Development of a carbon mesh supported thin film microextraction membrane as a means to lower the detection limits of benchtop and portable GC-MS instrumentation

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ABSTRACT

In this work, a durable and easy to handle thin film microextraction (TFME) device is reported. The membrane is comprised of poly-divinylbenzene (DVB) resin particles suspended in a high-density polydimethylsiloxane (PDMS) glue, which is spread onto a carbon fiber mesh. The currently presented membrane was shown to exhibit a substantially lesser amount of siloxane bleed during thermal desorption, while providing a statistically similar extraction efficiency towards a broad spectrum of analytes varying in polarity when compared to an unsupported DVB/PDMS membrane of similar shape and size which was prepared with previously published methods. With the use of hand-portable GC-TMS instrumentation, membranes cut with dimensions 40 mm long by 4.85 mm wide and 40+/-5 µm thick (per side) were shown to extract 21.2, 19.8, 18.5, 18,4, 26.8, and 23.7 times the amount of 2,4 dichlorophenol, 2,4,6 trichlorophenol, phorate D10, fonofos, chloropyrifos, and parathion, respectively, within 15 minutes from a 10 ppb aqueous solution as compared to a 65 µm DVB/PDMS solid phase microextraction (SPME) fiber. A portable high volume desorption module prototype was also evaluated, and shown to be appropriate for the desorption of analytes with a volatility equal to or lesser than benzene when employed in conjunction with TFME membranes. Indeed, the coupling of these TFME devices to hand-portable gas chromatography toroidial ion trap mass spectrometry (GC-TMS) instrumentation was shown to push detection limits for these pesticides down to the hundreds of ppt levels, nearing that which can be achieved with benchtop instrumentation. Where these membranes can also be coupled to benchtop instrumentation it is reasonable to assume that detection limits could be pushed down even further. As a final proof of the concept, the first ever, entirely on-site TFME-GC-TMS analysis was performed at a construction impacted lake. Results had indicated the presence of contaminants such as toluene, ethylbenzene, xylene, 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate, and Tris(1-chloro-2-propyl)phosphate, which stood out from other naturally occurring compounds detected.

INTRODUCTION

Since being introduced in 1989, solid phase microextraction (SPME) sampling techniques have demonstrated steady growth in the field of analytical chemistry.[1-3] Of the many formats available today, the original SPME fiber-based geometry has been by far the most widely used worldwide, largely due to its miniaturized, easy-to-handle design that lends itself well to both high throughput and on-site applications.[1-3] This has been prominently exemplified with a plethora of environmental, biological, industrial, food, and fragrance targeted analytical approaches, which are generally coupled to hyphenated gas chromatographic (GC) techniques.[3-9] However, standard fiber based SPME is not without its limitations; the same miniaturization which allows the SPME fiber to be directly introduced into a GC injector inherently limits the surface area and volume of the sorbent coating.[10-11] A limited sorbent volume, in turn, fundamentally limits the amount of a given analyte that can be extracted at equilibrium, as dictated by the fiber-sample partitioning coefficient, K_{fs}.[1,3,12] In addition, the small surface area available on a fiber directly controls the rate of analyte uptake, and consequently, method sensitivity during the linear pre-equilibrium regime of extraction.[1,3,12] Hence, surface area becomes highly important when rapid, pre-equilibrium analyses of semi-volatile components, such as pesticides, are performed. To account for these shortcomings, recent work in microextraction technology has shifted towards the development of high surface area, membrane-based SPME samplers.[11,13-16]

Membrane SPME, also known as thin-film microextraction (TFME), is a relatively new avenue in microextraction techniques that has been successfully used for both GC- and high performance liquid chromatography (HPLC) based applications.[10,13] Membranes developed for GC applications have generally employed similar polymeric make-ups commercially used in standard SPME fibers, including polydimethylsiloxane(PDMS), polydivinylbenzene (DVB), and Carboxen.[12-15] Initial works with TFME-GC techniques employed the use of pre-manufactured thin sheets (127 or 254 µm) of pure PDMS as an extraction phase.[13,17,18] Using this PDMS design, Qin *et al*. were able to demonstrate that a 10 cm^2 membrane provided approximately 10x the extraction efficiency for fluoranthene and pyrene when compared to commercially available PDMS sorptive stir bar technology (area = 1cm^2).[14] Such a result was directly in line with what was expected theoretically, as shown in Equation 1 below, where the amount of analyte extracted as a function of time (is directly proportional to the surface area (A) if all other factors are kept constant.[1,14,17] Despite this marked improvement, such pre-constructed membranes are limited to PDMS in terms of available sorbent phases. Additionally, such large membranes required the construction of a supporting frame for direct immersion sampling with agitation.[14] Further works in the

area have explored the in-house preparation of particle-loaded PDMS membranes and implementation of inert support materials.[14-16]

(1)

