

SYNTHETIC PYRETHROIDS DETERMINATION FROM FUNCTIONALIZED TEXTILE MATERIALS - PERMETHRIN

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Cell Solution® Protection fibers are natural cellulosic manmade fibers and provide effective and durable protection against insects - such as ticks and mosquitoes. Cell Solution® Protection fibers can be easily processed into textiles and have consistent dyeability when following the recommended processing/finishing method. Permethrin is a chemical categorized in the pyrethroid, insecticide group. Permethrin is used as an insecticide in agriculture or as a personal protective measure (cloth impregnant, used primarily for US military uniforms and mosquito nets). The objective of this work was the determination of Permethrin from functionalized textile materials. Permethrin has four stereoisomers (two enantiomeric pairs), arising from the two stereocenters in the cyclopropane ring. (1R,3S)-trans and (1R,3R)-cis enantiomers are responsible for the insecticidal properties of permethrin. We performed the extraction of Permethrin from textile materials using accelerated solvent extraction (ASE), followed by identification of permethrin and quantification by liquid chromatography with spectrophotometric detection (HPLC-MWD) and we confirmed the results by gas chromatography with mass spectrometric detection (GC-MS). Both analytical methods have contributed to determination of trans and cis-permethrin.

Keywords: Permethrin-impregnated clothing, Cell Solution® Protection Fibers, chromatography

INTRODUCTION

Permethrin is an insecticide in the Pyrethroid family, which are synthetic chemicals that act like natural extracts from the chrysanthemum flower. Clothing, shoes, bed nets, and camping gear can be treated with a pesticide called permethrin to kill or repel insects such as mosquitoes and ticks. Clothing and other products can be purchased pre-treated, or products can be treated using EPA-registered products. The U.S. Military has been using permethrin to treat combat uniforms for over 20 years to protect soldiers from diseases carried by insects. Permethrin is the only pesticide approved by the EPA for these uses. When it is applied properly, permethrin binds tightly to the fabrics, resulting in little loss during washing and minimal transfer to the skin. Permethrin is poorly absorbed through the skin, although sunscreens and other products may increase the rate of skin absorption (<http://npic.orst.edu/pest/mosquito/ptc.html>). Personal protective measures against hematophagous vectors constitute the first line of defense against arthropod-borne diseases. In this regard, a major advance has been the development of residual insecticides that can be impregnated into clothing (Faulde *et al.*, 2016). Cell Solution® Protection fibers provide effective and durable protection against insects - such as ticks and mosquitoes. Via direct spinning, the insect repellent permethrin is embedded in the Cell Solution® fiber core and migrates to the fiber surface in a tightly controlled manner. The patented technology ensures that a small, but just enough amount of permethrin is diffused from the inner of the Protection fiber to the surface. The direct contact with high concentration of active ingredients for example, in a coating, is avoided because the stored permethrin from the interior of the Cell Solution® Protection fiber is resupplied in small doses. Due to the limited availability of the active substance at the fiber's surface it is avoided that the active

substance is lost rapidly by environmental influences. Impregnation by dipping, spraying or even covering of polymer-insecticide blends on the fabric's surface give long-term permanent anti-insecticide activity at very high concentration only.

Our study was focused on the extraction of Permethrin from textile materials using accelerated solvent extraction (ASE), followed by identification of permethrin and quantification by two chromatographic methods, HPLC-MWD and GC-MS.

EXPERIMENTAL

We used 3 textile materials in our study: Raw Cell Solution Protection knit, Bleached Cell Solution Protection knit and Dyed Cell Solution Protection knit.

The three test specimens were subjected to accelerated solvent extraction. Approximately 1 g of material was weighed out of each sample. These were cut into pieces and introduced into extraction cells (22 mL volume) which were filled with diatomaceous earth and subjected to methanol-accelerated extraction.

