ISO 9001
REGISTERED

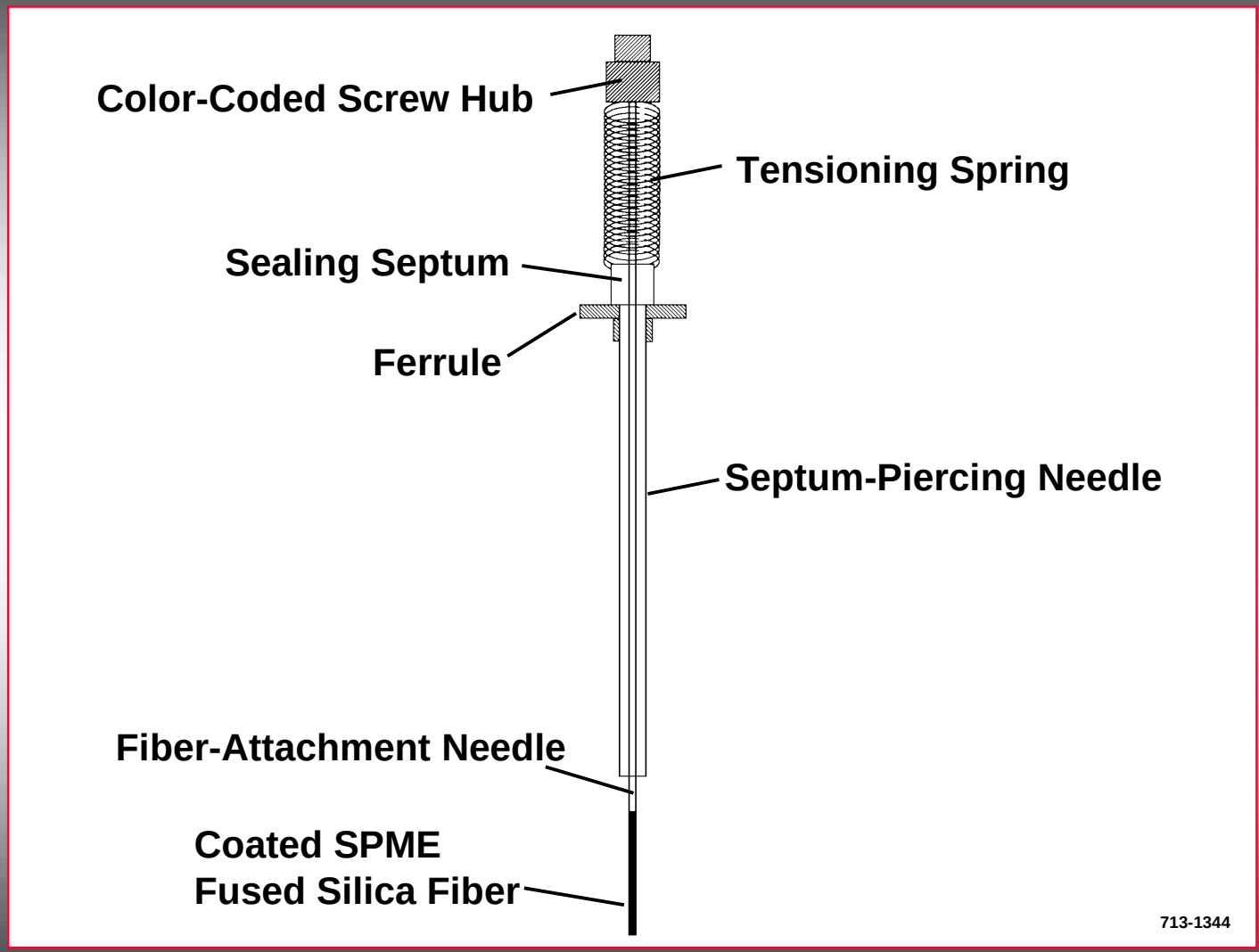
SUPELCO

Improved Performance of SPME Fibers and Applications

Ray Mindrup, Robert E. Shirey

Supelco, Supelco Park, Bellefonte, PA, 16823 USA

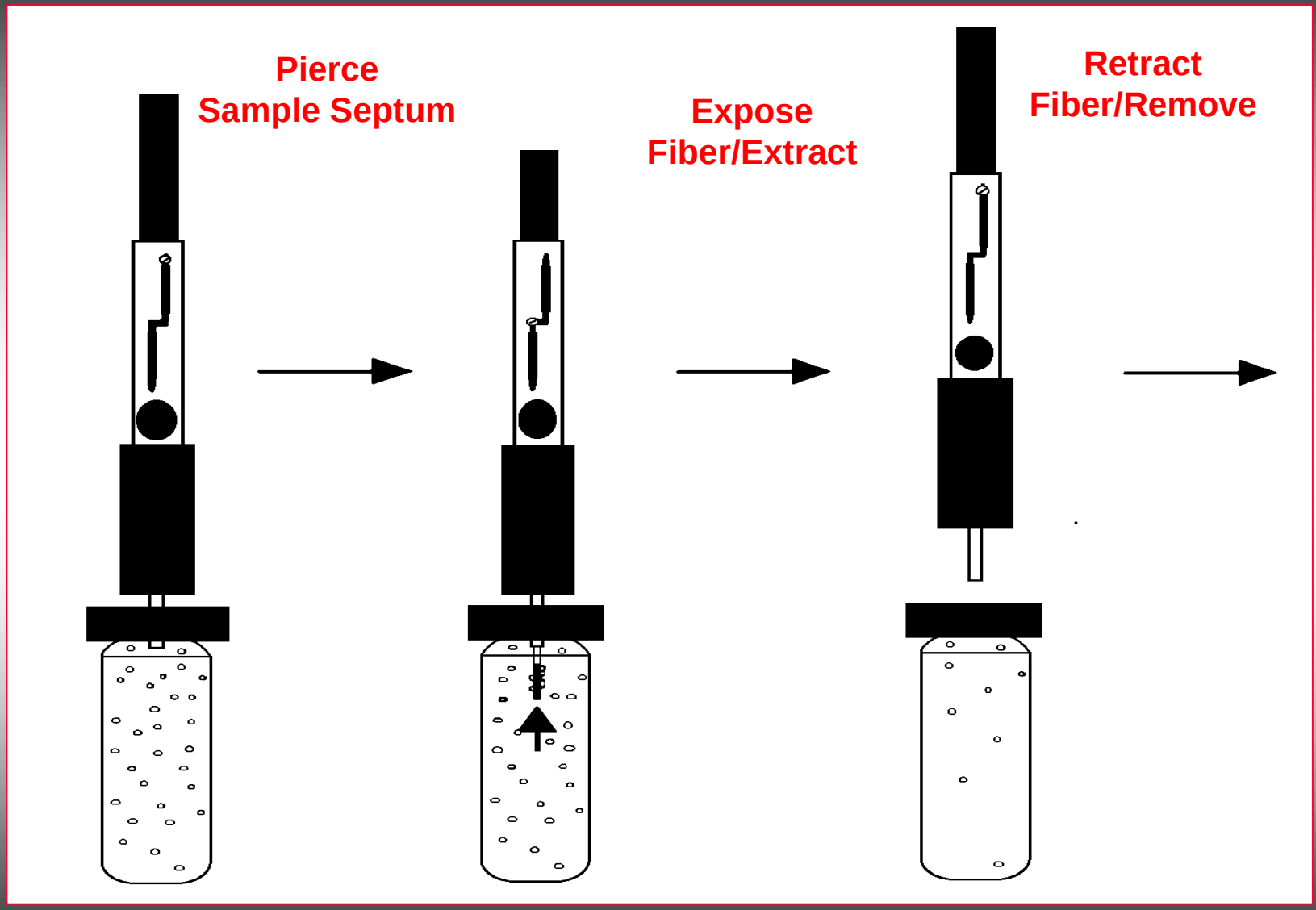
SPME Fiber Assembly Detail (Manual)



