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DIRECT GAS CHROMATOGRAPHIC DETERMINATION OF CARBAMATE PESTICIDES USING CARBOWAX 20M-MODIFIED SUPPORTS AND THE ELECTROLYTIC CONDUCTIVITY DETECTOR

RANDALL C. HALL* and DONALD E. HARRIS*

Environmental Toxicology Division, Health Effects Research Laboratory, Environmental Protection Agency, Research Triangle Park, N.C. 27711 (U.S.A.)

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SUMMARY

The gas chromatographic behavior of 32 carbamate pesticides was investigated using the Hall electrolytic conductivity detector. Relative retention indices were successfully determined for 24 carbamates on six different columns. Columns investigated included Ultra-Bond, 3% OV-101 on Ultra-Bond, 1% OV-17 on Ultra-Bond, 1% OV-210 on Ultra Bond, 1% Carbowax 20M on Ultra-Bond and 0.5% OV-210 + 0.65% OV-17 on Ultra-Bond. Chemical-ionization gas chromatography–mass spectrometry was used to verify that the carbamates were chromatographed intact. Chemical-ionization mass spectra are reported. Analytical procedures are demonstrated for the determination of carbamate residue in soil.

INTRODUCTION

The multi-residue analysis of carbamate pesticides by gas chromatography (GC) has been complicated by the instability of most N-methylcarbamates under common chromatographic conditions and the previous lack of suitable detectors. Considerable effort has thus been devoted to the development of derivatization procedures for the conversion of carbamates to thermally stable products that also possess high sensitivity to the electron-capture detector. These methods have been reviewed recently by Dorough and Thorstenson[1] and Kuhr and Dorough[2]. The development of special columns for the analysis of intact carbamates has also received some attention.

Although a number of carbamates can be converted to suitable derivatives[3–6], derivatization procedures suffer several limitations that often reduce their sensitivity and versatility. The most important limitations include the presence of contaminants from side reactions, unknown identity of the derivative in some procedures, and the

* Present address: Tracor, Inc., Analytical Instruments, 6500 Tracor Lane, Austin, Texas 78721, U.S.A.

limited number of pesticides that can be analyzed by a given method[2]. Involved cleanup procedures which increase time and cost of analyses must often be used to remove interfering products.

Direct GC analysis of the parent carbamate is the obvious method of choice. However, most N-methylcarbamates are either retained on the chromatographic column or are decomposed to the corresponding phenols[7–9]. Consequently, few reports of direct analyses have been published. In general, utilization of glass columns, low-polarity methyl and phenyl silicone stationary phases, special column conditioning techniques and moderate column temperatures has resulted in the greatest success[10–12].

Wheeler and Strother[13] were able to determine Baygon, mexacarbate and Matacil without difficulty on an OV-17 column operated at 180°. However, only approximately 30% of the injected quantity of Mesurol and carbaryl could be detected. Laski and Watts[14], on the other hand, were able to analyze carbaryl with only slight decomposition on a DC-200 column operated at 180°. The same compound was analyzed on a 3% SE-30 column at 145° with detectable decomposition[15–16]. The column, however, was equilibrated with microgram quantities of carbaryl during conditioning and with 50- to 100-ng quantities just prior to analysis. Carbofuran and 3-hydroxycarbofuran were analyzed similarly with good results[17].

Various analysts[18–21] have analyzed methomyl as the corresponding oxime. However, this method requires that methomyl be converted to the oxime prior to GC analysis. Aldicarb and its sulfoxide and sulfone metabolites can also be analyzed in a similar manner. Usually, aldicarb, aldicarb sulfoxide and aldicarb sulfone are isolated by Florisil-column chromatography and then converted to the oxime of aldicarb sulfone for analysis[22–24]. A procedure for "total aldicarb residues" utilizes peracetic acid oxidation for aldicarb and its metabolites and analysis of the sulfone oxime with prior separation[25]. This method has been used to determine "total aldicarb residue" in soils, crops and animal tissues[26–29].

A method that perhaps has the greatest potential for the direct GC analysis of intact carbamates was recently described by Lorah and Hemphill[30]. These authors used a column prepared with a highly deactivated Chromosorb W support that was surface modified with Carbowax 20M. The support, which was originally developed by Aue *et al.*[31], was prepared by heat-treating 6% Carbowax 20M on acid-washed Chromosorb W at 260 to 280° overnight under low carrier gas flow, and then exhaustively extracting the support with methanol and toluene. The modified support is believed to possess an ultra-thin layer of surface bonded Carbowax 20M, and shows excellent inertness to polar compounds such as alcohols and ketones. It can be used by itself or with an additional coating of stationary phase[32].

Lorah and Hemphill[30] achieved excellent sensitivity and peak shape for carbaryl, promecarb, mexacarbate and dimethylamino-3,5-xylanol when chromatographed on this support and detected with an alkali flame-ionization detector. Detector response was reported linear for these compounds over the range 4 to 2000 ng. Peak shape and linearity were not as good for Mesurol, which was believed to be due to the detector. Mesurol was detected by the negative response of the alkali flame-ionization detector which was linear to only 50 ng. Application of this technique to the analysis of fortified tomato and lettuce samples using the cleanup procedure of Holden[33] produced excellent results for carbaryl, Mesurol and promecarb. How-

ever, mexacarbate and 4-dimethylamino-3,5-xylanol were not recovered from the cleanup procedure.