One such design, suggested by Jiang *et al.*, utilized a platinum catalyzed PDMS preparation kit (SILGARD 184), such that macroporous DVB resin particles (diameter of 3-5 µm) could be suspended into the membrane [15]. The optimal DVB:PDMS ratio was found to be 20:100 (16.7%) w:w, with a compromise being made between extraction efficiency and the mechanical stability of said membrane.[15] Results from this study indicated that the composite membranes were much more efficient at extracting highly volatile and polar compounds such as toluene and benzaldehyde, respectively.[15] However, without an appropriate support, these membranes proved to be very difficult for highly turbulent or agitated direct-immersion sampling. Additionally, experience has shown that inserting membranes greater than 6 mm in diameter into the thermal desorption unit (TDU) desorption tube commonly results in breakage. A final observation indicated that these membranes exhibited considerable siloxane bleed/background even after 10 hours of thermal conditioning. Prior to the abovementioned study, Riazi-Kermani *et al.* employed a similar polymeric mixture onto a thin fiberglass mesh to prepare the first ever composite, supported TFME membrane.[14] These supported membranes were found to be much more physically stable than the composite TFME membranes introduced by Jiang *et al.*, withstanding aqueous agitation rates of 800 rpm without folding, while surviving at least 50 consecutive injections.[14] These 10 cm^2 membranes were also shown to extract between 46 to 117 times the amounts of analyte compared to traditional DVB/PDMS SPME fibers.[14] However, one major limitation of this study was that it failed to address the likely presence of major siloxane bleeding that would occur when desorbing a composite membrane of this size. It is expected that if selected ion monitoring (SIM) had not been used, background siloxane levels would have completely overloaded the detector, making such a membrane inappropriate for untargeted analysis. With this in mind, the choice of a more thermally stable PDMS glue for the preparation of a supported DVB/PDMS composite membrane would be ideal for untargeted analysis.

In the present work, one such membrane is proposed. By use of a high density PDMS pre-polymer in combination with DVB particles, spread onto a carbon-based mesh support, similar extraction efficiencies could be obtained while substantially lowering the inherent siloxane background. Furthermore, the carbon mesh was also found to provide some affinity for the analyte, which would provide an advantage over a comparable fiberglass-supported membrane in equilibrium conditions. These low-bleed membranes were also coupled with hand-portable GC-TMS technology, which allows

for on-site detection limits well below what is currently thought possible.[19] Most impressively, these membranes are herein demonstrated to allow for sub-ppb detection of multiple organochlorine and organophosphorus pesticides from an aqueous matrix on the aforementioned portable GC-TMS instrument.

EXPERIMENTAL SECTION

Reagents and supplies

2,4 dichlorophenol, 2,4,6 trichlorophenol, carbofuran, atrazine, fonofos, chloropyrifos, and parathion standards were purchased from Sigma-Aldrich (Mississauga, ON, Canada). Phorate D10 was purchased from CDN isotopes Inc. (Quebec, Canada). HPLC grade methanol, isopropanol, hexane, and acetonitrile were obtained from Caledon laboratories Ltd. (Georgetown, ON, Canada). Ultra-pure water was obtained using a Barnstead/Thermodyne NANO-pure ultrapure water system (Dubuque, IA, USA). The SYLGARD 184 silicone elastomer mix was acquired from Dow Corning (Midland, MI, U.S.A.). The 5 µm diameter DVB particles and high density PLOT PDMS were provided by Supelco (Bellefonte, PA, U.S.A). The carbon fiber mesh weave (Panex® 30) was provided by Zoltec Co. (Bridgetown, Mo, U.S.A.).250 mL Wheaton glass bottles were purchased from Thermo-Fischer Scientific (Ottawa, ON, Canada). Liquid nitrogen and ultra high purity helium were supplied by Praxair (Kitchener, ON, Canada). Miniature helium cylinders (99.5%) were supplied by Torion Technologies Inc. (UT, U.S.A). 65 µm divinylbenzene/polydimethylsiloxane (DVB/PDMS) SPME fiber assemblies and empty stainless steel (SS) sorbent tubes were provided by Sigma-Aldrich. The Tenax/CAR Custodian needle trap device and Calion™- 13 standard mixture (containing: acetone, methyl-tert-butyl ether, methylene chloride, heptane, methylcyclohexane, toluene D8, perchloroethylene, bromopentafluorobenzene, bromoform, 1,2-dibromo tetrafluorobenzene, methyl salicylate, tetrabromoethane, and tetradecane, ordered by volatility) were supplied by Torion Technologies Inc. (American Fork, UT, U.S.A.). The Twister sorptive PDMS stir bar (1.5 cm long) was supplied by GERSTEL Co. (Mülheim an der Ruhr, GE). The membrane conditioning unit was developed at the University of Waterloo Science Electronics Shop (Waterloo, ON, Canada). Stainless steel cotter pins were supplied by Spaenaur Inc. (Kitchener, ON, Canada). Teflon holders were created by the University of Waterloo Science Shop (Waterloo, ON, Canada). The Elcometer 4340 motorized automatic film applicator and coating bar (adjustable gap of 0-250 µm) were acquired from Elcometer Ltd. (Rochester Hills, MI, U.S.A.). The Mastercraft Maxxam 18 V powerdrill was purchased from Canadian Tire (Waterloo ON, Canada).

Instrumentation

Analytical instrumentation used for separation and quantitation included an Agilent 6890 GC and a 5973 quadrupole MS (Agilent Technologies, CA U.S.A.) coupled with a Gertsel cooling injection system (CIS) 4, Twister thermal desorption Unit (TDU), and a MPS2 autosampler for membrane desorption and injection (GERSTEL, Mülheim an der Ruhr, GE). Additionally, a Torion Tridion-9 GC- toroidal ion trap MS coupled with a prototype high volume desorption (HVD) module (Torion Technologies Inc. UT, U.S.A) was used to evaluate and compare membrane sensitivity for on-site analysis.

Chromatographic separations on the Agilent 6890-5973n were performed on a 30 m × 0.25 mm I.D × 0.25 µm SLB-5 fused silica column (Sigma-Aldrich, Mississauga, ON, CA). Helium carrier gas was used at a flow rate of 1 mL/min. The column temperature was initially held at 40 °C for 2 min, ramped to 200 °C at a rate of 10 °C min^{-1}, then kept for 2 min. The MS detector transfer line temperature, MS quadrupole, and MS source temperature were set at 300, 150, and 230 °C, respectively. Gas phase ions were generated using electron impact ionization, and the quadrupole was operated in full scan mode in the ranges of 35−400 m/z.