01-0062

SUPELCO

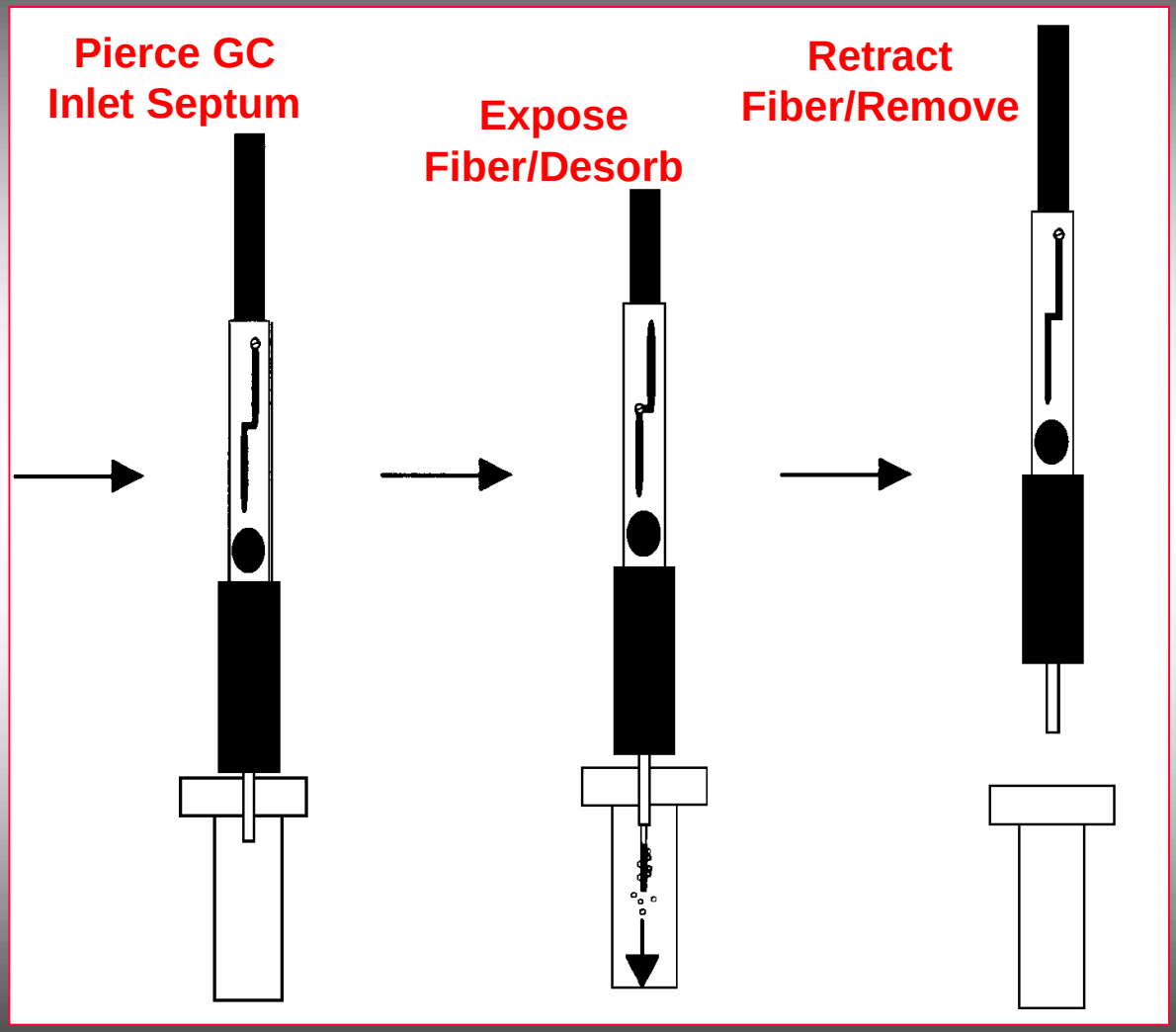
Extraction Procedure for SPME



01-0063

SUPELCO

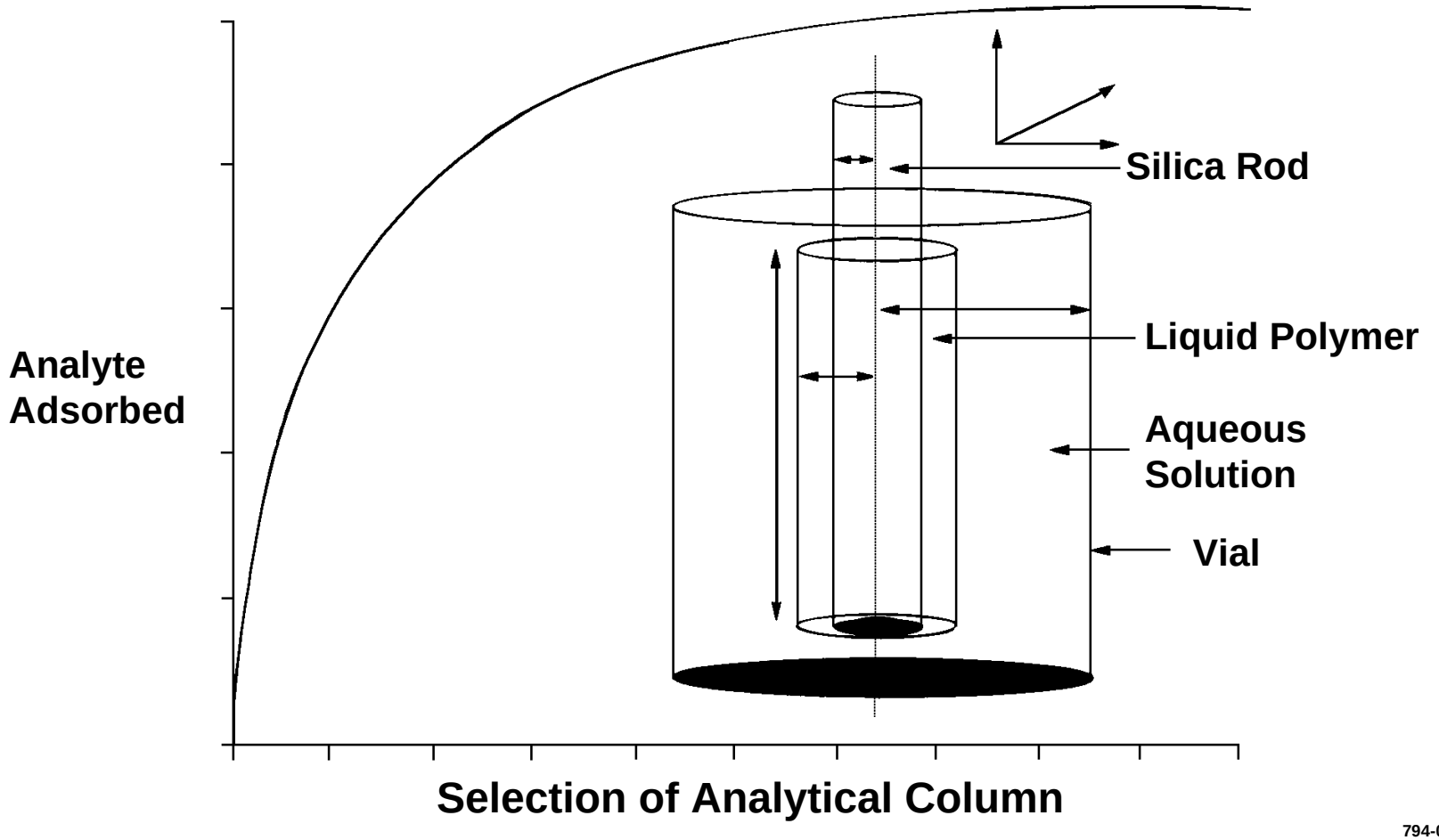
Desorption Procedure for SPME



01-0064

SUPELCO

Adsorption Mechanism for SPME



SUPELCO

Distribution Constant

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

$$K = n_s/V_1C_2^\circ$$

K	=	Distribution constant
n_s	=	Moles of analyte in stationary phase
V_1	=	Volume of stationary phase
C_2°	=	Final analyte concentration in water

SUPELCO

01-0067

