

Solid Phase Microextraction Theory and Basics of a modern Sample Preparation Technique



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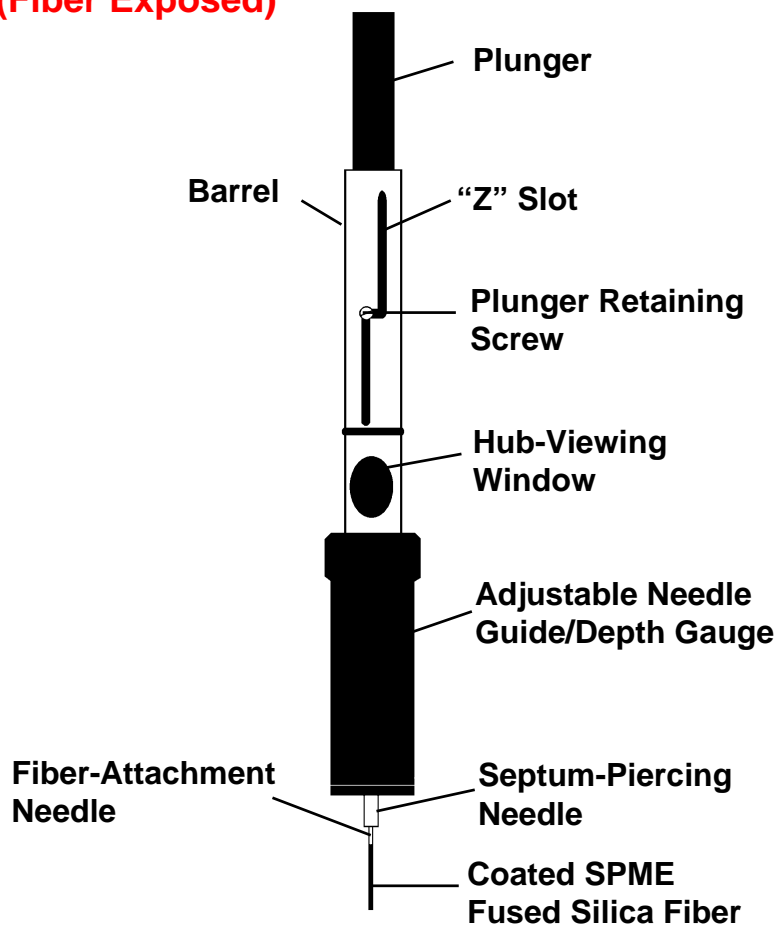


SPME History

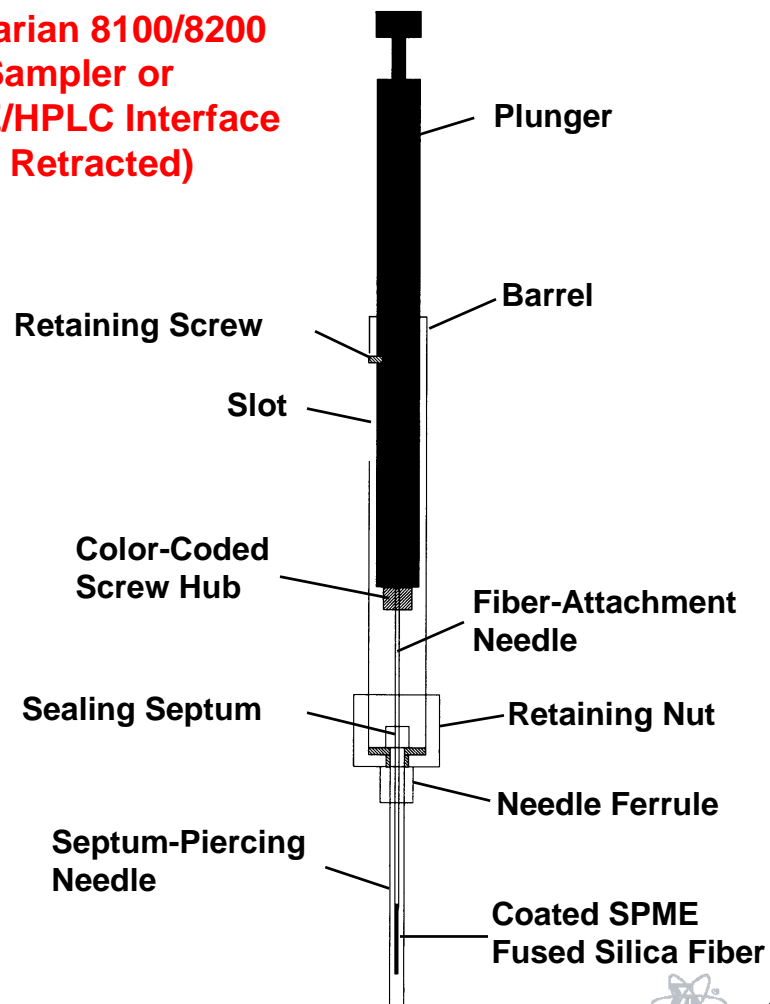
- Patented Technology of the University of Waterloo, Canada
- Inventor: Janusz Pawliszyn, Ph.D.
- Automisation by Varian (AS 8200 & CTC CombiPal).
 - CTC CombiPal makes the SPME compatible with most GCs

SPME Holders

For Manual Sampling
(Fiber Exposed)



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



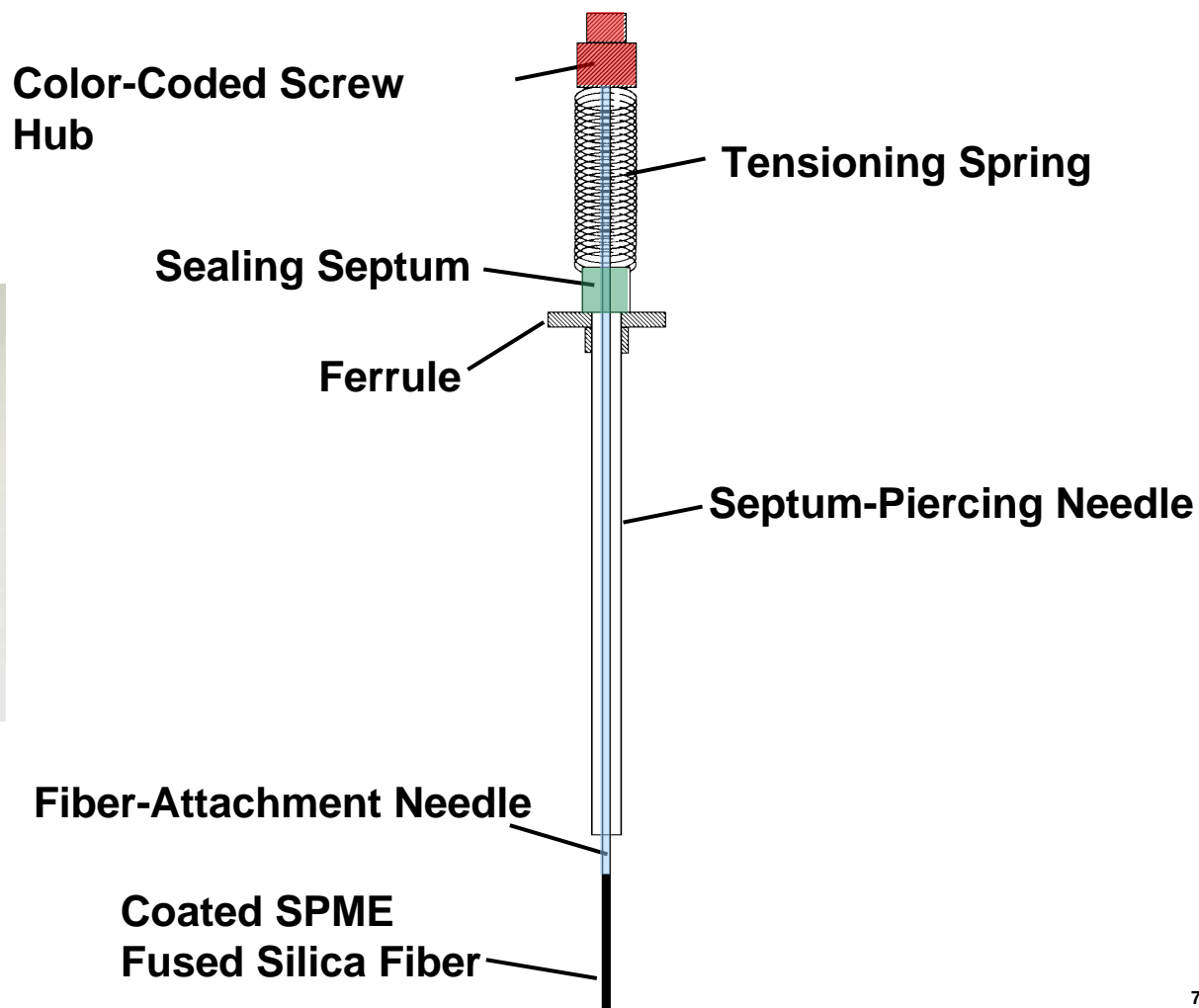
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SPME Fiber Assembly Detail (Manual)





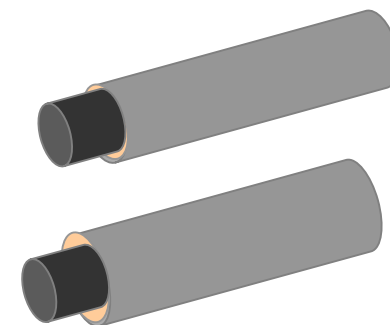
Types of SPME Fiber Assemblies

- **Assemblies for holders**

- manual
- autosampler style (no spring)