Chromatographic separations for untargeted analysis on the Tridion-9 were performed using a low thermal mass (LTM) MXT-5 (5 m x 0.1 mm x 0.4 µm) Siltek ® - treated stainless steel column (Restek Co. Bellefonte, PA, U.S.A.) Helium carrier gas was used at a flow rate of approximately 0.3 mL min^{-1}. Different oven methods were used depending on the experiment being performed, and will hence be disclosed in their own section. To maximise sensitivity while preventing any needle carryover, desorption of the Tenax/CAR 19-gauge needle trap transfer device was carried out at 280 °C for 20 s in splitless mode, followed by opening of the 10:1 split for 10 s, and then further opening of the 60:1 split for a final 10 s. The ion-trap heater was set to 155 °C with a transfer-line temperature of 250 °C during analysis. Ionization was performed using an electron-gun EI ion-source, and the trap was operated in a reduced scan mode in the ranges of 43-325 m/z).

Operation of the high volume desorption modules

In order to perform membrane desorption on the Twister TDU, an inert glass bead was first placed into the tapered 5 mm I.D. glass desorption tube to prevent the flat membranes from falling through the tube bottom. Desorption was carried out at 250 °C using a helium stripping gas flow of 60 mL min^{-1} for 5 minutes. The desorbed analyte was then cryo-focused at -80 °C within the CIS module for the duration of the 5 minute desorption. Following desorption, the CIS was then ramped to a temperature of 270°C at a rate of 10 °C s^{-1} so as to perform splitless transfer of the analyte onto the Agilent 6890 GC-column for separation and quantitation.

In order to perform membrane desorption on the portable HVD prototype, membranes were placed into empty 3.5 inch stainless steel sorbent tubes. Next, the tubes were placed into the conventional trap holder, which was then fit into the body of the HVD module. Following, an adapter was placed on top of the conventional trap holder, which creates an air-tight seal between the 3.5 inch sorbent tube and the 19-gauge Tenax-CAR needle trap device (NTD). A pair of heated clamps placed within the HVD module were then secured onto the sorbent tube, allowing for the 250 °C thermal desorption of the contained membrane. Subsequently, helium stripping gas was passed through the sorbent tube and into the attached NTD for 5 minutes. This process, outlined graphically in Supplementary Figure S.1, allows analytes to be transferred from the thin film membrane and onto the commercially available 19-gauge NTD, which can then be injected directly onto the Tridion-9 portable GC-TMS for separation and analysis. The HVD prototype system was thoroughly tested to ensure complete transfer of the analytes from the membrane to the NTD, ensuring no membrane carry-over or needle trap breakthrough was occurring. This validation is comprehensively discussed in supplementary Section S.1.

Preparation of the carbon mesh particle-loaded membranes

Following the methodology described by Jiang *et al.*, in order to first disperse the 5 µm DVB particles, a solvent was used to ensure homogenous distribution of these particles [15]. To accomplish this, 0.450 +/- 0.005 g of DVB particles were accurately weighed into a 20 mL headspace vial. 16 mL of hexane was then pipetted into this vial, and the mixture was vortexed for 1 minute, and then sonicated for 30 min. After mixing, 2.450 +/- 0.02 g of the high density PDMS pre-polymer was weighed into the same vial and vortexed for an additional 2 minutes, followed by 1 hour of sonication. Most of the hexane was then volatilized from the mixture by purging the vial with nitrogen gas. Optimal viscosity was chosen subjectively, when the mixture appeared to just barely flow when inverted in the vial. Future improvements upon this method could be made by weighing the mixture when this viscosity is achieved such that the same mass could be used in future preparations, lending to improved inter-batch reproducibility. Following these steps, 120 µL of the peroxide-based catalyst was pipetted into the mixture and manually mixed using a spatula for approximately 1 minute.

Concurrently, a 25 x 60 cm (approx.) sheet of the carbon mesh was cut and secured to the Elcometer 4340 motorized film applicator. The coating mixture was then manually placed in a thin strip along the top of the carbon mesh sheet. The coating bar gap was adjusted to the thinnest setting available, and then used to slowly spread the sorbent mixture across the carbon mesh surface. The

coating was then cured inside a nitrogen-purged vacuum oven at a pressure of -15 mmHg (approx.), and at 190-200 °C for a period of at least 16 hours. As the membranes are double sided, the entire process needed to be performed a second time to complete the membrane. Once both sides were cured, individual membranes were manually cut into 2 different, instrument-dependant sizes (2 cm x 4.85 mm for the Gerstel TDU and 4 cm x 4.85 mm for the prototype HVD module). A brass template and sharp utility knife were used to make these cuts. It is important to note that it is essential to make a clean cut when preparing membranes so as to avoid the loss of small strands of carbon, which can block the injector during desorption. Coating the membrane edges in polytetrafluoroethylene (PTFE) was also found to further prevent this loss; however, this will not be further discussed herein, as it falls outside the scope of the current research.

Membranes were conditioned under nitrogen at 250 °C for 4 hours using a membrane conditioning unit developed in house by the University of Waterloo electronics shop. Once cooled, these membranes were washed in a 25:25:25:25 water:methanol:isopropanol:acetonitrile v:v:v:v mixture for 2 hours, and then air dried on Kimwipes. Before use, all membranes were submitted to a final 30 minute conditioning step at 250 °C inside the respective thermal desorption unit. In line with standard SPME procedure, it is also recommended that this final conditioning step be re-performed whenever the membranes have been stored without use for long periods of time.

