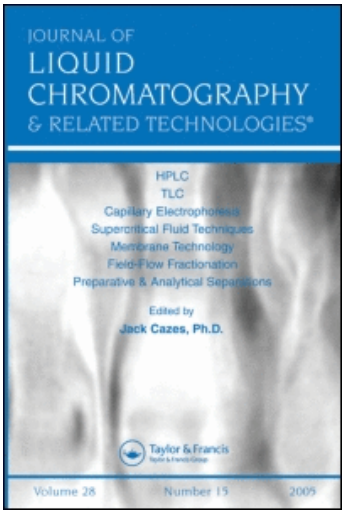

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FILTER COLLECTION OF AIRBORNE PERMETHRIN WITH DETERMINATION BY HPLC

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ABSTRACT

Glass microfiber filter was evaluated for the collection of permethrin aerosols. Determination and quantification of collected permethrin isomers by high performance liquid chromatography was developed on an octadecyl bonded phase column with an aqueous acetonitrile solvent and ultra-violet detection. Sampling of a test atmosphere of permethrin aerosol indicated a filter collection efficiency greater than 96%. The detection limit of the method for permethrin in air was estimated to be 8 $\mu g/m^3$ for a 20 L air sample.

INTRODUCTION

The pyrethrins are a class of very effective insecticides noted for their low mammalian toxicities and biodegradability. The prototype compounds were natural products isolated from chrysanthemum flowers and were characterized by photosensitivity and instability in air. To alleviate these problems, much effort has been devoted to the preparation of synthetic pyrethrins with

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properties more appropriate for commercial insecticidal application. One of the most effective of these new synthetic pyrethrins is (3-phenoxyphenyl)methyl(+-)-cis, trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate, (permethrin).

Permethrin is characterized by photostability, low vapor pressure ($3.4x10^{-7}$ mm Hg at 25°C) and low solubility in water (<0.1 mg/L at 20°C). These properties make it particularly useful for insect control on premises.

The toxicity of permethrin in non-target organisms is dependent on the ratio of the cis/trans isomers in the sample. For a cis:trans ratio of 40:60, typical of many commercial formulations, the oral LD_{50} in rats ranges from 430 to 4000 mg/kg (1). In contrast to its low toxicity in mammalian species, permethrin is quite toxic to fish; the 96 hour LC_{50} in rainbow trout is 9 µg/L (1).

Although no specific federal standard for occupational exposure to permethrin currently exists, the Occupational Safety and Health Administration (OSHA) does have an exposure standard for pyrethrum of 5 mg/m³ in air, time weighted average for an 8 hour working day (2). This is equivalent to the recommendations of the American Conference of Governmental Industrial Hygienists (ACGIH). In addition, the ACGIH recommends a short-term excursion limit of 10 mg/m³ averaged over a fifteen minute period (3).

The pyrethrins are particularly amenable to analysis by high performance liquid chromatography (HPLC) due to their low volatility and good ultraviolet absorbence. Recent work has been directed toward the determination of pyrethrins in various matrices using HPLC. Permethrin and its metabolites, m-phenoxyphenyl alcohol and m-phenoxybenzoic acid, were separated and determined by reversed-phase HPLC with UV detection at 254 nm (4). The sample matrix was not specified. The National Institute for Occupational Safety and Health (NIOSH) recommends an HPLC technique for the determination of airborne pyrethrum (5). The method involves collection of pyrethrum on glass fiber filter, desorption of the collected pyrethrum, and RP-HPLC with detection at 225 nm.

Using the NIOSH method as a base, we have evaluated and optimized the collection and analysis techniques for the determination of airborne permethrin.

METHODS AND MATERIALS

Permethrin, 98% purity, approximately 60% trans/ 40% cis, was obtained from Chem Service, Inc. This material was used as a standard for all analyses.

