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# **A Systematic Approach for Selecting the Appropriate SPME Fiber**

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T400156  
DKF

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# Overview of Presentation

- Factors that affect fiber selection
- Description of various types of fibers
- Extraction of low-molecular-weight analytes by various SPME fibers
- Extraction of semi-volatile analytes by various SPME fibers
- The effects of analyte size on SPME fibers
- Capacity of SPME fibers

# Factors Affecting Fiber Selection

- Analyte molecular weight and shape
- Analyte polarity and functionality
- Minimum detection limits
- Linear range requirements
- Fiber polarity
- Fiber extraction mechanism

# Adsorbent vs. Absorbent Fibers

## Adsorbent type fibers

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

## Absorbent type fibers

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

# Types of SPME Fibers

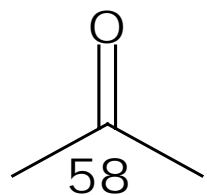
<u>Bare Fused Silica</u>	<u>Adsorbent</u>	<u>Unknown</u>
7µm Polydimethylsiloxane (PDMS)	Absorbent	Nonpolar
30µm PDMS	Absorbent	Nonpolar
100µm PDMS	Absorbent	Nonpolar
85µm Polyacrylate (PA)	Absorbent	Polar
65µm PDMS-DVB, StableFlex™	Adsorbent	Bipolar
65µm CW-DVB, StableFlex	Adsorbent	Polar
85µm Carboxen-PDMS, StableFlex	Adsorbent	Bipolar
55µm/30µm DVB/Carboxen™-PDMS, StableFlex	Adsorbent	Bipolar

# Physical Properties of Divinylbenzene and Carboxen-1006

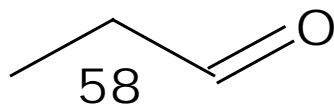
Material	Surface Area (m <sup>2</sup> /g)	Porosity (mL/g)*			Total
		macro	meso	micro	
Divinylbenzene	750	0.58	0.85	0.11	1.54
Carboxen™ 1006	720	0.23	0.26	0.29	0.78

\*Macropore = >500Å, Mesopore = 20-500Å, Micropore = 2-20Å

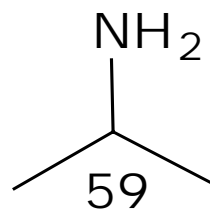
# Analytes in Volatile Study



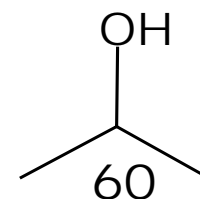
Acetone



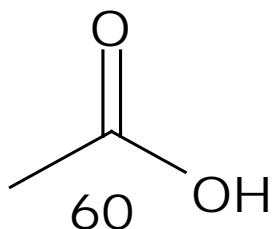
Propanal



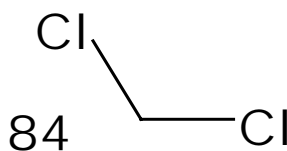
Isopropylamine



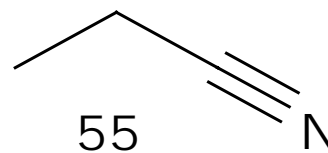
Isopropanol



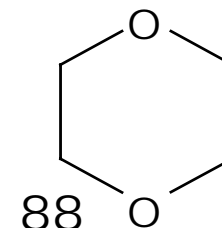
Acetic acid



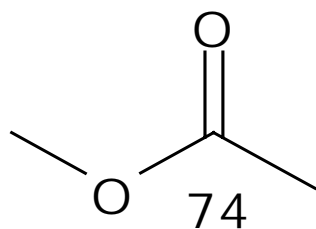
Dichloromethane



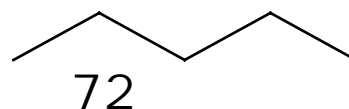
Propionitrile



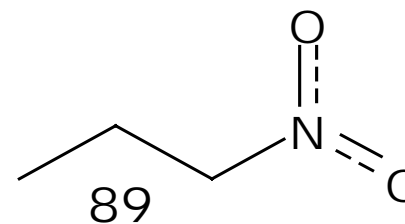
1,4-Dioxane



Methylacetate



Pentane



Nitropropane

# FID Response Factors for Analytes

Analyte	Response Factor
Acetone	1.78
Isopropanol	1.79
Methylacetate	3.11
Propanal	2.11
Methylene chloride	7.13
Acetic acid	6.41
1,4-Dioxane	2.60
Isopropylamine	1.93
Propionitrile	1.73
Nitropropane	2.15



# Analytical Conditions for Evaluation of Fibers with Volatile Analytes

**Sample:** Water containing 25% NaCl and appropriate 0.05M phosphate buffer, spiked with analytes to a final concentration of 2ppm

**Extraction:** 15 min with agitation, using Varian 8200 autosampler

**Desorption:** 2 min, temperature varies, depending on fiber

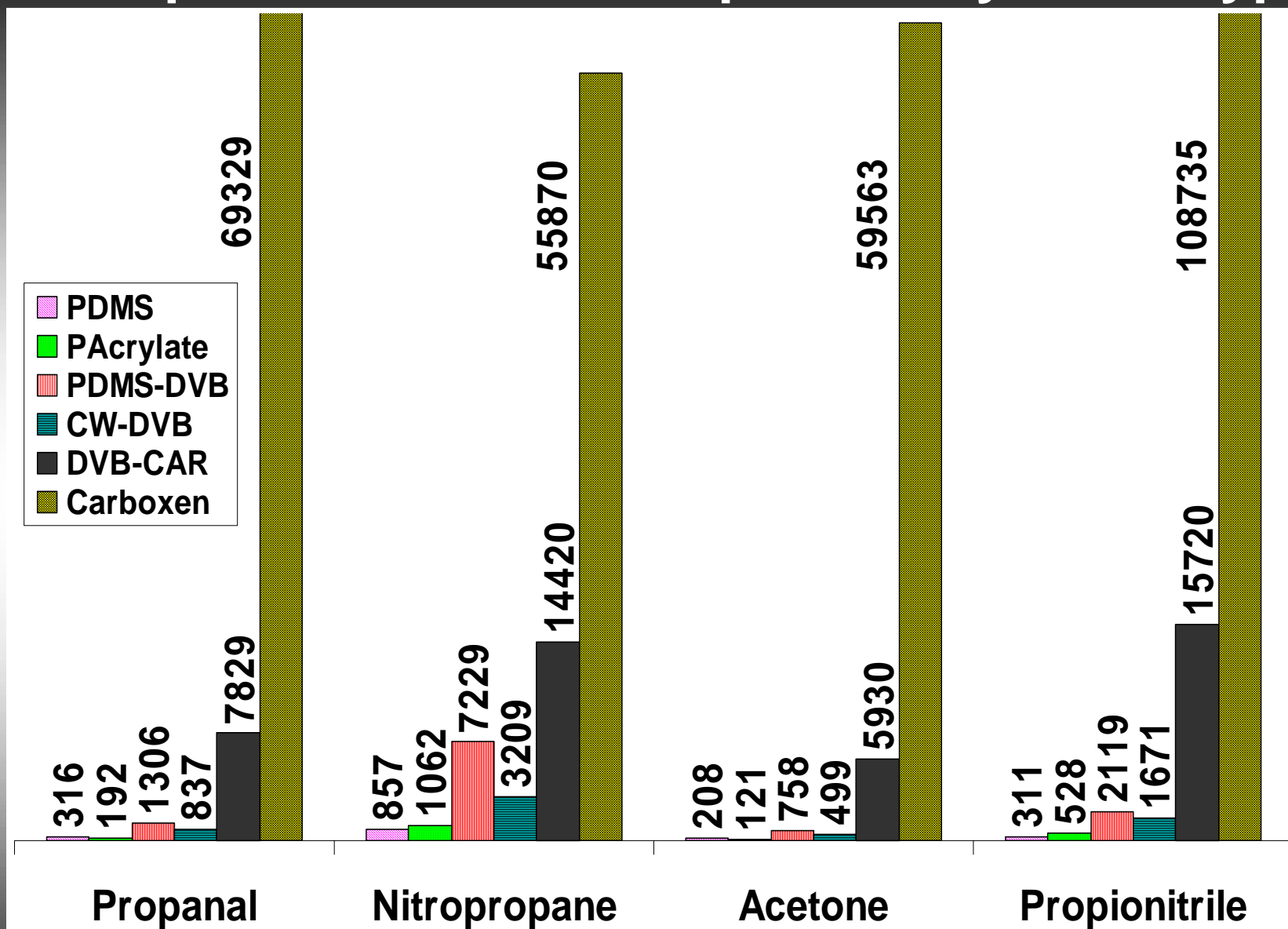
**Column:** 30m x 0.32mm x 4.0 $\mu$ m SPB<sup>TM</sup>-1 SULFUR

