Supporting Information

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

Jonathan J. Grandy, Ezel Boyacı, Janusz Pawliszyn*

Department of Chemistry, University of Waterloo, Ontario, Canada, N2L 3G1

Fax: +1 519 746 0435. E-mail: janusz@sciborg.uwaterloo.ca.

Table of Contents:

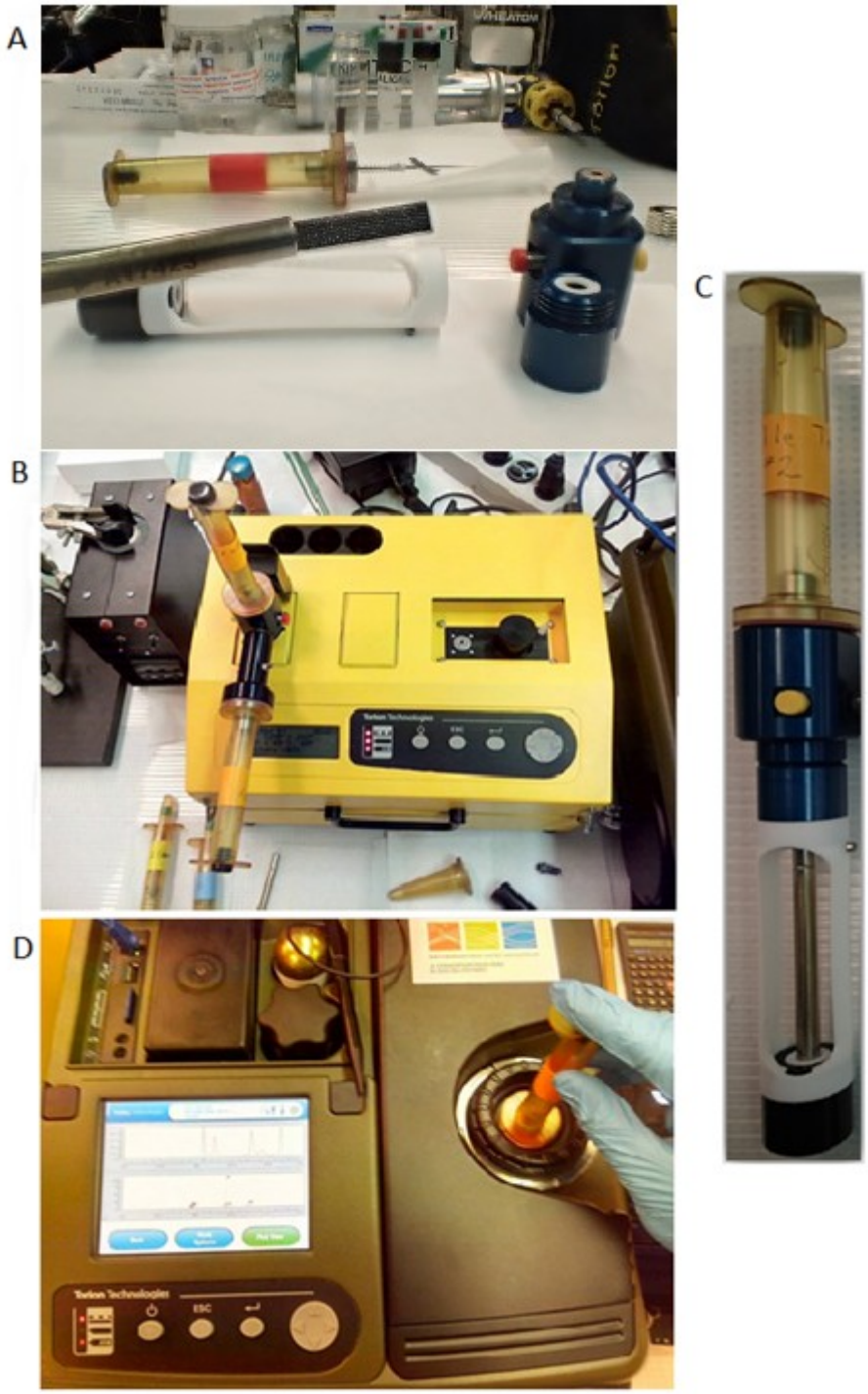

Figure S.1. Desorption of TFME membranes onto the portable high-volume desorption module:
(A) Insertion of membrane into 3.5“ sorbent tube, and into conventional trap holder
(B) Transfer of analytes from TFME membrane to the needle trap using SPS-3 desorption unit (in breakthrough test configuration)
(C) Non-leaking linkage between the sorbent tube and 19-gauge needle trap device
(D) Desorption of needle trap onto portable GC-TMS for separation and analysis

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

To verify that the portable high volume desorption module was capable of completely transferring all of the analyte to the needle trap device, a series of membrane carryover and needle trap breakthrough tests were performed. 3-second TFME extractions were performed from the heavily concentrated Calion-13 standard tuning mixture at room temperature. Such short extraction times had to be used, as longer extractions would result in overloading of the portable GC-TMS instrument. Highly concentrated standards were chosen so as to represent a worst case scenario where NTD breakthrough and TFME carryover were most likely to occur. For this experiment, the GC column was initially held at 50 °C for 10 seconds, and then ramped to 270 °C at a rate of 2 °C s^{-1}.

