Solid Phase Microextraction

Basics, Theory and Environmental Analysis

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SUPELCO™ Analytical

SPME® SUPELCO

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SPME History

- Patented Technology of University of Waterloo, Canada
- Inventor: Prof. Dr. Janusz Pawliszyn
- Automation by Varian (AS 8200 & CTC CombiPal).
  - CTC CombiPal makes the SPME compatibel with most GCs

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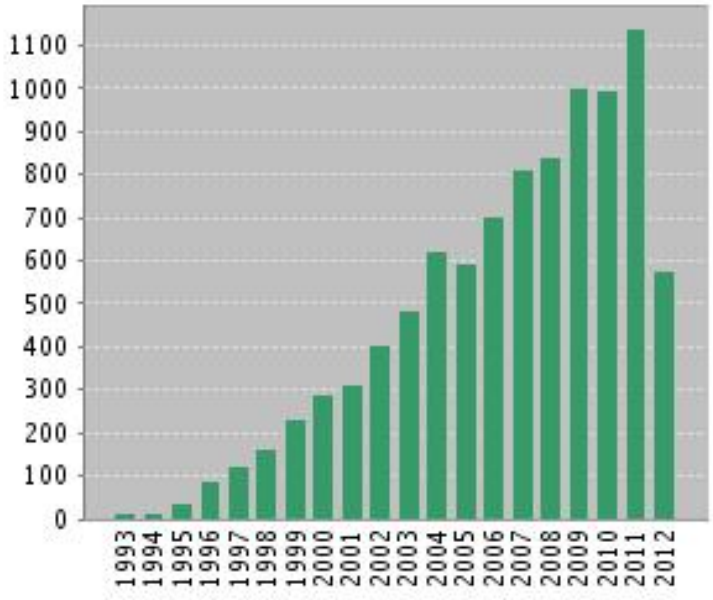
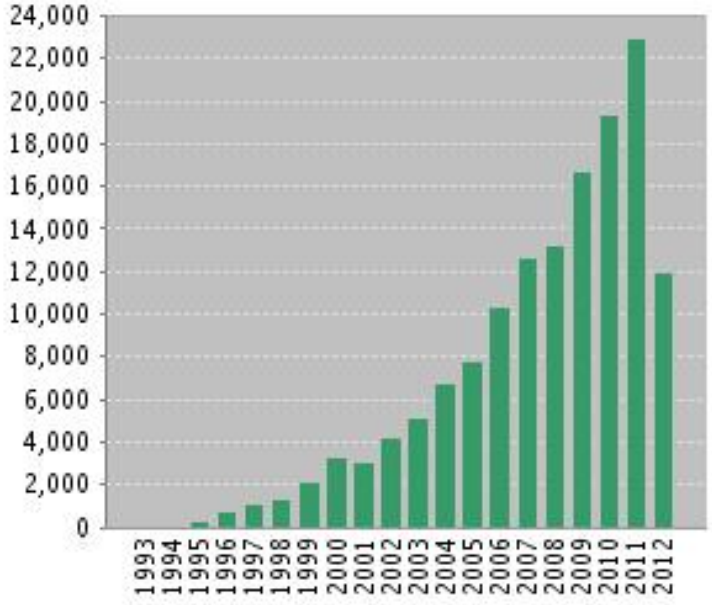
SPME: used in thousands of applications

Source ISI Search: Solid Phase Micro Extraction and SPME

Published Items in Each Year



Citations in Each Year



Items: 10720
Total Citations: 143140 (reviews not included)
H-index: 104 (reviews not included)

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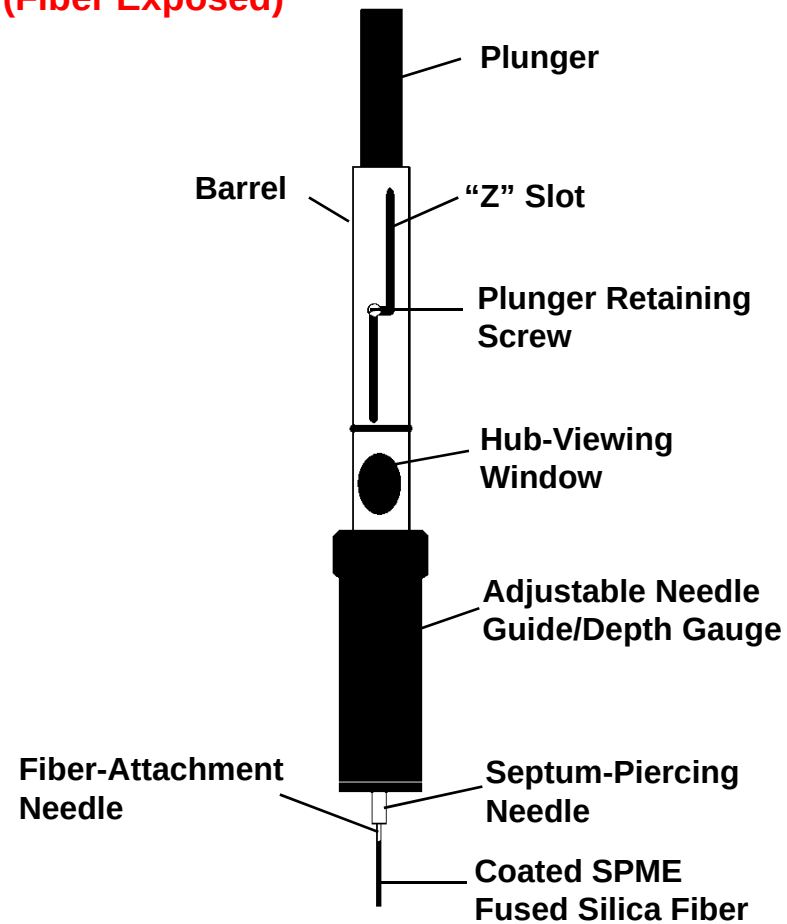
SPME Holders

For Manual Sampling (Fiber Exposed)



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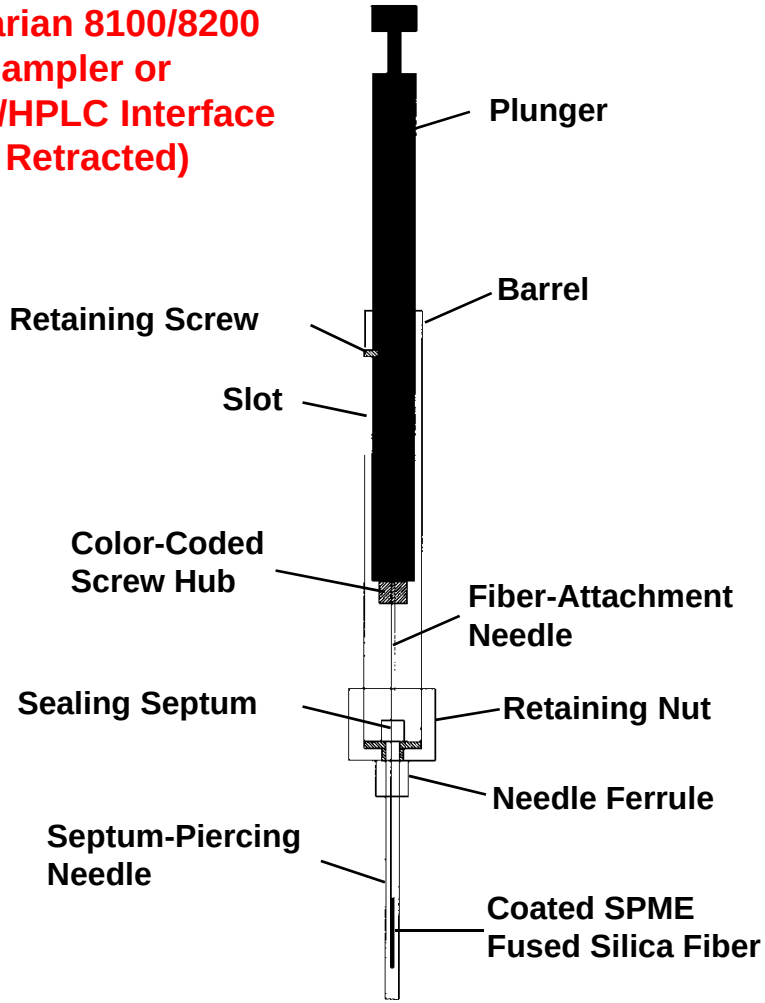
For Varian 8100/8200 AutoSampler or SPME/HPLC Interface (Fiber Retracted)



