Journal of Chromatography A, xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Development and validation of eco-friendly strategies based on thin film microextraction for water analysis☆

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ARTICLE INFO

Article history:
Received 1 July 2018
Received in revised form 6 October 2018
Accepted 14 October 2018
Available online xxx

Keywords:
Thin film microextraction
In-bottle TFME
On-site sampling
Portable GC/MS
On-site river monitoring

ABSTRACT

The aim of the current study is the establishment of Green Analytical Chemistry strategies for water analysis by elimination/reduction of hazardous chemicals, energy consumption, and waste generation throughout the entire analytical workflow. The first approach introduced in this manuscript consists of addition of water to a sampling vessel that contains a thin film microextraction (TFME) device, followed by removal of the device after equilibration, and subsequent quantification of the extracted components by thermal desorption GC/MS. In this approach, namely the in-bottle TFME approach, analyte-loss associated errors that stem from analyte adherence to glass surfaces and/or degradation are avoided as extraction occurs in situ, while analytes are isolated from a complex matrix that contains degradation agents (bacteria, oxidizing or reducing species, etc.). This procedure also circumvents the splitting of original samples into sub-samples. The second approach involves the use of portable TFME devices that facilitate on-site extraction of compounds, therefore eliminating the use of collection vessels, a factor known to potentially introduce errors into analysis. The herein described procedure involves attachment of the TFME device to drill accessories, analyte extraction via direct immersion into sampled site, and subsequent on-site instrumental analysis, which is carried out with the use of a portable GC/MS containing an appropriate thermal desorption interface, or alternatively, by transferring the membrane to the laboratory for bench-top GC/MS analysis. To facilitate a better understanding of the processes governing the developed approaches, modeling by COMSOL Multiphysics® software was performed. The findings of this study were applied for further method optimization, and the optimized developed methods were then applied for on-site surface water analyses. Finally, the greenness of the developed methods was evaluated with use of the eco-scale assessment, with obtained scores compared to that of the US EPA 8270 method.

1. Introduction

Given the impact of pesticide residues on the environment and human health, several priority lists comprising maximum contaminant levels (MCLs) have been established by the US environmental protection agency (US EPA) and EU regulations [1–4] to monitor the quality of drinking, surface, and ground water. Today, several official techniques [2,3], including liquid-liquid extraction (LLE) and solid phase extraction (SPE), are available for determination of contaminants (*e.g.* pesticides and polycyclic aromatic hydrocarbons, PAHs [2,3]) in water samples. As well known by analysts, losses of compounds during transfer of water samples from the sampling site to the laboratory are common sources of errors in many analytical procedures involving determination of compounds characterized by medium to high hydrophobicity. In such cases, compound loss may stem from the adsorption of target analytes to the surface of the sampling/collection bottle, and/or their degradation during transportation. LLE is currently one of the most popular techniques used in contract laboratories for analyses of water samples [2], since the method allows for accurate quantification of hydrophobic compounds in cases where extraction is performed in the original bottle. However, LLE is a time-consuming and tedious method that employs toxic solvents for extraction, a process which subsequently generates hazardous waste [2,5,6]. Aiming to reduce the use of organic solvents, SPE has also become established as a well-known official method for analysis of water samples in contract laboratories. However, losses of hydrophobic compounds during transportation to laboratories, requisite elution of samples through the cartridge, and often, the need to add a filtration step to facilitate

☆ Selected paper from the 42nd International Symposium on Capillary Chromatography and 15th GCxGC Symposium, 13–18th May 2018, Italy.

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https://doi.org/10.1016/j.chroma.2018.10.026
0021-9673/

removal of suspended particles are often cited as major drawbacks of this technique. To address the above challenges associated with application of traditional methods, microextraction methodologies such as solid phase microextraction (SPME), which replaces organic solvent with a solid phase, have been introduced as alternative approaches that move towards green sample preparation. SPME was developed in the early 1990s [7] as a promising and innovative solvent-free technique that eliminates the need for toxic solvent use while simplifying the workflow of extraction and analysis for a wide range of applications [8–19]. Indeed, SPME has been demonstrated to provide similar accuracy and precision figures as those offered by the accredited method for water analysis [5,20]. Given the several features afforded by SPME, such as various available geometries [21–23], biocompatibility [9], and open-bed extraction, SPME-based technologies have enabled several new analytical applications (*e.g.* in-vivo and on-site extraction) that could not otherwise be carried out by application of LLE and SPE techniques [6,24–27]. However, SPME and SPE share a common limitation in regards to the analysis of hydrophobic compounds. While previous SPME-based studies have had some success in improving the accuracy of results for hydrophobic compounds [28,29], the development of environmentally friendlier, simplified, and more universal methodologies that can be adopted for industrial applications and routine analyses is still highly demanded. Aiming to increase extraction efficiency without sacrificing extraction time, a new geometry of SPME, namely thin film microextraction (TFME), was introduced in 2003 by Bruheim et al. [30], using a pure polydimethylsiloxane (PDMS) sheet as extraction phase for semi volatiles extraction. Since then, several improvements to the TFME morphology, which have increased its robustness (*i.e.* coating the extraction phase on fabric substrate) [12,20] and extraction efficiency [31,32], have enabled expansion of its applicability towards a range of new analytical applications. Further, the possibilities presented by TFME have inspired the development of a range of different formats of SPME that function very similarly in principle, such as fabric phase sorptive extraction [33,34], and thin film extraction based on molecularly imprinted polymers on a glass substrate [35]. In terms of validation of optimal coating chemistry, recent studies have fully validated the use of membranes based on PDMS/divinylbenzene (DVB) (both on a carbon fabric substrate [12] and self-supported [31]) for routine laboratory analysis, fully demonstrating TFME as a sensitive and rapid technique with performance comparable to traditional methods [20]. Herein, we moved toward development of on-site extraction/analysis strategies as a means to further reduce analytical errors as well as improve the greenness of the method.

The goal of the current study encompasses the development of new green strategies to improve the accuracy of quantitation, particularly for hydrophobic compounds, by application of two new approaches utilizing in-bottle TFME and on-site TFME. Aiming to provide a procedure that allows for implementation of the entire analytical procedure on-field, a method based on drill-TFME for extraction of compounds from free flowing river water, followed by on-site portable GC/MS analysis was also designed. In addition, preliminary experiments were performed as part of this work to assess the feasibility of untargeted analysis via portable GC/MS following on-site sampling.

