HPTLC Analysis of Octachlorodipropyl Ether in Insecticide Formulations

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Key Words

HPTLC
Octachlorodipropyl ether
Insecticide formulation
Silica gel
Densitometry

Summary

A simple, rapid, and sensitive high-performance thin-layer chromatographic method for analysis of octachlorodipropyl ether (OCDPE) in insecticide formulations has been established and validated. Known amounts of analytical grade OCDPE and its emulsifiable concentrate (EC) or wettable powder (WP) formulations were characterized by HPTLC on silica gel with toluene–acetic acid–water 20:20:1 (*v*/*v*) as mobile phase; detection was by spraying with silver nitrate–2 M alcoholic potassium hydroxide as chromogenic reagent and exposure to UV light. The plates were evaluated densitometrically at 399 nm. The results indicated that the calibration plot for OCDPE was logarithmic in the range 0.2–5.0 µg per band, and the correlation coefficient for the calibration equation in this range was 0.99. Recoveries from laboratory-prepared test EC and WP formulations using this method were 98.5–103.9% and 95.3–104.3%, respectively, and the respective RSDs were 3.39–4.89% and 2.92–5.33%. The accuracy and precision of the method were suitable for analysis of OCDPE in pesticide formulations.

1 Introduction

Octachlorodipropyl ether (bis(2,3,3,3-tetrachloropropyl) ether; OCDPE; CAS registry no. 127-90-2; commercial name S-2, S-421) is a chloroalkyl ether (**Figure 1**) first prepared in 1959 by *Becke* and *Sperber* [1] and soon discovered to have insecticidal and synergistic activity [2, 3]. It has been used as an insecticide synergist for pyrethroid, organophosphorus, and carbamate insecticides, which are widely used in commercial agricultural and household insecticides [4, 5]. It has been reported that an estimated 700 tons of OCDPE were produced in China in 1998 [6]; in Japan OCDPE had been produced at approximately 200 tons a year from 1972 to 2001 [7]. The acute toxicity of OCDPE is low, but it is now clear that OCDPE has subacute or chronic toxicity, for example subacute hepatotoxicity, cytotoxicity, carcinogenicity, and contact allergenicity [8, 9]. Because OCDPE is a substantial health risk to humans and other nontarget life forms during its production and use in pest control, the Ministry of Agriculture of the People's Republic of China proclaimed a law in 2006 that pesticides containing OCDPE that have not been registered in China from March 1st, 2007, cannot be sold in China from Jan 1st, 2008. It is known that an estimated 30% of pesticides marketed in developing countries do not meet internationally accepted quality standards [10]. In China, some pesticide products, especially agricultural insecticides containing OCDPE, do not list OCDPE on the label. Consequently, it is necessary to perform analysis for OCDPE in pesticide formulations.

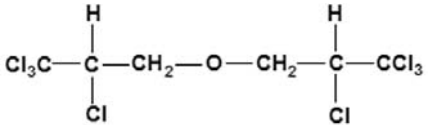

Figure 1

The structure of octachlorodipropyl ether (OCDPE).

The literature contains reports of analysis of OCDPE in household insecticides (mosquito coils or aerosol insecticide) based on gas chromatographic analysis with mass spectrometric detection (GC–MS) [5] or flame ionization detection (FID) [11]. As far as we are aware no published methods are available for analysis of OCDPE in agricultural insecticide formulations.

Modern quantitative HPTLC (high-performance thin-layer chromatography), when properly performed by well-trained analysts, has many advantages over high-performance liquid chromatography (HPLC) or gas chromatography (GC) in pesticide separation, detection, identification, and quantification, including:

– simplicity of operation;

– the availability of many sensitive and selective reagents for detection and confirmation without interference from the mobile phase;

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Table 1

Composition of emulsifiable concentrate (EC) formulation of OCDPE.

Test formulation	Technical grade OCDPE [g]	Emulsifier[a)] [g]	Solvent[b)]
10% OCDPE EC	5.40	5.0	Added to 50 g
1.0% OCDPE EC	0.54	5.0	Added to 50 g
0.1% OCDPE EC	0.054	5.0	Added to 50 g

[a)]Emulsifier 2201

[b)]Dimethylbenzene

Table 2

Composition of wettable powder (WP) formulation of OCDPE.