The utility of Carbowax 20M surface-modified supports, with and without additional liquid phase coatings, for the direct chromatographic determination of a wide variety of carbamate pesticides is reported in this paper. The identity of the compound eluted from the column was determined with a gas chromatograph–mass spectrometer operated in the chemical-ionization mode. The method is demonstrated for the analysis of soil samples using an electrolytic conductivity detector operated in the reductive mode.

EXPERIMENTAL

Gas chromatography

A Tracor Model 560 gas chromatograph equipped with a Model 700 Hall electrolytic conductivity detector was used. The detector was operated in the reductive mode with a nickel wire catalyst (Ventron) and a strontium hydroxide scrubber. An ion-exchange resin bed similar to that described by Patchett[34] was used to deionize the 15% isopropanol (in water) conductivity solvent. Solvent flow-rate to the detector was 0.5 ml/min. Helium purified with a General Electric Go Getter was used as a carrier gas at a flow-rate of 25 ml/min. Hydrogen produced with an Elhygen hydrogen generator was used as the reaction gas at a flow-rate of 80 ml/min. The chromatograph inlet temperature was maintained approximately 10° above the column temperature. Transfer and furnace temperatures were 200 and 720°, respectively.

Glass columns (6 ft. × 2 mm I.D.) were silanized with Sylon CT (dimethyldichlorosilane in toluene) purchased from Supelco (Bellefonte, Pa., U.S.A.). Silanized glass wool was used to plug the column ends. A commercially prepared Carbowax 20M-modified support, Ultra-Bond (available from RFR, Hope, R.I., U.S.A.) was coated with stationary phases by the evaporation technique. A rotary evaporator was used for solvent removal, and was operated at approximately 20 rpm. The columns were packed with the aid of a slight vacuum and gentle tapping with a plastic rod. They were conditioned at 190° for 24 h with normal carrier gas flow.

Gas chromatography–mass spectrometry (GC–MS)

A Finigan Model 3200 gas chromatograph–mass spectrometer equipped with a chemical-ionization source and a Model 6100 data system was used with isobutane as the reaction gas. Silanized glass columns (5 ft. × 2 mm I.D.) were operated with isobutane as the carrier gas. The carrier gas also served as the reaction gas. Source pressure was maintained at 550 μm. Column, source, transfer and separator temperatures were 170, 60, 190 and 220°, respectively. The electron energy was 82 eV. The emission current was 1.03 mA.

Soil analysis

Air dried and sieved (20 mesh) soil samples (50 g) were fortified at 0.1 and 1.0 ppm by the addition of 2 ml of a benzene solution of the pesticides. The soil was thoroughly mixed and extracted by shaking with 100 ml of an extraction solution on a "wrist-action" shaker for 10 min. The solution consisted of 80 ml of acetone, 20 ml of aqueous 2% sodium chloride and 1% sodium hydrogen carbonate. The extract

was filtered through Whatman No. 1 filter paper and the filter cake rinsed with 100 ml of the aqueous extraction solution. The filtrate was diluted with an additional 100 ml of the aqueous solvent and extracted 3 times with 50 ml of benzene. The extracts were combined and dried on a sodium sulfate column (40 g, prewashed with 50 ml of benzene). Any residual extract was eluted with an additional 25 ml of benzene. A 1-ml volume of 2% tetradecane in benzene was added to the dried extract as a keeper, and the extract volume was then evaporated to approximately 15 ml on a rotary evaporator. The concentrated extract was quantitatively transfered to a 25-ml Kuderna-Danish concentration tube and the volume reduced at room temperature to 0.75 to 1.0 ml on a rotary evaporator. The concentrated sample was quantitatively transfered to a 200 mm × 9 mm cleanup column that contained 1.5 g of Florisil (10% water) and 1 g of sodium sulfate (top), and eluted with 25 ml of 25% diethyl ether in benzene. The eluate was concentrated to 2.5 ml for analysis of samples fortified at 0.1 ppm and 25 ml for analysis of samples fortified at 1.0 ppm.

RESULTS AND DISCUSSION

Chromatography

The successful initial results of Lorah and Hemphill[30] indicate that the development of GC procedures for the direct determination of multiple carbamate residues is feasible. A study was thus undertaken to determine the full potential of Carbowax 20M-modified supports for the chromatography of nanogram quantities of carbamate pesticides. We initially utilized hydrochloric acid-treated Anakrom U (90–100 mesh) modified with Carbowax 20M by heat treating the coated support (6% phase loading) at 270° as originally described[31], followed by a simple chloroform extraction to remove the soluble residue. Although initial results with a limited number of carbamates were excellent, the laboratory prepared support was discarded in favor of a commercial version (introduced after the study was initiated) since it would be readily available to any residue laboratory.

A total of 32 carbamates, thiocarbamates and dithiocarbamates containing a wide variety of moieties, such as aniline, ether, ester, halogen, nitrogen heterocyclic, oxygen heterocyclic, oxime, sulfoxide, sulfone and urea, were used to determine the utility of the Carbowax 20M-modified support as a general support for the analysis of carbamates. The support was evaluated using quantities (10 to 20 ng) of carbamates that would normally be encountered in residue samples. No attempt was made to improve performance by conditioning the column with large quantities of carbamates as done in some instances[15,16]. Also, no particular precautions or conditioning techniques were employed.

The columns were evaluated using the Hall electrolytic conductivity detector. This detector was chosen because its response is uniform to various organic nitrogen compounds and directly proportional to the nitrogen content of the molecule. Consequently, the detector response on a gram of nitrogen basis can be used as a measure of compound decomposition.