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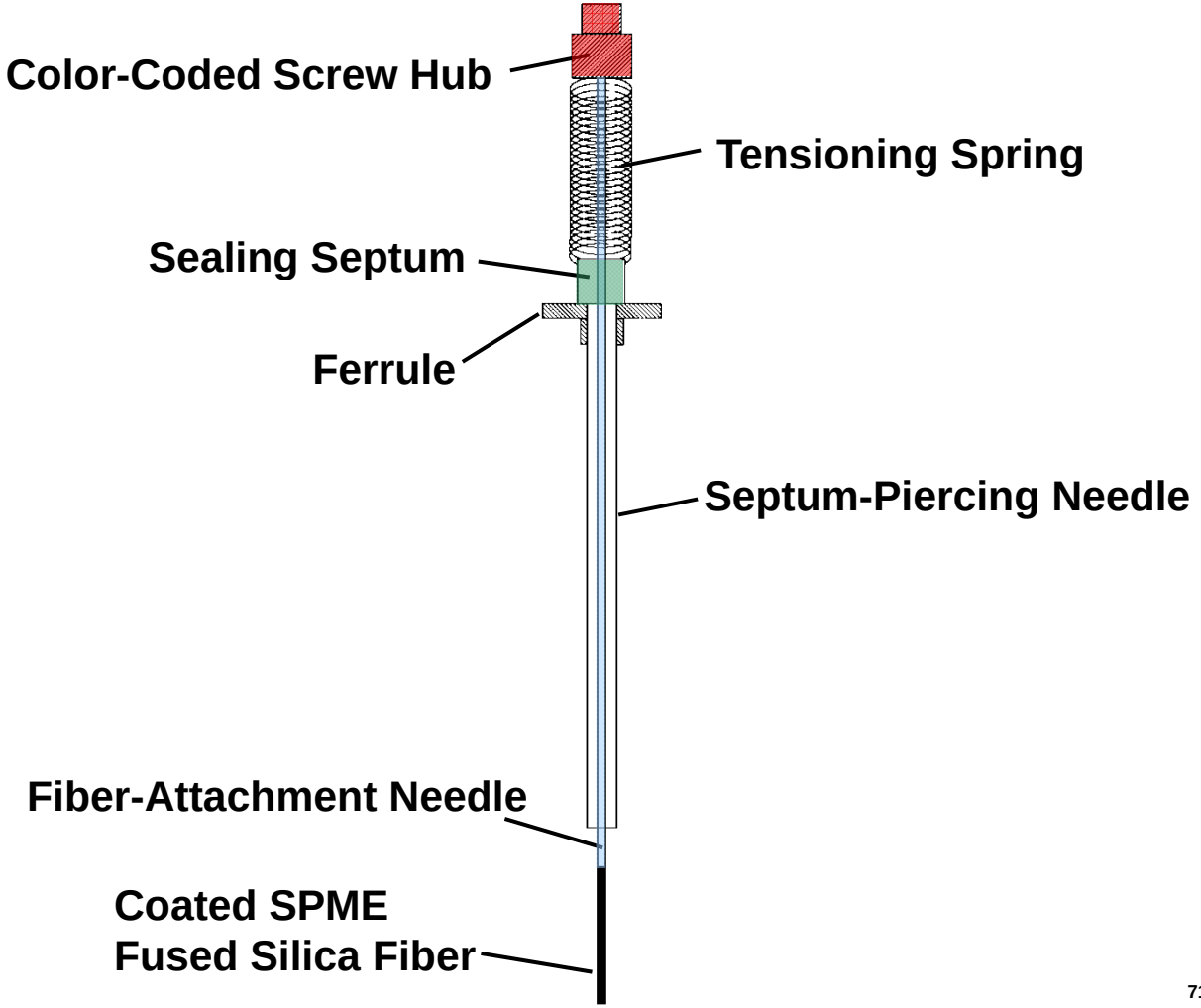
SPME Fiber Assembly Detail (Manual)



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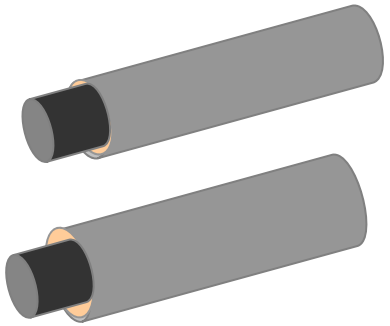
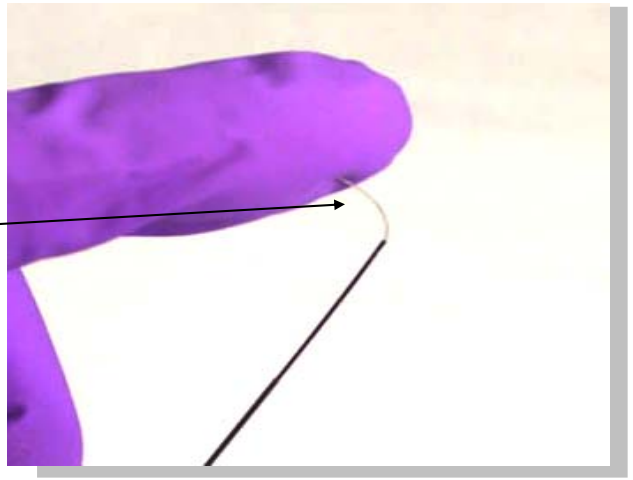
Types of SPME Fiber Assemblies

- Assemblies for holders
  - manual
  - autosampler style (no spring)



- Gauge size of piercing needle
  - Standard size - 24 GA
  - Larger bore size - 23 GA (for septum free inj. ports)

- Types of fiber core
  - Fused silica
  - Stableflex
  - Metal NEW!



