

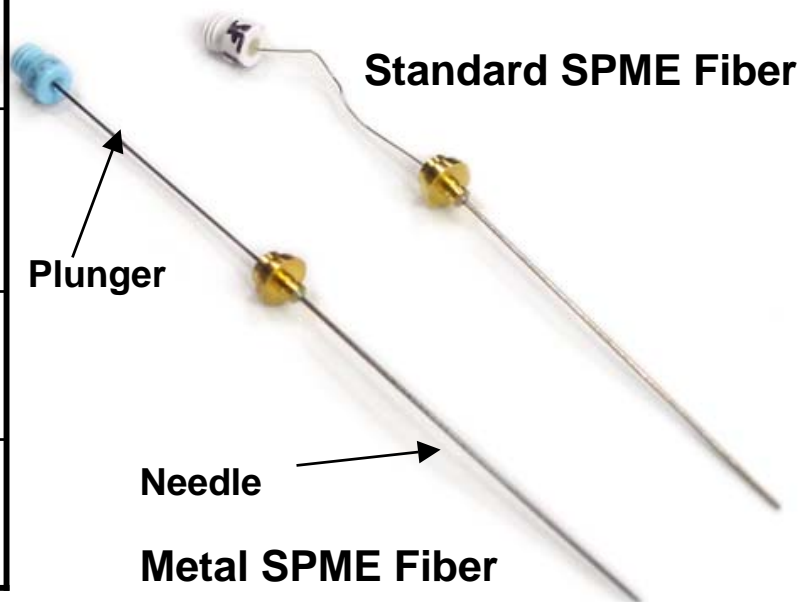
Topics in Presentation

- New Super-elastic metal fiber assemblies
- New metal fiber core
- New polyethylene glycol fiber (PEG) (Carbowax) phase coating



Super Elastic vs. Standard SPME Fiber Assemblies

	Super Elastic SPME Fibers	Std SPME Fibers
Needle	23 gauge metal alloy Beveled tip	24 or 23 gauge SS Blunt tip
Fiber Core	Metal alloy	Fused silica or Stableflex
Plunger	Solid metal alloy	SS tubing



Why Develop New SPME Metal Fiber Assemblies?

- Extend assembly lifetime
- Improve the durability and reproducibility of the extraction fiber
- Enhance compatibility with the CTC autosampler



CTC Analytics CombiPal

- The Combi Pal contains a rapid orbital shaker.
- This type of agitation is very useful to the analyst when SPME extraction is completed especially in the direct immersion mode.
- The fiber assembly is subjected to an intense wagging motion which place intense strain on its mid section pf the assembly needle where it is in contact with the sample vial septa.
- The needle can bow and not properly hit the GC inlet hole or not properly pierce the next vial and destroy the needle.



Advantages Of The New Assembly Design

- Increased durability – up to 10 times longer than stainless steel assemblies
- Stronger, more flexible plunger
- Beveled needle tip for easier septa penetration
- Needle tip is compatible with Merlin Microseals and other septum free inlet sealing systems
- Contains fiber coatings on metal core



The Future is Just Around the Bend

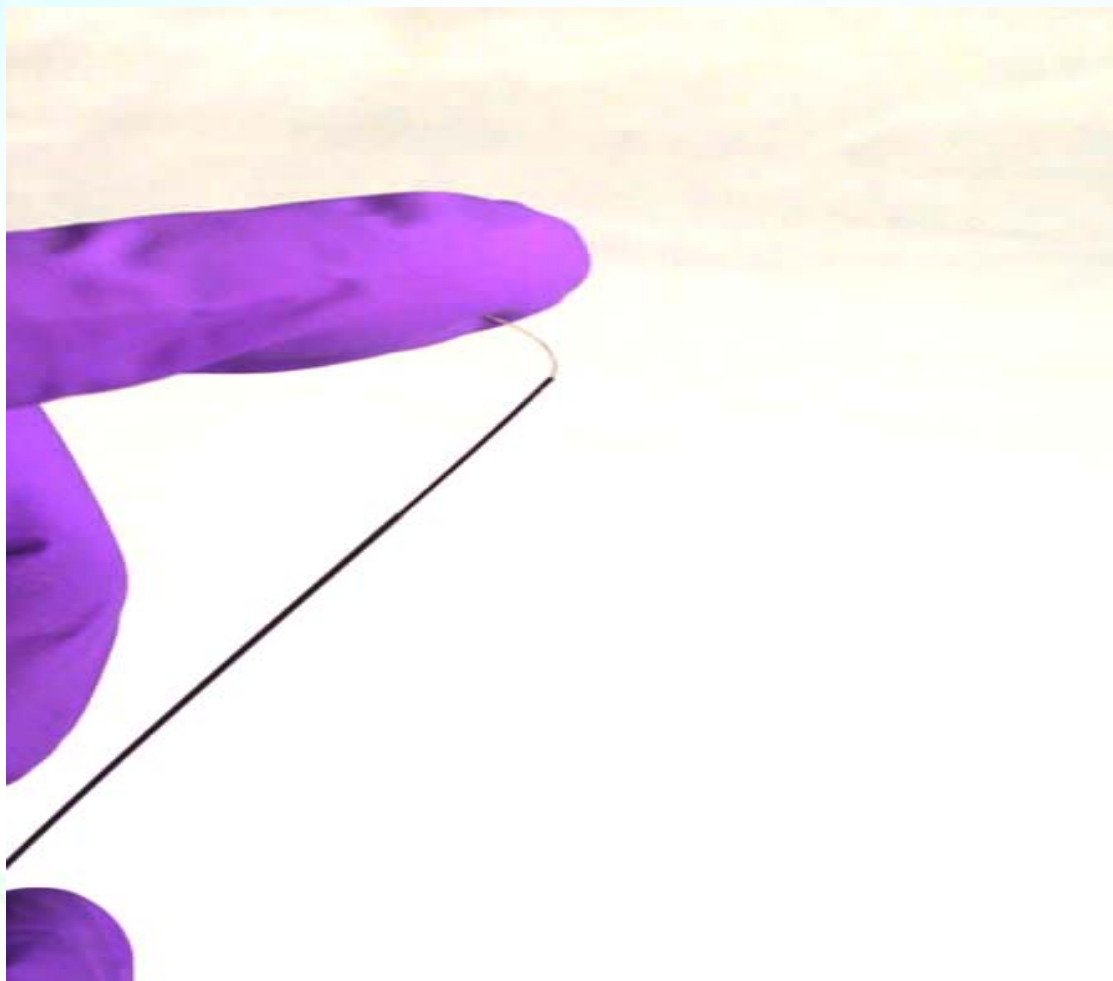


Qualities of Metal Fiber Core

- Inert metal fiber core, does not contain iron
- Coating bonds better to the metal core compared to the Stableflex core
- Does not produce extraneous peaks
- Metal fiber can be crimped into assembly without glue



Metal Fiber Core



Comparison of Fiber Cores (PDMS-DVB)

1. Methylamine
2. Dimethylamine
3. n-Propanol (IS)
4. Diethylamine
5. Triethylamine

sample: 1 ppm each in water
with 25 NaCl, 0.05 M
phosphate Buffer pH 11

fiber: PDMS-DVB various
core

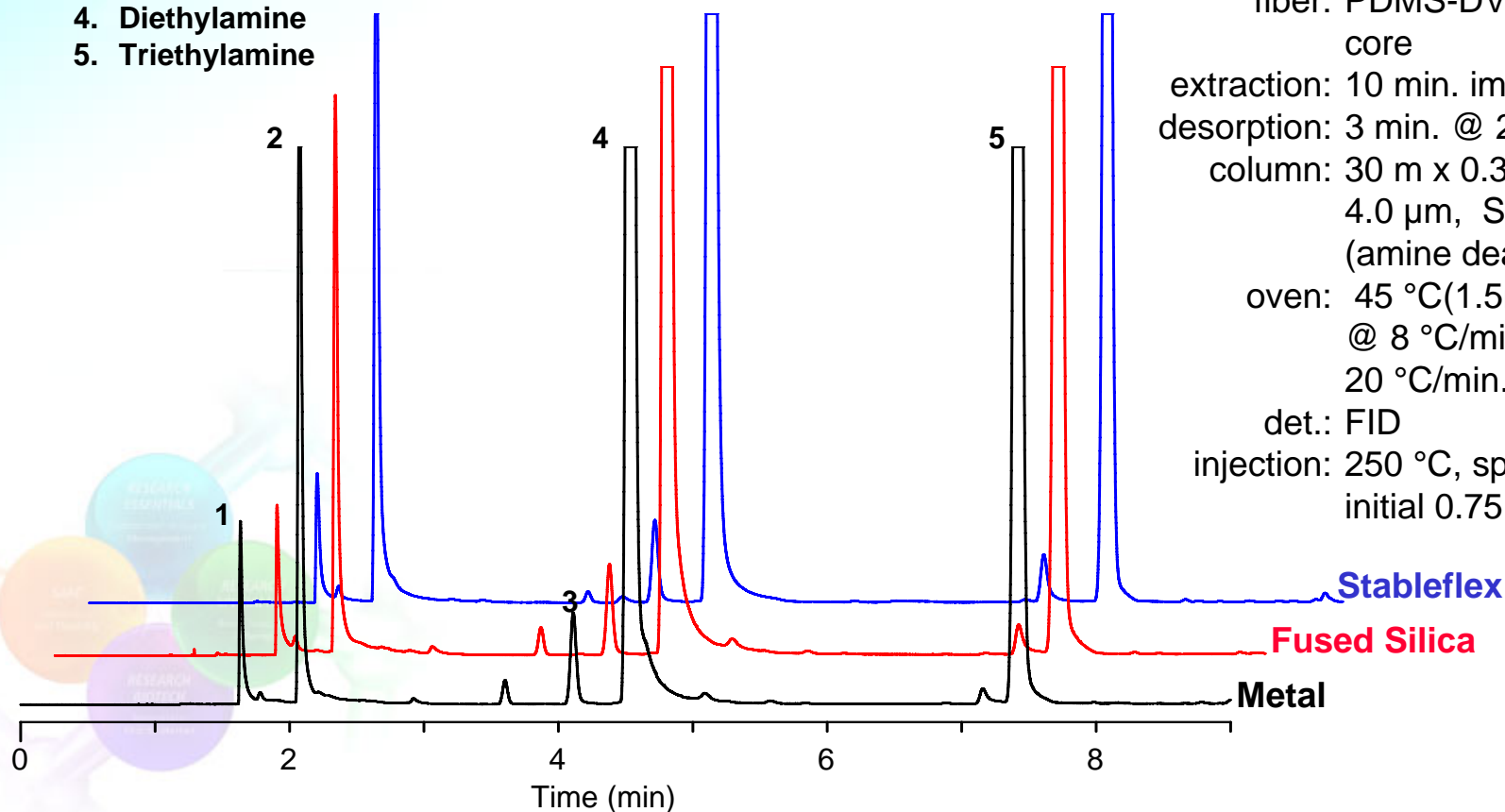
extraction: 10 min. immersion
desorption: 3 min. @ 250 °C

column: 30 m x 0.32 mm x
4.0 µm, SPB-1 sulfur
(amine deactivate)

oven: 45 °C(1.5min) to 80 °C
@ 8 °C/min. to 200 °C @
20 °C/min.