SUPELCO

Evaluation of Crimped Design

48 injection

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

100µm PDMS
50psig inlet pressure using Varian 8200 Autosampler,
30 sec extraction, 4ppm benzene in 25% NaCl water

SUPELCO

Available SPME Fibers, by Polarity

Nonpolar Fibers

Polydimethylsiloxane (PDMS): 100µm, 30µm, 7µm

Polar Fibers

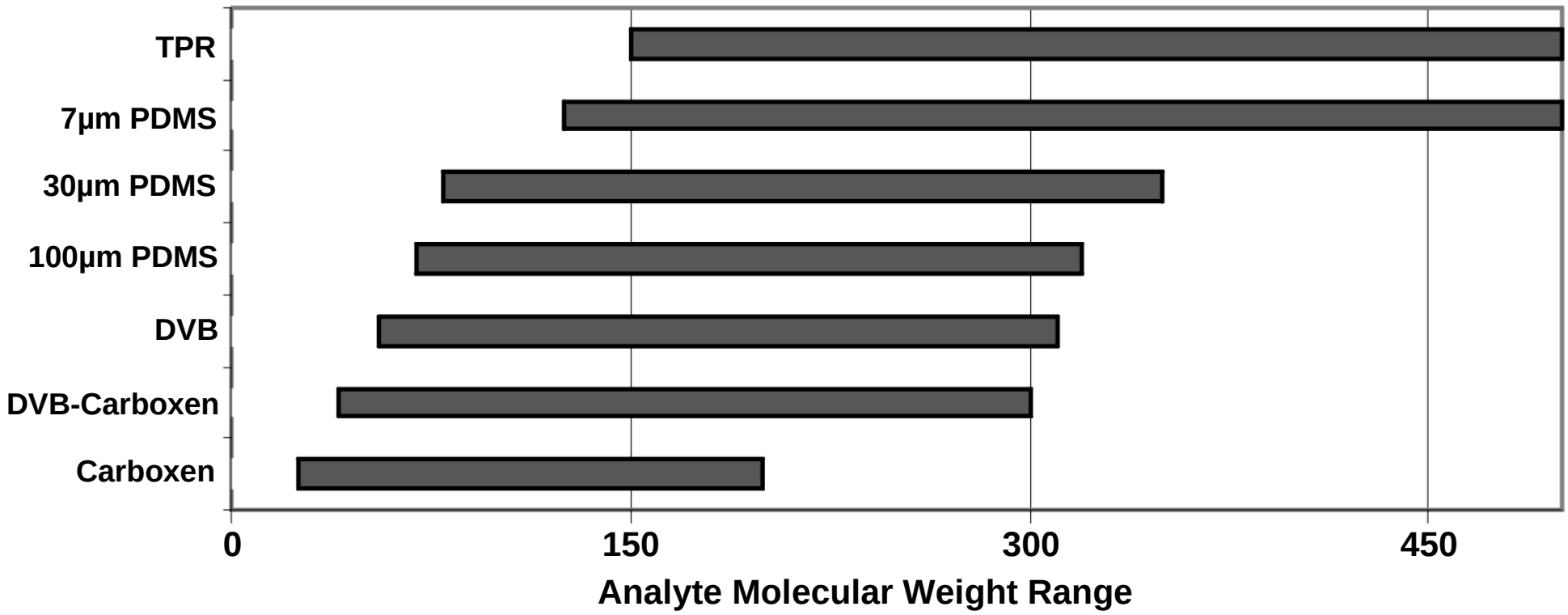
85µm Polyacrylate
65µm Carbowax®-divinylbenzene StableFlex ™ (CW-DVB)
50µm CW-templated resin (CW-TPR) (HPLC only – crimped)

