Development and Coupling of a Thin Film Microextraction Membrane to Portable GC-MS Instrumentation for the Sub-ppb Detection of Pesticides from Surface Waters

Jonathan J. Grandy
Ezel Boyacı
Janusz Pawliszyn

3rd Advances in Environmental Analysis
E-Seminar

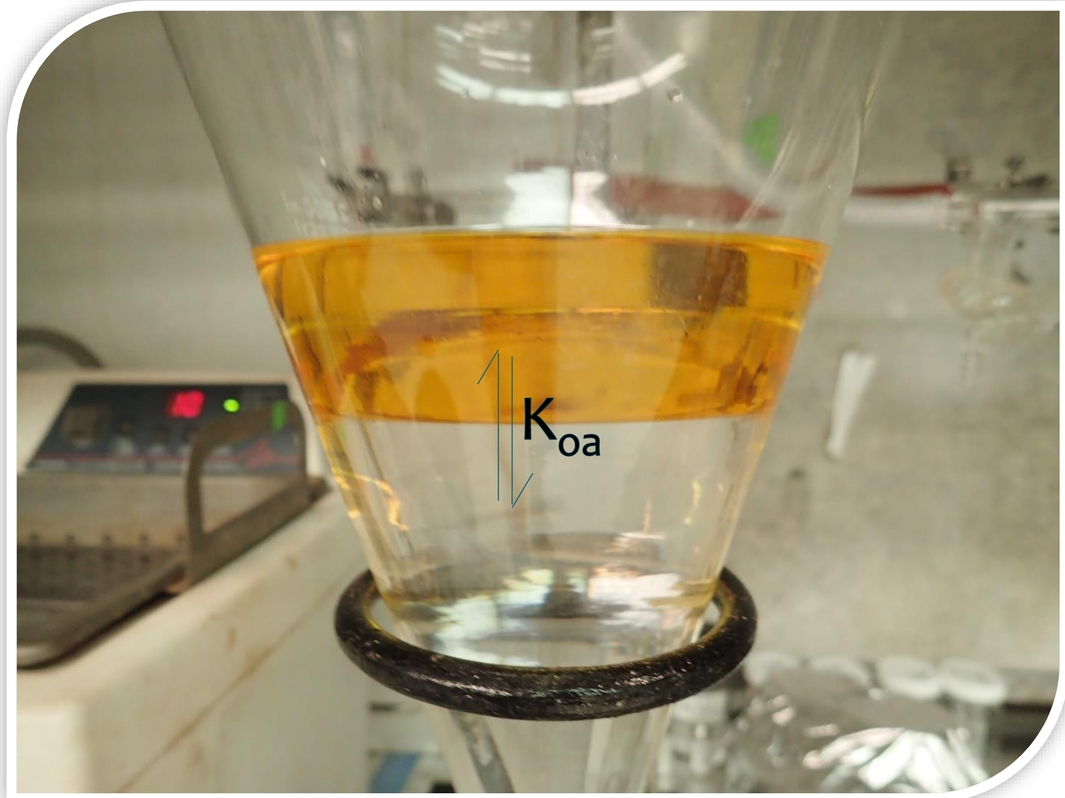
Jonathan J. Grandy
PhD Candidate
University of Waterloo, Ontario, Canada

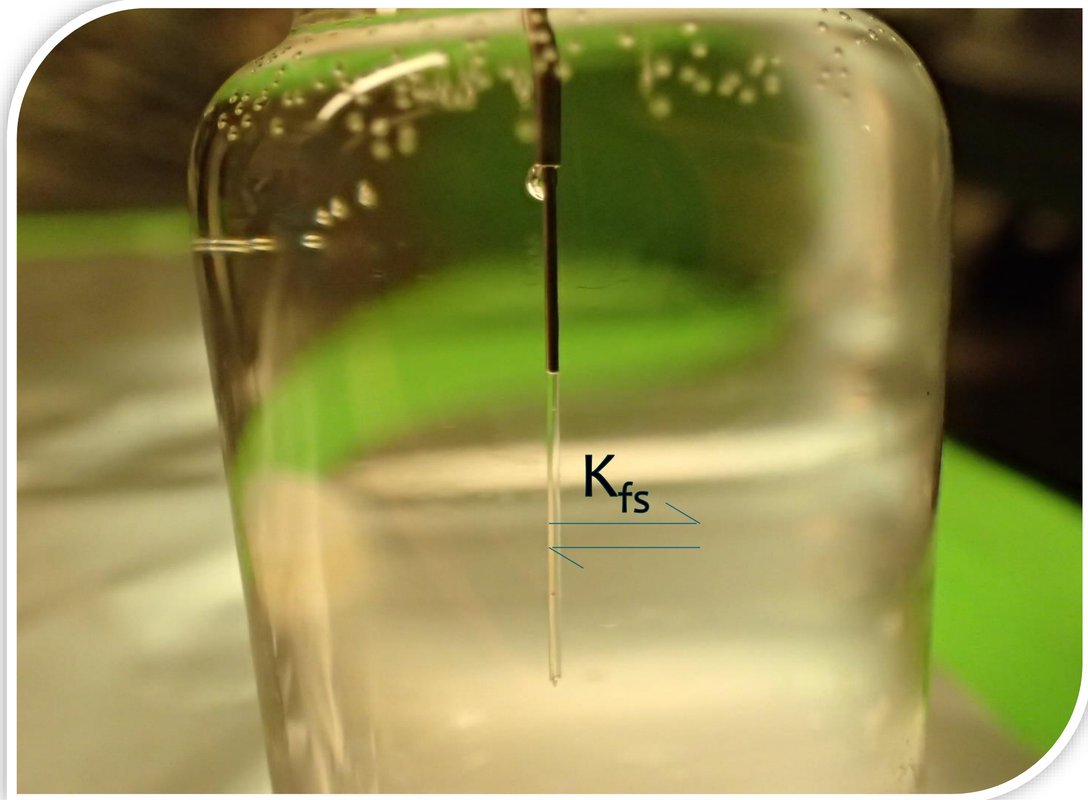
Dr. Janusz Pawliszyn Research Group

Environmental | SAMPLE PREPARATION | MASS SPECTROMETRY

Grandy, J. J.; Boyacı, E.; Pawliszyn, J. *Anal. Chem.* **2016**, *88* (3), 1760–1767.

Why use solid phase microextraction (SPME)? Vs. LLE





Liquid-liquid extraction $K_{oa} = \frac{[x]_o}{[x]_a}, x_o \gg x_a$

- Near exhaustive extraction of analyte
- Only small fraction of extract analyzed
- Uses hazardous organic solvent
- Cannot perform on-site

SPME extraction $K_{fs} = \frac{[x]_f}{[x]_s}, x_f \ll x_s$

- Minimal extraction of analyte
- Equilibrium dependant extraction
- All of the extract is analyzed
- Solvent free
- Environmentally friendly
- Field portable

K = distribution constant, o = organic layer, a = aqueous layer, f = fiber, s = sample, x = analyte

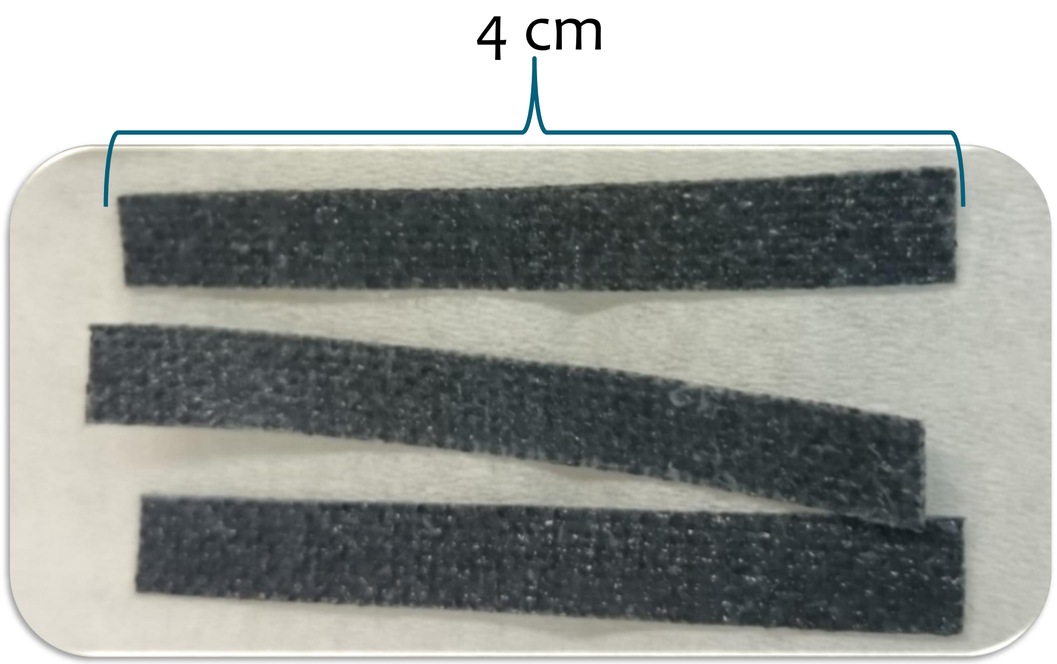
What is thin film microextraction? an extension of SPME

- A thin film membrane can be prepared with larger surface area and volume than a cylindrical SPME fiber.
- In pre-equilibrium, more surface area means a greater amount of analyte extracted per unit time
- More sorbent volume will result in more analyte extracted at equilibrium

Hence, a 4 cm by 4.9 mm membrane with a total coating thickness of 80 µm (40 µm each side) should extract **25x** more analyte in pre-equilibrium applications while extracting **18x** at equilibrium.[1]

DVB/PDMS fiber

Vs.



