The Introduction of PDMS-Overcoated Adsorbent-Based Fiber Coatings

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Abstract

A 10 µm layer of a proprietary PDMS has been applied over the PDMS-DVB fiber coatings. The PDMS overcoat reduces the adhesion of non-volatile matrix components on the surface of the fiber coating. The overcoat slightly reduces the polarity of the PDMS-DVB coating but increases the lifespan of the fiber coating by making them more durable, sealing the ends, and reducing matrix build-up on the surface. On average, the application more than doubles the life of the coating compared to PDMS-DVB coated fibers without the PDMS overcoat.

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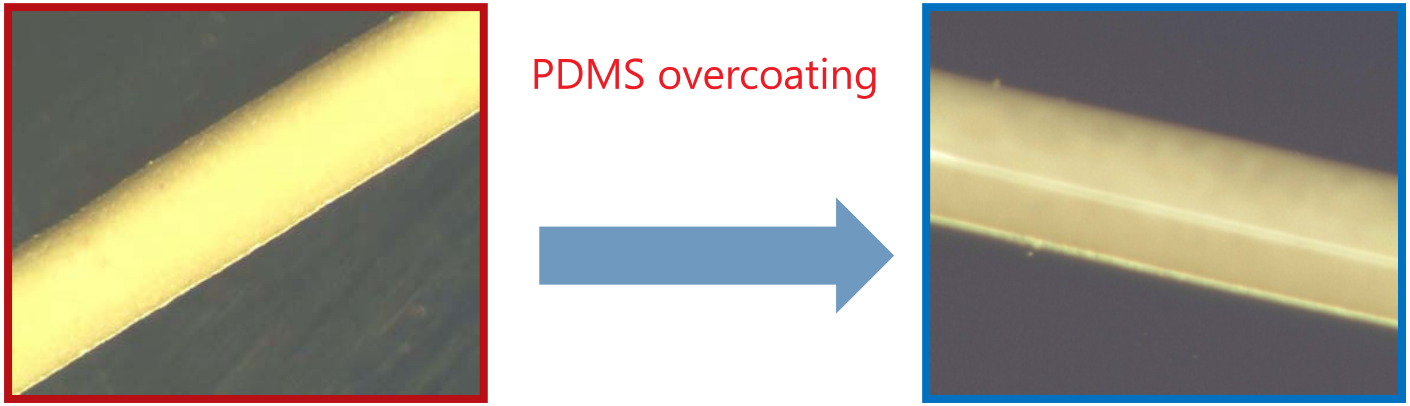
Introduction

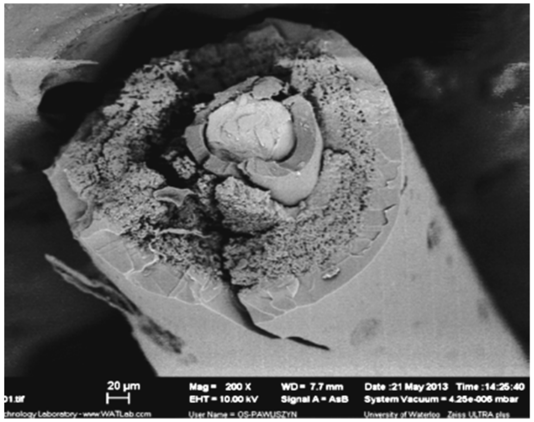
When SPME adsorbent-based fibers are immersed in a complex matrix solution, large, non-volatile components in the matrix tend to stick to the portion of the adsorbent that is exposed to the solution. During desorption of the fiber, the non-volatile components can buildup on the fiber coating and wick into the fiber ends, shortening the lifespan of the coating. This presentation shows the results of applying a PDMS overcoat on the PDMS-DVB fiber with the extraction of semi-volatile compounds out of grape juice.