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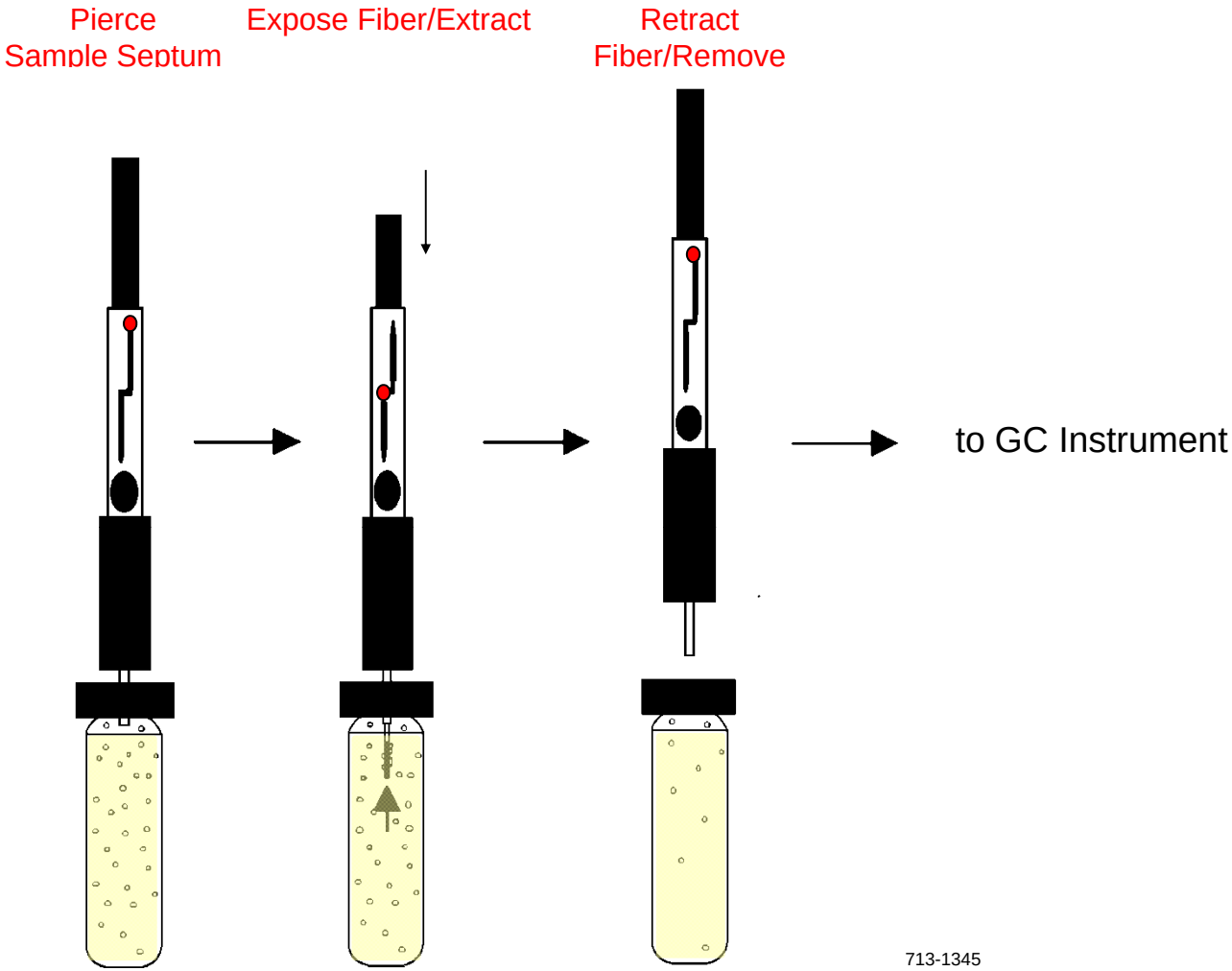
Extraction Procedure for SPME



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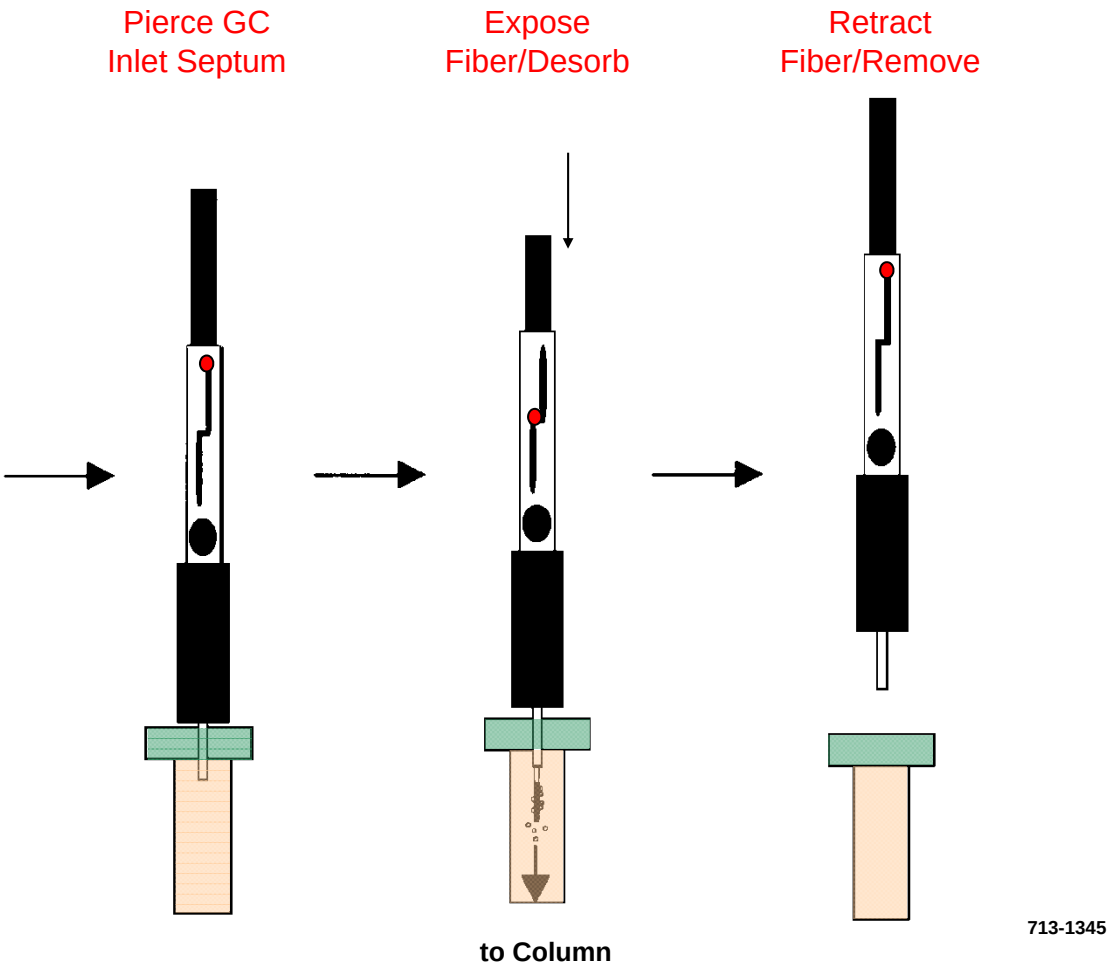
Desorption Procedure for SPME



