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Note

Determination of carbamic herbicides by high-performance liquid chromatography

III. Triallate

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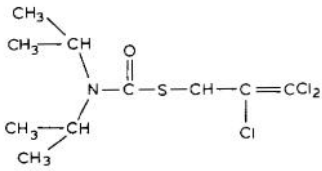
Triallate is the ISO common name for S-(2,3,3-trichloro-2-propenyl) bis(1-methylethyl)carbamothioate:



the herbicidal properties of which were described by Friesen[1]. It is commercially available as Avadex BW in the form of an emulsifiable concentrate (EC) with an active ingredient content of 400 g/l. As a herbicide it is particularly useful for the control of wild oats in cereals and peas, by incorporation into the soil in a pre-sowing or pre-emergence treatment.

It is of a low toxicity and various methods have been proposed for the analysis of technical and formulated products. Henriet[2] suggested its hydrolysis by acids, liberating diisopropylamine, which is distilled and collected in excess standard hydrochloric acid, the excess being back-titrated with standard sodium hydroxide solution. This method is not specific. Povlsen[3] used a gas–liquid chromatographic (GLC) method with a hot-wire detector, but there was slight decomposition of the product at the high temperature used. Beckmann[4] proposes the use of an IR method, which is very specific but not sufficiently precise or sensitive. The present authors[5] have already described two high-performance liquid chromatographic (HPLC) methods for the determination of chlorpropham, another carbamic herbicide. Residues may be determined by GLC with an electron-capture[6] or a nitrogen–phosphorus detector[7].

Two reversed-phase HPLC methods, with (A) external and (B) internal standards, are described here for the determination of triallate in EC formulations.

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EXPERIMENTAL

Eluent

Acetonitrile (HPLC quality, Merck, Darmstadt, G.F.R.)–doubly distilled water (60:40) was filtered through appropriate Millipore filters and degassed under a light vacuum.

For Method A

Stock solution. A 2.0 mg/ml solution in methanol (ACS Fisher Scientific, Pittsburgh, PA, U.S.A.)–doubly distilled water (90:10) is prepared. Weigh approximately 0.100 g of pure triallate (Monsanto, St. Louis, MO, U.S.A.) into a 50-ml volumetric flask and dissolve it in and dilute to volume with methanol–water (90:10).

Standard solution. Dilute 10 ml of the above, stock solution in a 50-ml volumetric flask with methanol–water (90:10). Filter through an appropriate Millipore filter into a small vial and cap.

40% EC solution. Weigh approximately 0.250 g of Avadex BW (Monsanto) into a 50-ml volumetric flask and dilute to volume with methanol–water (90:10). Dilute 10 ml of this solution in a 50-ml volumetric flask with the same solvent. Filter through an appropriate Millipore filter into a small vial and cap.

Linearity checking solutions. Eleven solutions of Avadex BW were prepared by serial dilution (1:2) from an initial solution having a triallate concentration of about 12 g/l.

For Method B

Internal standard solution. Weigh 0.800 g of di-*n*-pentyl phthalate (e.g., practical grade, Eastman-Kodak, Rochester, NY, U.S.A.) into a 200-ml volumetric flask and dissolve it in and dilute to volume with methanol–water (90:10).

Standard solution. Transfer 10 ml of the stock solution from method A and 10 ml of the above internal standard solution into a 50-ml volumetric flask and dilute to volume with methanol–water (90:10). Filter through an appropriate Millipore filter into a small vial and cap.

40% EC solution. Transfer 10 ml of the 40% EC solution from method A, at a concentration of approximately 0.250 g per 50 ml, and 10 ml of the above internal standard solution into a 50-ml volumetric flask and dilute to volume with methanol–water (90:10). Filter through an appropriate Millipore filter into a small vial and cap.

Linearity checking solutions. Eleven solutions of Avadex BW were prepared by serial dilution (1:2) from an initial solution with a triallate concentration of about 12 g/l, all of them having the same concentration of the internal standard, di-*n*-pentyl phthalate (0.8 g/l).

Apparatus

A Hewlett-Packard 1084B high-performance liquid chromatograph equipped with a microprocessor, electronic integrator, 79875A variable-wavelength detector (190–600 nm), etc., as decribed in a previous paper[8], was used. The column (Hewlett-Packard 79918A) was 200 nm × 4.6 mm I.D., stainless steel, packed with LiChrosorb RP-8 (10 μm).