Permectrin II, a commercial 10% emulsifiable permethrin formulation, was obtained from Anchor Laboratories, Inc., and was used for the generation of test atmospheres of permethrin aerosol.

A Beckman Model 25 UV-VIS spectrophotometer was used to obtain an absorbence spectrum of the standard permethrin. The instrument was operated with a 1.0 mm slit width. A solution of 60 µg/mL permethrin in acetonitrile (J.T. Baker, HPLC grade) was contained in a 1 cm quartz cuvette. The absorbence of this solution was measured from 180 to 325 nm vs. an acetonitrile blank.

Liquid chromatographic analyses were performed using a Waters Model 6000A pump and Model U6K injector. The column chosen for the analyses was 3.9 mm x 30 cm, packed with µ-Bondapack C18 (Waters). Detection was accomplished via UV absorbence with a Waters Model 450 Variable Wavelength detector operated at 234 nm. The output of the detector was fed to a strip chart recorder for documentation.

Chromatographic conditions were optimized using a mobile phase of 80% acetonitrile/ 20% water. Flow through the column was 1.5 mL/min. Injection volumes were held constant at 25 µL. The column was kept at room temperature, generally between 22 and 25°C.

In order to assay the Permectrin II sample, 15 µL of the material was diluted to 50.0 mL with acetonitrile. Sonication was necessary to completely dissolve the sample. It was then analyzed by HPLC and quantitated by comparison to a standard curve.

A test atmosphere of permethrin aerosol was generated in a chamber with dimensions 2.25 m x 1.89 m x 2.55 m. The temperature

and relative humidity were 23°C and 65%, respectively. Approximately 2.5 mL of a 10% solution of Permectrin II in distilled water was placed in the liquid reservoir of a Model 40 glass nebulizer (DeVilbiss Co., Somerset, Pa.). The nebulizer was placed inside the test chamber. To generate the permethrin aerosol, the nebulizer was operated with compressed breathing air at a pressure of 10 psi across the nebulizer jet. The nebulizer was operated until no further aerosol was being produced, as determined by visual inspection. This was approximately 3 minutes after the beginning of aerosolization.

The test aerosol produced in the chamber was sized by using an Andersen 2000 Inc., 1 ACFM Ambient Particle Sizing Sampler. This instrument is a cascade impactor capable of sizing particles in the size range of 11 to 0.43 micron (μm). Glass plates, 82 mm in diameter, were used as the impaction/collection stages for the impactor.

The impactor was operated at a sampling rate of 28.3 liters per minute (Lpm) for 5.5 minutes, beginning simultaneously with the start of nebulization. After collection, the glass impaction stages were washed with 10 mL of acetonitrile; the washings were transferred to individual containers, placed in a 40°C water bath and evaporated to dryness under a gentle stream of dry NF nitrogen. The residue was redissolved in 1.0 mL of acetonitrile and submitted for analysis by HPLC.

Samples for the determination of airborne permethrin levels were collected on 25 mm glass fiber filters (Gelman Sciences, Type A/E) contained in stainless steel filter holders (Gelman No. 1209). The air samples were collected at a flow rate of 1.0 Lpm maintained by use of a critical orifice and high vacuum pump.

A set of sequential samples was collected beginning at the onset of aerosol generation and ending 72 minutes later. The sampling times ranged from 14.5 to 16.5 minutes.

In order to determine the collection efficiency of the glass fiber filter for the permethrin aerosol, two sets of samples were collected in which two filters were connected in series and

attached to the sampling pump. The two filters were contained in separate filter cassettes. After collection, the primary and back-up filters for the two runs were prepared and analyzed separately.

All filter samples were prepared for analysis by placing the filter in a 20 mL development vial. To the sample was added 1.0 mL of HPLC grade acetonitrile. The sample was then sonicated for 10 minutes to desorb collected permethrin. The supernate was pipetted from the vial and transferred to a 5 mL glass conical centrifuge tube. This was then centrifuged at 800 x g. for 10 minutes to precipitate suspended glass microfibers. The clear supernate was then injected (25 µL) into the HPLC for quantitation of permethrin.

