INNOVATIONS IN SAMPLE PREP FOR GC & GC-MS

ISCC 2016

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MilliporeSigma is a business of Merck KGaA,
Darmstadt, Germany

Agenda

Over coated SPME Fibers

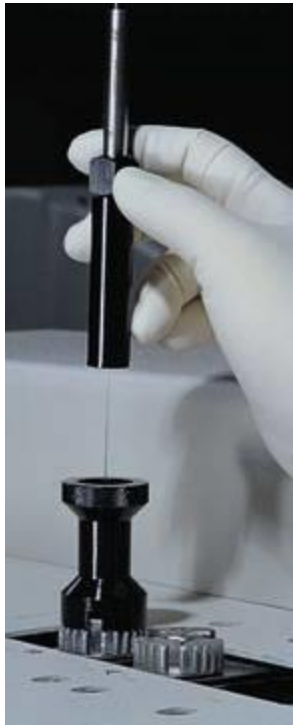
Sampling Tube for Fence Line Monitoring- EPA Method 325

Device Coatings

SPME – the Basics
Versatile and Green

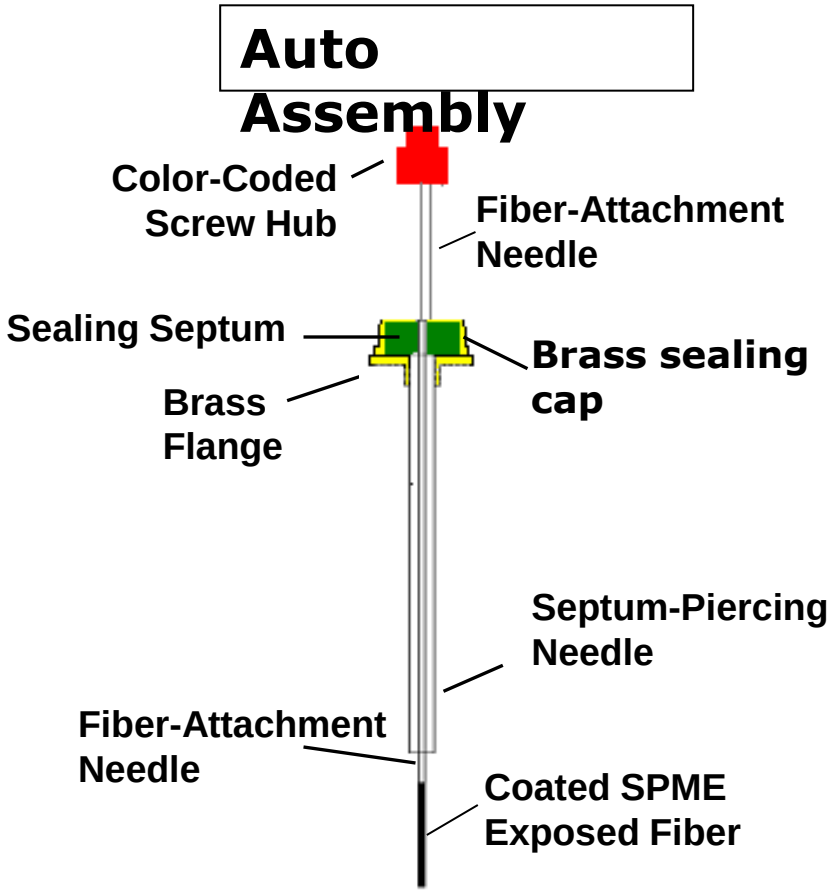
- Solvent-free extraction technique for nearly any sample or matrix
- Can sample from gas, liquid and solid matrices
- Can extract volatile, semi-volatile and non-volatile analytes
- Alternative to head-space GC, solid phase extraction (SPE), and purge & trap techniques
- Directly interfaced with GC inlets
- Non-destructive to sample
- Reusable (50-100+ times)
- Inexpensive
- Fast

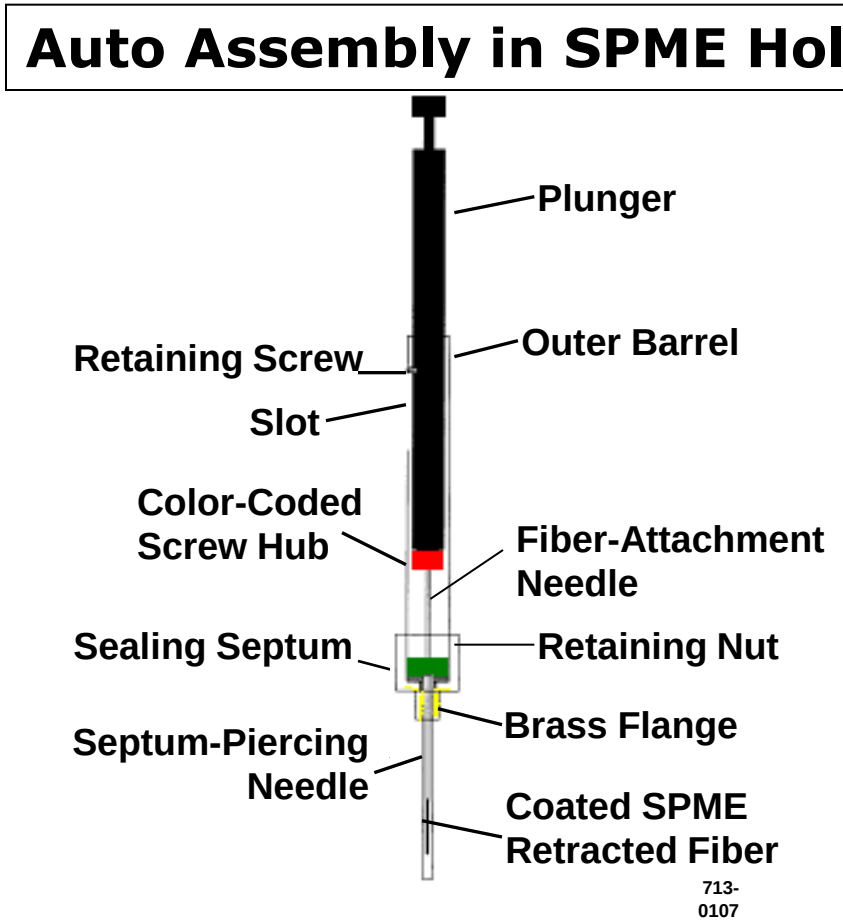
Assembled SPME fiber and holder with fiber immersed in a liquid sample.