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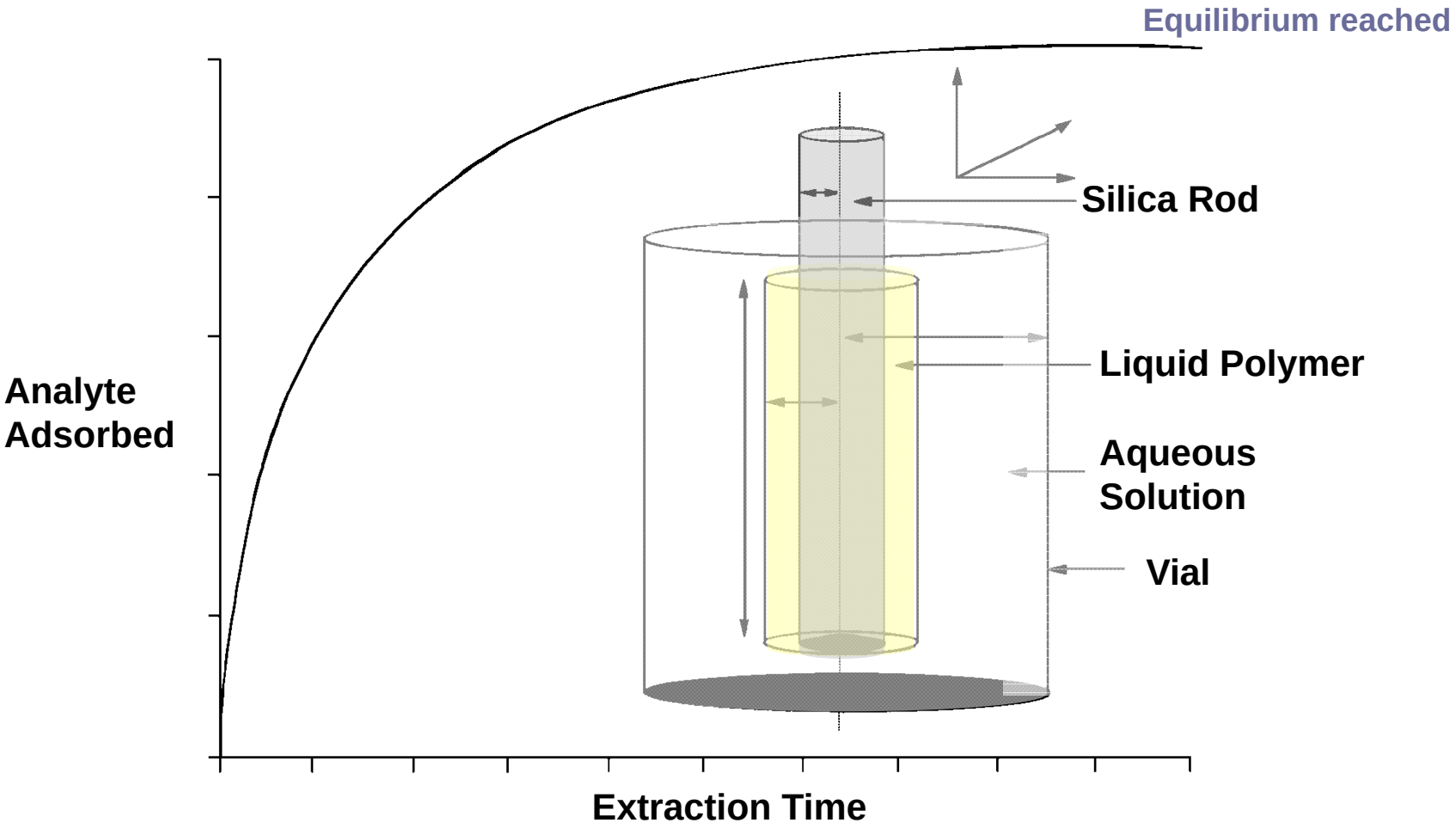
Adsorption Mechanism for SPME



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Amount of Analyte absorbed by the Fiber at Equilibrium

- for small sample volumes (2-5ml):

$$n_s = \frac{KV_f C_0 V_s}{KV_f + V_s}$$

- at infinite volume of samle ($V_s >> V_f$):

$$n_s = KV_f C_0$$

K	Distribution Costant fiber/sample
n_s	Analyte moles into the Stationary phase
V_f	Stationary Phase Volume
V_s	Sample Volume
C_0	Concentration of the Analyte in water

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Adsorption-time Profile for BTEX Compounds Using SPME

- K is compound specific
  - Also dependend of fiber & matrix
- Kinetics of analytes are different
  - Higher k values require longer equilibrium times

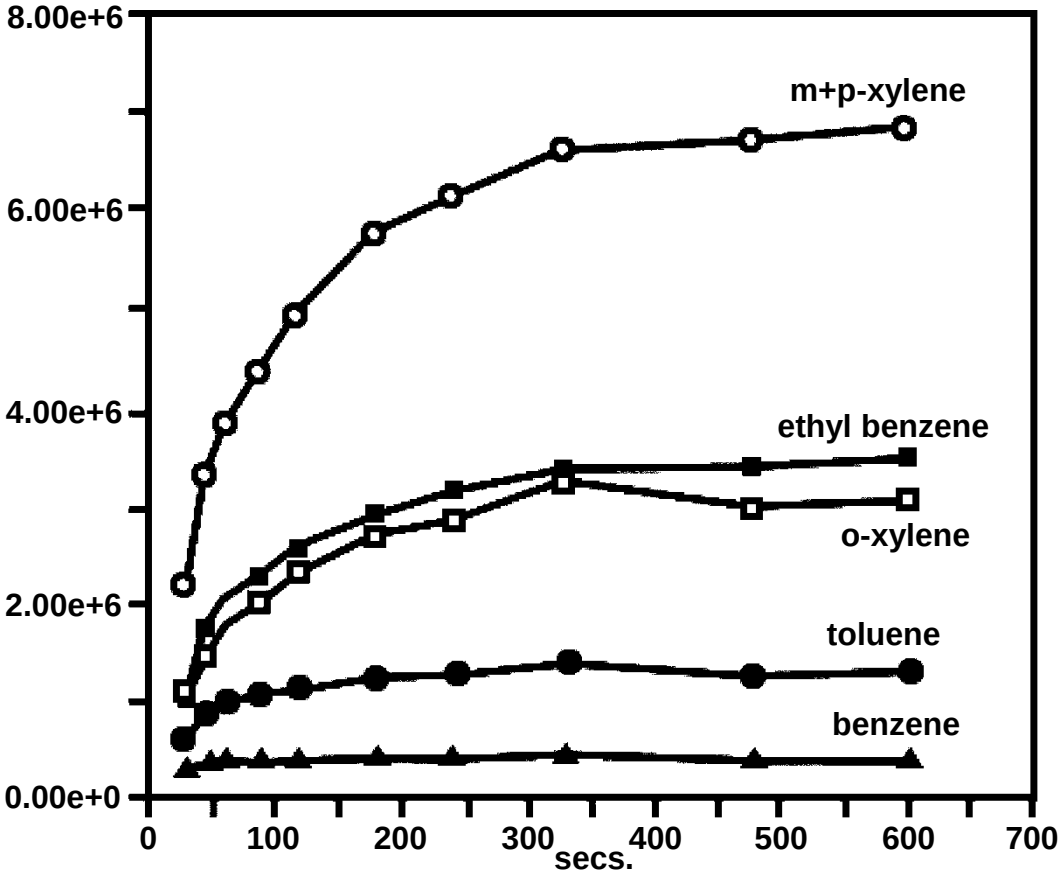

Figure courtesy of J. Pawliszyn, et al., University of Waterloo, Ontario, Canada.

