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Note

Gas–liquid chromatographic analysis of aminocarb and seven derivatives

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The analysis of carbamates and other related compounds by gas–liquid chromatography (GLC) has always posed a problem because these compounds are generally heat sensitive and often degrade at high column temperatures[1]. Thermally stable derivatives can usually be prepared with suitable reagents but there is always the possibility of reactions with co-extractives and the procedure is tedious and time-consuming[2]. Nevertheless, thermal degradation may sometimes be reduced considerably by optimizing GLC parameters and a judicial choice of columns and some carbamates have been analysed directly[3,4].

Aminocarb (4-dimethylamino-3-methylphenol methylcarbamate) sold under the trade name Matacil has been used increasingly in our country to control the spruce budworm (*Choristoneura fumiferana* Clemens). Its chemistry has been reviewed by Maguire[5] and he has emphasized the need for better analytical methodology for aminocarb and its derivatives.

Initially the problem of thermal instability was circumvented by derivatization with chemicals such as heptafluorobutyric anhydride[6] and the method has been used to analyse for aminocarb in water, soil and spruce foliage[7]. Recently, Brun and MacDonald[8] showed that aminocarb may be separated without significant degradation on a 183 cm GLC column containing 3% OV-17 and analysed using a Hall detector. Mamarbachi[9] used a similar column and a selective nitrogen–phosphorus (N–P) thermionic detector to analyse aminocarb in spruce foliage and he obtained greater than 90% recovery at the 6 ppb* level. More recently Sundaram *et al.*[10] analysed aminocarb and its phenol derivative in environmental water using a gas chromatograph equipped with a Hall electrolytic detector. They studied the recovery of the two compounds using Amberlite XAD-2 resin while controlling the pH but were only able to recover aminocarb (79.5%) at 0.01 ppm.

In this work it was intended to study not only aminocarb but to include seven possible degradation products most likely to be found in various substrates, and determine the possibility of using GLC without derivatization to analyse them simultaneously.

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

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EXPERIMENTAL

Materials

Aminocarb (Matacil) and seven derivatives namely, Matacil phenol, methyl formylamino Matacil, formylamino Matacil phenol, methylamino Matacil, formylamino Matacil, amino Matacil and amino Matacil phenol, were obtained as analytical standards from Chemagro (Mississauga, Canada). Standard solutions were prepared 1000 ppm in methylene chloride except for amino Matacil phenol and formylamino Matacil which were dissolved in acetone, while absolute ethanol was used with formylamino Matacil phenol. Solutions were kept refrigerated.

Apparatus

A Tracor Model 560 gas chromatograph equipped with a selective N–P thermionic detector was used. A glass column (122 cm × 0.64 cm I.D.) containing 3% OV-17 on Chromosorb W AW DMCS, 60–80 mesh, was utilized for separation.

Method

Aliquots of 5 μl taken from diluted solutions of the stock were injected directly in the chromatograph. The following operating parameters were maintained constant: flow-rates, helium 60 ml/min; air 125 ml/min; hydrogen 3.0 ml/min; polarization voltage, low. Other parameters were varied to obtain optimum conditions. For example, injection port, 250°C; detector, 260°C; oven, 145°C (initial temp) for 4 min; temperature programmed at 6°C/min until 195°C, remain at 195°C for 8 min.

RESULTS AND DISCUSSION

The importance of developing analytical capabilities for aminocarb and its degradation products stems from the fact that the chemical may be sprayed in high quantities over large areas and is basically non-persistent. Even a few hours or a few days after spraying the parent compound is hard to detect but the degradation products may be on the increase. Therefore it becomes desirable to be able to monitor simultaneously the parent compound and some of the most obvious degradation products.

The chemicals obtained from Chemagro (Table I) have been suggested as possible derivatives of aminocarb in water and biological tissues[11]. They usually occur as a result of chemical hydrolysis, bacteriological action, the effects of sunlight, and so on.

In a first series of experiments, we studied the behavior of each individual compound. The data in Table II give the optimum oven temperature for the independent determination of each compound, considering an eventual separation in presence of other derivatives and also sensitivity, while other conditions remained constant. A column containing OV-17 was chosen because of successful results with aminocarb by other authors[8,9]. A shorter column was judged preferable to minimize thermal degradation and give a shorter analysis time. Under these optimized condition one should expect the retention times and detection limits given in Table II. The detection limit is particularly good for most compounds. Thermal degradation is by far the

TABLE I

COMPOUNDS USED IN THIS STUDY

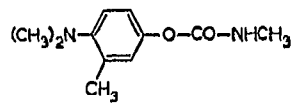
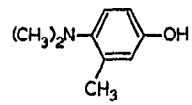
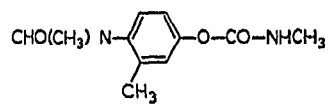
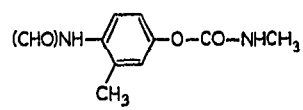
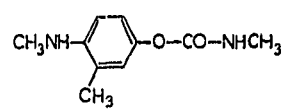
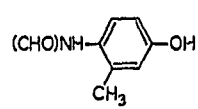
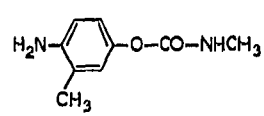
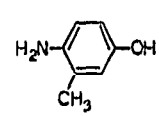
Common name	*Chemical name*	*Structure*
Matacil	4-(Dimethylamino-3-methylphenol methylcarbamate	
Matacil phenol	4-(Dimethylamino)-3-methylphenol	
Methyl formylamino Matacil	4-(N-Methyl-N-formylamino)-3-methylphenol methyl-carbamate	
Formylamino Matacil	4-(Formylamino)-3-methylphenol methylcarbamate	
Methylamino Matacil	4-(Methylamino)-3-methylphenol methylcarbamate	
Formylamino Matacil phenol	4-(Formylamino)-3-methylphenol methylcarbamate	
Amino Matacil	4-Amino-3-methylphenol methylcarbamate	
Amino Matacil phenol	4-Amino-3-methylphenol	

