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Isolation and Analysis of Aminocarb and its Phenol from Environmental Waters

by

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ABSTRACT

Recovery of aminocarb (4-dimethylamino-m-tolyl methylcarbamate) and its phenolic metabolite [aminocarb phenol, (4-dimethylamino-m-cresol)] from aqueous solution by column chromatography on Amberlite XAD-2 resin was investigated. Adsorption of the chemicals onto the column was influenced by the pH of the solution and a correlation existed between recovery levels and pH. The adsorbed parent material was stable in the column for 2 weeks. Desorption of the materials from the resin column by suitable solvent elution and quantitation by Hall gas-liquid chromatography (GLC) showed near quantitative recoveries for the parent material. Optimization of experimental conditions, column and GLC parameters, recovery levels, standard deviations and minimum detection levels of the chemicals are discussed. The procedure developed is simple and readily applicable to environmental monitoring and quality control programs.

RESUME

On a étudié la récupération de l'aminocarb (4-diméthylamino-m-tolyl méthylcarbamate) et de son métabolite phénolique [aminocarb phénol, (4-dimethylamino-m-crésol)] à partir d'une solution aqueuse, par chromatographie sur colonne de résine Amberlite XAD-2. L'adsorption des composés chimiques sur la colonne subissait l'effet du pH de la solution et il existe une corrélation entre les taux de récupération et le pH. La substance apparentée adsorbée est demeurée stable dans la colonne pendant deux semaines. La désorption des substances de la colonne de resine, par élution avec un solvant approprié, et la détermination quantitative par chromatographie (de partage) gaz-liquide (GLC) Hall ont révélé des récupérations quantitatives presque totales pour la substance apparentée. L'optimisation des conditions expérimentales, la colonne utilisée, les paramètres de la chromatographie gaz-liquide, les taux de récupération, les écarts-type et les taux minimums décelables de produits chimiques sont traités dans cet article. Le mode opératoire mis au point est simple et facilement applicable aux programmes de surveillance du milieu, et de contrôle de la qualité.

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INTRODUCTION

The forests of Canada, covering nearly half of the land area (43.2×10^6 ha), are an important renewable natural resource which contributes significantly to the national economy and well-being of all Canadians. The forests support a large manufacturing industry which not only provides a sizable portion of Canada's total exports but also offers extensive employment and income opportunities. Frequent outbreaks of insect pests are a significant threat to our forest resources and consequently effective and environmentally acceptable pest control practices are required to minimize such losses.

The spruce budworm (Choristoneura fumiferana Clemens) is a severe defoliatior of fir (Abies) and spruce (Picea) forests and is presently epidemic in Eastern North America. Aerial application of effective and less persistent insecticides that cause minimum ecological disturbance, is the most powerful tool currently available to reduce spruce budworm-occasioned losses to acceptable levels. Consequently, various labile organophosphorus and carbamate insecticides are currently being sprayed on the forest environment over vast areas. However, it is recognized that the chemicals dispersed may have a long-term detrimental effect on many non-target physical and biological resources in the natural environment. Although controversy exists at present on the reliance on, and extensive use of, chemical pesticides, the benefits from using them far exceed the risk

involved provided that the spray programs are adequately planned, managed, monitored and properly assessed for any side-effects on non-target resources in the environment.

The chemical insecticide, aminocarb (4-dimethylamino-m-tolyl methylcarbamate; trade name: Matacil) is one of the most promising materials and has proven highly effective in field experiments and at operational levels. The chemical has been aerially sprayed in increasing amounts on budworm infested forests in Canada since 1973 usually at a dosage rate of 0.070 kg AI in 1.46 l of an oil solution/ha. At this rate, budworm larval populations have been reduced by 70-80 percent after a single and 95 percent and above after second application against third and fourth instar larvae (Kettela et al., 1977) with good foliage protection resulting. Although the insecticide is effective, its environmental effects, especially its distribution, persistence, cycling, toxicity, metabolism and ultimate fate and accountability in different components of the forest environment including non-target organisms are not yet fully explored. Knowledge in these areas is essential in order to determine environmental and ecological damage. As a result, the Toxic Chemicals Section at the Forest Pest Management Institute, Canadian Forestry Service, Department of Fisheries and the Environment, launched a research program to find answers for some of the problems involved in assessing the overall accountability of aminocarb in the ecosystem. Begun in early 1975, the work has already resulted in new information on the fate and persistence of this chemical in some of the components of the forest environment that can be worked into practical

guidelines for forest management and insect control. This report summarizes the substantial progress made recently in the development of analytical methods for aminocarb and its phenolic metabolite, their recovery and stability in different types of water samples (pure, potable and natural) at various pH levels.

