

ISO 9001
REGISTERED

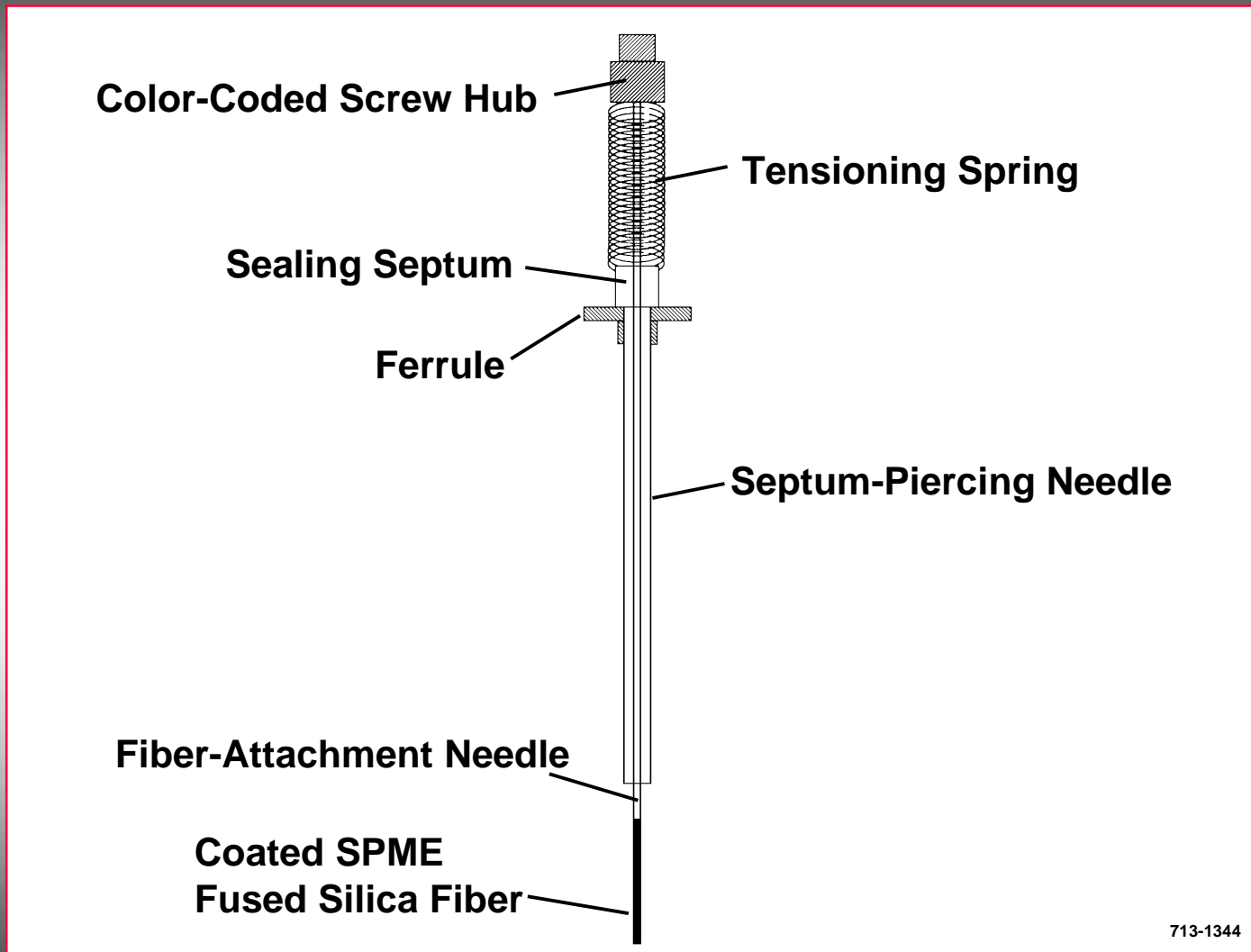


Improved Performance of SPME Fibers and Applications

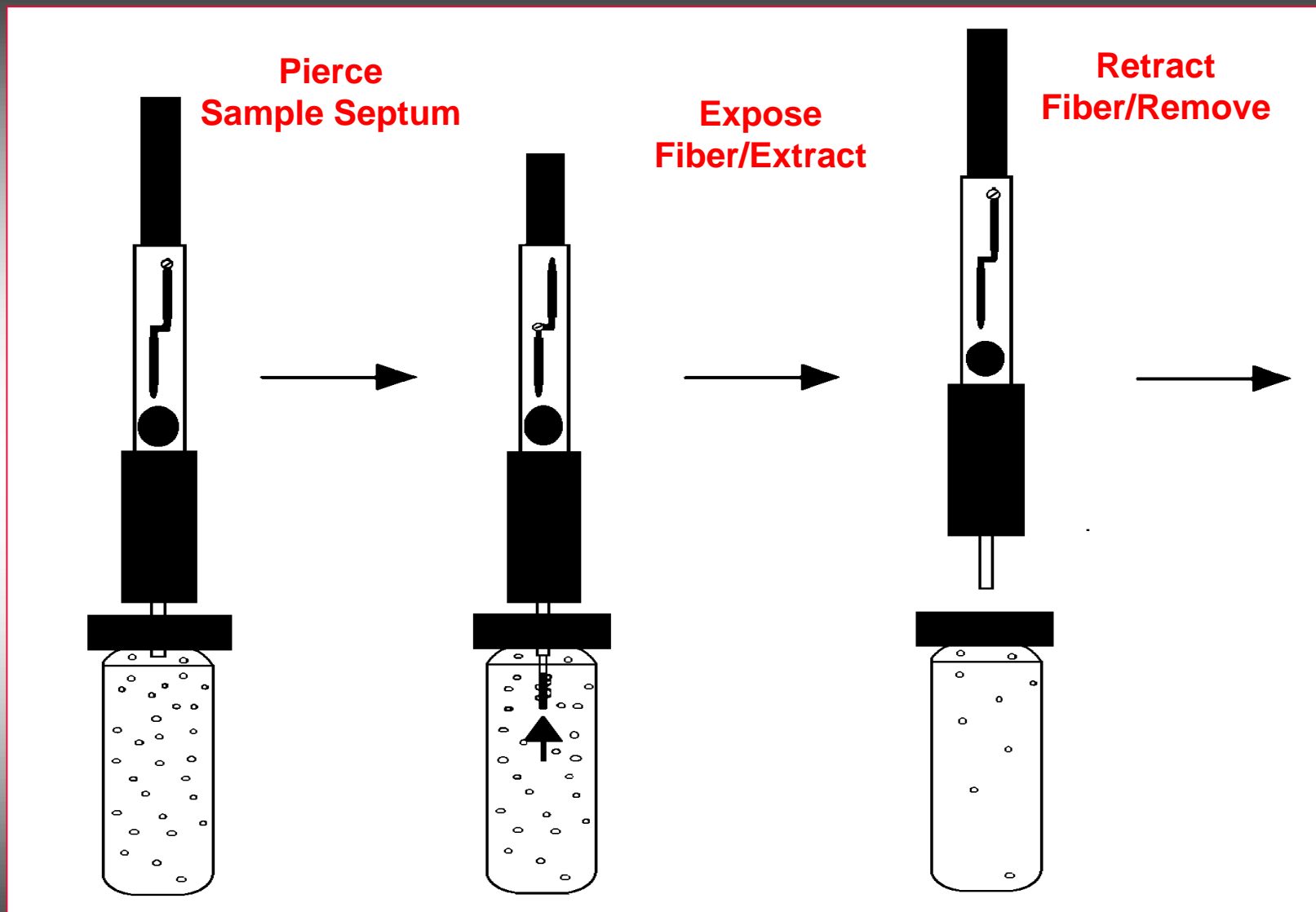
Ray Mindrup, Robert E. Shirey

Supelco, Supelco Park, Bellefonte, PA, 16823 USA

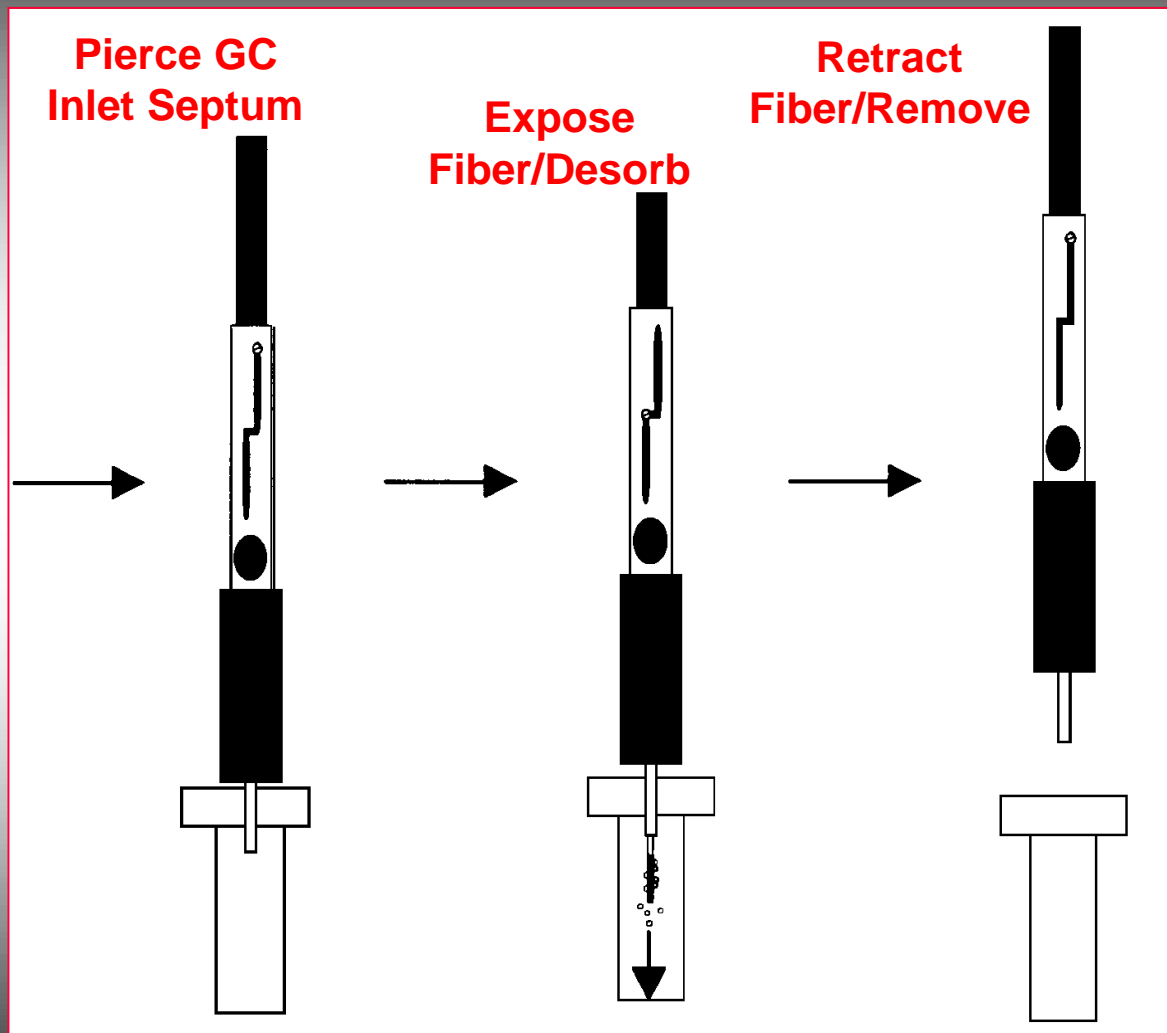