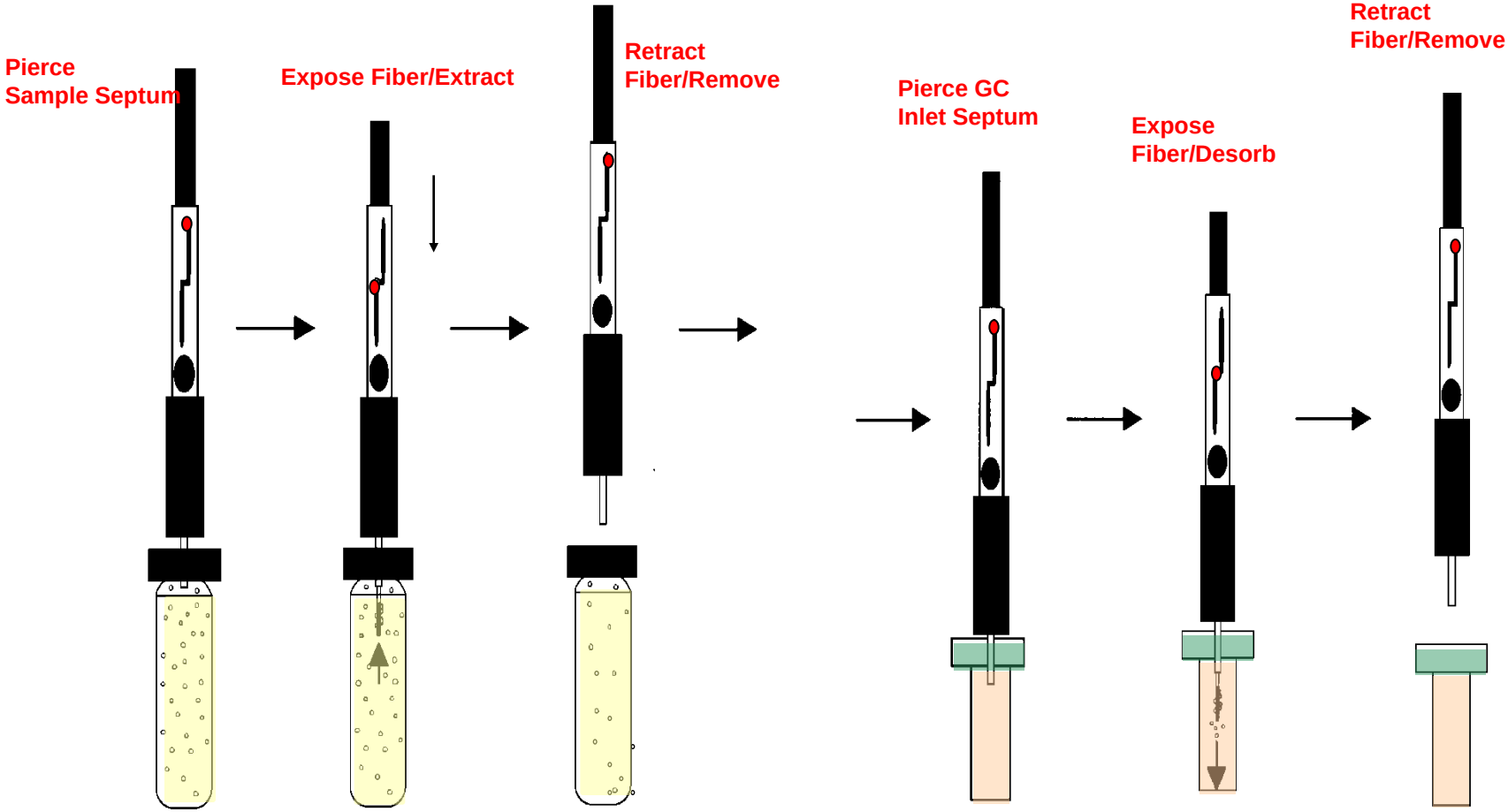
Manual SPME holder and inlet guide.

Standard SPME Assembly and Holder





Manual Procedure for Using SPME



Purpose for Over-coating Adsorbent Fibers

1. Matrix components such as sugars & other non-volatile components tend to stick to adsorbent coatings that reduces fiber life.

2. PDMS over-coating extends fiber life when fibers are immersed in the matrix solution

3. PDMS coating serves as a barrier to the matrix. The matrix components tend not to stick to PDMS.

4. Analytes migrate through the PDMS coating onto the adsorbent surface or into the pores where they are more tightly retained.

5. Fibers are more durable.

6. Overcoat reduces matrix competition with analytes

Coating Modification Optimization

✓ Overcoating commercial PDMS/DVB with a PDMS

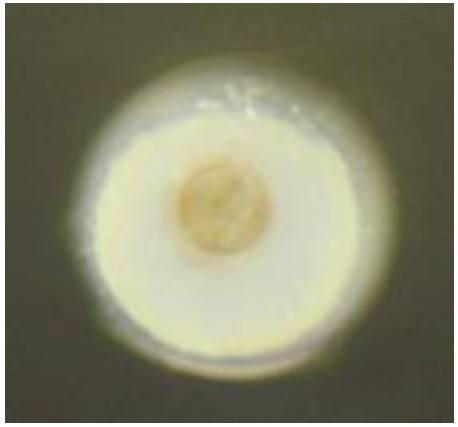
Microphotographs of a PDMS/DVB fibre as commercially available, and the same fibre coated with an external PDMS layer.

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

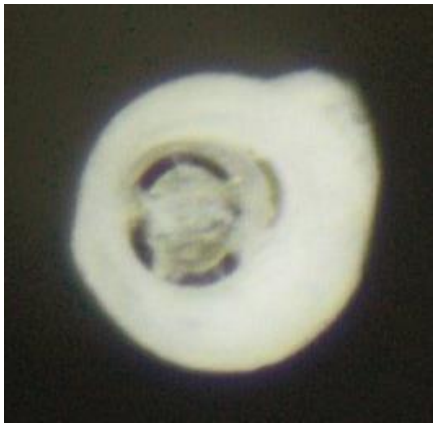
Images of Fiber End Cuts of PDMS-DVB Fibers with Light Microscopy and SEM

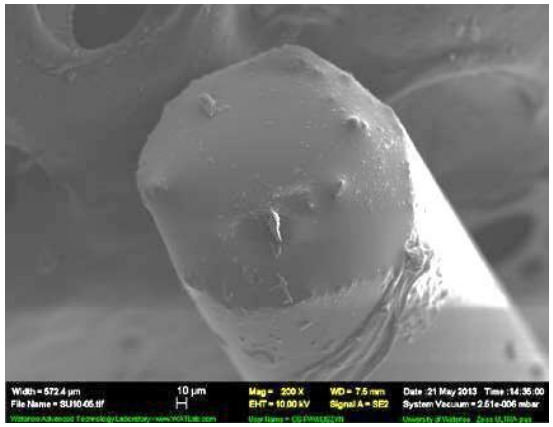
Overcoated Fiber Images

Standard Fiber Images



Light Microscopy





SEM

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

Analytes Evaluated in Study (Extraction of Semi-volatile Analytes from Grape Juice)

	Conc ug/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

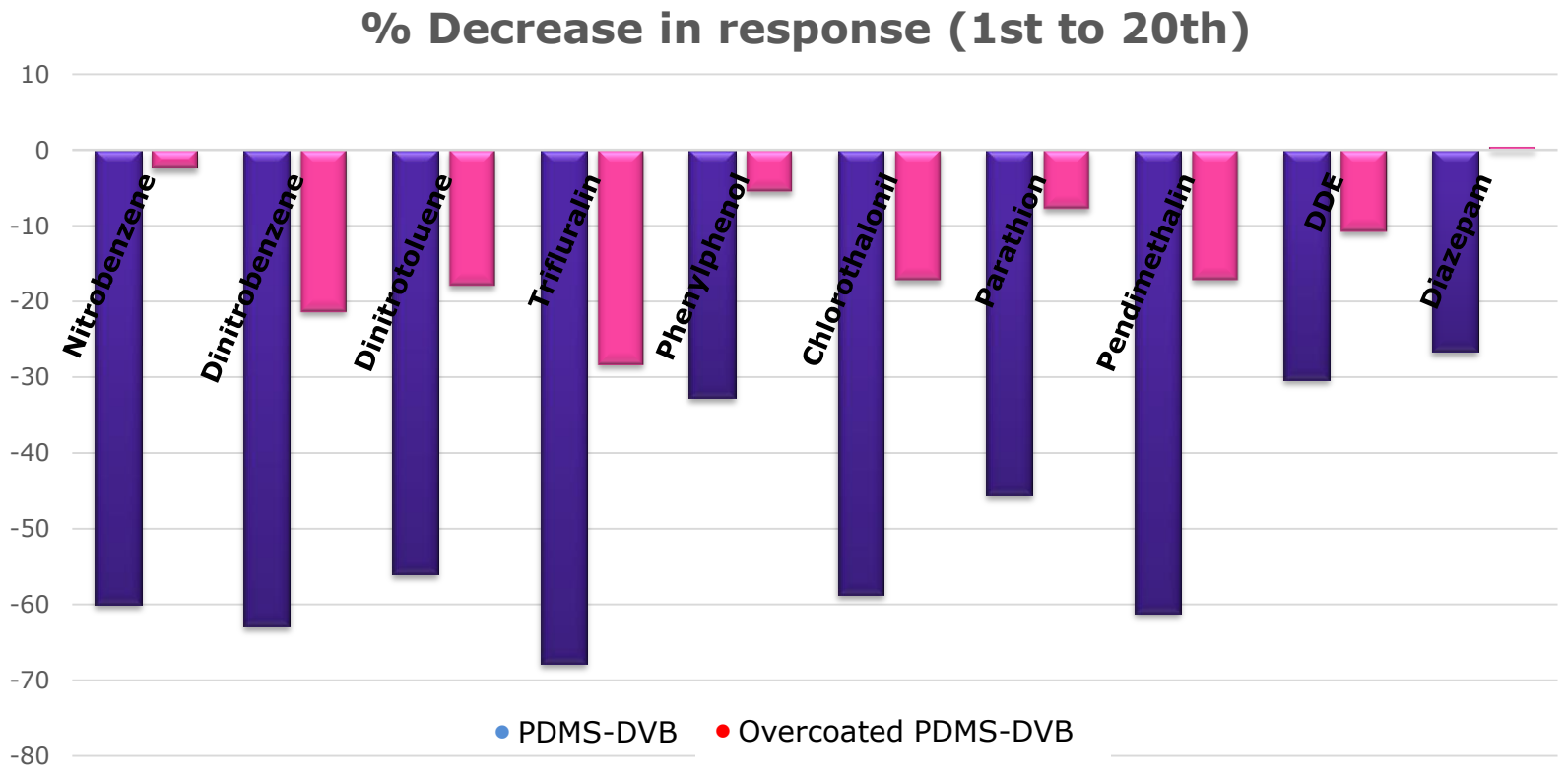
Why Extraction out of Grape Juice?