DVB/PDMS/Carbon mesh membrane

$$n(t) = C_s t \frac{B_3 D_s A}{\delta}$$

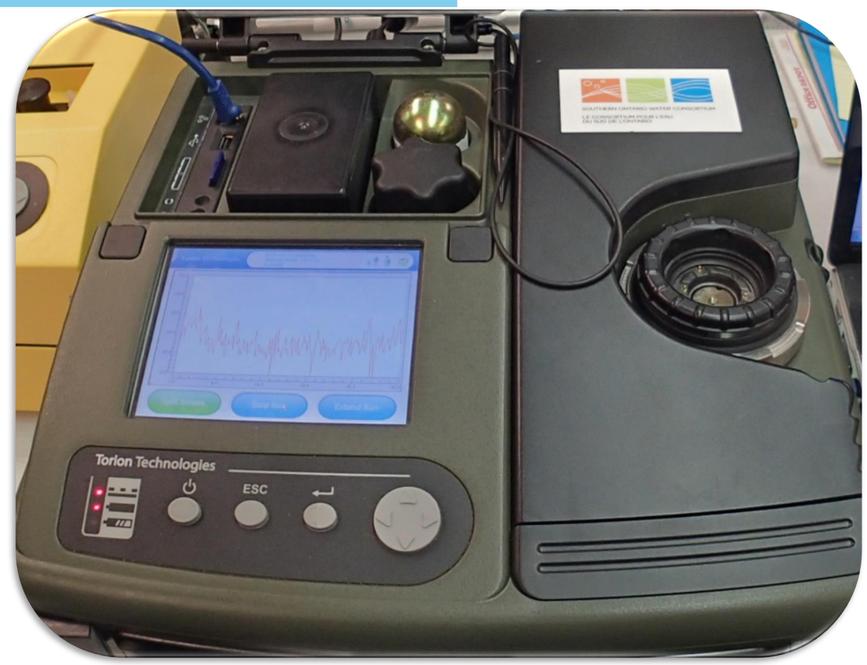
Where: n(t) = the amount extracted as a function of time C_s = the sample concentration t= the sampling time B_3 = the geometric factor D_s = the diffusion coefficient A = the sorbent surface area δ = the thickness of the boundary layer

Pawliszyn, J; Handbook of Solid Phase Microextraction; 2009

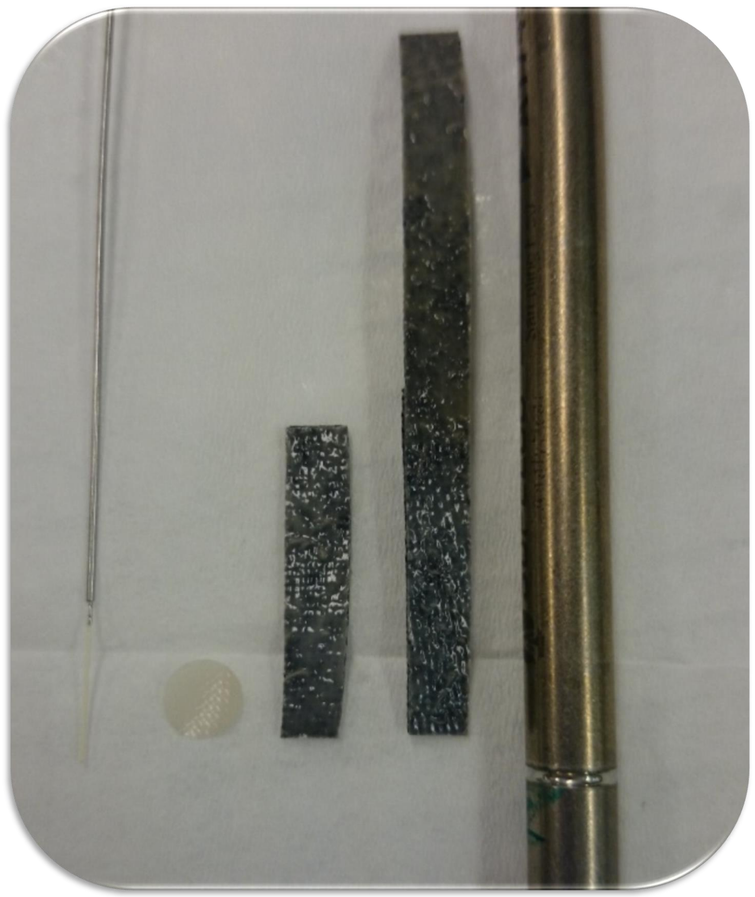
Coupling TFME with portable GC-MS: Background and motivation

- Portable GC-MS instrumentation offers an inherent advantage in generating immediately available results with no need for sample transport

- However portable instruments lack the sensitivity of their benchtop counterparts. Hence by coupling with more sensitive sampling technologies such as TFME this loss of sensitivity can be overcome



Tridion-9 GC-TMS



Evolution of TFME technology

Evolution of Thin Film Microextraction Techniques

1. Bruheim I, Liu X, Pawliszyn J **(2003)** Thin-Film Microextraction. 75:1002–1010.
   - ❑ First TFME membrane work using 25 µm thick PDMS sheets
   - ➢ Improved sensitivity vs standard PDMS fiber but lacked solid sorbent
2. Riazi Kermani F, Pawliszyn J **(2012)** Sorbent coated glass wool fabric as a thin film microextraction device. Anal Chem 84:8990–8995.
   - ❑ First described fabric (fiberglass) supported, particle loaded membrane
   - ➢ Highly sensitive membrane with great physical strength however the high volume of platinum catalyzed PDMS resulted in major background bleed
3. Jiang R, Pawliszyn J **(2014)** Preparation of a particle-loaded membrane for trace gas sampling. Anal Chem 86:403–410.
   - ❑ Highly sensitive particle loaded, unsupported membrane applied on-site
   - ➢ Again the use of Pt catalyzed PDMS resulted in substantial background

❖ Unpublished, Grandy JJ, Pawliszyn J **(2013-2014)** Preparation of a highly cross-linked PDMS, particle loaded, unsupported TFME membrane

- ❑ The more highly cross-linked PDMS resulted in greatly lowered background but the membranes were exceedingly fragile for real world application

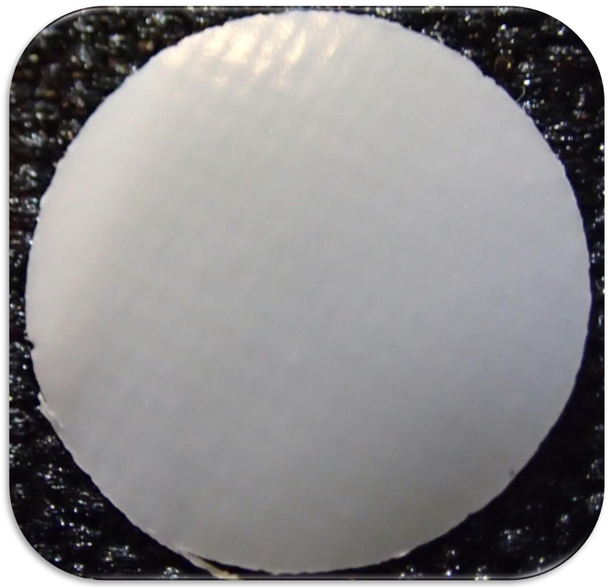
4. Grandy JJ, Boyacı E, Pawliszyn J **(2015)** Development of a Carbon Mesh Supported Thin Film Microextraction Membrane As a Means to Lower the Detection Limits of Benchtop and Portable GC/MS Instrumentation. Anal Chem 88:1760–1767.
   - ❑ A highly sensitive, low bleed, and durable TFME membrane was developed

The new DVB/PDMS/Carbon mesh membranes: A comparison to prior tech

Standard SPME fiber (65 µm DVB/PDMS)

- Advantages
  - Easy introduction to instrumentation
  - Easiest operation
  - Well established
- Disadvantages
  - **Lower sensitivity**

Former platinum catalyzed DVB/PDMS*



- Advantages
  - Easy preparation
  - Very flexible
  - Can be folded
- Disadvantages
  - **Heavy bleeding**
  - Difficult to handle
  - Bend in high flows

New DVB/PDMS/Carbon mesh TFME membrane (high X-link density PDMS)