Bi-Polar Fibers

65µm PDMS-DVB StableFlex
75µm Carboxen™-PDMS StableFlex
55/30µm DVB-Carboxen-PDMS StableFlex
60µm PDMS-DVB (HPLC only – crimped)

SUPELCO

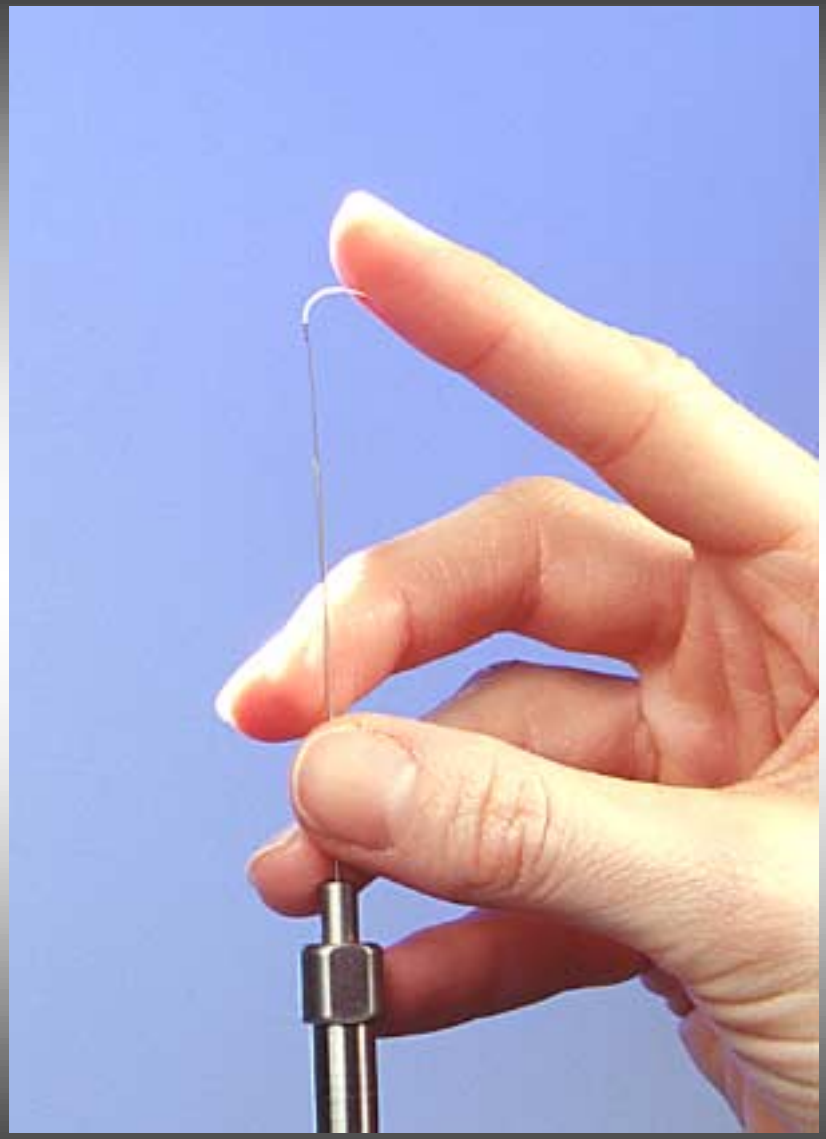
SPME Fibers, by Adsorption Strength



01-0070

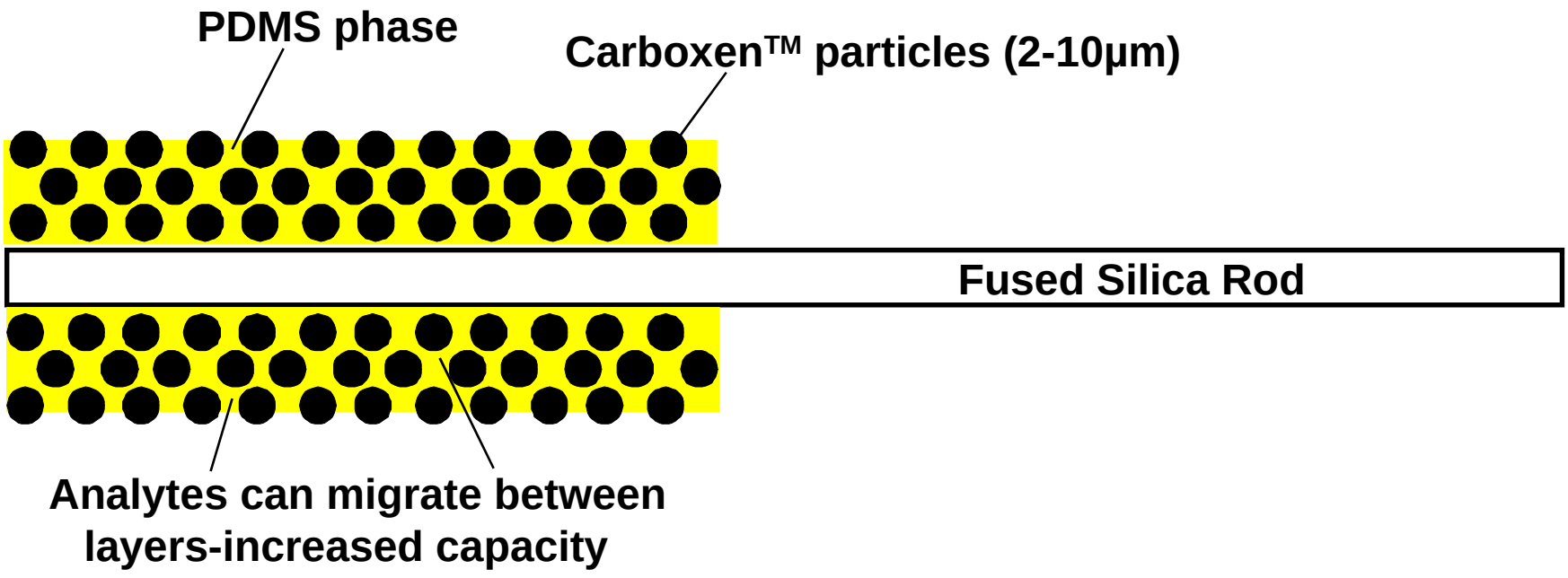