- Very high sugar content - 157 mg/mL of juice
- Dark color easily detect if adsorbed
- Large amount of polyphenols
- Consistency between bottles – Name brand juice

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

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

Analyte Response between 1st and 20th Extraction with One Fiber out of Grape Juice



Comparison of Std. PDMS-DVB and OC PDMS-DVB Fibers versus Extraction Number

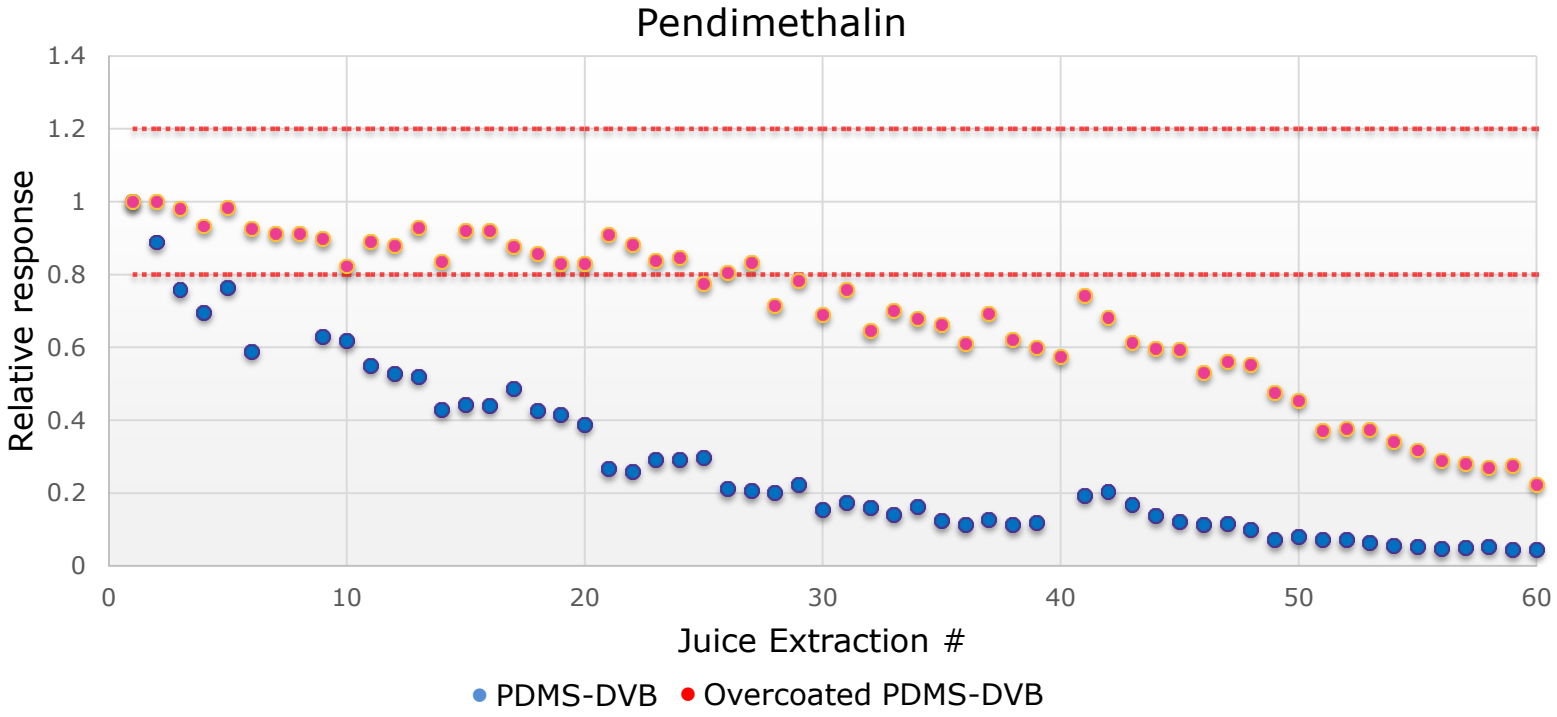
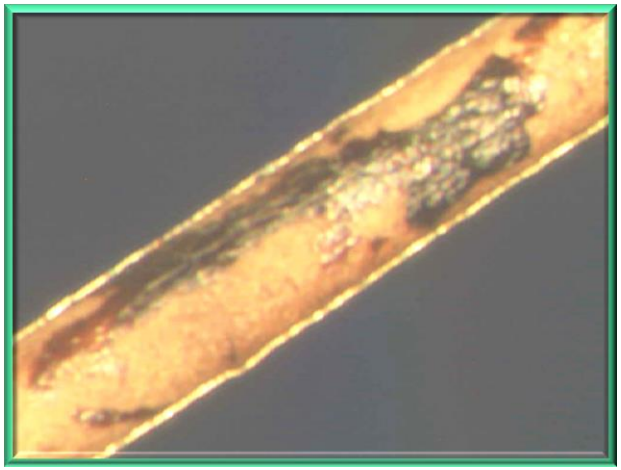
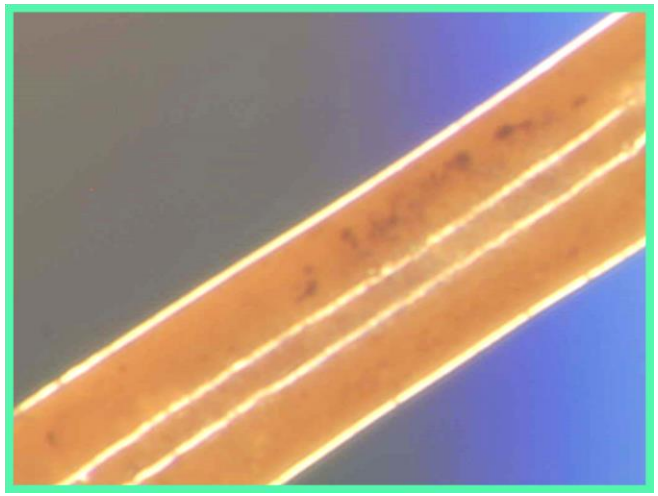


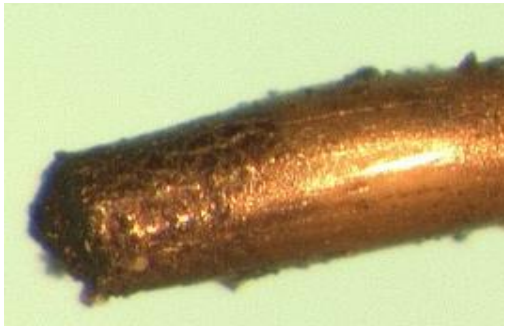
Chart courtesy Erica Sousa-Silva
& Emanuela Gionfriddo,
University of Waterloo

How much improvement?