det.: FID

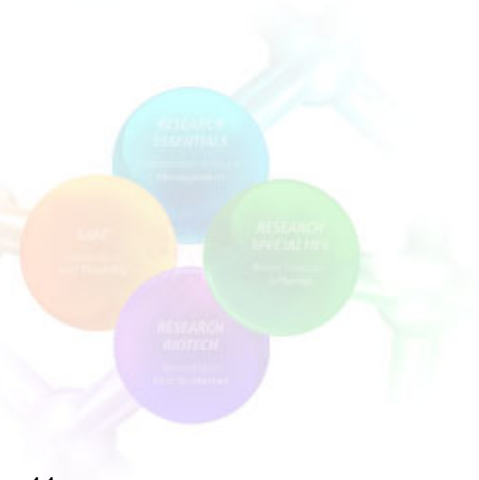
injection: 250 °C, splitless closed
initial 0.75 min.



Inertness of 3 Different Fiber Cores

All responses relative to n-propanol, all at 1 ppm.

Fiber core	Methylamine	Dimethylamine	Diethylamine	Total
Metal alloy	1.14	4.85	38.12	44.11
Fused silica	1.02	4.21	38.67	43.90
Stableflex	1.04	5.43	37.49	43.96

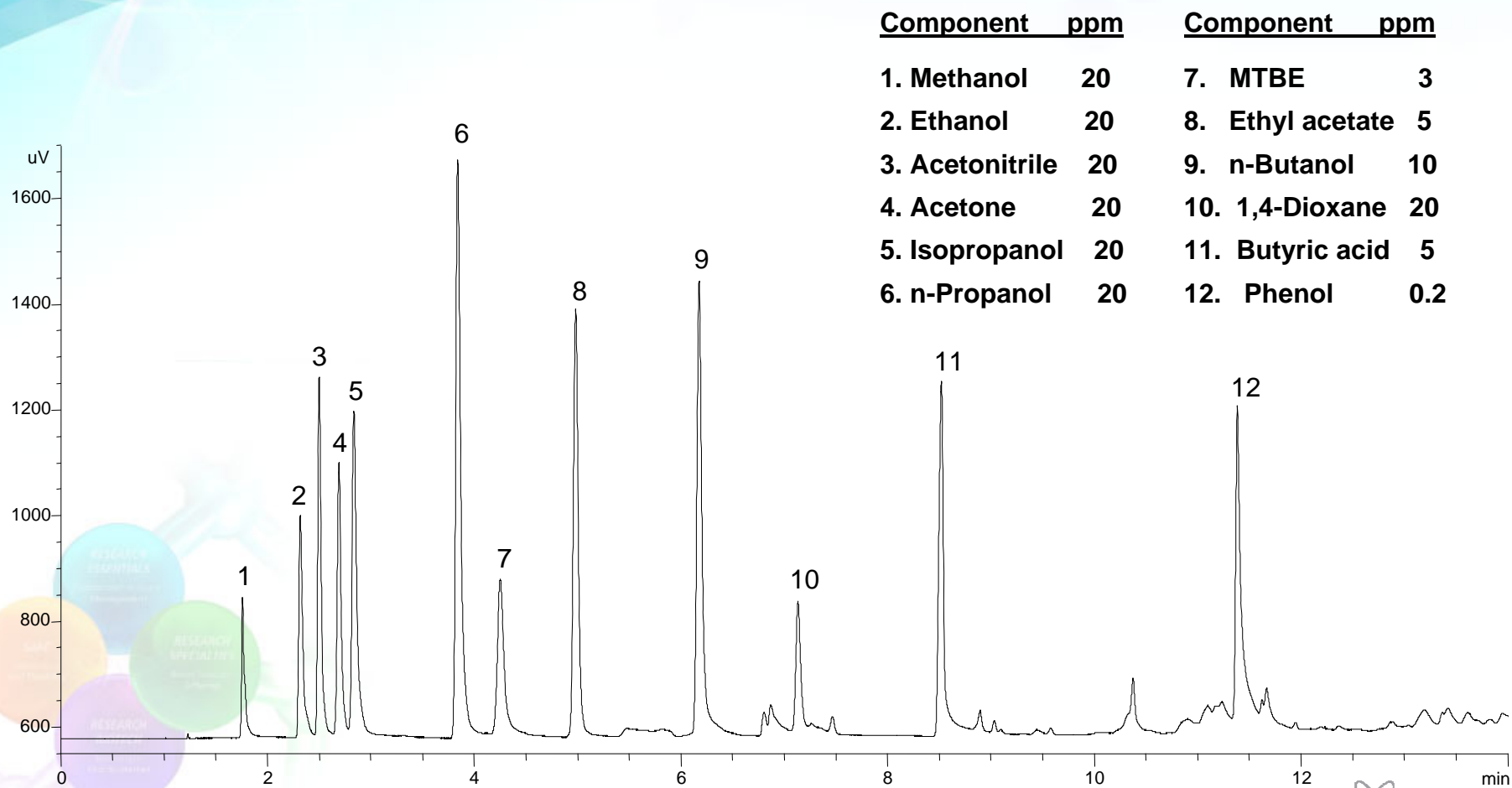


Goals for Development of New Polar Fiber

- Develop a polar fiber with a durable coating that will withstand multiple extractions from water
- Develop a polar fiber that does not contain an adsorbent
- Put the coating on an unbreakable metal fiber core
- Compare new coating with other fiber coatings
- Develop a fiber that enhances selectivity for polar analytes



Extraction of Solvents in Water with 60 μm PEG Fiber



Conditions for Analysis of Polar Solvents in Water using SPME

sample: Polar solvents in water with 25% NaCl

fiber: 60 μm PEG

extraction: 10 min., direct immersion with 60 μm PEG Fiber, with agitation using Varian 8200 autosampler

desorption: 5 min. at 240 $^{\circ}\text{C}$

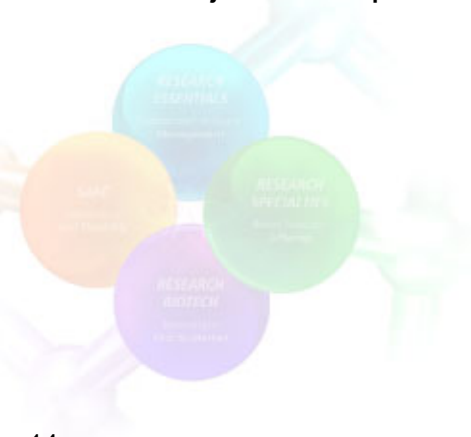
column: SPB-1 Sulfur, 30 m x 0.32 mm, 4.0 μm

oven: 45 $^{\circ}\text{C}$ (1.5 min.) to 80 $^{\circ}\text{C}$ at 8 $^{\circ}\text{C}/\text{min}$ to 230 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$. (10 min.)