Comparison of membrane bleed and instrument background

To contrast the levels of detectable bleed, 3 of the DVB/PDMS/Carbon mesh membranes described herein were compared with 3 DVB/PDMS unsupported membranes that were prepared using the method described Jiang *et al.* [15]. As membranes typically produce more bleeding after sitting for a greater period of time, a single blank desorption was performed 24 hours prior to the comparative runs. Desorption and analysis were carried out on the Agilent 6890-5973n instrument, with a GC runtime of 20 minutes.

Comparison of TFME extraction sensitivity using portable instrumentation

In order to determine the signal enhancement provided by the DVB/PDMS/Carbon mesh TFME membrane for portable GC-MS instrumentation, aqueous samplings of various pesticides were performed using 4 different extraction materials. These sorbents included: 2 separate DVB/PDMS/Carbon mesh membranes (4 cm x 4.85 mm L x W), 1 DVB/PDMS unsupported membrane (4 cm x 5.0mm, L x W), 1 Gerstel PDMS sorptive stir bar (1.5 cm long), and a 65 µm DVB/PDMS SPME fiber.

The 10 ppb aqueous pesticide test mixture consisted of 2,4 dichlorophenol, 2,4,6 trichlorophenol, phorate D10, carbofuran, atrazine, fonofos, chloropyrifos, and parathion. Direct immersion extractions were performed at a magnetic stir rate of 1000 rpm from 300 mL of the 10 ppb pesticide standards, using the same sampling set-up described by Riazi Kermani *et al*. [14] A relatively short extraction time of 15 minutes was chosen to more closely replicate a realistic time that could be allotted for sampling when performing analyses on-site under the constraint of battery power. Three replicate extractions were performed for each of the aforementioned samplers, and runs were randomized to account for any potential signal drift of the mass analyzer. For this experiment, the column temperature was initially held at 65 °C for 35 seconds, increased to 285 °C at a rate of 1.0 °C s^{-1}, and then held for 60 seconds at this final temperature.

Untargeted on-site determination of water contaminants in an industrially impacted lake

As a proof of concept, an entirely on-site TFME analysis of environmental lake water was performed at Silver Lake, located in Waterloo, Ontario. Water temperature was measured as 16.5 °C at the time of analysis. TFME Extractions were performed for 10 minutes at approximately 350 rpm using a modified power drill attachment, as shown in Figure 1. After sampling, the membrane was blotted dry with a Kimwipe, and immediately inserted into the 3.5” sorbent tube for desorption, which was undertaken with the use of the prototype HVD module. The portable GC-MS was operated out of the back of a car parked next to the sampling site, using an on-site configuration constrained by a miniature helium cylinder and battery power. For this experiment, the column temperature was initially held at 45 °C for 35 seconds, then increased to 285 °C at a rate of 1.5 °C s^{-1}, and held there for 60 seconds. For untargeted analysis, the signal was reported as the peak height of the respective quantitative ion.

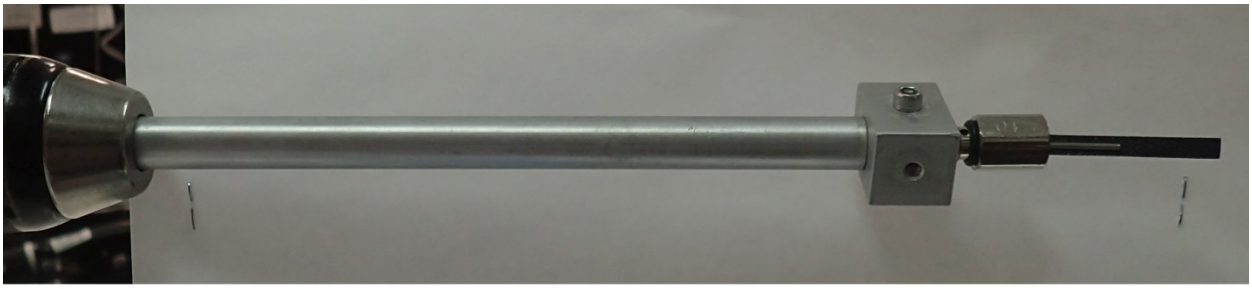

Figure 1. Modified power drill set-up holding a 4 cm x 5 mm DVB/PDMS/Carbon mesh TFME membrane

Safety Considerations

A wide variety of pesticides, including 2,4 dichlorophenol, 2,4,6 trichlorophenol, phorate D10, carbofuran, atrazine, fonofos, chloropyrifos, and parathion were used throughout this study. These compounds are well known to exhibit potentially life threatening neurotoxic, hepatotoxic, and various other acute toxic effects on the human body if mishandled. Therefore, stock solutions with concentrations greater than 1 ppm were always prepared and handled in a fume hood with nitrile gloves while working solutions of 50 ppb or less were handled in the lab using nitrile gloves, safety googles and a lab coat.

Furthermore all pesticide mixtures were disposed of in an appropriately labeled glass waste bottle which was then handled by the University of Waterloo Environmental Safety Facility which coordinates the disposal of hazardous waste.

Secondly, bubbling off of excess hexane from the DVB/PDMS preparation mixture was always performed in a fume hood as to avoid the inhalation of the volatile hexane.

Lastly, the various compounds contained in the Calion-13 standard mixture are commercially prepared in a sealed, usable headspace generating vial which is generally safe to handle so long as the vial is not dropped or otherwise broken.