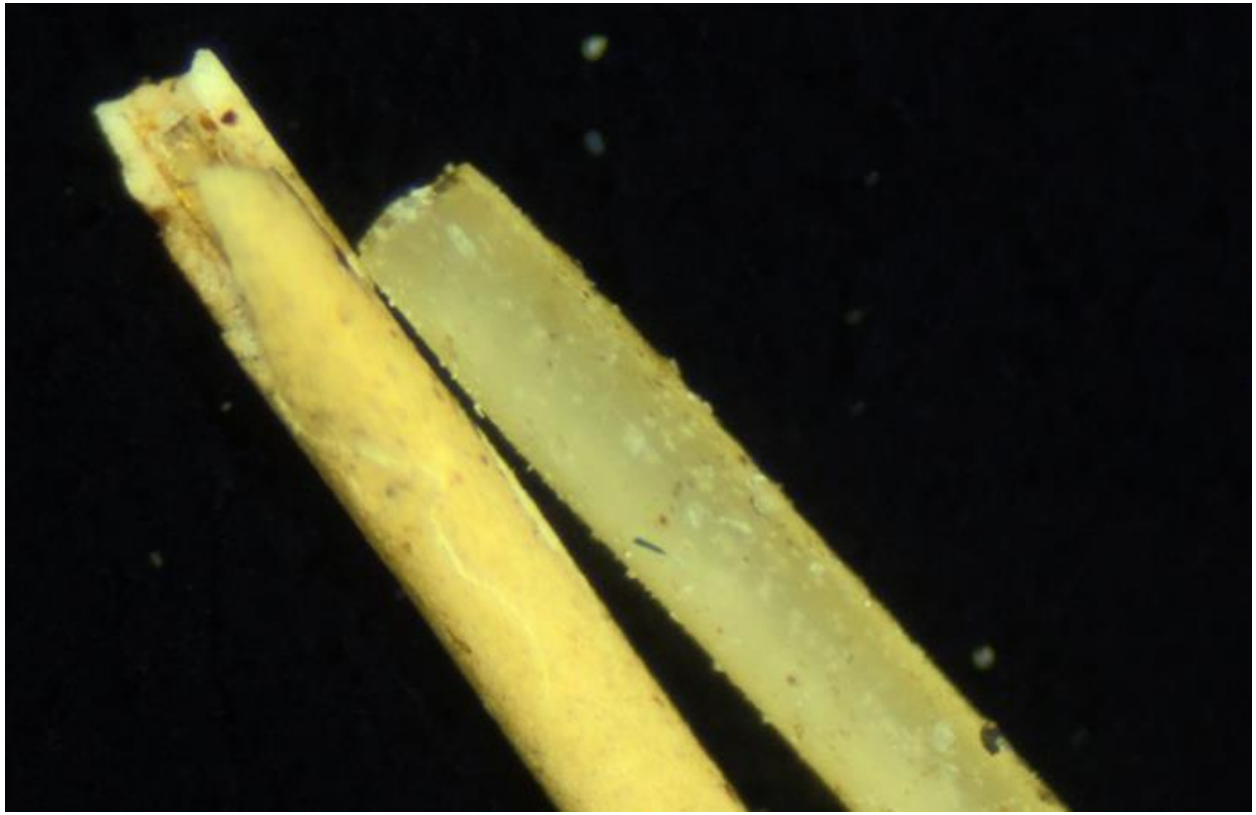
Left: PDMS/DVB after 20 extractions in unfiltered grape juice
Right: modified-PDMS after 130 extractions in whole grape pulp



Carbon building-up on surface of untreated fiber

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

Ends of fibers- note damage on standard fiber



SPME fibers after durability test sequence; 39-42 runs of baby food/pea samples.

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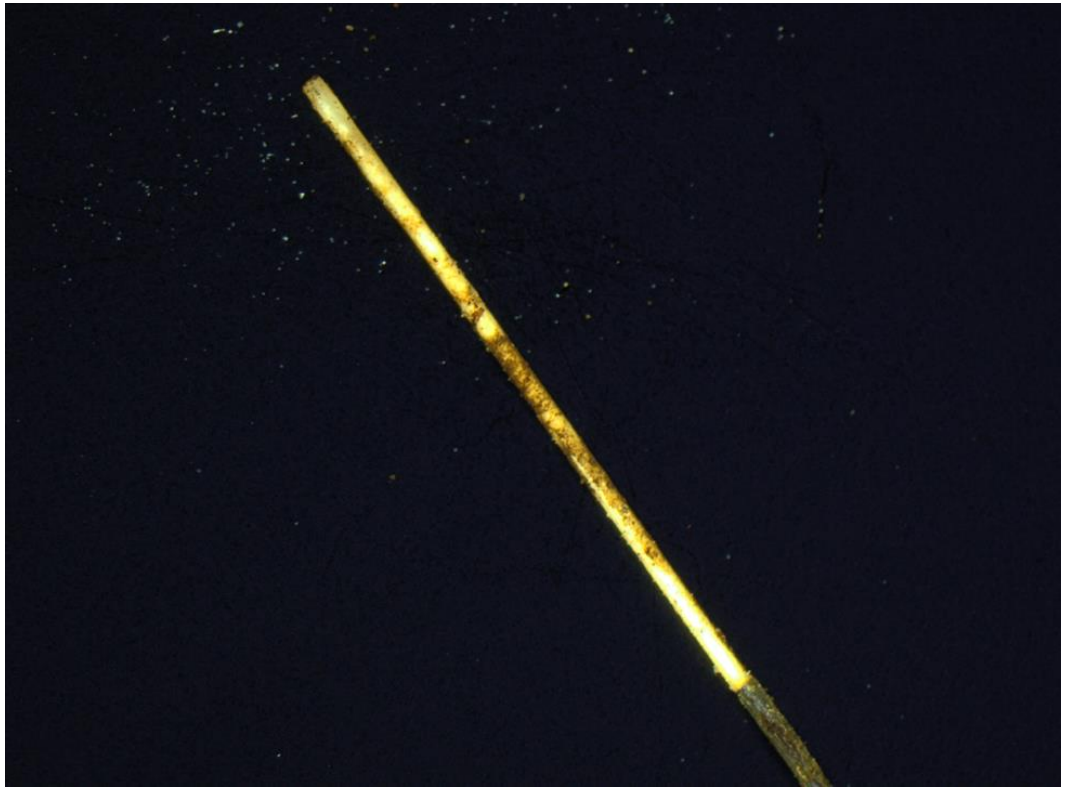
Standard fiber is on the left, OC on the right

PDMS-DVB OC fiber after 31 extractions of prune samples.



Standard fiber was lost during extraction sequence

Direct Immersion into Spaghetti Sauce

- Used a list of pesticides (32 total)
- Sample diluted 1:1 with phosphate buffer at pH 7.
- Addition of salt increased response of most pesticides
- An extraction temp. of 50°C significantly improved reproducibility over 30°C.
- Used post-extraction wash without cloth fibers
- Other parameters for SPME method the same as previous
- Matrix interference prevented analysis of some pesticides (both fibers)

Pesticide List for Spaghetti Sauce

Compound name	CAS #	Log P
Dimethoate	60-51-5	0.34
Mevinphos	7786-34-7	0.50
Dichlorvos	62-73-7	1.37
Malathion	121-75-5	1.86
Metalaxyl	57837-19-1	2.12
Iprodione	36734-19-7	2.29
Parathion-methyl	298-00-0	2.60
Endosulfan I, II	115-29-7	4.7-4.8
Pirimiphos-methyl	29232-93-7	2.96
Disulfoton	298-04-4	3.03
Fenitrothion	122-14-5	3.12
Phorate	298-02-2	3.16
Azinphos-methyl	86-50-0	3.24
Phenthoate	2597-03-7	3.36
Alachlor	15972-60-8	3.59
Vinclozolin	50471-44-8	3.74
Phosalone	2310-17-0	3.75
Ethion	563-12-2	3.93
Chlorpyrifos-methyl	5598-13-0	4.07
Diazinon	333-41-5	4.19
gamma-BHC	58-89-9	4.35
Heptachlor	76-44-8	4.78
Chlorpyrifos	2921-88-2	4.78
Profenophos	41198-08-7	4.88
Quintozene	82-68-8	4.93
Methoxychlor	72-43-5	4.93
Cypermethrins	52315-07-8	5.44
Hexachlorobenzene	118-74-1	5.50
Permethrins	52645-53-1	5.70
4,4'-DDT	50-29-3	6.46
Aldrin	309-00-2	7.4

Experimental Conditions:

Final SPME Method:

Sample: 8 mL vial containing 4 g spaghetti sauce and 4 mL phosphate buffer at pH 7 containing 25% NaCl

Fiber: PDMS/DVB, 24 gauge OC and non-OC

Incubation: 50°C, 6 min, with agitation at 600 rpm

Extraction: 30 min at 50°C, with agitation at 250 rpm; Fiber penetration set to 30 mm