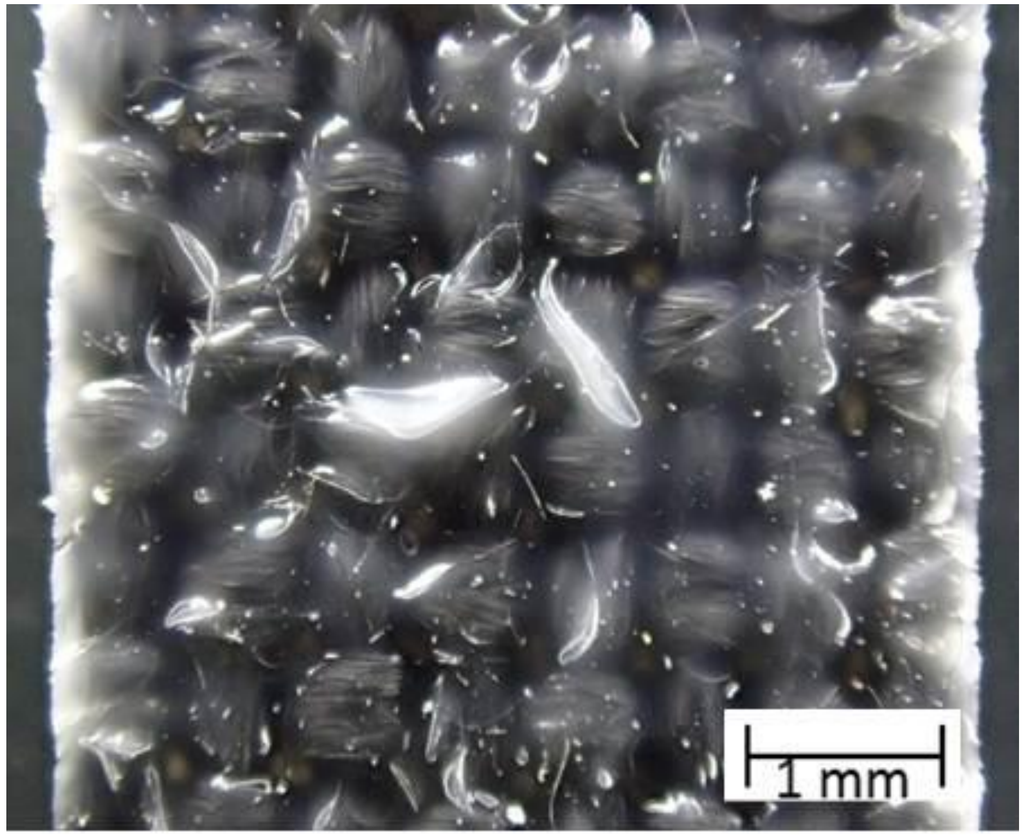
- Advantages
  - Very rigid
  - Highly durable
  - Easier to handle
  - Gives 3 phase sorbent
- Disadvantages
  - Challenging preparation
  - Low ductility

* Jiang, R; Pawliszyn, J; Preparation of a Particle-Loaded Membrane for Trace Gas Sampling; Anal. Chem., 2014, 86 , pp 403–410

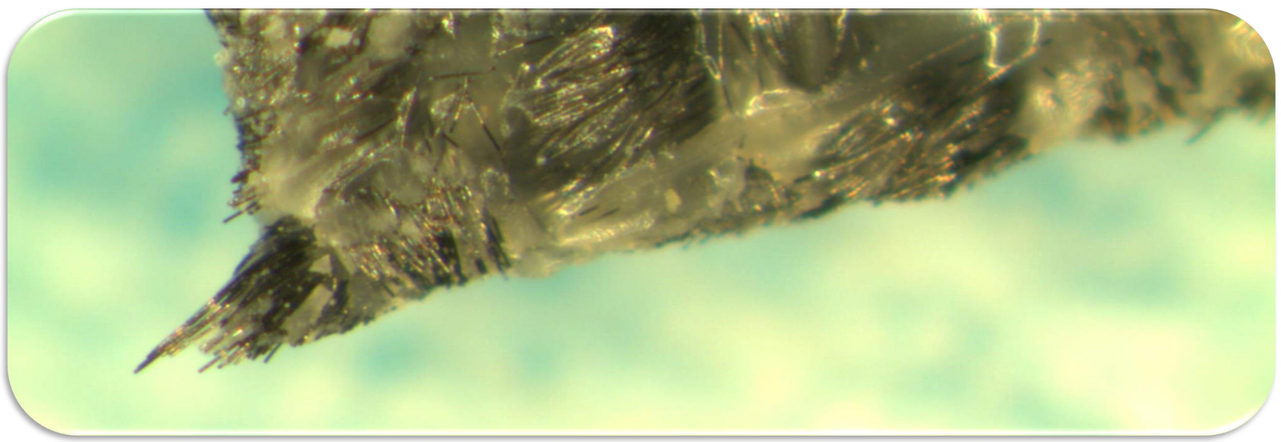
Properties of the carbon mesh supported TFME membranes

Physical membrane characteristics:

- Dimensions: 40 mm x 4.9 mm L x W
  *(20 mm x 4.9 mm for Gerstel TDU)
- Coating polymer: DVB/PDMS
- Coating thickness: 40 +/- 5 µm (per side)
- Support: Zoltek weaved carbon mesh
- Support thickness: 250 µm aprox.
- Maximum temperature: 270 °C
  (200-250 °C recommended)



Surface of a DVB/PDMS/Carbon Mesh Membrane



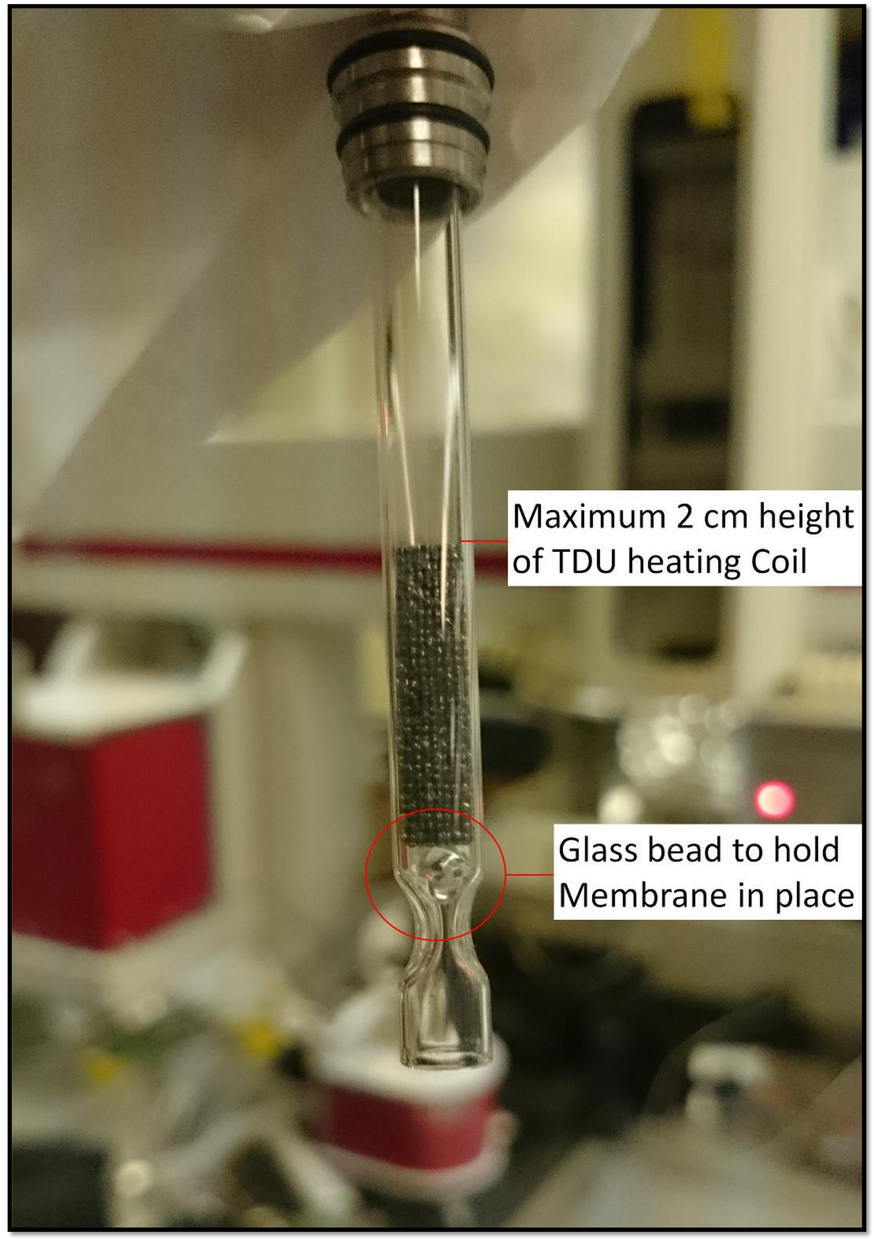
Care must be taken to ensure a clean cut!

