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## Note

# Analysis of aminocarb formulations by high-performance liquid chromatography

MONIQUE LANOUETTE and RICHARD K. PIKE
*Laboratory Services Division, Agriculture Canada, Ottawa, Ontario K1A 0C5 (Canada)*
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Aminocarb (4-dimethylamino-*m*-tolylmethylcarbamate) also known as Matacil® is a carbamate insecticide currently finding effective use against the epidemic spruce budworm (*Choristoneura fumiferana* Clemens). Niessen and Frehse[1] have proposed a non-specific method for the analysis of aminocarb in formulations by ultraviolet (UV) absorption. Direct gas chromatographic (GC) analysis of carbamate pesticides is difficult because of their tendency to break down to the corresponding phenols on GC columns[2,3]. Methods for the high-performance liquid chromatography (HPLC) of carbamate pesticides have been outlined[4], of these none specifically address the analysis of aminocarb in formulations. However, two methods for aminocarb residue analysis are documented, the first[4] using normal-phase chromatography on a LiChrosorb Si 60 (5 μm) gives an extended retention time (*ca.* 20 min) for aminocarb, the second[5] using reversed-phase chromatography on a Partisil 10 ODS column draws attention to the broad tailing nature of aminocarb in this system. The approach taken in this study was to develop a system which exploits the tendency of buffered mobile phases to overcome these drawbacks and give sharpened peaks with reproducible retention times.

## EXPERIMENTAL

### *Equipment and materials*

A Waters M6000 analytical pump coupled with a Waters dual-channel 440 UV detector and a Rheodyne 7105 closed-loop (175 μl) injection valve was used in this study, with a Westronics 10 mV, 15 in./h chart speed, recorder. In addition, electronic analytical information was collected and processed by a Hewlett-Packard 3354 B/C computerized laboratory data system. The UV detector was operated at 254 nm. During part of this study use was made of an electrochemical detector(ElCD)(Bioanalytical Systems) equipped with a glassy carbon electrode and operated at a positive voltage of 1.1 volts. The LC column was stainless steel, 25 cm × 4.6 mm I.D., packed with 10-μm particles of silica to which $C_8$ alkyl groups have been chemically bonded. The column was obtained prepacked from Brownlee Labs. (Santa Clara, Calif., U.S.A.). The mobile phase pH 7.97 was phosphate buffer–methanol (50:50). The phosphate buffer, pH 6.85, was made by dissolving $KH_2PO_4$ (3.393 g) and $Na_2HPO_4$

(3.53 g) in 1 l of filtered deionized water. A flow-rate of 2 ml/min was optimum for aminocarb analysis.

Aminocarb standard (99%) was supplied by the Canada Centre for Pesticide Analytical Standards. (Agriculture Canada, Ottawa, Canada). Samples of commercially formulated aminocarb containing 19.5% (w/w) (18 pounds per imperial gallon) of active ingredient and also samples of forest spray solutions 6.7% (w/w) (2 oz./20 fl. oz. (U.S.)) were collected by inspectors of the Plant Products Division of Agriculture Canada at four airstrips in New Brunswick.

*Sample preparation*

To evaluate the method five samples (each *ca.* 0.1 g) were taken from each of four commercial spray solutions. Each sample was weighed (*ca.* 0.1 g) into a 100-ml volumetric flask, made to volume with absolute methanol and 5 $\mu$l of each was analysed by LC. Each replicate was injected three times, each set of three sample injections were bracketed by 5-$\mu$l injections of the standard aminocarb solution. Standard aminocarb solution was prepared by taking a 10-ml aliquot of a solution of 0.1954 g of aminocarb in 100 ml of methanol and making up to volume in a 100-ml volumetric flask with absolute methanol (approximate concentration is 0.1954 $\mu$g/$\mu$l).

*Calculations*

The percentage of aminocarb in a formulation is determined by the expression

$$\text{aminocarb (\%)} = A_{\text{sam.}}/A_{\text{std.}} \times C_{\text{std.}}/W_{\text{sam.}} \times P$$

where $A_{\text{sam.}}$ is the mean peak area of three successive injections of the sample, $A_{\text{std.}}$ is the mean peak area of the standard injected immediately prior to and after the sample injections, $C_{\text{std.}}$ is the concentration of the standard in mg/100 ml, $W_{\text{sam.}}$ is the weight of sample taken for analysis and $P$ is the percent purity of the standard.

## RESULTS AND DISCUSSION

To evaluate this method five samples were taken from each of four commercial spray solutions and the results of the analysis for aminocarb content are shown in Table I. An example of the LC chromatogram is illustrated in Fig. 1, the retention time for the compound was 6.7 min.

During this study 44 samples of commercial spray solutions were examined, each formulation was sampled once and analysed by LC three times, standard solutions were injected after every batch of three samples. Provincial recommendations for aerial spray solutions suggest an aminocarb content of 6.8% (1.23 oz./20 Pl. oz. U.S.). The mean analytical value of 44 determinations by LC was 6.47% with a standard deviation of 0.45.