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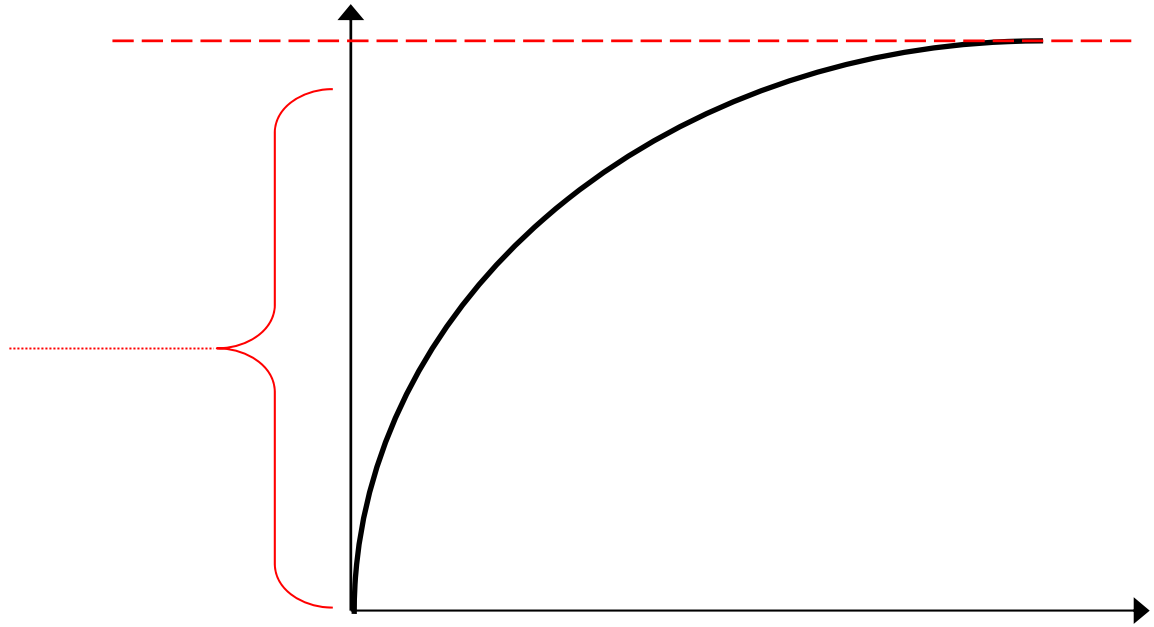
Physical Factors Affecting Sample Recovery

- Influence on Equilibrium
- Influence on Kinetics
  - Stiring
  - (Temperature)



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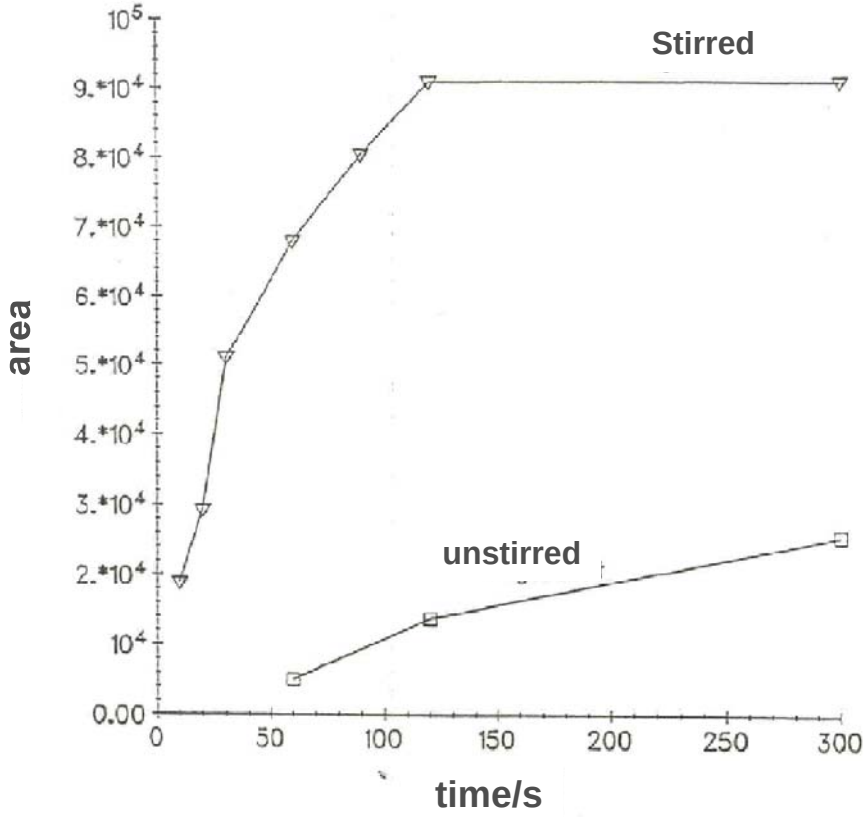
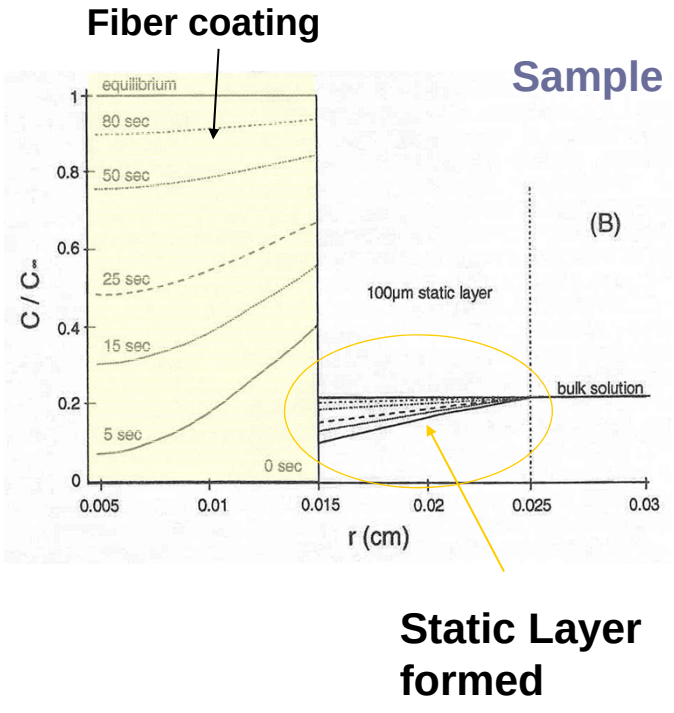
Stirring in SPME

Time dependence
Extraction of 1,3-Dichlorobenzene





Static Layer formed

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Factors Affecting Sample Recovery

- Fiber Selection
- Sample Modifications
- Extraction Time
- Desorption Conditions
- Inlet Design
- Column Selection

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Available SPME Fibers, by Film Type

- Absorption Fibers
  - Polydimethylsiloxane (PDMS) 7, 30, and 100µm — Unpolar
  - Polyacrylate (PA) — Polar
  - Polyethyleneglycol (PEG) — Polar
- Adsorption fibers (with particles)
  - Carboxen-polydimethylsiloxane(CAR-PDMS) — Adsorption
  - Polydimethylsiloxane-divinylbenzene (PDMS-DVB) — Adsorption
  - Divinylbenzene/Carboxen- Polydimethylsiloxane (DVB-CAR-PDMS) — Adsorption

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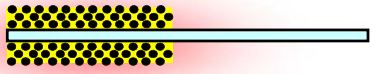
Adsorbent vs. Absorbent Fibers

Adsorbent (particle) fibers

- **Physically traps or chemically reacts bonds with analytes**
  - **porous material**
  - **high surface area**
- **Analytes may compete for sites**
- **Fibers have limited capacity**

Absorbent (film) fibers

- **Analytes are extracted by partitioning**
  - **liquid phase**
  - **retains by thickness of coating**
- **Analytes do not compete for sites**
- **Fibers can have high capacity**