The Millipore filters (Millipore, Bedford, MA, U.S.A.) used were type HAWP for water, EHWP for methanol and FHLP for acetonitrile, pore size 0.5 μm.

Chromatographic conditions

The following conditions were used: flow-rate, 1.8 ml/min; column temperature 40°C; variable-wavelength detector, UV–visible, wavelength 250 *vs.* 430 nm; injection volume, 10 μl; attenuation, 2^8; chart speed, 0.5 cm/min; slope sensitivity, 0.6; time, 6.5 min at wavelength 220 *vs.* 430 nm.

The detector can be programmed in order to change automatically the wavelength of measurement at different times throughout the development of the chromatograms. Hence wavelength time programming was established to measure at 250 *vs.* 430 nm from the beginning of the chromatogram to time 6.5 min and at 220 *vs.* 430 nm from time 6.5 min to the end of the chromatogram.

This procedure was used both to determine the peak corresponding to triallate at an absorbance close to one of its absorption maxima and to minimize the magnitude of the previous peaks, produced by the formulation additives, which also show a strong absorbance at 220 nm.

Calibration and quantitation

Inject 10-μl aliquots of the corresponding standard solution, method A or B, into the chromatograph until the variation in the standard peak areas is less than 1%. Adjust the detector sensitivity in order to obtain peak heights of *ca.* 60–80% full-scale. Calibrate and inject 10 μl of the samples to be analysed. Results will be obtained in absolute or relative amounts, according to our needs, by automatic integration of the peak areas.

RESULTS AND DISCUSSION

Some preliminary tests were carried out to find out how many analyses should be made for every sample and how many injections for every analysis, in every method, in order to maintain a precision lower than 1% ($P = 0.01$)[9]. One analysis and two injections are enough for the external standard method (A). In contrast, two analyses and one injection are necessary for the internal standard method (B). Nevertheless, more data were used in some instances, as they had been already obtained for the statistical calculation mentioned above.

The chromatography of pure triallate and Avadex BW, with an external standard, is shown in Fig. 1. The retention time is approximately the same in both instances (7.50 and 7.44 min). The concentration of active ingredient in the Avadex BW, labelled 40%, was 39.2 ± 0.18%, $s = 0.147\%$, $s_r = 0.375\%$ (mean of five determinations).

Triallate was found to have an absorption maximum at 208 nm; nevertheless, a wavelength of 220 nm was chosen for measurement in order to avoid interferences from the eluent.

The eleven linearity checking solutions from method A were analysed. Table I summarizes the amounts of triallate injected and found, and also the accuracy, precision and calculated correlation coefficient, only for those results in which linearity was achieved.

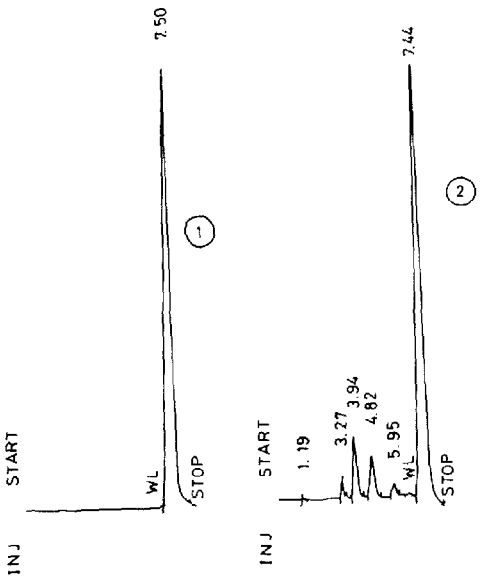

Fig. 1. Chromatography of (1) pure and (2) 40% EC triallate with acetonitrile–water (60:40) as eluent. WL = Moment in which the change of wavelength is produced.

The introduction of an internal standard, di-*n*-pentyl phthalate, improves the results slightly in spite of the very good repeatability of the automatic variable-volume injector.