2. Experimental section

2.1. Reagents and materials

Pesticide mixtures, including triazines, organophosphorus pesticides (OPPs), and carbamates 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). Internal standards, including 3,5-dichlorophenol-d3, trifluralin-d14 and metolachlor-d6, were prepared from stock solutions sourced from CDN Isotopes (Pointe-Claire, QC, Canada). DVB particles (5 μm diameter) and high-density PLOT PDMS, used in the preparation of the membrane, were obtained from Supelco (Bellefonte, PA, U.S.A). Nanopure water was sourced from a Barnstead/Thermodyne Nanopure ultra-pure water system (Type 1 water grade) for method development. A mixture of standards at different concentrations was prepared in ACN by diluting stock solutions for preliminary experiments, method development, and preparation of calibration levels. Properties of the selected pesticides are provided in Table S1 of Supporting Information.

2.2. Instrumentation

Analysis of the targeted pesticides on bench-top instrumentation was performed by the Agilent GC 6890 A instrument equipped with a thermal desorption unit (TDU) (GERSTEL, Mülheim an der Ruhr, GE), and hyphenated to a 5973C Series MS detector (Agilent Technologies, CA, U.S.A.) On-site GC–MS analysis was performed using a Tridion-9 portable GC–MS and a corresponding SPS-3 thermal desorption unit (Perkin Elmer, American Fork, Utah). Further details regarding chromatographic separation and SIM parameters are provided in section II of Supporting Information.

TFME devices were prepared with the use of an Elcometer 4340 automatic film applicator (Elcometer Inc., Manchester, UK) in accordance with the bar coating procedure developed by Grandy et. al [12]. The 19-gauge Tenax/Carboxen needle trap device (NTD) was purchased from the Torion Technology division of Perkin Elmer (American Fork, Utah).

2.3. Design of the in-bottle TFME, sampling case, and drill accessories

Fig. 1a shows the apparatus designed for the in-bottle TFME strategy. The designed equipment consisted of a 1 L bottle equipped with a Teflon home-built adaptor, which was employed to hold the membrane in the bottle through the use of a disposable fluorocarbon thread (Berkley fishing line). A PDMS/DVB thin film coated onto carbon mesh fabric was used for evaluation of the developed methods. The bottle was filled (1 L) with nanopure water for method development, while surface water was utilized in real sample analyses. The second employed strategy involved application of on-site TFME via deployment of a portable sampling case equipped with a drill to control the speed and time of agitation, and a head to hold the multi-TFME devices. Compared to a commercial drill, the newly designed sampling case provides higher agitation rates (up to 4500 rpm) with controlled sampling times, and a longer battery lifetime that exceeds several hours, facilitating on-site extractions from river waters. Fig. 1b shows the instrument set up used for on-site TFME, including the sampling case, multi-TFME holder, portable GC/MS, needle trap device (used to transfer analytes into the instrument), and standard gas generation vial (used to run QC).

2.4. LLE-GC/MS official method and split samples

One of the main goals of the current study was to demonstrate the feasibility of adopting SPME techniques as standard protocols in analytical laboratories for analysis of water samples [5,20]. To this end, the developed in-bottle TFME method was further validated by split blind analyses of surface water samples by TFME (at the University of Waterloo) and by LLE at Maxxam Analytics (Mississauga, ON). Surface water samples were collected from Grand River in Waterloo, ON, Canada. Samples fortified with the studied

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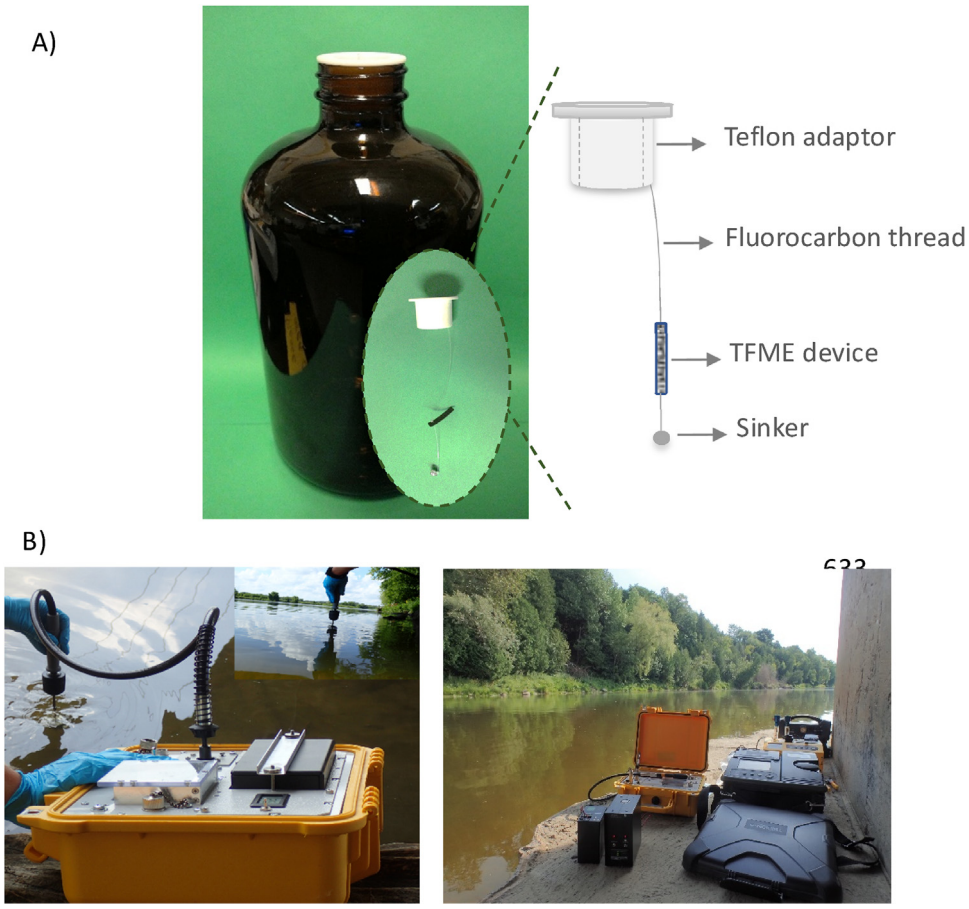

Fig. 1. Developed strategies based on a) In-bottle TFME, and b) On-site TFME using drill accessories and a portable GC/MS instrument.

pesticides were split, coded, and submitted to Maxxam Analytics and the University of Waterloo. An accredited method (Standards Council of Canada) based on LLE and GC/MS was applied for analysis of samples at Maxxam Analytics. The reference method was based on US EPA method 8270, with some modifications (Further details can be found in our previous studies [5,20]).