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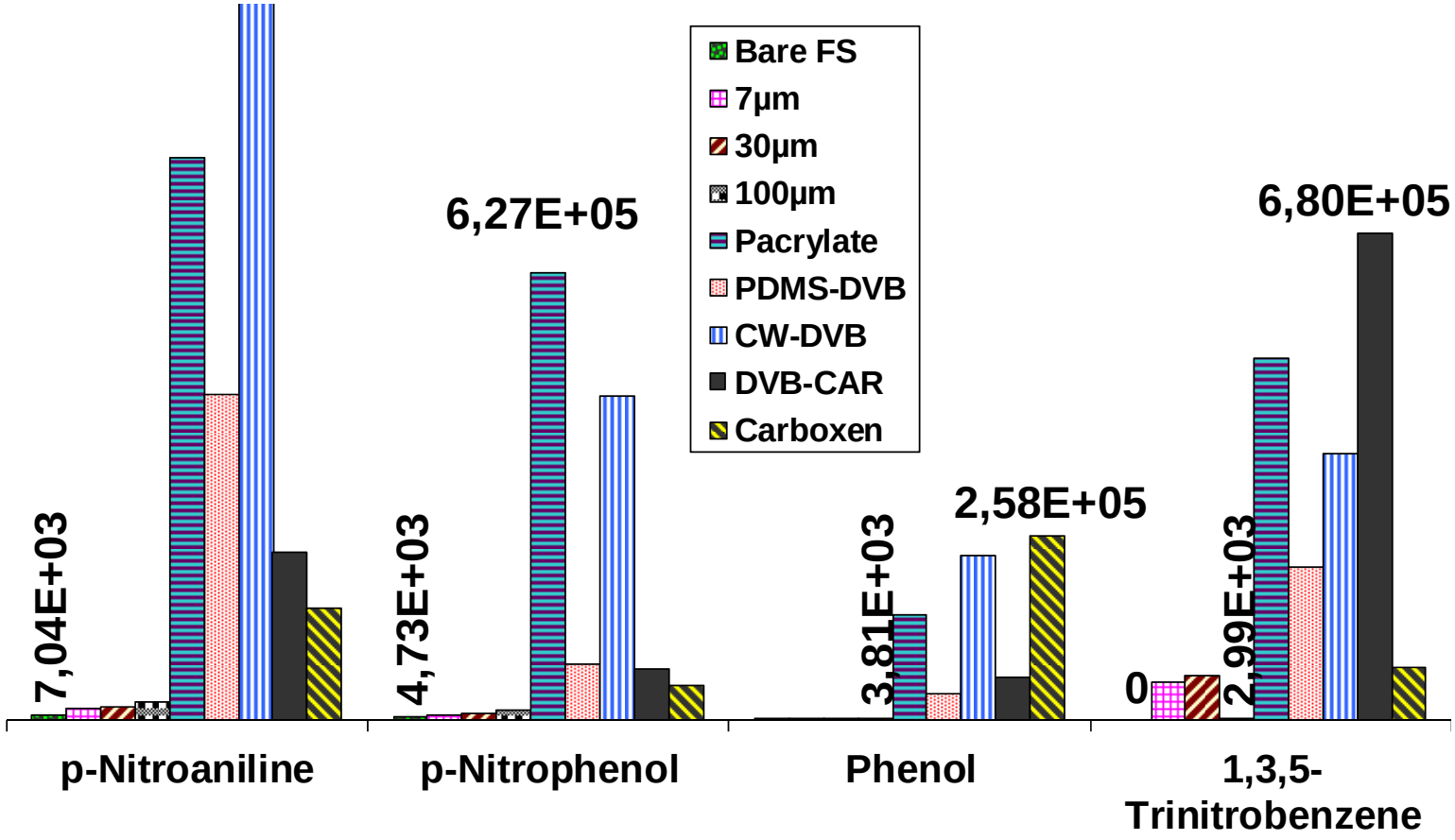
Area Response depending on Fiber Type



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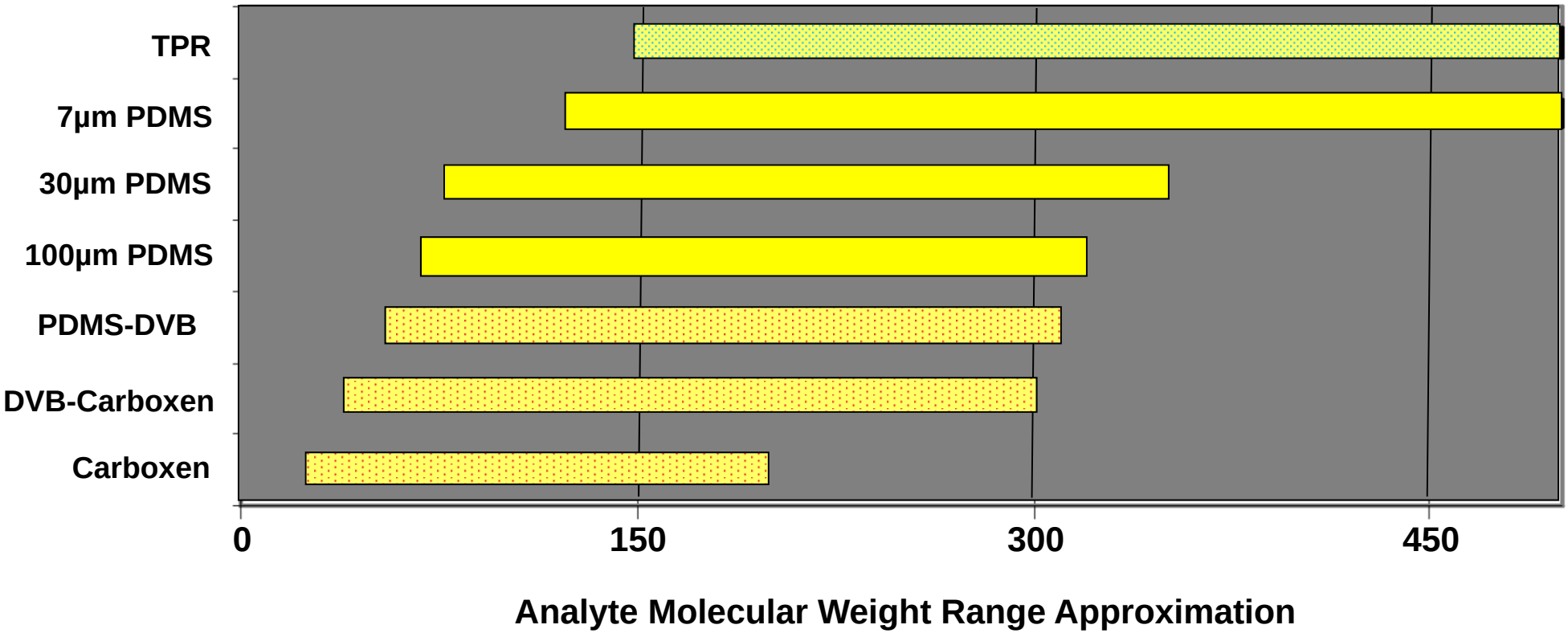
SPME Fibers by Adsorption Strength Estimation



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Comparison of SPME Fibers for the Extraction of Small Hydrocarbons

(Analytes at 1ppm in Air, Extracted for 10 Min)

Analyte	100µm PDMS	PDMS/DVB	Carboxen™/PDMS
Ethane	0	0	750
Propane	0	0	20000
Butane	0	340	72100
Pentane	230	2150	108000
Hexane	460	9280	105000

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SPME Fibers for the Extraction of Hydrocarbons

n=	Carboxen™-PDMS	Carboxen-DVB-PDMS	PDMS-DVB
2	200	80	
3	800	260	30
4	2600	1000	200
5	7000	3200	800
6	13000	7000	2200
7	10000	5000	2200
8	53000	29000	14000
9	49000	29000	14000
10	160000	100000	49000
12	230000	150000	90000
14	480000	300000	260000
16	490000	380000	360000
18	44000	110000	130000
20	18000	60000	110000
22	6600	24000	64000
24	3400	12000	46000