SUPELCO

StableFlex Fiber



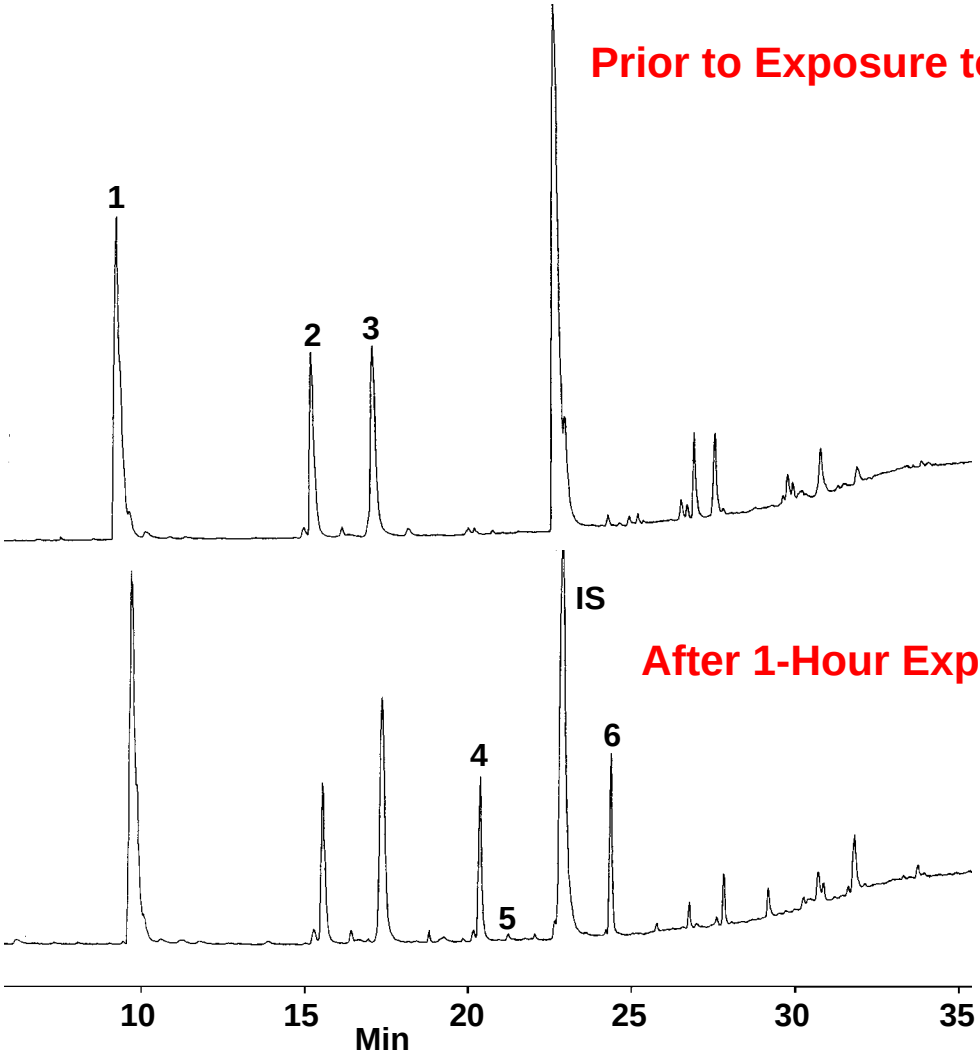
SUPELCO

Carboxen/PDMS Fiber



SUPELCO

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

01-0073

SUPELCO

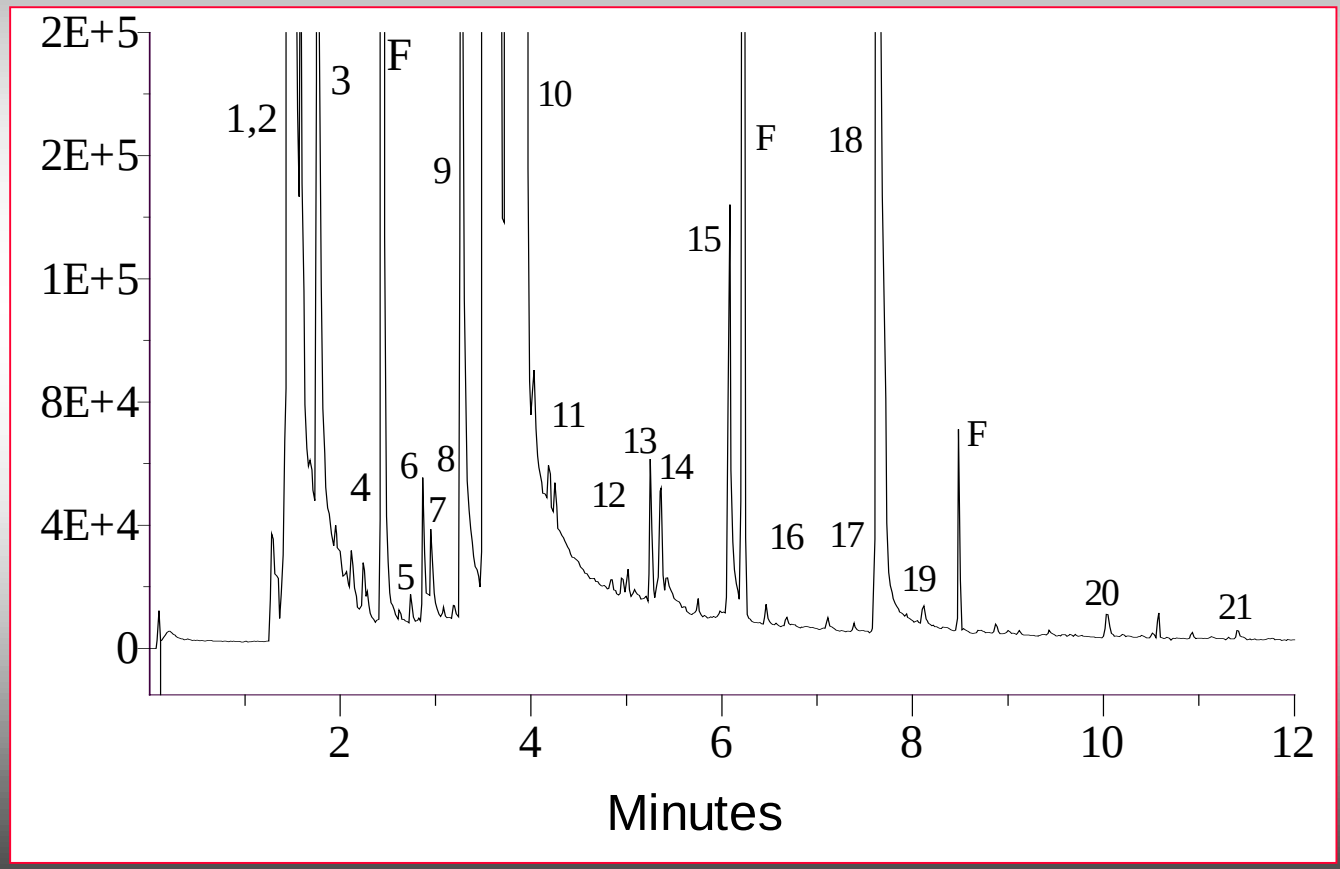
Conditions for Analysis of Milk Off-Flavors