SPME Fiber Assembly Detail (Manual)



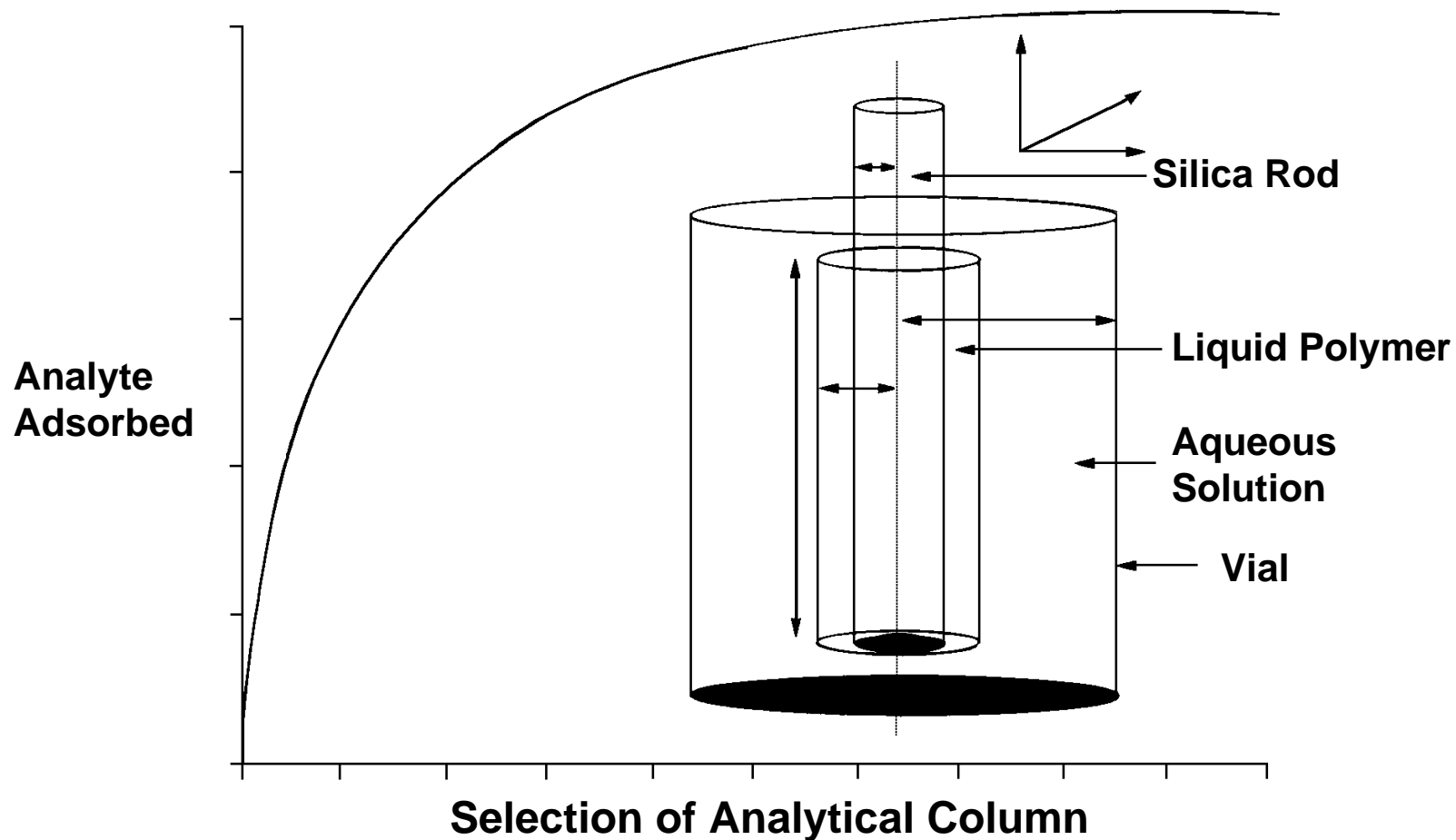
Extraction Procedure for SPME



Desorption Procedure for SPME



Adsorption Mechanism for SPME



794-0836

Distribution Constant

Concentration of analyte in stationary phase compared to concentration of analyte in solution:

$$K = n_s / V_1 C_2^\circ$$

K = Distribution constant

n_s = Moles of analyte in stationary phase

V_1 = Volume of stationary phase

C_2° = Final analyte concentration in water



Evaluation of Crimped Design

48 injection

1st injection	=	78082
48th injection	=	84001
Average	=	78675
		4.8% RSD

100 μ m PDMS

**50psig inlet pressure using Varian 8200 Autosampler,
30 sec extraction, 4ppm benzene in 25% NaCl water**

Available SPME Fibers, by Polarity

Nonpolar Fibers

Polydimethylsiloxane (PDMS): 100 μ m, 30 μ m, 7 μ m

Polar Fibers

85 μ m Polyacrylate

65 μ m Carbowax[®]-divinylbenzene StableFlex™ (CW-DVB)

50 μ m CW-templated resin (CW-TPR) (HPLC only – crimped)

Bi-Polar Fibers

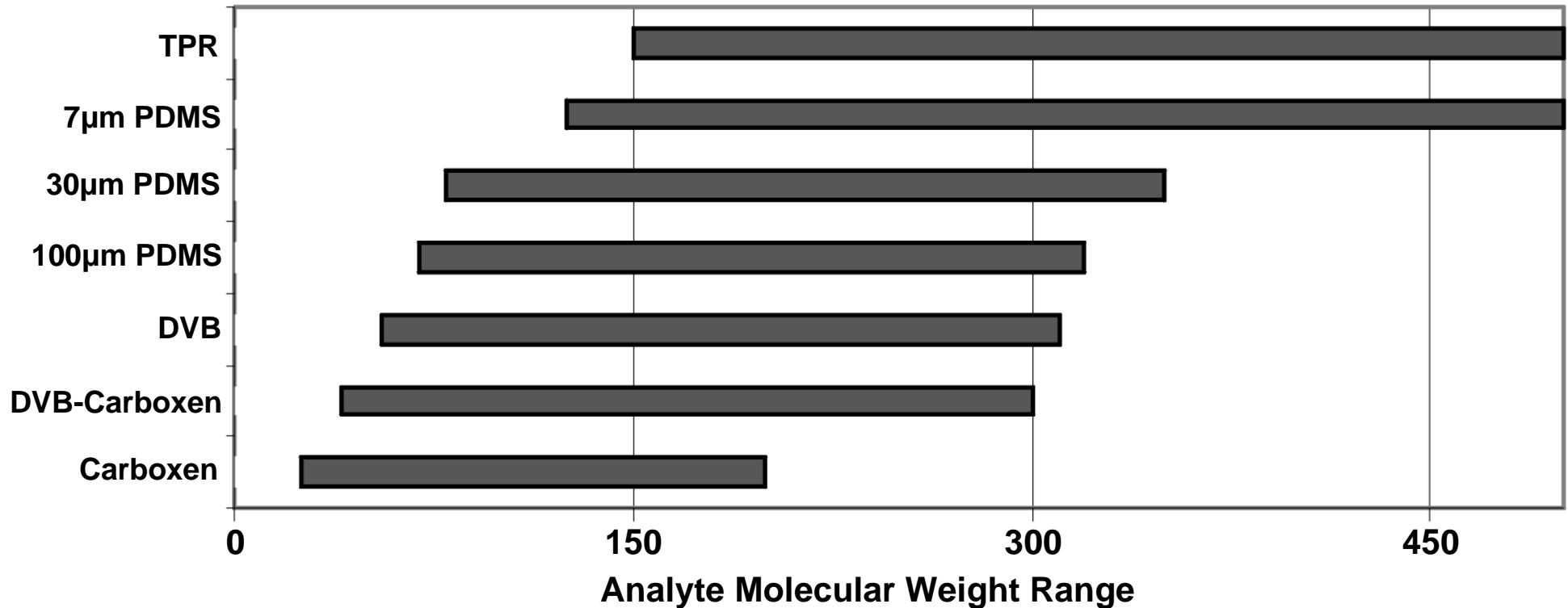
65 μ m PDMS-DVB StableFlex

75 μ m Carboxen™-PDMS StableFlex

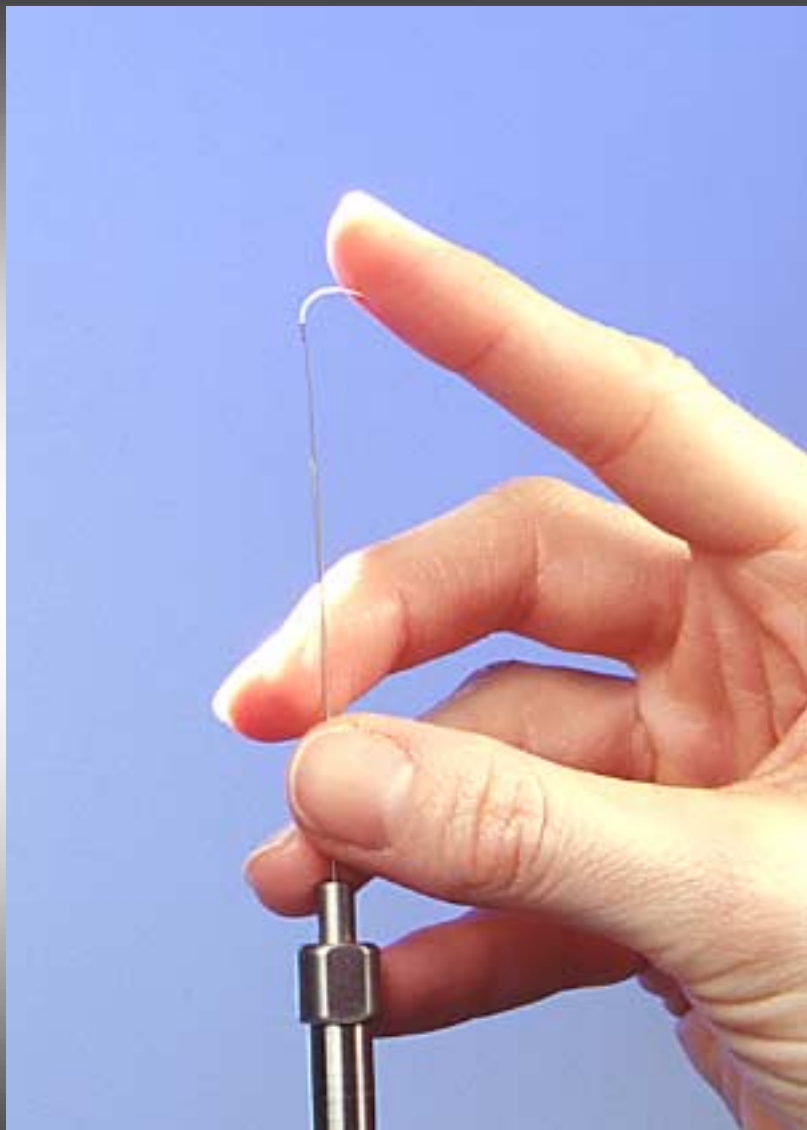
55/30 μ m DVB-Carboxen-PDMS StableFlex

60 μ m PDMS-DVB (HPLC only – crimped)