Test formulation	Technical grade OCDPE [g]	Wetting and spreading agent[a)] [g]	Carrier[b)]
10% OCDPE WP	1.1	5.0	Added to 10 g
1.0% OCDPE WP	0.11	5.0	Added to 10 g
0.1% OCDPE WP	0.011	5.0	Added to 10 g

[a)]Dregs of oil-tea-seed

[b)]Kaolin

– the ability to repeat detection and quantification at any time under different conditions, because the entire sample is stored on the plate;

– in-system calibration for quantitative analysis; and

– cost effectiveness, because many samples can be analyzed on a single plate with low solvent usage [12].

As an example, an HPTLC–densitometric method has been developed for analysis of commercial EC formulations of the synthetic pyrethroids cypermethrin, α-cypermethrin, and ë-cyhalothrin. Calibration plots for these insecticides were linear in the range 8–24 ng and the correlation coefficients ranged between 0.97 and 0.99. Recoveries from laboratory-prepared test samples of the EC formulations were in the range 95–99% [13]. Similar methods have been described for analysis of formulations of the pyrethroids fenvalerate and deltamethrin [14].

The purpose of this study was the development and validation of a HPTLC method for quantitative determination of OCDPE in commercially available agricultural insecticide formulations.

2 Experimental

2.1 Materials and Chemicals

Analytical grade octachlorodipropyl ether standard (98.0%) was obtained from *Dr Ehrenstorfer* (Augsburg, Germany). Technical grade octachlorodipropyl ether (93%) was obtained from Zhejiang Changxing Zhongshan Chemical Industry (Zhejiang, China). Emulsifier 2201 was obtained from Anhui Jintai Pesticide Chemical (Hefei, China). Methanol, acetonitrile, chloroform, toluene, acetic acid, ethyl acetate, dimethylbenzene, and 95% ethanol were analysis-grade from Shanghai Chemical Reagent (China Medicine Group, Shanghai, China).

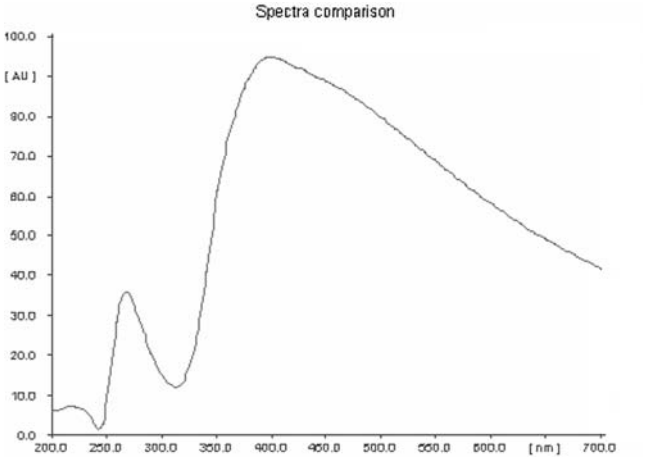

Figure 2

Overlaid spectra of OCDPE acquired in absorption mode by use of the Camag TLC scanner 3.

To prepare 2 M alcoholic potassium hydroxide 11.2 g potassium hydroxide was dissolved in 10 mL water and the total volume was adjusted to 100 mL with 95% ethanol.

2.2 Standard Solutions

A standard solution of 1.0 mg mL^{-1} OCDPE was prepared by dissolving 5.0 mg analytical-grade OCDPE in 5 mL acetonitrile in a volumetric flask and diluting to volume with acetonitrile. A standard solution of 0.1 mg mL^{-1} OCDPE was prepared by diluting the 1.0 mg mL^{-1} standard solution with acetonitrile.

2.3 Preparation of Test Formulations

Test formulations of OCDPE were prepared in the laboratory by mixing a known weight of technical grade OCDPE with solvent and emulsifier (for the EC formulation) or with wetting and spreading agent and carrier (for the WP formulation). The compositions of the EC and WP formulations are listed in **Tables 1** and **2**.

2.4 Sample Solutions

2.4.1 EC Formulations

Laboratory-prepared or commercially available EC formulations (0.500 ± 0.0002 g) were weighed into 10-mL volumetric flasks, dissolved in acetonitrile, diluted to volume with acetonitrile, and filtered through 0.45-µm syringe filters for chromatographic analysis. Five replicates were prepared for each treatment.