Interfacing TFME with a benchtop GC-MS

- Benchtop analytical runs were performed on an Agilent 6890-5973n GC-MS equipped with a Gerstel Twister thermal desorption unit (TDU) with cryofocussing and a MPS2 autosampler unit

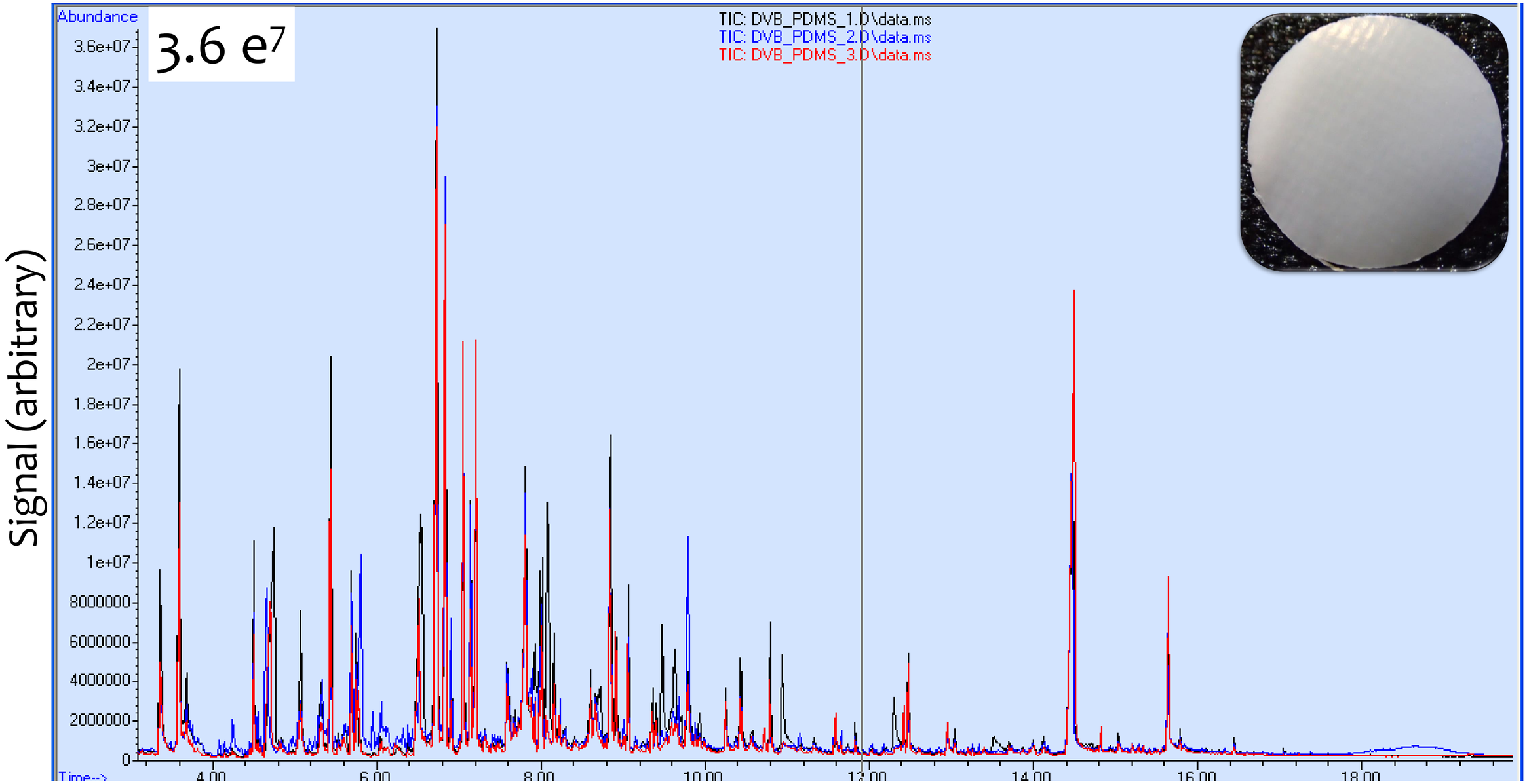
- TFME coupling accomplished by simply inserting a glass bead into the TDU tube

- Optimal desorption conditions were:
  - Temperature: 200-**250** °C
  - Flow rate: 60 mL min^{-1}
  - Time: 5 minutes
  - Cryo focussing temperature: -80 °C



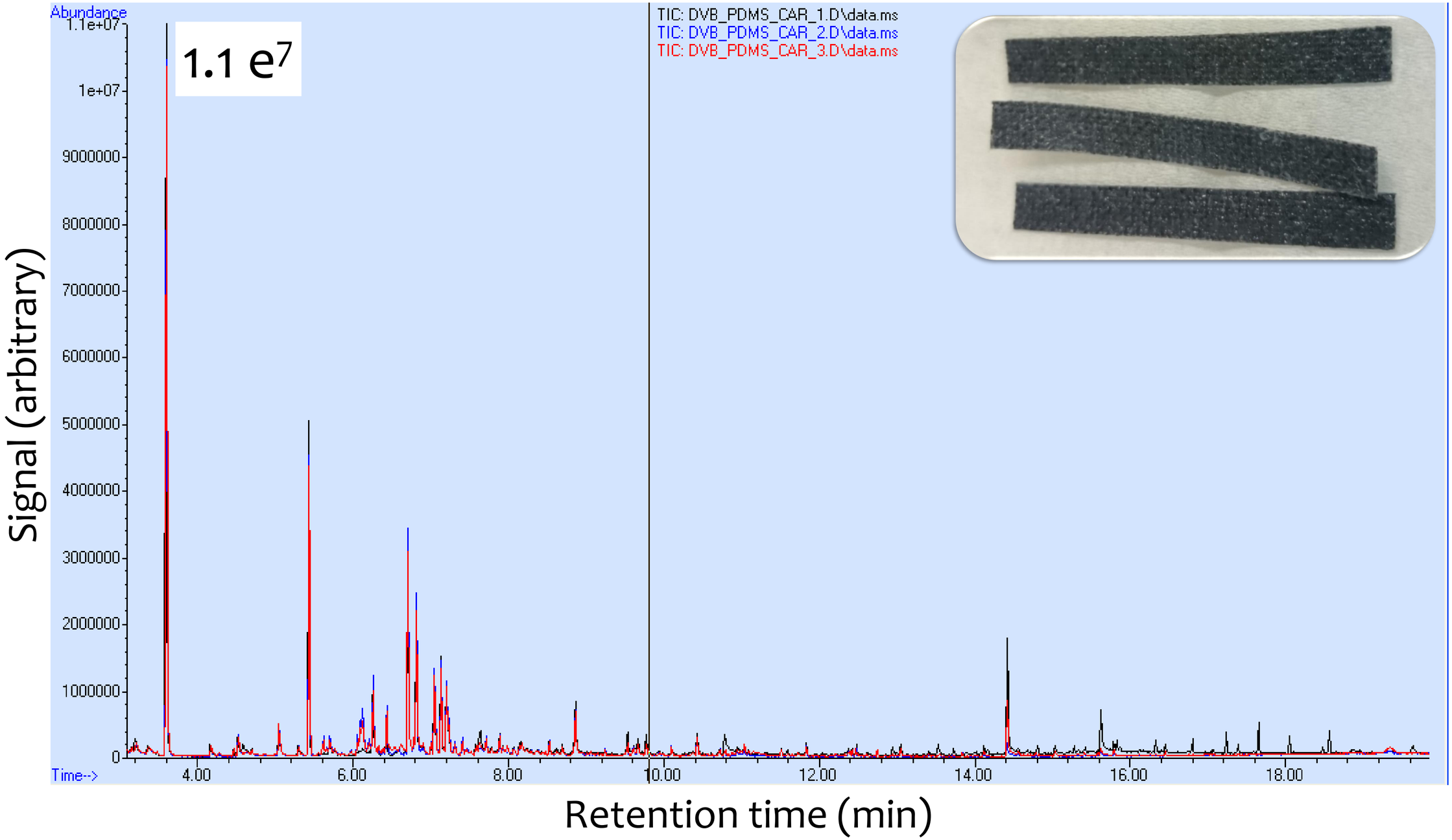
Insertion of TFME membrane into TDU thermal desorption tube

Representation of membrane bleed:
Blank run of the former platinum catalyzed DVB/PDMS membrane