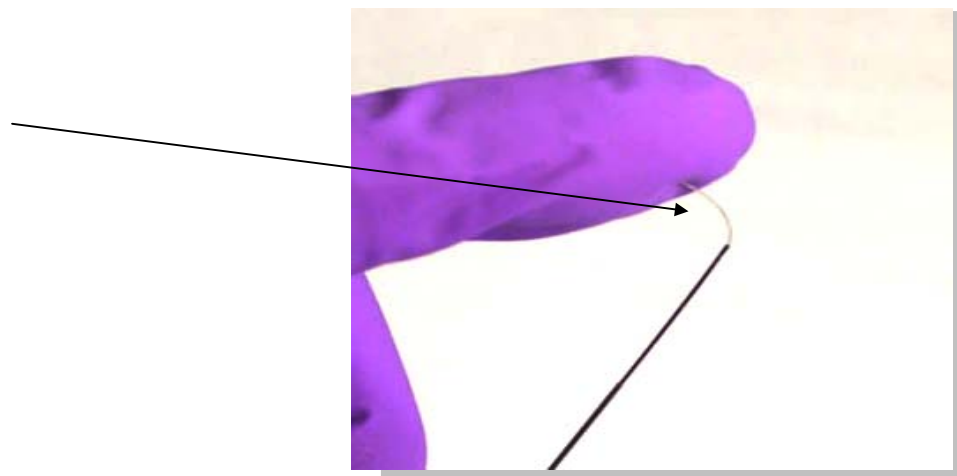
- **Gauge size of piercing needle**

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



- **Types of fiber core**

- Fused silica
- Stableflex
- Metal **NEW!**

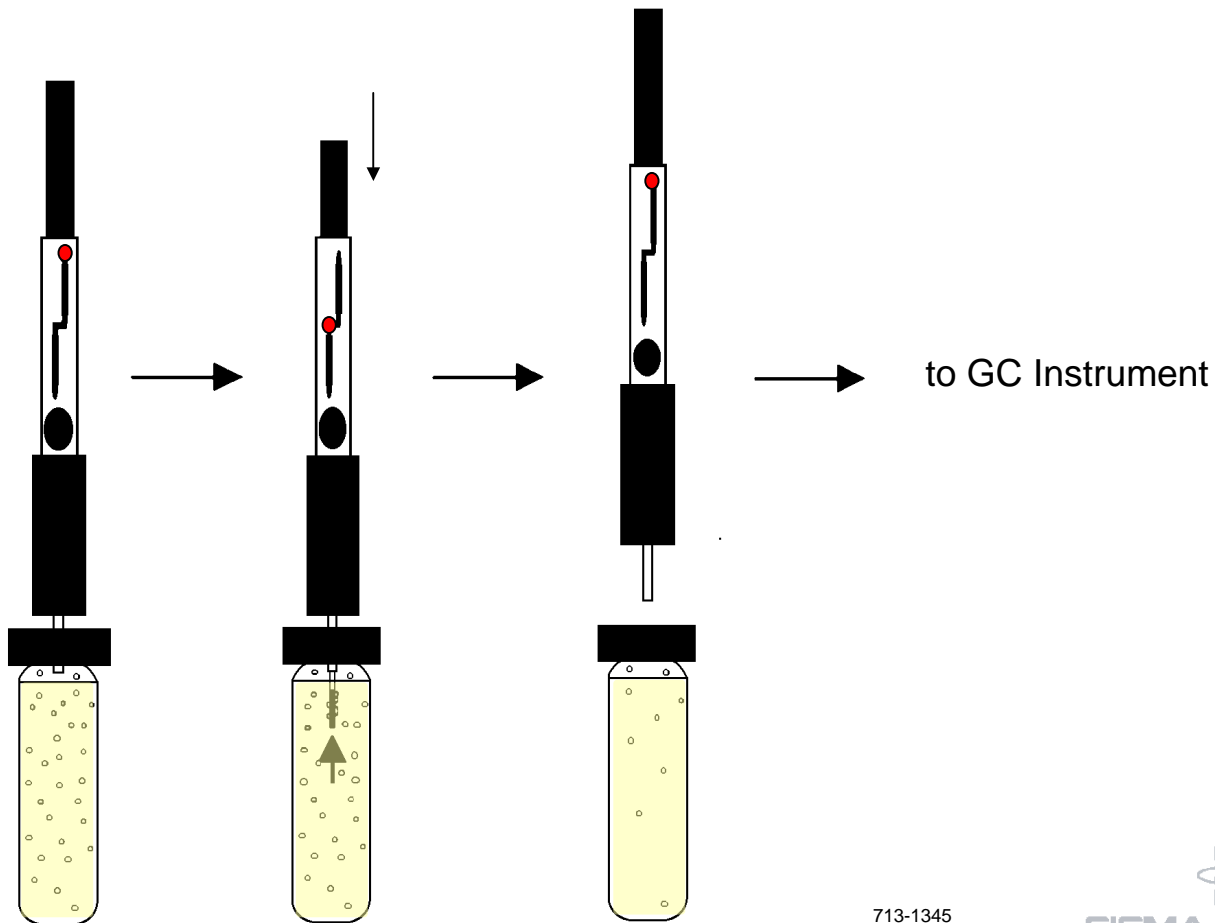


Extraction Procedure for SPME

Pierce
Sample Septum

Expose Fiber/Extract

Retract
Fiber/Remove



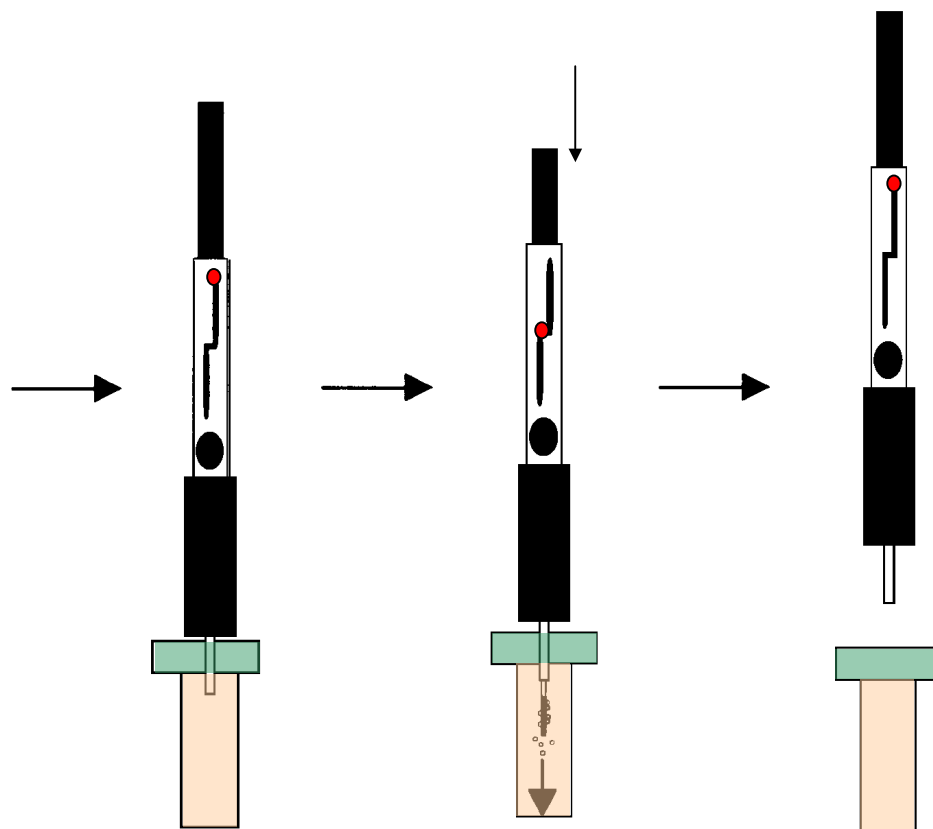


Desorption Procedure for SPME

Pierce GC
Inlet Septum

Expose
Fiber/Desorb

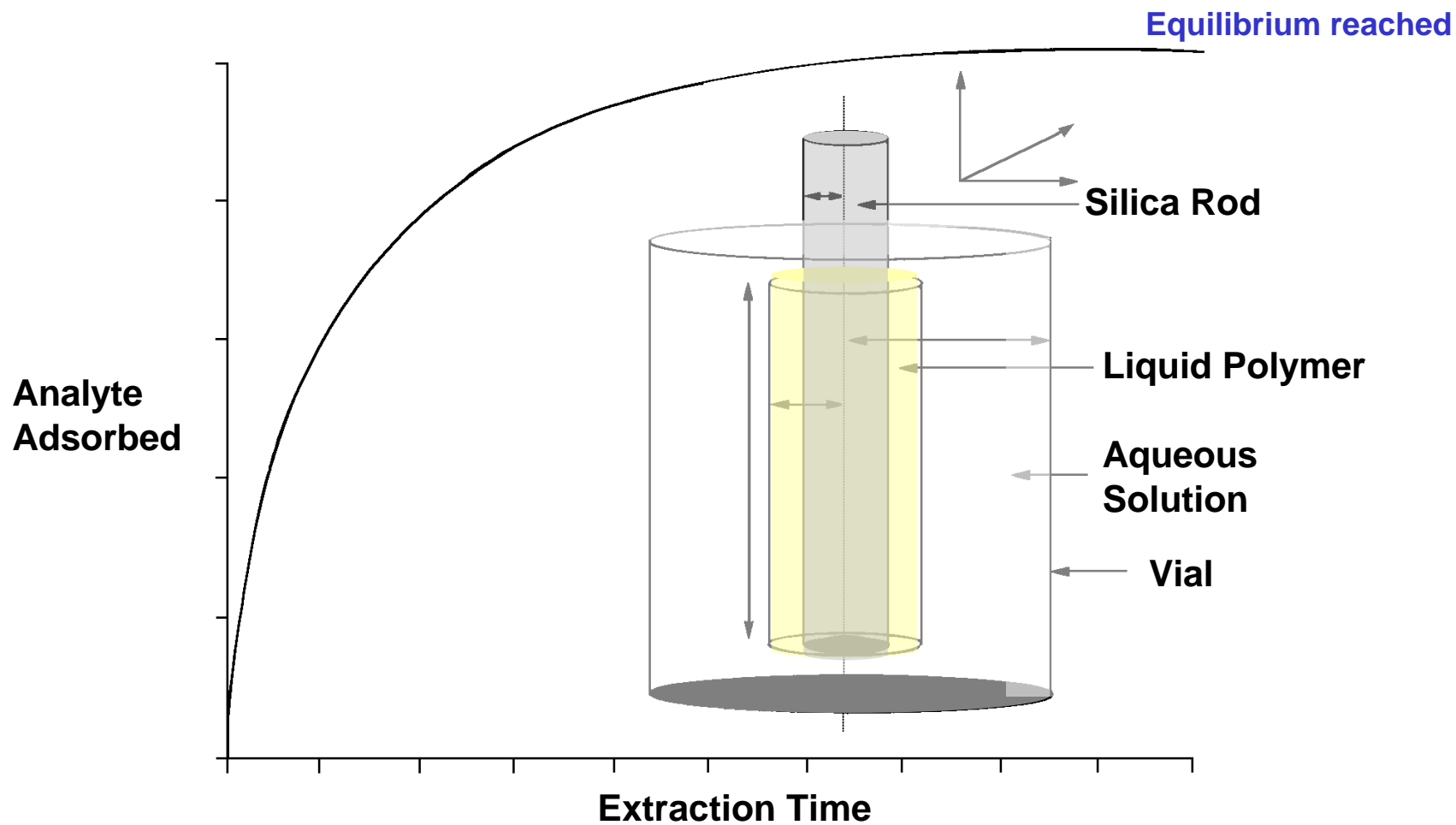
Retract
Fiber/Remove



to Column

713-1345

Adsorption Mechanism for SPME





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 sample ($V_s \gg V_f$):

