

Short Communication

Gas chromatographic and mass spectrometric investigation of seven carbamate insecticides and one metabolite

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ABSTRACT

Eight thermally labile N-methylcarbamates, aldicarb, carbaryl, carbofuran methiocarb, methomyl, oxamyl and propoxur, the active ingredients of insecticides, and 3-hydroxycarbofuran, the metabolite of carbofuran were separated on a gas chromatographic column, detected by a mass spectrometer and confirmed by positive ion electron impact (PIEI) spectra and ammonium positive ion chemical ionization spectra. The characteristic ions suitable for selected ion monitoring using PIEI are presented. The fragmentation patterns of these carbamates demonstrated that thermal degradation has not occurred under the reported conditions.

INTRODUCTION

To demonstrate food safety, Agriculture Canada has a program to monitor annually the residues of over 120 pesticides and metabolites in many samples of fruits and vegetables using a multi-residue method [1,2]. The sample extract in acetonitrile, after being cleaned up with a Nuchar–Celite column, can be analyzed by gas chromatography coupled with mass-selective detection (GC–MS) using the selected ion monitoring (SIM) mode. Automation allows for the rapid analysis of a large number of samples for residues of organochlorines, organophosphates and nitrogen-containing pesticides. However, N-methylcarbamate insecticides, being thermally

labile, have to be analyzed separately by high-performance liquid chromatography with post-column fluorescence detection [3]. This analytical method is time consuming involving a separate analytical system and preparation of post-column reaction reagents.

GC determination of certain carbamates using various temperature profiles and injection techniques [4–6], GC–MS determination of carbamates after derivatization with acetic anhydride [7] and with trimethylsulfonium hydroxide in a programmed-temperature vaporizer (PTV) [8] have been reported. In an effort to increase the output of this program by shortening the analysis time, a preliminary study of their GC behaviour and MS fragmentation was necessary. This paper reports the results of the investigation of seven carbamates (aldicarb, carbaryl, carbofuran, methiocarb, methomyl, oxamyl and propoxur)

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and three metabolites (aldicarb sulfoxide, aldicarb sulfone and 3-hydroxycarbofuran). Aldicarb, aldicarb sulfoxide and aldicarb sulfone have been analyzed by GC using a packed column and very low column temperatures (95°C for aldicarb and 130°C for aldicarb sulfoxide and aldicarb sulfone) [6]. On the other hand, direct GC of aldicarb, methiocarb, 3-hydroxycarbofuran and oxamyl using a capillary column and higher column temperatures (50–230°C) has not been previously reported.

EXPERIMENTAL

Analytical standards

Aldicarb (99.9%), aldicarb sulfoxide (99.2%) and sulfone (99.4%) were obtained from Union Carbide (Research Triangle, NC, USA); carbaryl, methomyl, oxamyl and propoxur (all 99.0%) from Caledon (Georgetown, Canada), carbofuran (99.5%) and 3-hydroxycarbofuran (99.0%) from FMC (Middleport, NY, USA) and methiocarb (98.7%) from Mobay (Kansas City, MO, USA).

Stock standard solutions of individual carbamates (100 ng/μl) were prepared in acetone. Composite standard solution 1, which contained aldicarb (20 ng/μl), carbaryl, methiocarb and propoxur (10 ng/μl each) was prepared by combining and diluting appropriate aliquots of the stock solutions with acetone. Composite standard 2, containing methomyl, 3-hydroxycarbofuran (21 ng/μl each), carbofuran (11 ng/

μl) and oxamyl (47 ng/μl) was prepared in the same manner as for composite standard 1.

