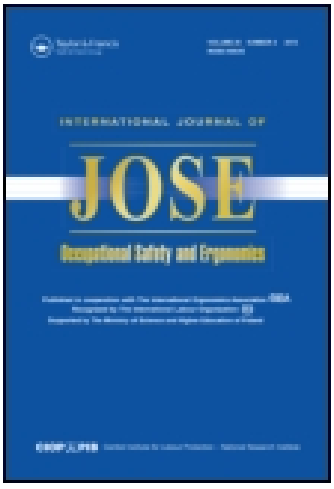

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Determination of Alphacypermethrin in the Air by Capillary Gas Chromatography

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A new method for sampling and chemical analysis of alphacypermethrin in workplace air has been described. Air samples were taken using a glass tube filled with silica gel with chemically bounded octadecyl phase. Chromatographic determinations were conducted using an HP-5 capillary column (10 m × 0.53 mm) and an electron-capture detector. Alphacypermethrin recovery was 100.15%. The calculated detection limit for a 60-L air sample was 0.0001 mg/m^3.

alphacypermethrin determination Fastac capillary gas chromatography

1. INTRODUCTION

Pyretroids are applied in plant protection as insecticides. Alphacypermethrin (CAS No. 67375-30-8) belongs to the group of synthetic pyrethroids. These compounds constitute a group of pesticides that are analogues of natural pyrethrines. Natural pyrethrines cover derivatives of pyrethrine acid as well as compounds without a typical cyclopropane cycle.

The following synthetic pyrethroids are currently applied in plant protection: deltamethrin, cypermethrin, permethrin, fenpropathrin, and fenvalerate. They are present in a wide range of pesticide products. Alphacypermethrin is an active component of the following preparations: Fastac 10 EC, Alfamor 05SC, Alfasekt 050SC, Alfazot 50 EC, Alphaguard 10 EC, Insektum A 01 AL, Ripcord New 050 EC, Ripcord.

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Considering their irritant properties, pyrothroids in workplace air may induce pathological symptoms in workers (Perkow, 1985). A reliable method for determining pyrethroids in the air is needed to control human exposure in the working environment. There is no literature on methods for determining alphacypermethrin in the air.

Based on references (Bottomley & Baker, 1984; Chapman, 1983; Ludwicki, Góralczyk, & Czaja, 1989; Nakamura et al., 1994; Nehmer & Dimov, 1994; Papadopoulu-Morkidou, 1988; Walters, 1983) and our earlier studies (Pomorska, 1993a) concerning the determination of synthetic pyrethroids, gas chromatography was selected for determining alphacypermethrin. A sampling cartridge filled with silica gel with chemical bounded phase C18 was used.

Earlier studies of pesticides sorption on silica gel with chemically bounded octadecyl phase (ODS-C18) showed that the sorbent was useful for chlorfenvinfos (Suprymowicz, Buszewski, & Pomorska, 1981). This publication presents results of studies characterizing this sorbent in detail. Studies of sorption of other pesticides (methydation, diazinon, malathion) on silica gel with ODS-C18 phase are presented in Pomorska (1993b).

2. MATERIALS

2.1. Reagents and Solutions

Nitrogen from a cylinder of 99.995% purity; acetone analytical grade; alphacypermethrin [(s)-cyano-3-phenoxybenzyl (1R,3R)-3-(2,2-clichloro-vinyl) 2,2-dimethylcycloprapanecarboxylate] standard, 99.0% (m/m) Dr Ehrenstofer GmbH; 1 g/L standard stock solution of alphacypermethrin in acetone. A standard solution of Fastac 10 EC in acetone 1 mg/ml.

2.2. Equipment and Materials

A Hewlett-Packard 5890 II gas chromatograph with an electron-capture (EC) detector equipped with

- a glass capillary column HP-5 (95% dimethyl-5% diphenyl polysiloxane) with the inside diameter equal to 0.53 mm and the length of 10 m;

- a sampling cartridge (Airsep), that is, glasses tubes with the inside diameter up to 10 mm and the length of 100 mm, filled with silica gel with chemically bounded phase C18. The mass of sorbent was 0.80 ± 0.02 g for one cartridge. The sorbent protected with glass wool stoppers. These cartridges were produced by the Industrial and Trade Enterprise Odczynniki Chemiczne (Lublin, Poland). Before use, acetone was passed through the sampling cartridge and dried with a stream of nitrogen;
- an aspirator type AP-2 (Technical Experimental Medical Institution, Łódź, Poland) with a flowmeter. The flow rate was 2 L/min;
- a unipam vacuum evaporator type 350.

