiocarb, and carbaryl) or herbicidal properties (*N*-arylcarbamates: carbendazim, propham, swep, chlorpropham and phenmedipham).

Their thermolability complicates gas chromatographic (GC) determination by forming the corresponding phenols and other fragments in unreproducible amounts through thermal degradation inside the injector or during the GC run (Thier and Frehse, 1986). Such difficulties may be overcome by using special conditions (Hall and Harris, 1979; Dorough and Thorstenson, 1975) or by derivatization of either the intact substances or the phenols after complete hydrolysis (Greenhalgh and Kovacicova, 1975).

Fishbein and Zielinski (1965) described the preparation of thermally stable trimethylsilyl derivatives of some carbamates. Bromilow and Lord (1976) used trimethylanilinium hydroxide (TMAH) for flash-heater methylation of carbamates and presented yields and retention times of the derivatives. Wien and Tanaka (1977) also used TMAH for the methylation of some carbamates in the hot split/splitless injector (SSL) and made investigations of the methylation reaction at different conditions. Ogierman (1982) investigated carbamate pesticide formulations with the same technique (TMAH/SSL/FID detection) and published IR, UV, NMR, and MS data of the derivatives.

However, none of those publications described a complete determination method with recoveries at low concentrations.

As an alternative, high-performance liquid chromatography (HPLC) and automated multiple development (AMD) techniques became more important for routine residue analysis of carbamates in recent years (Blaicher et al., 1980; Lawrence, 1977; Burger, 1988).

This work modifies and improves the earlier described "flash-heater methylation" of carbamates (Wien and Tanaka 1977; Ogierman, 1982). The new combination of solid-phase extraction, programmed temperature vaporizer (PTV), trimethylsulfonium hydroxide (TMSH), and high-resolution gas chromatography/mass spectrometry (HRGC/MS) provides low determination limits and allows simple, quick, and reliable derivatization and determination of 13 carbamates.

Table I. Peak Assignment and Quantitation Masses

peak	compound	M^+/fragment ions, (*m/z*)	derivate of
1	fenobucarb	164/135	phenol
2	propoxur	166/124/109	phenol
3	promecarb	164/149	phenol
4	trimethacarb	150/135	phenol
5	bendiocarb	180/165	phenol
6	carbofuran	178/163	phenol
7	propham	193/151/106	original
8a	phenmedipham a	179/164/120	fragment
8b	phenmedipham b	195/180/136	phenol
9	methiocarb	182/167/152	phenol
10	carbaryl	158/115	phenol
11	chlorpropham	227/185/140	original
12	swep	233/188/174	original
13	carbendazin	219/160	original

EXPERIMENAL PROCEDURES

Chemicals and Materials. Pesticides (see Table I) were obtained from Fa. Ehrenstorfer, Augsburg, FRG. Standard solutions for external quantitation were prepared in ethyl acetate (0.2 and 0.5 mg/L). A methanolic standard solution (1 mg/L) was prepared to fortify the water samples.

All solvents (methanol, ethyl acetate) used were of residue analysis quality.

Trimethylsulfonium hydroxide solution (0.2 M) was prepared as described by Schulte and Weber (1989).

Solid-phase extraction cartridges (RP C18, 1 g, 6 mL) and vacuum manifold (SPE 21) were obtained from J. T. Baker Inc., Gross-Gerau, FRG.

Instrumentation. GC, Carlo Erba, Mega 5160; column, DB 17 cb, 30 m, 0.25 mm i.d., 0.25 μm df; retention gap, 2 m, 0.32 mm i.d., Phenyl-Sil deactivated; injector, OC/PTV (multinjector) Carlo Erba (insert filled with silanized glass wool, injection volume 8 μL); control unit, MFA 515 (program 5—initial temperature 60 °C; purge time 180 s; splitless time 60 s; final temperature 260 °C; split ratio 1:10); carrier gas, He, 2 mL/min, 120 kPa; MS, Finnigan-MAT, ITD 700, EI 70 eV, full-scan mode; computer, IBM AT, software ITDS 4.0, external quantitation mode; transfer line, 200 °C; direct coupling; temperature program, 60 °C (1 min), 15 °C/min to 180 °C, 10 °C/min to 240 °C, 40 °C/min to 280 °C (5 min).