Excellent results were obtained for 24 of the carbamates when chromatographed on Ultra-Bond or Ultra-Bond coated with a stationary phase. Representative chromatograms of several mixtures of pesticides are reproduced in Figs. 1–3. As shown in these figures, peak symmetry is excellent. Of the 24 compounds that can be easily

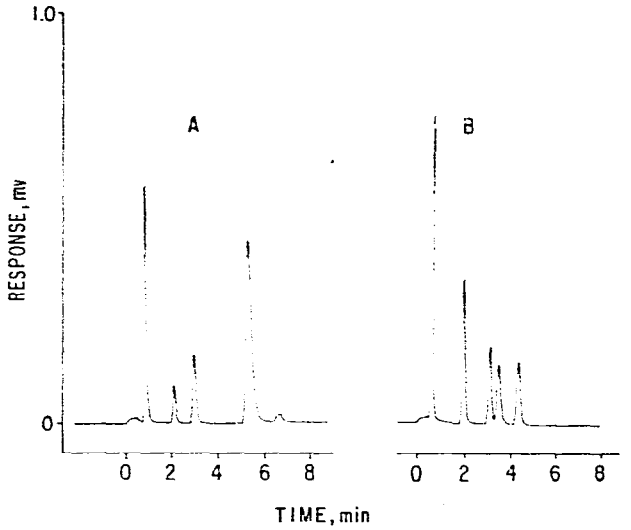

Fig. 1. Chromatograms of carbamates pesticides separated on a 3% OV-101 on Ultra-Bond column operated at 170°. Sensitivity: 10 × 8. Compounds in order of elution are: (A) butylate, CDEC carbofuran, Dimetilan and methiocarb; (B) EPTC, chlorpropham, triallate, SWEP and terbutol. Sample quantity: 10 ng each.

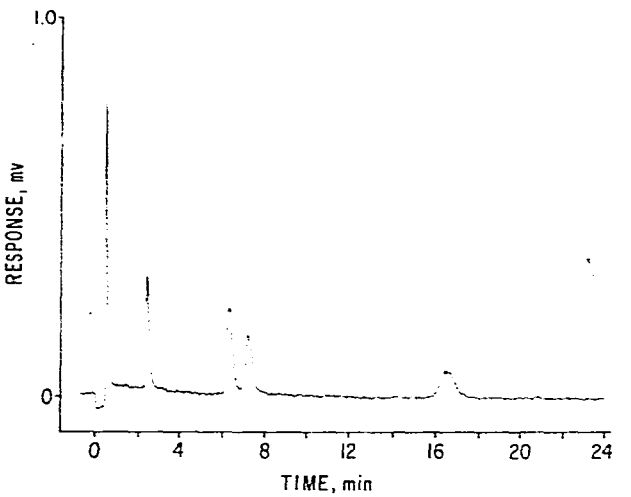

Fig. 2. Chromatogram of carbamate pesticides separated on a 1% Carbowax 20M column operated at 170°. Sensitivity 10 × 8. Compounds in order of elution are EPTC, chlorpropham, triallate, SWEP and terbutol. Sample quantity: 10 ng each.

chromatographed, pyramat was the only compound that exhibited some peak tailing. This may have been due to co-eluted impurities since distinct "shoulders" were noticed on the OV-210-coated column.

Poor results were obtained for aldicarb, aldicarb sulfoxide, aldicarb sulfone, Karbutylate, methomyl, phenmedipham and thiophanate. Either no response or distorted peaks were observed for these compounds. Although there are few similarities

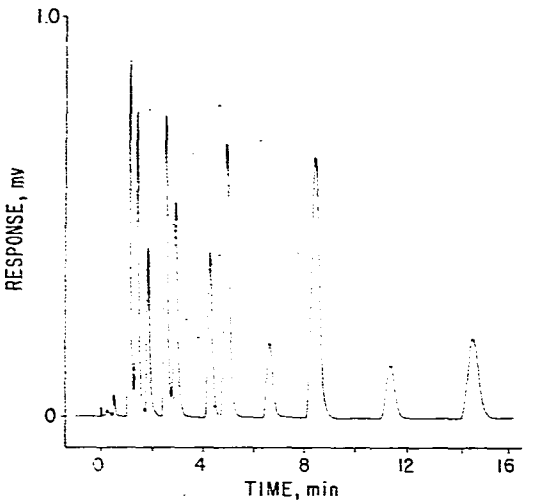

Fig. 3. Chromatogram of carbamate pesticides separated on a 0.65% OV-17 + 0.5% OV-210 on Ultra-Bond column operated at 170°. Sensitivity: 10 × 8. Compounds in order of elution are: Propham, diallate, triallate, meobal, 3,4,5-Landrin, carbofuran, mexacarbate, SWEP, Dimetilan, methiocarb and carbaryl. Sample quantity: 10 ng each with the exception of diallate at 5 ng.

in the structures of these pesticides, they do have moieties other than the carbamate unction (*i.e.* oxime, urea) that are known to be thermally labile.

Although peak shape was excellent for the compounds that could be readily chromatographed, some decomposition was indicated for carbaryl, methiocarb and meobal. Carbaryl exhibited the greatest degree of decomposition. Temperature-progammed analysis using a flame-ionization detector showed one major decomposition product and several minor products. Electrolytic conductivity detector response was approximately 50% of that expected. However, the electrolytic conductivity detector does not respond to the decomposition products (unless they contain nitrogen) and only the parent peak is observed. Thus, multiple carbamate determinations are not necessarily precluded by the presence of the degradation products.