Post extraction wash: 30 sec. in deionized water

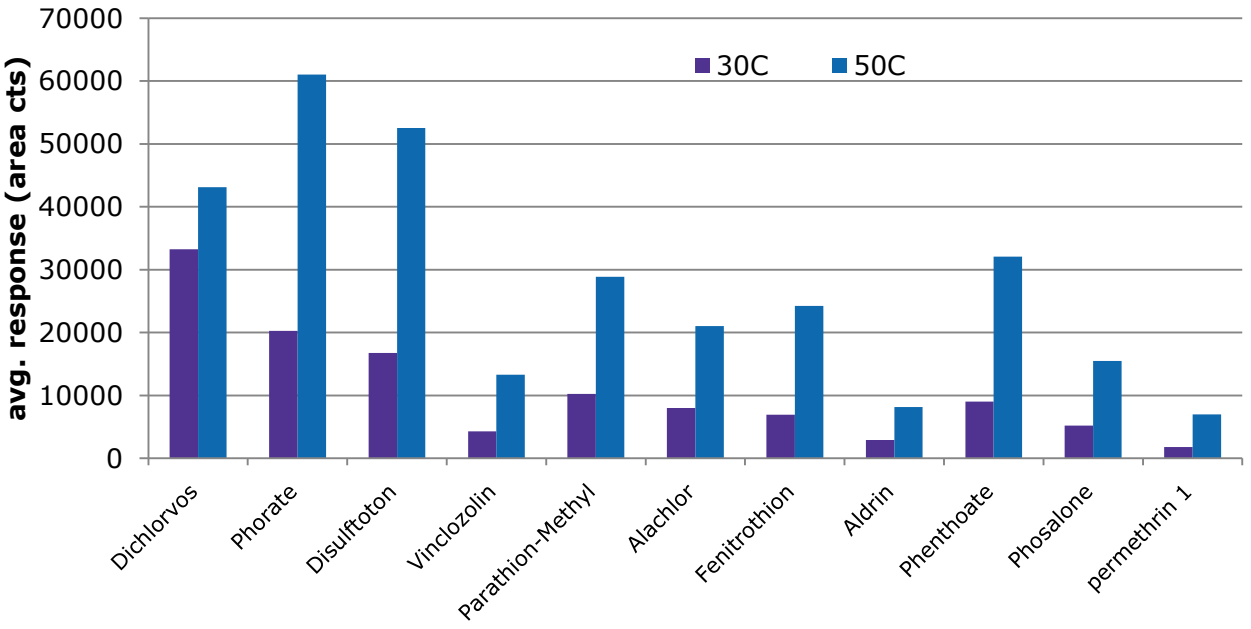
Desorb: 250°C, 3 min; Fiber penetration set to 45 mm

Postbake: 260°C, 5 min

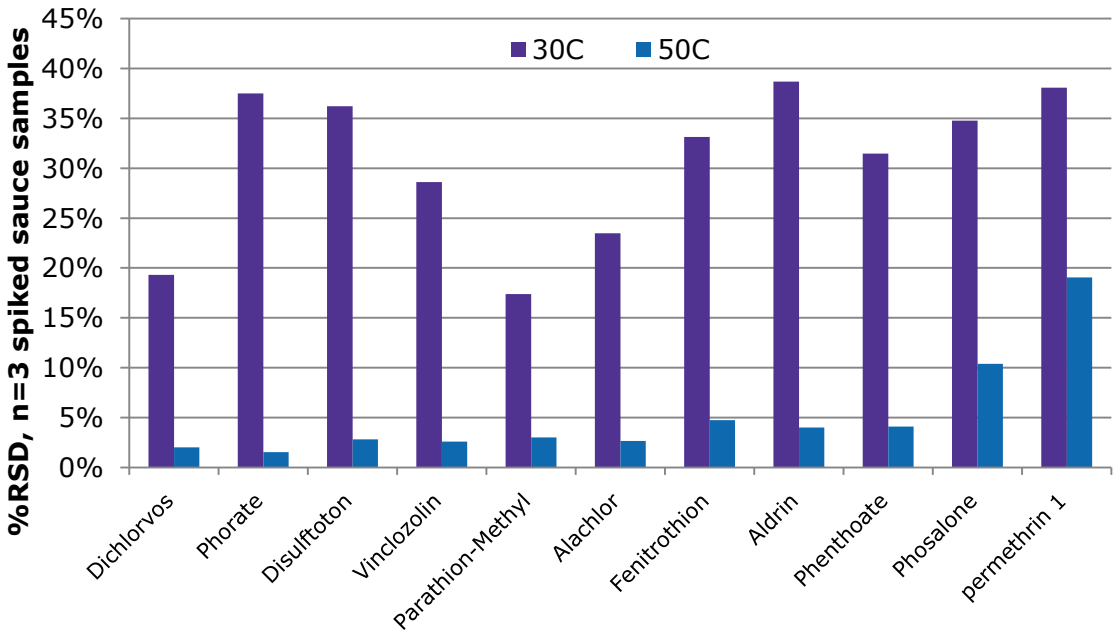
GC/MS conditions

Column: SLB-5ms, 30 m x 0.25 mm I.D. x 0.25 µm
Inj. Temp.: 250°C
Oven: 50°C (3 min), 10 °C/min to 325°C (5 min)
Carrier: helium, 1 mL/min constant flow
MS temps: source at 230°C, quads at 150°C

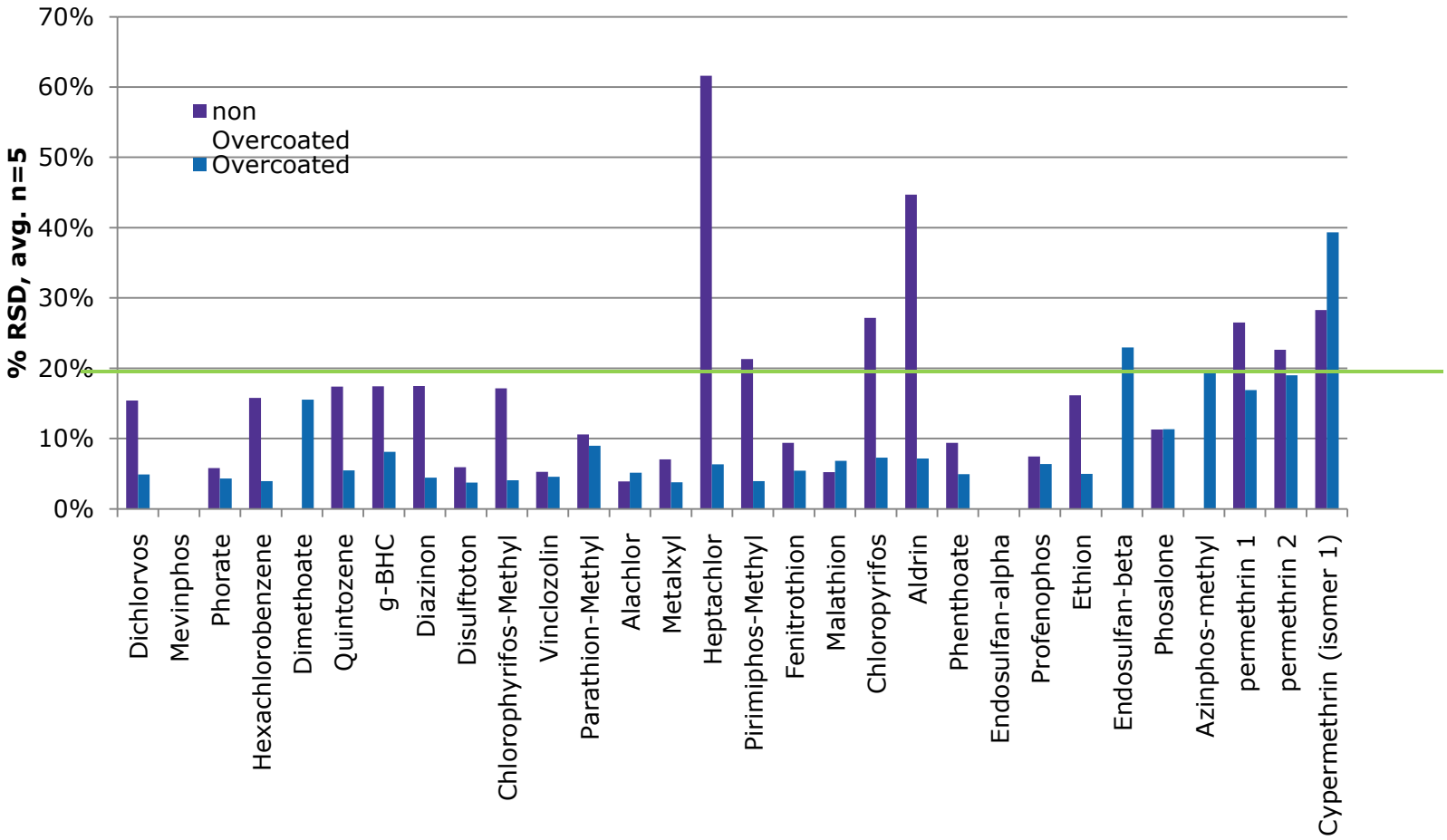
Effect of extraction temperature on pesticide response - Spaghetti sauce (*n*=3)