3. Results and discussion

3.1. Development of bottle sampling TFME

3.1.1. Extraction time profile

The designed in-bottle TFME (Fig. 1a) allows for extraction of compounds to begin taking place from the moment that the bottle is filled with water sample in the field. However, given the significant variations in time associated with the transportation of samples from site to laboratory, as well as the variations in waiting time for analysis between samples, it thus becomes necessary to carry out all experiments under the equilibrium regime so as to ensure accurate quantitation. Evaluation of extraction time profiles was carried out by spiking nanopure water with the selected compounds, ten pesticides from different classes and polarities, at a concentration of 100 ng L^{-1}. Three internal standards, 3,5-DCP-d3, Trifluralin-d14, and Metolachlor-d6, were also added to the sample. The orbi-shaker was selected as apparatus to agitate the water sample in the 1 L bottle at 200 rpm. Extraction time profiles were investigated from 30 min to 4 days, with results showing that the majority of the studied compounds reached equilibrium after 24 h (Fig. 2a). To ensure equilibration of all compounds, a period of three days was selected as extraction time for further evaluation of the method.

3.1.2. Method validation

Validation of the method was based on an industry standard validation protocol consisted of four steps: evaluation of method blank and carryover; limit of detection (LOD) and quantitation (LOQ); calibration curve and linear range; and finally, precision and accuracy of the method at different concentration levels.

At first, a blank of the method was evaluated by analysis of nanopure water, using a PDMS/DVB thin film device under the previously selected conditions (*i.e.* 3 days as extraction time; agitation at 200 rpm, using orbi-shaker). Newly prepared TFME devices and clean bottles were used so as to ensure no carryover of compounds from previous experiments. The obtained results showed that most of the targeted pesticides were present in nanopure water at pg L^{-1} and low ng L^{-1} levels. In our previous study [20], nanopure water was identified as a "non-detect" for the selected pesticides due to the use of a smaller sample volume (30 mL), as well as the shorter extraction time (30 min) selected for that application. However, in the current study, given the larger sample volume, 1 L, and equilibrium time of extraction (3 days), significant enhancement in sensitivity was achieved. Table S3 of Supporting Information also shows total recoveries of the studied compounds via the developed in-bottle TFME method. Succinctly, the preconcentration capability of the developed TFME method under the selected parameters (large volumes of sample and equilibrium extraction), once coupled with the cryofocusing in the TDU/CIS system in splitless mode, allowed for a sensitive method able to detect ultra-trace amounts

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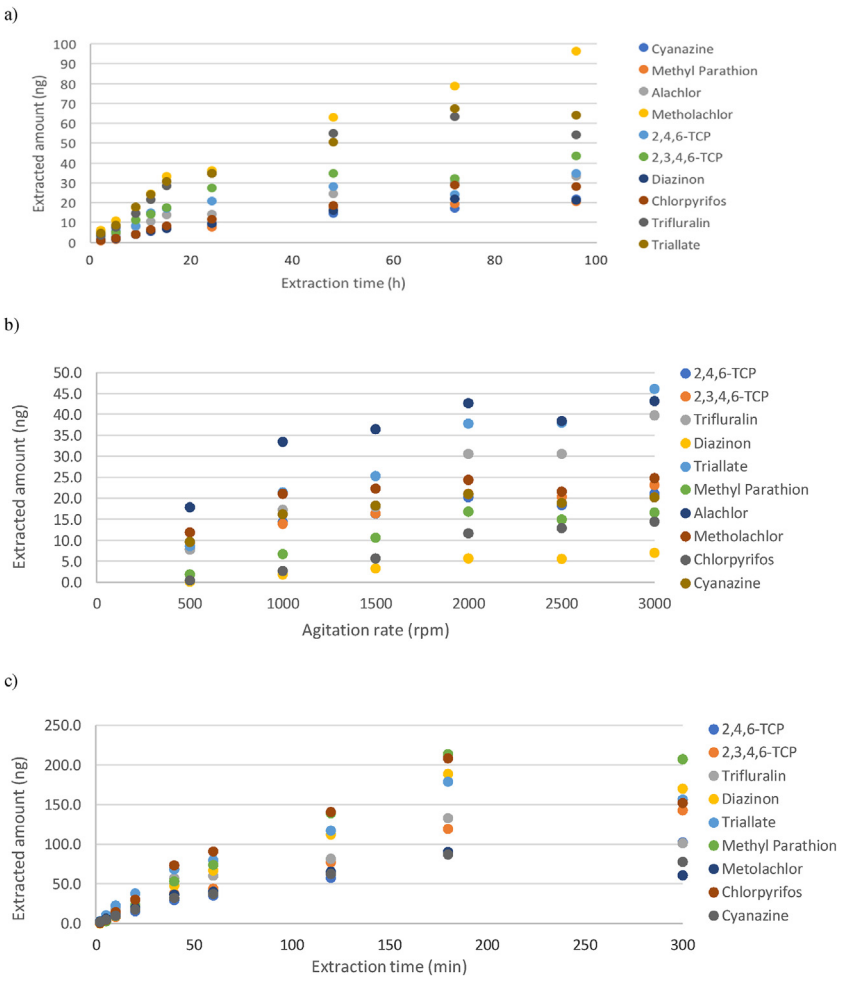

Fig. 2. a) Extraction time profile for in-bottle TFME strategy (1 L of nanopure water spiked at 100 ng L^{-1}); b) Agitation rate of drill TFME sampler (1 L of nanopure water spiked at 1 μg L^{-1}, extraction time of 20 min); c) Extraction time profile of drill-TFME approach (1 L of nanopure water spiked at 1 μg L^{-1}, agitation rate of 2000 rpm); PDMS/DVB thin films were run in a TDU-GC/MS instrument.

of the studied compounds. Several experiments were performed to confirm the blank of the method; further details are provided in section IV of Supporting Information.