Results and Discussion

Physical characterization of the DVB/PDMS/Carbon mesh thin film membrane

Sufficient physical strength and ease of handling are of upmost importance when considering the development and use of any new sampling device. If a membrane-based sampler is especially flimsy or fragile, it may prove inappropriate for the sampling of turbulent aqueous flows or when agitation is applied. Additionally, such a membrane would likely break after being submitted to a few desorptions. Furthermore, if any portion of the analytical operating procedure for the membrane is found to be exceedingly difficult or tedious, few analysts will be interested in adopting the technique, especially when non-technical end users are concerned. In view of these requirements, the new DVB/PDMS/Carbon mesh supported membranes were shown to exhibit great physical characteristics, while being much simpler to insert and remove from the desorption tubes than previous designs.

The first thing to note when viewing the new membranes would be the rectangular 4.85 mm-wide design shown in Figures 2 and 3 below. This design is in stark contrast to the 6 mm circular, and house-shaped membranes previously discussed in the literature [11,14,15]. By limiting membrane width to just under the 5 mm inner diameter of the desorption tubes, insertion and removal of the samplers for analysis were made abundantly simpler. Conversely, even the small, 6 mm diameter membranes

commonly proved difficult to desorb. Said membranes had a tendency to stick to the inside of the desorption tube, requiring a metal wire to be pierced through their surface, which could periodically lead to membrane breakage after prolonged use. It is worth noting nonetheless that the rollable house design possesses a surface area of 10 cm^2, which is markedly larger than the 3.88 cm^2 provided by the 4 cm long rectangular membrane. However, to make up for this size difference, an analyst could simply insert multiple rectangular membranes side by side into the same desorption tube.

The combination of high-density PDMS with the carbon mesh support was found to be advantageous for a multitude of reasons. First, although initial trials involving the preparation of unsupported DVB/PDMS membranes with the new high-density PDMS had shown a substantial decrease in the amount of siloxane background upon analysis by GC-MS, these membranes were found to be exceedingly fragile, often breaking after the first use. In addition to providing additional extraction phase, the incorporation of the carbon mesh support had a rebar-in-concrete-like effect on the membrane structure, making the structure incredibly resistant to impact, and without a propensity to elongate or bend under stress. This rigidity proved especially useful for aqueous sampling. As shown in Supplementary Figure S.4, the 4 cm DVB/PDMS/Carbon mesh membranes were shown to resist bending when direct immersion sampling was performed at 1000 rpm. Moreover, this strength allowed the membranes to be attached to a modified power drill, such that agitation could be performed during on-site water analysis. In fact, upon testing of the membrane architectures of both unsupported and supported designs, only those possessing a carbon mesh support resisted wrapping around the cotter pin when agitated at 1300 rpm, although the 4 cm long carbon-supported membrane was observed to bend into a persistent “J” shape at these speeds. Furthermore, the only unsupported membrane to resist wrapping at 350 rpm was the smallest, 2 cm by 5 mm design. These results are graphically illustrated in Supplementary Figure S.5. Such physical stability is essential for reliable environmental sampling of high-flow waterways such as river systems. Additionally, quicker extraction kinetics can be obtained by applying higher agitation rates; accordingly, this would allow for greater method sensitivity with shorter sampling times [1,12].

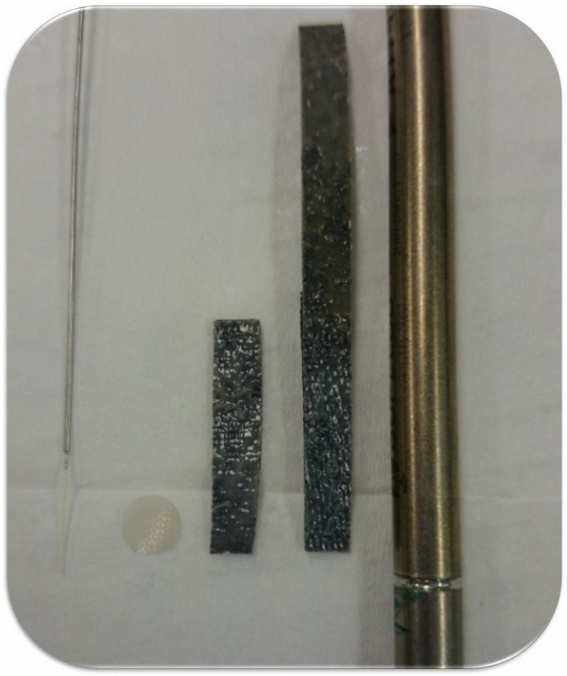

Figure 2. Evolution and design of DVB/PDMS extraction materials with (1) a 65 µm DVB/PDMS SPME fiber; (2) an unsupported 6 mm diameter DVB/PDMS membrane; (3) a 2 cm x 4.85 mm DVB/PDMS/Carbon mesh membrane; (4) a 4 cm x 4.85 mm DVB/PDMS/Carbon mesh membrane; (5) a standard 3.5“ sorbent tube

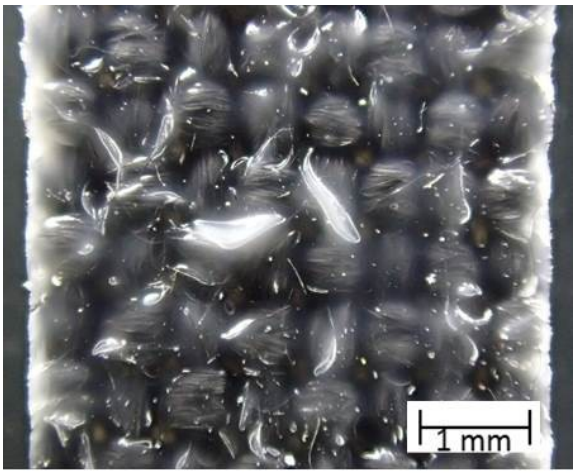

Figure 3. Surface of a DVB/PDMS-coated carbon mesh support with optical magnification of 11x