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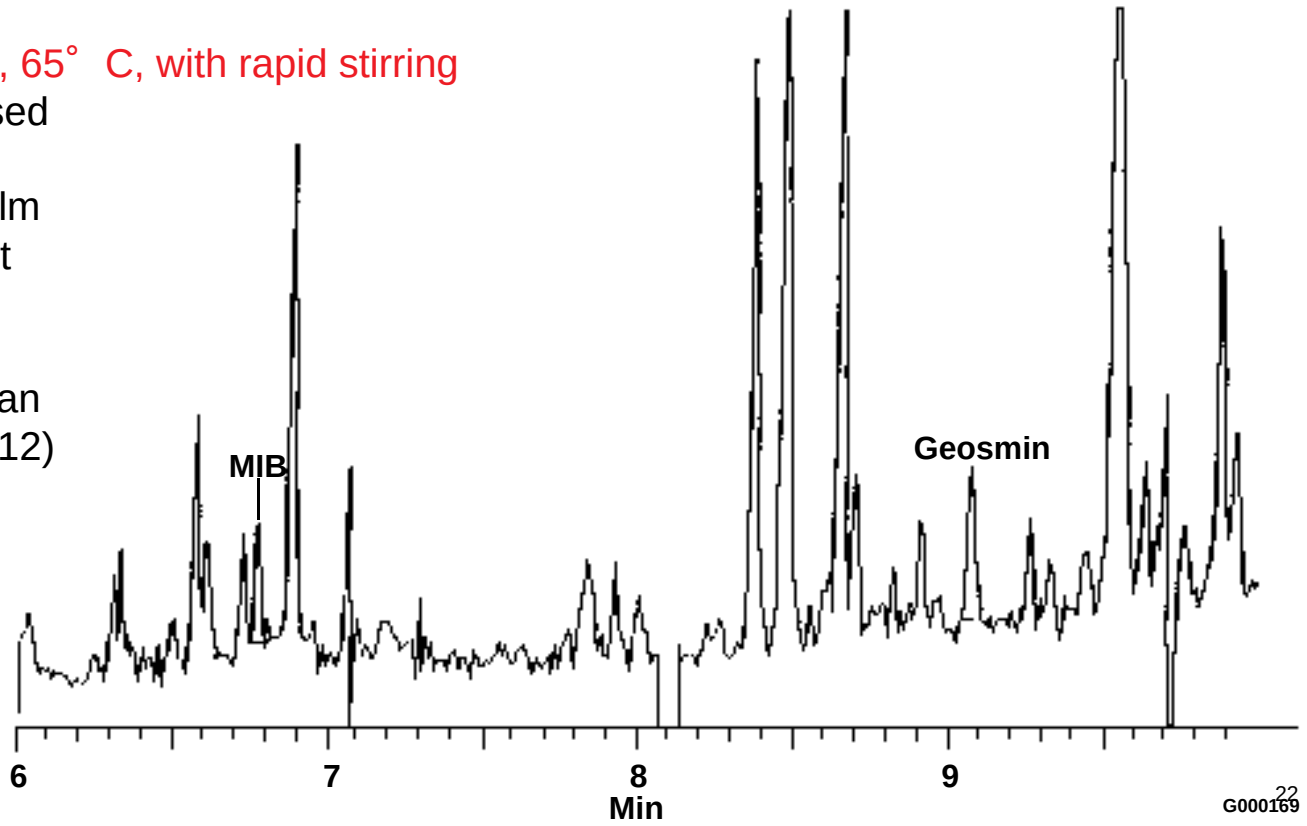
Odor Agents at 1ppt in Water by SPME-GC/MS

Sample: 30mL water containing MIB and geosmin at 1ppt and 25% NaCl in a 40mL vial, at 65° C
SPME Fiber: DVB/Carboxen™/PDMS
Extraction: heated headspace, 30 min, 65° C, with rapid stirring
Desorption: 3 min, 250° C, splitter closed
Column: Meridian MDN-5, 30m x 0.25mm x 0.25µm film
Oven: 60° C (1 min) to 250° C at 15° C/min
Det.: mass spectrometer, m/z = 75-180 at 0.6 sec/scan (quantitation ions 95 and 112)



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SPME Technique

- Extraction conditions
  - Headspace
  - Direct Imersion
- Desorption temperature
- Liner Diameter
- Sample Modifications

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Headspace vs. Direct Immersion

- Volatility of Sample
- Extraction Time concerns
- Sample Matrix
- Selectivity of Analytes

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Fruit Punch Flavor by Headspace SPME
Elimination of Glycerin Interference

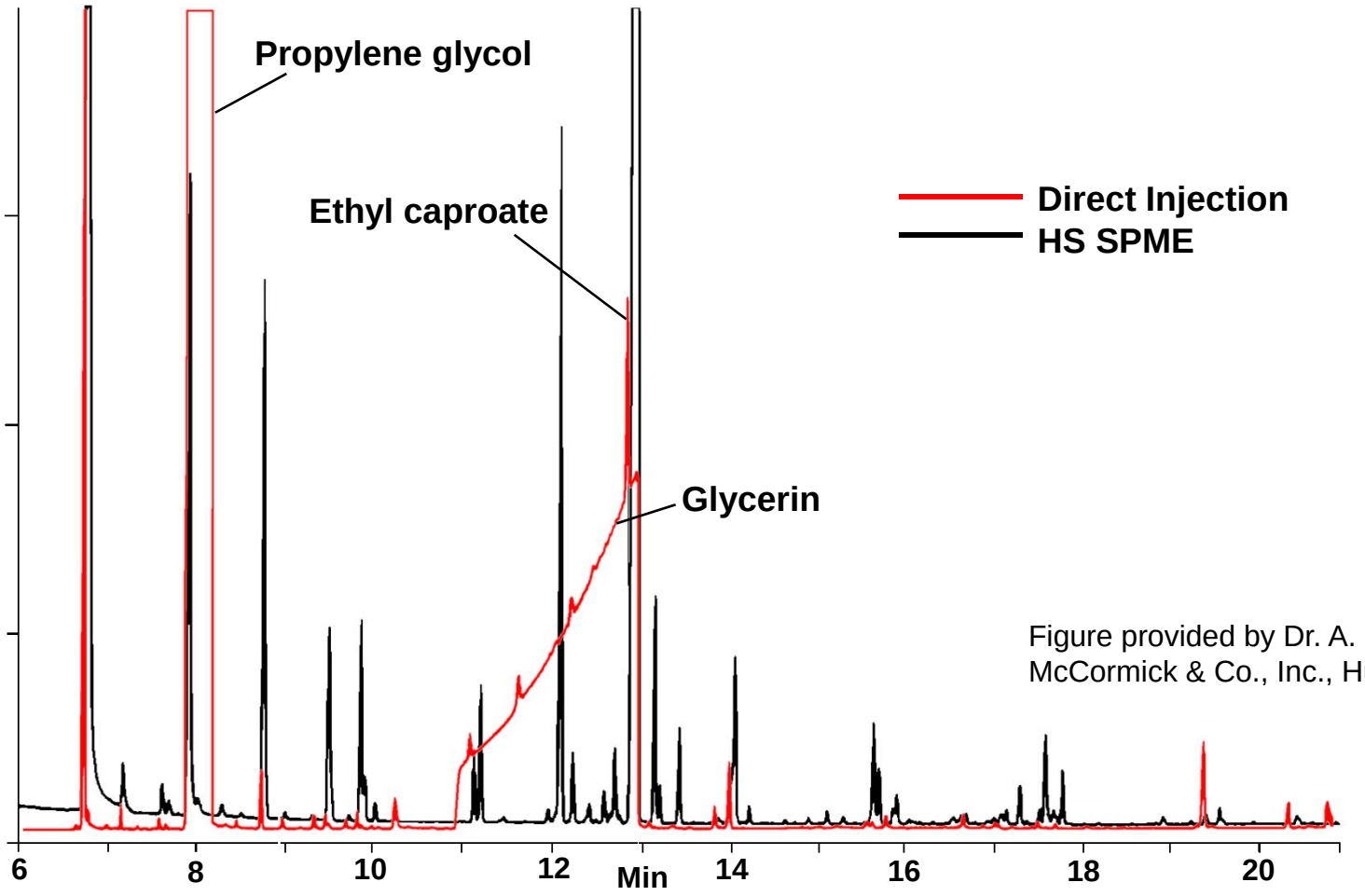

Figure provided by Dr. A. Harmon,
McCormick & Co., Inc., Hunt Valley, MD, USA.