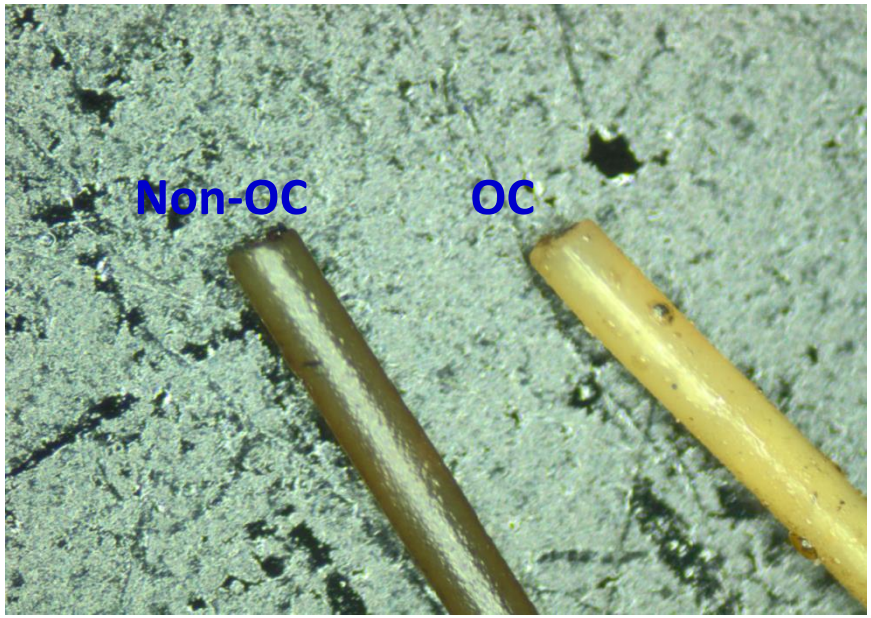
Effect of extraction temperature on reproducibility
Spaghetti sauce

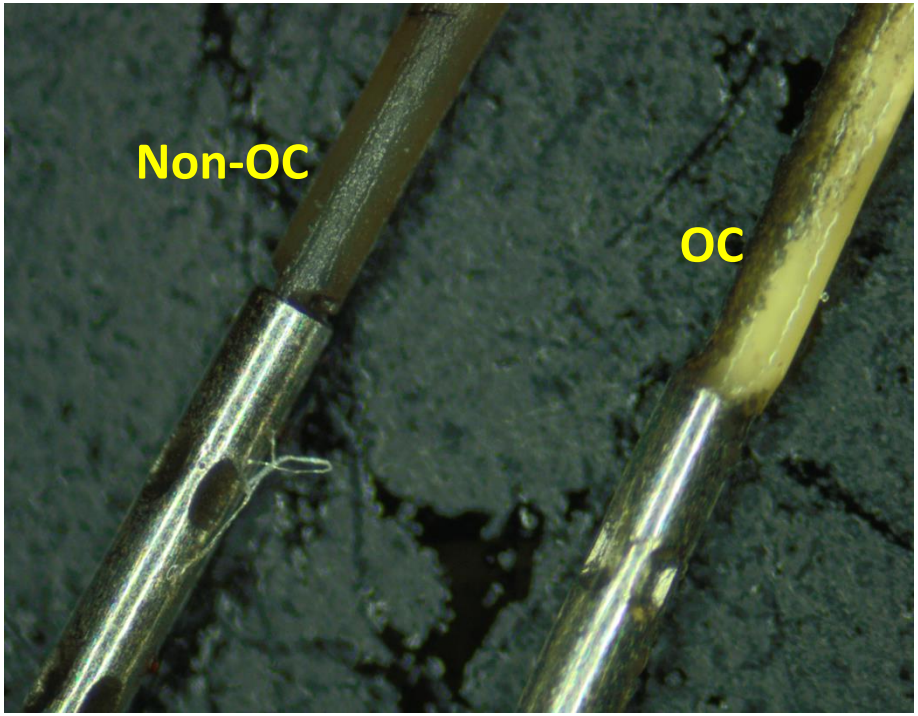


Reproducibility
10 ng/g spiking level, avg. *n*=5



SPME fibers after 38-40 spaghetti sauce





Conclusions

- SPME is a versatile and green extraction method
- SPME is cost effective
- SPME is suitable for many food and beverage applications
- Detection limits are similar to other extraction methods
- SPME is quantifiable
- Over-coated SPME fibers can extend fiber life when extracting out of complex matrices

New EPA Rule (Method 325 A&B)

On September 29, 2015, the U.S. EPA issued a final rule - requiring all U.S. Petroleum Refineries to conduct passive air sampling along the perimeter of their properties.

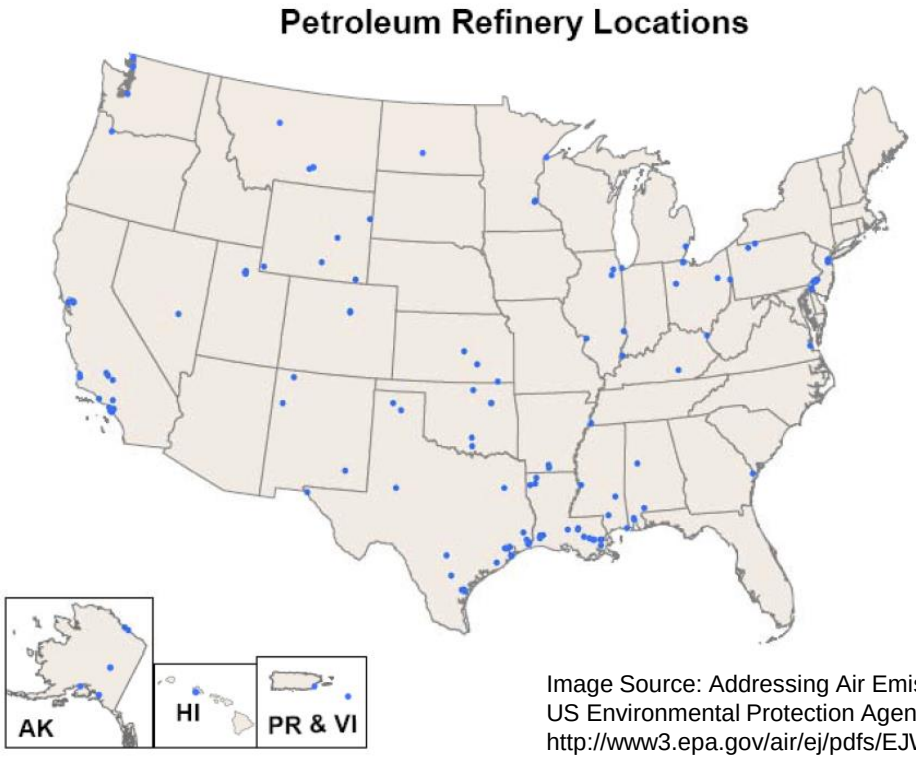


Image Source: Addressing Air Emissions from the Petroleum Refinery Sector US Environmental Protection Agency. http://www3.epa.gov/air/ej/pdfs/EJWebinar20111018.pdf