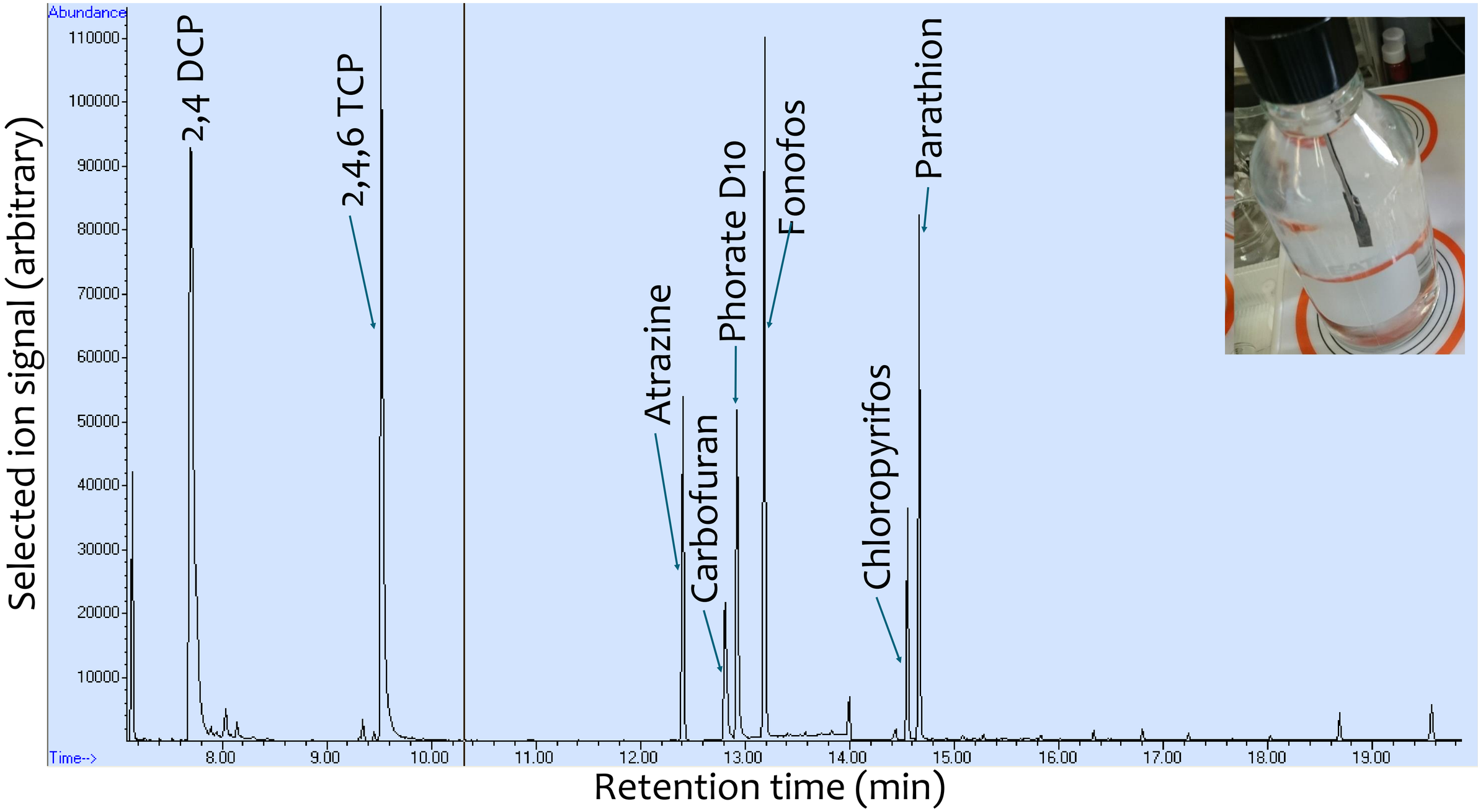
Desorption was carried out using a Gerstel thermal desorption unit at **250 °C** with a **60 mL/min** flow for **5 minutes.** Analysis was performed using an Agilent 6890-5973 in full scan mode.
The **3 membranes** had dimensions **20 mm x 5.0 mm (**L x W) with a coating thickness of **100 µm**

Representation of membrane bleed: Blank run of the new DVB/PDMS/carbon mesh membrane



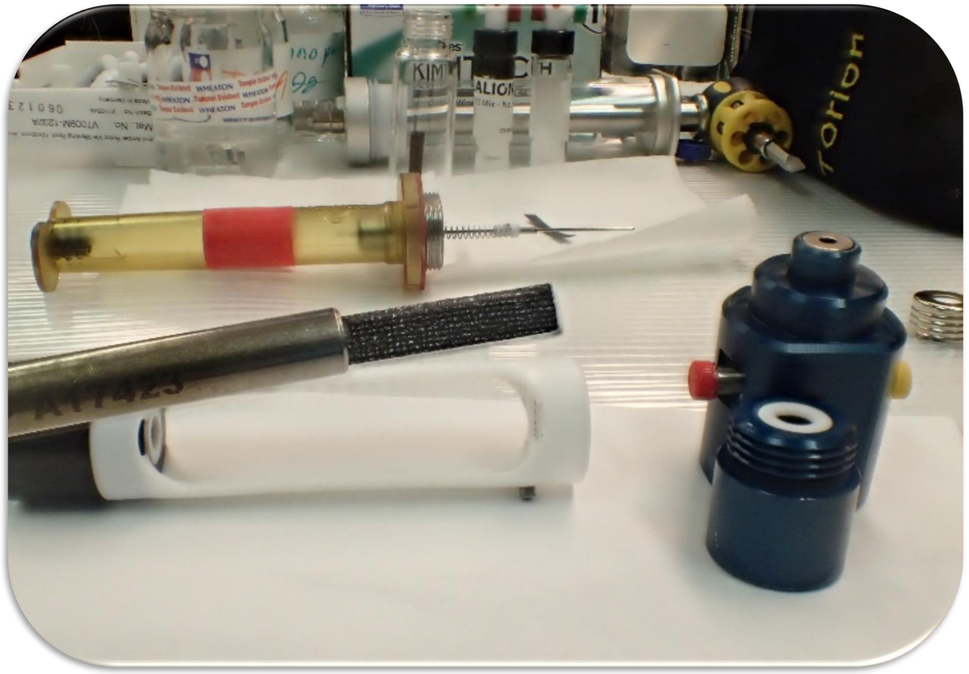
Desorption was carried out using a Gerstel thermal desorption unit at **250 °C** with a **60 mL/min** flow for **5 minutes.** Analysis was performed using an Agilent 6890-5973 in full scan mode. The **3 membranes** had dimensions **20 mm x 4.9 mm (**L x W) with a coating thickness of **80 µm**

Demonstration of detection capability: Pesticide mixture at 1 ppb on benchtop instrumentation

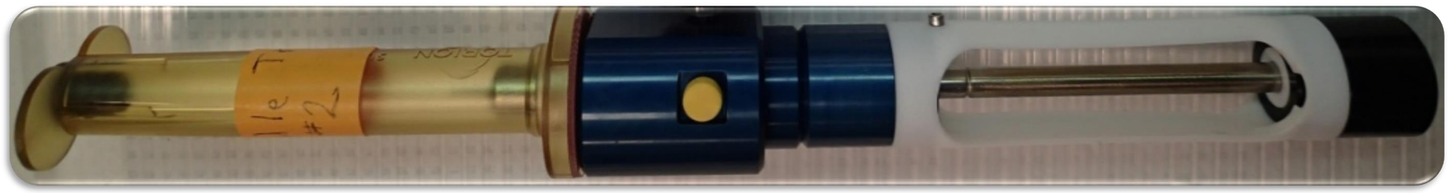


TFME extractions were performed for **15 minutes** directly from **300 mL** a **1 ppb** aqueous solution of pesticides using **1000rpm** agitation. Analysis was performed on a benchtop Agilent 6890-5973n instrument in **SIM** mode using a Gerstel thermal desorption unit

Interfacing TFME with portable GC-MS instrumentation



Step 1: insertion of membrane into 3.5“ sorbent tube and then into conventional trap holder

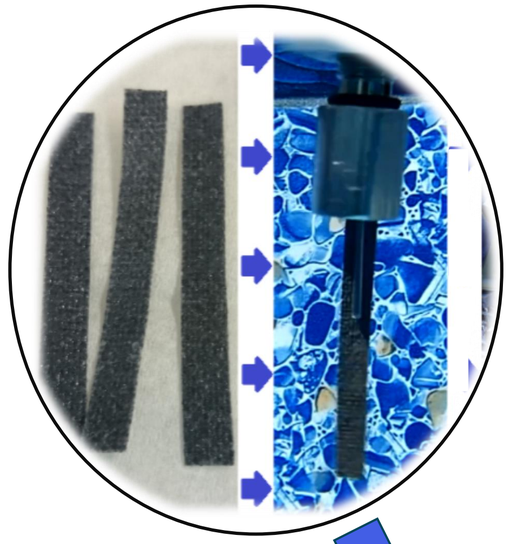


Step 2: needle trap device (NTD) is linked with the conventional trap holder such that analyte will be transferred from the TFME membrane to the NTD once inserted into the SPS-3 high volume desorption unit