TABLE II

RETENTION TIMES AND DETECTION LIMITS FOR INDIVIDUAL COMPOUNDS UNDER ISOTHERMAL CONDITIONS

Compound	*Oven temperature (°C)*	*Retention time (min)*	*Detection limit (ng)*
Matacil	185	6.70	0.05
Matacil phenol	185	0.80	0.1
Methyl formylamino Matacil	200	4.40	0.1
Formylamino Matacil*	235	1.90	20
Methylamino Matacil	175	2.30	1
Formylamino Matacil phenol**	210	5.20	0.1
Amino Matacil	185	11.60	10
Amino Matacil phenol	185	1.45	0.05

* Injection port 270°C.
** Injection port 275°C.

limiting factor. Matacil was analyzed up to 185°C, above that degradation occurs apprecially to Matacil phenol. The latter compound may be analyzed up to 200°C without apparent degradation. With methylamino Matacil a degradation peak peak appears above 185°C. The expected degradation product is methylamino Matacil phenol but the compound was not available for comparison. In summary the temperatures given in Table II are optimum in the sense that maximum sensitivity can be obtained without appreciable degradation while maintaining a good resolution. These experimental conditions could be used appropriately for the independent determination of each of the compounds listed.

A mixture of aminocarb and its derivatives, however, could not be separated under isothermal conditions since not one particular oven temperature could be found that would give good resolution and good detection limits. The data in Table III give the retention times and detection limits under temperature programming. The latter yields good separation of the components while thermal degradation is kept at a minimum. The detection limits are not as good and the main reason is probably the additional time spent in the column which increases the chances for thermal degradation. In addition detection limit is sometimes hampered by closely

TABLE III

RETENTION TIMES AND DETECTION LIMITS UNDER PROGRAMMED TEMPERATURE

Compound	*Retention time (min)*	*Detection limit (ng)*
Matacil	12.90	0.05
Matacil phenol	3.50	0.2
Methyl formylamino Matacil	11.90	1.0
Formylamino Matacil	15.10	25
Methylamino Matacil	2.50	10
Formylamino Matacil phenol	17.90	1.0
Amino Matacil*	—	—
Amino Matacil phenol	5.70	1

* This compound was not available anymore.

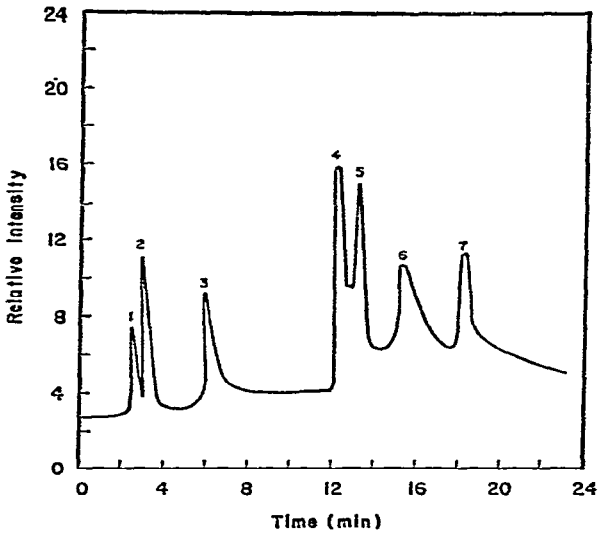


Fig. 1. GLC chromatogram of aminocarb and derivatives. 1 = Methylamino Matacil (0.2 ng); 2 = Matacil phenol (0.8 ng); 3 = Amino Matacil phenol (0.4 ng); 4 = methyl formylamino Matacil (100 ng); 5 = Matacil (40 ng); 6 = formylamino Matacil (4 ng); 7 = formylamino Matacil phenol (4 ng).

resolved peaks. The separation is better illustrated in a typical chromatogram shown in Fig. 1.

The next phase of this research is to successfully complete the extraction of aminocarb and its degradation products from environmental samples, and the most obvious substrate is water. Aminocarb itself is difficult to recover quantitatively from water without controlling the pH although good results may be expected using XAD resins. Attempts by Sundaram *et al.*[10] to recover simultaneously the hydrolysis product using XAD-2 were not very successful. We have also tried to extract aminocarb and its degradation products from water using XAD resins and we have found that aminocarb may be recovered quantitatively (< 90% recovery using either XAD-2 or XAD-4 at the 0.1 ppb level) but the results with the derivatives are not satisfactory and more experimental work has to be done. The problem is that certain derivatives extract well with one type of resin but the other derivatives do not and in addition the pH of the medium has an important effect. However, we feel that it will be possible enventually to develop a multi-residue extraction technique for aminocarb derivatives using XAD-resins and work along this line is continuing.

CONCLUSION

The results obtained in this work clearly demonstrate that GLC may be used for the separation of aminocarb and seven degradation products without chemical derivatization provided they can be extracted from a particular substrate.

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