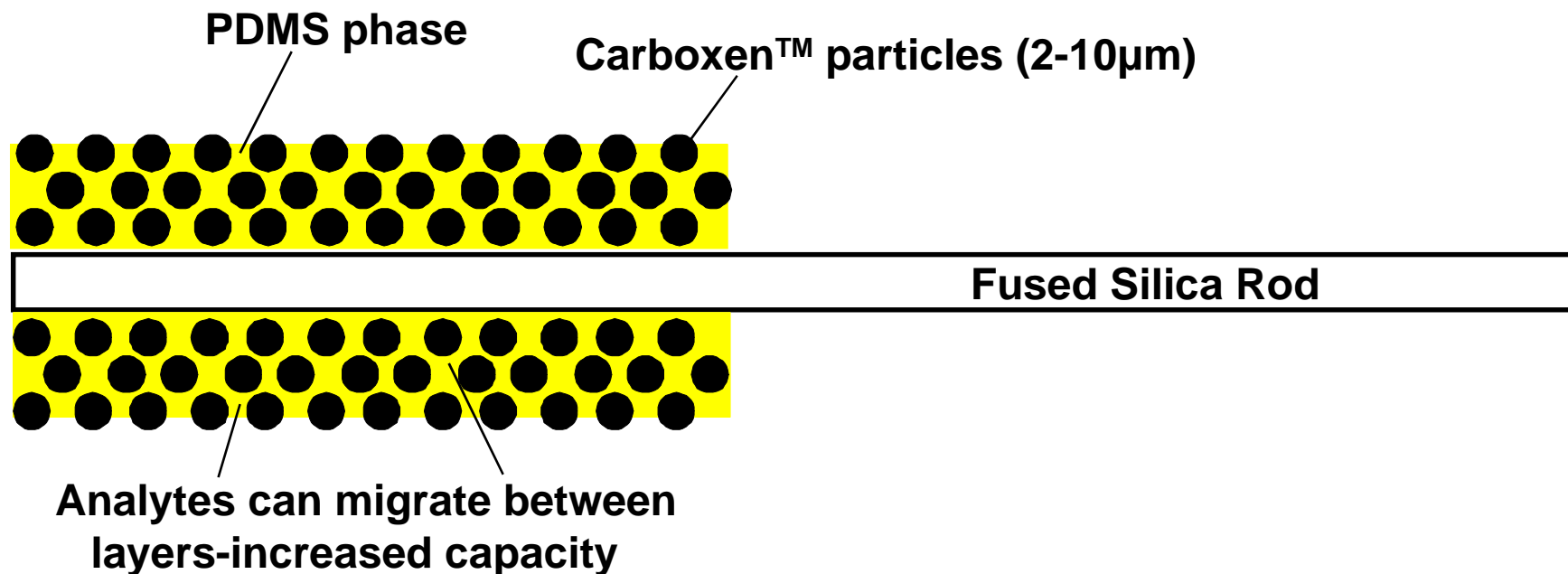
SPME Fibers, by Adsorption Strength



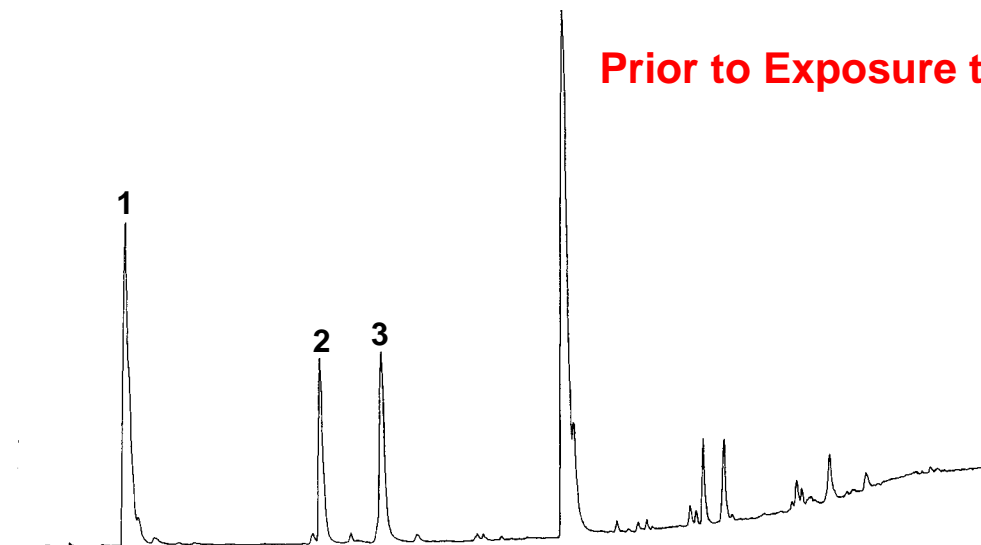
StableFlex Fiber



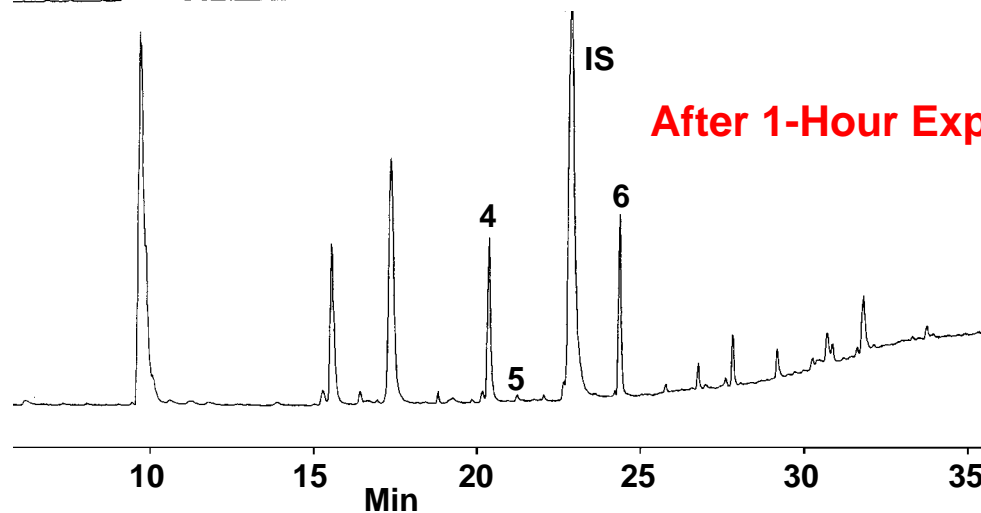
Carboxen/PDMS Fiber



Milk Sample Off-Flavors by SPME-GC/MS



1. Acetone
 2. 2-Butanone
 3. 3-Methylpentane
 4. Pentanal
 5. Dimethyldisulfide
 6. Hexanal
- IS 4-Methyl-2-pentanone (int. std.)