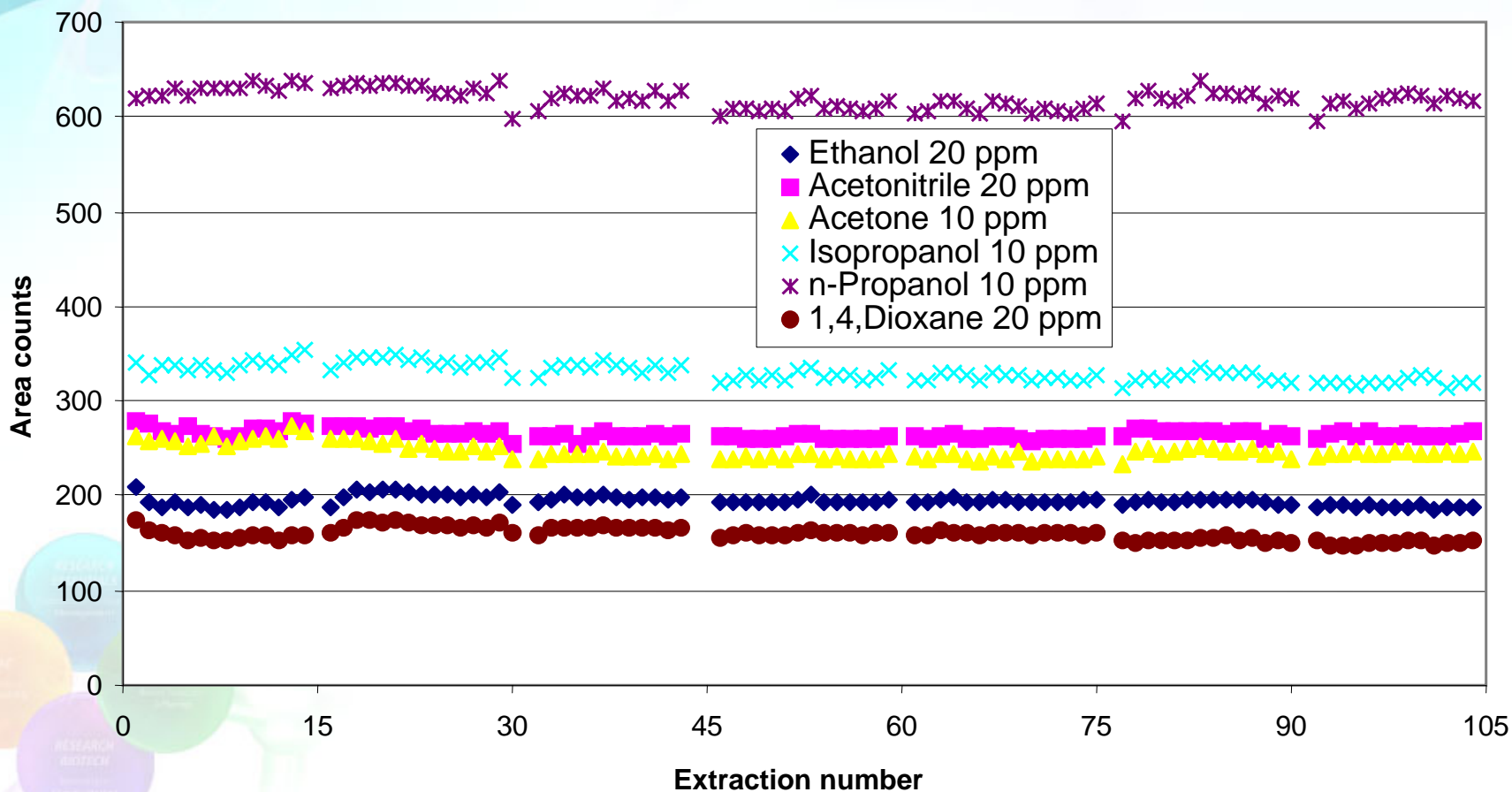
det.: FID at 300 $^{\circ}\text{C}$

carrier gas: helium at 13 psi constant pressure, 40 cm/sec. at 40 $^{\circ}\text{C}$

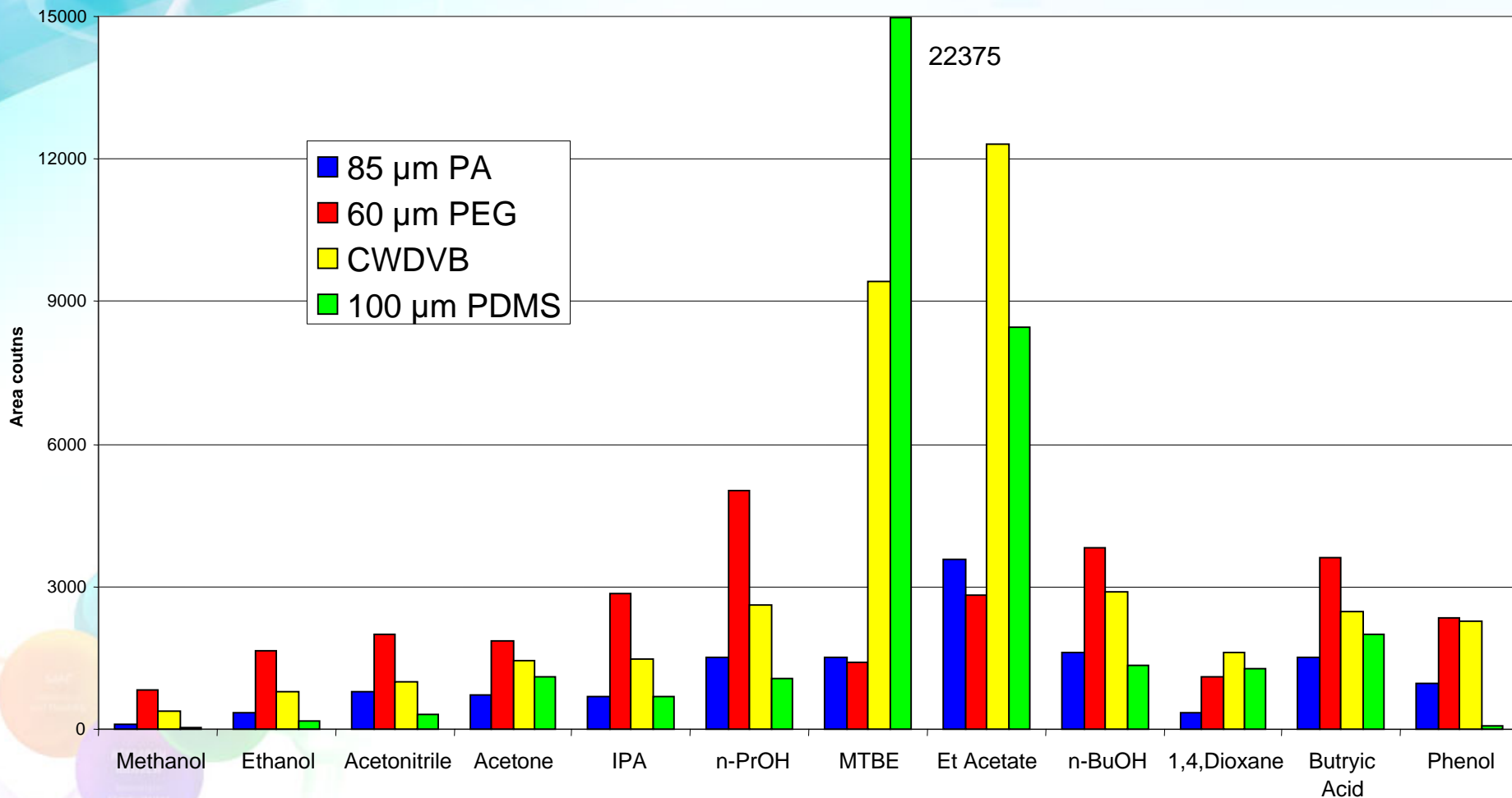
injection: splitless/split, closed initial 0.75 min. than opened 50:1 with 0.75 mm I.D. liner



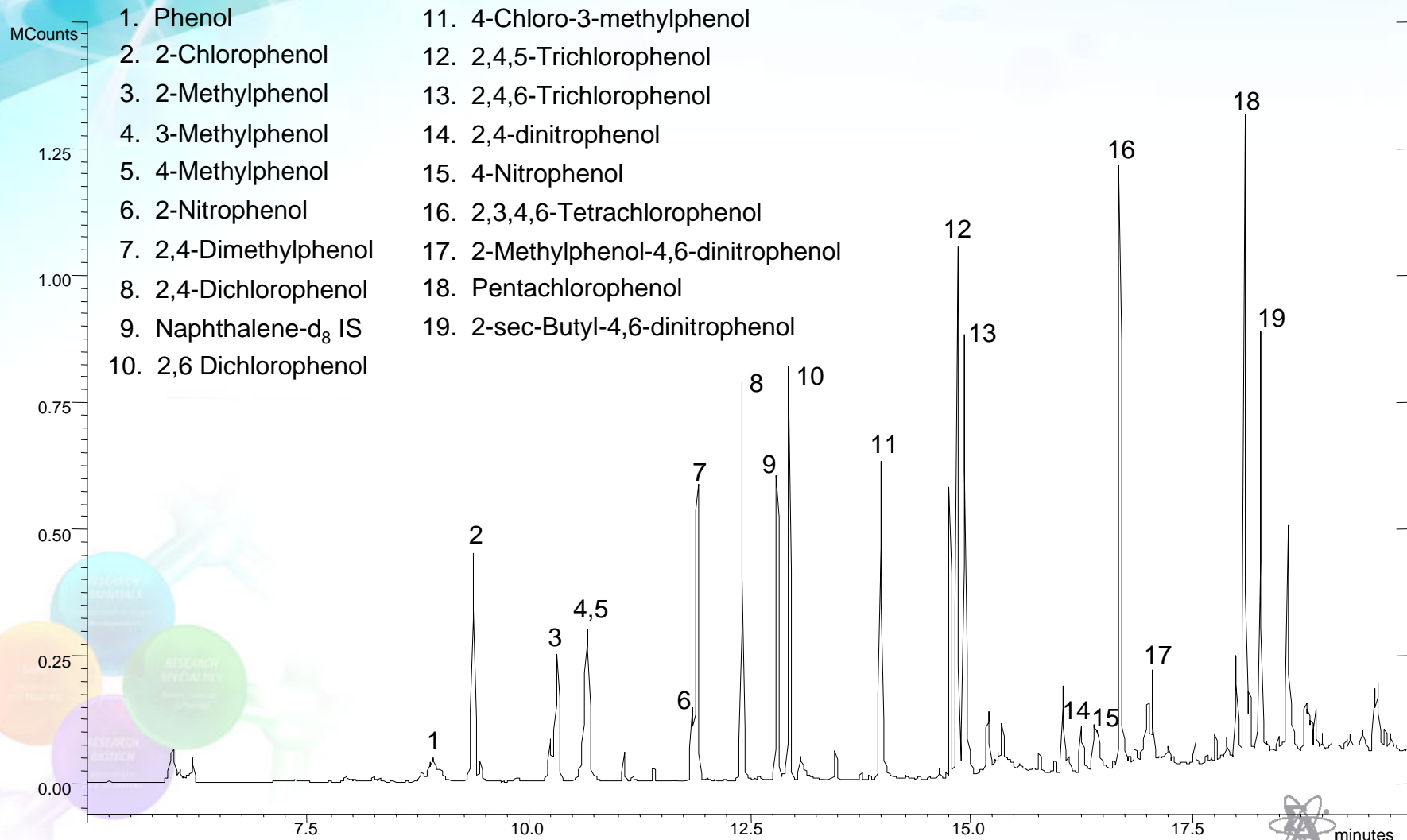
Durability of PEG Fibers with Repeated Extractions