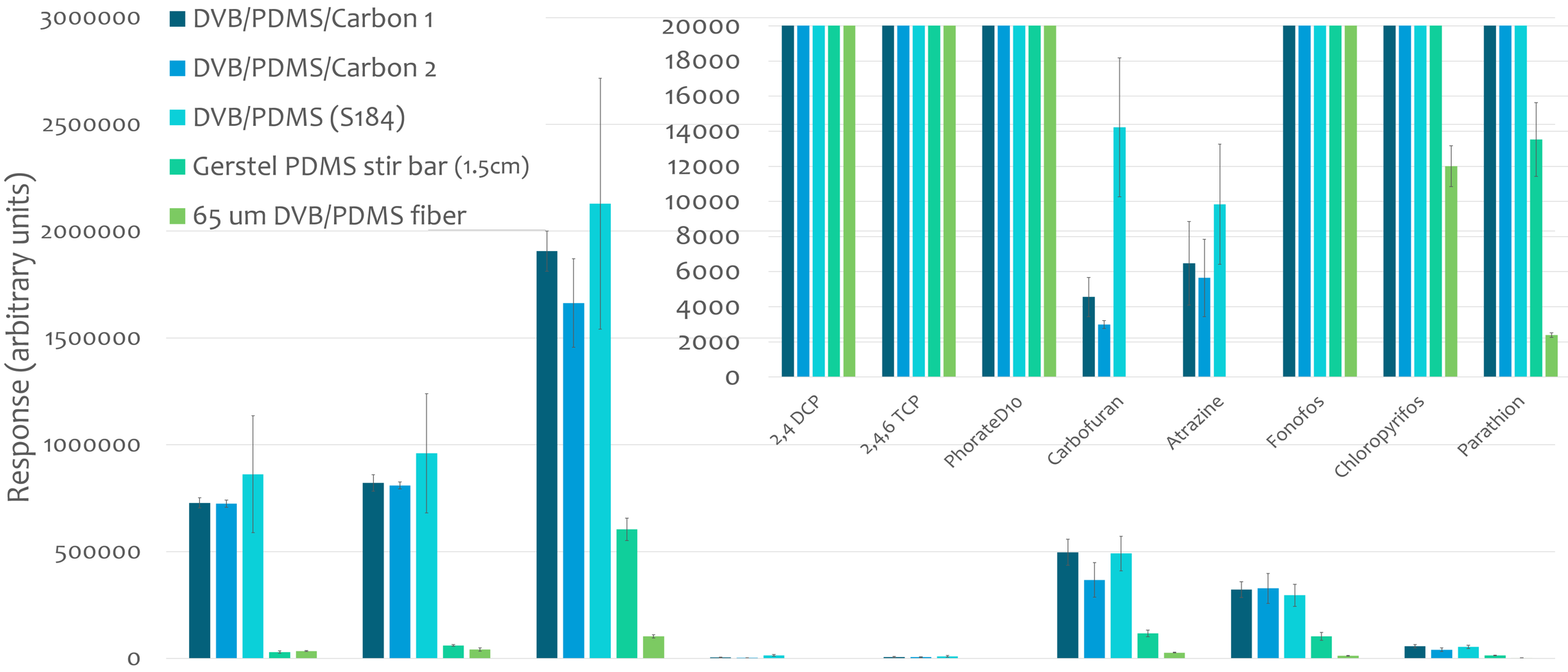
Step 3: Transfer of analytes from TFME membrane to needle trap using SPS-3 prototype desorption unit

Step 4: desorption of NTD into instrument for analysis

So, does it work ???



Comparison of extraction efficiency: SPME,TFME,SBSE

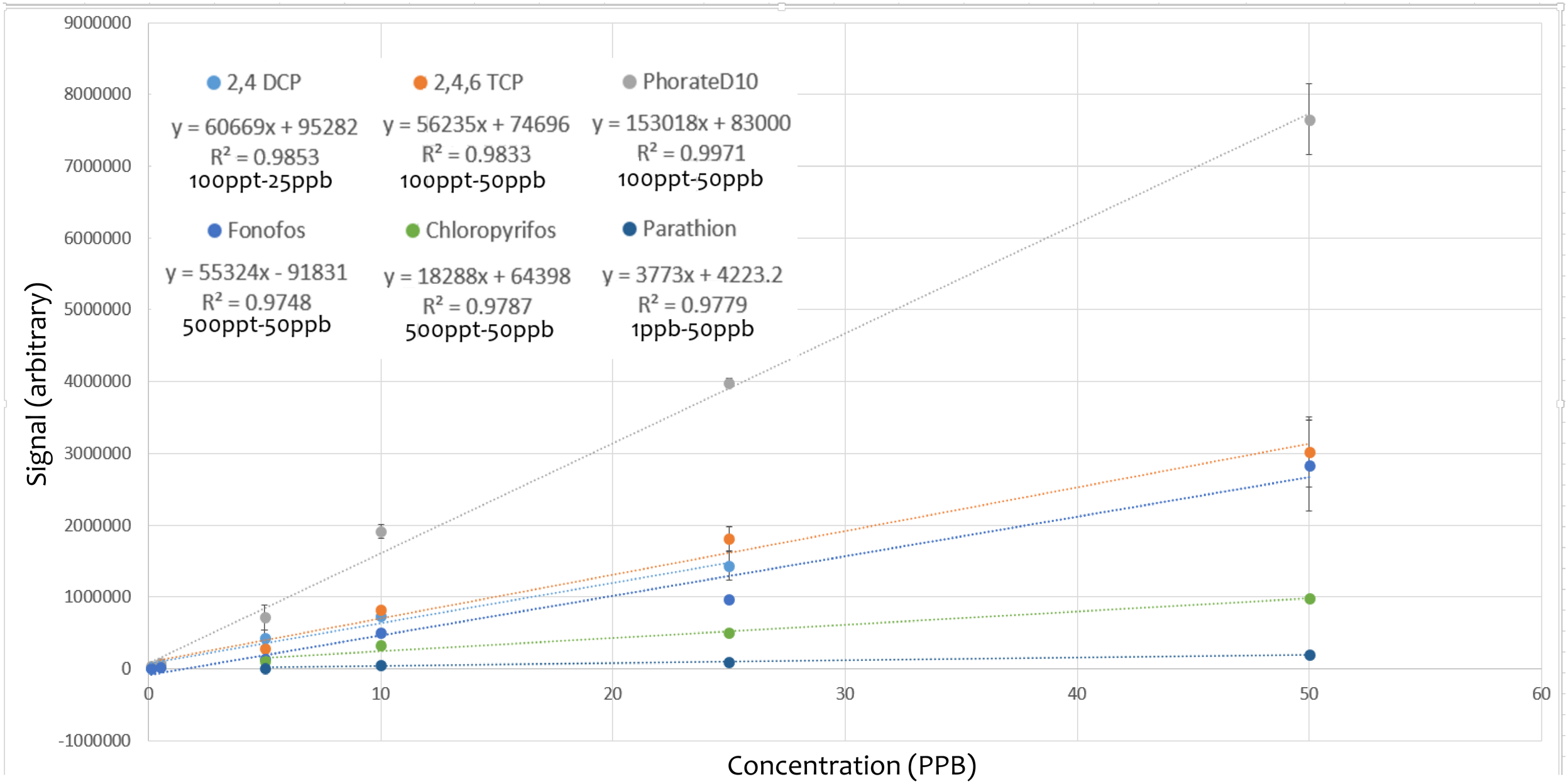


SPME Vs. TFME	2,4 DCP	2,4,6 TCP	PhorateD10	Carbofuran	Atrazine	Fonofos	Chloropyrifos	Parathion
	x21.2	x19.8	x18.5	N/A*	N/A*	x18.4	x26.8	x23.7