Figure 1. Overcoating Standard PDMS/DVB with PDMS

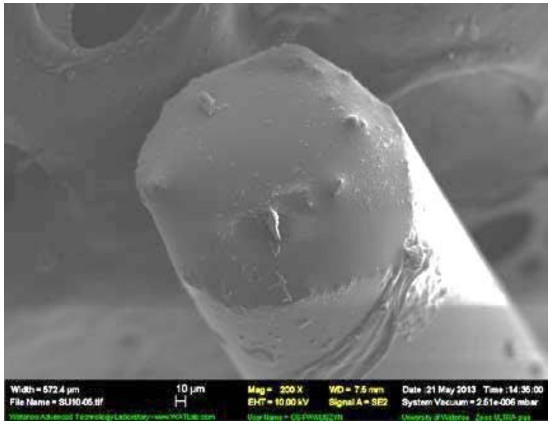


Microphotographs of a standard PDMS/DVB fiber and the same fiber coated with an external PDMS layer (PDMS-DVB OC).

E. A. Souza-Silva, J. Pawliszyn, *Anal. Chem.* 84 (2012), 6933-6938.



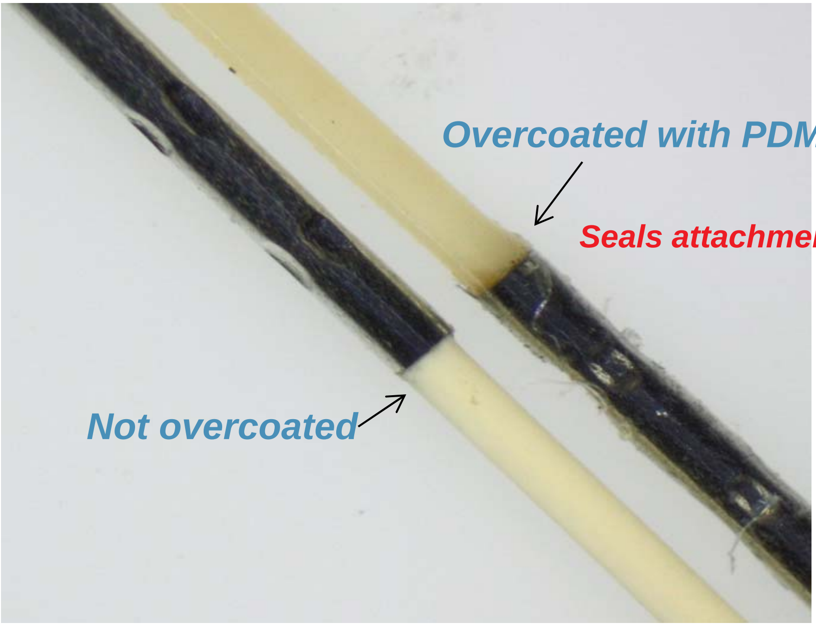
SEM Images of PDMS-DVB Fiber End Cuts



Not overcoated

Overcoated with PDMS

Light Images of Fiber Attachment to Tubing



SEM Images courtesy of
E.A Souza-Silva University of Waterloo.

Experimental

Extraction of Semi-volatile Analytes out of Grape Juice.

Table 1. Analytes Evaluated in Study

	Conc µg/mL*	Log P @ pH 7	MW g/mole	Quant Ion
1,3-Dinitrobenzene	150	1.43	168	168
Nitrobenzene	50	1.90	123	77
2,4-Dinitrotoluene	75	2.42	182	165
Diazepam	100	2.80	284	256
Chlorothalonil	15	2.94	266	266
4-Phenylphenol	20	3.20	170	170
Diazinon	7.5	3.40	304	304
Parathion	5	3.83	291	291
Trifluralin	5	5.07	325	306
Pendimethalin	5	5.18	281	252
p,p'-DDE	2.5	6.00	318	318

*Concentration in standard, sample concentration in ng/mL

Conditions for Analysis of Semi-volatiles in Grape Juice and Water

Sample Matrix:	7 mL of grape juice in 10 mL vial spiked with 7 µL of standard mix shown in Table 1 with no pH adjustment
Fibers:	Standard PDMS/DVB and PDMS/DVB OC Fibers
Extraction:	Direct immersion with agitation at 300 rpm at 35 °C for 40 min, CombiPAL
Needle Depth:	11 mm
Injection Penetration:	38 mm
Rinse Step:	30 sec in 7.5 mL of DI water, no agitation
Desorption Process:	2 min at 270 °C
Injection Port:	Splitless/split, closed initial 0.75 min then opened at 30:1 split, 0.75 mm liner
Column:	SLB®-5ms, 30 m x 0.25 mm I.D., 0.25 µm
Carrier Gas:	Helium at 1 mL/min constant flow
Oven:	60 °C (1.5 min) to 180 °C @ 10 °C/min to 320 °C @ 20 °C/min (4.5 min hold)
Detector:	Ion trap MS, m/z=70-340 @ 0.2 sec/scan, Quant ions listed in Table 1