Note: Program 5 is a specific temperature program for the PTV. Its operational sequence is controlled by the unit MFA 515, which allows editing of *initial* (injection) *temperature, purge*

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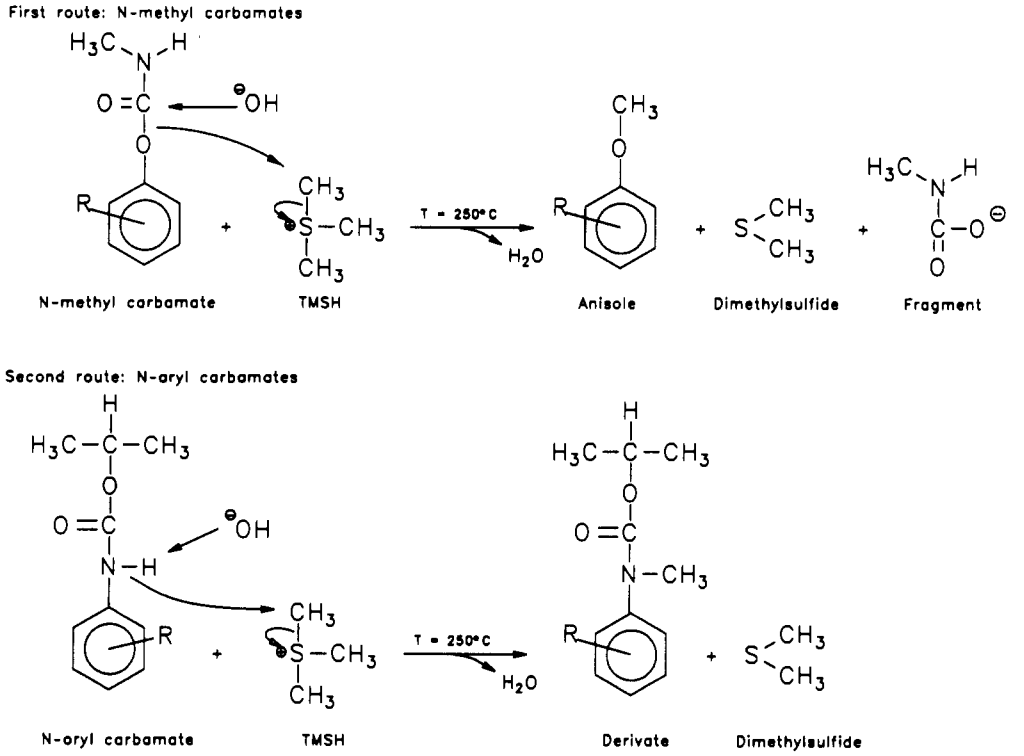

Figure 1. Reaction of carbamates with TMSH.

time for solvent elimination (with split valve open at the initial temperature), *splitless time* (during the heating step and at the final temperature), and *final temperature* of the PTV insert.

Methods. *Extraction.* Recovery data and determination limits of the 13 investigated carbamates (see Table I) were obtained by solid-phase extraction of fortified water samples (pH 7–8) at 0.025, 0.05, 0.1, and 0.2 μg/L levels.

Fortifications were done by adding aliquots of the methanolic standard solution (1 mg/L). The mixture was shaken thoroughly. The weighted RP C18 cartridges (1-mg accuracy) were first washed twice with 3 mL of methanol and with 3 mL of water (pH 7). The water samples (1000 mL) were extracted by percolating through the cartridges with a flow rate of about 10 mL/min, maintained by gravitation.

For this purpose the bottles were fixed on a board at the wall and connected with the lower cartridges (height difference, 1.4 m) by polyethylene tubes. It is suggested that the investigated carbamates were not adsorbed on the tube walls, because we did not find significant differences in recovery data compared with extractions carried out using a commercial vacuum manifold without polyethylene tubes.

After sample application, the sorbent bed was dried with nitrogen at 40 °C until weight constancy (ca. 45 min). The cartridges were eluted with 2 mL of methanol into a graduated vial, and the eluate was evaporated under a gentle stream of nitrogen to a volume of 0.1–0.2 mL. Ethyl acetate was added up to 0.5 mL, which corresponds to an enrichment factor of 2000.

Five extractions of each fortification level were carried out.

Derivatization and Gas Chromatography/Mass Spectrometry. Ten microliters of the TMSH solution was added to the extract and mixed well. Eight microliters of this mixture was injected into the insert of the PTV at 60 °C, where the compounds underwent methylation during the following PTV program.

After solid-phase extraction, methylation, and separation using GC, the derivatized compounds were detected and quantitated using a mass specific detector (EI, 70 eV).