Comparison of siloxane backgrounds using different TFME chemistries

As previously stated, the main motivation of this study was to minimize the amount of siloxane bleed occurring from TFME membranes upon thermal desorption. Although a small amount of background may be considered acceptable for most GC methods, if too much background occurs, it may become difficult to resolve which peaks are associated with the sample, versus those attributed to the

background. This difficulty holds especially true when untargeted analysis is performed. Additionally, excessive background can also contaminate the electron impact ion source of the mass spectrometer, resulting in fluctuations in the ionisation of target analyte, and an overall reduction in the life of the source. With these facts in mind, background levels of blank desorptions from 3 different DVB/PDMS/Carbon mesh membranes were compared with levels found for 3 DVB/PDMS unsupported membranes.

As demonstrated in Figure 4 below, the amount of bleed and associated background were substantially less when the high-density PDMS was used to prepare the TFME coating. Although it is difficult to comparatively quantitate background, a visual observation of the 2 stacked chromatograms clearly shows that the platinum catalyzed PDMS-based membranes exhibit a greater number of large bleed peaks than seen with the high density PDMS-based design. Additionally, the height of these peaks was found to be much higher for the platinum catalyzed PDMS-based membranes. Hence, the newer membrane design was found to be far superior in terms of bleeding. In addition, considering that the larger 1.1 x 10^7 (height) siloxane peak obtained from the DVB/PDMS/Carbon mesh membrane occurred so early in the chromatogram, this could be easily prevented by setting the solvent delay to 4 minutes.

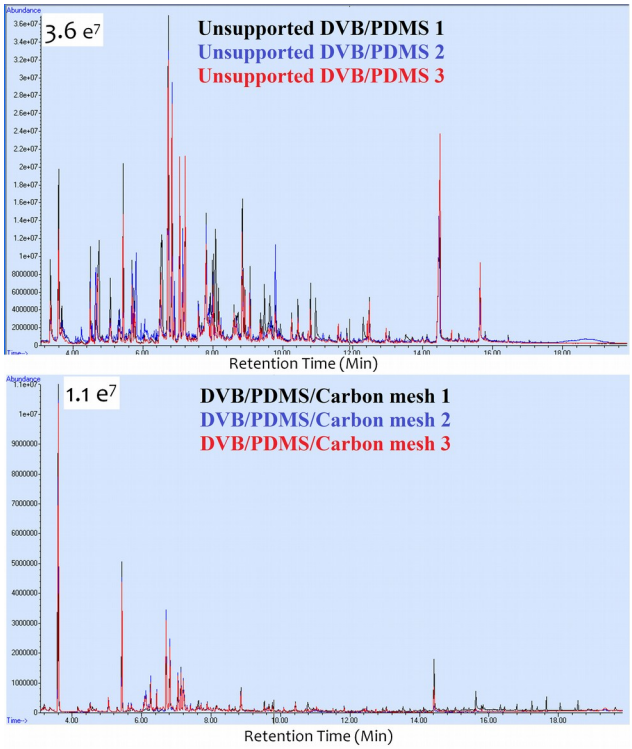

Figure 4. Comparison of membrane bleed and associated siloxane background for: (A) 3 unsupported platinum catalyzed DVB/PDMS membranes; (B) 3 high-density PDMS DVB/PDMS/Carbon mesh supported membranes. All membranes were of similar size, and desorbed at 250 °C using 60 mL min^{-1} of helium for 5 minutes

Improvement upon the sensitivity of portable GC-TMS instrumentation by use of DVB/PDMS/Carbon mesh membranes to extract a mixed pesticide sample

As a demonstration of the advantages of the new DVB/PDMS/Carbon mesh supported membranes, its extraction efficiency towards a pesticide mixture was directly compared with that of a standard 65 µm DVB/PDMS fiber, a 1.5 cm Twister PDMS sorptive stir bar, and an unsupported DVB/PDMS membrane of approximately the same size (4 cm x 5 mm). As the TFME membranes possessed a similar sorbent phase and dimensions, one would expect that they should extract a similar amount of analyte. Theoretically, this amount should be 25.3 times the amount extracted via SPME at pre-equilibrium, and 17.6 +/- 2.2 times that amount once equilibrium had been achieved.

As shown in Figure 5 below, this result was accomplished with a surprising amount of congruency to this theory. With the exception of carbofuran, the 2 DVB/PDMS/Carbon mesh membranes were shown to extract a statistically identical amount of analyte as the unsupported DVB/PDMS membrane. However, standard deviations observed for the unsupported membrane were found to be much higher than any other sampler tested. As can be seen in Supplementary Figure S.4, this was likely due to the unsupported membrane flapping and folding during agitation at 1000 rpm. The amounts of 2,4 dichlorophenol, 2,4,6 trichlorophenol, Phorate D10, fonofos, chloropyrifos, and parathion extracted by TFME were found to increase by factors of 21.2, 19.8, 18.5, 18,4, 26.8, and 23.7, respectively, when compared with a standard 65 µm DVB/PDMS fiber. Unfortunately, carbofuran and atrazine generated poor signals on the portable GC-TMS system, resulting in no detection for either compound when the SPME fiber and Twister sorptive stir bar were used. This result was a bit perplexing, as both compounds generated good signals when analyzed using benchtop GC-MS instrumentation. Additionally, when TFME was used, the signal for earlier eluting analytes was only found to increase by an approximate factor of 20, instead of 25.3. A potential explanation for this finding could be that more volatile analytes were beginning to approach equilibrium within the thinner membrane coatings (40 +/- 5 µm per side). Conversely, the thicker 65 µm fibers would instead require a greater amount of time to begin exhibiting non-linear extraction kinetics. Hence, equilibrium kinetics may explain why the factors for these more volatile analytes fell closer to the theoretical value of 17.6 +/- 2.2 expected for an equilibrium extraction, where sorbent volume V_f, fiber constant K_{fs}, and sample concentration C_s determine the amount of analyte extracted, as shown in Equation 2.[1,4,12]