The desorption procedure described above was evaluated for the efficiency of recovery of collected permethrin. Three filters were prepared to which 100 µL of a solution of 30 µg/mL of permethrin in acetonitrile was added. The acetonitrile was evaporated from the filter by gentle ventilation with nitrogen for several minutes. The filters were then stored overnight at 5°C. Subsequently, the filter samples were heated to room temperature and carried through the desorption procedure described above. The samples were analyzed and compared to standards to determine the recovery efficiency.

RESULTS AND DISCUSSION

Figure 1 illustrates the ultraviolet absorbence spectrum of the standard permethrin solution. The absorbence maximum occurs at a wavelength of 234 nm. This is in contrast to the NIOSH method for pyrethrum which uses a detection wavelength of 225 nm (5). Of interest is the relatively low absorbence of the compound at 254 nm, a major mercury vapor lamp emission line and the most common wavelength of operation for fixed wavelength UV detectors. The absorbence of permethrin at 234 nm is approximately one order of magnitude greater than that at 254 nm. Detection at 254 nm would greatly diminish the sensitivity of analysis by HPLC.

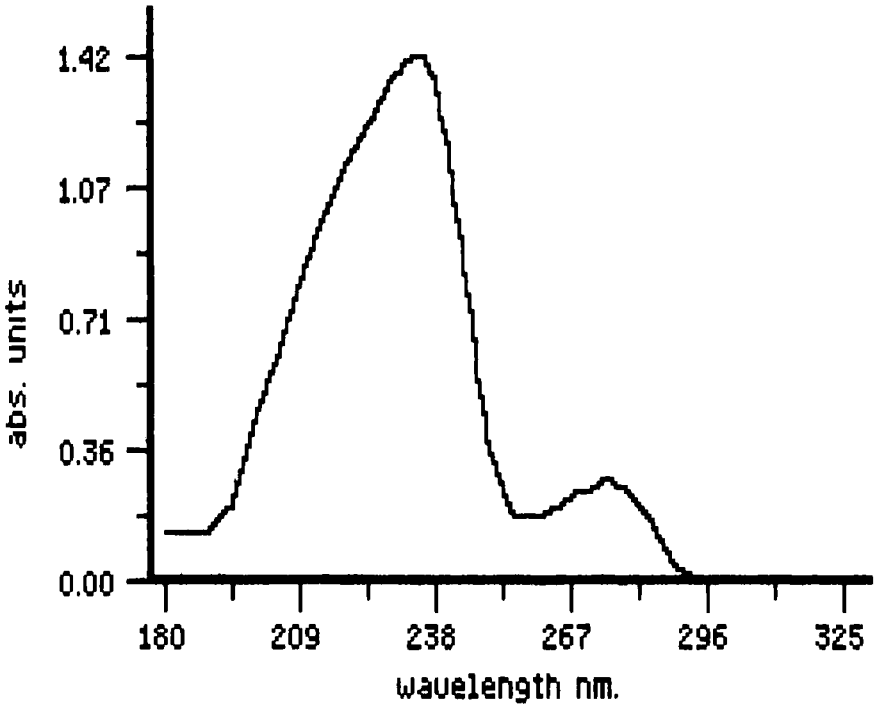

FIGURE 1 - UV absorbence spectrum of permethrin standard.

A chromatogram of a standard sample of permethrin is shown in Figure 2A. Excellent resolution of the cis/trans isomers is obtained under the isocratic chromatographic conditions. The permethrin isomers elute within 10 minutes, enabling rapid analysis of samples.