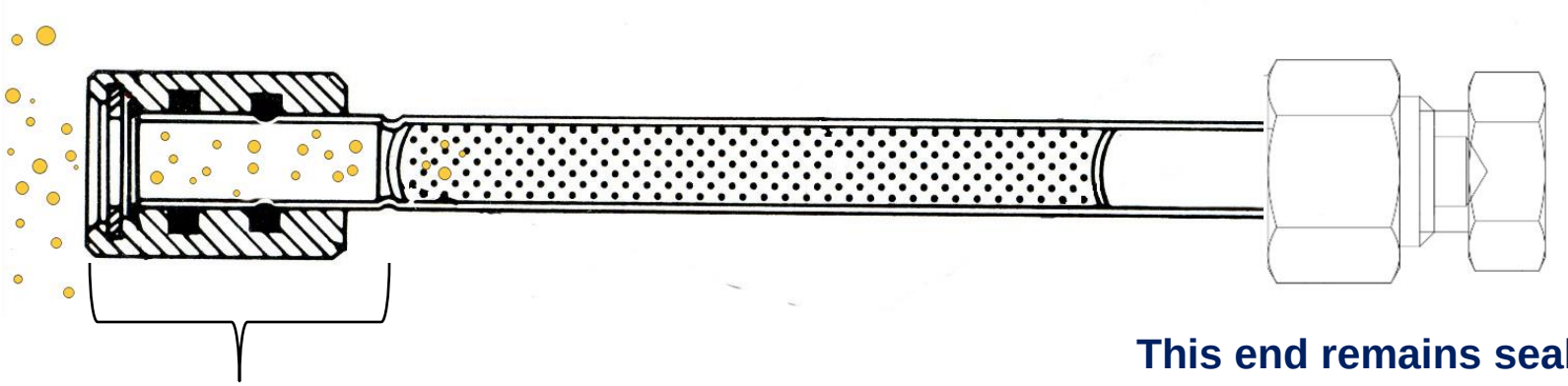
Introduction

EPA Method 325 uses passive (diffusive) samplers to collect air samples at specific intervals along the fence line of the petroleum refineries property[1]. The target compound is Benzene.

These passive air samplers are comprised of a inert-coated stainless steel thermal desorption tube packed with a graphitized carbon adsorbent. Carbopack™X is listed as the primary adsorbent. The I.D. of the stainless steel tube are coated with a protective layer, which masks any active sites that could be present on the inside of the tube.

How it works (Diffusive Sampling)

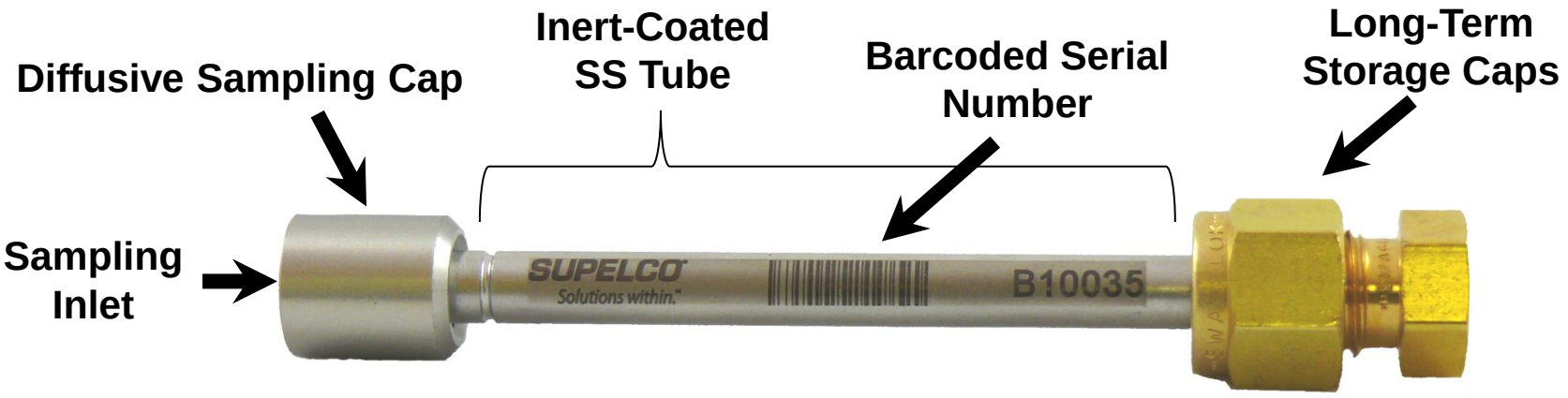
The air sample is collected by the natural movement of the contaminant molecules across a concentration gradient of the air gap and onto the adsorbent. (Fick's Law)



Diffusion Path
"Air Gap"

This end remains sealed during sampling

Passive Sampling Tube



Tube Dimensions: 6.35 mm O.D. x 5 mm I.D. x 89 mm Long

Inert-Coated Tubes

- Method 325 specifies the stainless steel tubes have an inert coating on the inside.

- This process produces a ceramic like protective coating to the inside of the stainless steel tube. The coating covalently bonds to the steel surface and protects the surface from oxidation.

- The coating is stable to (>400°C), and creates a reproducible surface that withstands multiple uses.

Conclusions

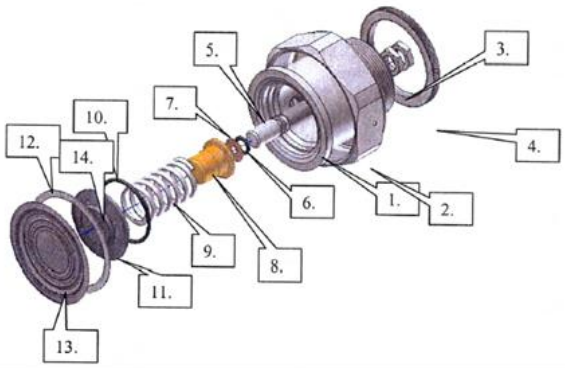
Tubes packed with Carbopack-X will retains a wide range of VOC’s

The recovery of key analytes, 1,3 Butadiene, Benzene, Toluene, remain at 100% when sampling large volumes with Carbopack-X tubes.

Carbopack-X is hydrophobic, so when sampling in high humidity no water will be retained by the adsorbent.

Carbopack-X has low background levels.

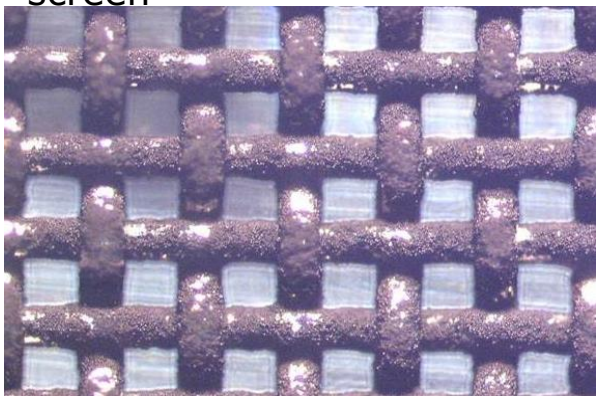
Regulator Passivation



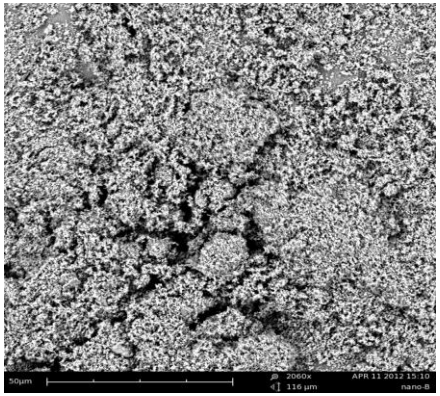
- Very thin coating of regulator parts
- Allows for the analysis of active components without adsorption to the metal surface
- Faster equilibration times during analysis
- Original application was for an EPA method for Hg (ruling pending)
- Expanding into analysis of HCl gas and sulfur containing mixtures for fossil fuels