**Oven:** 40°C (2 min) to 140°C at 8°C/min (1 min)

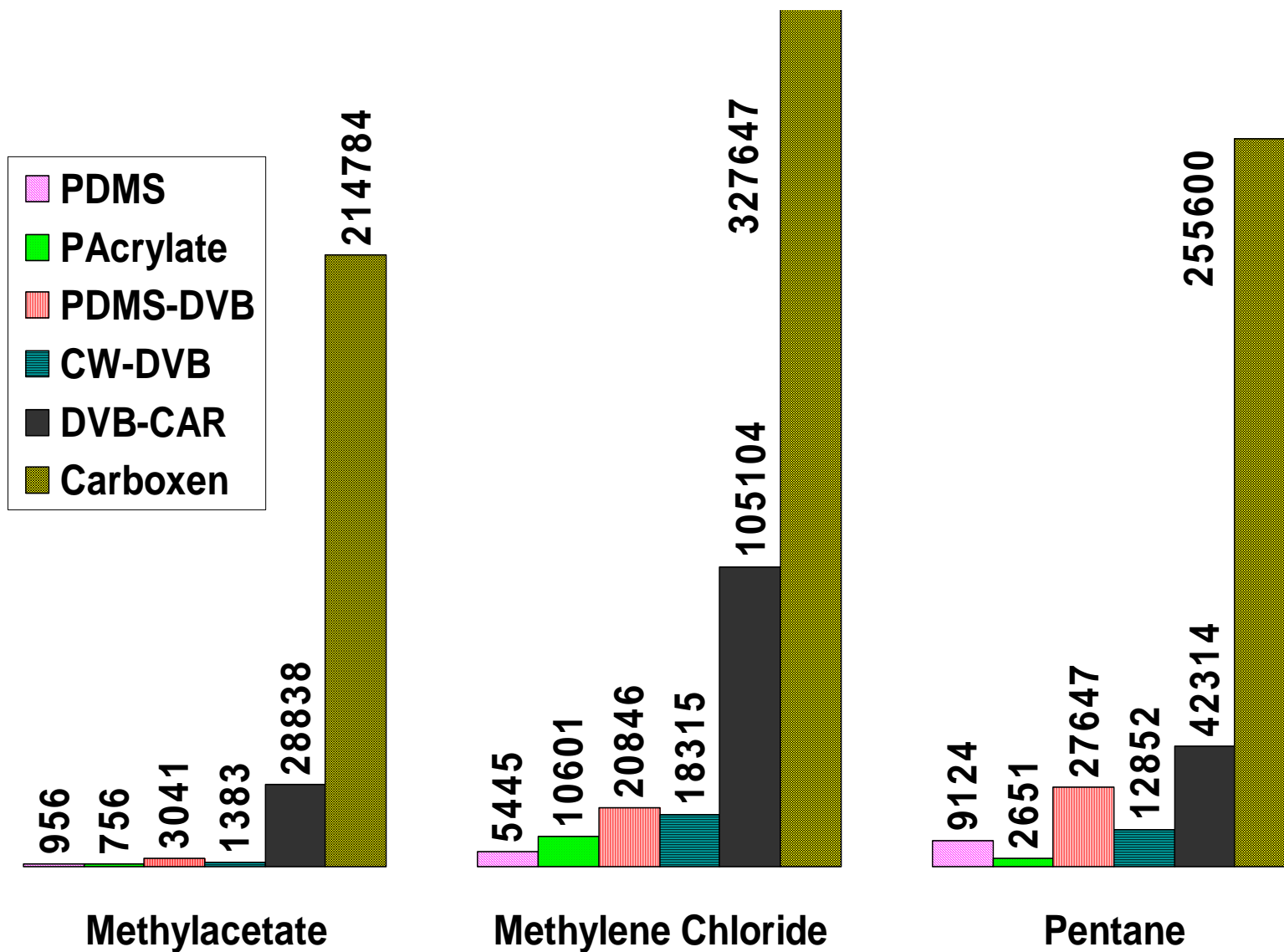
**Inlet:** Split/splitless, closed 0.5min, 0.75mm ID liner

**Detector:** FID

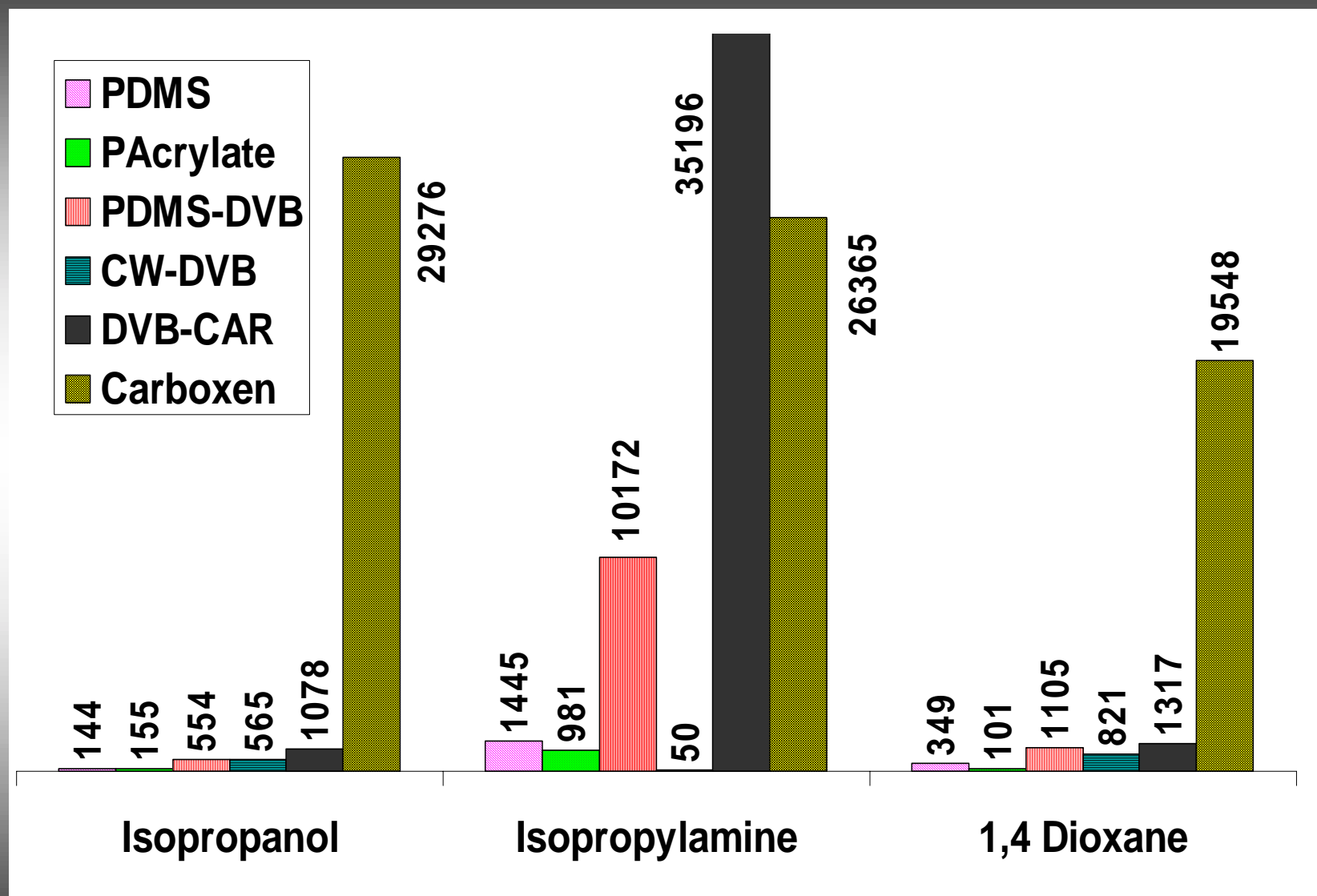
# Comparison of Area Responses by Fiber Type