Chromatogram provided by Ray Marsili, Dean
Foods Technical Center, Rockford, IL, USA.

G00507, 508

Conditions for Analysis of Milk Off-Flavors

Sample: 3g of 2% milk + 10 μ L internal standard solution
(20 μ g/mL 4-methyl-2-pentanone) (9mL GC vial)

SPME Fiber: PDMS/CarboxenTM, 75 μ m film

Extraction: headspace, 15 min with constant stirring at 45°C

Desorption: 5 min, 250°C

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

Oven: 70°C (2 min) to 140°C at 6°C/min (2 min hold)
then to 220°C at 6°C/min (5 min hold)

Carrier: helium, 35cm/sec

Inj.: splitless (closed 2 min)

Det.: GC/MS ion trap, m/z = 33-300

Compounds in Salivary Headspace by Dynamic HS-SPME

Sample: 3ml. saliva solution
w/thioglycollate medium

Fiber: 75 μ m Carboxen-PDMS

Extraction: headspace,
15 min. @ 22°C, stirred

Desorption: 1 min., 250°C

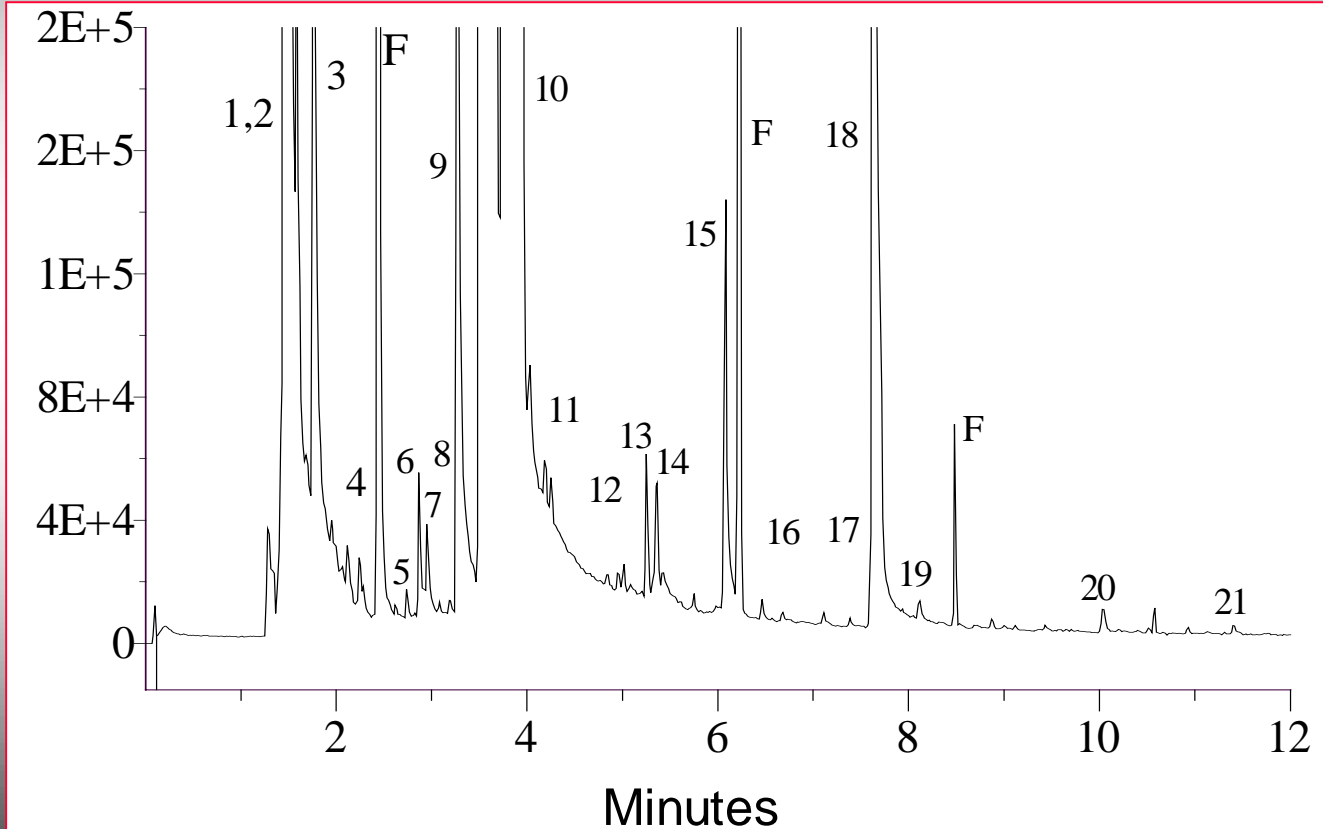
Column: 30m x 0.25mm x 0.25 μ m,
Supelcowax 10

Oven: 50-200°C, 10°C/min hold
5 min. @ 200°C

Carrier: Helium @ 30cm/sec.

Injection: 250°C, 0.75mm ID
inlet liner, splitless

Detector: GC-MS ion trap



Peak No.	Compounds	Ret. Time (min)	ID ^a
2	Methyl Mercaptan	1.55	rt,ms
3	Dimethyl Sulfide	1.63	rt,ms
4	Acetone	1.82	rt,ms
5	Butanone ^b	2.15	rt,ms
6	Z-1-(methylthio)-1-propane*	2.77	T,ms
7	E-1-(methylthio)-1-propane*	2.97	T,ms
8	S-methyl ethanethioate	3.28	T,ms
9	Dimethyl disulfide	3.55	rt,ms
10	Limonene ^b	4.97	rt,ms
11	Amyl alcohol ^p	5.02	rt,ms
12	S-methyl pentanethioate*	5.25	T,ms
13	S-Methyl 3-methyl butanethioate*	5.35	T,ms
14	Thiocyanic acid methyl ester*	6.08	T,ms
15	2,5-dimethyl pyrazine ^b	6.68	rt,ms
16	5-methyl-6-hepten-2-one ^b	6.88	T,ms
17	4-hydroxy-4-methyl-2-pentanone ^b	7.25	T,ms
18	Dimethyl trisulfide	7.65	rt,ms
19	Alkyl Benzene ^b	8.12	T,ms
20	Acetic acid	8.58	rt,ms
21	Dimethyl sulfoxide*	10.02	rt,ms
22	Methyl(methylthio)methyl disulfide	11.14	T,ms
23	Benzyl alcohol ^p	13.85	rt,ms
24	Phenol	15.32	rt,ms
25	Indole	23.32	rt,ms

^a Identification was by GC retention times (rt) and mass spectrometry (ms) of authentic compounds.