A standard curve covering a range of approximately 1 to 100 µg/mL permethrin is shown in Figure 3. The linearity of response over a range of two orders of magnitude is evident. The limit of detection under the instrumental conditions used for the standard curve is estimated to be 0.15 µg/mL for either isomer. For this work, the detection limit is defined as the quantity of permethrin necessary to give a detector response (peak height) equal to twice

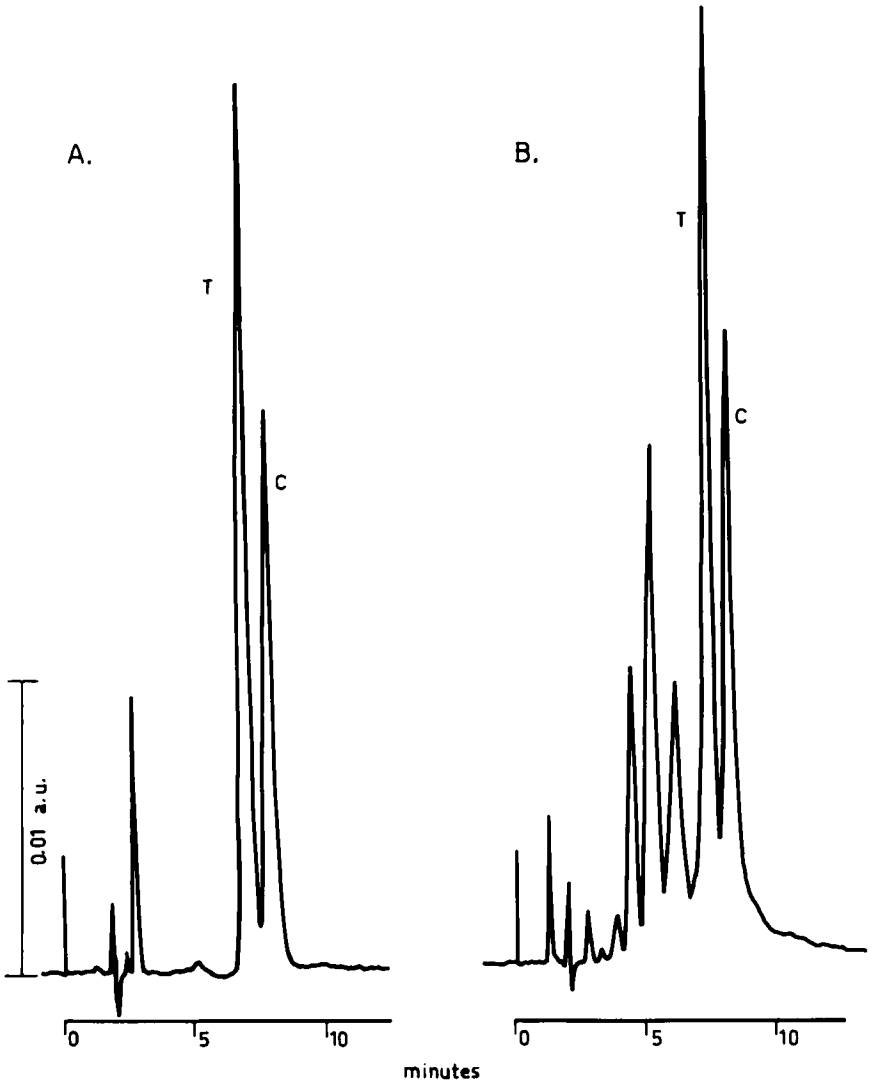

FIGURE 2 - Sample chromatograms. A: standard permethrin. B: Permectrin II sample. T = trans-permethrin; C = cis-permethrin. 30 cm x 3.9 mm column packed with μ-Bondapack C18. Mobile phase: 80% acetonitrile, 20% water, 1.5 mL/min. Absorbence measured at 234 nm.