In order to test for needle trap breakthrough, 2 NTDs were linked in series, as shown in Supplementary Figure S.2. Hence, if breakthrough of the more volatile analytes from the first needle were to occur, they would be trapped onto the second for detection .[22,23] Membrane carryover was evaluated by simply performing a second desorption from the same membrane. This allowed for confirmation as to whether any residual analyte remained from the first analytical run. Each step of the validation process was performed a total of 3 times to ensure reproducibility of the system.

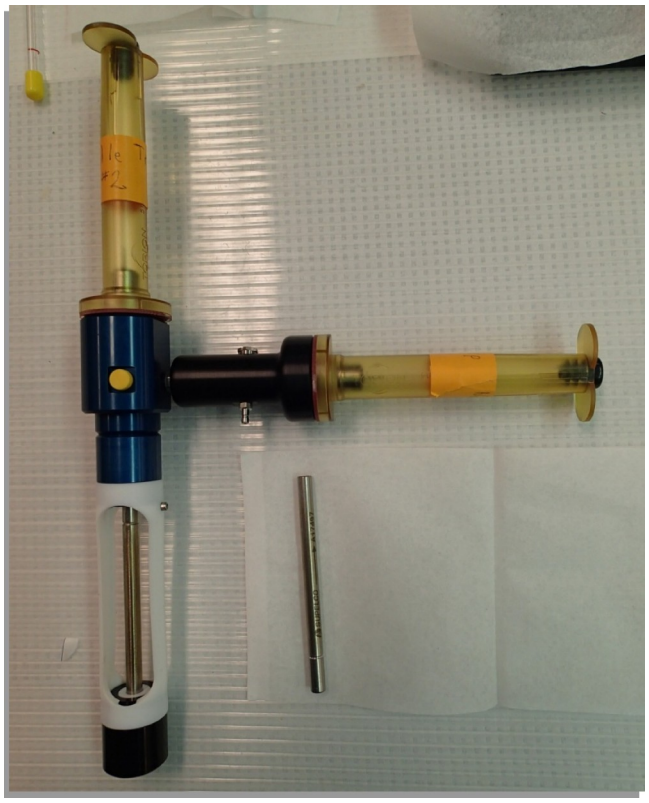

Figure S.2. 19-gauge NTD Breakthrough test configuration for the desorption of thin film membranes

Results and Discussion

Achieving complete desorption and transfer of all compounds extracted using TFME techniques is of the upmost importance when considering any new high-volume desorption device. Hence, care was taken to ensure that minimal or no membrane carryover and needle trap breakthrough were observable from the portable HVD prototype. Generally speaking, one would expect membrane carryover to be most prominent with semi-volatile, heavier compounds while the lighter, more volatile compounds would be the first to breakthrough a needle trap device.[12,23] With this in mind, the acetone and tetradecane components of the Calion -13 standard were the most critical for the evaluation.