Though a wide variety of carbamates can be readily analyzed on Ultra-Bond or Ultra-Bond coated with a polar or non-polar stationary phase, it appears to be important to use moderate column temperatures and fairly short retention times. Relatively poor peak shapes and sensitivities were observed for 3% OV-17 and 3% Carbowax 20M columns operated at 190 to 200°. Retention times at these temperatures were approximately twice that achieved with the 1% phase loadings. A phase loading of 1% was therefore used for all stationary phases, except OV-101 which was used at 3% loading. Retention times were short on OV-210 and a higher loading could have been used. However, the electrolytic conductivity detector is sensitive to bleed from this phase. Elution times generally ranged from 1 to 15 min on these columns when operated at 170°.

Temperature-programmed and isothermal analyses are compared in Figs. 3 and 4. Temperature-programmed analysis enables 15 carbamates to be separated on the OV-210 + OV-17 column within 19 min. The absence of baseline drift during

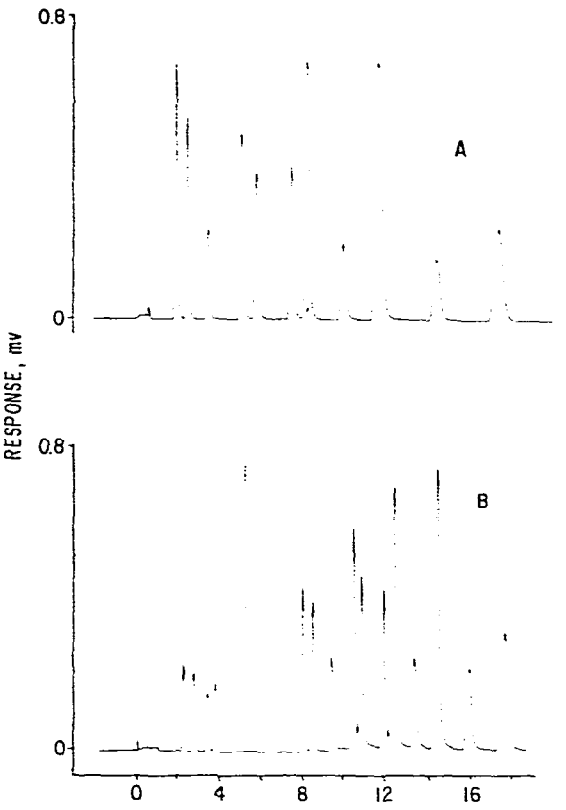

Fig. 4. Chromatogram of carbamate pesticides separated on a 0.65% OV-17 + 0.5% OV-210 on Ultra-Bond column. (A) Temperature-programmed from 115–175° at 10°/min. Sensitivity: 10 × 8. Compounds in order of elution: propham, diallate, triallate, meobal, 3,4,5-Landrin, carbofuran, mexacarbate, SWEP, Dimetilan, methiocarb and carbaryl. Sample quantity: 10 ng except for diallate at 5 ng. (B) Temperature-programmed from 110–185° at 10°/min. Sensitivity: 10 × 8. Compounds in order of elution are: EPTC, butylate, vernolate, pebulate, propham, diallate, triallate, meobal, 3,4,5-Landrin, carbofuran, mexacarbate, SWEP, Dimetilan, methiocarb and carbaryl. Sample quantity same as in A.

programmed analyses should be noted. Isothermal operation enables 11 compounds to be resolved on the same column in approximately 15 min.

Relative retention properties for a number of carbamate pesticides are reported in Tables I and II. EPTC, butylate, vernolate and pebulate could not be resolved from the solvent front on the Ultra-Bond, OV-210 and OV-210 + OV-17 columns under conditions suitable for chromatographing the bulk of the carbamates (Table I). All compounds, however, could be analyzed at a single temperature on the 3% OV-101, 1% OV-17 and 1% Carbowax 20M columns. Relative retention indices for the "volatile" carbamates on Ultra-Bond at several different column temperatures are reported in Table II. Of these compounds, EPTC was the only pesticide whose relative retention index displayed a significant temperature dependency.

In general, the best performance (peak symmetry and sensitivity) was achieved on the Ultra-Bond, 3% OV-101, 1% OV-17 and the mixed phase 0.5% OV-210 +

TABLE I

RELATIVE RETENTION INDICES FOR CARBAMATE PESTICIDES

Column temperature is 170°.

*Compound**	*Purity***	*Ultra-Bond*	*3% OV-101*	*1% OV-17*	*1% Carbowax 20M*	*1% OV-210*	*0.5% OV-210 + 0.65% OV-17*
EPTC	99.5	—	0.20	0.08	0.07	—	—
Butylate	99.5	—	0.25	0.09	0.07	—	—
Pebulate	99.0	—	0.25	0.12	0.09	—	—
Vernolate	99.0	—	0.28	0.12	0.08	—	—
Propham	100.0	0.19***	0.31	0.19	0.22	—	0.22
Diallate	99.0	0.20***	0.67	0.31	0.21	0.32	0.28
Meobal	99.0	0.33	0.59	0.42	0.52	0.56	0.50
CDEC	99.5	0.34	0.66	0.40	0.30	0.40	0.37
Pyramat	98.0	0.35	0.62	0.43	0.29	0.39	0.36
Triallate	99.5	0.53	1.01	0.48	0.26	0.39	0.38
Propoxur	98/99	0.55	0.55	0.48	0.53	0.63	0.52
2,3,5-Landrin	98.0	0.60	0.69	0.51	0.58	0.65	0.58
Chlorpropham	99.5	0.61	0.66	0.45	0.59	0.56	0.55
Bux	98.0	0.78	1.04	0.72	0.71	0.75	0.71
Terbutol	98.0	0.82	1.47	0.91	0.66	0.82	0.78
3,4,5-Landrin	98.0	0.85	0.94	0.78	0.85	0.88	0.85
Benthiocarb	98.0	0.85	1.80	1.26	0.82	0.75	1.02
Aminocarb	98.0	0.93	1.07	0.89	0.95	1.02	0.94
Mexacarbate	99.0	0.98	1.32	0.98	0.94	1.02	0.96
Carbofuran	99.5	1.00	1.00	1.00	1.00	1.00	1.00
SWEP	98.0	1.36	1.19	0.97	1.47	1.19	1.28
Dimetilan	98.0	1.37	1.79	1.93	1.38	1.86	1.64
Methiocarb	99.0	2.10	2.25	2.13	2.28	1.96	2.20
Carbaryl	99.5	2.75	2.48	2.41	3.10	2.81	2.82

* Compounds are listed by common names.