2.4.2 WP Formulations

Laboratory-prepared or commercially available WP formulations (0.500 ± 0.0002 g) were weighed into 25-mL centrifuge tubes and 10 mL acetonitrile was added. The samples were sonicated in an ultrasonic water bath at room temperature for 3–5 min then centrifuged for 10 min at 5000 rpm. The liquid

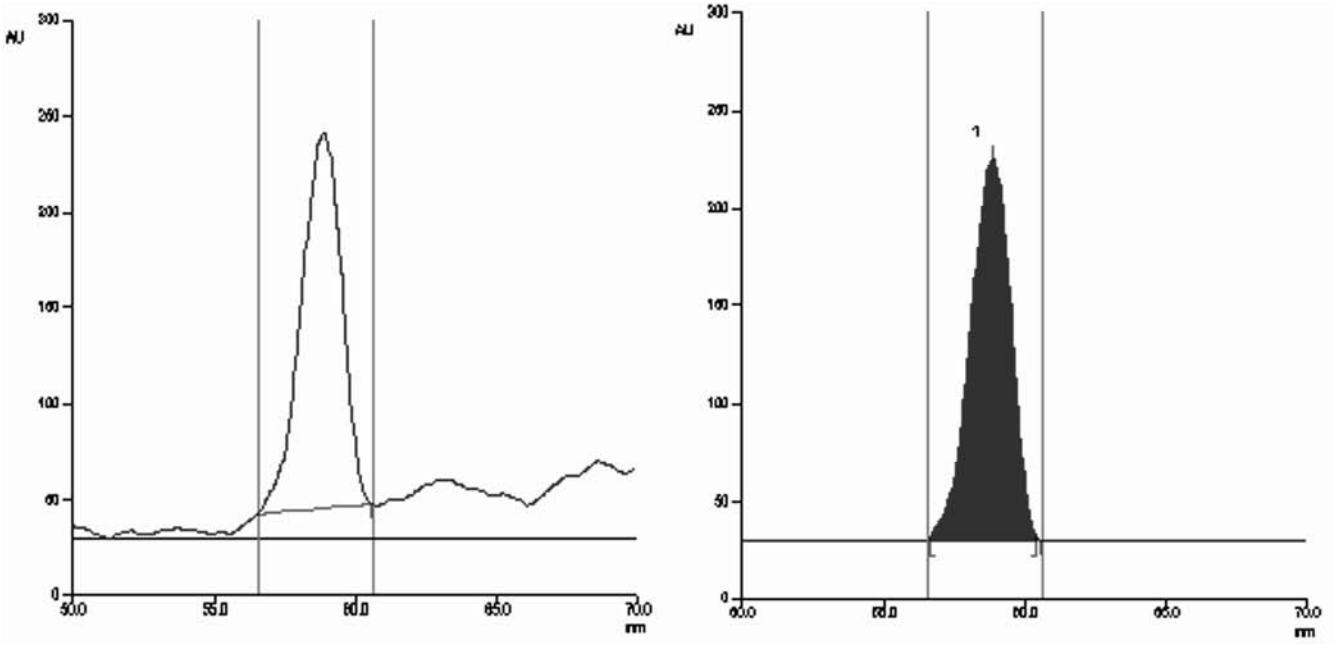

Figure 3

HPTLC chromatogram obtained from OCDPE standard.

phase was decanted into a 10-mL volumetric flask, diluted to volume with acetonitrile, and filtered through 0.45-µm syringe filters for chromatographic analysis. Five replicates were prepared for each treatment.

2.5 Chromatography

TLC was performed on 10 cm × 20 cm glass-backed silica gel 60 HPTLC plates (Qingdao Haiyang Chemical, China) previously prewashed by development with methanol–chloroform 1:1 (*v*/*v*) then activated at 110°C for 30 min. Solutions were applied to the plates as 5.0 mm bands by means of a Camag (Muttenz, Switzerland) Linomat IV applicator equipped with a 100-µL syringe. The plates were developed by the linear ascending technique with toluene–acetic acid–water 20:20:1 (*v*/*v*) as mobile phase in an unsaturated Camag glass twin-trough chamber. The development distance was 60–65 mm. The developed plates were freed from mobile phase, sprayed with 2 M alcoholic potassium hydroxide, heated for 30 min at 120°C, oversprayed with 1% silver nitrate in 30% nitric acid, then exposed to unfiltered UV illumination for approximately 15 min. Finally, evaluation of the HPTLC plates was performed densitometrically with a Camag TLC Scanner 3 controlled by an external PC running Wincats software (Version 1.1.2), absorbance was measured at 399 nm (**Figure 2**). Peak heights were recorded for all the tracks.