As demonstrated in Supplementary Figure S.3, no needle trap breakthrough was detected in any of the 3 replicate analyses performed. However, a very small amount (<2%) of tetradecane was found to carryover during one of the 3 runs performed. Considering that the levels of tetradecane extracted in this test were close to those required to overload the portable GC-TMS, this miniscule amount of carryover was not considered to be greatly significant. However, similar to precautions taken for standard SPME methods, it may be prudent to perform a carryover test on this system whenever a new type of sample is analysed.

A more interesting point of discussion to be made from these results would be the poor chromatographic performance observed for early eluting analytes. This limitation is well known to occur with the Tridion-9 GC-TMS when highly volatile and concentrated compounds are analysed using NTDs and, to a lesser extent, SPME while using a low-or no split-flow. This occurs due to the relatively small amount of helium being passed through the NTD or past an SPME fibre as under splitless conditions, only 0.3 mL min^{-1} of helium passes through the injector and into the column during analysis. Hence, in splitless mode, any compound that is not completely refocused at the head of the GC column prior to oven ramping will have its peak width dictated by the time required to complete the desorption.

As mentioned, a similar effect may be observed even when a regular SPME fiber is used. The standard operating procedure for the portable GC/MS includes an opening of the 10:1 split anytime high concentrations of volatile organic compounds (VOCs) are analyzed. This effect is markedly worse when NTD injections are performed. However, it was found that by using a modified GC-method, decent chromatography could still be obtained for compounds as volatile as benzene while performing splitless desorption. Additionally, good signal and chromatography were still attained for semi-volatile components, suggesting that these issues should not hinder pesticide analysis.