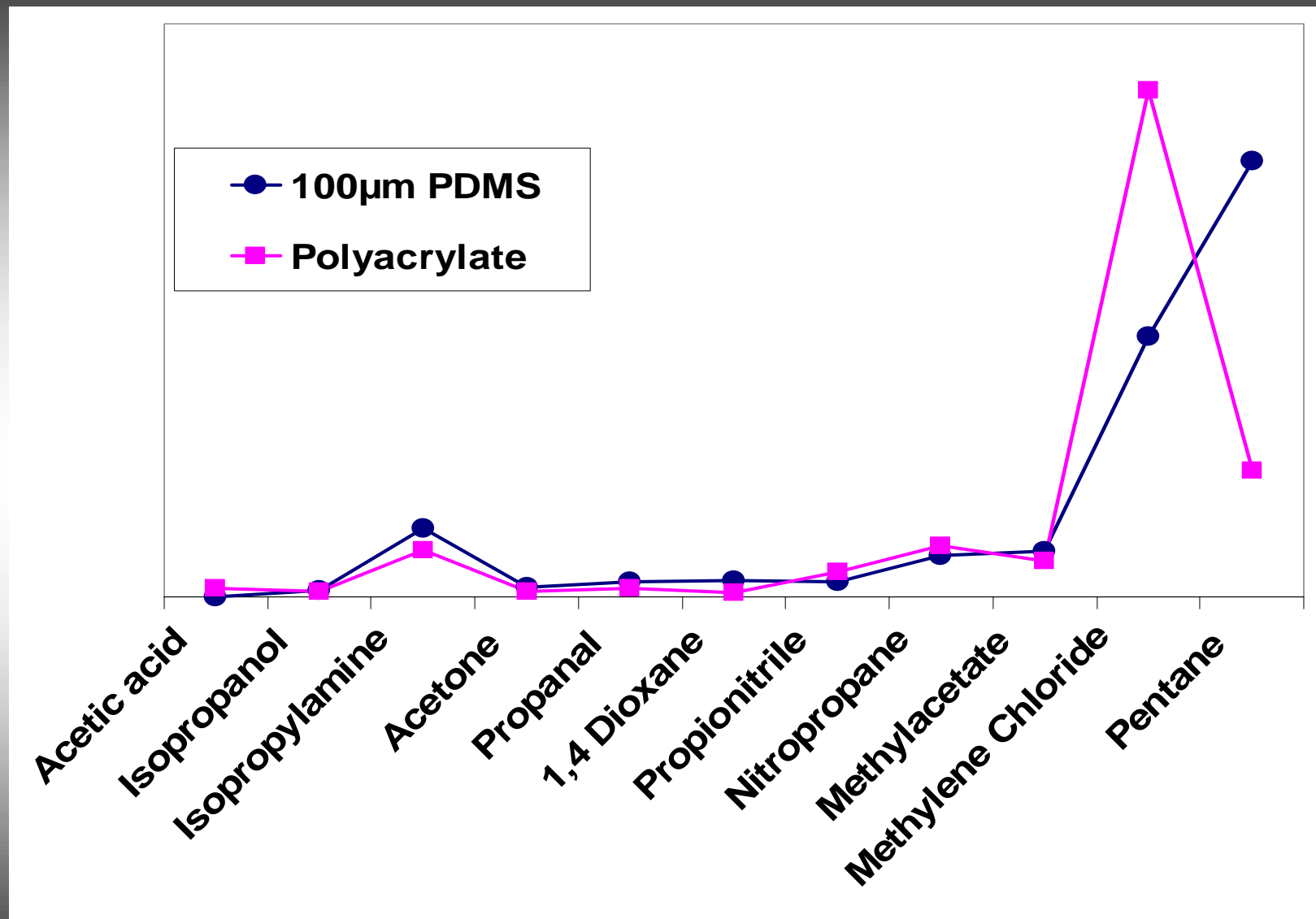
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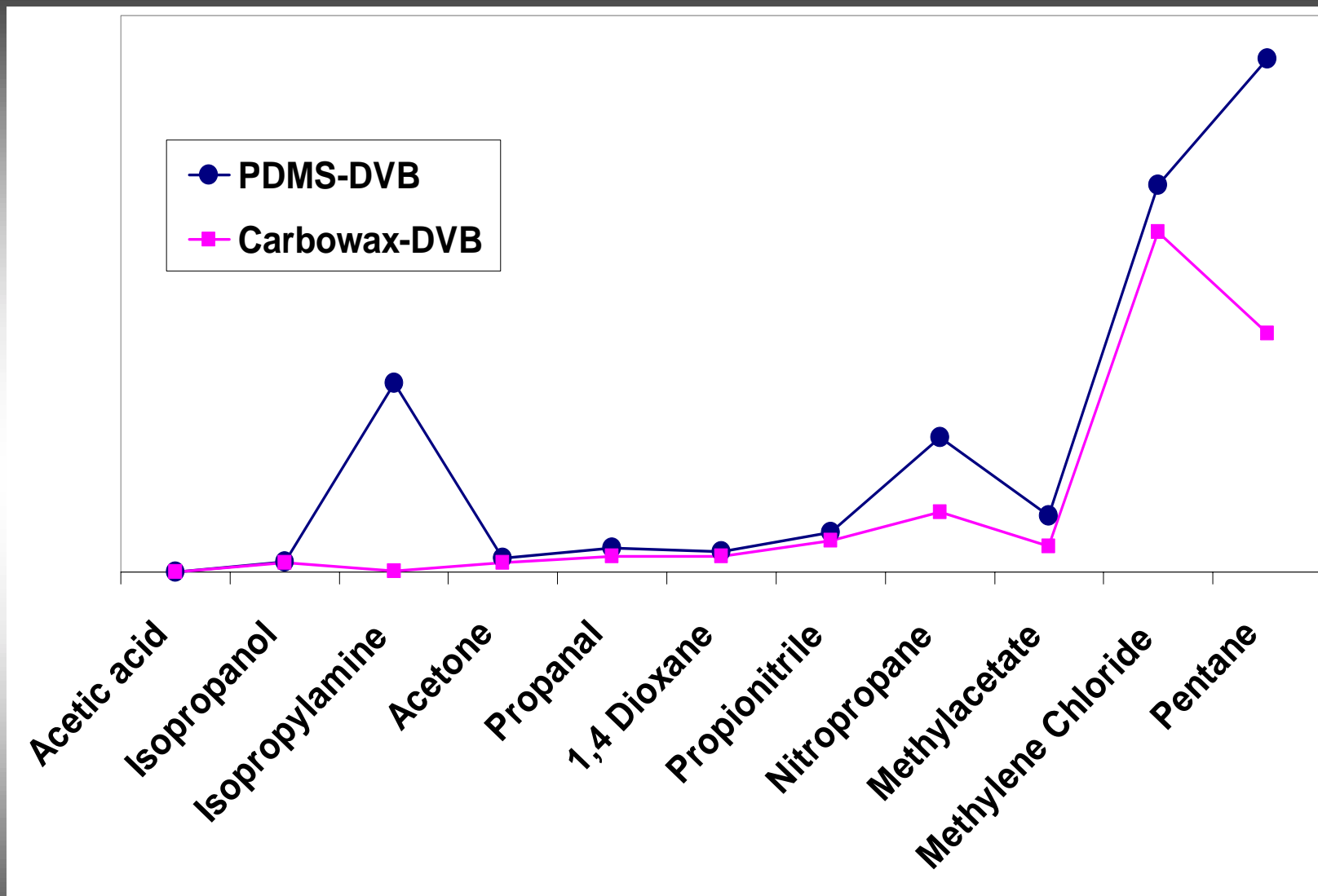
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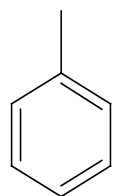
# Analyte Polarity vs. Area Response



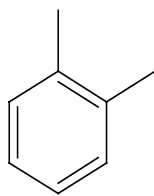
# Fiber Polarity vs. Area Response



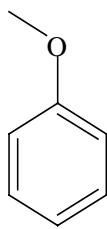
# Semi-Volatile Analytes Used in Study



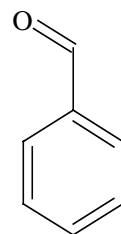
Toluene  
92



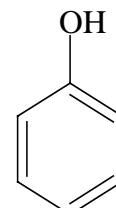
o-Xylene  
106



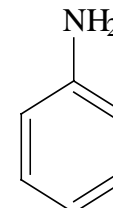
Anisole  
108



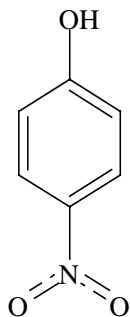
Benzaldehyde  
106



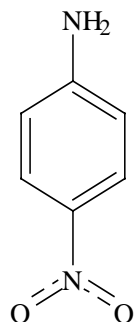
Phenol  
94



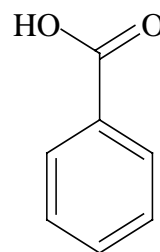
Aniline  
93



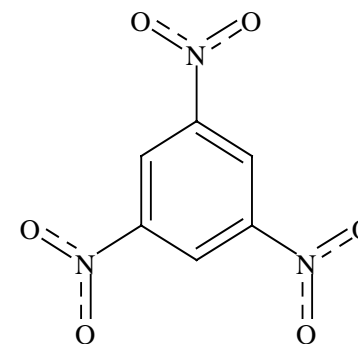
p-Nitrophenol  
139



p-Nitroaniline  
138



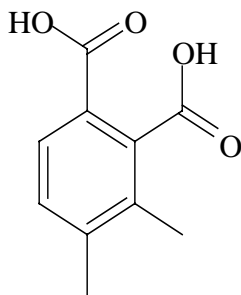
Benzoic acid  
122



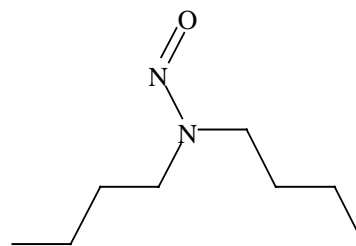
1,3,5-Trinitrobenzene  
213

G00129  
8

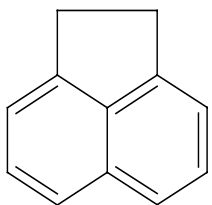
# Semi-Volatile Analytes Used in Study (contd.)



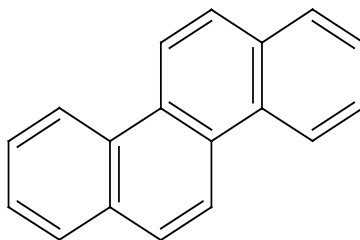
Dimethylphthalate  
194



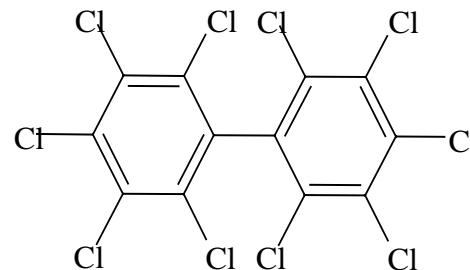
N,N-Nitrosodibutylamine  
158



Acenaphthene  
154



Chrysene  
228



Decachlorobiphenyl  
499

G001299



# Response Factors for Semi-Volatile Compounds in Study

Analyte	Response Factor
Toluene	0.72
o-Xylene	0.83
Anisole	1.13
Benzaldehyde	2.28
Aniline	0.83
Phenol	0.87
Benzoic acid	3.93
n-Dibutylnitrosoamine	2.53
Dimethylphthalate	0.42
Acenaphthene	1.00
p-Nitrophenol	3.87
p-Nitroaniline	3.16
1,3,5-Trinitrobenzene	4.64
Chrysene	0.69
Decachlorobiphenyl	3.16

# Analytical Conditions for Evaluation of Fibers with Semi-Volatile Analytes

**Sample:** Water containing 25% NaCl and appropriate 0.05M phosphate buffer, spiked with analytes to a final concentration of 75 ppb