RESULTS AND DISCUSSION

After sample injection (extract/TMSH), the PTV began to run the operational sequence of program 5: at first the solvent was purged (180 s at 60 °C, split valve open) and a nonvolatile ionic complex, consisting of the trimethylsulfonium cation and the corresponding phenolate anion

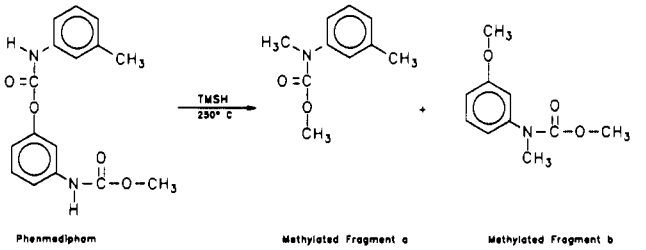

Figure 2. Reaction of phenmedipham with TMSH.

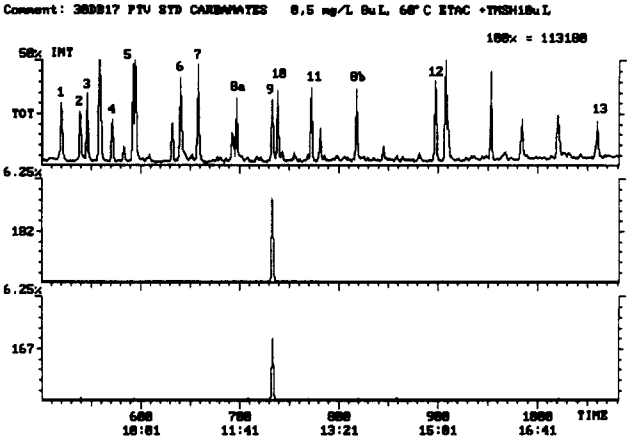

Figure 3. Total ion chromatogram (above) of the carbamate derivatives and two specific mass chromatograms with *m/z* 182 and 167 of methiocarb anisole.

or the parent carbamate anion (see Figure 1) was formed and remained on the surface of the glass wool. Carbamates may react with TMSH via two different routes (Wien and Tanaka, 1977), depending on their structure (see Figure 1).

First Route. *N*-Methylcarbamates are completely hydrolyzed by the alkaline reagent and create the phenolates and probably the carbamic acid anion, if no decarboxylation occurs. These anions form subsequently the ionic complexes with TMSH.

Table II. Recoveries and Ranges of Carbamates in Percent (n = 5; RP C18 1 g)

peak	compound	ng/L 25	50	100	200
1	fenobucarb	98 ± 8	95 ± 5	97 ± 10	102 ± 5
2	propoxur	96 ± 16	99 ± 7	90 ± 13	87 ± 8
3	promecarb	94 ± 7	100 ± 2	101 ± 11	103 ± 5
4	trimethacarb	95 ± 14	90 ± 16	104 ± 11	104 ± 7
5	bendiocarb	66 ± 11	89 ± 7	92 ± 10	85 ± 7
6	carbofuran		75 ± 15	90 ± 12	97 ± 12
7	propham	87 ± 15	72 ± 13	73 ± 8	70 ± 12
8b	phenmedipham		48 ± 5	60 ± 12	55 ± 14
9	methiocarb	67 ± 13	81 ± 13	88 ± 6	81 ± 5
10	carbaryl	89 ± 13	94 ± 8	82 ± 8	95 ± 5
11	chlorpropham	98 ± 22	71 ± 11	65 ± 14	74 ± 9
12	swep	75 ± 15	96 ± 7	86 ± 6	82 ± 9
13	carbendazim		46 ± 14	50 ± 6	53 ± 5

Second Route. Only the acidic N–H group of the N-aryl compounds reacts without hydrolysis to the carbamate anions, which also associate with the TMSH cation. The ballistical (flash) heating step (split valve now closed) of the PTV completes the reaction by destroying the ionic complexes and forming dimethyl sulfide, the corresponding anisoles (first route), or the methylated intact carbamate (second route).

The N-methylcarbamic acid (fragment in Figure 1) anion reacts either to give the N-dimethylcarbamic acid methyl ester or decarboxylates to generate methylamine, neither of which was detectable in our investigations.

Excessive TMSH creates only volatile dimethyl sulfide and methanol. Therefore, no contamination of the gas chromatographic system takes place. The use of TMAH generates less volatile N,N-dimethylaniline, which can raise disturbing memory effects.

The reaction products are swept into the GC column by the carrier gas and separated as usual.

The reaction of carbendazim generated only the dimethyl derivative; the monomethyl product could not be observed, which confirms the results of Ogierman (1981a).

Benomyl, another investigated N-arylcarbamate, was also found to produce two derivatives with TMSH: methylated benomyl, as expected, and dimethylcarbendazim, which is created after partial hydrolysis and subsequent methylation of the resulting NH groups, as Ogierman (1981b) described earlier.

