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Note

Quantitative determination of ppb* levels of carbamate pesticides in water by capillary gas chromatography

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The recent discovery[1] of groundwater contaminated with carbamate pesticides has made it imperative to have reliable methods for detecting low levels (ppb*) of these environmentally persistent pesticides in soil and water. One of the most toxic of these pesticides used on crops is aldicarb [2-methyl-2-(methylthio)propionaldehyde-O-(methylcarbamoyl) oxime]. Its residues primarily consist of the parent compound and two principal oxidation products, aldicarb sulfoxide and aldicarb sulfone. Extensive contamination of groundwater by aldicarb metabolites has been discovered in over one thousand wells on eastern Long Island[1]. This contamination resulted from the use of aldicarb on potato fields to protect the crop from the Colorado potato beetle and the golden nematode. The residues found in the groundwater consist on the average of equal parts of the sulfoxide and sulfone both of which are similar in toxicity to aldicarb.

Numerous methods for the determination of aldicarb and its oxidation products have been reported in the literature[2–6]. Gas chromatography is often the method of choice for quantitative determination of residues in crops and more recently soil and water. Since aldicarb and aldicarb sulfoxide are not resolved from the solvent peak, the usual procedure is to oxidize these species to the sulfone with peracetic acid. After bulk extraction and cleanup, the total aldicarb residue can then be quantified by gas chromatography with a flame photometric detector[2–4], an electrolytic conductivity detector[5], or a nitrogen phosphorus detector[7]. If quantification of the individual metabolites is desired it is necessary to separate them by column chromatography after the extraction step. Aldicarb and aldicarb sulfoxide would then be oxidized separately to aldicarb sulfone before analysis. These procedures are both time consuming and contribute to inaccurate determinations.

High-performance liquid chromatography has also been used for quantification of low levels of aldicarb and its oxidation products in water[5–6]. Analysis of the three species after bulk extraction was reported using a two injection procedure[5]. A method of direct analysis of aldicarb after a preconcentration step has also been developed[6].

* Throughout this article the American billion (10^9) is meant.

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In this paper a new gas chromatographic method is reported for the quantification of aldicarb and its oxidative metabolites. The method has also been modified for quantification of carbofuran, oxamyl and methomyl. An open tubular column and a nitrogen phosphorus detector are used to quantify nanogram levels of aldicarb, aldicarb sulfoxide and aldicarb sulfone in a one injection procedure. Linear calibration curves are obtained for each species. The method is particularly useful for environmental sampling and for degradative studies in soil–water systems in the laboratory since all three metabolites can be determined in one sample. Thus, degradation of the parent compound can be followed under varying conditions.

EXPERIMENTAL

Materials

Samples of aldicarb sulfoxide (98% pure), aldicarb sulfone (99% pure), aldicarb oxime, aldicarb sulfoxide oxime, aldicarb sulfoxide nitrile, aldicarb sulfone oxime and aldicarb sulfone nitrile were supplied by Union Carbide. Reference standards of aldicarb, carbofuran, oxamyl and methomyl were obtained from the United States Environmental Protection Agency, Quality Assurance Section. Distilled, deionized and then glass distilled water was used throughout except for the experiments with actual groundwater from a well in Oakdale, New York on Long Island. Methylene chloride used for bulk extractions was recovered, distilled, and used again. Methylene chloride blanks were run through the system to insure that there was no carry-over of the pesticide. Analytical reagent grade chemicals and solvents were used in all experiments.

Procedures

A 100-ml aqueous sample (either distilled water or well water) containing the appropriate concentration of pesticide standard or mixture of standards is placed in a 250-ml separatory funnel to which 30 g of sodium chloride and 0.5 ml of acetone has been added. The solution is extracted three times with a total of 150 ml of methylene chloride. The organic layer is dried by passage through a glass column (5 × 1.5 in.) packed with granular anhydrous sodium sulfate (80 g). The column is then rinsed with 20 ml of fresh methylene chloride. The rinse is combined with the extracts, and the solvent is evaporated in a Buchi Rotovap at 38°C with a gentle stream of dry air just until dryness is attained. Since no oxidation of aldicarb to aldicarb sulfoxide or of the sulfoxide to the sulfone was observed under these conditions (*vide infra*) the above procedures were followed in all experiments. The residues are dissolved in 1 ml of acetone (1°C) and stored in the refrigerator for analysis by gas chromatography.

