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## EVALUATION OF AMBERLITE XAD-2 AS THE EXTRACTANT FOR CARBAMATE INSECTICIDES FROM NATURAL WATER

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### SUMMARY

A rapid and sensitive analytical technique to quantify carbamate insecticides at nanogram levels is reported using resin column and sorption, and desorption followed by N-P gas-liquid chromatography (GLC) analysis. The carbamates were extracted from natural water by percolation through a column of Amberlite XAD-2, followed by elution with ethyl acetate. The carbamate residues were directly analyzed by GLC with a Tracor Model 702 N-P detector. The recoveries for several carbamates including aminocarb, mexacarbate, carbaryl, propoxur, carbofuran, pirimicarb and methiocarb were from 86 to 108% at 1.0 and 0.01 ppm levels. Only 41 to 58% was recovered for methomyl.

The extraction efficiency of Amberlite XAD-2 was pH-dependent as indicated in the extraction of aminocarb. More than 90% of the added aminocarb was recovered from phosphate buffer by the described method at pH 5.0 to 7.5 at 5.0 and 0.5 ppm levels.

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### INTRODUCTION

The use of carbamate insecticides for pest control has increased steadily in the past few years after the phasing out of organochlorine insecticides due to their biomagnification in the food chain and adverse effect on the ecosystem. Aminocarb, 4-dimethylamino-*m*-tolyl N-methylcarbamate, a broad spectrum non-systemic insecticide, has been used in large scale aerial spraying in eastern Canada for spruce budworm control since 1976<sup>1,2</sup>. Other carbamates such as carbaryl (1-naphthyl N-methylcarbamate), carbofuran (2,3-dihydro-2,2-dimethyl benzofuran-7-yl methylcarbamate), methomyl (S-methyl N-[(methylcarbamoyl)-oxy] thioacetimidate), mexacarbate (4-dimethylamino-3,5-xylol methylcarbamate) and propoxur (*o*-isopropoxyphenyl N-methylcarbamate) have been used for controlling various forest pests on an experimental scale<sup>3</sup>. A rapid and sensitive method for the extraction and analysis of these carbamates is required for the environmental monitoring program in forestry.

Amberlite XAD-2® (Rohm & Haas, Philadelphia, Pa., U.S.A.), a synthetic non-polar macroreticular styrene-divinylbenzene copolymer, has been used successfully

in column chromatography for the extraction of drugs and organic contaminants from aqueous systems at trace levels<sup>4-7</sup>. Coburn *et al.*<sup>8</sup> reported the use of XAD-2 for multiresidue extraction of organochlorine pesticides and polychlorinated biphenyls from natural waters. Also, fenitrothion and the hydrolytic products of some organophosphorus insecticides were successfully extracted from water with this resin<sup>9,10</sup>. An evaluation of Amberlite XAD-2 resin as the extractant for several carbamate insecticides is reported in this paper. Using aminocarb as an example of the carbamate group of insecticides, the effect of pH was also investigated.

## EXPERIMENTAL

### *Preparation of Amberlite XAD-2 column*

Shell type Pyrex glass columns (35 × 1.5 cm O.D.) with reservoir, sealed-in coarse fritted disc and PTFE stopcock were used in this study. An amount of 2.5 g of Amberlite XAD-2 resin was suspended in 50 ml distilled water and after the resin had settled down, the supernatant was discarded. This procedure was repeated several times more until all the attrition fines had been removed. The resin-water slurry was slowly poured into the chromatographic columns to form an adsorption bed of about 6.5 cm. The columns were rinsed with methanol (2 × 20 ml) followed by distilled water (3 × 50 ml) and the water level maintained at about 1 cm above the resin bed until the introduction of natural water containing carbamate insecticides.

### *Preparation of carbamate insecticide standards and phosphate buffers*

The carbamate insecticides used in this study were aminocarb, mexacarbate, carbofuran, propoxur, carbaryl, methomyl, pirimcarb (2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyl dimethylcarbamate) and methiocarb (4-(methylthio)-3,5-xylyl N-methylcarbamate). Stock solutions in acetone (1000 µg/ml) were prepared from these carbamates (analytical grade) for the fortification of water samples.

Phosphate buffers of pH 3.0, 4.0, 5.0, 6.0, 7.5 and 9.0 were prepared by titration with 0.2 M solutions of mono-, di- and tribasic sodium phosphate and phosphoric acid for the study of the effect of pH on the extraction efficiency.

### *Extraction of carbamate insecticides from natural waters*

Natural waters were collected from the St. Mary's River near the Sault Lock, and from the Root River in Sault Ste. Marie, Ontario. The natural waters were stored in clean 20-l Nalgene bottles. The pH of the samples ranged from 6.4 to 6.8.