Extraction Method

The condition of the extraction method are the following:

Solvent: Methanol;

Preheat time: 5 min;

Analysis time: 40 min;

Extraction cycles: 3;

Temperature: 80°C;

Washing: 60% with methanol

After extraction, the resulting solutions were allowed to cool and subsequently filtered through 0.45 µm PTFE filters and transferred to vials for further analysis by HPLC-MWD and GC-MS. For the quantification of permethrin in the textile samples a calibration curve was made by diluting stock solution of permethrin to the following concentrations: 2400 ppm, 1800 ppm, 1200 ppm, 600 ppm and 300 ppm.

Liquid Chromatography with Spectrophotometric Detection (HPLC-Equipment Agilent Technologies 1100 series MWD)

Conditions of the detection method used are the following:

Eluent: Acetonitrile / HOH: 90/10, isocratic

Stationary phase: Zorbax Eclipse XDB C18 column (3.5 µm); (150 x 4.6) mm

Flow rate: 0.5 mL / min

Column temperature: 32°C

Volume injected: 10 µl

Detection: MWD (spectrophotometer) at 275 nm.

Gas Chromatographic Method Coupled with Mass Spectrometry (GC-MS 6890N / 5793 Agilent Technologies)

Capillary column: DB-35MS (J & W)®, length: 35 m, inside diameter 0.25 mm

Injection system: splitless; Injector temperature: 250°C;

Carrier gas: helium;

Flow rate: 1.24 mL / min

Temp. program: Initial temp.: 70°C (1min), Heating rate: 25°C/min., Final temp.: 280°C (8min);

Injection volume: 1 µl; Detector: MS (mass spectrometer)