Instrumentation

For GC-MS a Varian Model 3400 gas chromatograph was used with Varian Model 1095 on-column capillary injector and direct capillary coupling to a MAT 90 (Finnigan-MAT) mass spectrometer. The analytical parameters were: column, DB-5 (10 m × 0.32 mm I.D. with 0.25 μm coating); temperatures: injector, 60–200°C at 20°C/min; oven, at 50°C for 7 min, increased to 150°C at 20°C/min, at 150°C for 1 min, to 230°C at 10°C/min and held at 230°C for 4 min; interface, 230°C; source, 250°C for positive ion electron impact (PIEI) mode and 150°C for positive ion chemical ionization (PICI) mode; source pressure for PICI, 3 · 10⁻⁴ Torr (1 Torr = 133.322 Pa); emission current, 0.35 mA for PIEI and 0.20 mA for PICI; carrier gas, helium at 4 ml/min; injection volume, 1 μl.

RESULTS AND DISCUSSION

GC investigation of these carbamates began with injection of individual carbamates on a gas chromatograph with a flame ionization detector using two different 30-m columns coated with 0.25 μm film thickness of (a) SE-54 (0.32 mm I.D.) or (b) DB-5 (0.2 mm I.D.). Two different temperature profiles were used, (a) injection, splitless, 260°C; oven, 60–260°C at 18°C/min and (b) injection splitless, 250°C; oven, 70°C (2 min),

TABLE I

EIGHT N-METHYLCARBAMATES [R-O-C(O)-NHCH₃] ANALYZED BY GC-MS

M_r = Molecular mass.

No.	Carbamate	R	<i>M_r</i>
1	Aldicarb	CH ₃ S(CH ₃) ₂ CCH = N-	190
2	Carbaryl	α-Naphthyl	201
3	Carbofuran	2,3-Dihydro-2,2-dimethyl-7-benzofuranyl	221
4	Methiocarb	4-(Methylthio)-3,5-dimethylphenyl	225
5	Methomyl	CH ₃ S(CH ₃)C = N-	162
6	Oxamyl	(CH ₃) ₂ NC(O)C(SCH ₃) = N-	219
7	Propoxur	2-Isopropoxyphenyl	209
8	3-Hydroxycarbofuran	2,3-Dihydro-2,2-dimethyl-3-hydroxy-7-benzofuranyl	237

increased to 130°C at 25°C/min, to 220°C at 2°C/min, to 280°C at 10°C/min and held there for 4.6 min. The latter temperature profile is normally used for the multiresidue analysis of all other pesticides by GC–MS in our laboratory. Separate injections of individual pesticides showed that all carbamates were degraded except carbaryl, carbofuran, methiocarb and propoxur while 3-hydroxycarbofuran was not degraded when a DB-5 column and the second temperature profile was used. Suzuki *et al.* [4] have demonstrated that when a short wide-bore column (10 m × 0.52 mm I.D.) was used, due to the short column residence time, degradation of carbamates could be avoided; thus a short DB-5 (10 m × 0.32 mm I.D.) column was investigated. A short column with 0.32 mm I.D. offers the advantages of higher resolution and fast analysis time and can result in performance improvement. In addition, to further prevent thermal degradation, a PTV injection technique was used. Under these conditions, regular single peaks were achieved for 7 carbamates and 1 metabolite (Table I) with aldicarb sulfoxide and sulfone showing slow degradation into broad overlapping multiple peaks which were not identified.

Because flame ionization detection is non-selective, a GC–MS system was substituted. The GC–MS chromatograms (Fig. 1A and B) show baseline separation with symmetrical peak