Comparison of Fibers for Extraction of Solvents



Phenols at 25 ppb in water by SPME PEG Fiber



Conditions for Extraction of Phenols

sample: phenols at 25 ppb in 0.1M phosphate buffer, pH 2, with 25% NaCl, 9 mL in 10 mL screw cap vial

fiber: 60 μm Carbowax (PEG)

extraction: 30 min., direct immersion with agitation using CombiPAL

desorption: 2 min. at 250 $^{\circ}\text{C}$, splitless for 0.75 min. then opened

column: SLB-5ms 30 m x 0.25 mm I.D., 0.5 μm film

det.: ITMS $m/z = 45-275$ @ 0.7 μs sec. per scan, transfer line 310 $^{\circ}\text{C}$

oven: 50 $^{\circ}\text{C}$ (2.0 min.) to 160 $^{\circ}\text{C}$ @ 10 $^{\circ}\text{C}/\text{min.}$ to 280 $^{\circ}\text{C}$ @ 20 $^{\circ}\text{C}/\text{min.}$

carrier gas: helium, 1 mL/min. constant flow, 8.7 psi

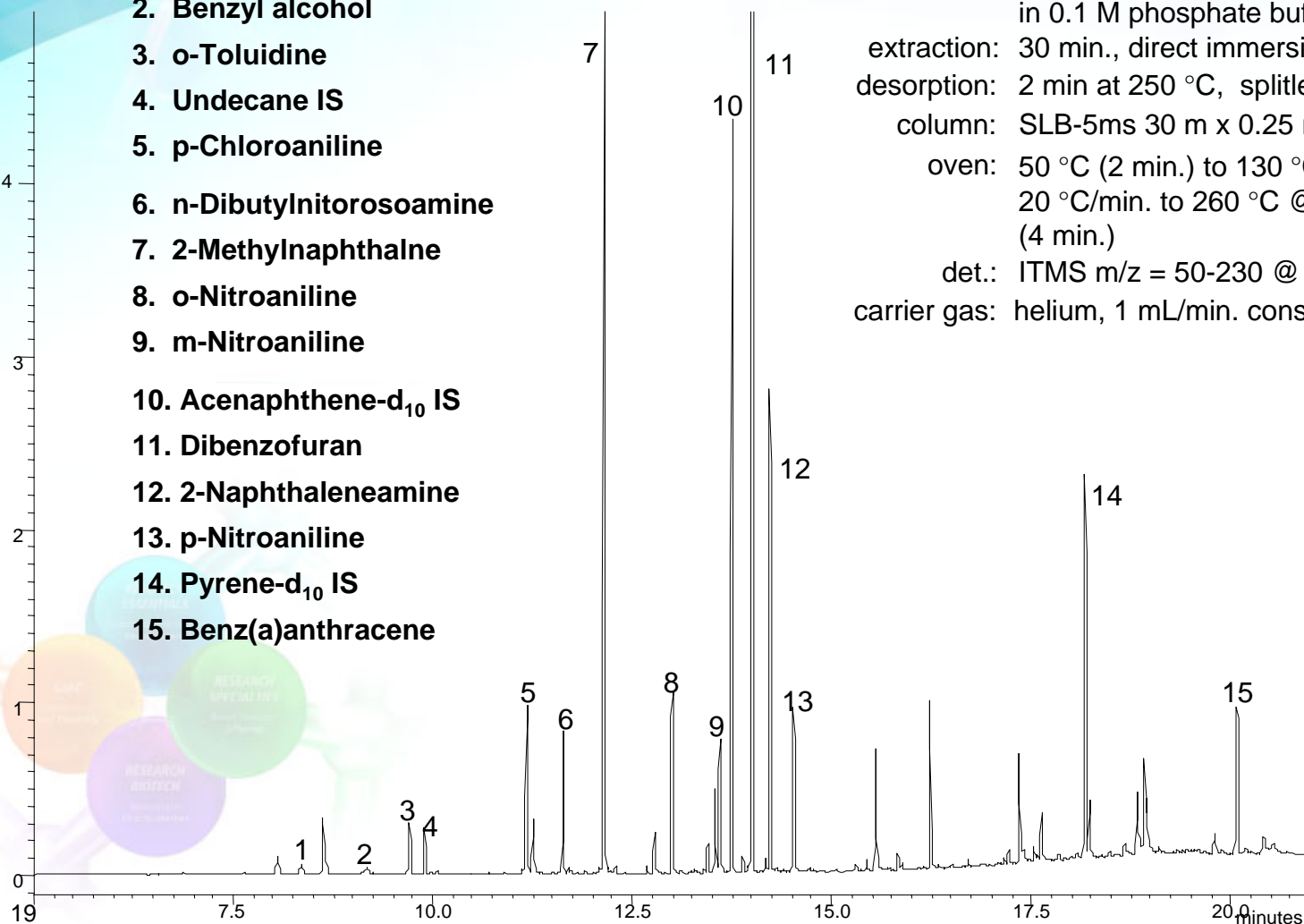
injection: splitless/split with 0.75 mm I.D. liner and Merlin Microseal



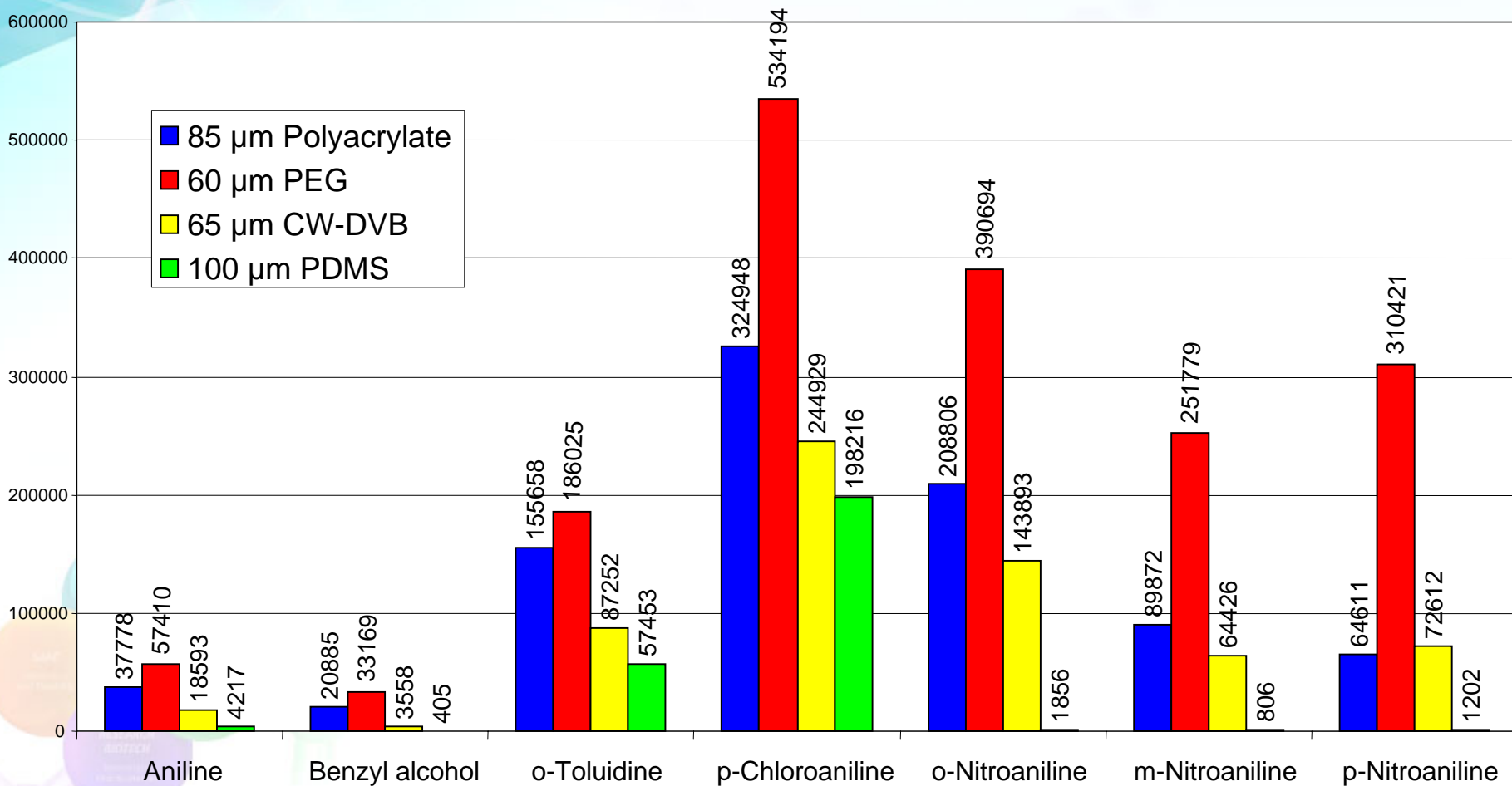
Base Neutral Analytes at 50 ppb with PEG Fiber

1. Aniline
2. Benzyl alcohol
3. o-Toluidine
4. Undecane IS
5. p-Chloroaniline
6. n-Dibutylnitrosoamine
7. 2-Methylnaphthalne
8. o-Nitroaniline
9. m-Nitroaniline
10. Acenaphthene-d₁₀ IS
11. Dibenzofuran
12. 2-Naphthaleneamine
13. p-Nitroaniline
14. Pyrene-d₁₀ IS
15. Benz(a)anthracene

