Journal of Chromatography, 195 (1980) 151–153
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 12,821

Note

Analysis of barban formulations by high-performance liquid chromatography

CARLA BARRY and RICHARD K. PIKE*
Laboratory Services Division, Agriculture Canada, Ottawa, Ontario K1A 0C5 (Canada)
(First received January 21st, 1980; revised manuscript received March 7th, 1980)

Barban (4-chloro-2-butynyl N-(3-chlorophenyl)carbamate) also known as Carbyne® is a post-emergence herbicide used for the control of wild oats (*Avena fatua*). It is formulated as an emulsifiable concentrate at either 1.2 or 2.4 pounds per imperial gallon. The present method[1] of formulation analysis involves the separation of the active ingredient from its impurities by column chromatography using neutral alumina and graded solvent elution followed by quantitation on the basis of the product's absorbance at 277.5 nm. Two methods are documented for residue analysis. One[2] requires hydrolysis of the barban residue followed by diazotization and determination of absorbance at 500 nm, the other[3] requires barban to be converted to its tribromo derivative prior to gas chromatography. The method described below is direct, rapid and applicable to the routine analysis of barban formulations.

EXPERIMENTAL

Equipment and materials

A Spectra-Physics SP3500B pump coupled with a Waters dual-channel 440 ultraviolet (UV) detector (operated at 254 nm), a Waters U6K injection valve, and a Westronics 10 mV, 15 in./h chart speed, recorder were used in this study. Analytical data from the UV detector were collected electronically and processed by a Hewlett-Packard 3354 B/C computerized laboratory data system. The column (Zorbax ODS purchased prepacked from DuPont, Wilmington, DE, U.S.A.) was 25 cm × 4.6 mm I.D. stainless steel packed with particles (5 μm) of silica to which C_{18} alkyl groups were chemically bonded. The mobile phase (pH 5.1) was phosphate buffer–acetonitrile (40:60). The phosphate buffer (pH 4.5) was made by dissolving 13.6 g KH_2PO_4 in 1 l of filtered deionized water. A flow-rate of 2 ml/min was optimum for barban analysis.

Barban standard (99%) was supplied by the Canada Centre of Pesticide Analytical Standards. Samples of commercially formulated barban containing 1.2 lb./imp.gal. of active ingredient were collected by inspectors of the Plant Products Division of Agriculture Canada. Solvents were of HPLC grade (Caledon, Georgetown, Canada).

Sample preparation

To evaluate the method five samples were taken from each of four commercial

0021-9673/80/0000–0000/$02.25

formulations. An aliquot (1 ml) of formulation was pipetted into a 10-ml volumetric flask and made up to volume with HPLC-grade methanol and filtered. From this solution 1 ml was pipetted into a 10-ml volumetric flask and made up to volume with HPLC-grade methanol and 4 μl were analyzed by liquid chromatography. Standard barban solution was prepared by taking a 1-ml aliquot of a solution of 0.1022 g of barban in 10 ml of methanol and making up to a volume in a 10-ml volumetric flask with methanol (concentration of standard is 1.022 μg/μl); 4 μl of this solution were analyzed by liquid chromatography. Each sample was injected three times, each set of three triplicate injections was bracketed by injections of the standard.

Calculations

The amount of barban in a formulation is determined by the expression

$$\text{barban (lb./imp.gal.)} = 1.00224 \times \frac{A_{\text{sam}}}{A_{\text{std}}} \times \frac{1}{C_{\text{std}}} \times \frac{P}{100}$$

where A_{sam} is the mean peak area/μl of three successive injections of the sample, A_{std} is the mean peak area/μl of the standard injected immediately prior to and after the sample injections, C_{std} is the concentration of the standard in μg/μl and P is the percent purity of the standard.

RESULTS AND DISCUSSION

Early development of this method was made using Partisil 10 ODS, a 10-μm C_{18} reversed-phase column obtained from Whatman (Clifton, NJ, U.S.A.). The pH of the mobile phase was varied from 2.95 to 8 and near baseline resolution of the peak due to barban was observed at pH 5.1; both higher and lower values caused other peaks in the chromatograms to interfere with the barban peak. Baseline separation of the barban peak was effected by changing the silica particle size to 5 μm. An example of the liquid chromatogram is illustrated in Fig. 1. To evaluate this method five samples were taken from each of four commercial formulations and the results of the analysis for barban content are shown in Table I. The retention time for barban was 4.71 $\pm$ 8%. Although the retention time was stable for each batch of mobile phase; the variations were observed between different batches of mobile phase. The analyses were made by one analyst over a period of 3 weeks and it was observed that the shorter a period over which a set of analyses were made the smaller the relative standard deviation. Sample B was formulated with a different wetting agent than the other three samples and may have caused a more reproducible draining of the pipette used to sample these viscous formulations.