The results of the analysis for aminocarb content in six commercial formulations as determined by both UV and ElCD are shown in Table II. The detectors were connected in series, the UV detector being upstream (comparison of the standard deviations indicate that UV detection is more consistent than ElCD and has a lower variation).

The linearity of the UV detector was examined across the range of 10 ng to

TABLE I

AMOUNT (% w/w) OF AMINOCARB FOUND IN COMMERCIAL SPRAY SOLUTIONS
*Number of determinations: 5.*

| *Sample No.* | *Commercial spray solutions* | | | |
|---|---|---|---|---|
| | *A* | *B* | *C* | *D* |
| 1 | 6.66 | 7.03 | 6.80 | 6.79 |
| 2 | 6.71 | 6.81 | 6.83 | 6.78 |
| 3 | 6.88 | 6.72 | 6.87 | 7.00 |
| 4 | 6.79 | 6.69 | 6.97 | 6.96 |
| 5 | 6.64 | 6.69 | 6.79 | 6.94 |
| Average | 6.74 | 6.79 | 6.85 | 6.89 |
| Standard deviation | 0.10 | 0.14 | 0.07 | 0.10 |
| Coefficient of variation (%) | 1.47 | 2.12 | 1.06 | 1.48 |

10 μg and that of the ElCD across the range of 10 ng to 1 μg. (Analysis of a 19.5% formulation by this method corresponds to an injected amount of 0.977 μg of aminocarb). A linear regression of the data points (amounts injected and corresponding area counts) throughout these ranges gave a correlation coefficient of 0.9999 in both cases.

The minimum detectability (defined as a signal twice the magnetude of noise) was 3 ng for both UV and ElCD. Repeat analysis using the amounts described in this method led to deterioration in sensitivity of the ElCD probably due to excessive

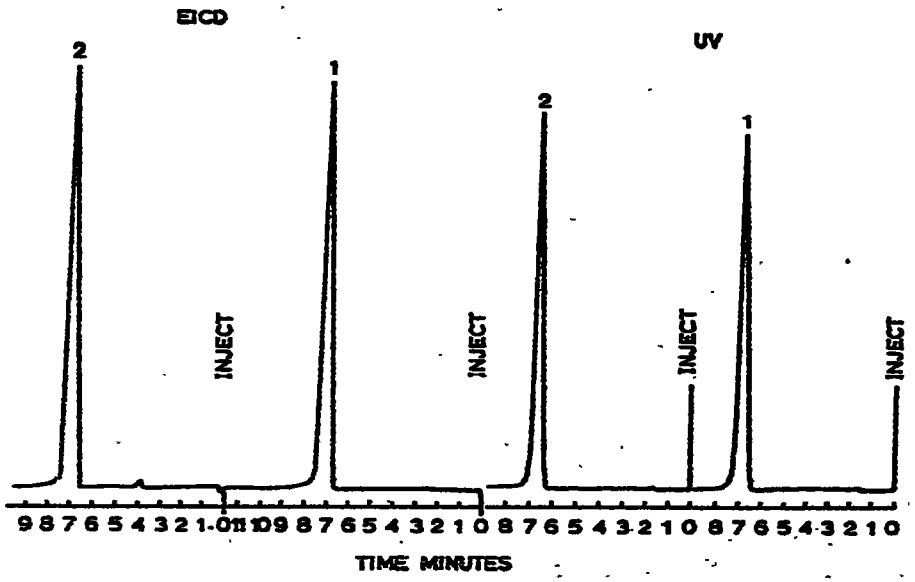


Fig. 1. LC curves of aminocarb by UV and ElCD. (1) Analytical grade aminocarb 0.98 μg/5 μl and (2) commercial aminocarb spray solution. Conditions: UV detector, UV range 254 nm; range setting 0.05; ElCD; 1.1 V; range setting 500B; LC column of stainless steel, 25 cm × 4.6 mm I.D. packed with $C_8$ reversed-phase silica; flow-rate 2 ml/min, mobile phase phosphate buffer (pH 6.85) in absolute methanol (50:50); observed pressure 1100 p.s.i.

TABLE II

AMOUNT OF AMINOCARB (% w/w) FOUND IN COMMERCIAL FORMULATIONS BY TWO METHODS OF DETECTION

Manufacturer's label indicated that commercial formulation contained 1.8 lb. per gallon (19.5%) aminocarb.

| *Sample No.* | *Aminocarb (%)* | |
|---|---|---|
| | *UV* | *ElCD* |
| 1 | 19.60 | 20.53 |
| 2 | 18.48 | 18.82 |
| 3 | 19.00 | 18.54 |
| 4 | 19.37 | 19.66 |
| 5 | 19.43 | 19.42 |
| 6 | 18.69 | 18.94 |
| Average | 19.1 | 19.32 |
| Standard deviation | 0.45 | 0.72 |
| Coefficient of variation (%) | 2.33 | 3.73 |

build-up of reaction products on the surface of the detector electrode. This problem can be eliminated by making a ten-fold dilution of the sample prior to injection when electrochemical detection is to be used.

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