After evaluation of blank and noise levels, LOD and LOQ values were obtained, using an S/N of 3 and 10, respectively. As shown in Table 1, LOD and LOQ values in low ng L^{-1} were achieved by the in-bottle TFME method in 2–3 orders of magnitude higher sensitivity than that obtained by EPA method 8270, where limits of detection are based on the standard deviation of low level analyses (More detail of LOD and LOQ obtained by Maxxam Analytics can be found in our previous inter-laboratory study [5]). Successively, a calibration curve was obtained using weighted linear regression. Good linearity was achieved in the range of 3–1000 ng L^{-1}, with R^2 > 0.99 for most of the compounds. The accuracy and repeatability of the developed method were studied at two levels of concentration, with acceptable accuracy (in the range of 71–124 %) and repeatability (percent relative standard deviation, %RSD between 1–21). Finally, the method was evaluated by split blind analyses of four surface water samples fortified with the selected pesticides. The bottle was completely filled with surface water samples, and quantitation was performed using the external calibration method. The pH of surface water samples was adjusted with phosphate buffer (pH ~ 5.5) to match the nanopure water calibration. For future studies, in cases where filling the bottle to full capacity (1 L) might prove difficult, the amount of the sample can be calculated by weighting the bottle.

Table 2 presents a comparison of the results obtained by both methods, showing distinctive features of the current study in terms of sensitivity and accuracy. The first feature is related to the high sensitivity of the method, capable of quantitation of the selected compounds even at the low nanogram per liter level, while the LLE method was only able to quantify compounds mainly present at the microgram per liter level. While the method detection limit of the LLE procedure carried out as part of this study meets US EPA requirements, it is nonetheless always beneficial to push down LOQ levels to lower concentrations that allow the method to be more universally well received, as well as applied in simultaneous determinations of a wide range of compounds. Such a feature is particularly relevant for compounds characterized by MCLs lower than those established by the US EPA, as is the case for certain compounds under the established EU quality standards [1,2]. As Table 1 shows, the in-bottle TFME method is very sensitive, such that the upper limits of the calibration curves are 300, 500, and 1000 ppt for the compounds under study. For SW1, as the concentrations of a few compounds were above these upper limits and hence, no longer in the linear dynamic range, these concentrations could not be quantified, and are thus denoted as N/A in Table 2. The in-bottle TFME is effectively used for ultra-trace analysis and might be too sensitive to analyze sample concentrations in the ppb level.

In the LLE technique, analytes need to be present in the medium in their neutral form due to the exhaustive calibration nature of this technique; as such, in order to extract pesticides that contain acidic,

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Table 1
In-bottle TFME Method validation data summary.

Pesticides	LOD ng L^{-1}	LOQ ng L^{-1}	LDR ng L^{-1}	R^2	Slope	Intercept	Accuracy (%)		RSD %	
							30ng L^{-1}	300ng L^{-1}	30ng L^{-1}	300ng L^{-1}
Cyanazine	3.0	10	10–300	0.9983	0.007	−0.003	96	73	6	17
Methyl-parathion	30	100	100–1000	0.9907	0.011	−0.354	NA	126	NA	6
Alachlor	3.0	10	10–300	0.9982	0.014	−0.018	91	96	21	6
Metolachlor	1.0	3.0	3–300	0.9994	0.041	0.001	90	115	3	14
2,4,6-TCP	3.0	10	10–1000	0.9993	0.041	−0.170	93	101	7	7
Diazinon	30	100	100–1000	0.9983	0.028	−1.745	NA	112	NA	19
2,3,4,6-TeCP	1.0	3.0	3–1000	0.9996	0.040	−0.065	86	124	9	20
Chlopropyrifos	4.0	10	10–500	0.9982	0.012	−0.028	91	91	9	6
Trifluralin	1.0	3.0	3–500	0.9997	0.023	−0.025	93	110	3	1
Triallate	1.0	3.0	3–500	0.9928	0.037	−0.054	109	110	12	9

Table 2
Split sample analyses of surface water samples by in-bottle TFME and US EPA 8270 methods.

Pesticides	SW1(fortified at 900 ng L^{-1})		SW2(fortified at 190 ng L^{-1})		SW3(fortified at 62.5 ng L^{-1})		SW4(fortified at 300 ng L^{-1})	
	TFME Conc.	LLE Conc.	TFME Conc.	LLE Conc.	TFME Conc.	LLE Conc.	TFME Conc.	LLE Conc.
Cyanazine	N/A	ND	210	ND	74	ND	257	ND
Methyl-parathion	938	ND	326	ND	NA	ND	460	ND
Alachlor	NA	860	164	ND	49	ND	195	ND
Metolachlor	NA	880	182	ND	69	ND	239	ND
2,4,6-TCP	931	620	191	ND	59	ND	307	ND
Diazinon	1150	ND	248	ND	NA	ND	286	ND
2,3,4,6-TeCP	936	750	183	ND	50	ND	340	ND
Chlopropyrifos	N/A	ND	359	ND	80	ND	514	ND
Trifluralin	N/A	ND	307	ND	76	ND	530	ND
Triallate	N/A	ND	291	ND	70	ND	527	ND

ND: Not detected.
N/A: Not applicable (analyte concentration in sample was higher than the upper level of calibration curve, and thus not in the linear dynamic range).

basic, and neutral (ABNs) compounds, three separate extractions need to be performed at different pH levels so as to match each condition. Addition of these extraction steps, however, makes the method cumbersome and time consuming, while the use of sodium hydroxide and hydrochloric acid adversely affect the greenness of the method. On the other hand, for TFME analysis, sample pH does not need to be adjusted as long as sensitivity is not an issue, as the method is based on microextraction calibration; as such, only the pH and temperature of the sample and calibration curve must be matched.

Table 2 also depicts the appreciable accuracies attained in this study. As can be seen, accuracies higher than 85% (except for one point) were obtained for all studied compounds in surface water samples, even for triallate and trifluralin, which have log P values of 6.18 and 5.41, respectively. The high accuracies attained in this work certainly support the hypothesis that circumvention of the use of sub-samples ('sub-sample' denotes the transfer of sample from the original sampling bottle to a secondary vial/tube/bottle for subsequent experiments), even in cases where compounds adsorb on the surface of the bottle, can greatly facilitate attainment of high accuracy in quantitation. Given that the same procedure was followed to both obtain the calibration curves and carry out analysis of real samples, the free concentrations of the compounds under study can then be assumed to be similar, leading to improved accuracy of quantitation. A comparison between the results obtained in the present study and findings from our previous study [5,20] also shows improvement in accuracy for hydrophobic compounds, from the range of 40–70 % to an acceptable range (*i.e.* ≥ 70%). While the accuracy of the method for a few compounds was observed at 150%, such figures can be corrected in future studies by selecting a deuterated internal standard for each compound to accurately correct instrumental fluctuations.