** Standards came from the EPA Protection Agency, Health Effects Research Laboratory, Environmental Toxicology Division, Research Triangle Park, N.C. 27711, U.S.A.

*** Column temperature is 150°.

TABLE II

RETENTION PARAMETERS FOR VOLATILE CARBAMATE PESTICIDES ON ULTRA-BOND

t_R = retention time; t'_R = relative retention.

Compound	*Purity*	*Temperature (°C)*					
		90°		*100°*		*120°*	
		t_R *(min)*	t'_R	t_R *(min)*	t'_R	t_R *(min)*	t'_R
EPTC	99.5	3.27	0.69	2.00	0.73	1.09	0.87
Butylate	99.5	4.72	1.00	2.75	1.00	1.25	1.00
Vernolate	99.0	5.29	1.12	3.06	1.11	1.42	1.14
Pebulate	99.0	6.00	1.27	3.44	1.25	1.55	1.24

0.65% OV-17 columns. The other columns are still useful, particularly for confirmation and analysis of certain compounds. For instance, relative retention indices for diallate, CDEC, pyramat, triallate, terbutol, SWEP, dimetilan and carbaryl were

either distinctly smaller or greater on Carbowax 20M than on the other phases. OV-210 was the only phase on which a response for barban was observed ($\alpha = 11.6$, relative to carbofuran).

Gas chromatography–mass spectrometry

The nature of the compound actually observed with the electrolytic conductivity detector was investigated by chemical-ionization MS. Isobutane was used as the reaction gas in order to minimize fragmentation. Total ion-current chromatograms were obtained and used to check for chromatographic decomposition products. Specific ion searches for expected phenol or isocyanate decomposition products (*i.e.* the M + 1 ion of 1-naphthol for carbaryl) were also conducted.

All carbamates investigated were readily protonated by isobutane to form the M + 1 ion, which was the most significant ion for all compounds. A number of the compounds produced significant M − *n* ions (Table III). In all case, these could be attributed to the ions of the corresponding phenols or isocyanates. It could not be determined from the spectra, however, whether these ions were fragmentation ions or the M + 1 ions of the decomposition products formed in the transfer line from the column to the ion source. Although the transfer line was stainless steel, it is unlikely that significant decomposition occured since the residence time was very short and the M − *n* ions were major ions produced from compounds that exhibited little or no column decomposition. Representative spectra are shown in Figs. 5 and 6.

TABLE III

PRINCIPAL IONS FORMED IN THE GC–CHEMICAL-IONIZATION MS OF CARBAMATE PESTICIDES USING ISOBUTANE AS THE REACTION GAS

Compound	*Molecular formula*	*Molecular weight*	*Parent ion*	*Secondary ions (intensity)*
EPTC	$C_9H_{19}NOS$	189	190	128 (34)
Butylate	$C_{11}H_{23}NOS$	217	218	156 (48)
Pebulate	$C_{10}H_{21}NOS$	203	204	128 (25)
Vernolate	$C_{10}H_{21}NOS$	203	204	128 (28)
Propham	$C_{10}H_{13}NO_2$	179	180	—
Diallate	$C_{10}H_{17}Cl_2NOS$	269	270	128 (65)
Meobal	$C_{10}H_{13}NO_2$	179	180	—
CDEC	$C_8H_{14}ClNS_2$	223	224	—
Pyramat	$C_{11}H_{17}N_3O_2$	223	224	—
Triallate	$C_{10}H_{16}Cl_3NOS$	303	304	128 (79)
Propoxur	$C_{11}H_{15}NO_3$	209	210	153 (48)
2,3,5-Landrin	$C_{11}H_{15}NO_2$	193	194	—
Chlorpropham	$C_{10}H_{12}ClNO_2$	213	214	172 (15)
Bux	$C_{13}H_{19}NO_2$	221	222	—
Terbutol	$C_{17}H_{27}NO_2$	277	278	222 (61)
3,4,5-Landrin	$C_{11}H_{15}NO_2$	193	194	—
Benthiocarb	$C_{12}H_{16}ClNOS$	257	258	—
Aminocarb	$C_{11}H_{16}N_2O_2$	208	209	—
Mexacarbate	$C_{12}H_{18}N_2O_2$	222	223	—
Carbofuran	$C_{12}H_{15}NO_3$	221	222	165 (33)
Swep	$C_2H_7Cl_2NO_2$	219	220	—
Dimetilan	$C_{10}H_{16}N_4O_3$	240	241	—
Methiocarb	$C_{11}H_{15}NO_2S$	225	226	—
Carbaryl	$C_{12}H_{11}NO_2$	201	202	—