Four 1000-ml aliquots of natural water were fortified by adding 1.0 ml of the acetone solution containing 1000 µg/ml or 10 µg/ml of the carbamate insecticide to give a concentration of 1.0 or 0.01 ppm. The fortified water samples were shaken well and allowed to equilibrate for 30 min. Then they were allowed separately to pass through the Amberlite XAD-2 columns by gravitation at the rate of 20 ml/min. After completion of the elution, the residual water was removed from the columns under aspiration for 5 min. The erlenmeyer flasks containing the water samples were thoroughly rinsed with pesticide-grade ethyl acetate (2 × 10 ml) and the rinsings were transferred to the resin columns. A 40-ml volume of ethyl acetate was used for eluting the carbamates from the resin columns at the rate of 10 ml/min. Each ethyl acetate eluate was dried by passing through a column of granular anhy-

drous sodium sulfate (10 g). The sodium sulfate columns were then washed with ethyl acetate ( $2 \times 10$  ml) and the combined eluates evaporated gently to dryness in the flash evaporator at  $40^\circ$ . The residues of carbamates were dissolved in a known volume of ethyl acetate or acetone for gas-liquid chromatographic (GLC) analysis.

*The effect of pH on the extraction efficiency of Amberlite XAD-2 resin*

Four 100-ml aliquots of phosphate buffer were fortified by adding 0.5 ml of the acetone solution containing 1000  $\mu\text{g/ml}$  or 100  $\mu\text{g/ml}$  aminocarb to give a concentration of 5.0 or 0.5 ppm. After equilibration, the aminocarb residues were extracted from the buffer as described above.

*GLC analysis*

A Tracor Model 550 gas chromatograph, equipped with a Hall 310 electrolytic conductivity detector and a Model 702 N-P detector was used for the analysis of carbamate residues present in the extracts of water samples. Three Pyrex glass columns (75 cm  $\times$  4.0 mm I.D.) were used: (1) 1.95% QF-1 plus 1.5% OV-17, (2) 3% OV-25 and (3) 3% Carbowax 20M TPA; all on Chromosorb W HP, 80-100 mesh. The operating conditions are given in Table I.

TABLE I  
OPERATING CONDITIONS FOR GLC

Parameter	Hall 310 electrolytic conductivity detector	Tracor Model 702 N-P detector
Detector temperature	$850^\circ$	$240^\circ$
Inlet temperature	$210^\circ$	$210^\circ$
Outlet temperature	$300^\circ$	$210^\circ$
Column temperature	$160^\circ$	$160^\circ$
Carrier gas (helium) flow-rate	80 ml/min	80 ml/min
Reaction gas (hydrogen) flow-rate	20 ml/min	—
Solvent flow-rate	50% isopropanol in distilled deionized water at 1 ml/min	—
Plasma gas flow-rate	—	hydrogen 2.5 ml/min air 120 ml/min

Calibration curves were prepared daily before and after sample analysis to confirm the stability of the detectors. Quantification of carbamates was based on external standardization.

*Regeneration of the Amberlite XAD-2 column*

After each extraction of the carbamate residues, the Amberlite XAD-2 columns were regenerated by washing with methanol ( $2 \times 10$  ml) followed by distilled water ( $3 \times 100$  ml). The columns did not show any noticeable signs of deterioration and were reused for the extraction of carbamate residues from natural waters.

RESULTS AND DISCUSSION

*Influence of pH on the extraction of aminocarb residues*

The results obtained for the extraction of aminocarb residues from phosphate

buffers (pH 3.0 to 9.0) by Amberlite XAD-2 columns are given in Table II. The recoveries of the insecticide at 0.50- and 5.00-ppm levels above pH 4.0 were 91–104%. The results were reproducible as indicated by the small standard deviation for the four replicates in each extraction study. However, at acidic pH, namely 3.0 and 4.0, the Amberlite XAD-2 did not adsorb all aminocarb residues present in the water. At concentration levels of 0.5 and 5.0 ppm, only 62 and 52% of the fortified aminocarb were extracted by the resin columns. The unadsorbed aminocarb residues present in the water samples were quantitatively recovered by neutralizing the samples with saturated aqueous sodium carbonate solution, re-percolating the water through the same resin columns and eluting with ethyl acetate. The lower extraction efficiency of Amberlite XAD-2 for aminocarb residues at low pH was probably due to the formation of quarternary ammonium ion ( $R_2R'NH^+$ ) from the parent molecule by protonation, thus decreasing the hydrophobic nature of the molecule. The extent of adsorption of the aminocarb molecule on the resin column depended upon its hydrophobicity and since the formation of ionic species at low pH destroyed this property, the insecticide residues were not readily adsorbed on the resin columns. Consequently, low recovery was obtained. To extract quantitatively aminocarb or other carbamate residues from water with Amberlite XAD-2, the pH of the water should be at or near neutral.