**Extraction:** Directly immersed for 30 min with agitation

**Desorption:** 3 min, temperature varies, depending on fiber

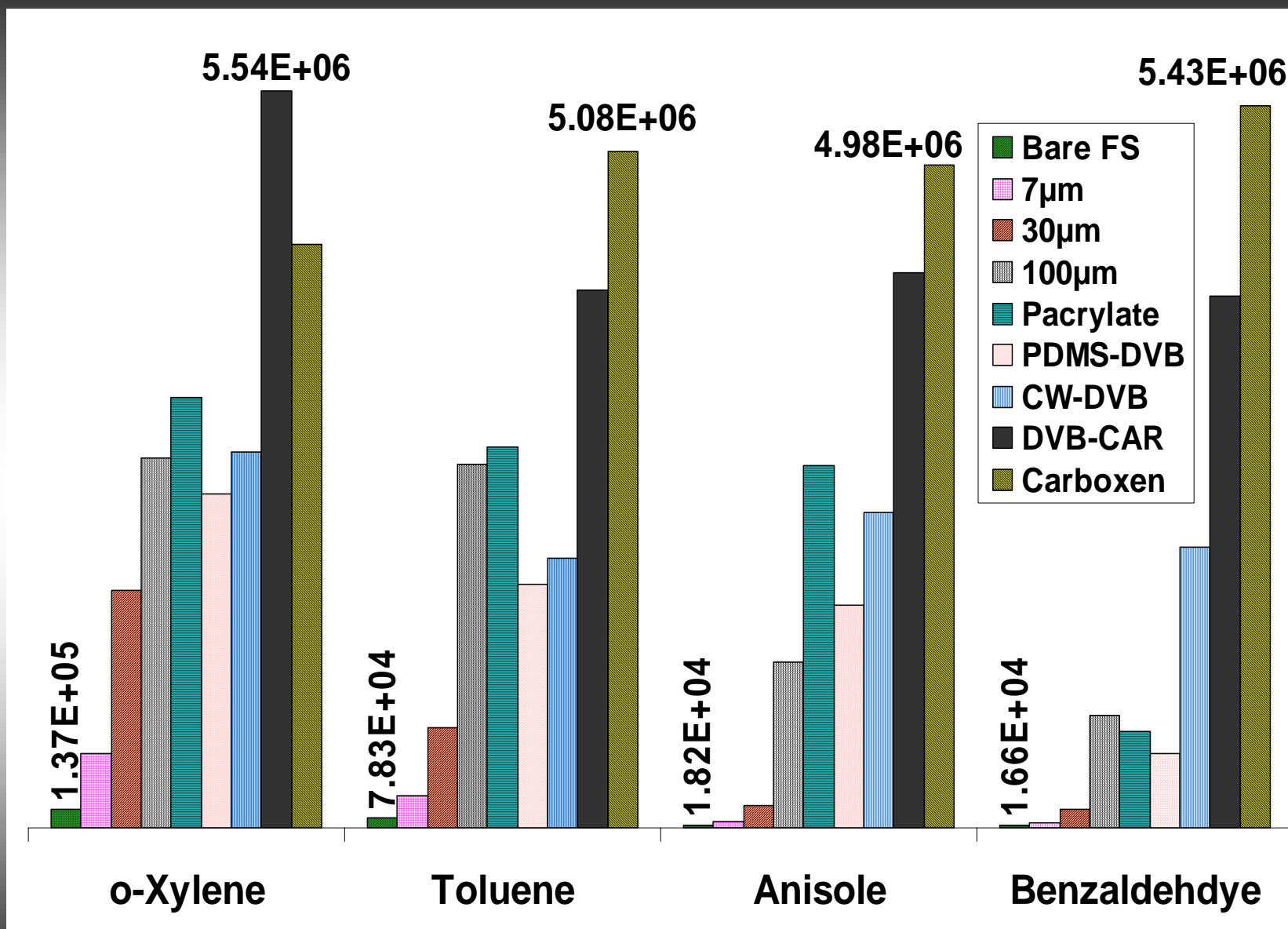
**Column:** 30m x 0.5mm x 0.25 $\mu$ m PTE™-5

**Oven:** 45°C (2 min) to 210°C at 10°C/min, then to 320°C at 20°C/min (10 min)

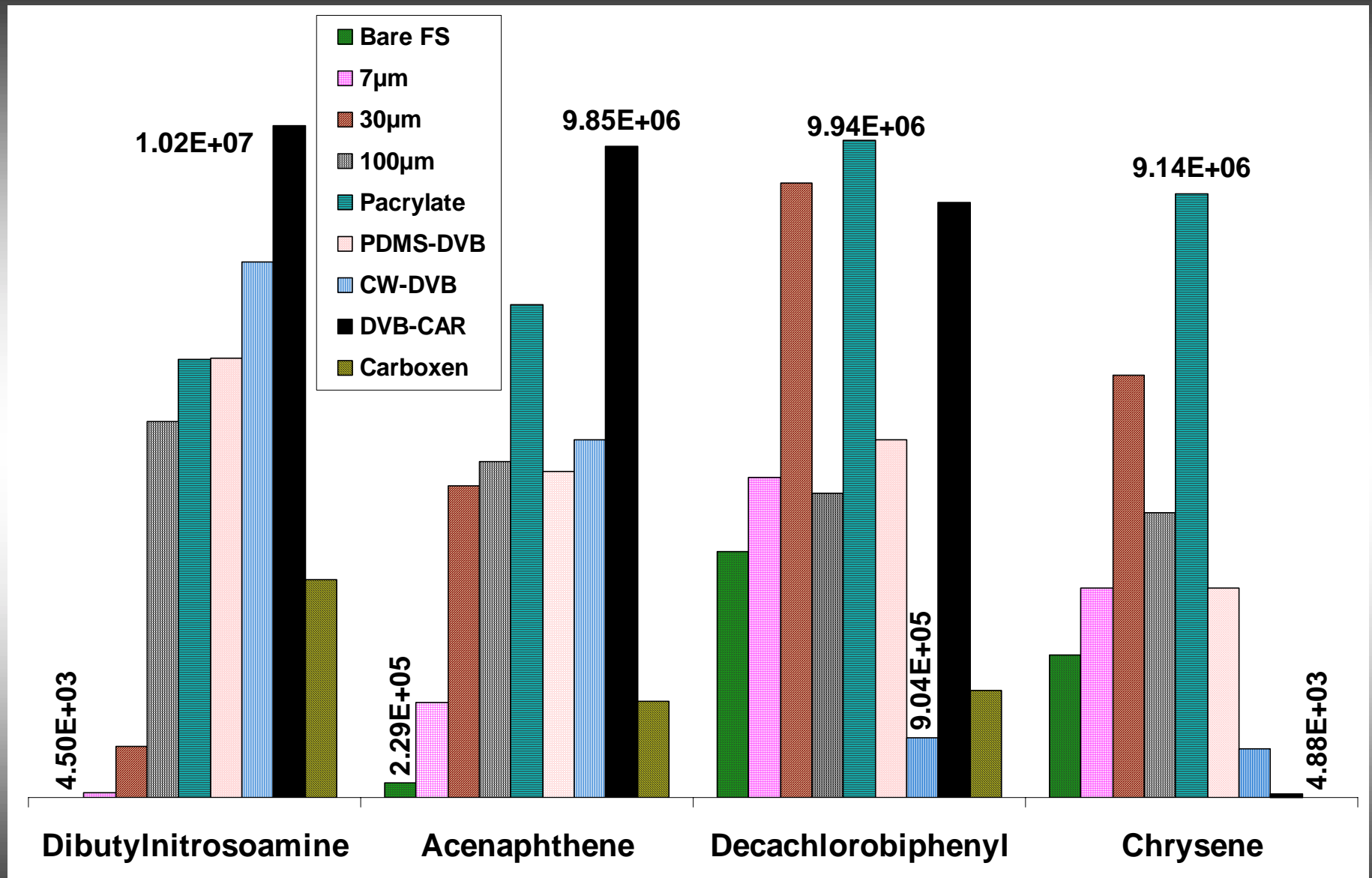
**Inlet:** Split/splitless, closed 1 min, 0.75mm ID liner