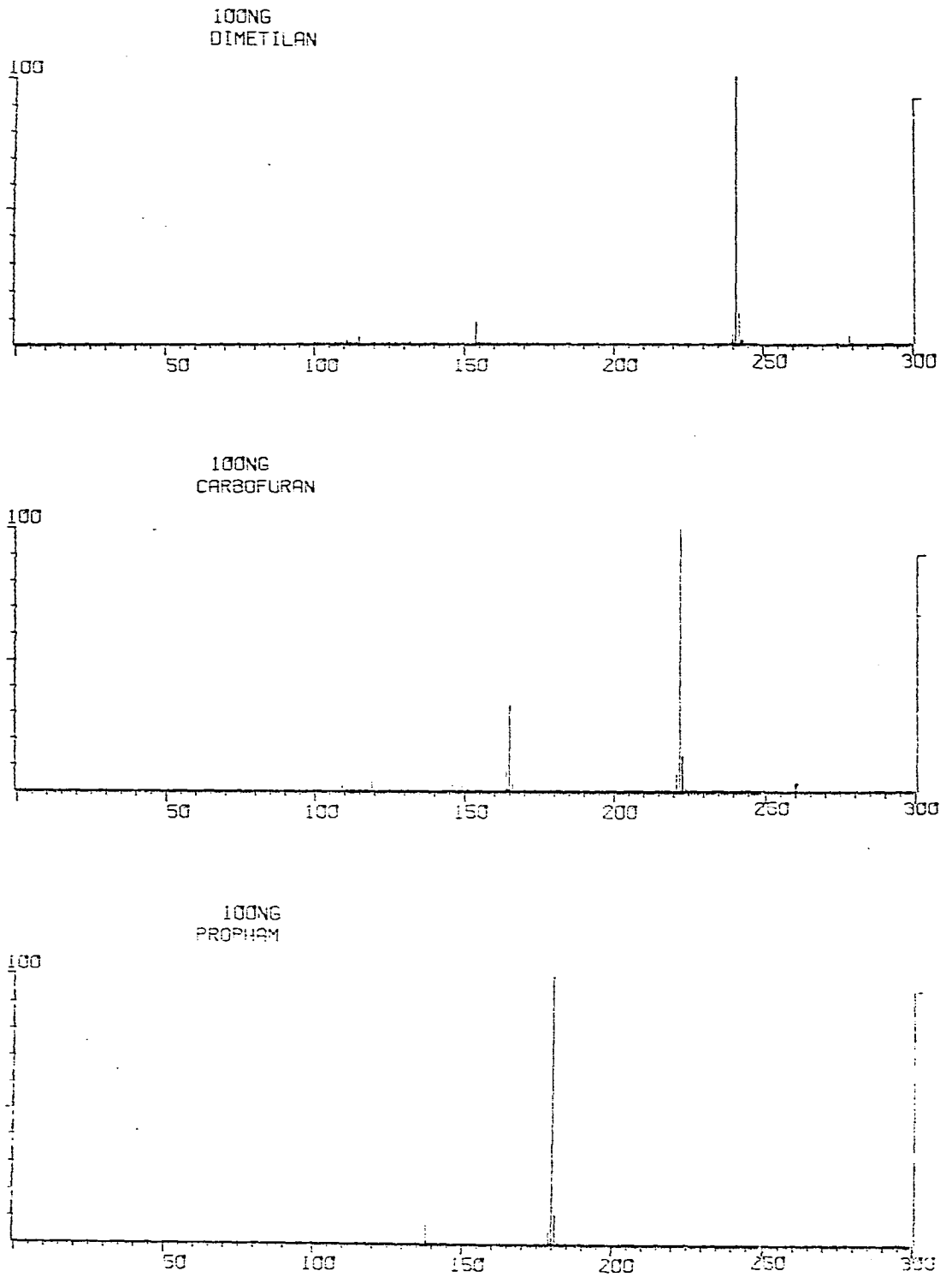

Fig. 5. Chemical-ionization mass spectra of dimetilan, carbofuran and propham.