The quantitative analysis was carried out on a level 4 Hewlett-Packard 5880A gas chromatograph equipped with a splitless injection port and a nitrogen–phosphorus detector. A fused-silica wall-coated open tubular column coated with methyl silicone (12 m × 0.2 mm I.D.) supplied by Hewlett-Packard was used. The detector and injector port temperatures were maintained at 300 and 200°C, respectively, for the analysis of aldicarb and its oxidation products. Knaak *et al.*[8] in an earlier work used an injection port temperature of 350°C. We found that peak areas were sensitive to the injection port temperature and measured this variability from 125 to 350°C. As can be seen in Fig. 1, the optimum temperature for quantitative analysis of the three aldicarb species is 200°C.

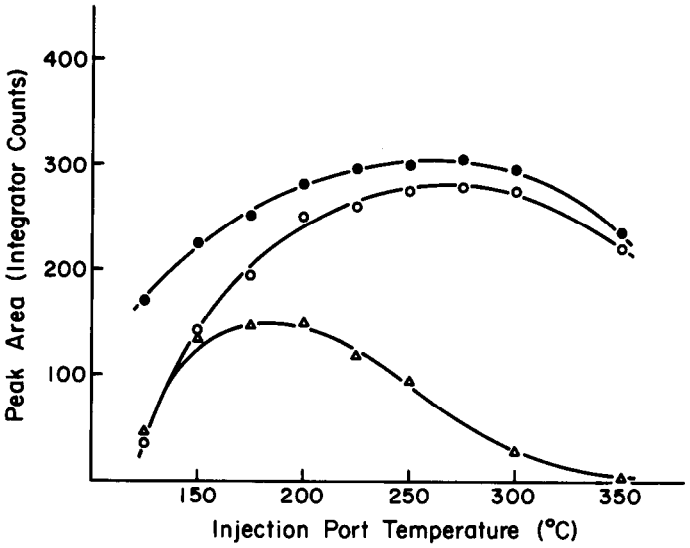

Fig. 1. Peak areas of aldicarb (●), aldicarb sulfoxide (△), and aldicarb sulfone (○) at varying injection port temperatures.

For analysis of carbofuran, the detector and injector temperatures were also 300 and 200°C, respectively, and the oven temperature was programmed from 100 to 190°C at a rate of 30°C/min. Oxamyl analyses were made with both injector and detector temperatures at 300°C and the oven temperature programmed from 50 to 120°C at 25°C/min intervals. Methomyl analyses were made with the injector at 200°C, the detector at 300°C and the oven temperature programmed from 100 to 170°C at 30°C/min intervals. Helium carrier gas was used at a flow-rate of 1.0 ml/min with a splitting ratio of 1:100. The detector auxiliary gas (helium), hydrogen gas and air flow-rate were 30 ml/min, 3 ml/min and 100 ml/min, respectively. Injections of 1 μl were made manually.

RESULTS AND DISCUSSION

Typical chromatograms of aldicarb, aldicarb sulfoxide and aldicarb sulfone, appear in Fig. 2A, B and C. Aldicarb, aldicarb sulfoxide and aldicarb sulfone are quantified as aldicarb nitrile, aldicarb sulfoxide nitrile, and aldicarb sulfone nitrile, respectively: the major thermal degradation products obtained with an injection temperature of 200°C. The identity of the decomposition products was determined by comparison of these chromatograms with those obtained by chromatographing the three nitrile standards. In addition, preliminary work using mass spectrometry confirms these results[9]. Reproducibility of peak area measurements for 1 and 2 ng injections at an injection temperature of 200°C is shown in Table I. Detection limits under the conditions used for these experiments was 0.1 ng. The detection limits can be lowered further by raising the temperature of the source in the nitrogen phosphorus detector, but this shortens lifetime.

