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Note

High-performance liquid chromatographic determination of cyhexatin in technical and wettable pesticide powders

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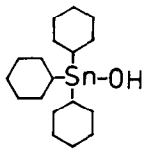
Cyhexatin (tricyclohexyltin hydroxide, Cy_3SnOH) (I) is a contact acaricide effective in the control of a wide range of phytophagous mites on apples, pears, citrus and ornamentals.



Various methods for the analytical determination of this acaricide involve acidic digestion of the compound to inorganic tin, followed by the colorimetric determination of the released tin with various colorimetric reagents[1–6]. These methods, in addition to being difficult to perform, are not specific for the actual active compound tricyclohexyltin hydroxide as they are designed for the determination of total tin.

For the determination of cyhexatin in the technical or formulated product, a non-aqueous titration method is available[7] in which the material is dissolved in 2-butanone and titrated to a potentiometric or colorimetric end-point with a standard solution of perchloric acid in 2-butanone. The main disadvantages of this procedure are that it is non-specific, insensitive and the end-point of titration is difficult to detect either potentiometrically or colorimetrically leading to poor accuracy and precision.

Gauer *et al.*[8] have described a gas-chromatographic (GC) procedure for the determination of cyhexatin residues in fruit crops. This method, which involves derivatisation of the compound to its bromide derivative, Cy_3SnBr, leads to losses and poor peak shape due to the apparent adsorption or decomposition of the cyclohexyltin bromide on column packing, walls and fittings. A GC method not involving derivatisation has been described by Camoui *et al.*[9] and although several columns and conditions were tried, peak tailing was still a problem. Stewart and Cannizzaro[10] have recently described the analysis of several organotin pesticides including cyhexatin by a procedure involving the formation of the methyl derivative of the pesticide, this being Cy_3SnCH_3 in the case of cyhexatin, and its determination by combined gas

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chromatography–mass spectrometry (GC–MS). The procedure described, while undoubtedly giving excellent specificity and sensitivity, uses instrumentation not readily available in most commercial laboratories.

In view of the difficulties with the present methods for the determination of cyhexatin as discussed above, a reversed-phase high-performance liquid chromatographic (HPLC) procedure has been developed in this laboratory for the routine determination of cyhexatin in the technical material and in a wettable pesticide powder. After suitable extraction the material is separated on an octylsilane reversed-phase column using methanol–water–phosphoric acid (82:18:1) as eluent. Detection is by UV at 220 nm. Using the recommended extraction time, the mean recovery of cyhexatin is 98.3% with a standard deviation of 0.9% for wettable powders containing 12.5–75% active material.

EXPERIMENTAL

Apparatus

The liquid chromatograph used consisted of a Kortec Model K-35 pump (Kortec, Ramsgate, N.S.W., Australia) and Altex 210 injector with 20-μl loop, and an Erma Model ERC-7210 variable wavelength UV detector (both supplied by Edwards Instrument Co., Sydney, N.S.W., Australia). Separations were performed on a Brownlee RP-8 reversed-phase column and chromatograms were recorded on an Omniscribe Model B5117-2 recorder (both supplied by Activon Scientific Service, Granville, N.S.W., Australia).

Reagents and standards

Cyhexatin Analytical Standard (99.0%, w/w) and cyhexatin technical material (94.2%, w/w) from Oxonitalia (Sompiong, Italy). Methanol (HPLC Grade, Burdick and Jackson) from Alltech Associates (Sydney, N.S.W., Australia). Orthophosphoric acid (85%, w/w) and sodium hydroxide, both analytical grade, from Ajax Chemicals (Auburn, N.S.W., Australia).

Preparation of mobile phase

To 820 ml of HPLC grade methanol, were added 180 ml of distilled water and 10 ml of 85% (w/w) orthophosphoric acid. This solution was then adjusted to pH 3.0 with a 50% (w/w) solution of sodium hydroxide.