Please note that the University of Waterloo added a second rinse step after desorption.
The fibers were rinsed in 20% methanol:water for 2 minutes.

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Figure 2. Effects of Overcoat on Analyte Recovery from Water (Arranged by Increasing Log P Left to Right)

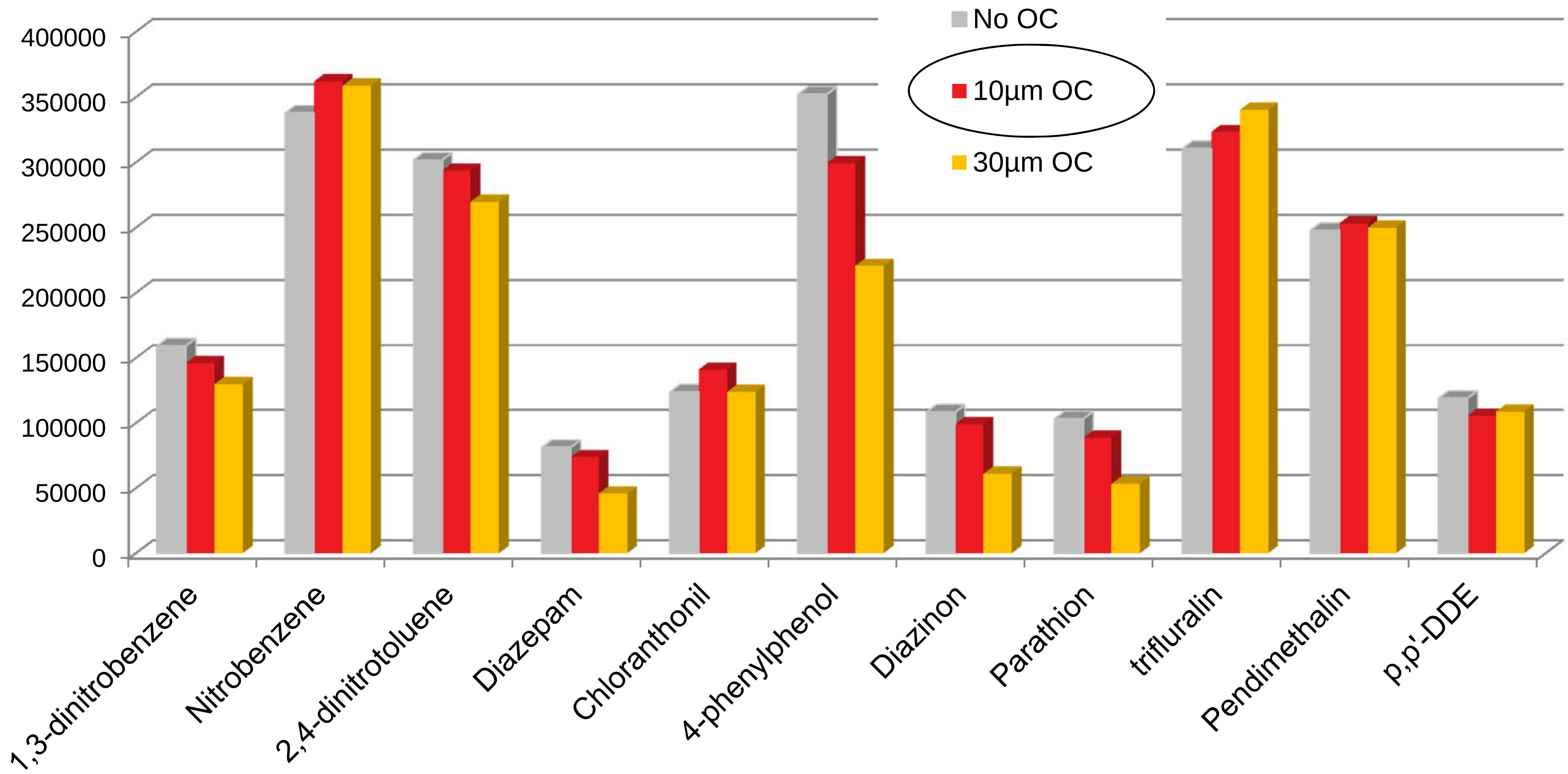

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Figure 2 shows that the application of a PDMS overcoat slightly reduces the uptake of polar analytes. The reduction was greater with the 30 µm coating compared to the 10 µm PDMS coating. The 30 µm coating was not a better barrier than the 10 µm coating, so 10 µm was selected as the thickness for the PDMS overcoat.

Figure 3. The Effect of Rinsing Fibers after Extraction Prior to Desorption (30 seconds, no agitation)