**Detector:** MS ion trap, m/z = 50-515 at 0.6 sec/scan

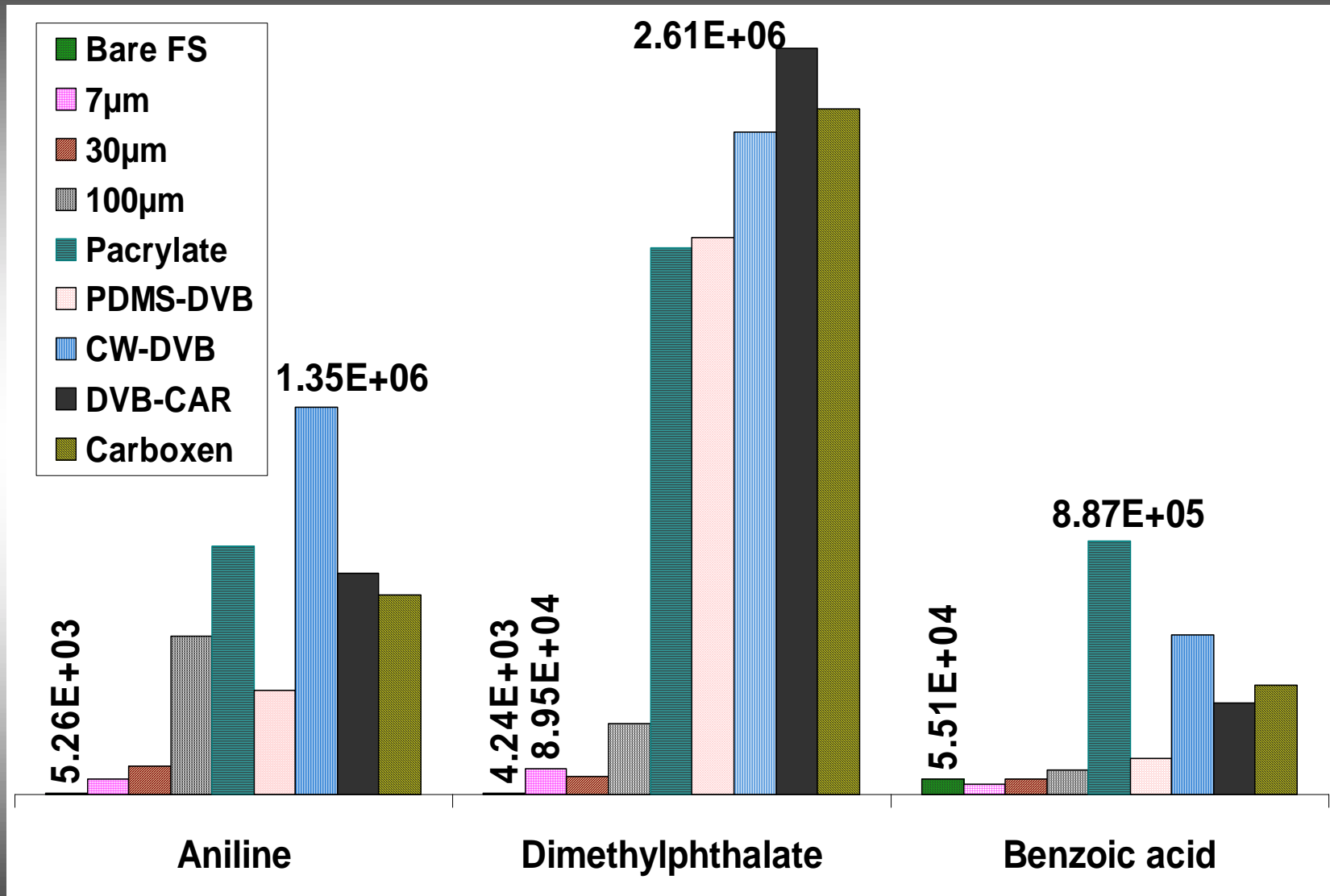
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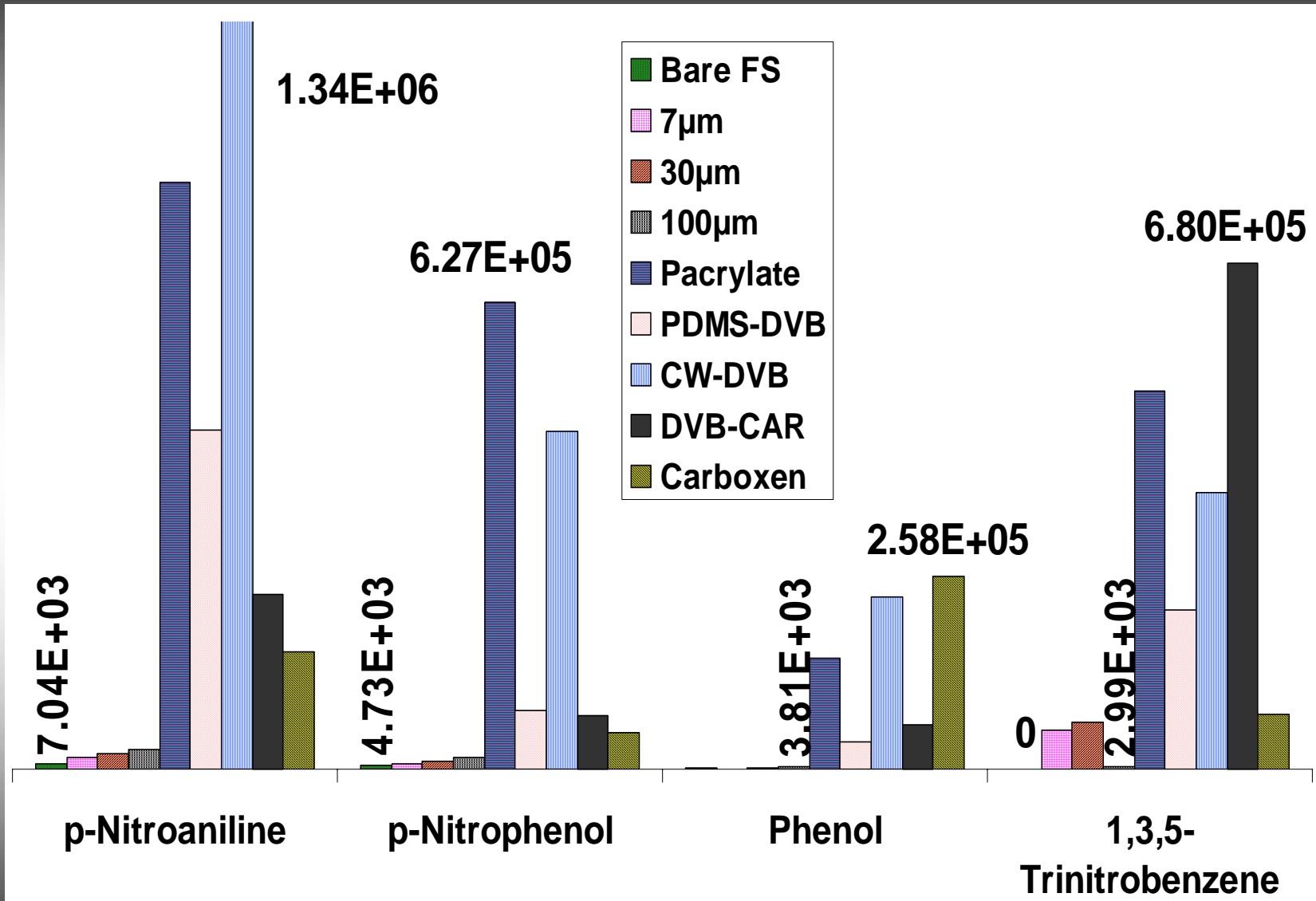
# Area Response vs. Fiber Type