TABLE I

LABORATORY PREPARED CYHEXATIN WETTABLE POWDER FORMULATION

Component	*% Added*			
	1	*2*	*3*	*4*
Cyhexatin	12.5	25.0	50.0	75.0
Wetting/dispersing agent	9.0	9.0	9.0	9.0
Clay	78.5	66.0	41.0	16.0

TABLE II

RECOVERY OF CYHEXATIN FROM A 50% (W/W) CYHEXATIN WETTABLE POWDER AGAINST EXTRACTION TIME WITH METHANOL–WATER (80:20)

Extraction time (min)	*Recovery (%)*
30	79.8
60	98.2
120	99.0
180	98.7
240	99.5
	Mean: 95.0

Preparation of working standard

A working standard solution was prepared by transferring 0.0553 g of analytical grade cyhexatin (99.0%, w/w) to a 500-ml volumetric flask. About 200 ml of methanol–water (80:20) were added to the flask and the flask shaken for 15 min by mechanical shaker. The volume was then adjusted to 500 ml with the same solvent and approximately 3–4 ml filtered through a Millipore 0.5-μm filter syringe.

Preparation of wettable powder formulations

Four wettable powder formulations containing cyhexatin were prepared as shown in Table I. These formulations were subsequently analysed by the method shown below and the results used to determine the linearity of the analytical method.

Determination of extraction efficiency

The extraction efficiency was determined by accurately transferring approximately 0.055 g of a 50% (w/w) wettable powder to four separate 500-ml volumetric flasks. To each flask was added 200 ml of methanol–water (80:20). The flasks were then shaken for periods varying from 0.5 to 4.0 h as shown in Table II. The volume in each flask was then adjusted to 250 ml with methanol–water (80:20) and a few ml of each solution filtered through a Millipore syringe filter containing a 0.5-μm filter. These solutions were then analysed using the chromatographic conditions shown below.

TABLE III

RECOVERY OF CYHEXATIN FROM LABORATORY PREPARED WETTABLE POWDER FORMULATIONS

As determined from duplicate 20-μl injections.

Sample	*% Added*	*% Found*	*% Recovery*
1	12.5	12.4	99.2
2	25.0	24.6	98.6
3	50.0	49.3	98.4
4	75.0	73.6	97.1
		Mean:	98.3
		S.D.	0.89%

Extraction of samples

Technical material. 0.0548 g of cyhexatin technical were added to a 500-ml volumetric flask and 200 ml of methanol–water (80:20) added to the flask and the flask shaken for 15 min by mechanical shaker. The solution was then made to volume (500 ml) with methanol–water (80:20) and approximately 3–4 ml filtered through a Millipore syringe filter containing 0.5-μm filter.

Cyhexatin 50 wettable powder. 0.0565 g of the formulated material were added to a 250-ml volumetric flask and 200 ml of methanol–water (80:20) added. The flask was then shaken for 1 h to extract the cyhexatin, the volume was adjusted to 250 ml and several ml of solution filtered through a Millipore filter syringe. This same procedure was used to determine the cyhexatin content of the laboratory prepared formulations.