3.2. On-site TFME

3.2.1. Optimization

Prior to on-site deployment, the drill-TFME method was optimized in the laboratory with respect to influential parameters, such as the extraction time profile and the agitation rate of the drill. The agitation rate was the first parameter investigated, as it controls the thickness of the boundary layer, and affects the mass transfer of compounds to the coating. In the pre-equilibrium regime, improved sensitivity is expected to be achieved at higher agitation rates due to a decrease in the thickness of the boundary layer. Application of high agitation rates are beneficial for on-site extractions, since a short extraction is preferred due to practical limitations (*e.g.* lifetime of the battery, sampling difficulties related to the accessibility of the site and sample). In view of this, agitation rates in the range of 500–3000 rpm were investigated in 1 L of nanopure water spiked with the target pesticides at 1 μg L^{-1}. The highest sensitivity increases were observed for most compounds at 2000 rpm (Fig. 2b).

An extraction time profile was then obtained using the optimized stir rate of 2000 rpm in 1 L nanopure water spiked at 1 μg L^{-1}. As shown in Fig. 2c, after three hours, all spiked compounds were shown to reach equilibrium. However, as previously mentioned, a shorter extraction time needed to be selected so as to simplify the on-site TFME procedure. Therefore, 10 min was selected as extraction time for further evaluation of the method.

3.2.2. COMSOL-based modeling

It was anticipated that given the directional stream-line velocity of the sample around the membrane, one side of the membrane would have a thicker boundary layer, and therefore, lower extraction efficiency within the pre-equilibrium regime. COMSOL-based modeling was used to simulate the boundary layer around the

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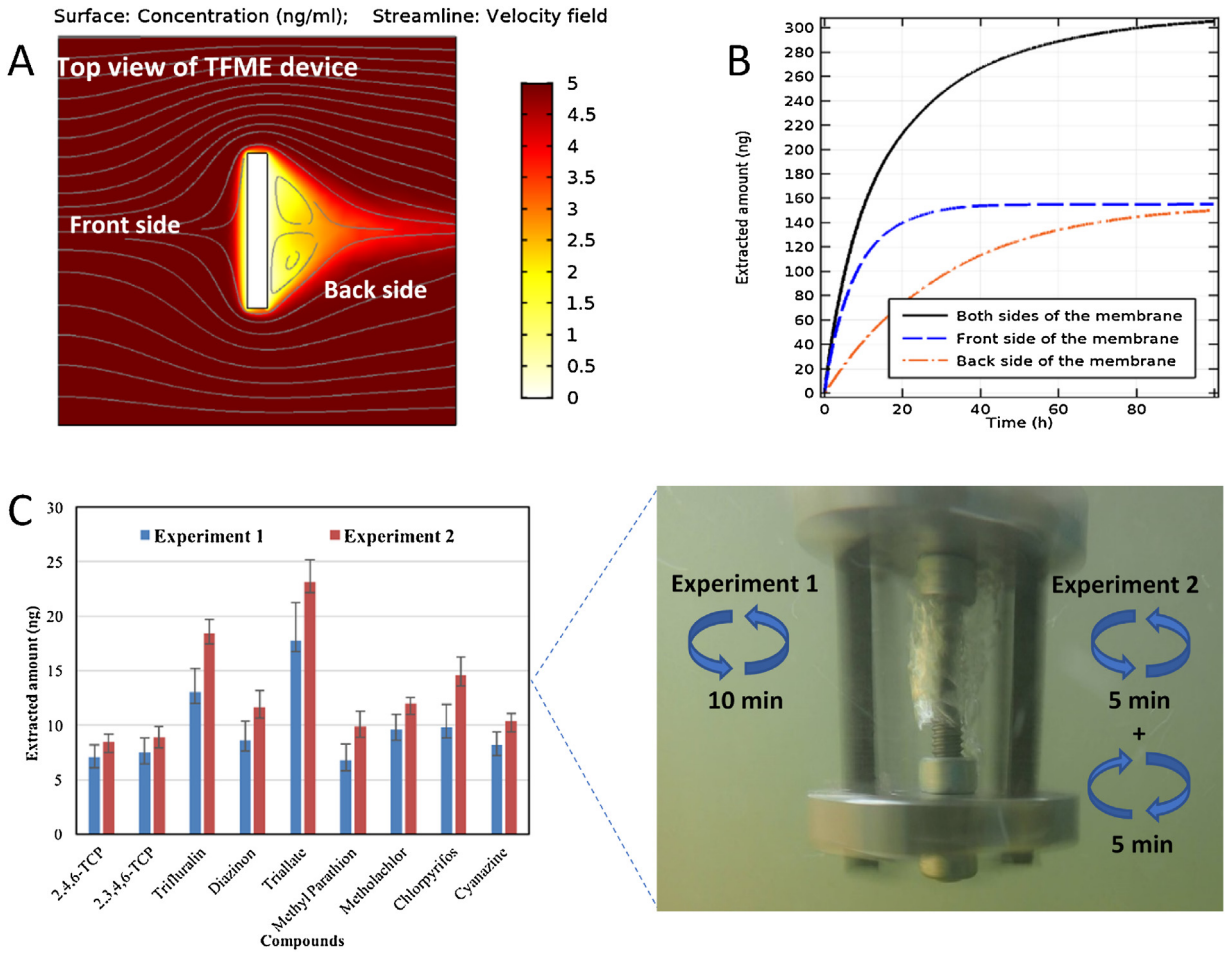

Fig. 3. Numerical (a and b) and experimental (c) validation of the effect of flow on the uptake of compounds and the thickness of the boundary layer. a) Visualization of the diffusion boundary layer around the membrane during the initial stage of sample extraction by COMSOL modeling; b) Variation of equilibration time with respect to the selected surface of the membrane by COMSOL modeling; and c) Comparison of extraction efficiency of the membrane at two conditions (1 L of nanopure water spiked at 1 μg L^{-1}, agitation rate of 2000 rpm).