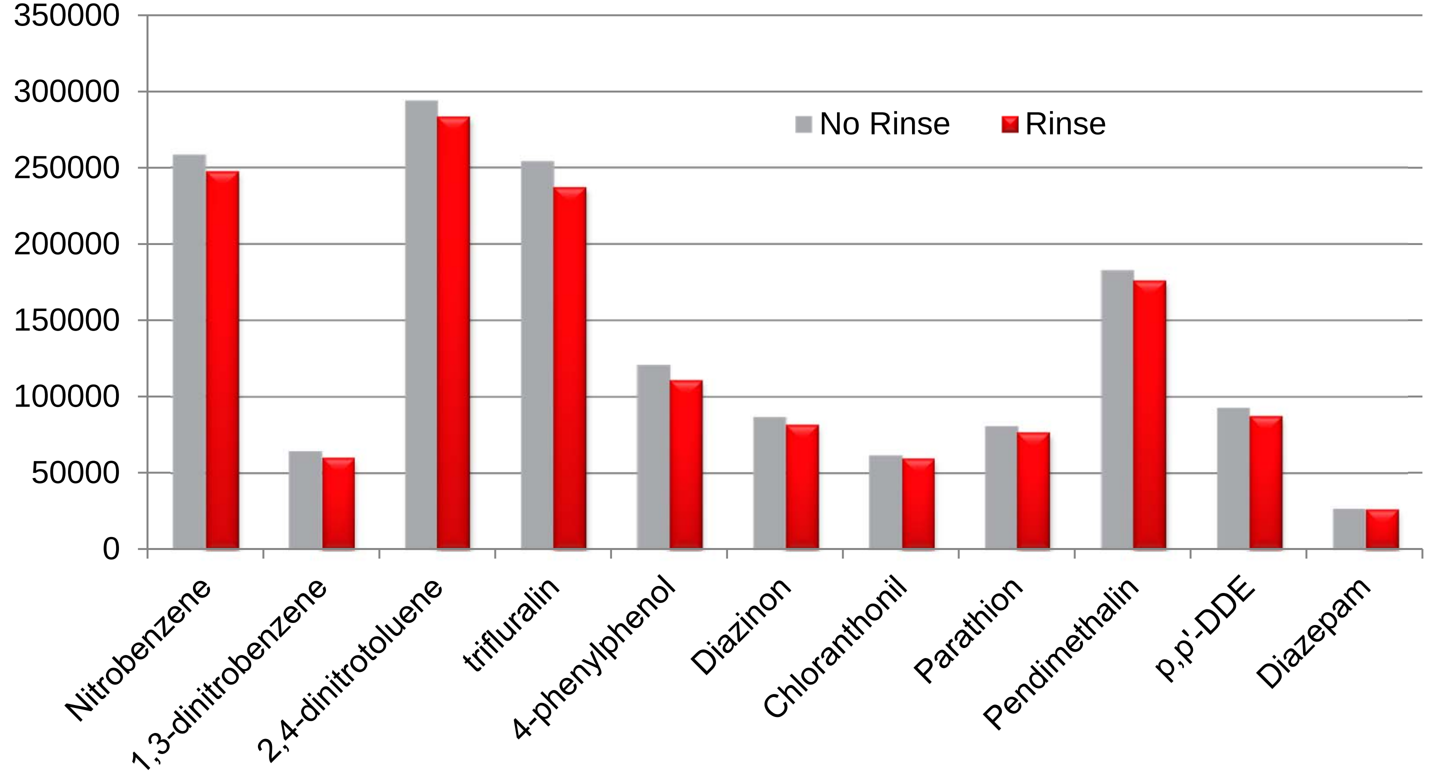
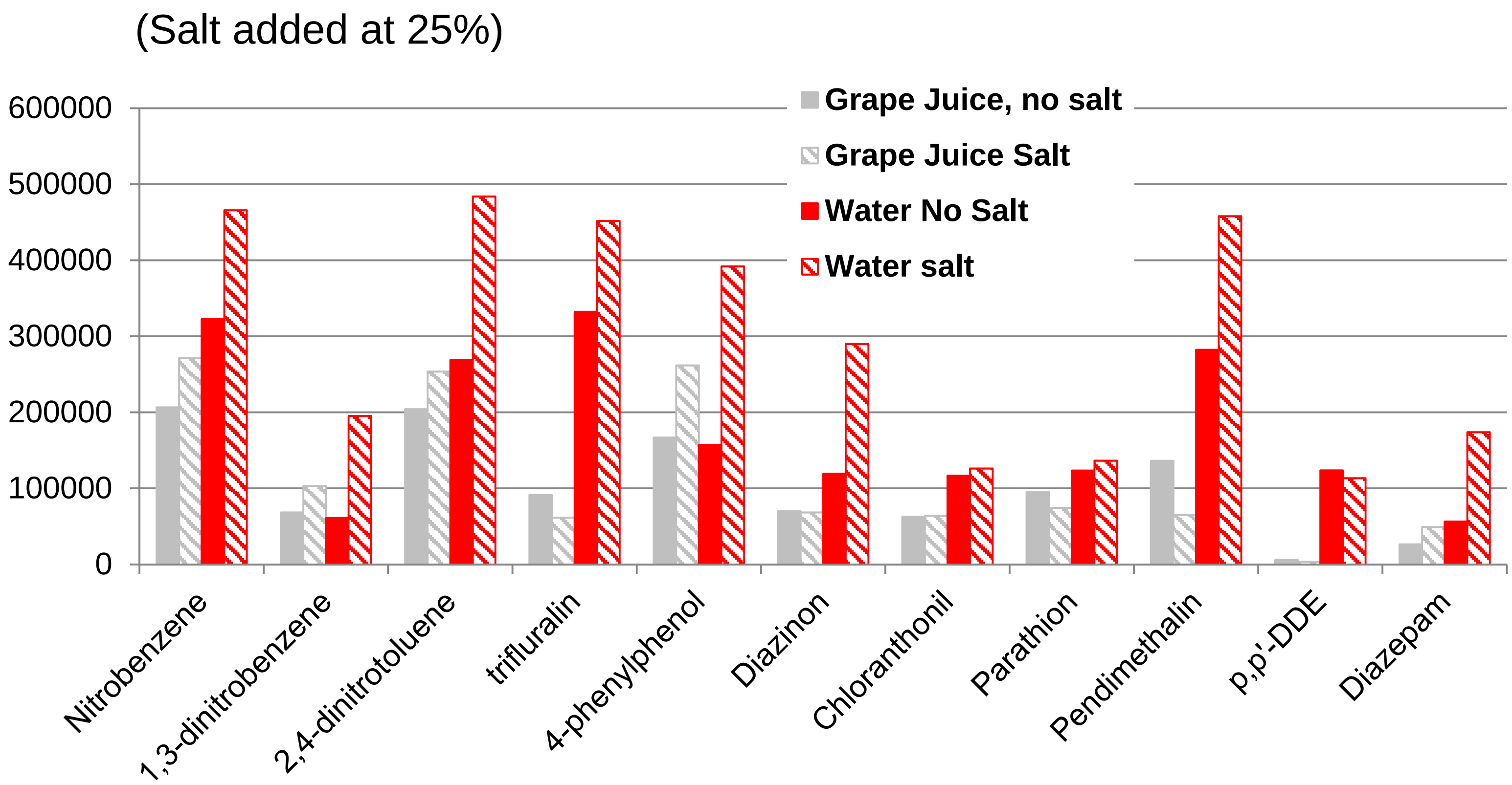


Figure 3 shows that a 30 second rinse step resulted in a very slight loss of analyte response, but without the rinse, buildup was faster. A longer rinse step resulted in a greater loss of analyte response.