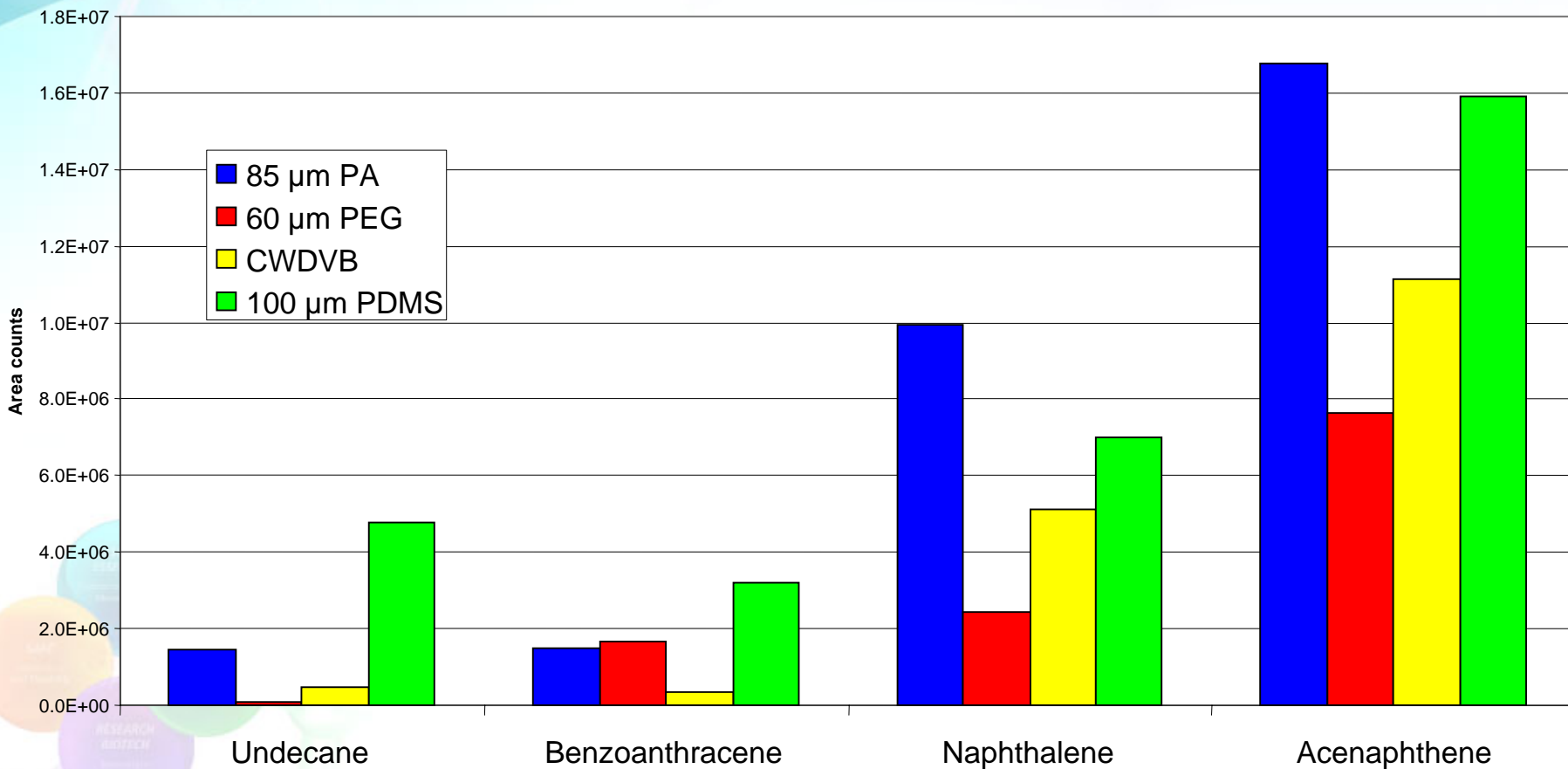
sample: base-neutral analytes, 50 ppb, Int Stds 25 ppb
in 0.1 M phosphate buffer, pH 9, with 25% NaCl
extraction: 30 min., direct immersion with agitation
desorption: 2 min at 250 °C, splitless for 0.75min than opened
column: SLB-5ms 30 m x 0.25 mm I.D., 0.5 µm film
oven: 50 °C (2 min.) to 130 °C @ 12 °C/min. to 200 °C @
20 °C/min. to 260 °C @ 15 °C to 310 °C at 20 °C
(4 min.)
det.: ITMS m/z = 50-230 @ 0.65 µm sec. per scan
carrier gas: helium, 1 mL/min. constant flow, 8.7 psi



Comparison of SPME Fibers Base-Neutrals (Basic Fraction)



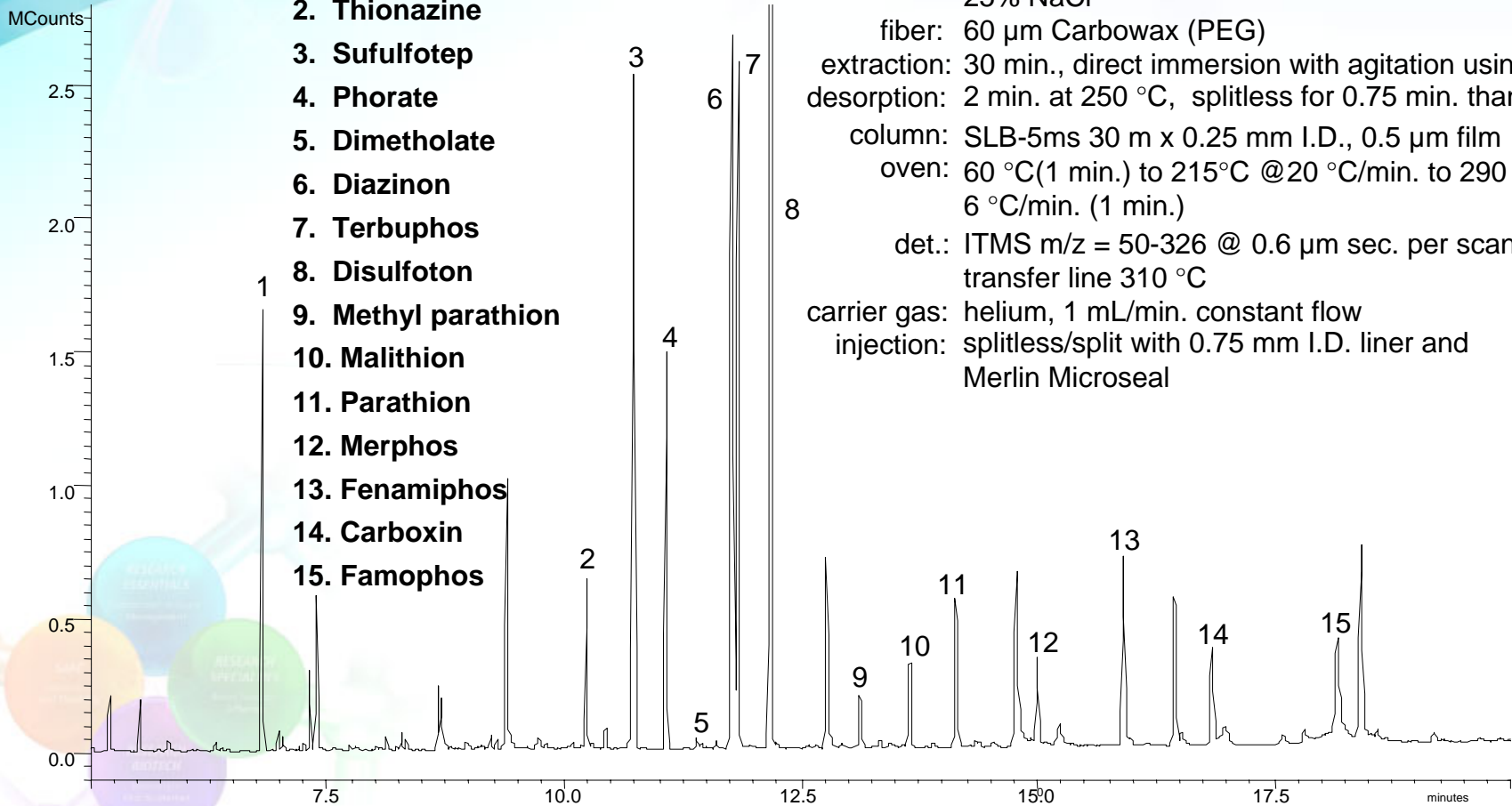
Comparison of SPME Fibers Base-Neutrals (Neutral Fraction)



Organophosphorus Pesticides at 10 ppb by SPME

1. Triethylthiophosphodiate
2. Thionazine
3. Sufultotep
4. Phorate
5. Dimetholate
6. Diazinon
7. Terbutphos
8. Disulfoton
9. Methyl parathion
10. Malithion
11. Parathion
12. Merphos
13. Fenamiphos
14. Carboxin
15. Famophos