membrane so as to gather a better understanding of the obtained results. Alam et al. have recently described a computational model that accounts for the analyte transport processes occurring during extraction by an SPME coating [36]. This model has been employed to estimate the diffusion boundary layer formed around the SPME membrane during the kinetic regime of extraction. As depicted in Figure S2 of Supporting Information, the model considered a two-dimensional segment of a sample-extractant system. Here, the flow field is assumed to be normal to the membrane, since the membranes (three and six assembled in the holders in the current study) orbit around an axis of fixed distance. The flow in the sample domain is governed by the Navier-Stokes equation and treated as steady state. The time-dependent partial differential equations for each of these physical processes were solved simultaneously according to the procedure mentioned in the associated literature [37]. In the sample matrix, chemicals are transported via convection and diffusion, while diffusion is the only transport process involved within the static boundary layer domain of the coating. Due to the concentration gradient at the sample-coating interface, mass fluxes are established across the interface. COMSOL Multiphysics 5.1, a finite element method (FEM) based software package, was utilized in this modeling and simulation study. The parameters used in the simulation are given in Table S5. As the boundary layer thickness around the membrane controls the mass transfer of analytes to the membrane, a decrease in this thickness results in an increase in the uptake (mass transfer) of analytes during the pre-equilibrium regime, as well as shorter equilibrium times. Fig. 3a shows COMSOL-based modeling visualization of the diffusion boundary layer around the membrane during the initial stage of sample extraction. The surface plot presented in Fig. 3a shows the simulated concentration (ng/ml) profile and the streamline representing the water velocity field around the membrane. The color bar represents the range of concentrations in and out of the diffusion layer that are present around the membrane. Results of this simulation support that the boundary thicknesses are different at both sides of the membrane; therefore, the extraction efficiency of one side of the membrane is expected to be higher in the pre-equilibrium regime (Fig. 3b). Therefore, by switching the rotational direction of the drill mid-extraction, a higher extraction efficiency can be achieved.

3.2.3. On-site sampling TFME and bench-top GC/MS analysis

The experiment was optimized based on the modeling simulation results to improve the extraction efficiency of the methods under similar conditions, which included a sample volume of 1 L of nanopure water spiked at 1 μg L^{-1} and an agitation rate of 2000 rpm (Fig. 3c). On-site river sampling using a thin film equipped drill was conducted at an agitation rate of 2000 rpm for 10 min (5 min for each side). Following conclusion of the sampling procedure, the deployed thin film devices were brought back to the laboratory for bench-top GC/MS analysis.

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Table 3
Comparison of method detection limit between in-bottle TFME, Drill-based TFME, and LLE (US EPA 8270) method for pesticides under study.

Analytes	In-bottle TFME* (ng L^{-1})	Drill-based TFME* (ng L^{-1})	LLE** (US EPA 8270)(ng L^{-1})
2,4,6-TCP	10	100	500
2,3,4,6-TeCP	3.0	250	500
Trifluralin	3.0	50	1000
Diazinon	100	1000	1000
Triallate	3.0	50	1000
Methyl parathion	100	1000	1000
Alachlor	10	100	500
Metalachlor	3.0	250	500
Chlorpyrifos	10	1000	1000
Cyanazine	10	100	1000

* Results obtained using bench-top GC/MS instrument; based on S/N = 10.
** Reporting limits (roughly equivalent to LOQ); further details can be found in a previous report [5].

Table S6 of Supporting Information shows the LOD and LOQ values of the drill-based TFME method (in the range of 20–300 ng L^{-1}) using a 10 min extraction time and 2000 rpm agitation rate. Table 3 also compares the method detection limits of the in-bottle TFME, drill TFME, and US EPA 8270. Quantitation can be performed either by using an external calibration curve obtained under negligible depletion conditions or by obtaining the sampling rates of individual compounds [26,38]. It is worth mentioning that at negligible depletion conditions, the amount of analyte extracted is independent from the sample volume; therefore, the calibration curve obtained in-lab can be used for on-site analysis and quantitation from river waters [26]. Further information regarding quantitation using sampling rates is provided in section VII of Supporting Information.

3.2.4. On-site sampling TFME and portable GC/MS analysis

The last approach developed as part of this work concerned on-site extraction and subsequent quantitation of compounds via portable GC/MS for rapid screening and monitoring of water samples, as an alternative to transporting extraction devices to a laboratory for instrumental analysis [39,40]. For on-site analysis, the stability and repeatability of the portable GC/MS instrument are critical parameters that need to be frequently monitored by running an extensive quality control (QC) protocol. Unlike benchtop instrumentation, battery operated, portable GC/MS instruments must be powered off after each use. As such, a reusable standard BTEX gas-generating vial held carefully at 35 °C with a portable block heater was used to monitor the status of the instrument in field [41,42]. In cases where the portable GC/MS was not directly equipped with the TDU unit, a secondary SPS-3 thermal desorption module was first used to transfer analytes from the TFME membranes to a needle trap device, which could then be directly introduced into the instrument [12]. All optimizations of the drill-TFME method were performed in a temperature controlled laboratory at 22.5 °C. It is also important to note that if external calibration is to be used for real on-site TFME experiments, the temperature of the sample matrix must match or be close to that of the external calibration experiment. Alternatively, the kinetic calibration [43] method, performed by loading internal standard on the coating, can be used to justify any temperature variations. However, the kinetic calibration can only be performed with a proper coating material that assure adsorption-desorption symmetry for analyte and internal standard, respectively.

Finally, analyses of real water samples along 4 sampling sites (2 affected and 2 low-impact) within the Grand River and Credit River (Ontario, Canada) were performed by three methods, including i) in-bottle TFME, ii) on-site TFME and bench-top GC/MS analysis, and iii) on-site TFME-portable GC/MS analysis. These sites included the small community of West Montrose (clean), downstream of multiple Kitchener/Waterloo golf courses (affected) within the Grand River, and both up and downstream of a covered dumpsite near the Forks of the Credit Provincial Park. River temperature was monitored using a thermometer and found to be relatively consistent between the four sites, ranging from 22 °C +/− 1 °C for the Credit River sites, and 25 °C +/− 1 °C for the Grand River sites. Therefore, in the current study, there were no considerable temperature variations between the external calibration curve and real samples. For validation of the methods, one grab sample from each location was taken and submitted to Maxxam Analytics (Mississauga, ON).

Real sample analysis revealed that the levels of the targeted pesticide compounds were well below the limits of detection of most of the methods being tested. This was further confirmed by the accredited method (US-EPA 8270) performed by Maxxam Analytics. Although these results are great news in terms of the water quality of the tested rivers at the time of sampling, the results of this real-life application failed to yield much in terms of engaging in scientific comparison. Nonetheless, the more sensitive TFME bottle sampling method still enabled identification and quantitation of selected compounds. These levels were found to be 19 and 3 ng L^{-1} for 2,4,6 TCP, trifluralin, and methyl-parathion on the Credit River dumpsite respectively, whereas 2,4,6 TCP, metholachlor, chlorpyrifos, and cyanazine were quantified at 9, 10, 11, 14 ng L^{-1} at the golf course site (Grand River), respectively. Many other compounds were detected using the TFME-bottle methodology but were at levels just under the method LOQ; these findings can be viewed in Tables S9 and S10.

