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A One-Step Derivatization Procedure for Several Carbamate Pesticides

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A review by KUHR & DOROUGH (1976) discusses several procedures for the direct conversion of carbamates to compounds amenable to GC analysis.

The purpose of this study was to determine if any of these carbamate derivatization procedures could be applied to a wide range of carbamate pesticides at the residue level and still use the standard gas chromatographic columns and operating conditions as described in the EPA manual (THOMPSON 1977) for ECGC. Herein, we report the results of the use of pentafluorobenzyl bromide as a derivatization reagent with 23 carbamates of widely different structure.

MATERIALS AND METHODS

Reagents and solvents. Alcoholic KOH: 1.0 g of solid KOH was dissolved in 100 mL of 95% ethanol.

Derivatizing reagent: 0.1 mL of α-bromo-2,3,4,5,6-pentafluorotoluene (Aldrich Chemicals,* Milwaukee, WS) was diluted to 10 mL with 95% ethanol.

Carbamate standards: Analytical grade aldicarb, aminocarb, asulam, barban, benthiocarb, carbaryl, carbofuran, CDEC, chlorpropham, desmedipham, formetanate hydrochloride, karbutilate, meobal, methiocarb, methomyl, pebulate, phenmedipham, promecarb, propham, propoxur, thiophanate-methyl, triallate, and vernolate standards (Pesticide Repository, U. S. Environmental Protection Agency, Research Triangle Park, NC) were dissolved in either pesticide quality benzene, n-hexane, or toluene (1 mg/mL). Working standards for derivatization were prepared from these stock solutions.

Equipment. Gas chromatograph equipped with a ^{63}Ni electron capture detector. Glass columns (183 x 0.2 cm i.d.) containing either 1.50% OV-17/1.95% OV-210 or 4% SE-30/6% OV-210 on 80-100 mesh Gas Chrom Q were used. All columns were pre-conditioned at 225°C for 24 h. Operating parameters were: inlet, 220°C; column oven, 220°C; detector, 350°C; nitrogen carrier gas, 100 mL/min.

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*Mention of trade names is for identification only and does not constitute endorsement by the U. S. Environmental Protection Agency.

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Procedure. Pipet 1 mL of alcoholic KOH, 0.1 mL of derivatizing reagent and 1 mL of carbamate standard into a 15-mL culture tube. Seal with a teflon-lined screw cap and place the tube in a pre-heated (95 ± 1°C) tube block heater for 2 h. The length of time and temperature are critical, for overheating can cause an increase in the formation of extraneous gas chromatographic peaks (AGEMIAN & CHAU 1976). Remove, allow to cool at room temperature, and add 5 mL of distilled water followed by 4 mL of n-hexane to the culture tube. Place the culture tube on a tube rotator (60 rpm) for 2 min and at the end of this time transfer the n-hexane layer to a 15-mL centrifuge tube. Add an additional 4 mL of n-hexane to the culture tube, and place in the tube rotator for an additional 2 min. Combine n-hexane layer with the previous n-hexane extract. Bring the final volume of the centrifuge tube to 10 mL with n-hexane. The sample is now ready for either further cleanup if necessary or direct GC analysis.

Characterization. Each PFB derivative was characterized by electron capture GC and the derivatization procedure evaluated utilizing the following criteria:

1. GC retention time relative to aldrin

2. Linearity of electron capture detector response and Quantity of derivative required to give 50% full scale deflection (FSD). The response linearity of the derivatives was determined on two gas chromatographic columns. A concentration of the derivative was selected so that a 5-µL injection would produce a peak height of approximately 40-45% full scale deflection (FSD). Injections of 2 to 8 µL, at 1 µL increments, were made, with an allowance of ± 10% tolerated in determining linearity. The quantity required for 50% FSD was determined from this procedure.

3. Derivatization linearity. Linearity was checked over a concentration range from 0.1 to 1,000 ng/µL, if possible, or to the limits of detection. Allowances of ± 15% were tolerated in determining the range of derivatization linearity.

4. Minimum detectable level. Minimum detectable level was defined to be 10% full scale deflection, provided that this was at least twice the background noise. (This might be a combination of gas chromatographic baseline and background from the derivatization procedure.) The theoretical concentration for this response was calculated from the detector response before solutions of the proper concentration were prepared and tested.

5. Storage of derivatized samples. For each carbamate derivative, one sample was stored at 4°C and a second sample was stored in the dark at 25°C. These samples were analyzed at 0, 1, 2, 4, and 8 days to determine their stability under storage conditions.