The monitoring and quantitative evaluation of aerially sprayed insecticides deposited on surface waters in the forest environment are relatively more difficult than, for example, water samples derived from agricultural spray programs. Inherent difficulties include obtaining, storing and transporting samples, usually from remote forest areas, without degradation, if labile insecticides are involved, to residue laboratories for analysis. Considerable research is necessary to minimize these problems and to establish a standardized approach to sampling, storage and transportation methods required for monitoring of residues present in natural waters from the forest environment. Further, environmental waters normally contain various volatile and nonvolatile organic impurities and when contaminated by insecticides, isolating the latter from natural impurities and studying their persistence especially when they are present in trace amounts, is quite difficult and challenging.

Amberlite XAD-2 (registered trademark of Rohm and Haas, Philadelphia, PA), a synthetic nonpolar macroreticular styrene-divinylbenzene copolymer, has been used extensively since 1970 in column chromatography for the isolation and recovery of trace levels of various organic materials from aqueous systems (Fujimoto and Wang,

1970; Burham et al., 1972; Stolman and Pranitis, 1977; Gelbke et al., 1978). After Musty and Nickless (1974) and Junk et al. (1974) first reported on the use of column chromatography on Amberlite XAD-2 for the isolation and quantification of organochlorine insecticides and polychlorinated biphenyls from water, Coburn et al. (1977) extended the technique to develop a multiresidue method for the quantitative determination of these materials in natural waters. Quantitative experiments were also carried out by Richard et al. (1975) to determine some chlorinated insecticides and herbicides present in various Iowa water samples.

Daughton et al. (1976) showed that various organophosphate insecticides and their hydrolytic products in water were adsorbed readily and selectively by the nonionic Amberlite resin and could be separated into their individual components by selective elution. They were subsequently quantified by suitable analytical methods. Highly satisfactory results were thereby obtained concerning the practicability of this technique as well as the separation and recovery of various types of pesticides after Amberlite resin treatment of the water. These findings prompted Berkane et al. (1977) to extend the application of the Amberlite XAD-2 procedure to natural water samples containing fenitrothion (O,O-dimethyl O-4-nitro-m-tolyl phosphorothioate), an organophosphorus insecticide extensively used in budworm control operations in Canada. They amply demonstrated that by using the Amberlite XAD-2 column, not only could fenitrothion be separated quantitatively from aqueous environmental samples collected from spray area but also the adsorbed in-

secticide is stable on the column for extended periods of time, thus making the procedure suitable as a preservation technique.

Because of the above mentioned investigations, it was felt that the Amberlite XAD-2 technique might prove to be a valuable tool for monitoring trace levels of aminocarb present in natural waters sampled from forest areas following aerial applications of this insecticide. In the present study, we found that among the various adsorbents used to remove aminocarb from water, Amberlite XAD-2 resin was a very useful trapping medium because of its high affinity for the chemicals and low affinity for water. Once the isolation had been completed, the adsorbed insecticide was found to be stable on the column at ambient temperature for two weeks. It was subsequently eluted by using a suitable solvent, identified and quantified by gas chromatography. The technique developed is simple, reliable and easy to adapt to forestry situations and could be used routinely to sample surface waters from spray areas by chemists, field biologists, ecologists and limnologists involved in large scale investigation of the fate of the chemical in a hydrologic environment.

MATERIALS AND METHODS

1. Apparatus and Reagents Used In This Study

Evaporative Concentrator:	Buchi Rotavapor-RE Flash-evaporator
Chromatographic Columns:	1.5 cm o.d. x 35 cm Shell type Pyrex glass column with reservoir, sealed-in coarse fritted disc to support column packing and teflon stopcock for column flow control.
Amberlite XAD-2 Resin:	Manufactured by Rohm and Haas Co., U.S.A. and supplied by BDH, Toronto, Ont.
Sodium sulfate (Anhydrous):	Fisher S-421, heated overnight to ca 200°C, cooled and stored in air-tight bottles.
Phosphoric acid	Fisher A-242, 85%, ACS certified.
Sodium phosphate-monobasic, $NaH_2PO_4.H_2O$	Fisher S-369, ACS certified
Sodium phosphate-dibasic, Na_2HPO_4	Fisher S-374, ACS certified
Sodium phosphate-tribasic, $Na_3PO_4.12H_2O$	Fisher S-377, ACS certified
Solvents	Methanol, ethyl acetate, benzene, chloroform and acetonitrile are pesticide grade solvents supplied by Caledon Laboratories Ltd.
pH Meter	Fisher Accumet® Model 320
Gas Chromatograph	Tracor model 550 equipped with a Tracor 310 Hall electrolytic conductivity detector.

2. Preparation of Amberlite XAD-2 Column

Two and one-half grams of resin were suspended in 50 ml distilled water and after the material had settled down, the supernatant was discarded. The procedure was repeated once more and the resin-water slurry was slowly poured into the chromatographic column to form an

adsorption bed of ca 6.5 cm (Fig. 1). The column was rinsed with 2 x 20 ml of methanol followed by 3 x 50 ml of distilled water and the water level was maintained at about 1 cm above the XAD-2 resin bed until the introduction of environmental water samples containing aminocarb.

