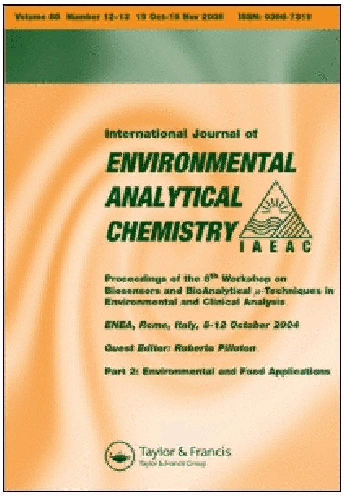

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D. Levesque[a]; V. N. Mallet[a]
[a] Départment de chimie et biochimie, Université de Moncton, Moncton, Canada

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Development of an Analytical Method for Aminocarb and some Derivatives in Water using XAD Resins and Gas Chromatography

D. LEVESQUE and V. N. MALLETT†
Départment de chimie et biochimie, Université de Moncton, Moncton, N.-B. E1A 3E9 Canada

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The recovery from water of aminocarb and several of its derivatives using Amberlite XAD resins and the subsequent analysis by GC using a nitrogen-phosphorus detector, was studied. The results show that aminocarb and three derivatives namely, MATACIL phenol, methyl formylamino MATACIL, formylamino MATACIL phenol, may be extracted from water at pH 7.0 using Amberlite XAD-4, with over 80% recovery. A fourth derivative, formylamino MATACIL may be recovered at close to 70%. The use of other resins such as Amberlite XAD-2 and 7 is more limited although each one may be used for the extraction of aminocarb from water. The amphoteric derivative, amino MATACIL phenol may be recovered with XAD-7 but the column has to be eluted with methanol. One derivative, namely methylamino MATACIL could not be recovered successfully. Experiments with environmental water show that the % recoveries were good for aminocarb, MATACIL phenol, methyl formylamino MATACIL and formylamino MATACIL.

INTRODUCTION

The chemical insecticide aminocarb, 4-dimethylamino-3-methylphenyl *N*-methylcarbamate (Bayer 44646), has been used increasingly in Canada since 1973 to help control epidemics of

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†To whom correspondence should be sent.

spruce budworm (*Choristoneura fumiferana* Clemens). It is usually sprayed aerially as the formulation MATACIL^R at a dosage of 70 g of active ingredient per hectare. In New Brunswick alone, 0.74 and 2.1 million hectares were sprayed with MATACIL^R in 1978 and 1979, respectively.[1] Other Provinces namely Quebec and Newfoundland are currently using MATACIL^R.

General reviews by Maguire[2] and others[3,4] describe the chemical properties of aminocarb, some of its biological and environmental reactions and methods for its chemical analysis. In terms of chemical properties, hydrolysis in alkaline medium seems prominent. With regards to biological and environmental degradation, experiments conducted with rats, human liver and bean plants have led to the identification of several metabolites. It is claimed that some of the degradation products may be up to ten times more toxic than the parent compound. Thus in practice it is also necessary to develop analytical methods suitable for the parent compound and its known degradation products.

The analysis of carbamates and other related compounds by Gas Chromatography (GC) has always posed a problem because these compounds are generally heat sensitive and often degrade at high column temperatures.[5] In the past thermally stable derivatives of aminocarb were prepared with reagents such as heptafluorobutyric anhydride[6] and the technique has been used to analyse aminocarb in water, soil and spruce foliage samples.[7] More recently, Brun and MacDonald[8] showed that aminocarb could be separated by GC without significant degradation on a 1.8 m column containing 3% OV-17 and detected using a Hall electrolytic detector. Mamarbachi[9] used a similar column and a selective nitrogen–phosphorous (N–P) thermionic detector to detect aminocarb in spruce foliage extracts. Sundaram *et al*[10] used a Hall detector to analyse aminocarb and its phenol derivative in environmental water by GC. Since then, Levesque and Mallet[11] have successfully separated aminocarb and seven known degradation products by GC with a column containing 3% OV-17 and they detected the chemicals using a N–P thermionic detector.

Another problem encountered in the analysis of carbamates, such as aminocarb, is the difficulty in extracting simultaneously and quantitatively the parent compound and its degradation products using traditional techniques such as liquid–liquid partition.