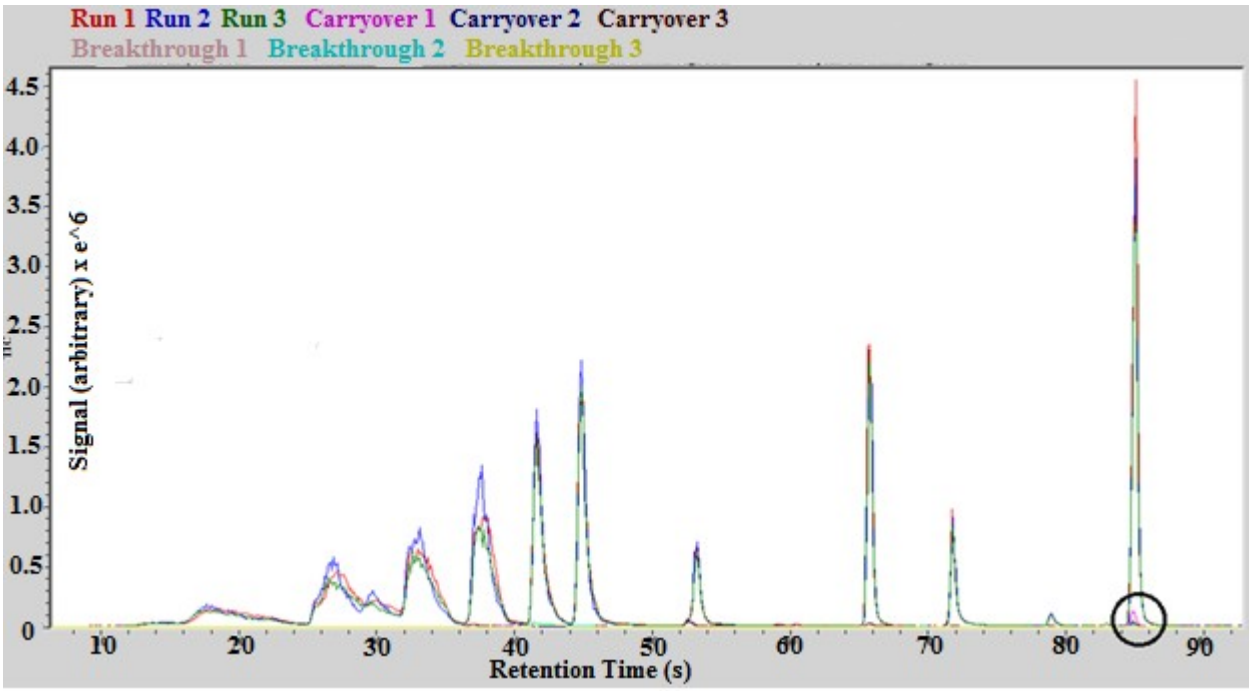

Figure S.3. Examination of TFME membrane carryover and NTD breakthrough obtained with use of the portable high-volume desorption prototype. 3 second TFME extractions were performed at room temperature from a highly concentrated Calion-13 standard mixture, with a small amount (<2%) of tetradecane carryover detected for one of the 3 replicates.

A B C

Figure S.4. Direct immersion sampling of pesticides at 1000 rpm with:
(A) a 2 cm long, unsupported DVB/PDMS membrane;
(B) a 2 cm long DVB/PDMS/Carbon mesh supported membrane;
(C) a 4 cm long DVB/PDMS/Carbon mesh supported membrane.