3. EXPERIMENTAL

Properties of alphacypermethrin: a crystalline powder; melting point 80.5 °C; vapour pressure 1.7×10^{-7} Pa at 20 °C; solubility 0.01 mg/L water, 515 g/L cyclohexanon, 420 g/L chlorobenzene, 620 g/L acetone, 350 g/L xylene (Worthing, 1991).

3.1. Chromatograph Operation Conditions

Alphacypermethrin was determined under the following conditions: EC detector, temperature 300 °C; column temperature 260 °C; inlet temperature 275 °C; carrier gas (N_2), total flow 60 ml/min; injection volume 1 μl, retention time 189 s. Figure 1 presents a chromatogram of a standard solution of 0.3 mg/L.

3.2. Calibration Graph

An alphacypermethrin standard solution with concentration ranging from 0.1 to 1.5 mg/L was prepared by diluting the 1-g/L stock solution with acetone. The standards were injected into the chromatographic column in 1-μl doses. The correlation between the mean areas below peaks and alphacypermethrin concentrations within the range (0.1–1.0 μg/ml) was linear. Table 1 presents calibration data. Figure 2 presents the calibration graph.

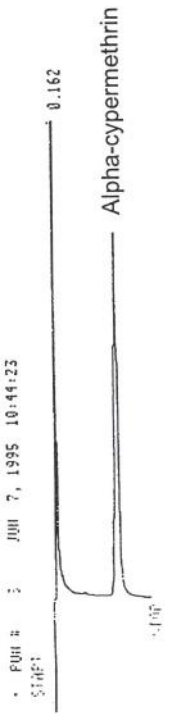

Figure 1. A chromatogram of a standard solution of alphacypermethrin 0.3 mg/L.

TABLE 1. Correlation Between Detector Readings and Alphacypermethrin Concentration

Sample Number	Alphacypermethrin Concentration (mg/L)	Area of Peaks	Mean Value
1	0.1	57,971 59,112 57,010	58.031 ± 1.052
2	0.3	150,168 146,814 147,632	148.205 ± 1.749
3	1.0	514,083 415,014 412,839	415.312 ± 2.603
4	1.5	884,885 884,988 907,867 909,315	896.762 ± 23.677

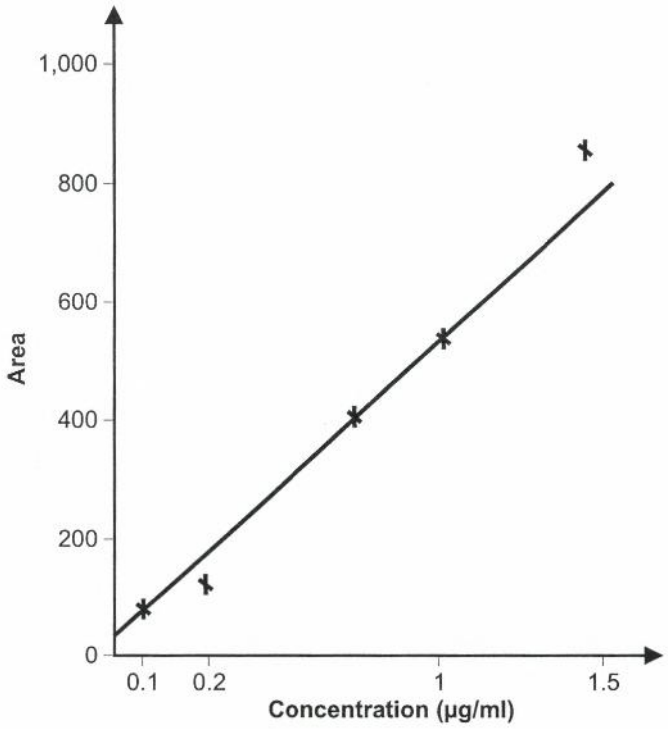

Figure 2. Relationship between the detector response and the concentration of alphacypermethrin.