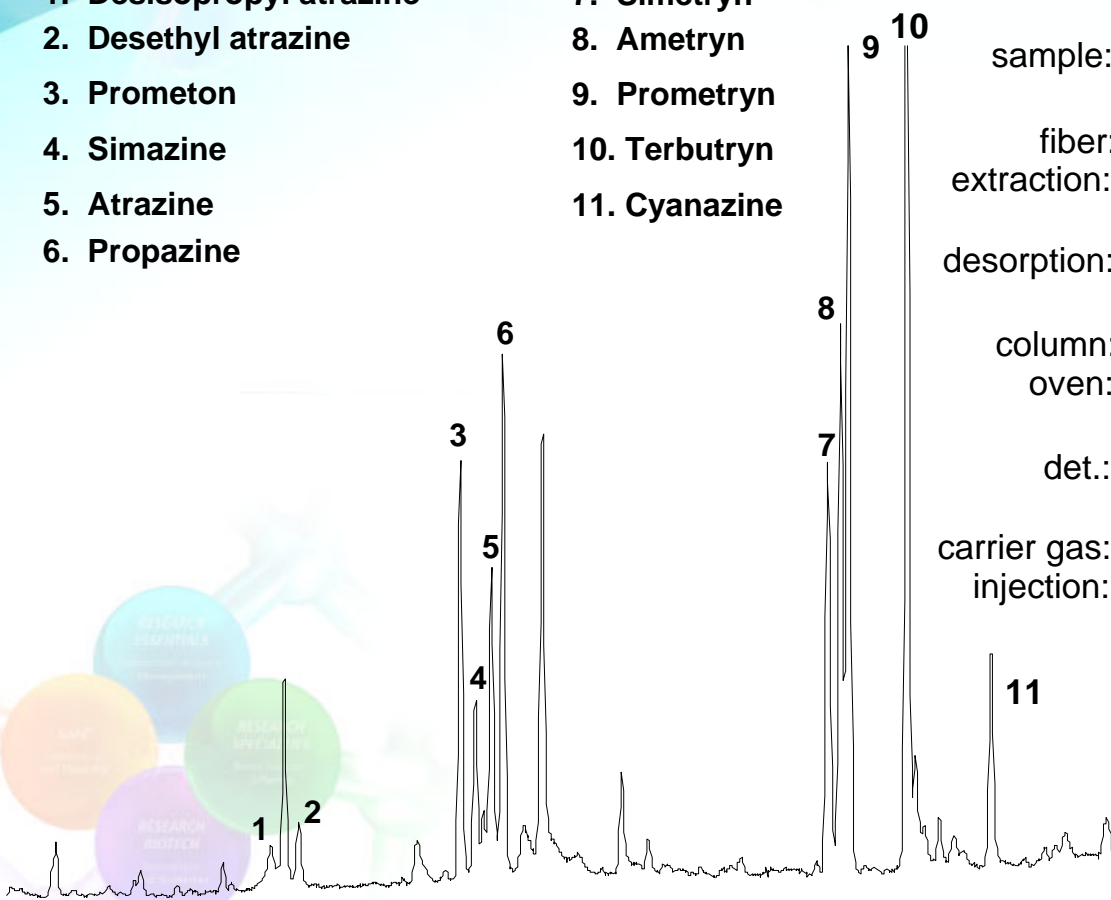
sample: OPPs at 10 ppb in 0.1 M phosphate buffer, pH 7, 25% NaCl
fiber: 60 μm Carbowax (PEG)
extraction: 30 min., direct immersion with agitation using CombiPAL
desorption: 2 min. at 250 °C, splitless for 0.75 min. than opened
column: SLB-5ms 30 m x 0.25 mm I.D., 0.5 μm film
oven: 60 °C(1 min.) to 215°C @20 °C/min. to 290 °C @ 6 °C/min. (1 min.)
det.: ITMS m/z = 50-326 @ 0.6 μm sec. per scan, transfer line 310 °C
carrier gas: helium, 1 mL/min. constant flow
injection: splitless/split with 0.75 mm I.D. liner and Merlin Microseal



Triazine Herbicides at 2 ppb by SPME

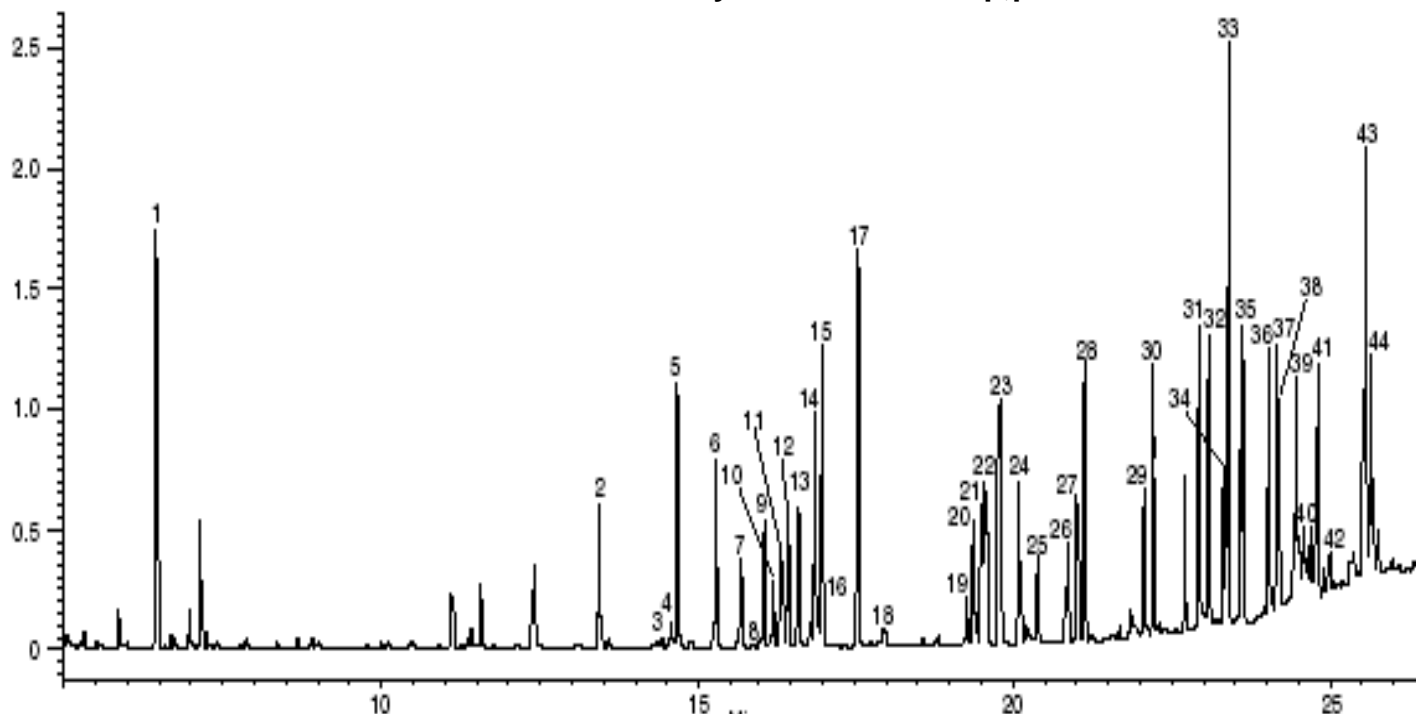
1. Desisopropyl atrazine
2. Desethyl atrazine
3. Prometon
4. Simazine
5. Atrazine
6. Propazine
7. Simetryn
8. Ametryn
9. Prometryn
10. Terbutryn
11. Cyanazine

sample: triazine pesticides at 2 ppb in 0.1 M phosphate buffer, pH 7, with 25% NaCl, 9 mL in 10 mL vial
fiber: 60 μ m PEG
extraction: 30 min., direct immersion with agitation using CombiPAL
desorption: 2 min. at 250 °C, splitless for 0.75 min. than opened
column: SLB-5ms 30 m x 0.25 mm I.D., 0.5 μ m film
oven: 60 °C(1 min.) to 150 °C @ 25 °C/min. to 230 °C @ 5 °C/min. (5 min. hold)
det.: ITMS m/z = 150-250 @ 0.5 μ m sec. per scan, transfer line 310 °C
carrier gas: helium, 1 mL/min. constant flow
injection: splitless/split with 0.75 mm I.D. liner and Merlin Microseal



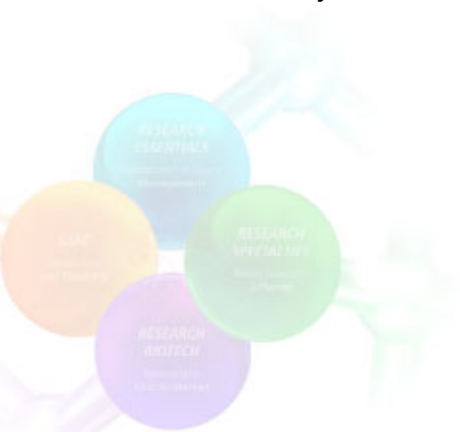
Extraction of 44 Pesticides with PEG SPME Fiber

- | | | | |
|-----------------------------|----------------------|-------------------------|------------------------|
| 1. Triethylthiophosphodiate | 12. Propazine | 23. Heptachlor | 34. Carboxin |
| 2. Thionazine | 13. Beta BHC | 24. Terbutryn | 35. Dieldrin |
| 3. Desisopropyl atrazine | 14. Terbuphos | 25. Malithion | 36. Endrin |
| 4. Desethyl atrazine | 15. Deta BHC | 26. Cyanazine | 37. m,p'- DDD |
| 5. Sulfotep | 16. Diazinon | 27. Parathion | 38. Endosulfan II |
| 6. Phorate | 17. Disulfoton | 28. Aldrin | 39. Endrin aldehyde |
| 7. Alpha BHC | 18. Gamma BHC | 29. Merphos | 40. Famophos |
| 8. Dimetholate | 19. Methyl parathion | 30. Heptachlor expoxide | 41. p,p'- DDT |
| 9. Prometon | 20. Simetryn | 31. Fenamiphos | 42. Endosulfan sulfate |
| 10. Simazine | 21. Ametryn | 32. Endosulfan I | 43. Methoxychlor |
| 11. Atrazine | 22. Prometryn | 33. p,p'- DDE | 44. Endrin ketone |