$$n_s = KV_f C_0$$

K Distribution Constant 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

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

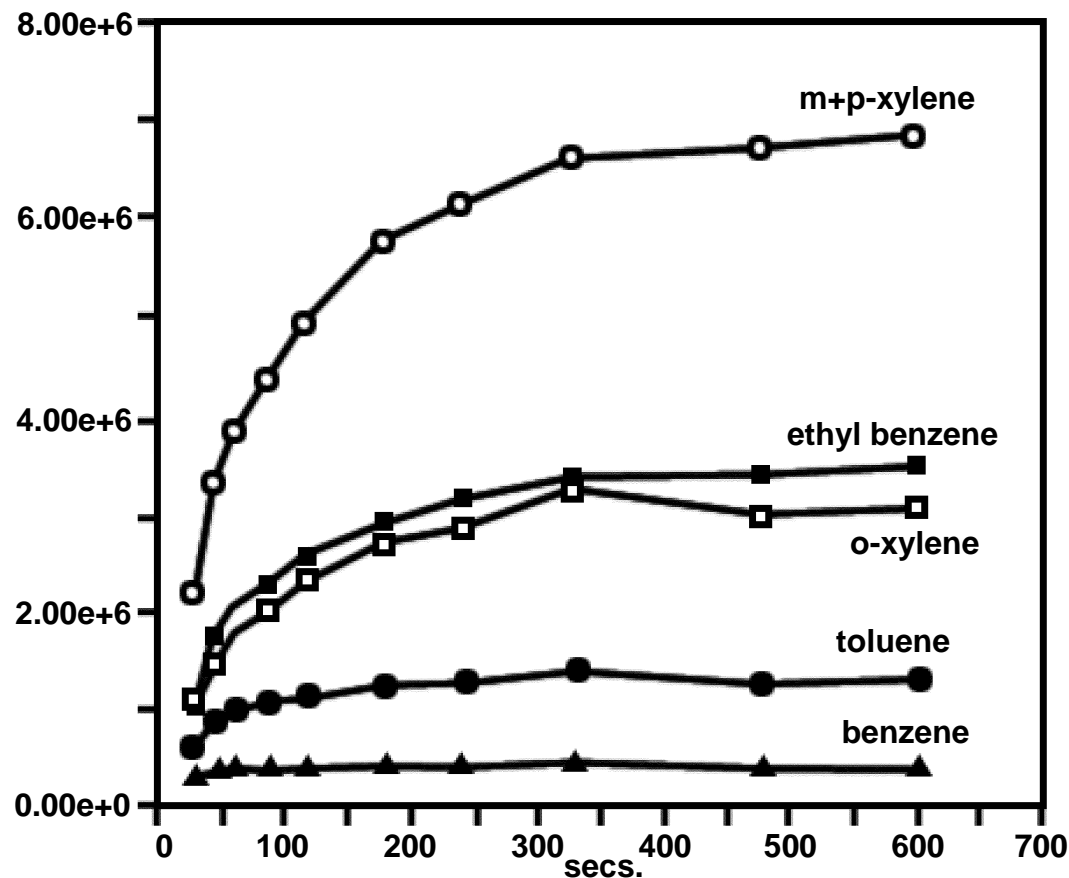


Figure courtesy of J. Pawliszyn, et al., University of Waterloo, Ontario, Canada.



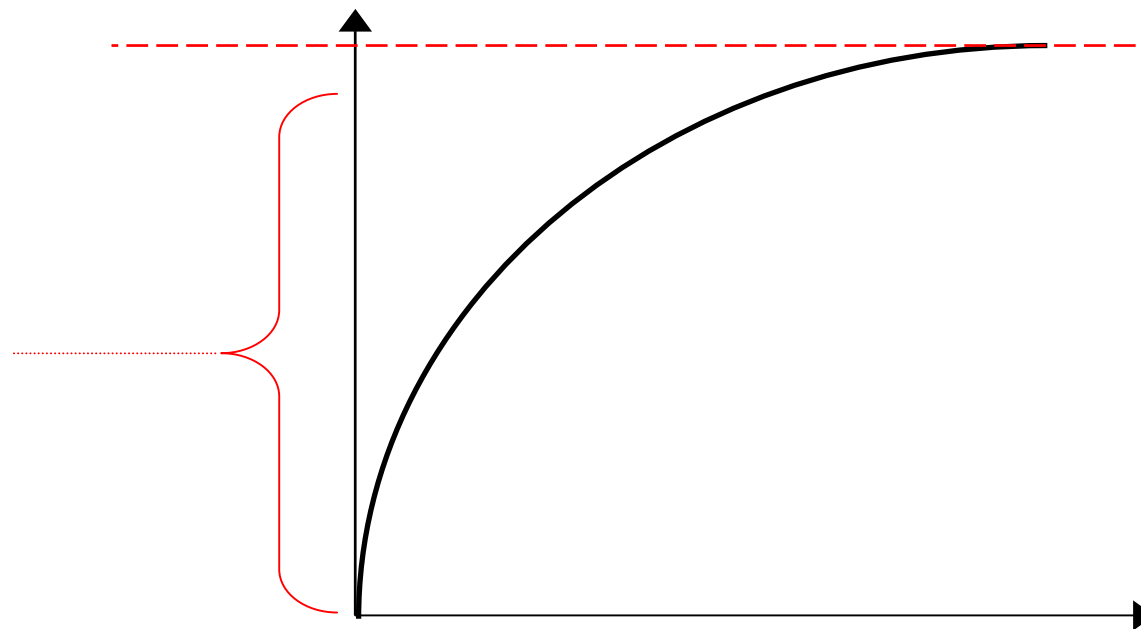


Physical Factors Affecting Sample Recovery

Influence on Equilibrium

Influence on Kinetics

- Stiring
- (Temperature)

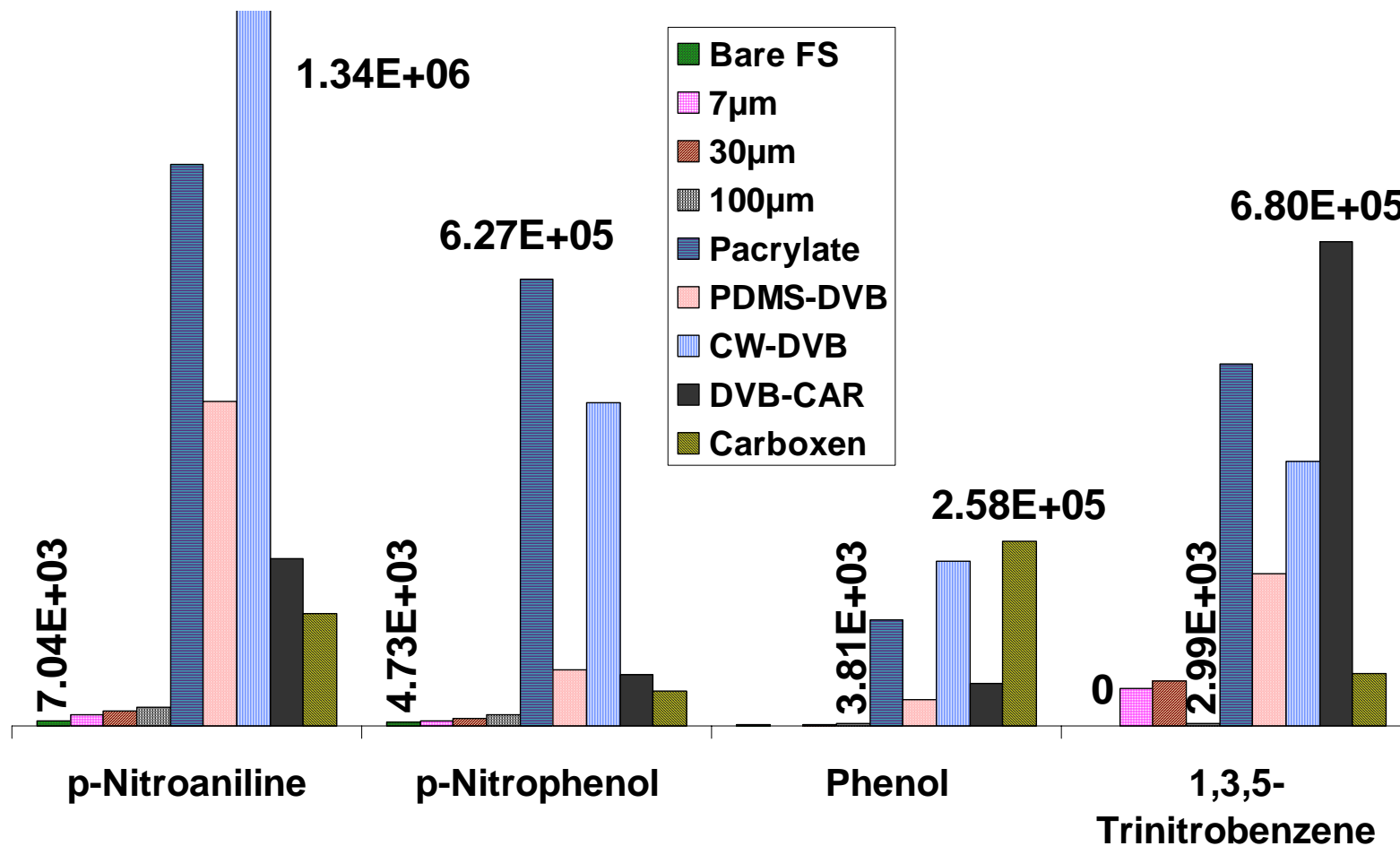




Factors Affecting Sample Recovery

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

Area Response depending on Fiber Type





Available SPME Fibers, by Film Type

- **Absorption Fibers**

- Polydimethylsiloxane (PDMS) 7, 30, and 100µm
- Polyacrylate (PA)
- Polyethyleneglycol (PEG) **NEW!**