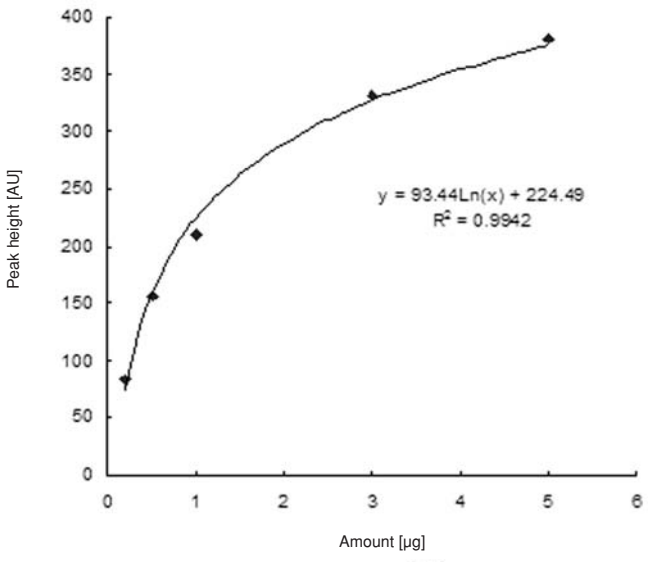

Figure 4

Calibration curve for determination of OCDPE.

3 Results and Discussion

3.1 Optimization of Chromatography

Initial trial experiments were conducted to select a suitable mobile phase for accurate analysis of OCDPE; this led to selection of toluene–acetic acid–water 20:20:1 (*v*/*v*). This optimum mobile phase furnished a dense, compact band on the plate and a well resolved peak on the densitogram; the R_F value of OCDPE was 0.93. A typical chromatogram obtained from OCDPE is shown in **Figure 3**.

3.2 Calibration Plot

A series of OCDPE calibration solutions was prepared from the standard solution and 0.2–5.0 µg OCDPE per band was applied to the plate. A calibration plot for OCDPE was constructed by plotting peak height (*Y*-axis) against amount of OCDPE (*X*-axis). The logarithmic regression equation for OCDPE was