Fig. 2 shows the chromatography of pure and 40% EC triallate with an internal standard. The retention times are approximately the same in both instances (7.62–9.62 and 7.63–9.62 min). The concentration of the active ingredient in the EC, labelled 40%, was 39.2 ± 0.17%, s = 0.156%, s_r = 0.404% (mean of six determinations).

TABLE I

AMOUNTS OF TRIALLATE INJECTED AND FOUND AND THE CORRELATION COEFFICIENT, ACCURACY AND PRECISION, USING THE EXTERNAL STANDARD METHOD (A)

$$\text{Accuracy (\%)} = \frac{\text{injected } (\mu g) - \text{found } (\mu g)}{\text{injected } (\mu g)} \cdot 100$$

Injected (μg)	*Found (μg)**	*Accuracy (%)*	*Precision (%)***
15.604	16.341	−4.72	1.51
7.802	7.984	−2.33	2.63
3.901	3.935	−0.87	0.97
1.951	1.958	−0.36	0.75
0.975	0.981	−0.62	1.04
0.488	0.475	2.66	0.63
		Correlation coefficient: 0.9999	

* Average value.

** Relative standard deviation of three determinations (see first paragraph of Results and discussion).

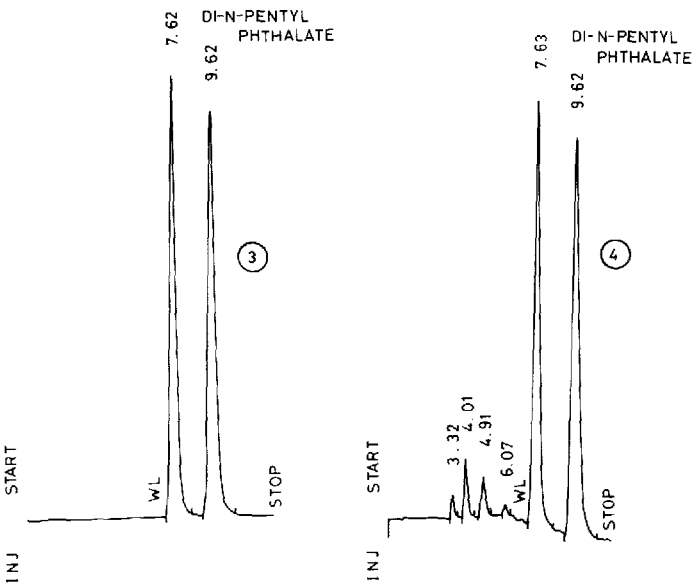

Fig. 2. Chromatography of (3) pure and (4) 40% EC triallate with acetonitrile–water (60:40) as eluent and di-*n*-pentyl phthalate as internal standard. WL = Moment in which the change of wavelength is produced.

The eleven linearity checking solutions from method B were analysed. Table II shows the amounts of triallate injected and found and also the accuracy, precision and calculated correlation coefficient, only for those results in which linearity was achieved.

Lower concentrations of the linearity checking solutions from method A were employed, using a signal-to-noise ratio of 2:1, to establish the detection limit, which was found to be 7.8 ng of triallate, equivalent to 10 μl of a $7.8 \cdot 10^{-4}$ g/l solution.

TABLE II

AMOUNTS OF TRIALLATE INJECTED AND FOUND AND THE CORRELATION COEFFICIENT, ACCURACY AND PRECISION, USING THE INTERNAL STANDARD METHOD (B)

$$\text{Accuracy (\%)} = \frac{\text{injected } (\mu g) - \text{found } (\mu g)}{\text{injected } (\mu g)} \cdot 100$$

Injected (μg)	*Found (μg)**	*Accuracy (%)*	*Precision (%)***
31.245	31.967	−2.31	1.08
15.622	15.242	2.43	0.28
7.811	7.998	−2.39	0.07
3.906	3.928	−0.56	0.18
1.953	1.958	−0.26	0.32
0.976	0.960	1.64	0.32
0.488	0.463	5.12	0.25
		Correlation coefficient: 0.9997	

* Average value.

** Relative standard deviation of three determinations (see first paragraph of Results and discussion).

In conclusion, both methods work satisfactorily for the determination of EC triallate, the confidence limits and relative standard deviations being approximately the same. The internal standard method has slightly better linearity, 0.5–30 compared with 0.5–15 μg of triallate.

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