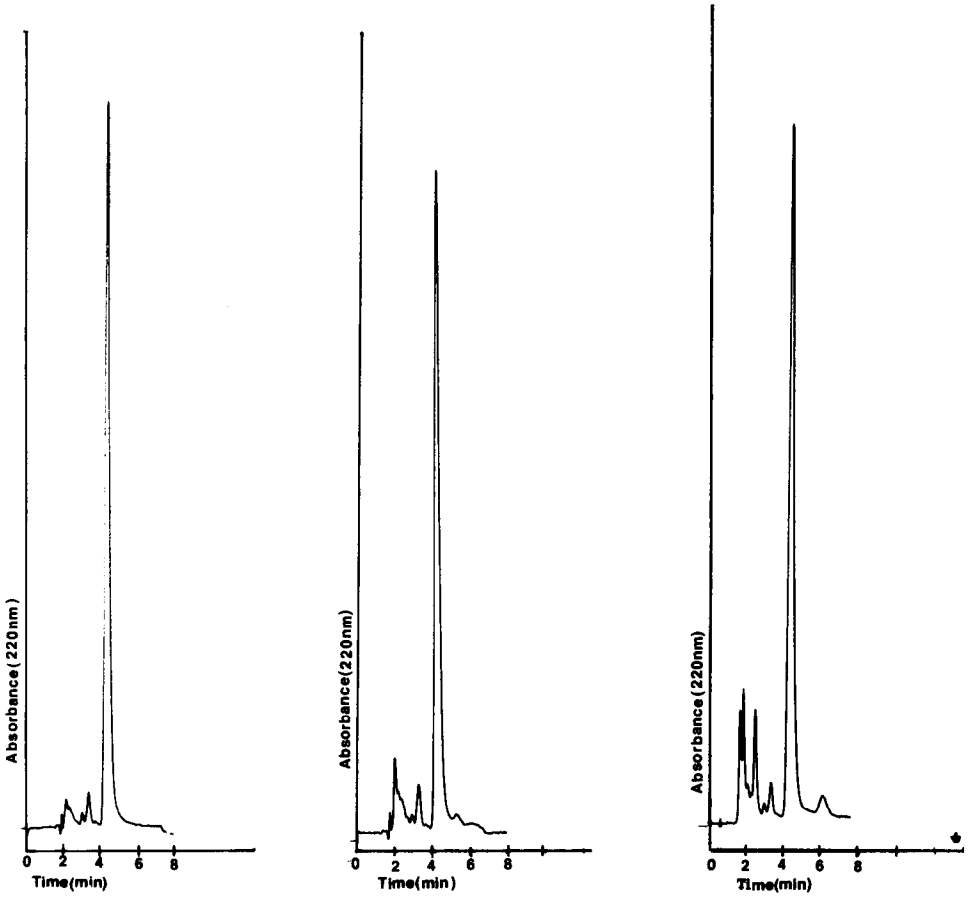

Fig. 1. Chromatogram of a cyhexatin working standard solution. For chromatographic conditions see Experimental section.

Fig. 2. Chromatogram of technical cyhexatin solution. For extraction and chromatographic procedure see Experimental section.

Fig. 3. Chromatogram of commercially produced cyhexatin 50 wettable powder. For extraction and chromatographic procedure see Experimental section.

Chromatographic conditions

Flow-rate, 2 ml min^{-1}; detector settings, 220 nm and 0.08 a.u.f.s.; chart speed, 0.5 cm min^{-1}; injection volume, 20 μl, each in duplicate.

RESULTS AND DISCUSSION

The recovery of cyhexatin from a 50% (w/w) cyhexatin wettable powder formulation after various periods of shaking with 200 ml of methanol–water (80:20) is shown in Table II. As can be seen from this table, extraction of cyhexatin is essentially complete after shaking with the above solvent for 2 h. Furthermore, shaking of the formulation in excess of 1 h leads to an only marginal increase in recovery ($\approx$ 1%) and so it was decided that for routine method application a 1-h extraction period would suffice.

Using a 1-h extraction period, the average percentage recovery of cyhexatin for wettable powder formulations containing 12.5–75% (w/w) cyhexatin is 98.3% (Table III). As expected, the greater the amount of cyhexatin in the formula the lower is the percentage recovery for equal extraction periods due to the low solubility of cyhexatin.

A typical chromatogram of a standard solution of cyhexatin is shown in Fig. 1, while Fig. 2 is a chromatogram of a solution of the technical material. A typical chromatogram of a commercially formulated and produced wettable powder is shown in Fig. 3 and, as can be seen, the wetting and dispersing agents commonly used in this type of formulation do not interfere with the cyhexatin peak, leading to excellent quantitation as is evident from Tables III and IV. Table IV also shows that the standard deviation is 0.18% for six determinations of a commercially produced batch of wettable powder containing a nominal 50% (w/w) cyhexatin.

TABLE IV

RECOVERY OF CYHEXATIN FROM SINGLE SAMPLE OF COMMERCIALLY PRODUCED WETTABLE POWDER FORMULATIONS CONTAINING A NOMINAL 50% (w/w) ACTIVE INGREDIENT

As determined from duplicate 20-μl injections.

Run	*% Found*
1	50.6
2	50.2
3	50.5
4	50.2
5	50.4
6	50.2
Mean	50.4
S.D.	0.18

For the concentration range 1–250 ppm detector response was linear with the calibration curve going through the origin. Using the above mobile phase (methanol–water–phosphoric acid, 82:18:1) it was found that it required approximately 30

column volumes of mobile phase to pass through the column, before a stable baseline was obtained. In addition, if the orthophosphoric acid was not added to the mobile phase, the retention time of cyhexatin increased from 4.4 min to more than 1 h.

With the detector set at its maximum sensitivity of 0.005 a.u.f.s., the minimum detectable concentration of cyhexatin was found to be 0.070 ppm (2 × noise level). While the above described procedure is intended for determination of cyhexatin in technical and formulated products, with a suitable extraction method, the chromatographic conditions and low detection limit should be suited for its determination at the residue level.

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