Considering successful results obtained earlier[12] in the extraction of fenitrothion (an organophosphorus insecticide) and several of its degradation products from water, the use of XAD resins seemed promising. In fact Amberlite XAD resins have been tested in our laboratory for the extraction of aminocarb[13] as early as 1977. At the time, good recoveries were obtained for aminocarb in water with XAD-2, 4 and 7. Since then, Sundaram *et al.*[14] have reported recoveries of 103% ± 2.00 at 1.0 ppm and 98.0% ± 3.00 at 0.01 ppm ($n=4$) for aminocarb using Amberlite XAD-2. They also attempted to extract simultaneously the hydrolysis product MATACIL phenol, but the recoveries were low. Brun and MacDonald[8] extracted aminocarb from lake water using Amberlite XAD-4 at 1.0 ppb and obtained recoveries of 84% ± 5.7.

Thus, it was intended in this study, to evaluate XAD resins for the recovery of aminocarb and several of its degradation products from water using a similar procedure that had been developed previously for fenitrothion and some of its degradation products.[12]

EXPERIMENTAL PART

Chemicals, reagents and solvents

Aminocarb (A) and six degradation products, namely MATACIL phenol (MP), Methylamino MATACIL (MAM), Methylformylamino MATACIL (MFAM), Formylamino MATACIL (FAM), Amino MATACIL Phenol (AMP) and Formylamino MATACIL Phenol (FAMP) were all obtained as analytical standards from Chemagro Ltd., Mississauga, Ont. The structures and chemical names are presented in Table I.

Standard solutions of aminocarb and some derivatives were prepare 1000 mg/L in methylene chloride (pesticide grade). Amino MATACIL phenol and formylamino MATACIL were dissolved in acetone, while absolute ethanol was used with formylamino MATACIL phenol. Solutions were kept refrigerated in amber bottles. Even then solutions in methylene chloride were stable for about 3 months, while in the polar solvents degradation was significant within a few weeks.

Amberlite XAD-resins (2, 4, 7 and 8) were obtained from BDH

TABLE I

Structures of aminocarb and some known derivatives.

Abbreviation	Chemical name	Structure
A	4-(dimethylamino-3-methylphenol methyl carbamate	
MP	4-(dimethylamino-3-methylphenol	
MFAM	4-(*N*-methyl-*N*-formylamino)-3-methylphenol methylcarbamate	
FAM	4-(formylamino)-3-methylphenol methyl carbamate	
MAM	4-(methylamino)-3-methylphenol methyl carbamate	
FAMP	4-(formylamino)-3-methylphenol	
AMP	4-amino-3-methylphenol	

Laboratory Reagents, Toronto, Ontario. All the solvents used for extraction were pesticide grade.

Apparatus

A Tracor Model 560 gas chromatograph (GC) equipped with a thermionic N–P detector (TRACOR 702) was used for all quantitative studies. The glass column was 1.2 m × 4 mm I.D. and contained 3% OV-17 on CHROMOSORB W, 60/80 AW-DMCS.

Methods

General procedure for the recovery of aminocarb and degradation products from water using XAD resins

One litre of water was spiked with the desired chemical(s) then adjusted to pH 7.0 with sodium bicarbonate, 0.1 M. It was passed through a glass column (30 cm × 1.9 cm I.D.) containing 12 cm of an Amberlite XAD resin. The column was then eluted with 3 × 30 mL of ethyl acetate. The eluate was dried by passing through a Whatman no. 2 filter paper, containing anhydrous sodium sulfate. It was then evaporated to 1.0 mL for GC.