The toroidal ion trap of the portable GC–MS was run in full-scan mode (43–500 AMU), allowing for a determination of the repeatability of the method, which was carried out by defining the identity of a select few of the unknown compounds that were extracted. In fact, the ability to quickly determine whether or not a target compound is present in a sample remains one of the key advantages of portable instrumentation. As such, various non-target analytes were identified and selected based on their molecular functional group from extracts obtained from the affected sites of both river systems. These unknown features were preliminarily identified using the NIST mass spectral database (Fig. 4), followed by tentative verification via a linear retention index (LRI) plot (Figure S.3), which was generated using a C7-C20 n-alkanes generating standard gas-generating vial. These results can be seen in Tables 4 and S10 for extracts obtained from the Credit River and Grand River sites, respectively. It was promising to see that RSD% levels (n = 5) for all compounds tested were around the +/- 20% range. This repeatability was further supported by favorable control chart data (Figure S.4) set at 2 standard deviations of the mean, which was generated using the field portable BTEX standard gas-generating vial. To prepare this plot, 2 BTEX extractions were performed onsite before and after every sampling (equaling 4 total extractions per site). Furthermore, previous works performed by Grandy et al. have demonstrated sub-ppb detection limits for similar pesticides, including 2,4 dichlorophenol, 2,4,6 TCP, phorate D_{10}, fonofos, chlorpyrifos, and parathion with LOQ values of 100, 100, 100, 500, 500,

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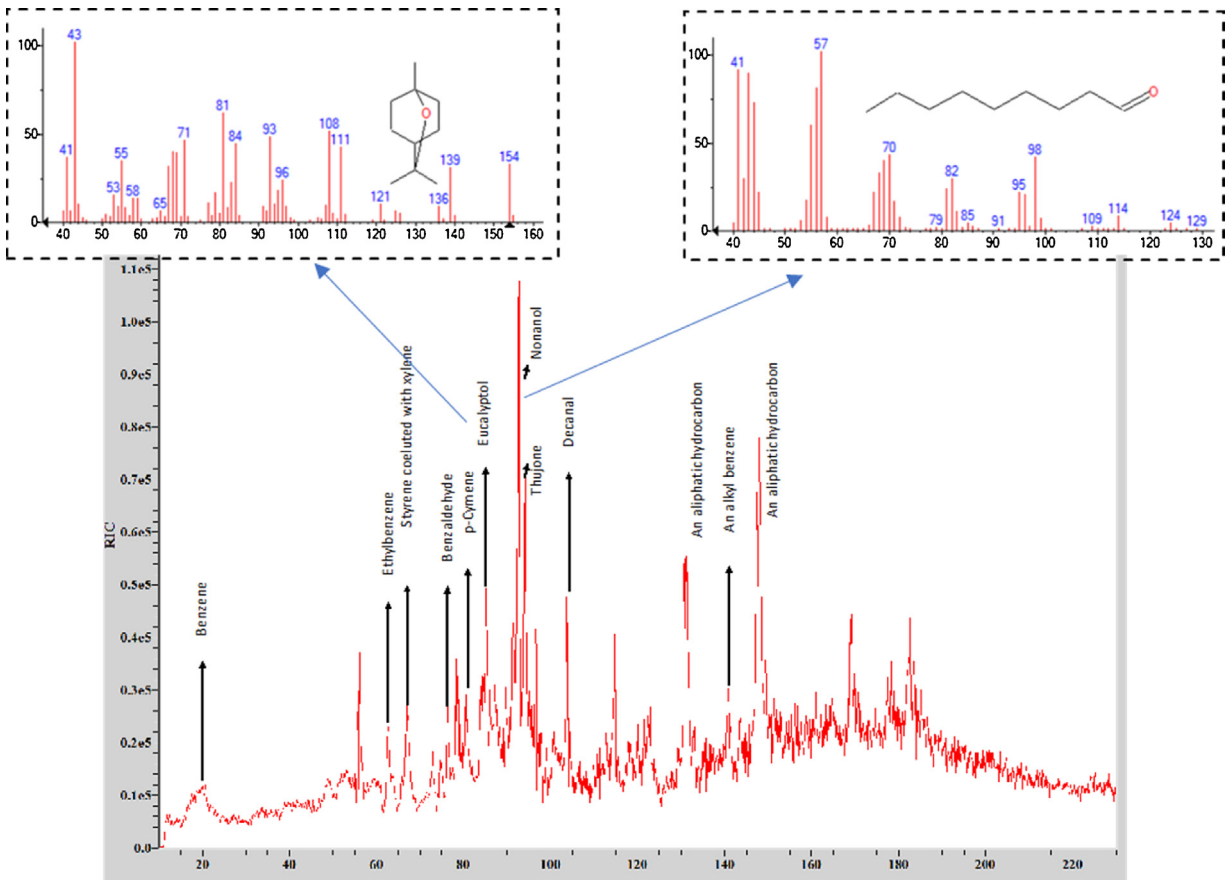

Fig. 4. Untargeted water analysis using TFME-portable GC/MS. Downstream of Credit dump site using completely on-site analytical methodology.

Table 4
Selected unknown identifications downstream of Credit dump site, attained completely via on-site analytical methodology; not shown are another 6 aliphatic hydrocarbons, 2-alkyl-benzenes, 4 alcohols, 5 aldehydes, and 1 ester (n = 5).

Analyte	RT (s)	$LRI_{(exp)}$	$LRI_{(lit)}$	Average	SD	%RSD
Benzene	19.1	N/D	/	5464	1302	24
Ethylbenzene	62.7	863	864	5585	878	16
Benzaldhyde	76.5	966	965	4333	853	20
p-Cymene	83.8	1026	1025	7724	1573	20
Eucalyptol	85.3	1039	1035	4396	491	11
Nonanal	92.6	1103	1108	22826	4471	20
an alkylbenzene	144.0	1647	N/D	5634	737	13

$LRI_{(exp)}$ experimental linear retention index.
$LRI_{(lit)}$ linear retention index from literature.
%RSD percent relative standard deviation.

1000 ng L^{-1}, respectively, which are in the same order of magnitude as those reported in the current study.[10] The findings of this work certainly support application of the developed field portable analysis method as a quick and efficient solution to analytical tasks that require fast, on-site absence-presence determination of target analytes.