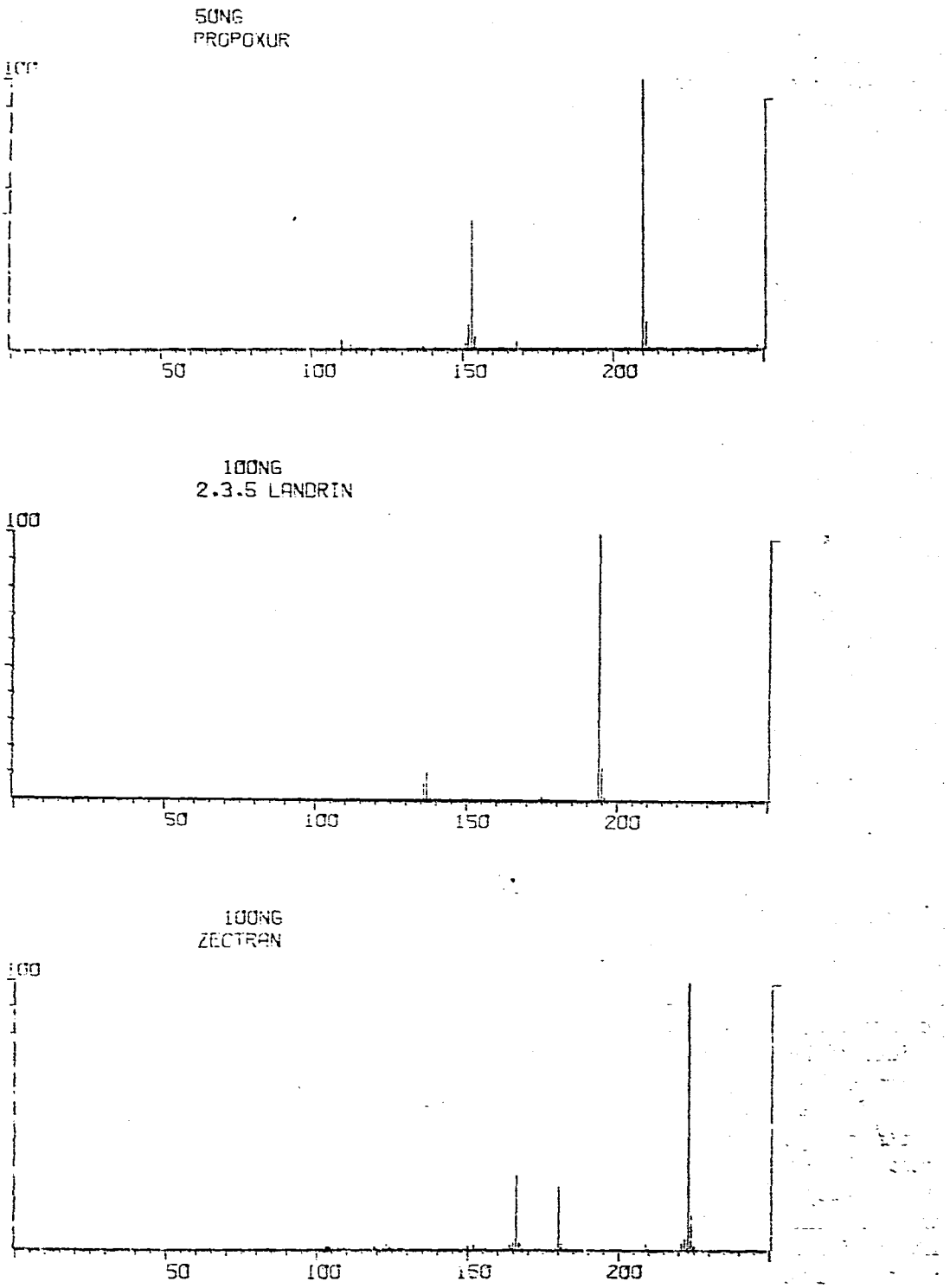

Fig. 6. Chemical-ionization mass spectra of propoxur, 2,3,5-Landrin and mexacarbate.

Except for carbaryl, total ion-current chromatograms were free of extraneous peaks, and specific ion searches for expected decomposition products were negative. The decomposition product of carbaryl, 1-naphthol, displayed approximately 1.5 times the area of carbaryl in the total ion-current chromatogram. Results obtained with a flame-ionization detector were similar.

From the above results, it can be concluded that the compounds detected with the electrolytic conductivity detector were the intact carbamates. Of these compounds, carbaryl was the only pesticide that was significantly degraded when chromatographed on Ultra-Bond or Ultra-Bond coated with a stationary phase. It should be noted, however, that decomposition products would have to be present in a quantity greater than 10% of the parent carbamate in order to be detected above the GC–MS background.

Soil analysis

The extraction of carbamate pesticides from soil has received only limited attention. Chromatographic methods for aldicarb[35], carbaryl[36], carbofuran[37], landrin[38] and methomyl[39] have been reported recently. Initial investigations using several published procedures provided satisfactory results for only a limited number of compounds. Particular difficulty was encountered with the basic carbamates such as aminocarb and mexacarbate. Since these published procedures were developed for the determination of specific compounds and not meant to be used as multi-residue techniques, it was decided to develop a new procedure rather than extend existing methods.

A number of solvent systems, including water–acetone, alcohol, alcohol–benzene, water–benzene and benzene, were evaluated using a wide variety of carbamates. Halogen- and nitrogen-containing solvents were not investigated since they are not compatible with the electrolytic conductivity detector. A slightly basic solution containing sodium chloride, sodium hydrogen carbonate, water and acetone provided the best results. Recovery data for this extraction solvent is presented in Table IV.

As shown in Table IV, the water–acetone–sodium hydrogen carbonate–sodium chloride solution is very effective for the extraction of parent carbamate pesticides. All compounds, except CDEC, were recovered with better than 70% efficiency. The overall average recovery of the compounds investigated (excluding CDEC) was 89%. The recovery of CDEC diminished with the length of time that the fortified soil was allowed to sit prior to extraction, which indicates that soil decomposition may preclude meaningful residue determinations for this pesticide. Decomposition of the other pesticides was not obvious. The samples, however, were extracted within 0.5 h of preparation.

Representative chromatograms of soil extracts are shown in Figs. 7 and 8. Extraneous peaks were not observed in the 1-ppm samples, but two peaks were present in the 0.1-ppm samples. These soil impurities exhibited similar chromatographic properties on various cleanup columns (alumina–10% water, Florisil–10% water and silica gel–10% water), and could only be partially removed. These impurities interfered somewhat with the determination of butylate, pebulate, EPTC, mexacarbate and vernolate when chromatographed on the OV-101 column.