Subsequent studies showed that instead of using the expensive Shell type adsorption columns, laboratory burettes, general purpose chromatographic columns etc. could be used successfully by inserting small glass-wool plugs instead of sintered glass filter to hold the resin bed.

3. Preparation of Phosphate Buffers

Bulk quantities of 0.2 M solutions of mono, di- and tribasic sodium phosphates and phosphoric acid were prepared in distilled water and their pH measured. The values obtained were respectively 4.5, 9.2, 11.7 and 1.6. Measured quantities of the acid and various volumes of one or more of the salt solutions were mixed with distilled water to yield bulk quantities of 7 buffer solutions named respectively as A to G with pH's 3.0, 4.0, 5.0, 6.0, 7.5, 8.0 and 9.0. The pH's of these solutions were checked with a pH meter. The buffer solutions were stored in tightly sealed plastic bottles at 4°C to protect from carbon dioxide and mold formation.

4. Sampling of Natural Water

Natural water was collected in bulk on a single occasion from the St. Mary's River near the Sault Lock, Sault Ste. Marie,

Ontario and stored in a clean 20 l Nalgene bottle. The water sample was taken downstream to industrial plants whose effluents contributed to the organic content of the river.

5. Preparation of Aminocarb and its Phenol Standards

Analytical grade aminocarb and its phenol were obtained from Chemagro Chemical Company Ltd., Mississauga, Ont., and stock solutions in acetone (1 µg/µl were prepared to fortify the water samples used in the study.

6. Fortification of Water Samples

Two sets of recovery experiments, one for aminocarb and another for its phenol, in potable (tap) water, river water and buffer solutions were conducted in quadriplicate. Experimental conditions (volume of aqueous samples used, their pH values, fortification levels of the toxicants etc.) are summarized in Table I. All water and buffer solutions were fortified by adding 0.5 ml of acetone solution containing 1000 µg/ml, 100 µg/ml or 10 µg/ml of aminocarb and its phenolic metabolite separately. These solutions were shaken well and allowed to equilibrate for 30 min before the isolation of the chemicals from the systems using Amberlite XAD-2 resin column chromatography.

7. Recovery studies

One hundred-ml aliquots of phosphate buffers containing either 0.50 or 5.0 ppm of aminocarb, or 0.50 ppm of aminocarb phenol; 1,000-ml aliquots of tap water and natural water containing 0.01 ppm of aminocarb and 0.10 ppm of its phenol were allowed

separately to pass through the XAD-2 resin columns by gravitation at the rate of 20 ml/min. Application of slight vacuum to increase the flow rate to ca 100 ml/min did not affect the adsorption efficiency of the resin and hence percent recovery when the residue concentration was low but a slow flow rate was preferred when the fortification level was high. After completion of elution, the residual water was removed from the columns under aspiration for 5 min. The conical flasks containing the water samples were thoroughly rinsed with 2 x 10 ml of ethyl acetate and the rinsings were transferred to the XAD-2 resin columns. Fifty ml of ethyl acetate were used for eluting aminocarb from the columns at the rate of about 15 ml/min. The ethyl acetate eluates were dried by passing through chromatographic columns (2.5 cm o.d. x 20 cm) packed with 8 cm anhydrous sodium sulfate. The sodium sulfate columns were then washed with 20 ml of ethyl acetate and the combined eluates evaporated gently to dryness in the flash evaporator at 40°C. The residues of aminocarb and its phenol were dissolved in a known volume of benzene for GLC (gas liquid chromatographic) analysis.

Although other solvents such as dichloromethane, benzene, acentonitrile, chloroform etc. generally yielded satisfactory results, the use of ethyl acetate was preferred in this study for its moderate polarity and volatility.

Buffer solutions with pH 3 and 4 containing aminocarb showed less than 80% recovery of the insecticide probably due to the formation

of cationic species that were not retained on the column bed. These column eluates were carefully neutralized with saturated sodium carbonate solution to a pH of 7.5 and repercolated through the same resin column to obtain acceptable recovery levels. Similarly the phenol metabolite showed poor recoveries due to the formation of cationic and anionic species respectively outside the pH range 6.0 to 8.0. Careful neutralization of the column eluates with either hydronium or hydroxyl ions to a pH of 7.5 and recirculation through the same resin column for adsorption gave near quantitative recoveries.

8. Stability Study of Aminocarb and Its Phenol on the Column

One thousand ml of the tap and river water samples containing 0.01 ppm of aminocarb and aminocarb phenol were allowed to pass through different XAD-2 resin columns. When the water had completely drained, the columns were either stoppered or a glass-wool plug inserted on the top of resin bed, wrapped in aluminum foil to protect from light and stored at room temperature. The residues of aminocarb and its phenol were eluted from the columns by the procedure described after 7 and 14 day intervals and analyzed by GLC.