For recovery studies, the following amounts of aminocarb and derivatives were added to 1 litre of water: 2 mg for MAM, 40 μg for MP, 200 μg for AMP, 200 μg for MFAM, 10 μg for A, 200 μg for FAMP and 5 mg for FAM. These concentrations were chosen so as to take into account the respective detection limits as already reported.[11]

RESULTS AND DISCUSSION

In this study the simultaneous recovery from water (adjusted to pH 7.0 with sodium bicarbonate) of aminocarb and three degradation products was attempted with a column containing Amberlite XAD-4. The % recoveries reported in Table II were excellent for aminocarb and MATACIL phenol, acceptable for MFAM and low for FAM. Amberlite XAD-4 was first tested because it had proven very reliable in studies with fenitrothion.[12]

In another series of experiments the simultaneous recoveries of aminocarb and six degradation products was tried at various pH using Amberlite XAD-4. The results in Table III confirm that aminocarb and MATACIL phenol may be recovered successfully at pH 7.0. At lower pH values (4.0 and 3.0) the percentage recoveries were not good while at higher pH values (> 7.0) reasonable recoveries were still possible in the case of aminocarb when the extraction step was done immediately following spiking of the

TABLE II

Extraction of aminocarb and three degradation products from distilled water using amberlite XAD-4.

Chemical (concentration)	Recovery (%) ($n=3$)
Aminocarb (10 ppb)	98
MATACIL phenol (40 ppb)	102
Methylformylamino MATACIL (200 ppb)	85
Formylamino MATACIL (5 ppm)	61

TABLE III

Recovery of aminocarb and six degradation products from distilled water with amberlite XAD-4 at various pH.

Chemical (concentration)	Recovery (%) ($n=3$)					
pH[a]	3.0	4.0	7.0	7.5	8.5	9.0
MAM (2 ppb)	N.D.[b]	N.D.	N.D.	N.D.	N.D.	N.D.
MP (40 ppb)	1	7	97	75	64	54
AMP (200 ppb)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
MFAM (200 ppb)	44	42	85	87	88	(—)[c]
A (10 ppb)	34	60	92	90	80	29
FAMP (200 ppb)	40	27	80	81	80	29
FAM (5 ppm)	24	25	69	5	10	13

[a] pH 3.0 and 4.0 were adjusted with HCl, 0.1 M and 0.01 M; pH 7.0 was adjusted with sodium bicarbonate 0.1 M; pH 7.5, 8.5 and 9.0 were adjusted with NaOH, 0.1 M and 0.01 M.

[b] N.D.: not detectable.

[c] (—): the compound was not included.

sample, i.e. before hydrolysis became important. But extraction in basic medium is not recommended for this reason. The pH variations (3.0–9.0) did not improve recoveries for the degradation products and some, namely MAM and AMP, were never detected. Thus, the optimum pH for extraction of aminocarb and its related chemicals seems to be close to seven.

A study of other Amberlite XAD-resins was initiated to determine their capabilities for the recovery of aminocarb and its degradation products. The results in Table IV indicate that in general XAD-4 gives better recoveries for a larger number of chemicals. Also MP was recovered at 99% with XAD-7 and XAD-2 gave good recoveries with A and FAMP. It should be taken into consideration, however, that in all of the above experiments, only ethyl acetate was used to eluate the resins.

Presumably most of the degradation products are not retained by the resins. Repeated elutions of the columns with ethyl acetate did not improve the recoveries. However, in the case of AMP, elution of the XAD-7 column with methanol revealed that this degradation product was in fact retained by the resin and that ethyl acetate was not hydrophilic enough to elute it (see Table IV).

TABLE IV

Recovery of aminocarb and six degradation products from distilled water at pH 7.0 using various amberlite resins.

Chemical (concentration)	Recovery (%) ($n = 3$)				
Resin	XAD-2	XAD-4	XAD-7	XAD-8	XAD-2: XAD-7[a]
MAM (2 ppb)	6	N.D.	21	26	52
MP (40 ppb)	61	97	99	21	20
AMP (200 ppb)	N.D.	N.D.	N.D. (101)[b]	N.D.	N.D.
MFAM (200 ppb)	42	85	36	48	43
A (10 ppb)	93	92	87	75	93
FAMP (200 ppb)	98	80	85	104	103
FAM (5 ppm)	11	69	14	14	21

[a] The XAD-2:XAD-7 mixture was prepared 1:1, volume:volume.

[b] Result in bracket indicates elution of the column with 3 × 40 mL of methanol.