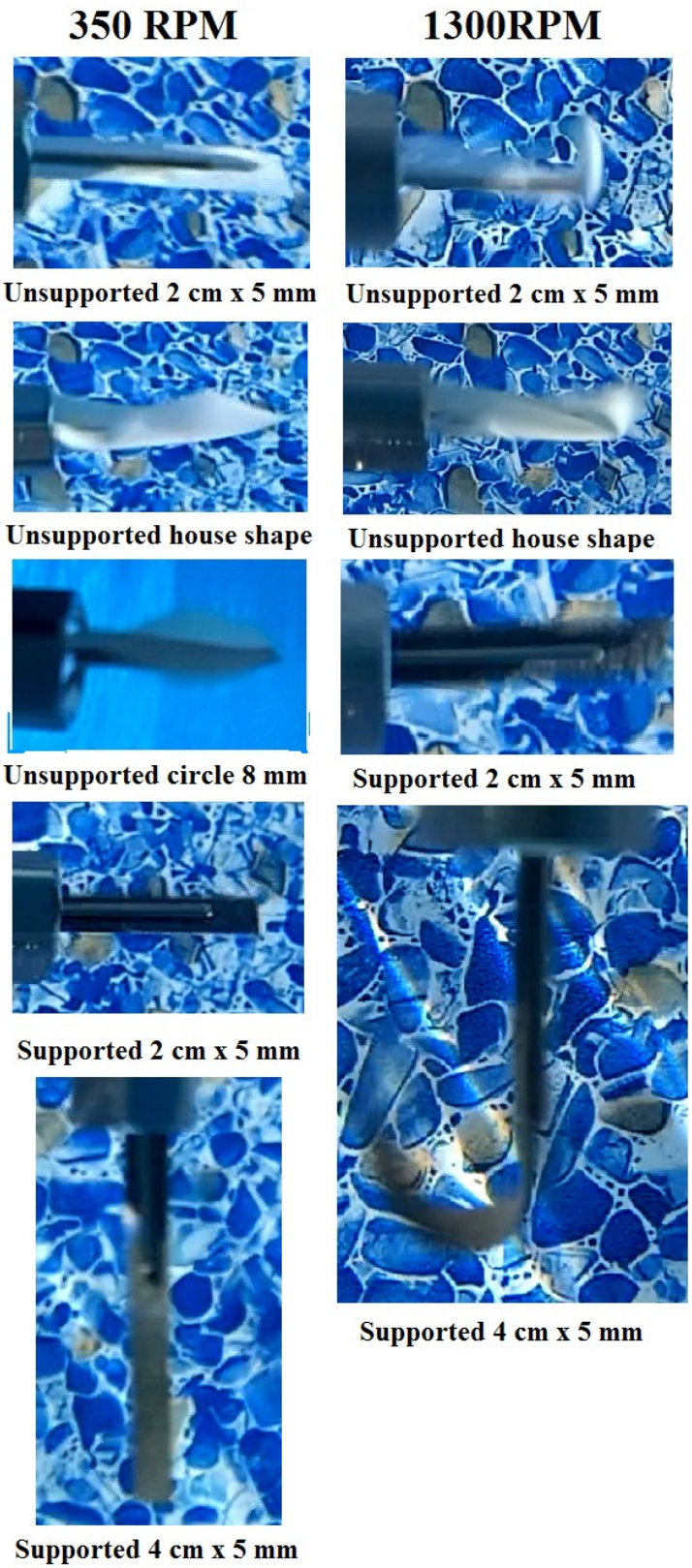

Figure S.5. Direct immersion sampling of various TFME membrane designs using the modified drill sampler at 350 rpm and 1300 rpm

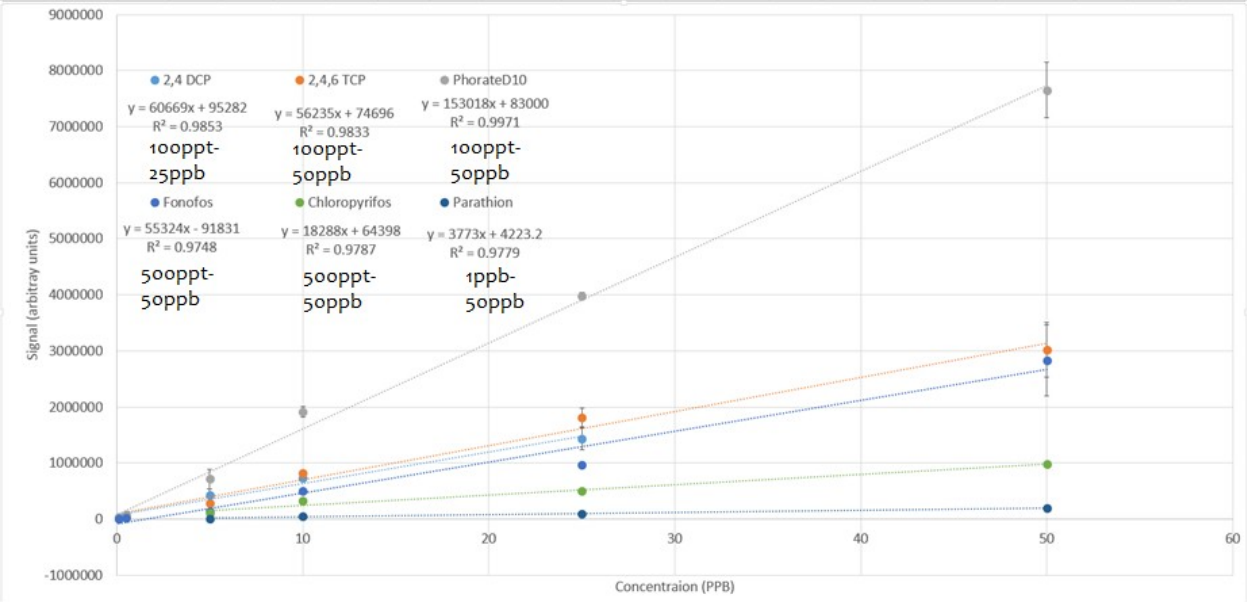

Figure S.6. External calibration curve and linear range of the pesticide mixture using TFME on the Portable GC-TMS instrument. Direct immersion extractions were performed with a DVB/PDMS/Carbon mesh membrane (3.88 cm^2) from 300 mL of the appropriate concentration pesticide mixture for 15 minutes at room temperature, and applying 1000 rpm agitation