9. Regeneration of the XAD-2 Resin Column

After each extraction of aminocarb and its phenol residues, the XAD-2 resin columns were regenerated by washing twice with 10 ml of methanol and three times with 50 ml of distilled water. The columns did not show any noticeable signs of de-

terioration and were reused for further recovery studies.

10. Gas Liquid Chromatographic (GLC) Analysis

A Tracor Model 550 gas liquid chromatograph, equipped with a Hall 310 electrolytic conductivity detector was used for the analysis of aminocarb residues present in the extracts of water. The operating parameters are given in Table II.

The gas chromatograph was standardized on the same day as the samples were analyzed. Aliquots (1-4 µl) of analytical grade aminocarb and its phenol standards in benzene (5 µg/ml) were injected and calibration curves prepared by plotting the peak heights vs concentration. The calibrations were checked before and after each sample analysis to confirm the stability of the gas liquid chromatograph. Quantification of aminocarb and its metabolite were based on external standardization.

TABLE I

Experimental Conditions in Recovery Studies

Aqueous samples	pH	Vol. of Samples Used in spiking (ml)	Fortification levels of aminocarb (ppm)	Fortification levels of aminocarb phenol (ppm)
Potable water	8.4	1000	0.01	0.10
River water	7.5	1000	0.01	0.10
Buffer solution A	3.0	100	5.0 and 0.50	0,50
" B	4.0	100	5.0 and 0.50	0,50
" C	5.0	100	5.0 and 0.50	0,50
" D	6.0	100	5.0 and 0.50	0.50
" E	7.5	100	5.0 and 0.50	0,50
" F	8.0	100	5.0 and 0.50	0.50
" G	9.0	100	5.0 and 0.50	0.50

TABLE II

Gas Chromatographic Parameters

Gas Chromatograph	: Tracor (Model 550).
Detector	: Tracor (Model 310) Hall electrolytic conductivity detector (Nitrogen Mode).
Column	: 75 cm x 6.3 mm O.D. pyrex glass packed with 1.95% QF1 plus 1.5% OV17 on Gas-Chrom Q mesh 80/100.
Solvent	: 50% Isopropanol in distilled de-ionized water.
Solvent Flow Rate	: 1 ml/min.
Column Oven Temperature	: 155°C (aminocarb), 125°C (aminocarb phenol).
Injection Port Temperature	: 210°C.
Outlet Temperature	: 310°C.
Carrier Gas (Helium) Flow Rate	: 80 ml/min.
Reaction Gas (Hydrogen) Flow Rate	: 20 ml/min.
Attenuation	: 2
Range	: 1
Recorder	: Linear Instruments Model 261/MM, 1 mV
Chart Speed	: 76 cm/h
Retention Time (min)	
Aminocarb	: 3.0
Aminocarb phenol	: 1.0

TABLE III

Percent Recovery* of Aminocarb and its Phenol from Phosphate Buffer Solutions After Column Chromatography on Amberlite XAD-2 at various pH Levels

pH	Aminocarb Fortification Level (ppm)		Aminocarb Phenol Fortification Level (ppm)
	0.50	5.00	0.50
3.0	62 ± 5**	52 ± 4**	6 ± 2**
4.0	89 ± 2**	84 ± 5**	27 ± 2**
5.0	91 ± 4	98 ± 5	44 ± 7**
6.0	101 ± 1	103 ± 2	75 ± 8**
7.5	104 ± 3	97 ± 4	95 ± 3
8.0	-	-	88 ± 4
9.0	98 ± 2	104 ± 4	84 ± 3

* Average of four replicates

** Neutralization of the eluate with Na_2CO_3 (aq) to pH 7.5 and recirculation on the resin column gave near theoretical recoveries for aminocarb and ca 85% for the phenol. Minimum detection limit 1×10^{-4} ppm

TABLE IV

Percent Recovery* of Aminocarb and Its Phenol from Potable and River Waters After Using XAD-2 Amberlite Resin

Water Samples	pH**	Fortification Level (ppm)	Aminocarb Recovery			Aminocarb Phenol Recovery
			0 Day	7 Days	14 Days	0 Day
River	7.5	0.01	98 ± 3	96 ± 2	92 ± 3	<45
Potable	8.4	0.01	100 ± 1	100 ± 5	95 ± 4	<5