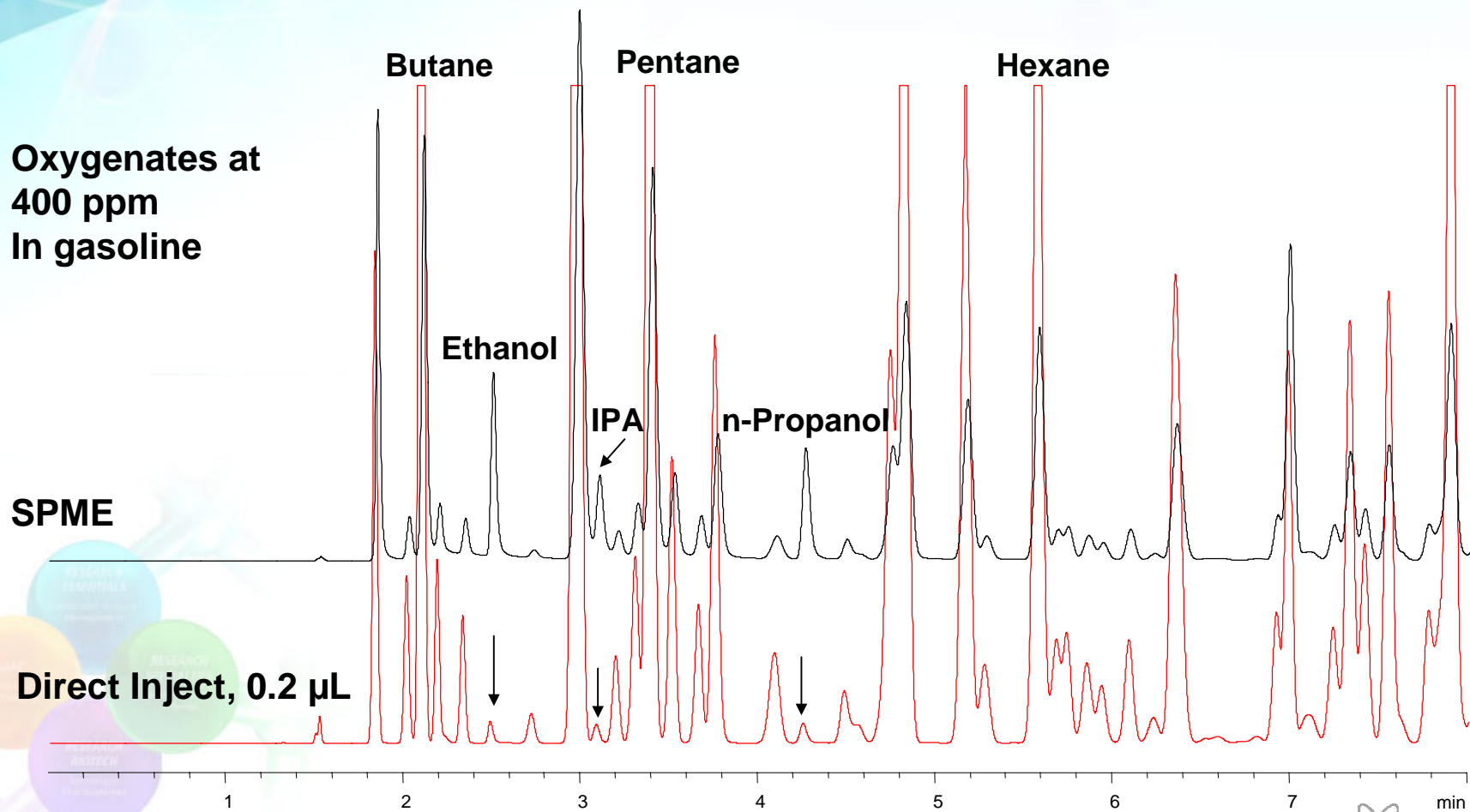


Conditions for Analysis of Chlorinated Pesticides

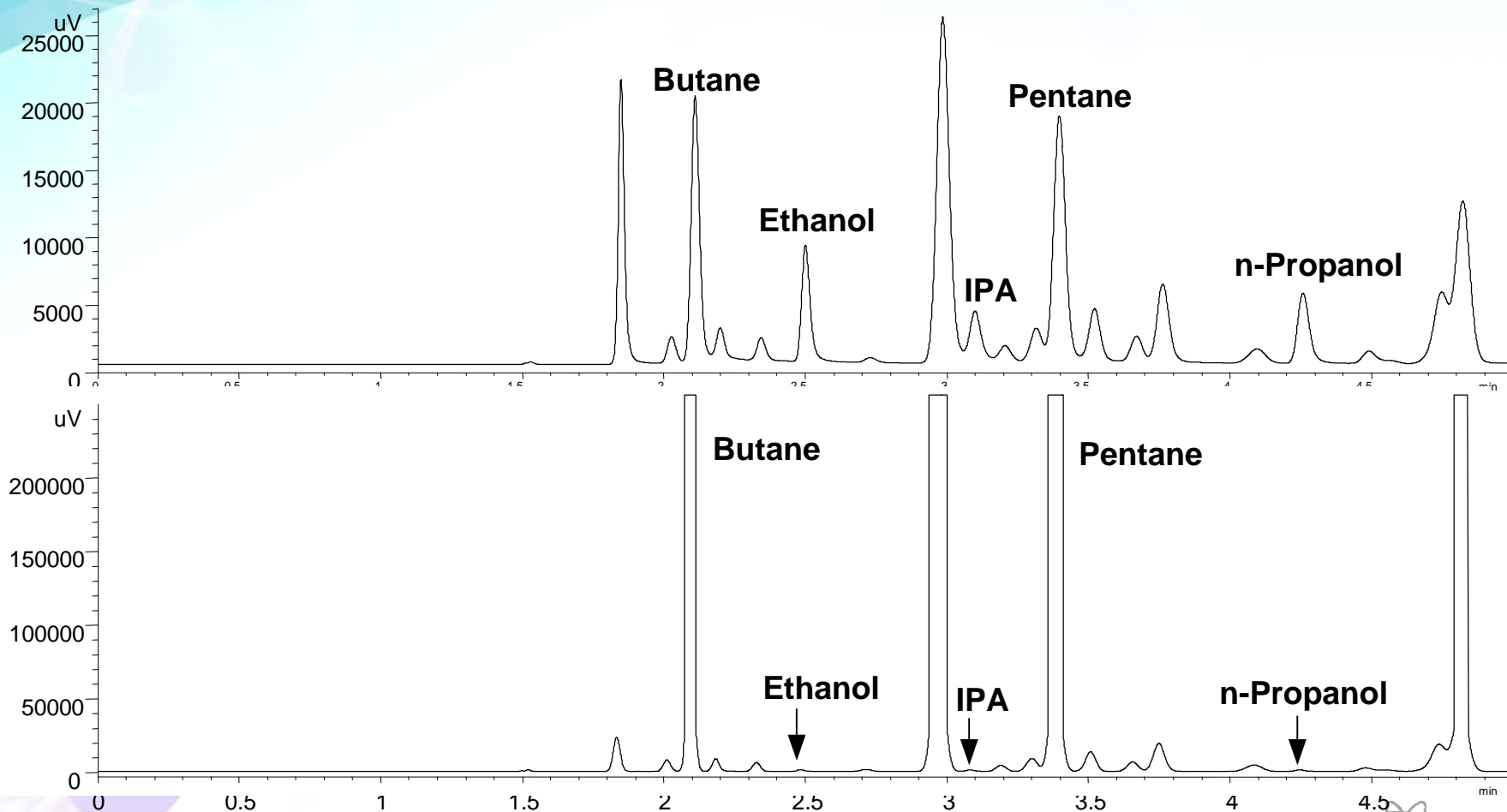
- sample: All pesticides at 10 ppb in 0.1 M phosphate buffer, pH 7 with 25% NaCl, 9 mL in 10 mL screw cap vial
- fiber: 60 μm Carbowax (PEG)
- extraction: 30 min., direct immersion with agitation using CombiPAL
- desorption: 2 min. at 250 $^{\circ}\text{C}$, splitless for 0.75 min. than opened
- column: SLB-5ms 30 m x 0.25 mm I.D., 0.5 μm film
- oven: 60 $^{\circ}\text{C}$ (1 min.) to 150 $^{\circ}\text{C}$ @ 25 $^{\circ}\text{C}/\text{min.}$ to 230 $^{\circ}\text{C}$ @ 5 $^{\circ}\text{C}/\text{min.}$ to 310 @ 18 $^{\circ}\text{C}$ (3 min.)
- det.: ITMS $m/z = 60\text{-}450$ @ 0.9 μm sec. per scan, transfer line 310 $^{\circ}\text{C}$
- carrier gas: helium, 1 mL/min. constant flow
- injection: splitless/split with 0.75 mm I.D. liner and Merlin Microseal



Comparison of Oxygenates in Gasoline by Direct Injection and by SPME with PEG Fiber (Same Y scale)



Comparison of Oxygenates in Gasoline, Direct Injection vs. SPME (Chromatograms normalized)



Enhancement of Oxygenates in Gasoline using SPME

Oxygenates in gasoline at 400 ppm (0.4%)

	Area Counts		Relative to Butane		SPME
	SPME	Injection	SPME	Injection	Enhancement
Ethanol	21214	2055	0.493	0.003	155
Isopropanol	12403	2191	0.288	0.003	85
n-Propanol	16212	2636	0.376	0.004	92
Butane IS	43071	644669			

Direct injection of gasoline, 0.2 μ L, split 50:1

SPME Extraction 15 min., direct immersion with PEG Fiber, split 50:1



Analytical Conditions for Analysis of Oxygenates in Gasoline using SPME

- sample: oxygenates at 400 ppm in gasoline, 3.5 mL in 4 mL vial
- fiber: 60 μm PEG metal
- extraction: 15 min., direct immersion with 60 μm PEG fiber
- desorption: 5 min. at 240 $^{\circ}\text{C}$
- column: SPB-1 sulfur, 30 m x 0.32 mm, 4.0 μm
- oven: 40 $^{\circ}\text{C}$ (1.5 min.) to 80 $^{\circ}\text{C}$ at 8 $^{\circ}\text{C}/\text{min.}$ to 260 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min.}$ (10 min.)
- det.: FID at 300 $^{\circ}\text{C}$
- carrier gas: helium at 13 psi constant pressure, 40 cm/sec. at 40 $^{\circ}\text{C}$
- injection: split 50:1, 240 $^{\circ}\text{C}$

Findings Concerning 60 μm PEG Fiber

1. Methanol may be produced by the fiber under acidic conditions for the first several extractions. A trace amount of inhibitor, that can generate methanol, in the phase may still be present after conditioning.
2. The fiber can swell either in headspace or immersion mode when exposed to water samples with total soluble organic content exceeding 200 ppm. Elongation of the fiber coating can occur. The fiber is best suited for trace level analyses.
3. The fiber does not swell when immersed in hydrocarbon solvents making it suitable for extraction of polar analytes out of hydrocarbon solvents.