TABLE II

## RECOVERY OF AMINOCARB FROM AMBERLITE XAD-2 AT VARIOUS pH LEVELS

$\bar{X}$  = mean recovery; S.D. = standard deviation ( $n = 4$ )

pH	Aminocarb fortification (ppm)	
	0.50	5.00
	$\bar{X} \pm S.D. (\%)$	$\bar{X} \pm S.D. (\%)$
3.0	61.8 $\pm$ 5.99	51.8 $\pm$ 5.12
4.0	89.1 $\pm$ 1.84	83.8 $\pm$ 6.03
5.0	91.5 $\pm$ 4.82	98.0 $\pm$ 5.41
6.0	101 $\pm$ 1.15	103 $\pm$ 2.45
7.5	104 $\pm$ 3.23	97.2 $\pm$ 4.00
9.0	98.5 $\pm$ 1.91	104 $\pm$ 4.03

*Recovery of carbamates from natural water*

Eight carbamates, namely aminocarb, mexacarbate, carbaryl, propoxur, carbofuran, pirimicarb, methiocarb and methomyl were extracted from natural water by Amberlite XAD-2 columns. Except for methomyl, the recoveries were better than 85% (Table III). They ranged from 91.4 to 106% at 1.0-ppm level and 86.4 to 108% at 0.01-ppm level (Table III). However, the recovery for methomyl was poor. At 1.0- and 0.01-ppm levels, only 58.4 and 41.7% respectively were recovered from natural water (Table III). It is known that methomyl is soluble in water. At 25°, its solubility in water is 5.8 g/100 ml (ref. 11). The poor extraction efficiency of Amberlite XAD-2 for methomyl may well have been due to its water solubility as the extent of adsorption of the solute molecules on the resin depended upon the hydrophobicity of the solute. Other adsorbents such as Amberlite XAD-7 and

XAD-8, which are capable of retaining both hydrophobic and hydrophilic solute molecules from the aqueous medium, could be used for the extraction of methomyl and other water soluble carbamates.

TABLE III

## RECOVERY OF CARBAMATE PESTICIDES FROM NATURAL WATER

$\bar{X}$  = mean recovery; S.D. = standard deviation ( $n = 4$ )

Compound	Fortification (ppm)	
	1.0	0.01
	$\bar{X} \pm S.D. (%)$	$\bar{X} \pm S.D. (%)$
Aminocarb	103 $\pm$ 2.00	98.0 $\pm$ 3.00
Mexacarbate	91.4 $\pm$ 1.69	101 $\pm$ 2.73
Carbaryl	91.5 $\pm$ 1.32	108 $\pm$ 2.86
Propoxur	102 $\pm$ 2.22	94.5 $\pm$ 11.0
Carbofuran	95.3 $\pm$ 0.96	97.8 $\pm$ 9.74
Pirimicarb	106 $\pm$ 7.76	88.3 $\pm$ 6.24
Methiocarb	105 $\pm$ 1.63	86.4 $\pm$ 3.25
Methomyl	58.4 $\pm$ 5.91	41.7 $\pm$ 3.05

Coburn *et al.*<sup>12</sup> reported a procedure for the extraction and analysis of N-methyl carbamates in natural water. Their procedure involved the extraction at pH 3–4 by solvent partitioning with methylene chloride, salting out with sodium sulfate, hydrolysis of the extracts by methanolic potassium hydroxide to form the corresponding phenols, re-extraction of the phenols at pH  $\leq$  2 with methylene chloride, chemical derivatization with pentafluorobenzyl bromide (PFB) to form the PFB ether derivatives, clean-up on a silica gel microcolumn and analysis by GLC–electron-capture detection. Their recoveries were from 87 to 98% for several carbamates, namely propoxur, carbofuran, 3-ketocarbofuran, metmercapturon, carbaryl and mobam. However, their procedure required considerably longer analysis times. Furthermore, the determination of mexacarbate and aminocarb was not possible with this procedure as their phenolic products obtained on hydrolysis were not extracted from the acidified media. Since the sensitivity and stability of the alkali flame-ionization detector has been greatly improved in the past few years, the method described in this paper provides a simple, time and labor saving approach to the extraction and analysis of carbamates from natural water at the sub-part per billion ( $10^{-9}$ ) level.

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