Several different cleanup columns were investigated. The carbamates were

TABLE IV

RECOVERY OF CARBAMATE PESTICIDES FROM FORTIFIED SOIL

Compounds	*Recovery (%)*	
	0.1 ppm	*1.0 ppm*
Aminocarb	85 ± 7*	85 ± 4
Benthiocarb	82 ± 20	92 ± 5
Butylate	95 ± 3	86 ± 2
Bux	88 ± 6	99 ± 5
Carbaryl	—**	85 ± 0
Carbofuran	92 ± 4	86 ± 5
CDEC	33 ± 5	66 ± 3
Chlorpropham	92 ± 9	80 ± 5
Dimetilan	83 ± 3	71 ± 2
EPTC	75 ± 5	87 ± 3
2,3,5-Landrin	112 ± 8	96 ± 4
3,4,5-Landrin	96 ± 8	98 ± 4
Meobal	87 ± 2	92 ± 5
Methiocarb	84 ± 8	—
Mexacarbate	86 ± 7	85 ± 1
Pebulate	105 ± 7	94 ± 3
Propham	101 ± 4	94 ± 4
Pyramat	99 ± 5	92 ± 5
SWEP	85 ± 8	82 ± 6
Terbutol	90 ± 6	83 ± 6
Triallate	92 ± 9	75 ± 6
Vernolate	87 ± 2	90 ± 4

* Standard deviations for three determinations.

** Determination precluded by insufficient response.

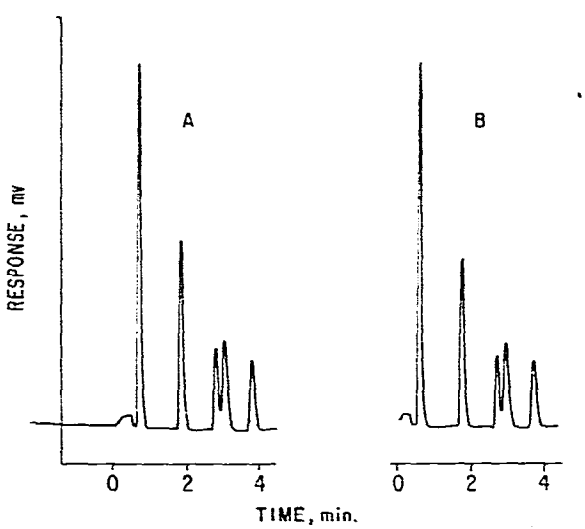

Fig. 7. Chromatograms of soil extract of carbamate pesticides separated on a 3% OV-101 on Ultra-Bond column. Compounds in order of elution are: pebulate, 2,3,5-Landrin, 3,4,5-Landrin, aminocarb and benthiocarb. (A) 10 ng standard; (B) extract of fortified soil.

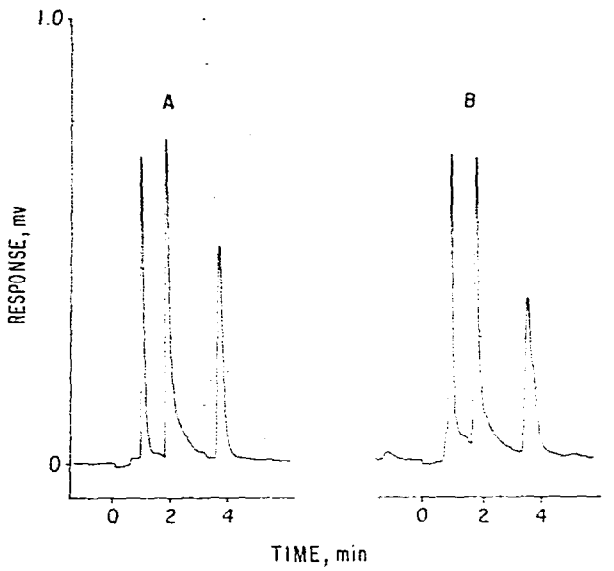

Fig. 8. Chromatograms of soil extract of carbamate pesticides separated on a 3% OV-101 on Ultra-Bond column. Compounds in order of elution are: propham, pyramate and mexacarbate. (A) 10 ng standard; (B) extract of fortified soil.

readily decomposed on activated materials such as Florisil, alumina or silica gel. Deactivation of the absorbents with 10% water eliminated any detectable decomposition on cleanup columns packed with 1 to 1.5 g of material. Some decomposition was noticed with larger quantities of Florisil. An ether–benzene (1:3) solution provided adequate sample cleanup and near quantitative recovery of the pesticides with Florisil, alumina or silica gel columns. Coconut charcoal was also evaluated, but recoveries for most of the carbamates were too low to be useful.

CONCLUSIONS

A wide variety of carbamate pesticides can be chromatographed as the intact compounds using Carbowax 20M-modified supports with or without additional liquid phase coatings. It appears to be important, however, that moderate column temperatures ($<185°$) and relatively short analysis times be employed. Of the 24 pesticides that could be readily chromatographed, carbaryl was the only compound that exhibited significant degradation ($\approx 50\%$). The retention time of carbaryl was considerably longer than the other pesticides, which probably contributed to its degradation. Eleven carbamate pesticides can be separated on a OV-210–OV-17 mixed phase column under isothermal conditions. A total of 15 carbamates can be separated with baseline resolution on the same column with temperature programming.

Chemical-ionization MS using isobutane as the reaction gas revealed that the carbamates were chromatographed as the parent compounds. The parent compounds were readily protonated to form a M+1 ion, which was the major ion in all cases. Some compounds also produced a few significant secondary ions. These ions can be

attributed to the ions of the corresponding phenols and isocyanates. Total ion-current chromatograms showed extraneous peaks for only carbaryl. Specific ion searches for expected decomposition products were positive for only carbaryl.

Soil samples fortified with carbamates were readily analyzed by electrolytic conductivity detection down to levels of 0.1 ppm. A slightly basic water–acetone–sodium hydrogen carbonate–sodium chloride solution provided excellent recoveries. The average recovery of 22 carbamates pesticides was 89%. Florisil–10% water provided adequate cleanup for most samples.

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