3.3. Air Sampling

Alphacypermethrin was collected by passing air through an Airsep sampling cartridge. Air passing was facilitated by the use of an AP-2 aspirator with a flowmeter. Usually 30–60 L of air were passed at a flow rate of 2 L/min.

3.4. Sample Preparation and Determination

Samples were extracted from approximately 20 ml of acetone. The extracts were evaporated at room temperature using a rotary evaporator.

The dry residue was reconstituted with 1 ml of acetone and a 1-μl sample was injected into a chromatographic column. In quantitative analysis the areas below peaks for the standard and tested solutions were compared.

3.5. Recovery Test

The recovery test was carried out using Fastac 10 EC standard solutions. Fastac 10 EC solutions equivalent to 0.1, 0.3, and 1.5 μg of alphacypermethrin were applied. Cartridges containing silica gel ODS-C18 were spiked with the alphacypermethrin 0.1, 0.3, and 1.5 μg. Six samples for each concentration were prepared. After spiking, clean air (60 L) was passed through the cartridges at a rate of 2.0 L/min by using an AP-2 aspirator with a calibrated flowmeter.

The sampling cartridges were extracted according to the procedure described in section 3.4. Table 2 presents the data recoveries.

TABLE 2. Alphacypermethrin Recovery From Silica Gel ODS–C18 Filled Sampling Cartridges

Number of Samples	Mass of Alphacypermethrin Spiked Cartridges (μg)	Recovery Value[a] (%)	Mean Recovery Value (%)
6	0.1	89.00 ± 8.15	
6	0.3	109.00 ± 11.15	100.15
6	1.5	102.46 ± 1.40	

Notes. a—each value is mean ± percentage of relative standard.

3.6. Stability of Samples During Storage

Six cartridges containing silica gel ODS-C18 were spiked with known amounts of technical alphacypermethrin (0.001 mg). Clean air flow was passed (average of 30 L) by them. Polyethylene adapters were attached to both sides of cartridges and stored at 4 °C.

The analyses were done after 24 hrs, 1, and 2 weeks according to the procedure described in section 3.4. Table 3 presents the results.

TABLE 3. Stability of Technical Alphacypermethrin on Silica Gel ODS–C18 Filled Cartridges at Trap Temperature of 4 °C[a]

Number of Samples	Mass of Alphacypermethrin Spiked Cartridges (μg)	Recovery Value (%)		
		24 hrs	1 week	2 weeks
6	0.3	99.50 ± 9.10	101.16 ± 1.50	101.00 ± 1.60

Notes. a—$n = 6$, each value is mean ± percentage of relative standard.

4. RESULTS AND DISCUSSION

The method developed for determining alphacypermethrin concentrations in air samples utilizes a sampling tube called Airsep (Odczynniki Chemiczne; Lublin, Poland), which is available on the market. The sampling tube is filled with silica gel with chemically bounded octadecyl phase. Gas chromatography with an electron capture detector and an HP-5 column capillary is used for determining alphacypermethrin. Figure 1 presents a sample chromatogram of the pattern substance.

Figure 2 shows correlation between the detector readings and the range 0.1–1.5 μg/ml. This dependence was linear of the range 0.1–1.0 μg/ml.

The collection efficiencies were estimated from the retention efficiencies because it is difficult to prepare air standards containing technical alphacypermethrin. Cartridges containing silica gel with chemically bounded octadecyl phase (ODS-C18) were spiked with a Fastac 10 EC solution (equivalent to 0.0001–0.001 mg of alphacypermethrin), and clean air was passed through the cartridges at a rate of 2.0 L/min. Table 2 shows that recoveries varied between 89 and 109%, mean 100.15%.

The stability of alphacypermethrin on cartridges containing silica gel with chemically bounded octadecyl phase (ODS-C18) was determined by spiking the cartridges with a Fastac 10 EC solution (equivalent to 0.001 mg of alphacypermethrin) and storing them at 4 °C. The analyses were done after 24 hrs, 1, and 2 weeks. The results in Table 3 show that samples collected on these cartridges can be kept for up to 2 weeks before analysis.

5. CONCLUSION

We have shown sampling, extraction, and determination for alphacypermethrin in the air. The following results of determining alphacypermethrin in the air were obtained:

- detection limit based on a 60-L air sample was 0.0001 mg/m^3, detectability of the analysis 0.1×10^{-9} g,
- recovery of alphacypermethrin from the sorbent was 100.15% (mean value).

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