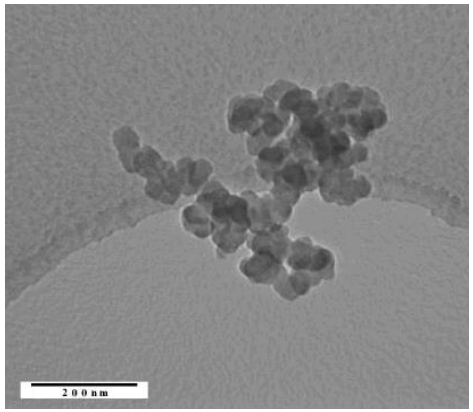
Carbon Coatings

GCB bonded 100um screen screen

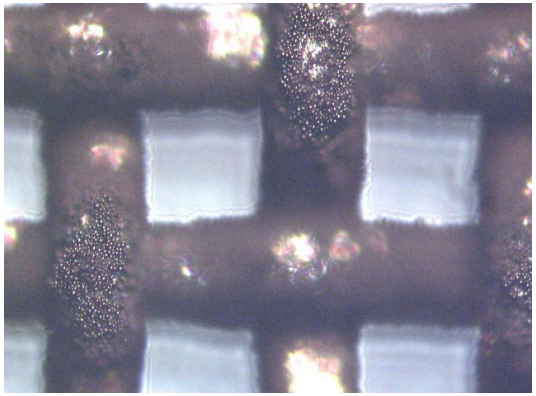


nanoGCB on metal baffle





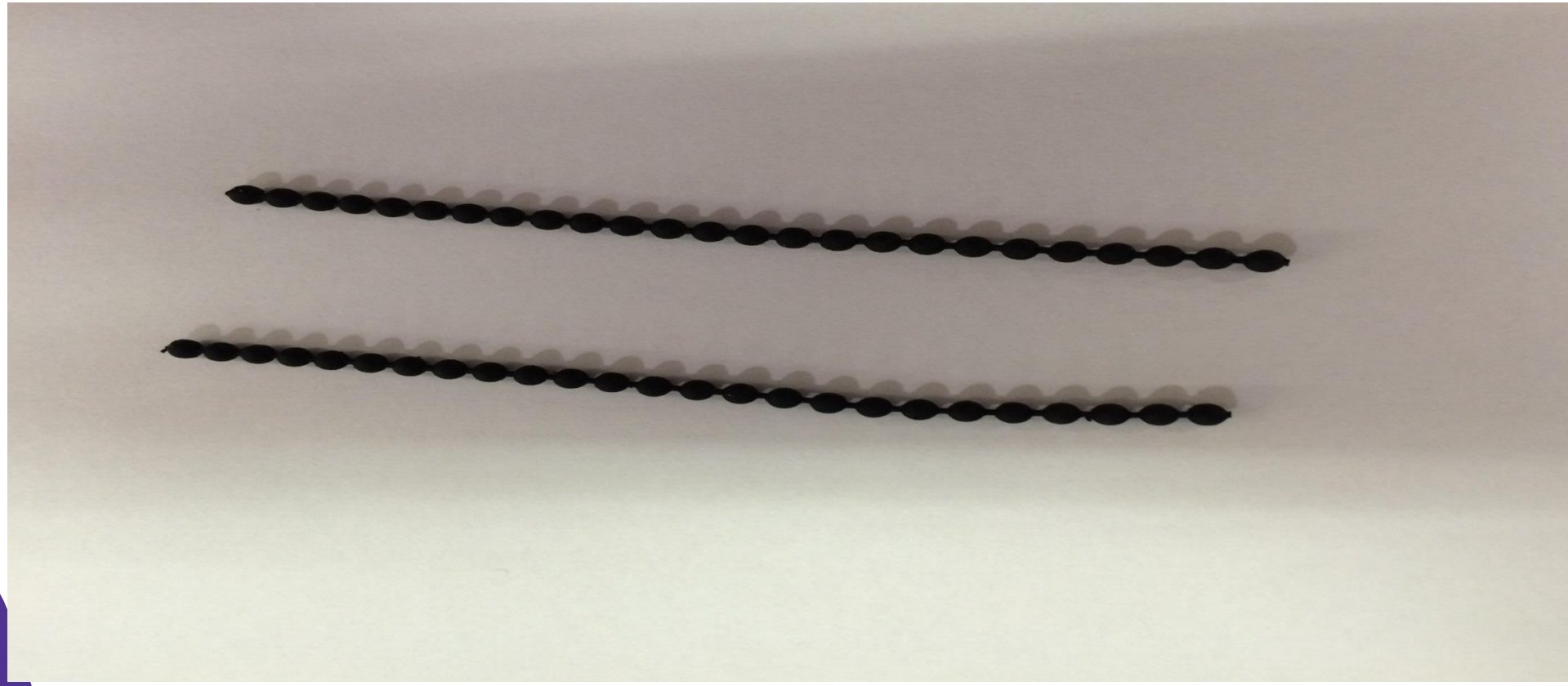
2.0um CMS bonded 100um



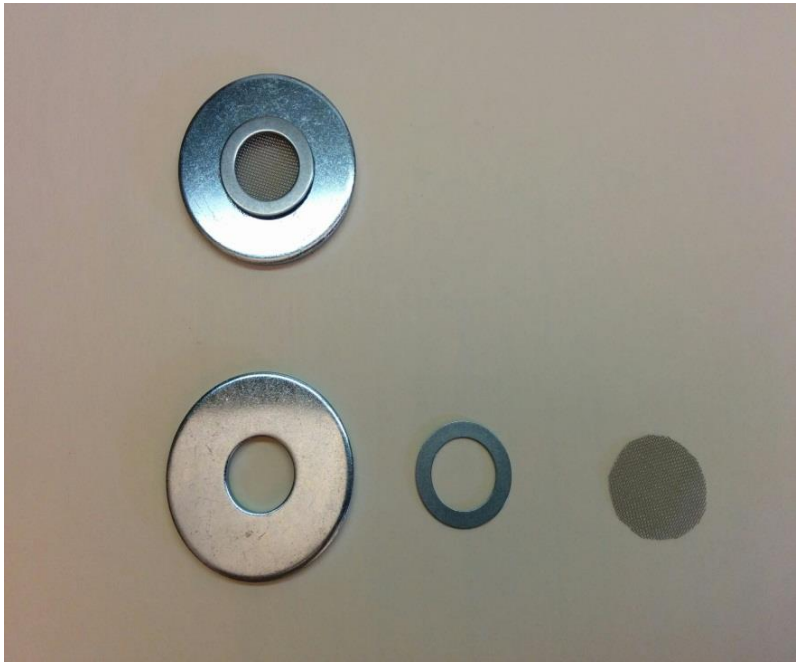
Sampling Devices

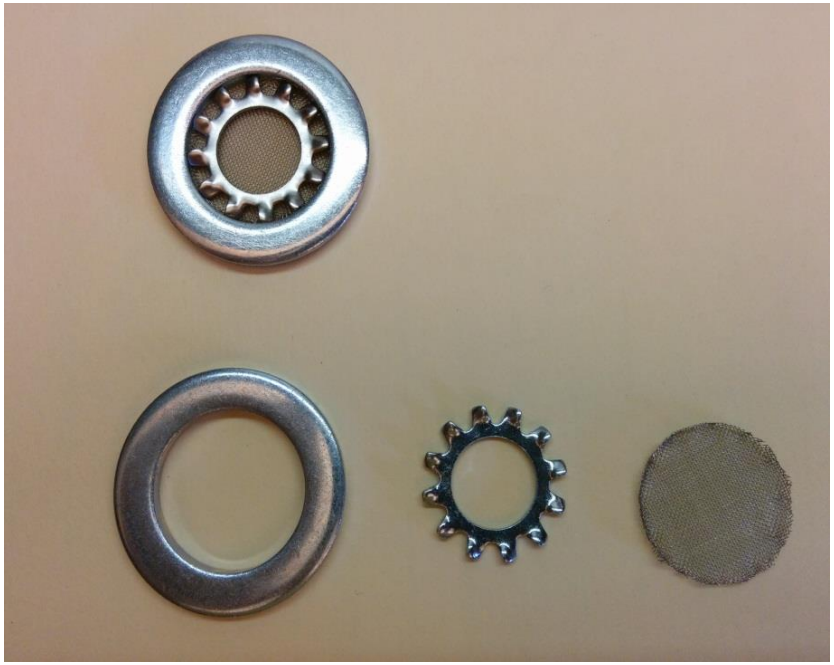
- Sampling device used with a portable mass spectrometer
- Nichrome mesh coated with adhesive and carbon adsorbents (allows for resistive heating)
- Commercial technology actively being marketed outside the defense arena
- Recent applications: evaluation of milk spoilage, VOCs in potato chips factories

Device Coating
Pull Chains coated with Carboxen 569



Technology Overview- SPME Device Coating DART System





Summary

- SPME- Overcoated fibers
- Air Monitoring- New Fence line Monitoring Tubes
- Device Coating- Regulators , Screens and other Devices