Sample:	**3g of 2% milk + 10µL internal standard solution (20µg/mL 4-methyl-2-pentanone) (9mL GC vial)**
SPME Fiber:	**PDMS/Carboxen™, 75µm film**
Extraction:	**headspace, 15 min with constant stirring at 45°C**
Desorption:	**5 min, 250°C**
Column:	**Supel-Q™ 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**

SUPELCO

Compounds in Salivary Headspace by Dynamic HS-SPME

Sample:	**3ml. saliva solution w/thioglycollate medium**
Fiber:	**75µm Carboxen-PDMS**
Extraction:	**headspace, 15 min. @ 22°C, stirred**
Desorption:	**1 min., 250°C**
Column:	**30m x 0.25mm x 0.25µm, 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**



01-0075

SUPELCO

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[b]	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[b]	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.

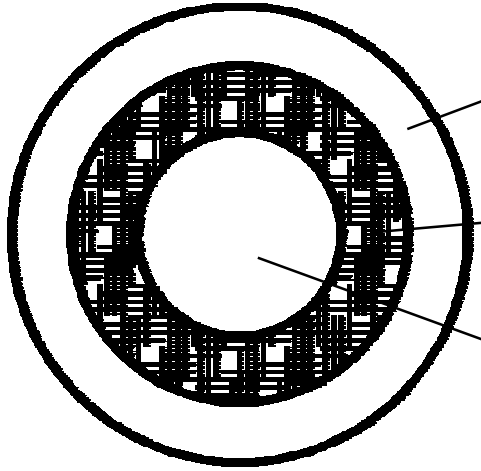
[b] Probable exogenous sources.

** Not previously identified in saliva.*

SUPELCO

Dual-Coated SPME Fiber

Front View

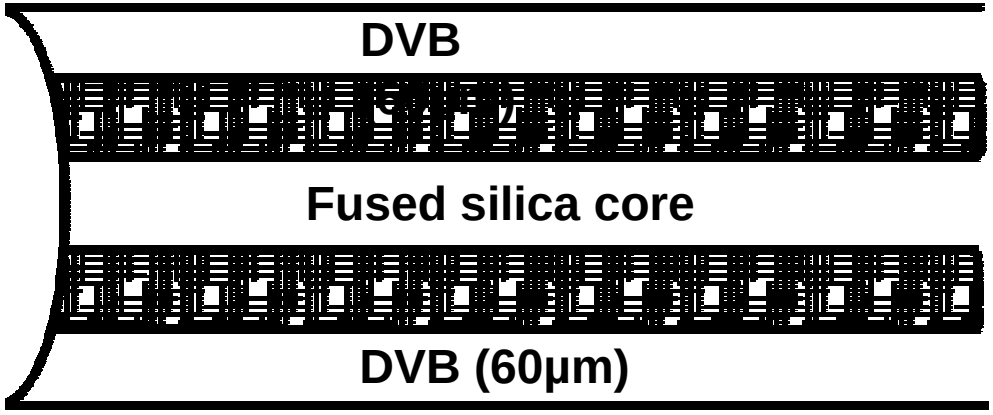


DVB (60µm)

Carboxen™-1006 (25µm)

Fused silica core (110µm)

Side View



Carboxen-1006 (25µm)

Carboxen-1006 (25µm)

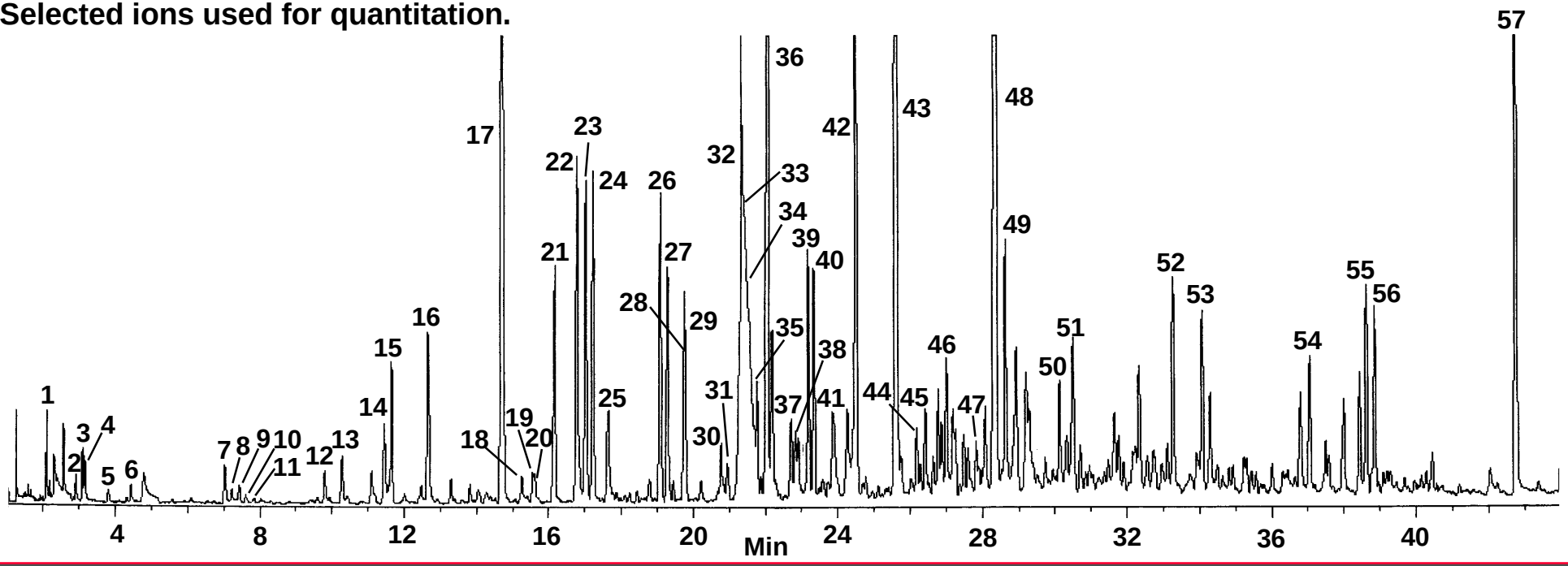
01-0077

SUPELCO

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.