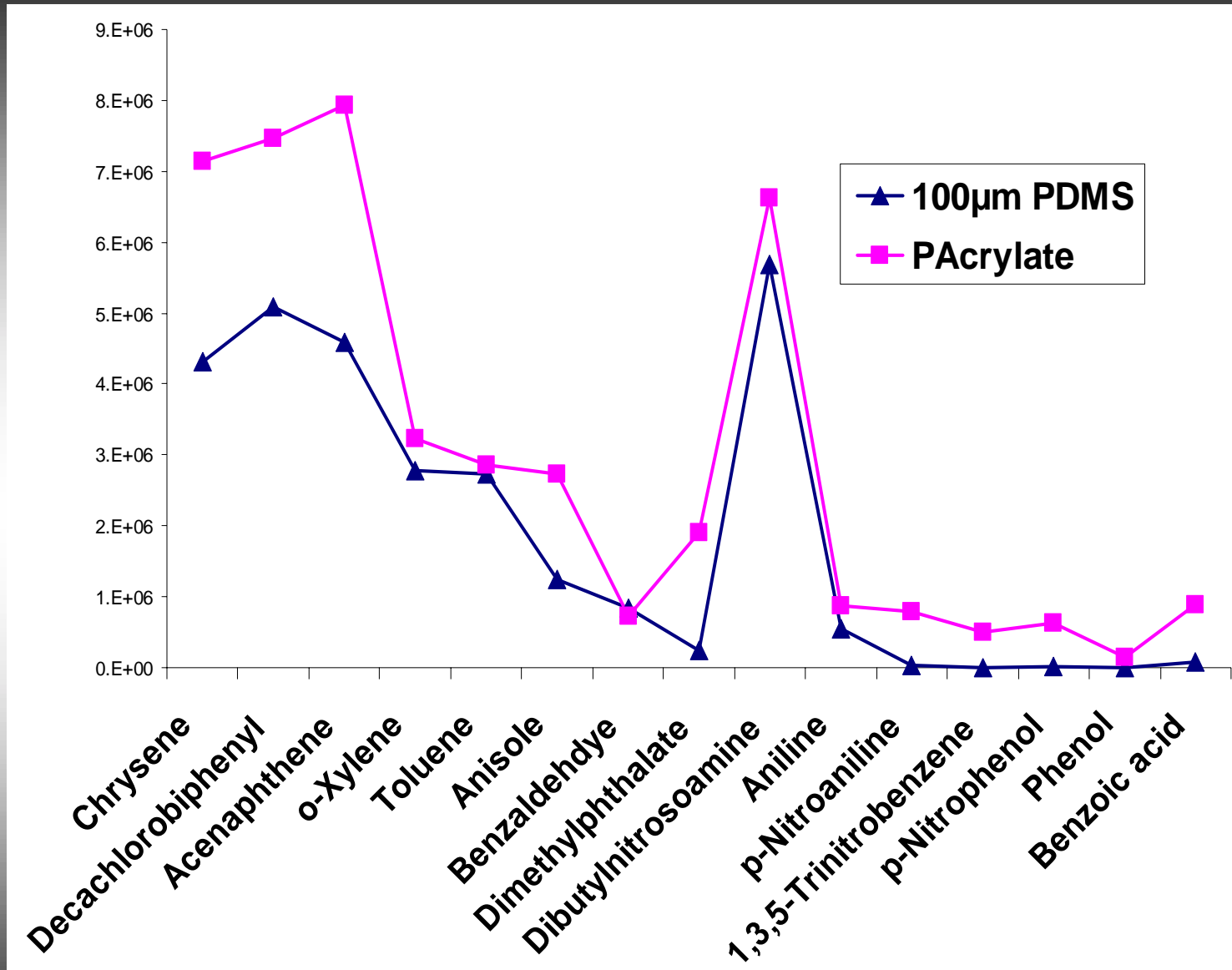
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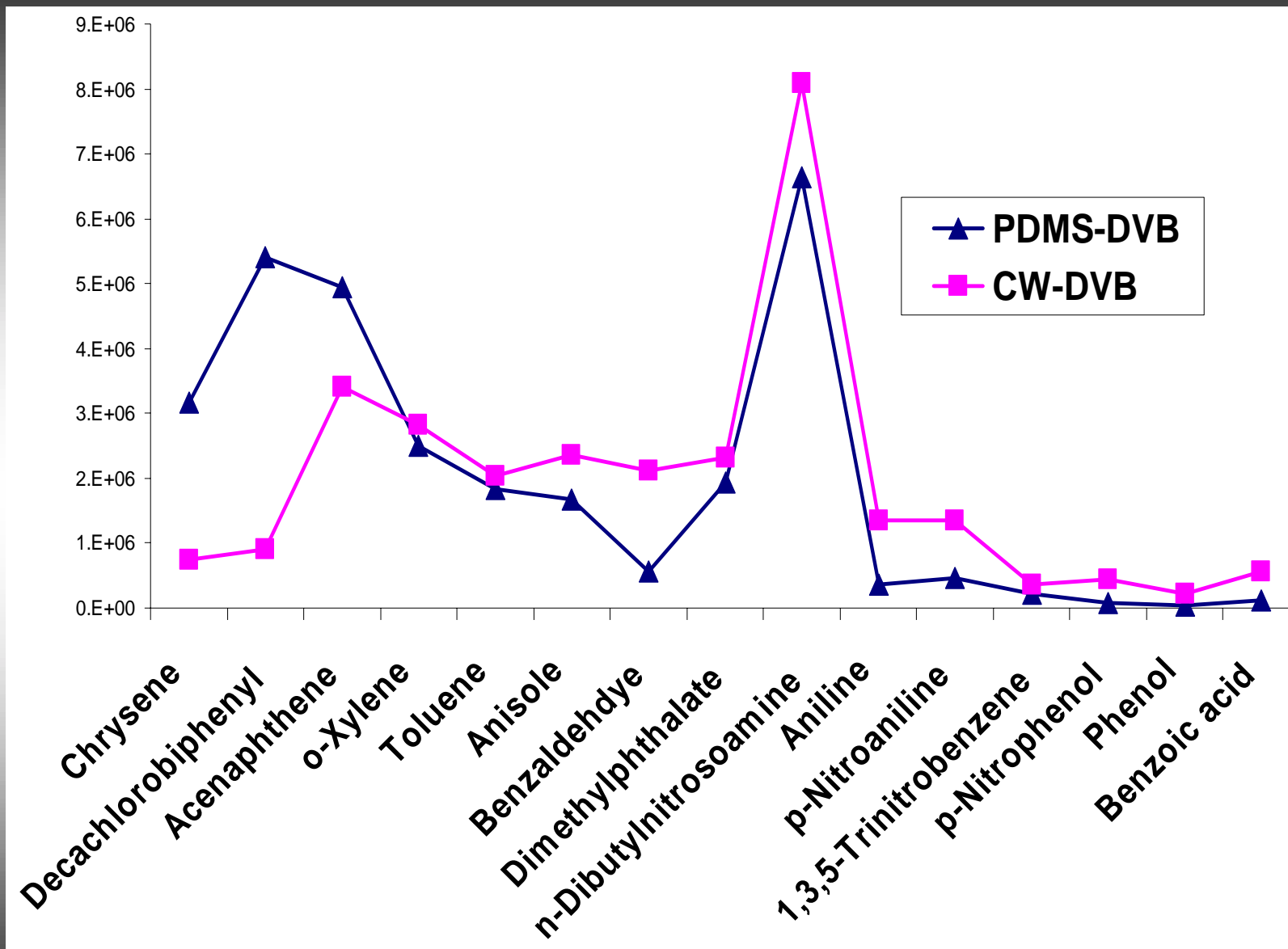
# Area Response vs. Fiber Type