Figure 4. The Effect of Salt on Extraction Efficiency of Analytes out of Water and Grape Juice



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The addition of 25% salt in DI water enhances the recovery of polar analytes; however, when 25% salt was added to grape juice, the response of some polar analytes decreased. The addition of salt may drive the matrix on the fiber and may increase binding of some analyte to the matrix. We decided not to add salt to grape juice.

Figure 4. Change in Analyte Response between 1st & 20th Extraction with One Fiber out of Grape Juice

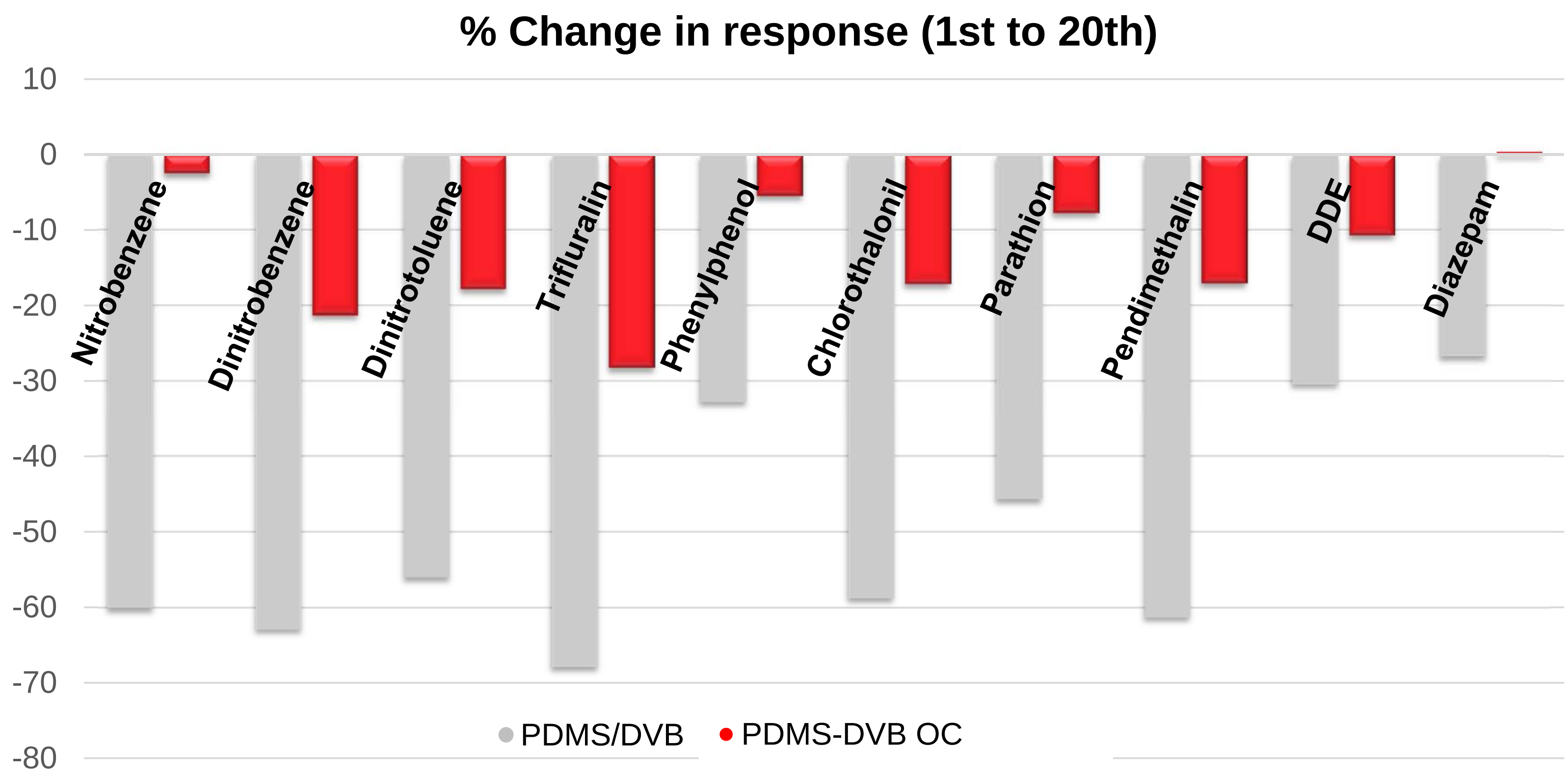

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Figure 4 shows that with the standard PDMS-DVB fiber, there was on average about a 50% drop in analyte response between the 1st and 20th extraction of the analytes out of grape juice. The PDMS-DVB OC fiber showed an average loss of only 20% in analyte response between the 1st and 20th extraction.

Figure 5. Relative Response to 1st Extraction with Std. PDMS-DVB and PDMS-DVB OC Fibers versus Extraction No. out of Grape Juice

