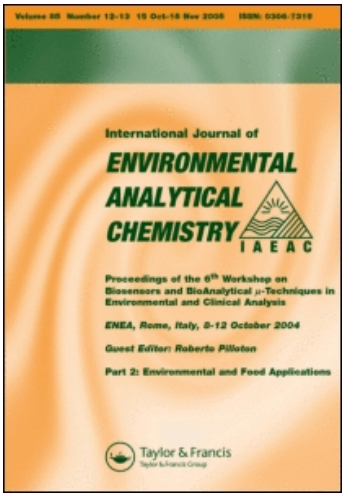

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Use of XAD-2 Macroreticular Resin for the Recovery of Aldicarb and its Metabolites in Drinking Water

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Use of XAD-2 Macroreticular Resin for the Recovery of Aldicarb and its Metabolites in Drinking Water

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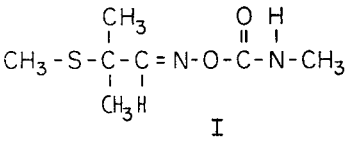
A simplified method for the determination of aldicarb and its oxidation products, aldicarb sulfoxide, and aldicarb sulfone, in water has been developed. Aldicarb and its metabolites are adsorbed on Amberlite XAD-2 polymer resin and then eluted with acetone. The eluate is analyzed for aldicarb and aldicarb sulfoxide by high performance liquid chromatography (HPLC) with UV detection at 254 nm. Total aldicarb residues can be determined by a colorimetric method. Typical detection limits in drinking water are 1 μg/l.

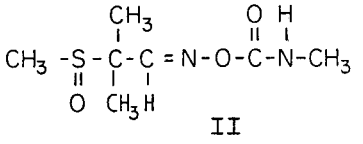
KEY WORDS: Aldicarb, XAD-2 Resin, HPLC, colorimetric method.

Aldicarb, 2-methyl-2-(methylthio) propionaldehyde-0-(methylcarbamoyl) oxime (Union Carbide 21149), is a widely used broad spectrum soil-applied systemic pesticide with insecticidal, acaricidal, and nematocidal properties.[1,2] Its chief mode of action appears to be cholinesterase inhibition.

Recently significant concentration of aldicarb (I), its sulfoxide (II), and sulfone (III) have been detected in large numbers of well water samples from Eastern Long Island, N.Y.[3] Since the concentration of these powerful cholinesterase inhibitors was often in excess of the NYS Department of Health guideline (7 μg/l), the need for a rapid low cost analysis that could be performed without using sophisticated equipment became apparent.



I



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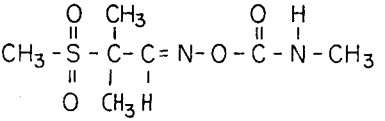

III

The existing gas chromatographic method[4-6] for the determination of aldicarb residues in water involves oxidation of aldicarb and aldicarb sulfoxide to aldicarb sulfone with peracetic acid followed by liquid–liquid extraction. The extract may further require a florisil clean-up before gas chromatography-detection is accomplished with a sulfur-specific flame photometric detector. The GC method, though comprehensive in methodology, is not well suited to residue analysis on a routine basis for several reasons. This procedure determines only the total combined concentration of aldicarb, its sulfoxide, and its sulfone, and not the concentration of individual metabolites. This is a significant disadvantage since aldicarb sulfone is a markedly weaker cholinesterase inhibitor than aldicarb and its sulfoxide.[2,7] Further, the oxidation step is laborious and uses a reagent that is unstable and not generally available. The liquid–liquid extraction requires a large volume of chloroform for efficient extraction (H_2O–$CHCl_3$ ratio 1:2.5).

In recent years it has been shown that macroreticular Amberlite XAD-2 resin, a low polarity styrene-divinyl benzene copolymer with high sorptive capacity, is an effective extractant for a wide variety of organics and pesticides from water.[8-14] The method described here consists of extraction of aldicarb residues from well water samples by XAD-2 resin. However, the large differences between the solubilities of aldicarb and aldicarb sulfoxide and aldicarb sulfone in water (0.6, 33 and 0.8 % at 25°C respectively) presented a peculiar problem and a considerable experimentation was needed for optimization of the recoveries.