Unpolar

Polar

Polar

- **Adsorption fibers (with particles)**

- Carboxen-polydimethylsiloxane(CAR-PDMS)
- Polydimethylsiloxane-divinylbenzene (PDMS-DVB)
- Divinylbenzene/Carboxen- Polydimethylsiloxane (DVB-CAR-PDMS)
- ~~Carbowax-divinylbenzene (CW-DVB)~~
- ~~Carbowax-templated resin (CW-TPR) (HPLC only)~~

Adsorption

Adsorption

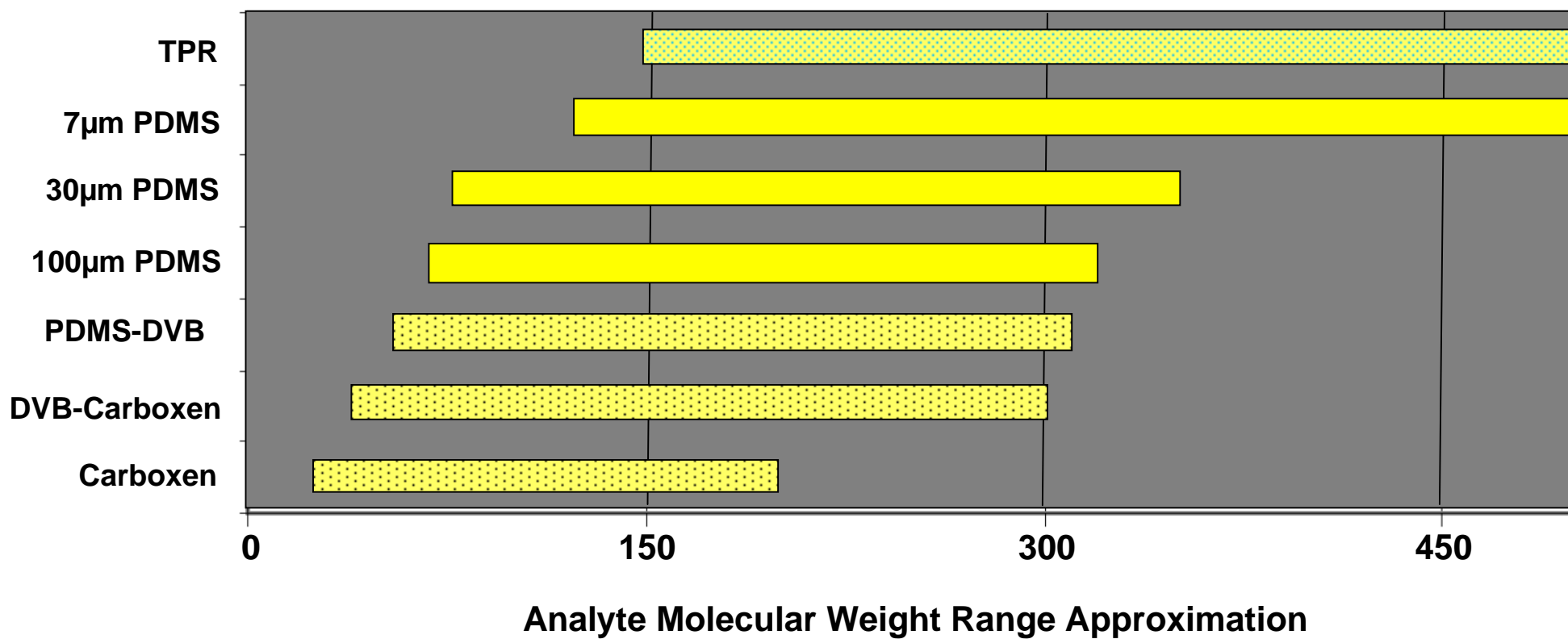
Adsorption

Polar & Adsorption

Polar & Adsorption



SPME Fibers, by Adsorption Strength Estimation





Effects of Fiber Coating Porosity

- **Better for trace level analyses**
- **Increasing porosity retains analytes more tightly**
- **Varying pore size increases analyte selectivity**
- **DVB: Primarily meso and macroporous**
- **Carboxen™: micro, meso, and macroporous**

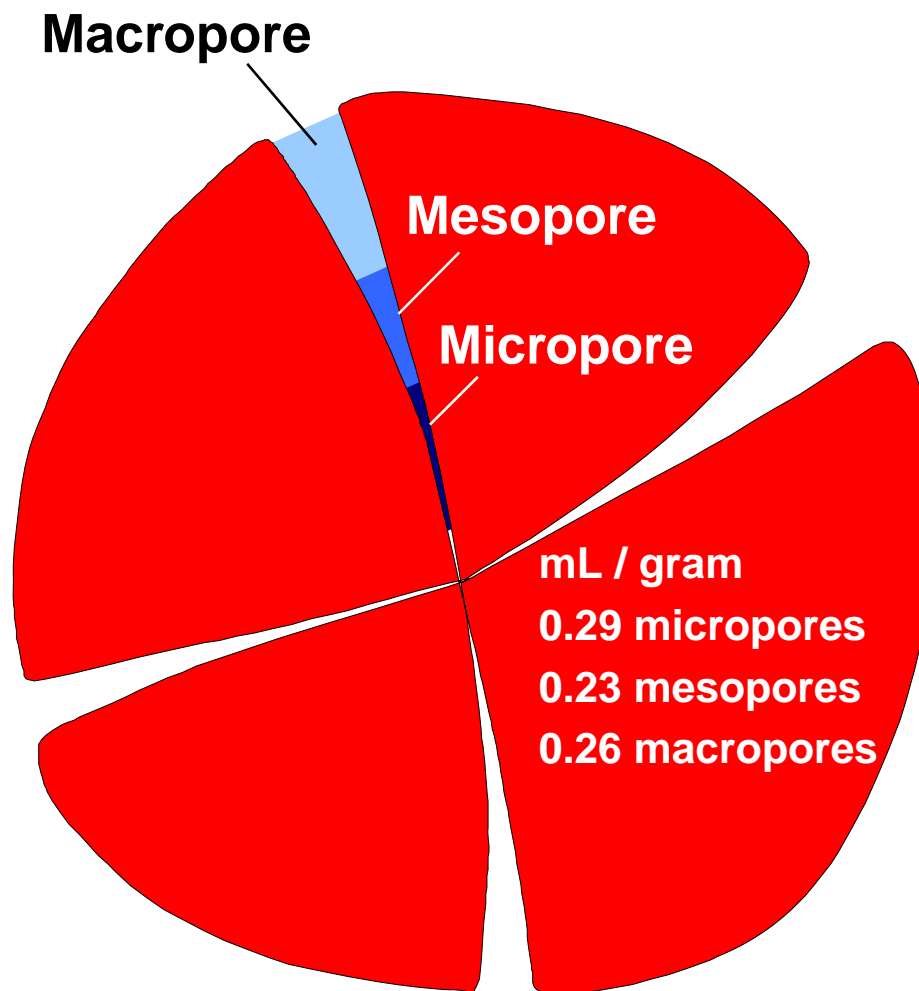
Carboxen™ Particle

Pores - Definition:

Any cavity present on a solid surface which has a depth:width ratio of ~10:1

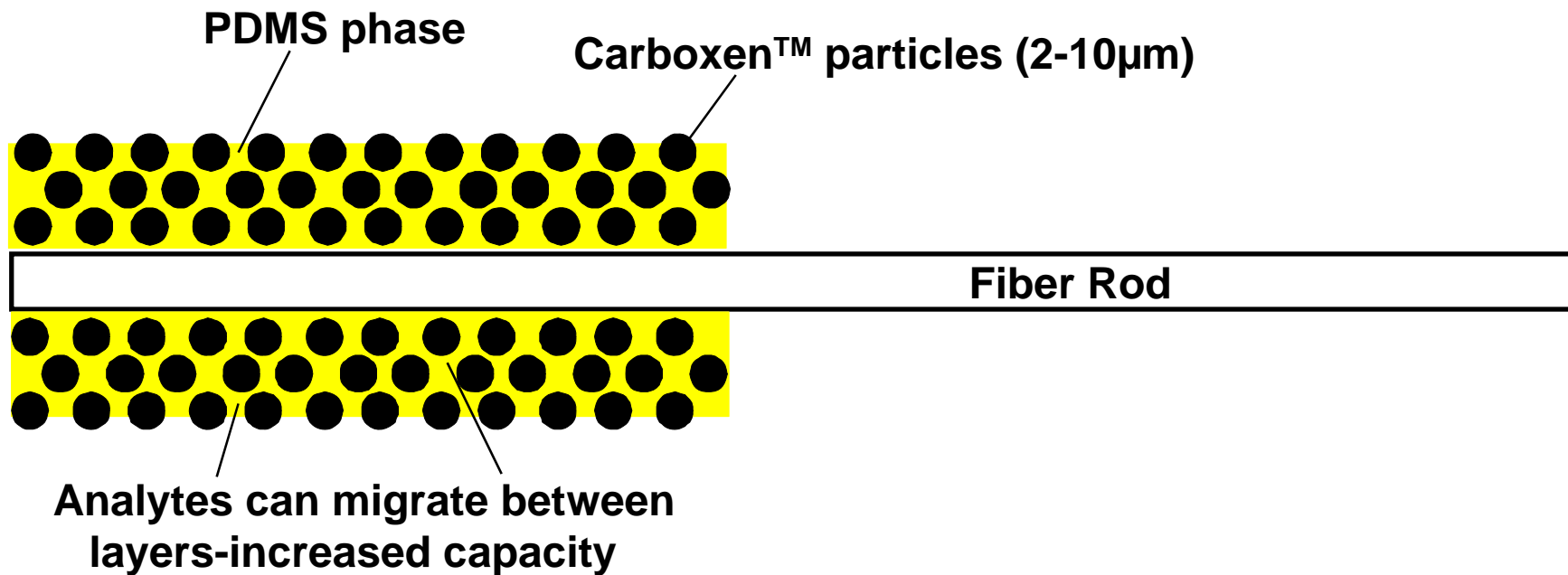
Pore sizes:

Macro: > 500Å
Meso: 20 - 500Å
Micro: < 20Å





Carboxen/PDMS Fiber





Comparison of SPME Fibers for the Extraction of Small Hydrocarbons

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

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



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

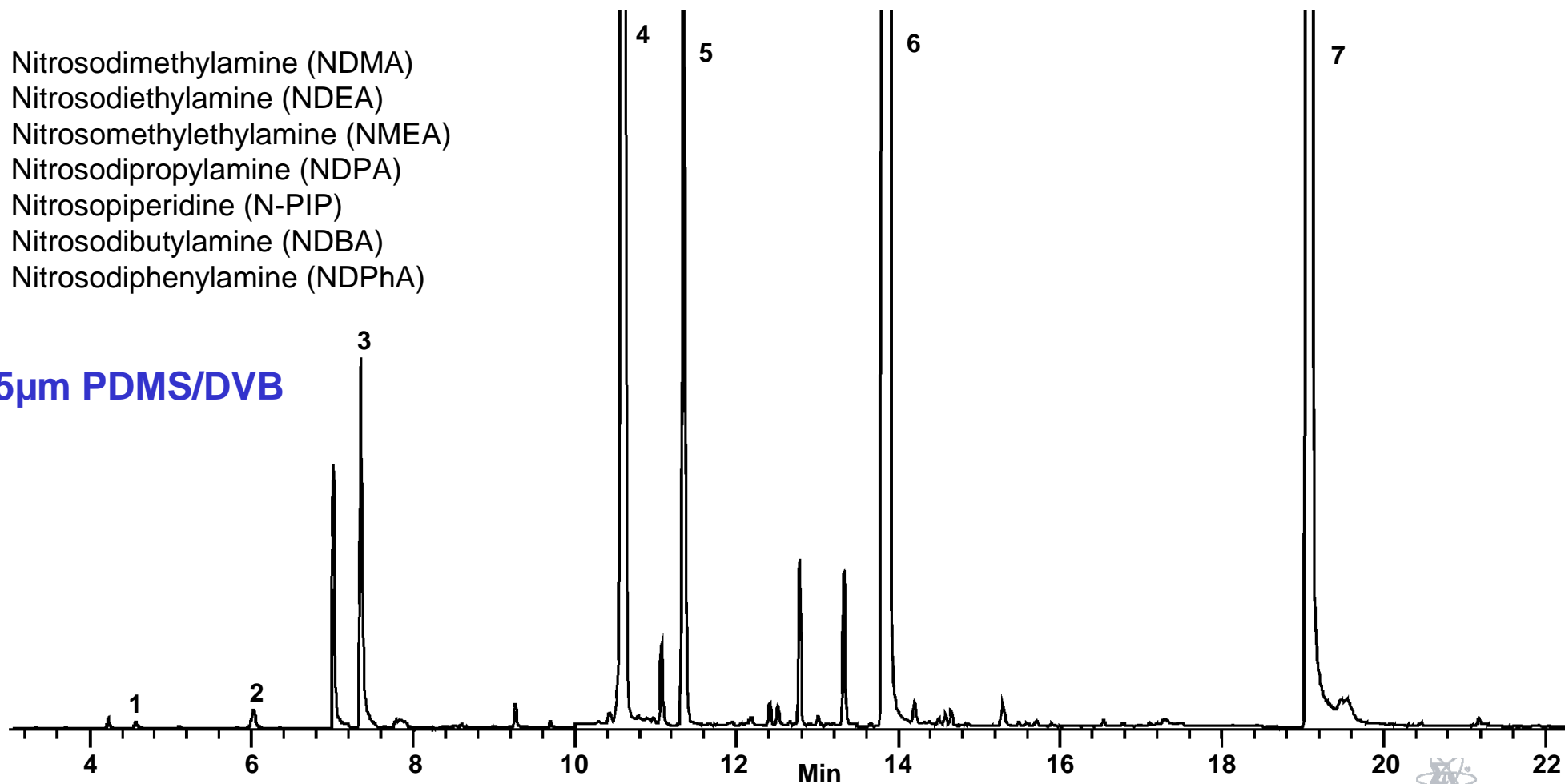
- Analytes are extracted by partitioning
 - liquid phase
 - retains by thickness of coating
- Analytes do not compete for sites
- Fibers can have high capacity



10ppb Nitrosamines in Water: SPME-GC/MS

1. Nitrosodimethylamine (NDMA)
2. Nitrosodiethylamine (NDEA)
3. Nitrosomethylethylamine (NMEA)
4. Nitrosodipropylamine (NDPA)
5. Nitrosopiperidine (N-PIP)
6. Nitrosodibutylamine (NDBA)
7. Nitrosodiphenylamine (NDPhA)

65 μ m PDMS/DVB



Chromatogram courtesy of J. Clark, Liggett Group, Inc.

Sulfur Gases at 1ppm by SPME

Carboxen™/PDMS Fiber

Extraction Conditions

Sample: Sulfur gases in air at 1ppm, 250mL bulb

Extraction: headspace, 5 min, ambient temp.

Desorption: 2 min, 250°C

Chromatographic Conditions

Column: Supel-Q™ PLOT, 30m x 0.32mm ID

Oven: 45°C (0.75 min) to 250°C at 25°C/min

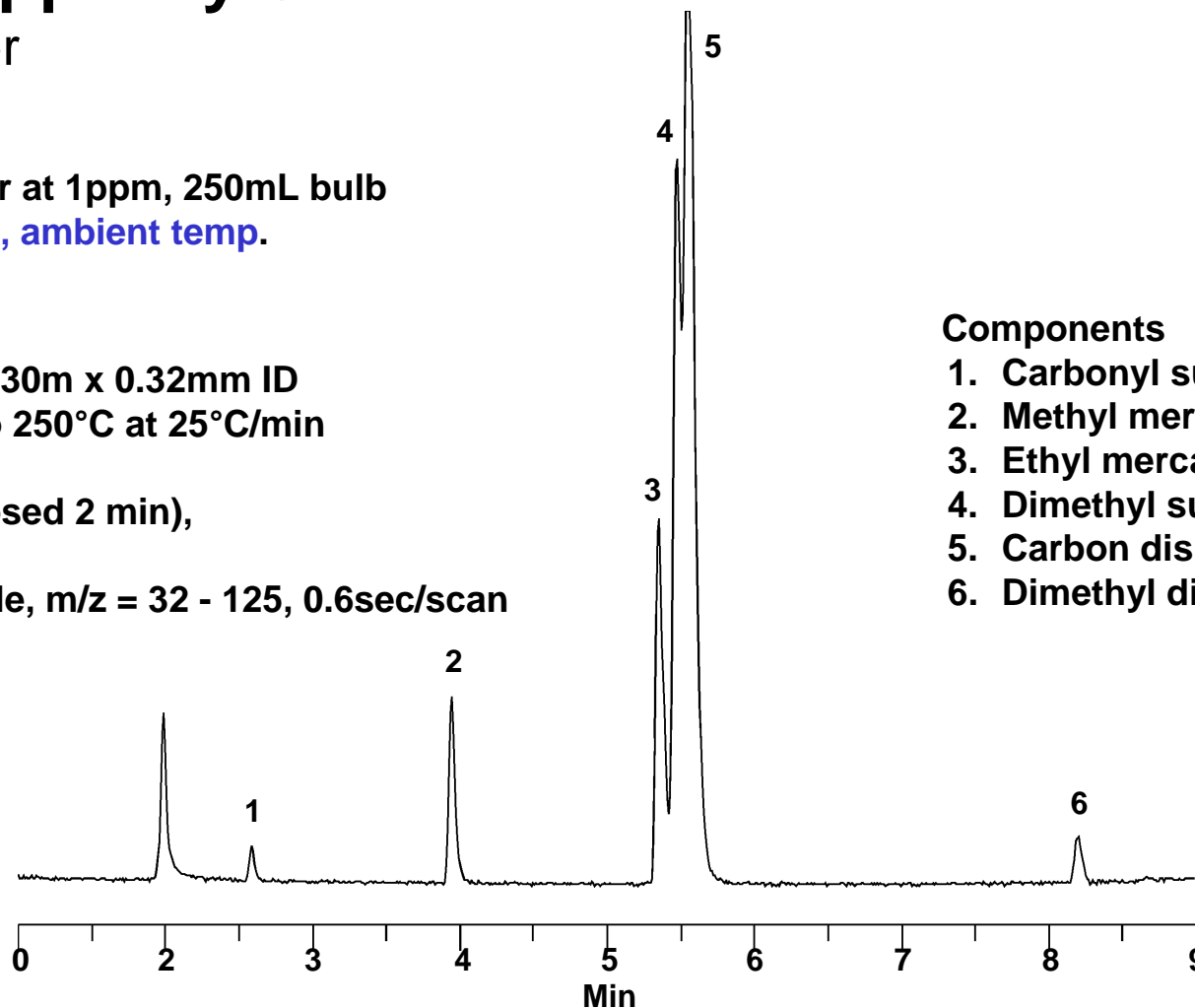
Carrier: helium, 25cm/sec

Injection: splitless/split (closed 2 min),
0.75mm ID liner

Detector: GC/MS quadrupole, m/z = 32 - 125, 0.6sec/scan

Components

1. Carbonyl sulfide
2. Methyl mercaptan
3. Ethyl mercaptan
4. Dimethyl sulfide
5. Carbon disulfide
6. Dimethyl disulfide



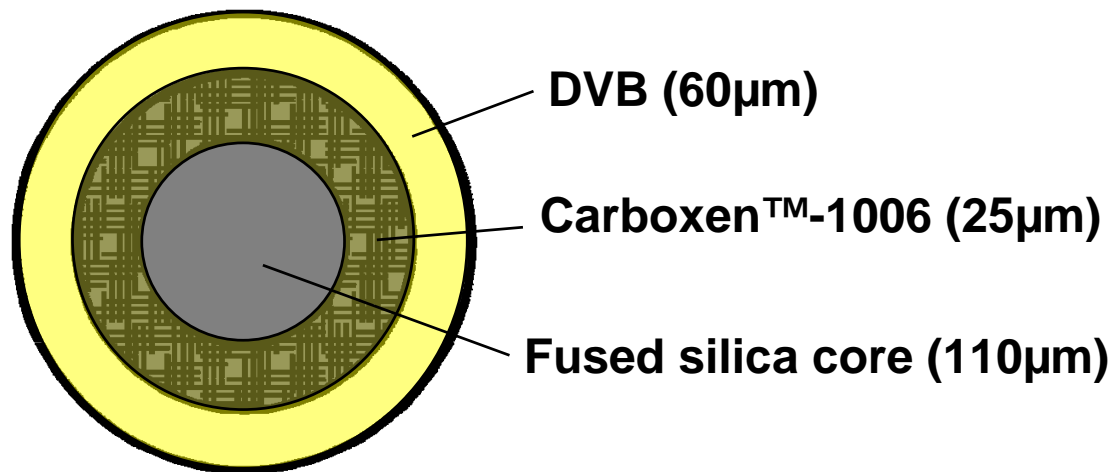
SPME Fibers for the Extraction of Hydrocarbons