The results of this study have shown that Amberlite XAD-4 is a promising resin because it may be used to recover simultaneously aminocarb and three of its degradation products from distilled water when the pH is adjusted to 7.0. Thus this resin was chosen to veryify the potential of the method with environmental water. The latter came from the St. John River, at Fredericton, N.B. (Can.). The results in Table V show that Aminocarb, MP, MFAM and FAM may be recovered reasonably well. In particular the recoveries for

TABLE V

Recovery of aminocarb and three degradation products in environmental water with amberlite XAD-4.

Chemical (concentration)	Recovery (%) ($n=6$)	Coefficient of variation (%)
MP (40 ppb)	95	9
MFAM (200 ppb)	84	13
A (10 ppb)	95	7
FAM (5 ppm)	72	8

aminocarb and MATACIL phenol were excellent. The other derivatives were not tested.

The coefficients of variation seem higher than one would expect considering that other authors[8, 14] have reported 2–5%. In fact coefficients of variation of 2–5% is what may be expected on the basis of our experiments with distilled water. The data in Table V were obtained two years later using a GC column containing OV-17 but the latter was not of AW-DMCS quality and as a result the resolution was not as good as had been obtained previously.

CONCLUSION

This study reveals that aminocarb and MP may be recovered quantitatively from distilled water at pH 7.0 using Amberlite XAD-4 or XAD-7 columns with ethyl acetate as elution solvent. Successful recoveries may be expected for MFAM and FAMP using XAD-4. The % recoveries with Amberlite XAD-7 were low for MFAM but the resin retained AMP particularly well. Elution of the column with methanol was necessary in this case. The other resins namely, XAD-2 and XAD-8 did not show as much potential.

The results indicate that the best recoveries were achieved when the pH was adjusted to 7.0. The method was tested successfully for the recovery of aminocarb and three degradation products in environmental water.

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References

1. I. W. Varty, Chairman (EMOFICO), *Environmental Surveillance in New Brunswick (1978–1979)—Effects of Spray Operations for Forest Protection,* (available from Dept. of Forest Resources, UNB, Fredericton, N.B., 1980).
2. R. J. Maguire, *Aminocarb: A Review of its Chemistry* (National Water Research Institute, Environment Canada, Burlington, Ontario, May 1979).
3. J.-G. Davidson and L. Dorais, *Pulvérisations aériennes d'insecticides contre la tordeuse des bourgeons de l'épinette en 1981. Chapitre 2—Identification et Evaluation des Répercussions Environnementales.* (Québec, mars 1981, 400 pp),
4. Associate Committee on Scientific Criteria for Environmental Quality, *Aminocarb: The Effects of its Use on the Forest and the Human Environment,* (National Research Council, Ottawa, Canada, Report no. ISSN-0316-0114, 1982).
5. R. J. Kuhr and H. W. Dorough, in *Carbamate Insecticides; Biochemistry and Toxicology,* (CRC Press, Cleveland, Ohio, 1976).
6. J. F. Lawrence, *J. Chromatogr.* **123,** 287 (1976).
7. K. M. S. Sundaram, Y. Volpé, G. G. Smith and J. R. Duffy, *A Preliminary Study on the Persistence and Distribution of MATACIL in Forest Environment.* (Report CC-X-116, CCRI, Ottawa, 1976).
8. G. L. Brun and R. M. MacDonald, *Bull. Environ. Contam. and Toxicol.* **24,** 886–893 (1980).
9. G. Mamarbachi, *Bull. Environ. Contamin. and Toxicol.* **24,** 415 (1980).
10. K. M. S. Sundaram, Y. Volpé, S. Szeto and P. Hindle, *Isolation and Analysis of Aminocarb and its Phenol for Environmental Waters.* (Report FPM-X-18, Forest Pest Management Institute, Sault Ste Marie, June 1978).
11. D. Lévesque and V. N. Mallet, *J. Chromatogr.* **200,** 228–233. (1980).
12. G. G. Volpé and V. N. Mallet, *Intern. J. Environ. Anal. Chem.* **8,** 291 (1980).
13. P. Haché, *Utilisation des résins XAD: Nouvelle méthode de recouvrement d'aminocarb,* (4th year Honours Thesis, April 1978).
14. K. M. S. Sundaram, S. Y. Szeto and R. Hindle, *J. Chromatogr.* **177,** 29–34 (1979).