A colorimetric method of Johnson and Stansbury[15] based on generation of hydroxylamine by base-acid catalyzed hydrolysis of aldicarb, followed

by oxidation of hydroxylamine by iodine to nitrous acid, and quantitation of the latter by diazotization and coupling was applied for the determination of total aldicarb residues on a routine basis. However, for an accurate toxicity assessment the colorimetric method by itself is not adequate since, like the gas chromatographic method, it does not distinguish among aldicarb and its oxidation products. Thus there is a need to supplement this method by a more sensitive analytical procedure which could be directly applied for the determination of toxic compounds. The analysis of carbamate pesticides by high performance liquid chromatography (HPLC) using several techniques has been reported by a number of workers. Most of these involve derivitizations prior to analysis.[16-21] Sparacino and Hines[22] carried out a detailed HPLC study of a number of intact carbamates including aldicarb, its sulfoxide, and its sulfone. However, these studies were performed with pure samples, free of potential interferences. Significant modification of the methodology was necessary before HPLC (Fig. 1) could be successfully applied to quantitation of aldicarb and its sulfoxide in well water at concentrations below 10 μg/l.

EXPERIMENTAL

Reagents and Apparatus

All solvents used were spectrograde. Pre-distilled water was redistilled in an all-glass apparatus. Aldicarb, aldicarb sulfoxide, and aldicarb sulfone standards (Union Carbide, Agricultural Product Division, Jacksonville, Florida) were used as supplied. XAD-2 polymer resin (Rohm and Hass) 20–50 mesh was first ground in a ball and roller mill and sieved to 60–100 mesh. It was purified[8,13] by sequential extraction with acetone, diethyl ether, chloroform, and methanol in a soxhlet extractor for 12 hours per solvent and stored in methanol.

A Perkin-Elmer 559 UV–Vis spectrophotometer was used for colorimetric measurements at 530 nm in a 1 cm cell, using water to zero the spectrophotometer.

High performance liquid chromatography (HPLC) was accomplished with two μ-Bondpak C_{18} reverse phase columns (30 cm × 3.9 mm i.d.) on a Waters ALC/GPC-244 liquid chromatograph equipped with a Model 6000A solvent delivery system, a Model U6K universal injector, a Model 660 solvent programmer and a Model 440 UV detector at 254 nm (0.01 AUFS) (all equipment of Waters Associate, Milford, Mass). The recorder was a OmniScribe strip chart recorder Model B 5217–1 (Houston Instrument, Austin, Texas). Injections of 25 μl were made with a 25 μl