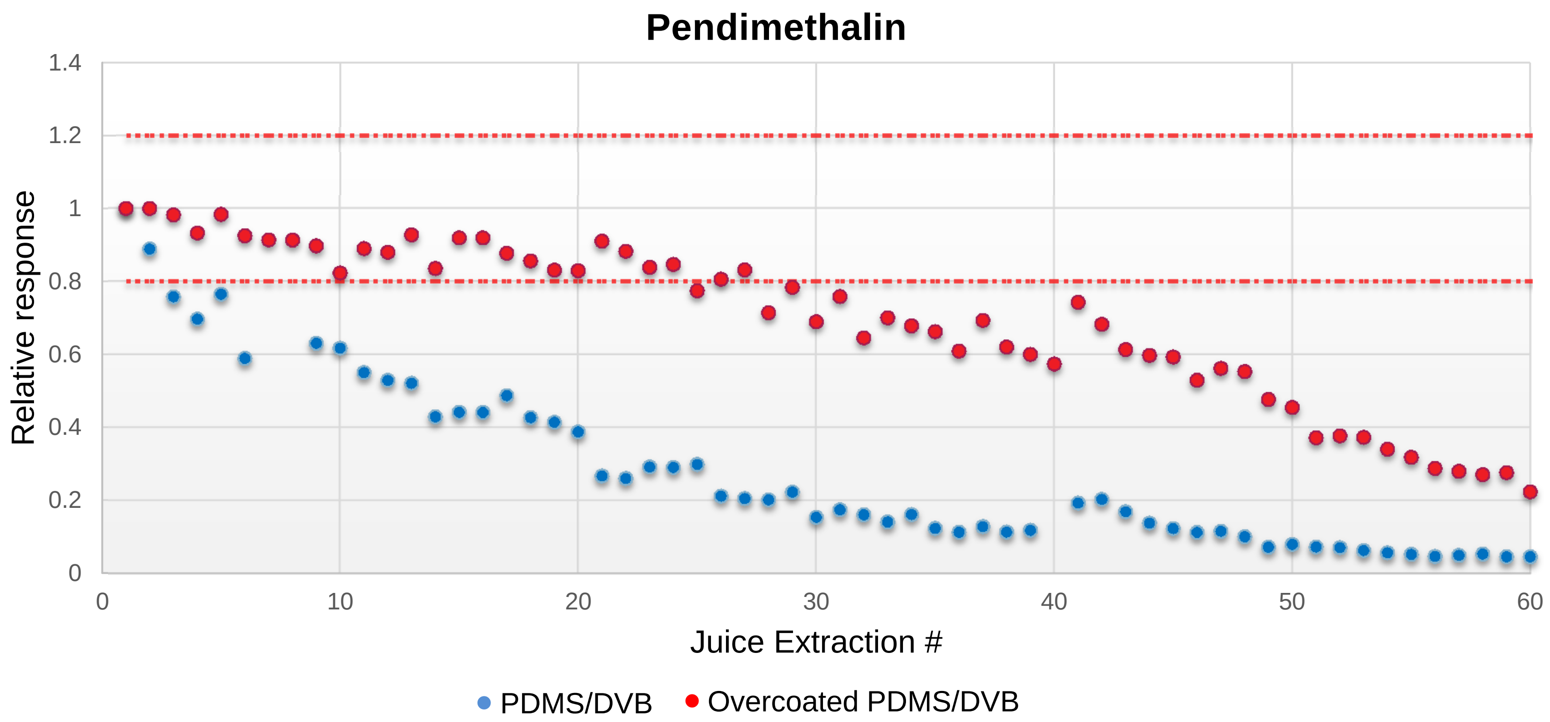
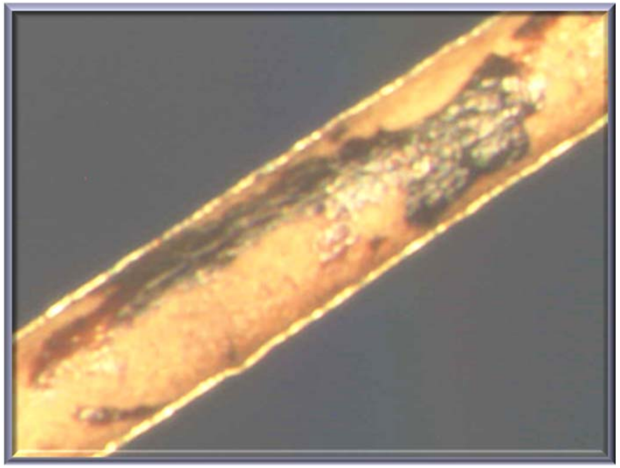
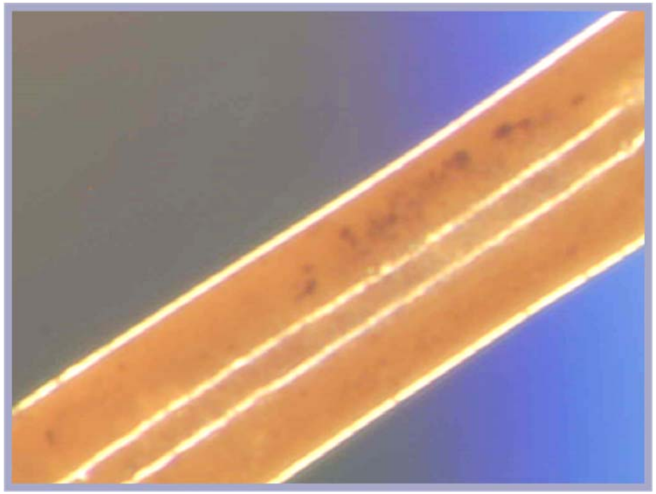


Chart courtesy of E.A. Souza-Silva & Emanuela Gionfriddo, University of Waterloo.

Figure 5 shows that the response for pendimethalin extracted with the standard PDMS-DVB fiber after 20 extractions was 40% less than the response of the first extraction. It took 50 extractions with the PDMS-DVB OC fiber before a 40% loss in response was observed. The PDMS-DVB-OC fiber lasted 1.5 times longer than the standard PDMS-DVB coated fiber.

How Much Improvement?





Left: PDMS/DVB after 20 extractions in unfiltered grape juice
Right: modified-PDMS after 130 extractions in whole grape pulp

Carbon building-up on surface of untreated fiber

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Conclusions

- Overcoating extends fiber life by 75-100% when fiber is immersed in samples.
  - By reducing matrix buildup on fiber coating
  - By increasing fiber durability
- Overcoating seals ends and prevents matrix wicking which improves quantification.
- Overcoating slightly reduces fiber polarity, but increases fiber capacity.
- Rinsing the fibers is necessary but not as effective as desired. An automated way to wipe the fibers would be more beneficial.
- Possibility of extending product line to other adsorbent coatings.

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