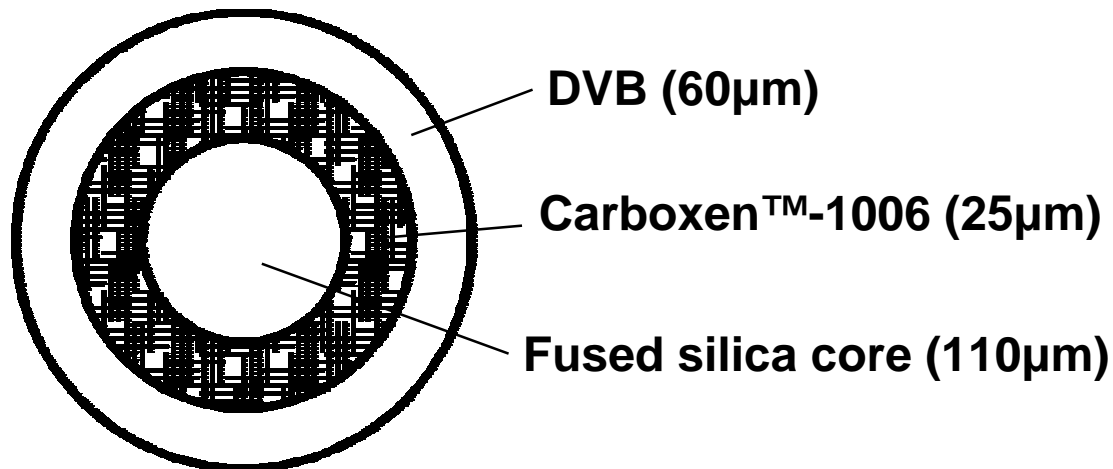
Tentative (T) identification by mass spectrometry only when authentic compound was not available.

^b Probable exogenous sources.

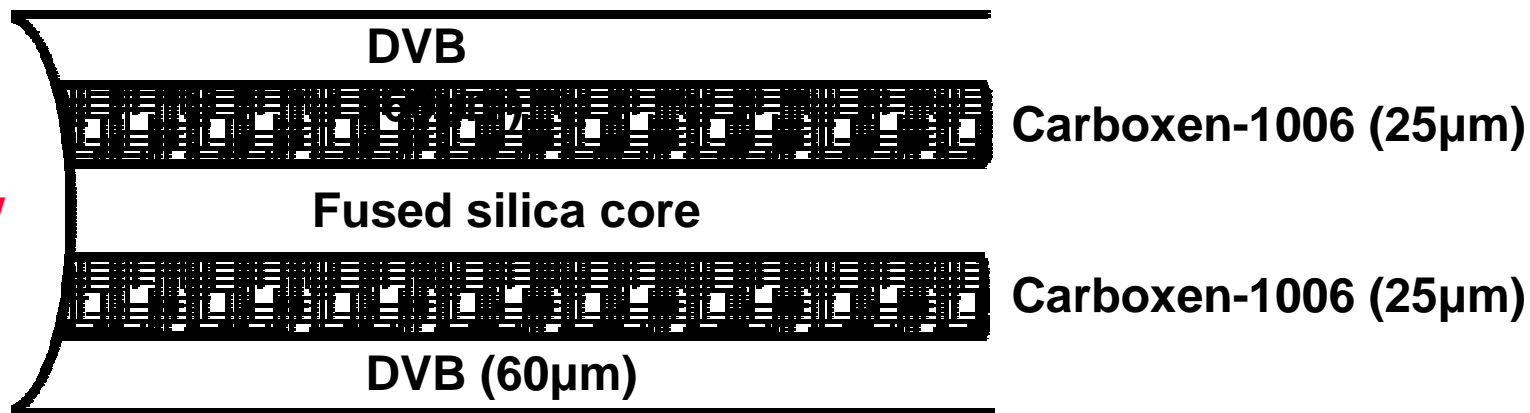
* Not previously identified in saliva.

Dual-Coated SPME Fiber

Front View



Side View



Regular Coffee Grounds by SPME

Sample: 5g coffee grounds in 40mL vial

SPME Fiber: DVB/Carboxen™/PDMS (StableFlex™ Fiber)

Extraction: headspace, 30 min at 65°C

Desorption: 270°C for 5 min

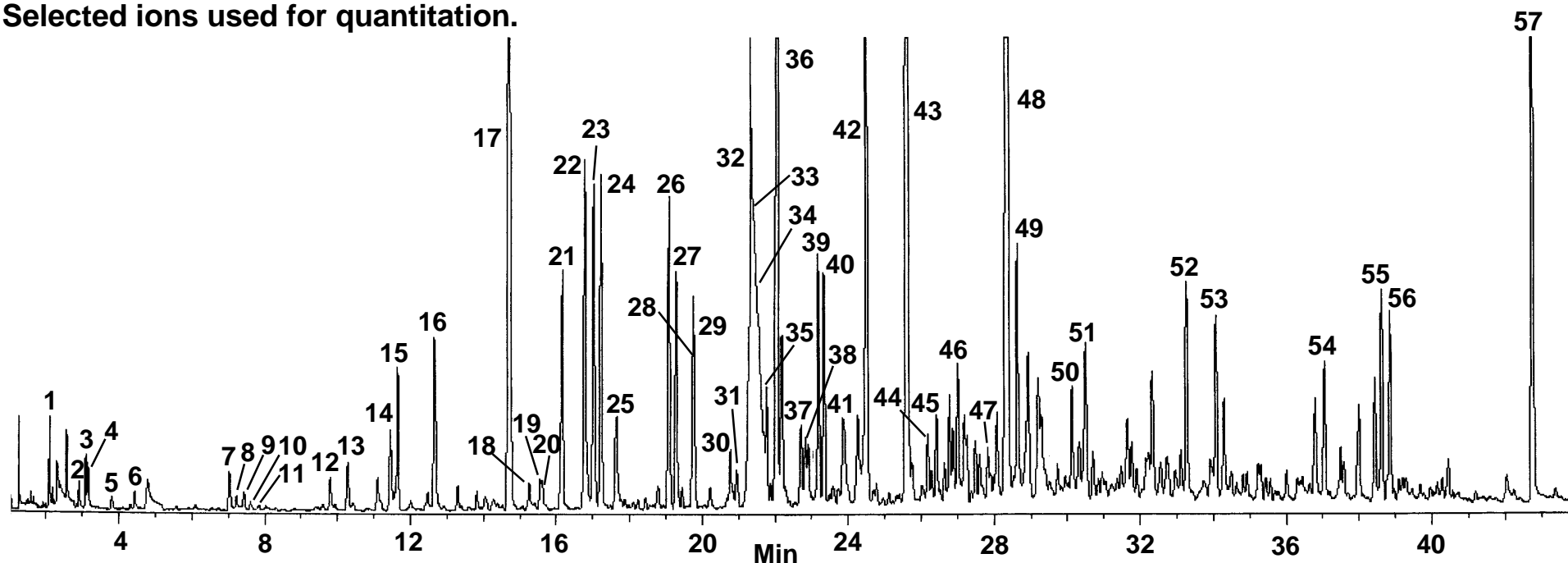
Column: SUPELCOWAX™ 10, 30m x 0.25mm x 0.25µm film