* Average of four determinations

** pH was adjusted to 7.5 prior to recovery by adding Na_2CO_3 (aq) dropwise
Minimum detection limit 1 x 10^{-4} ppm.

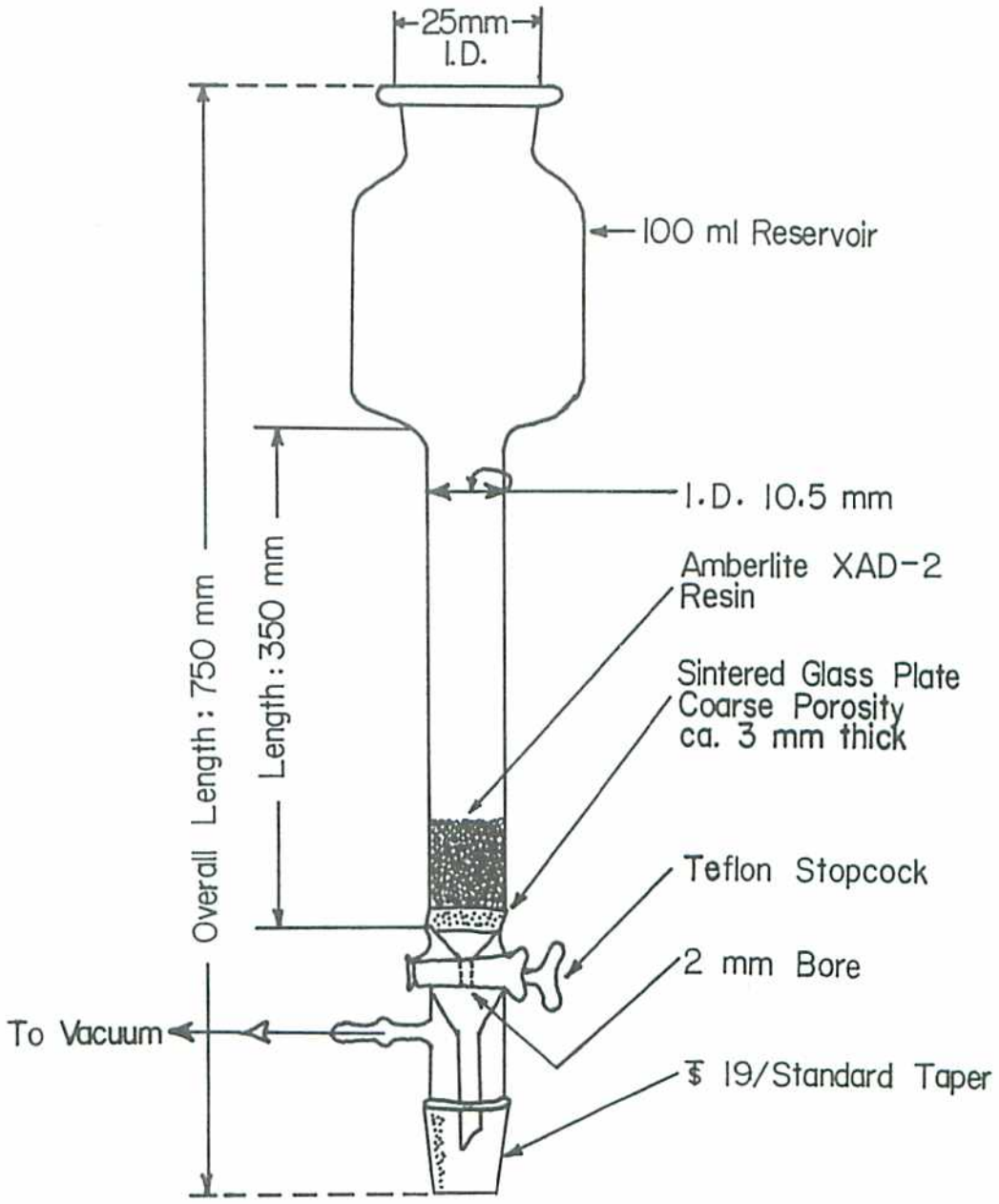