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

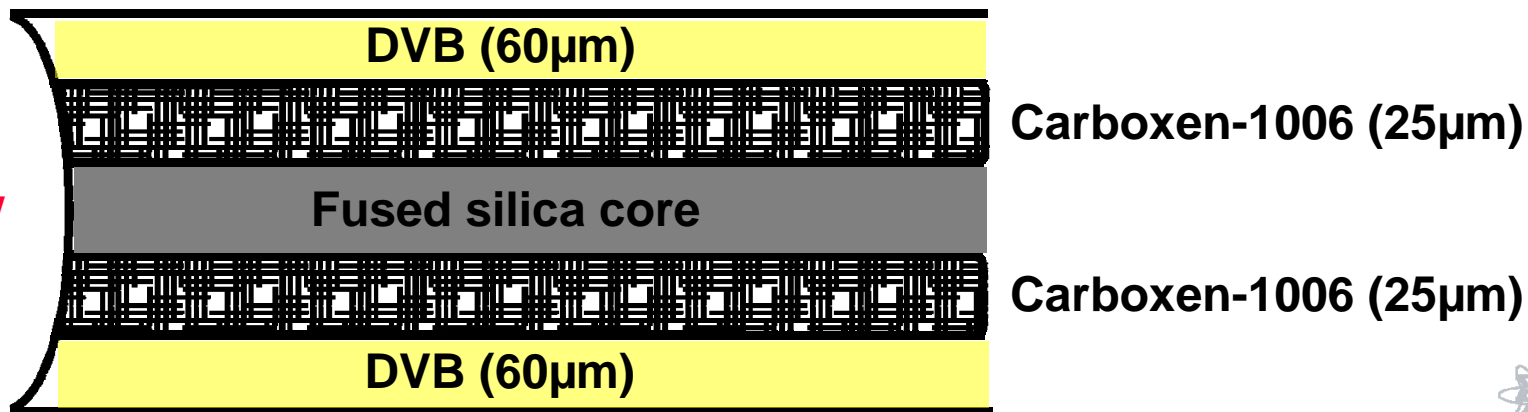


Dual-coated SPME Fiber

Front View



Side View



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

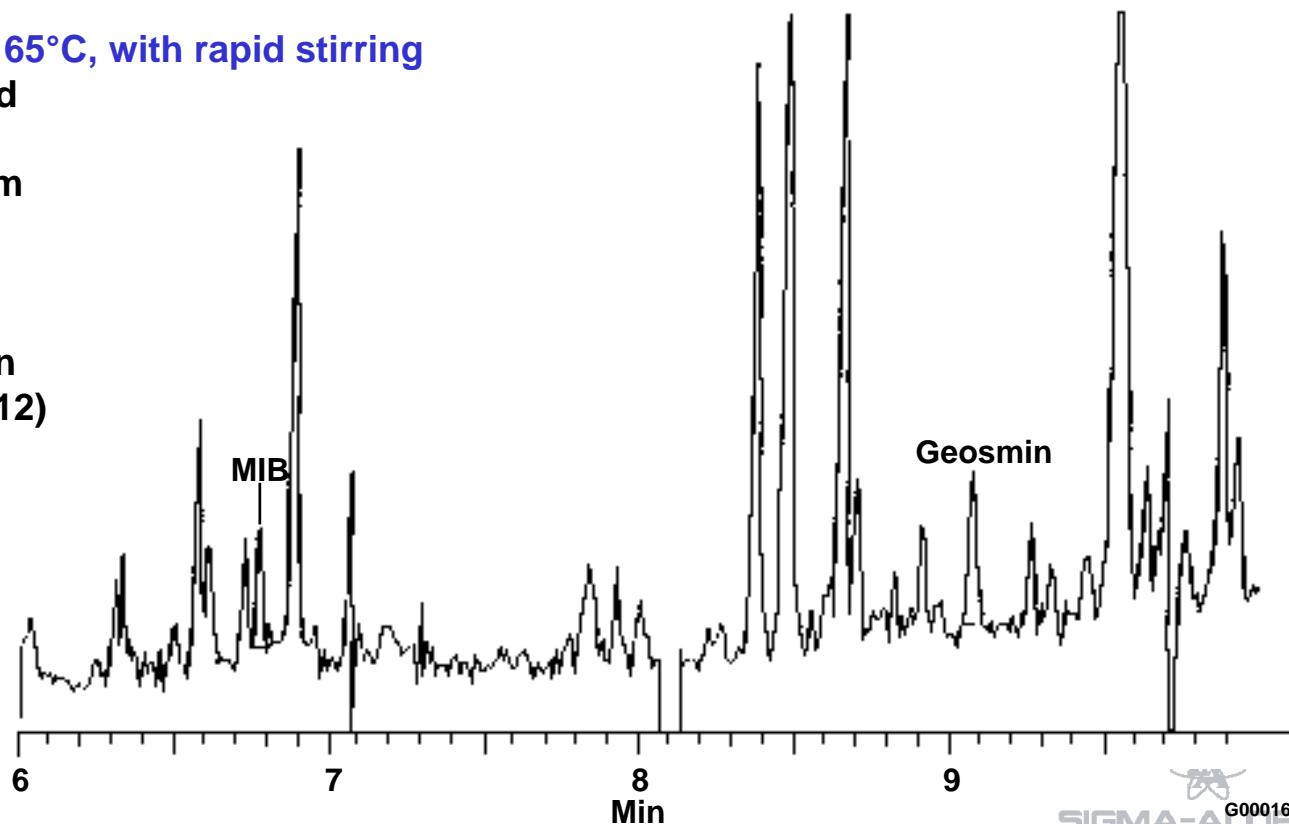
Extraction: heated headspace, 30 min, 65°C, with rapid stirring

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)





SPME Technique

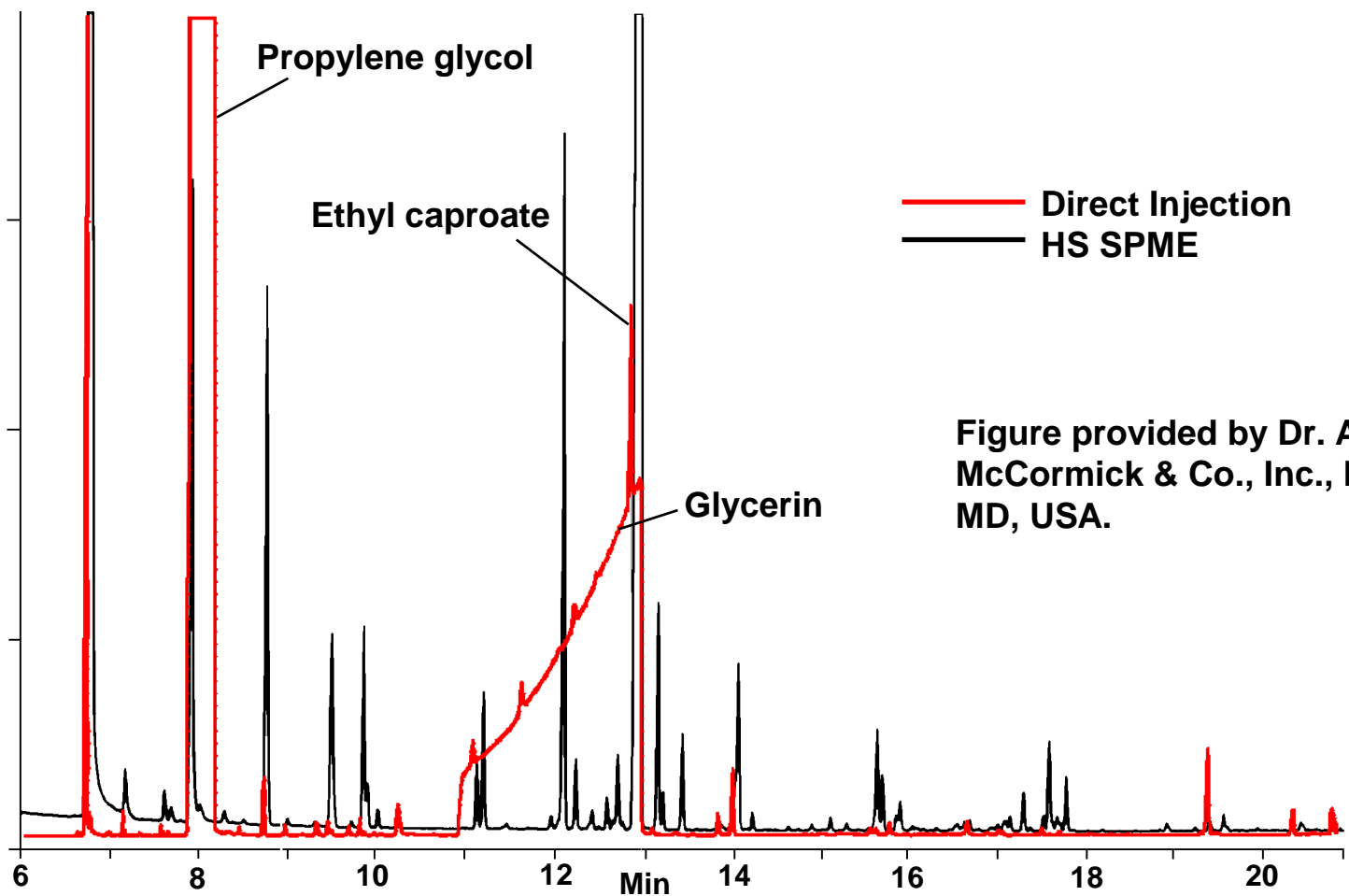
- **Extraction conditions**
 - Headspace
 - Direct Imersion
- **Desorption temperature**
- **Liner Diameter**
- **Sample Modifications**