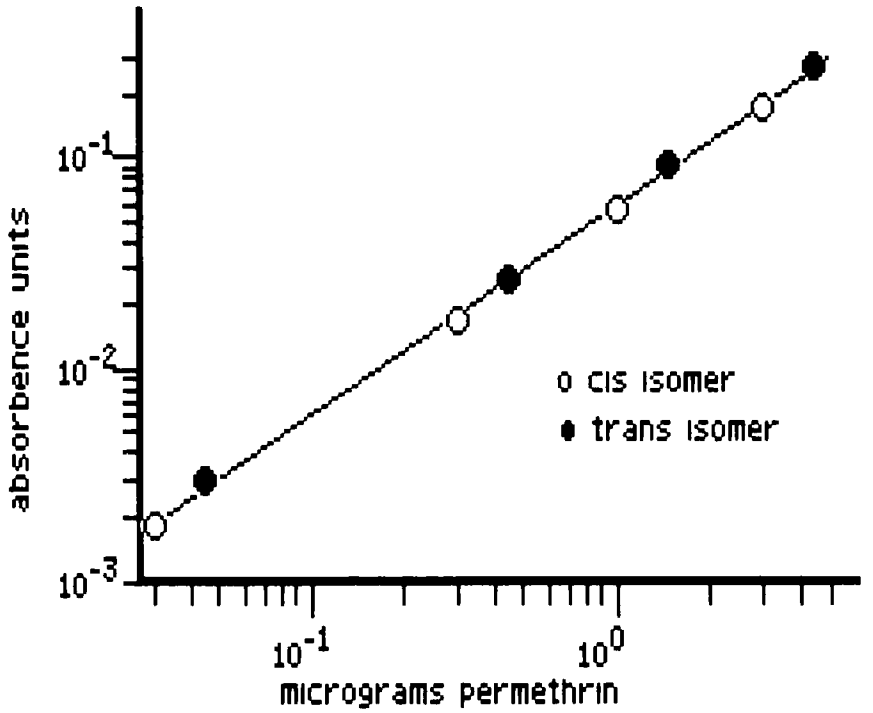

FIGURE 3 - Standard curve of cis, trans isomers of permethrin.

the least recordable deflection. This value is 2.5% of a full scale deflection for our instrumental set up. For a 20 L air sample, this would be equivalent to a concentration of approximately 0.008 mg/m³, or 0.2% of the comparable pyrethrum exposure standard.

The chromatogram shown in Figure 2B was produced from the assay of the Permectrin II sample. The permethrin isomers are easily separated from the other components of the sample, probably emulsifiers. The ratio of absorbences of the cis/trans isomers was shown to be 1.55 (trans/cis) for this sample as compared to a ratio of 1.59 for the permethrin standard. The results of the assay yielded a permethrin concentration of 10.2%; the nominal value supplied by the manufacturer was 10.0%.

Particle size analysis of the permethrin test aerosol used in the evaluation of the filter collection technique indicated a mass median diameter (MMD) of 3.1 μm and a geometric standard deviation of 2.49. These values are based only on permethrin content of the aerosol; i.e., 50% of the airborne permethrin was contained in aerosols of 3.1 μm aerodynamic equivalent diameter or smaller. This size particle is well within the respirable range and is generally of most import in terms of health effects.

The results of the recovery efficiency experiment are shown in Table 1. For either isomer of permethrin, essentially 100% of the spiked material was recovered under the conditions of desorption.

Likewise, evaluation of the collection efficiency of the glass fiber filter for permethrin aerosol indicated essentially complete collection by the primary filter cassette: 3.7 μg permethrin were found on each primary filter (aerosol concentration 0.24 mg/m³), while no permethrin was detected on either backup filter. Based on a detection limit of 0.15 μg per filter, the collection efficiency was at least 96%. Glass microfiber filters have been shown to be greater than 99% efficient at

TABLE 1
Recovery Efficiency of Collected Permethrin

Sample	μg Permethrin Spiked		μg Permethrin Recovered		% Recovery Efficiency	
	Trans	Cis	Trans	Cis	Trans	Cis
A	1.8	1.2	1.73	1.18	95.9	98.0
B	1.8	1.2	1.81	1.22	100.6	102.0
C	1.8	1.2	1.79	1.27	99.4	105.9
				Avg.	98.6	102.0
				S.D.	±2.4	±4.0

collecting 0.3 μm particles of dioctylphalate (6). Although the filters will not efficiently collect permethrin vapor, the vapor pressure of permethrin is so low at room temperature that the vapor concentration would be insignificant in relation to the aerosol concentrations of interest.