FIG. I AMBERLITE XAD-2 COLUMN

FIG.2 GAS CHROMATOGRAM OF 5·0ng AMINOCARB AND AMINOCARB PHENOL

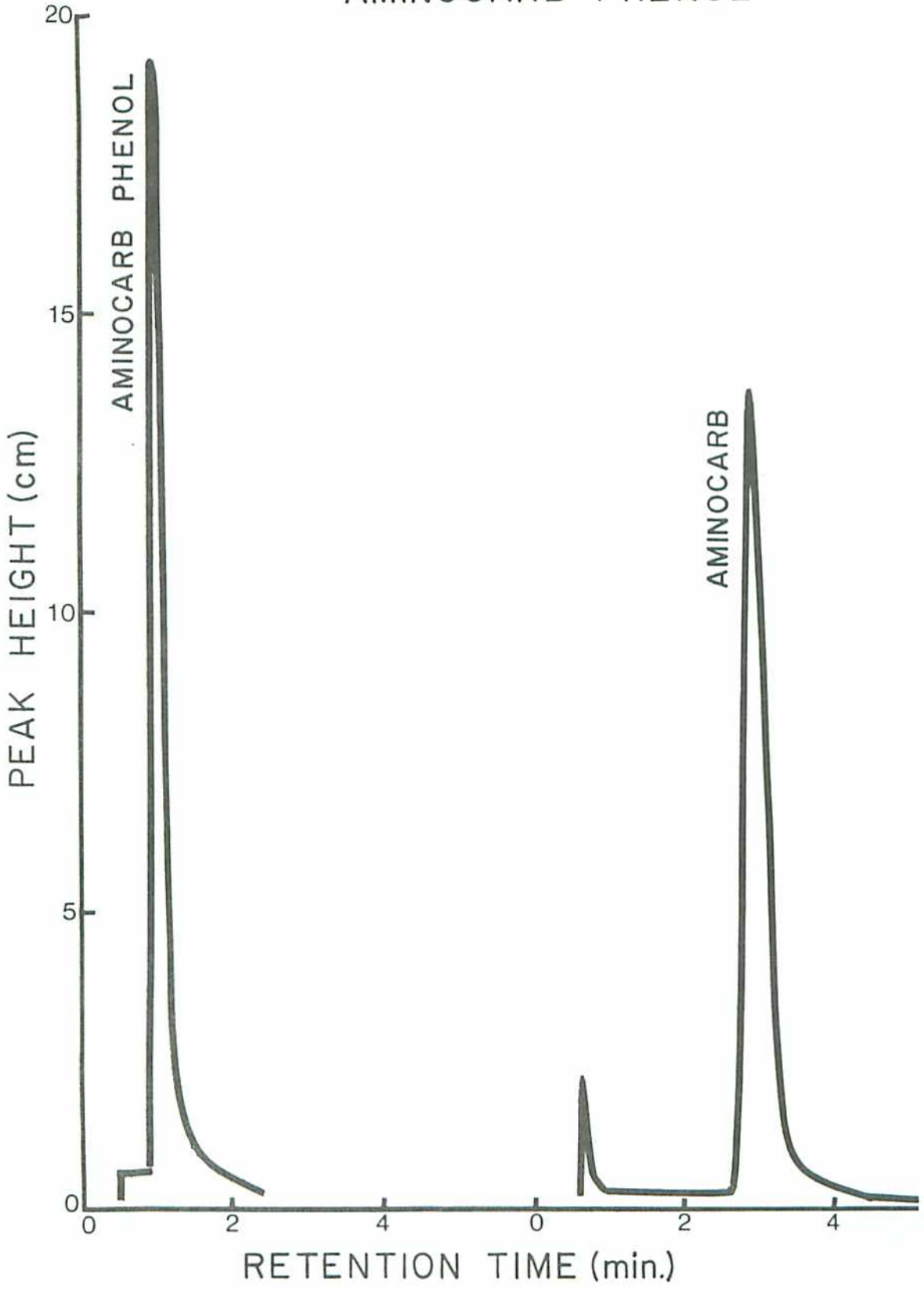
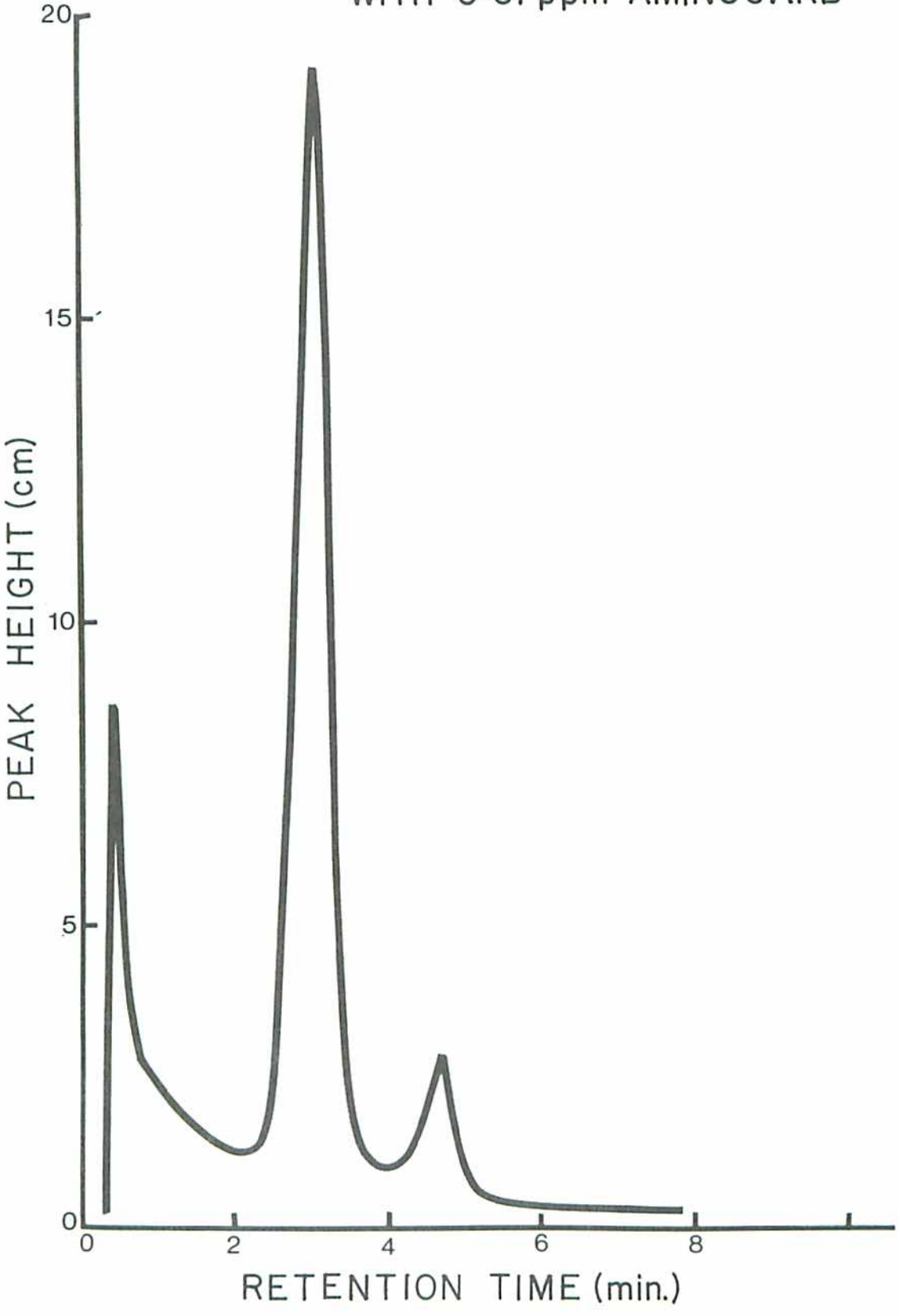