(2)

Additionally, to rule out non-linearity of the toroidal-ion-trap detector, a rough calibration curve from 100 ppt to 50 ppb was prepared using the DVB/PDMS/Carbon mesh membrane by applying the same extraction conditions as before. This plot can be found in the supplementary information as Figure S.6. The obtained results demonstrated that 2,4 dichlorophenol, 2,4,6 trichlorophenol, Phorate D10, fonofos, chloropyrifos, and parathion could all be detected using a selected ion chromatogram at 100 ppt. However, only 2,4 dichlorophenol, 2,4,6 trichlorophenol, and Phorate D10 gave a high enough signal to noise ratio at 100 ppt to be included in this calibration plot. It is also worth mentioning that a test for membrane carryover was also performed at 10 ppb, confirming that there was no detectable carryover.

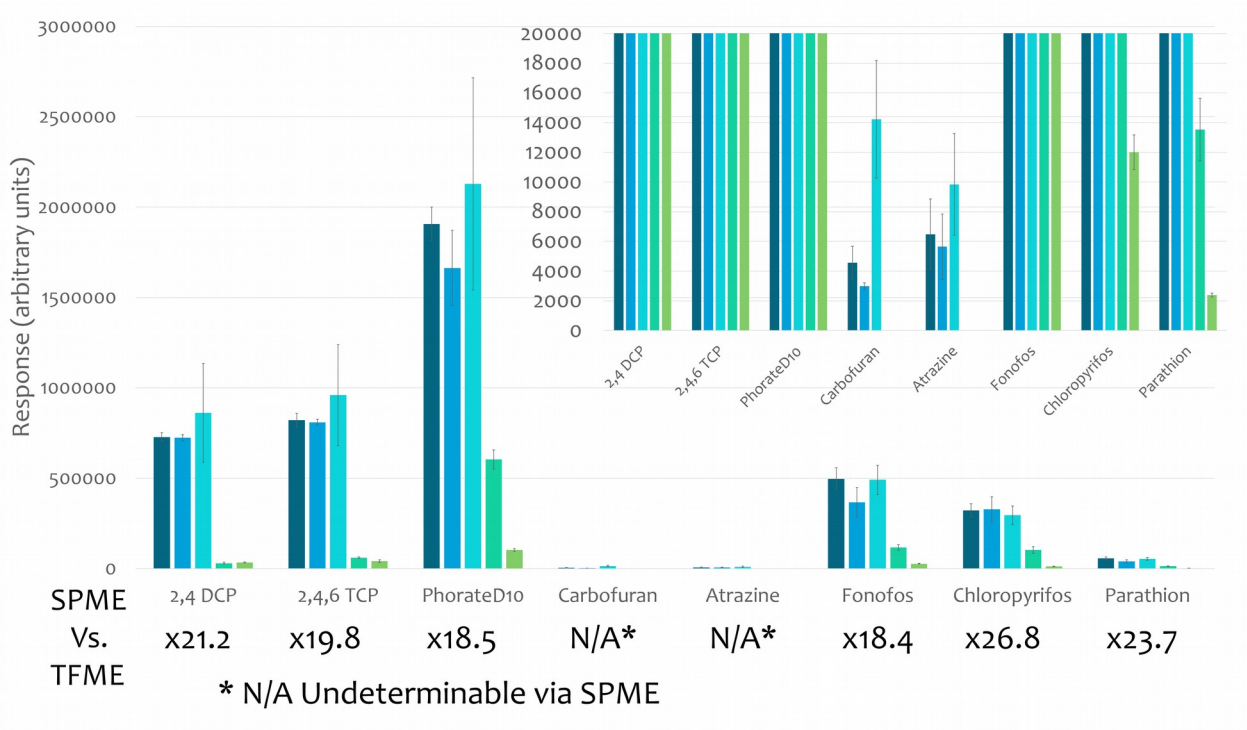

Figure 5. Comparative pesticide extraction efficiencies on portable GC-TMS instrumentation between 2 DVB/PDMS/Carbon mesh membranes (3.88 cm^2); an unsupported DVB/PDMS membrane (4.0 cm^2); a 1.5 cm Twister PDMS sorptive stir bar, and a standard 65 µm DVB/PDMS SPME fiber. Direct immersion extractions were performed from 300 mL of a 10 ppb pesticide mixture for 15 minutes at room temperature and 1000 rpm agitation. Sensitivity improvement factors obtained with the use of a DVB/PDMS/Carbon mesh in lieu of a standard DVB/PDMS fiber are also shown.

Untargeted on-site determination of water contaminants in an industrially impacted lake

As a final proof of concept, it was important to show that the entire system could be employed entirely on-site. Henceforth, an untargeted analysis was performed for Silver Lake, situated in Waterloo, Ontario. This location was chosen because of concurrent construction of a light rail bridge at the inlet of the lake. The portable GC-MS was run on battery power alone, hence, only 3 replicate 10 minute

extractions were performed from the lake. Adding in the 5 minutes required for desorption, and the 5 minutes needed for analysis, each run required 20-25 minutes in addition to 30 minutes required for the instrument to warm up and run performance validation. Recognizing these shorter extraction times, it was very advantageous to be able to perform sampling with the modified power drill to improve the extraction kinetics, and consequently, method sensitivity.