* N/A Undeterminable via SPME

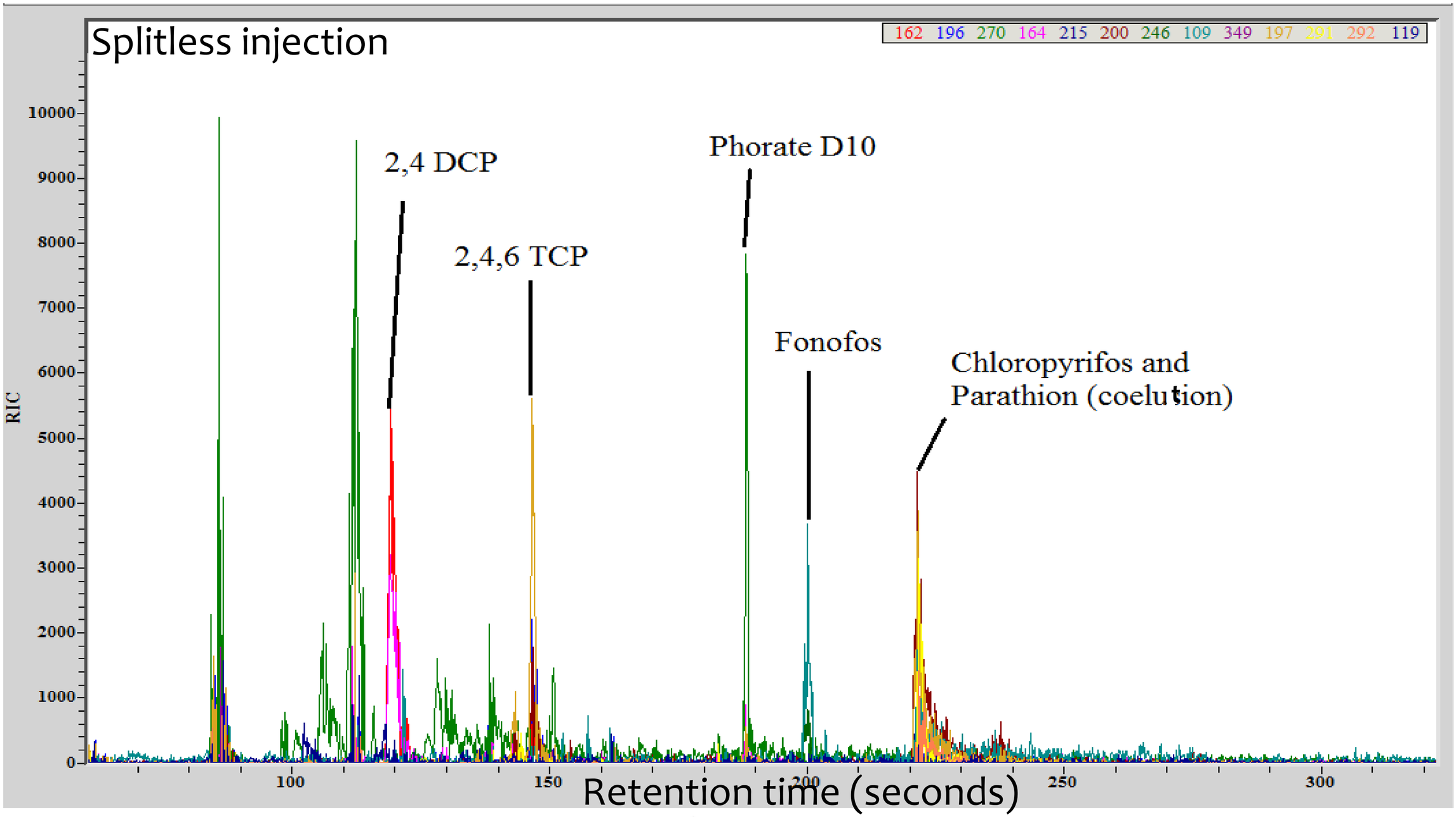
TFME extractions were performed for **15 minutes** directly from **300 mL** of a **10 ppb** aqueous solution of pesticides using **1000rpm** agitation. Desorption on the SPS-3 module was carried out at **250°C with 35 mL/min** of **He** for **5 minutes**. Analysis was performed on the Tridion-9 GC-MS.

TFME Calibration curve for select pesticides on portable GC-MS instrumentation



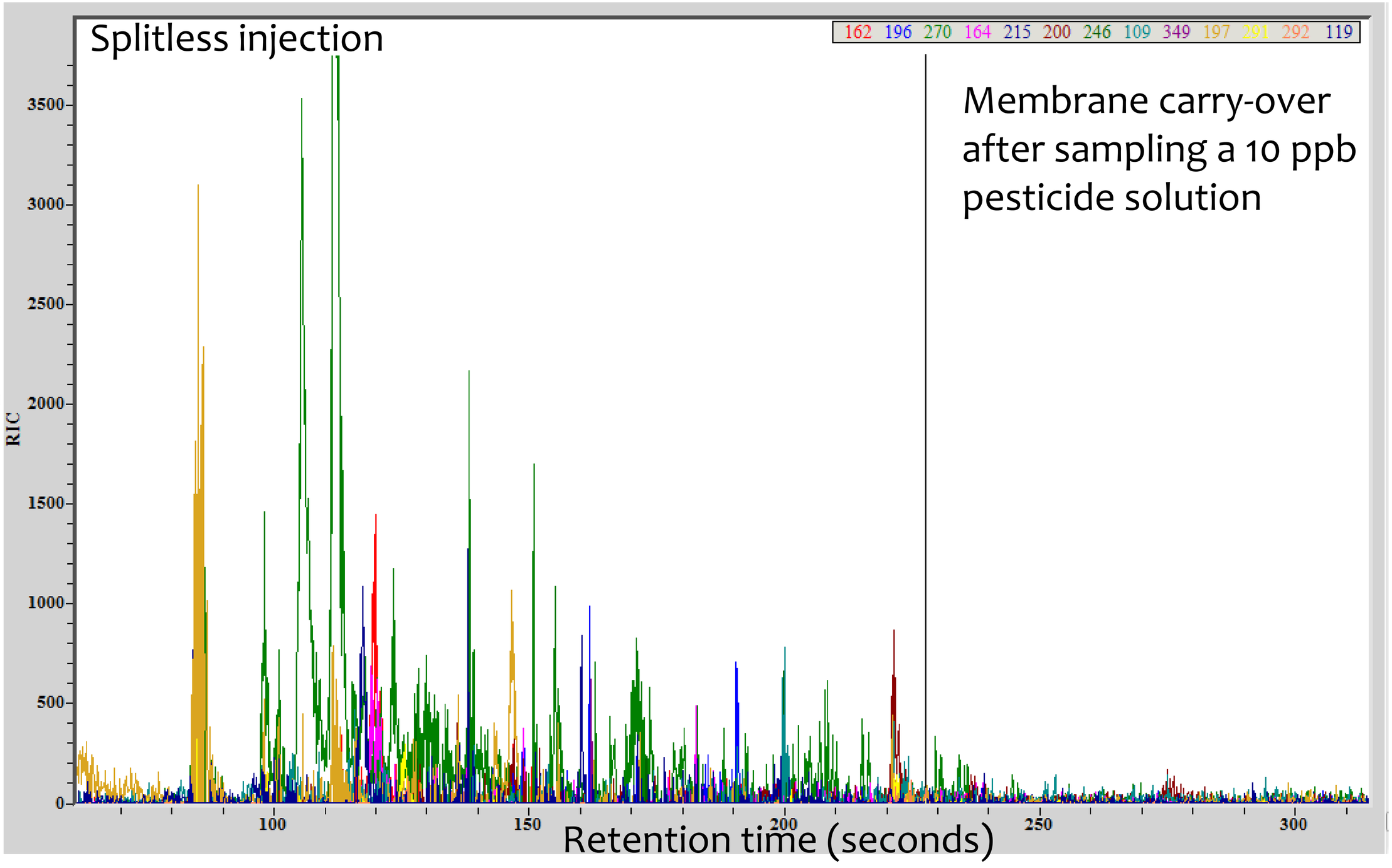
TFME extractions were performed for **15 minutes** directly from **300 mL** aqueous solution of pesticides using 1000rpm agitation. Desorption on the SPS-3 module was carried out at 250°C with **35 mL/min** of He for **5 minutes.** Analysis was performed on the Tridion-9 GC-MS

Demonstration of detection capability: Aqueous pesticides at 100 ppt on portable instrumentation



TFME extractions were performed for **15 minutes** directly from a **100 ppt** aqueous solution of pesticides using **1000rpm** agitation. Desorption on the SPS-3 module was carried out at **250°C** with **35 mL/min** of He for **5 minutes**. Analysis was performed on the Tridion-9 GC-MS

Test for carry-over : Prototype desorption module



The initial TFME extraction was performed for 15 minutes directly from a **10 ppb** aqueous solution of pesticides using **1000rpm** agitation. Both Desorption on the SPS-3 module was carried out at **250°C** with **35 mL/min** of HE for **5 minutes.** Analysis was performed on the Tridion-9 GC-MS

On-site analysis of a construction impacted lake: proof of concept

Location

Sampling location of the construction impacted Silver Lake of Waterloo, Ontario, Canada. The construction site is shown in RED while the sampling location is highlighted in GREEN

! This proof of concept represents the first ever documented completely on-site analysis using TFME !