3.3. Evaluation of greenness of the developed methods

Nowadays, the development of green techniques and strategies that have minimal impact on the environment plays a vital role in current, trending research in analytical chemistry [44–47]. In this regard, it is widely acknowledged that in analytical chemistry, 'green chemistry' is understood to encompass both separation science and sample preparation [44]. In this sense, green analytical chemistry techniques are focused on the "3R" and "4S" approaches. The approaches are based on "Reduction, Replacement, and Recycling" of hazardous solvents and materials (3R) and introduction of "Specific method, Smaller dimensions, Simpler methods, and Statistics"(4S) [44]. In this respect, an ideal 'green' method would thus have to integrate several steps into one, and preferably eliminate waste generation by performing the entire extraction and analysis on-site (or at least enable on-site extraction, with associated transportation of only the extraction device to the laboratory, rather than samples). With this in mind, several evaluations concerning the eco-scale greenness of methods have been introduced in different research areas, including analytical chemistry [48]. Such evaluations consider all the steps required for analysis of samples, including sample collection, preservation, transportation, sample preparation, and analysis. Further, these evaluations are carried out by assigning penalty points based on the i) reagents used, ii) method, iii) energy consumption, and iv) waste production. In this regard, a main advantage of using SPME is that the extraction phase is constituted by a polymeric coating rather than a toxic

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Table 5
Evaluation of greenness of the developed methods and US EPA 8270.

Steps in analytical process	Analytical method			
	In-bottle TFME	On-site TFME (Bench-top GC/MS)	On-site TFME and on-site analysis (Portable GC/MS)	LLE (US EPA 8270)
Sample collection	- Sampling: 1 - Transport: 1	- Transport*: 1	–	- Sampling: 1 - Transport: 1
Sample preparation	- ACN (100 μL) (Internal standard): 4 (0) - Isotopically labeled mixture: 4 (0) - Orbi-shaker: 1 - Waste production: 5 (0)	- Sampling case(drill): 1	- Sampling case(drill): 1	- Dichloromethane (50 ml × 2): 4 × 2 - ACN (Internal standard):4 - HCl: 4 - NaOH: 2 - Isotopically labeled mixture: 4 - Vortex: 1 - Tumbler: 2 - Turbovap: 2 - Occupational hazard: 1 - Waste production: 10
Analysis	- GC/MS with auto sampler: 3	- GC/MS with auto sampler: 3	- Portable GC/MS: 0 - Desorption chamber: 0	- GC/MS with auto sampler: 3
Penalty points (PP)	**19**	**5**	**1**	**43**
Eco-scale, 100-PP** (Without IS)	**81 (94)****	**95**	**99**	**57 (65)****

* Transport of the membrane (not the sample) after extraction.
** Penalty points associated with the calibration curve were not considered for evaluation of the greenness of the methods [48].
*** The numbers in parentheses denote the Eco-scale of the method without addition of IS.

organic solvent. While certain steps of the analysis workflow are inevitable (*e.g.* analysis by GC/MS, LC–MS/MS), penalty points can be reduced by eliminating the sampling step through employment of on-site extraction and analysis. An evaluation of the greenness of the developed methods presented in this study, also including the standard US EPA 8270 method for comparison, is shown in Table 5. As can be seen, the TFME method is significantly greener as compared to the standard method (Eco scale 81 vs 57). While the TFME method incurs 5 penalty points for waste generation, significant differences exist between the TFME and LLE methods in terms of generation of waste. In TFME, the waste generated during sample preparation is only related to water samples that are spiked with an internal standard mixture. To eliminate this source of waste generation, addition of internal standard can be avoided as long as there are no fluctuations in the instrument. In cases where internal standard is not added to the sample, the eco-scale greenness of the TFME method increases to 94. When considering applications that enable employment of on-site extraction and analysis strategies, the eco-scale for SPME techniques further increases to 99, becoming one of the greenest approaches in analytical chemistry, owing to the elimination of both sampling (transportation in the case of portable GC/MS analysis) and waste generation. It should be emphasized that penalty points associated with the establishment of the calibration curve, including employment of standard solutions, solvent use, and waste production, were not considered for this evaluation of the greenness of the method [48]

4. Conclusion

The developed in-bottle TFME extraction methodology herein presented was demonstrated to be a promising approach for accurate quantitation of compounds that may otherwise be lost during transportation to the lab and/or during sample-to-vial transfers. The obtained results demonstrated improvements on accuracy for hydrophobic compoundsand the sensitivity of the developed methods significantly outweighed previously reported methods, including the accredited US EPA method used for validation purposes in this study. Although the method was developed using thin film on fabric as the extractant, other geometries of SPME, such as fiber or stirrer (Twister) configurations, are currently being considered as future directions in this research. The attachment of TFME to a stirrer with extraction phase in future studies (using a PDMS/DVB coating as an efficient extraction phase) should further allow for significantly decreased equilibrium times, as higher stirring rates can be conveniently applied. It is important to ensure that extraction conditions, including temperature, are kept constant during calibration and throughout sample analysis. Also, the use of spikes of internal standard for calibration of complex water samples needs to be carried out appropriately so as to facilitate full dissolution of the spike. The second approach investigated in this study, namely on-site extraction TFME facilitated by a home-built, drill-based sampling device, opens new possibilities for rapid on-site screening and quantitation. In this approach, the transportation of samples to the laboratory is eliminated, thus showcasing this method as the ultimate green chemistry approach. Further, in addition to enabling accurate quantification of labile compounds by eliminating losses of analytes related to transportation and/or adhesion to apparatus, the developed method facilitates immediate decision-making for users as analytical results can be attained on-site almost immediately following sampling and portable instrumental analysis. However, careful attention should be paid to on-site temperature variations, as well as in cases where complex samples are analyzed; in such circumstances, the use of an in-coating calibration method should be considered if good accuracy and precision are desired rather than just the gathering of screening information.

Acknowledgements

This research was financially supported by the Ontario Research Fund, project number RE-WR-07. We wish to thank Maxxam Analytics (Mississagua, ON) for the in-kind financial support lent in the form of LLE analyses. H. Lord and T. Obal are appreciated for coordinating the LLE experiments at Maxxam Analytics. The authors thank J. Poole and F. Ahmadi for providing the split blind samples and sci-

entific discussion, respectively. We also thank the Science Shop of the University of Waterloo for construction of the Teflon adaptor for bottle sampling. D. Hein is thanked for the provided technical assistance related to the sampling case for on-site sampling.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.chroma.2018.10.026.

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