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Inter-laboratory validation of a thin film microextraction technique for determination of pesticides in surface water samples☆

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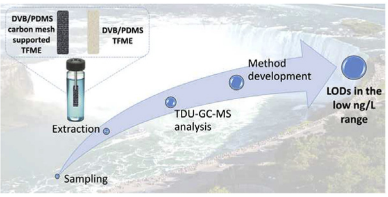
HIGHLIGHTS

- PDMS/DVB and carbon-mesh supported PDMS/DVB membranes as TFME devices.
- Validation of thin film microextraction (TFME) as a sensitive and green approach.
- Inter-laboratory study of TFME and LLE for water sample analyses.
- Achieving agreement of accuracy between TFME and LLE method (US EPA 8270).

GRAPHICAL ABSTRACT



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ABSTRACT

The primary goal of the present study is the inter-laboratory evaluation of a thin film microextraction (TFME) technique to be used as an alternative approach to liquid-liquid extraction (LLE). Polydimethylsiloxane/divinylbenzene (PDMS/DVB) and PDMS/DVB-carbon mesh supported membranes were used for the extraction of 23 targeted pesticides, while a thermal desorption unit (TDU) was employed to transfer these analytes to a GC/MS instrument for separation and detection. After optimization of the most critical parameters, both membranes were capable of achieving limits of detection (LOD) in the low ng L^{-1} range while demonstrating excellent robustness, withstanding up to 100 extractions/desorption cycles. Furthermore, limits of quantification (LOQ) between 0.025 and 0.50 μg L^{-1} were achieved for the 23 compounds selected from several classes of pesticides with a wide range of polarities. A wide linear range of 0.025–10.0 μg L^{-1} with strong correlation to response ($R^2 > 0.99$) was attained for most of the studied analytes. Both membranes showed good accuracy and repeatability at three levels of concentration. Moreover, the method was also validated through blind split analyses of 18 surface water samples, collected within 3 months, using TFME at the University of Waterloo and LLE at Maxxam Analytics (Mississauga, ON) which is an accredited commercial analytical laboratory. Good agreement between the two methods was achieved with accuracy values ranging from 70 to 130%, for the majority of analytes in the samples collected. At the concentration levels investigated, 90% of the analytes were quantifiable by TFME, whereas only 53% of the compounds were reportable using the LLE method particularly at concentrations lower than 1 μg L^{-1}. The comparison of TFME and LLE from several analytical aspects demonstrated that the novel TFME method gave similar accuracy to LLE, while providing additional advantages including higher sensitivity, lower sample volume, thus reduced waste production, and faster analytical throughput. Given the sensitivity, simplicity, low cost, accuracy,

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greenness and relatively fast procedure of TFME, it shows great potential for adoption in analytical laboratories as an alternative to LLE.

1. Introduction

Quality-control of public drinking water is one the priorities of government environmental agencies due to the increase of environmental pollutants, such as pesticides, in surface water as a result of the extensive usage of pesticides in agriculture [1–3]. Several potential health effects such as damage to the eyes, liver, kidneys and spleen, anemia and increased risk of cancer derive from long-term exposure to pesticides above the maximum contaminant levels (MCL) [4,5]. Determination of pesticides in water samples at low and sub μg L^{-1} levels is therefore necessary to meet the requirement of United States Environmental Protection Agency (US EPA) [6]. Among the sample preparation techniques used for extraction, enrichment and clean-up of pesticides from water samples, Liquid-liquid extraction (LLE) and solid phase extraction (SPE) represent two well-established techniques, widely employed as official methods of the US EPA [7]. LLE is a widely accepted method for routine analysis of drinking water samples in accredited contract analytical laboratories as it is an accurate technique and does not require any special apparatus. However, LLE is generally considered as a time-consuming and laborious technique, requiring large amounts of expensive and toxic organic solvents. SPE is a sample preparation technique poised to replace LLE as it requires small amount of organic solvent [8]. On the other hand, apart from difficulties in automation, filtering the suspended solids and particulate prior to the SPE procedure may result in loss of target compounds which may be difficult to account for in a supposedly exhaustive technique.