This indicates that detected carbendazim residues may stem from either benomyl or carbendazim. Therefore, the selective quantitation of carbendazim or benomyl is not practicable when both compounds are present in the sample.

The methylation of the N-methylcarbamate phenmedipham produced two peaks with similar responses (see chromatogram in Figure 3), which can be explained by hydrolysis (first route, see Figure 1) and complete methylation of the resulting fragments a and b (see Figure 2).

Other compounds under investigation such as asulam, ethiofencarb, carbetamide, or fenoxycarb gave no specific derivatives. For that reason no mass spectra or quantitation data of the latter mentioned substances could be obtained.

All mass spectra of the derivatives showed significant fragmentation patterns with molecular ions and resulting fragment ions. A total ion chromatogram (TIC) and two specific mass chromatograms (m/z 182/167: methiocarb–anisole) are shown in Figure 3. The quantitation masses in m/z are listed in Table I, the average recoveries and ranges are presented in Table II, and the mass spectra of two derivatives are depicted in Figure 4.

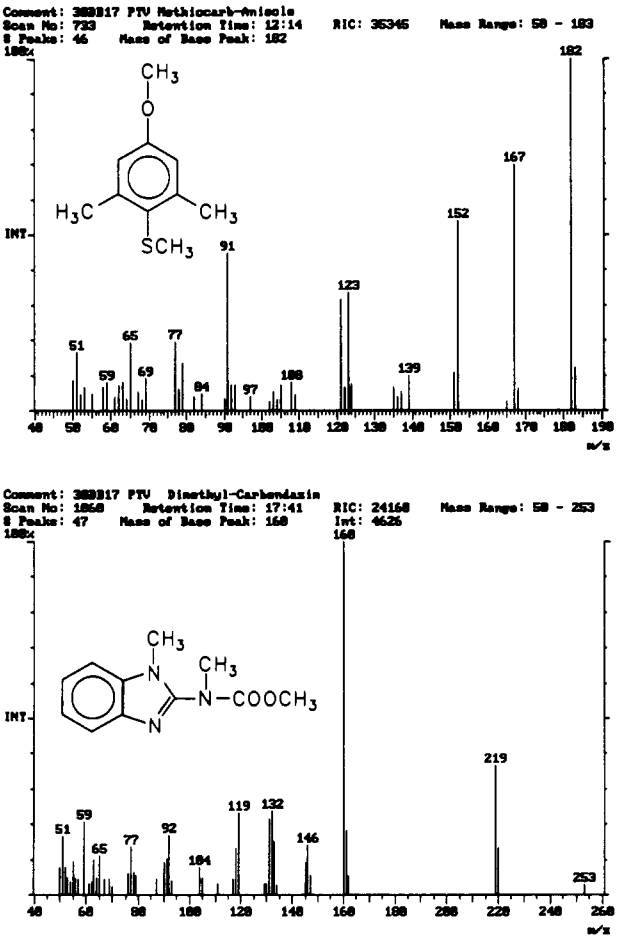

Figure 4. Mass spectra of methiocarb anisole and dimethylcarbendazim (EI; 70 eV).

All mass spectra and quantitation data were recorded using a personal computer. The recoveries were calculated vs two external standard solutions (0.2 and 0.5 mg/L) of the investigated compounds with the same concentration of TMSH.

The determination limits of all compounds with the exception of phenmedipham, carbendazim, and carbofuran, which had values of 50 ng/L, were 25 ng/L. Therefore, the described method is suitable for controlling carbamate concentrations in the water below the limit values for pesticides and related compounds specified in the German "Drinking Water Regulation". That regulation allows residues of up to 0.1 μg/L of any single pesticide or 0.5 μg/L total pesticides in drinking water (Trinkwasserverordnung, 1986). A false positive determination of N-methylcarbamates, caused by phenols already present in the

water sample, can be excluded as those phenols are not extractable at the used extraction conditions (pH 7–8).

Conclusions. The described PTV methylation technique for carbamates is time-saving and easy to handle as TMSH provides simultaneously a hydrolyzing and methylating effect. The reaction products are volatile, and no contamination of the PTV insert or GC column was observed. Other main advantages are the low determination limits—as a result of the high injection volume—and the high reliability, which makes the method suitable for residue analysis of carbamates at the 0.1 μg/L level.

The presented technique may be regarded as a multiderivatization method, which has other successful applications such as the methylation of chlorophenoxy acids and urea herbicides (Färber et al., 1991; Färber and Schöler, 1991). The latter compounds may be determined as their methyl derivatives in the same GC run as the carbamates.

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