RESULTS AND DISCUSSION

The derivatization procedure used is similar to that of COBURN et al. (1976). The hydrolysis and derivatization steps have been combined into one step to save time and minimize chances for error.

Of the 23 cambamate pesticides tested with this method, only five (asulam, pebulate, propham, triallate, and vernolate) did not form a derivative amenable to GC analysis.

Most derivatives give only one well-formed symmetrical peak. However, there was one minor peak each for chloroproham and meobal and two minor peaks each for methomyl and phenmediphan. All characterizations were made on the major peaks.

The data characterizing the derivatives are presented in Table 1. All derivatives formed gave linear electron capture detector responses on both columns. No loss of derivative was noted following storage either at 4 or 25°C. During the course of the characterization of the carbamate derivatives, two major difficulties were encountered. These difficulties were a decrease in the extent of reaction at low concentrations (i.e., $\geq$ 10 ng/µL) and large background interference caused by the derivatization reagent. A decrease in the extent of the reaction at low concentrations, could be caused by competing reactions of the PFBB with ethoxide ions. Also, a small loss of derivative absorbed on the glassware could become an important portion of the derivative at very low concentrations. With some of the carbamate derivatives, the background interference was so great that dilution of the final extract by a factor of 100 to quantify the GC peaks was required. These interferences were especially troublesome when retention times of the derivatives were short (less than 0.6 relative to aldrin) or when retention times were near 1.2. The level of interference can be expected to increase when environmental samples are derivatized instead of analytical standards. Hence, the value of this method is limited without a suitable cleanup procedure. Several methods of cleanup are available. One involving a deactivated alumina column (COBURN et al. 1976) has been used with the PFB derivative. The intent of this work was to determine whether or not derivatization of carbamates with PFBB was widely applicable and amenable to GC analysis. Another limiting factor was that unless the carbamate can form a substituted phenoxide ion in the alkaline reaction mixture, the structure of the derivative will be difficult to predict. Mass spectrometric analysis (JACKSON et al. 1979) showed at least four different derivatives were formed; phenolic (aminocarb, carbaryl, meobal, and promecarb), amino (barban), oximino (aldicarb), and sulfide (thiophanate-methyl). However, in spite of this, PFBB derivatization is a sensitive method for the determination of carbamates which can form a substituted phenoxide ion in the reaction mixture.

TABLE 1. GC characteristics of PFB derivatives of carbamates

Carbamate	Derivatization linearity (µg/sample)	RRT (Aldrin)		10% FSD (ng)		50% FSD (ng)	
		OV-17/ OV-210	SE-30/ OV-210	OV-17/ OV-210	SE-30/ OV-210	OV-17/ OV-210	SE-30/ OV-210
Aldicarb	1-100	0.56	0.60	0.08[a]	0.04	0.08	0.07
Aminocarb	1-100	2.00	1.90	1.6[a]	0.49	2.7	2.6
Barban	100-1000	2.00	3.00	20[a]	33	34	100
Benthicarb	10-1000	0.91	1.00	0.65[a]	0.48	1.8	2.0
Carbaryl	1-1000	4.70	3.60	0.20	0.18	1.0	0.89
Carbofuran	2-1000	2.10	---[b]	0.70	---[b]	3.1	---[b]
CDEC	0.1-1000	0.64	0.62	0.024	0.024	0.15	0.15
Chlorpropham	10-1000	0.39	0.40	0.72	0.72	3.1	3.0
Desmedipham	100-1000	2.8	1.8	6.3	8.4	32	42
Formetanate·HCl	100-1000	1.7	2.2	4.7	4.1	23	20
Karbutilate	100-1000	2.5	2.1	9.7	9.9	49	49
Meobal	10-1000	1.2	1.2	0.091	0.096	0.46	0.48
Methiocarb	1-1000	3.7	3.1	0.35	0.30	1.8	1.5
Methomyl	1-100	1.3	1.5	0.031	0.026	0.16	0.13
Phenmedipham	100-1000	2.3	1.6	18	14	88	68
Promecarb	10-1000	1.4	1.4	0.14	0.14	0.68	0.70
Propoxur	10-1000	1.2	1.2	0.24	0.24	1.2	1.2
Thiophanate-methyl	10-100	3.0	3.3	0.009	0.012	0.044	0.057

[a]The 10% FSD is not one-fifth of the 50% FSD due to background.

[b]Characterization was not attempted due to high background interference.

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