A typical chromatogram of a mixture containing 2 μg/ml each of aldicarb,

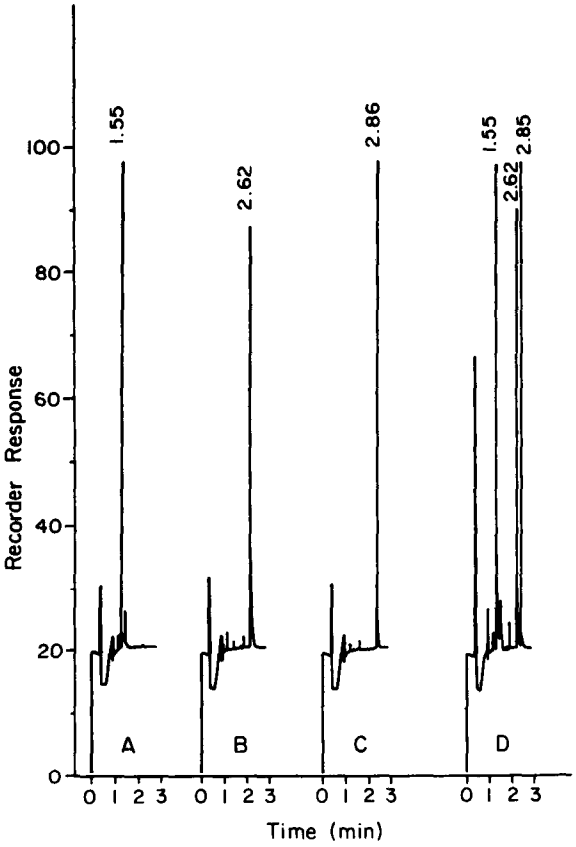

Fig. 2. (A) Aldicarb (2 ng), (B) aldicarb sulfoxide, (2 ng), (C) aldicarb sulfone (2 ng), (D) mixture of aldicarb, aldicarb sulfoxide and aldicarb sulfone (2 ng each). Oven temperature is programmed from 50 to 110°C at a rate of 25°C/min and held at the final temperature for 1 min. A post run to 200°C is made over a 4-min interval to clean the column.

TABLE I

PERCENT RELATIVE STANDARD DEVIATION OF PEAK AREAS (n = 4) AT AN INJECTION PORT TEMPERATURE OF 200°C

Compound	*Injection amount (ng)*	*Relative standard deviation (%)*
Aldicarb	1	2.11
	2	1.86
Aldicarb sulfoxide	1	2.22
	2	2.92
Aldicarb sulfone	1	2.38
	2	1.73

TABLE II

PERCENT RECOVERY OF ALDICARB AND ITS OXIDATION PRODUCTS FROM DISTILLED AND WELL WATER

Concentration (ppb)	*Aldicarb*		*Aldicarb sulfoxide*		*Aldicarb sulfone*	
	Distilled water	*Well water*	*Distilled water*	*Well water*	*Distilled water*	*Well water*
5	96.3	98.2	100	101	102	102
	97.3	96.7	98.4	104	100	105
10	96.5	97.5	98.6	99.5	104	103
	98.4	96.8	99.1	102	102	99.4
15	97.2	96.4	102	105	99.0	100
	96.1	96.9	97.5	98.8	104	104
20	97.9	97.8	99.0	100	104	98.5
	97.1	98.4	98.1	98.0	103	99.7

aldicarb sulfoxide and aldicarb sulfone is shown in Fig. 2D. By comparing peak areas obtained from injections of the individual compounds to those obtained from the mixture, it can be seen that there is no evidence of oxidation of the aldicarb or aldicarb sulfoxide to the next metabolite under the experimental conditions described. Five standard solutions containing 0.5, 1.0, 1.5, 2.0 and 2.5 μg/ml each of aldicarb, aldicarb sulfoxide and aldicarb sulfone gave linear calibration curves over a range from 0.1 to 5 μg/ml. The regression coefficients are 232 (r^2 = 0.999), 108 (r^2 = 0.997) and 213 (r^2 = 0.999) for aldicarb, aldicarb sulfoxide, and aldicarb-sulfone, respectively.

In addition, an experiment was carried out to determine the amount recovered by the extraction procedure for each metabolite in four standard aqueous solutions in both distilled water and well water ranging in concentration from 5 to 20 ppb. The results are illustrated in Table II. Recoveries ranged from 96 to 105%. There appears to be no difference in the recoveries from distilled water or well water. It is expected that this method would be quite effective when applied to environmental field studies. Further work on the effect of electrolytes, pH, and soil extraction is in process.

The high recoveries of aldicarb can only be achieved with slow evaporation of the solvent extract at a temperature less than 40°C. When evaporation is attempted at higher temperatures the aldicarb is easily oxidized to aldicarb sulfoxide. When the extraction is done without using sodium chloride to saturate the aqueous phase, the recovery of aldicarb sulfoxide is on the order of 80%. With the addition of sodium chloride at least 97% of this highly soluble metabolite is extracted from both distilled and well water.

A modified version of the same procedure was used to quantify nanogram quantities of carbofuran, oxamyl and methomyl. Each pesticide gave a major peak which can be calibrated for nanogram quantities. The retention times for carbofuran, oxamyl and methomyl were 4.00, 2.73 and 3.24 min, respectively.

In conclusion, the sensitivity and speed of capillary gas chromatography and the selective response of the nitrogen–phosphorus detector combine to provide an effective procedure for simultaneous quantitative analysis of aldicarb and its oxida-

tion products. It was also determined that an injection port temperature of 200°C converts all three species to nitriles which give reproducible and sensitive chromatogram peaks. The modified extraction procedure permits analysis of water samples with concentrations of aldicarb and its metabolites as low as 1 ppb. This method is easily adapted for analysis of the other carbamate pesticides studied: carbofuran, oxamyl and methomyl.

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