Oven: 40°C (5 min) to 230°C at 4°C/min

Inj.: splitless/split, closed 0.5 min, 270°C, with 0.75mm liner

Det.: ion trap mass spectrometer, m/z = 30-350 at 0.6 sec/scan

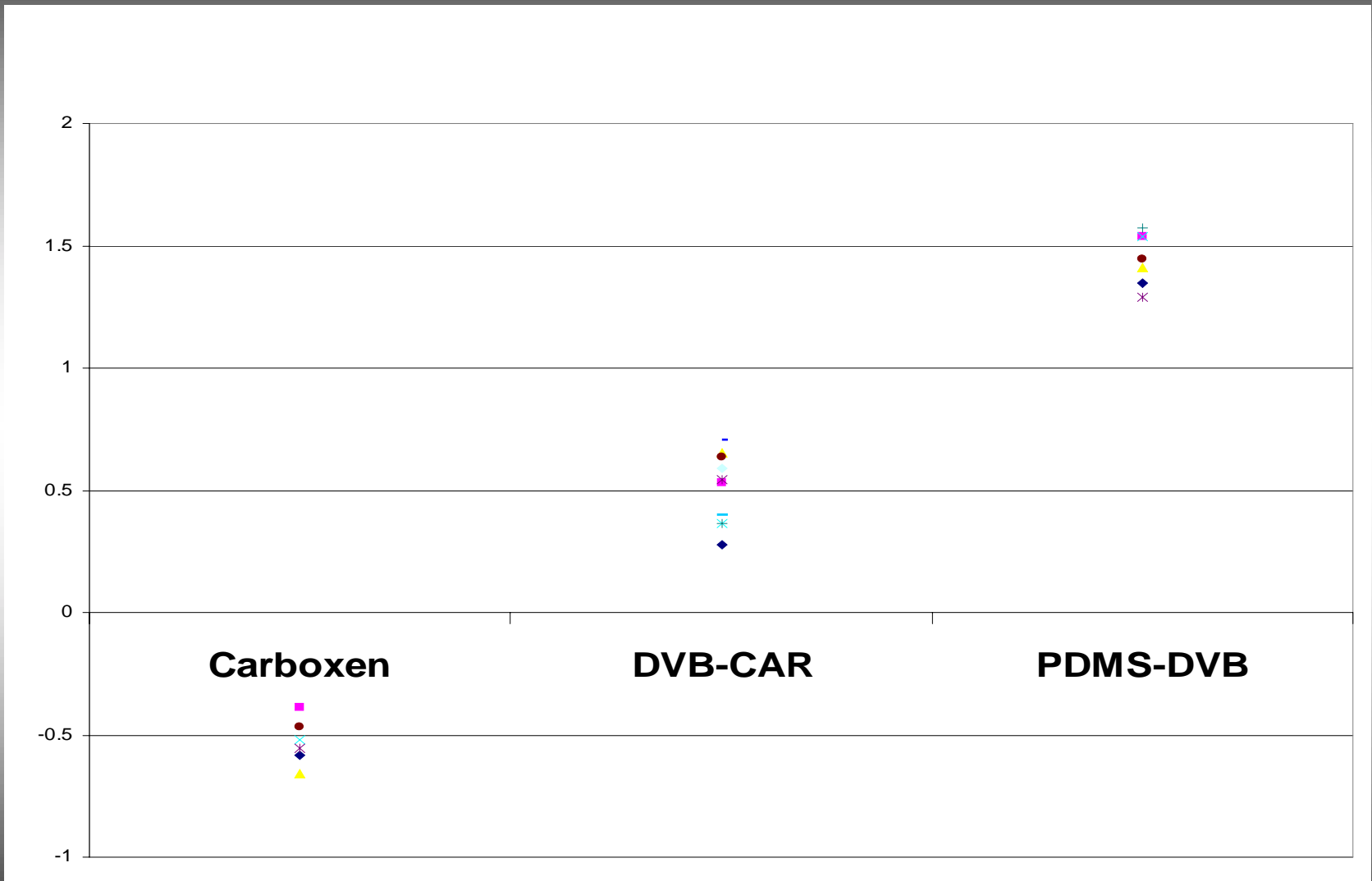
Selected ions used for quantitation.