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Sample Modifications

- Salt
- pH
- Derivatisation of analytes on the fiber
  - Fiber saturated with reagent put into sample extraction
  - Fiber with extracted analytes put into reagent

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Sample Modifications

The Effect of Salt and pH on Extraction of Phenols (50ppb) by SPME (PA)

	No Salt Neutral	No Salt pH = 2	Salt Neutral	Salt pH = 2
2-Chlorophenol	1800	2361	3952	14028
Phenol	810	1003	6425	6150
Methylphenol	761	882	5485	7434
3- & 4-Methylphenol	1795	1846	15337	19723
2-Nitrophenol	422	474	311	2315
2,4-Dimethylphenol	1344	1476	15000	20710
2,4-Dichlorophenol	5396	8138	19803	61664
2,6-Dichlorophenol	2991	5858	12511	48530
4-Chloro-3-methylphenol	2398	3137	24060	33529
2,4,5-Trichlorophenol	3115	11097	24270	96333
2,4,6-Trichlorophenol	9702	19307	35466	109492
2,4-Dinitrophenol	0	11	765	1182
4-Nitrophenol	626	730	11458	6536
2,3,4,6-Tetrachlorophenol	3108	27683	33938	70440
2-Methyl-4,6-dinitrophenol	55	47	920	1685
Pentachlorophenol	2305	40582	22056	143905
Dinoseb	68	2123	6676	37744

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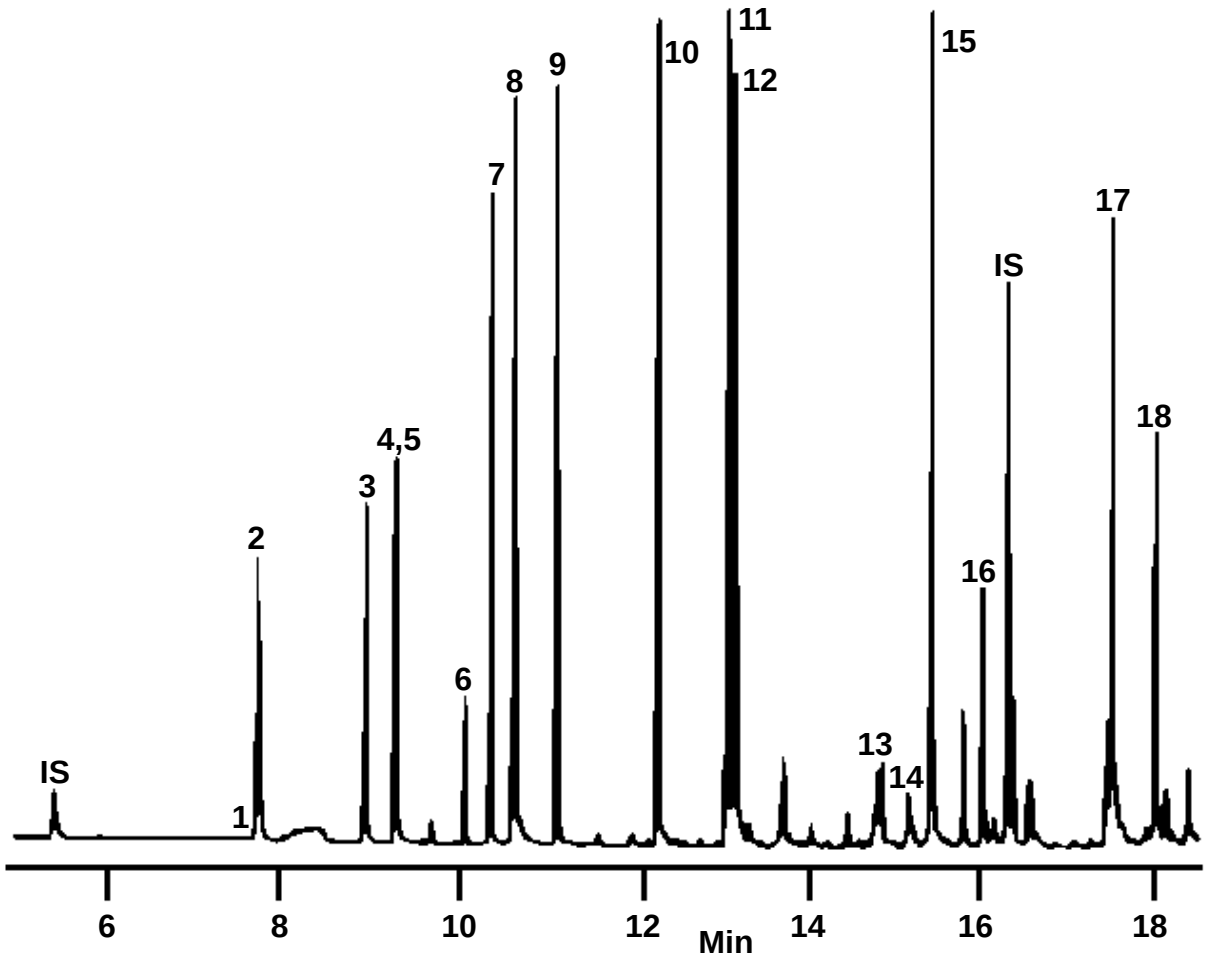
Phenols by SPME at 50ppb

(85µm Polyacrylate Fiber, pH 2)



IS 2-Fluorophenol (int. std.)
1. Phenol
2. 2-Chlorophenol
3. 2-Methylphenol
4. 3-Methylphenol
5. 4-Methylphenol
6. 2-Nitrophenol
7. 2,4-Dimethylphenol
8. 2,4-Dichlorophenol
9. 2,6-Dichlorophenol
10. 4-Chloro-3-methylphenol
11. 2,4,5-Trichlorophenol
12. 2,4,6-Trichlorophenol
13. 2,4-Dinitrophenol
14. 4-Nitrophenol
15. 2,3,4,6-Tetrachlorophenol
16. 2-Methyl-4,6-dinitrophenol

IS 2,4,6-Tribromophenol
17. Pentachlorophenol
18. Dinoseb

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Quantification

- Internal Standard !!
- For complex Matrices – Standard Addition
- Extraction is an Equilibrium!!
- Extraction parameter needs to be kept constant:
  - Stir velocity
  - Temperature
  - Sample matrix (Salt?)
  - Fiber position in the sample
  - Extraction time

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Conclusion

- One Step Extraction
- Micro Technology
- Trace Analysis
- 100% Solvent Free
- Equilibrium Technology
  - Control your T‘s (Time, Temp., Technique)
- Suitable for Liquids (Water), Gases or Solids
- Quantitative
- Automation possible
  - CTC
  - Gerstel
  - Varian
  - Thermo

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Supelco SPME Bulletins

925 “SPME-Applications Guide” **(only on CD & web)**

923 “Theory and Optimization of Conditions”

928 “Trouble Shooting guide”

929 “Practical Guide to Quantification SPME”

901 “Drugs, Alcohol, org. Solvents in Biological Fluids”

922 “Forensic Applications: Explosives, Fire Debris, and Drugs of Abuse”

869 “Flavour and Fragances”

All on the SPME-CD plus additional applications & videos

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Thank you!

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