Headspace vs. Direct Immersion

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

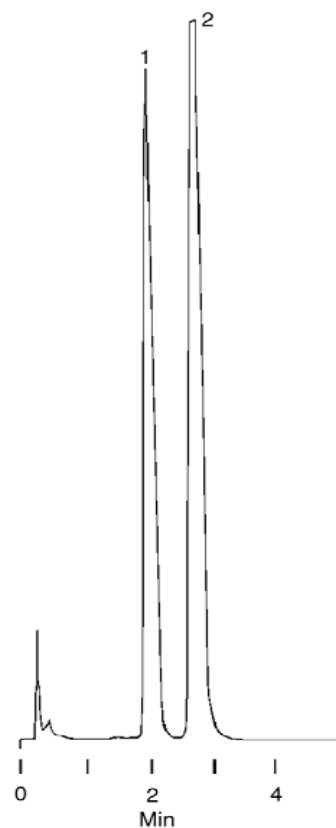
Fruit Punch Flavor by Headspace SPME Elimination of Glycerin Interference



Amphetamine and Methamphetamine in Urine

Sample: 1mL urine (100µg each analyte, 5µg d₅-methamphetamine, 0.7g K₂CO₃) in 12mL vial
SPME Fiber: **100µm polydimethylsiloxane**
Cat. No.: **5-7300** (manual sampling)
Extraction: headspace, 80°C, 5 min (sample incubated 20 min)
Desorption: 3 min, 250°C
Column: polydimethylsiloxane, 15m x 0.53mm ID, 2.0µm film
Oven: 110°C
Carrier: nitrogen, 25mL/min
Det.: FID, 250°C
Inj.: splitless, 250°C

Heated Headspace SPME



Conventional Heated Headspace

1. Amphetamine
2. Methamphetamine



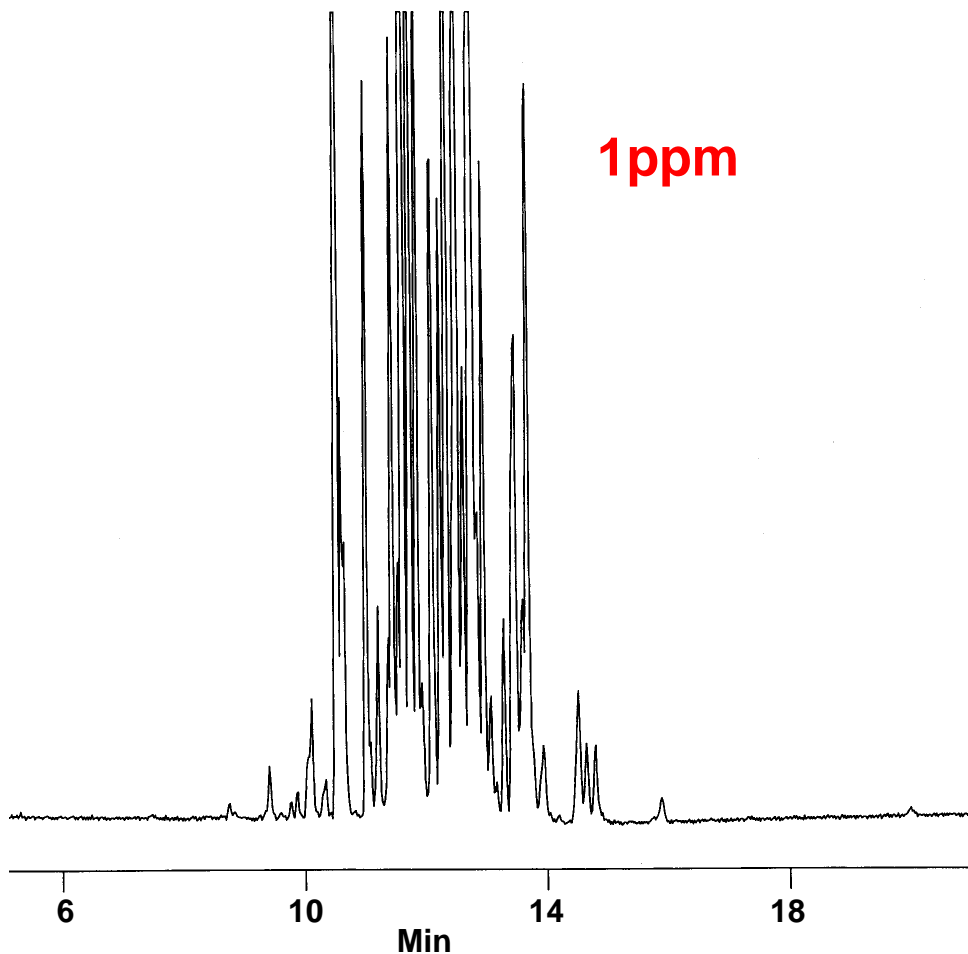
Figure provided by M. Yashiki, T. Kojima, T. Miyazaki, N. Nagasawa, and Y. Iwasaki, Dept. Legal Medicine, Hiroshima University School of Medicine, Hiroshima, Japan and K. Hara, Dept. Legal Medicine, Fukuoka University School of Medicine, Fukuoka, Japan.



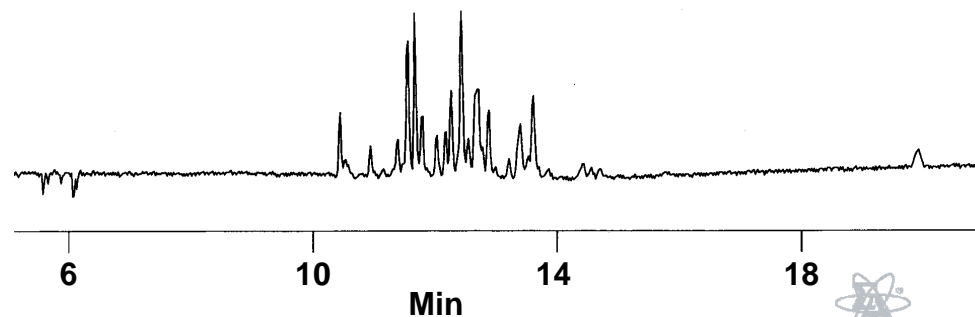
Analysis of PCBs From Soil

Sample: 0.5g soil + 15mL water in 40mL vial
SPME Fiber: 30µm PDMS
Extraction: headspace, 20 min, 45°C
Desorption: 5 min, 250°C
Column: SPB™-35, 15m x 0.20mm, 0.20µm film
Oven: 120°C (1 min) to 290°C at 15°C/min
Carrier: helium, 30cm/sec
Inj.: split, 100:1, 250°C
Det.: ECD, 300°C