FIG. 3 GAS CHROMATOGRAM OF RIVER WATER FORTIFIED WITH 0·01 ppm AMINOCARB



RESULTS AND DISCUSSION

1. Analytical Technique

The analytical technique developed earlier by Sundaram et al (1976) to quantify aminocarb residues present in water samples involved liquid/liquid extraction, partitioning, distillation, derivatization and final analysis by electron capture gas-liquid chromatography. The procedure was rather complicated, expensive, time consuming and not adequately suitable for environmental monitoring of natural waters. The present use of Amberlite XAD-2 resin column for adsorption of aminocarb residues and the use of a Hall GLC in nitrogen mode for the final quantitation of aminocarb and its phenol metabolite not only increased the sensitivity (minimum detection limit, MDL, $1x10^{-4}$ ppm) but also simplified the technique by eliminating the tedious solvent extraction, partitioning and derivatization steps used in the former method. The Hall GLC responses to the standards were sharp, symmetrical and well defined (Fig. 2) with retention time (RT) of 3.0 min. for aminocarb and 1.0 min for its phenolic metabolite.

2. Influence of pH on the Isolation of Aminocarb Residues

The results obtained for the isolation of aminocarb and its metabolite from phosphate buffers ranging from pH 3.0 to 9.0 by column chromatography on Amberlite XAD-2 are given in Table III. The recoveries of the insecticide at both fortification levels (0.50 and 5.00 ppm) above pH 4 were higher than 90% and the results were reproducible as indicated by the

small standard deviation for the four replicates in each extraction study. However, at lower pH levels, i.e. 3.0 and 4.0, the Amberlite XAD-2 did not adsorb all aminocarb molecules present in the percolated solutions. At concentrations of 0.50 and 5.0 ppm, only 62 and 52 percent, respectively were adsorbed on the resin columns and the rest were in the solutions collected. The unadsorbed molecules were quantitatively isolated by neutralizing the solutions with aqueous sodium carbonate to pH 7.5, repercolating them through the same columns and desorbing with ethyl acetate. The lower extraction efficiency of Amberlite XAD-2 resin for aminocarb at low pH levels 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 aminocarb on the resin column depended upon its hydrophobicity and since the formation of ionic species at low pH levels destroyed this property, the insecticide molecules were not readily adsorbed on the column. Consequently, low recovery levels were obtained.

Good recoveries (85%) were observed for the aminocarb phenol when the pH of the fortified buffer solutions were between 7.5 and 8.0 (Table III). Beyond this range, the recoveries were low, but improved considerably when the column effluents were adjusted to pH 7.5 by the addition of either Na_2CO_3(aq) or 0.1 M HCl as required, and repercolation through the same columns.

These findings indicate that the phenol moiety exists primarily as a cation, $R_2R'N^+H$ below pH 6.0 and as an anion, $R_2N\text{-}R'\text{-}O^-$ above pH 8.0 and that the resin being a nonpolar styrene-divinylbenzene copolymer, preferentially adsorbs nonionic and neutral species from solutions.

3. Recovery of Aminocarb from Natural Waters

Nearly quantitative recoveries (>95%) were obtained (Table IV) from the potable and river waters containing 0.01 ppm of the insecticide. Although the river water contained considerable amount of particulate matter, and effluents from industrial source, the recovery was excellent demonstrating the versatility of this method. Close inspection of Fig. 3 obtained for river water and a comparison with the sample chromatogram of the standard (Fig. 2) showed certain differences in peak profiles which are probably attributable to the plant effluents.