Interestingly enough, a number of anthropogenic compounds that could be attributed to the ongoing construction were detected during analysis. These compounds, which are listed in Table 1 below, included toluene (T), ethylbenzene (E), xylene (X), 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (TXIB), and Tris(1-chloro-2-propyl)phosphate (TMCP). Identification of the unknowns was performed by comparing the generated mass spectra to those within the NIST mass spectrometry database, followed by confirmation using an n-alkane linear retention plot which was generated via analysis of highly reusable C7-C20 n-alkane standard headspace generating vial.[20,21] The presence of T,E,X was not entirely surprising, considering that multiple gas-powered pumps were used to bypass the water around the railway bridge during construction. Hence, it is very likely that small amounts of gasoline may have been spilled into the waterway.

The detection of TXIB and TMCP proved to be a little bit more intriguing. These compounds, which are commonly used as a plasticizer and flame-retardant, respectively, were found to generate a considerable signal. Further investigation of the construction site indicated that on the day of sampling, workers were in the process of applying polymer-reinforced concrete to the bridge. It is possible that this polymer component may have contained the aforementioned compounds; however, this is purely speculation.

Regardless, for the purposes of this experiment, it could be concluded that the on-site method worked appropriately for qualitative untargeted aqueous sampling. Additionally, it was reassuring to see that the method response was, for the most part, reproducible even though only 3 runs were performed. This would indicate that if a target analyte were selected, it should be possible to perform semi-quantitative analysis completely on-site using this system.

Table 1. Compounds detected in Silver Lake, Waterloo, Ontario, with likely anthropogenic origins. Extractions were performed directly from 16.5 °C lake water with a DVB/PDMS/Carbon mesh membrane, using a modified power drill at 350 rpm for 10 minutes. Desorption and analysis were performed on-site using a portable GC-MS and desorption unit.

Compound	RT(s)	Quant ion	Exp LRI	NIST LRI	Signal (AVG)	SD	%RSD
Toluene	55.80	91	779	794	1740	72	4
Ethylbenzene	72.59	91	873	893	7035	1151	16
Xylene	77.13	91	901	907*	1913	592	31

TXIB	152.94	71	1612	1605	35725	2476	7
TMCP	169.68	99	1827	1814	14157	2865	20

* Reported for ortho-xylene
TXIB 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate
TMCP Tris(1-chloro-2-propyl)phosphate

CONCLUSION

A novel carbon-mesh-supported DVB/PDMS TFME membrane based on a high-density PDMS pre-polymer for the trace level detection of volatile and semi-volatile organic compounds is proposed in this study. Many benefits over the previous TFME designs were demonstrated herein. Use of the carbon mesh support was shown to greatly enhance the physical strength of these membranes, while limiting the membrane shape to a rectangle of width just under 5 mm allowed for easy operation and desorption. Furthermore, this design allowed for the direct immersion sampling of turbulent water systems without any major bending or twisting of the sorbent. More importantly, the use of a high density PDMS was shown to drastically reduce the amount of siloxane bleeding observed during thermal desorption. Furthermore, it was shown that these TFME membranes could not only be used on standard benchtop instrumentation, but could also be coupled to hand-portable GC-TMS instrumentation by use of a prototype high-volume desorption unit, and commercially available 19-gauge needle traps. It was demonstrated that no significant analyte loss could be detected from the HVD prototype, even when a large amount of a broad volatility multi-component standard was used. This concept was further explored by performing an entirely on-site investigation of water contamination in a construction-impacted lake, where a number of anthropogenic compounds were detected. Most importantly, when short 15-minute extractions were performed from a 10 ppb aqueous pesticide mixture, these membranes were shown to provide upwards of 26.8 times more signal than a comparable DVB/PDMS fiber. Hence, TFME can be used to perform much more rapid on-site sampling while still generating signals comparable to what could be attained from longer SPME extractions.

Ultimately, the work performed with these DVB/PDMS/Carbon mesh supported membranes could very well decrease the generally high detection limits associated with portable instrumentation to levels more in-line with those observed on benchtop GC-MS instrumentation. Furthermore, if coupled with these benchtop instruments, detection limits could be driven even lower than what is currently obtainable.

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SUPPORTING INFORMATION

Additional information as listed below and noted in text. This material is available free of charge at http://pubs.acs.org

Figure S.1. Desorption methodology of TFME membranes onto the portable high-volume desorption module

Section S.1 Validation of the portable high volume desorption interface

Figure S.2. 19-gauge NTD breakthrough test configuration for the desorption of thin film membranes

Figure S.3. Examination of TFME membrane carryover and NTD breakthrough obtained using the portable high-volume desorption prototype

Figure S.4. Direct immersion sampling of pesticides using thin film microextraction at 1000 rpm

Figure S.5. Comparison of direct immersion sampling stability using various TFME membrane designs with the modified power drill sampler at 350 and 1300 rpm

Figure S.6. External calibration curve showing linear range of the pesticide mixture on the portable GC-TMS using TFME

CONFLICT OF INTEREST DISCLOSURE

The authors of this manuscript herein declare that although we have received financial support from Torion Technologies of Perkin Elmer Co. we maintain our independence as a 3rd party academic body resulting in an un-biased representation of the results with no competing conflict of interest, financial or otherwise.

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