01-0078

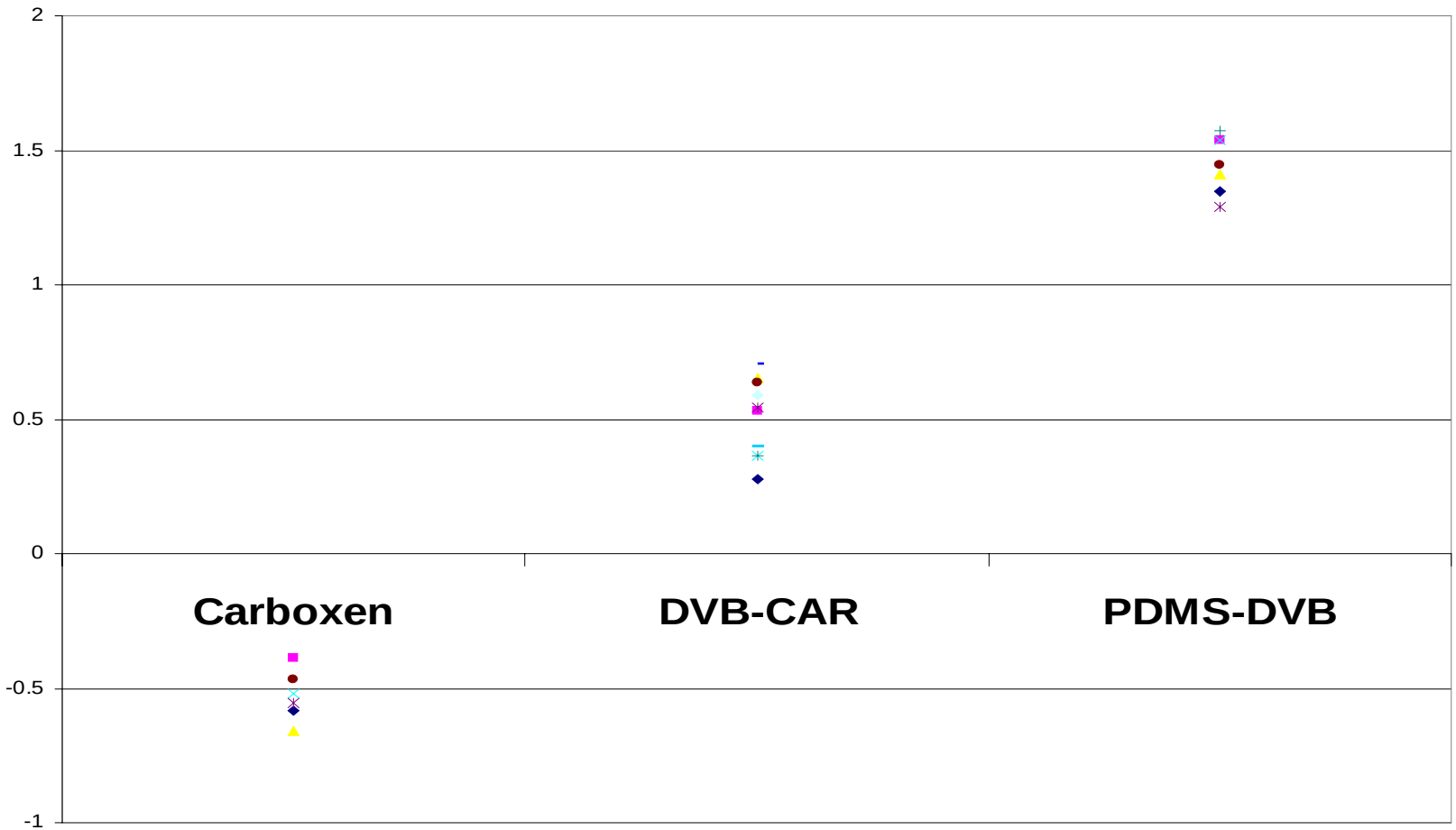
SUPELCO

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 proprionate
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