A comparison of the chromatograms obtained from a formulation and technical barban indicates that all the other peaks in the chromatogram are due to formulation adjuvants and not by-products from the manufacture of barban. No deterioration of the solutions of standard or samples was observed over the period of the study. During this study, a total of seven formulations (active ingredient guarantee of 1.2 lb./imp. gal.) were analyzed. The mean analytical value was 1.17 with a relative standard deviation of 3.9%.

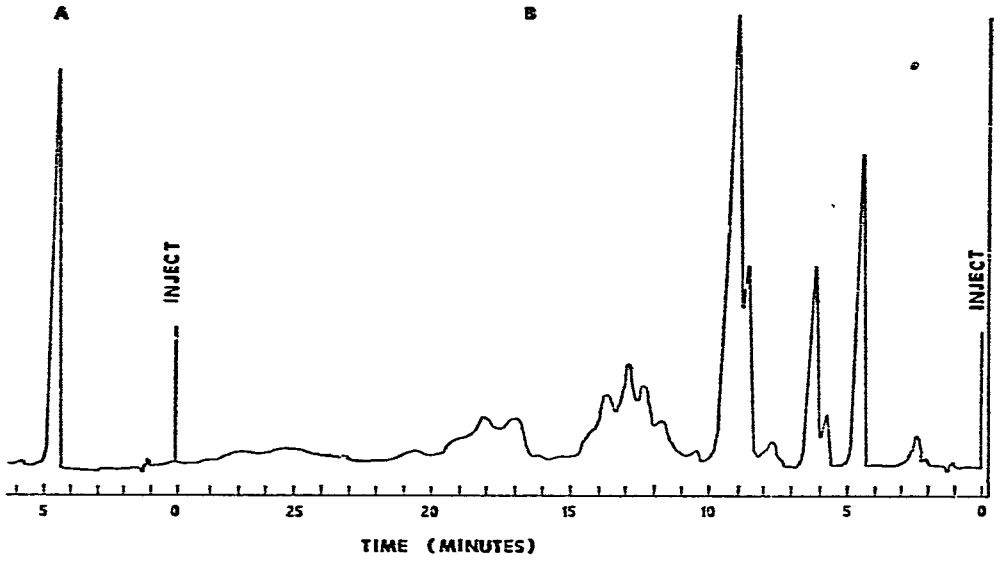

Fig. 1. Liquid chromatograms of barban in a standard solution (A) and in a commercial formulation (B).

TABLE I

AMOUNT (lb./imp.gal.) OF BARBAN FOUND IN COMMERCIAL FORMULATIONS

Sample No.	*A*	*B*	*C*	*D*
1	1.36	1.09	1.07	1.08
2	1.21	1.12	1.09	1.12
3	1.17	1.12	1.24	1.14
4	1.23	1.13	1.22	1.08
5	1.07	1.10	1.14	1.2
Average	1.21	1.11	1.15	1.12
Std. Dev.	0.105	0.016	0.076	0.050
Rel. Std. Dev.	8.69	1.48	6.59	4.43

The linearity of the UV detector was examined over the range of 4.048 ng to 4.048 μg (analysis of a 1.2 lb./imp.gal. formulation by this method corresponds to an injected amount of 4 μg barban). A linear regression of the data points (amounts injected and corresponding area counts) throughout this range gave a correlation coefficient of 0.998. The minimum amount of barban which could be detected (defined as a signal where magnitude was twice that of noise) was 2.024 ng.

To ensure the precision of future analysis of barban formulations, we would recommend that one batch of mobile phase be prepared in sufficient quantity to complete the analysis, and that a larger aliquot of the formulation be sampled.

REFERENCES

1 K. J. Bombaugh and W. C. Bull, *J. Agr. Food Chem.*, 9 (1961) 386.
2 J. R. Riden and T. R. Hopkins, *J. Agr. Food Chem.*, 9 (1961) 47.
3 R. J. Harris and R. J. Whiteoak, *Analyst (London)*, 97 (1972) 294.