RESULTS AND DISCUSSIONS

Sample Raw Cell Solution Protection Knit

Sample Name: Crud

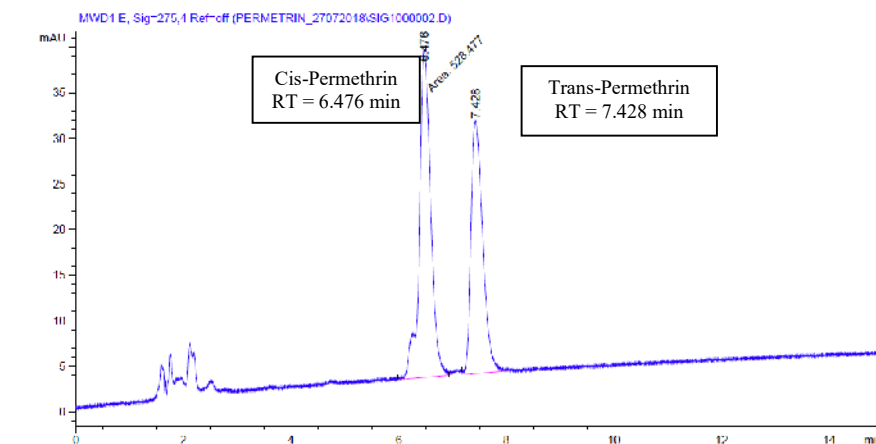


Figure 1. HPLC chromatogram of sample Raw Cell Solution Protection Knit

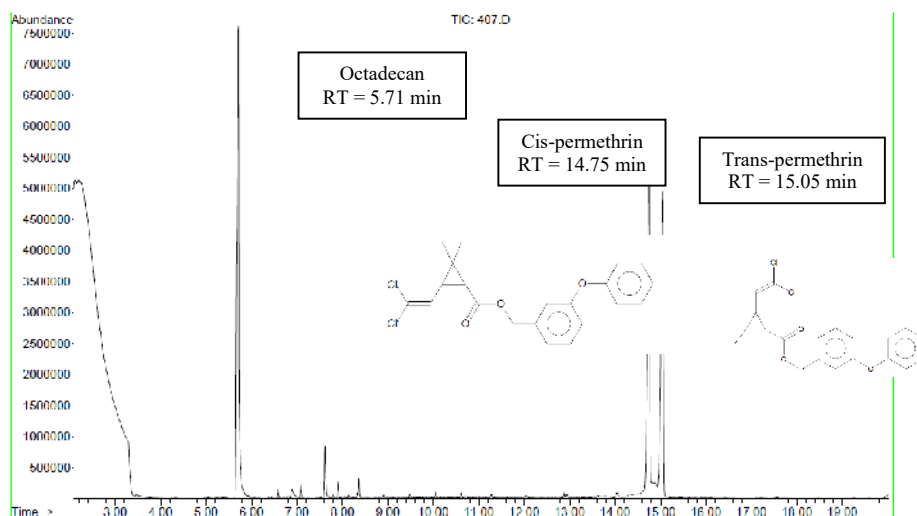


Figure 2. GC chromatogram of sample Raw Cell Solution Protection Knit

Bleached Cell Solution Protection knit

Sample Name: A1b1t

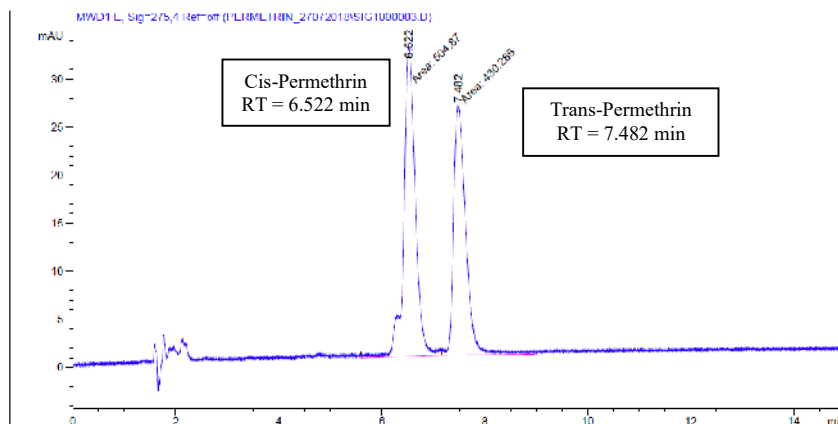


Figure 3. HPLC chromatogram of sample Bleached Cell Solution Protection Knit

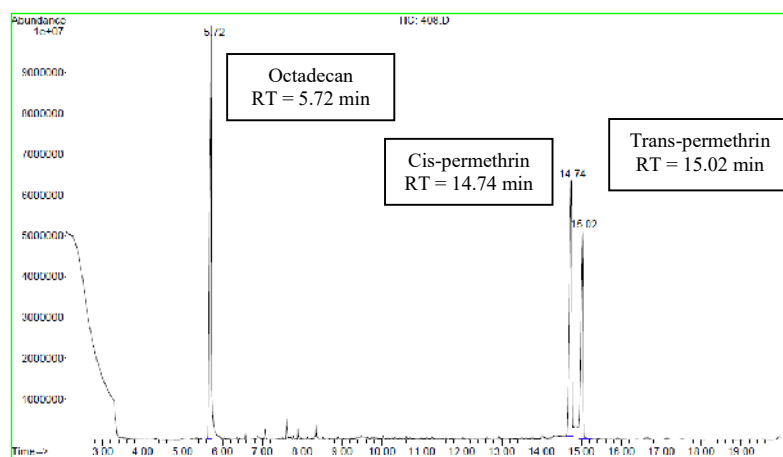


Figure 4. GC chromatogram of sample Bleached Cell Solution Protection Knit

Dyed Cell Solution Protection knit

Sample Name: Vopstt

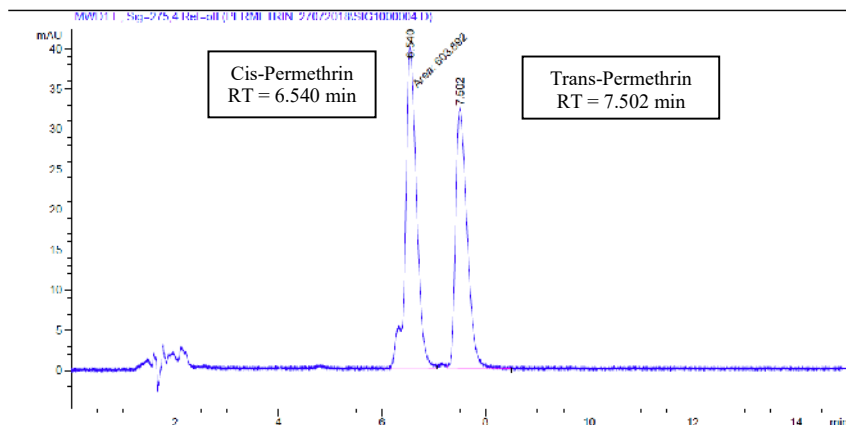


Figure 5. HPLC chromatogram of sample Dyed Cell Solution Protection Knit

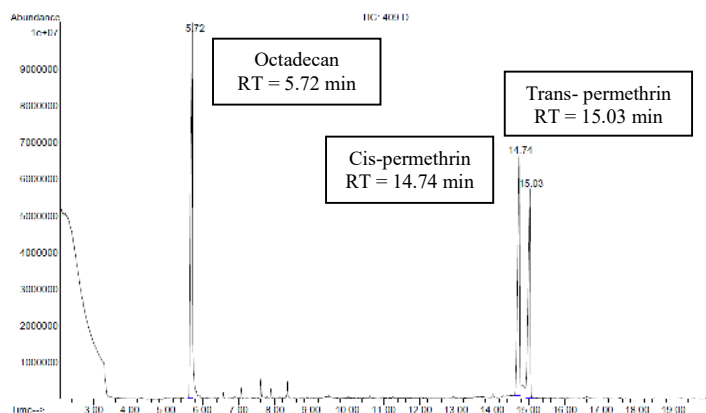


Figure 6. GC chromatogram of sample Dyed Cell Solution Protection Knit

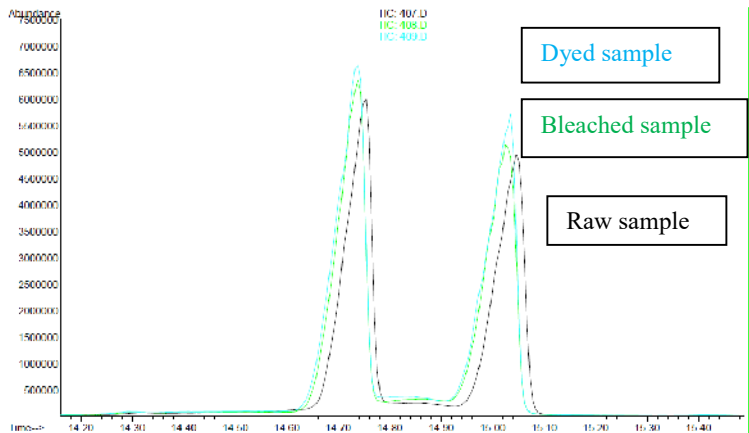


Figure 7. Overlaid GC chromatogram of the three sample: dyed, bleached and raw textile materials

Permethrin Quantification

Table 1. Quantification of permethrin in the textile samples

	Raw sample	Bleached sample	Dyed sample
Permethrin	595.68 µg/mL	592.26 µg/mL	702.59 µg/mL

CONCLUSIONS

As we can see in Figures 1-7, both Cis-permethrin and Trans-permethrin have been extracted and detected in the textile samples; HPLC method was useful in quantification of permethrin based on a calibration curve, and GC method confirmed the presence of both isomers. The highest quantity of permethrin was found in dyed sample, probably due to the fact that including the insecticide in the Cell solution fiber core followed by dyeing of textile materials ensures a better fixation of the protective agents against insects, thus resulting a greater amount of insecticide extracted from sample.

Acknowledgement

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REFERENCES

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*** <http://npic.orst.edu/pest/mosquito/ptc.html>