# Analyte Polarity vs. Area Response

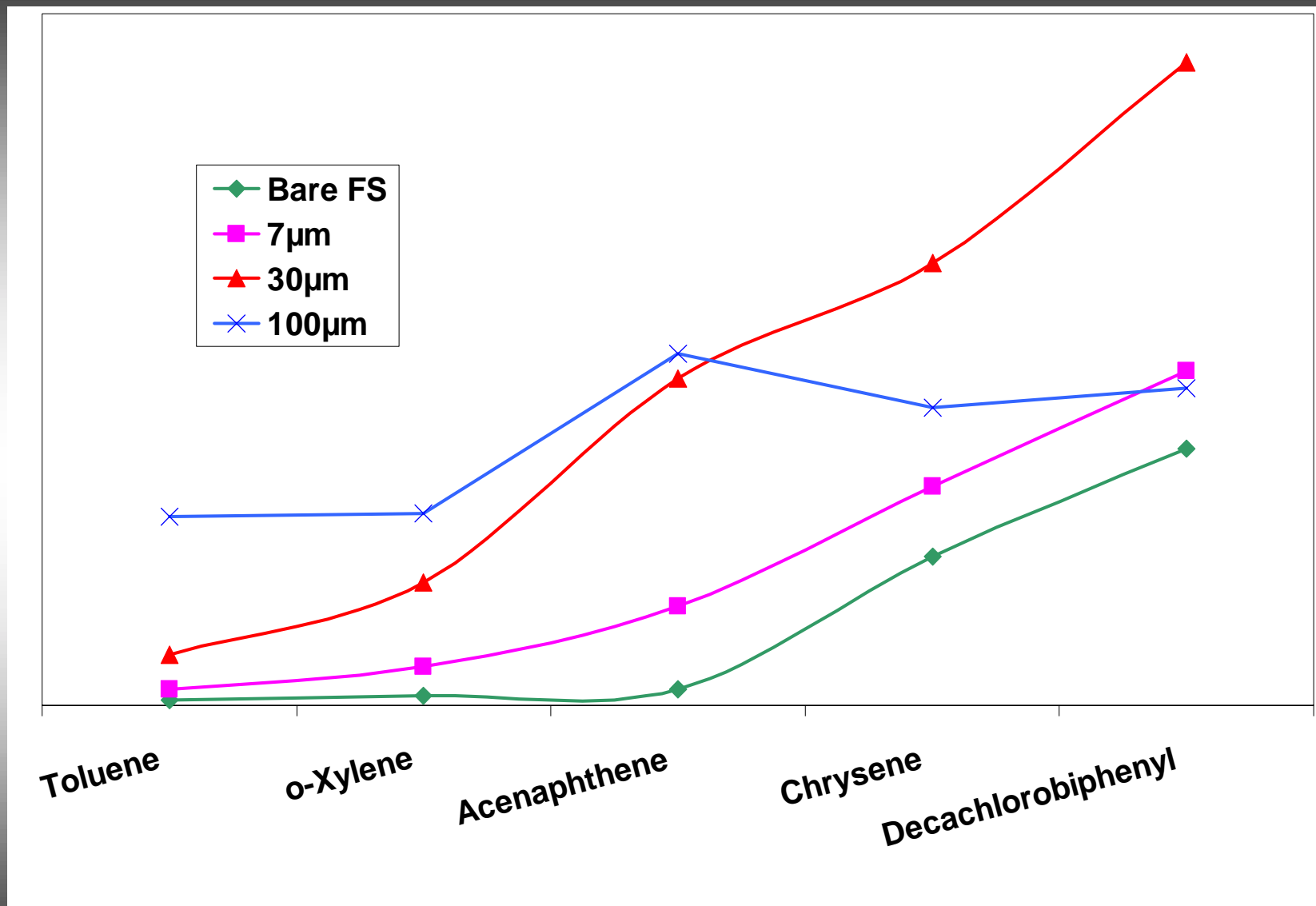


# Analyte Polarity vs. Area Response

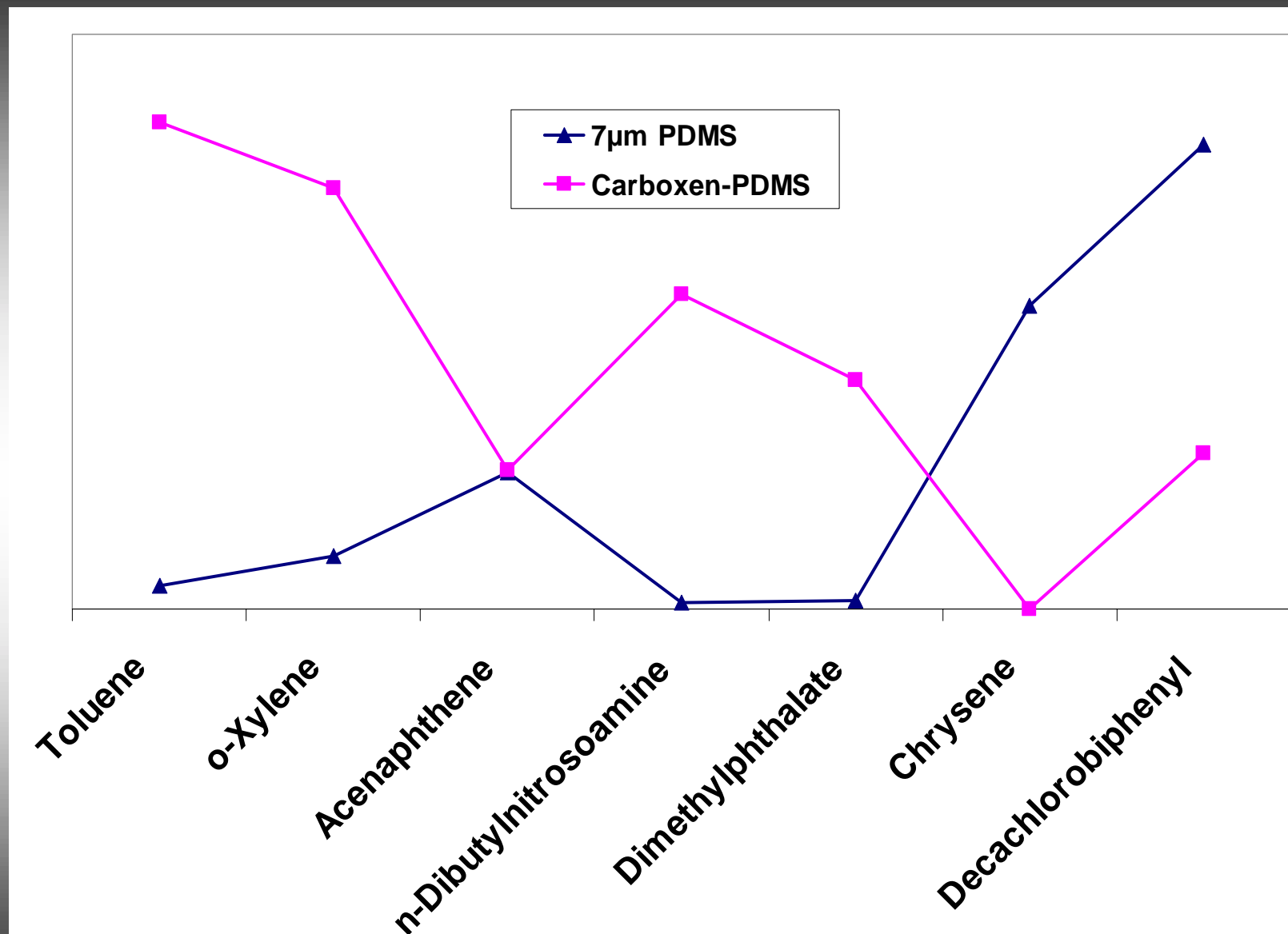




# Effects of Coating Thickness on Analyte Recovery



# Analyte Size vs. Area Response



# Classical Adsorption Mechanism for a Uniform Surface

$$\theta = \frac{\text{number of adsorption sites filled}}{\text{number of adsorption sites available}}$$

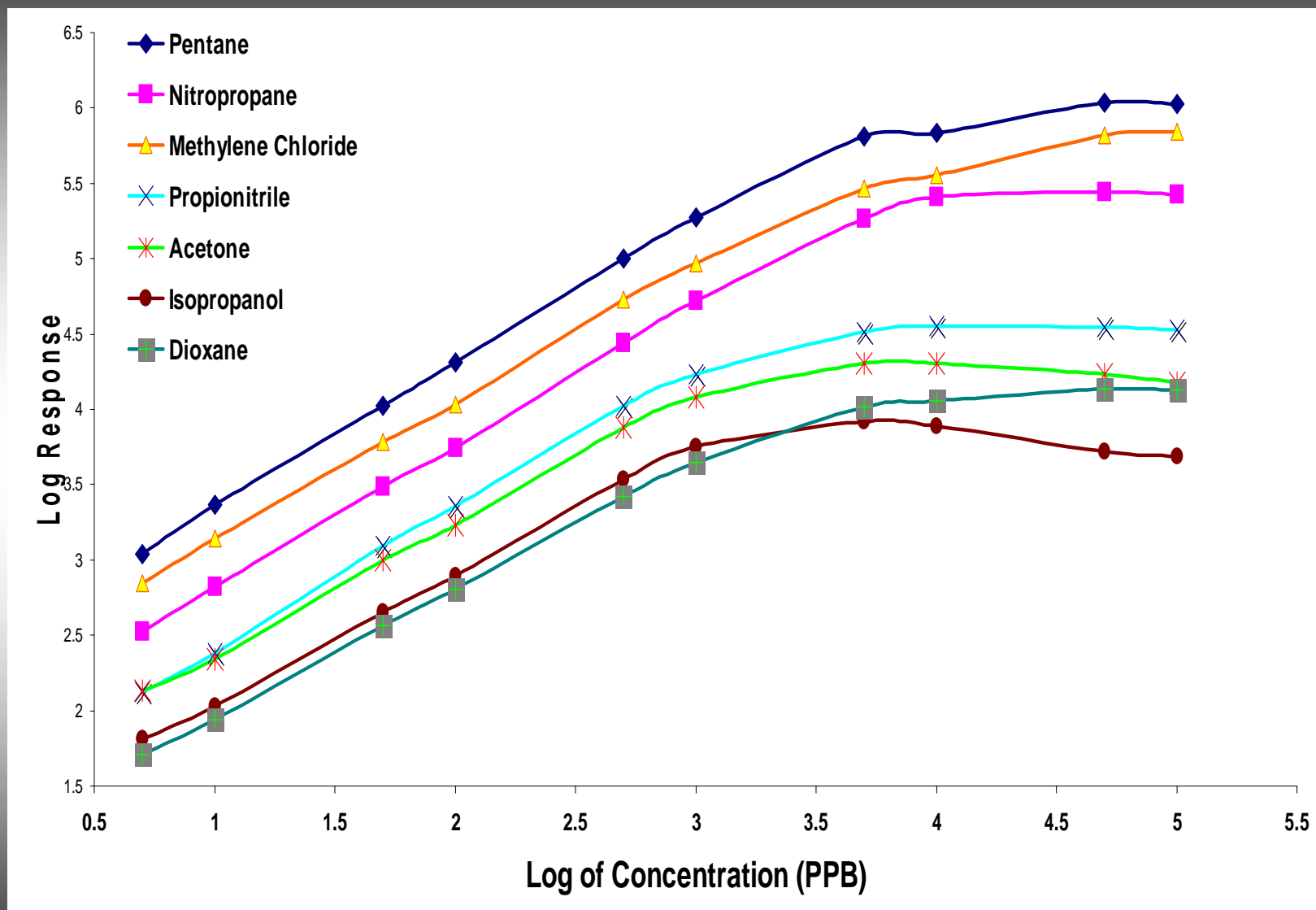
## Langmuir's Isotherm

$$\theta = \frac{K P_A}{1 + K P_A}$$

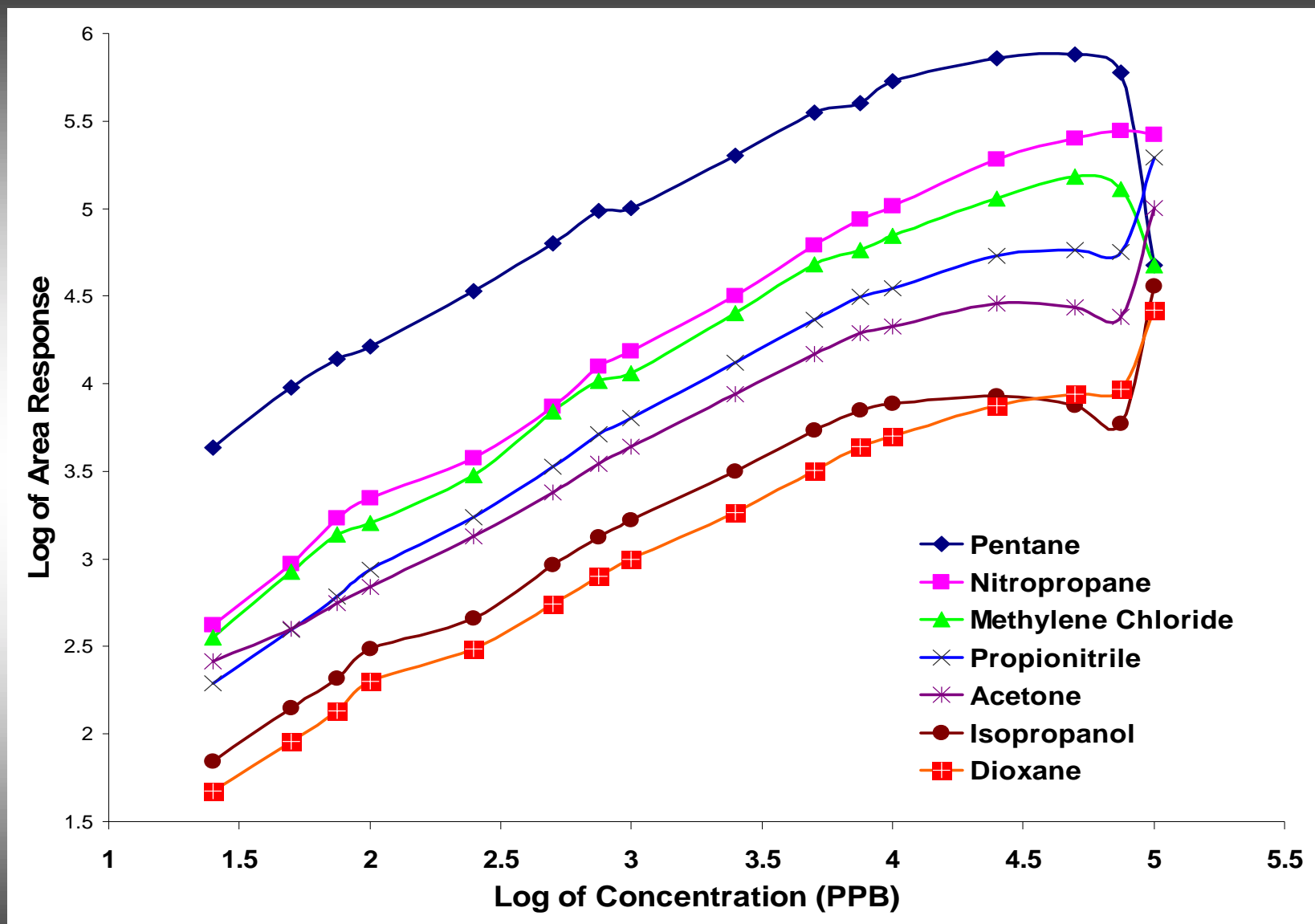
where  $K = k_a / k_d$      $k_a$  = rate of adsorption     $k_d$  = rate of desorption