4. Aminocarb Stability in the Column

Inspection of the results in Table IV showed that the aminocarb adsorbed by the Amberlite XAD-2 resin was stable and did not undergo significant degradation at ambient temperature for up to 14 days. The residues were recovered almost quantitatively from the stored columns 7 and 14 days after they had been extracted from natural waters. Since the compound is stable on the columns, the technique would be useful for collecting water samples for residue analysis after the aerial application of aminocarb. Water samples could be percolated through the resin

columns at the collection site, the column tops plugged or stoppered, the columns protected from light and transported to residue laboratory for subsequent solvent elution and GLC analysis. During this interval, aminocarb remains unchanged in the column and its concentration is respresentative of the time the water was sampled in the field. The technique developed at present is far superior to the conventional methods of solvent extraction in the field and/or freezing large quantities of water, where facilities exist, and rushing the samples to the laboratory for analysis. Such processes are not only cumbersome but also result in residue losses and in addition they involve considerable time and labour which could be saved by utilizing the present technique. Moreover the columns can be regenerated easily, as described earlier and reused. The columns used in this study had been regenerated at least ten times after repeated applications without apparent change in the performance of the resin.

Thus, adsorption of aminocarb residues on Amberlite XAD-2 is an extremely useful technique for recovering trace levels of the chemical from environmental waters. Also the results presented here confirm that eventually the procedure will greatly facilitate the task of residue chemists when environmental monitoring and quality control programs are to be conducted in forest areas sprayed with aminocarb.

5. Recovery of Aminocarb Phenol from Natural Waters

Although the macroreticular resin XAD-2 has been useful for the isolation of aminocarb from environmental waters, the results

in Table IV showed that it was not capable of extracting the phenol from potable and river water samples completely and the results were not reproducible. Repeated solvent (ether, chloroform, dichloromethane, benzene, etc.) extraction of the aqueous effluents from the columns revealed low (5-18%) but measurable amounts of the phenol indicating a small fraction of the fortified material did pass through the column. Chloroform rinsing of the interior surface of the columns for possible retention of the material was negative. The discrepancy in the recovery of the phenol (5 to 45%) from natural waters (Table IV) and from buffer solutions (Table III) was possibly caused by the affinity of the phenol for trace metal ions to form chelates and its interaction with other materials present in natural waters. Especially the low recovery (<5.1) of the phenol from tap water compared to the distilled water (>85%) was also, presumably because of reaction of the chemical with residual hypochlorous acid as a result of chlorination of the tap water. Similar observations were also made recently by Von Rossum and Webb (1978). In general, the XAD-2 resin is applicable to separate aminocarb found in environmental waters but unsuitable for its phenolic metabolite because of incomplete sorption as indicated by the column effluent data in Table IV.

In future, adsorbents of intermediate polarity or hydrophobicity such as Amberlite XAD-7 and Amberlite XAD-8 could be tried along with hydrophobic adsorbents such as Amberlite XAD-2 and 4 to separate aminocarb and its metabolites from natural waters. Possibly an equal weight mixture of the hydrophobic

(XAD-7 and 8) adsorbents could be more useful in isolating aminocarb and some of its metabolites. Work is proceeding in this direction to evaluate systematically which of these resinous materials or their combinations will be suitable for adsorbing quantitatively aminocarb and its metabolites from aqueous solutions.

SUMMARY AND CONCLUSIONS

1. A new GLC method using Tracor Model 550 chromatograph fitted with a Hall detector (model 310) in nitrogen mode for quantifying trace levels of aminocarb and its phenolic metabolite present in environmental waters has been reported.
2. Use of the Amberlite XAD-2 resin columns to isolate quantitatively the insecticide from natural waters by selective adsorption, solvent elution and subsequent GLC analysis is an efficient and sophisticated technique compared to the conventional multistage liquid/liquid extraction, derivatization and quantitation by EC-GLC.
3. Using column chromatography on Amberlite XAD-2, recovery of aminocarb and its metabolite from phosphate buffers with pH 3.0 to 9.0 showed that the adsorption of the chemicals was pH dependent. At pH 7.5 and above the adsorption of aminocarb was maximum; at lower pH levels the recovery was poor due to the formation of cationic species. Similar optimum pH levels did exist for the phenolic metabolite. These findings showed that Amberlite XAD-2 would not preferentially and quantitatively adsorb ionic and highly polar species from solutions. The basis of separation was adsorption on the surface of the resin; no ion exchange or pore exclusion mechanisms were involved.
4. One unique feature of the Amberlite XAD-2 method is that the adsorbed species are stable in the column for two weeks, con-

sequently the method serves as a preservation technique for aminocarb present in environmental waters.

The new technique will be a valuable tool in the hands of residue chemists, field biologists, limnologists and other environmentalists and will help them immensely in their monitoring and quality control programs undertaken after every forest pest control operation in which aminocarb insecticide has been sprayed.

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