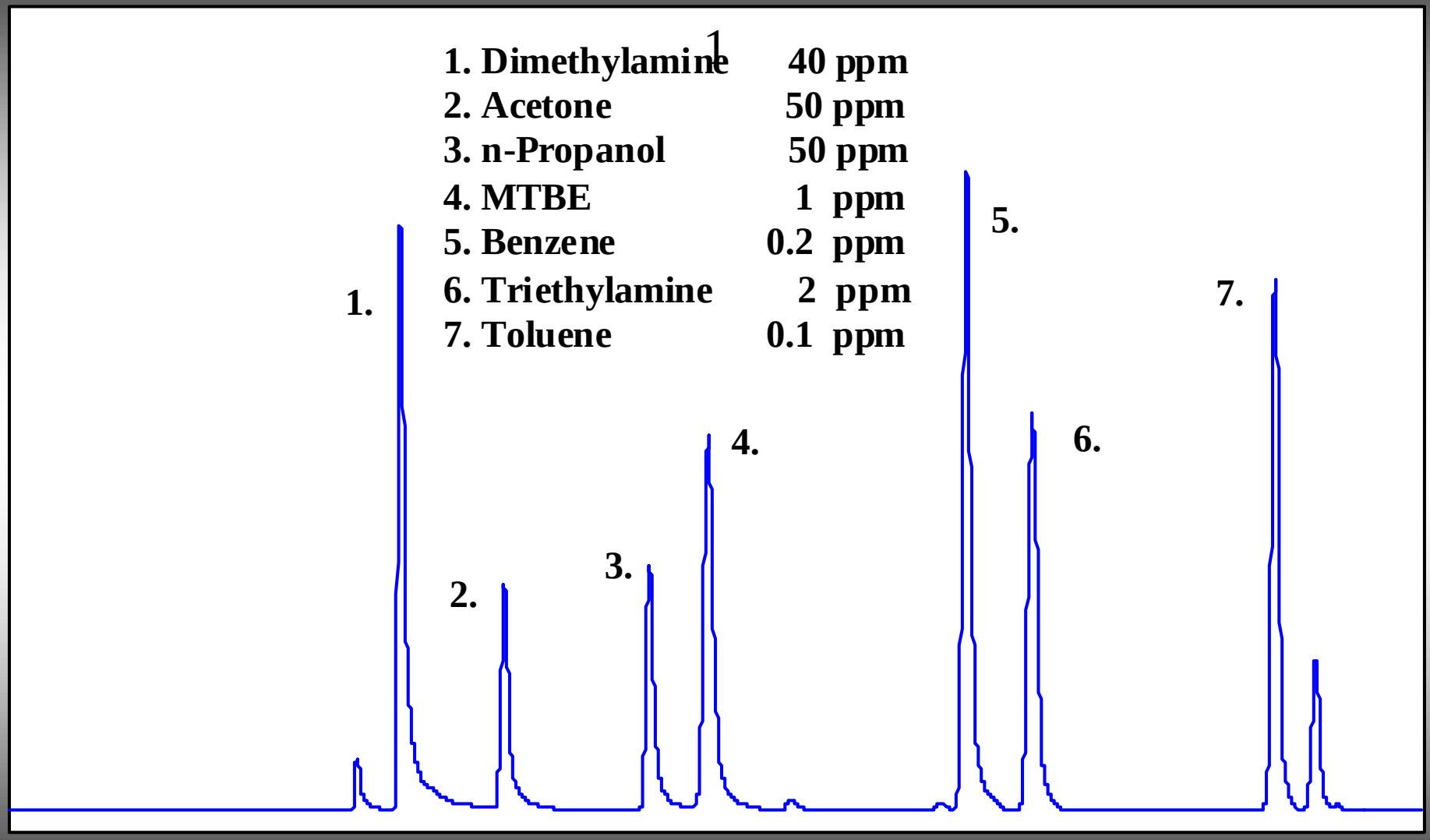
SUPELCO

Log Plot of Acenapthene/Heptane Responses



SUPELCO

Analytes in Test Mixture



01-0081

SUPELCO

Conditions for Analysis of Test Mix

Extraction Conditions

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

Fiber: 65µm PDMS-DVB StableFlex

Extraction: Headspace (amibient) 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 4.0µm

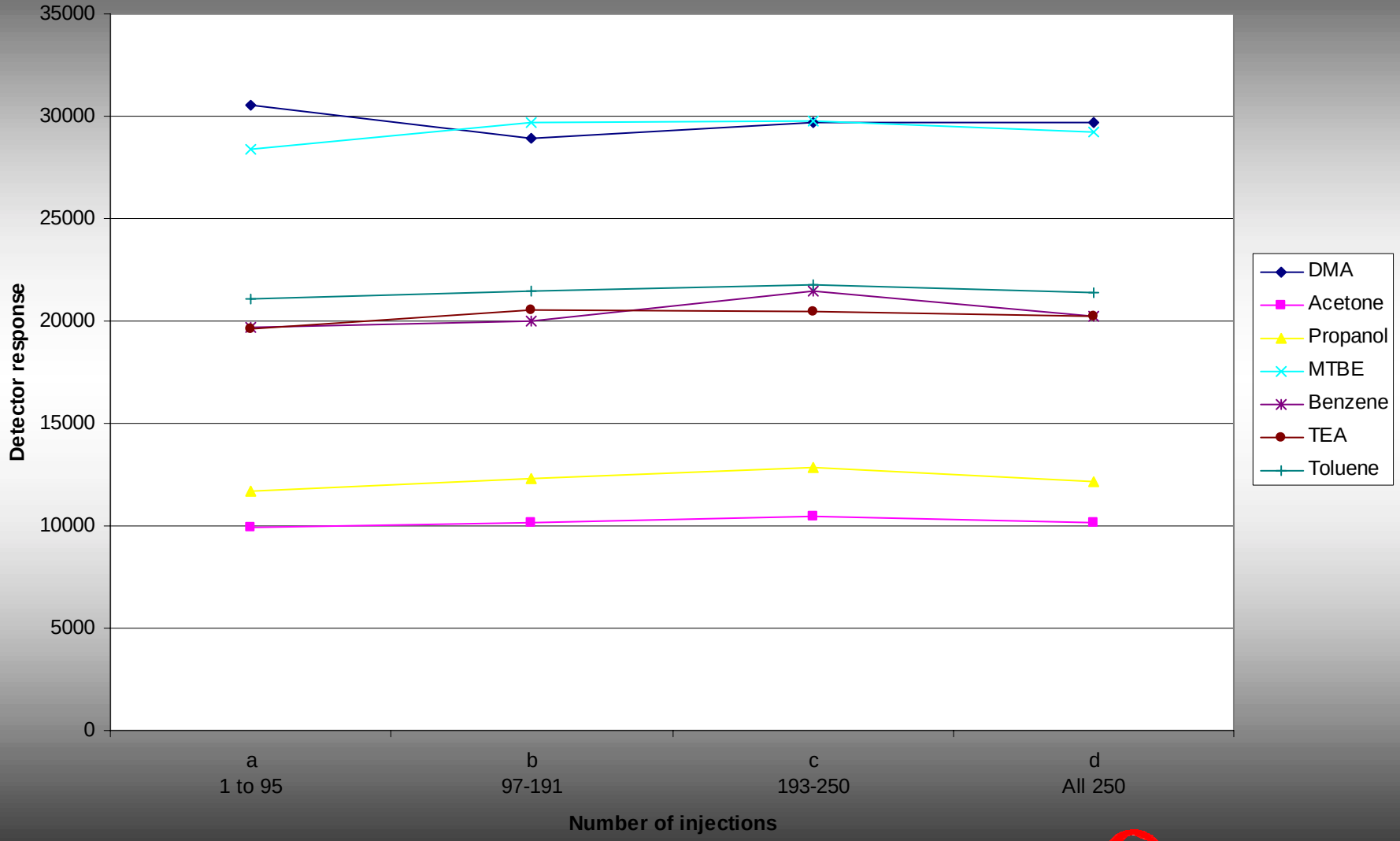
Oven: 50°C(0.5min) to 150°C@20°C/min.

Injector: Splitless/split, 250°C, 0.75mmID liner

Detector: FID, 280°C

SUPELCO

Precision for DVB/PDMS fiber



01-0083

SUPELCO

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

SUPELCO

- **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**

SUPELCO