# Analyte Response vs. Conc. (Carboxen-PDMS)

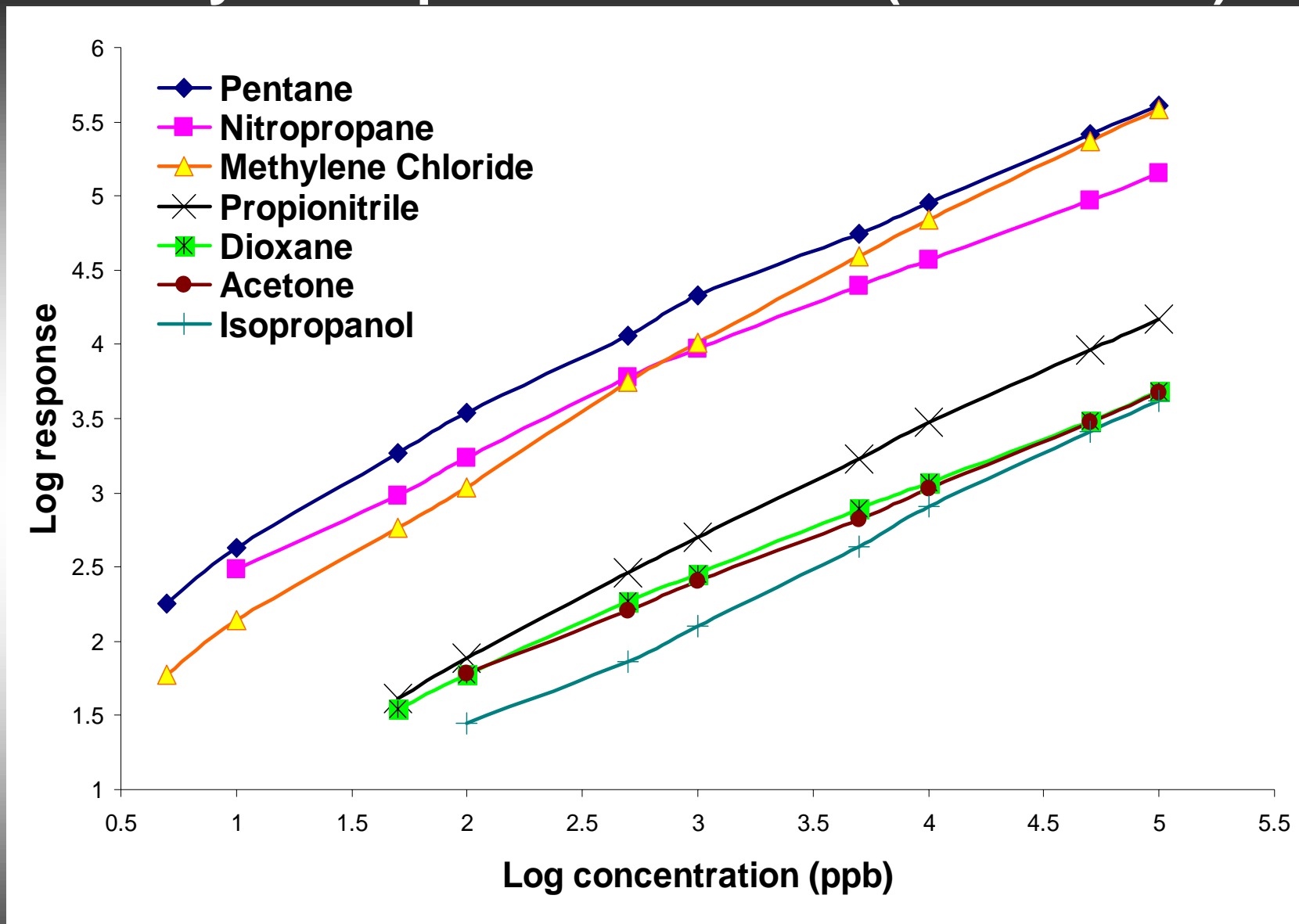
## 15 Min Ext.



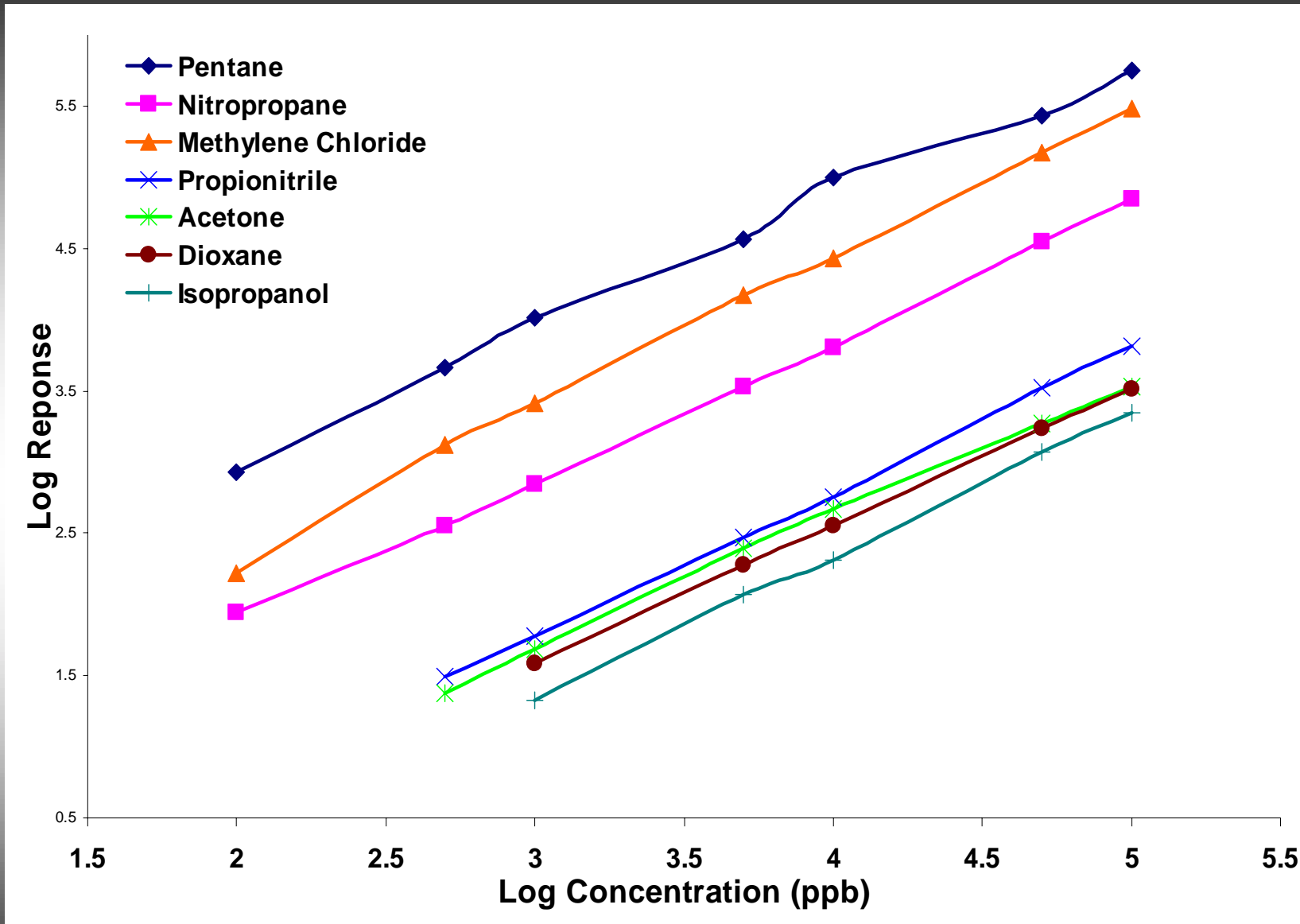
# Analyte Response vs. Conc. (Carboxen PDMS 2min Ext.)



# Analyte Response vs. Conc. (PDMS-DVB)



# Analyte Response vs. Conc. (100 $\mu$ m PDMS)



# Conclusions

- **Carboxen-PDMS is best for extracting small analytes (MW<90).**
- **For small analytes, analyte polarity has little affect on fibers.**
- **Analyte polarity affects fiber selection for larger analytes**
  - **the CW-DVB and Polyacrylate fibers are best or extracting polar analytes**
- **High MW analytes >150 amu and planar analytes are not extracted well by Carboxen containing fibers.**
- **Thin absorbent fibers are good for PAHs and PCBs.**
- **Adsorbent fibers are good for trace level extractions but have limited linear range.**
- **Absorbent fibers have higher minimum detection but larger linear ranges.**