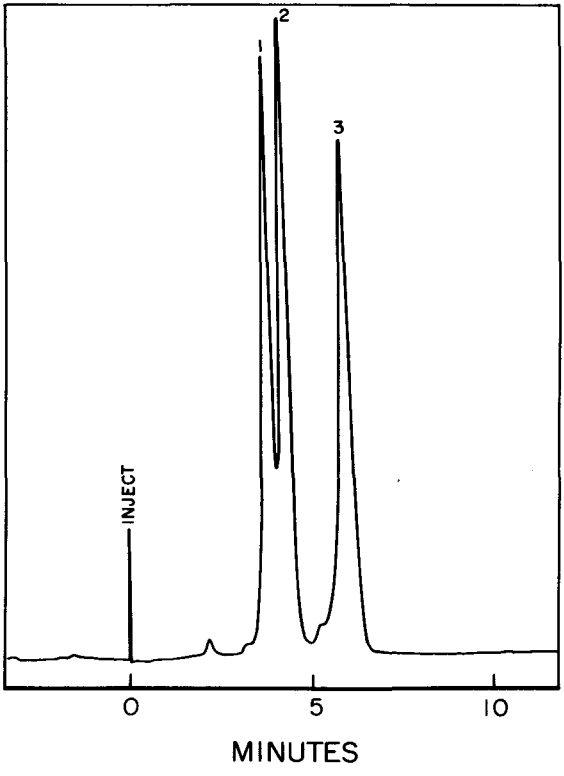

FIGURE 1 Separation of a mixture of aldicarb, aldicarb sulfoxide, and aldicarb sulfone. Chromatographic conditions. Column: two μ-Bondapak C_{18}; mobile phase: 60% CH_3CN in water; flow rate: 1.5 ml/min.; UV detector at 254 nm. (0.01 AUFS); Peaks: (1) = 0.4 μg Aldicarb Sulfoxide; (2) = 40 μg Aldicarb Sulfone; (3) = 0.4 μg Aldicarb.

syringe Model No. 802 (Hamilton) and the mobile phase was CH_3CN:H_2O (60:40) at a flow rate of 1.5 ml/min.

Analytical Procedure

Purified XAD-2 resin (25 ml) was poured as a methanolic slurry into a glass column (46 × 1 cm) plugged at the lower end with a silanized glass wool. A second silanized wool plug was inserted at the top of the resin bed and the methanol was drained until its level reached the top of the resin bed. A 500 ml reservoir was attached to the column and 300 ml of distilled water was poured in it. The reservoir was capped with a 24/40 ground glass joint adaptor connected to a nitrogen cylinder. A pressure of about 1 psi was applied using organic free nitrogen; water was allowed to

pass through the resin bed at a flow rate of 15–20 ml/min. The flow was stopped when the water level reached the top of the resin bed. Distilled water (333 ml), fortified with appropriate standard solution, was added to the reservoir and then drained through the column at a flow rate of 10 ml/min. After all the water had passed through the column, the resin bed was allowed to drain for 2–3 minutes. Acetone (100 ml) was added to the reservoir, a pressure of ~1 psi, was applied immediately and 6–8 ml of the effluent was collected. The stopcock was then closed and acetone was allowed to equilibrate with the resin bed for about ten minutes. This was run off and collected in a separate receiver. The flow was stopped when the acetone level reached the top of the resin bed. The first 6–8 ml of the effluent collected was extracted with methylene chloride (2 × 5 ml) and added to the acetone fraction. The combined extract was first concentrated to about 2–3 ml in a Kuderna–Danish apparatus on a steam bath, then blown gently to dryness, and diluted with acetonitrile to 0.5–1.0 ml.

It was first analyzed for aldicarb and aldicarb sulfoxide by reverse phase high performance liquid chromatography under the conditions mentioned previously. For the determination of total aldicarb residues the extract was again blown to dryness and subjected to colorimetric method. The column was regenerated, prior to reuse, by washing with about 300 ml of distilled water.

RESULTS AND DISCUSSION

Recovery studies were carried out on fortified distilled and well water samples in order to evaluate the overall performance of the XAD-2 polymer resin extraction technique and to compare it with liquid–liquid extraction (Table I). The mean recoveries at the 1 to 10 μg/l level determined by colorimetric method and high performance liquid chromatography ranged from $95 \pm 5\%$ and $95 \pm 3\%$, respectively. The volume of resin used for extraction and techniques for desorption are critical operations affecting recovery. Large volumes of the resin (>40 ml) resulted in good recovery of the aldicarb sulfoxide, the most soluble metabolite, but slightly reduced recovery of the aldicarb and its sulfone. A smaller volume of the resin (<15 ml) gave opposite results; considerable breakthrough of the aldicarb sulfoxide from the column was observed. A volume of 25 ml of resin gave maximum efficiency. The slightly reduced recovery of aldicarb and its sulfone from the large column bed is attributed due to poor desorption from the resin. A 60–100 mesh XAD-2 resin which provided a better packed and easier to handle column was preferred over the 30–60 mesh resin.