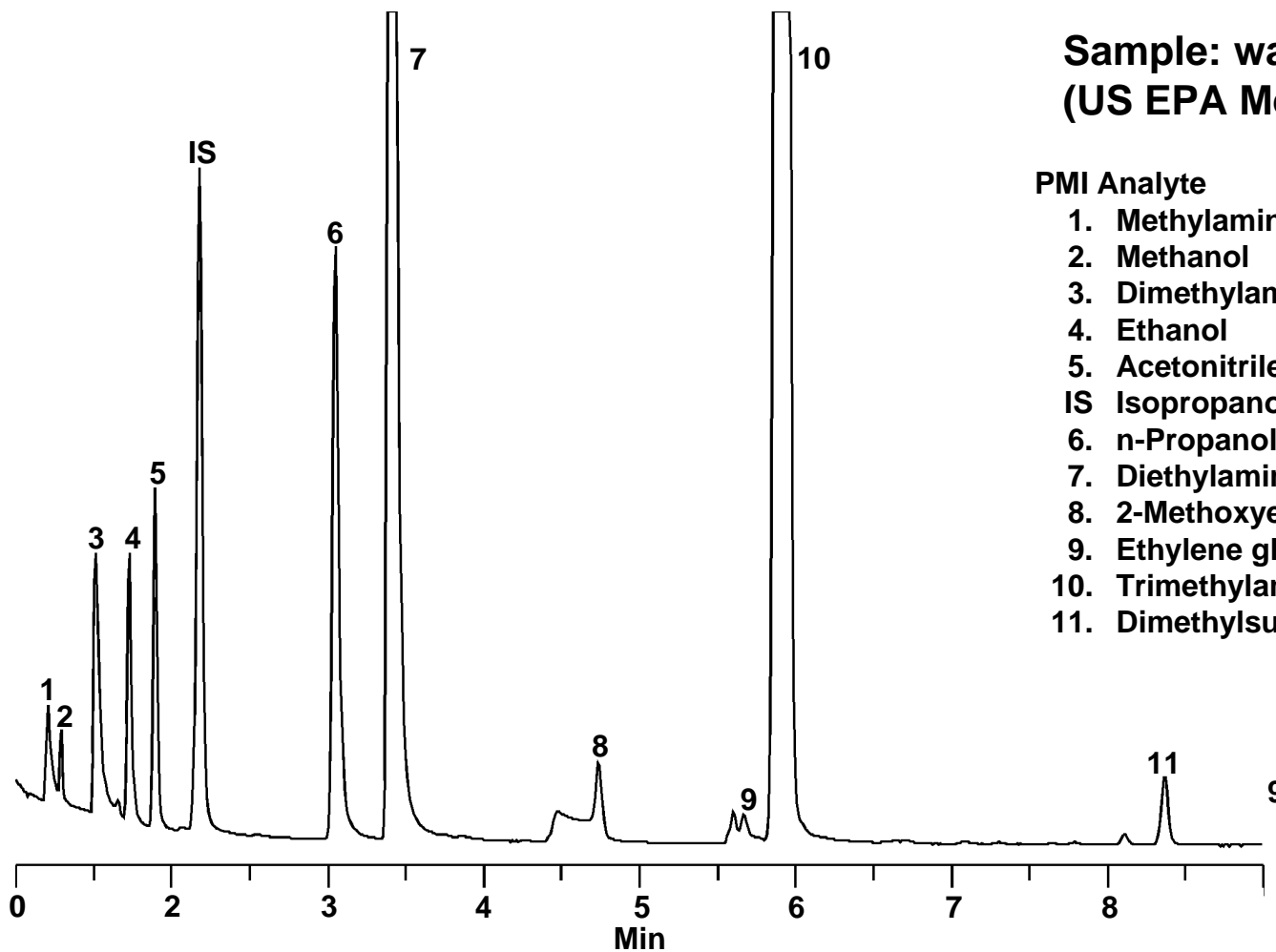
1ppm



50ppb



Nonpurgeables: Heated Headspace SPME-GC/MS

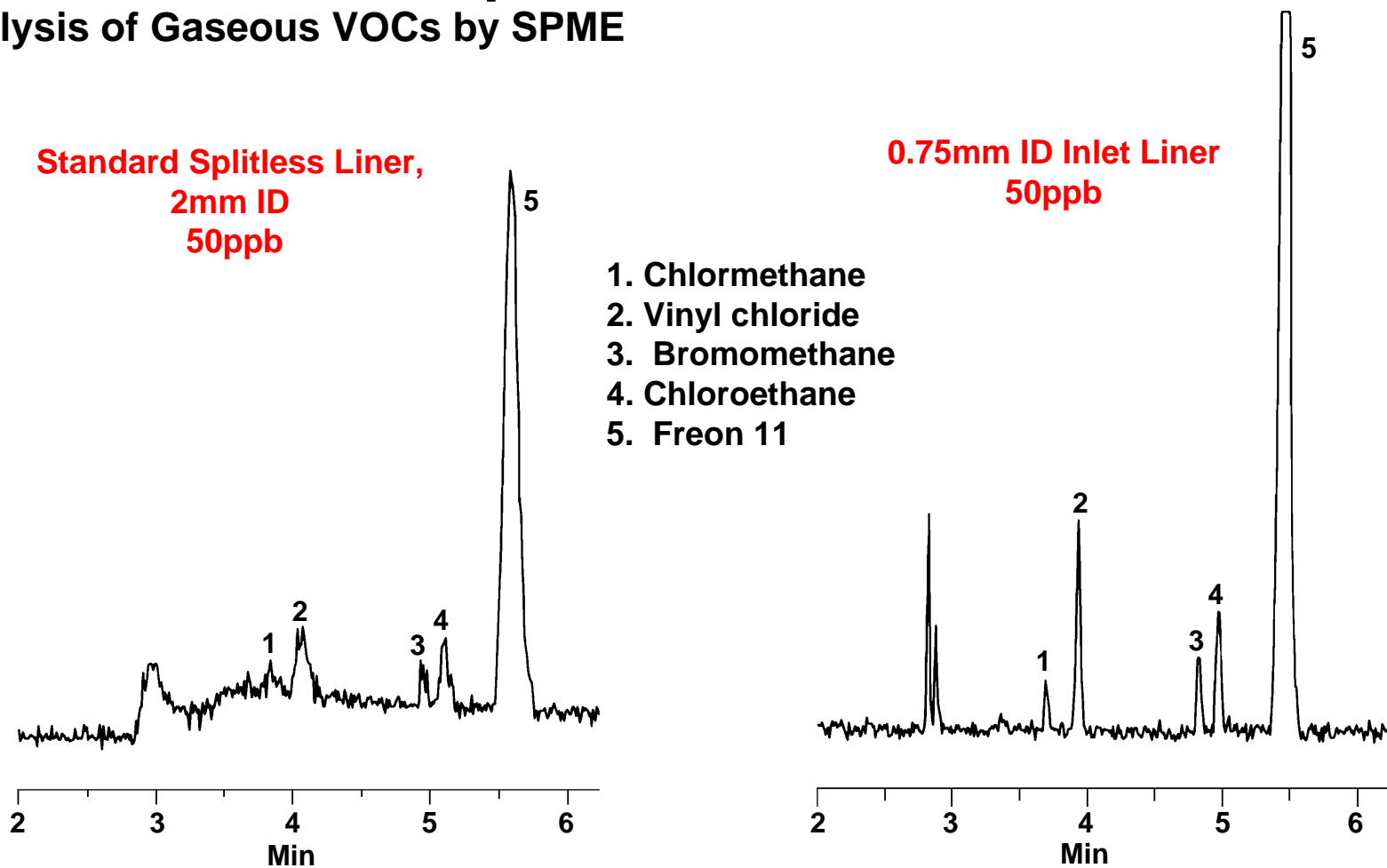


Sample: water + 27% NaCl, pH 11
(US EPA Method 1671)

PMI Analyte	Conc. (ppm)	MDL (ppm)
1. Methylamine	0.8	0.5
2. Methanol	10	5
3. Dimethylamine	0.8	0.5
4. Ethanol	10	5
5. Acetonitrile	10	5
IS Isopropanol (int. std.)	10	
6. n-Propanol	5	1
7. Diethylamine	0.8	0.1
8. 2-Methoxyethanol	25	10
9. Ethylene glycol	50	25
10. Trimethylamine	0.8	0.05
11. Dimethylsulfoxide (DMSO)	20	10

Liner Diameter - Comparison

for Analysis of Gaseous VOCs by SPME



794-0050, 0051



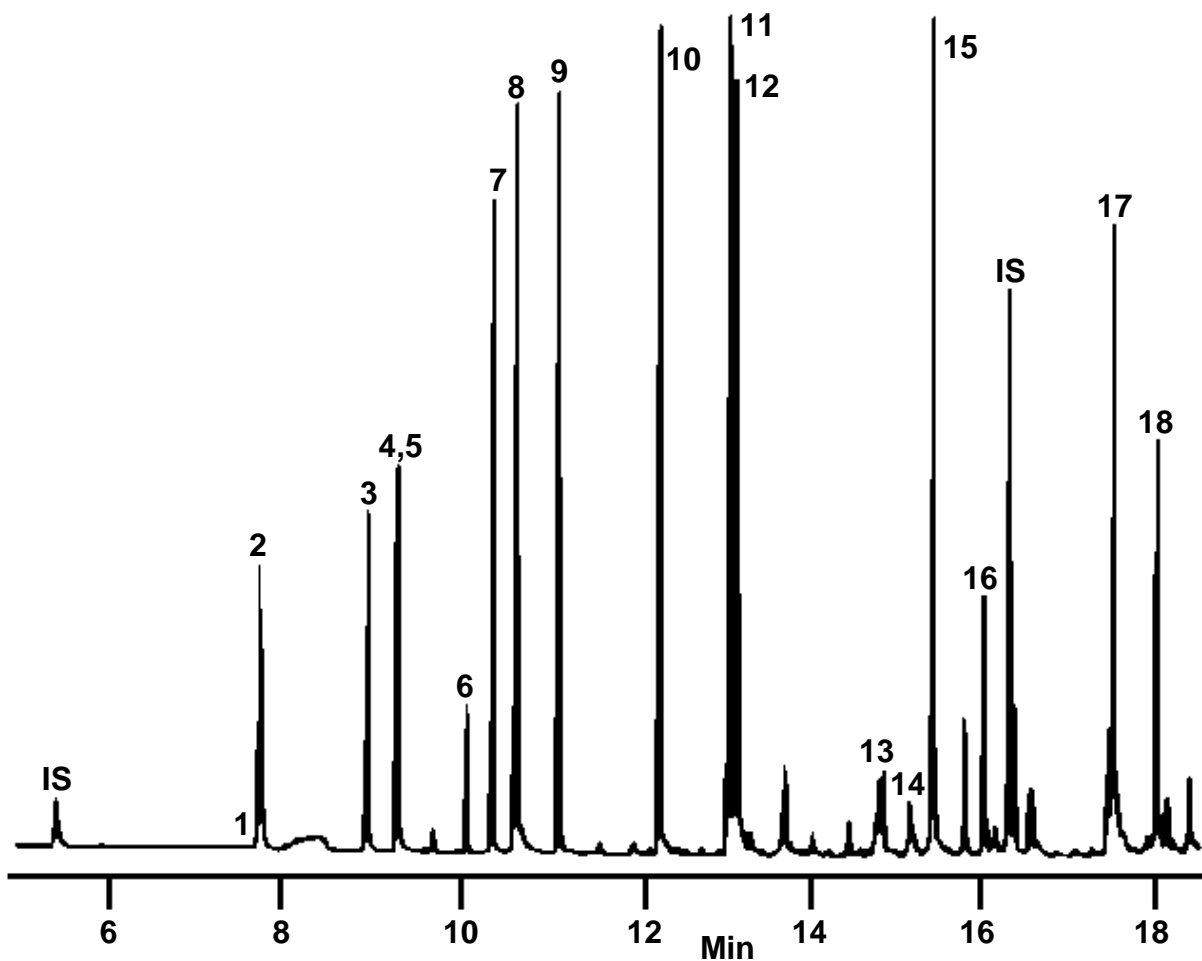
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Sample Modifications

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

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





Sample modifications

- **Salz**
- **pH**
- **Derivatisation of Analytes on the Fiber**
 - Fiber doted with Reagent put into Sample
 - Sampled Fiber put into Reagent



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**
- **Automatization possible (e.g. CTC)**





Supelco SPME Bulletins

- **# 925** “**SPME-Applications Guide**” (only on CD & web)
- **# 923** “**Theory and Optimization of Conditions**”
- **# 901** “**Drugs, Alcohol, org. Solvents in Biological Fluids**”
- **# 922** “**Forensic Applications: Explosives, Fire Debris, and Drugs of Abuse**”
- **# 869** “**Flavour and Fragrances**”

All on the SPME-CD plus additional applications.

Thank You!

SPME



S SUPELCO

Sample
Prep
Made
Easy