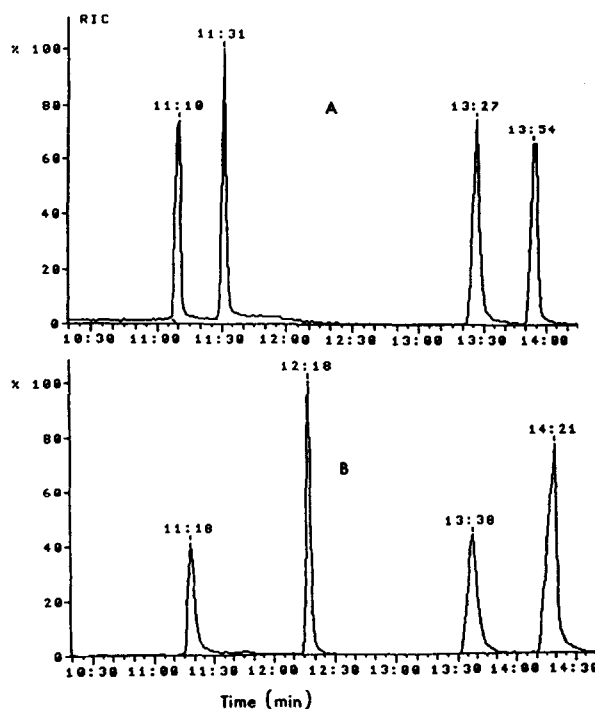


Fig. 1. GC–MS chromatograms of (A) aldicarb (11 min:10 s), propoxur (11 min:31 s), carbaryl (13 min:27 s) and methiocarb (13 min:54 s) and (B) methomyl (11 min:18 s), carbofuran (12 min:18 s), 3-hydroxycarbofuran (13 min:38 s) and oxamyl (14 min:21 s).

shape. Using the PIEI mode, molecular ions were detected for all carbamates except aldicarb, methomyl and oxamyl (see Table II). However,

TABLE II

INTENSITY AND THE CHARACTERISTIC m/z OBSERVED IN EIGHT N-METHYLCARBAMATES

m/z for (a) $[M - SCH_2]^+$, (b) $[M - SCH_2 - 58]^+$, (c) $[CH_3NHCO]^+$, (d) $[CH_3NCO]^+$ in PIEI, and (e) $[M + NH_4]^+$ in ammonium PICI.

Carbamate	Intensity (%)						
	M^+	144 (a)	$[R - OH]^+$	86 (b)	58 (c)	57 (d)	$[M + 18]^+$ (e)
Aldicarb	0	43		92	50	20	30
Carbaryl	1.8		100		0	10	100
Carbofuran	6		100		0	42	40
Methiocarb	4		100		0	10	100
Methomyl	0		75		80	100	100
Oxamyl	0		20		20	80	10
Propoxur	0.3		20		2	6	100
3-Hydroxycarbofuran	0.08		42		0	48	25

TABLE III

RELATIVE STANDARD DEVIATION (R.S.D.) ($n = 4$) OF GC-MS INJECTIONS FOR EIGHT N-METHYLCARBAMATES BY AREA COUNTS (A)

Carbamate	Mass (ng) ^a	Mean ($A \times 10^6$)	S.D. $\times 10^6$	R.S.D. (%)
Aldicarb	20	52.9	3.4	6.5
Carbaryl	10	71.0	4.0	5.7
Carbofuran	11	35.0	6.2	17.6
Methiocarb	10	60.5	3.8	6.3
Methomyl	21	26.0	3.1	11.8
Oxamyl	47	69.9	4.0	5.7
Propoxur	10	70.9	6.0	8.5
3-Hydroxycarbofuran	21	33.3	6.8	20.5

^a Mass of carbamates injected onto GC-MS.

using the PICI mode with ammonia, the ammonium adducts of these molecular ions, $[M + 18]^+$, were detected (see Table II). These characteristic masses together with the single sharp GC-MS peaks observed in the chromatograms supported the fact that all eight carbamates were eluted from the GC column without undergoing degradation. The acceptable relative standard deviation (R.S.D.) (see Table III) suggested that these carbamates can be quantitated using GC-MS. The R.S.D.s for carbofuran and 3-hydroxycarbofuran were relatively high (17.6 and 20.5%, respectively); however, using GC-flame ionization detection the corresponding R.S.D.s were 6.0 and 7.6% ($n = 6$). In addition, carbofuran has also been analyzed directly using GC with a nitrogen-specific detector [9].

When highly selective and sensitive detection of carbamates is desired, as in the case of residue analysis, the use of MS to monitor pre-selected ions is advantageous. In most cases, except for aldicarb, the ions from the C-O bond cleavage

giving the m/z corresponding to $[\text{ROH}]^+$ can be utilized for this purpose. For aldicarb, the m/z 144 representing $[\text{M} - \text{SCH}_2]^+$ can be used instead.

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