On-site analysis of a construction impacted lake:

Experimental

Extractions Conditions:

- Extraction time: 10 minutes
- Agitation: 350 rpm
- Water temperature: 16.5 °C
- Replicate extractions: 3

High Volume Desorption Conditions:

- Time: 5 minutes
- Flow Rate 35 mL/min
- Temperature: 250 °C

Portable GC/MS Parameters:

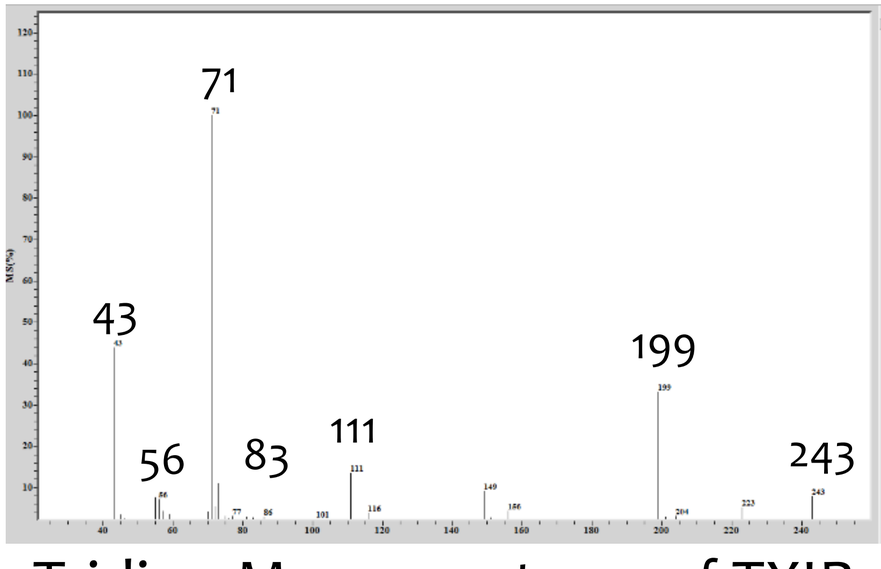
- Desorption time: 45 seconds
- Splitless injection Temp. 260 °C
- Temperature: 16.5 °C
- Oven ramp: 45-285°C at 1.5 °C/min
- Initial hold time : 35 seconds
- MS scan range : 45 – 400 AMU

On-site analysis of a construction impacted lake:

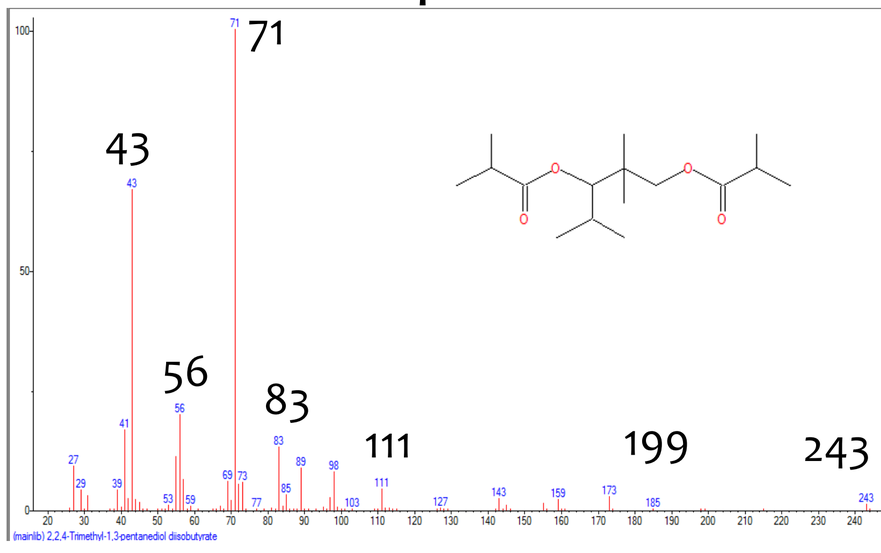
Results

Detected compounds with suspected anthropogenic origin

Compound	RT(s)	Quant ion	Exp LRI	NIST LRI
Toluene	55.80	91	779	794
Ethylbenzene	72.59	91	873	893
O-Xylene	77.13	91	901	907
TXIB	152.94	71	1612	1605
TMCP	169.68	99	1827	1814



Tridion Mass spectrum of TXIB



NIST Mass spectrum of TXIB

TXIB: 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate

-TXIB is a common plasticizer typically used for PVC rubbers

TMCP: Tris(1-chloro-2-propyl)phosphate

-Very common flame retardant found in many products, especially polyurethane spray in foams

- investigation of construction site it was found that the workers were in the process of using polymer reinforced concrete and polyurethane spray-in foams on the bridge

Concluding Remarks

- These new DVB/PDMS/ Carbon mesh membranes were shown to:

1. Exhibit substantially less bleed than the previous design

2. Demonstrate an easy to handle, durable and rigid construction

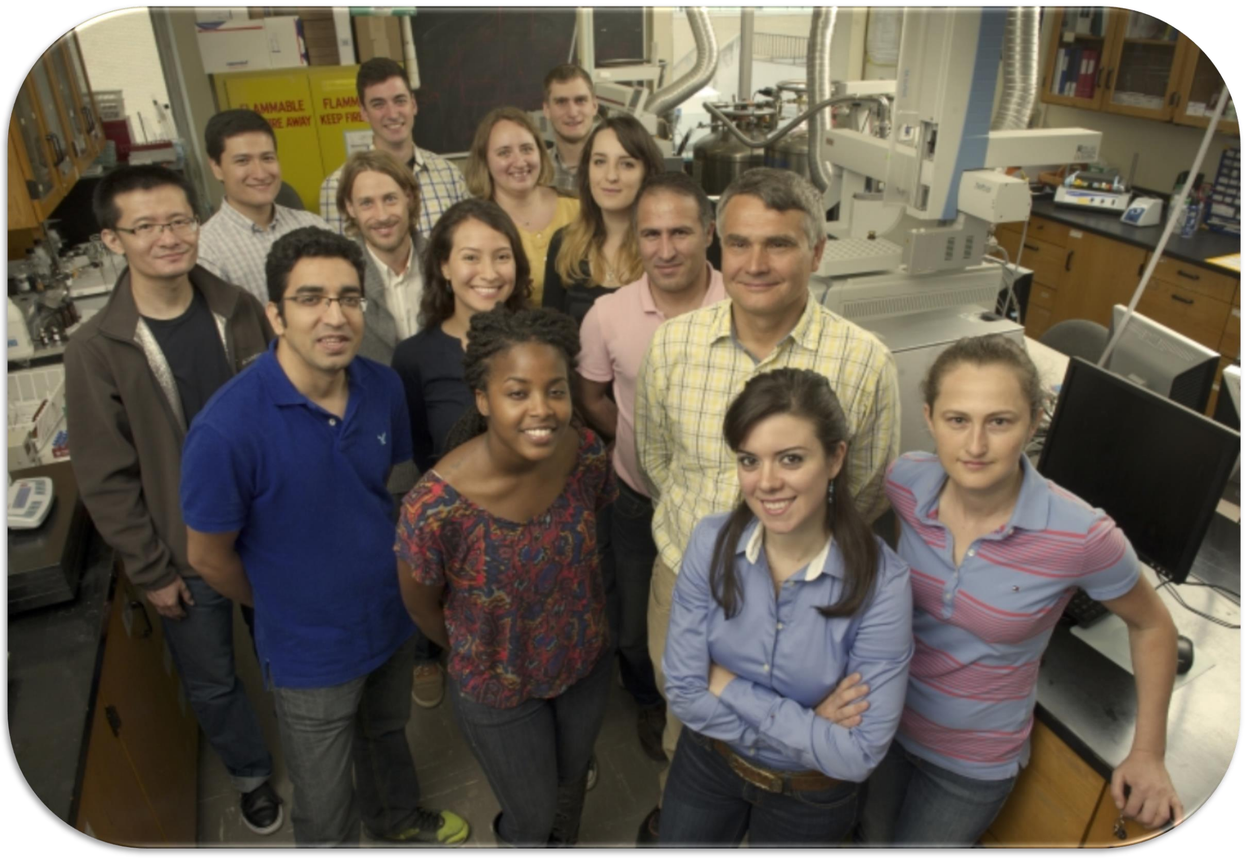
3. Extract up to 20-26x more analyte than standard DVB/PDMS fibers

4. Capability to be coupled with benchtop and portable GC-MS instrumentation
5. Allow the sub-ppb detection of a variety of pesticides (100 ppt shown!) matching LODs expected from benchtop instrumentation with standard SPME techniques

* Recent Results have also indicated that when used in a clean matrix a single membrane may be used in excess of 100 times!

Acknowledgements

- Torion Technologies Inc. of Perkin Elmer Co. with a special thanks to Dr. Ed Lee.
- Mr. Chuck Sadowski for his past collaboration and training
- Natural Sciences and Engineering Research Council of Canada (NSERC)
- Supelco Co. Of Sigma Aldrich
- All members of Prof. Pawliszyn Research Group for their continued help, time, and friendship!



thank you!

Questions?

Dr. Janusz Pawliszyn
Research Group

Environmental | SAMPLE PREPARATION | MASS SPECTROMETRY

5: Hand portable instrumentation: the Tridion-9 GC-TMS

Characteristics of the Tridion-9 GC-TMS	
Weight (kg)	14.5
Power (W)	60 (120 peak)
Battery life (hr)	2.5 (Li-ion)
Sample introduction	SPME, NTD, low volume LI (0.1 µL), 3.5” sorbent tube, TFME
Column	LTM, MXT-5 treated S.S. (5m x 0.1 mm x 0.4 µm)
Max oven ramp	2.5 $^{o}C\ s^{-1}$
Run-time (standard)	3 min plus 2 min cool down
Mass analyzer	Toroidal ion trap (TMS)
Mass range (m/z)	43-500 AMU
Mass resolution	Nominal at 500 AMU
Scan time (ms)	60 ms at 43-500 AMU 30 ms at 43-325 AMU

Tridion-9 portable GC-TMS

Prototype high volume desorption module (SPS-3)