TABLE I
Recovery of aldicarb, aldicarb sulfoxide, and aldicarb sulfone from fortified distilled water[a]

Concentration added μg/l	Aldicarb recovered[b] %		Aldicarb sulfoxide recovered[b] %		Aldicarb sulfone recovered[b]
	I	II	I	II	I
0		0		0	0
1	95±5	97±1	92±4	92±3	94±3
3	94±6	93±2	95±6	99±2	94±6
6	94±7	95±3	94±6	93±3	94±6
10	93±8	96±2	98±8	98±2	96±7
Average	94±5	95±2	97±5	96±3	92±3
	Total average = I = 95±5				
		II = 95±3			

[a]Recoveries from fortified well water known to contain no aldicarb residues were within the range given above. (Average of three runs).
[b]Average of three runs.
I—Determined by colorimetric method.
II—Determined by HPLC.

The adsorption efficiency of the resin at 10 μg/l was tested in two ways. The water effluent from one column was passed through another column and then eluted with an excess of acetone (200 ml). Alternatively, the water effluent from the column was extracted with a large excess of chloroform (5 × 200 ml). Neither extracts showed detectable aldicarb, aldicarb sulfoxide, or aldicarb sulfone. Although diethyl ether is a commonly used solvent to elute adsorbed pesticides from XAD-2 resin[7, 8, 10] it proved inefficient in the present study. Several solvent systems were tested for their ability to elute adsorbed aldicarb and its metabolites from XAD-2 resin column. These include chloroform, acetone, acetone-diethyl ether, acetone-chloroform, methanol-chloroform, and acetone-ethyl acetate. Certain combinations gave better recoveries than could be obtained with diethyl ether but acetone alone proved to be most suitable solvent for elution. This reduced the handling steps and improved recoveries. Initially the acetone was allowed to equilibrate with the resin immediately after draining water from the column. But residual water co-eluted from the column with acetone causes problems in the work up and results in low recoveries. Removal of the residual water from the column and extraction with small amounts of methylene chloride (2 × 5 ml), prior to equilibration of the acetone with resin, increased aldicarb, aldicarb sulfoxide and aldicarb sulfone recoveries by 15–20%.

The quantitation of aldicarb and aldicarb sulfoxide by reverse phase high performance liquid chromatography using one μ-Bondpak C_{18} column was precluded by background interferences. However, resolution was improved considerably by using two μ-Bondpak C_{18} columns and a mixture of CH_3CN:H_2O (60:40) as a mobile phase instead of 15–60% CH_3CN in water in a step gradient. Under these conditions, aldicarb and its sulfoxide are adequately separated from background interferences.

The method developed was applied for the analysis of aldicarb, aldicarb sulfoxide and aldicarb sulfone in a number of well water samples from Long Island, N.Y. (Table II).

TABLE II
Determination of aldicarb, aldicarb sulfoxide, and aldicarb sulfone in well water samples

Sample #	Aldicarb[a] μg/l	Aldicarb[a] sulfoxide μg/l	Total Aldicarb[b] residues μg/l
1	N.D.	3.0	20.0
2	N.D.	2.4	12.0
3	N.D.	3.0	12.0
4	N.D.	23.1	43.5
5	N.D.	2.5	9.0

[a]Determined by HPLC.
[b]Determined by Colorimetric method.
N.D. = None detected.

CONCLUSIONS

The extraction of aldicarb, its sulfoxide, and its sulfone from water with Amberlite XAD-2 polymer resin is superior to liquid–liquid extraction since it eliminates the use and disposal of large volumes of toxic solvent. HPLC, with UV detection at 254 nm is sufficiently sensitive to permit detection and quantitation of aldicarb and aldicarb sulfoxide in drinking water at levels well below the N.Y. State guidelines (the estimated detection limit is 12 ng/injection). This technique possesses some advantages over the conventional gas chromatographic procedure since it requires less sample preparation (oxidation step is omitted) and allows direct and independent quantitation of aldicarb and its sulfoxide, both powerful cholinesterase inhibitors. HPLC, with UV detection at 254 nm,[22] is insufficiently sensitive for the determination of the less potent aldicarb sulfone (estimated detection limit 2–3 μg/injection). However, since the total aldicarb can be quantitated either by the colorimetric method

described here or by the standard gas chromatographic method, the sulfone concentration can be readily calculated.

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