The results of the analysis of the permethrin test atmosphere are shown in Figure 4. The height of the bar is equivalent to the average concentration determined over the sampling period indicated as the width of the bar. The samples clearly illustrate the decay of the airborne permethrin as it diffuses, impacts and absorbs onto the surfaces of the test chamber.

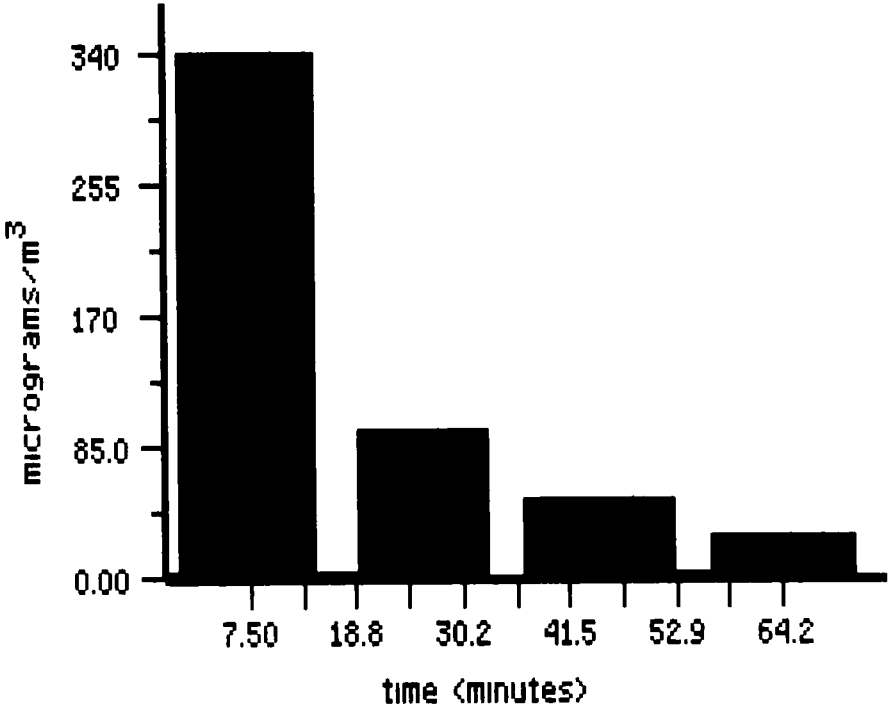

FIGURE 4 - Decay of permethrin aerosol test atmosphere.

The characteristics of the test atmosphere: particle size distribution and airborne concentration of permethrin, are similar to what may be expected during the use of an aerosol bomb in fumigation practices. The filter collection technique is clearly appropriate for accurate sampling of this type of atmosphere. The collection apparatus when used in conjunction with a small battery operated sampling pump is small and convenient for use in personal breathing-zone monitoring of worker exposure during the application of permethrin. Although the method was evaluated for test atmospheres similar to aerosol bomb applications, it should be amenable to sampling during the use of manual pressurized spray apparatus which generally produce a much larger aerosol than that evaluated here.

Reversed phase HPLC is an excellent technique for the determination of collected permethrin. The technique allows for rapid analysis along with chromatographic resolution adequate to not only separate permethrin from components of the sample matrix but also to resolve and quantitate the cis/trans isomers of the compound. The method should prove valuable both for compliance monitoring of worker exposure and for research into the environmental effects of airborne permethrin.

ACKNOWLEDGEMENT

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