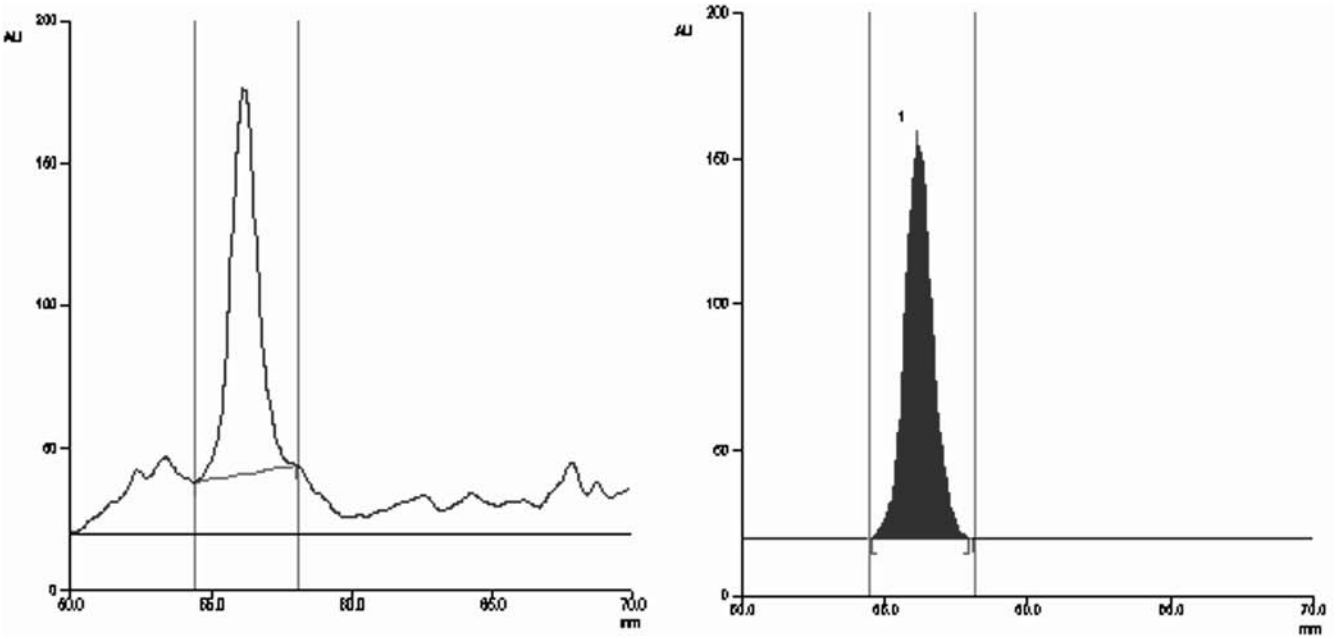

Figure 5

Chromatogram obtained from OCDPE from a laboratory-prepared EC formulation.

Table 3

Recovery of OCDPE from laboratory-prepared formulations.

Formulation	OCDPE content [%]	Amount on TLC plate [µg per band]		Recovery [%]	RSD [%]
		Applied	Found		
EC	0.1	0.30	0.295 ± 0.010	98.5 ± 3.34	3.39
	1.0	3.00	3.04 ± 0.15	101.2 ± 4.95	4.89
	10	3.00	3.12 ± 0.14	103.9 ± 4.55	4.37
WP	0.1	0.30	0.313 ± 0.012	104.3 ± 3.91	3.75
	1.0	3.00	2.86 ± 0.08	95.3 ± 2.78	2.92
	10	3.00	2.89 ± 0.15	96.3 ± 5.13	5.33

$Y = 93.44 \ln X + 224.5$, and the correlation coefficient for the calibration equation was 0.99. Under the conditions described above, the limit of detection for OCDPE was 0.1 µg for a 5-mm band. A typical calibration plot for OCDPE is shown in **Figure 4**.

3.3 Method Validation

Recoveries of OCDPE from laboratory-prepared formulations, determined by use of this analytical method, were 98.5–103.9% for EC formulations and 95.3–104.3% for WP formulations; the relative standard deviations (RSDs) were 3.39–4.89% and 2.92–5.33%, respectively. The precision and accuracy of this HPTLC method were suitable for pesticide formulation analysis.

The method is specific for determination of OCDPE in insecticide formulations, because there was no interference on the plate from other substances present in the formulations. An HPTLC chromatogram obtained from an extract from an EC formulation is shown in **Figure 5**.

3.4 Quantitation of OCDPE in Commercial Insecticide Formulations

Thirty-five commercial insecticide formulations were analyzed by use of this validated HPTLC method. Different amounts of standard OCDPE for the calibration plot and 5 µL sample solutions were applied to the plates and plate development and quantitation were performed as described in the experimental section. The results showed that 72.7% of test pyrethroid formulations contained OCDPE. As examples (**Table 4**), the OCDPE content of 2.5% cypermethrin EC formulation and of 2.5% β-Cyfluthrin EC formulation was 1.501% and 0.506%, respectively.

4 Conclusion

Quantitative HPTLC with densitometry can, when performed optimally, produce results comparable with those from gas chromatography (GC) and column liquid chromatography (HPLC).

Table 4

Concentrations of OCDPE in selected pyrethroid formulations, as determined by HPTLC.

Formulation	Replicate	Amount [µg per band]	OCDPE content [%]	Average ± SD [%]	RSD [%]
2.5% Cypermethrin EC	1	3.7796	1.512	1.501 ± 0.056	3.73
	2	3.5259	1.410		
	3	3.9054	1.562		
	4	3.7488	1.500		
	5	3.8026	1.521		
2.5% β-Cyfluthrin EC	1	1.3107	0.524	0.506 ± 0.013	2.63
	2	1.2617	0.505		
	3	1.2806	0.512		
	4	1.2531	0.501		
	5	1.2201	0.488		

The volume of sample solution was 5 µL

In the work discussed in this paper we successfully developed an HPTLC method for determination of octachlorodipropyl ether (OCDPE) in insecticide formulations. The method is simple, inexpensive, high-throughput, and precise and has been successfully used to estimate the OCDPE content of commercial insecticide formulations.

Acknowledgments

This work was supported by the Natural Science Key Research Project of Colleges and Universities in Anhui Province (Contract No KJ2007A020).

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Ms received: July 23, 2007
Accepted: September 29, 2007