As an alternative to these aforementioned exhaustive methods, solid phase microextraction (SPME), which was introduced by Pawliszyn et al., is a well-known, solvent-less sample preparation technique capable of performing extraction, pre-concentration and sample clean-up in a single step [9]. There are several geometries of SPME including fiber [10,11], coated-tip (miniaturized fiber) [12], in-tube [13,14] and membrane (self supported, blade and fabric support) [15,16,45,47] that makes it a robust technique for convenient coupling to different analytical instruments [12,13,16–25]. Furthermore, SPME has been widely used for several applications including water sampling and analysis [10,21,26], food analysis [27–29], bio-fluids, in-vivo and non-destructive analysis [30,31], metabolomics [25,32] and tissues sampling [23,33], among many others. Unlike LLE and SPE techniques, SPME is a non-exhaustive sample preparation method [34,35] for which quantitation may be performed by use of several different calibration methods chosen in accordance to the conditions, limitations, complexity of the matrix and goal of study [36]. It is worth noting that there are already some official methods which employ the SPME fiber, published by several agencies including US EPA [37], International Standard Organization (ISO) [38,39] and American Standards for Testing of Materials (ASTM) [40–43]. In addition to the aforementioned benefits of SPME, rapid extraction, easy automation, low cost and need for only a small volume of sample are among some of the other advantages which make this technique a green alternative approach to conventional solvent extraction methods. Validation of the SPME fiber as an alternative to LLE for determination of pesticides in surface and ground water samples was already conducted in multiple previous studies [21,22].

As an extension of the SPME method, sensitivity of the technique can be further enhanced by increasing the volume of the coating to achieve lower detection limits. However, sensitivity and extraction time are traded off when this is accomplished by simply increasing the thickness of the fiber [44]. Hence, thin film microextraction (TFME) was developed in 2003 by Bruheim et al. [15] to address this trade-off. This initial development employed a thin sheet of polydimethylsiloxane (PDMS) to be used as a membrane based SPME device. This membrane, provided an increased surface area-to-volume ratio resulting in higher extraction rate and increased sensitivity when compared to the fiber geometry [15]. PDMS/DVB and Carboxen(CAR)/PDMS membranes were also developed to further enhance the extraction efficiency of the pure PDMS membrane [45,46]. Recently, Grandy et al. [47] developed a carbon-mesh supported PDMS/DVB membrane as a robust TFME format for on-site sampling by use of portable GC/MS instrumentation. Furthermore, it was demonstrated that these membranes improved on-site method sensitivity for a variety of pesticides in water when compared to a traditional 65 μm PDMS/DVB SPME fiber. However, although this membrane geometry has been used for several applications [45–49], a comprehensive evaluation and optimization of TFME from several analytical aspects for the determination of pesticides with a wide range of polarities has not been fully explored. Furthermore, in spite of the many advantages offered by the SPME technique for analysis of water samples, many laboratories are still using LLE as the standard method. Hence, the validation of TFME techniques compared to reference methods approved by the US EPA through inter-laboratory studies can facilitate the adoption of SPME techniques in analytical laboratories for routine analysis of water samples.

It is therefore the intent of this study to validate a TFME method for the analysis of pesticides in surface water samples. The performance achieved by the validated method was then compared to results obtained by LLE as described by an official US EPA method carried out in an accredited analytical laboratory. PDMS/DVB and PDMS/DVB carbon mesh supported membranes were prepared and analysis was performed by use of a thermal desorption unit (TDU) equipped GC/MS instrument. The TFME devices were extensively evaluated from several analytical aspects including stability, lifetime, sensitivity, accuracy and repeatability. Limits of detection in the low ng L^{-1} range and satisfactory accuracy were obtained by both membranes.

2. Experimental

2.1. Chemicals and reagents

All stock solutions of pesticide mixtures, including triazines, organophosphorus pesticides (OPPs) and carbamates (100–1000 μg mL^{-1}) in acetonitrile (ACN) were purchased from AccuStandard (New Haven, CT, USA). Pure standards of chlorophenols, trifluralin, and methyl parathion were obtained from Sigma-Aldrich (Oakville, ON, Canada). A comprehensive list of the target analytes and their physical-chemical properties is shown in Table S1. Deuterated internal standards (3,5-dichlorophenol-d3, trifluralin-d14, phorate-d10, metolachlor-d6 and diazinon-d10) were obtained from CDN Isotopes (Pointe-Claire, QC, Canada) and