Conclusions

- New more durable and flexible metal alloy assembly has been designed
- Super-elastic properties make it more compatible with autosamplers
- Coatings on a new metal fiber core made with the same super-elastic properties have been developed
- The fiber core is inert, durable and the coating bonds well to it
- New PEG fiber coating has been developed without an adsorbent
- The coat is durable and long lasting
- The coating is on the inert metal fiber core
- PEG fiber is available in standard stainless steel assemblies
- PEG fiber is suitable for extraction of polar analytes out of hydrocarbon solutions



Product Information

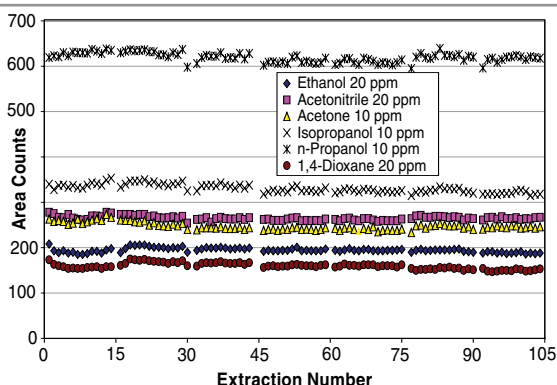
Polyethylene Glycol (PEG) SPME Fibers

A new polar SPME fiber has been developed with a polyethylene glycol phase coating. This new 60 µm PEG SPME fiber coating does not contain an adsorbent polymer. Eliminating the adsorbent produces a more polar, selective fiber. The new PEG phase is coated on an inert metal fiber core attached to the standard stainless steel assemblies. The metal fiber core also enables long lengths of the fiber to be coated continuously, helping improve reproducibility between fibers. Also, the metal fiber is unbreakable and the coating bonds to the metal core better than other surfaces.

Durability of Fiber Coating

Since Carbowax® is a water-soluble material, the durability of the coating often becomes a problem due to swelling and stripping when extracting analytes out of water. A top priority for the PEG fiber coating was to make it more durable and robust coating. To achieve this, the coating must bond securely to the fiber core and not swell significantly when inserted in water. This requires a highly cross-linked polymer. To demonstrate the durability of the PEG fibers, they were immersed for 10 minutes in water containing small polar solvents at ppm levels. The Varian 8200 autosampler was used, which agitates the fiber similarly to an electric razor. This fast vibration is often detrimental to fiber coatings. With the old CW-DVB fibers, the life of the fiber in the system ranged between 1 and 20 extractions before part or all of the coating came off the fiber core. With the new PEG fiber, the average life of the fibers was over 100 extractions. After 15 extractions, a water blank was extracted to remove salt on the fiber and the fiber was examined. Figure 1 shows the response of the solvents over 100 extractions. There was a slight reduction in analyte response of about 3% between the first 10 and the last 10 extractions. No visible decay in the appearance of the fiber coating was observed and the film thickness remained constant throughout the study.

Figure 1. Analyte Response from Repeated Extractions with 60 µm PEG SPME Fiber

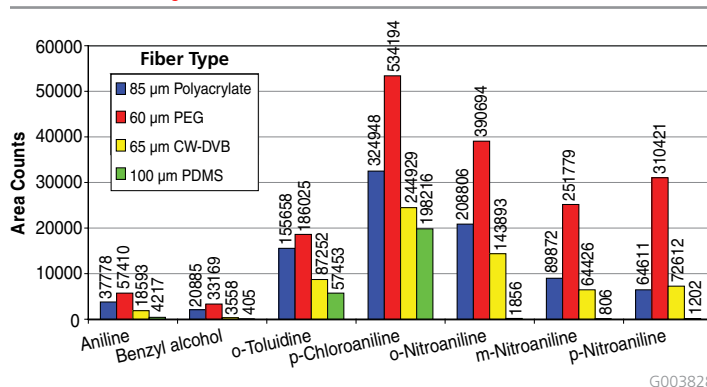


G003827

Applications Using 60 µm PEG Fiber

Since the 60 µm PEG fiber is being offered as a replacement for the CW-DVB fibers, applications comparing fiber performance is important. Several classes of analytes were evaluated and some examples are shown below. For a more detailed comparison please contact Supelco Technical Service (800-359-3041/814-359-3041) for additional information. A mixture containing base neutral analytes was evaluated with several different SPME fibers. Figure 2 compares the fibers for the extraction of the more polar analytes in the mixture. These analytes were extracted out of buffered salt water (pH 9) by immersion for 30 minutes with agitation using the CombiPAL™ autosampler.

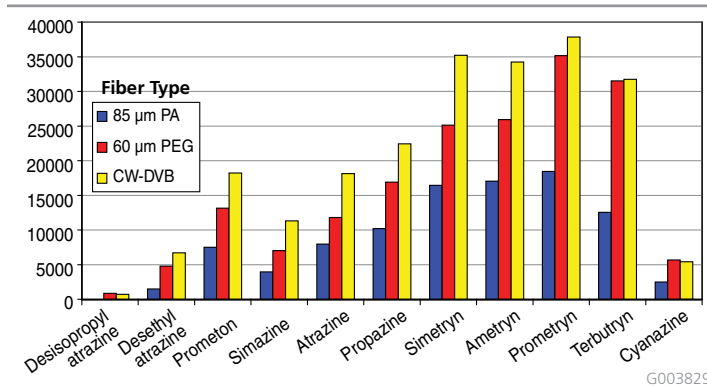
Figure 2. Comparison of SPME Fibers by the Extraction of Basic Analytes



G003828

The results show that the 60 µm PEG fiber extracts the more polar analytes better than the other fiber coatings, while it extracts less of the non-polar analytes compared to the other fibers. Triazine herbicides have both polar and non-polar properties and most of the analytes are extracted well with a variety of fibers. However, for the extraction of the metabolites of atrazine, desethyl atrazine and desisopropyl atrazine, more polar fibers are recommended. Figure 3 (over) shows a comparison of the fibers for the extraction of the herbicides.

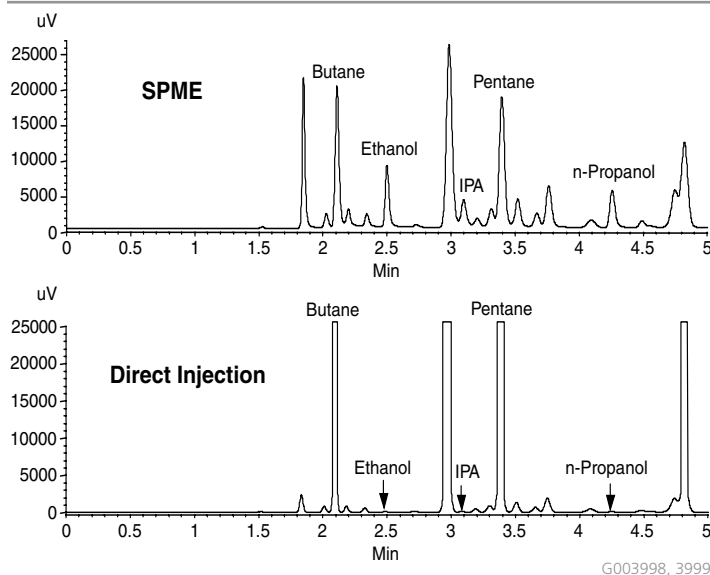
Figure 3. Comparison of Fiber Coatings for the Extraction of Herbicides



All three polar fibers extract the triazine herbicides well. The most polar analyte, desisopropyl is best extracted by the PEG fiber. Since the PEG fiber extracts polar analytes well, and reduces the amount of less polar analytes extracted, the fiber is ideal for samples containing both polar and non-polar analytes.

The PEG coating is suitable for the extraction of polar analytes out of a non-polar matrix. Figure 4 shows an example of the extraction of oxygenated compounds out of gasoline compared to a direct injection of the same sample. The fiber was immersed 15 minutes in gasoline containing 400 ppm each of several alcohols. The polar phase repels hydrocarbons and has a high affinity for the small polar alcohols.

Figure 4. Comparison of Oxygenates in Gasoline, Direct Injection vs. SPME (Chromatograms normalized)



Conclusions

The new polar, PEG SPME fibers are more durable and selective toward polar analytes. Also, the fiber is suitable for extracting polar analytes out of a hydrocarbon matrix. The PEG fiber coating should be a good complement to the PDMS fibers particularly for the extraction of semi-volatile analytes.

Ordering Information

Description

60 µm PEG SPME Fiber, autosampler
60 µm PEG SPME Fiber, manual

Cat. No.

57354-U
57355-U

Trademarks

Carbowax — Union Carbide Chemicals & Plastics Technology Corp.
CombiPAL — CTC Analytics

SPME - Technology licensed exclusively to Supelco. US patent #5,691,206; European patent #523,092

6th Edition SPME CD

To learn more about SPME and its applications for water analysis, request a free copy of the SPME Applications CD (CJQ), which includes:

- Video demonstrations
- Over 2200 references to SPME applications
- A comprehensive list of technical literature

You can also visit us online at sigma-aldrich.com/spme



World Headquarters

3050 Spruce St., St. Louis, MO 63103
(314) 771-5765
sigma-aldrich.com

Order/Customer Service (800) 325-3010 • Fax (800) 325-5052

Technical Service (800) 325-5832 • sigma-aldrich.com/techservice

Development/Bulk Manufacturing Inquiries **SAFC**™ (800) 244-1173

The SIGMA-ALDRICH Group



©2007 Sigma-Aldrich Co. All rights reserved.
SIGMA, SAFC, SAFC, SIGMA-ALDRICH, ISOTECH, ALDRICH, FLUKA, and SUPELCO are trademarks belonging to Sigma-Aldrich Co. and its affiliate Sigma-Aldrich Biotechnology, L.P. Riedel-de Haën® trademark under license from Riedel-de Haën GmbH. Sigma brand products are sold through Sigma-Aldrich, Inc. Sigma-Aldrich, Inc. warrants that its products conform to the information contained in this and other Sigma-Aldrich publications. Purchaser must determine the suitability of the product(s) for their particular use. Additional terms and conditions may apply. Please see reverse side of the invoice or packing slip.



SIGMA-ALDRICH

Accelerating Customers' Success
through Leadership in Life Science,
High Technology and Service