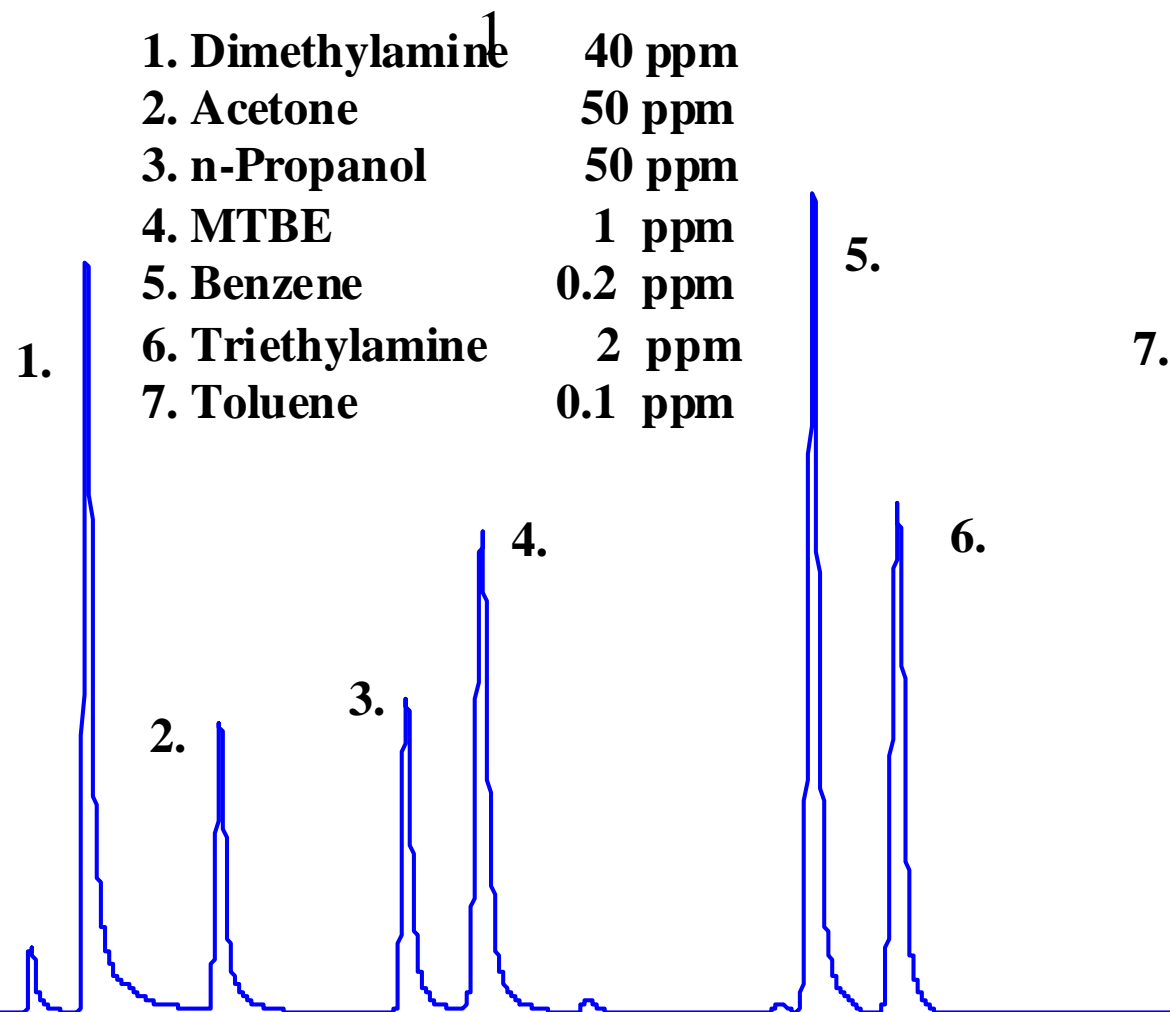
Components in Coffee

1. 2-Methyl furan
2. 2-Butanone
3. 2-Pentanone
4. 3-Methyl butanal
5. 2,5-Dimethylfuran
6. 2-Acetyloxy-2-propanone
7. 2-Ethyl hexanol
8. Dimethyldisulfide
9. Phenol
10. Hexanal
11. 2-Methyl thiophene
12. n-Methyl pyrrole
13. 4-Methylphenol
14. 2-Ethyl pyrrole
15. Pyridine
16. Pyrazine
17. Methyl pyrazine
18. 4-Methyl thiazole
19. 3-Hydroxy butanone
20. Dimethyl phenol (isomer)
21. 1,2-Ethanediol, monoacetate
22. 2,5-Dimethylpyrazine
23. 2,3-Dimethylpyrazine
24. 2-Ethylpyrazine
25. 2,6-Dimethylpyrazine
26. 2-Ethyl-6-methylpyrazine
27. 2-Ethyl-5-methylpyrazine
28. Trimethylpyrazine
29. 2-Ethyl-3-methylpyrazine
30. 2,6-Diethylpyrazine
31. 2-Ethenylpyrazine
32. 2-Ethyl-3,5-dimethylpyrazine
33. Glycerol
34. 2,3-Diethylpyrazine
35. 2-Ethyl-3,6-dimethylpyrazine
36. 2-Furancarboxaldehyde
37. 2-Isopropenylpyrazine
38. 3,5-Diethyl-2-methylpyrazine
39. Furfural formate
40. 2-Furonyl ethanone
41. Methyl benzoylformate
42. Furanmethanol acetate
43. 5-Methyl-2-furancarboxaldehyde
44. Furanmethanol propionate
45. Furfanyl furan
46. Pyridine methanol
47. 2-Methyl-5-propenylpyrazine
48. Furanmethanol
49. 3-Ethyl-4-methyl-2,5-furandione
50. Pyrazinecarboxamide
51. 2-Ethyl-3-hydroxy-4H pyran-4-one
52. 1-(2-Furanylmethyl)-pyrrole
53. 2-Methoxyphenol
54. 1-(1H-pyrrole-2-yl)-ethanone
55. 4-Ethyl-2-methoxy phenol
56. 3-Phenylpropenal or 2-Methylbenzofuran
57. 3,5-Dimethylbenzoic acid

Log Plot of Acenaphthene/Heptane Responses



Analytes in Test Mixture



Conditions for Analysis of Test Mix

Extraction Conditions

Sample: 0.8 μ l of test mix spiked in 0.8mL of water containing 25% NaCl and 0.1M phosphate buffer, pH 11 in 2mL vial.

Fiber: 65 μ m PDMS-DVB StableFlex

Extraction: Headspace (ambient) for 2 min with Varian 8200 autosampler with agitation

Desorption: 250°C for 2min

Chromatographic Conditions

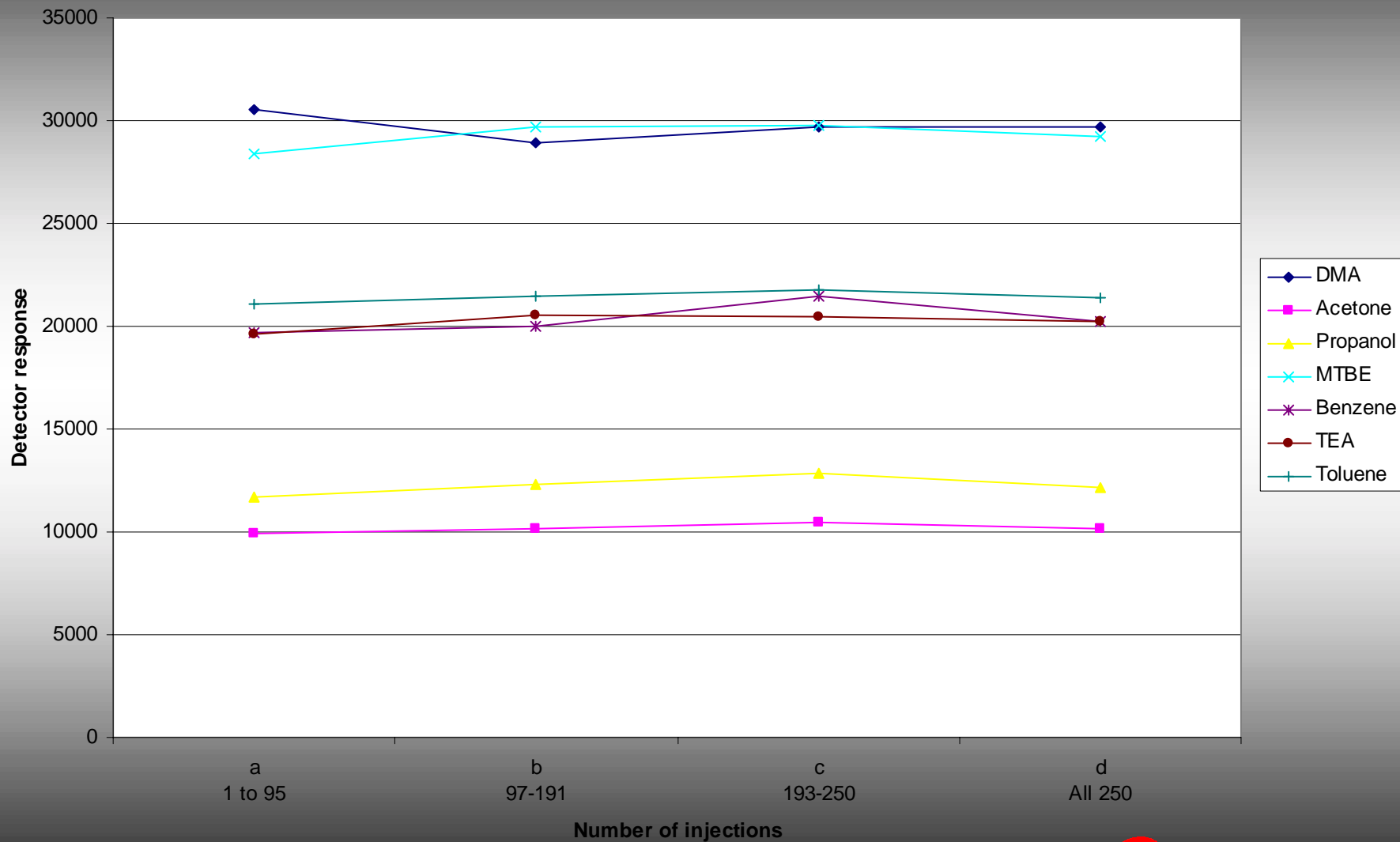
Column: SPB-1 Sulfur 30m x 0.32mm x 4.0 μ m

Oven: 50°C (0.5min) to 150°C @ 20°C/min.

Injector: Splitless/split, 250°C, 0.75mm ID liner

Detector: FID, 280°C

Precision for DVB/PDMS fiber



Precision Measurement -					
DVB/PDMS Fiber					
	1 to 95	97-191	193-250	All 250	% RSD
	a	b	c	d	
DMA	30535	28926	29719	29701	8.4
Acetone	9943	10161	10433	10132	4.3
Propanol	11661	12322	12817	12190	5.5
MTBE	28355	29729	29773	29224	5.9
Benzene	19658	20012	21439	20214	5.2
TEA	19649	20553	20491	20199	8.8
Toluene	21041	21434	21738	21363	4.3

- **Where are we going in Fiber development?**
- **Minimize the variability in Carboxen coatings by:**
 - a. controlling the porosity**
 - b. optimize the conditioning process**
- **Development of new fiber coatings**